Decreasing Corrodibility of Steel Rebars in Carbonated Concrete Solution

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Abstract:

Corrosion of steel rebars in reinforced concrete structure represents a major economic loss and a huge threat to people's lives. Corrosion of reinforcement can occur due to ingress of acidic gases (CO_2) in industrial areas or ingress of chloride in areas with marine atmospheres, into concrete pores. One of the most important methods utilized to decrease the corrosion of steel rebars is the use of inhibitors either with fresh concrete mixture or applied to concrete surface after hardening.

This study focuses on the corrosion occurring due to carbonation in simulated concrete solution and investigates the effect of inhibitors on decreasing corrosion in carbonated concrete solution.

In Simulated Concrete solution $Ca(OH)_2$ with (pH=12), corrosion rate was 2.84 mpy due to formation of passive film on rebar's surface. Due to carbonation of simulated concrete solution (pH= 8) resulting from ingress of CO_2, corrosion rate increased to 11.67 mpy due to the dissolution of passive film. Adding 200 ppm of Polyethylene glycol, Quaternary Amine and ginger extract has decreased the corrodibility of steel rebars in carbonated simulated concrete solution (pH=8) from 11.67 mpy to 8, 3.75 and 1.13 mpy, respectively.

X-Ray Diffraction (XRD) patterns showed the formation of passive films of iron oxides on rebar's surface. As for Quaternary Amine, XRD have shown the formation of iron nitride besides iron oxides which provided higher protection from corrosion.

1. Introduction:

Due to the poor tensile characteristics of concrete, steel rebars are embedded to compensate for tensile properties. It has been estimated that about 80% of the deterioration of reinforced concrete structures is mainly coming from the corrosion of the steel rebars.

The medium of concrete has a very high alkaline nature (pH =12 -13) which leads to the formation of a passive film on rebar surface. However, since concrete structure has a porous nature, corrosion of steel rebars occurs due to : (i) Ingress of chloride ions via concrete pores, attacking and breaking down the passive film formed on rebar surface, (ii) Ingress of acidic gases such as CO_2, bringing down the pH value of medium to 7 or 8 and breaking down the passive film [1].

After the passive film is broken down, active corrosion occurs leading to the formation of corrosion products. These Products exert internal forces onto the concrete cover leading to cracking and falling of concrete leaving the reinforcement material exposed to the surrounding environment and hence further corrosion [1].

One technique that is commonly used and applied widely is the use of corrosion inhibitors. Using corrosion inhibitors within concrete mixture enhances the performance of rebar reinforcement in aggressive environments by forming a passive film on steel surface. It is also considered an economic cost-saving choice as they are added in small concentrations. In fact, the use of corrosion inhibitors had undergone several stages. At first, inorganic compounds such as calcium nitrite, nitrates, Molybdates, chromates were used [2] [3].However, their usage have been limited due to their toxicity. Then, safe organic inhibitors have been utilized such as: amines, alkanol amines then plant extracts [4] [5].

These inhibitors can either be added to fresh concrete or can be applied to concrete surface after it hardens. The second method is usually used in repair works of concrete, while the first one is used in construction phase.

Zhang *et al* [6], achieved an inhibition efficiency of 83.15% using maize gluten meal extract as an ecologically friendly inhibitor for reinforcing steel in SCP containing 3.5 wt.%NaCl. Shanmugapriya *et al.* [7] , achieved an IE% of 98 in SCP using an aqueous extract of turmeric. A. Bahgat Radwan et al [8] used behentrimonium chloride (BTC, $C_{25}H_{54}ClN$) and were able to measure an inhibition efficiency of 91, 79, and 71% in SCP solution with 3.5% NaCl at pH of 12.5, 10 and 7, respectively without showing any effect on the mechanical properties on the cured mortars. Yongqi Liu et al [9] studied the effect of ginger extract as a green inhibitor on the performance of steel rebars in Simulated Concrete Pore solution to improve resistance to chloride induced corrosion. Trabanelli et al [10] studied the performance of sodium salts of benzoic acid and particularly, 2-amino benzoic acid on protection against carbonation using Simulated concrete pore solution and found that it provided inhibition efficiency of around 60%. Monicelli et al [11] made a study about the effectiveness of sodium 2-amino-benzoate and sodium glycerol phosphate in concrete pore solution simulating both chloride and carbonated environments and found to reach inhibition efficiency of nearly 87%.

In industrial regions, the atmosphere contains acidic gases such as: CO_2 along with humidity, the concrete structure is continuously exposed to the formation of acidic solutions that can bring down the basic nature of concrete structure towards neutral and acidic nature "pH = 8" leaving the reinforcement under attack. In this paper, effects of three organic inhibitors: Polyethylene glycol, Quaternary Amine and ginger extract on corrodibility of steel rebars in simulated concrete pore solution were emphasized by applying electrochemical measurements. Moreover, scanning electron microscopy (SEM) were used to characterize the passive layers formed on rebar's surface. X-ray diffraction (XRD) showed the products formed on the steel rebars surface under each condition.

2. Materials and Methods:

2.1. Preparation of steel bar specimen:

Medium carbon steel bars "Quenched and self-Tempered" of 14 mm diameter and 10 mm length of grade B500DWR according to Egyptian Standard ES 262-2-2015 were delivered by Ezz steel, El Sokhna Plant, Egypt. The chemical composition of specimen is listed in Table 1.

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

C	Mn	Si	P	S	Cu
0.28	1.45	0.22	0.01	0.017	0.35

The samples were prepared by cold mounting as shown in Fig.1.

Figure 1 shows the mounted sample.

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2.2. Corrosion inhibitors:

Three corrosion inhibitors were chosen: Polyethylene glycol, Quaternary Amine and ginger extract.

2.3. Preparation of simulated concrete pore solution:

A saturated Calcium Hydroxide solution was prepared after adding calcium hydroxide powder to distilled water then measuring the pH value of solution using both pH tapes and pH meter to assure the value is 12.

The carbonated solution was prepared by blowing CO_2 gas into the saturated calcium hydroxide solution to simulate the carbonated concrete and the pH was measured (pH=8) [12].

2.4. Experimental Procedures:

Corrosion performance of samples in SCP have been assessed by Potentiodynamic Polarization (PDP) technique using VersaSTAT 3 device. The conventional three electrode cell system was utilized. The potential range used in PDP test was from -2 V to 2 V vs. Open Circuit Potential (OCP). The scan rate was 3 mV/s.

SEM was used to obtain images of surface of steel rebars in different media. EDAX technique was also used to attain the characterization of elemental composition of the surface. Also, X-Ray Diffraction was used to characterize the corrosion products formed on the surface of steel rebars. So, Five specimens of steel bars were immersed for 2 weeks in the following media: (i) SCP solution "pH=12", (ii) Carbonated SCP solution "pH=8", (iii) Carbonated SCP solution "pH=8" with 200 ppm Quaternary Amine, (iv) Carbonated SCP solution "pH=8" with 200 ppm Polyethylene glycol, (v) Carbonated SCP solution "pH=8" with 200 ppm Ginger extract.

3. Results and Discussion:

The PDP curves of steel bars specimens at $Ca(OH)_2$ with (pH=12) and carbonated concrete solution with (pH=8) are shown in Fig.2.

Fig.2 shows that in SCP solution at (PH=12), passivation occurs and a passive layer is formed on surface of steel bar specimen as the formed corrosion products are insoluble and produce a very thin protective coating which limits the metal loss from surface. While, in carbonated concrete solution with (pH=8), active corrosion occurs as the passive film is broken down as the acidic gas (CO_2) neutralizes the pH of pore solution [1].
It is noticed that the passivation potential is -0.76 V. The corrosion current I_{corr} increased as the pH of solution decreased indicating active corrosion

and metal loss occurs.

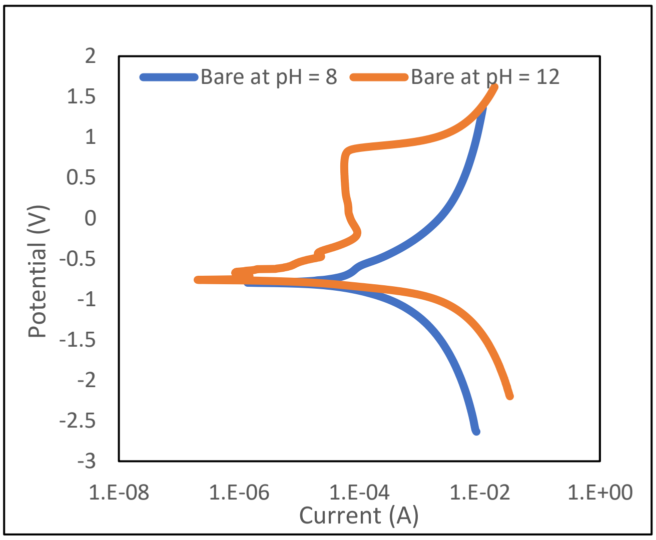


Figure 2 shows PDP curves of steel rebars specimens in SCP solution (pH=12) and carbonated SCP solution (pH=8)

PDP curves of three systems (Quaternary Amine, Polyethylene glycol and Ginger extract) are shown in figures 3, 4 and 5 respectively. It has been demonstrated that increasing the amount of each inhibitor leads to shifting polarization curves to left side i.e. less dissolution.

Table 2 shows comparison of corrosion potential and rate between the two conditions (pH=12 and pH=8)

Sample	E_{corr} (V)	Corrosion rate (mpy)
pH=12	-0.76	2.84
pH=8	-0.80	11.67

Table 3 shows a comparison of corrosion rate values of each system and exhibits the inhibition efficiency as a function of the inhibitor concentration. It is observed that Quaternary Amine, Polyethylene glycol and Ginger extract have achieved maximum inhibition efficiency of 90.30 %, 31.42 % and 67.89 % respectively. It is clear that Quaternary Amine and Ginger extract gave the better results. The inhibitor efficiency (IE) can be calculated from either of the following equations:

$$IE_n\ (\%) = \left(1 - \frac{C.R_n}{C.R_o}\right) \times 100$$

Where $C.R_o$ is corrosion rate of specimen when no inhibitor is added and $C.R_n$ is corrosion rate of specimen when a certain amount of inhibior is added to solution.

Figures 6, 7 and 8 shows the effect of each inhibitor's concentration on corrosion rate and inhibition efficiency.

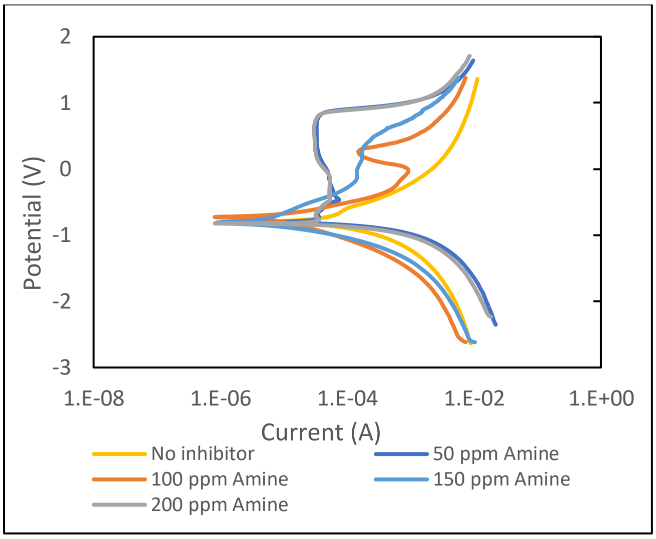


Figure 3 shows PDP curves of steel rebars specimens in Carbonated SCP solutions with different concentrations of Quaternary Amine.

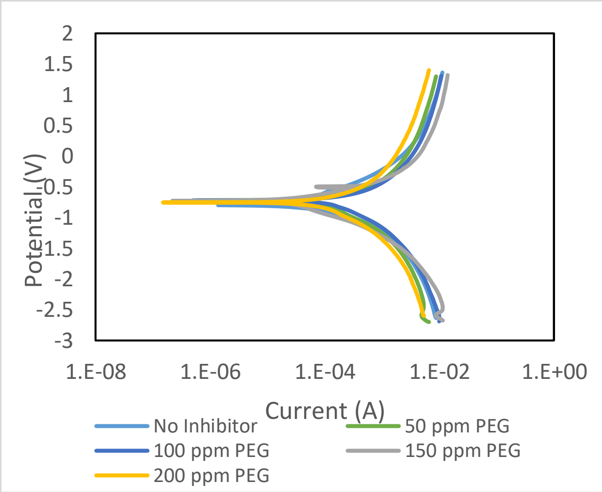


Figure 4 shows PDP curves of steel rebars specimens in Carbonated SCP solutions with different concentrations of Polyethylene Glycol.

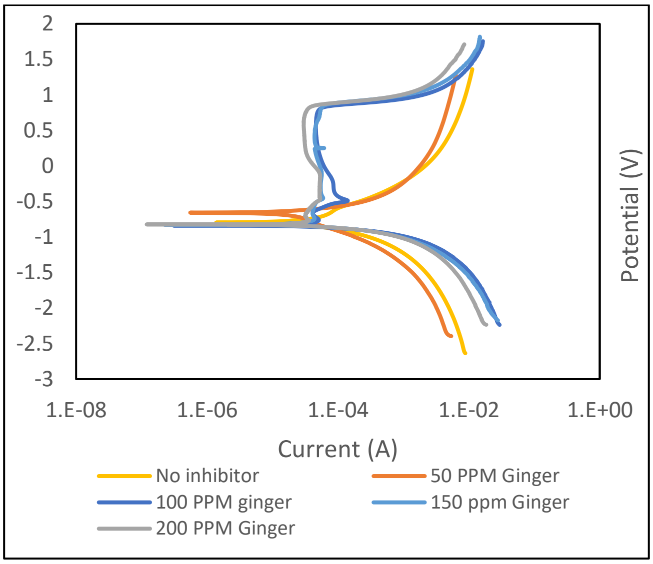


Figure 5 shows PDP curves of steel rebars specimens in Carbonated SCP solutions with different concentrations of Ginger Extract.

The formation of carbonaceous organic film is thought to occur via physical adsorption phenomenon. The presence of polar functional groups containing O, N and C atoms and the bonds C=O and N=O provide lone pair electrons and form co-ordinate bonds within the vacant d-orbitals of iron (Fe). This will make these organic species adhere to the surface of steel [6] [9]. In concrete, these inhibitors penetrate through concrete pores and get adsorbed on rebar surface. They inhibit corrosion via forming a protective film leading to inhibition of ferrous decomposition (anodic reaction) and restriction of oxygen access (cathodic reaction) to the rebar surface [12].

Table 3 shows corrosion potential, corrosion current and Inhibition efficiency of each inhibitor at different concentrations.

Inhibitor	Quantity added (ppm)	E_{corr} (V)	Corrosion rate (mpy)	Inhibitor efficiency (%)
Quaternary Amine	0	-0.80	11.67	0.0
	50	-0.80	7.23	38.07
	100	-0.73	4.10	64.91
	150	-0.81	1.83	84.31
	200	-0.82	1.13	90.30
Polyethylene Glycol	0	-0.80	11.67	0
	50	-0.75	11.43	2.06
	100	-0.73	11.03	5.50
	150	-0.72	9.90	15.14
	200	-0.72	8.00	31.42
Ginger Extract	0	-0.80	11.67	0
	50	-0.76	8.48	27.29
	100	-0.84	5.06	56.65
	150	-0.83	4.15	64.45

200	-0.82	3.75	67.89

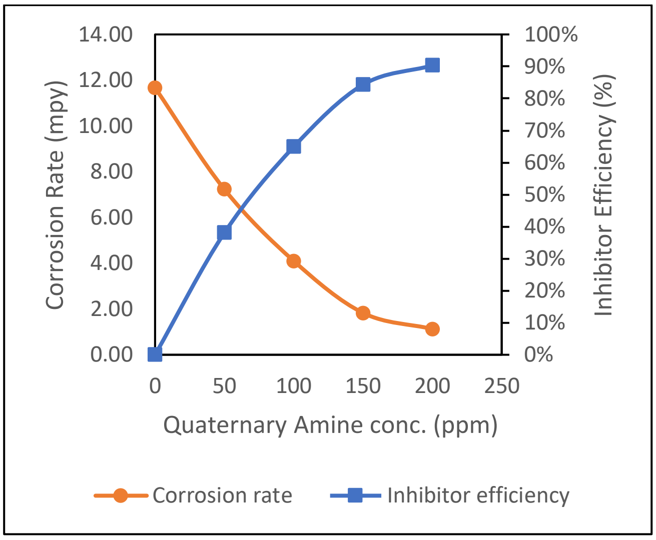


Figure 6 shows Corrosion Rate and Inhibition Efficiency of Quaternary Amine systems.

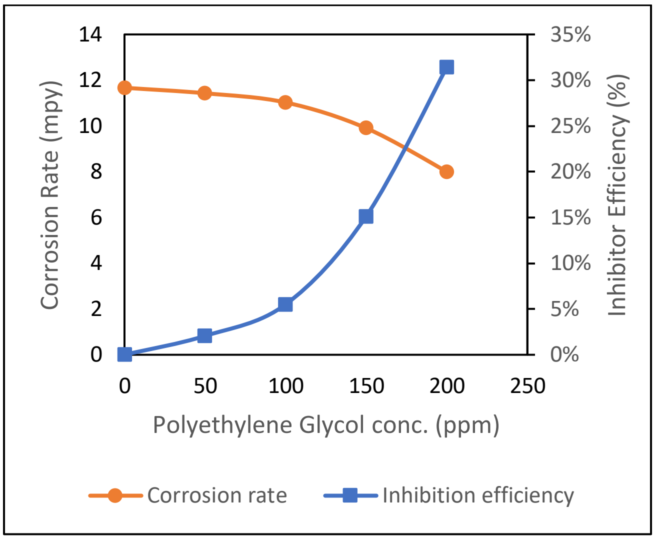


Figure 7 shows Corrosion Rate and Inhibition Efficiency of Polyethylene glycol systems.

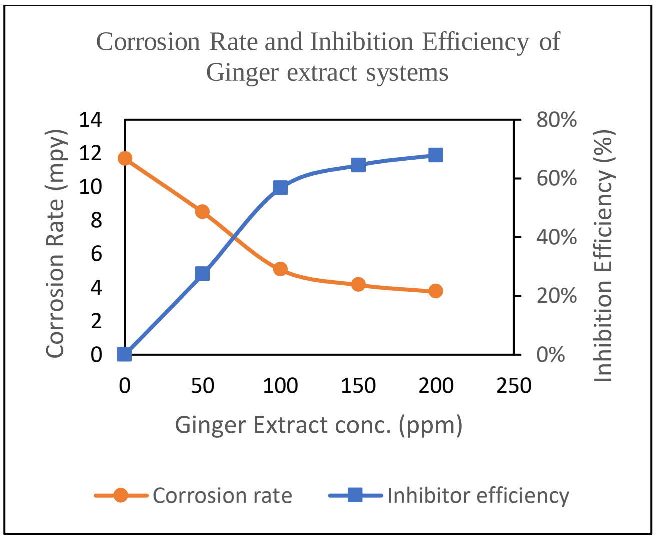


Figure 8 shows Corrosion Rate and Inhibition Efficiency of Ginger extract systems.

On basis of previous results, the inhibition behavior of the used inhibitors can be related to the adsorption of inhibitors' ingredients on rebar surface enhancing corrosion resistance of steel rebars in each condition.

To make sure of the formation of protective films, SEM-EDAX is used for characterizing the surface topography and for determining the chemical composition of elements present on surface. Fig.9 (a to e) shows surface morphologies of steel samples immersed in each medium. When looking at Fig 9(a) of steel rebar in simulated concrete solution, the surface is smooth -indicating formation of protective film- when compared to Fig 9(b) of carbonated concrete solution (pH= 8) which showed rough surface indicating higher corrosion rate. As for Fig 9(c, d, e), samples immersed in carbonated concrete solution (pH=8) with presence of inhibitors showed smoother surfaces and this can be ascribed to formation of protective carbonaceous organic films.

EDAX spectra are shown in Fig.10 for steel rebar specimen immersed in each medium along with the chemical composition of elements present in surface. Higher oxygen weight % in Fig 10(b) indicates existence of ferric oxides and formation of rust at low values of pH (pH= 8) due to corrosive medium and decomposition of protective passive film that was formed at higher values of (pH= 12). Fig 10(c,d,e) show the existence of C and O along with nitrogen in the sample immersed in solution containing Quaternary Amine Fig 10(d).

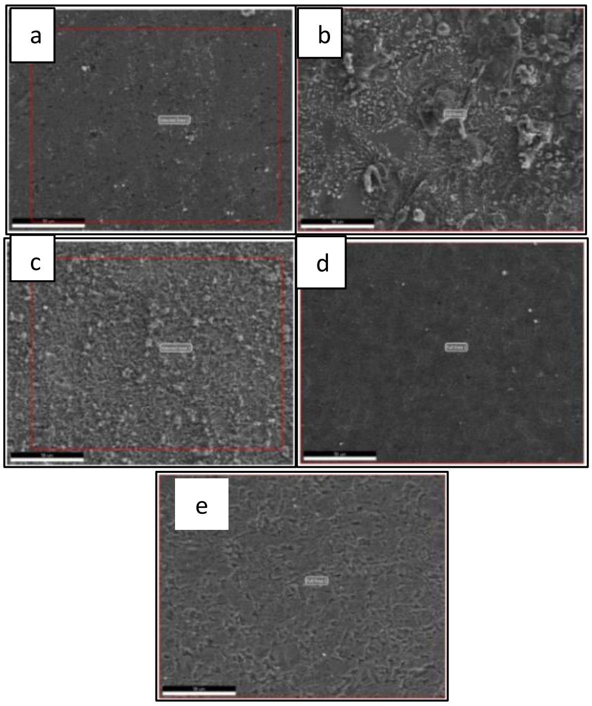
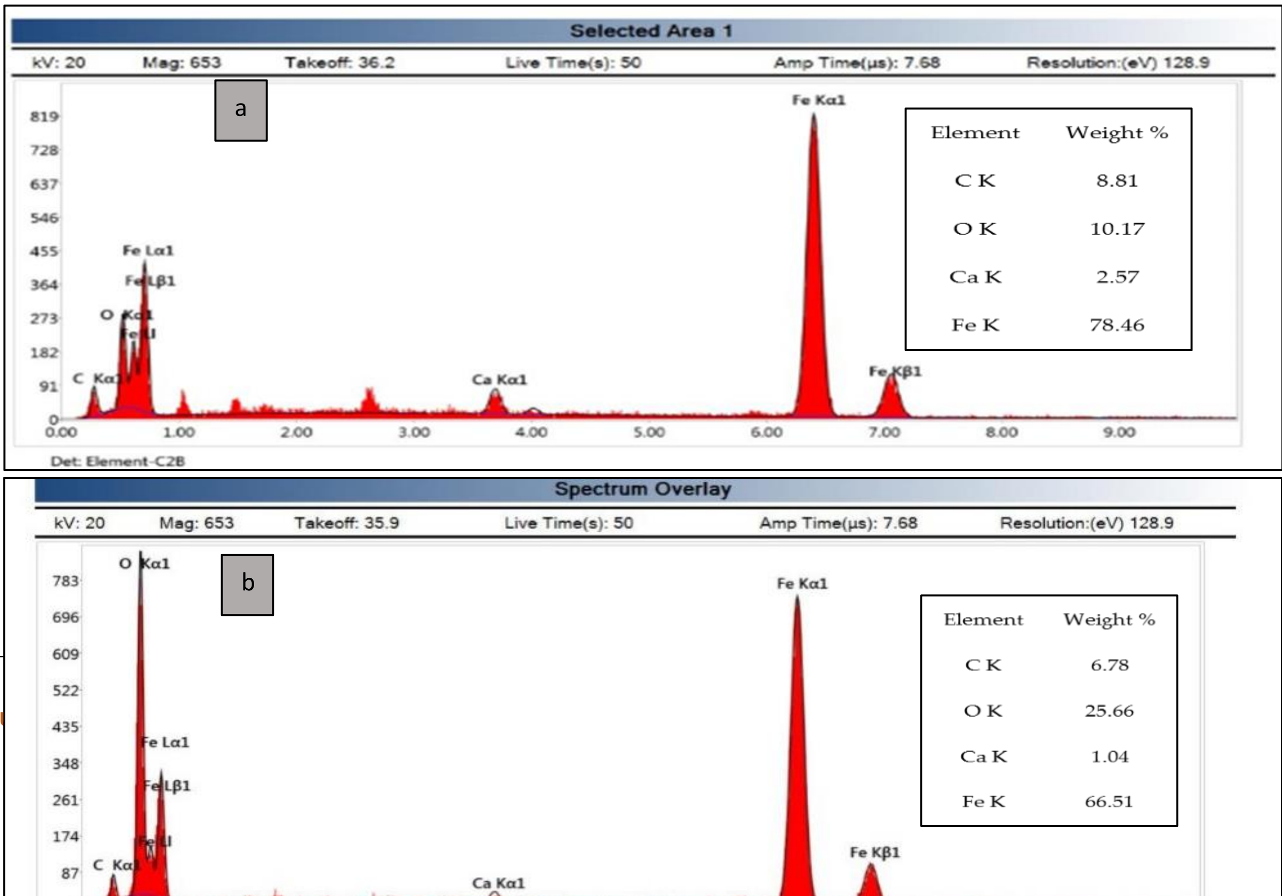


Figure 9 SEM images of steel rebar surface exposed to different media for 2 weeks (a: pH=12, b: pH=8, c: pH=8 in presence of 200 ppm PEG, d: pH=8 in presence of 200 ppm quaternary amine, e: pH=8 in presence of 200 ppm ginger extract.



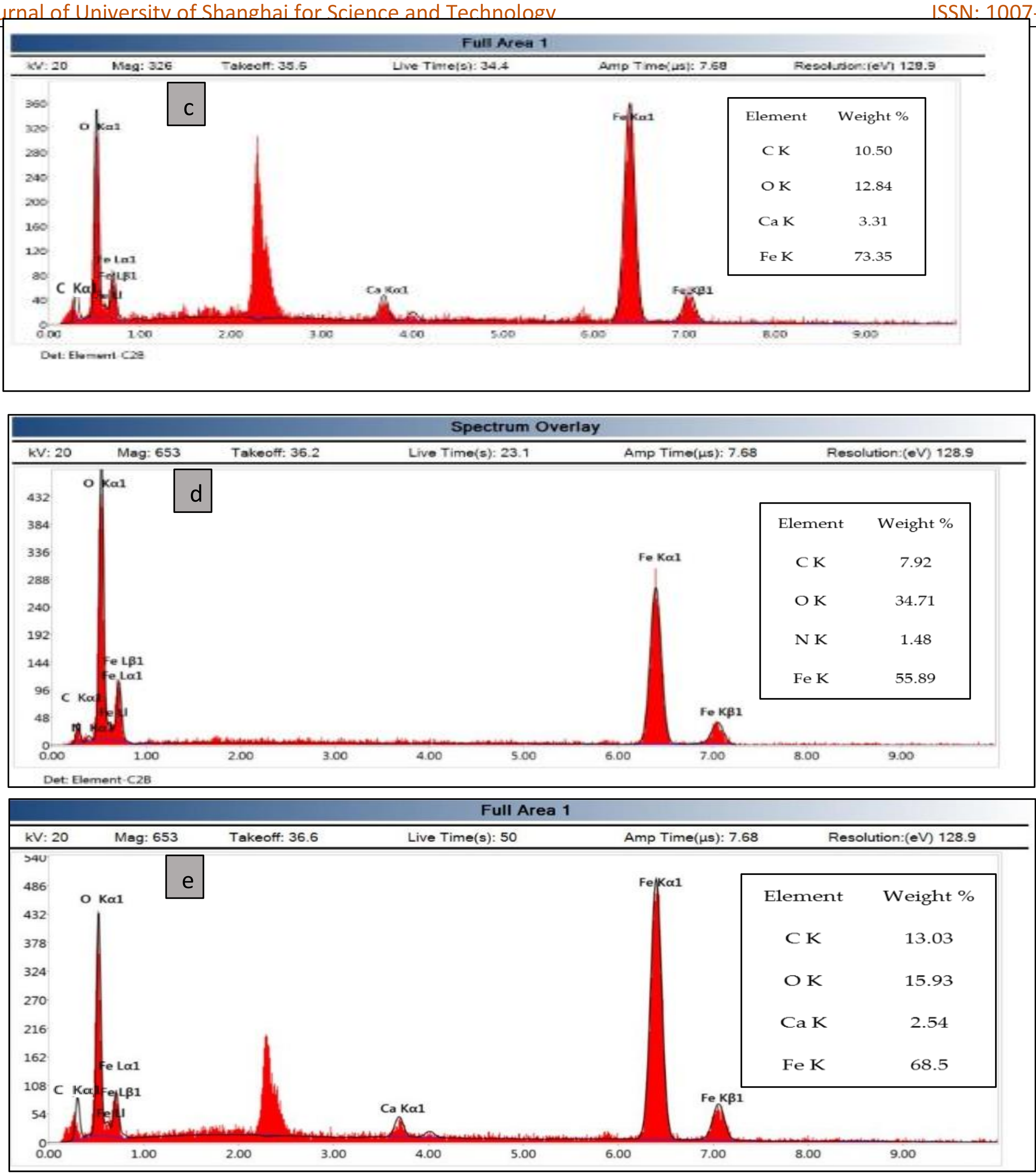
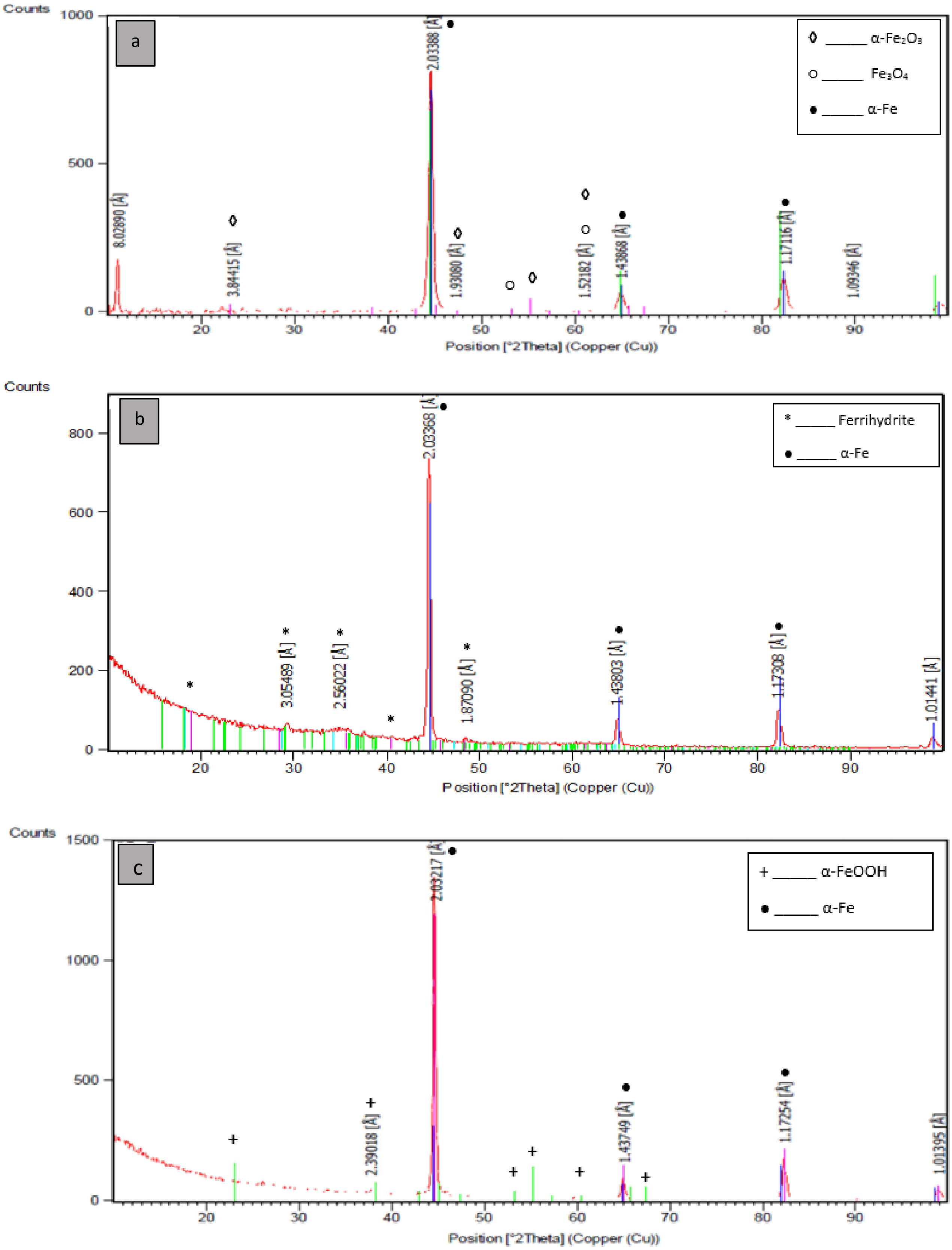


Figure 10 EDAX spectra of steel rebar surface exposed to different media for 2 weeks (a: pH=12, b: pH=8, c: pH=8 in presence of 200 ppm PEG, d: pH=8 in presence of 200 ppm quaternary amine, e: pH=8 in presence of 200 ppm ginger extract.


a
Counts
1000
500
0
20
30
40
50
60
70
80
90
Position [°2Theta] (Copper (Cu))
◊ α-Fe2O3
○ Fe3O4
● α-Fe
8.02890 [Å]
3.84415 [Å]
2.03388 [Å]
1.93080 [Å]
1.52182 [Å]
1.43868 [Å]
1.17116 [Å]
1.09346 [Å]
b
Counts
800
600
400
200
0
20
30
40
50
60
70
80
90
Position [°2Theta] (Copper (Cu))
* Ferrihydrite
● α-Fe
3.05489 [Å]
2.56022 [Å]
2.03368 [Å]
1.87090 [Å]
1.43803 [Å]
1.17308 [Å]
1.01441 [Å]
c
Counts
1500
1000
500
0
20
30
40
50
60
70
80
90
Position [°2Theta] (Copper (Cu))
+ α-FeOOH
● α-Fe
2.39018 [Å]
2.03217 [Å]
1.43749 [Å]
1.17254 [Å]
1.01395 [Å]

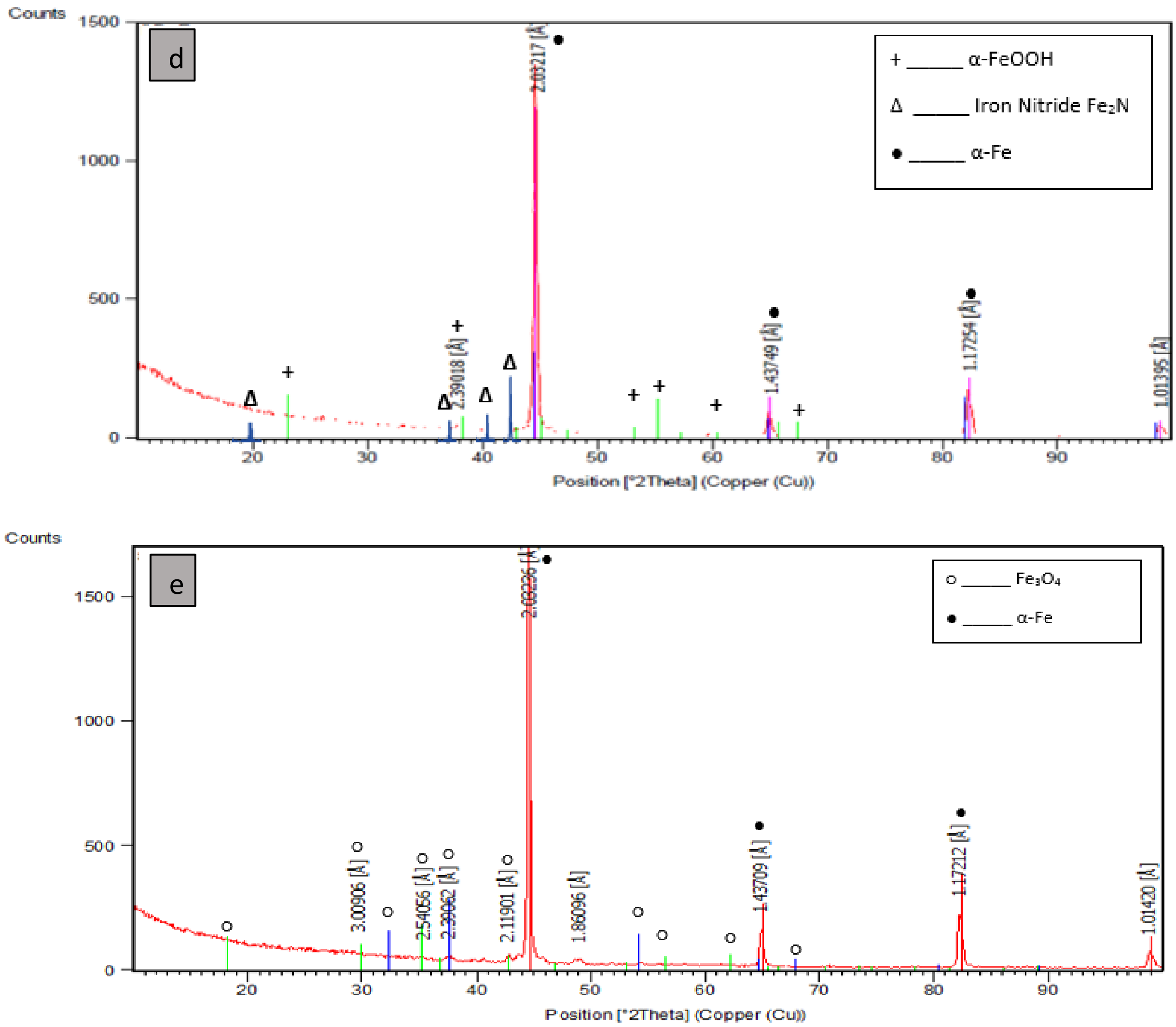


Figure 11 XRD patterns of steel rebar surface exposed to different media for 2 weeks (a: pH=12, b: pH=8, c: pH=8 in presence of 200 ppm PEG, d: pH=8 in presence of 200 ppm quaternary amine, e: pH=8 in presence of 200 ppm ginger extract.

XRD patterns in Fig.11 (a to e) shows a characterization of corrosion products formed on the surface of samples immersed in these five different media. These corrosion products are listed in table 4.

Table4 shows compounds formed on steel rebar surface immersed in each condition for 2 weeks according to XRD patterns (a: pH=12, b: pH=8, c: pH=8 in presence of 200 ppm PEG, d: pH=8 in presence of 200 ppm quaternary amine, e: pH=8 in presence of 200 ppm ginger extract.

Condition	Products Formed
Sample at pH = 12	α-Fe_2O_3 + Fe_3O_4 (Protective)
Sample at pH = 8	Fe_2O_3.0.5(H_2O) "Ferrihydrite" (rust)
Sample at pH = 8 , with Polyethylene	α-FeO(OH) (protective)
Sample at pH = 8 , with ginger	Fe_3O_4 (Protective)
Sample at pH = 8 , with Amine	α-FeO(OH) (protective) + Iron nitride (Protective)

4. Conclusions:

The following conclusions can be stated from this paper:

1) Steel rebar in concrete is passivated due to the high pH of concrete (pH=12) which causes the formation of passive film on its surface.
2) The ingress of acidic gases such as: CO_2 brings down the pH value of concrete medium to 8 causing decomposition of the passive layer on the surface and initiating corrosion.
3) The organic compounds of Polyethylene, Ginger and Quaternary Amine are environmentally friendly corrosion inhibitors for steel rebars in simulated concrete pore solution of calcium Hydroxide $Ca(OH)_2$. They decrease the corrosion rate of steel rebars in carbonated concrete solution of (pH= 8) from 11.67 mpy to 8, 3.75 and 1.13 mpy respectively.
4) Corrosion rate of steel rebars decrease by increasing inhibitor concentrations. Inhibition efficiency reached to 31.42%, 67.89% and 90.30% for the polyethylene and ginger and Amine respectively.
5) SEM images show uniform corrosion when immersing in test solution with pH = 8 and without inhibitors.
6) While those of the specimens after adding 200 ppm of polyethylene, Amine and ginger to test solutions, show the formation of protective film which decreases corrosion rate of rebar.
7) XRD patterns show the formed corrosion products in each case.

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