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ELECTROCHEMICAL BEHAVIOR OF STEEL FIBER REINFORCED CONCRETE
IN 3.5%NACL SOLUTION

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ABSTRACT

In this paper, potentiodynamic polarization and cyclic anodic polarization measurements were used to investigate the corrosion behavior of four samples of steel fibers, obtained from tyres, with or without addibond 65. The electrochemical tests in aerated 3.5 % NaCl showed that for steel fiber sample with or without concrete, a high amount addibond 65samples had the lowest corrosion rate as compared to the samples with low and without addibond 65. The results also indicated that the steel fibers corrosion rate decreases with increasing its diameter and the withdraw samples having the lowest corrosion rate.

KEYWORDS: Potentiodynamic, Polarization and Cyclic Anodic

INTRODUCTION

Steel – reinforcedconcrete is widely used in construction. It is one of the main causes for the deterioration of civil infrastructure. Corrosion occurs in the steel regardless of the inherent capacity of concrete to protect the steel fiber from corrosion; accelerated corrosion results from the loss of alkalinity in the concrete or the penetration of aggressive ions (such as chloride ions)[1]. It is hypothesized that corrosion, also an expansive process, can be mitigated with steel fibers as well. When reinforcing steel within concrete corrodes, the rust product applies expansive pressure on the surrounding concrete inducing cracking in the matrix in close vicinity to the reinforcing steel fiber. Corrosion then continues further and increased volume of rust product will propagate the microcrack and initiate others. When these cracks propagate far enough to reach the concrete surface, they become pathways allowing for the rapid ingress of water and chloride ions. Both agents accelerate the corrosion process, leading to further cracking and eventually to spalling [2]. Fibers have an advantage over because they can influence the cracking process in close vicinity to the steel reinforcing bars at onset due to their small diameter. The fibers will result in a higher required expansive pressure for cracks to initiate and propagate. Thus, for a constant corrosion rate, it will take longer for cracking to initiate in fiber-reinforced specimens. Delaying crack formation will slow the corrosion process by preventing the corrosion products from leaving the reaction site.

The present work was mainly concerned with the study of the electrochemical behavior of different width steel fiber in different amount of addibond 65 with or without concrete.

EXPERMENTAL

Materials

A newly designed concrete were prepared in Central Metallurgical Research and Development Institute by the authors. An ordinary Portland cement was used to prepare the mortar specimens. Fine aggregate between 0-1ml diameter, coarse aggregate between 4-14ml diameter and tap water were employed at laboratory temperature (20-250C). Composition

of the concrete is given in Table (1). A cylindrical fiber reinforced concrete samples with 20 cm diameter and 15 cm in hight were used as shown in Fig(1). An embedded steel fibers of 9 cm in height and (1ml and 2ml) in diameter in addition withdraw steel fibers with 1ml in diameter were used. The chemical composition of steel fibers is given in Table (3)

Four samples of steel fiber with and without concrete are used for electrochemical measuerments. Sample 1, as received steel fibers while sample 2, steel fiber after treatment with HCl 1:1, rinsed with water, Na₂CO₃ solution and finally with water. Samples 3 and 4 were treated steel fiber with different amount of addibond 65. Addibond 65 used as surface hardener for concrete and cement plastering surface. It is latex dispersion admixture based on styrene butadiene rubber so it is used for improving the properties of cement mortar and concrete. For every diameter of steel fiber and withdraw steel fiber the four samples were used. Table (2) includes the identification of the four tested samples.



Figure 1: Steel Fibers in Concrete

Table1: Concrete Composition

Cement(Gm)	Water(Ml)	Fine Aggregate (Gm)	Coarse Aggregate (Gm)	Steel Fiber (Gm)
833	520	1666	833	41.6

Table 2: Steel Fibers Chemical Composition

C	Mn	Si	S	P	Fe
0.8%	0.58%	0.2%	0.012%	0.008%	ball.

Table 3: The Four Samples Identification

Sample No	Name
1	As received
2	After treatment with HCl
3	With normal amount additiond 65
4	With over amount additiond 65

Adopted Techniques

The major electrochemical techniques used in this study were potentiodynamic polarization, cyclic anodic polarization measurements and surface examination by S.E.M and EDXA.

A three – electrode cell, working electrode, platinum sheet (counter electrode) and Ag/AgCl calomel electrode (reference electrode), was used for measurements. Electrochemical polarization experiments were conducted using VoltaLab 40(PGZ301)-Radiometer, connected to a potential and current X-Y recorded. The results were finally processed in a personal computer using a data acquisition program. All the measurements were performed in freshly prepared

solution at room temperature (25+ 20C).

The potentiodynamic polarization was performed at scan rate of 2mV/s from -1000 to 1000mV. The cyclic anodic polarization was measured at scanning rate 5 mv/sec swepting from -1000 mv to 1000 mv. The identification of the elements present in the surface of specimens before and after immersion in test solution will be performed using EDXA analysis. This technique is used in conjunction with SEM.

RESULTS AND DISCUSSION

Potentiodynamic Polarization Measurements of Steel Fibers, Without Concrete, in 3.5% Nacl Solution

As cleares from Fig. 2 and the electrochemical parameters listed in Tables (4-6) there is significant decreasing in current density, $I_{corr.}$, in the active dissolution region and lower maximum current density in samples with addibond 65, samples 3 and 4, compared samples without it, samples 1 and 2. In general, the corrostion current denisty is decreasing in the following order:

Sample 4 < Sample3 < Sample2 < Sample1

A possible reason for this phenomenon is attributed to the fact that addibond 65 acts as isolator for steel fibers from the external environment so by increasing the addibond 65 content, sample 4, the corrosion rate show the lowest values.

Fig. 2 and Tables (4-6) indicate also that, the corrosion rate is decrease by increasing the steel fiber diameter. Therefore, steel fiber with 2ml diameter has lower corrosion rate than steel fiber with 1ml diameter. However, withdraw steel fibers is the lowest in the corrosion rate for the foure steel fiber samples tested. Withdraw steel fibers waere the less in corrosion rate for the four steel fibers because there are rubber layer on the steel fiber, which make as isolator in the corrosive media.

Table 4: The Corrosion Parameters of Four Fire Steel Fiber Samples (1ml) in 3.5% Nacl, Solution

Sample No.	I _{corr} μ A/cm ²		Slopes nVβ _c	Corrosion rate µm/y
1	8.02	281.6	-112.5	93.87
2	7.21	105.9	-140.4	84.39
3	3.17	133.4	-84.0	37.13
4	2.44	107.6	-55.7	28.56

Table 5: The Corrosion Parameters of Four Fire Steel Fiber Samples (2ml) in 3.5% Nacl, Solution.

Sample No.	I _{corr} μ A/cm ²	Tafel Slopes β _a mV β _c		Corrosion rate µm/y
1	3.30	82.6	-313.9	38.66
2	2.48	19.9	-35.3	29.11
3	1.76	50.7	-37.2	20.61
4	1.60	12.7	-22.3	18.75

Sample No.	I _{corr} μA/cm ²		Slopes 1Vβ _c	Corrosion rate µm/y
1	2.37	728.1	-304.0	27.73
2	2.33	11.6	-14.8	27.34
3	1.28	199.9	-80.6	14.98
4	0.99	265.3	-121.8	11.62

Table 6: The Corrosion Parameters of Four Withdraw Steel Fiber Samples(1ml) in 3.5% Nacl, Solution

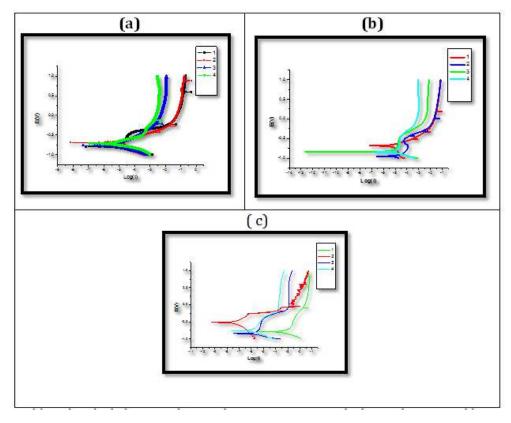


Figure 2: Anodic and Cathodic Potentiodynamic Polarization Curves in 3.5%Nacl Solution Without Concrete (A)
Four Steel Fiber Samples(1ml),(B)Four Steel Fiber(2ml) and (C.) Four Withdraw Steel Fiber (1ml)

Potentiodynamic Polarization Measurements of Steel Fiber Samples with Concrete in 3.5% Nacl Solution

Fig.(3) shows polarization response of the concrete contain four steel fiber samples in aerated 3.5% NaCl solution using scan rate 2mV/sec. in the potential range from -1000 to 1000 mV at 25 · C.

Tables (7,8) show that, there are decrease in corrosion rate with increasing amount of addibond 65. The values of corrosion rate for 1 ml fire steel fiber samples 1,2,3 and 4 are 43.99, 21.98,17.18 and 15.34 μ m/y respectively while for 1 ml withdraw steel fiber for the same samples are 13.46,8.91, 2.39 and 1.20 μ m/y respectively. It is clear that withdraw steel fibers have lower corrosion rate than fire steel fibers. Withdraw steel fibers waere the less in corrosion rate because there are rubber layer on the steel fiber, which make as isolator in the corrosive media.

The mechanisms of corrosion in a steel fiber reinforced matrix need to be isolated and examined in detail. Postulate that the fibers can influence both the cathodic and anodic reactions in a corrosion cell. From the standpoint of the cathodic reaction, the addition of steel fibers is immediate. The cathodic reaction can control by the concentration of oxygen Eq. (1),

$$O_2 + H_2O + 2e^- \longrightarrow 2OH^-[1]$$

So reductions in O₂ concentrations reduce the amount of available oxygen to carry out this reaction. Studies have demonstrated that steel fibers show increased corrosion resistance when compared to conventional steel reinforcement [3-5]. Coupled with the fact that corrosion was not observed on any of the fibers in this study, it is most likely that the fibers were in a passive state. Trejo [6] stated that the formation of the passive layer for steel in a cement based matrix is an oxygen intensive process. Whether by formation of stable oxides or direct adsorption of the oxygen to the surface of the steel fibers.[2]

It is also anticipated that an environment devoid of available oxygen may modify the species of iron oxides that typically form in the wake of iron oxidation. Iron oxide species with lower oxygen content have a lower molecular volume and hence are less expansive. In terms of cracking due to corrosion, expansive stresses due to the formation of corrosion products will be reduced in oxygen deprived environments. [2]

In terms of anodic control, after sufficient concentrations of Cl⁻ are present the surface of the steel, corrosion can propagate unimpeded. In the case of conventional plain concrete, the formation of iron oxides induces expansive stresses which cause microcracking. Once a crack has formed, the magnitude of expansive stress required to propagate the crack are reduced [7,8] and the rate of ingress of deleterious compounds and the rate of egress of corrosion products is increased due to the crack opening. Cracks can only propagate under increases in the magnitude of expansive stress[7]. Under this confined condition, the solid products formed from the corrosion process will fill surrounding voids and any cracks that may have initiated, locally densifying the cement matrix and cutting off the further ingress of deleterious compounds.[2]

While conventional reinforcing bars are efficiently placed according to the direction of the principal tensile stresses, fibers are randomly oriented. Because of this, fibers cannot replace conventional steel reinforcement but can be incorporated into the cement matrix to improve the response of reinforced cracked concrete. In particular, fiber reinforcement mainly enhances the toughness of the concrete's brittle matrix and leads to a more ductile material behaviour. The increased ductility is due to the ability of the fibers to transfer tensile stresses across a crack.[9]

Studies on the influence of steel fibers idicated that, the splitting cracks were effectively controlled by adding fibers and that transverse cracks were smaller and more closely spaced than were in specimens without steel fibers (10). In a similar study Bischoff [11], concluded that the ability of steel fiber reinforced concrete led to reduced crack spacing, which contribute to an improved crack control.

Sample No.	I_{corr} $\mu A/cm^2$		Slopes 1V β _c	Corrosion rate µm/y
1	3.76	412.3	-299.2	43.99
2	2.73	310.6	-274.4	21.98
3	1.46	357.0	-158.0	17.18
4	1.31	312.6	-196.1	15.34

Table 7: The Corrosion Parameters of Four Fire Steel Fiber Samples(1ml) With Concrete in 3.5% Nacl, Solution

Table : The Corrosion Parameters of Four Withdraw Steel Fibersamples(1ml) with Concrete in 3.5% Nacl, Solution.

Sample No.	I _{corr} μA/cm ²		Slopes nVβ _c	Corrosion rate µm/y
1	1.51	155.4	-170.2	13.46
2	0.762	73.5	-72.8	8.91
3	0.20	274.2	-336.4	2.39
4	103.4X10 ⁻³	79.0	-85.6	1.20

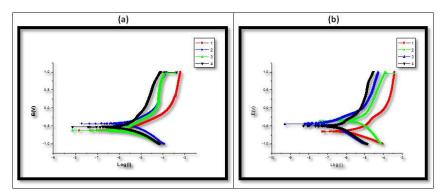


Figure 3:Anodic and Cathodic Polarization Curves of Steel Fibers with Concrete (A) Four Steel Fiber Samples(1ml)(B) Four Withdraw Steel Fiber (1ml) in 3.5%Nacl Solution.

Cyclic Anodic Polarization Measurements for Steel Fiber Samples in Sodium Chloride solution with and without concrete

Figs.(5,6) represent the cyclic anodic polarization measurements for test samples in 3.5% NaCl using scan rate 5 mV/sec in potential range from -1000 to 1000 mV at 25°C

It is clear that, the anodic current density starts to increase to form the active region. The increasing of the potential in the positive direction lead to increasing of the anodic current, which corresponds to oxidation of iron to iron ions, with increasing the potential a passive film[Fe(OH)₂, Fe₃O₄ and or Fe₂O₃]is formed[13]. When the potential move towards more anodic, the current density starts to increase again, forming the transpassive region before oxygen evolution. The current rises suddenly without any sign of oxygen evolution for samples 1 and 2, denoting break down of the passive layer.

Hysteresis loop area is a rough measure of the intensity of pitting corrosion. Larger size of loap means greater intensity of pitting corrosion[14]. For samples 3 and 4. in 3.5% NaCl solution, the cyclic polarization curves don't have a hysteresis loop where the forwards scan current density are higher than back words at the same potential, indicating the

good stability and self repairing ability of the passive film. For the rest samples, the hysteresis loops was observed.

As shown from Figs. (5,6), the hysteresis loop area is decreasing with increasing in the amount of addibond 65. This is due to the formation of the iron – rich oxide layer that accounts chiefly for the corrosion resistance of steel fibers. However this layer is susceptible to damage, particularly in the presence of chlorides, and such damage can lead to the onset of localized corrosion such as pitting and crevice corrosion. Addibond 65 does not influence the initiation phase, but is important in reducing the rate at which both pitting and crevice corrosion propagates. This is critical in determining how serious corrosion will be and this explain the highly pitting resistance of sample No.4.Sample 4, the improvement in the pitting resistance and the stability of passive film is related to the addition of over amount of addibond 65 at steel fibers.

The stability of a corroding pit depends on the potential drop, the composition of the pit electrolyte and the pH drop. pH shifts have often served to explain the stability of a corroding pit. The hydrolysis of metal ions lead to acidification according to:

$$Me^{+2} + H_2O = MeOH^{(z-1)} + H^+$$
 (2)

The corrosion parameters for steel fiber samples in 3.5% sodium chloride solution are given in Tables(9- 13). As clear from these tables, the value of corrosion rates for samples 1,2,3 and 4 are 60.26, 54.05,39.37 and 17.45 μ m/y respectively for (1ml) steel fibers without concrete, while for (2ml) steel fibers samples 1,2,3 and 4 are 52.20,49.42, 20.48 and 15.61 μ m/y respectively. On the other side (1ml) withdraw steel fiber without concrete for samples 1,2,3 and 4 are 43.86,33.44,21.95 and 11.48 μ m/yrespectively. In case of steel fibers with concrete, the value of corrosion rates (1ml) for steel fiber for samples 1,2,3 and 4 are 47.12, 42.39,19.83 and 14.78 μ m/y respectively while for(1ml) withdraw steel fibers the value of corrosion rates for samples 1,2,3 and 4 are 34.45,18.02,11.77and0.41 μ m/y respectively.It can concluded that corrosion rate decreases and pitting potential E_{pit} , increases with increasing addibond 65 contents in all cases. Withdraw steel fibers have better corrosion resistance than steel fibers. The value of E_{pit} for all samples in 3.5% NaCl solution follows the sequence

Sample
$$1 < 2 < 3 < 4$$

It is clear that higher content of addibond65, sample 4, not only reduce susceptibility to pit nucleation, but also diminish the rate of pit growth.

Table 9: The Corrosion Parameter of Fire Four Steel Fiber (1ml) Sampleswithout Concrete in 3.5% Nacl Solution

Sample No.	E _{pit} (mV)	I _{corr} μA/cm ²	Corrosion rate µm/y
1	0.10	5.2	60.26
2	0.13	4.62	54.05
3	0.19	3.36	39.37
4	0.21	1.49	17.45

Table 10: The Corrosion Parameter Of Fire Four Steel Fibersamples(2ml) Without Concrete In 3.5% Nacl Solution

Sample No.	E _{pit} (mV)	I _{corr} μA/cm ²	Corrosion rate µm/y
1	0.19	4.46	52.20

2	0.22	4.22	49.42
3	0.27	1.78	20.84
4	0.29	1.33	15.61

Table 11: The Corrosion Parameter of Four Withdraw Steel Fiber Samples (1ml) Without Concrete In 3.5% Nacl Solution

Sample No.	E _{pit} (mV)	I _{corr} μA/cm ²	Corrosion rate µm/y
1	0.20	3.8	43.86
2	0.24	2.85	33.44
3	0.32	1.87	21.95
4	0.39	0.98	11.48

Table 12: The Corrosion Parameter of Fire Steel Fiber Samples (1ml) with Concrete in 3.5% Nacl Solution

Sample No.	E _{pit} (mV)	I _{corr} μA/cm ²	Corrosion rate µm/y
1	0.17	4.025	47.12
2	0.2	3.62	42.39
3	0.25	1.69	19.83
4	0.30	1.26	14.78

Table 13: The Corrosion Parameter of with Draw Steel Fiber Samples (1ml) with Concrete in 3.5% Nacl Solution

Sample No.	E _{pit} (mV)	I _{corr} μA/cm ²	Corrosion rate µm/y
1	0.20	2.94	34.45
2	0.25	1.54	18.02
3	0.29	1.006	11.77
4	0.37	0.03	0.41

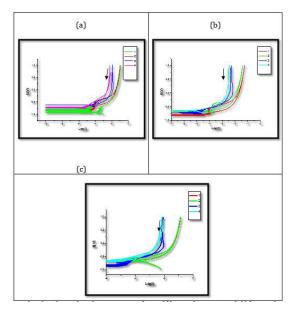
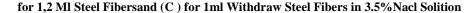


Figure 5a-C:Cyclic Anodic Polarization Curves For Steel Fibers Without Concrete (A,B)



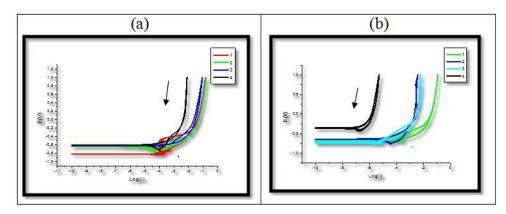


Figure 6 A,B:Cyclic Anodic Polarization Curves for Steel Fiber With Concrete in 3.5% Nacl Solution. Four Steel Fiber Samples (1ml), Four Withdraw Steel Fiber (1ml).

SURFACE EXAMINATION

Scanning Electron Microscope (SEM)

To confirm the results obtained after potentiodynamic polarization measurements, the tested steel fiber samples were observed under the scanning electron microscope (SEM). Fig.(7-10) illustrates the surface morphology of steel fiber samples after potentiodynamic polarization in 3.5 % NaCl solution. Fig.(7-a) for as received sample No.1 showed that, the surface of the sample was highly corroded. The corroded areas are shown as grooves in the sample with gray and white products. fig. (7b,c) show no evidence of corrosion attack and formation of passive film on alloy surfaces. This observation indicates that samples No. 3 and 4, which contain high percentage of addibond 65 gave excellent corrosion resistance due to the protective passive film formed on the surface of the samples.

(Fig. 8-a) For withdraw steel fiber sample No.1 without addibond 65, a heterogeneous, non-protective iron oxide, possibly rust product is observed. Fig. (8,b,c) for samples No. 3 and 4 show uniform surface free of corrosion attack, due to the existence of addibond 65 on their surfaces. Figs. (9,10) withdraw and steel fibers in concrete, Sample No.1 shows heterogeneous oxide film formed on the surface with some pitting corrosion. Samples 3 and 4 covered with thin and thick concrete layers which preventing from seeing the surface. SEM results are in good agreement with the electrochemical measurements results.

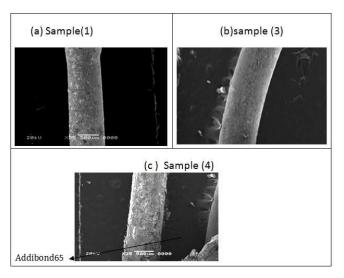


Figure 7:Surface Morphology of Three Fire Steel Fiber Samples in 3.5% Nacl Solution.

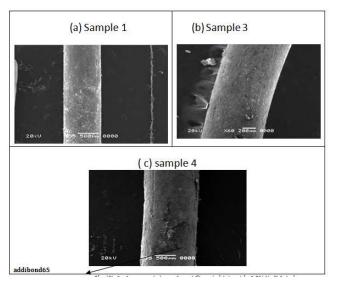


Figure.8: Surface Morphology of Steel Fibesr (Withdraw) in 3.5% Nacl Solution.

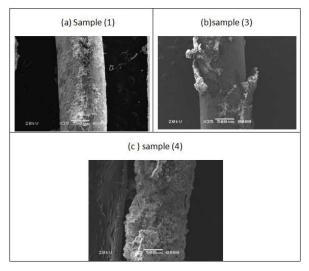


Figure.9:Steel Fibers in Concrete

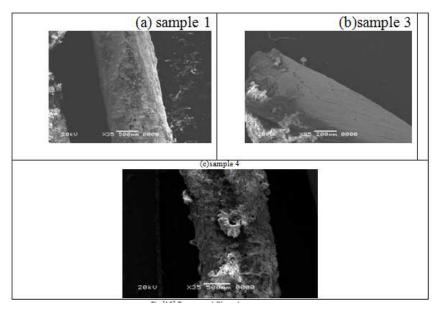


Figure.10:Draw Steel Fibers in Concrete

Energy Dispersive X-Ray Analysis (EDXA)

It is important to take into consideration the percentage of element and oxide formed on the surface of the samples. This percentage was obtained from analyzed element composition by energy dispersive X-ray analysis (EDXA). Fig.(11-13) show the energy dispersive X-ray analysis (EDXA) for samples No. 1, 3 and 4 in 3.5% NaCl. The observed spectra indicated the presence of Fe, and S in steel fibers. According to the peak strength Fe dominates the component of the film. The presence of chloride ion on the passive film knows to create a concentration gradient that facilitates its diffusion into the film, where it undergoes hydrolysis and reduces the local pH, causing dissolution of the film [15].

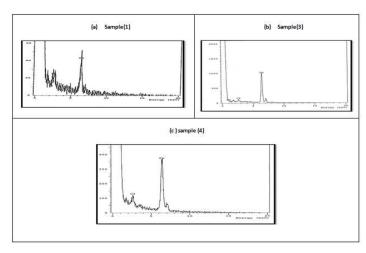


Figure. 11:EDAX Spectra of Steel Fibers In 3.5% Nacl Solution.

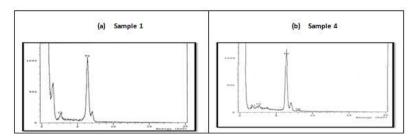


Figure 12: EDAX Spectra of Withdraw and Steel Fiber in 3.5% Nacl Solution.

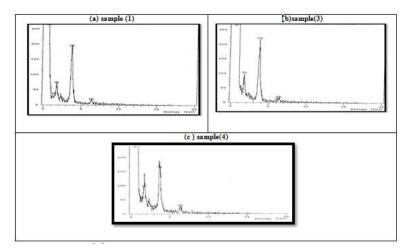


Figure 13: EDAX Spectra of Fire Steel Fibers in 3.5% Nacl Solution. with Concrete

CONCLUSIONS

- From this work, we conclude that
- From potentiodynamic polarization techniques, the value of I_{corr} and corrosion rate decrease in the order:samples 4 < 3 < 2 < 1.

- From potentiodynamic cyclic anodic polarization we noted that corrosion rate decrease in the sequence samples 4<3<2<1.
- The samples with fiber size of (2ml) showed lower corrosion rate than samples of (1ml).
- Steel fiber samples showed more active corrosion compared to the withdrawn steel fiber samples.
- SEM and EDAX analysis are in good agreement with the results from electrochemical techniques used.

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