

MECHANICAL PROPERTIES AND CORROSION BEHAVIOR OF REINFORCING STEEL IN DIFFERENT CEMENT WITH ADDITION OF NANO-SILICA ON BLENDED CEMENTIN TAP WATER

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ABSTRACT

The effect of Nano-silica on blended cement was studied in tap water by using mechanical properties such as compressive strength and different electrochemical technique studied on reinforcing steel in addition of Nano-silica. Different electrochemical techniques namely: open circuit potential, Tafel polarization and EIS. The results refer to an increase in Nano-silica by 7 % leads to an increase in the compressive strength and its further increase leads to reducing the compressive strength. The study is also tackling the tap water effects up to 90 days on ordinary Portland cement and both slag cement. It is also tackled the continuous hydration in the presence of slag cement which indicates an increase in compressive strength with long interval time. Furthermore, the presence of water as a medium never had a negative effect on all hydrated cements. These results have been confirmed through the IR and SEM. The polarization resistance in all cement types increases with time, except in OPC and SRC. The increase in polarization resistance has shown the formation of stable passive layer and reduction of pores during the hydration.

KEYWORDS: Mechanical Properties, Corrosion Behavior, Reinforcement Nano-Silica, Electrochemical Techniques, Tap Water

1. INTRODUCTION

The durability of reinforced concrete depends on the surrounding environmental and exposure conditions. The alkaline phase from hydrated cement has a protective effect for the embedded reinforcing steel bars. Reinforcement corrosion is one of the major causes of degradation in concrete structure [1].Nanosilica is the extremely fine silica that has been used for years as cement admixture both in the oil field and in construction and civil engineering industries. Because of its extremely fine nature and high reactivity pozzolanic material, Nanosilica has been used to improve slurry impermeability and the mechanical properties of the hardened material [2].

The studies, regarding the improvement of the mechanical, shrinkage, and some durability properties of the concrete by NS have been carried out [2-7]. Li et al.[8] reported the mechanical properties and the SEM observation of mortars mixed with nano-silica. They replaced 3, 5 and 10 % of the cement with nano-silica with 99.9 % SiO_2 at water -binder (w/b) ratio of 0.5 for all the mixes. The compressive strength for all the specimens at 7 and 28 days of curing

were higher than for the plain cement mortar with the same w/b ratio. The nano-silica was effective in improving the strength, with increasing amount cement replaced. The SEM observations also revealed that the Nano-silica was not only acting as filler, but also as an activator to promote hydration.

The cement which is alkaline (pH 13.5) oxidizes embedded steel bars, forming a chemically and electrically inactive layer (passive film) of ferric oxide [1]. Corrosion of the reinforcing steel bars is initiated to form inactive thin layer which can be broken when immersed in carbonate, chloride or sulphate solutions. Carbonates, chlorides and sulphates media can be found in concrete when using contaminant aggregates, or adding CaCl₂ (as an accelerator) during the mixing step or they are found under the effect of sea-water or ground-water on concrete and they can also result from attack of concrete by the surrounding environment in coastal regions [1].

In the production of iron, iron ore, iron scrap, and fluxes (limestone and/or dolomite) are charged into a blast furnace along with coke for fuel [9]. The coke is combusted to produce carbon monoxide, which reduces the iron ore to a molten iron product. This molten iron product can be cast into iron products, but is most often used as a feedstock for steel production. Blast furnace slag is a nonmetallic coproduct produced in the process. It consists primarily of silicates, aluminosilicates, and calcium-alumina-silicates. The molten slag, which absorbs much of the sulfur from the charge, comprises about 20 percent by mass of iron production. Different forms of slag product are produced depending on the method used to cool the molten slag. These products include air-cooled blast furnace slag (ACBFS), expanded or foamed slag, pelletized slag and granulated blast furnace slag (GBFS).

The present work aims to study the mechanical properties of different cement paste with mineral additive Nanosilica to improve the properties of the cement pastes. Also, the effect of cement types on the electrochemical behavior of reinforcing steel in tap water.

2. EXPERIMENTAL PROCEDURE

2.1. Materials Used

Materials used in this investigation were ground granulated blast furnace slag (WCS) which produced from Iron and Steel Company, Ordinary Portland Cement (OPC) produced from National Cement Company and Sulphate Resistance Cement (SRC) produced from Egypt Cement Company. On the other side, air-cooled blast furnace slag (ACBFS) used as reference sample. The chemical analyses of these raw materials are shown in Table (1.2). Material properties of Nanosilica (NS) (in liquid form) are shown in Table (2.2).

Chemical	Types of Cement					
(%)	OPC	SRC	WCS(Slag A)	ACBFS(Slag B)		
Na ₂ O	0.601	0.215	1.399	0.566		
MgO	2.208	1.446	5.501	1.156		
Al ₂ O ₃	4.227	1.358	12.137	3.749		
SiO ₂	15.892	8.374	31.303	15.907		
P_2O_5	0.175	2.472	0.020	0.355		
SO ₃	2.539	0.518	2.358	2.614		
K ₂ O	0.103	0.049	1.356	0.197		
CaO	67.330	41.971	33.179	66.986		
TiO ₂	0.510	0.251	0.607	0.516		
MnO	0.047	8.535	5.547	1.038		

 Table 1.2: Chemical Composition of Starting Materials, (Wt %)

Fe ₂ O ₃	5.292	3.378	0.504	6.467
BaO	0.019	0.389	5.730	0.169

Composition (Mass %)	SiO ₂ (30%), H ₂ O (70%)
Diameter (nm)	50
pH value	10
Density (g/cm^3)	1.03

2.2. Sample Preparations

Cylindrical specimens of 60 mm diameter and 100 mm height were cast with an embedded steel bar of 12 mm in diameter and 100 mm in height were prepared for corrosion test. The steel bars were mechanically polished to remove the firmly adherent mill scales on the surface and cleaned by deionized water, dried with acetone then coated with epoxy leaving 1 cm² uncoated. The chemical compositions of reinforcing steel are shown in Table (3.2).

Table 3.2: Chemical Composition of Reinforcing Steel

Element	C	Si	Mn	Р	S	Cr	Ni	Al	Fe
Wt %	0.323	0.169	0.782	0.0321	0.0186	0.0188	0.0135	0.0333	bal

Different mixtures were prepared from ground granulated slag (WCS) or reference granulated slag (ACBFS) as well as Nano-silica (NS) with Ordinary Portland Cement (OPC) and Sulphate Resistance Cement (SRC). The cylindrical specimens were vibrated mechanically to assist compaction. After 24 h of setting the cylindrical specimens were demoulded and subjected to water curing for 7 days in order to avoid any contamination.

2.3. Method of Mechanical Properties

The compressive strength measurements were carried out by preparing neat cement cubes $2.5 \times 2.5 \times 2.5$ cm, which were cured for 24 h, demoulded and continuously cured in a humidity chamber till the time of testing. A set of 3 cubes were used for each compressive strength determination [10]. Compressive strength measurements were carried out using two tones Amsler testing machine with a loading rate of 100 kg/min determined according to Khater et al.[11].

2.4. Corrosion Measurements

Three different electrochemical methods were used to evaluate the corrosion behavior of reinforcing steel bar. The open circuit potential, Tafel Plot polarization measurements and EIS were performed using the Voltalab 40 Potentiostat PGZ301 made in Germany. The Volta Master 4 software is designed to measure and analyze corrosion rate.

2.4.1. Open Circuit Potential (OCP)

OCP measurements were often used as an indication of the corrosion risk of the steel. The reinforcing steel embedded in the cement paste was employed as working electrode and a saturated calomel electrode (SCE) as reference electrode. Bi-weekly readings were recorded for potential till 90 days of exposure period. Before each measurement, the potential was recorded until it reached an almost stable value, which was the corrosion potential, E_{corr} .

2.4.2. Tafel polarization experiments

Tafel polarization technique was used to determine the corrosion parameters; corrosion potential, corrosion current and corrosion rate of reinforcing steel bars embedded in cement paste. The potential of the steel electrode was scanned at a scan rate of 2 mV/s. The tests were initiated at 250 mV below the corrosion potential (E_{corr}) and terminated at 250 mV above it, while recording the polarization current density (i). The Tafel equation is an empirical relation between the over potential of the electrode and the current density passing through the electrode:

$$\eta_{a+b \log i} \tag{1}$$

Where η is the over potential; i is the current density; a and b are characteristic constants of the electrode system. A plot of electrode potential against the logarithm of the current density is called the "Tafel plot" and the resulting straight line the "Tafel line". "b" is the "Tafel slope" that provides information about the mechanism of the reaction, and "a" the intercept, provides information about the rate constant (and the exchange current density) of the reaction.

The corrosion rate, C.R. (µm consumption of steel per year) can be computed using Faraday's Law as follows

C.R.
$$(\mu m/year) = 3.3 i_{corr} M/zd$$

Where; z = ionic charge (3 for iron), M = atomic weight of metal (55.85 for iron), d = density of iron, 7.9 g/cm³, and $i_{\text{corr.}} = \text{corrosion current density}$, $\mu A/cm^2$.

2.4.3. Electrochemical Impedance Spectroscopy (EIS) Measurements

Electrochemical Impedance spectroscopy (EIS) is a powerful technique for investigating electrochemical and corrosion systems. The main advantage of this technique is the use of a purely electronic model (equivalent circuit) to represent the electrode/electrolyte interface. An interface undergoing electrochemical reaction is typically analogous to an electronic circuit consisting of resistors and capacitors. Thus, an electrochemical system can be characterized in terms of its equivalent circuit. According to AC (alternating current) circuit theory, an impedance plot obtained for a given electrochemical system can be correlated with one or more equivalent circuits. The information is used to verify a mechanistic model for the system or at least to rule out incorrect models. Once a particular model is chosen, physical or chemical properties can be correlated with circuit elements and numerical values can be obtained by fitting experimental data to the circuit model.

For impedance measurements a 10 mV amplitude signal in normally used, since the impedance data were found to be dependent of the perturbation signal amplitudes in the range 5 - 15 mV. The normal working frequency range is 1 mHz to 100 kHz. The measurements, processing, storage, retrieval and analysis of data generated has been automated. After preliminary setting-up measurements, the electrode impedance data can be obtained over a wide frequency range (1 mHz - 100 kHz). These data are fitted to the suggested equivalent circuit from this circuit useful information is obtained and plots can be obtained [92, 95].

2.5. Spectroscopic Analysis

2.5.1. Infrared Spectroscopic Analysis

The infrared spectrum of compound can be used as a finger print to provide qualitative and quantitative analysis of mixture. IR spectral analysis was carried out for some selection sample of hydrated pastes to provide additional information on the hydrated products, and it is sometimes possible to have conclusions concerning aspects of the structure from their appropriate spectrum. The samples were prepared using alkali halide (KBr) pressed disk techniques as it gives a

(2)

further reduction in scattering. 1.0 mg of the hydrated powder sample was ground with 99 mg of potassium bromide in an agate mortar to produce a homogeneous mixture. The mixture was pressed under vacuum to give a transparent disk of 1.0 cm in diameter. Transfer the KBr disc to a sample holder and place it in the spectrometer. The infrared spectral analysis was recorded from KBr discs using Genesis-II IR spectrometer in the range 400-4000 cm⁻¹.

2.5.2. Scanning Electron Microscope (SEM) Analysis.

The SEM was used to observe the surface morphology and the grain size. The examination was carried out on different samples using JEOL JSM 5410 (Japan). The data that presented and discussed in this paper are divided into two main parts. The first part is concerned with determining the mechanical properties for many designed mixtures containing both types of slag with OPC. In addition, mineral additive Nanosilica was added to improve the properties of the cement pastes. The second part is ascribed to electrochemical behaviors of reinforcing steel imbedded in OPC, SRC and blended cements in tap water.

3. RESULTS AND DISCUSSIONS

3.1. Mechanical Properties

3.1.1. Effect of Cement Types on the Mechanical Properties

The mix designs of the prepared cements are given in Table (4.3). The values of compressive strength of the hydrated slag cement pastes as well as OPC and SRC cured in tap water up to 28 days are given in Table (5.3). These are also graphically represented as a function of curing times in Figure (1.3).

Mix No.	OPC	SRC	Slag A	Slag B
OPC	100	-	-	-
SRC	-	100	-	-
SA5	95	-	5	-
SB5	95	-	-	5

Table 4.3: Mix Composition of the Prepared Cements, (wt %)

 Table 5.3: Compressive Strength (Kg/Cm²) of Hydrated Slag Cement Pastes as Well as

 OPC and SRC as a Function of Curing Time

Time(Dava)	Compressive Strength(kg /cm ²)					
Mix No.	3 Days	7 Days	15 Days	28 Days		
OPC	398	438	476	503		
SRC	420	451	484	535		
SA5	430	446	504	563		
SB5	350	420	502	551		



It is clear that the compressive strength for all cement pastes increases with curing time due to the increase of the amounts of hydration products, such as calcium silicate and aluminosilicate hydrates. As the hydration proceeds, more cementing materials are formed and accumulated in water-filled pores to give a more compact body.OPC pastes give the lower compressive strength values at all immersing ages. This is mainly due to the high content of portlandite, which formed during the hydration.

3.1.2. Effect of Nanosilica Addition on Cement Types in the Mechanical Properties

In this part of investigation, a trial is made to increase reactivity of the pozzolanic part by using Nanosilica. The values of compressive strength of hardened blended cement pastes cured in tap water up to 28 days are given in Table (7.3). These are also graphically represented as a function of curing times in Figure. (2.3).

Mix No.	OPC	SRC	Slag A	Slag B	NS
OPC+1NS	99	-	-	-	1
SRC+1NS	-	99	-	-	1
SA5+1NS	94	-	5	-	1
SB5+1NS	94	-	-	5	1

Table 6.2: Mix Composition of the Prepared Cements, (wt %)

 Table 7.3: Compressive Strength (Kg /Cm²) of Hardened Blended Cement

 Pastes as Function of Curing Time

Time(days)	Compressive Strength(kg /cm ²)						
Mix No.	3Days	7 Days	15 Days	28 Days			
OPC+1NS	426	461	472	501			
SRC+1NS	405	470	514	549			
SA5+1NS	455	525	536	579			
SB5+1NS	443	487	523	553			



It can be seen that the compressive strength was developed in cement pastes containing Nanosilica particles in every case higher than that of containing cement. The difference in the strength development of the cement pastes can be attributed to pozzolanic reaction. Nano particles are thought to be more effective in pozzolanic reaction than slag cement. Also, the Nanosilica would fill pores to increase the cement paste strength. Therefore, it is confirmed that the addition of Nanosilica to cement pastes improves their strength characteristics. This is may be due the fact that highly reactive Nanosilica will consume the liberated hydrated lime from hydration reaction and result in the formation of CSH that acts as nucleating sites [11].

3.1.3. Effect of Nano-silica Concentration on Blended Water Slag Cement in the Mechanical Properties

A series of tests were performed to study the effect of Nano-silica on the mechanical properties of the blended water slag cement paste. The influence of Nano-silica on the microstructure of slag cement pastes was also investigated using SEM analysis. The values of compressive strength of blended water slag cement pastes of various proportion of Nano-silica cured in tap water up to 28 days are given in Table (9.3). These are also graphically represented as a function of curing times in Figure. (3.3).

Mix No.	OPC	Slag A	NS
1NS	94	5	1
3NS	92	5	3
5NS	90	5	5
7NS	88	5	7
9NS	86	5	9

Table 8.3: Mix Composition of the Prepared Cements, (wt %)

Table (9.3): Compressive Strength (Kg/Cm ²)	of Blended Water Slag Cement Pastes as
Function of Curing Time of Vari	ous Proportion of Nano-Silica

Time(days)	Compressive Strength (kg /cm ²)						
Mix No.	3 Days	7 Days	15 Days	28 Days			
1NS	422	436	458	493			
3NS	444	447	483	517			
5NS	448	452	502	547			
7NS	458	466	513	562			
9NS	412	432	447	459			



The compressive strength increases with the increase of the amount of NS until it reaches an optimal amount of 7% and then drops to some lower values at 9 % addition. It is obvious that increase in the Nano-silica content beyond 7% did not change the compressive strength significantly. It is found that large amounts of Nano-silica decrease the compressive strength of the cement paste instead of improving it. Because when the content of Nano-silica is large, Nano particles are difficult to disperse uniformly **[8]**. Therefore, they create a weak zone in the form of voids, consequently the homogeneous hydrated microstructure cannot be formed and a lower strength will be probable. Strength enhancement of NS can be attributed to reduction in the content of $Ca(OH)_2$ which does not have any cementing property and production of hydrated calcium silicate (CSH) that plays a vital role in mechanical characteristics of cement paste[**14.15**].

Generally, two fundamental mechanisms can be deduced for strength enhancement of slag cement paste by Nanosilica: first, strength enhancement by matrix densification and paste-aggregate interfacial zone refinement. Evidence from numerous studies has shown that the microstructure of transition zone between aggregates and cement paste strongly influences the strength and durability of concrete [16]. The presence of Nano-silica particles reduces the wall effect in transition zone between the paste and the aggregates and strengthens this weaker zone due to the higher bond between those two [17]. Strength enhancement by pozzolanic reactions is the second mechanism. Pozzolanic materials are generally able to combine with the hydrated calcium hydroxide $Ca(OH)_2$) which has a low cementing property forming the hydrated calcium silicate (C–S–H), which is the principal responsible for the strength of hydrated cement pastes [15]. The SEM analysis was carried out on some selected samples of hardened cement pastes at 28 days for OPC, Blended slag cement and mix Nanosilica are shown in Figure.(12 a, b, c).

The results showed that nano-SiO₂ particles formed very dense structure and compact formation of the hydrated products and decreased the size of big crystals such as $Ca(OH)_2$ [18,8]. The effect of nano-SiO₂ on the microstructure of blended slag cement paste was evaluated. It can be seen that the slag cement paste has a porous microstructure, but when 7% nano-SiO₂ was added, the microstructure significantly changed. The nano-SiO₂ particles improved the microstructures of paste containing slag cement on dense and compact form and generated more homogenous distribution of the hydrated products.



Figure (12): SEM Micrographs of Cement Pastes Immersed in Tap Water at 28 Days. (A). OPC. (B). OPC+ Slag A. (C). OPC + Slag A + 7 NS.

3.1.4. Effect of Tap water on Blended Slag Cement and Plain Cement

The influence of tap water was studied on blended slag cement pastes and OPC pastes up to 90 days. In the beginning, samples of hardened cement pastes were cured under tap water up to 28 days (zero time), then continued in tap water up to 3, 7,15,28, 60 and 90 days. The mix composition of blended slag cement and plain cement are given in Table (10.3). The values of compressive strength of the hardened blended slag cement and plain cement pastes cured in tap water up to 90 days are given in Table (11.3). These are also graphically plotted as a function of curing times in Figure (5.3).

Table 10.3: Mix	Composition of	of Blended Slag	Cement and Plain Cement
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Slag A	(95% OPC+5% WCS)
Slag B	Reference sample (95% OPC+5% ACBFS)
OPC	100% OPC

Table 11.3: Compressive Strength (Kg /Cm²) of Hardened Blended Slag Cement and Plain Cement Pastes as a Function of Curing Time in Tap Water

Immersing	Compressive Strength (kg /cm²)			
Time (Days)	OPC	Slag A	Slag B	
3	403	408	405	
7	429	490	460	
15	447	516	496	
28	456	519	502	
60	476	521	512	
90	497	540	531	



The results show that the compressive strength increases for all cement pastes with the increasing of curing time due to the nature of hydrated phases that formed during the hydration process. The results can be summarized as follow: The gain in the strength for the specimens having OPC is mainly attributed to the hydration of aluminate, ferroaluminate and $C_{3}A$ in addition to $C_{2}S$ phase. The hydration products fill the pores and have binding characteristics [19].

Microstructure: As the physical properties of concrete particularly strength and permeability significantly depend on its pore structure, the application of scanning electron microscopy (SEM) will improve our ability to evaluate the effect of supplementary cementing materials on the strength and durability of the products. Figure.(6.3 a, b, c) are shown SEM micrographs of blended slag cement and plain cement pastes immersed in tap water at 90 days for a) OPC , b) Slag A and c) Slag B. The number of pores increases but the size of each pore decreases shapely due to the hydration process which reacts with Portlandite to form CSH and various phases in the pore.



Figure 6.3: SEM Micrographs of Cement Pastes Immersed In Tap Water at 90 Days. (A) OPC, (B) Slag A and (C) Slag B

I.R. Spectroscopy

The IR spectral for blended slag cement and plain cement pastes cured in tab water at 90 days are given in Figure.(7.3).It is clear that, the absorption band at 3640 cm⁻¹ which is due to the stretch vibration of OH⁻ group of Portlandite (CH). The peak at 3437 cm⁻¹ is due to water this band increases with curing time due to the large incorporation of H₂O molecules in the formation of hydrated product. The band at 1424 cm⁻¹ is attributed to presence of CaCO₃ (calcite), possibly formed due to carbonation of the pastes. This band increases as the following order:

This behavior may be pointing to the porosity of cement pastes. The intensity of the band at 971 cm⁻¹ is due to Si – O stretching vibration of CSH. The IR spectral at 710 cm⁻¹ may be attributed to the alumina content and this band could be assigned to (Al-O) vibrations of aluminate mineral component, this band also get the same behavior in vibration band 971cm⁻¹.



3.2. Corrosion Measurements

The data presented and discussed in this part covers the effect of different cement pastes (Sulphate Resistance Cement (SRC), Ordinary Portland Cement (OPC), water slag cement (slag A), air slag cement (slag B), Mix water slag cement (Mix A) and Mix air slag cement (Mix B)) on the electrochemical behavior of reinforcing steel in tap water. The electrochemical measurements used through this investigation include Open circuit potential measurement, Tafel Polarization measurements and Electrochemical Impedance Spectroscopy (EIS).

3.2.1. Open Circuit Potential (OCP)

Open circuit potential (OCP) has been studied the electrochemical behavior of reinforcing steel in different types of cement immersed in Tap Water. The open circuit potential measurements for the plain OPC, SRC, Slag A, Slag B, Mix A and Mix B blends are presented in Figure. (8.3). The open circuit potential was monitored periodically for a period of 90 days of exposure.

In cases of OPC and SRC, the open potential values were observed a steady state potential and remained passive state. While in case of Slag A, Slag B, Mix A and Mix B, open potential values shifts towards more negative value up to 28 days, then sharply shifts towards more nobler direction. The pore size distribution may be the reasons for the cement paste has significantly reduced potential, which acts as filler material. The increases of potential indicate passive state. At the end of exposure period, the potential for Slag B was found to be lesser than other types of cement.



3.2.2. Tafel Polarization Experiments

The progress of the corrosion and consequently the performance of the MK admixed concretes was monitored by means of the corrosion current density and the corresponding corrosion rates. Tafel polarization technique had employed at scan 2 mV/s. The linear polarization resistance curves for reinforcing steel embedded in Ordinary Portland Cement (OPC), Sulphate Resistance Cement (SRC), water slag cement (Slag A), air slag cement (Slag B), Mix A and Mix B on the electrochemical behavior of reinforcing steel immersed in tap water for 3, 7, 15, 28, 60 and 90 days at scan rate 5 mV/sec., are shown in Figures.(9.3-14.3). The values of different corrosion parameters are calculated and presented in Tables (12.3-17.3). Inspection of Tables (12.3, 13.3) in case of OPC and SRC, it is found that E_{corr} values and also polarization resistance (R_p) values decreased with increasing the exposure period, while I_{corr} and corrosion rate values increased with increasing exposure period. The low corrosion potentials have been observed due to compactness which developed as the CSH gel (3CaO.SiO₂) formed **[20]**.

During the first hour of the hydration of the cement, the pH originates partly from production of the super saturated calcium hydroxide and partly from sodium and potassium hydroxide in the pore liquid, as the time goes mainly the sodium and potassium hydroxide in the solution will determine the pH [21]. The amount of calcium hydroxide will be determined by amount of C_3S and C_2S in the Portland cement clinker. Furthermore, C_3A is very low ($\leq 3.5\%$) causing decrease in the pH of pore solution. At 60, 90 days the corrosion potentials (E_{corr}) decrease and this is mainly due to the low alkalinity of Portlandite which produced during the hydration process and precipitated in pores. Differences in the types of cement are a result of variation in composition or fineness or both, and as such, not all types of cement have the same ability to provide protection of the embedded steel [22].

To compare the results in Tables (12.3,13.3), it is found that, R_p value in case of SRC paste is more than that in case of OPC paste and also, C.R value in case of SRC paste is lower than that in case of OPC paste. Most of the work reported previously on the performance of OPC and blended cements are done on hardened cement pastes **[20]**. However, if chloride is present inherently by the use of the contaminated water or aggregate or a freshly set cast is immersed in contaminated environment then most of the damage through corrosion will be experienced during the time of hydration.

Slag improves the mechanical and physicochemical properties of the cement paste. Blast furnace slag is the most useful latent hydraulic material, because the amount produced is very large and its properties are very stable composed with other industrial by-products **[9]**. Water slag cement (slag A) created by grinding mixture of 5 percent water granulated slag and 95 percent Portland cement. In this case, Figure.(11.3) and Table (34), the free corrosion potential shifts towards

more positive values up to 90 day due to the hydration of slag, which consumed large amount of $(Ca(OH)_2)$ to produce C-S-H. Air slag cement (slag B) created by grinding mixture of 5 percent air granulated slag and 95 percent Portland cement. Inspection of Figure (12.3) and Table (15.3), it is found that the free corrosion potential shifts towards more negative values up to 90 day and the potential values changed from (- 315.2 mV to - 472.2 mV). The decreasing in free corrosion potential at 90 day is attributed to the reducing effects of sulfur species, such as S, SO₂, S₂O₃, etc., derived from slag. These sulfur species can reduce the potentials to much lower values depending on the concrete environment [23].

The amount of buffering substance $(Ca(OH)_2)$ for the penetrating CO_2 decrease with the amount of slag or pozzolanic material. However, the additional reaction within blended cement leads to less or much less permeable concrete. The pozzolanic reaction leads to filling of pores. The decrease in buffering capacity or even decrease in pH is therefore counter act by the decrease in permeability. Additionally, the pozzolanic reaction leads to increase of the electrical resistivity, and decrease of mobility of aggressive ions and therefore decreasing the corrosion [22].

Mix A created by grinding mixture of 5 percent water granulated slag, 7 percent NS and 88 percent Portland cement. Mix B created by grinding mixture of 5 percent air granulated slag, 7 percent NS and 88 percent Portland cement. Inspection of these curves in Figures.(13.3,14.3) and Tables (16.3,17.3), it is found that, the free corrosion potential shifts towards more positive values. The high values of the free corrosion potential at early days of hydration is due to the high amount of OPC in cement mix, and formation of the high amount of Portlandite (Ca(OH)₂) during the hydration of ordinary Portland cement. The increase in potential is mainly due to increase in the Portlandite concentration with time. Furthermore, NS in this type of cement reduces the effect of internal sulphide attack during the reduction of pores.

The use of large quantities of cement produces increasing CO_2 emissions. A method to reduce the cement content in concrete mixes is the use of silica fines. One of the silica fines with high potential as cement replacement and as concrete additive is Nano-silica (NS) [24]. In addition, a mix design tool used for self-compacting concrete (SCC) will be modified to take into account particles in the size range of 10 to 50 nm. From the results in Tables (16.3, 17.3), for Mix A and Mix B, respectively, it is found that corrosion rate values decreased with increasing the exposure period in case of Mix B than these values in case of Mix A and that confirmed by (SEM) analysis.

The corrosion current density values of slag A, slag B, Mix A and Mix B decreased with time. The decreasing values of I_{corr} are mainly due to the physical and chemical protection. The physical protection is attributed to the formation of dense passive layer on the surface of steel. The chemical protection can be explained through two reactions: the first reaction is related to the formation of discontinuous layer of Portlandite (Ca(OH)₂), the second reaction includes the hydration of cement and the formation of Calcium-Silicate-Hydrate (CSH) gel which imparts an additional physical protection to the steel matrix.



Immersing	E _{corr}	Icorr	R _p	Corrosion Rate
Time (Days)	(mV)	$(\mu A/cm^2)$	$(\mathbf{k}\Omega.\mathbf{cm}^2)$	(µm/y)
3 days	-246.8	1.6240	24.70	18.99
7 days	-249.4	1.8282	23.20	21.38
15 days	-255.1	1.9320	21.62	22.59
28 days	-255.9	2.0176	21.51	23.59
60 days	-475.5	2.0653	21.08	24.15
90 days	-554.2	2.2216	16.55	25.98

Table 12.3: Corrosion Parameters of Reinforcing Steel Presented in OPC Paste in Tap Water

Immersing Time (Days)	E _{corr} (mV)	$I_{corr} \\ (\mu A/cm^2)$	$\frac{R_{p}}{(k\Omega.cm^{2})}$	Corrosion Rate (µm/y)
3 days	-109.2	0.4636	53.60	5.42
7 days	-111.8	0.4752	51.57	5.558
15 days	-124.4	0.6109	50.69	7.144
28 days	-131.6	0.6541	49.67	7.650
60 days	-135.2	0.6708	44.76	7.846
90 days	-156.0	0.9569	42.89	11.19

Table 14.3: Corrosion Parameters of Reinforcing Steel Presented in Slag a Paste in Tap Water

Immersing Time (Days)	E _{corr} (mV)	$I_{corr} (\mu A/cm^2)$	$\frac{R_{p}}{(k\Omega.cm^{2})}$	Corrosion Rate (µm/y)
3 days	-447.5	1.9092	14.16	22.33
7 days	-417.3	1.8999	14.59	22.22
15 days	-357.8	1.6109	15.73	18.84
28 days	-343.0	1.3208	19.11	15.44
60 days	-310.0	1.2473	21.01	14.58
90 days	-227.3	1.0489	27.01	12.26

Table 15.3: Corrosion Parameters of Reinforcing Steel Presented in Slag B Paste in Tap Water

Immersing Time (Days)	E _{corr} (mV)	$\frac{I_{corr}}{(\mu A/cm^2)}$	R_{p} (k Ω .cm ²)	Corrosion Rate (µm/y)
3 days	-315.2	2.7620	12.21	32.30
7 days	-386.7	2.2728	12.53	26.58
15 days	-399.6	2.2118	13.28	25.87
28 days	-421.2	2.1297	13.52	24.90
60 days	-448.6	1.8920	14.66	22.12
90 days	-472.2	1.8013	17.05	21.06

Table 16.3: Corrosion Parameters of Reinforcing Steel Presented In Mix a Paste in Tap Water

Immersing Time (Days)	E _{corr} (mV)	$I_{corr} (\mu A/cm^2)$	$\frac{\mathbf{R}_{p}}{(\mathbf{k}\boldsymbol{\Omega}.\mathbf{c}\mathbf{m}^{2})}$	Corrosion Rate (µm/y)
3 days	-354.1	0.9831	45.02	11.49
7 days	-305.7	0.7404	46.70	8.660
15 days	-299.6	0.5877	47.50	6.873
28 days	-264.5	0.5787	50.26	6.769
60 days	-189.3	0.5533	57.90	6.471
90 days	-146.6	0.4772	58.25	5.581

Immersing Time (Days)	E _{corr} (mV)	$I_{corr} (\mu A/cm^2)$	$\frac{R_{p}}{(k\Omega.cm^{2})}$	Corrosion Rate (µm/y)
3 days	-344.6	0.5982	49.82	6.996
7 days	-343.9	0.4921	53.60	5.755
15 days	-326.1	0.4913	55.10	5.746
28 days	-317.9	0.4273	60.61	4.997
60 days	-312.2	0.3217	62.91	3.762
90 days	-267.5	0.2821	86.93	3.300

Table 17.3: Corrosion Parameters of Reinforcing Steel Presented in Mix B Paste in Tap Water

3.2.3. Electrochemical Impedance Spectroscopy

The electrochemical impedance spectroscopy (EIS) has been studied the electrochemical behavior of reinforcing steel embedded in cement pastes. Nyquist diagrams of reinforcing steels in difference types of cement immersed in Tap water are shown in Figures (15.3-20.3). These figures represent the relation between the resistive Z real (Zr) against the capacitive Z imaginary (Zi). The calculated equivalent circuit parameters for the investigated reinforcing steel of Nyquist diagrams are reported in Tables (18.3-23.3). These tables include the equivalent parameters at low frequency, such as, the solution resistance (R_s), double layer capacitance (C_{dl}) and polarization resistance (R_p). At low frequency, an electric resistance in series with (R-C) network can describe the spectra of peaks. The series resistance represents the solution resistance (R_s), which increases with time for all types of cement except for OPC and SRC. This is due to the formation of

protected layers (passive layer and cement phases). After 90 days, the solution resistances are in the following order

Mix B > Mix A > Slag A> Slag B > SRC > OP

The solution resistance in presence of OPC and SRC get lower value compared to the other types of cement due to the degree of permeability in OPC and SRC cements, which increases in presence of slag cement.

The polarization resistance (R_P) increased with time in all types of cement except in presence of OPC and SRC, this mainly attributed to the growth of passive layer on the surface of steel, which formed in alkaline pH during the formation of Portlandite. The polarization resistances at the 90 days are in the following order

$$Mix B > Mix A > Slag B > Slag A > SRC > OPC.$$

In the presence of Mix A and Mix B, the passivation process record high values especially at early days due to the internal sulphide attack. Both OPC and SRC get low values due to the hydration process on steel surface, which produce large amount of heat that increases the activity of steel. It is concluded that, in case of OPC and SRC, R_p values decrease with time. The decrease in resistance is due to the penetration of chloride ion from the tap water. While in cases of Slag A and Slag B, R_p values increase with time due to the formation of passive layer on surface of steel and the physical protection by the cement layer.

In case of presence of (NS), and that in Mix A and Mix B paste, it is found that a high values of R_p . Therefore, adding (NS) to concrete effectively reduced the corrosion rate and also increased the polarization resistance [25].

The double layer capacitance of reinforcing steel imbedded in tap water (C_{dl}) decreases with time due to the absence of aggressive ions. At 90 days, the double layer capacitances are following the order

Slag B > Mix A > SRC > Mix B > Slag A > OPC

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The recorded values for slag cement and mix slag cement are related to the presence of active sulphide in internal solution. While in case of OPC, the capacitance recorded very low value due to the formation of thin and dense oxide layer. Furthermore, thickness of passive layer in presence of OPC records the best result compared to the thickness of passive layer in other types of cement. As it is known, oxygen input into the concrete is facilitated at higher porosities. Oxygen and water are definitely required in order to enable the corrosion to continue in a neutral environment [26].Water normally enters the concrete through capillary action; the fewer and smaller the capillary pores are the less water enters the concrete and the lower the rates of oxygen diffusion. Due to the high alkalinity in concrete, there are very few H^+ ions to be consumed in the cathodic reaction, so that the oxygen has to be reduced in order to sustain the cathodic reaction. Low air void content and low water absorptivity help keep chloride ions from going through the concrete and reaching the surface of the steel [25].





Table 18.3: Impedance Parameters of Reinforcing Steel Presented in OPC Paste in Tap Water

Immersing Time (Days)	R _s (kohm.cm ²)	R _p (kohm.cm ²)	$C_{dl}(\mu F/cm^2)$
3 days	8.489	14.1	22.70
7 days	2.437	4.662	3.806
15 days	2.285	4.335	1.771
28 days	2.075	3.914	1.739
60 days	2.025	3.6	1.409
90 days	2.001	3.023	1.352

Table 19.3: Impedance Parameters of Reinforcing Steel Presented in SRC Paste in Tap Water

Immersing Time (Days)	R _s (kohm.cm ²)	R _p (kohm.cm ²)	С _{dl} (µF/сm²)
3 days	3.307	13.70	80.86
7 days	2.559	6.998	67.43
15 days	2.505	6.878	61.50
28 days	2.453	6.575	65.59
60 days	2.374	5.975	50.21
90 days	2.352	4.658	49.59

Table (20.3): Impedance Parameters of Reinforcing Steel Presented in Slag a Paste in Tap Water

Immersing Time (Days)	R _s (kohm.cm ²)	R _p (kohm.cm ²)	C _{dl} (µF/cm²)
3 days	1.277	3.017	53.03
7 days	1.320	4.482	52.74
15 days	1.400	5.834	35.50
28 days	1.439	6.00	27.27
60 days	1.672	7.585	20.98
90 days	2.448	8.367	19.02

Table 21.3: Impedance Parameters of Reinforcing Steel Presented in Slag B Paste in Tap Water

Immersing Time (Days)	R _s (kohm.cm ²)	R _p (kohm.cm ²)	C _{dl} (µF/cm ²)
3 days	1.126	9.418	168.9
7 days	1.137	9.607	165.6
15 days	1.179	10.93	145.5
28 days	1.223	12.59	126.3
60 days	1.886	14.89	106.8
90 days	2.370	15.07	105.5

Table 22.3: Impedance Parameters of Reinforcing Steel Presented in Mix a Paste in Tap Water

Immersing Time (Days)	R _s (kohm.cm ²)	R _p (kohm.cm ²)	$C_{dl}(\mu F/cm^2)$
3 days	1.229	6.046	147.3
7 days	1.348	15.73	101.1
15 days	1.405	16.45	96.73
28 days	1.542	21.67	73.44
60 days	1.763	24.57	64.76
90 days	2.635	25.44	62.55

Table 23.3: Impedance Parameters of Reinforcing Steel Presented in Mix B Paste in Tap Water

Immersing Time (Days)	R _s (kohm.cm ²)	R _p (kohm.cm ²)	$C_{dl}(\mu F/cm^2)$
3 days	1.150	13.62	93.43
7 days	1.389	17.51	90.85
15 days	1.485	28.11	56.60
28 days	1.884	45.10	35.28
60 days	1.936	49.51	31.54
90 days	2.704	50.45	28.80

3.2.4. Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high energy beam of electrons in a raster scan pattern. The electrons interact with the atoms (at or near surface of the sample) that make of the sample producing signals that contain information absent the sample's surface. Figure (21.3), shows SEM image of the surface of reinforcing steel embedded in Mix B cement specimens after 90 days immersions in tap water.

The resulting micrographs appear formation of film on the surface of rebar which increases its resistance. This attributed to good rebar protection by Mix B concrete specimens. **Ji[18]** demonstrated that NS can react with $Ca(OH)_2$ crystals, and reduce the size and amount of them, thus making the interfacial transition zone (ITZ) of aggregates and binding cement paste denser. The NS particles fill the voids of the CSH-gel structure and act as nucleus to tightly bond with CSH-gel particles. This means that NS application reduces the calcium leaching rate of cement pastes and therefore increasing their durability. This result is in agreement with the result of open circuit potential measurement, tafel polarization measurement and electrochemical impedance microscopy measurements.



Figure 21.3: Surface Morphology for Reinforcing Steel Embedded in Mix B Paste for 90 Days in Tap Water

4. CONCLUSIONS

- The mechanical properties of cement pastes were studied in tap water up to 28 days of hydration such as compressive strength of cement pastes. The factor being changed is the average amount of Nano-silica and replaced by ordinary Portland cement with stability of the amount of slag cement added at 5 % to increasing the quality of cement.
- The effect of cement types on the electrochemical behavior of reinforcing steel immersed in tap water solution was studied. In cases of OPC and SRC, the open potential values were observed a steady state potential and remained passive state. While in case of Slag A, Slag B, Mix A and Mix B, the potential values shifted towards more negative up to 28 days, then sharply shifted towards nobler direction. At the end of exposure period, the potential for Slag B was found to be lesser than other types of cement.
- Tafel polarization r curves showed that corrosion current density and corrosion rate values in case of OPC and SRC increased with increasing exposure period. While their values decreased with time in case of slag A, slag B, Mix A and Mix B. The polarization resistance in all cement types increased with time, except in OPC and SRC. The increase in polarization resistance showed the formation of stable passive layer and reduction of pores during the hydration.
- The electrochemical impedance spectroscopy data observed, for polarization resistance (R_p), were in agreement with those obtained from the Tafel polarization measurements. The polarization resistances at the 90 days were in the following order: Mix B > Mix A > Slag B > Slag A > SRC > OPC.

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