Enhancing Physical and Mechanical Properties of Cement Based Morters and Corrosion Resistance of Reinforcing Steel using Nano - SiO_2

Prof. Dr. Magdy A. El Aziz
Professor Of Materials Properties nd Resistance
Faculty of Engineering, Fayoum University,
Fayoum, Egypt

Eng.Taher Anwer Tawfik
Assistant at the Higher Institute of Engineering
6 October
Fayoum, Egypt

Dr. Ahmed Serrag
Lecturer, Department of Civil Engineering,
Faculty of Engineering, Fayoum University ,
Fayoum, Egypt

Dr. Ghada M. Abd El Hafez
Lecturer, Department of Chemistry
Faculty of Science, Fayoum University
Fayoum, Egypt

***Abstract*-This paper investigates the effect of replacement of cement with different percentages of Nano-SiO2 and with constant percentage of silica fume. Nano-Sio2 is used to reduce the corrosion in reinforcement bars. The physical and mechanical properties of cement mortars and corrosion resistance property was studied to estimate the effect of Nano-SiO2 additive. A control specimen is prepared without Nano-SiO2. Further, four more specimens are prepared by replacing the amount of cement with different percentages of Nano-SiO2 with silica fume. In these four specimens, the amount of Nano-SiO2 are varied by 0%, 1%, 2%, 3% and 4%, respectively with constant 10% silica fume. The specimens are treated with different types of water as tape water and Qarun lake water. Comparing the observed responses, it is found that the addition of Nano-SiO2 with silica fume is effective in increasing the compressive and flexural strengths of cement mortar in addition to decreasing permeability and corrosion (with different mixing and type of treatment water). Thus this paper presents the recent progress and advancement in Nano-engineering and Nano modification in cement concrete.**

Keywords: Nano-Silica, Silica fume, Compressive strength, flexural strength, permeability, corrosion

I.INTRODUCTION:

Recently, Nano technology has attracted considerable scientific interest due to the new potential uses of particles in nanometer (10^{-9} m) scale. The nano scale-size of particles can result in improving properties from conventional grain-size materials of the same chemical composition. Thus, industries may be able to re-engineer many existing products and to design new products that function at unprecedented levels. There are few reports on mixing Nano-particles in cement-based building materials. **Li et al [1]** investigated cement mortars with Nano-SiO_2 or Nano-Fe_2O_3 to explore their super mechanical and smart (temperature and strain sensing) potentials. The **Fuji Chimera Research Institute [2]** addressed functional applications of SiO_2 in Nano scale.

However, until now, research performed over the years aimed largely at achieving high mechanical performance with cement replacement materials in micro size. **Lu and Young [3]** obtained 800 MPa strengths on compressed samples. **Richard and Cheyrezy [4]** developed Reactive Power Concretes (RPCs) ranging from 200 to 800 MPa and fracture energies up to 40 kJ m^{-2}. The development of an ultrahigh strength concrete is made possible by the application of DSP (Densified System containing homogeneouslyarranged ultra-fine Particles) with superplasticizer and silica fume content. In the light of these developments, this study aims at investigating the influences of Nano-SiO_2 in cement mortars and reinforced concrete. Therefore, it is plausible to add Nano-SiO_2 of a high purity (99.9%) and in order to improve the characteristics of cement mortars. The use of Nano-SiO_2 to improve the properties of concrete has opened a vast view to the concrete structures **Scrivener, K.L., R.J. Kirkpatrick [5, 6, 7]**.

The aim of the present work is to evaluate the influence of using Qarun lake water on corrosion (with different cases of mixing and treatment) to investigate the durability of concrete with Nano-SiO_2.

II. EXPERIMENTAL TECHNIQUES

The materials used in this work were ordinary Portland cement (OPC), fine aggregate, coarse aggregate, superplasticizers, silica fume powder (SF) and Nano-SiO_2 particles (NS).The physical properties of cement is shown in Table (1) . The specific gravity of sand and basalt are 2.65 and 2.75 respectively. The cement is replaced by 10% silica fume [8]. The mix composition of the investigated mixes is seen in Table (2). Superplasticizers have density

1.07± 0.02 kg/l, total soluble chloride ion content max 0.1% chloride free, pH value 6-10 and brown liquid color.

Table.I Physical properties of cement

Cement Properties	Result
Specific gravity	3.17
Fineness	2000 cm^2/g
Initial setting time	85 minutes
Final setting time	180 minutes
Compressive strength	Kg/cm^2
3 days	205
7 days	300
28 days	435
Soundness	1 mm

Table II Mix composition of the investigated mixes

Mix No	% O.P.C	% S.F	% N.S
M0	100	0	0
M1	89	10	1
M2	88	10	2
M3	87	10	3
M4	86	10	4
C0	100	0	0
C1	89	10	1
C2	88	10	2
C3	87	10	3
C4	86	10	4

M: cement mortar with 0,1,2,3 and 4% nano-SiO_2
C: reinforced concrete
O.P.C: ordinary portland cement
S.F: silica fume
N.S: nano-SiO_2

Nano-SiO_2 has a significant role. The changes recorded in modified mixtures with Nano-SiO_2 particles are due to the chemical reaction between SiO_2 and $Ca(OH)_2$ which is released during cement hydration and also due to physical alterations such as the packing factor improvement [9]. Electron micrographs of Nano-SiO_2 (SEM) are shown in Fig (1). Qarun Lake water is used as mixing water for concrete samples and it is used in curing other samples. The chemical analysis of Qarun Lake water is given in table (3)

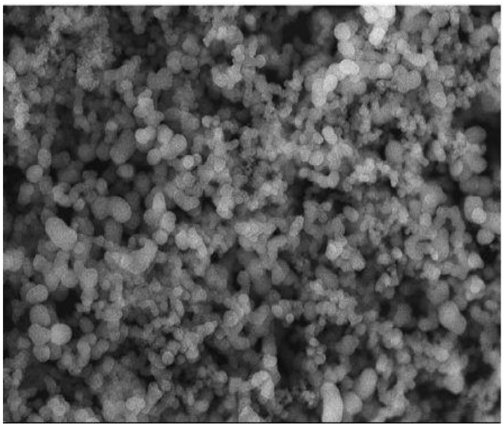

Fig 1. SEM of Nano-SiO_2.

Table III: The chemical analysis of Qarun Lake water

Content	Quantity
Density (gm/cm3)	1.025
Soluble salts (gm/l)	35.438
Ions	———
Carbonates (gm/l)	0.030
Bicarbonate (gm/l)	0.305
Sulfate (gm/l)	9.712
Chlorides (gm/l)	12.985
Calcium (gm/l)	0.500
Magnesium (gm/l)	1.325
Sodium (gm/l)	10.109
Others	0.472

A. Compressive strength and flexural test

The percentages of Nano-SiO_2 (NS) are 1, 2, 3, and 4% for these experimental studies. The compressive strength is determined for cement mortar according to (ASTM) **[10]**. The flexural strength is determined for cement mortar using prisms 40x 40 x 160 mm .At least three samples are tested in each experiment. The ratio of blended cement to sand is 1: 3 by weight throughout the tests. The specimens are cured in a humidity chamber at 23 ± 1^0C for 24 hours, and then immersed in tap water until the time of testing 3 ,7 and 28 days. The result of each test is the average of three specimens, which are tested at the same curing time.

B. Water permeability test

These tests are carried out to assess the permeability of the concrete specimens, based on water permeation depth. In permeability test method used in this work, the permeability criterion is based on the permeation depth according to DIN1048Part1 standard. The 10×20 centimeter cylindrical samples are initially brought out of the water after 28 days of curing and are dried for 24 hours in 100-110◦C in an oven before the permeability tests. The water pressure imposed to the end of the samples is five bars. The samples are subjected under such pressure for 24 hours in permeability device and then are immediately broken using the Brazilian method to record the water permeation depth. In order to determine the permeability depth ratio, this depth is measured in three different points and the average of them is noted as the water permeability depth in the samples. The permeability factor is calculated for concrete by using the following relation and in respect with Darsi law **[11]**:

K=Q/AI

In this relation, the parameter I is the hydraulic gradient, Q is the discharge, and A is the cross section area of the sample, where I=H/d and H is the hydraulic load difference imposed to the sample and d is the permeation depth.

C. Corrosion test

The corrosion test is determined for reinforced concrete using cylinder 7.5 x 15 cm , a bar steel diameter 10mm and length 15cm.This test aims to measure the value of corrosion at different periods 2, 4 and 6 months. Samples are divided into groups: the first group is mixed and treated with tape water, the second group is mixed with Qarun Lake water and treated with tape water and the third one is mixed with tape water and treated with Qarun Lake water.

The samples are tested by Volta Lab PGZ301,"potentiostate/Galvanostate system France. The latest analoge and microcomputer design advances to provide high performance, ease of use, and greater versatility in electrochemical measurements. The instrument is interfaced to an external IBM 1200 CPU computer. The Volta Master 4 software is designed to measure and analyze corrosion quickly, easily and reliably, using a variety of techniques. The experimental set up allows the direct application of the required techniques. In our experiments both linear polarization and Tafel techniques were carried out. The electrochemical cell is consist of a reference electrode = saturated calomel electrode (SCE) and also contains auxiliary electrode = counter electrode (pt electrode) is used to measure the current between it and the sample. The sample is defined as the working electrode and the cell is connected to the Volta Lab PGZ 301 device. The rate of corrosion in steel samples is measured through the equation:

$$\text{Corrosion rate } (\mu m/year) = I_{corr} \times M \times 3270 / D \times V \quad (1)$$

Where I_{corr}= corrosion current density in A/cm^2
M = atomic weight (g)
V=Valance
D = density (g/cm^3)

III. RESULT AND DISCUSSION:

A. Compressive strength and flexural strength test:

According to the test results shown in Figure (2, 3) and the Table (3), the specimens containing 4% Nano-SiO_2 shows the highest increase in the compressive strength and flexural strength during 28 days compared with that of control specimens. However, it is specified that using Nano-SiO_2 beside constant percentage of silica fume lead to more increase in compressive strength of the concrete. It is shown in table (4), the specimens containing 10% silica fume and 4% Nano–SiO_2 have 424 kg/cm^2 in their compressive strength in comparison with that of control specimens whereas it is 352 kg/cm^2.Flexural strength results show that the specimens containing 10% silica fume and 4% Nano–SiO_2 have 52.18 kg/cm^2 in their compressive strength in comparison with that of control specimens whereas it is 36.25 kg/cm^2

Table IV: Compressive strength and flexural strength results

Mixture no.	**Compressive strength kg/cm2**			**Flexural strength kg/cm2**		
	3 days	***7 days***	***28 days***	***3 days***	***7 days***	***28 days***
M0	275	317	352	17.4	23.52	36.25
M1	286	330	368	19.8	27.18	40.31
M2	316	366	404	20.6	29.34	43.93
M3	325	380	415	23.8	33.06	48.56
M4	336	396	424	24.75	35.50	52.18

Table V: Percentage of increase in compressive strength and flexural strength of cement mortars

Mixture no.	**Compressive strength**			**Flexural strength**		
	3 days	***7 days***	***28 days***	***3 days***	***7 days***	***28 days***
M1	4.00	4.1	4.50	13.79	15.56	11.20
M2	14.91	15.46	14.77	18.39	24.74	21.02
M3	18.18	19.87	17.89	36.78	40.65	33.95
M4	22.18	24.92	20.45	42.24	50.93	43.94

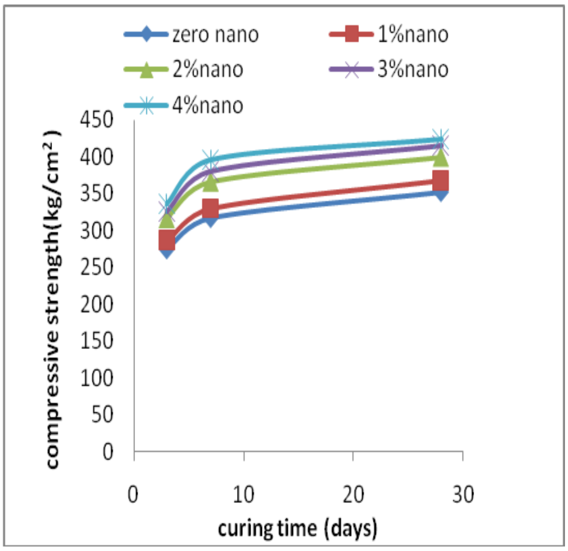

Fig 2. Compressive strength of specimens containing Nano-SiO_2 particles with curing time.

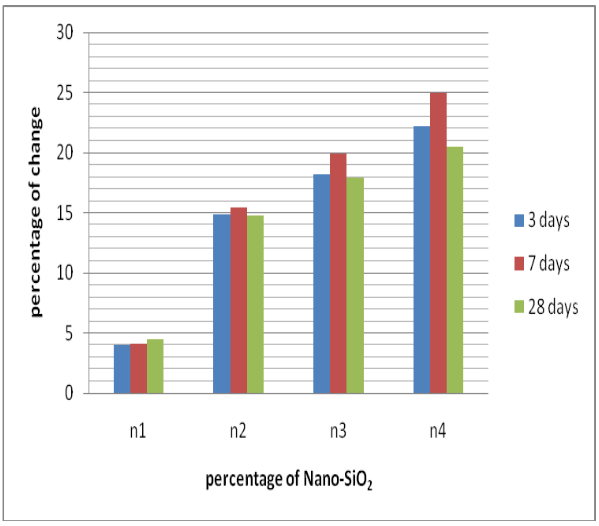

Fig 4. Percentage of increase in compressive strength of cement mortars containing different Nano-SiO_2 percentages at different ages

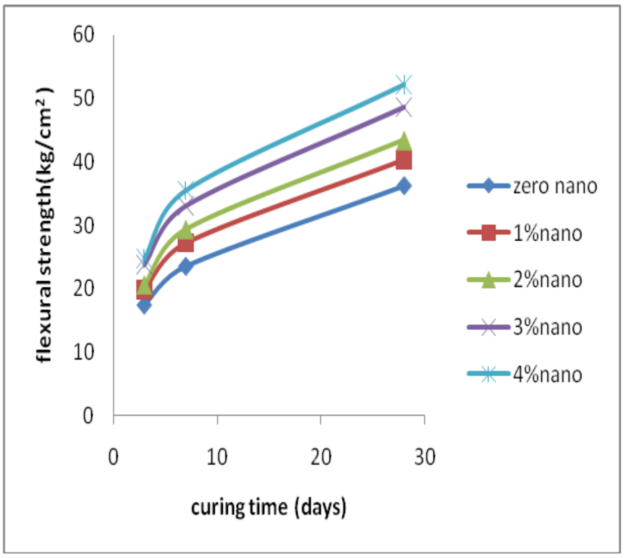

Fig 3. flexural strength of specimens containing Nano-SiO_2 particles with curing time.

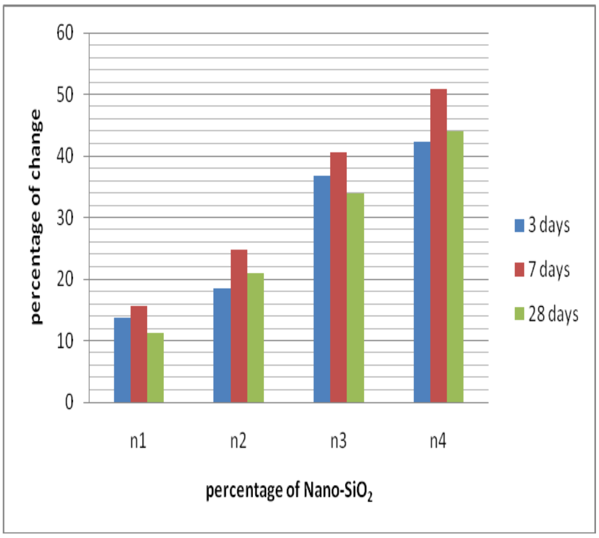

Fig 5. Percentage of increase in flexural strength of cement mortars containing different Nano-SiO_2 percentages at different ages

Figs. (4.5), respectively and table (5) represent the rates of increase of compressive and flexural strength of blended mortars incorporating Nano-SiO_2 and hydrated at the same curing times (3, 7 and 28 days). The specimens containing 1, 2, 3 and 4% Nano-SiO_2 the rate of increase ranges from 4.50% to 20.45 % in their compressive strength in comparison with that of control specimens at 28 days curing times. The results also indicate that, the rate of increase of flexural strength ranges from 11.20% to 43.94% in comparison with that of control specimens at 28 days.

The results show that, at the early ages (3 and 7 days) the mechanical properties percentage of increase (compressive and flexural strength) increase. On the other hand, at the late age (28 days) the percentages of increase of the mechanical properties decrease obviously.

B. Water permeability test

It is shown in Table (6) and Figure (6), the results of permeability test on different concrete specimens show that replacing a specific amount of the cement with Nano-SiO_2 and constant 10% silica fume would decrease the permeation of water in concrete. According to the test results, for the specimens containing different percentages of Nano-SiO_2, a minimum water permeation depth of 10mm is related to the specimens of 4% Nano-SiO_2. It has been shown that increasing Nano-SiO_2 percentage beside 10% constant silica fume led to more decrease in permeability of the concrete up to 66.71 % in comparison with that of the specimens which don't have Nano-SiO_2 as shown in figure 7.

Table VI: Water permeability test results

Mixture no.	The average penetration depth (mm)	The permeability 10-10(cm/sec)	% decrease
C 0	30	17.30	0
C 1	26	15.02	-13.18
C 2	19	10.97	-36.59
C 3	13	7.5	-56.65
C 4	10	5.76	-66.71

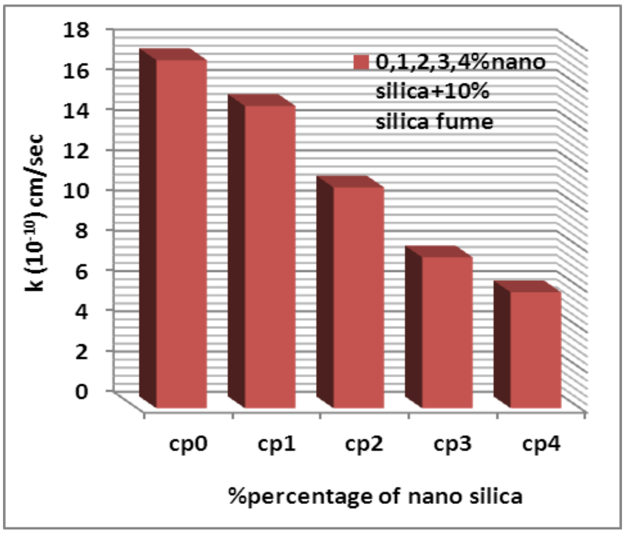

Fig 6.permeability test results of specimens containing 0, 1, 2,3and4 % Nano-SiO_2

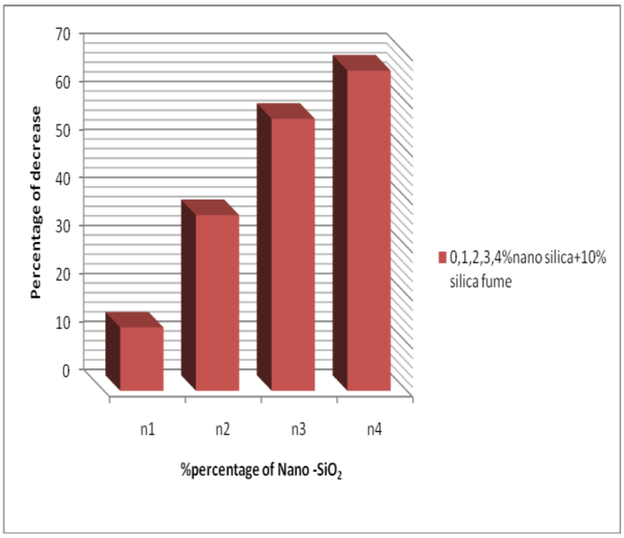

Fig 7. Percentage of decrease in permeability test at different Nano-SiO_2 percentages

C. Corrosion test

The corrosion parameters of the steel in concrete Nano-SiO_2 free and Nano-SiO_2 containing different concentrations are obtained from the potentiodynamic polarization experiments. Different concentrations of the Nano –SiO_2 ranging from 1% to 4% have been used. Figs (from 8 to 16) present potentiodynamic polarization curves of these measurements. In general, the presence of different concentrations of the Nano-SiO_2 in concrete decreases the anodic current density and the cathodic one. Also, the presence of Nano-SiO_2 in concrete shifts the corrosion potential to more positive values. The values of the corrosion current density i_{corr} and corrosion rate are calculated at different concentrations of the Nano-SiO_2 and are presented in Table (7) at different periods. In general, the corrosion rate decreases by increasing Nano-SiO_2 concentration. In most cases, the increase of the Nano-SiO_2 concentration shifts the corrosion potential to more positive values with a decrease in the anodic and cathodic current density, i.e. the studied Nano –SiO_2 concentrations act as mixed inhibitors, where they are absorbed on the metal surface, blocking the active sites for the corrosion process; thus decreasing the exposed free metal area to corrosive medium **[12]**.

Table 7: Corrosion test results
Specimens mixed and treated with tape water.

Mix. No.	Rate of corrosion (µm/year)		
	2months	*4months*	*6months*
C0	195.6	246.4	276.1
C1	152.4	194.2	219.8
C2	126.7	149.2	162.1
C3	112.5	122.2	154.6
C4	79.52	109.3	135.7

Specimens mixed with Qarun Lake water and treated with tape water

Mix. No.	Rate of corrosion (µm/year)		
	2months	*4months*	*6months*
C0	289.6	378.3	389.3
C1	199.5	274	283.2
C2	180.1	192.2	213.2
C3	154.7	178.8	195.3
C4	107.5	175.3	186.4

Specimens mixed with tape water and treated with Qarun Lake water

Mix. No.	Rate of corrosion (µm/year)		
	2months	*4months*	*6months*
C0	235.6	280.5	312.3
C1	192.3	224.5	242.6
C2	167.2	169.7	177.8
C3	133.9	149.8	165.1
C4	97.4	128	147.2

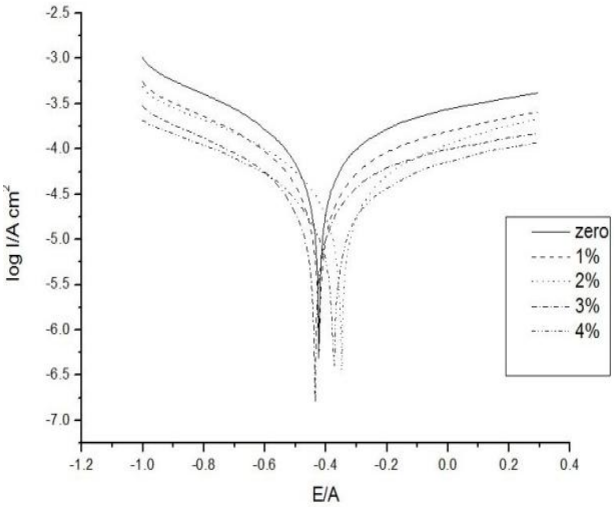

Fig 8. Different concentrations of the Nano-SiO_2 ranging from 1% to 4% at 2 months (first group)

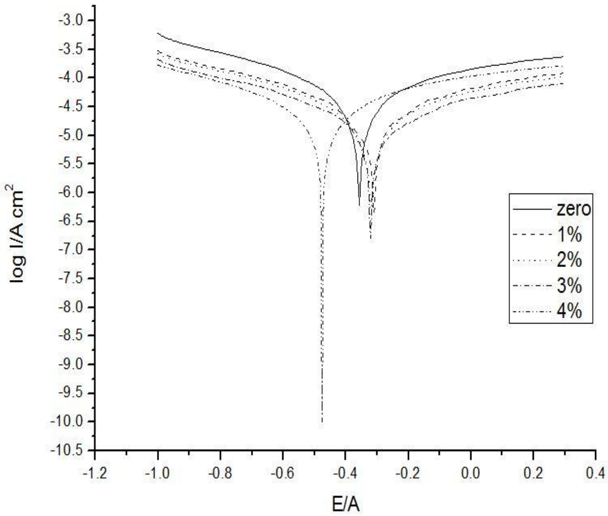

Fig 10. Different concentrations of the Nano-SiO_2 ranging from 1% to 4% at6 months (first group)

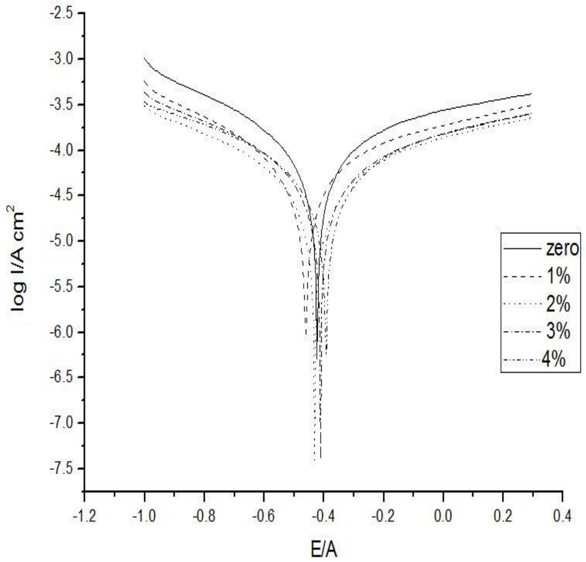

Fig 9: Different concentrations of the Nano-SiO2 ranging from 1% to 4% at 4 months (first group)

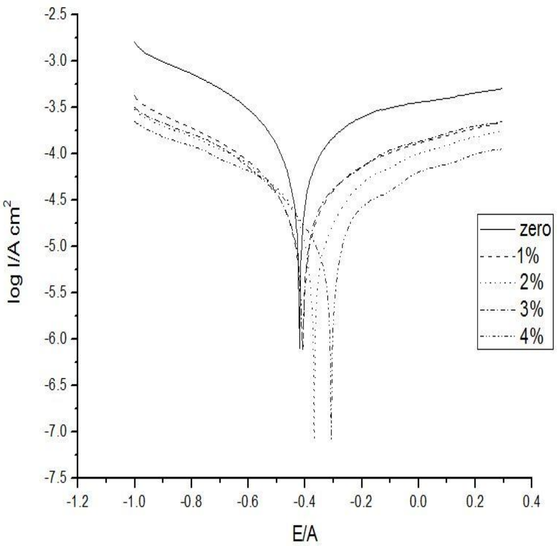

Fig 11. Different concentrations of the Nano-SiO_2 ranging from 1% to 4% at 2 months (second group)

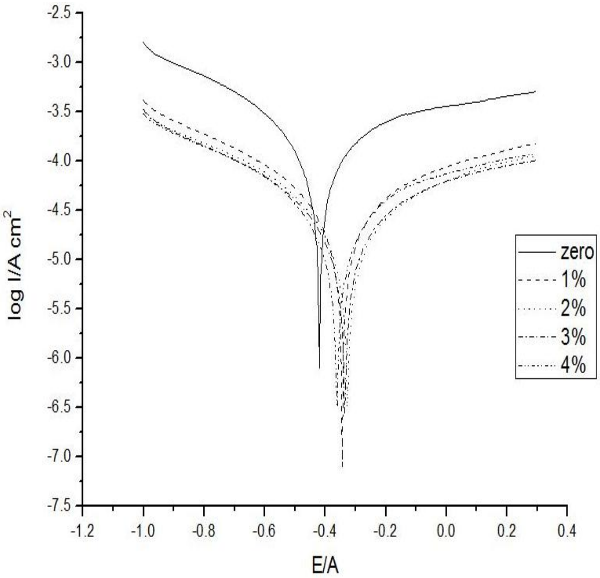

Fig 12.Different concentrations of the Nano-SiO_2 ranging from 1% to 4% at 4 months (second group)

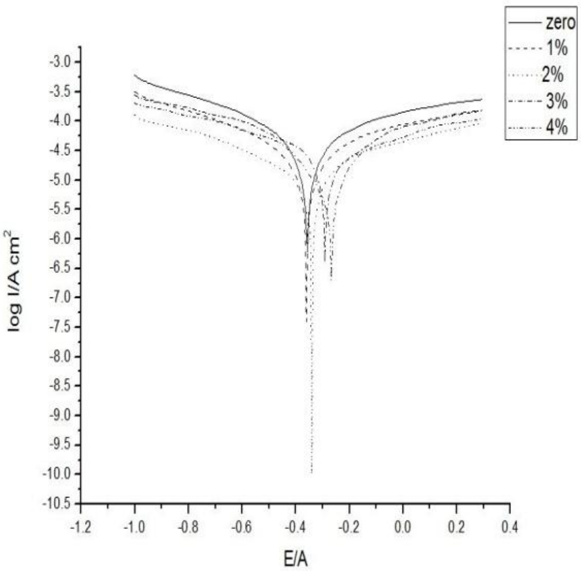

Fig 13. Different concentrations of the Nano-SiO_2 ranging from 1% to 4% at 6 months (second group)

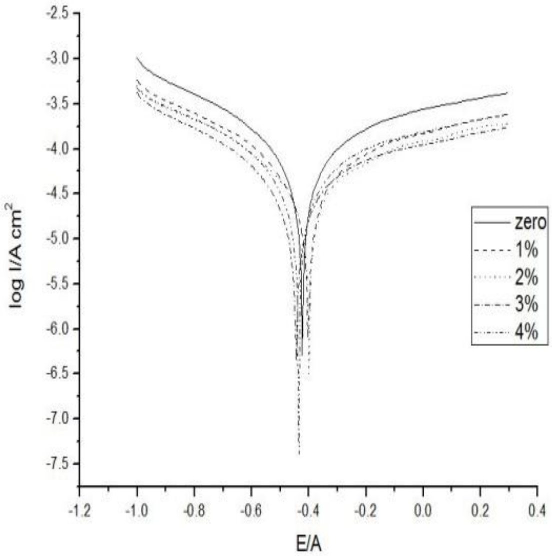

Fig 14. Different concentrations of the Nano-SiO_2 ranging from 1% to 4% at 2 months (third group)

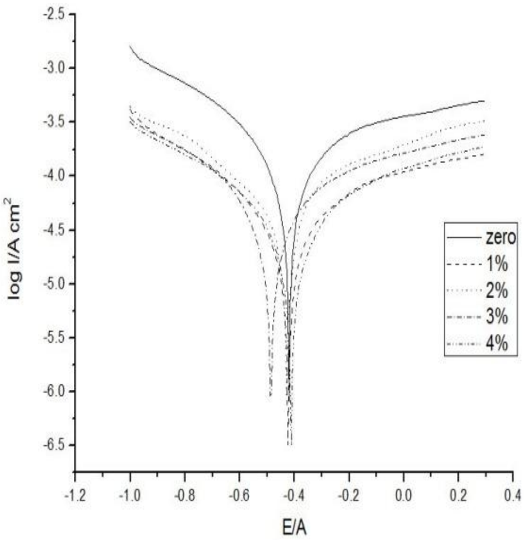

Fig 15. Different concentrations of the Nano-SiO_2 ranging from 1% to 4% at 4 months (third group)

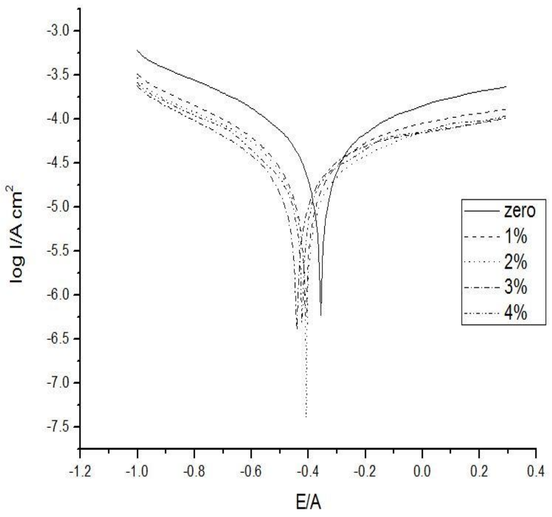

Fig 16. Different concentrations of the Nano-SiO_2 ranging from 1% to 4% at 6 months (third group)

Figures (17 to 19) show the comparison of different mixing and treating method at 2, 4 and 6 months explained that the highest rate of corrosion is when mixed with Qarun Lake Water and treated with tape water and the least rate of corrosion is when mixed and treated with tape water. Table 8 shows the percentage of decrease of rate of corrosion at different mixing and treating method at 2, 4 and 6 months

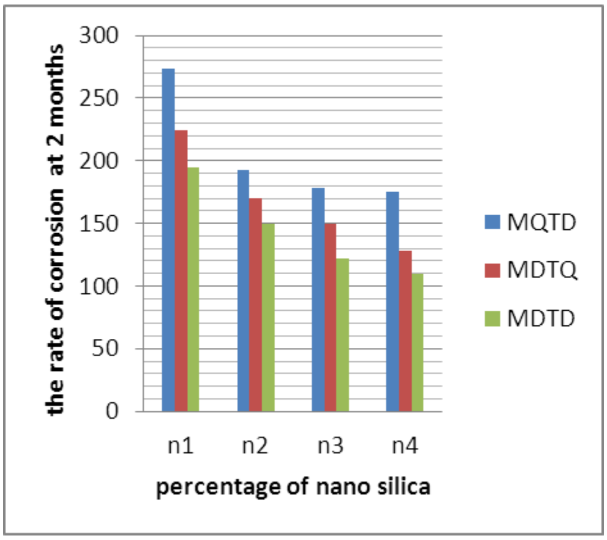

Fig 17. comparison of rate of corrosion at different cases with 1,2,3,4 % Nano-SiO_2 at 2 months

Note: MQTD samples mixed with Qarun lake water and treated with tape water
MDTQ samples mixed with tape water and treated with Qarun lake water
MDTD samples mixed with tape water and treated with tape water.

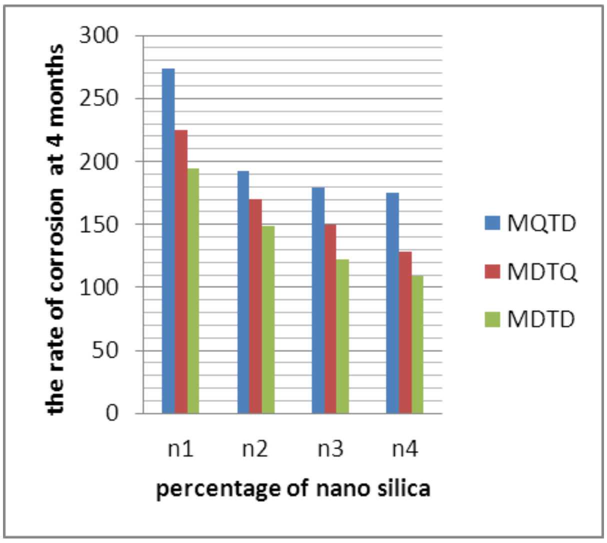

Fig 18. comparison of rate of corrosion at different cases with 1,2,3,4 % Nano-SiO_2 at 4 months

Note: MQTD samples mixed with Qarun lake water and treated with tape water
MDTQ samples mixed with tape water and treated with Qarun lake water
MDTD samples mixed with tape water and treated with tape water.

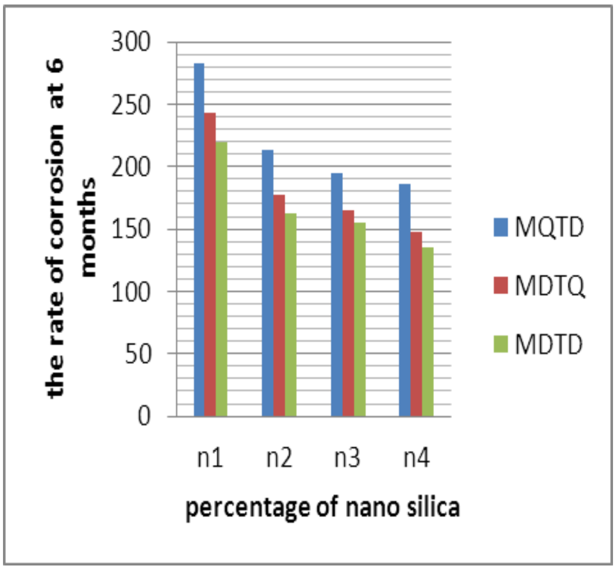

Fig19. comparison of rate of corrosion at different cases with 1,2,3,4 % Nano-SiO2 at 6 months

Note: MQTD samples mixed with Qarun lake water and treated with tape water
MDTQ samples mixed with tape water and treated with Qarun lake water
MDTD samples mixed with tape water and treated with tape water.

Table 8: Percentage of decrease of corrosion rate

Mixture No.	Percentage of decrease of corrosion rate at first group			Percentage of decrease of corrosion rate at second group			Percentage of decrease of corrosion rate at third group		
	2 months	*4 months*	*6 months*	*2 months*	*4 months*	*6 months*	*2 months*	*4 months*	*6 months*
C1	22.08	21.18	20.39	31.11	27.57	27.25	18.37	19.96	22.31
C2	35.22	39.44	41.28	37.81	49.19	45.23	29.03	39.50	43.06
C3	42.48	50.36	44.00	46.58	52.73	49.83	43.16	46.59	47.13
C4	59.34	55.64	50.85	62.87	53.81	52.11	58.65	54.36	52.86

First group: Specimens mixed and cured with tape water
Second group: Specimens mixed with Qarun Lake water and cured with tape water
Third group: Specimens mixed with tape water and cured with Qarun Lake water

D.SEM Test

To verify the mechanism predicted by the compressive strength test, scanning electron microscope (SEM) examinations are performed. Some samples from all experimental specimens are exposed for the electrographic at a specific period (28 days). This can be shown from Figures (20) a, b and (21) a, b that the Nano-SiO_2 samples have more consolidated and occupy structure compared with the control sample.

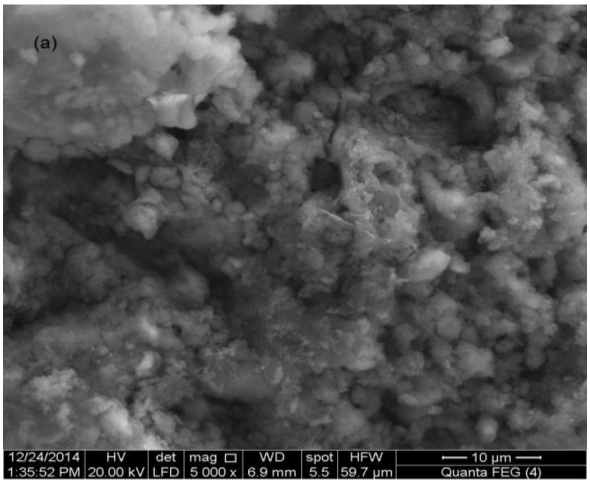

Fig 20. (a) SEM of ordinary Portland cement mortar

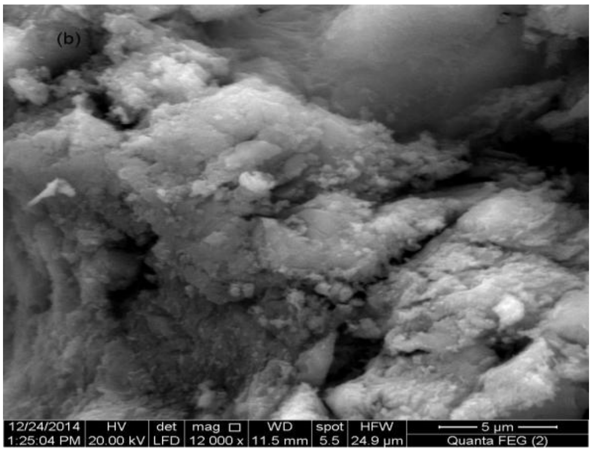

Fig 20. (b) SEM of cement mortar containing Nano-SiO_2

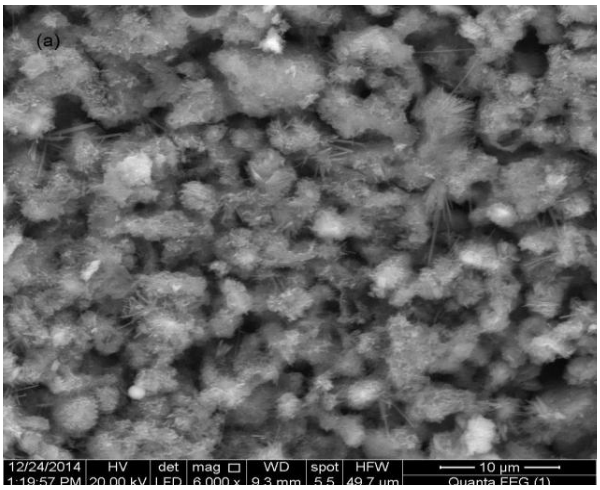

Fig 21. (a) SEM of control sample of concrete

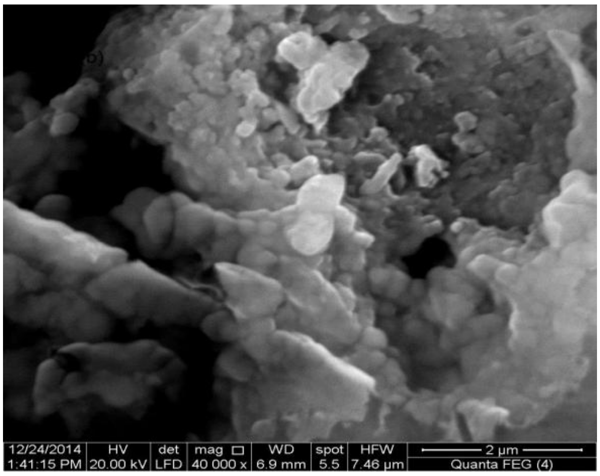

Figure 21: (b) SEM of concrete sample containing Nano-SiO_2

E.The X-Ray Diffraction Test

The XRD test is performed to reveal the amount of different crystals existing in concrete specimens. As it is obvious from Figures (22, and 23) there is an increase in the amount of the calcium silicate hydrate (C-S-H) crystal in the concrete containing Nano-SiO_2 compare with that of the normal concrete, but the amount of the Ca $(OH)_2$ crystals existing in the normal concrete, are more than that of the concrete containing the Nano-SiO_2 particles. Note that the sampling is conducted on the 28th day of the concrete specimens.

Therefore, applying Nano-SiO_2 particles to the concrete structure would increase the stability and improve the mechanical properties (compression and flexural strength), permeability and corrosion of the concrete.

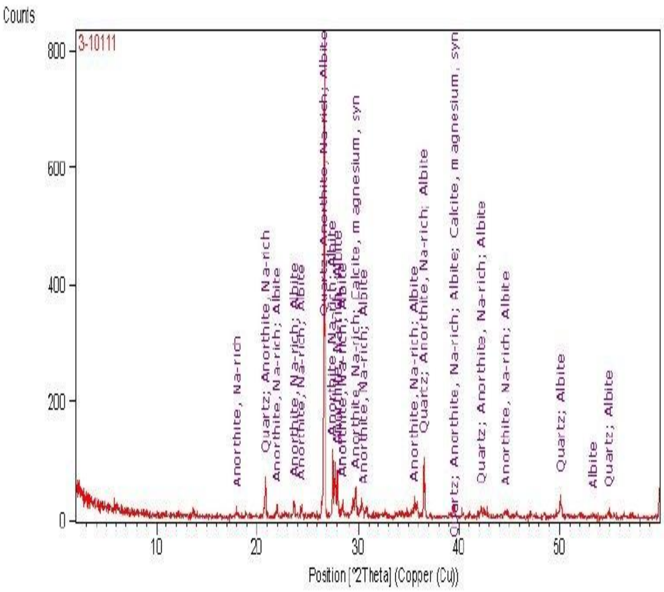

Fig 22. XRD shows results of curing concrete during 28 days (control concrete)

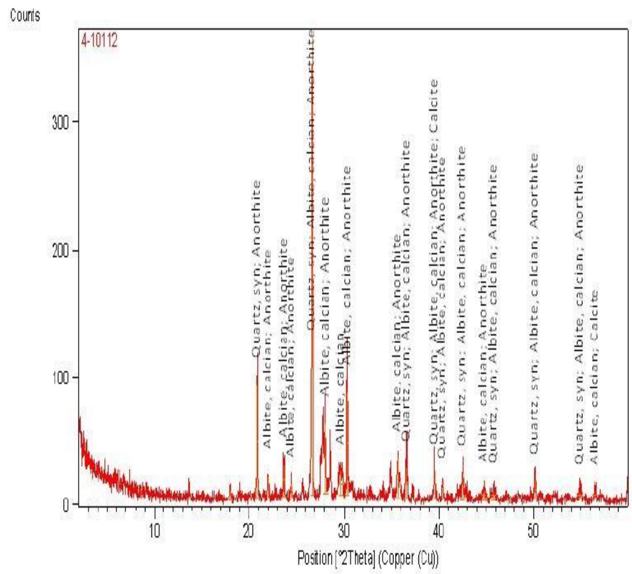

Fig 23. XRD shows results of curing concrete during 28 days concrete with Nano-SiO_2

IV. CONCLUSION

-The compressive and flexural strength of the cement mortars with Nano-SiO_2 with constant percentage of silica fume was higher than that of the plain cement mortar with the same w/c. The specimens containing 4% Nano-SiO2 the compressive strength increase with 20.45 % and the increase of flexural strength were 43.94%

.-The permeability of the concrete with Nano-SiO_2 with constant percentage of silica fume was lower than that of the plain concrete with the same w/c. The specimens containing 4% Nano-SiO_2 the permeability decrease with 66.71 %.

- The comparison of different mixing and treating method at 2, 4 and 6 months explained that the highest rate of corrosion is when mixed with Qarun Lake Water and treated with tape water and the least rate of corrosion is when mixed and treated with tape water
- The mechanical properties at the early ages (3 and 7 days) percentage of increase (compressive and flexural strength) increase. On the other hand, at the late age (28 days) the percentages of increase of the mechanical properties decrease obviously
- Nano-SiO_2 particles when used in concrete mixes result in decreasing the water permeability of the concrete.
- SEM test shows that Nano-SiO_2 samples have more uniformed and filled structure compared with the control sample.
- The XRD test performed to reveal the amount of different crystals existing in concrete specimens.
- An increasing percentage of Nano-SiO_2 the results showed a decrease in the rate of corrosion.
- It is observed that the compressive strength increases with SiO_2 Nano-particles up to 3% replacement (M3) and then it slight increases, although 4% replacement (M4) is still higher than those of the control cement mortar (M0). This may be due to the fact that the quantity of SiO_2 Nano-particles present in the mix is higher than the amount required to combine with the liberated lime during the

process of hydration thus leading to excess silica leaching out and causing a deficiency in strength as it replaces part of the cementitious material, but it does not contribute to its strength.

REFERENCES

1. Li, H.; Xiao, H. G.; Yuan, J.; and Ou, J., "Microstructure of Cement Mortar with Nano-Particles," Composites Part B: Engineering, V. 35, No. 2, Mar. 2003, pp. 185-189.
2. Fuji Chimera Research Institute Inc., "Fine (Impalpable) Powder Market 2002—Present and Future Outlook," 2002.
3. Lu, P., and Young, J. F., "Hot Pressed DSP Cement Paste," Material Research Society Symposium Proceedings, No. 245, 1992, pp. 321-328.
4. Richard, P., and Chyrezy, M. H.,(1994). "Reactive Powder Concretes with High Ductility and 200-800 MPa Compressive Strength," Concrete Technology Past, Present, and Future" , Proceedings of the V. Mohan Malhotra Symposium, SP-144, P. K. Mehta, ed., American Concrete Institute, Farmington Hills, Mich., , pp. 507-528.
5. Scrivener, K.L., R.J. Kirkpatrick. (2008). "Innovation in use and research on cementious material", Cement and Concrete research, 38: 128-136.
6. Li, H., H.G. Xiao, J.P. Ou. (2004). "A study on mechanical and pressure-sensitive properties of cement mortar with nanophase materials" Cement and Concrete Research, 34(3): 435-438.
7. Ji Tao, (2005). "Preliminary study on the water permeability and microstructure of concrete incorporating nano-SiO_2",Cement and Concrete Research, 35: 1943-1947.
8. V. M. Malhotra. and G. G. Carette. (1982) "silica fume a pozzolan of new interest for use in some concretes", concrete construction.
9. Byung Wan Jo, Chang Hyun Kim ,Jae Hoon Lim. (2007) "Investigations on the Development of Powder Concrete with Nano-SiO2 Particles". KSCE Journal of Civil Engineering; 11: 37-42.
10. ASTM Standards. (1992)"Standard test method for compressive strength for hydraulic cement mortars" ASTM Designation, C109-92, 62.
11. Mehta P. K., Paulo J., Monteiro M.(2006) Concrete (Microstructure, Properties and Materials), (Advanced concrete technology).third ed., McGraw-Hill.
12. N.H. Helal, M.M. El-Rabiee, Gh.M. Abd El-Hafez, W.A. Badawy, (2008) " Alloys and compounds", 456 -372.