

Investigation on Concrete Properties for Nano Silica Concrete by using Different Plasticizers

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Abstract

This paper presents results of the optimal dosage levels of polycarboxylate-based (PSP) (0.4 and 0.8%) and naphthalene-based (NSP) (0.8 and 1.6%) super plasticizers and different water to binder (w/b) ratios (0.4 and 0.45) that produce an adequate balance between strength and workability for concrete containing nano-SiO₂ (NS) of 1%, 2%, and 3% as cement replacement. These results indicate that For two types super plasticizers mixes. Increasing the w/c ratio from 0.40 to 0.45 increased the slump of all mixes. Either those containing polycarboxylate or naphthalene sulphonate super plasticizer or the control mixes. For polycarboxylate super plasticizer mixes. Decreasing the w/c ratio from 0.45 to 0.40 increased the compressive strength of all mixes. Either those containing polycarboxylate super plasticizer. For naphthalene sulphonate super plasticizer mixes. Increasing the w/c ratio from 0.40 to 0.45 increased the compressive strength of all mixes. Either those containing 0.8 % naphthalene super plasticizer or the control mixes. While decreasing the w/c ratio from 0.45 to 0.40 increased the compressive strength of all mixes. Either those containing 1.6 % naphthalene sulphonate super plasticizer. the use of (1.6 %) sulphonated naphthalene super plasticizer (NSP) with 0.4 w/c ratio reached a gain in strength equivalent to the use of (0.8 %) polycarboxylic super plasticizer (PSP) for mix containing 3 % nano silica . the use of (1.6 %) naphthalene super plasticizer (NSP) with 0.45 w/c ratio reached a gain in strength equivalent to the use of (0.8 %) polycarboxylic super plasticizer (PSP) for mix containing 2 % nano silica.

Keywords: Nano silica, concrete, plasticizers, workability, strength.

1. Introduction

The addition of nanosilica (NS) has attracted increasing interest because of the filling effect, which improves the particle size distribution, thus reducing porosity, and the pozzolanic reaction between NS and calcium hydroxide (CH) yielding calcium silicate hydrates (C-S-H). These actions result in enhanced mechanical strength (Bjornstrom J et al. 2004, Kong D et al. 2010). The filling of the inter-particle space leads to a denser packing and reduces the water demand, as there is no need to fill the space with water. In this case, the use of a superplasticizer is required in order to guarantee workability (Kirby Gh et al. 2004). Furthermore, the strong tendency of NS to agglomerate also may make it necessary to use a dispersing additive in order to overcome this problem and to ensure enough reactive surface for the filling effect and C-S-H formation (Thomas Jj et al. 2009, Deyu Kong et al. 2013, Diamond S et al. 2006). Dispersing additives are the so-called plasticizers or superplasticizers, which have a water reducing action on cement materials.

This study aims to estimate the optimal dosage levels of SP of various types and different w/b ratios for concrete with different nano-SiO₂ (nS) additions. The program addresses the relationship between the fresh and hardened states in concrete.

1.1. Polycarboxylates super plasticizers (PSP) compatibility:

- Polycarboxylates super plasticizers (PSP) is the most effective of all the chemicals. These can cause a reduction in water content of as much as 40%. Thus, they are highly preferred to make high and ultra high strength concrete, where the w/c may be as low as 0.20. Generally, these chemicals exhibit excellent slump retention characteristics and do not cause any delay in the gain of strength of the concrete. The downside of these admixtures is their high cost. However, as stated earlier, for the same category of concrete (workability) (PSP)

can work at lower dosages than Sulphonated naphthalene (NSP). Thus, the overall cost of concrete is not affected. Only in the case of special concretes such as self compacting concrete (SCC), the use of (PSP) can substantially increase the concrete cost. It must be stated, though, that making good quality SCC without these latest generation super plasticizers is almost impossible. Limited experience with these chemicals indicates that they work well at low water to cement ratios, and exhibit fewer compatibility problems compared to (NSP).

For fluidity retention, the main chain should be short, with large numbers of long side chains [Sugiyama et al., 2003]. Because of the steric repulsion mechanism, (PSP) are generally more effective than the sulphonate based admixtures, and generally do not experience much problems at low water to cement ratios. However, they are more sensitive to overdosing, and can lead to problems like excessive air entrainment and retardation. Apart from affecting the early age physical properties of concrete, SPs can also cause some changes in the morphology of hydration products. Size of portlandite crystals decreases with addition of admixtures [Grabiec, 1999]. Ettringite in the presence of SPs (at high dosage) crystallizes in small and massive clusters rather than the conventional needle shape [Hanna et al., 2000; w. Prince et al., 2002]. In general, SPs improve rheological properties by yielding smaller hydrate particles and preventing hydration products from bridging neighbouring cement particles. There is also a difference in porosity and pore size distribution of superplasticized concrete compared to normal concrete. Higher numbers of smaller pores are produced in superplasticized mixtures, which could have an influence on the degree of shrinkage.

1.2. Sulphonated naphthalene super plasticizer (NSP) compatibility:

Sulphonated naphthalene (NSP) based super plasticizer formaldehyde condensates possess all the necessary characteristics to make them suitable for hot weather concreting. Mainly, these possess good slump retention characteristics, enabling their use in ready mixed concrete where long hauls are common. The cost of (NSP) is also low.

Sulphonated naphthalene super plasticizer (NSP) work on the mechanism of lowering zeta potential that leads to electrostatic repulsion. On the other hand, polymers with backbone and graft chains, such as (PSP) cause dispersion of cement grains by steric hindrance [Uchikawa et al., 1997]. Electrostatic repulsion depends on the composition of the solution phase and the adsorbed amount of the SP (greater the adsorption, better the repulsion) (Y. Nakajima et al. 2004). On the other hand, steric repulsion depends on the length of main chain, length and number of side chains [Sugiyama et al., 2003]. The Sulphonated naphthalene (NSP) based admixtures are most prone to rapid loss of workability, particularly at low water to cement ratios, which are the norm for most special concretes today. The low molecular weight fractions cause excessive retardation by covering reactive sites on the cement surface and inhibiting reactions. Another factor affecting (NSP) effectiveness is the location of the sulphonate ($-HSO_3$) group in the naphthalene structure. It is well accepted that the presence of the sulphonate group in the β -position leads to a high polymer charge and better electrostatic repulsion. (NSP) admixtures are more prone to slump loss problems at low w/c, as compared to the (PSP). (R. Gettu et al. 1997). feels that the lower w/c in super plasticized concrete and the resulting lower interparticle separation of the cement particles makes it more sensitive to loss of water by evaporation or reaction with cement during transportation of the concrete. In general, most compatibility problems only exist at low w/c.

The placing of concrete at Low temperature has been reported to decrease fluidity. This decrease in workability at low temperature cannot be compensated with SP [Gettu et al., 1997]. On the other hand, high temperatures increase SP adsorption which increases fluidity. Conversely, temperature increase causes increase in reactivity of C3A which causes higher ettringite contents with fine morphology in the presence of SP, thus causing a higher rate of slump loss. The influence of temperature on cement – SP interaction is closely associated with the cement composition.

2. Experimental work

The experimental program was divided into two major phases. In the first phase the objective study aims to estimate the optimal dosage levels of polycarboxylate super plasticizer (PSP) and different water to binder (w/b) ratios that produce an adequate balance between strength and workability of concrete with different nano-SiO₂ (NS) additions through a full factorial design and statistical analysis. In the second phase, the study aims to estimate the optimal dosage levels of naphthalene sulphonate super plasticizer (NSP) and different water to binder (w/b) ratios that produce an adequate balance between strength and workability for concrete containing nano-SiO₂ (NS) of 1%, 2%, and 3% as cement replacement will be introduced comparing the effect of the two types of super plasticizers on concrete behavior and performance. A total of 40 mixtures were prepared consisting each of sets of 6 cubes (15*15*15 cm³) to evaluate compression strength after 7, and 28 days of water curing. While for the fresh state measurements, the workability of concrete mixtures is measured by means of the standardized slump test as outlined by ASTM C-143.

2.1. Characterization of Used Materials:

Ordinary Portland Cement (OPC) conforming to ASTM C150 standard is to be used as received. The chemical and physical properties of the cement are shown in Table 4.1. SiO₂ amorphous and agglomerated nano particles with average particle size of 30 nm and 45 m²/g Blaine fineness produced from WINLAB laboratory chemicals, UK is to be used as received. The properties of SiO₂ nano particles are shown in Table 2.1. Transmission electron micrographs (TEM) and powder X-ray diffraction (XRD) diagrams of amorphous SiO₂ nano particles.

Table 2.1: Chemical composition of Portland cement and Nano SiO₂ (wt%).

Element	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	L.O.I	P ₂ O ₅
Cement	20.13	5.32	3.61	61.63	2.39	2.87	0.37	0.13	1.96	0
NS	99.17	0.13	0.06	0.14	0.11	0	0.40	0	0	0.01

For concrete production; Crushed limestone aggregates, as well as sand free of alkali-reactive materials are to be used to insure producing durable concretes. The aggregates are mixed by percentages of 65% for coarse aggregate, and 35% for fines by volume. The water used in the mix design was potable water from the water-supply network system. It was free from suspended solids and organic materials, which may affect the properties of the fresh and hardened concrete. A polycarboxylate with a polyethylene condensate de-foamed based admixture (Glenium C315 SCC) was used. A naphthalene sulphonate with a synthetic polymers, which allow mixing water condensate de-foamed based admixture (Rheobuild 1200) was used. Table 2.2 shows some of the physical and chemical properties of polycarboxylate and naphthalene sulphonate admixtures used in this study. The superplasticizer type was chosen for its electrostatic-steric behavior, which is thought to be more effective with nano silica dispersion.

Table 2.2: Physical and chemical characteristics of the polycarboxylate and naphthalene sulphonate admixtures.

	polycarboxylate admixture	naphthalene admixture
Appearance	Off white opaque liquid	Brown free - flowing liquid
Specific gravity	1.095 ± 0.02 g/cm ³ @ 20°C	1.190 - @ 24°C
PH-value	6.5 ± 1	-
Air – entrainment	-	Maximum 1 %
Alkali content (%)	Less than or equal to 2.00	-
Nitrate content (%)	-	Nil
Chloride content (%)	Less than or equal to 0.10	Nil to BS5075

Table 2.3: Samples of the polycarboxylate and naphthalene sulphonate super-plasticizers mixes, concrete mixtures composition by weight (kg) per 1 m³..

Mix	Cement	Aggregate		Water	P.S.P	N.S	Mixing Notes
		Coarse	Fine				
A0 P0	450	1168	629	180	0	0	Control mix
A1 P0	445.5	1168	629	180	0	4.5	Control mix
A2 P0	441	1168	629	180	0	9	Control mix
A3 P0	436.5	1168	629	180	0	13.5	Control mix
B0 P0	450	1168	629	202.5	0	0	Control mix
B1 P0	445.5	1168	629	202.5	0	4.5	Control mix
B2 P0	441	1168	629	202.5	0	9	Control mix
B3 P0	436.5	1168	629	202.5	0	13.5	Control mix
A0 P4	450	1168	629	180	1.6	0	Polycarboxylate plasticizer
A1 P4	445.5	1168	629	180	1.6	4.5	Polycarboxylate plasticizer
A2 P4	441	1168	629	180	1.6	9	Polycarboxylate plasticizer
A3 P4	436.5	1168	629	180	1.6	13.5	Polycarboxylate plasticizer
B0 P4	450	1168	629	202.5	1.6	0	Polycarboxylate plasticizer
B1 P4	445.5	1168	629	202.5	1.6	4.5	Polycarboxylate plasticizer
B2 P4	441	1168	629	202.5	1.6	9	Polycarboxylate plasticizer
B3 P4	436.5	1168	629	202.5	1.6	13.5	Polycarboxylate plasticizer
A0 P8	450	1168	629	180	3.3	0	Polycarboxylate plasticizer
A1 P8	445.5	1168	629	180	3.3	4.5	Polycarboxylate plasticizer
A2 P8	441	1168	629	180	3.3	9	Polycarboxylate plasticizer
A3 P8	436.5	1168	629	180	3.3	13.5	Polycarboxylate plasticizer
B0 P8	450	1168	629	202.5	3.3	0	Polycarboxylate plasticizer
B1 P8	445.5	1168	629	202.5	3.3	4.5	Polycarboxylate plasticizer
B2 P8	441	1168	629	202.5	3.3	9	Polycarboxylate plasticizer
B3 P8	436.5	1168	629	202.5	3.3	13.5	Polycarboxylate plasticizer
A0 N8	450	1168	629	180	3.3	0	Naphthalene plasticizer
A1 N8	445.5	1168	629	180	3.3	4.5	Naphthalene plasticizer
A2 N8	441	1168	629	180	3.3	9	Naphthalene plasticizer
A3 N8	436.5	1168	629	180	3.3	13.5	Naphthalene plasticizer
B0 N8	450	1168	629	202.5	3.3	0	Naphthalene plasticizer
B1 N8	445.5	1168	629	202.5	3.3	4.5	Naphthalene plasticizer
B2 N8	441	1168	629	202.5	3.3	9	Naphthalene plasticizer
B3 N8	436.5	1168	629	202.5	3.3	13.5	Naphthalene plasticizer
A0N16	450	1168	629	180	6.5	0	Naphthalene plasticizer
A1N16	445.5	1168	629	180	6.5	4.5	Naphthalene plasticizer
A2N16	441	1168	629	180	6.5	9	Naphthalene plasticizer
A3N16	436.5	1168	629	180	6.5	13.5	Naphthalene plasticizer
B0N16	450	1168	629	202.5	6.5	0	Naphthalene plasticizer
B1N16	445.5	1168	629	202.5	6.5	4.5	Naphthalene plasticizer
B2N16	441	1168	629	202.5	6.5	9	Naphthalene plasticizer
B3N16	436.5	1168	629	202.5	6.5	13.5	Naphthalene plasticizer

N.S: "nano silica, "A"0.40%(w/b), "B"0.45%(w/b) ratios, p0:non super plasticizer
 P.S.P:" a Polycarboxylate - N.S.P:" a naphthalene sulphonate super plasticizers

3. Results and Discussion

3.1. Slump test

3.1.1: The effect of nano silica on slump for polycarboxylate super plasticizer mix.

- As it can be seen from figures 1(a, and b), representing the non super plasticizer mixes, the slump decreased

by increasing the nano silica from 0% to 3% for the studied w/c ratios. The difference in the overall decreased slump reached 5 cm for 0.4.%w/c and 6cm for 0.45%w/c. while for mixes containing 0.4 % polycarboxylate super plasticizer, the slump decreased by 6 cm for 0.4.%w/c. for the 0.45 w/c mixes the slump decreased significantly after adding the nano silica (1%) to reach 8cm instead of 19cm for the control mix (0% ns). Increasing nano silica percentage over 1% decreased the slump more and more to reach a value of 4cm by adding 3% nano silica.

The mentioned above loss in slump by increasing the nano silica addition can be attributed to the fact that the silica nano-particle is almost a kind of in adhesive material, and by adding the feature of owning ultra high specific area and high surface energy of these particles, physical reaction would happen between nano-particles which will result in attraction of each other (Li et al. 2004, 2006). The more the number of silica nano-particles the higher the capability of these particles to gather around each other in the concrete matrix.

- For representing the 0.8 % polycarboxylate super plasticizer mixes, the slump decreased by increasing the nano silica from 0% ,to 3% . The difference in the decreased slump reached 10 cm for 0.45.%w/c . while with w/c 0.40% the slump values followed different pattern, the slump increased by adding 1% nano silica (5cm) then a significant drop in slump is reported for 2% and 3% nano silica addition .

The mentioned above gain in slump by adding 1% nano silica is a result of the fact that the well dispersed ultra fine particles have a higher workability as a consequence of high free water among the particles where the rolling effect can be observed. The earlier mentioned rolling effect is similar to the effect of fly ash (E.B. Nelson et al. 2006). It improves or facilitates the flowing of the cement paste, resulting in a lower water demand to obtain the same slump (G. Quercia et al. 2012). This conclusion was also mentioned by (Erich D. Rodriguez et al. 2012). While by increasing the nano silica percentage the slump starts to decrease because of the use of densified silica particles has a negative effect on the workability of fresh mixes, where this rolling effect disappears due to the presence of large irregular agglomerates.

3.1.2 The effect of the polycarboxylate super plasticizer percentages on slump

- Figures from (a and b), showed that the slump increased by increasing the polycarboxylate super plasticizer from 0% to 0.80% for all mixes.

The a above mentioned improvement in concrete workability by increasing polycarboxylate super plasticizer from 0% to 0.80%, at constant water/cement ratio is due to the adsorption of the plasticizer molecules on the solid particles, either by modifying the surface charge (zeta potential) of the particles, thus increasing the electrostatic repulsion, or by steric hindrance, causes a dispersing action, which has been claimed to be responsible for the increase in fluidity of the cement paste (A. Papo et al. 2004).

3.1.3. The effect of nano silica on slump for naphthalene sulphonate super plasticizer mixes

In order to understand the compatibility between nano silica and naphthalene sulphonate super plasticizer . we will first introduce based on previous literature the effect of superplasticiser dosage on workability of cement containing different percentage of silica fume. For a limited cement replacement by silica fume a lower superplasticiser content is needed to obtain a similar workability. For higher cement replacements, the required superplasticiser dosage is increasing with increasing cement replacement level. The influence of cement replacement level by silica fume on the required superplasticiser dosage seems to be similar for both cement types. Based on the work of (Jolicoeur et al. 1994), the optimal cement replacement level (in terms of required superplasticiser dosage) could be explained by two different phenomenons. The first phenomenon is linked to the adsorption of admixture molecules. Within their experiments, (Jolicoeur et al. 1994).found that silica fume adsorbs relatively low amounts of naphthalene sulphonate. The adsorption data for ordinary Portland cement normalised at unit surface area, show up to 10 times higher adsorption values. Adsorption of naphthalene sulphonate molecules in case of a blended binder system (Portland cement + 8% silica fume) is of the same order of magnitude as for ordinary Portland cement, although clearly somewhat lower (about 10% reduction when normalised at unit surface area). This first phenomenon could be called a 'dilution effect', due to the cement replacement by silica fume. The second phenomenon is determined by the increasing surface area with increasing cement replacement by silica fume. As silica fume is much finer than Portland cement particles, the blended binder system has a larger surface area per unit of mass. Even when only low amounts of naphthalene sulphonate molecules are adsorbed on silica fume particles (according to (Jolicoeur et al. 1994). about 0.2 mg/m²), the cumulated adsorption becomes relevant for higher cement replacement level. This second phenomenon could be called a 'surface area effect'. For limited replacement levels, the dilution effect is more important than the surface area effect, resulting in a decreasing required superplasticiser dosage. For higher replacement levels, the surface area effect becomes dominant, leading to increasing super plasticizer dosage. At intermediate replacement levels, an optimal superplasticiser dosage can be found (E.-H. Kadri et al. 2009).

- As it can be seen from figures 2 (a and b) . for the 0.80 % naphthalene sulphonate super plasticizer mixes, the slump decreased by increasing the nano silica from 0% ,to 3% . the difference in the overall decreased slump is 6 cm for 0.4.%w/c ,

- while for the 0.45 w/c mixes the slump decreased significantly after adding the nano silica (1%) to reach 4 cm instead of 20 cm for the nano silica mix (0% ns). Increasing nano silica percentage over 1% decreased the slump more and more.

For the above mentioned results, the surface area effect is dominant over the dilution effect due to the use of relatively small dosage (less than saturation =1.2%) of naphthalene sulphonate super plasticizer (0.8%), resulting in a increasing required superplasticiser dosage by increasing the nano silica from 0% ,to 3% and consequently decrease in slump.

- For the 1.60 % naphthalene sulphonate super plasticizer mixes the increase of nano silica percentage till 2% hasn't any significant effect on the slump results , while a significant drop is reported by the adding of 3% nano silica . by about 15cm for both 0.40 and 0.45.%w/c.

For the results of 0% to 2% nano silica addition, both ; the dilution and the surface area effects occurred together due to the use of relatively high dosage (more than saturation =1.2%) of naphthalene sulphonate super plasticizer (1.6%),and small amounts of nano silica resulting in keeping slump results constant. While by increasing the nano silica from to 3% the surface area effect dominates and consequently a decrease in slump is reported. an optimal superplasticiser dosage can be found between 0% to2% nano silica at 1.60 % naphthalene sulphonate super plasticizer .As it can be seen from figures 2 (a and b).

3.1.4. The effect of the naphthalene sulphonate super plasticizer percentages on slump

- As it can be seen from figures 2 (a and b), For naphthalene sulphonate super plasticizer mixes. Increasing the w/c ratio from 0.40 to 0.45 increased the slump of all mixes. Either those containing naphthalene sulphonate super plasticizer mixes on the control mixes
- The slump increased by increasing the naphthalene sulphonate super plasticizer from 0% to 1.60% .

The above mentioned increase in slump by increasing naphthalene sulphonate percentage can be attributed to the fact that naphthalene sulphonate based superplasticizer work on the mechanism of lowering zeta potential that leads to electrostatic repulsion. [Uchikawa et al., 1997] increasing the free water amount needed for mixing and consequently increasing slump.

3.1.5. The effect of nano silica on slump for polycarboxylic super plasticizer (PSP) and sulphonated naphthalene super plasticizer (NSP)

- As it can be seen from figures 1, and 2, the increase in w/c ratio from 0.40% and 0.45% increased the slump for all mixes except for the 1.60 % naphthalene sulphonate super plasticizer adding that showed equal slump for 0.80% polycarboxylate super plasticizer mixes

The naphthalene sulphonate admixtures are more prone to slump loss problems at low w/c, as compared to the polycarboxylate super plasticizer. feels that the lower w/c in super plasticized concrete and the resulting lower interparticle separation of the cement particles makes it more sensitive to loss of water by evaporation or reaction with cement during transportation of the concrete. In general, most compatibility problems only exist at low w/c.

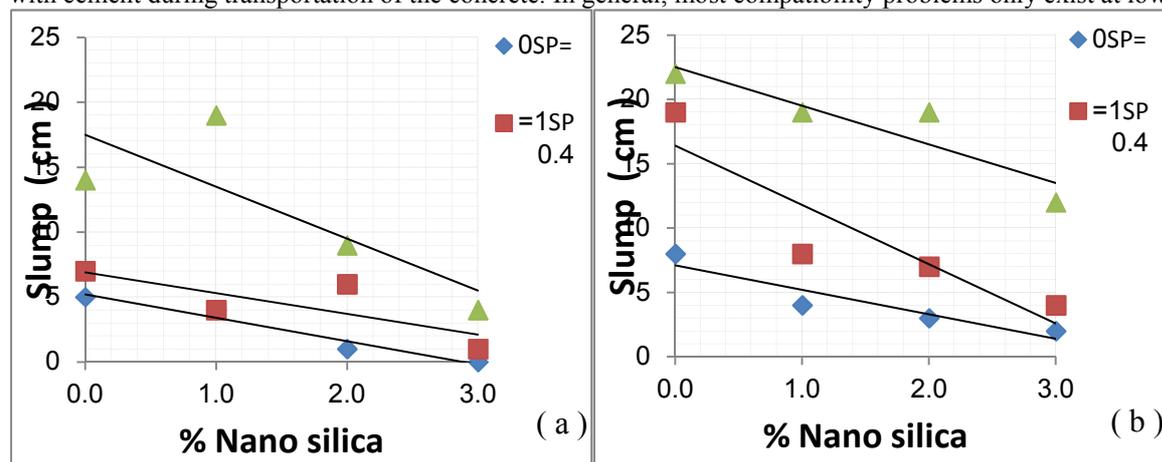


Figure 1 : the effect of Polycarboxylate super plasticizer on slump as compared to (a) 0.40% w/c, and (b) 0.45% w/c concrete mix

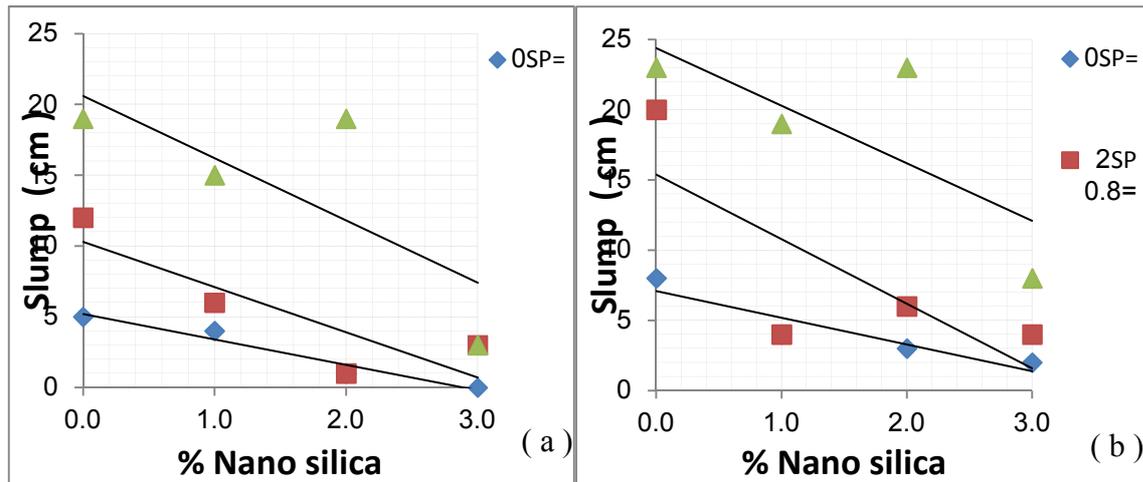


Figure 2 : the effect of naphthalene sulphonate super plasticizer on slump as compared to (a) 0.40% w/c, and (b) 0.45% w/c concrete mix

3.2. compressive strength

3.2.1 The effect of polycarboxylate super plasticizer and nano silica on Compressive strength for concrete mixes

As it can be seen from figures 3 and 4. for the non superplasticizer mixes, we can conclude the following :

- The compressive strength increase by increasing the w/c from 0.40 to 0.45 ranges from (4% to 33%) at 7 days of curing, and from (8% to 34%) at 28 days of curing.
- The compressive strength increased by adding 1 % nano silica then a significant loss in strength appeared for the 2 and 3 % nano silica for both w/c . at 7 days and 28 days of curing
- For w/c=0.4 , the compressive strength is decreased for (2 and 3%) nano silica to 0% nano silica . while the compressive strength is increased for w/c =0.45

The mechanical strength of tested mixes increased with increasing the amount of the silica nano particles up to 1%, and then slight reduction in compressive strength was reported. The results can be attributed to the fact that silica nano-particle is almost a kind of inadhesive material, and by adding the feature of owning ultra high specific area and high surface energy of these particles, physical reaction would happen between nano-particles which will result in attraction of each other (Li et al. 2004, 2006) . The more the number of silica nano-particles the higher the capability of these particles to gather around each other in the concrete matrix. This fact can contribute to conglomeration of nano-particles in concrete matrix (without happenstance of any chemical reaction) and subsequently strength loss; because the newly formed conglomerations are weak and alterable. In addition for the contents higher than 1%, the nano particles cannot easily disperse within the cement matrix, and due to their high surface energy, they become more agglomerated, hence a weak area of empty spaces such as voids appeared. Consequently, the structure formed in such conditions cannot be homogenous and compacted (Meral Oltulu et al. 2014). It was found that C-S-H gels from pozzolanic reaction of the agglomerates cannot function as binder. The gels from cement hydration did not penetrate into the pozzolanic gels. There even existed ITZ between the large reacted agglomerates and the bulk paste (Deyu Kong et al. 2012).

Similar results were reported by (Meral Oltulu et al. 2014). they concluded that among the mortars containing NS powder, the largest pore volume belongs into 2.5% NS group, while the lowest porosity was displayed by 1.25 % NS group. Since the pore sizes in S1.25NS group were mostly in the interval of 4–10 nm , it could be stated that the pores became finer after the addition of NS powder by 1.25%. The addition of nanosilica to mortar changed dramatically the pore distribution due to the proven behavior as nanofiller that caused a decrease of the pores in the range 10–100 nm [46]. The increasing pore volume of mortars after the addition of NS by 2.5% is associated with the drop in workability during the course of production induced by the agglomeration of powders. Increasing levels of NS powder, leads to the agglomeration of particles and hence the powders cannot be homogeneously dispersed within the mixture. Kuo et al. [21] also supported this assessment. The influence of NS powder on the pore structure was also validated through other supplementary tests, use of NS powder at proportions of 0.5% and 1.25% increased the compressive strength in parallel to decreasing capillary absorption coefficient of the mortars, while a proportion of 2.5% displayed the opposite effect. In consideration of these findings, it could be stated that the addition of NS powder enhances the compactness of mortars containing silica, up to a certain threshold – that was determined to be proportions greater than 1.25% within the scope of their study.

From the tested samples, the strength of early specimens (7 days) is dependent on the concentration of

CSH, produced from C3S, C2S, and CH (pozzolanically transformed). The contributions of early strength for all three mixes can be attributed to the cementitious and pozzolanic reaction. When agglomeration exists, high surface interaction occurs, and consequently the available SiO_2 free ions decreases, and so the early compressive strength decreases which can also be attributed to the water that was intended for hydration was hindered by the agglomerated particles. That is why by increasing NS%, the early strength decreases. As it can be seen from figure 4

Although in early stages, agglomerates affected the gain in strength significantly. Larger and/or agglomerated particles in the mix that had not completely dissolved in solution will reduce porosity in the pores/capillaries of the CSH gel by packing into some of these voids. In doing so, the density of the CSH will slightly increase in the plastic form and convert into a denser compressive bearing structure after hydration completes by the 28th day (Jonathan S. Belkowitz and Dr Daniel Armentrout. 2010) [101]. That explains why increasing agglomerated nano silica particles decreases early strength, while slightly increases late strength. As it can be seen from figure 4

The decrease in strength by decreasing w/c ratio can be a result of the presence of agglomerates that were unable to act as fillers will consume some free water that originally contributes to fluidity. They may also push away the cement particles around them, causing an increase of the void space. While by increasing the w/c ratio some of the consumed water is added.

As it can be seen from figures 3 and 4, for the 0.4% polycarboxylate superplasticizer, we can conclude the following:

- The compressive strength increase by decreasing the w/c from 0.45 to 0.40. the gain in strength ranges from (10% to 37%) at 7 days of curing, and from (5% to 21 %) at 28 days of curing
- The compressive strength increased by adding 1 % nano silica then a slight drop in strength appeared for the 2 and 3 % nano silica for both w/c . at 7 days and 28 days of curing
- The compressive strength increased by increasing the nano silica from 0 to 1 % at 7days and 28 days of curing for all mixes except for the 2% and 3 % nano silica where the strength decreased for 0.45% w/c.
- The highest compressive strength of all mixes was reached by the addition of 3% nano silica.by increasing the polycarboxylate super plasticizer from 0 to 0.40 to reach 394 kg/cm², with an increase of 75 % for 0.40 w/c and 356 kg/cm² , with an increase of 20 % for 0.45w/c at 7 days of curing,mix.
- The highest compressive strength of all mixes was reached by the addition of 3% nano silica.by increasing the polycarboxylate super plasticizer from 0 to 0.40 to reach 427 kg/cm² at 28 days of curing, with an increase of 66 % for 0.40 w/c mix.
- The highest compressive strength of all mixes was reached by the addition of 1% nano silica for 0.45w/c mixes then slight reduction in compressive strength was reported by increasing the polycarboxylate super plasticizer from 0 to 0.40 to reach 403 kg/cm² at 28 days of curing, with a decrease of 4 %

For the 0.80 % polycarboxylate superplasticizer, we can conclude the following :

- The compressive strength increase by decreasing the w/c from 0.45 to 0.40 ranges from (11% to 48%) at 7 days of curing, and from (14 % to 32 %) at 28 days of curing
- The compressive strength increased by increasing the nano silica for all mixes, at 7 and 28 days of curing.
- For polycarboxylate super plasticizer mixes. decreasing the w/c ratio from 0.45 to 0.40 increased the compressive strength of all mixes. Either those containing polycarboxylate super plasticizer.

The mentioned above gain in the compressive strength by increasing the nano silica from 0 to 3 % at 7days and 28 days of curing for all mixes is a result of the polycarboxylate superplasticizer addition which enhanced the dispersion of some of the nano silica particles. In addition, According to Yamakawa, the utilization of superplasticizer will have positive effects on properties of concrete, both in the fresh and hardened states. In the fresh state, utilization of superplasticizer will normally reduce tendency to bleeding due to the reduction in water/ cement ratio or water content of concrete. However, if water/ cement ratio is maintained, there is tendency that superplasticizer will prolong the time of set of concrete as more water is available to lubricate the mix.

The reported loss in compressive strength by increasing w/c from 0.4 to 0.45% can be attributed to the increase in entrapped water that promote hydration of cement. increase in w/c will reduce the compressive strength. This phenomenon will cause bleeding and segregation, which will affect the cohesiveness and uniformity of the concrete.

The above mentioned improvement in compressive strength concrete by increasing polycarboxylate super plasticizer from 0% to 0.80%, at constant water/cement ratio is due to the adsorption of the plasticizer molecules on the solid particles, either by modifying the surface charge (zeta potential) of the particles, thus increasing the electrostatic repulsion, or by steric hindrance, causes a dispersing action, which has been claimed to be responsible for the increase in fluidity of the cement paste (A. Papo et al. 2004).

3.2.2. The effect of nano silica on Compressive strength for naphthalene sulphonate super plasticizer mixes

As it can be seen from figures 5 and 6, for the 0.80 % naphthalene sulphonate superplasticizer, we can conclude the following:

The compressive strength increase by increasing the w/c from 0.40 to 0.45 ranges from (8% to 22%) at 7 days of curing, and from (4 % to 29 %) at 28 days of curing

The highest compressive strength of all mixes was reached by the addition of 1% nano silica then slight reduction in compressive strength was reported for all mixes.

The gain in strength increased by increasing sonicated nano silica to 1 % then a significant drop appeared, this can be attributed to that the nano silica particles cannot easily disperse within the cement matrix, and due to their high surface energy, they started to be agglomerated

by comparing figures 5 and 6, increasing the naphthalene sulphonate super plasticizer from 0 to 0.80, we can find the following :

- The highest compressive strength for 0.45w/c mixes was reached by the addition of 1% nano silica then slight reduction in compressive strength was reported for all mixes.

For the contents higher than 1%, the nano particles cannot easily disperse within the cement matrix, and due to their high surface energy, they become more agglomerated, hence a weak area of empty spaces such as voids appeared. Consequently, the structure formed in such conditions cannot be homogenous and compacted (Meral Oltulu et al. 2014). It was found that C–S–H gels from pozzolanic reaction of the agglomerates cannot function as binder. The gels from cement hydration did not penetrate into the pozzolanic gels. There even existed ITZ between the large reacted agglomerates and the bulk paste (Deyu Kong et al. 2012).

The above mentioned improvement in compressive strength concrete by increasing naphthalene sulphonate super plasticizer from 0% to 0.80%, at constant water/cement ratio is due to the main effect of traditional superplasticizer that induce the dispersion of cement particles by an electrosteric mechanism favouring mutual repulsion and hindering flocculation (OlgaBurgos et al. 2012).the adsorption of the plasticizer molecules on the cement solid particles, either by modifying the surface charge (zeta potential) of the particles, thus increasing the electrostatic repulsion, causes a dispersing action, which has been claimed to be responsible for the increase in fluidity of the cement paste (A. Papo et al. 2004).

Loss in in compressive strength concrete by increasing nano silica from 0 to 3 % is due to the bad dispersion of the nano silica addition particles in the presence of naphthalene sulphonate super plasticizer, since the admixture present in the liquid, is not adsorbed onto the nano silica particles (OlgaBurgos et al. 2012).

The decrease in strength by decreasing w/c ratio can be a result of the presence of agglomerates that were unable to act as fillers will consume some free water that originally contributes to fluidity. They may also push away the cement particles around them, causing an increase of the void space. While by increasing the w/c ratio some of the consumed water is added.

As it can be seen from figures 5 and 6, for the 1.60 % naphthalene sulphonate superplasticizer, we can conclude the following:

- The compressive strength increased by decreasing the w/c from 0.45 to 0.40 % at 7days and 28 days of curing for all mixes
- The compressive strength increase by decreasing the w/c from 0.45 to 0.40 ranges from (8% to 32%) at 7 days of curing, and from (4 % to 47 %) at 28 days of curing
- The compressive strength decreased by increasing the nano silica from 0 to 3 %, at 7days and 28 days of curing for 0.45 % w/c mixes.
- The highest compressive strength of all mixes was reached by the addition of 0% nano silica for 0.45 w/c mixes, by increasing the naphthalene sulphonate super plasticizer from 0 to 1.60 % to reach 442 kg/cm² at 28 days of curing, with an increase of 37 %
- The highest compressive strength of all mixes was reached by the addition of 3% nano silica for 0.40 w/c mixes, by increasing the naphthalene sulphonate super plasticizer from 0 to 1.60 % to reach 387 kg/cm² at 28 days of curing, with an increase of 32 % .
- For naphthalene sulphonate super plasticizer mixes. decreasing the w/c ratio from 0.45 to 0.40 increased the compressive strength of all mixes. Either those containing 1.6 % naphthalene sulphonate super plasticizer

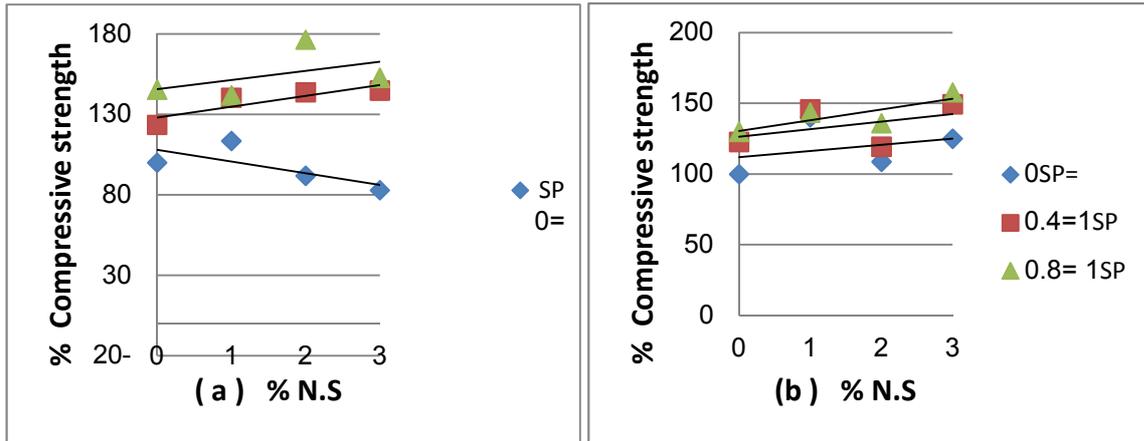


Figure 3 : the effect of Polycarboxylate super plasticizer on Compressive strength of 7 days as compared to (a) 0.40% w/c, and (b) 0.45% w/c concrete mix

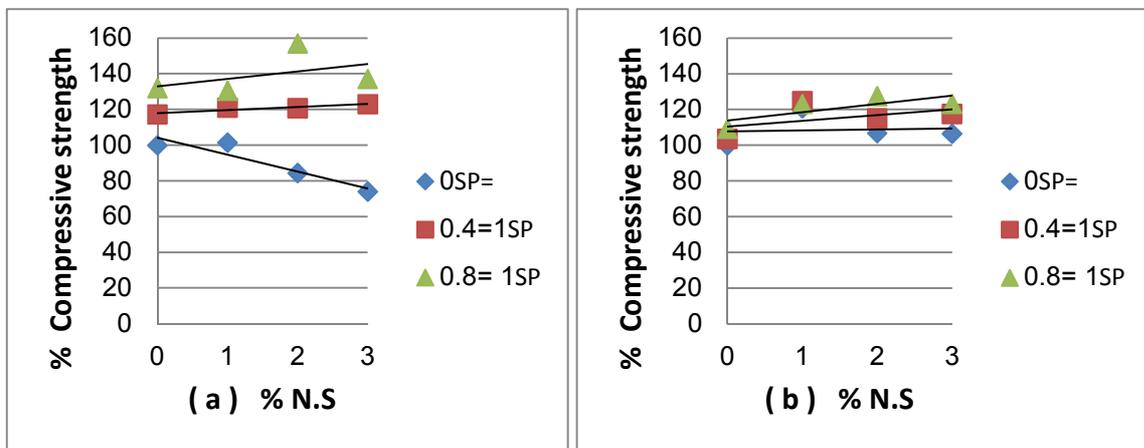


Figure 4 : the effect of Polycarboxylate super plasticizer on Compressive strength of 28 days as compared to (a) 0.40% w/c, and (b) 0.45% w/c concrete mix

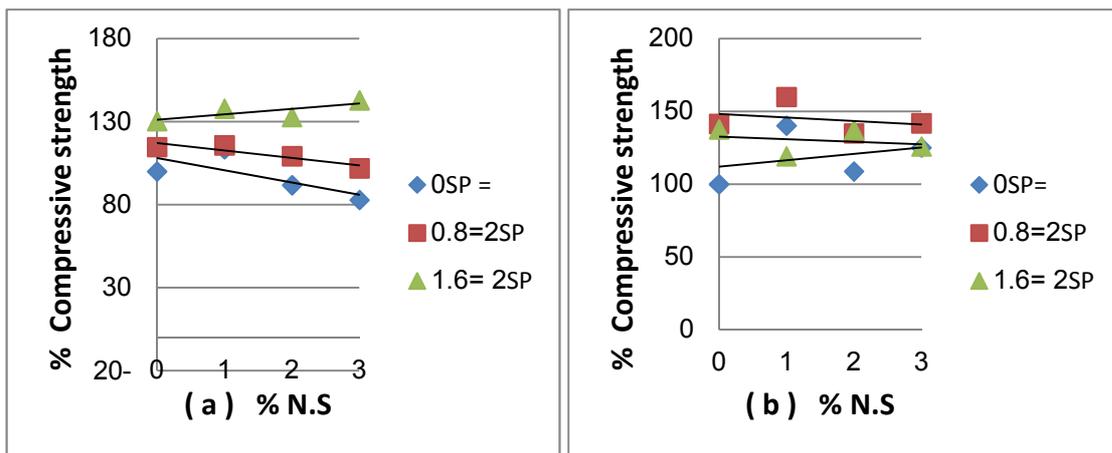


Figure 5 : the effect of naphthalene sulphonate super plasticizer on Compressive strength of 7 days as compared to (a) 0.40% w/c, and (b) 0.45% w/c concrete mix

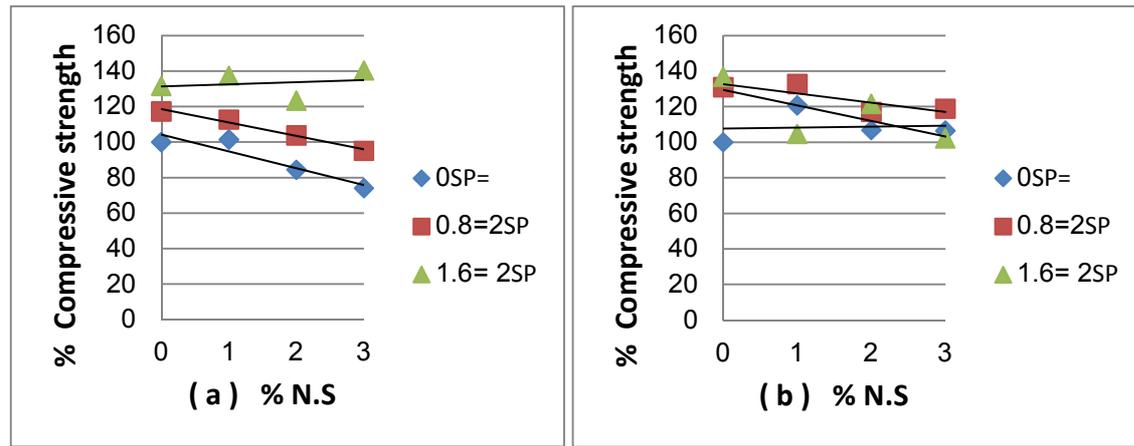


Figure 6 : the effect of naphthalene sulphonate super plasticizer on Compressive strength of 28 days as compared to (a) 0.40% w/c, and (b) 0.45% w/c concrete mix

4. Conclusion

- For polycarboxylate super plasticizer mixes. Increasing the w/c ratio from 0.40 to 0.45 increased the slump of all mixes. Either those containing polycarboxylate super plasticizer or the control mixes.
- For naphthalene sulphonate super plasticizer mixes. Increasing the w/c ratio from 0.40 to 0.45 increased the slump of all mixes. Either those containing naphthalene sulphonate super plasticizer or the control mixes.
- The compressive strength increased by increasing the w/c from 0.40 to 0.45 at 7days and 28 days of curing for all mixes except for the 0% nano silica where the strength decreased by increasing w/c ratio. for the non superplasticizer mixes
- The compressive strength increased by decreasing the w/c from 0.45 to 0.40 at 7days and 28 days of curing for all mixes either those containing nano silica or the control mix. For both 0.4 %, and 0.80 % polycarboxylate superplasticizer
- These results indicate that increasing the polycarboxylate-based superplasticizer content beyond 0.8 % could positively affect the development of compressive strength, the superplasticizer plays a role for dispersing the cement and nano silica particles through the adsorption mechanism, resulting in improvement of compressive strength at early and late ages.
- For naphthalene sulphonate super plasticizer mixes. Increasing the w/c ratio from 0.40 to 0.45 increased the compressive strength of all mixes. Either those containing 0.8 % naphthalene sulphonate super plasticizer or the control mixes. while decreasing the w/c ratio from 0.45 to 0.40 increased the compressive strength of all mixes. Either those containing 1.6 % naphthalene sulphonate super plasticizer
- the use of (1.6 %) sulphonated naphthalene super plasticizer (NSP) with 0.4 w/c ratio reached a gain in strength equivalent to the use of (0.8 %) polycarboxylic super plasticizer (PSP) for mix containing 3 % nano silica .
- the use of (1.6 %) sulphonated naphthalene super plasticizer (NSP) with 0.45 w/c ratio reached a gain in strength equivalent to the use of (0.8 %) polycarboxylic super plasticizer (PSP) for mix containing 2 % nano silica
- by increasing nano silica from 0 to 3 %, the strength increased by using the two types of super plasticizers (0.8%) either with 0.4 or 0.45 w/c ratios. As compared to the non- super plasticizer mix.

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