

Corrosion Performance of Medium-Strength and Silica Fume High-Strength Reinforced Concrete in a Chloride Solution

¹Prof, Hany A. El-Ghazaly¹, Prof. Magdy Abdelaziz², Ass. Prof. Mohamed El-Rabiei³, Eng. Hala Emad⁴

^{1,2,4}Structure. Dep. Faculty of Engineering, Fayoum University, Egypt

³Chemistry Dep. Faculty of Science, Fayoum University, Egypt

ABSTRACT - In the present study, corrosion rate of reinforcing carbon steel bars with ultimate strength of 360 MPa and diameter 12 mm in different concrete mixes made of sulphate resistance cement 42.5, was measured using electrochemical methods. The effect of different parameters such various additives like silica fume, superplasticizer, water/cement ratios and concrete cover thickness on corrosion rate of reinforcing steel bars embedded in concrete submerged into different aggressive solutions was studied. Four aggressive solutions were utilized in the experimental work, namely, tap water, natural chloride solution, natural sulphate solution and natural sulphate-chloride solution for different time intervals. The physical and mechanical properties of different samples were examined in the laboratory. Then, the corrosion parameters were observed through two stages: In the first stage, the corrosion potential of steel in the concrete was measured after 1 hour, 3, 7, 28 and 90 days in accordance with ASTM C 876 standard using open circuit measurements. In the second stage, "potentiodynamic polarization" anodic and cathodic polarization values of this steel were measured and then the corrosion rate was determined using linear polarization technique. Results showed that adding of 10% silica fume and 1% superplasticizer (both by weight of cement) to concrete with w/c ratio 0.4 gives the highest value of resistance of compressive strength, tensile strength, workability, permeability and corrosion. For ratios more than 10% of silica fume, the concrete durability decreases.

Key Words - Corrosion, Sulphate Resistance Cement, Silica fume, Water Content, Concrete, Reinforcing Steel, Linear Polarization.

1- INTRODUCTION

Reinforced concrete structures provide excellent service under certain environmental conditions[1]so the reinforcement corrosion is the primary cause of concrete deterioration in many parts of the world. It is now a well-known fact that reinforcement corrosion is predominantly mostly caused by the chloride ions[2]. High quality and durable concrete is required to reduce the rapid deterioration of concrete in severe conditions. Among the factors related to declining concrete durability such as carbonation, corrosion, alkali-silica reaction,

freezing/thawing, and so on, the penetration of chloride-ions into concrete has been regarded as the major

deterioration problem[3, 4]. Chloride induced corrosion as the major cause for degradation of reinforced concrete has been the subject of great research efforts over the last fifty years. As chloride ions destroys the passivity and the binder type of the surface of reinforcing steel which can have a more dominant influence on the result[5]. Thus, insufficient concrete cover or poor quality concrete accelerates reinforcement corrosion [6]. These corrosion problems lead frequently to early deterioration and eventually to risky situations for the stability of structures. In any case, the economic costs inherent to reparation works are considerable. So it is very important to evaluate the performance of some proprietary and generic inhibitors in decreasing the rate of reinforcement corrosion in the inhabitations as silica fume cement concrete[2]. And it is not possible to select a reliable range of chloride threshold values and thus the current practice of condition assessment as well as service life design cannot be improved[5]. Numerous research studies have been performed on the factors affecting the corrosion of reinforcing steel embedded in concrete in recent years [2, 3, 7-15]. During studies on real concrete samples or in equivalent alkali solvent, the corrosion rate of reinforcing steel usually at chloride ion concentrations and the minimum limit value that results in the corrosion of chloride ions were determined. For the studies about the effect of Silica Fume, w/c ratio and the concrete cover depth on the corrosion of reinforcing steel, different ratios of Silica Fume were compared and their effects on steel corrosion were investigated. In this study, When SF was added to the concrete specimens with super plasticizer, it improved both the strength and other performance parameters (capillary absorption, porosity and ultrasonic pulse velocity). Since SF consist of very fine particles, pores in the bulk paste or in the interfaces is filled by this mineral admixture, therefore, the strength of concrete specimens with SF increased after the addition of super plasticizer. The aim of the study is to investigate the corrosion behavior of reinforced steel in different concrete mixes immersed in different aggressive media (chloride and sulphate binding) depending on permeability and strength. For this purpose, the corrosion potential of reinforcing steel embedded in concrete samples is studied. The corrosion rate is measured after 3, 7, 28 and 90 days in

accordance with ASTM C 876 standard. At last, the corrosion rates of the steel are determined by using the linear polarization technique and the cyclic voltammetry technique. Furthermore, the influences of mix design and the type of binder are evaluated and related to porosity. The chlorides destroy the protective oxide film which develops on the steel surface as a result of the highly alkaline conditions found in concrete and in the presence of oxygen and moisture this corrosion occurs. Moreover, sulphate destroys the concrete by accelerating corrosion process.

2- MATERIAL AND METHOD

SRC batches were prepared with water cement ratios of 0.4 to 0.64, silica fume ratios of 0 to 20 % and superplasticizer with ratios of 0 to 1.27% related to cement weight. 20 batches are obtained.

2.1 Prepare of Electrodes

As an electrode, Carbon Iron and Steel Factories Ahmed Ezz steel bar, which is the fundamental construction material of construction industry, was selected for the present study. The asreceived material was in the form of 12 mm diameter. The chemical composition of this steel is given in Table 1.40 pieces of reinforcing steel were machined to 12 mm diameter and 150 mm length and the sample surfaces were polished with 1200 mesh sandpaper. The polished surfaces were cleaned with ethyl alcohol. 3.77 cm² surface areas were left open in the tips of electrodes which would be embedded in the concrete. Screw thread was machined in other ends of steel electrodes and cables were connected to these ends in order to easily make measurements during the experiment. Remaining sections of the electrodes were protected against external effects by covering with epoxy resin at first and exposed to chloride salts.

2.2 Design of Concrete Samples

The steel electrodes prepared in advance were embedded in cylindrical concrete samples 100*200 mm to evaluate corrosion behavior. 42.5 S. R cement was used in order to prepare all concrete samples with and without silica fume included in the experiments in scope of the study. Tap water was used as mix water while preparing the concrete batches. The concrete samples were kept in molds for 24 hours, and then unmolded. After 28-days, the specimens were tested for compressive strength. The compressive strength of the normal strength concrete were found to be 250, 310 and 350 kg/cm², and 456 & 535 kg/cm² for high strength concrete. is presented in Table 2.

While the specimens were being prepared, cement dosage, water/cement ratio, aggregate amount, silica fume and super plasticizer amount which were added for create least corrosive environment. Five batches were chosen to cover various compressive strength. The chosen five batches were tested for permeability and absorption before conducting electrochemical tests. For electrochemical tests and for calculating corrosion rate, 40 cylindrical samples for batches were used. Chemical compositions of the Components for themixes are given in Table 3.

2.3 Corrosion Tests

Corrosion experiments were conducted in two stages. In the first stage, the corrosion potential of steel in the concrete was measured after 1 hour, 3, 7, 28 and 90 days in accordance with ASTM C 876 standard using open circuit measurements. In the second stage, "potentiodynamic polarization" anodic and cathodic polarization values of this steel were measured and then the corrosion rate was determined using linear polarization technique. The working electrode (steel) is covered by epoxy resin except one centimeter is left uncovered as shown in **figure 1**. The steel bar is actually surrounded by concrete with a certain volume and height.

2.4 Electrochemical system and Computer software

The electrochemical impedance investigations and polarization measurements are performed using the Volta lab 40 PGZ 301 ". All-in-one "potentiostat/ Galvanostat. The latest analogue and microcomputer design advances to provide high performance, ease of use, and greater versatility in electrochemical measurements. The instrument is interfaced to an external IBM 1200 CPU computer. The volta master 4 software is designed to measure and analyze corrosion quickly, easily and reliably, using a variety of techniques, cyclic voltammetry (CV) and potentiodynamic polarization ... etc.

2.5 Potentio-dynamic polarization techniques.

After measuring the potential voltage, a passive layer is formed at certain value (steady state voltage). The entire potential scan is programed to take place within ± 400 mV of the steady state to accelerate the corrosion process by cracking the layer protection of steel and hence determination of the corrosion rate. In Tafel extrapolation, the evaluation is based on the concept of the mixed potential theory for aqueous corrosion as shown in figure 2[16] shows more details about the anodic branch and the cathodic branch.

The slope of the anodic branch is equal to:

$$(1-a) nF/ 2.3RT$$

And the cathodic branch slope is equal to:

$$-a nF/ 2.3RT$$

where, a is the transfer coefficient which can range from zero to unity, n is the number of electrons oxidized or reduced, F is the Faraday constant, R is the gas constant and T is the temperature.

3. RESULTS AND DISCUSSION

The open-circuit potential, OCP, of reinforced steel was recorded over a period of 90 min in stagnant naturally aerated aqueous chloride solution. Generally, the steady state potential in a narrow range (≈ 150 mV).

3.1 Polarization measurements in natural Chloride solution

The effect of cement types on the electrochemical behavior of reinforcing steel in different samples was investigated under polarization conditions. The linear polarization and tafel extrapolation techniques were used. The polarization experiments were carried out at a scan rate of 5 mVS^{-1} . The data obtained from **figure 3, 4** reveal that the potentiodynamic polarization curves of the different samples after holding the electrodes at the open circuit potential for at least 60 min in natural chloride solution at cover thickness 1.95, 4.5cm respectively change due to the concrete samples contents. The values of corrosion parameters, corrosion potential, E_{corr} , corrosion current density, i_{corr} , and corrosion rate were calculated.

The decrease in free corrosion potential declined slowly with the decreasing of compressive strength. This decrease, is mainly related to the quantity of portlandite $[\text{Ca}(\text{OH})_2]$ in the sulphate resistance cement (SRC) which is produced by the hydration of Portland cement. Such a quantity is solely dependent on the C3S & C2S ratio. In this case, C3S & C2S ratio is 2.5 [17], C3A is very low ($\leq 3.5\%$) causing decrease the pH of pure solution. Furthermore, the addition of silica fume fill the small pores and the superplasticizer decrease the w/c ratio and increase the compressive strength for the samples [18]. Also, the silica fume showed low carbonation depth and the lowest corrosion rate, close to of undamaged specimens.

This is attributed to the formation of C-S-H compounds at the interface between these mixtures and cement mortar, resulting in the creation of good binding properties of the repair materials [14]. Superplasticizers reduce chloride ingress by allowing the use of lower water-to-cement ratios [19], and they help to decrease the corrosion rate.

3.2 Polarization measurements in natural Sulphate solution

The polarization resistance in all cement types increases with increasing of compressive strength and the sulphate resistance cement content. The increase in polarization resistance is mainly due to the formation of passive layer and reducing the activity of steel. The variation in the resistance is attributed to the sulphate attack and destruction of passive layers. The corrosion rate in SRC > Silica fume > Silica fume + Super plasticizer. **Figure 5, 6** presents the potentiodynamic polarization curves of the different samples after holding the electrodes at the open circuit potential for at least 60 min in natural sulphate solution at cover thickness 1.95, 4.5cm respectively. The values of corrosion parameters, corrosion potential, E_{corr} , corrosion current density, i_{corr} , and corrosion rate were calculated. The data obtained from **figure 5, 6** reveal that the corrosion rate changes in natural sulphate due to the concrete samples contents

3.3 The effect of immersion time on corrosion rates for steel in natural sulphate solution

Corrosion potential changes versus time of the reinforcing steels embedded in the concrete samples. In case of (SRC) only without inhabitations the later product was

limited, where the amount of calcium aluminate hydrate is less than <3.5 , at earlier ages, these two reactions lead to a denser structure because of precipitation of the product with voids and micro pores. So that the diffusion of sulphate ions decrease at early days of hydration, and the alkaline medium increases the passivation process on steel surface [20] as shown in **figure 7**.

3.4 The effect of immersion time on corrosion rates for steel in natural sulphate-chloride

a) Cover thickness 1.95 cm

This behavior changes due to the acidity of sulphate-chloride ions, which the sulphates decrease the stability of passive layer, but the chloride destroys the steel as shown in **figure 8**.

b) Cover thickness 4.5 cm

The corrosion potential values changed to more negative values up to 70 days then it decreased at 90 days as in cover thickness 1.95cm but in cover thickness 4.5 cm is more. The current density (I_{corr}), increases with time for every sample up to 70 days then it shifted to decrease at 90 days as shown in **figure 9**. Also, the corrosion rate values for the different samples are in the order $E > D > A$ as the decrease of the cement SRC ratio and increasing the water ratio in sample E and the decrease in current density is due to physical protection at sample A, and for sulphate-chloride solution more than this in sulphate solution only. The variation in the resistance is attributed to the sulphate-chloride attack and destruction of passive layers. The corrosion rate shifted.

SRC > SRC + Silica fume > SRC + Silica fume + Super plasticizer

at 28 days > 7 days > 3 days

at cover thickness 1.95cm > cover thickness 4.5cm
at sulphate-chloride solution > sulphate solution only

This situation was interpreted that the corrosion still continued even at the end of 90th day in A, B, C and D samples by taking ASTM C876 [14] as a reference. From the results of corrosion potentials by ASTM C876 standard, it can be said that the steels in the concrete sample which has been produced with E cement has higher corrosion resistance than the other concrete samples. It is expected that the corrosion rate values of reinforcing steel embedded in concrete samples which were prepared with CEM II /B-M 32.5 R cement, should be practically similar. However, at the end of the 90th day, it was found that the corrosion rate of steel in sample A was the highest and corrosion rate of the steel in sample E was the lowest. At the same time, the corrosion rate values of the B and C, A and D samples are close. Besides of these reasons, corrosion rate of the steel may have been change pH value of the sample. Because, acid oxide amount ($\text{SiO}_2 + \text{SO}_3$) is higher and base oxide amount ($\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO}$) is lower in specimen A in comparison to the other samples. This would be increased corrosion rate of the reinforcing steel in sample A by decreasing the pH value. Moreover, as understood from

Because, corrosion rate of the steels increase along with the increasing of total additives in the cements. For example,

highest total additive amount is in A sample which has highest corrosion rate.

4. CONCLUSIONS

Results showed that adding of 10% silica fume and 1% superplasticizer (both by weight of cement) to concrete with w/c ratio 0.4 gives the highest value of resistance of compressive strength, tensile strength, workability and permeability. For ratios more than 10% of silica fume, the concrete durability decreases. From electrochemical perspective, which aimed to study the electrochemical behavior of reinforced steel in different media with the presence of Cl^- ions, SO_4^{2-} ions and $(\text{SO}_4^{2-} + \text{Cl}^-)$ ions using linear polarization, cyclic Volta metric and open circuit methods. Several results were concluded by the preceded electrochemical experimental work. It could be briefed as :

For the highest corrosion resistance, the best concrete mix can be obtained with the following ingredients: 10% silica fume and 1% superplasticizer, w/c ratio 0.4 and cover thickness not less 4.5 cm.

-The corrosion rate increases to a certain limit in a time interval ranges from 28 to 70 days, after that a decrease takes place.

-The effect of the aggressive media on corrosion rate can be presented in ascending fashion as follows:

-Tap water, sulphate, composition (chloride + sulphate) and chloride media

5 REFERENCES

1. Felekoglu, B., et al., Sulfate resistances of different types of Turkish Portland cements by selecting the appropriate test methods. *Construction and Building Materials*, 2006. 20(9): p. 819-823.
2. Al-Mehthel, M., et al., Performance of generic and proprietary corrosion inhibitors in chloride-contaminated silica fume cement concrete. *Construction and Building Materials*, 2009. 23(5): p. 1768-1774.
3. Oğuzhan Keleştemur, M.A., Servet Yıldız, Effect of Oxide Compositions in the Portland Cement on Corrosion Behavior of Reinforcing Steel Embedded in Concrete, in *Construction Education 2009*, Firat. p. 39-43.
4. Al-Amoudi, O.S.B., Durability of plain and blended cements in marine environments. *Adv. Cem. Res.*, 2002. 14(3): p. 89-100.
5. Angst, U., et al., Critical chloride content in reinforced concrete -- A review. *Cement and Concrete Research*, 2009. 39(12): p. 1122-1138.
6. Ann, K.Y. and H.-W. Song, Chloride threshold level for corrosion of steel in concrete. *Corrosion Science*, 2007. 49(11): p. 4113-4133.
7. Grubb, J.A., et al., Effect of steel microfibers on corrosion of steel reinforcing bars. *Cement and Concrete Research*, 2007. 37(7): p. 1115-1126.
8. Tan, Z.Q. and C.M. Hansson, Effect of surface condition on the initial corrosion of galvanized reinforcing steel embedded in concrete. *Corrosion Science*, 2008. 50(9): p. 2512-2522.
9. Gürten, A.A., K. Kayakırılmaz, and M. Erbil, The effect of thiosemicarbazide on corrosion resistance of steel reinforcement in concrete. *Construction and Building Materials*, 2007. 21(3): p. 669-676.
10. Oğuzhan KELEŞTEMUR, S.Y., Effect of Various NaCl Concentration on Corrosion of Steel in Concrete Produced by Addition of Styrofoam. *G.U. J. Sci.*, 2006. 19(3): p. 163-172.
11. Garcés, P., et al., Corrosion of steel reinforcement in structural concrete with carbon material addition. *Corrosion Science*, 2007. 49(6): p. 2557-2566.
12. Gadve, S., A. Mukherjee, and S.N. Malhotra, Corrosion of steel reinforcements embedded in FRP wrapped concrete. *Construction and Building Materials*, 2009. 23(1): p. 153-161.
13. Venkatesan, P., N. Palaniswamy, and K. Rajagopal, Corrosion performance of coated reinforcing bars embedded in concrete and exposed to natural marine environment. *Progress in Organic Coatings*, 2006. 56(1): p. 8-12.
14. Kasselouri, V., N. Kouloumbi, and T. Thomopoulos, Performance of silica fume-calcium hydroxide mixture as a repair material. *Cement and Concrete Composites*, 2001. 23(1): p. 103-110.
15. Vennesland Ø, a.G., O.E, Silica Concrete Protection Against Corrosion of Embedded Steel. Fly Ash, Silica fume, Slag and other Mineral by products in Concrete, 1983. 2, SP-79, American Concrete Institute: p. 719-729.
16. Faulkner, A.B.a.L., "Electrochemical Methods", John Wiley & Sons, U.S.A. 1980, p.106.
17. Al-Amoudi, O.S.B., *Construction and Building Materials*. 1995. 9(1): p. 25-33.
18. ACI Committee 549.1R-93, reapproved 1999, Guide for the Design, Construction, ACI Committee 549 Report, American Concrete Institute, Farmington Hills, Michigan 1999.
19. Berke, N.S., and Rosenberg, R, Technical Review of Calcium Nitrite Corrosion Inhibitor in Concrete. *Concrete Bridge Design and Maintenance: Steel Corrosion in Concrete*, Transportation Research Record 1211, Transportation Research Board, National Research Council, Washington, DC, 1989: p. 18-403, vol 119.
20. E.E.Hekal et al. "Cement and Concrete Research". 2002. 32: p. 1421-1427.

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

C	Mn	Si	P	S	Fe
0.193	0.650	0.188	<0.001	0.0057	98.8 Balanced

Table 2. Mixture proportion of the concrete batches (kg/m³)

Sample	Cement	Water	Sand	Gravel	Silica fume	Superplasticizer
A	400	160 (0.40)	620.92	1243.7	40	4
B	400	188 (0.47)	575	1150	40	4.4
C	400	188 (0.47)	604.5	1210.8		
D	400	218 (0.55)	578	1156.2	40	
E	400	240 (0.60)	558.6	1118.9		

Table 3. The Components for the mixes

Compositions	Contents type				
	Cement(SRC)	Steel	Gravel	Sand	Silica fume
Silicon dioxide (SiO ₂)	21.7		90.97	78.1	97
Aluminum oxide (Al ₂ O ₃)	3.97		1.73	6.5	0.2
Iron oxide (Fe ₂ O ₃)	4.95		0.78	1.9	0.5
Calcium oxide (CaO)	63.5				0.2
Magnesium oxide (MgO)	2.1		0.92		0.5
Sulfur trioxide (SO ₃)	1.94		0.19		0.15
Chloride (Cl ⁻)			0.023	0.035	0.2
Loss of Ignition (LOI)	0.94		1.58		0.55
Unknown			3.25		
K ₂ O	0.11		0.23	1.4	0.5
Na ₂ O	0.13		0.35	2.3	0.2
H ₂ O				7	

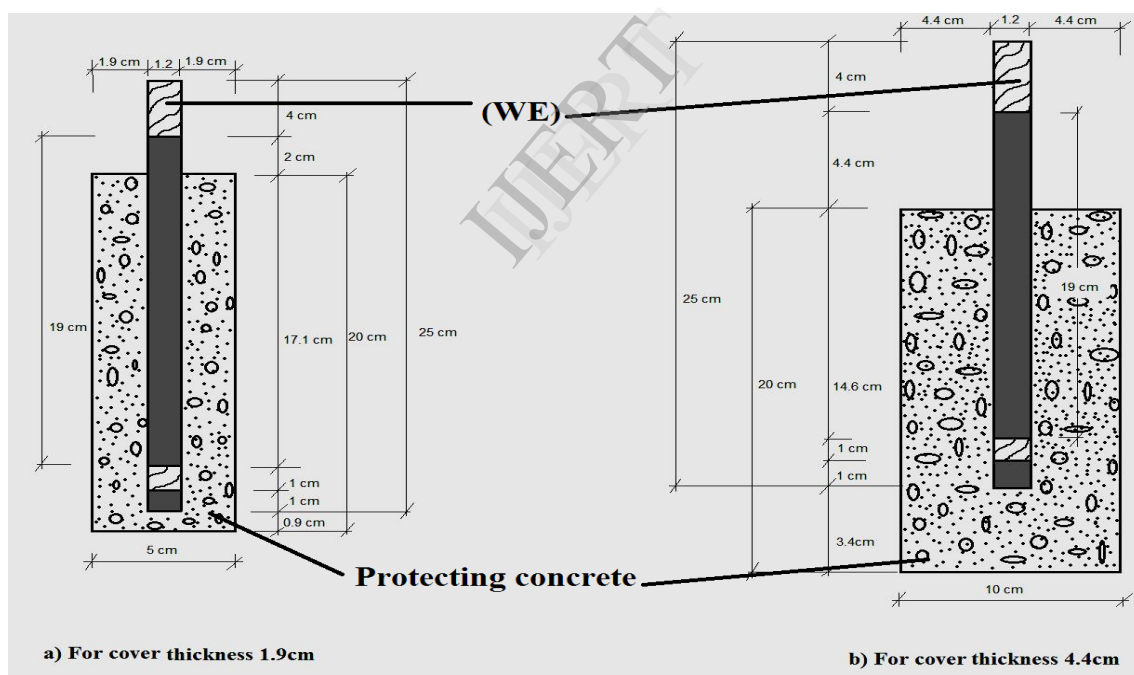


Figure 1. Schematic illustration of electrochemical corrosion test specimen

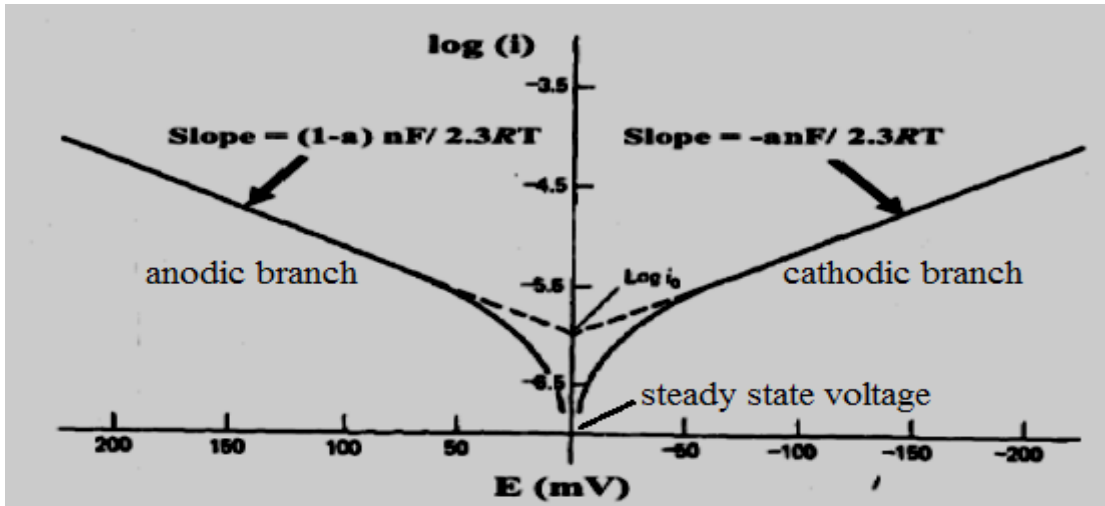


Figure 2. Anodic and cathodic slopes in tafel extrapolation plot.

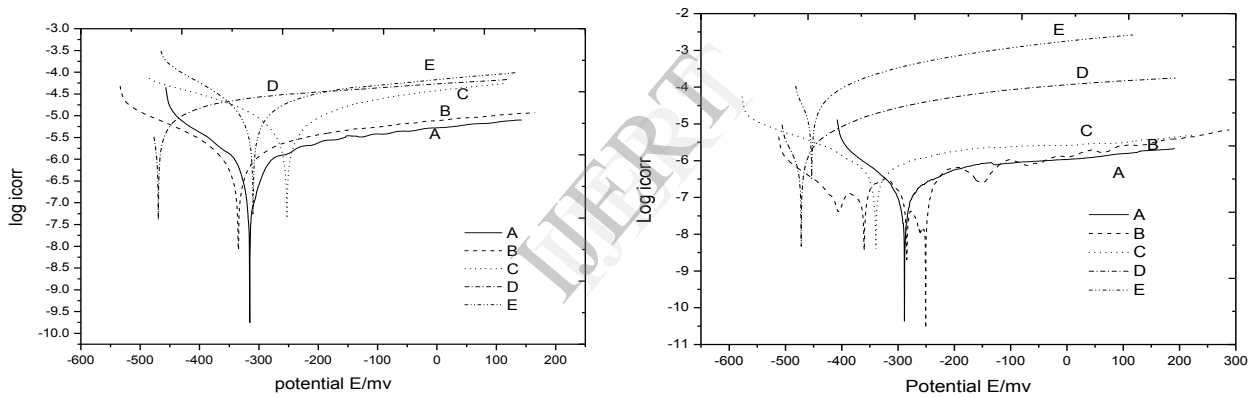


Figure 3. Potentiodynamic polarization curves of reinforced steel at different concrete samples after one hour immersion in natural chloride solution with cover thickness 1.95 and 4.5 cm and scan rate 5 mVS-1 at 25° C.

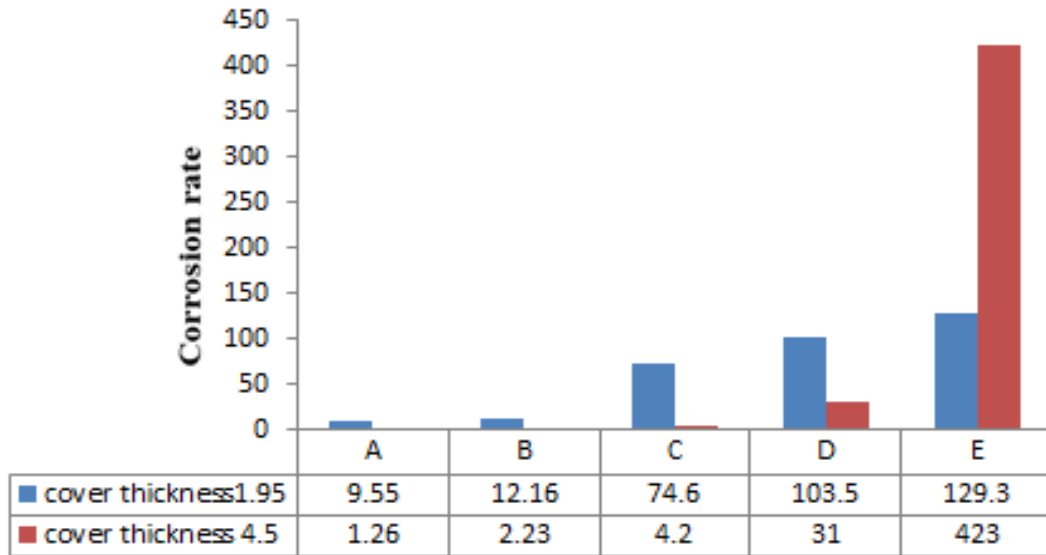


Figure 4. Variation of Corrosion rate (μmY^{-1}) of reinforced steel at different concrete samples after one hour immersion in natural chloride solution with cover thickness 1.95 cm using polarization method at 25°C.

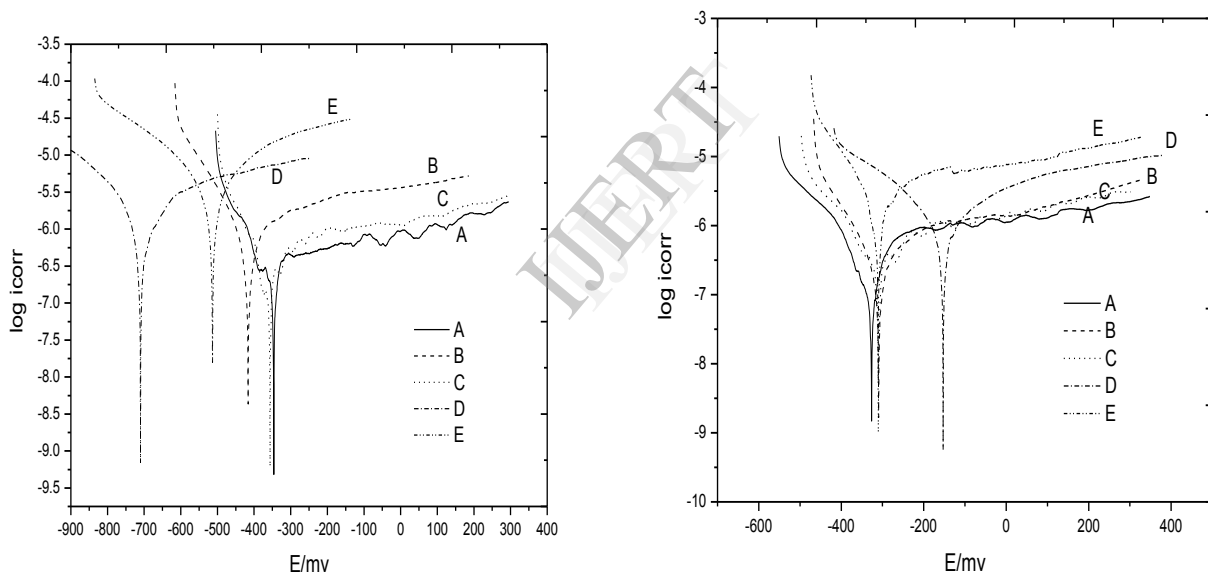


Figure 5. Potentiodynamic polarization curves of reinforced steel at different concrete samples after one hour immersion in natural sulphate solution with cover thickness 1.95 and 4.5 cm and scan rate 5 mVS⁻¹ at 25°C.

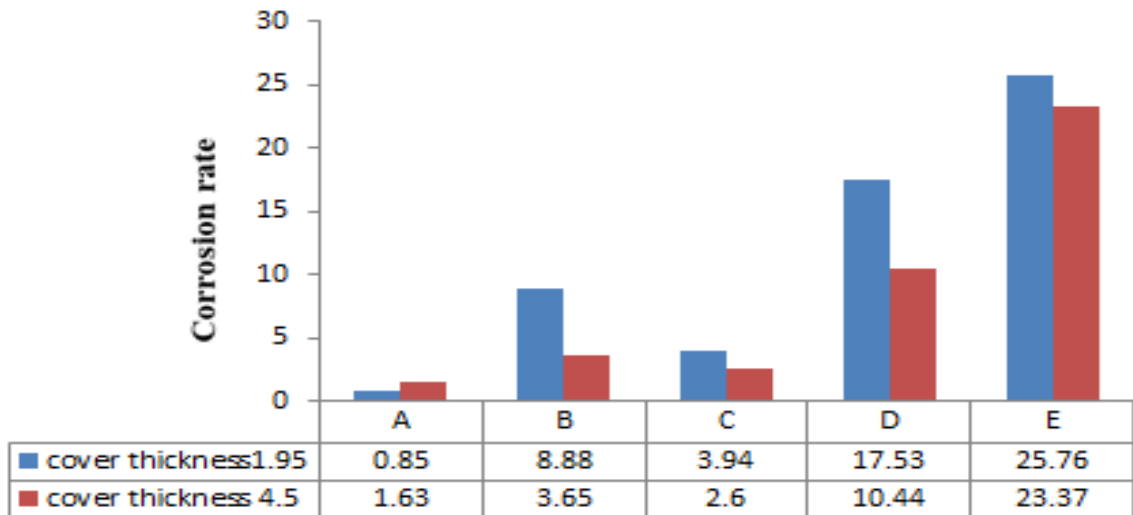


Figure 6. Variation of Corrosion rate of reinforced steel at different concrete samples after one hour immersion in natural sulphate solution with cover thickness 1.95 cm using polarization method at 25°C.

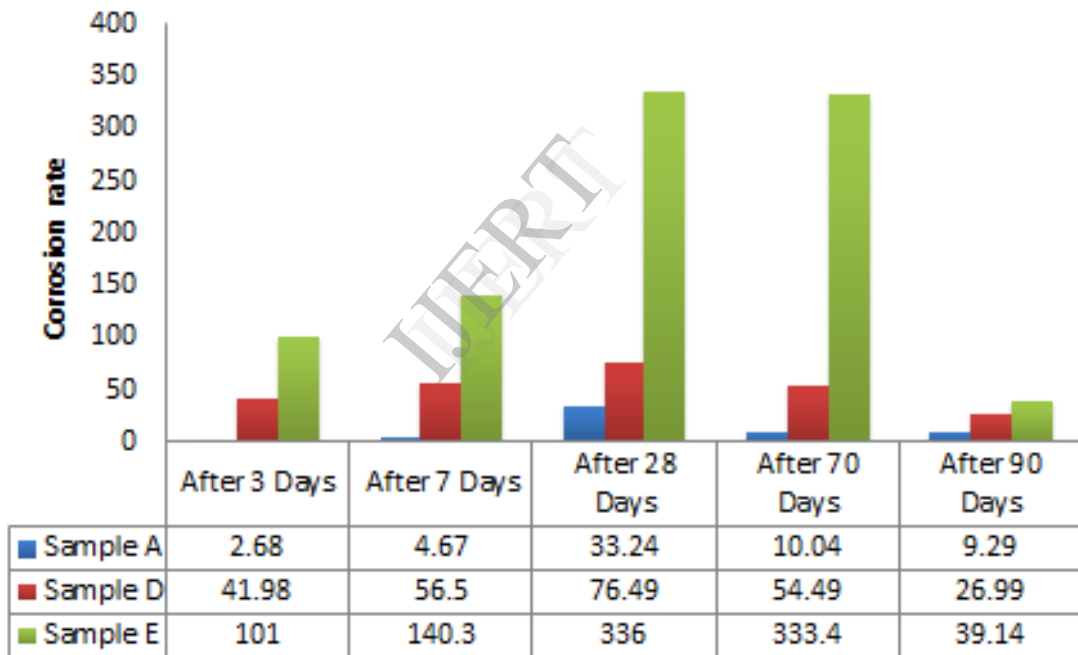


Figure 7. The effect of immersion time on corrosion rates for steel in natural sulphate solution with cover thickness 4.5 cm

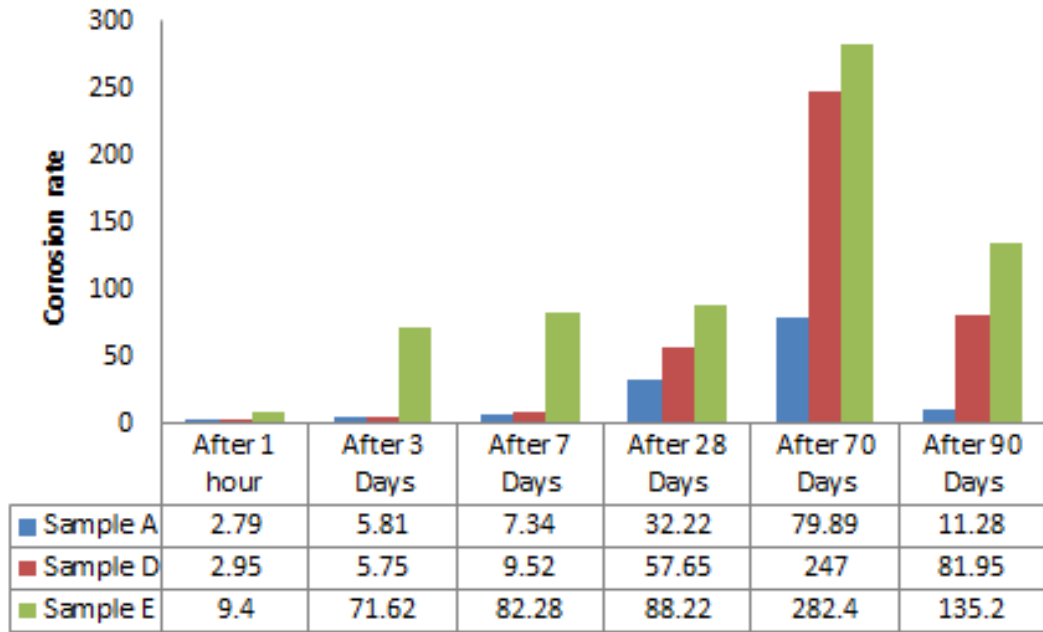


Figure 8. The effect of immersion time on corrosion rates for steel in natural sulphate-Chloride solution with cover thickness 1.95 cm

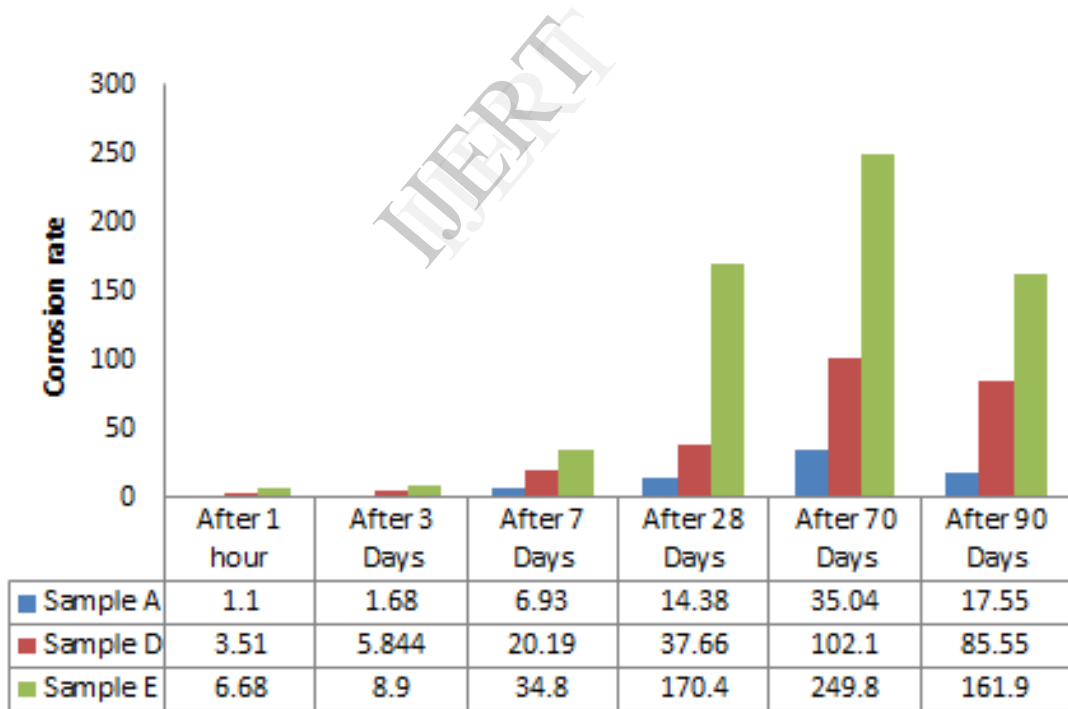


Figure 9. The effect of immersion time on corrosion rates for steel in natural sulphate-Chloride solution with cover thickness 1.95 cm.