IJCPE
Iraqi Journal of Chemical and Petroleum Engineering

Iraqi Journal of Chemical and Petroleum Engineering
Vol.14 No.1 (March 2013) 15- 24
ISSN: 1997-4884

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College of Engineering

Reinforcement Steel Corrosion Reduction by Using Fly Ash from South Baghdad Power Plant

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Abstract

Corrosion- induced damage in reinforced concrete structure such as bridges, parking garages, and buildings, and the related cost for maintaining them in a serviceable condition, is a source of major concern for the owners of these structures.

Fly ash produced from south Baghdad power plant with different concentrations (20, 25 and 30) % by weight from the cement ratio were used as a corrosion inhibitor as a weight ratio from the cement content.

The concrete batch ratio under study was (1:1.5:3) cement, sand and gravel respectively which is used in Iraq. All the raw materials used were locally manufactured.

Concrete slabs (250x250x70) mm dimensions were casted, using Poly-wood molds. Two steel bars were embedded in the central position of each slab at the mid- height (about 35 mm), with a space of 100 mm between each other.

A 16 concrete slabs were prepared (0, 20, 25 and 30) wt. % of fly ash. The specimens were partially immersed in 3.5 wt. % NaCl solution in order to predict the corrosion.

Half-cell potential test technique was used to estimate the corrosion rate which is occurred in the steel bar due to the migration of chloride ions through the concrete, depending on the ASTM C876-08.

The result shows that the potential values of steel in concrete were shifts to the positive direction with increasing the percentage of fly ash, because the reduction of porosity by the addition of fly ash which fill the pores and inhibit the chloride ions to reach to steel.

The results also show that the further increase of fly ash (30%) the possibility of carbonation is increased which result in reduction its alkalinity, thereby permitting corrosion of embedded steel.

Introduction

Reinforced concrete is a versatile, economical and successful construction material. It can be molded to a variety of shapes and finishes. Usually it is durable, performing well throughout its service life. However, sometimes it does not perform adequately as a result of poor design, poor construction, inadequate materials selection, a more severe environment than anticipated or a combination of these factors.

The corrosion of reinforcing steel in concrete is a major problem facing civil engineers and surveyors today as they maintain an ageing infrastructure. Potentially corrosion rehabilitation is a very large market for those who develop the expertise to deal with the problem. It is also a major headache for those who are responsible for dealing with structures suffering from corrosion [1].

The deterioration of reinforcement concrete structure is major problem. The cost of repairing or replacing deterioration structures has become a major liability for highway, agencies. The primary cause of this deterioration (cracking, delamination, and spilling) is the corrosion of steel reinforcing bars due to chlorides. The two main sources of chlorides are deicing chemical and seawater. The most common chemical used has been sodium chloride. Many bridges have also been built in coastal areas and are exposed to seawater.

Bridges built with black reinforcing steel are showing progressive concrete deterioration as the concentration of chloride ions increases. The average bridge deck located in a snow -belt State with black reinforcing steel and 40 mm (1.5 in) of concrete cover has shown spalling in about 7 to 10 years after construction and has required rehabilitation in about 20 years after construction.

For most corrosion–protection measures, the basic principle is to prevent the chloride ions from reacting with the steel surface and also to increase the time needed for the chloride ions to penetrate through the concrete cover. While these measures generally do not stop corrosion from eventually initiating, they do increase the service life of reinforced concrete structures by slowing the corrosion process. Cathode protection, however, has proven to be a successful corrosion –protection measure for conventionally reinforced and pretension, pre-stress concrete bridge members [2].

When corrosion occurs as shown in Fig.(1), the steel reinforcement basically “dissolves” in the pore water, giving up electrons and forming cations (positively charged ions). The process of losing electrons is known as oxidation. The following chemical reaction represents the fundamental oxidation of steel reinforcement at the anode (the location that releases electrons).

The anodic reaction:

$$Fe \rightarrow Fe^{+2} + 2e^{-} \qquad \ldots(1)$$

Where: Fe is iron, Fe^{+2} is ferrous-ion, and 2e are two free electrons.

In the presence of water molecules and the free electrons, oxygen is transformed from a neutral molecule to an anion, which has become more negatively charged by gaining released electrons. This process is called reduction. The gain of electrons comes from a loss of electrons from two substances that react with each other. The following chemical equation illustrates the cathodic reaction (the reaction at the location that gains electrons) [3].

The cathodic reaction:

$$O_2 + 2H_2O + 2e^{-} \rightarrow 2OH^{-} \qquad \ldots(2)$$

Where: O_2 is oxygen, H_2O is water, and OH^{-} is a hydroxyl ion.

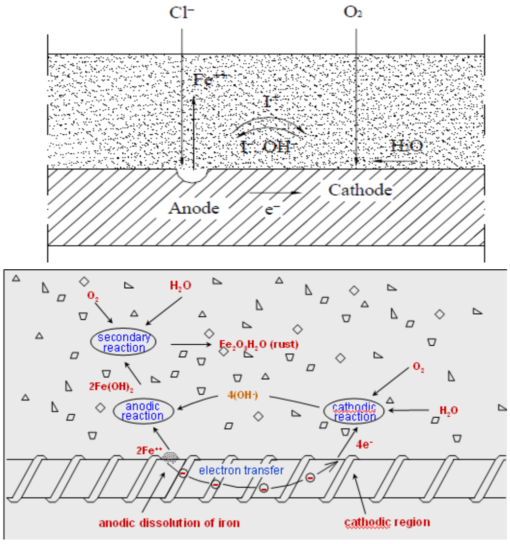


Fig. 1, Schematic of the corrosion process

The surface of the iron, at which oxidation occurs, serves as an anode. The two free electrons, $2e^{-}$, created in the anodic reaction must be consumed elsewhere on the steel surface to preserve electrical neutrality in the system. In other words, it is not possible for a large amount of electrical charge to build up at one location. Another chemical reaction must consume the electrons. Oxidation and reduction are coupled together as electrons are transferred between them. This reaction consumes both water and oxygen.

Several more "downstream" reactions must occur for corrosion products to form. This process can be expressed through the following steps. First, as shown in Eq.(3), the products of the anodic reaction, Fe^{+2}, and the cathodic reaction, OH^{-}, react, producing ferrous hydroxide, $Fe(OH)_2$ [3].

$$Fe^{+2}+2OH^{-}\rightarrow Fe(OH)_2 \qquad ...(3)$$

In Eq. (4), ferrous hydroxide, $Fe(OH)_2$, is further oxidized to form ferric hydroxide, $Fe(OH)_3$.

$$4Fe(OH)_2+O_2+2H_2O\rightarrow 4Fe(OH)_3 \qquad ...(4)$$

As a result of dehydration (from exposure to the environment), Eq. (5) shows how ferric hydroxide becomes ferric oxide, Fe_2O_3, commonly referred to as rust.

$$2Fe(OH)_3\rightarrow Fe_2O_3.H_2O+2H_2O \qquad ...(5)$$

The electrical current flow resulting from the above process and the generation and consumption of electrons in the anode and cathodereactions are used in macrocell and half-cell potential measurements to assess corrosion activity. Interestingly, the fact that the anodic and cathodic reactions must balance each other for corrosion to proceed is the reason that epoxy coating are believed to protect steel reinforcement [3].

Deterioration of concrete due to ingress of chloride ions is considered the major cause of premature corrosion of steel reinforcement, which may be internationally added most often as a constituent of accelerating admixtures. Dissolved chloride ions also may penetrate unprotected hardened concrete in structures exposed to marine environments or to deicing salts.

The reactions involved on the anodic and cathodic areas are:-

$$Fe^{+2}+2Cl^{-}\rightarrow FeCl_2 \qquad ...(6)$$

$$FeCl_2+2H_2O\rightarrow Fe(OH)_2+2HCl \qquad ...(7)$$

Fly ash blended cements are more suitable as binders for marine concrete structures than Portland cements. The use of fly ash blended cement in marine concrete will lead to higher resistance to chloride attack and good resistance to seawater damage. The overall results are longer service life in marine exposure [8].

Fly ash react with the cement hydration products, notably calcium hydroxide; hydraulic materials, such as granulated blast furnace slag, undergo direct hydration reactions for this reason it can improve the strength and durability of concrete [4].

Thilgavathi et .al [2010] presents the laboratory investigations conducted to study the chloride permeability characteristics of admixed concrete specifically with Fly Ash (FA). Rapid Chloride Permeability Test (RCPT) was used to study the chloride permeability characteristics of concrete.

The result suggests an optimized percentage of FA suitable for concrete in an aggressive environment and to develop correlation between various parameters, which are responsible for chloride permeability [5].

Reddy D.V., et.al [2011] studied the durability characteristics of low calcium fly ash-based geopolymer concretes subjected to the marine environment, compared to ordinary Portland cement concrete with similar exposure. To achieve this goal, 8 Molar Geopolymer, 14 Molar Geopolymer and Ordinary Portland Cement Concrete (OPC) mixes were prepared and tested for exposure in seawater.

The results show that the Geopolymer Concretes (GPC) excellent resistance to chlorideattack, with longer time to corrosion cracking, compared to ordinary Portland cement concrete [6].

Experimental work

Materials

Cement

Resisting Portland cement produced by Iraqi State Company at Al-gesser plant was used in this work. The chemical and physical properties of cement are listed in Table (1) and (2) respectively. Results confirmed to the Iraqi standard specification (I.O.S) No. 5/1984[24].Chemical and Physical tests were carried out by Specification Institute for Engineering Industry (S.I.E.I) from Table (1) to (6).

Table 1, Chemical composition and main compounds of the cement used

Item	Chemical Formula	Oxides Content %	Limits of (I.O.S.) No.5/1984
Iron Oxide	Fe_2O_3	5	-
Sulfate	SO_3	2.5	< 2.5
Silica	SiO_2	26.2772	-
Alumina	Al_2O_3	4.5	-
Magnesia	MgO	2.2084	< 5
Insoluble	-----	0.3578	< 1.5
C_3A	-----	3.475	< 3.5
CaO	-----	Rem	Rem

Table 2, Physical properties of the cement used

Physical Properties	Test results	Limits of (I.O.S.) No.5/1984
Specific surface area m^2/kg	330.2	≥ 250
Setting time Initial setting, h: min Final setting, h: min	 1:45 4:05	 ≥00:45 ≤10:00
Compressive strength, N/mm^2 3- days 7- days	 26.5 38.4	 ≥ 15.0 ≥ 23.0

Fine Aggregate

Normal weight natural sand from Al-Ekhaider region was used as fine aggregate. Table (3) and Fig.(2) shows the sieve analysis of the fine aggregate used throughout this work. Results show that the sand grading was within the requirements of the Iraqi specification (I.O.S) No.45/1984. Table (4) illustrates the chemical properties of the used sand.

Table 3, Grading of fine aggregate

Sieve size (mm)	% passing	Limits of (I.O.S.) No.45/1984	% retained
10	100	100	0
4.75	94.5	90-100	5.5
2.36	83.1	75-100	16.9
1.18	72.6	55-90	27.6
0.60	58.8	35-59	41.2
0.3	20.7	8-30	79.3
0.15	3.9	0-10	96.1
Fineness modulus = $\sum$ % retained/100=2.666mm			

Table 4, Chemical properties of fine aggregate

Properties	Test results	Limit of Specification	
Sulfate content as SO_3 %	0.08	≤1	(I.O.S.) No.45/1984

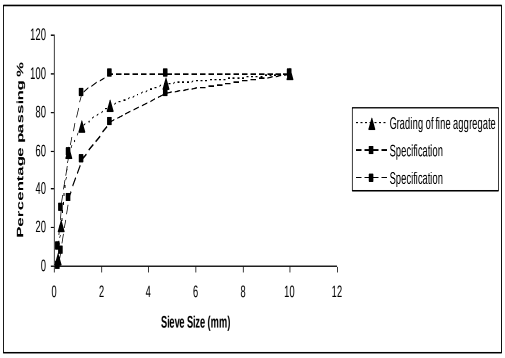


Fig. 2, Grading curve for fine aggregate with (I.O.S.) limits

Coarse Aggregate

Gravel of 37.5 mm maximum size was used as coarse aggregate. Table (5) with Fig. (3) shows the grading of coarse aggregate conforms to the Iraqi specification No.45/1984. Table (6) illustrates the chemical properties of the coarse aggregate in the present work.

Table 5, Grading of coarse aggregate

Sieve size (mm)	passing %	passing % Limits of (I.O.S.) No.45/1984 (5-40 mm)
75	100	100
37.5	100	95-100
20	68.6	35-70
10	11.9	10-40
5	1	0-5

Table 6, Chemical properties of coarse aggregate

Chemical properties	Test results	Limit of Specification	
Sulfate content %	0.088%	≤ 0.1%	(I.O.S.) No.45/1984

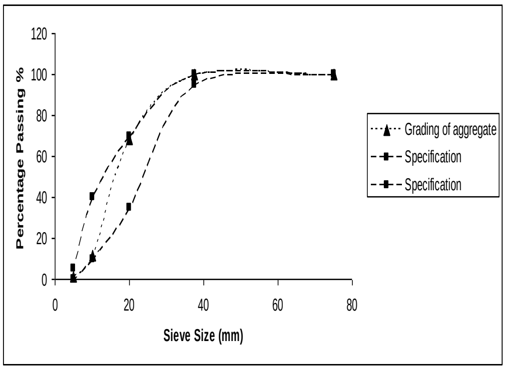


Fig. 3, Grading curve for coarse aggregate with (I.O.S.) limits

Mixing Water

Tap water was used for all batches. Table (7) shows the chemical analysis of tap water. Chemical and Physical tests were carried out by Ministry of Science and Technology /Research Center and laboratories water.

Table 7, Chemical and physical analysis of tap water

Test	Value ppm
$SO4^{-2}$	81
Cl^{-1}	80
Ca^{+2}	128
Mg^{+2}	44
$HCO3^{-2}$	122
$CO3^{-2}$	0.0
Na^{+1}	50
K^{+1}	2.5
PH- value	8

Steel Reinforcement

Deformed steel bars of diameter 10 mm were used as reinforcement in concrete. The steel bars were cleaned with degreasing agent followed with acetone. The end of each steel bar was coated with cement grout followed with epoxy paint to avoid unexpected crevice corrosion. Fig. (4) Shows the main reinforcement details.

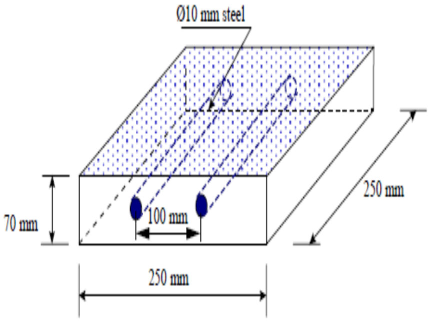


Fig. 4, Illustration of concrete specimens with two embedded steel bars

Corrosion Inhibitors

Fly Ash (FA)

Fly ash produced from south Baghdad power plant was used as a corrosion inhibitor with a different concentration (20, 25 and 30) % by weight of cement. Table (8) shows the chemical and physical analysis of fly ash. The tests were carried out at state Company of Geological Survey and Mining.

Concrete Mixes

Locally resistance Portland cement, sand and gravel were used to prepare concrete batch with mixing ratio 1:1.5:3 which are used in Iraq. The three components with the above fixed ratios were mixed for (4 minutes); the standard consistency was done to estimate the true w/c ratio, which differs in the range (0.48 – 0.53), and slump ≈2.

Table 8, Chemical analysis of fly ash

Item	composition	Chemical composition %
Iron Oxide	Fe_2O_3	6.7
Sulfate	SO_3	0.6
Silica	SiO_2	34.76
Alumina	Al_2O_3	16.341
Magnesia	MgO	0.437
CaO	-----	1.216
Organic compounds	CO_2	≈ 42

Mixing of Concrete

A mixer of about 0.1 m3 capacity was used to mix concrete ingredient. Dry materials of reference concrete(without fly ash) were placed in mixers pan after it was cleaned from any remaining materials, and they were initially mixed before adding the required quantity of water to get uniform mixture. Then the mixing water was added and the whole constituents were mixed for (4) minutes.

The fly ash dried in electrical furnace at 40˚C for (24) hours and then sieved then the required quantity of fly ash was measured as a percentage from the binder (cement).

Preparations, Casting and Curing of the Test Specimens

With dimension (250x250x70) mm the poly-wood molds were used for casting the specimens used in the corrosion test. Two steel bars were embedded in parallel in the center portion of each slab at the mid-height (about 35 mm), with a space of 100 mm between each other, Before casting the molds were cleaned and oiled by Gas oil, the steel bars were cleaned with degreasing agent followed with acetone. The ends of each steel bar were coated with cement grout followed with epoxy paint to avoid unexpected crevice corrosion compaction was performed by means of vibrating table for about (2) minutes to remove any entrapped air; the concrete surfaces were leveled and smoothed by means of trowel and covered with nylon sheets to assure humid air for about (24) hours, the specimens were demolded and immersed in 3.5 wt % NaCl of solution.

Measuring the Density of Hardened Concrete Using a Buoyancy Balance Device

The device as shown in Fig. (5) consists of rigid support frame, incorporating a water tank mounted on a platform. A mechanical lifting device is used to raise the water tank through the frame height immersing the specimen suspended below the balance. The balance supplied may also be used as a standard weighing device.

Fig. 5, The illustration of Buoyancy balance Device

The weight of the specimen were measured, and the density computed using the following formulas.

Volume density=m/V (Kg/m^3) …(8)

Where: m:The weight of specimen,
V:The volume of specimen

Preparation of Curing Solution

Pure salt was used to prepare salt solution 3.5% NaCl in tap water analyzed in Table(7) Two tanks are provided with pump to circulate the saltwater is used to immerse the slabs of concrete partially(3/4 of each specimen). Twice daily, the water is circulated for one hour to ensure uniform chloride content within the tanks, and full aeration of the water. Water depth and salt content were adjusted weekly.

Half- Cell Potential Measurement

It is an electrochemical technique commonly used by engineers to assess the severity of corrosion in reinforced concrete structure. The electrochemical potential of the reinforcing steel was measured against potassium chloride (KCl) electrode (SCE), Fig (6).

The reference electrode accordance with the ASTM C876-91 standard, consists of the rigid tube or container shall have an inside diameter of not less than 1 in. (25 mm); the diameter of the porous plug shall not be less than 1⁄2 in. (13 mm); the diameter of the immersed copper rod shall not be less than 1⁄4 in. (6 mm), and the length shall not be less than (50) mm [7].

Instrumentation

The measuring setup Fig (**7**) consists of:-

1. Reference Electrode (RE); A potassium chloride (KCl) electrode (SCE) half –cell was used, consists of the rigid tube an inside diameter (10 mm); the diameter of the porous plug (4 mm); the diameter of the immersed rod (6 mm), and the length (110 mm).
2. Digital voltmeter, Aswar digital Model DT830D was used for this purpose. The D.C voltage measurement was 2000 m V.

Test Procedure

1. The reference electrode (RE) was held vertically with the sponge folded around and attached to the tip of the half cell so that it provides electrical continuity between the porous plug and the concrete member. Fig. (6).
2. Electrically connect one end of the lead wire to the half cell and the other end of the same lead wire to the negative (ground) terminal of the voltmeter, the working electrode (steel reinforcement) was electrically connected to the positive terminal of D.C voltmeter Fig. (6)
3. The half-cell potential can be read directly on the display of the voltmeter.
4. The results of half-cell potential measurements are interpreted as allows[27]:-

a. If potentials over an area are more positive than −0.20 V SCE, there is a greater than 90 % probability that no reinforcing steel corrosion is occurring in that area at the time of measurement
b. If potentials over an area are in the range of −0.20 to −0.35 V SCE, corrosion activity of the reinforcing steel in that area is uncertain.
c. If potentials over an area are more negative than −0.35 V SCE, there is a greater than 90 % probability that reinforcing steel corrosion is occurring in that area at the time of measurement.

Fig. 6, The reference electrode

Results and Discussion

Corrosion-induced deterioration of reinforced concrete structures occurs when the environmental loading on the structure is greater than ability of the structure to resist the environmental loading (environmental resistance).

Slump and Standard Consistency

The slump and the standard consistancy of the prepared slubs, were tested, Table (9) shows the result for concrete with and without fly ash. It is appeared that the w/c ratio and the slump increased due to addition of fly ash which contains mainly SiO_2 and Al_2O_3 as shown in Table (8).

Table 9, The slump and standard consistency

	W/(Cement + Fly ash)	Slump (mm)
Without fly ash	0.33	1
With 20% fly ash	0.37	2
With 25% fly ash	0.38	2
With 30% fly ash	0.38	2

Density Computation

The density of the prepared slubs was measured using the formulas (8). Table (10) shows the result which gives values with increasing fly ash; this is due to the reduction of the permability by adding the fly ash which lies in the pores formed through the concrete.

Table 10, The density Computation of specimens

Specimens	Density (Kg/m^3)
Without fly ash	2340
20% Fly ash	2372
25 % Fly ash	2400
30% Fly ash	2409

Corrosion Rate Prediction

Figs. (7) to (10) illustrate the results of corrosion potential measurements of reinforcement steel reference to potassium chloride electrode, when partially immersed in salt solution for a period of about 60 days. Results indicate that the half cell potential of steel was divided in two different ranges of values. The first (E >-250 mV) was observed during the first few days which is a characteristic of passive state. The second range (-250, -550 mV) was observed after 30 days and the passive film has been destroyed by the aggressive ions[7].

So the potential of steel after 60 days of immersion in NaCl solution was (-550,-500 and -175) mV for (20, 25 and 30) % FA concrete respectively, while the potential of steel in concrete specimen without FA was (-400) mV.

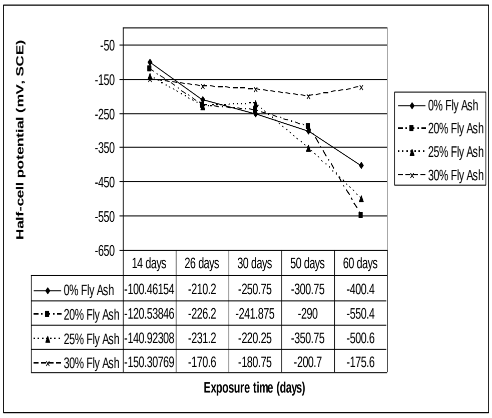
Results show that the potentials value of steel in concrete were shifts to the positive direction(noble direction) with increasing the percentage of fly ash, but the values were oscillated due to the short periods of immersion in salt solution, were the periods may be reached to 480 days as in some researches.

Furthermore, the use of fly ash has a beneficial effect on corrosion resistance of steel in concrete due to the decreased permeability of chloride ions, through the concrete, which is clear from the values of the potential difference in figures.

The addition of fly ash increase the time required to initiate corrosion of reinforcement steel in concrete due to the inhibition of chloride ions to penetrate through the concrete, reaching to the steel bars.

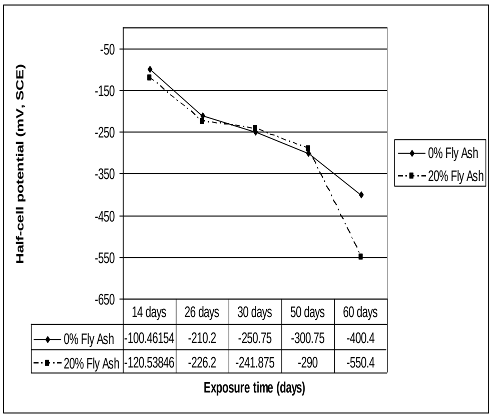
This is in good agreement with other literatures which present that the addition of fly ash reduce the corrosion rate[8].

The corrosion of steel in concrete happened due to the chlorides and carbonates ions[28], from the results shown in figures below it is cleared that the largest ratio of fly ash give more resistance to corrosion of steel in concrete ,this is may be due to the high ratio of carbon in fly ash as appeared in table (8)



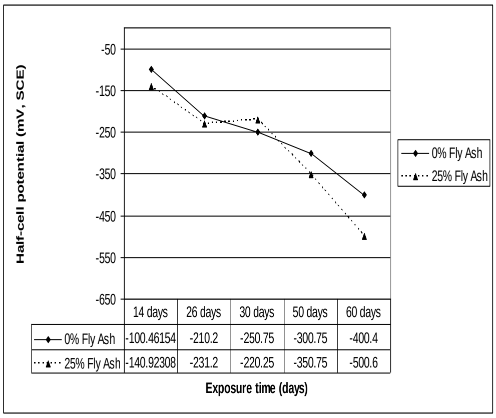
	14 days	26 days	30 days	50 days	60 days
0% Fly Ash	-100.46154	-210.2	-250.75	-300.75	-400.4
20% Fly Ash	-120.53846	-226.2	-241.875	-290	-550.4
25% Fly Ash	-140.92308	-231.2	-220.25	-350.75	-500.6
30% Fly Ash	-150.30769	-170.6	-180.75	-200.7	-175.6

Fig. 7, Half-Cell potentials of reinforcing bars in concrete with and without fly ash exposed in a 3.5% NaCl solution



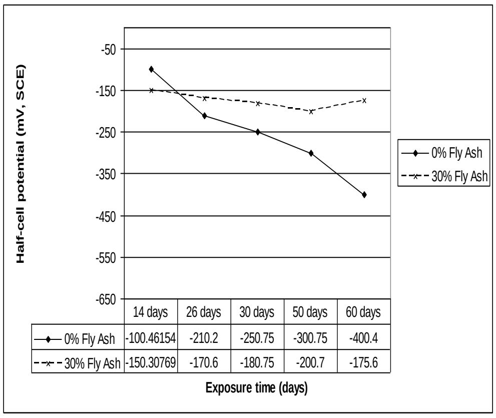
	14 days	26 days	30 days	50 days	60 days
0% Fly Ash	-100.46154	-210.2	-250.75	-300.75	-400.4
20% Fly Ash	-120.53846	-226.2	-241.875	-290	-550.4

Fig. 8, Half-Cell potentials of reinforcing bars in concrete with 20% fly ash from the binder and without exposed in a 3.5% NaCl solution



	14 days	26 days	30 days	50 days	60 days
0% Fly Ash	-100.46154	-210.2	-250.75	-300.75	-400.4
25% Fly Ash	-140.92308	-231.2	-220.25	-350.75	-500.6

Fig. 9, Half-Cell potentials of reinforcing bars in concrete with 25% fly ash from the binder and without exposed in a 3.5% NaCl solution



	14 days	26 days	30 days	50 days	60 days
0% Fly Ash	-100.46154	-210.2	-250.75	-300.75	-400.4
30% Fly Ash	-150.30769	-170.6	-180.75	-200.7	-175.6

Fig. 10, Half-Cell potentials of reinforcing bars in concrete with 30% fly ash from the binder and without exposed in a 3.5% NaCl solution

Conclusions

1. The addition of fly ash to the concrete batch increases the water cement ratio from 33% to 38% as shown in Table (3.11).
2. The increasing in water ratio leads to increase the time required for solidification.
3. The density also increased.
4. The half-cell corrosion rate data shows detectable values for potential difference which give estimation for the migration of chloride ions within the concrete.
5. The potential value shifts to the positive direction (noble direction) with increasing of fly ash ratios.
6. The limited values for the potential difference ensure that the corrosion

of the steel bars initiate after long time period (may be 3 months) but it can be increased steeply after that.

7. The corrosion of steel affected by the composition of fly ash, this is clear from the reduction of corrosion resistance by increasing the fly ash ratio because the effect of corrosion by carbonate.

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