NANO - SILICA (SiO₂) CONTRIBUTION TO MECHANICAL AND MICROSTRUCTURAL CHARACTERISTICS OF HIGH PERFORMANCE CONCRETE PAVEMENT

* Dr. Nahla Yassoub Ahmed [1]　　　　　***Fatimah Fahem Alkhafaji [2]**

1) Prof. Civil Engineering Department, College of Engineering, University of Babylon, Iraq, Babil .

2) Ph.D. Student, Highway and Transportation Engineering Department, Mustansiriyah University, Baghdad, Iraq.

Abstract: High performance concrete pavement appears to be the best choice for layer with high strength and low cost. In this paper, the mechanical properties were investigated which considered essential for design and requirements of rigid highway pavement. These properties were examined by compressive strength, flexural strength and modulus of elasticity. Previous test investigations were imposed for concrete mixes with different Nano SiO2 (size of 30 nm) percentage (0, 0.5, 1,1.5, & 2) % by wright of cement as mineral admixture . Also, X- Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) tests were conducted to indicate the chemical composition of the used admixture. Energy Dispersive Spectroscopy (EDS) was conducted to visualize the micro structural behaviour of concrete during hydration process. Wet and dry mixing methods were utilised to prepare the modified concrete mixes and the results of the more effective method, were adopted. Scanning electron microscopy (SEM) was utilized to investigate the microstructure and morphology of nano concrete mixes. The results of SEM indicated that the microstructural distribution of C-S-H gel were comparable for all the nano mixes. The decrease in thickness of nano concrete layer was associated with the increment in the percentage of nano silica add to the mixes when the other factors remain the same. The best percentage of nano silica was 1.5% by weight of cementitious materials (by using dry mixing method). This percentage satisfied all requirements of fresh and hardened concrete mixes for highway pavement and achieved well microstructure with significant decrement in the thickness of concrete layer which positively reflected on construction cost .

1. Introduction

Rigid Highway pavement plays a significant role in the nation's infrastructure. The construction and maintenance of them consume large amount of energy resulting in environmental impact and reduction of covetable source. Therefore, any method reducing the above harmful impact may reflect positivity on sustainable development [1] .

One of main recent technology is the use of nano concrete mixes to construct rigid highway pavement. The use of nano materials in cement-based mixes have sustainable merits due to the advantages related to the final product. The incorporation of nano materials into matrix improves the mechanical properties of nano composite [2].

Usually, the high specific surface of nano silica particles cause high adsorption of Ca+ ions as well as accelerate the dissolution rate of C3S which in turn increase the hydration rate and the formation of the cement hydration products. In addition, nano silica acts as reactive filler which increase the packing density and reduce the voids within the concrete mass [3].

Corresponding Author: Fatima_alkhafaje86@yahoo.com

The chemical effect of nano silica that reacts with CH (calcium hydroxide) from cement hydration to form calcium Silica hydrate C-S-H. The formation of C-S-H increases the strength and durability of concrete relative to control one. Thus, the nano silica of new composite enhanced the general properties of concrete [4].

The porosity of control hardened concrete mix is approximately high and the mechanical characteristics are comparably low. The use of nano silica initiates the early pozzolanic reaction on the silica products to form C-S-H gel and increase the viscosity of cementitious mix. This process may impose negative or positive effect on microstructural development depending on the percentage of nano silica [5].

1.2. Nano Silica Admixture (SiO₂)

Pozzolanics are known as siliceous and alumina particles reacting with $Ca(OH)_2$-CH to form cementitious products. The mineral characteristics such as particle size and the amorphousness are the main parameter related to Pozzolanic activities. The ultra-size of nano silica causes packing that work as filler inside the matrix of hardened cement paste increasing the strength, durability and sulphate resistance of mixes [6].

2. Experimental Work

2.1. Material

The materials used to prepare the test samples in this research are:

- Water: Tap (drinking) water, free of oils, acids, alkaline, is suitable for sample preparations.
- Fine aggregate: Al-Gkaider natural sand with most particles smaller than 4.75 mm, based on Iraqi requirements (No.45/1984-Fine aggregate based on gradation Zone No.2) [7].

- Coarse aggregate: generally all particles smaller than 20 mm, based on Iraqi requirements (No.45/1984) [7].
- Cement: Al Jeser sulfate resisting cement produced in Iraq was used. The cement conforms to the Iraqi requirements (No.5/1984-type V) [8].
- Nano material: Nano silica (SiO_2) has high purity reaches to 99% and particle size of about (30 nm) with different contents (0%, 0.5%, 1%, 1.5%, 2%) by weight of cement.
- High range water reduces admixture (superplasticizer). Hyperplastic (PC 175) is high performance super plasticizer used as dispersing addition in order to overcome the nano particles agglomeration and ensure reactive surface for the filling effect and C-S-H formation. [9].
- Colloidal polymer resins admixture Poly Vinyl Alcohol (PVA) is colloidal material (solid white granules) in water help dispersion of micro material [10].

2.2. Concrete Mix

The concrete mix was prepared to achieve the requirements of concrete mixture construction (C30) according to ACI 211.1) [11].

2.2.1. *Types of Nano Mixing Method*

For better performance, the following main mixing methods [6], which were used to solve the problem of nano agglomeration during addition to cement binder within nano modified concrete mixture:

1. Wet Mixing Method

Nano silica admixture was mixed with first part of mixing water in the presence of Polyvinyl alcohol (PVA) (1% by weight of cement binder) by using stirring device as shown in plate (1-a) for (10 min period) . Then, the solution was treated by sonication device with 50W power for (5 min period) and temperature (25 ℃) as shown in plate (1-b).

The second part of mixing water was mixed with superplastizer (0.5 liter/100 kg of cementitious material) by using electrical mixer. The final step of preparing nano modified concrete mixes was achieved by adding all mentioned solution with the residual mixing water to the other concrete components (aggregate) and the concrete mixes were poured into steel models of specimens, compacted by vibratory table for (3-4) seconds and cured in water bathes at 20-25 °C temperature. [12].

a- Stirring Device   b- Sonication Device

Plate 1. Devices for Wet Mixing Method (Nano Material Laboratory, College of Materials Engineering, University of Babylon)

2. Dry Mixing Method

Nano silica material was added to part of cement binder in a small container and mixed by using rotary mixer for (25 min., period) as shown in plate 2 .

The first part of mixing water was mixed with the superplastizer (0.5 liter/100 kg of cementitious material) by using electrical mixer . The Final step of preparing nano silica concrete mixer was done by adding solution and modified cement to the other components (aggregate) and the concrete mixes were poured into steel models of specimens, compacted by vibratory table for (3-4) seconds and cured in water bathes at 20-25 °C temperature.

a- Rotary Device   b- Nano Silica and Cement Before and After Mixing

Plate2. Rotary Device for Dry Mixing Method (Nano Material Laboratory, College of Materials Engineering, University of Babylon)

- X-Ray Detraction Test of Nano Silica Admixture

The crystallinity of Nano-silica particle was determined by X-ray diffraction (XRD) which is considered the most useful technique for identification of microstructure was shown in Figure (1). The analysis was compatible with the powder is amorphous silica with little impurities.
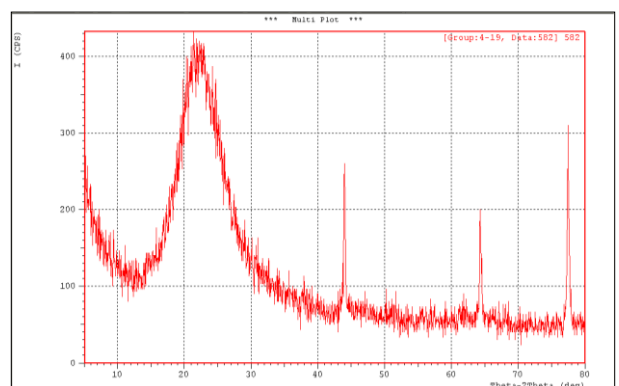

Figure1. XRD Analysis of Nano (SiO_2) Particles (Germany-Iraqi Laboratory, College of Science, University of Baghdad)

- X-Ray Florescence Test of Nano Silica Admixture

It is a simple non-distractive method for testing the quantitative and qualitative analysis of chemical composition of Nano silica material to achieve the purity and chemical composition of the admixture as shown in Table (1).

Table1. XRF Results of Nano (SiO_2) Particles Germany-Iraqi laboratory, College of Science, University of Baghdad.

Sample Name Description	**SiO2** nano			Date of Receipt Method	03/11/2019 12:40 TurboQuant-Powd
Z	Symbol	Element	Norm. Int.	Concentration	Abs. Error
12	MgO	Magnesium	0.0000	< 0.0034 %	(0.0) %
13	Al2O3	Aluminum	92.1309	1.337 %	0.021 %
14	SiO2	Silicon	35531.9665	217.3 %	0.1 %
15	P2O5	Phosphorus	321.0287	0.9260 %	0.0036 %
16	SO3	Sulfur	30.5036	< 0.00050 %	(0.0) %
17	Cl	Chlorine	157.2908	0.02818 %	0.00017 %
19	K2O	Potassium	0.0000	< 0.0012 %	(0.0) %
20	CaO	Calcium	32.8700	0.1493 %	0.0023 %
22	TiO2	Titanium	18.3218	0.0745 %	0.0016 %
23	V2O5	Vanadium	0.6745	0.0059 %	0.0027 %
24	Cr2O3	Chromium	5.3519	0.00088 %	0.00005 %
25	MnO	Manganese	7.9706	0.00504 %	0.00021 %
26	Fe2O3	Iron	343.9652	0.1341 %	0.0005 %
27	CoO	Cobalt	1.6885	< 0.00090 %	(0.00020) %
28	NiO	Nickel	14.2836	0.00205 %	0.00006 %
29	CuO	Copper	5.7928	0.00069 %	0.00006 %
30	ZnO	Zinc	21.8309	0.00190 %	0.00004 %
31	Ga	Gallium	0.0000	< 0.00005 %	(0.0) %
32	Ge	Germanium	0.0000	< 0.00005 %	(0.0) %
33	As2O3	Arsenic	0.0000	< 0.00007 %	(0.0) %
34	Se	Selenium	0.0000	< 0.00005 %	(0.0) %
35	Br	Bromine	2.6583	0.00007 %	0.00001 %
37	Rb2O	Rubidium	10.0029	0.00017 %	0.00001 %
38	SrO	Strontium	52.2717	0.00086 %	0.00001 %
39	Y	Yttrium	62.2349	0.00085 %	0.00001 %
40	ZrO2	Zirconium	10.7622	0.00327 %	0.00009 %
41	Nb2O5	Niobium	0.5148	0.00013 %	0.00004 %
42	Mo	Molybdenum	5.2111	0.00089 %	0.00005 %
47	Ag	Silver	1.7532	0.00054 %	0.00013 %
48	Cd	Cadmium	1.9281	0.00002 %	0.00001 %
50	SnO2	Tin	0.0000	< 0.00039 %	(0.0) %
51	Sb2O5	Antimony	2.1855	< 0.00040 %	(0.0) %
52	Te	Tellurium	0.0000	< 0.00030 %	(0.0) %
53	I	Iodine	0.0000	< 0.00030 %	(0.0) %
55	Cs	Cesium	0.0000	< 0.00040 %	(0.0) %
56	Ba	Barium	2.6371	< 0.00020 %	(0.0) %
57	La	Lanthanum	2.2632	< 0.00020 %	(0.0) %
58	Ce	Cerium	2.3554	< 0.00020 %	(0.0) %
72	Hf	Hafnium	3.1036	0.00034 %	0.00003 %
73	Ta2O5	Tantalum	31.8206	0.00795 %	0.00014 %
74	WO3	Tungsten	2.2527	0.00016 %	0.00002 %
80	Hg	Mercury	3.1389	0.00018 %	0.00002 %
81	Tl	Thallium	4.9419	0.00020 %	0.00001 %
82	PbO	Lead	11.9427	0.00073 %	0.00003 %
83	Bi	Bismuth	0.0000	< 0.00010 %	(0.0) %
90	Th	Thorium	13.6399	0.00056 %	0.00002 %
92	U	Uranium	12.4055	0.00019 %	0.00001 %
		Sum of concentration		220.03 %	

2.3. Testing Procedure

2.3.1. *Fresh Concrete Test*

For all the natural and nano SiO_2 concrete mixes, slump test was conducted immediately after mixing in accordance to (ASTM C-143-89) [13].

2.3.2. **Hardened** *Concrete Test*

- Compressive strength: The cubic samples for the test were manufactured with dimensions (150×150×150 mm) in accordance with (BS 1881-Part 116) [14]. The cubes were tested utilizing the standard testing machine having a capacity of 2000kN.
- Flexural strength test: The samples of modulus of raptures were fabricated in accordance to (ASTM C 78-02) [15] with dimension (100×100×400 mm). These primes were tested by Flexural machine of (2000 kN) capacity.
- Static Modulus of Elasticity: The related test was carried out in accordance to ASTM (469-02) [16]. The cylindrical samples were manufactured with dimensions (150×300 mm). Then, they fixed in compressive machine with attaching stain measuring equipment, and the dial gauge with average of 0.001 mm.

2.3.3. *Microstructural Analysis (SEM Test)*

Scanning electronic microscopy (SEM) is utilised to investigate the Microstructure and the morphology of control mixes and these with Nano silica admixtures as shown in plate (3).

Plate3. Scanning Electronic Microscopy (SEM) with Sputter Coating Device (Microscopic Laboratory, College of Science, University of Kufa)

3. Results and Discussion

3.1. Fresh Properties of Control and Nano Cement Mix

Due to the large surface area of Nano silica (smaller particle size of Nano silica admixture), the initial setting time is reduced and the slump value is decreased that have a significant effect on workability behaviour of Nano concrete mix due to high degree of agglomeration but still within the adopted limitation (25-75 mm slump) except for2% Nano silica content. Thus, there was a greater demand for the superplastizer to achieve the required workability as shown in Figure (2).
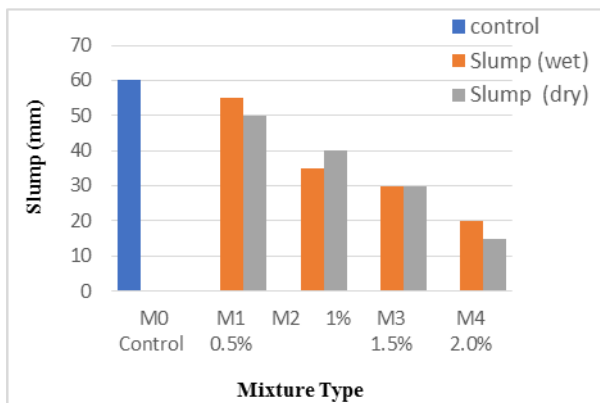

Figure2. Effect of Fresh Mix Type According Nano Silica Addition Content on Slump Value

3.2. Hardened Properties of Control and Nano Concrete Mixes

Nano silica gives both pozzolanic activities due to high surface area and packing ability with significant role in filling voids, thus it increases the mechanical properties.
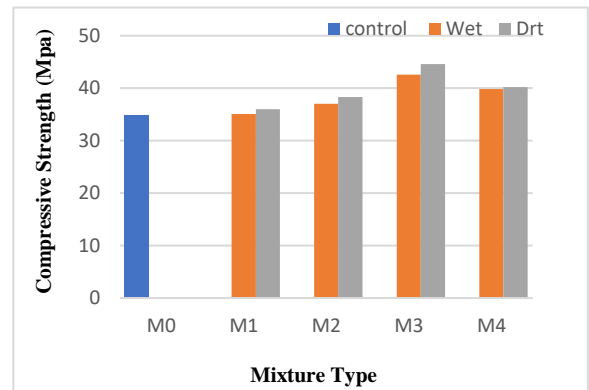

Figure3. Effect of Mix Type According Nano Silica Addition Content on Compressive Strength at Age (28) Days

Moreover, it can participate in the hydration process to create C-S-H product through reaction with $Ca(OH)_2$ [17] .

The increase of strength is the most important benefit of using nano materials like Nano silica as shown in Table (2) and Figure (3, 4, & 5).
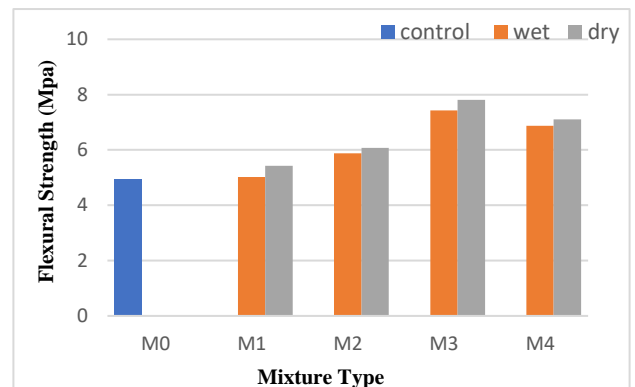

Figure4. Effect of Mix Type According Nano Silica Addition Content on Flexural Strength at Age (28) Days
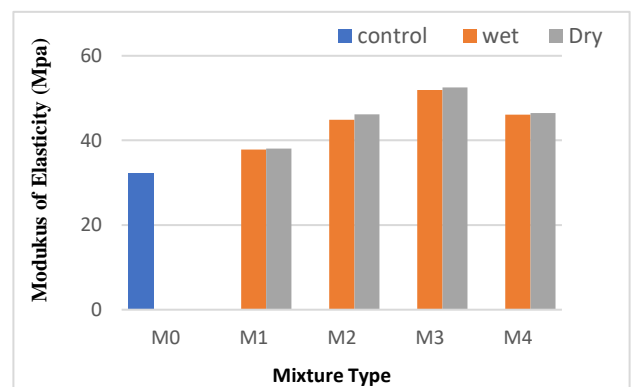

Figure5. Effect of Mix Type According Nano Silica Addition Content on Modulus of Elasticity at Age (28) Days

Table 2. Tests Values of Compressive Strength, Flexural Strength and Modulus of Elasticity at Age 28 Days for Control Concrete and Nano Silica Concrete Mixes

Mix Type	Compressive strength (MPa)		Flexural strength (MPa)		Modulus of Elasticity (GPa)	
	Wet	Dry	Wet	Dry	Wet	Dry
M0	34.78		4.95		32.21	
M1	35.10	35.98	5.02	5.43	37.88	38.07
M2	37.04	38.32	5.88	6.07	44.89	46.19
M3	42.57	44.59	7.43	7.81	51.93	52.51
M4	39.83	40.17	6.87	7.11	46.12	46.50

3.3. Microstructure Analysis of Control and Nano Concrete Mixes

In SEM analysis of concrete mixes, it can be noticed the absence of well-developed $Ca(OH)_2$ plates and the presence of relatively high porosity. When nano particles are uniformly distributed in concrete mix, they fill cement panes and act as concrete core. Due to its intense activity, cement hydration becomes rapid and concrete strength measures especially modulus of elasticity increase that agree with [18].

The microstructure of hydrated cement paste of M3 (1.5% of nano silica addition) was shown in Figure (6-a). The considerable strength obtained in this mix was due to the pozzolanic activity of the Nano silica. The chemical reaction of nano silica with the portlandite $Ca(OH)_2$ leads to production of additional C-S-H gel and less voids. The nano structure is very dense and many crystalic lumps can be observed. From EDS test shown in Figure (6-b), the purity observed matches the specification which presents the predominant phases Oxygen (O), silicon (Si) and Calcium (Ca). That shows a good reaction between silica and $Ca(OH)_2$.
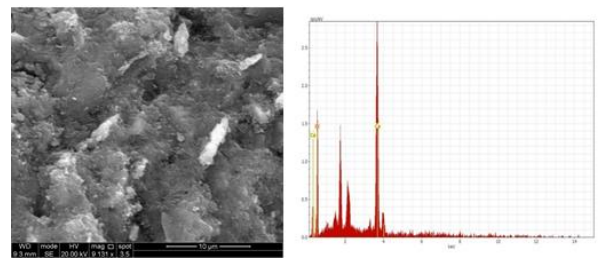
a. SEM Micrograph of M_3.   b. EDS Images of M_3

Figure 6. Microstructure Analysis of M_3 (1.5% Nano Silica Modified Concrete)

From SEM micrograph shown in Figure (7-a), it was observed that C-S-H gel was rapidly spread on the M_0 (control mix) which was the main cause for the effective strength but with Ettringite appearance extend in relatively high air voids. The microstructure looks to contain many amorphous substances. EDS test given in Figure (7-b) presents the predominant phase oxygen (O) and calcium (Ca) only. High concentration of Ca due to the formation of $Ca(OH)_2$ crystals.
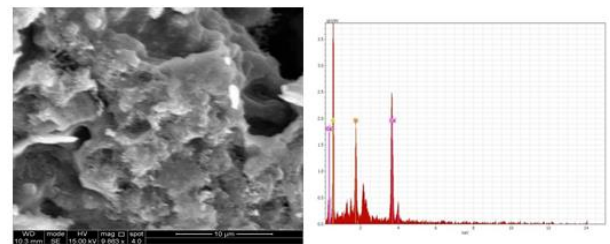
a. SEM Micrograph of M_0 b. EDS Images of M_0

Figure 7. Microstructure Analysis of M_0 (Control Concrete)

4. Thickness Design of Nano Concrete Layer

The thickness of the concrete layer within rigid highway pavement is fabricated in accordance to AASHTO Guide [19]. All mixes are designed to withstand the same conditions. Table (3) shows the comparison which is based on layer thickness between control mix (0% Nano silica addition) and mixes contain different percentages of Nano silica admixture (0.5, 1, 1.5, and 2% %). As given in previous table, the mixes contain Nano silica admixture gives lower thickness than control mixes due to high value of modulus of elasticity and Flexural strength.

This may make saving in construction cost with taking in consideration the Nano silica cost.

Table3. Calculated Thickness Values of Highway Layer For Control and Nano Silica Concrete Mixes

Mix Type	W $18×10^6$	K (pci)	MR (psi)		E×10^6 (psi)	
			Wet	Dry	Wet	Dry
M0	60	200	718		4.7	
M1	60	200	728	787	5.49	5.52
M2	60	200	853	880	6.51	6.69
M3	60	200	1077	1132	7.53	7.61
M4	60	200	996	1031	6.68	6.74

H (in)		Recommended H (in)	
Wet	Dry	Wet	Dry
13.93		14	
13.90	13.36	14	14
12.89	12.70	13	13
11.49	11.20	12	12
11.91	11.71	12	12

5. Conclusions

According to the mechanical properties, with microstructure analysis of nano silica concrete and the results of experimental investigation that are presented in the research, the following conclusions are obtained:

1. The workability of nano concrete decreases with the increase in percentage of nano silica particles, but still within the required limitation except for 2% nano silica.

2. Two nano mixing methods were utilized, wet mixing method by stirring device and sonication device to overcome the agglomeration phenomena and dry mixing method by using rotary device . The results showed that the dry method was better than wet method.

3. An increase in all results of related hardened properties is noticed for nano concrete mix compared to control one regardless to the percentage of Nano SiO_2 added. The increment rate reaches 28%, 57%, 62% of original values of control mixes for compressive strength, flexural strength and modulus of elasticity.

4. The decrement in the thickness of concrete layer was related to the increment in the percentage of nano silica addition in a mix when all other factors are held constant. These decrement rate reaches to 19% of original thickness value of control mix.

5. The SEM analysis of Nano concrete layer with percentage of 1.5% Nano silica admixture showed that high C-S-H hydration product with the uniformly distrusted, few air voids and dense structure were achieved.

6. From the aforementioned results, it can be concluded that the nano concrete layer had a better microstructural and mechanical performance than control layer with preference to use 1.5% nano silica admixture for economical purposes and good pavement performance.

6. References

1. R.Shoshonk and E.Ealayi (2016*)" Flexural Behaviour of Nano Silica Concrete"* IRJ ET val 03 Issue 04, Apr.

2. Saba J.and Seyed K. (2014) *"Effect of Nano-Alumina (N-AL) and Nano silica (NS) as Admixture on Concrete Behaviour"* ICABES -Oct 15-16 Dubai (UAE).

3. Ghalib M.H. and Zainab A.G (2015) *"Effect of Accelerated Curing on Compressive Strength of High Strength Concrete with Nano Silica "Publication* 3073552-Article Dec.

4. Saad I.S.(2016) *" Influence of Nano Materials Action as Partial Replacement of Cement in The Properties of Concrete Pavement"* journal of Nano Silica and Nano Engineering vol2.No.1 pp 1-5.

5. R.Yu, P.Spere and H.J.H Bravuers (2014) *" Effect of Nano Silica on The Hydration*

and Micro Structure Development of Ultra High Performance Concrete (UHPC) With A low Binder Amount " Construction and Building Materials 65 (140-150). .

6. A.E.Al-Salami and M.A.AL-Gawati (2013) *"Pozzolanic Activity of Nano-Silica and Its Application for Improving Physical, Mechanical and Structural Properties of Hardned Cement"* International Journal of Applied Physics and Mathematics Vol.3 No.6 November.

7. Iraqi Organisation of Standard IOS/45-1984 for Aggregate.

8. Iraqi Organisation of Standard IOS/5-1984 for Portland cement.

9. El-Sayed A.R., Hala E. and Mohamed R. (2014) *" Investigation on Concrete Properties For Nano Silica Concrete By Using Different Plasticizers "* Civil and Environmental Research Vol.6, No.9.

10. Tesanex P., Prosek Z. and F Josef (2017) *" Effect of Poly (Vinyl-Alcohol) Amount on Flexural Strength of Cement Mortars With Micronized Recycled Concrete "* 55th, conference on experimental stress analysis.

11. American Concrete Institute ACI 211-91 (2008) Standard Practice For Selecting Properties Normal, Heavy Weight and Mass Concrete.

12. M.I.Serag., Hala.E and Muhammad 'S. E. (2014) *" The Effect of Induced Sonication on The Reactuty of Nano Silica Concrete "* IJSER, Vol.5, issue 12.Decemeber.

13. ASTM (C143-89) Standard Test Method For Slump of Hydrated Cement Concrete.

14. BS 1881-116:1983. Testing concrete. Method for determination of compressive strength of concrete cubes.

15. ASTM (C78-02) Standard Test Method For Flexural Strength of Concrete Specimens.

16. ASTM (C469-02) Static Modulus of Elasticity and Poison Ratio of Concrete Specimens.

17. Saleh, Najat J., Raheek I. Ibrahim, and Ali D. Salman. *"Optimization Process for Using Prepared Nanosilica in Concrete."* The 2nd International Conference of Buildings, Construction and Environmental Engineering, BCEE2-2015.

18. Saloma, Amrinsyah Nasution, Iswandi Imran, and Mikrajuddin Abdullah. (2013) *"Mechanics Properties of Nano-Silica Material Concrete."* International Journal of Engineering & Sciences.

19. AASHTO Guide (1993) For Design of Pavement Structure.