

Characterization of Nano Silica prepared from Iraqi Rice Husk and its Application in Oil Well's Cement

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Abstract

Iraqi Rice husk (IRH) was used to produce nanosilica by precipitation method. The prepared silica nanoparticles samples were characterized using different analytical techniques, these included FTIR, XRD, SEM, AFM and TEM. X-Ray fluorescence (XRF) was used for the quantitative determination of chemical composition of rice husk which reveal that it contains 94.22% silica, after acid leaching it gave 99.04% silica. at 700 °C. FTIR showed bending and stretching absorption bands Si-O-Si at (797) cm^{-1} , (1078) cm^{-1} . X-Ray diffraction shows a strong broad characteristic peak of nano pure silica at $\approx 22^\circ$. Electron microscope image characterize particles size of \sim (60) nm in spherical shape and agglomerated form. The observation by Atomic Force Microscope shows that the average diameter of particles 88.87 nm. The prepared nanosilica from rice husk has a surface area of (194 m^2/g) and pore volume of (0.275 cm^3/g).

Nanosilica pozzolanic material was used as cement admixture in oil field cement to improve compressive strength. The nanosilica cement admixture compressive strength was increase 8%, 9% and 4% at 1.5%, 2%, 2.5% nanosilica percentage adding respectively by weight of cement at 38 °C and 0.1%, 9%, 7% compressive strength percent increase at 60 °C.

Keywords: Iraqi rice husk, Nanosilica, Oil well, cement-admixture.

1. Introduction

Rice husk (RH) is an agro- residue matter that must be excluded. Its composition is similar to the normal synthetic fibers; contains silica as well as other organic ingredients. On ignited, organic content such as cellulose, lignin, hemicelluloses is disintegrated and the resultant is rice husk ash (RHA) [1-3].

RHA is almost silica- wealthy crude substances contains close by 90% to 98% silica with rather significant quantity of metallic ingredients amongst the class of another agricultural residues [4-8].

The silica in RHA must has elevated surface area and found in the amorphous status [9-13]. For this reason, silica has variety of utilization, such as origin for artificial adsorption substances [14-16], bearers, medical additives, composite material fillers [17,18], and obtains superiority when achieved at nanometer dimensions.

In nature, silica endures as sand, glass, quartz. Natural silica is crystalline, while man-made silica is amorphous in form. Silica employed in chemical utilizations is prepared from either silane reagents or silicate solution [19].

The synthesis of nanosized silica from rice husk (RH) is not complicated method and it becomes economical method due to a big obtainable of cheap waste crude material with highly purification percent, elevated surface area, extreme reactivity, and amorphous in shape. This financial method when fasten to residue matter gives also many superiorities to the neighborhood agricultural -industry [20-28]. The sol–gel method [22-24] is practically common process for silica preparation. It consists coincident hydrolysis and condensation reaction. In such process, a sol of silicon alkoxide or sodium silicate changed to gel(a polymeric network).

A variety of process have been inspected for reprovig amorphous silica from rice husk and rice husk ash [29]. Whereas silica nanoparticles synthesized by different methods. Adam et al. prepared spherical silica nanoparticles with extraordinary surface area of (245 m²/g) and narrow pore size distribution (5.6–9.6 nm) with an average diameter of 50.9 nm., from rice husk by solvent extraction and sol–gel technique at room temperature (30⁰C) .[30]

Jal et al. [31] synthesis nano sized silica via precipitation process, and the outcome nanosilica were establish to have a particle dimension of 50 nm. Oil well cement (OWC) slurries is commonly more complex than of normal cement paste, to contend with bottom hole circumstances (broad scope of pressure and temperature), a number of additives are commonly utilized in the OWC slurries, which display various representative properties depending on the union of mixture employed incorporating various chemical and mineral admixtures used [32]. Several researchers have been proposed that nanoparticles can be incorporated into conventional building materials in order to improve some physicochemical properties for instance, silica nanoparticles used as an additive for high performance and self-compacting concrete [33].

2. Experimental Work

2.1. Materials

Rice husk samples were collected from Al-Najaf province in Iraq. Sodium hydroxide was obtained from (LoBAChemie) India, Hydrochloride acid (37%, analysis grade) (Thomas Baker) India, Nitric acid HNO₃ (BDH) England.

2.2. Pretreatment of the Rice husk ash (RHA)

RH was washed by distilled water and then dried; muffle furnace was utilized for calcinations RH at 700 °C for 6 h.

2.3. Preparation of Nanosilica

To ten grams of RHA samples 80 ml of 3.0 N sodium hydroxide solution were added and the mixture was heated and stirred for 3 h , equation (1) shows the reaction:



The solution was filtered and the resultant residue was washed thoroughly with (20) ml hot water. 5N(H₂SO₄) was introduced to the filtrate with continuous stirring of the solution until the pH of the solution reached (2). Then pH of the solution was then raised to (8.5)by the

addition of ammonium hydroxide solution then filtration and drying were carried out at 120°C for 12h. Pure silica was extracted from the above solution using 6N HCl under reflux for 4 h. In order to make the solution acid free deionized water was used to wash it repeatedly. The resultant silica was dissolved in 3N NaOH with continuous stirring for 10 h. A concentrated H₂SO₄ was used to adjust the pH in the range of 7.5-8.5. Warm deionised water was used to wash the prepared nanosilica repeatedly till the filtrate becomes totally alkali free. Nano-sized silica then dried in the oven at 50°C for 48h.[34]

2.4. Acid Leaching Treatment

The metallic components posse a significant impact on the characteristic of produced silica from RH, also an efficient interaction takes place between the silica and metallic ingredient which gives to a substantial diminish in the surface area. It is desired to handle RH with a prime acidic solution such as HCl.

2.5. Cement and Nanosilica Admixture

Cement slurry was prepared (the required mass of water)was placed in the mixing container, then different percentages of nanosilica (1.5,2 and 2.5%) were added to it then it was mixed at 4000 rpm while the cement sample is added at uniform rate is not more than 15 sec.when all mass of cement type G has been added the mixing continued at 12000 rpm for 35 sec The slurry was transfer then to the mould .The curing of the specimens were carried out in curing bath preheated to the test temperature of 38°C and 60⁰ C respectively. Specimens cured at previous temperatures were removed from the curing bath at 45 min.before testing were they removed from their moulds and transfer to a water bath and maintain at 270⁰C for 40 minute specimen are placed in the testing machine to measure compressive strength [35]. The silica samples for compressive strength measurement were prepared according to API spec 10A.ISO10426-1 [33, 36].

3.Result and discussion

3.1. Chemical Analysis of Rice Husk Ash

Ashing in general is carried out to remove undesirable component (metallic ingredients) , increase silicon dioxide percent, and reduce carbonaceous materials. (RHA) when burned at governed atmosphere, highly reactive amorphous silica is obtained. The chemical compositions of the RHA before and after acid treatment were determined by XRF and the results are presented in Table (1)

Table (1): Quantitative chemical analyses of rice husk ash (RHA) before and after acid leaching

SiO₂	Al₂O₃	CaO	SO₃	Fe₂O₃	MgO	K₂O	LOI
94.2	0.15	2.47	0.15	0.5	0.57	0.67	0.2
99.04	0.07	0.11	0.09	0.02	0.06	0.11	0.22

The RHA is an agro- residue, which bears some prime non-essential components. The thermal and acid treatments are consider to be effective in removing these ingredients, thus resulting in a substance with great diminish in Al₂O₃,CaO,SO₃, Fe₂O₃, MgO, and K₂O contents. Since the silica (SiO₂) in the RHA is not soluble in the acid. Its percent in the RHA increases from 94.2% to 99.04%. It's also clearly seen that ashing temperature at (700°C) was chosen, due to amorphous structure of nanosilica which is obtained .This nanosilica has a pozzalonic activity which is necessary when used in cement and concrete [37].On the other hand using of high temperature cause surface soften and speeds up the crystallization of amorphous silica and carbon fixation, which consequently result in crystalline structure of nanosilica produced. The results are agreed well with results obtained by [20, 38]

This acid reacts chemically with metallic impurities, the reacted metals leached from acidic solution trough filtration. Thus effective removal of impurities occurs. The acid leaching does not attack the structure of the nanosilica obtained, whether crystalline or amorphous. Therefore, no change of phase from amorphous to crystalline occurs; the pretreatment method employed has not attacked nanosilica produced. [38, 39].

3.2. Characterization Of Nanosilica

3.2.1. FTIR Spectra for Nanosilica

A-FTIR spectra of the powder prepared from pure silica nanosize particles are shown in figure 1; the predominant peaks at 797 cm⁻¹ and 1087 are due to the symmetric and asymmetric stretching manners of (Si-O-Si) respectively. No band was observed between 1800 and 2300 cm⁻¹, which means there were no primary organic compounds in the silica after governed ignition and extrication. Our results are agreed well with results obtained in work by [34].

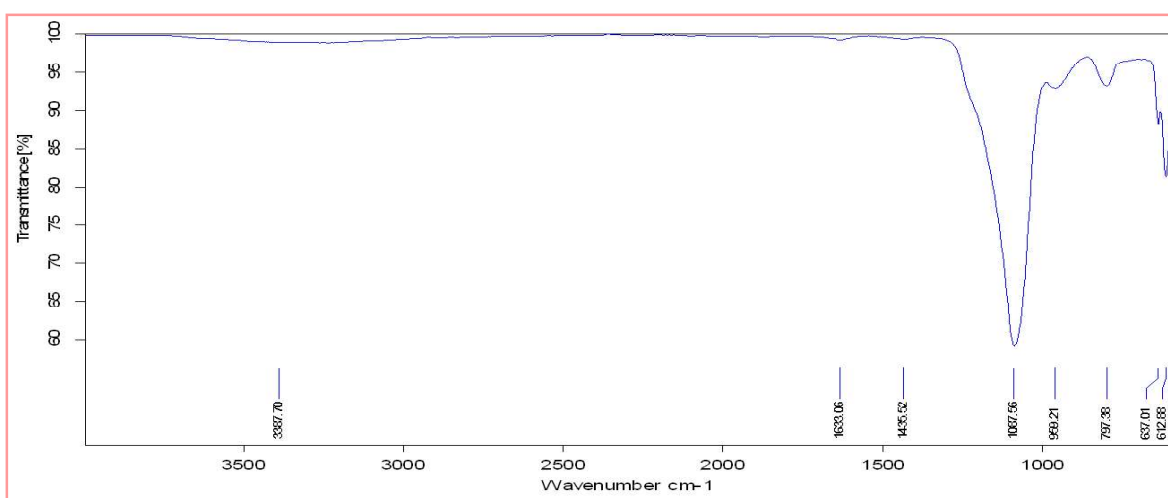


Fig.(1) FTIR spectra of the nanosilica particles from (RH)

3.2.2. X-Ray diffractograms

X-Ray diffract diagrams for nanosilica is displayed in figure 2; a strong broad characteristic peak of nano pure silica at $\approx 22^\circ$ (2θ), which show the amorphous nature of the prepared nanosilica particles. The lack of sharpened peaks confirmed the lack of orderly crystallize configuration in the primed RH-nanosilica, the result obtained here are agreed well with the result get by [34, 40].

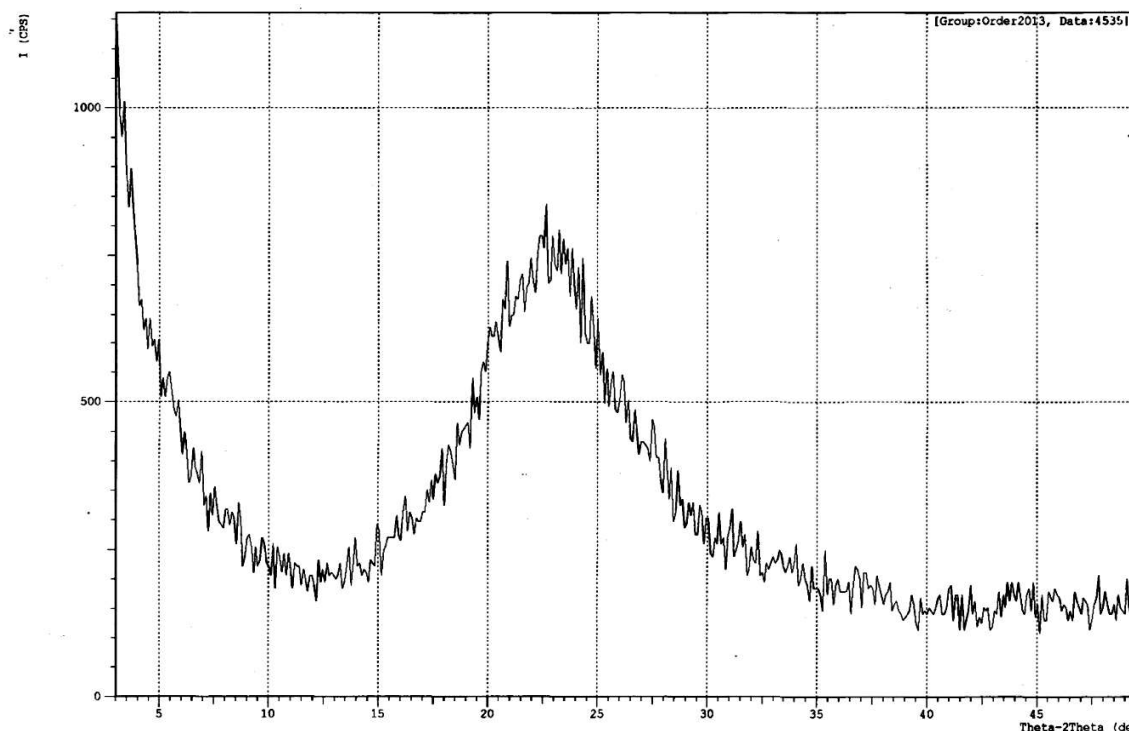


Fig. (2) XRD diagram of the nanosilica particles from (RH)

3.2.3. Surface area and Pore volume

It concluded that the amorphous nanosilica particles is of high purity, relatively high surface area(194) m^2/g and pore volume (0.275) cm^3/g . Silica with this specification is suitable compound to be used as support for catalyst or as adsorbent. On the other hand the conductivity of silica is straight associate to its surface area. The high surface area and pore volume is due that fact that the organic material has been fragmented through the thermal broken up of RH therefore depart a greatly spongy configuration. The enlarging pore volume of nanosilica particles approves this event.

3.2.4. Scanning Electron Microscope for Nanosilica (SEM)

SEM images were utilized to identify the size, shape and dispensation of the nanosilica. Figure 3 shows the SEM image of synthesized nanostructures products prepared by precipitation method from rice husk. Nanosized silica with a mean diameter of ~ 60 nm recognized in highly agglomerated form, due to Van Der Waals forces into larger aggregated nanoparticles. This distinct

capability for aggregation which is extant in the particles was due to the Van-der-Waal forces acting between the specific particles. Agglomeration was due to the hydrogen bonding between silanol groups on the surface. Thereafter rice husk SiO₂ nanoparticles have large extent of shape from random aggregates to spherical nanoparticles. As can be seen in results obtained that the particle size of nano-silica is not uniform and various primary particles appear to gathering or coalesce at their faces. These results agree well with the result obtained by [23].

3.2.5. Transmission electron microscope (TEM)

Figure 4 displays the morphology of nanosilica prepared by precipitation method. The TEM figure shows various structures of the (NS) particles including irregular shape particles, spherical in shape and highly agglomerated in form due to Van der Waals force on the particle surface and confirms the solid structure of nanosilica. The range of diameters is 60 nm for the sample tested.

3.2.6. Atomic Force Microscopy (AFM)

Figure 5 shows the AFM topography were studied with (496 - 499) pixel density for nanosilica by precipitation method indicates that particles in spherical form. Figure 6 shows a three-dimensional surface profile atomic force microscope observation identified the diameters of prepared nanosilica. Particle size distribution shown in Table (2) indicates that nanosilica was in range of (50-140 nm) and average diameter of 93.40 nm.

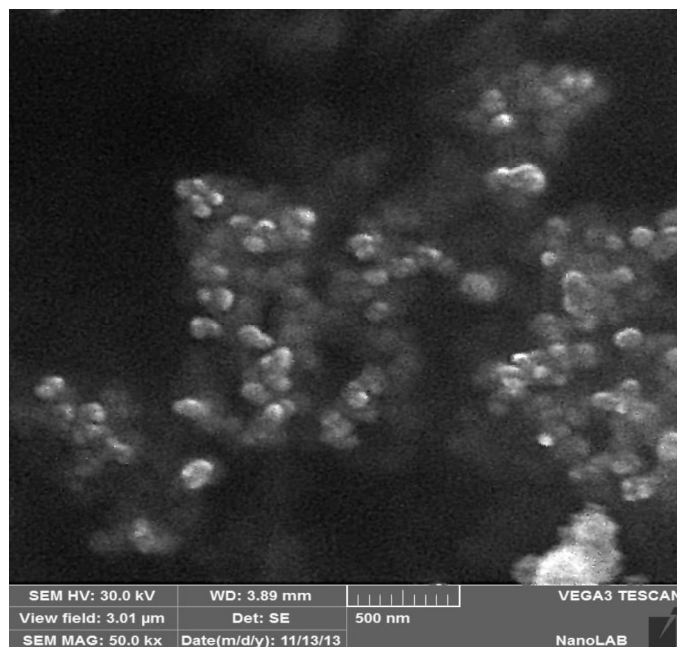


Fig.(3) SEM of nanosilica produced.



Fig.(4)TEM of nanosilica by precipitation method.

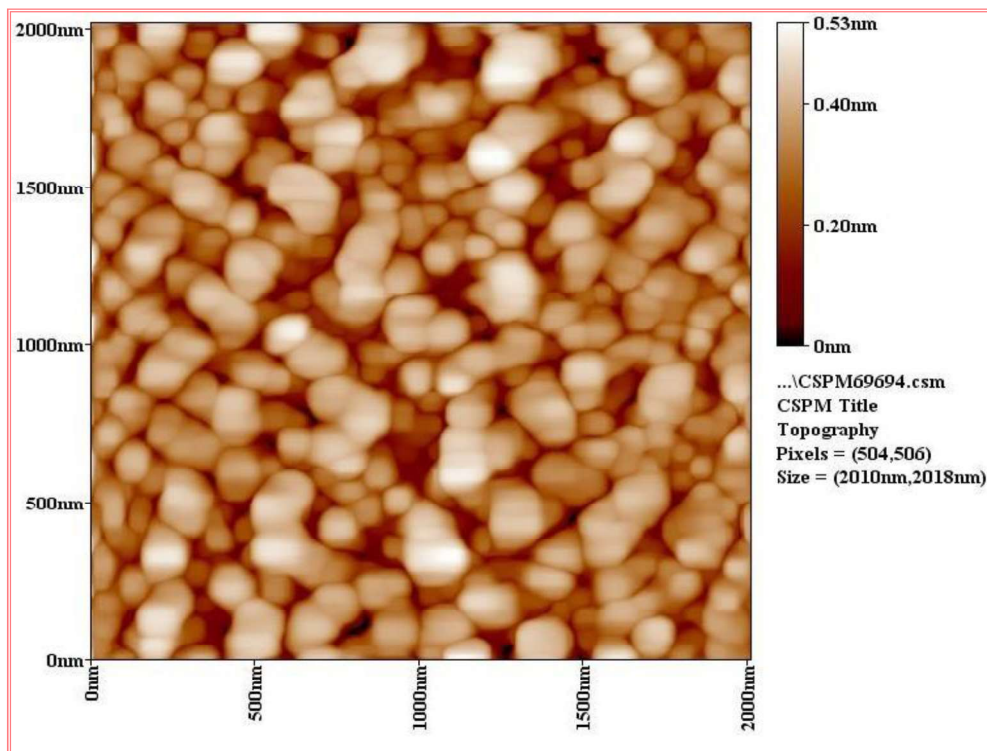


Fig.(5) AFM for Nanosilica.

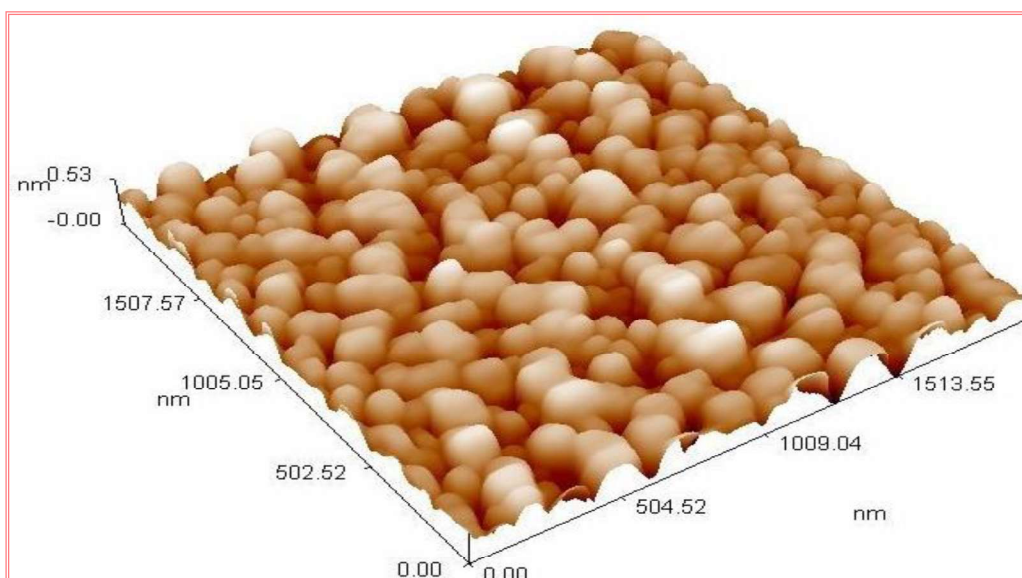


Fig.(6) AFM three-dimensional surface profile for nanosilica particles.

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The three dimensional surface image shown in figure (6) confirms that nanosilica particles are spherical in shape and agglomerated in form.

Table (2): Particle size distribution for nanosilica (Avg. Diameter: 93.40 nm)

50.00	2.14	2.14	85.00	7.14	41.43	120.00	2.86	81.43
55.00	2.86	5.00	90.00	5.71	47.14	125.00	5.00	86.43
60.00	2.86	7.86	95.00	5.00	52.14	130.00	6.43	92.86
65.00	3.57	11.43	100.00	5.71	57.86	135.00	5.00	97.86
70.00	7.86	19.29	105.00	5.00	62.86	140.00	2.14	100.00
75.00	9.29	28.57	110.00	12.86	75.71			
80.00	5.71	34.29	115.00	2.86	78.57			

Table (2) and figure (7) show the particle size distribution for nanosilica and the results obtained confirms the most volume percentage 12.86 % of particle size distribution was at 110 nm and the lowest volume percentage 2.14% was at 140 nm.

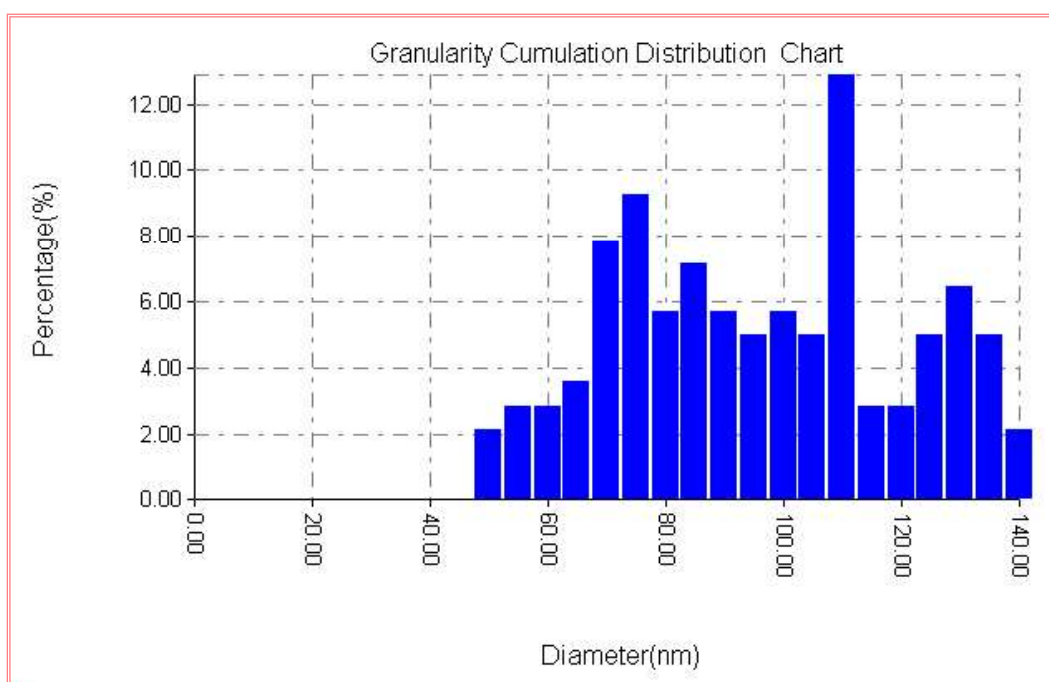


Fig.(7) Bar chart of particle size distribution for nanosilica .

3.3. Composition of Cement

Tables (3) and (4) show the physical properties and chemical composition of oil well cement class G used in the experimental work based on API standard. These properties indicated that this cement is suitable to be used since it is in the successful range of API specification standard [36].

Table (3): Physical properties of oil well cement

Property	API Standard	API Result
Density	1.9	1.82
Free water	5.9	3.75
Thickening time	(90-120)	96

Table (4): Chemical composition of oil well cement

Component	API standard	API result
MgO	6	0.2
SO ₃	8	1.9
Na ₂ O	0.75	0.52
C ₃ S	65	61.33
C ₃ A	3	1.72
Tetra- C ₃ A C ₄ AF +2 C ₃ A	24	21.8
Insoluble residue	0.75	0.25
Loss on ignition	3	2.1

3.4. Characterization of Nanosilica Admixture

3.4.1. Scanning Electron Microscope for Nanosilica Admixture

4. Figures (8,9) show the SEM micrographs of the cement mixture; demonstrate porous structure that is full of large size pores and presence of $\text{Ca}(\text{OH})_2$ that over-shadowed. Also it can be seen from same figures the existence of many CH crystals connected to the C-S-H gel which indicates that the hydration process is not completed and also explains the low results of compressive strengths for the blank mixture. Also, the same photos show that the concentration of the CH is higher than the C-S-H gel concentration and that the CH hydrate needles cover a large area. Our results are agreed well with the results obtained by [34].

5. The SEM images of admixture with added nanosilica as shown in Figures (10&11) that is prepared with 2% nano-silica of nominal particle size (60) nm. These Figures (10&11) show that the microstructure of the cement mixture after incorporating (NS) is dense and more organized with a small number of $\text{Ca}(\text{OH})_2$ crystals and small sized pores as compared with the blank mixture. The C-S-H gel existed in the form of clusters lapped and jointed together by many CH needles hydrates, it can also be noticed from the same photo that the CH needles are visible and there is a compact structure with the absence of the unhydrated crystals and voids and more uniform and homogeneous than that of the blank sample, which explains the superior compressive strength results. This could be due to the high activity of many particles that promote the pozzolanic reaction to developed more than C-S-H gel in order to record high compressive strength which is confirmed by the strength results, that is in good agreement with [34]

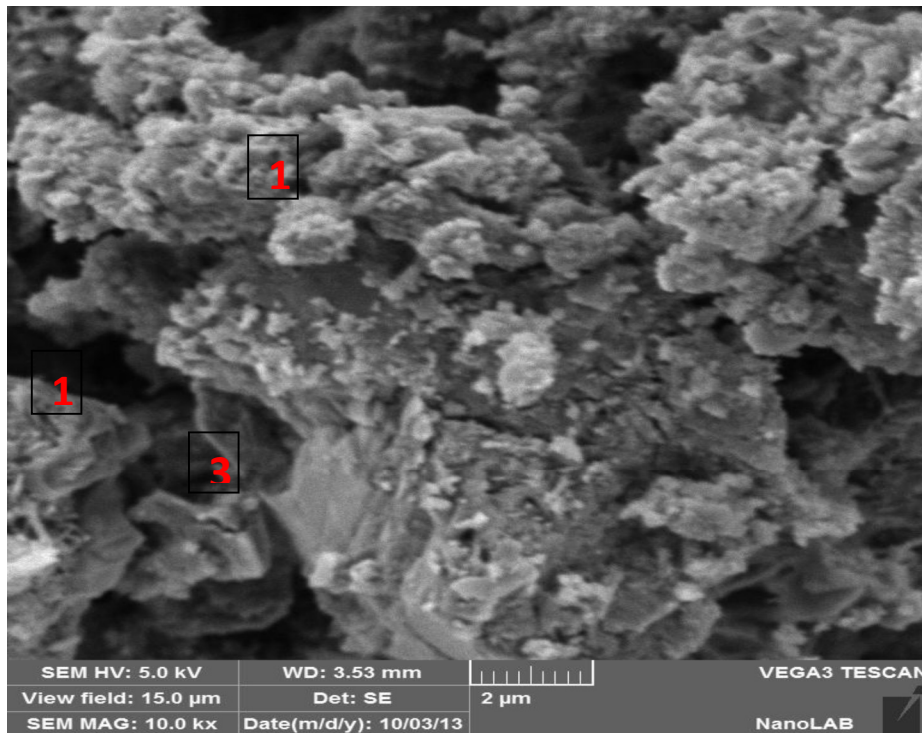


Fig.(8) Cement without nanosilica at 38°C.1 =Ca(OH)₂crystal,2= C-S-H,3 = pore.

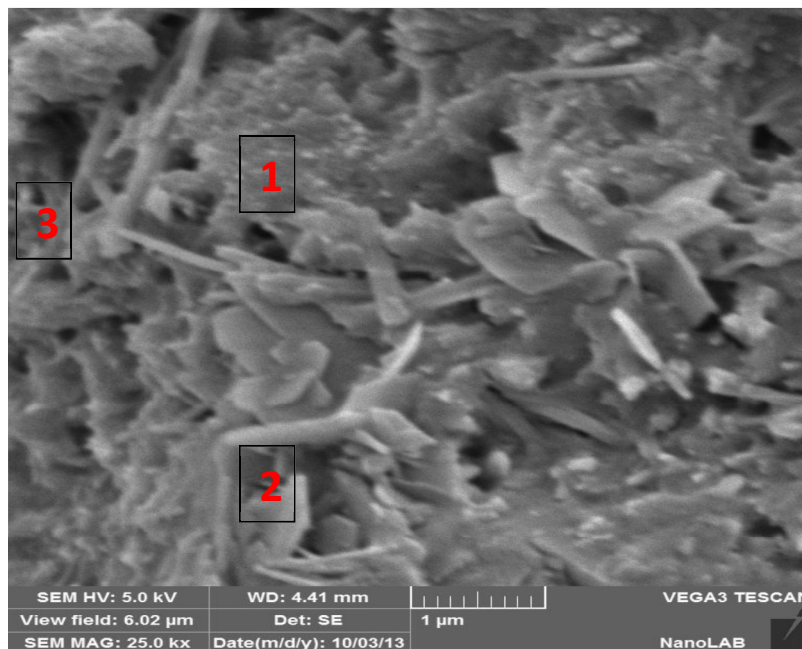


Fig.(9) Cement without nanosilica at 60°C.1 =Ca(OH)₂ crystal,2= C-S-H,3 = pore.

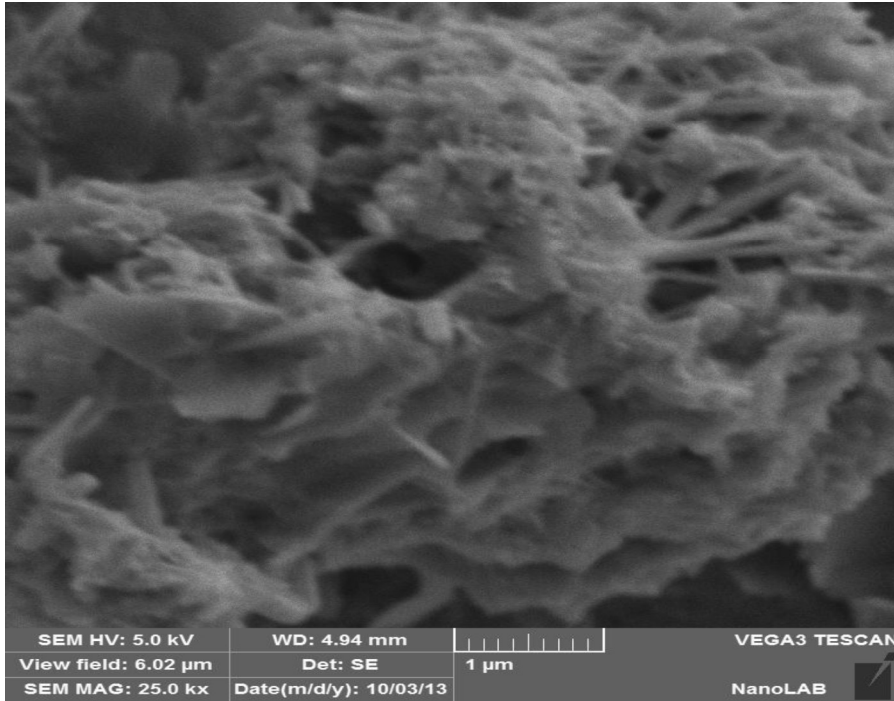


Fig.(10) Cement and 2%nanosilica at 38°C.

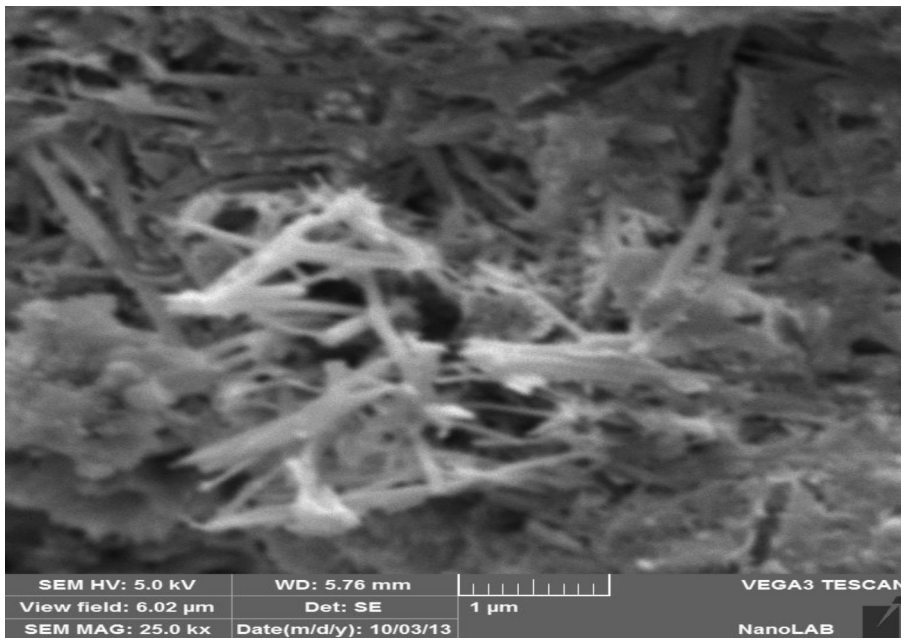


Fig.(11) Cement and 2%nanosilica at 60 oC.

5.1.1. XRD for Cement and Nanosilica Admixture

Figures (12, 13) show XRD for oil well cement (OWC) before and after adding nanosilica particles. Calcium hydroxide (CH) was found out, at 17.90, 47.10 and C₃S was found out at 28.80, 32.40, and 33.70. It is clear from Figure 15, calcium hydroxide (CH) is almost decreased after the addition of nanosilica particles and can conclude from that these nanoparticles react with (CH) during the hydration process. However more alite (C₃S) and belite (C₂S) known as a contributor for late strength of cement pastes are appeared after incorporating of 2% nanosilica under ambient conditions as it is inferred in Figure (13) which indicates extra quantity of C-S-H was produced. The pozzolanic reactivity of nanosilica particles at prematurely situation of hydration is obviously extraordinary and improves the microstructure of OWC system, thereby enhancing the compressive strength of OWC.

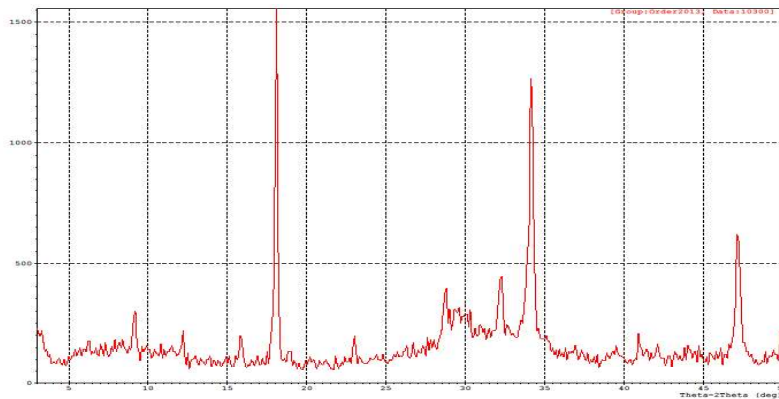


Fig.(12) XRD of oil well cement class G.

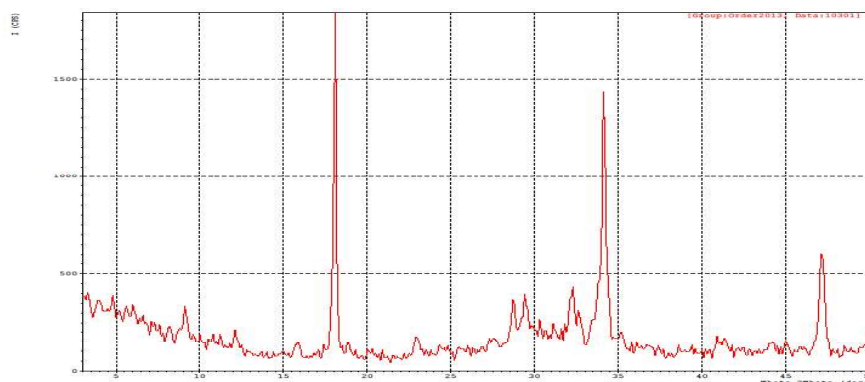


Fig.(13) XRD of cement with 2% nanosilica.

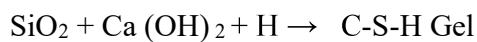
1.1.Compressive Strength Test of Cement

Table (5) shows the affect of adding nanosilica particles on compressive strength of oil well cement class G.The test was carried out for 8h at temperature 38°C and 60 °C as specified in API specification (10A) for cements and materials for well cementing [36].

Table (5): Compressive strength tests

Compressive strength	Without nanosilica	With nanosilica		
		1.5%	2%	2.5%
(8 h psi and 38 °C)	879	953	963	919
(8 h psi and 60 °C)	2090	2094	2306	2262

Table (5) showed that the maximum compressive strength of oil well cement class G was obtained when 2% nanosilica particles were added to the cement. Nanosilica particles can block the pores in the (C–S–H) gels, behaving as a nano-filler. In addition, the amount of (C–S–H) increases as result of the pozzolanic reaction of nanosilica with calcium hydroxide, which upgrades the strength and durability of the material [41].



A cement paste is comprised of C-S-H gels, pores. These pores represent spaces that accommodate nanosilica particles, consequently increase the compressive strength of pure cement paste; however, as nanosilica particles are facile to accumulate because of their great surface energy, thus a large quantity of these particles cannot be uniformity displeased. It is obviously noted that compressive strength increased with increasing the percentage of nanophase additives; In this case, nanosized silica, but enlarging in quantity tof nanosilica decrease the compressive strength as it occur when 2.5% nanosilica added. This attributed to nanosilica is considered as a lighten agent, therefore it was showed this condition as a result of fitness of the particles and accumulation attribute by problems to disperse the particles during mixing, thus intensifying the quantity of nanosilica percentage lowered slurry density which finally leads to lower compressive strength of cement. [33]

6. Conclusions

Nano-silica was successfully synthesis from local Iraqi rice husk by precipitation method, such process is basic and protective way for the preparation of particle in nanoscale. The Characterization of Nano-silica by SEM , AFM ,FT-IR and TEM showed the ultrafine product of nanosilica were spherical particles and agglomerates form with amorphous structure and high specific surface area of $194 \text{ m}^2/\text{g}$ and pore volume $0.275 \text{ cm}^3/\text{g}$, this leads to incorporation of cheap nanosilica produced in low cost at various application such as oil well cement(OWC). Moreover, reaction of nanosilica particles with CH crystals of cement produced higher amount of C-S-H which in turn increase the strength and durability of the cement. The Nanosilica cement admixture compressive strength was increase 8%, 9% and 4% at 1.5%, 2% , 2.5% nanosilica percentage adding respectively by weight of cement at 38 °C and 0.1% , 9% , 7% compressive strength percent increase at 60 °C.

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