Evaluation of the Performance of Steel in Reinforced Concrete by Electrochemical Methods

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Abstract- **The effect of different dosages of the high range water reducing admixture–additive- (HRWRA), the commercially polymeric material (Plastocrete-N), on the corrosion resistance of embedded steel in concrete exposed to chloride solution in the absence and presence of sulfate ions was studied. In the present study, four levels of polymeric material (Plastocrete-N) (0.125%, 0.250%, 0.375%, and 0.500% by weight of cement) were used to prepare HRWRA treated concrete. The concrete specimens exposed to chloride and chloride–sulfate solutions at concentrations of (3.5% NaCl and 5% Na2SO4), at ambient temperature. The electrochemical behavior of steel in both reference and HRWRA concretes was studied under the effect of corrosive environments using corrosion measurement systems such as: a) half – cell potentials measurement system and b) accelerated corrosion test system. The results showed that a longer time of corrosion initiation (180 day) observed with 0.500% HRWRA containing concrete compared to other different HRWRA percentage including the reference concrete. It was concluded that the use of 0.500% HRWRA provided superior protection to steel reinforcement in concrete that subjected to corrosive environments. Furthermore, the steel with 0.500% HRWRA was subjected to corrosion test by mass loss, it is evident that a reduction in mass loss by about 90.2% and 85.2% in both solutions, respectively.**

Key wards: Internally finned tubes, Turbulent flow model, helix angle, apex angle and fin height

1. Introduction:

The corrosion of the metals, especially steel, in concrete has received increasing attention because of its widespread occurrence in certain types of structures and the high cost of repairs [1]. There are two consequences of corrosion of steel; first, the products of corrosion occupy a volume several times larger than the original steel so that their formation results in cracking, spalling or delaminating of concrete. This makes it easier for aggressive agents to ingress toward the steel, with a consequent increase in the rate of corrosion; second, the progress of corrosion at the anode reduces the cross-sectional area of steel, thus reducing its load-carrying capacity [2]. Concrete construction in middle east seaboard countries shows an alarming degree of deterioration within the short span of 10 to 15 years. The two most familiar modes of concrete deterioration are concrete spalling due to reinforcing bar corrosion and expansive cracking due to sulfate attack. The deterioration is accentuated by the climatic environmental conditions which are characterized by marginal aggregates, high temperature-humidity regimes, and severe ground and ambient salinity [3].

When steel is embedded in concrete, a passive film develops and covers the steel surface. Cement paste is alkaline and enables the formation of the passive thin film coating on steel that protects the steel from corrosion. The factors that promote corrosion include oxygen, water and aggressive ions such as chloride. Thus, the corrosion to be occurred need that the steel reinforcing bar to be depassivated. Furthermore, the presence of high concentration of salts in concrete i.e. resulted in low resistivity will accelerate the corrosion process of steel [4, 5, and 6].

Steel-reinforced concrete is widely used in construction of buildings, bridges, decks, etc. The corrosion of the steel reinforcing bars in the concrete limits the life of concrete structures. Corrosion occurs in the steel regardless of the inherent capacity of concrete to protect the steel from corrosion; imposed by the loss of the alkalinity in the concrete or the diffusion of aggressive ions (such as chloride and sulfate ions) [26]. However, there are many ways to prevent the penetration of aggressive ions into a concrete. Among these methods the use of chemical admixtures. There are many researches and papers published in this field. Studies conducted by Lukas [7] have confirmed that under the action of aggressive solution, HRWRA- treated concrete have a smaller tendency to absorb chloride than reference concrete of the same w/c ratio. Therefore, it reduced the corrosion activity. Limited data developed by Al-Hubbouby and Dhir, et al. [8 and 9] indicated that the use of HRWRA admixture led to minimize the corrosion risk of embedded steel in concrete. In these studies [7 – 9] only one concentration of HRWRA were investigated.

This study was conducted to assess the a) effect of different concentrations of HRWRA on reinforcement corrosion in concretes and b) effect of corrosives such as chloride and chloride-sulfate concentration on the corrosion of reinforcement.

2. Experimental work

2.1 Materials

Ordinary Portland cement, type V, ASTM C 150 [10], commercially known (valkon), produced in Pakstan and natural sand from Al-Zubair, Basra south region were utilised in the present study. The maximum size of Crushed gravel of 19 mm was used as coarse aggregate.

A Modified Lignosulphonate - based super plasticizer called Plastocrete-N, supplied by Sika Company, was added to the mix. The maximum water reduction attained at the optimum dosage of 0.500% HRWRA by weight of cement is 17.78%.

2.2 Solutions
The solutions used in the present study are:

3.5% sodium chloride (NaCl) solution was prepared by dissolving 35 g commercial NaCl (purity~90% w/w) in one liter distilled water.

5% sodium sulfate (Na2SO4) solution was prepared by dissolving 50 g Na2SO4 (purity of 99 %, BDH chemical company) in one liter distilled water.

2.3 Reinforcement Steel

For corrosion testing measurements, deformed steel bars of 12 mm diameter and 200 mm length were used for the test of reinforcement specimens. The chemical composition (wt %) was carried out which is shown in Table 1. All bars were treated according to the procedure given by ASTM G1-03 [10] by pickling with a 10% sulfuric acid (H2SO4) solution for 5 minutes, and then rinsed in water prior to wire brushing to remove any remaining rust. The bars were wipped with clean cloth and allowed to air-drying. Then un-embedded end of the bar was coated with chemical resistance epoxy paint by a thin layer to covering with electroplater's tape in order to eliminate the crevice corrosion , leaving an inside 112.5 mm length of bar uncovered.

2.4 Mix Specifications, Preparation, Casting of the Concrete Specimens.

Concrete mixes were designed according to the absolute volume method, and proportioning of materials was carried out on weight basis. A concrete mix with cement content of 405 kg/m3, while the effective water to cement ratio of 0.45. The mixing ratio 1: 1.5: 3 for cement, sand, and gravel respectively were utilized in all the concrete mixtures. The materials were mixed by an electrically driven batch mixer. For normal concrete and HRWRA-containing concrete, the following procedures were performed according to the method given in BS 1881: parts108 [11] and 110:1983 [13].

The test specimens were taken out from the molds after 24 hours of casting and completely immersed in desalinated water. Then, the specimens partially immersed in corrosive solutions mentioned earlier.

2.5 Corrosion Monitoring Techniques
2.5.1 Half-cell potential Measurements

The half-cell potential as an electrochemical potential system was employed including reinforcing steel as working electrode. The potential was measured with respect to reference electrode i.e. saturated calomel electrode (SCE). The measurements were carried out according to the method given by ASTM C876-80 standard [14].

A) Test specimens

The concrete cylinders of 75x150 mm reinforced with central deformed bar of 12 mm diameter were used as illustrated in Fig.1. The working electrode is presented by 1 m long an isolated copper wire welded to the upper portion of reinforcement bars that's exposed to air.

B) Test procedure

The half-cell potential measurements were carried out using a) reference electrode-SCE and b) high performance digital voltmeter, as D.C. potential measuring instrument and can be explained as follows:

1. The reinforcing steel is electrically connected to the positive terminal of voltmeter and the reference electrode to the negative terminal of the same voltmeter, Fig.2.
2. The reference electrode was placed adjacent to the working electrode of the test specimen and only the porous end immersed in the solution, Fig.3.
3. The function switch of the voltmeter is turned to D.C , and the range switch to 2 volt range, then "the half-cell potential" can be read directly on the display of voltmeter. The results of half-cell potentials can be interpreted according to ASTM C876 [14] as in Table 2 .
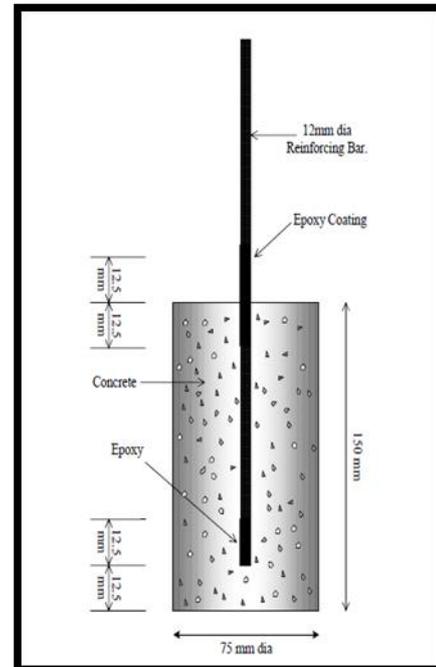

Fig.1 Concrete specimens utilized to evaluate the corrosion of reinforcement.

2.5.2 Accelerated Corrosion and Current Measurements System.

A cylindrical concrete specimen 75 mm in diameter and 150 mm height with embedded steel bars were cast. Epoxy paint was applied to the un-embedded end of the bar and at the interface of concrete and air to avoid the initiation of corrosion at those critical locations. These specimens were then subjected to an accelerated corrosion test to determine the susceptibility of reinforcing steel to corrosion [15]. The accelerated corrosion setup used in the present study consisted of plastic tank filled with electrolytic solution (aggressive solutions 3.5% sodium chloride and 5% sodium sulfate) and steel mesh placed at the

bottom of the tank. The concrete cylinders were then placed in a (600 mm length, 500 mm width and 400 mm depth) tank. Each cylinder was partially immersed in the electrolyte up to two-thirds of its total height. To eliminate any variation in the concentration of the salts and pH of the electrolytic solution, it was renewed on a weekly basis. The specimen's steel bars and the bottom steel mesh in the tank were connected to a 12 V DC power supply. The direction of the current was arranged so that the steel mesh served as a cathode while the specimen bars served as anodes, Fig.4. After the power supply was turned on, the current flowing through the system was

recorded at one-hour intervals. The current supplied to each of the specimens was plotted against time and the time–current curves were utilized to evaluate the time to cracking of concrete due to reinforcement corrosion [16].

2.5.3 Measurements of Weight Loss.
After the reinforced concrete specimens were corroded and the measurements of half-cell and current values were taken, the concrete were jack hammered to remove the corroded bars. The corroded bars were cleaned with a wire brush to ensure they were free of any adhering concrete or corrosion products, and then soaked in a chemical solution (1:1 of HCl and water) according to ASTM G1-03 method [11]. The clean bars were then reweighed and the percentage mass loss for each bar was calculated based on Eq. below

% mass loss = (initial mass – final mass)*
(100 / initial mass)

3. Test Results and Discussions

3.1 Half-Cell Potential
The average half-cell potential values of reinforcement steel as referenced to a saturated calomel electrode (SCE) were plotted against the period of immersion in chloride and chloride-sulfate solutions in Figs. (6 – 11). The corrosion potential curves were utilized to assess the time to initiation of reinforcement corrosion. For this purpose, ASTM C 876 - criterion was utilized. According to this criterion, if the corrosion potentials are numerically less than i.e. more negative -270 mV SCE, then there is 90% probability of reinforcement corrosion.

After a specified period of exposure to aggressive solutions, the reinforcing steel potentials dropped suddenly to threshold value (-270 mV specified by ASTM C 876) which was indicated 90% probability the active reinforcement corrosion. This change in the electrochemical status may be attributed to the moisture penetration which enhances the ingress of all aggressive ions and may promote electrochemical corrosion activity [17]. The corrosion activity is more pronounced in concretes in chloride-sulfate solution than in the chloride solution. It was stated by many researchers that an increase in corrosion activity in the specimens exposed to sodium chloride plus sodium sulfate environments compared to the specimens exposed to only sodium chloride environments. It would be expected that the presence of sulfate ions would affect the mineralogical composition of hardened concrete and hence its corrosion–resisting characteristics [18 - 21]. The time-corrosion potential curves in the Figs.(6 – 11) were evaluated to study the effect of HRWRA on the time to initiation of reinforcement corrosion.

For reference concrete, as shown in Figs. (6 and 7), the data developed in the present study show that the sulfate ions have little effect on the time to initiation of reinforcement corrosion (was nearly the same; for 80 and 72 days in chloride and chloride – sulfate solutions, respectively). This may be attributed to the fact that the corrosion initiation, when exposed to mixed chloride and sulfate environments, is predominantly governed by the relative diffusivity of these two ions. Several studies [22 - 25] have indicated that

chloride ions diffuse much faster than sulfate ions into hardened cement paste. But, in 0.125% HRWRA concrete specimens, corrosion initiation was noted after 95 and 80 days of exposure to chloride and chloride–sulfate solutions respectively, (See Figs. 8 and 9).

The effect of 0.250% HRWRA on the time to initiation of reinforcement corrosion in the concrete specimens also studied. It was noticed that a delay in the time to corrosion initiation after 133 and 121 days in both solutions respectively. These data depict the beneficial effect of HRWRA in delaying the corrosion process.

Further increase of HRWRA concentration had resulted in delaying the corrosion initiation as shown with (0.375% and 0.500%) HRWRA in both corrosive solutions, (Refer to Figs. 10 - 11). The 0.500% HRWRA addition was the most effective in delaying the corrosion initiation, as it took 180 days for chlorides to depassivate the protective layer on reinforcement and 169 days in aggressive solution containing sulfate. This performance is due mainly to the significant reduction in water content of the concrete, leading to low permeability, hence, reducing the penetrability of aggressive ions [26].

The percentage improvement in the time to initiation of reinforcement corrosion when HRWRA were used in mix is summarized in Table 3. The concrete specimens prepared with the HRWRA showed a significant improvement in thetime to initiation of reinforcement corrosion compared to that observed on the reference concrete specimens, in the range of 135)% approximately (19 to 125)% and (11 to in chloride and chloride-sulfate solutions respectively.

3.2 Accelerated Corrosion
During the accelerated corrosion test, the relationship between the current in mA and the immersion time in days for reference and HRWRA concrete specimens exposed for aggressive solutions was shown in Figs. (12 – 14). In general, the current-immersion time relationship for all concrete specimens showed an initial decrease in the current, followed by a gradual increase. The decrease of the current in the first few days is an indication of the formation of the passive film around the reinforcing steel bar, which protects the steel from corrosion. When depassivation of the steel occurs due to the presence of aggressive ions, corrosion starts and then the rate of corrosion increases significantly [27].

Reference concretes showed higher current values in the early stages of the test, approximately (14.3 and 15.5 mA) in chloride and chloride-sulfate solutions respectively, compared to HRWRA concretes which showed current values in the ranges (0.3 to 7.2 mA) and (0.8 to 8.2 mA) in chloride and chloride-sulfate solutions, respectively. HRWRA concretes exhibited sudden jump in the time–current curve after relatively steady slope compared to reference concretes which showed relatively gradual increase of the current with the time. The sudden jump in HRWRA concretes time – current curves was the indication of the concrete cover spalling due to reinforcement corrosion [27].

Figs. (12 – 14) showed that the current in all concretes exposed to chloride-sulfate solution was higher than that exposed to chloride solution during the whole test period. The lower current passing through the concrete specimens is an indication of the higher resistivity of the concrete. Permeability of the concrete is the main factor influencing the concrete resistivity [28].

The point of first increase of the slope in the time – current curve indicates the time to initiation of concrete cracking due to reinforcement corrosion. Reference concretes showed earlier time to cracking due to reinforcement corrosion than all HRWRA concrete specimens, where started after 10.5 and 9 days in chloride and chloride-sulfate solutions, respectively, compared to (13, 15, 19 and 23) and (10.5, 12, 14 and 17.5) days in HRWRA concretes exposed to both solutions, respectively, (See Table 4). The increase of the time to cracking in HRWRA concretes compared to reference concrete was related to significant reduction in water content of the concrete, leading to low permeability, hence, reducing the penetrability of aggressive ions to steel surface, thereby delaying the process of reinforcement corrosion. Also, it was noted that all concretes exposed to chloride plus sulfate solution showed earlier time to cracking due to reinforcement corrosion than those exposed to chloride solution alone. This may be attributed to an increase in the concentration of free chloride ions in the pore solution due to the concurrent presence of sulfate and chloride ions [27]. The percentage improvement in the time to cracking in the concrete specimens imposed by the use of adding different concentrations of HRWRA in mixes design is tabulated in Table 4. The highest the percentage improvement in the time to cracking due to reinforcement corrosion was noted with 0.500% HRWRA addition to mix, which was 119.1% in chloride solution, while it was 94.4% in chloride-sulfate solution.

3.3 Mass Loss Testing Results (Gravimetric Technique)

The mass loss and consequently corrosion rates was nearly similar in the reference concrete specimens and those with 0.125% HRWRA. While there was a decrease in the mass loss of the steel bars in the concrete specimens with other percentages of HRWRA. The lowest mass loss of steel was noted in the concrete specimens with 0.500% which exposed to chloride and chloride-sulfate solutions was 90.2% and 85.2%, respectively, (See Fig. 15). In this present study, the mass loss of steel in the concrete specimens exposed to chloride–sulfate environment was more than that in the specimens exposed to only chloride environment. This may be attributed to increases the concentration of free chloride ions in the pore solution. This increase in the free-chloride ion concentration is ascribed to the simultaneous reaction of tri calcium aluminates (C3A) with both chloride and sulfate ions. Chloride ions normally react with C3A in cement to form an insoluble compound known as calcium chloro-aluminate hydrate (C3A. CaCl2.10H2O(, also known as Friedel's salt. This chemical reaction reduces the quantity of free chloride ions in the pore solution thereby decreasing the chances of steel depassivation. When both chloride and sulfate ions are present, C3A reacts concomitantly with both sulfate and chloride ions, as a result the proportion of chloride ions bound is less than that when only chlorides salts are present [27].

4. Conclusions

1. The time to initiation of reinforcement corrosion and time to cracking of concrete increased with increasing addition of HRWRA percentage by weight of cement. The effective dosage was 0.500% by weight of cement which delayed the time to initiation of reinforcement corrosion by about 125% and134.7% for concretes immersed in chloride and chloride–sulfate solutions, respectively. At the same dosage, the time to cracking of concrete due to accelerated corrosion was also delayed by about 119% and 94% for concretes immersed in chloride and chloride–sulfate solutions, respectively compared to their reference concrete.

2. All concrete specimens exposed to chloride plus sulfate showed a relatively shorter time to initiation of reinforcement corrosion and cracking of concrete due to accelerated reinforcement corrosion than those exposed to chloride solution alone.

3. The mass loss of steel bars was decreased with the increase in HRWRA percentage. But, the reduction in mass loss of reinforced steel was found less in chloride plus sulfate solution than that in chloride solution alone. The 0.500% HRRWA percentage led to a reduction in reinforced steel mass loss of about 90.2% and 85.2% compared to their reference concrete in chloride and chloride–sulfate solutions, respectively.

5. References

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Table 1: Chemical composition (wt %) of the used steel.

Fe	C	Si	Mn	P	S	Cr	Mo
98.500	0.200	0.080	0.900	0.005	0.005	0.085	0.003
Ni	Al	Co	Cu	Nb	Ti	V	W
0.025	0.010	0.010	0.028	0.003	0.003	0.003	0.025

Table 2: Corrosion interpretations (ASTM C876) [14].

Half-cell potential reading,mV SCE	Corrosion activity
< -400	Severe corrosion
< -270	High risk of corrosion (90%)
-120 to -270	uncertain corrosion risk
> -120	Low risk of corrosion (10%)

Table 3: Percentage improvement in time to initiation of reinforcement corrosion found at different additions of HRWRA to concrete mix.

Mix type	Time to Initiation of Corrosion (Days)		Improvement %	
	in Chloride solu.	In Chloride-Sulfate solu.	in Chloride solu.	in Chloride-Sulfate solu.
Ref.	80	72	-	-
MS1	95	80	18.75	11.11
MS2	133	121	66.25	68.06
MS3	165	150	106.25	108.33
MS4	180	169	125.00	134.72

Table 4: Improvement percentage in time to cracking of concrete due to reinforcement corrosion.

Type of mix	Time to cracking , days		% Improvement in time to cracking	
	In chloride solu.	In chloride-sulfate solu.	In chloride solu.	In chloride-sulfate solu.
Ref.	10.5	9.0	-	-
MS1	13.0	10.5	24	17
MS2	15.0	12.0	30	33
MS3	19.0	14.0	43	55
MS4	23.0	17.5	119	94
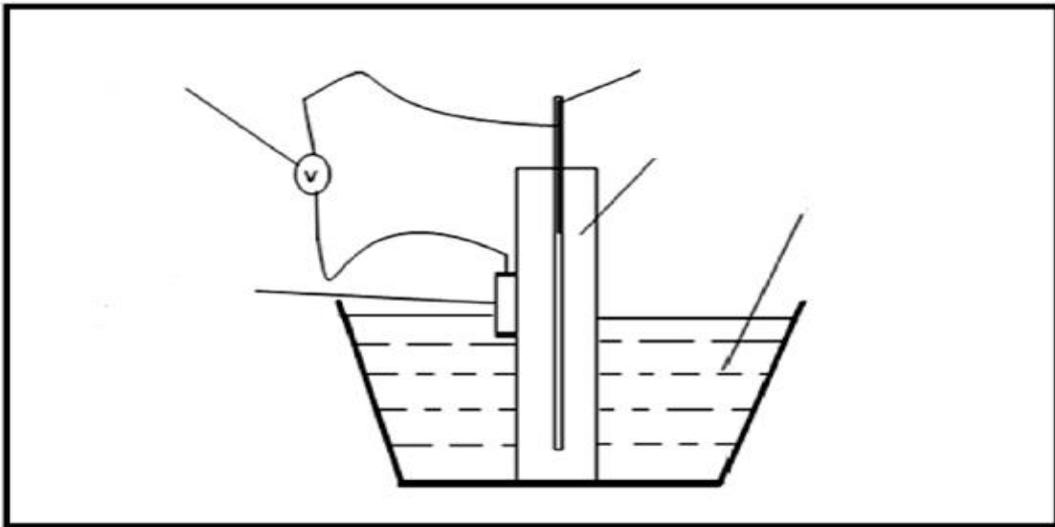
Fig. 2 Half-cell potential measurements circuit for the present corrosion study.
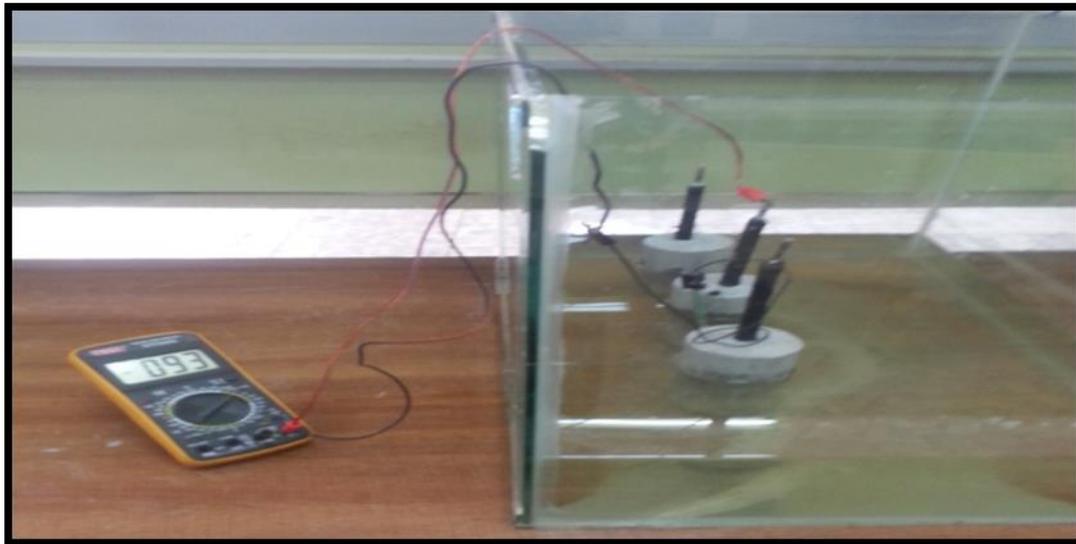
Fig. 3 Half- cell potential measurements system.
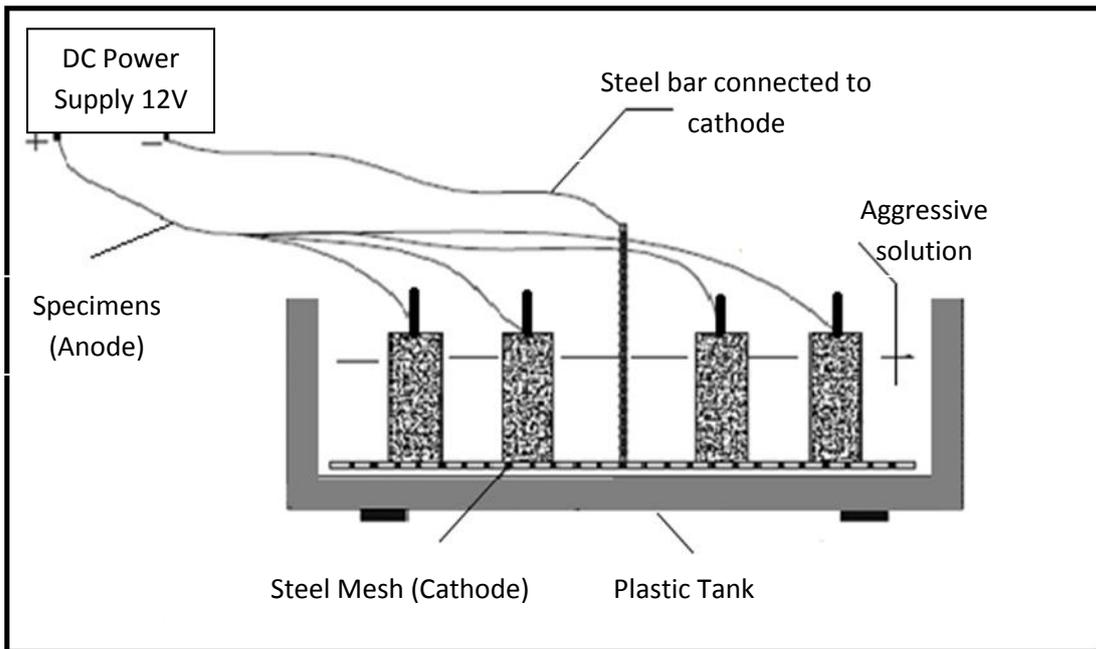
Fig.4 Schematic representation of the accelerated corrosion test system [15].
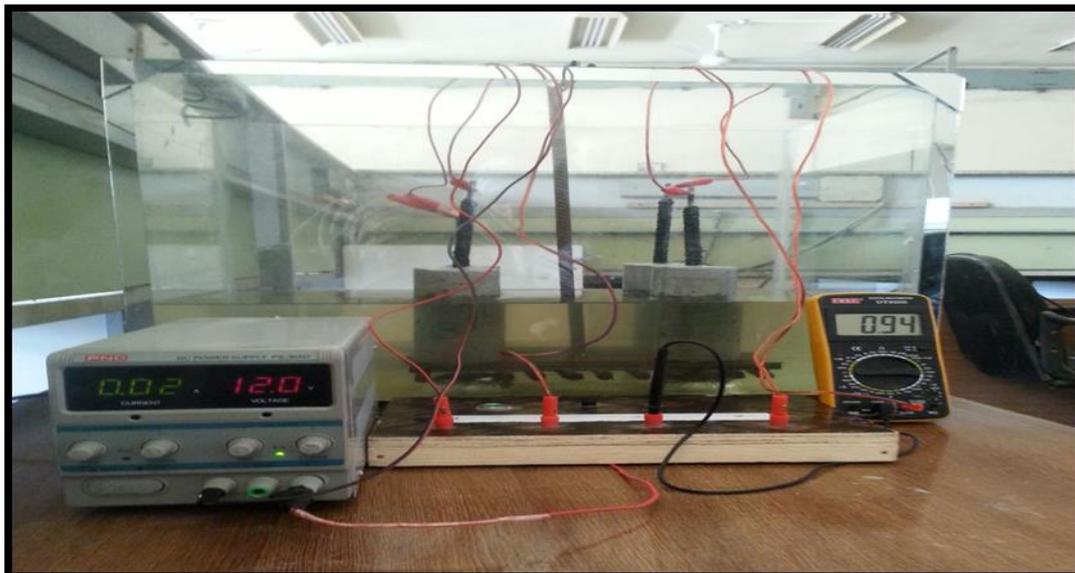
Fig.5 The accelerated corrosion system set up of the present study.
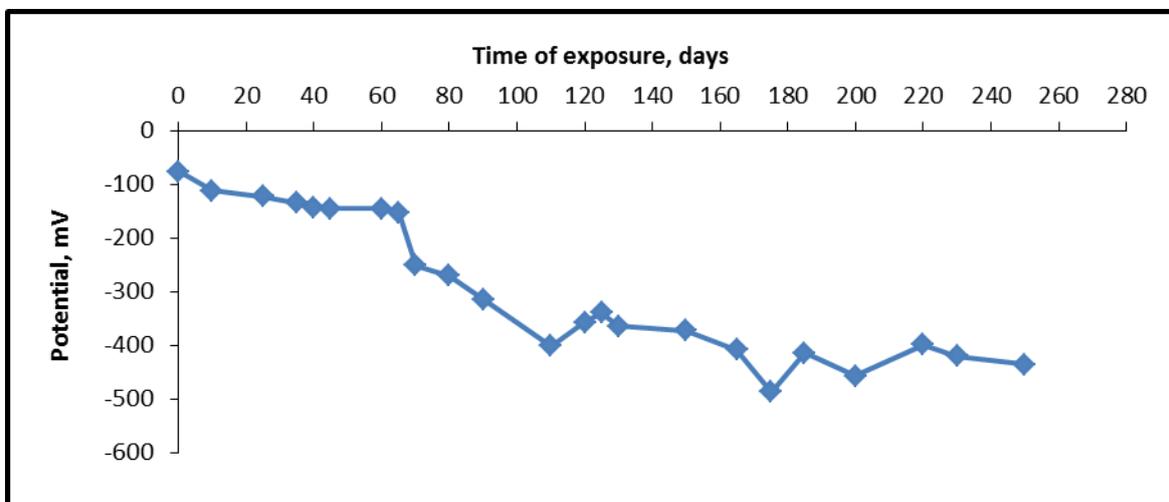
Fig.6 Half-cell potentials of reinforcing bars in reference
concrete exposed to chloride solution.
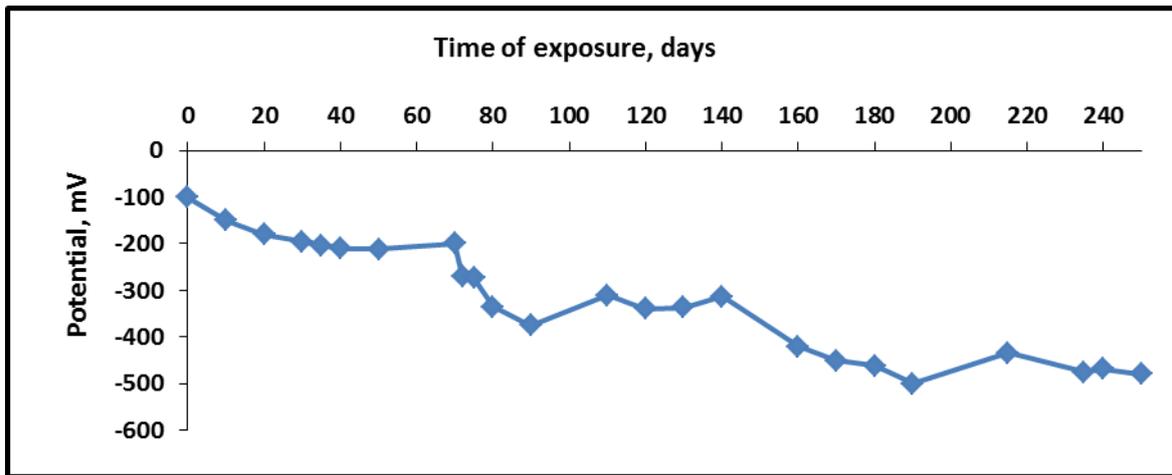
Fig.7 Half-cell potentials of reinforcing bars in reference
concrete exposed to chloride-sulfate solution.
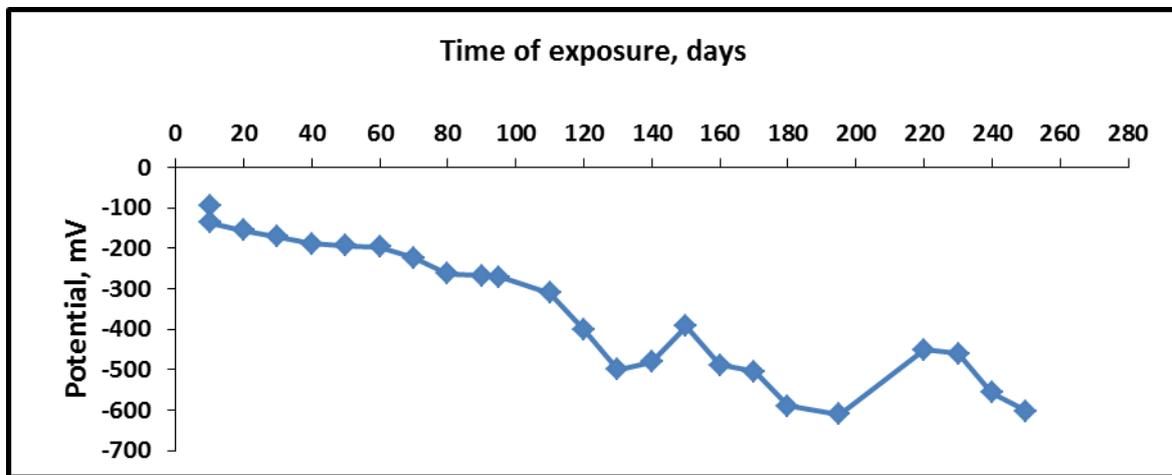
Fig.8 Half-cell potentials of reinforcing bars in 0.125% HRWRA
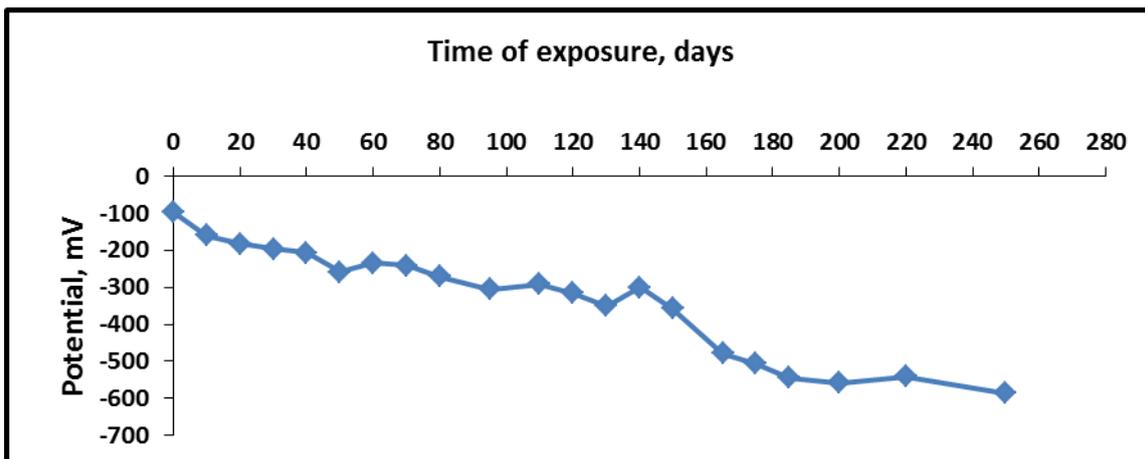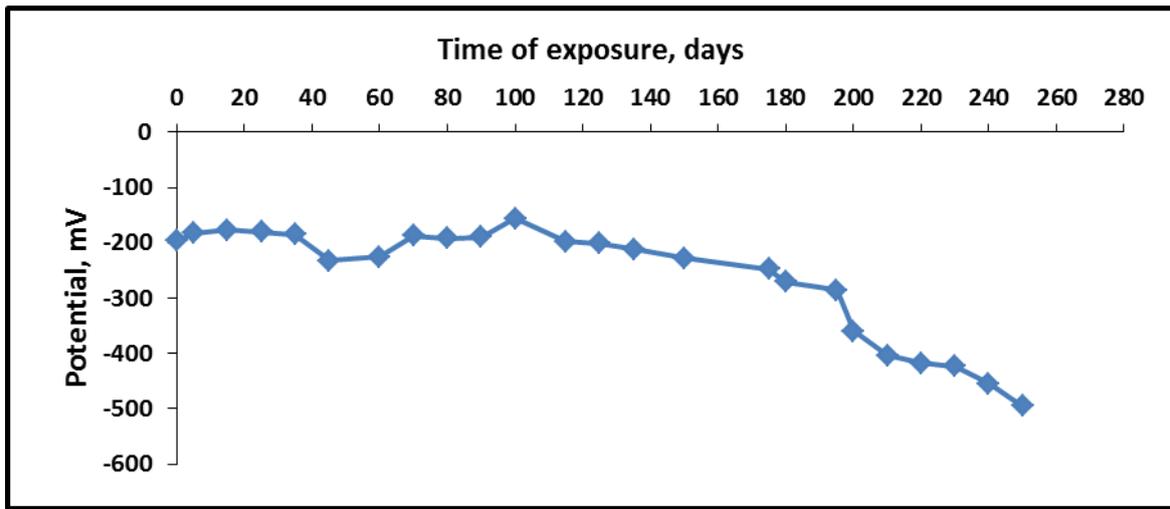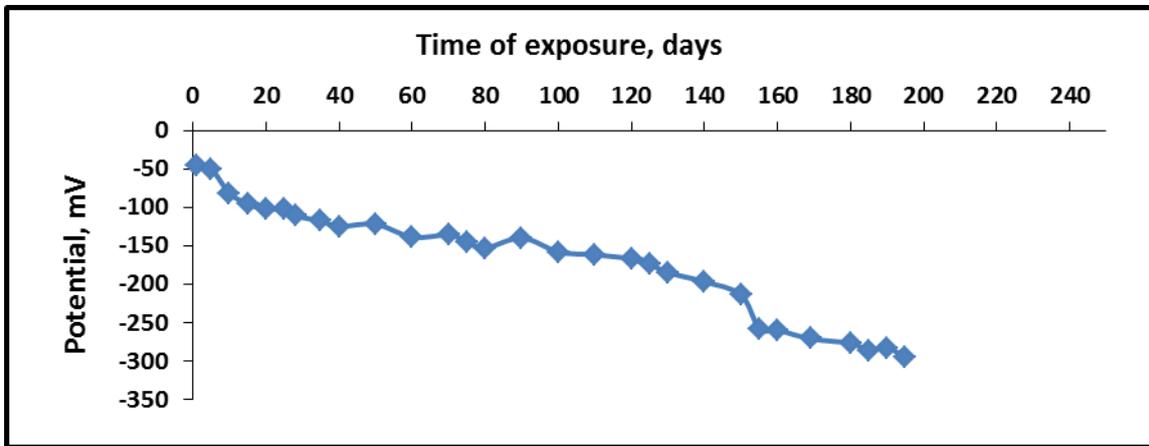concrete exposed to chloride solution.

Fig.9 Half-cell potentials of reinforcing bars in 0.125% HRWRA
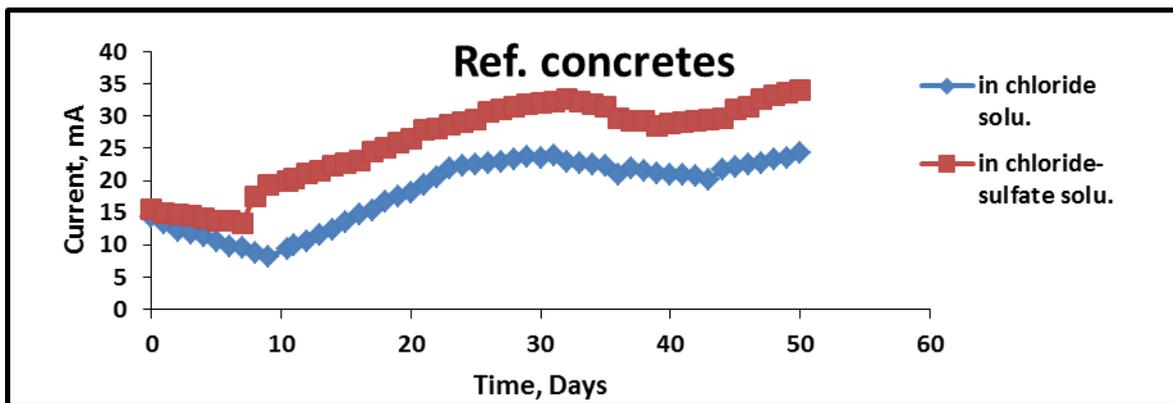concrete exposed to chloride-sulfate solution.

Fig.10 Half-cell potentials of reinforcing bars in 0.500% HRWRA
concrete exposed to chloride solution.

Fig.11 Half-cell potentials of reinforcing bars in 0.500% HRWRA
concrete exposed to chloride-sulfate solution.

Fig.12 Variation of current with time in the reference concrete
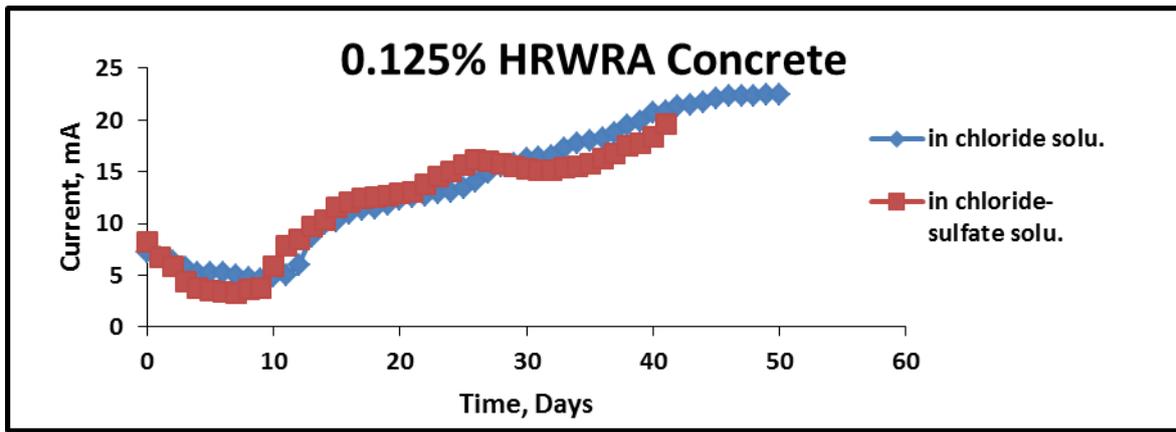specimens in chloride and chloride-sulfate solutions.

Fig.13 Variation of current with time in the concrete specimens
prepared with 0.125% HRWRA in chloride and chloride-sulfate solutions.
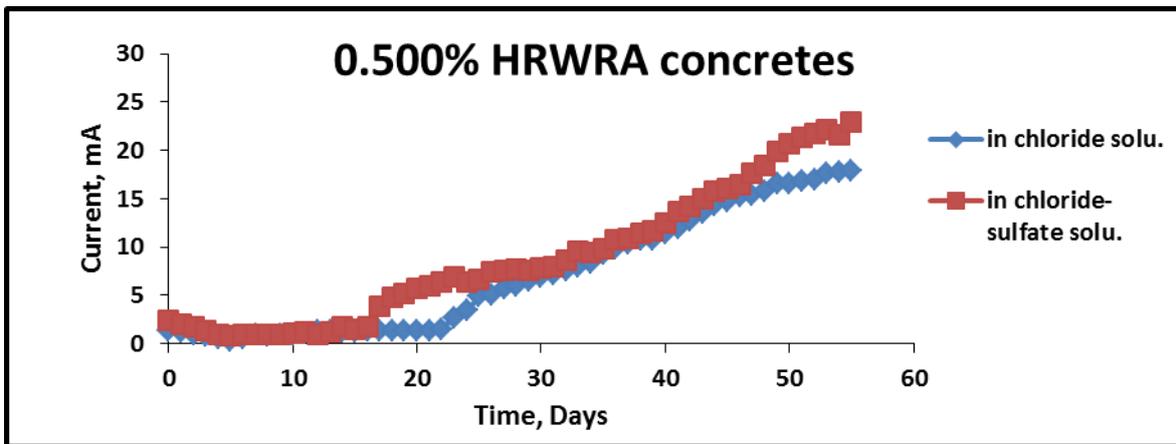

Fig.14 Variation of current with time in the concrete specimens prepared with 0.500% HRWRA in chloride and chloride-sulfate solutions.
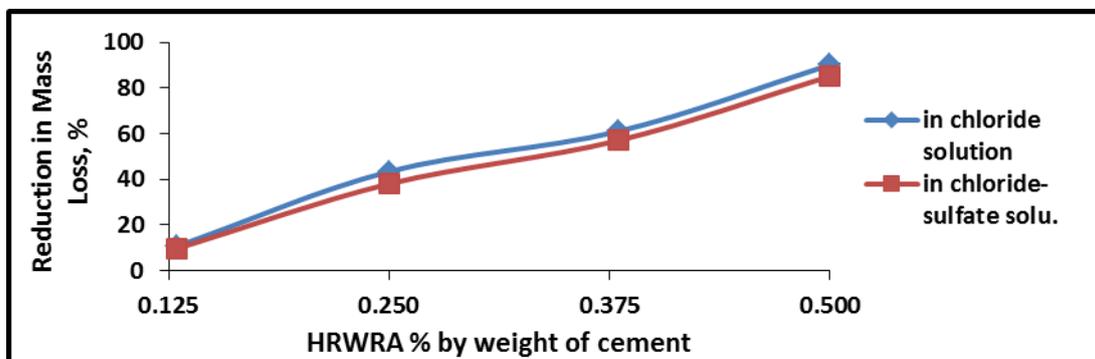

Fig.15 Reduction in mass loss percentage with increasing of HRWRA concentration in both aggressive solutions.