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ARTICLE

The Effect of Various Polynaphthalene Sulfonate Based Superplasticizers on the Workability of Reactive Powder Concrete

Anthony Torres[1*] Federico Aguayo[1] Srinivas Allena[2] Michael Ellis[1]

1. Texas State University, San Marcos, TX, 78666
2. Cleveland State University, Cleveland, 44115

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ABSTRACT

A superplasticizer is a type of chemical admixture used to alter the workability (viscosity) of fresh concrete. The workability of fresh concrete is often of particular importance when the water-to-cement (w/c) ratio is low and a particular workability is desired. Reactive Powder Concrete (RPC) is a high-strength concrete formulated to provide compressive strengths exceeding 130MPa and made of primarily powders. RPC materials typically have a very low w/c, which requires the use of a chemical admixture in order to create a material that is easier to place, handle and consolidate. Superplasticizer are commonly used for this purpose. Superplasticizers are developed from different formulations, the most common being Polycarboxylate Ether (PCE), Polymelamine Sulfonate (PMS), and Polynaphthalene Sulfonate (PNS). This study investigates the effect of various PNS based superplasticizers on the rheological performance and mechanical (compressive strength) performance of a RPC mixture. Six distinctive types of PNS based superplasticizers were used; three of various compositional strengths (high, medium, low range) from a local provider, and three of the same compositional strengths (high, medium, low) from a leading manufacturer. The properties investigated were the individual superplasticizers' viscosity, the concrete workability, determined through a mortar spread test, the concrete viscosity, and the compressive strength of the hardened RPC mixtures measured at 7, 14, and 28 days. Two separate RPC mixtures were prepared, which contained two different water-to-cementitious ratios, which consequently increases the dosage of superplasticizer needed, from 34.8L/m3 to 44.7L/m3. The results show that the name brand high range composition produced the overall highest spread, lowest viscosity, and a highest compressive performance. However, the local provider outperformed the name brand in the mid and low range compositions. Lastly, the rheology assessment also confirmed that the name brand high range, and RPC fabricated with the name brand high range, developed the lowest viscosities.

**Corresponding Author:*
Anthony Torres,
Texas State University, San Marcos, TX, 78666;
Email: ast36@txstate.edu

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1. Introduction

As the world's structures increase in height and overall size, so does the necessity for higher performance building materials. Concrete is the most used building material in the world, but conventional concretes are lacking in the necessary performance for the next generation of structures. Higher strength and performance concretes meet this demand, however, not all aspects are currently known and therefore, require more investigation. A particular type of high strength concrete is known as Reactive Powder Concrete (RPC). RPC is a concrete with highly reactive constituents that results in a high strength and highly ductile material. RPC type concretes typically have compressive strengths at or above 130 MPa. RPC mixtures typically consist of only powders that react well with each other to produce high performance properties. These materials typically consist of Portland cement, Silica Fume, Fly Ash, Slag, fine (powdered) aggregate, and fibers. RPCs also typically require the use of admixtures to adjust certain properties. These admixtures are commonly a superplasticizer type, which typically increases the workability of the fresh concrete and helps with high early-age strength. The admixtures also help to provide an increase in compressive and tensile strength as well as other durability properties. The nature of a superplasticizers is to allow for an effective dispersion of cement particles to ensure complete hydration, packing density, and workability within the mixture. RPCs typically have very low water-to-cementitious (w/cm) ratios, which typically results in a very viscous mixture and the possibility of conglomerated un-hydrated cement particles. A superplasticizer will not only help to break up these conglomerations, ensuring all particles are properly hydrated, it will also improve the workability for easier handling and placing.

There are typically three compositional strengths for these superplasticizers, which consist of high, medium, and low range. These three strengths are commonly used to change the viscosity of the fresh concrete. Requirements for these admixtures are outlined by ASTM C494 "Standard Specifications for Admixtures in Concrete" [1]. Common examples of superplasticizers include, Polymelamine Sulfonate, Polynaphthalene Sulfonate (PNS), and (PMS) and Polycarboxylate Ether (PCE) based polymers. These admixtures are all used to deflocculate the cement particles and increase the workability of the fresh concrete mixture [1-5]. The effectiveness of an individual superplasticizer is a result of the chemical structure, main backbone length, composition of functional groups, side chain length, degree of backbone polymerization, and charge density differentiation [4-5].

This study focuses on investigating the impact of different PNS based superplasticizers on the workability and compressive strength of RPC. Six various PNS based superplasticizers were obtained and implemented; three different PNS based superplasticizers (high, medium, and low) from a local manufacturer (PNS-L-high, PNS-L-medium, PNS-L-low), and three PNS-based superplasticizers from a name brand manufacturer, also in a high, medium, and low composition (PNS-N-high, PNS-N-medium, PNS-N-low). The products produced and provided by a local company are understood to produce comparable results to the name brand products. The focus of this study is to determine the effect of various Polynapthalene Sulfonate (PNS) superplasticizers have on the compressive strength and rheological performance of RPC. The workability of the concrete was measured via a mortar spread test. To compare the viscosity properties of the superplasticizer and the RPC mixtures a viscometer was used.

2. Experimental Program

2.1 Materials and Mixture Design

Ordinary Portland Cement (Type I/II) cement was used in all concrete mixtures, which conforms to ASTM C150 Standard Specification for Portland Cement [6]. Powdered silica fume was also used, to help improve particle packing of the mixtures. The very fine particle size of silica fume is known to enhance particle packing and increase the cement reaction to improve strengths in RPC. The only aggregate used in the mixtures was a river sand. The sand was sieved over a #30 sieve and was then washed on a #200 sieve. After washing, the rive sand was then dried in a laboratory oven at 110ºC for 24 hours prior to mixing. Based off of a literature review, two RPC mixtures were designed [7-10] that contained two different w/cm., The two w/cm will elucidate the impact of the amount of superplasticizer used. Table 1 shows the mixture design proportions used for the two mixtures. Table 2 contains information about each superplasticizer used.

Table 1. RPC mixture quantities

Materials	w/cm = 0.20 (kg/m^3)	w/cm = 0.15 (kg/m^3)
Type I/II Cement	880	880
Silica Fume	220	220
River Sand	830	1010
Superplasticizer	34.8 (L/m^3)	44.7 (L/m^3)
Water	220	165

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Table 2. Superplasticizer Properties

	PNS-L-high (Yellowish Liquid)	PNS-L-med (Yellowish Liquid)	PNS-L-low (Gold/Brownish Liquid)
pH, 25ºC	6.11	6.08	6.19
Density (g/cm³)	1.11	1.09	1.08
Mass average molecular weight	49,000	50,000	41,000
Side chain density of carboxylic acid groups	1:4	1:3	1:5
Appearance	PNS-N-high (Gold/Brownish Liquid)	PNS-N-med (Gold/Brownish Liquid)	PNS-N-low (Gold/Brownish Liquid)
pH, 25ºC	6.12	6.10	6.14
Density (g/cm³)	1.15	1.16	1.15
Mass average molecular weight	49,000	47,000	45,000
Side chain density of carboxylic acid groups	1:4	1:3	1:5

Note: *PNS = Polynapthalene Sulfate; **L = Local Provider; ***N = Name Brand

2.2 Sample Preparation

The mixing method was completed based off of experience and a review of the literature [7-10]. The mixing procedures consisted of mixing of all of the constituents was completed for 15 minutes using a pan mixer. The dry constituents were mixed for the first 5 minutes followed by the addition of 75% of the water. After an additional 5 minutes, the desired superplasticizer was added with the remaining 25% of the water, followed by 5 minutes of mixing. In order to ascertain the impact of the three compositional ranges as well as the difference between the various types of superplasticizers one dosage amount was selected despite the compositional range of the three types. Additionally, one specific curing treatment was used for the compression testing samples. The curing treatment was originally developed by Shaheen and Shrive [9] and demonstrated replicable results. First the samples are cured at room temperature 23ºC (73ºF) for the first 24 hours, and after demolding, the specimens were then heat cured in a water bath at 50ºC (122ºF) until 2 days prior to testing. At two days prior to testing, the specimens were removed from the water bath and dry cured at 200ºC (392ºF).

Compressive strength specimens were casted into 50-mm (2-in.) cube molds. All samples were compacted according to the mortar cube compaction method described in ASTM C109 [11] "Compressive Strength of Hydraulic Cement Mortars". Cubes specimens were used to avoid issues with end preparation of cylindrical specimens [11]. After the specimens were properly cured, they were individually tested according to BS 12390-3- 2019 [12]. An average of three samples was tested per individual data point described in the results section.

2.3 Testing Equipment

Testing of the mortar flow (spread) was completed in accordance to ASTM C1437-20 [13], which was completed immediately following mixing of the RPC mixtures. The rotational viscosity was also obtained. Both the superplasticizer was measured as well as the freshly mixed RPC. A Brookfield model DV-II+ rotational viscometer was used for all superplasticizers and the RPC mixtures. Viscosity measurements of the fresh concrete was done in parallel with the flow spread test and casting of the compressive strength cubes.

3. Results

The viscosity of each superplasticizer was recorded at 3 different rates (20, 50 and 100 rpm) shown in Figure 1. The viscosity measurements were recorded in centipoises, cP at three different angular speeds to investigate how the viscosity changes with different speeds (sheer capacity). In addition to the superplasticizer viscosity the spread flow data measured from the fresh RPC mixtures can be seen in Table 3.

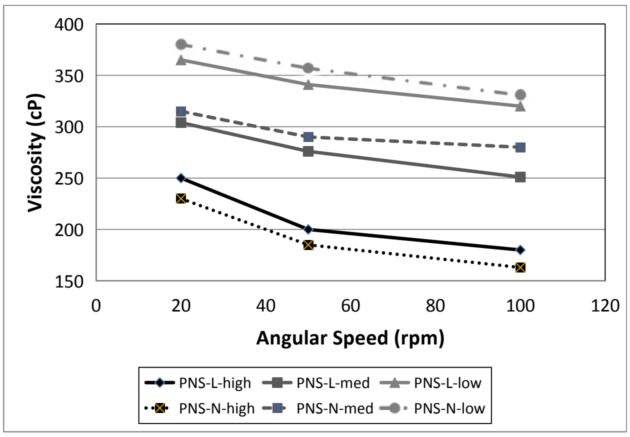

Figure 1. Viscosity measurement of each superplasticizer at individual rotational speeds

Table 3. Spread flow results of the RPC mixtures

Superplasticizer	w/cm = 0.20 (mm)	w/cm = 0.15 (mm)
PNS-L-high	205.9	196.4
PNS-L-med	187.3	175.6
PNS-L-low	169.1	153.3
PNS-N-high	210.6	202.2
PNS-N-med	181.2	169.4
PNS-N-low	163.0	147.1

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Both Figure 1 and Table 3 demonstrate that the viscosity of each superplasticizer dosed in the RPC mixture has an effect on the workability of the mixtures. The results demonstrate that the PNS-N-high produced the lowest viscosity measured, and the RPC mixtures also made with the PNS-N-high resulted in the highest spread. The general trend seen in both the viscosity measurements and spread test is that the high composition superplasticizer produced the lower viscosity and highest spread, followed by the medium range composition, then lastly the low range composition. This result is as expected as the broader the range, the higher the impact on the viscosity and spread at the same dosage level [1-5]. In general, RPC mixtures have a high viscosity and low spread, which results in lower workability and a less pumpable mixture [7-10]. Therefore, a higher spread and lower viscosity is generally preferable, however, this does depend on the application. What can also be seen is that the name brand superplasticizer does not always produce a lower viscosity and higher spread. In fact, the name brand only outperformed the locally provided PNS in the high range category. Based off of these results there seems to be a difference in composition between the different superplasticizers despite the marketed similarity. Both manufactures do not reveal their specific chemical composition due to their proprietary ingredients. Despite this fact, this study still provides beneficial information on the impact of various PNS based superplasticizers on RPC types of concretes. The results also elucidate that despite the increase in superplasticizer dosage between the two w/cm mixtures, the workability (spread flow) still decrease for the 0.15 w/cm ratio concrete.

The outcome of the viscosity measurements of the RPC mixtures produced with the various superplasticizers can be found in Figures 2-3.

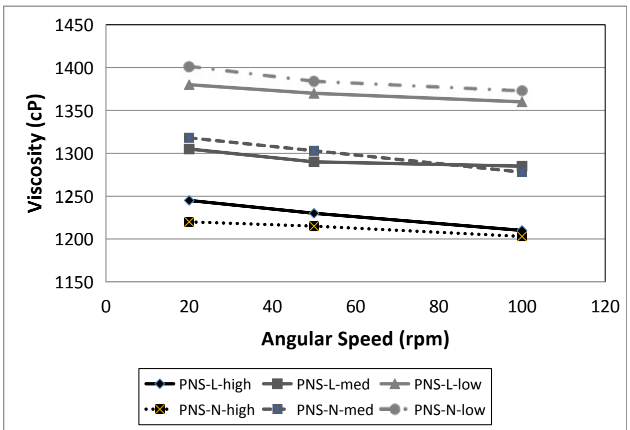

Figure 3. Viscosity measurements of the RPC produced with the six PNS-based superplasticizers at a 0.20 w/cm

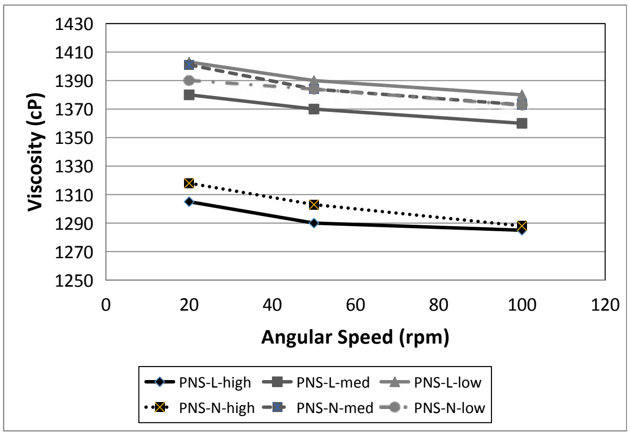

Figure 4. Viscosity measurements of the RPC produced with the six PNS-based superplasticizers at a 0.15 w/cm

The results shown in Figures 3 and 4, ultimately demonstrate that the viscosity of the RPC mixture is considerably higher than that of the pure superplasticizers. Despite this increase, the high results are not as expected for this type of concrete, as these types of concretes traditionally only contain high amounts of powders, which typically results in a viscous mixture. These mixtures also typically contain a high amount of silica fume, which is spherical in nature, and very fine. The particle morphology of this powder will help to improve the workability of these types of concrete, and this is likely the case in the results of this study. It can be seen in Figures 3-4 that the various superplasticizers produce an effect on the workability (measured viscosity) of the RPC mixtures at the three measured rotational speeds, which is expected. A correlation is observed between the viscosity of the of the superplasticizer compositional range and its influence to the RPC mixtures. This correlation can be seeing in Figures 2-4. As with just the viscosity of the superplasticizer, the higher the range of the superplasticizer the higher the impact on the concrete's viscosity. Additionally, there is a correlation between the viscosity of the superplasticizers and the viscosity of the RPC mixtures, such that the lowest measured superplasticizer produced the lowest measured RPC viscosity and similarly with the highest viscosity superplasticizer and the highest RPC viscosity. Hence, the order from lowest to highest of just the superplasticizer liquids are in the same order as the RPC produced with the same superplasticizers, aside from PNS-L-high, which performed with a slightly lower viscosity than its counterpart. This only occurred at the lower w/cm of 0.15 and not in the w/cm of 0.20. The overall correlation is expected as the superplasticizer is creating the desired viscosity within the concrete as per its design due to its inherent properties. The difference in the PNS-L-high versus PNS-N-high is very close to each other, therefore this difference is likely negligible. Also note that at an angular speed of 100, the viscosity of the PNS-L-high and PNS-N-high are essentially the same. The results in Figures 3-4, also reveal that the overall viscosity increases marginally with the lower w/cm. This result is expected as a lower w/cm means less water, and less water tends to have a higher viscosity. This result is still observed despite the additional dosage of superplasticizer used. These results are also similar with the mortar flow test. It can also be seen that the superplasticizer properties seen in Table 2 have no effect on the viscosity of the superplasticizers or the RPC. It is noticed that the main property affecting the viscosity of the RPC mixtures is the viscosity of the superplasticizer itself.

The compressive strength results were obtained in accordance to BS EN 12390-3-2019 [12] which uses 50-mm (2-in.) cubes. The results of this testing can be seen in Figure 4.

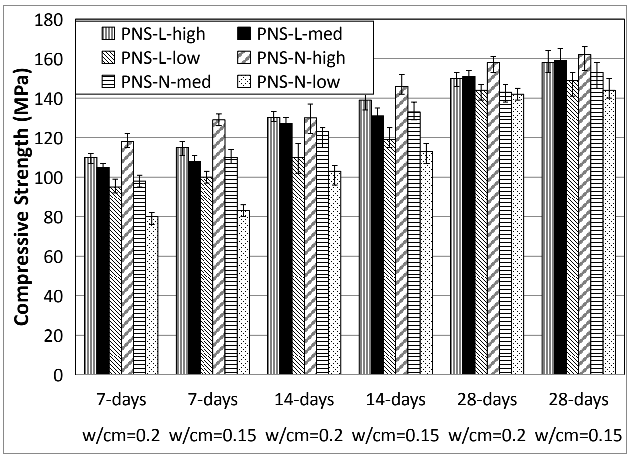

Figure 4. Compressive strength results

The outcome of the compression strength testing showed results that are similar with the viscosity and spread tests discussed previously. These results are as expected based off of the literature. Specifically, the compressive strengths are proportional with curing age, in that they increase with age. Additionally, also as expected, the compressive strengths increase with a decrease in w/cm. The highest strength achieved was 162MPa produced by the 28-day, 0.15 w/cm, PNS-N-high mixture. The lowest compressive strength recorded was the 0.20 w/cm measured at an age of 7-days. This result was from the PNS-N-low with a strength of 80MPa. Although this is a lower strength than expected this strength should be noted as a sufficiently high compressive strength when related to standard concretes. It is also noticed that the PNS-N-high regularly yielded the highest results with the PNS-L-high following. The next highest performing mixtures were the PNS-L-med, PNS-N-med, PNS-L-low and PNS-N-low for the remaining compressive strengths. Therefore, the name brand only outperformed the counterparts in the high range categories. It can also be observed that PNS-N-low always produced the lowest strengths, which also corresponds to the highest superplasticizers' viscosity and also the highest RPC mixture viscosity. It is observed that all of the compressive strength measurements have an inverse relationship to the spread test and viscosity amounts of both the individual superplasticizers and the RPC mixtures. Hence, the superplasticizer and corresponding mixture with the lowest viscosity produced the highest compressive strengths. Therefore, the less workable the mixture the higher the compressive strength. This outcome is expected as the only variable changing is the superplasticizer itself, which only impacts the workability. A lower workability, typically signifies a denser mixture, which results in a higher compressive strength concrete. The workability is a performance measure that relates to the ease of placement and compaction of the material, therefore, a compromise between strength and ease of placement must be made. Based off the results of this study and similar studies in the literature, the impact of a superplasticizer on the workability and compressive strength of a concrete is directly proportional to the viscosity of the superplasticizer itself.

4. Conclusions

This study demonstrated the influence that six different PNS based superplasticizers has on two RPC mixtures. Of the six superplasticizers three were from a leading name brand company and three were provided from a local competing company. One overall type of superplasticizer was used (PNS), with three different compositions of high, medium, and low. The high range superplasticizers overall yielded the best performance, however only the high range from the name brand provider outperformed its counterparts. The outcome from the viscosity testing revealed how each superplasticizer performed at different rotational speeds. This data elucidated the effect that each superplasticizer had on the two RPC mixtures. The results showed that the locally provided superplasticizers in the mid and low range produced lower viscosities, which led to a higher mortar spread of the corresponding RPC mixture, which in turn resulted in a more workable concrete, which ultimately led to higher compressive strengths at all ages versus the name brand counterparts. The lowest viscosity concretes were produced by the low range superplasticizers. The lower workable RPCs also corresponded to lower compressive strengths, which is likely a result of a lower hardened density (not measured) and less hydration of all cementing particles. The findings produced in

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this study demonstrate how various PNS based superplasticizers impact the performance of RPC type concretes.

References

[1] ASTM C494. Standard Specifications for Admixtures in Concrete. ASTM International, ASTM Standard C 494 (2020), West Conshohocken, Pa, USA, 2020. https://www .astm.org

[2] Torres, A., Aguayo, F., Allena, S., Ellis, MG. Investigating the Rheological Properties of Ultra High Strength Concrete Made with Various Superplasticizers. Journal of Advances in Science and Engineering, 2019, 11(2).

[3] Alsadey, S. Effect of Superplasticizer on Fresh and Hardened Properties of Concrete. Journal of Agricultural Science and Engineering, 2015, 1(2): 70-74

[4] Rendon Diaz Miron, L., Lara Magaña, M. Superplasticizer for High Strength Concrete. MRS Proceedings, 2015, 1768, Imrc2014-6d-019. DOI: 10.1557/opl.2015.324

[5] Mardani-Aghabaglou, A., Tuyan, M., Yılmaz, G., Arıöz, Ö, & Ramyar, K. Effect of different types of superplasticizer on fresh, rheological and strength properties of self-consolidating concrete. Construction and Building Materials, 2013, 47: 1020-1025. DOI: 10.1016/j.conbuildmat.2013.05.105

[6] ASTM C150. Standard Specification for Portland Cement. ASTM International. ASTM Standard C150-20 (2020), West Conshohocken, Pa, USA, 2020. https://www .astm.org

[7] ACI Committee 239. 239R-18: Ultra-High Performance Concrete: An Emerging Technology Report. American Concrete Institute, 2018, 1: 1-41.

[8] Torres, A., Aguayo, F., Allena, S. Developing Sustainable Ultra High Strength Concrete Mixtures Using Spent Foundry Sand. Journal of Civil Engineering and Architecture, 2019, 13: 343-352

[9] E. Shaheen, N. G. Shrive. Optimization of mechanical properties and durability of reactive powder concrete. ACI Materials Journal, 2006, 103(6): 444-451.

[10] Aguayo, F., Torres, A., Talamini, T.U, Whaley, K.U. Investigation into the Heat of Hydration and Alkali Silica Reactivity of Sustainable Ultrahigh Strength Concrete with Foundry Sand. Advances in Materials Science and Engineering, Article ID 2096808, 2017, 2017: 11. DOI: 10.1155/2017/2096808

[11] NF EN12390-3. Testing hardened concrete - Part 3: Compressive strength of test specimens. 2019: 18.

[12] ASTM C109. Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens). ASTM Standard C 109-16a (2019) West Conshohocken, Pa, USA, 2019. https://www .astm.org

[13] ASTM C1437. Standard Test Method for Flow of Hydraulic Cement Mortars. ASTM International, ASTM Standard C 39-15a (2020), West Conshohocken, Pa, USA, 2020. https://www .astm.org