Some Durability Characteristics of Micro Silica and Nano Silica Contained Concrete

Mohammed Salah Nasr
Al-Diwaniya Technical Institute/
Al-Furat Al-Awsat Technical University
msn_alamar@yahoo.com

Shakir Ahmed Salih
Building and Construction Department/
University of Technology
professorshakir@yahoo.com

Maan Salman Hassan
Building and Construction Department/
University of Technology
maan_s_h@yahoo.co.uk

Abstract

This paper aims to investigate the influence of replacement of cement with nano and micro silica admixtures on some durability properties of concrete such as water absorption, chloride content and pH tests. Three replacement ratios (5%,10%,15%) of micro silica and four replacement proportions (0.5%,1.5%,3%,5%) for nano silica were used in this study. Two exposure conditions were considered for chloride content test: wetting-drying and full immersing exposure in 6% of chloride ions solution, NaCl type.

Results showed that mixes of %5 micro silica and 5% nano silica had lower content of chloride (about 0.19% and 0.18%) for wetting-drying and full immersing exposure respectively. For water absorption test, all mixes incorporated micro and nano silica, except for %5 micro silica mix, showed lower absorption than control mixes. For pH test, results indicated that the adding of nano and micro silica didn't affect adversely the alkalinity of concrete.

Key wards: Nano silica; micro silica; chloride content; water absorption; pH.

الخلاصة

تهدف هذه الدراسة الى التحري عن تأثير استبدال السمنت بمضافات النانو والمايكرو سليكا على بعض خواص الديمومة للخرسانة مثل امتصاص الماء، محتوى الكلوريد و فحص القاعدية. تم استخدام ثلاث نسب استبدال (5%،10%،15%) للمايكرو سليكا واربع نسب استبدال (0.5%،1.5%،3%،5%) للنانو سليكا. تم اعتماد اسلوبي تعرض لفحص محتوى الكلوريد: تجفيف–ترطيب وغمر كلي في محلول 6% ايونات الكلوريد، نوع كلوريد الصوديوم.

اظهرت النتائج بان الخلطات 5% مايكرو سليكا و5% نانو سليكا امتلكت اقل محتوى كلوريد (حوالي 0.19 % و 0.18 %) لأسلوبي التعرض تجفيف–ترطيب وغمر كلي على التوالي. بالنسبة لفحص الامتصاص، فان نتائج جميع الخلطات الحاوية على مايكرو ونانو سليكا، عدا الخلطة 5% مايكرو سليكا، اظهرت امتصاص اقل من الخلطات المرجعية. بالنسبة لفحص درجة القاعدية، فقد اشارت النتائج بان اضافة النانو والمايكرو سليكا لم تؤثر سلبيا على قاعدية الخرسانة.

الكلمات المفتاحية: نانو سليكا؛ مايكرو سليكا؛ محتوى الكلوريد؛ امتصاص الماء؛ درجة القاعدية.

1. Introduction

Concrete represents one of the vastly anticipated building materials due to its pretty mechanical and durability properties. By reinforcing concrete with steel rebar or else item, it has good construction properties permitting it to be used in different structures such as, bridge decks, parks and other building types. Due to its alkaline properties, which come from Portland cement and its reactions, steel bars embedded in concrete are protected from corrosion **(Berke,2005)**.

One of the main causes of reinforcement corrosion is caused by chloride ions. Incorporating of pozzolanic materials in concrete can enhance its durability properties against many aggressive agents especially,the diffusion of chloride ions.The densification of concrete microstructure, restricting the fluids movement inside it by cutting the continuity of capillary pores and pores refinement, are some of the pozzolanic materials impacts that influence the durability aspects, especially, the reinforcement corrosion. Other admixtures (called nano materials) which recently began to be used in concrete, revealed positive effect on some concrete mechanical, microstructure and durability properties. Discovering the effect of these materials on some durability properties and comparing their action with conventional pozzolanic materials may be considered as one of the worthy studying issues.

(Abyaneh *et. al.*, 2013) studied the synergic effect of nano and micro silica on concrete water absorption, electrical resistivity and compressive strength. The used proportions were 2% for the former and 10% for the latter as replacement of cement weight. Plain and 10% micro silica concrete mixes were also made for comparison. It was found that mix including (2%+10%) nano and micro silica, respectively, had higher electrical resistance and lower water absorption when compared with other mixes. Similar results were noticed for compressive strength test at the researched ages: 7, 14 and 28 days.

(Du *et al*, 2014) studied the durability properties of concrete containing nano silica in proportions 0.3% and 0.9%. It was found that incorporating nano silica, though in small dosages (0.3%), decreased the apparent chloride diffusion and migration coefficient, depth of water penetration by about 31%, 28.7% and 45% respectively. Also, concrete microstructure became more homogenous and the interfacial transition zone was densified due to the nano-filler influence and pozzolanic reaction. At early ages, it was deduced that the calcium hydroxide was reduced and the compressive strength was increased after using nano silica.

2. Research significance

This paper aimed to investigate about the effect of including nano and micro silica in concrete and their effect on its durability properties. Three durability tests: water absorption, chloride content and pH tests are chosen for these purposes. The importance of water absorption test comes from that the lower absorption, the lower permeability is of concrete, and subsequently, the lower introducing of aggressive ions (such as chloride and sulfate ions) into concrete. Chloride content of concrete directly influences the steel reinforcement corrosion. The alkalinity or pH test also affects passivity of the rebar corrosion. So, these tests specifically affect the corrosion of steel reinforcement in concrete. Thus, investigation of nano silica effect, which has unique aspects due to the small size influence (large surface area), on these durability tests and comparing it with micro silica (pozzolanic material) may be considered as a significant issue.

3. Experimental works

3.1 Materials

1. Cement

Commercially available ordinary Portland cement, named Karasta, is used in this study. Chemical properties of cement are shown in Table 1. It is conformed to Iraqi specifications No. 5/1984 **(I.Q.S No. 5, 1984)**.

2. Fine aggregate

Natural sand brought from Al-Amara city is used in this work. The fine aggregate is conformed to Iraqi specifications No. 45/1984, zone two **(I.Q.S No. 45, 1984)**.

3. Coarse aggregate

Crushed gravel with size range (5-19 mm) and compatible with Iraqi specifications No. 45/1984 **(I.Q.S No. 45, 1984)** is used as coarse aggregate.

4. Micro silica (M)

Micro silica purchased from BASF Company is used as pozzolanic admixture. Physical and chemical specifications of micro silica are shown in Table 2. These properties are provided by the manufacture, except for activity index property, which was determined experimentally.

5. Nano silica (N)

Amorphous nano silica bought from Evonik Company; Turkey, is used as concrete admixture in this research, see Figure 1. It's called commercially as Aerosil 150. The number 150 refers to specific area of the product, as shown in Table 3 which includes as-received properties of nano silica.

6. Superplasticizer

Glenium 54 (G54) high range water reducing admixture, purchased form BASF Company, is used as workability adjusting material for concrete mixtures.

7. Water

Tap water is used for mixing and curing of all concrete mixes and specimens.

Table 1: Chemical composition of cement.

Oxides Composition	Content, %	Iraqi specifications (No.5/1984), %
CaO	63.5	-
SiO_2	21.9	-
Al_2O_3	4.3	-
Fe_2O_3	4.5	-
MgO	3.8	<5
SO_3	2.1	<2.5
Free lime	0.8	-
L.O.I.	3.4	<4
L.S.F.	0.88	0.66- 1.02
Insoluble residue	1.2	<1.5

Table 2: Specifications of micro silica.

Property	Value or description
Material structure	Densified micro silica
Color	Gray
Specific gravity	2300 kg/m^3
Fineness (blain)	> 15000 m^2/kg
SiO_2	> 85 %
CaO	< 1 %
Chloride content	< 0.1 %
SO_3	< 2 %
Activity index	> 105 %

Table 3: Specifications of nano silica.

Property	Value or description
Specific surface area (BET)	150 ± 5 m^2/g
Color	white
Primary particle size	14 nm
SiO_2 content	99.8 %
Loss on ignition	≤ 1 %
Moisture (after 2 hour at 150 □C)	≤ 1.5 %
pH (in 4% dispersion)	3.7-4.7
Bulk density (approximate value)	30 g/l
Tapped density (approximate value)	50 g/l

Figure 1: Nano silica used

3.2 Concrete proportions

Eight types of concrete mixes (nine mixes in total) are depended. Without adding (Nil)- type (two mixes) is used as control. Other mixes types contained admixtures (micro or nano silica). Micro silica (M) admixture is used in three proportions (mixes): 5, 10, 15% as a partial replacement of cement weight, while, nano silica (N) is used in four proportions (mixes): 0.5, 1.5, 3, 5% as a partial replacement of cement weight.

Several trial mixes included different amounts of superplasticizer (Glenium 54) are executed to make mixes slumps within the range of 140- 170 mm. Procedure provided by ASTM C143 **(ASTM C 143, 2003)** is adopted to test the slump. So, the fixed parameters for all mixes are: water/cement, slump, coarse and fine aggregate fractions, and binder (cement, cement and micro or nano silica) content. Table 4 shows mixes details and symbols.

Table 4: Mixes symbols and proportions

Mix symbol	Cement, kg/m^3	Sand, kg/m^3	Gravel, kg/m^3	Water/ binder	Superplasticizer, kg/m^3	Micro silica, kg/m^3 (rep. %)	Nano silica, kg/m^3 (rep. %)
Nil	400	725	1050	0.45	1.859	---	---
5M	380	725	1050	0.45	2.118	20 (5%)	---
10M	360	725	1050	0.45	2.518	40 (10%)	---
15M	340	725	1050	0.45	3.2	60 (15%)	---
0.5N	398	725	1050	0.45	2.8	---	2 (0.5%)
1.5N	394	725	1050	0.45	3.718	---	6 (1.5%)
3N	388	725	1050	0.45	5.318	---	12 (3%)
5N	380	725	1050	0.45	9.718	---	20 (5%)

3.3 Concrete mixing procedure

Before description of mixing procedure of concrete ingredients, it is important to note that due to the high surface area of powder nano silica used (150 m^2/g) which required special treatment, it was not directly added to the mixer with other concrete materials but it was dry-batched separately (using hand-held mixer) with cement for specific time to have acceptable homogeneity. For unifying purposes, micro silica was also batched with cement using the same hand-held mixer but with different batching time before following the mixing steps of whole concrete mixes. The depended batching time for nano silica and cement was 10 minutes, while, 2 minutes were considered for batching of micro silica and cement due to the lower surface area of micro silica compared to nano silica. After batching, each mixture (cement + nano silica or cement + micro silica) was treated as one material (binder or cementitious material) in the mixer, as mentioned in the next paragraph.

Mechanical mixing using 0.1 m^3 electrical mixer is used for all concrete mixtures. The general procedure of mixing is adapted from ASTM C192 **(ASTM C192, 2012)** with some variations. Mixing steps can be summarized as follows:

- Mixing water is divided into two parts, the major one (about 75%) is mixed separately with the whole amount of super plasticizer (G54) for nearly 1 minute;
- Before mixer operating, coarse aggregate with a part of mixing water (about 25%) is added and the mixer is operated for few revolutions (≤ 0.5 minute) then it is stopped;
- After that, binder materials (cement and micro silica or nano silica which were batched together previously); fine aggregate and the major part of mixing water plus G54 are fed to the mixer then it is operated for 3 minutes;
- Thereafter, the mixer is rested for 1 minute;
- Finally, concrete ingredients are mixed for additional 2 minutes.

So, the total mixing time is about 5.5 minutes, excluding rest time.

3.4 Casting and curing

All concrete specimens are cast in previously-oiled molds directly after end of mixing. After about 24 hours, the specimens are de-molded. Thereafter, concrete specimens of chloride and water absorption tests are cured in tap water for 28 days. After that, chloride test specimens are removed from curing and exposed to chloride solution as mentioned in the following section. While, water absorption specimens remained in water until test.

3.5 Tests

3.5.1 Chloride content test

Powder collected from concrete specimens are used to measure chloride ions concentration (acid chlorides) according to BS 1881- Part 124 **(BS 1881-124, 1988)**. Concrete cubes with 150 mm size are cast and exposed to 6% external chloride ions (Cl^-) solution. Sodium chloride (NaCl) is used as a source of chloride ions. Two exposure conditions for chloride solution are considered: wetting-drying and full immersed exposure. In wetting-drying exposure, the concrete cubes are exposed to two weeks of wetting and two weeks of drying, so each wetting-drying cycle consists of four weeks. All cubes are placed in galvanized metallic tanks for chloride solution exposure. One cube is made for each mix, thus, a total of 18 cubes (9 for each exposure condition) are cast. One test at exposure age of 23 weeks is taken into consideration. Concrete powder is obtained by drilling 20 mm diameter holes using drilling hummer machine. Concrete powder for each mix and exposure condition state are collected from three holes drilled at a depth of 20-30 mm from the same cube face, as illustrated in Figure 2. Then the powders are mixed together to get one sample to be tested. Concrete powder for all mixes is passed on 300 μm sieve opening.

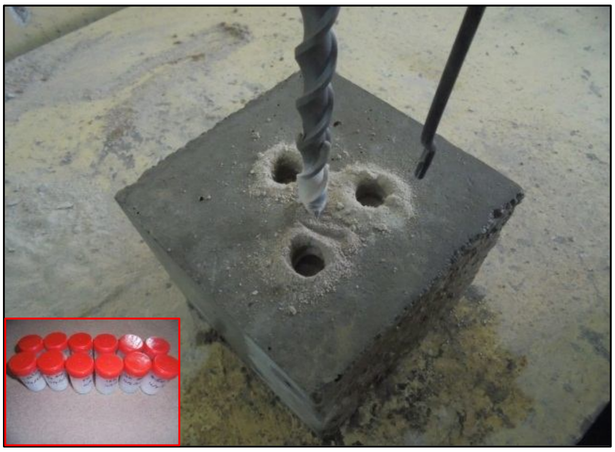

Figure 2: Concrete drilled holes for chloride content test.

3.5.2 Water absorption test

This test is conformed, according to ASTM C642 **(ASTM C 642, 2006)**, for concrete mixes incorporated with micro silica, nano silica and without adding mixes. A total of 24 concrete specimens (discs) with dimensions of 50×100 mm (height× diameter), considering two replicate specimens for each mix, are cast. Two mixes are considered as control. One age test (240 days age) is taking into account. Testing procedure included removing the specimens from tap water at 240 days age and placing it in an oven with a temperature set of 100-110°C for about 24 hours. After that, the oven is switched off and the specimens stilled in it for a specific period to be cooled then lifted from the oven and weighed. Thereafter, it returned to the oven and heated again as mentioned above. The process is repeated until the decrease in mass between two successive values becomes equal or less than 0.5%. The final dried mass is recorded (let is called as D_m). Then the oven-dried specimens placed in tap water for about 24 hours then removed from water and weighed. After that, they immersed in tap water for additional 24 hours, then removed and weighed. The operation is continued until the increase in mass between two successive values becomes equal or less than 0.5%. The final wetted mass is recorded (let is called as W_m). Thereafter, the water absorption of concrete specimens is calculated as percentage of concrete weight by the following equation:

$$\text{Water absorption, \%} = 100 \times (W_m - D_m) / D_m \qquad (1)$$

Where; W_m and D_m are over-dried and wetted mass of concrete specimens respectively.

3.5.3 pH test

Small parts got from broken concrete cubes under compressive strength tested at 90 days age (90 days curing in water) are used for measuring the alkalinity (pH) of concrete mixes. Note that this test (compressive strength test) is not included in this paper. These ports are crushed, then ground to a powder for one minute using grinding machine. The total weight of prepared sample was about 75g. Powder suspension method as in reference **(Rasanen** and **Penttala, 2004)** is depended for this test. The fixed considered parameters are: particle size, liquid: solid ratio, stirring time, extraction time (time between end of stirring and beginning of testing) and reading stabilizing time (time between introducing of pH probe in the suspension, and stabilizing the reading). The later parameter is not defined clearly by the literature, where, some researchers **(Rasanen** and **Penttala, 2004)**recorded the measurement when the change in the reading of pH device was less than 0.01 unit per minute. But, it is believed that it is suitable to fix this time to a limited period, including the above condition (< 0.01 unit per minute). So, the following values are taking into account:

- liquid to solid ratio: 1:1 (0.5)
- particle size: powder is passed through 300 μm.
- stirring time: 15 minutes using glass rod
- extraction time: 60 minutes
- reading stabilizing time (determined after trials): 25 minutes

Crushing and grinding processes are executed not less than two months after compressive strength test, which, as stated above, its results are not included in the present paper. During this period these parts are stored indoor inside closed polyethylene bags. Hanna 211 pH meter is used in the current test. A 15 g (±0.01) of concrete powder and 15 g (±0.01) of distilled water are weighed (using 0.01g precision scale) and mixed, then the suspension is stirred, extracted and the pH measurements are taken considering the above periods.

4. Results and discussions

4.1 Chloride content

The total chloride content (acid soluble) results, as percent of concrete weight, of concrete mixes for the tested age (23 weeks) are shown in Figures 3 and 4. Figure 3 is for wetting-drying exposure, while the other is for full immersing exposure. Chloride contents for all mixes are determined, as mentioned previously, at depth of 20-30 mm.

For wetting-drying exposure, results indicated that the lower chloride concentration value is obtained by 5M mix (about 0.19%). While the larger value is attained by 3N mix (about 0.3%). For full immersing exposure, lower chloride content is found in 5N mix (about 0.18%). However larger value is recorded in 0.5N mix (about 0.29%).

It was found also that, for wetting-drying exposure, mixes incorporated nano and micro silica, except of 10M and 3N mixes, had chloride content less than control mixes. For full immersing exposure, it is cleared from Figure 4 that the higher replacement of cement with nano silica was, the lower was the chloride concentration in concrete mixes.

This may be a result of nano and micro silica effect in pore refinement and densification of concrete microstructure that led to reduce the ingress of aggressive ions into concrete.

In general, chloride content alone is not considered as an evidence of high or low activity of corrosion of reinforcement. Several Other factors (like, alkalinity; type of chloride: bound or free; etc.) are affected.

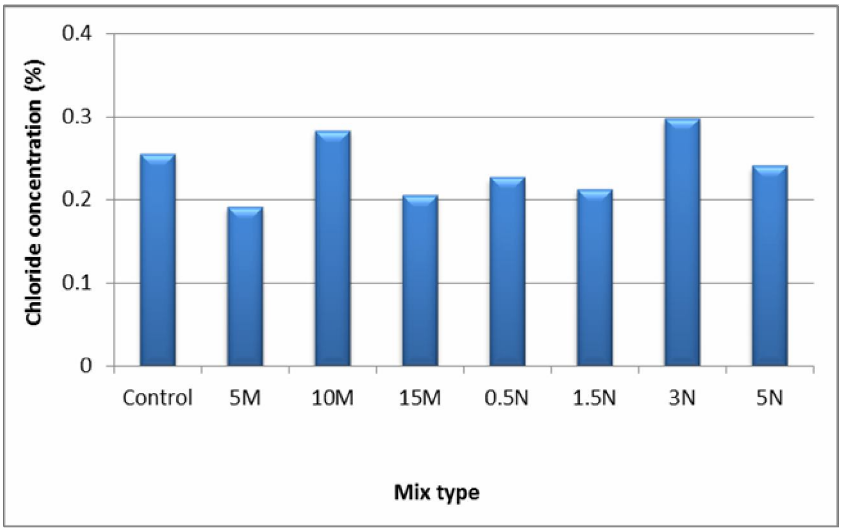

Figure 3: chloride content of concrete mixes after 23 weeks of wetting-drying exposure.

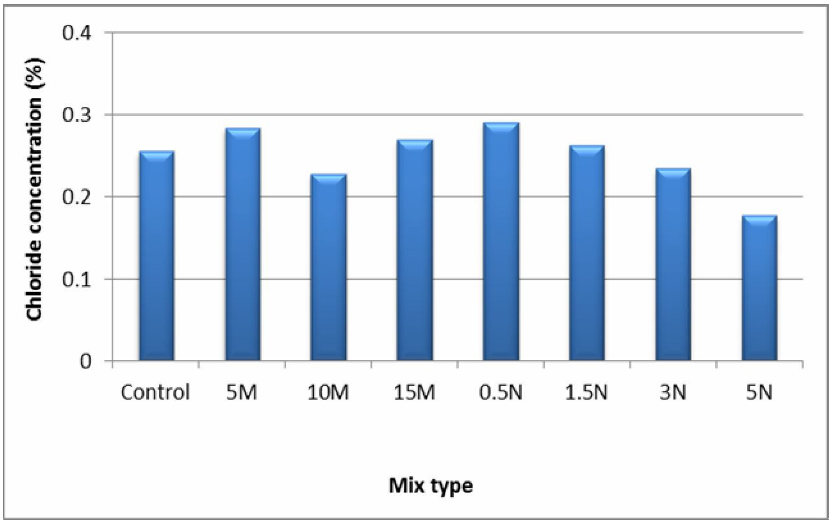

Figure 4: chloride content of concrete mixes after 23 weeks of full immersing exposure.

4.2 Water absorption

Results of water absorption test (% of specimens weight) of concrete mixes at 240 days age (one age) are described in Table 5 and Figure 5. Each result refers to the average of two specimens, except of control mixes results which refer to the average of four specimens.

It can be seen from Table 5 that 5M mix imparted higher absorption percentage (6.97 %) compared with control and all other mixes, while, lower water absorption percentage is given by 0.5N mix (5.13%). It is also noticed that there were slight decreasing in absorption of 10M and 15M mixes in comparison with control mixes (reduction percent was 2-3%) .

Results revealed also that Nano silica mixes, except of 1.5N mix, had significant reduction in water absorption relating to without adding (control) mixes. Replacing of cement by 1.5% nano silica (1.5N mix) led to somewhat decrease in absorption (less than 1%).

Table 5 water absorption of concrete mixes.

Mix type	Water absorption (%)	Reduction % of control
Control	6.26	---
5M	6.97	-11.40 *
10M	6.11	2.35
15M	6.07	3.04
0.5N	5.13	18.00
1.5N	6.22	0.63
3N	5.44	13.03
5N	5.46	12.69

* The negative sign means that the absorption was increased not decreased.

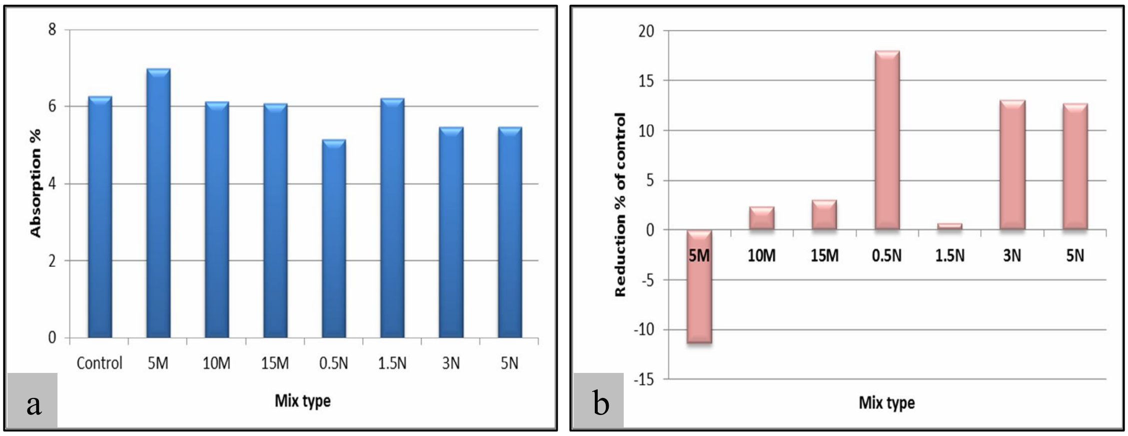

Figure 5: (a) Water absorption %; and (b) Reduction % of control mixes

It was reported in previous work **(Parrott, 1992)** that water absorption of concrete is related to its durability aspects such as chloride entry. Thus, the decreasing of absorption percentage has an advantage effect on concrete durability, and subsequently corrosion of reinforcement. Based on this concept and on water absorption results in this test, it is cleared that incorporating of nano and micro silica in specific proportions (excluding 5M mix) can enhance impermeability properties of concrete mixes, but the improvement was more significant in nano silica mixes than that in micro silica mixes.

4.3 pH of concrete

Results of pH test for concrete mixes for one age (90 days in tap water) are illustrated in Table 6 and Figure 6. Because of the weight of powder sample (15g) used in pH measurement represents a part of about 75g (about 5 times) prepared and mixed together before test, thus, the variation of readings form sample to sample is diminished. For this reason, one reading (except of control which calculated from the average of two readings) is considered for each result in this test.

It is cleared from Table 6 that, for the considered mixes, there was no significant difference in pH values. Where, the change in results between all mixes was less than 0.15 unit. Higher pH value (12.64) is obtained by control mix. The lower ranges of pH magnitude are given by micro silica mixes, where it imparted approximately comparable values, 12.53. The micro silica results are in agreement with previous works **(Gjorv, 1995)** which stated that up to 20 % replacement of cement by silica fume, the pH value didn't drop less than 12.5 unit. Nano silica mixes showed higher alkalinity (pH ≈ 12.6) than micro silica mixes but lower than control mixes.

Concerning of corrosion, the proportions used of nano and micro silica had no negative effect on corrosion resistance of steel reinforcement because the pH values of all concrete mixes were above than 12.5 unit is which considered within the usual alkalinity of concrete (12-13).

Table 6 pH values of concrete mixes

Mix type	pH value
Control	12.64
5M	12.53
10M	12.52
15M	12.53
0.5N	12.60
1.5N	12.60
3N	12.62
5N	12.61

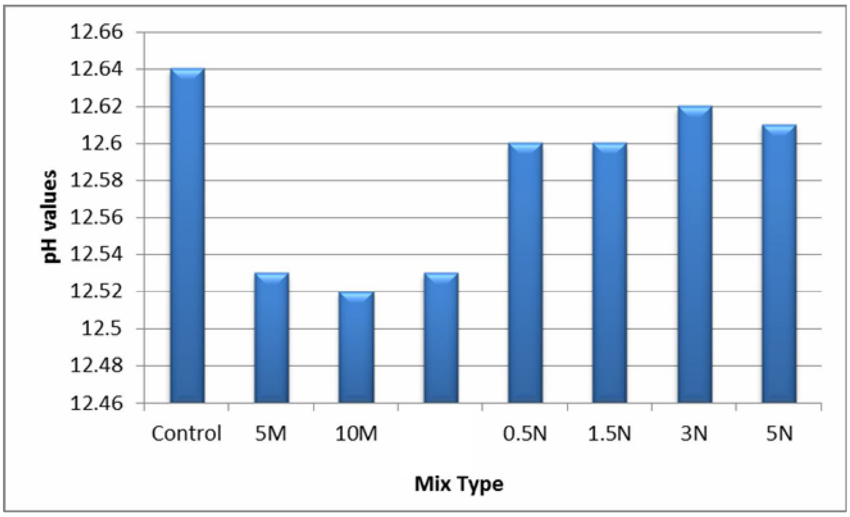

Figure 6: Graphical representation of pH results.

5. Conclusions

Based on experimental results of this work, the following conclusions are reported:

1. For chloride content test, it can be concluded that in full immersed exposure, the chloride concentration into concrete mixes was decreased with increasing of nano silica replacement ratio. This behavior was not cleared in wetting-drying exposure,

however, in this exposure, all mixes incorporated admixtures, except of 10M and 3N mixes, appeared lower chloride content than without adding or control mixes.

2. For water absorption test, all mixes incorporated micro and nano silica, except of 5M mix showed lower absorption than control mixes. Lower absorption was found in 0.5N mix (5.13%) while 5M mix revealed higher absorption, about 6.97%.
3. For pH test, it was found that there was no important difference in pH values for all concrete mixes, where the varying in pH values was less than 0.15 unit. In other words, the adding of nano and micro silica didn't affect adversely the alkalinity of concrete.
4. By considering the three tests together, it can be concluded that the replacement of cement by nano and micro silica in concrete with specific proportions can improve concrete durability properties. However, the optimum proportion may differ for each property , thus it is important to choose the suitable replacement proportion according to the expected conditions in the fields.

References

Abyaneh, M.R.Z., Mousavi S.M.,Mehran A.,Hoseini S.M.M.,Naderi S.,and Irandoost F.M.,2013,"Effects of Nano-Silica on Permeability of Concrete and Steel Bars Reinforcement Corrosion", Australian Journal of Basic and Applied Sciences, Vol. 7, No. 2, pp. 464-467.

ASTM C 143/C 143M –03,2003,"Standard Test Method for Slump of Hydraulic-Cement Concrete", ASTM, West Conshohocken, PA, USA.

ASTM C 642 –06,2006,"Standard Test Method for Density, Absorption, and Voids in Hardened Concrete", ASTM, West Conshohocken, PA, USA.

ASTM C192/C192M −12a, 2012, "Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory", ASTM, West Conshohocken, PA, USA.

Berke, N.,"Concrete". In: Baboian R.,2005,"Corrosion tests and Standards: Application and Interpretation", 2nd edition, ASTM International, West Conshohoken, PA.

BS 1881-124,1988,"Testing Concrete-Part 124:Methods for Analysis of Hardened Concrete", British Standard.

Gjorv, O.E.,1995,"Effect of Condensed Silica Fume on Steel Corrosion in Concrete", ACI Materials Journal,V. 92, No. 6, pp.591-598.

Iraqi Standard Specification No.45,1984,"Aggregate from Natural Sources for Concrete and Building Construction",Central Organization for Standardization and Quality Control, Iraq.

Iraqi Standard Specifications No.5,1984,"Portland Cement", Central Organization for Standardization and Quality Control, Iraq.

Du,H., Du S.and Liu X.,2014,"Durability Performances of Concrete with Nano-Silica", Construction and Building Materials, Vol. 73, pp. 705–712.

Parrott, L.J.,1992,"Water Absorption in Cover Concrete", Materials and Structures, Vol. 25, pp. 284-292.

Rasanen, V. and Penttala V.,2004,"The pH Measurement of Concrete and Smoothing Mortar Using a Concrete Powder Suspension", Cement and Concrete Research, Vol. 34, pp. 813–820.