The Influence of Nano Silica Surface Area on Its Reacitivity in Cement Composites

Passant Youssef, M. S. El-Feky, Mohamed I.Serag

Abstract— nowadays, nanotechnology is the main trend of research in different areas due to the new potential of using nanometre materials scaled less than 100nm. Nano materials are needed with cement to react with excess CH, produce additional C-S-H, and refine the pore structure to densify the cement matrix, reduce permeability of gases and water in concrete and replace cement to reduce CO2 emission. The present study focuses on the effectiveness of superplasticizers and ultrasonic processing on the dispersion of Nano Silica at first in water and then in cement composites. A qualitative analysis using compressive and flexure strength tests were conducted with a view to investigate the influence of different dispersion techniques on the mechanical properties of cement composites containing Nano Silica (NS) particles with different percentages. In addition micro-structural analysis was carried out to understand the surface morphology and microstructure of cement composites with different dosages of NS addition. The investigational study results showed that the strength can be improved by the the optimum NS concentration by consequence time of sonication was 2.5% by cement weight sonicated for 12 minutes using indirect sonication method. Gain in compressive strength was 97% and 40% for 7 and 28 days respectively as compared to the reference mortar. the experimental program helped in achieving about 100% gain in flexure strength using 0.5 wt. % NS sonicated for 1.5 minutes or 2 wt.% NS sonicated for 3 minutes.

Index Terms— Nano Silica, surface area, sonication, optimization, Nano materials, agglomeration, strength.

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1 INTRODUCTION

The cement industry has a bad effect to eco-system, physical, chemical and biological components of the environment. It is one of the most energy consuming industries due to high amount of CO2 emission, 5% of these emissions are caused by global manmade; 50% by chemical manufacturing and 40% due to burning fuel. Many researchers worked to solve the problem of cement industry either by improving the process of cement manufacturing efficiency or by replacing cement with supplementary cementitious materials, which partially replace the cement weight such as Nano materials, fly ash, slag, natural pozzolans, and Silica fume [1]. Nano materials, such as Nano Silica, are needed with cement to react with excess CH, produce additional C-S-H, refine the pore structure to densify the cement matrix, reduce permeability of gases and water in concrete, solve corrosion problem in the reinforcement and replace cement to reduce CO2 emission [2; 3], by consequence improve compressive strength of cement composites [4]. It also acts as filler in the Nano pores due to its fine particle size, decreasing the water absorption and thus increasing the durability of the matrix. However, when fine NS particles are added to cement, they will coagulate immediately with allowance to form settlements or agglomerates especially when they contact water. This phenomenon affects the rheological behavior of the cement composite and the ultimate mechanical hardened properties Thus; there is a need to increase the repulsive forces between adjacent particles to

disperse the NS particles in aqueous solution. We can conclude that the major problem in the utilization of nano particles is the high agglomeration if used directly as received in a composite; they lose their surface area due to grain growth.

As a result, it is believed that whether by using NS powder, dispersion, or colloidal sol, it is the behavior of the final agglomerates, rather than that of the individual nano silica particle, which controls the pozzolanic, the filling and the nucleation site effects. That's why the main aim of the proposed research plan is to study extensively dispersing nano silica within the cement matrix using ultra sonication under different concentrations and for different durations and finding out the effect of the finally reached surface area of these nano silica particles on the major mechanical properties of cement composites.

In order to achieve the previously mentioned goal, experimental and statistical research plan is to be implemented. The influence of the method and duration of applying direct or indirect sonication energy to disperse Nano Silica will be studied. Particle size distribution will be introduced to investigate the effect of sonication power on NS particles dispersion. Characterization of the main properties of prepared cement mortars containing Nano Silica will be investigated using different techniques; scanning electron microscope (SEM), transmission electron microscope (TEM), X-Ray diffraction (XRD), to reach optimum, and most desirable content of NS by weight of cement.

2 EXPERIMENTAL WORK

The major problem in utilizing Nano Silica is that it is highly agglomerated particles which cause loses in their high-surface area due to grain growth. Effective de-agglomeration and dispersion for Nano-particles is needed to overcome the bonding forces after wetting the powder; the ultrasonic power breakup of the agglomerate structures in aqueous and non-

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aqueous suspensions allows utilizing the full potential of Nano-sized materials [5]. This research discusses the optimum method for Nano Silica dispersion.

Contents of Nano Silica used are (0.5%, 1%, 1.5%, 2% and 2.5%) by cement weight, and sonicated with indirect method for 1.5 min, 3 min, 4.5 min, 6 min, 7.5 min, 9 min, 12 min, 15 min and 18 min. Superplasticizer is added 0.45% by cement weight and water cement ratio is 0.4. 18 mortar samples compose of cubes (5*5*5 cm3) and prisms for compressive and flexure strength tests after 7 and 28 days, water curing. Cement content is 1 kg; sand is 2 kg, 0.4 w/c and 0.4 wt. % superplasticizer. The addition of proper chemical dispersing admixtures like superplasticizer helps in the de-agglomeration of Nano-particles in order to cause electrostatic repulsive forces, as well as cement mixtures compressive strength as some investigators have first dispersed Nano materials in water by using surfactants and sonication and then added the dispersed materials to cement composites [6]. Guidance and evaluation of experimental program of the preparation of Nano Silica particles are made through particle size distribution, scanning electron microscope (SEM), X-ray diffraction (XRD) and thermo gravimetric analysis (TGA). Table 1 shows the constituents of the mixtures. The mixing sequence of the samples is mentioned in figure 1.

TABLE 1

Mixtures composition (gm.)

SAMPLE	CEMENT	SAND	WATER	S.P.	N.S.%	SONICATION TIME
NS 0/0	1000	2000	400	4.5	0	0
NS 0.5/1.5 NS 0.5/3	1000	2000	400	4.5	0.5	1.5 3
NS 1/3 NS 1/6 NS 1/9 NS 1/12	1000	2000	400	4.5	1	3 6 9 12
NS 1.5/3 NS 1.5/4.5 NS 1.5/6	1000	2000	400	4.5	1.5	3 4.5 6
NS 2/3 NS 2/6 NS 2/9 NS 2/12	1000	2000	400	4.5	2	3 6 9 12
NS 2.5/7.5 NS 2.5/12 NS 2.5/15 NS 2.5/18	1000	2000	400	4.5	2.5	7.5 12 15 18

Example:

NS 2/3: Nano Silica 2% of cement weight / 3 min sonication

NS 2.5/15: Nano Silica 2.5% of cement weight / 15 min sonication

1- Cement + SP + water

2- NS + water
Sonication time depends on NS content
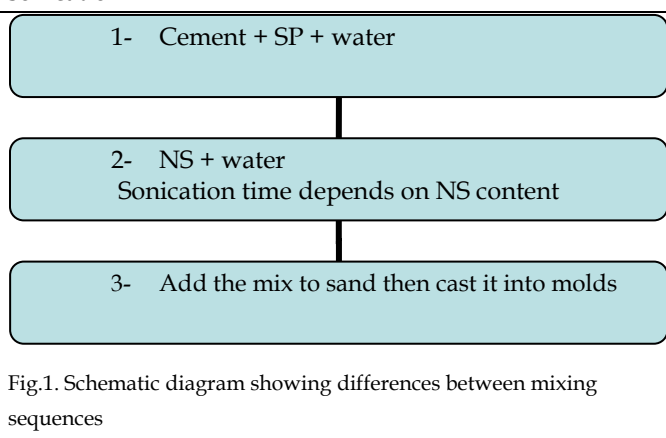
3- Add the mix to sand then cast it into molds

Fig.1. Schematic diagram showing differences between mixing sequences

3 RESULTS AND DISCUSSION

This paper presented the effect of changing sonication time for different dosages of NS in the cement matrix. The results were introduced using compressive and flexure strengths, SEM, TEM, TGA and XRD.

3.1 Compressive Strength and Particle Size Distribution

Figures (2-5) showed the early and late age compressive strength for 1% and 2% NS by cement weight sonicated for different times, the results showed that:

- For 1% NS, increasing sonication time increased both; the early and late compressive strengths of the cement mortars as compared to the control mix.

- Increasing the sonication time over 3 mins, decreased the early compressive strength significantly to reach 266 kg/cm2 at 12 min instead of 394 kg/cm2 at 3 min. This can be attributed to reduction in electrostatic forces, which promoted the particle agglomeration with increasing sonication time and reduced dispersion.

- Increasing sonication time for higher dosages of NS (2%) helped its particles to disperse well, and consequently the early compressive strength increased for all mixes as compared to the control mix, this can be attributed to the fact that increasing NS dosage needed more sonication time to reach a well dispersed condition.

- The optimum specific surface area for 1% NS sonicated for 3 minutes was approximately the same value of that of 2% NS sonicated for 12 minutes, which confirm that increasing sonication time is

required for higher dosages of NS for an effective dispersion, as shown in figures (10-11).

- The optimum sonication time for 1% NS was 3 minutes which lead to a gain in 7 and 28 days compressive strength 84% and 37% respectively.

- The cement mortar contains NS sonicated for 3 min gained most of its compressive strength at the early age, as it reached 92% of its strength after 7 days of curing due to the observed increase in the sub Nano metric particles after 3min of sonication.

- The agglomerated particles of NS dispersed well in samples contained 1% NS sonicated for more than 3 minutes, this was observed from the difference of compressive strength compared to control specimen.
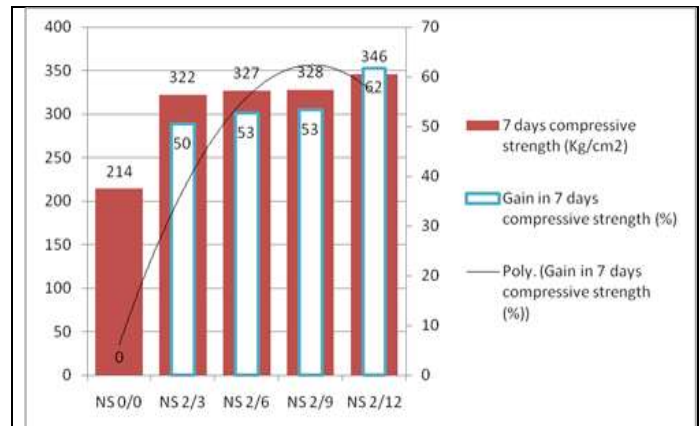
Fig.4. 7 days compressive strength for cement mortars containing 2% NS under the effect of sonication for 3, 6, 9 and 12 minutes
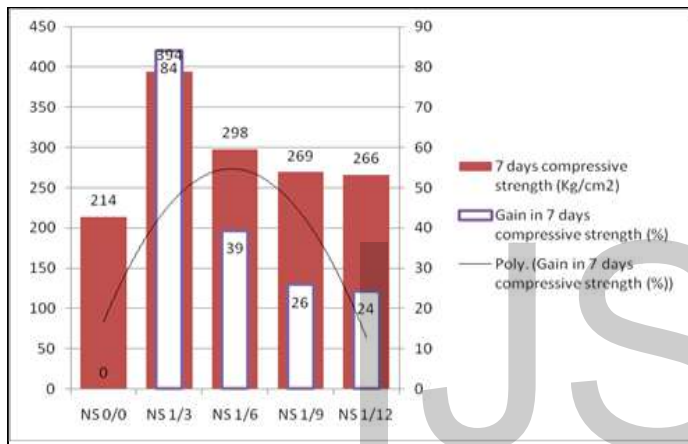
Fig.2. 7 days compressive strength for cement mortars containing 1% NS under the effect of sonication for 3, 6, 9 and 12 minutes
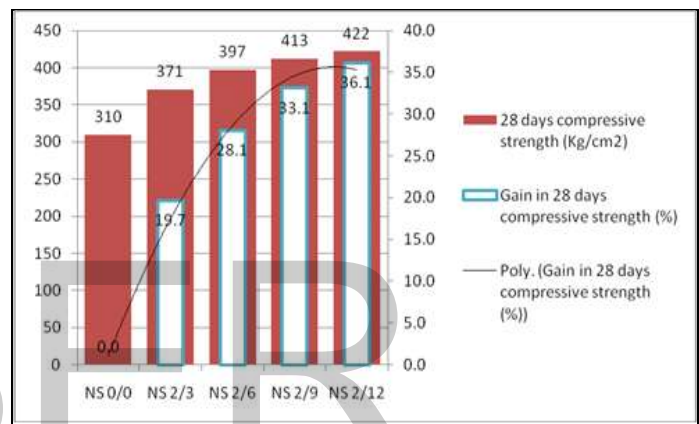
Fig.5. 28 days compressive strength for cement mortars containing 2% NS under the effect of sonication for 3, 6, 9 and 12 minutes
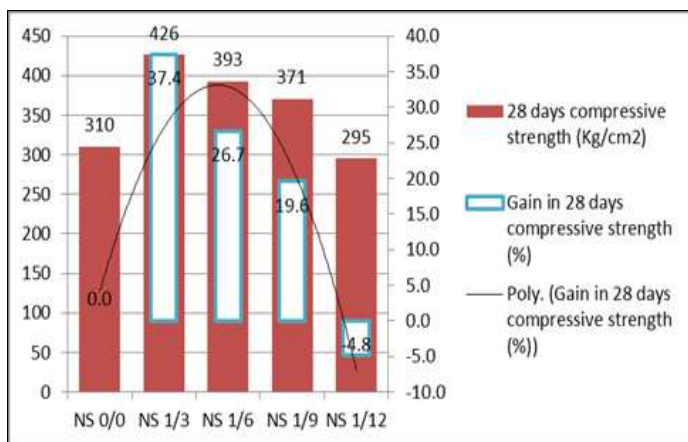
Particle size distribution showed in figures (6-9) confirmed the behavior of the compressive strength;

- Sub-Nanometric content increased to reach an optimum value at 3 min sonication as compared to control for 1%.

Fig.3. 28 days compressive strength for cement mortars containing 1% ns under the effect of sonication for 3, 6, 9 and 12 minutes
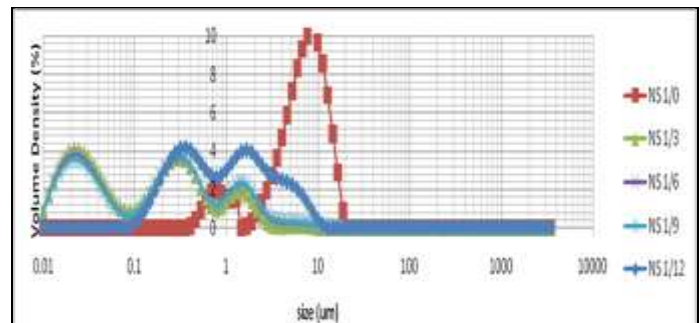

Fig.6. Particle size distribution of 1% NS particles size dispersed in water under the effect of sonication for 0, 3, 6, 9 and 12 minutes
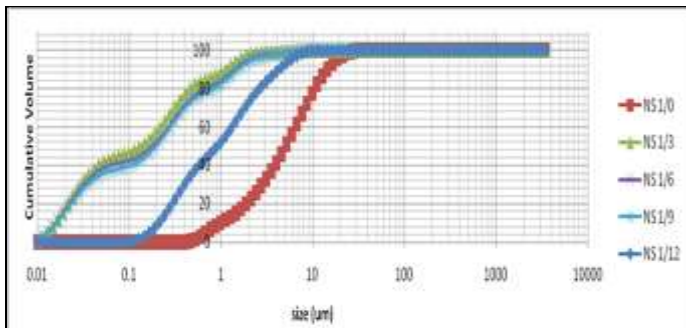
Fig.7. Cumulative density of 1% NS particles size dispersed in water under the effect of sonication for 0, 3, 6, 9 and 12 minutes
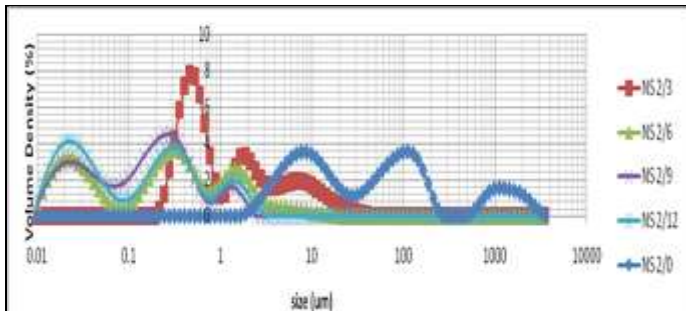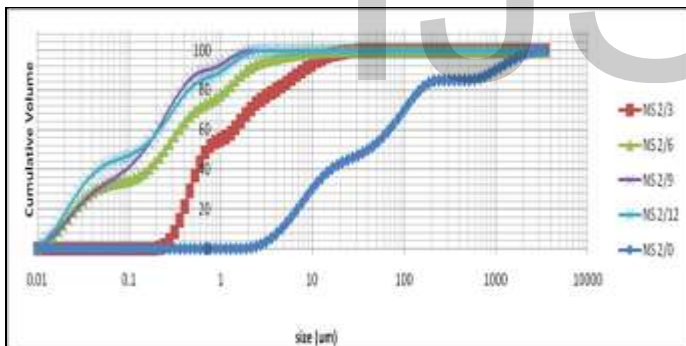

Fig.8. Particle size distribution of 2% NS particles size dispersed in water under the effect of sonication for 0, 3, 6, 9 and 12 minutes
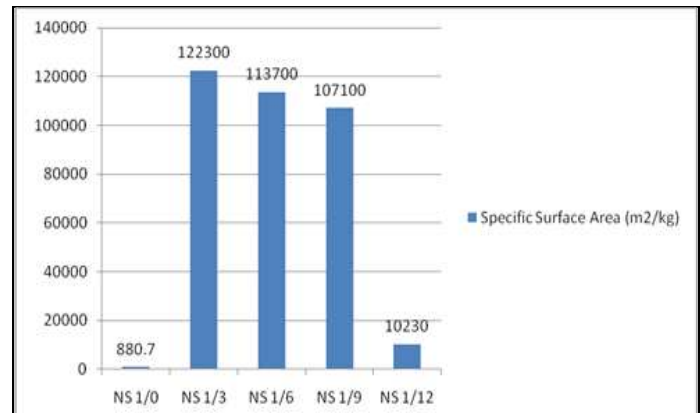

Fig.9. Cumulative density of 2% NS particles size dispersed in water under the effect of sonication for 0, 3, 6, 9 and 12 minutes

Fig.10. Specific surface area for 1% NS dispersed in water under the effect of sonication for 0, 3, 6, 9 and 12 minutes
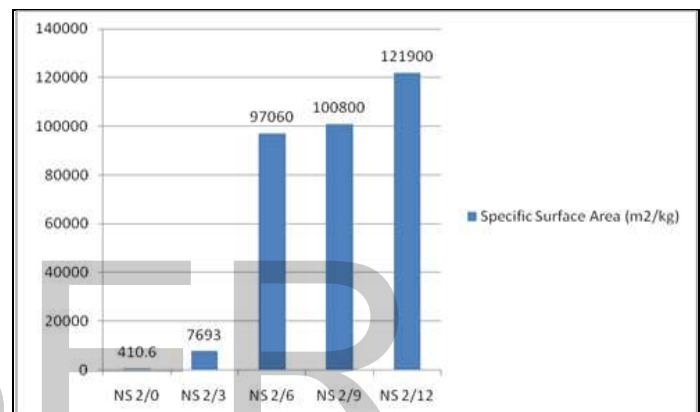
Fig.11. Specific surface area for 2% NS dispersed in water under the effect of sonication for 0, 3, 6, 9 and 12 minutes

- Specific surface area, shown in figures (10-11), for the optimum sonication time for 1% NS is approximately the same value of the optimum time (12 min) for 2% NS.
- Specific surface area is the dominant factor to determine the optimum dispersion for NS.

Figures (12, 13 and 14) showed the early compressive strength for different NS dosages sonicated for the same time 3, 6 and 12 minutes which concluded that:

- Increasing NS dosage need more time of sonication and increasing sonication time for the same dosage causes reduction in compressive strength. This was attributed to re-agglomeration of NS particles and electrostatic repulsion between particles.

- The optimum dosages of NS for the sonication times 3, 6 and 12 minutes were 1%, 1.5% and 2.5% by cement weight.

- The same behavior showed in the latter ages of compressive strength in figures (12-14).
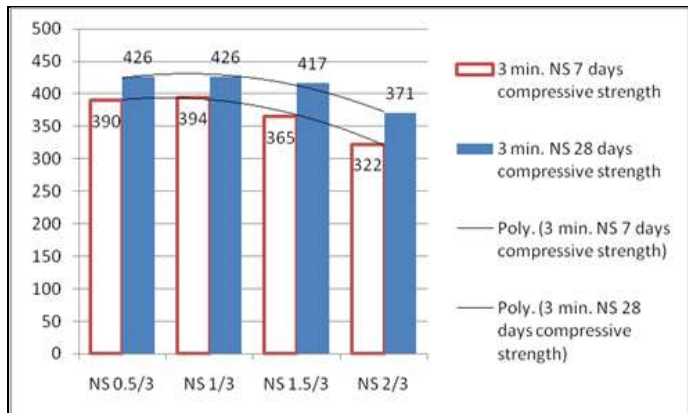
Fig.12. 7 and 28 days compressive strength for cement mortars containing 0.5, 1, 1.5 and 2% NS under the effect of sonication for 3 minutes
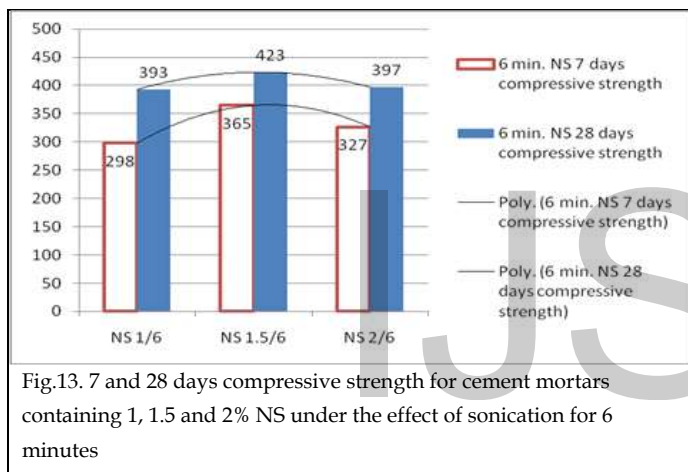

Fig.13. 7 and 28 days compressive strength for cement mortars containing 1, 1.5 and 2% NS under the effect of sonication for 6 minutes
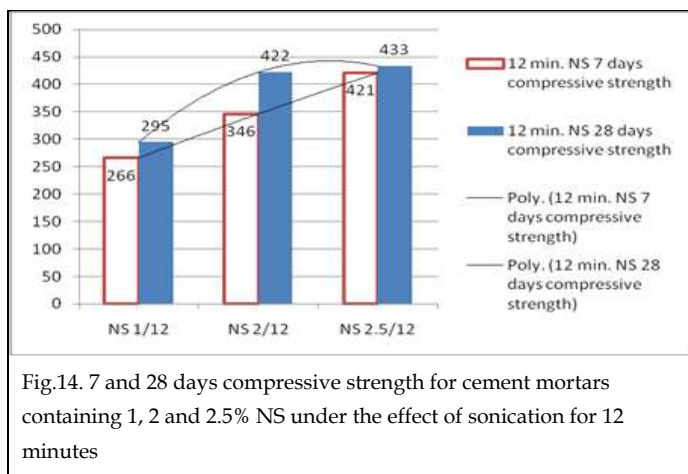

Fig.14. 7 and 28 days compressive strength for cement mortars containing 1, 2 and 2.5% NS under the effect of sonication for 12 minutes

Figure 15 showed the optimum dosages of NS and their optimum time of sonication;

- All dosages got approximately the same compressive strength with average gain 37.5% in 28 days compressive strength.

- The optimum sonication time for 0.5%, 1%, 1.5%, 2% and 2.5% NS was found to be 3, 3, 6, 12 and 12 minutes respectively.

Results displayed in figures (16-18), revealed that:

- No matter the percentage used of ns and no matter the sonication time, the final dispersion condition of ns particles within the cement matrix represented by the specific surface area and the particle size distribution is the dominant factor in determining the compressive strength.

- Changing sonication time had the same effect on the different dosages of NS.

- The optimum NS concentration by consequence time of sonication was 2.5% by cement weight sonicated for 12 minutes using indirect sonication method. Gain in compressive strength was 97% and 40% for 7 and 28 days respectively as compared to the reference mortar.
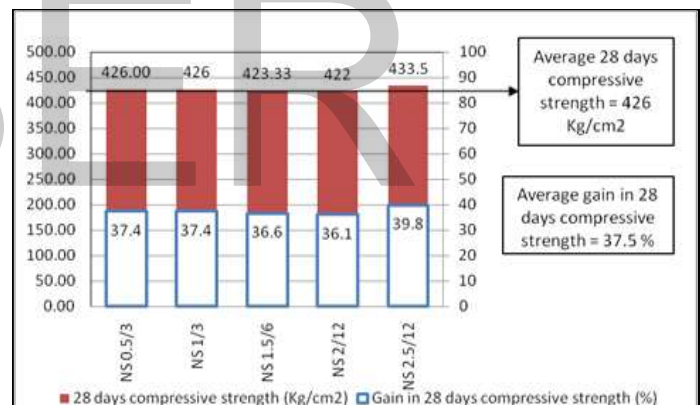

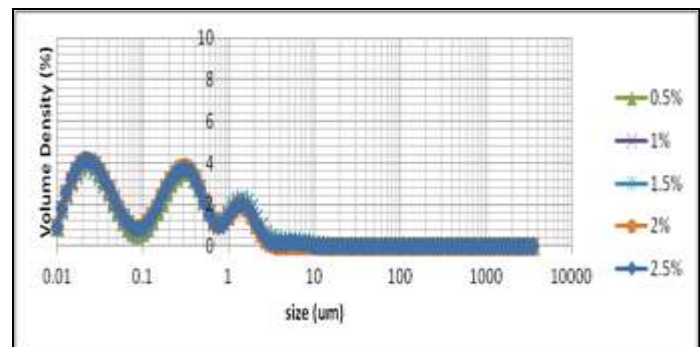Fig.15. 28 day compressive strength for optimum NS sonication time for each concentration

Fig.16. Particle size distribution of optimum NS sonication time for each concentration
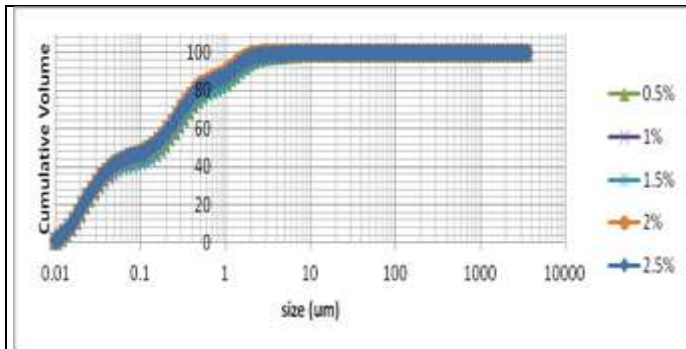
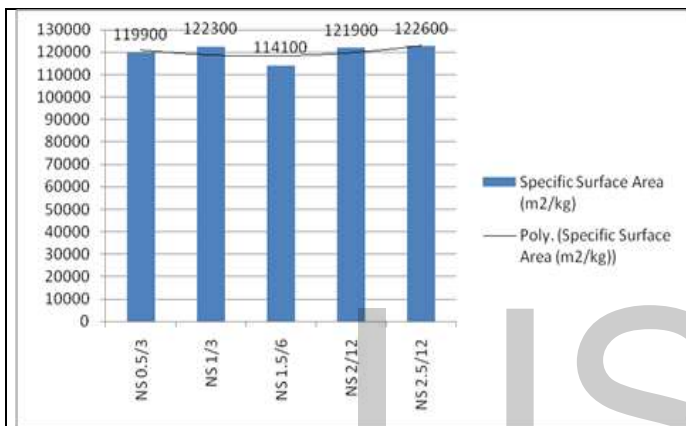Fig.17. Cumulative density of optimum NS sonication time for each concentration

Fig.18. Specific surface area for optimum NS sonication time for each concentration

3.2 Flexure Strength

Figures (19-20) showed that:

- The optimum time of sonication for 1% NS was 3 minutes.
- The sample contained 1% NS sonicated for 3 minutes (NS 1/3) got a gain 67% in flexure strength.
- The flexure strength increased by 100% in the sample contained 2% NS sonicated for 3 minutes (NS 2/3).
- The highest flexure strength was reached using 0.5 wt. % NS sonicated for 1.5 minutes and 2 wt. % NS sonicated for 3 minutes. The gain in flexure strength was 100% as compared to the reference beam.
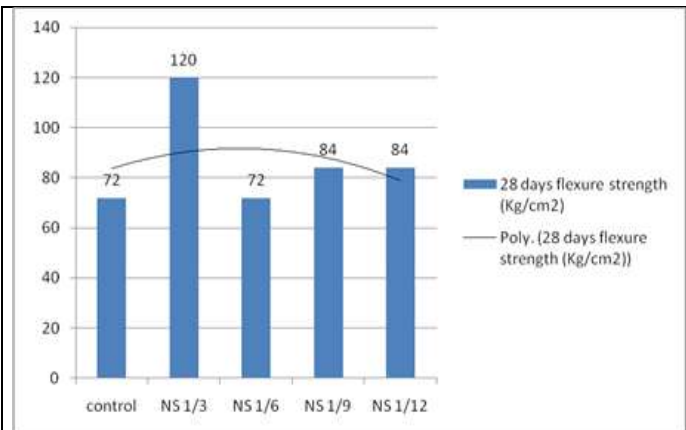

Fig.19. Flexure strength for beams with 1% NS sonicated for 3, 6, 9 and 12 minutes compared by the control batch
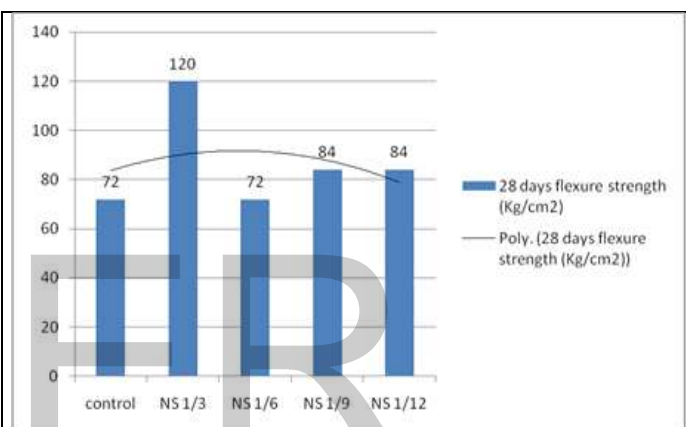

Fig.20. Flexure strength for beams with 2% NS sonicated for 3, 6, 9 and 12 minutes compared by the control batch

Figures (21-22) noted that the agglomeration of NS increased the flexure strength, however well dispersed NS decreased the amount of ettringite needles in the matrix.
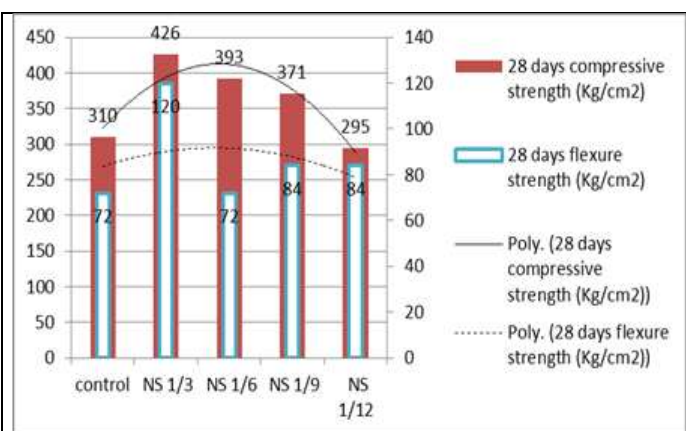

Fig.21. Comparison between compressive and flexure strength for beams with 1% NS sonicated for 3, 6, 9 and 12 minutes compared by the control batch
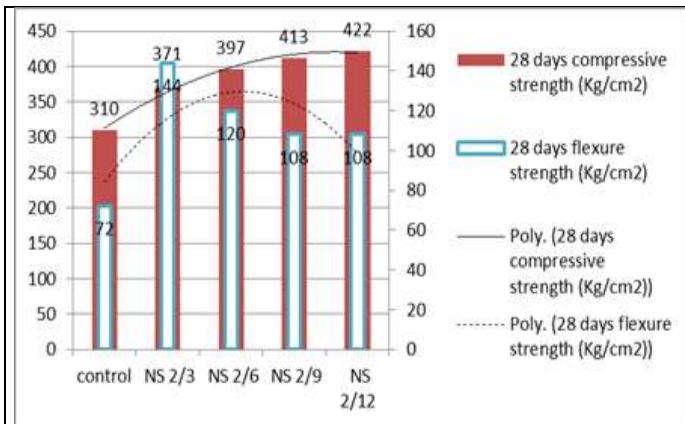
Fig.22. Comparison between compressive and flexure strength for beams with 2% NS sonicated for 3, 6, 9 and 12 minutes compared by the control batch

Figures (23-25) showed the relation between the effect of NS on the compressive and flexure strengths, they concluded that: The flexure strength trend was opposed proportional with compressive strength due to the reaction of NS in early ages so ettringite needles had the opportunity to increase the flexure strength at the latter age.
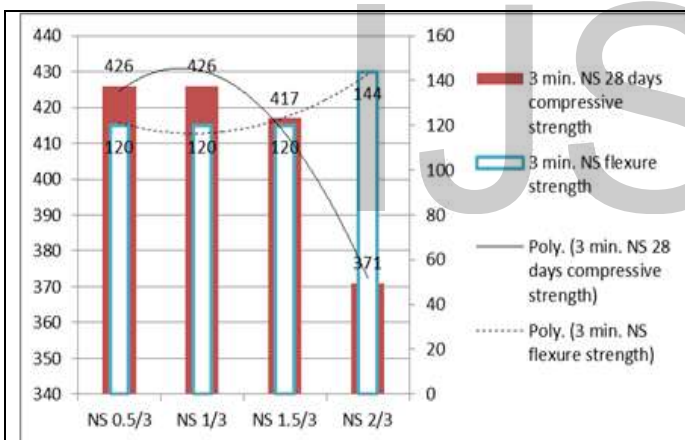

Fig.23. Comparison between compressive and flexure strength for beams with different percentages of NS sonicated for 3 minutes
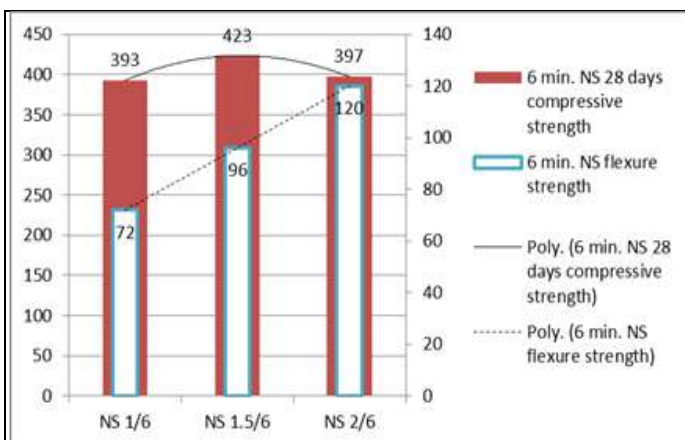

Fig.24. Comparison between compressive and flexure strength for

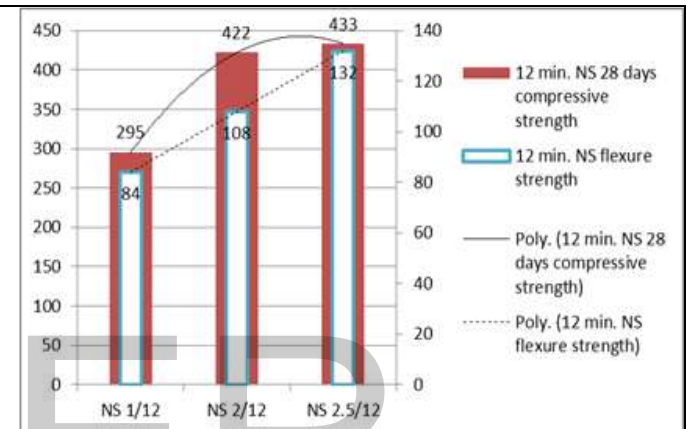beams with different percentages of NS sonicated for 6 minutes

Fig.25. Comparison between compressive and flexure strength for beams with different percentages of NS sonicated for 12 minutes

3.3 Microstrucrure Analysis

SEM micrographs of the optimum cement mortar contained 2.5% NS sonicated for 12 minutes as compared to plain cement mortar were showed in figure (26). The Scanning Electron Microscope (SEM) images were investigated to study the microstructure for the materials.

As for SEM plates, when compared the morphology structure for control samples versus NS system, is in agreement with the poor properties in the fresh state of materials and with the compressive results.

Calcium Silicate hydrate (C-S-H) plates as well as calcium hydroxide crystals were able to be recognized in the control specimen as well as the porous structure of paste as it can be seen in part (a). While for Nano Silica specimen seen in part (b), the calcium Silicate hydrate plates were clearly dominating with a well compacted structure, as a conclusion NS presence contributed to producing higher levels of C-S-H, as the NS's high reactivity acts as a nucleating spot to bind the hydration products together which can explain the high strength of specimens containing NS.

Nano Silica can absorb the Ca(OH)2 crystals, and reduce its size and amount, therefore making the interfacial transition

zone (ITZ) of aggregates and densify the matrix. The NS particles can act as filler material for the voids of the C–S–H structure and act as nucleus to bond with C–S–H gel particles, densify the matrix, and increase its durability.
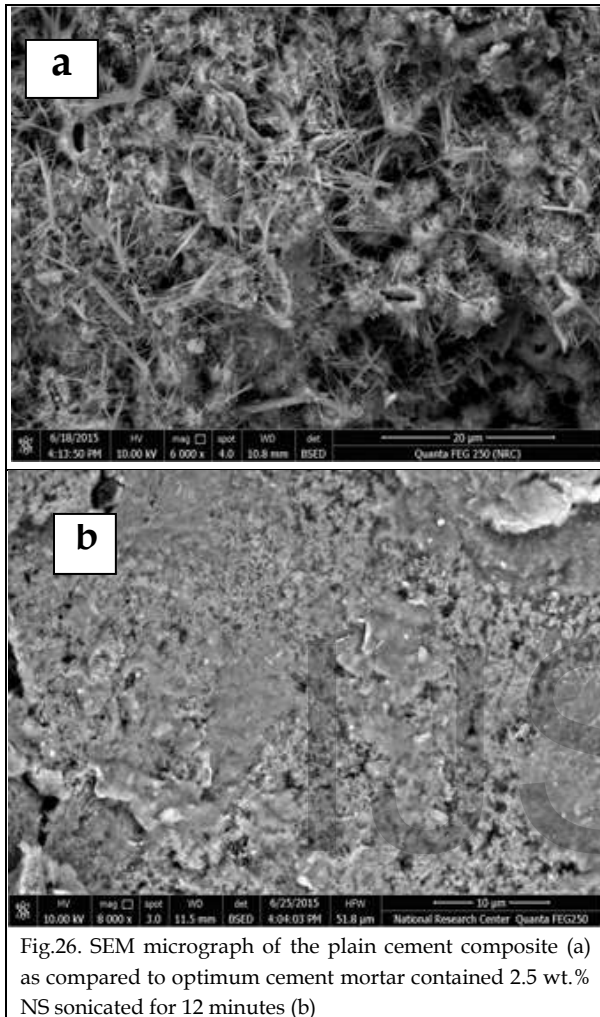

Fig.26. SEM micrograph of the plain cement composite (a) as compared to optimum cement mortar contained 2.5 wt.% NS sonicated for 12 minutes (b)

Fig.27. XRD the plain cement composite

Fig.28. XRD the cement mortar containing 2.5% NS sonicated for 12 min (NS2.5/12)

XRD results were presented in figures (27-28). XRD was carried out to detect changes in the hydration process due to the addition of NS. Due to their crystalline nature, calcium hydroxide Ca(OH)2, calcium Silicate and Silica SiO2 peaks can clearly be observed in the XRD diagrams, while amorphous materials cannot be directly observed using this technique. NS addition caused in a significant decrease in the peaks of calcium hydroxide compared to control specimens. As it can be observed from the semi quantitative analysis where the CH content decreased from 4 % for the CO Mix to 1 %, in the sample contained 2.5% NS sonicated for 12 minutes. While some peaks disappeared due to the high pozzolanic reactivity of NS that produced high amounts of C-S-H, which explains the high strength results for these specimens.
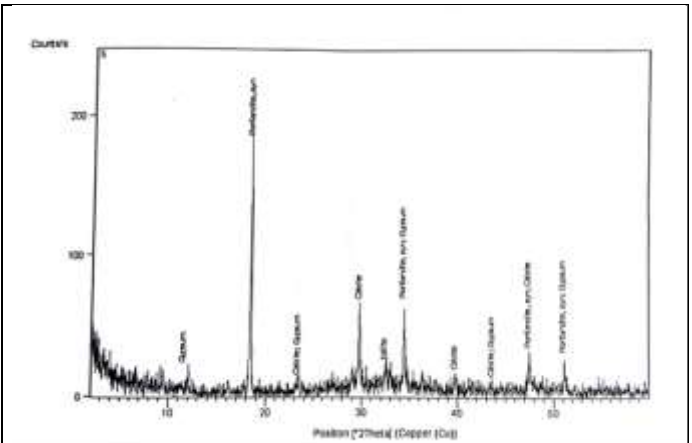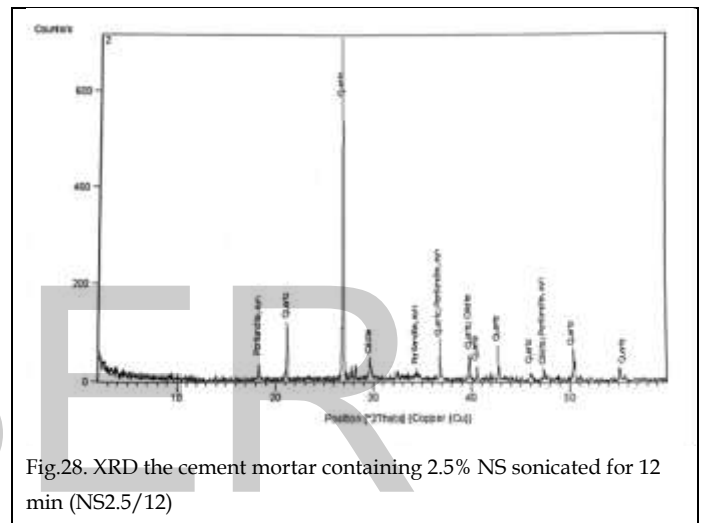
Thermal analysis techniques such as thermo gravimetric analysis (TGA) has been used to determine the changes in hydration products for cement composites after being exposed to high temperatures versus time. A number of studies showed that the increase in temperature in cement pastes causes the release of physically absorbed water, chemically bonded water and the decomposition of hydration products. Figures (29-30) showed TGA micrographs of plain cement composite as compared to the mix containing 2.5% Nano Silica.

Three major peaks can be observed through the DSC curves. The first one is between 80 C and 150 C, which occurred from the loss of the physically absorbed water from the pastes. The second peak, between 400 C and 500 C corresponded to the de-hydroxylation of calcium hydroxide and the loss of some of chemically bonded water from C-S-H. The third peak, between 700 C and 800 C, corresponded to the complete dehydration of calcium hydroxide, which is in agreement with the XRD results, and the dehydration of C-S-H. Moreover, the DSC curves showed that during the temperature increase, the behavior of the specimens with NS is more stable compared to the control specimens. This phenomenon is most probably due to the high amount of high density C-S-H in the specimens that was not affected by high temperature

exposure.

The same figures show the results of TGA, which represents the change in mass for the specimens before and after exposure to high temperatures from 30 C to 900 C. Three main mass losses were observed at 150 C, 450 C and 750 C in the specimens. A dramatic increase in mass loss has been observed in the specimens starting at 650 C approximately. This result can be considered as a start point for the hydration products disintegration, which defines the decrease in strength for specimens exposed to higher temperature.

The loss in weight observed for the control Mix from 30 to 400 (13%) was much higher than the mix containing Nano Silica (2%), this can be attributed to the larger amount of CH in the control mix as compared to the mixes containing Nano Silica. This is in good agreement with the compressive strength results.
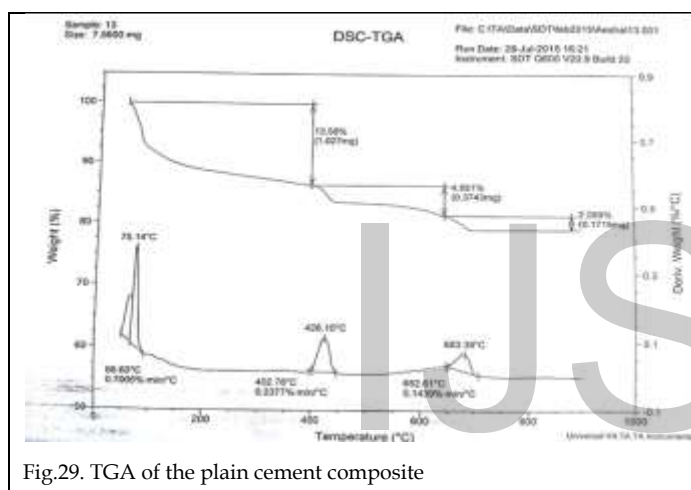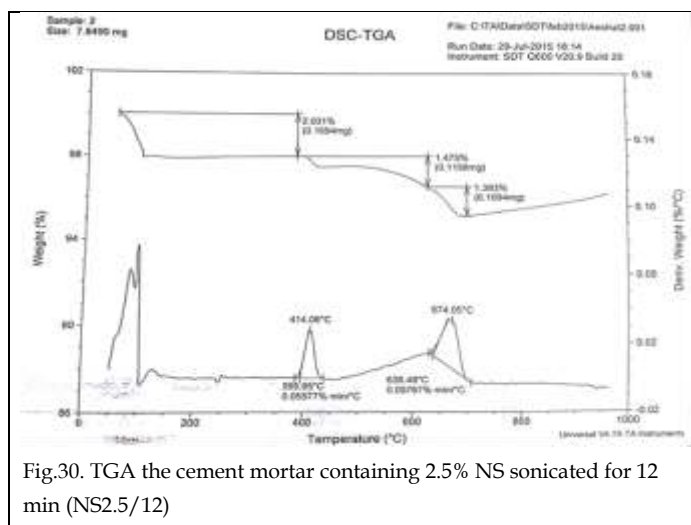

Fig.29. TGA of the plain cement composite

Fig.30. TGA the cement mortar containing 2.5% NS sonicated for 12 min (NS2.5/12)

3 CONCLUSIONS

- The compressive strength increased by adding different dosages of NS (up to 1% by cement weight) at 3 min. sonication time and then re-agglomerated for the higher percentages; the same trend occurred for 6 and 12 min. sonication time.
- Flexure strength trend is opposed proportional with compressive strength due to the reaction of NS in early ages so ettringite needles had the opportunity to increase the flexure strength at the latter age.
- The optimum time of sonication for the following percentages of NS by cement weight 0.5%, 1%, 1.5%, 2% and 2.5% was 3, 3, 6, 12 and 12 minutes respectively. In general, the gain in compressive strength in early age was higher than that in latter age because most of NS reacted with CH early.
- The optimum NS concentration by consequence time of sonication was 2.5% by cement weight sonicated for 12 minutes using indirect sonication method. Gain in compressive strength was 97% and 40% for 7 and 28 days respectively as compared to the reference mortar.
- Specific surface area is the dominant factor to determine the optimum dispersion time and dosage of NS.
- The highest flexure strength was reached using 0.5 wt. % NS sonicated for 1.5 minutes and 2 wt.% NS sonicated for 3 minutes. The gain in flexure strength was 100% as compared to the reference beam.

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