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Effect of Nano SiO₂ and Nano CaCO₃ on The Mechanical Properties, Durability and flowability of Concrete

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Abstract. This study investigated the effect of using nano CaCO₃ and nano SiO₂ as partial replacement of cement on the mechanical properties, durability and flowability of concrete. Nano materials were added in four different dosages of 1%, 2%, 3% and 4% by weight of cement in concrete mixture. Mechanical properties of hardened concrete (compressive strength, flexural strength and split tensile strength) have been done after 28 days of water curing. Also water absorption test was carrying out for obtaining the durability properties of concrete specimen. slump flow for fresh concrete was measured for all mixes. Binary combination of nanoCaCO₃ + nanoSiO₂ were also studied the combined effect of the nano particles. The results showed that incorporation of nano CaCO₃ and nano SiO₂ particles lead to increase the packing and enhance the mechanical properties and durability of concrete. A significant performance was observed in case of nano silica addition to the concrete in comparing with nano CaCO₃. The results showed that the workability of fresh concrete was decreased by increasing the content of nano particles.

1. Introduction

With increasing societal demands to make concrete a more sustainable infrastructural material, the replacement of cement with supplementary cementitious materials (SCMs) has been widely recognized as a viable solution [1]. With the development of nanotechnology, nanomaterial known as one of the most promising materials in 21st century has drawn attention from researchers successfully [2]. Nano particles have high interaction because their high surface area, these interactions offer the possibility of modifying cement reactions, creating new surface chemistries, developing new products for the concrete industry, and allowing more controlled and ecologically friendly manufacturing route to cement and concrete [3]. Faiz A. et.al studies the effects of CaCO₃ nanoparticles on compressive strength and durability properties of high volume fly ash and found concretes containing 1% CaCO₃ nanoparticles have reasonably higher compressive strength, lower volume of permeable voids, porosity, higher resistance to water absorption, chloride permeability and chloride ion diffusivity than the counterpart concretes. It is also found that 1% CaCO₃ nanoparticles improves the microstructure by forming additional calcium silicate hydrate gels and decreases the calcium hydroxide [4]. M. Stefanidou et.al. found that nano-SiO₂ appears to affect the mechanical properties and the structure of high-strength cement pastes even in low concentration, microstructure observation also recorded a denser structure in nano-modified samples. Zemei Wu et.al. indicated that both the nano-CaCO₃ and nano-SiO₂ decreased the flowability and accelerated the heat of hydration of UHSC, the addition of nanomaterials also leads to improve the compressive and flexural strength of concrete. For the same content, the use of nano-CaCO₃ resulted in greater flowability and lower strength compared to nano-SiO₂[5].



2. Materials

Commercially Iraqi available ordinary Portland cement Type I, named Karasta, is used in this study. Chemical and physical properties of cement, which are indicated that the cement is conformed to Iraqi specifications (I.Q.S.) No. 5/1984[6], are shown in Table 1 and Table 2 respectively. Natural sand (from Al- Akhedher in Karbala) was used. Table (3) shows the grading of the fine aggregate and sulfate content according to the limits of the Iraqi Specification No. 45 /1984[7]. To obtain high strength concrete crushed gravel used throughout this work of maximum size (14) mm. Table (4) shows the grading of the fine aggregate and sulfate content according to the limits of the Iraqi Specification No. 45 /1984[7]. Nano SiO_2 , nano CaCO_3 , were used as concrete admixture in this work figure (1) showed the XRD spectra for each admixture while figure (2) showed AFM analysis of nano particles.

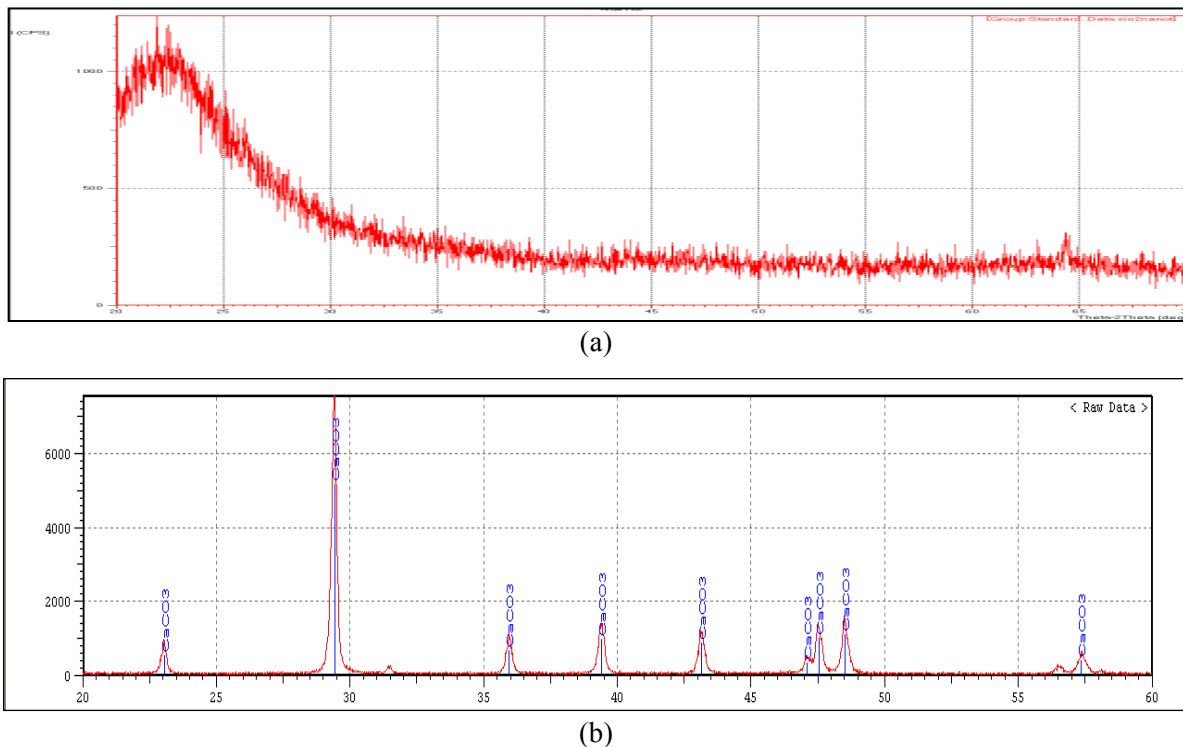
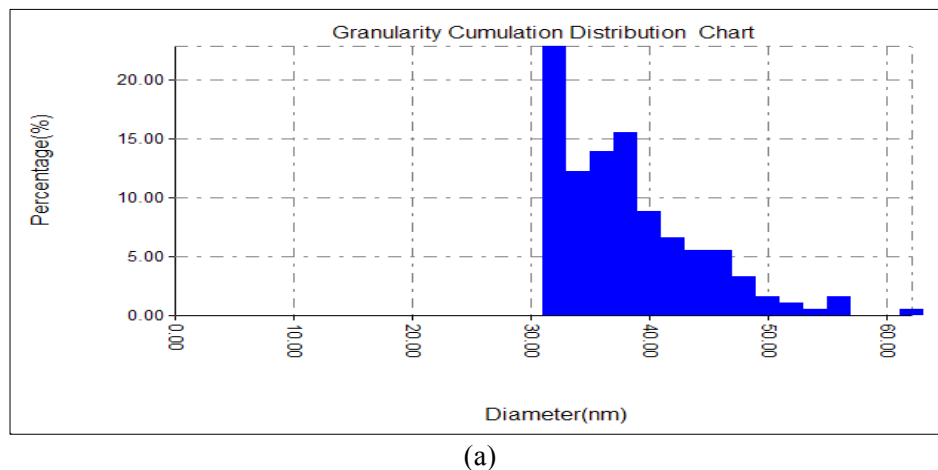


Figure 1. (a)XRD spectra of nano silica. (b) XRD spectra of nano CaCO_3 .



(a)

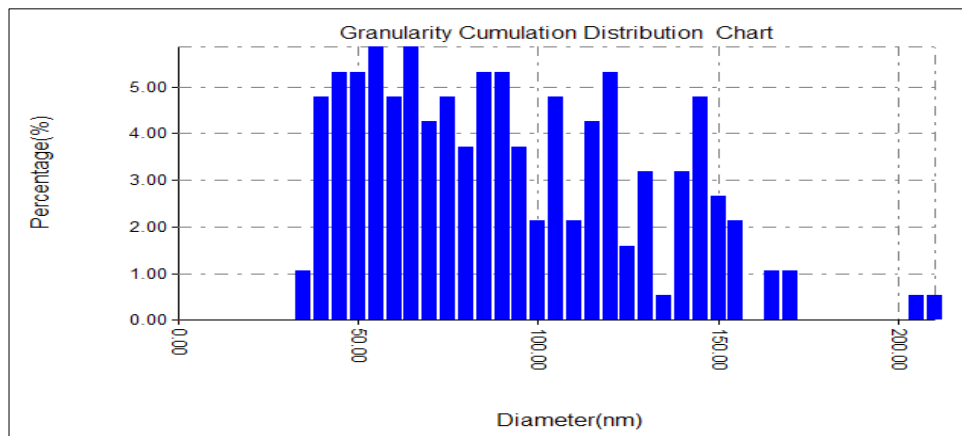


Figure 2. (a)AFM analysis of nano silica . (b) AFM analysis of nano CaCO₃

Table 1. Chemical analysis of cement.

Oxide	%	I.O.S.	5: 1984 ^l	Limits
CaO	66.11		—	
SiO ₂	21.93		—	
Al ₂ O ₃	4.98		—	
Fe ₂ O ₃	3.10		—	
MgO	2.0		< 5.0	
K ₂ O	0.75			
Na ₂ O	0.35			
SO ₃	2.25		< 2.8	
Compound	%	I.O.S.	5: 1984 ^l	Limits
C ₃ S	50		—	
C ₂ S	20.48		—	
C ₃ A	4.0		—	
C ₄ AF	13.17		—	

Table 2. Physical Properties of Cement test

Physical Properties	Test Results
Fineness , Blaine , cm ² /gm	3300
Setting Time :	
Initial hrs. ; min	2;05
Final hrs. ; min	4;00
Compressive Strength MPa	
3-days	20,0
7-days	25,0

Table 3. Sieve analysis and sulfate content of fine aggregate.

Sieve opening (mm)	Accumulative passing, %
10	100
4.75	94
2.36	85.6
1.18	76.9

0.60	46.3
0.3	10.8
0.15	1.1
0.075	0.5
Property	Result
SO ₃ , %	0.4

Table 4. Sieve analysis and sulfate content of gravel

Sieve opening (mm)	Accumulative passing, %
14	97
10	62
5	10
0.075	0.037
Property	Result
SO ₃ , %	0.09

3. Specimens

The types and dimensions of specimens that used were cubic with 150x150x150 mm for compressive strength test according to BS 1881-Part 101 [8], split tensile strength specimens for concrete were cylinder (100x200) mm according to ASTM C31/C31M [9], flexural strength test specimens were prism (100x100x400) mm according to ASTM C31/C31M [9]. and cylindrical 100x50 mm for absorption test according to ASTM C 642[10]

3.1 Mix Proportions

Target design strength of 50, 70 MPa was designed according to British mix design method BS5328. Part 2:1991[11], thirteen types of concrete mixes are implemented in this study. The fixed parameters for all mixes are: water/cementitious, coarse and fine aggregate fractions, and superplasticizer contents. Mixes details and symbols can be seen in Table (5).

Table 5. Symbols, content and quantity
Table (5) Mixes

Mix symbol	Cement, kg/m ³	Sand, kg/m ³	Gravel, kg/m ³	w/b %	G54 kg/m ³	NS kg/m ³ (rep. %)	NC kg/m ³ (rep. %)
Control	515	721	1030	0.32	6.43	---	---
1NS	509.85	721	1030	0.32	6.43	5.15	
2NS	504.7	721	1030	0.32	6.43	10.3	
3NS	499.55	721	1030	0.32	6.43	15.45	
4NS	494.4	721	1030	0.32	6.43	20.6	
1NC	509.85	721	1030	0.32	6.43		5.15
2NC	504.7	721	1030	0.32	6.43		10.3
3NC	499.55	721	1030	0.32	6.43		15.45
4NC	494.4	721	1030	0.32	6.43		20.6
1NS+NC	509.85	721	1030	0.32	6.43	2.575	2.575
2NS+NC	504.7	721	1030	0.32	6.43	5.15	5.15
3NS+NC	499.55	721	1030	0.32	6.43	7.725	7.725
4NS+NC	494.4	721	1030	0.32	6.43	10.3	10.3

NS: mixes with nano silica
NC: mixes with nano CaCO₃

4. Tests

4.1 Compressive Strength Test

This test was carried out according to BS 1881-Part 116 [12]. The curing age was 28 days. Three cubes were made for each mix at the specified age.

4.2 Split Tensile Strength Test

This test done according to ASTM C 496/C 496M – 04[13]. The curing age was 28 days. Three cylinders were made for each mix at the specified age.

4.3 Flexural Strength

This test is carried out according to ASTM C293-02 [14]. Duplicate beam specimens were tested and the average results were considered.

4.4 Water absorption test

The water absorption was conducted according to ASTM C642 [10], the water absorption test is carried out using (50x100 mm) cylinder specimens, and the average water absorption of two samples were recorded and considered.

4.5 Slump Flow Test

A slump cone with flow table, the flow table is wetted and the cone is placed in the center of the flow table and filled with fresh concrete in two equal layers. Each layer is tamped 10 times with a tamping rod. wait 30 seconds before lifting the cone. then cone is lifted, allowing the concrete to flow, the flow table is then lifted up 40mm and then dropped 15 times, causing the concrete to flow after this the diameter of flow of the concrete is measured.

5. Results

5.1 Result of Mechanical Properties

Compressive strength test results as indicated in fig. (3) showed improvement in compressive strength with increasing the content of nanoparticles, greater increment were founded at 3% nano SiO₂ 78 MPa compared with 53 MPa for control mix, in binary mixes the maximum compressive strength recorded 67 MPa at 3%(nano SiO₂+nano CaCO₃) while for mixes with nano CaCO₃ the greater value recorded were 63 MPa with content 4%. Splitting strength results were indicated in fig. (4) showed the same trend where the greater strength founded at 3% nano SiO₂ 13.5 MPa compared with 8MPa for control mix, maximum strength for mixes with nano CaCO₃ founded also at 3% content was 11MPa. Moderate strength was achieved by binary mixes 3%(nano SiO₂+nano CaCO₃) 12 MPa. Fig (5) explained the results of flexural strength higher improvement also recorded at 3% nano SiO₂ was 18 MPa compared with 11 MPa for control mix, maximum strength for mixes with nano CaCO₃ founded also at 4% content was 15MPa, also moderate strength was achieved by binary mixes 4%(nano SiO₂+nano CaCO₃) was 15.7 MPa. Nano silica showed higher improvement because nano silica reacts with the CH produced during cement hydration and results in more strength carrying C-S-H into the paste. As a more pozzolanic reaction occurs in the mix, more strength-carrying C-S-H is produced, which ultimately leads to a higher overall strength [15] these results were agree with Madhuwanthi R. et.al [15], and Wengui Li et.al [16]. Nano CaCO₃ can react with C3A to form mono-carbonate, which is a substance with special framework with strong hydrogen bonds between oxygen atoms and interlayer waters carbonate groups[5],CaCO₃ nanoparticles changed the formation of hydration products, hence contributed to the improvement of early-age compressive strength and durability properties of concrete [4]. Binary mixes showed moderate values due to the dual effect of nano SiO₂+nano CaCO₃ on the concrete properties.

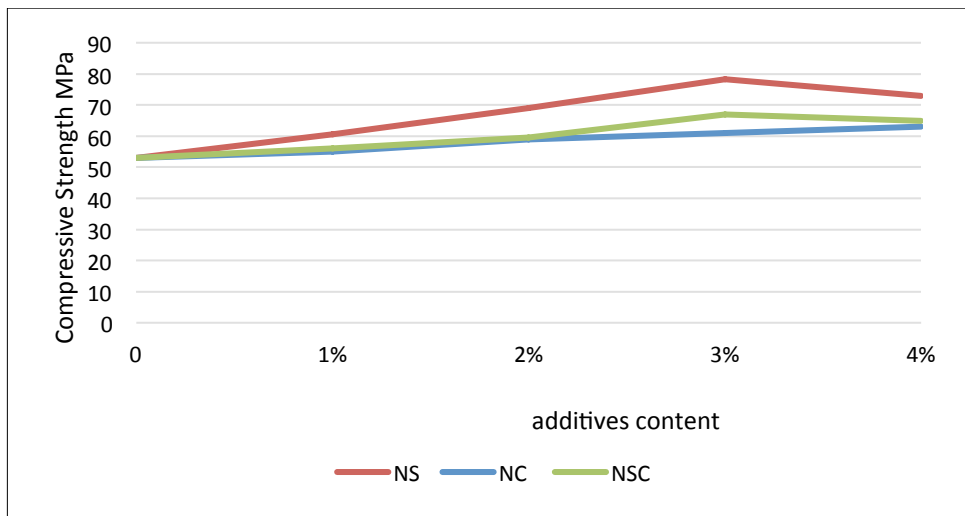


Figure 3. The results of compressive strength.

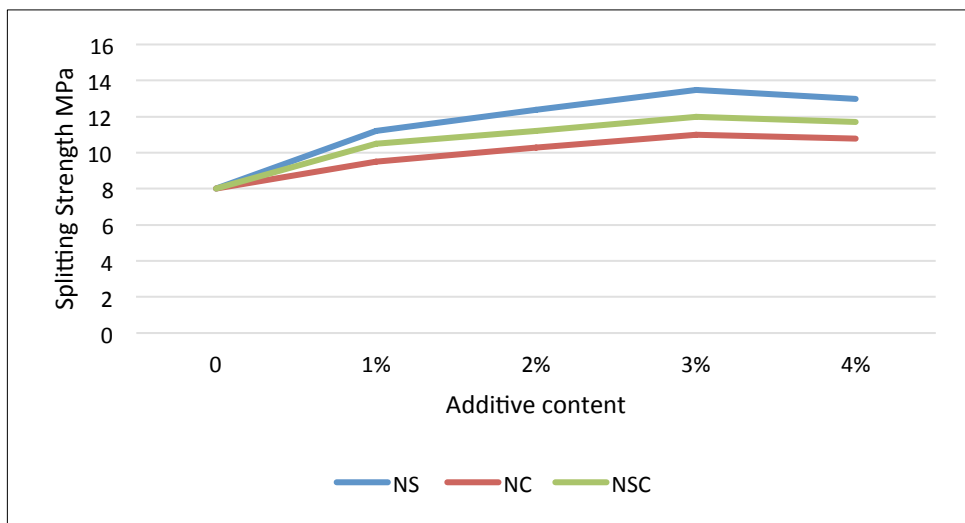


Figure 4. The results of splitting tensile strength.

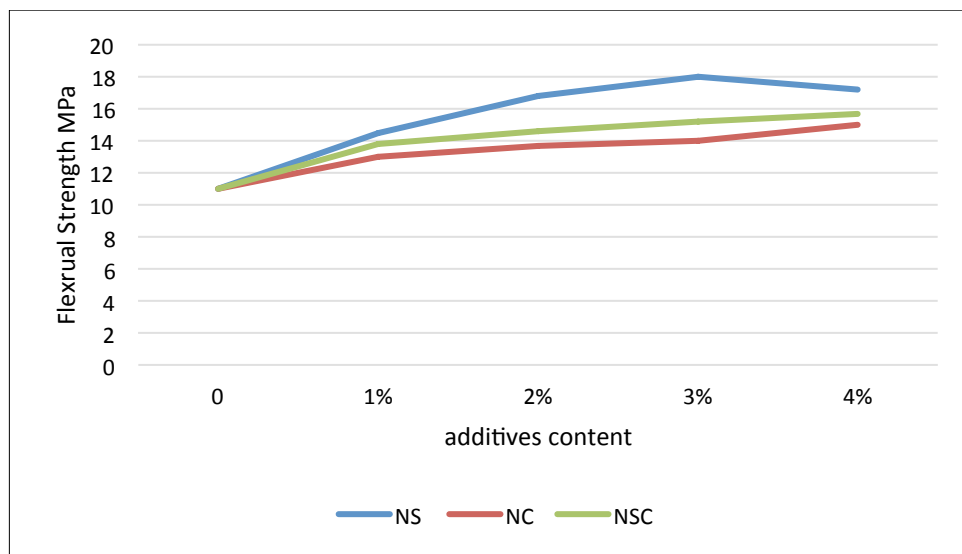
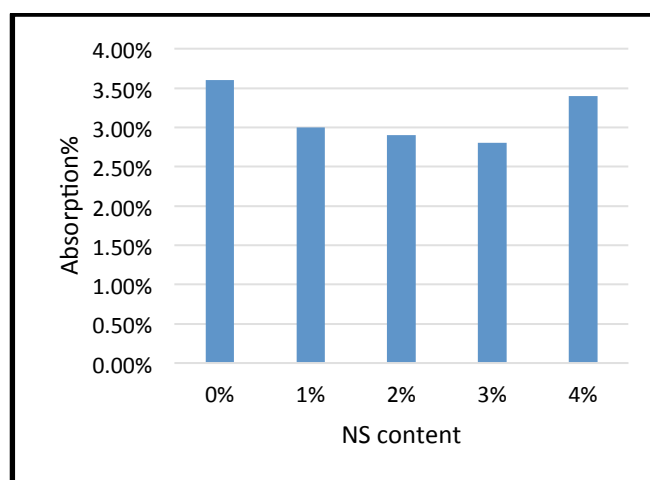


Figure 5. The results of flexural strength.

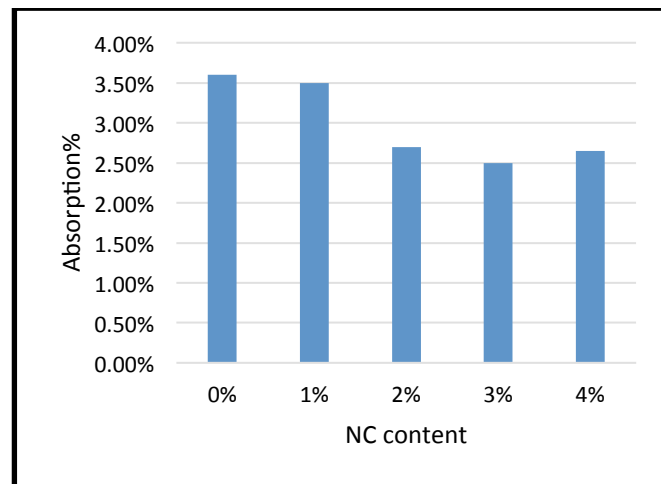
5.2 Result of Water Absorption Test

Nano silica implemented in this work generally exhibits a reduction in the water absorption potential of concrete this reduction, increased with the content of nano silica until reaching to 4% as replacement of cement as presented in fig (4-a), however, it's still lower than control mix this result agrees with the work achieved by S SANJU et.al [3]. The low water absorption values in nano silica mixes were attributed due to the higher pozzolanic effect of nano silica which made the concrete more compact and dense. Also the pore filling improved the pore structure of concrete, whoever S.Chirthra et.al[17], Ali Riza et.al[18], Peng Zhang et.al[19] and many researcher's work supported these results. the addition of CaCO₃ nanoparticles not only led to much denser microstructure in concrete matrix but also changed the formation of hydration products, hence contributed to the improvement of early-age compressive strength and durability properties of concrete [4].

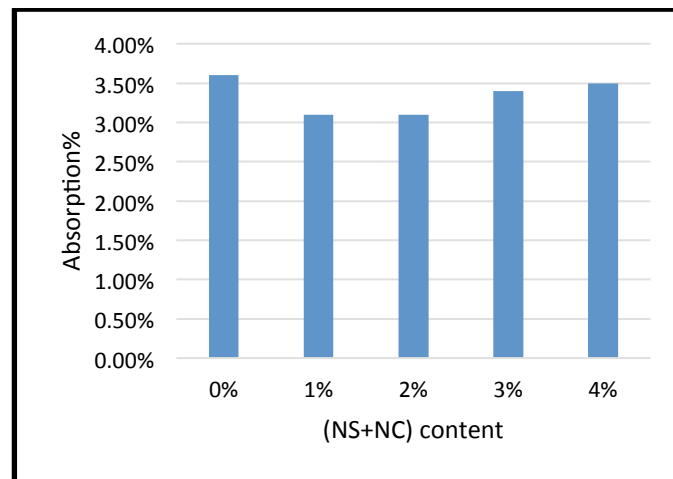
the best result was with binary mixes too. This reduction resulted from the tiny particles of nanosilica place in pores in micron size and lead to porosity and permeability reduction, increasing the amount of nanosilica lessened slurry density, thus the permeability of slurries increased [20] so the water absorption increase beyond 3% nanosilica content.



(a)



(b)



(c)

Figure 6. The results of water absorption test(a) For mixes with Nano SiO₂(b) For mixes with Nano CaCO₃(c) For mixes with (Nano SiO₂+ Nano CaCO₃)

5.3 Results of Flowability Test

The effects of nano-CaCO₃ and nano-SiO₂ contents on slump flow of concrete mixtures are illustrated in Fig. 3. It can be seen that the slump flow gradually decreased with the increase of nano-CaCO₃ and nano-SiO₂ contents. Wengui Li founded that greater cement replacement amounts achieve lower flowability. This phenomenon is due to the fine particle size of nano materials which have much higher surface areas that absorb water leaving less free water to contribute to the flowability [21]. Erhan reported that the addition of nano silica to the mixture decrease the spread on flow table due to the increase of cohesion in the mortar [22]. The flowability for NC series was greater than that of NS series at the same content. This might be attributed to different particle size and reactivity for nano silica and nano CaCO₃, same results were proved by Zemei Wu how indicated that due to its surface effect, smaller particle sizes and higher surface energy, Ca²⁺ and OH⁻ produced by cement hydration could be adsorbed in the surface of NC more easily, and the reduction of Ca²⁺ and OH⁻ in cement paste solution led to speeding up the hydration reaction of cement [5].

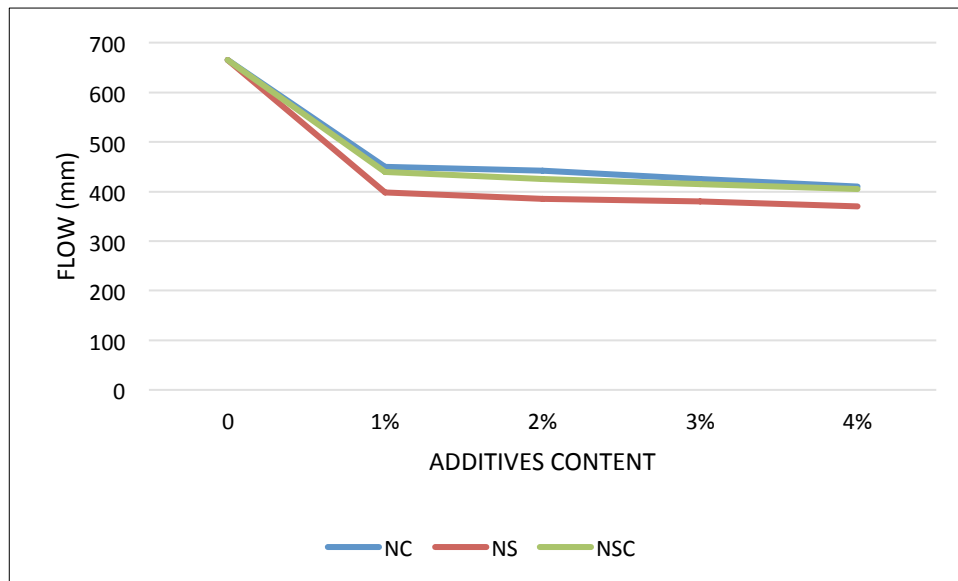


Figure 7. The results of slump flow test.

6. Conclusion

Based on the results presented in this study, the following conclusions can be drawn

- The optimal dosages for nano-CaCO₃ and nano-SiO₂ were 4% and 3% respectively for improvement the mechanical properties of concrete, mixtures with nano-SiO₂ showed larger strengths than that with nano-CaCO₃ for the same content while binary mixes showed moderate effect.
- Both the nano-CaCO₃ and nano-SiO₂ decreased the flowability and accelerated the heat of hydration of UHSC. For the same content, the use of nano-CaCO₃ resulted in greater flowability compared to nano-SiO₂.
- All admixtures used in this work showed good resistance to water absorption in addition to strength enhancement.

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