Development of Poly-Naphthalene Sulphonate Based Concrete Admixture

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ABSTRACT: *In this research, Poly-Naphthalene Sulphonate (PNS) properties and working in concrete are enhanced to get the required workability and high strength of 10000psi. PNS usually does not work in high-strength concrete due to the presence of more cement content in its mix design. PNS dispersing effect in cement particles decreases as the cement content is increased. Therefore, its dispersion property and zeta potential are enhanced to make it compatible with high-strength concrete. Before modification, PNS is optimized in a mixed design of 10000psi concrete. When targeting dispersion, firstly PNS is modified by removing its oligomers which were creating a hindrance for cement particles. The required strength cannot be achieved while the required slump is achieved. In the other trial, sodium sulfate was added to concrete to increase dispersion by increasing sulfate ions in it, this sample did not work due to the presence of silica fume in the mix design. Similarly, many additives are added to increase dispersion like sulphonic acid with the defoaming agent, and by increasing gluconate dosage in the admixture solution. From the gluconate increment, get nearer to the required strength, which was not the exact required one. In the second phase, the hydration of cement is targeted by adding sodium lauryl ether sulfate to increase the viscosity of mixing water by which the active point of cement will increase but it gave the strength failure. Similarly, polytetrafluoroethylene was added which gave a better result but not the required strength. This additive is also tried with a gluconate-incremented sample to target both factors simultaneously. But the strength cannot be achieved and in the last by adding sulfuric acid to the mixing water rate of hydration of cement is slowed down by the water absorption principle and the required strength. The workability was achieved at a very cheap cost.*

KEYWORDS: *Admixture additives, Concrete; Poly-Naphthalene Sulphonate; Polytetrafluoroethylene; Sodium sulfate; Water absorption; Cement hydration reaction.*

INTRODUCTION

The two types of cementitious materials are; hydraulic and supplementary cementitious materials. The purpose of cement is to bind the constituents together and harden the concrete. Portland cement is the most common hydraulic

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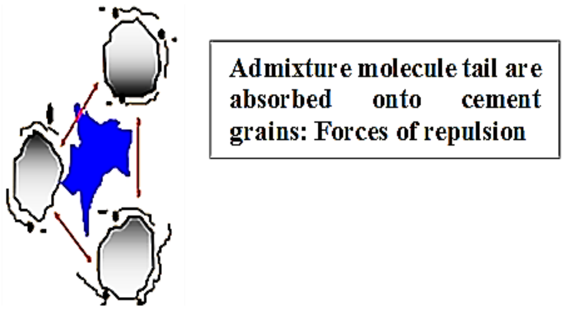


Fig. 1: Chemistry of admixture

cement used which undergoes a reaction of hydration when compounds of calcium silicate and aluminum silicate react with water in which heat is given off which can cause thermal cracking, hence supplemental cementitious materials are used in conjunction with hydraulic cement which reduces the heat of hydration and also improves workability. Fly ash, natural pozzolans, blast furnace slag, and silica fumes are the supplementary cementitious materials used with Portland cement, silica fume is used in our concrete to attain better strength. When high-quality quartz is reduced with coal and wood chips, silica fumes are produced as a byproduct. Typically, silica fume has a specific gravity of around 2.2. Because it has lower specific gravity than Portland cement when replacement is done based on weight, more silica fumes are introduced than cement is taken out. So, the volume of cementitious pastes increases, and typically water-cementitious material ratio decreases on a volume basis. Particle size distribution of silica fumes shows that most particles are smaller than one micrometer (1 µm with an average diameter of about 0.1 µm, which is approximately one hundred times smaller than the average size of cement particles). It is a highly powerful pozzolanic substance because of its extreme fineness and high silica fume content [1, 2]. During the hydration of cement, the silica fumes react pozzolanically with the calcium hydroxide and form a stable compound which is Calcium Silicate Hydrate (CSH). Sand and crushed stone are two fundamental elements in aggregates, which are inert granular substances. 60 to 75 percent of the entire volume of concrete is made up of aggregates. There are two types of aggregates: fine and coarse. Sand or crushed stone with the majority of the particles having a maximum length of 3/8 inch make up fine aggregates, whereas coarse aggregates come in lengths between 3/8 inch and 1.5 inches. The sources of this aggregate are pits, rivers, lakes, and sea beds and recycled concrete is also a good source of aggregate. Aggregates make concrete more compact, decrease the amount of cement and water required, and contribute to the mechanical strength of the concrete. Concrete's characteristics can be changed with additives to make it more pliable, robust, and cost-effective [3, 4].

Conforming to ASTM C 494 there are types of admixtures with different purposes (Dixon). Water reduction is used to reduce the water needed in the concrete mixture. Workability is an important factor that improves workability at the expense of a reduction in strength. This admixture is added to improve workability with reduced water so that the strength is not compromised. Retarding admixtures inhibits the rate of hydration of cement which helps in increasing the setting time of concrete. They are added in concrete where it is to be used in high-temperature environments so that it does not dry out before setting appropriately. Accelerating admixtures increases the rate of hydration reaction which helps the concrete to reach its maximum strength early. Water-reducing and retarding admixtures provide workability at reduced water content as well as reduce the setting time of concrete by slowing down the process of hydration. Water-reducing and accelerating admixtures provide workability at reduced water content as well as increase the hydration reaction and help them to reach their maximum strength faster. Water-reducing high-range admixtures provide workability at reduced water content as well as increase the strength of concrete. Water-reducing high-range and accelerating admixtures provide workability at reduced water content reduce the setting time and provide strength to the concrete [5, 6].

Preferred Admixture

Fresh or hardened concrete's characteristics can be changed by chemical admixtures. The majority of the admixtures are employed as high-range or water reducers. "An admixture that reduces the amount of mixing water for concrete for a specified workability" is the definition of a water reducer admixture. It slows down cement hydration, which is primarily influenced by the admixture's dosage and molecular composition. Hardened concrete's qualities are improved, as are its strength and durability. As shown in Fig. 1 the admixture molecules get adsorbed onto cement molecules by steric and repulsive forces and release the entrapped air for giving higher

Table 1: Different grades of concrete according to ACI and IS456:2000

Concrete Type	Concrete Grade	Mixed Ratio (Cement: Sand: Crush)	Strength at 28 days according to ACI 318 (MPa)
Normal concrete	M5	1:5:10	5
	M7.5	1:4:8	7.5
	M10	1:3:6	10
	M15	1:2:4	15
	M20	1:1.5:3	20
Standard concrete	M25	1:1:2	25
	M30	Design Mix	30
	M35		35
	M40		40
	M45		45
	M50		50
High strength concrete	M55	Design Mix	55
	M60		60
	M65		65
	M70		70

workability at a constant water-cement (w/c) ratio. Concrete water requirements can be reduced by up to 10% with normal water reducers, but they can be reduced by 25% to 30% with high-range water reducers (SPs). The molecular weight affects both the rate and volume of SP adsorption. The amount of SPs that are adsorbed increases as the admixture's molecular weight rises. The selected water-reducing admixture is the poly naphthalene sulphonate-based second-generation concrete admixture [7, 8].

PNS is a superplasticizer that is a high-range water-reducing agent and falls into types of chemical admixtures. Since the introduction of superplasticizers in the 1930s, the use of such plasticizers provides more control over the rheological and mechanical properties of both fresh and hardened concrete, which makes them a crucial component in the manufacture of concrete. PNS is one of the most widely utilized superplasticizers in the building industry. It can help in reducing the water-cement ratio which can in turn strengthen the concrete. It is also a raw material for many additives in the construction industry such as compound accelerators, antifreeze, and retarder. It is reliable for producing construction materials that can be used to build highways, bridges, dams, tunnels, and in various other projects [4, 9]. The first step of the synthesis of PNS involves a reaction of naphthalene with sulfuric acid, this reaction is called sulfonation reaction and is shown in Eq. (1). The position of hydrogen sulphonate occurs in two possible positions α and β. β sulfonation occurs at a temperature of about 150°C. The preference is β-type sulfonation. In a well-controlled synthesis process, the sulfonation degree can be achieved by up to 90%. The next step is to react with the β-naphthalene sulphonic acid with formaldehyde. This reaction is a condensation reaction that produces polynaphthalene sulphonic acid [10, 11]. The formaldehyde becomes reactive following the protonation of the carbonyl function and is then added to the aromatic ring via an electric addition process. Following condensation, the new compound's methyl-ol function combines with a second naphthalene molecule to create

a methylene bridge between these two naphthalene molecules. Upon reaching the optimum level of polymerization, move forward to the last step which is the neutralization reaction of poly-methylene-naphthalene-sulfonate with sodium hydroxide given in Eq. (2) [10, 11].

$$nC_{10}H_8 + nH_2SO_4 \rightarrow nC_{10}H_7SO_3H \quad (1)$$

$$\mathrm{nC_{10}H_7SO_3H + nCH_2O} \xrightarrow{\mathrm{H+/NaOH}}$$

$$\mathrm{nC_5H_3SO_3NaC_5H_3CH_2O} \quad (2)$$

The PNS that was acquired can be classified as linear, branching, or cross-linked. Commercially synthesized PNS has up to 10% oligomers with a degree of polymerization between 1 and 4, has monomers in the greatest abundance, and 20-30% are linear molecules with a maximum degree of polymerization equal to 20, about 35% having a degree of polymerization between 20 and 40 which might have slight branching and cross-linking and 25% of species have degrees of polymerization that can exceed 200 due to strong cross-linking. This concludes that commercially synthesized PNS contains a large amount of non-linear molecules [12, 13].

Concrete mix design is a procedure of finding the right amounts of the mentioned materials to achieve the desired strength. An accurate concrete mix design makes concrete construction economical for the required conditions. To calculate the right amount of cement, sand, and aggregate required in 1m^3 of concrete there are different grades as shown in Table 1 [4, 14]. Since our mixed design is of M70 grade (High strength concrete) which does not have a fixed proportion of components therefore it is designed by Bond Chemicals (Pvt.) Ltd., which gives us the strength of 10000psi (70MPa) at a constant water-cement ratio. Concrete compressive strengths, slump or slump flow, water cementitious material ratio (w/c or w/c+p), kind of cement, coarse aggregate size, and source, if required, are all qualities that a correctly designed concrete mix should have. The density of concrete, proportions of additional cementitious materials, use of specified admixtures, and avoidance of prohibited admixtures. Additional qualities and material parameters, such as those relating to entrained air content, total chloride limits, or other durability or exposure standards as well as economy [11, 15].

Procedure for selection of mix proportion

The term slum is the consistency of freshly mixed concrete before it sets, the higher slump shows mean higher fluidity note that for ready mix concrete high slump and workability are required for placement and transportation (ASCI 304R), and therefore mix proportion should design by the necessarily required slump. The desired slum in this mixed design is 200mm initially. Aggregate is defined as reinforcing material in the concrete same as aramid or Kevlar fiber in the case of polymeric composite, they are either rounded or angular. Fine aggregate and coarse aggregate are the two classifications for concrete. Crushed stone or gravel is utilized as the coarse aggregate, and sand is used as the fine aggregate. According to ASTM C30-37, large nominal-size aggregates reduce voids, which in turn reduces the volume of mortar, which is the cement, water, and sand mixture used in concrete. Generally speaking, the nominal maximum aggregate size should be the largest that is both economically feasible and consistent with the structure's dimensions. The size of the structural member and the spacing of the reinforcing steel within a member must be taken into account when determining the maximum aggregate size. But in the case of the congested steel, these are omitted. If high-strength concrete is going to be designed then a small size of aggregate is required because high strength is attained either at a lower or fixed w/c or w/(c+p) ratio. The size analysis is done by sieve analysis by ASTM C33. Here in our mixed design, the size of the aggregate is 20mm.

A certain amount of water (~23% by weight) is required for the hydration of water, excess water increases the fluidity of the concrete on the cost of strength because as the number of water increases the number of voids which is entrapped in air increases due to evaporation of water during concrete setting and cement heat generation. In general, the size, shape, and grading of the aggregate, the amount of entrained air, and the temperature of the concrete all affect how much water is needed per unit volume of concrete to generate a certain slump. In case of excess air voids air entrained admixture (ASTM C260) is used and for given fluidity strength are increased by using water-reducing admixture (ASTM C494). The total amount of cementitious material or the net amount of water used per unit of cement is what determines the strength of concrete for a specific set of components and conditions. In addition to Portland or blended cement, cementitious materials other than hydraulic cement are frequently used in concrete for a variety of reasons, including economy, reduced heat of hydration, improved workability, increased strength, and/or improved durability under the expected service environment. These substances include fly ash, GGBF slag (ASTM C 989), natural pozzolans (ASTM C 618), and silica fume. In this mixed design for the strength of 10000psi (70MPa) silica fume is used as a pozzolanic material. The net amount of water utilized per unit of cement or cementitious material determines the component's strength. It is inversely related to strength. For a w/c ratio given, strength can also be varied by the amendments in other components. The constant water-cement ratio in this design is 2.5 for an initial slump of 200mm. The PNS normally gives an optimum strength of 3000-4000 psi and does not provide the required strength of 10000Psi. Since PNS is relatively cheaper than other chemical admixtures that can provide the strength of 10000 psi thus, have to modify PNS or modify the effect that the PNS creates in the concrete so that it can provide the required strength of 10000 Psi [3, 6].

Concrete and its mix proportion

Standard practice for proportioning concrete mixtures expects that for a given most extreme size of the coarse total, the workability or consistency of cement is an immediate capability of the water content; that is, inside restricts it is free of different factors, for example, total evaluating and concrete substance. It is to be referenced that in foreseeing the impact of combination extents on usefulness, among the elements water content, concrete substance, and total evaluating, simply two have been accounted for to be autonomous. At the point when the total concrete proportion is decreased at consistent water cement proportion, the water content and consequently functionality increments. Substantial blends with high water content will quite often isolate and drain consequently unfavorably influencing the usefulness. Blends with too low water content might be hard to place and smaller and the coarse total might isolate on position. Workability is impacted by concrete substances moreover. Researchers in their reading material detailed that with ordinary Portland concrete cement, at given water content, an exceptional decrease of concrete substance would create a cruel combination with unfortunate finish ability. Substantial combinations containing exceptionally high concrete substance or a high extent of the sand tend to be cohesive but become sticky. They investigated that a modern type of concrete is a mixture of aggregates, water, cement, different additives, and admixtures. In specific, polymer additives appear to be favorable ingredients. It can significantly change the properties of concrete and mortar. Today's most common polymer additives include latexes, superplasticizers, and dispersal powders. Furthermore, to develop the properties of concrete-based composite admixtures that enrich crack resistance, freeze-thaw, strength, workability, and fluidity of the concrete. Various polymer materials are widely used in the construction industry. This article, there is a summary of the current situation and knowledge of different categories of common polymeric additives. It also explains the context between the chemical structure of the additive and the macroscopic behavior of the resulting concrete [7, 16].

The Portland cement concrete has been studied by Akoba A.S, Phulari R.C, and Kembhavi S.B by adding some additional compounds known as admixtures. The composition of Portland cement is 51.8% (C_3S), 23% (C_2S), 7% (C_3A), 11% (C_4AF), 2.9% MgO, 2.5% (SO_3), 0.8% ignition loss, and 1.0% free CaO. Every admixture performs differently from the others and is tailored to meet a certain demand. The goal of the current study is to gather more detailed information in this area so that users of this chemical admixture in concrete can more clearly understand the suggested usage. The tests on compressive strength and workability of the concrete with standard Portland cement and Portland pozzolana cement with GGBS and admixture are given at various curing periods for M45 grade of concrete in this investigation on the performance of concrete with GGBS and different PCE-based water-reducing admixture to determine its behavior [17]. Superplasticizers are the most significant admixtures boosting concrete performance, according to Literature. The most significant advancements in the field of concrete construction in terms of greater strength, longer durability, less shrinkage, and safer installation have been made in recent decades as a result of the invention of new superplasticizers. The current experimental investigation examined the effects of several superplasticizers (PCE) in combination with various cement kinds. On M45 concrete, a chemical additive (PCE) was assessed. It was found that regardless of the kind of cement and addition, the compressive strength of PCE-based concrete was higher after 1 day, 3 days, 7 days, and 28 days than it was at those times for conventional concrete. Data on concrete compressive strength can be used to establish a good correlation [13, 17].

The adsorption behavior of a Poly-Naphthalene Sulfonate (PNS) superplasticizer and its relationship to the fluidity of cement paste has been studied for six types of cement. The adsorption behavior of a PNS superplasticizer and its relationship to the fluidity of cement paste are discussed in this article at a specific PNS superplasticizer dosage. The results show that incompatible cement has a greater PNS superplasticizer adsorption capacity due to the absence of soluble alkali sulphates. The amount of PNS adsorbed has an inverse relationship with the mini-slump area value of cement paste after 30 minutes, which means that the more PNS adsorbed, the lower the initial slump value and the greater the slump loss. Na_2SO_4 helps to widen the slump area since less PNS is absorbed as a result. More recently, it has been found that adding more calcium sulphate does not impair sodium sulfate's capacity to stop PNS from sticking to cement particles in cement pastes with W/C = 0.35. The impact of alkali sulphate on the dispersing process of PNS super-plasticized cement pastes is discussed concerning the first slump and its elimination [3, 13]. It is well accepted that when the dosage of superplasticizer rises, cement paste fluidity typically rises as well. This effect was explained in literature as follows: the higher the dose of Poly-Naphthalene Sulfonate (PNS), the greater PNS that has been adsorbed on cement particles, and the more fluid cement pastes are. These phenomena are based on the fact that PNS adsorption can give cement particles a net negative electrical charge on their surface and short-range steric hindrance, which causes repulsive interactions to exist between nearby cement particles and enhances dispersion. The electrostatic repelling forces that the superplasticizer caused were found to exist. It has been shown that the PNS superplasticizer increases the negative zeta potential of cement particles [2, 3].

According, to previous studies the steric-repelling forces produced by superplasticizer molecules are just as significant as the dispersing mechanism. Some researchers corroborated these findings because high-molecular-weight polymers produce additional short-range repulsive forces while low-molecular-weight polymers often have moderate water reduction and low paste fluidity properties. Studies have more recently thought about the relative significance of electrostatic and steric influence on particle repulsion. They concluded that whereas electrostatic forces are important for the dispersion of PNS superplasticizer, steric forces are important for a copolymer of acrylic acid and acrylic ester superplasticizer. However, it is commonly believed that superplasticizer molecules must be adsorbed on surfaces before these two dispersing methods. The results in this study confirmed that the behavioral changes in the properties of the mixture are only because of the non-adsorbed polymer as well as the adsorbed polymer, which in turn affects the mixture's viscosity because of the increased amount of air added. Because the polymer with the lowest molecular weight delays hydration the most, high-dose polymers vary the most whereas the effect is similar across the board for low dosage in all polymers because the addition of PNS superplasticizers starts a process that is extremely complex because of several processes starting side by side [1, 18]. This study the processes which involved the mechanisms and their impact on the cementitious system. It showed that all of the PNS showed the same behavior and macroscopic involvement up to Critical Dosage (CD) but the molecules with higher molecular weight required greater concentrations to start the plasticizing effect but the reduction of viscosity was unaffected. The polymer with the lowest molecular weight showed hydration retardation over CD, so can say that the mechanisms can be explained concerning CD and Saturation Dosage (SD). Furthermore, PNS also harms cement hydration and can conclude that using superplasticizers (PNS to be specific) can have a major effect on the processes that occur therefore a complete understanding of the effect it has is vital to develop better methods and additives that can enhance the final qualities of cement and concrete manufacture.

Utilizing solely PNS in unsaturated doses results in a gradual decrease in fluidity and an increase in the amount of PNS adsorbed onto particle surfaces for cement. An appropriate SG dosage can minimize the fluidity loss of the cement when PNS is not at the saturated level. The amount of adsorbed PNS reduces as SG is added, and the magnitude of the decline increases over time. Similar patterns are shown for cement, suggesting that SG's ability to retain fluidity is not only due to the suppression of cement hydration. On the surface of the powder particle, PNS and SG are competing for adsorption. Because SG can prevent the PNS adsorption model from switching from a caudal style to a ring and horizontal style, fluidity loss in pastes containing PNS is reduced. The influence of SG on the rate at which a caudal style changes into a ring style and then into a horizontal style, in addition to its ability to prevent cement hydration, is a crucial element in minimizing the paste's loss of fluidity [15, 19].

EXPERIMENTAL SECTION

To achieve the objective, the research is divided into two phases which are to determine the optimum amount of PNS in M70 concrete mix design and modification. This research is being carried out with the collaboration of Bond Chemicals Pvt Ltd, hence are provided with the mix design of concrete that has the potential to give a compressive strength of 10000psi and Poly Naphthalene-Sulphonate (PNS) admixture must be used. Various solution samples were prepared by varying PNS amounts from 20%, 30%, 40%, 50%, and 60% of PNS by weight of solution keeping a constant dosage of molasses and gluconate (2.2%) along with water on application. After these samples, it was concluded that the optimum lay between the 40% to 50% dosage of PNS. Thus, to find the best amount more samples were made in which the PNS amount was set to be 44%, 48% and 52% by weight was admixture solution.

Slump testing (ASTM C143)

The slump is then taken, in the slump cone or Abram's cone. The cone normally measures 300mm tall, 200mm in diameter at the bottom, and 100mm at the top. It has a connected handle and is open on both ends. Following American standards, the concrete is poured into the cone using a scup in three stages, with each layer being tapped 25 times (15 times near the circumference and 10 times in the middle) with a 600 mm long bullet-nosed metal rod of 16 mm diameter. The concrete is struck off flush with the top of the mold at the third stage's conclusion. With care, the mold is raised vertically and away from the concrete cone. Since 120mm slump is much low thus not acceptable for the workability and playability of high-strength concrete. Therefore, the percentage of admixture solution is increased until the required slump is attained at constant w/ (c +p).

Casting and curing of cylinder (ASTM C31)

After the initial slump of concrete, the slump is again taken at 30 min and 60 min. After attaining the optimum value of the slump, the casting of cylinders is done within 15 min after slump taking. The concrete is poured in a cylindrical mold of 150mm x 300mm, and placed in three equal layers (two scoops for each layer). Each layer is tapped 25 times by the same metal rod used for the slump. The voids which are left by a tamping rod are removed by tapping the outside of the cylinder 10-15 times. To develop a flat and even surface, the surface is struck off with a handheld float and trowel. The cylinder is then stored at room temperature (60ºF-80ºF) for 24-48 hours this is called initial curing. After initial curing of 24-48 hours, cylinders are removed from the mold. For final curing, the concrete cylinders are then placed in a water bath within 30 min of mold removal to make sure the proper hydration of cement.

Compressive strength testing (ASTM C39-86)

One cylinder is taken out from the curing tank to check the 7 days strength of the cylinder. The cylinder is then placed at room temperature for a certain period to wipe out the excess water from the surface. The cylinder is then vertically placed on the platform of the compressive testing machine. Caps pad at the ends of the cylinder to facilitate uniform load application and distribution.

Preparation and mixing of PNS-44, PNS-48, and PNS-52

To check the impact of PNS on dispersion and fluidity in concrete. In this sample, increased the amount of PNS from 444g to 522g which is 44%, 48%, and 52% by weight in the solution of admixture. 444 g (44%) of the PNS-44, 488 g (48%) of the PNS-48, and 522 g (52%) of the PNS-52 are taken in three beakers. About 22gm of molasses and sodium gluconate is measured in three beakers, as a further increase in amount will result adversely. Both were stirred with PNS in an automatic stirrer along with 512 g water for 5 mins to ensure the proper mixing in different beakers. Now pour the brownish thick liquid into a separate beaker that will be used in the prepared mix design. The pH is measured by the pH tester which is 8 (PNS-44), 8.3 (PNS-48), and 8.3 (PNS-52). By dipping a hydrometer into a test tube containing a solution, the specific gravity of PNS-44, PNS-48, and PNS-52 is measured at 1.27. The amounts of components shown in Table 2 are used in high-strength concrete (M70) to see the workability and strength. The proportions are designed for one cubic meter of cement and these proportions are reduced for the four cylinders of 150mm diameter, and 300mm height casting, the reduced proportion. The application involves the preparation of concrete mix design in a pan mixer and during mixing, an admixture solution is added. Slump is then measured and the prepared concrete is then cast in the cylinders. Since the concrete is designed to give the strength of 1000psi according to the objective (M70) for a given w/(c+p) ratio.

Table 2: Admixture solution

Cement (c) (kg)	Silica (p) (kg)	Sand (Kg)	Crush (kg)	Water (w) (kg)	w/(c+p)
Admixture Solution of PNS44					
13.5	1.25	17.8	24.15	4.2	0.25
Mix design proportions of M70 concrete for 1m^3 concrete					
550	50	712	966	168	0.25
Mix design proportions of M70 concrete for 4 cylinders					
13.5	1.25	17.8	24.15	4.2	0.25

The sample PNS44 is mixed according to the steps. The concrete mix design is weighed by M70 proportion as shown in Table 2, to attain a strength of 10000Psi (70 MPa) at 28 days according to ACI-318. All the concrete components except water are mixed in a pan mixer. 75% of weighed water is then added to a mixture during the mixing of dry components and mixing is continued for 2 minutes. The remaining 25% water is added with 1.5% admixture in the mixer, followed by 2 minutes of mixing. Then after the mixing of sample slump is taken according to the ASTM C143. The uniform load is continuously applied without shock at the rate of 78683 lb. per min, this is continued until the specimen failed and maximum strength of 4452 psi PNS-44, 4431 psi PNS-48, and 4770

Table 3: Concrete mix design for PNS-44, PNS-48, and PNS-52

Mix Design					Sol. (%)	w/c+p	Slump (mm)			Strength (psi)	
Cement (c) (Kg)	Sand (p) (Kg)	Water (w) (Kg)	Crush (Kg)	Silica (Kg)			0 (min)	30 (min)	60 (min)	7 days	28 days
13.75	17.8	4.2	24.15	1.25	For PNS-44						
					1.5	2.5	120	100	70	-	-
					1.6		130	110	80	-	-
					1.8		190	170	130	4452	6360
					For PNS-48						
					1.5		140	110	90	-	-
					1.6	2.5	170	120	100	-	-
					1.8		190	170	130	4431	5895
					For PNS-52						
					1.5	2.5	120	100	70	-	-
					1.6		170	110	80	-	-
					1.8		230	210	190	4770	5247

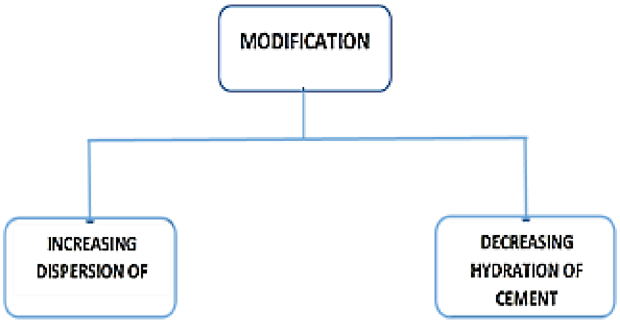


Fig. 2: Modification of the selected base sample

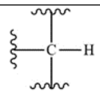
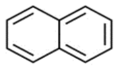
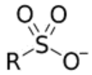
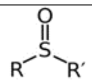
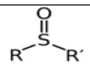
psi PNS-55 at 7 days is recorded. Similarly, the 2nd cylinder is taken out from the curing bath after 28 days, and its strength is found to be 6360 psi PNS-44, 5895 psi PNS-48, and 5247 psi PNS-52 as shown in Table 3.

Modifications

From the samples, it was concluded that the optimum amount of PNS for M70 concrete was 44% as shown in sample 1 application Table 3 because it gives the best strength of 6360 psi, among all the casted samples. Thus, all the samples were prepared by modifying this optimum amount of PNS, considering this as a base sample. The modification of the above-selected base sample is done by increasing the dispersion of PNS and secondly by controlling the hydration of cement as shown in Fig. 2. The plasticizing effect of the PNS is related to its adsorption and dispersing effect. The PNS has poor compatibility with cement that causes a great slump loss because when PNS reacted with cement by hydration causes an organic mineral phase that causes a decrease in fluidity but apart from hydration, the transformation of PNS adsorptive style is mainly by caudal style or ring style is also responsible for the fluidity loss. The dispersion is affected by the structure; therefore, the effect of structure change by removing oligomers was investigated. Moreover, numerous studies showed that an increase in the amount of sodium gluconate, and the addition of sodium sulphate and sulphonic acid also affect the dispersion hence the change in strength was observed by modifying the PNS concrete admixture using these additives. When the hydration of cement occurs, new active points generate. Initially, the concentration of PNS is high and active points are low in the paste, then with time, PNS gets adsorbed onto these new active points. But due to the remaining insufficient amount of PNS, the adsorption style may transform to a horizontal style by caudal or ring style. By these transformations, the zeta potential and the steric or repulsive effect decrease causing a reduced fluidity of paste. In different studies, the hydration of cement was controlled by adding sodium Lauryl ether sulphate (SLS), polytetrafluoroethylene (PTFE), and sulfuric acid. Hence, in this study SLS, PTFE and H_2SO_4 were used to observe the change in the hydration of cement. [4, 20].

Normally Poly Naphthalene Sulfonate (PNS) is used as a concrete admixture in normal concrete and for other grades of concrete other high range water reducing concrete admixture (for instance; Poly carboxylate Ether-PCE) is used which is a high-cost, while PNS is cheap. The aim and objective of the research are to modify the properties of Poly naphthalene sulfonate such that it could be used in high-strength concrete instead of PCE to make our concrete cost-effective. Simply the motive of this work

Table 4: FT-IR results of poly-naphthalene sulphonate

Sr. No.	Functional Groups	Molecular Vibrations/ Bands	Wavelength (cm^{-1})
1		C-H stretching band	3425
2		Aromatic rings	1595 and 1505
3		Sulphonate groups	1175 and1031
4		S=O Stretch sulphoxide	1356
5		S=O group	676

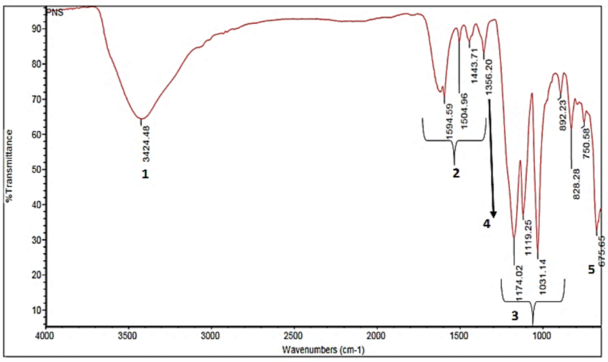


Fig. 3: FTIR Poly-naphthalene sulphonate

is to get the same benefits of the costly product from the cheap product by modification. Hence before modification, it was necessary to find the optimum amount of PNS which gives better workability in the high-strength concrete mix design.

RESULTS & DISCUSSION

Effect of sodium gluconate and molasses

Due to the adverse effect of PNS on fluidity and workability, it is being compounded with sodium gluconate (SG) which is used as a retarder and accelerator in concretes. The use of retarder is beneficial because it inhibits the amount of PNS adsorbed or wrapped onto cement molecules, thereby overcoming the fluidity loss. After adding SG in PNS, adsorption occurs between both because of the low molecular weight of SG that causes fast diffusion. As a result, sodium gluconate reduces the amount of adsorbed PNS on cement, which is why the setting and hardening behavior is regulated. Additionally, sodium gluconate can stop the PNS from changing from its caudal or ring style to its horizontal adsorption style, which will lessen fluidity loss. PNS initially caudally adsorbed on the cement molecules. The PNS's adsorptive style eventually altered to a caudal style as a result of the SG adhering to particular action locations, increasing the initial fluidity [13, 21]. The use of superplasticizers in the production of mortar or concrete influences the hydration kinetics and the amount of total heat and it adversely affects the workability due to slump loss and reduced water/cement ratio Therefore, a retarding agent is required to postpone hydration. Molasses' sugar serves as a potent retardant and causes a considerable increase in initial and final setting time. It coagulates the cement particles thereby decreasing the rate of cement hydration, thus inhibiting the setting of cement without influencing the strength. From the research, it is concluded to use molasses up to 0.05%, and on further increase in the amount, it will decrease the setting times.

Poly-Naphthalene sulphonate FT-IR results

To identify the components, an FT-IR (Fourier Transform InfraRed spectroscopy) test was conducted. The FTIR spectra were collected with 32 scans and a resolution of 4 cm^{-1}. It is an analytical technique used to recognize organic (and in rare cases inorganic) material as well. Using this method, you may measure how much-infrared light a sample material absorbs with wavelength. Infrared adsorption reveals the parts and structures of molecules. So, in comparison to the standard FT-IR report from the literature, the obtained results were checked and it was found that it is a pure PNS compound shown in Fig. 3 and Table 4 [12, 22].

Table 5: PNS structural composition

Categories	Chains (%)	Degree of Polymerization	Molar Mass (g/mol)
Oligomers	10	1- 4	900
Linear chains	20-30	20	5000
Branched chains	35	20-40	10,000
Cross linking chains	25	200	50,000

Targeting dispersion of poly-naphthalene sulphonate

The dispersion of the PNS is taken into account to increase the strength of the concrete. Commercially used poly naphthalene sulphonate generally has a high degree of polydispersity index. The structure of PNS is classified into three linear groups, cross-linked, branched molecules as shown in Table 5. It is concluded that a large number of nonlinear molecules in more or less 3D structures is present in commercial PNS. The dispersion properties of PNS in cement molecules affects by its structure. The dispersion of the polymer in cement suspension is reduced due to the presence of high molar mass cross-linked molecules and also by smaller molecules with a lesser degree of polymerization (monomers and oligomers), but their amount can't be controlled during the reaction. To remove the cross-linked molecules from PNS it is dissolved in water. By dissolving, cross-linked molecules should be settled down. Then the crosslinked free PNS is then separated as a filtrate. On testing, the results showed that PNS was free from crosslinking molecules. PNS is dissolved in alcohol to remove the oligomers. Oligomers will be dissolved and removed with alcohol. On this test using industrial-grade isopropyl alcohol oligomers were removed from PNS [1, 23].

Preparation of samples admixture

500 g was dissolved in 5 dm^3 isopropyl alcohol. Oligomers were removed with alcohol by filtration. The remaining filtrate was dried in an oven at 60ºC. The weight of dried filtrate was found to be 466g means that about 34g oligomers were present in the polymer. Now admixture solution is prepared by taking 444g oligomer-free PNS with 22 g gluconate and molasses stirred in an automatic stirrer along with 512 g water for 5 mins to ensure the proper mixing is shown in Table 6. Now pour the brownish thick liquid into a separate beaker that will be used in the prepared mix design.

The prepared sample is applied to the concrete of the same mixed design mentioned in Table 4. The admixture ratio is first taken at 1.5% which gives the slump of 210mm but to see the further effect the admixture is increased to 1.6% (amount of PNS in 1.6% admixture solution is 77) and at this initial slump of 230mm is recorded as shown in Table 7. The 28 days strength was found to be 7000 Psi.

The aim of the modification in this sample 2 was also to increase the dispersion of the cement particles. In this sample, sodium sulphate is used to control the production of tri-calcium aluminate and ettringite. The sodium sulphate is directly added to cement during application along with base sample admixture. The mixed design used was the same as the M70. In sample 3 to increase the dispersion effect of PNS in cement molecules, 50% concentrated sulphonic acid was used as a dispersing agent. As know that zeta potential is inversely related to pH. So, to decrease the pH, acid is directly added to the concrete of M70 along with the PNS-44 admixture recipe. The pH of concrete after adding the acid was found by pH-paper, which decreased to 12 from 13.5. Note that there is a restriction according to American Standard that the allowable pH is 12. But due to the presence of foams in sulphonic acid "Light Weight Concrete "was produced, which has high air entrainment and is less dense. It is primarily used for freeze-thaw resistance in freeze events as a result of the pressure relief sites that air gaps offer, the water inside the concrete can freeze, preventing significant internal tensions. The slump was recorded at 220mm initially but it cannot give us the required strength due to the presence of a large number of air voids.

Sample 4 to increase the dispersion effect of PNS in cement molecule 50% concentrated sulphonic acid with approximately 20 gm of the antifoaming agent was used and directly added into the concrete of M70 along with the PNS-00 admixture recipe. The pH of concrete after adding the acid was found by pH-paper, which decreased to 13. The initial slump of 300mm is recorded. The 28 days strength was found to be 7849 psi as shown in Table 7.

Sample 5 to check the impact of gluconate on dispersion and fluidity in concrete. Sodium gluconate is utilized as a retarder in admixture which delays the setting time

Table 6: Admixture solution sample 1

Solution Recipe				Physical Properties	
Oligomer free PNS	Molasses (g)	Gluconate (g)	Water (g)	Specific Gravity	pH
444	22	22	512	1.256	7.9

Table 7: Concrete mix design for samples

Mix Design					Sol. (%)	w/c+p	Slump (mm)			Strength (psi)	
Cement (c) (Kg)	Sand (p) (Kg)	Water (w) (Kg)	Crush (Kg)	Silica (Kg)			0 (min)	30 (min)	60 (min)	7 days	28 days
13.75	17.8	4.2	24.15	1.25	For sample 1						
					1.5	2.5	210	170	160	-	-
					1.6		230	220	210	5565	7000
					1.8		Collapse	-	-	-	-
					For sample 4						
					1.5	2.5	Collapse	250	230	4757	7849
					For sample 5						
					1.5	2.5	210	150	170	-	-
					1.6		240	170	110	5963	9262
					For sample 6						
					1.5	2.5	200	170	140	-	-
					1.6		230	210	200	5150	6996
					For sample 7						
					1.5	2.5	210	150	70	-	-
					1.6		230	170	100	-	-
					1.8		240	200	170	6360	8228
					For sample 8						
					1.5	2.5	210	150	100	-	-
					1.6		230	200	170	-	-
					1.8		Collapse	250	200	7060	8500
					For sample 9						
					1.5	2.5	Collapse	240	230	7990	10534

of concrete. In this sample, 5% gluconate by weight of admixture was increased to reduce the active point formation during the hydration of cement which reduces the PNS adsorption. Admixture of the sample prepared the amount of gluconate varied from 22gm to 23.10 gm which is a 5 % increment by weight of PNS. Both were stirred with PNS in an automatic stirrer along with 512 g water for 5 mins to ensure the proper mixing. They are used in high-strength concrete (M70) to see the workability and strength. The prepared sample of high gluconate dosage is applied on the concrete of the same mixed design mentioned in Table 4. The admixture ratio is first taken at 1.5% which gives the slump of 210mm but to see the further effect the admixture is increased to 1.6% (amount of PNS in 1.6% admixture solution) and at this initial slump of 240mm. is recorded as shown in Table 7. The 28 days strength was found to be 9262 psi.

Targeting hydration of cement

Now the hydration phenomenon is targeted to achieve the required strength in the samples. Cement hydration is an exothermic reaction, it is defined in the stages. Stage I mixing period, during which time various phases enter the solution and form various ions. The breakdown happens quickly and generates heat. Ettringite, a hydrated trisulfide-aluminate salt of calcium, is formed by the combination of Ca^{2+}, AlO_2^-, SO_4^{2-} and OH^- ions originating from the interstitial phase and from the various forms of calcium sulphate that are present in the cement. Together, these ions come from the silicate phases of the clinker and cover a portion of the cement surface. In stage II dormant period, the pH and Ca^{2+} both increases, and the solution is become saturated with Ca^{2+}, which reduces the amount of dissolution of the clinker phase. The rate of formation of ettringite and the rate of heat production also a slowdown in dormancy. The stage III setting period or acceleration of hydration usually occurred five to six hours after mixing. The setting is "triggered off" by the sudden precipitation of portlandite crystal (lime), the chemical trigger of hydration. The precipitation of lime is due to the decrease in the concentration in the aqueous phase of silicate. The anhydrous phase of clinker dissolves more quickly due to the quick consumption of Ca^{2+} and OH^- during lime production. Because CH precipitation is endothermic and consumes some heat, the heat creation starts slowly and then picks up speed as it progresses. Less calcium sulphate than is necessary to react with the aluminate stage is present in stage IV hardening, which causes SO_4^{2-} particles to initially be consumed by the ettringite development. This often occurs between nine and fifteen hours after the initial blending. Ettringite then serves as a source of sulphate to combine with the remaining aluminate stage to form mono-sulfoaluminate. This reaction produces heat and accelerates the hydration of the silicate phases. The concrete grains are covered by a coating of hydrates that thickens during Stage V slow down, making it logically more difficult for water particles to reach the still-unhydrated portions of the concrete grains via this thick layer. Since hydration is mostly governed by the rate at which water atoms diffuse through the hydrate layers, it slows down. As a result, the hydrated cement paste, also known as an internal product, manifests as an extremely dense, "amorphous," enormous paste [10, 21].

Samples 6 and 7

In this sample 6, Sodium Lauryl Ether Sulphate (SLES) is used to target the cement hydration. Sodium lauryl ether sulfate (SLES) is an anionic surfactant extensively used, especially in industrial applications. In this sample, SLES is dissolved in the mixing water of concrete along with the antifoaming agent (silicon-based) because dissolution in water increases the viscosity of the water as well as creates some foam. In this sample, about 80 g of SLES is added to half of the mixing water (2.1 Kg) to achieve the acceptable viscosity to slower down the cement hydration reaction. Note that the SLES is added till the water changes to gel-like material but the viscosity should be in that range that gives proper mixing of concrete components. The prepared mixing water is then applied to the concrete of the same mixed design. The admixture ratio is first taken at 1.5% which gives the slump of 200mm but to see the further effect the admixture is increased to 1.6% and this initial slump of 230mm is recorded as shown in Table 7.

In sample 7, 5g PTFE was added to half of the mixing water of concrete (2.1 Kg). A further amount of PTFE is increased but it makes the water highly viscous (like wax) so it can't give the slump. The prepared mixing water is then applied to the concrete of the same mixed design. The admixture ratio is first taken at 1.5% and then 1.6% but doesn't give enough fluidity to see the further effect the admixture is increased to 1.8% and at this initial slump of 240mm is recorded as shown in Table 7. The 28 days strength was found to be 8228 psi.

Sample 8 targeting dispersion and hydration (addition of PTFE+ 5% gluconate)

This sample was the trial based on the hypothesis to target affecting factors that are increasing dispersion and decreasing hydration. In this sample, both dispersion and hydration are targeted by adding PTFE in the mixing water of concrete and the admixture used in this sample was a 5% incremented gluconate admixture (admixture of sample 5). In the sample, the admixture solution was used the same as sample 5 to check the impact of gluconate on dispersion and fluidity in concrete. In this sample, 5% gluconate by weight of admixture was increased to reduce the active point formation during the hydration of cement which reduces the PNS adsorption. In this sample, PTFE was mixed with the mixing water of the concrete mix design same as in sample 6. The admixture ratio is first taken at 1.5% then 1.6% but didn't give enough fluidity to see the further effect the admixture is increased to 1.8% and at this initial slump of 290mm is recorded is considered to be collapse as shown in Table 7. The 28 days strength was found to be 8500 psi.

Sample 9 targeting hydration by H_2SO_4

In this sample, hydration is slowdown by adding oil of vitriol that is H_2SO_4 (60%-70% conc.). As H_2SO_4 is hygroscopic so it readily absorbs water at a very slow rate.

Table 8: Sample 9 on different dosages

Dosage of Acid	Slump			Strength (psi)
	0 (min)	30 (min)	60 (min)	28 Days
20 g	Collapse	230	200	7643
30 g	Collapse	240	230	10800
40 g	Collapse	270	250	8067

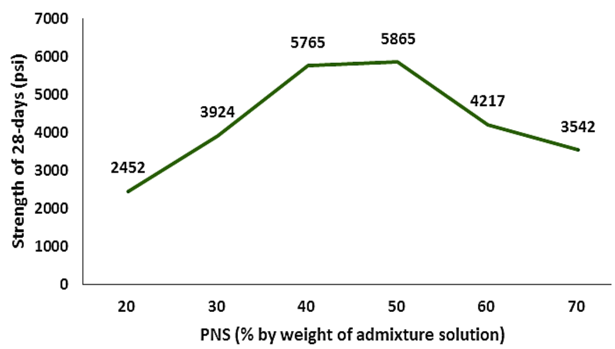


Fig. 4: Amount of PNS in solution and strength

The other aim was to lower the pH to increase the zeta potential which increases the early strength of the concrete. In this sample, about 70 % concentrated acid was used in this sample. These three different grams of acid were added to study the effect of the dispersion of hydration in presence of sulphuric acid which is 20g, 30g, and 40g as shown in Table 8. In this sample, it was added to the mixing water of concrete by which it was dissociated. When water is added to the application of concrete, the hydration becomes slowed down which allows cement to give better strength [5, 24]. The admixture ratio is first taken from 1.5% to 1.8% but the fluidity was not acceptable for the placement of concrete. Thus, then all the samples were run on a 2%. Among all the samples in Table 8, 30 g was the most suitable of all in terms of strength. It also fulfills the objective strength. When 30g acid (60 % conc.) was added in the half mixing water it gives the initial slump of 300mm which is called collapse and the 28 days strength was recorded to be 10,800 psi.

Optimization of Poly Naphthalene Sulfonate (PNS)

To find the optimum amount of PNS in admixture solution for 1000 psi concrete mixed design various samples are prepared at 25% to 70% PNS dosage by weight of admixture solution. The strengths are recorded at a constant dosage of admixture in concrete (1.8% by weight cementitious material in concrete) as shown in Fig. 4. It shows that as optimum amount of PNS lies between 40-50 percent. In the initials stage as the amount of PNS increases strength also increases but after the optimum range strength decreases with the increment of PNS this is because the increase in PNS causes more active points in the cement by which the rate of hydration of cement particles increases and ettringite will form rapidly which reduces the strength [1, 2, 6].

Since the suitable range of dosage is 40-50 percent of PNS. So, to find the optimum point from this range further optimization is done at the constant dosage of admixture in the concrete as shown in Figs. 5 and 6. Further samples are prepared in the optimum range by adding 44% (PNS44), 48% (PNS48), and 52% (PNS52) dosage of PNS by weight of the solution, and slump and strengths were recorded as shown in Figs. 5 and 6. The optimum point is found at 44% dosage where the slump was found to be 190mm and the strength was 6360psi. This point is selected because it gives the highest strength among all others.

Modification targeting dispersion samples

In sample 1 oligomer-free PNS was used. The oligomers were removed by using industrial-grade iso-propanol (ISP). 500g PNS was dissolved in 5L ISP which results in the removal of 34g oligomers from it. The oligomers are a short chain that does not disperse the cement particle and similarly the cross-linking hinder the cement particle dispersion. Only the normal chains give the proper dispersion to the cement particles by which free water will be able to release. Samples results are shown in Figs. 5 and 6. The results show that the removal of oligomers increased dispersion by which the slump was increased to 230mm at the dosage of 1.6% of cementitious material (while the slump of sample1 was 190mm at 1.6 % admixture dosage by weight of cementitious material). If this dosage is further increased it would increase the retention time. But this modification was failed due to the strength was found to 7000psi which is less than our objective strength (10000psi). It is not feasible for the factory to set up the plant for alcohol usage and its recovery due to its flammable nature [11, 13]. It is not cost-effective due high cost of alcohol.

In sample 2, the aim of the modification was also to increase the dispersion of the cement particles. In this sample, sodium sulphate is mixed with concrete. The presence of Na_2SO_4 will increases the concentration of sulphate ions formation during cement hydration which allows the cement particles to disperse easily due to the presence of more charges over them. But in our case silica fume is used as a pozzolan due to high-strength concrete so silica is would not allow Na_2SO_4 to make better dispersion. Hence in this sample concrete become chock and will give zero slumps so it failed. In sample 3 the dispersion in increased by adding sulphonic acid to the mixing water of concrete. As it is known that pH is inversely proportional to dispersion so to increase the dispersion sulphonic acid was added but when sulphonic is missed in water it created foams which made the concrete to be lightweight. So. The sample failed but this sample is further modified to sample 4.

In sample 4 silicon-based antifoaming agent was used along with sulphonic acid. The sulphonic acid is mixed in water and the results are shown in Figs. 5 and 6. It shows that sulphonic acid with PNS-based admixture increases the dispersion of cement particles by which the slump was increased to 230mm at the dosage of 1.6% of cementitious material in concrete. The pH of concrete was found to be 13.5 (according to ASTM the minimum pH for concrete should be 12 because if the pH will be lower than it, it will corrode the steel fibers) while normal concrete has a pH of 14. But in this sample required strength is not achieved [1, 3, 24].

In sample 5 dispersing ability of PNS is increased by increasing the dosage of sodium gluconate in the admixture solution. Sodium gluconate is used as a retarder in admixture which delays the setting time of concrete, by increasing the rate of activity of active points of types of cement. Gluconate molecules have fewer atomic radii as compared to PNS so it is easily penetrated between the gap left by PNS molecules between cement particles and increases the active points by which more free water comes out retention time increases. Not that its higher dosage will increase the retention time and may cause reduce in fluidity. So, in this sample, 5% gluconate (by weight of the previous amount of gluconate 22g) is increased and the results are shown in Figs. 5 and 6. The results show that the increment of gluconate in the sample increased the dispersion and the fluidity increased to 240mm (usually called a collapse slump) and the strength at 28-days was found to be 9262 psi which was very nearer to our required strength. Furthermore, the amount of gluconate is also increased to get better strength but it caused a delay in the setting time of concrete [10, 22].

Modification targeting hydration of cement samples

In sample 6 Sodium Lauryl Ether Sulphate (SLES) is used to target the cement hydration. When SLES is dissolved in the mixing water of concrete along with the antifoaming agent because on dissolution in water it creates foam (used with sulphonic acid) it increases its viscosity by which the hydration reaction was reduced. On reducing the hydration reaction rate ettringite formation decreases which increases the slump and strength as shown in Figs. 5 and 6. The results show that on the slowdown of hydration reaction the strength is increased to 6996 psi at 1.6% dosage of admixture by weight of cementitious and slump was found to be 230mm because the active points remain stable for more time. But this sample did not give the required strength. Further increase in the amount of SLES dosage may reduce the fluidity of concrete.

In sample 7 hydration of cement is targeted by adding polytetrafluoroethylene (PTFE) in the mixing water of concrete. Since PTFE is hydrophobic but it has a backbone chain of fluoride atoms and therefore has high electronegativity which allows it to interact with water and form hydrogen bonding. The interaction with water increases the viscosity of water. Therefore, 5g PNS was added to the mixing water of concrete and the results are shown in Figs. 5 and 6. The results show that strength and fluidity are increased due to the long stay of the active point of cement particles but the strength is lower than the requirement. A further amount of PTFE is increased but it makes the water highly viscous (like wax) so it can’t give the slump.

In sample 8 both dispersion and hydration are targeted by adding PTF in the mixing water of concrete and the admixture used in this sample was a 5% incremented gluconate admixture (admixture of sample 5). By targeting both factors rate of active points active points was to be increased and the results were recorded as shown in Figs. 5 and 6. The results show that the number of active points increased because the slump was 290mm (higher than sample 7) but the strength (become less than sample 7 where only PTFE is used). The decrease in strength as compared to alone samples where alone PTFE is used (sample 7) and only incremented gluconate solution is used alone (sample 5). This is because

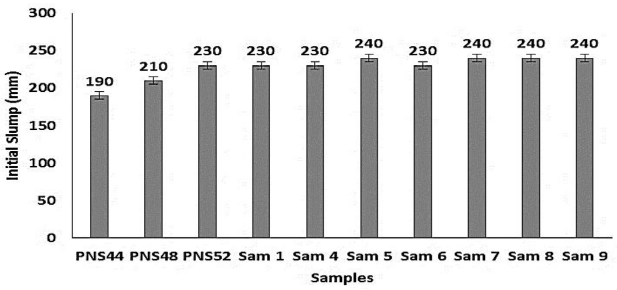


Fig. 5: Comparison of all samples for the initial slump

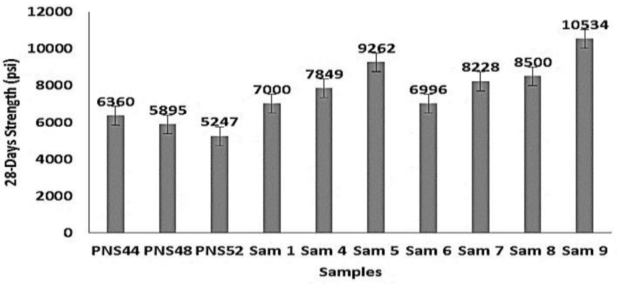


Fig. 6: Comparison of all samples for 28 days of strength

the active points formed were decreased after a while and hydration becomes rapid which results in a decrease in strength [2, 5, 6].

In sample 9 hydration is a slowdown by adding oil of vitriol H_2SO_4 (60%-70% conc.). As H_2SO_4 is hygroscopic so it readily absorbs water at a very slow rate. In this, it was added to the mixing water of concrete by which it was dissociated. When the water of the cement is absorbed by it, the hydration becomes slowed down which allow the cement to give better strength and binding force while the formation of SO_4^{-2} is also increased during 1st and 2nd stage of hydration which helps in better fluidity after some time (3-4 hours). It'll lose its fluidity because of the rapid reduction of active points and water absorption [25, 26]. So, in this sample, various amounts of H_2SO_4 were added to the mixing water of concrete to find the best suitable amount as shown in Fig. 7. The results show that 30g H_2SO_4 (which is 0.31% by weight of cementitious material) gives the required strength at the dosage of 2% by weight of cementitious material in concrete (along with the margin required commercially due to error if concrete prepared in bulk quantity) that is 10534psi. Note that all the above samples gave the collapse slump (>230mm). Hence the required slump (collapse for M70 concrete for ease of workability) and strength are achieved from these samples [3, 4, 15].

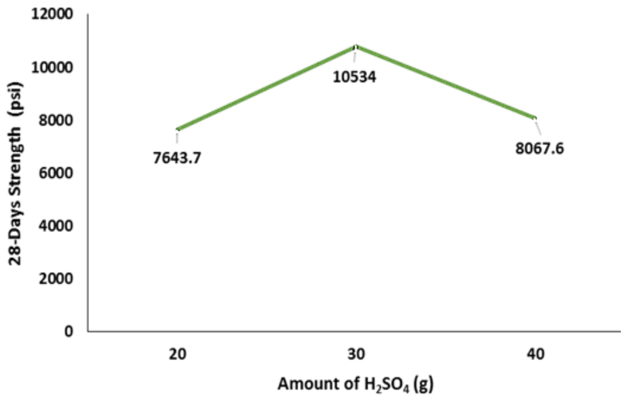


Fig. 7: Strength at various dosages of H_2SO_4

The samples formed by modification are tabulated in Table 9 according to the output that is it fails or gives better results. Since nine samples were made by modification by targeting the two factors, from both factors dispersion and hydration of cement two samples (sample 5 and sample 9 respectively) gave the desired results their slumps were founded to collapse (>230mm) and strengths (at 28-days) were found to be 9626psi (nearer to the requirement of 1000psi) and 10534psi respectively.

CONCLUSIONS

This research aims to make the cost-effective 2nd Generation concrete admixture such that it'll be able to run on the mix design of 1000psi strength (M70). It can provide 10000psi strength along with the high fluidity (slump) required for ease of workability. Normally on a 10000psi mix design, 3rd Generation admixture is used while PNS is used over less strength mix design proportion because in the M70 mix design high amount of cement is added where PNS does not work properly, workability and strength. In this research, PNS properties are enhanced to make it usable for M70 (10000psi) concrete such that it can be able to give high fluidity and required strength. The concrete admixture solution is composed of four components water, sodium gluconate, molasses, and PNS. In the first part of the research optimum amount of PNS was founded keeping constant other components of the solution and varying PNS that is to obtain the amount which gives better strength and slump on mixing it with concrete. Since by varying PNS dosage in the admixture solution various benchmarking different samples were prepared and tested, from these testing it is concluded that the admixture solution should consist of 44% PNS by its weight to give better results in the high strength concrete

Table 9: Modified samples and their outputs

Targeted Factor	Sample	Modification By	Achievements		Failure
			Slump	Strength and Slum Both	
Dispersion	Sample-1	Removal of Oligomers by using ISP	✓	-	-
	Sample-2	Addition of Na_2SO_4	-	-	✓
	Sample-3	Addition of Sulphonic acid	-	-	✓
	Sample-4	Addition of Sulphonic + Deformer	✓	-	-
	Sample-5	Increment of Gluconate	-	✓	-
Hydration of cement	Sample-6	Addition SLES	✓	-	-
	Sample-7	Addition of PTF	✓	-	-
	Sample-8	Addition of PTFE + Gluconate 5%	✓	-	-
	Sample-9	Addition of H_2SO_4	-	✓	-

mix design. In the 2nd phase of the research, modifications were done to this PNS-optimized admixture solution. Since there were two reactions hydration of cement and interaction of PNS and cement. So, based on these reactions two main factors were targeted for modification those were dispersion of cement particles and hydration of cement. It is evident from the results that among different additives, H_2SO_4 provided high strength which is 10534 psi by reducing the hydration of cement. Therefore, H_2SO_4 is considered the best additive for concrete in combination with PNS. In the future, the dispersion of the PNS in concrete can be targeted to further improve the strength of PNS concrete admixture.

List of Abbreviations

PIC	Polymer impregnated concrete
PMC	Polymer modified concrete
PC	Polymer concrete
SP	Superplasticizers
ASTM	American Society for Testing and Materials
RPC	Reinforced polymer concrete
PE	Polyethylene
EVA	Ethylene vinyl acetate
RDP's	Re-dispersible polymers
VAEC	Vinyl acetate and ethylene copolymer
SSC	Sea water and sea sand cement
W/C	Water to cement ratio
S/C	Sand to cement ratio

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