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Application the Principle of Sacrificial Anodes to Corrosive Cells Created in Different pH Media

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Abstract

Corrosion is a common concern that arises from the use of iron metal components in daily life, both at home and industrial scale. Cathodic protection employing a sacrificial anode is one of several ways for preventing iron corrosion and it is a common industrial method for preventing corrosion in underground pipes, ships, and storage tanks. The two basic components of the cathodic protection method are the metal to be protected, a second metal is used as a sacrificial anode to prevent corrosion. This study involved preparing corrosive cells with different pH corrosive media (1,3,5,7,9 and11) in different immersion times (30, 60, and 90 days). It aimed to apply the principle of sacrificial anodes by using zinc and iron as sacrificial anodes for the protection of iron and copper respectively. The magnitudes of the percentage of corrosion (% corrosion) and corrosion rate (CR) were observed by the weight loss method for Fe without protection, Fe/Zn couple, and Fe/Cu couple. The CR varies with varied immersion times and acid-alkaline concentrations. The results show a large % corrosion and CR in acidic media, with varying degrees, compared to the alkaline and neutral media. At pH=1 and 90 days immersion time, the % corrosion reached 92.26% and CR reached 102.33 mpy, this proved that the acidic media accelerated the corrosion of iron. Promising results were obtained in which corrosion rates were reduced and determined by applying for protection with the sacrificial anode. The CR of iron declined from 102.33 mpy to 13.31 mpy at pH=1 and after 90 days for Fe/Zn couple. Whereas, CR of Fe/Cu couple increased significantly from 13.31 mpy to 30.94 mpy at pH=1 and after 90 days when it compared with the CR of Fe/Zn couple.

Keywords: metallic corrosion, corrosion control, cathodic protection, sacrificial anodes.

1. Introduction

Nowadays, corrosion of metallic equipment has emerged as one of the most difficult problems in the industrial sector. Many industries have lost billions of dollars because of corrosion [1]. The environment's corrosive attack on metallic components may have an impact on the overall process's functionality. Corrosion-induced component failure causes direct and indirect economic losses, as well as product quality issues and delays in plant shutdown owing to necessary repairs [2]. Iron and its alloys, such as steel, have been widely used as a primary component in the production of a wide range of metallic equipment for use in crude oil and natural gas refineries, petrochemical plants, agriculture, and civil construction [3]. Despite its benefits such as low cost, good malleability and formability, and customizable surface hardness, steel's limited corrosion resistance in severe settings remains a prohibitive, difficult, and problematic issue [4].

Metals are stable in a vacuum for long periods of time, but when exposed to the atmosphere or aqueous environments without protection, they corrode. The metal's surface oxidizes, and electrochemical processes occur at the metal's interaction with the environment. The production of local microcells is caused by the development of localized anodes and cathodes on the metallic surface. At the anodes, the metal is oxidized, whereas, at the cathodes, the corrosion process is maintained by the reduction of some species from the environment (namely protons in acidic solutions, or oxygen in neutral and moderately alkaline media) [5].

Corrosion control is a technique for preventing damage. Controlling can be done in a variety of ways, including using numerous approaches, such as coatings, inhibitors, electrochemical methods (anodic and cathodic protection) [6–12]. Cathodic protection with sacrificial anodes is one of the many ways available to prevent or control corrosion. The principle of cathodic protection using sacrificial anodes is the same as that of galvanic cells [13–16]. Metals having a greater or higher potential for oxidation in the Electromotive-Emf series (more active) become

anodic to metals with a lower potential for oxidation and are consumed during electrochemical processes in these cells. Cathodic protection is applied to the surface of less active metals. The current flowing through anodic metal electrolytes is the cause of this [5,17].

The findings of this study designed to investigate the effect of various pH corrosive media (1,3,5,7,9 and11) in different immersion times (30, 60, and 90 days), on the percentage of corrosion (% corrosion) and the corrosion rate (CR) of steel, as well as to examine the effectiveness of zinc and iron as sacrificial anodes for the protection of iron and copper, respectively. Its aim at investigating the effect of varying anode material on the rate of corrosion and the corresponding protection effectiveness of the anode at room temperature.

2. Experimental
2.1. Preparation of specimens
All of the metallic elements used in this work were the local source, including the iron nails (steel 65x 3 mm), zinc strips, and copper wires. The nominal chemical composition of the iron (steel) nails was 0.130 C, 0.031 S, 0.147 Cu, 0.010 Co, 0.173 Si, 0.397 Mn, 0.017 P, 0.021 Zn, 0.0005 Ca, and the rest 99.2 Fe [18]. The zinc anode utilized had a zinc content of 99.4% while the copper wire had a copper content of 99.7%.

2.2. Preparation of corrosive media
The corrosive media used in this work were water with various pH (1,3,5,7,9 and11). The pH measured using a pH meter was adjusted by adding varying amounts of dilute HCl and NaOH for preparing acidic and alkaline media respectively.

2.3. Weight Loss Experiments

Part 1- Fe without protection: Iron nails were weighted separately, then fully were immersed in Petri dishes with various pH corrosive media (1,3,5,7,9 and11) for different immersion times (30, 60, and 90 days).

Part 2- cathodic protection with Fe/Zn couple: Iron nails were weighted separately, then tightly wrapped each one with zinc stripe metal after that fully immersed in Petri dishes with various pH corrosive media (1,3,5,7,9 and11) for different immersion times (30, 60, and 90 days).

Part 3- cathodic protection with Fe/Cu couple: Iron nails were weighted separately, then tightly wrapped each one with copper wire metal, after that fully immersed in the same Petri dishes that used in part 2 with various pH corrosive media (1,3,5,7,9 and11) for different immersion times (30, 60, and 90 days).

After immersion times, each of the iron nails, in these three parts, was taken out and washed with tap water followed by soaks in acetic acid (5%) for 15 min. in order to remove all products of corrosion on the surface of the iron nails. Washed again with distilled water then dried by clean tissue and hot air, final weight, and kept in a desiccator for 3 hours.

The corrosion rate CR of iron (with and without protection) in different pH corrosive media for exposure time (30, 60, and 90 days) has been determined by weight loss at room temperature. From the weight losing data, the CR was calculated by applying Eq. (1) [19].

$$CR(mpy) = \frac{534W}{DAT} \quad ......(1)$$

Where:
CR (mpy): is the corrosion rate in mills per year.
W: is weight losing (mg).
D: density (g/cm^3).
A: area of the iron nail (in^2).
T: time exposure (h).

3. Results and discussion
3.1. Corrosion mechanism of iron in different pH corrosive media
Corrosion of iron and its alloys, such as steel, is known as rusting. Although other metals oxidize in the same way, these oxides are not typically referred to as rust. There must be certain circumstances for rusting to occur. Iron undergoes this reaction in the presence of oxygen and water or moisture, resulting in a sequence of iron oxide, a reddish-brown color compound is known as rust. Rust is typically composed of hydrated iron (III) oxide $Fe_2O_3.3H_2O$, as well as iron (III) hydroxide $Fe(OH)_3$ in wet conditions [20].

Rusting begins when solid iron oxidizes in water (anode reaction). Iron atoms transfer 2e$^-$ and form Fe^{+2} as follows in Eq. (2):
$$Fe_{(s)} \longrightarrow Fe^{+2}{}_{(aq)} + 2e^- \quad ......(2)$$
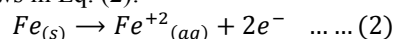
In aerated water, these electrons will quickly react with H$^+$ and dissolved O$_2$ in water (cathode reaction), Eq. (3):

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O_{(l)} \quad ......(3)$$
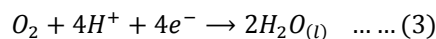
In the presence of acids, the reactions listed above are accelerated. The hydrogen ions react with electrons at extremely low pHs, creating hydrogen gas, accompanied by the cathodic reaction that corresponds, Eq. (4):

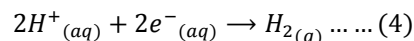$$2H^+{}_{(aq)} + 2e^-{}_{(aq)} \longrightarrow H_{2(g)} ......(4)$$

Figure -1 reveals the rusting of iron in acidic media. The hydrogen evolution reaction controls the corrosion of metals in neutral or acidic solutions cathodically [20,21].
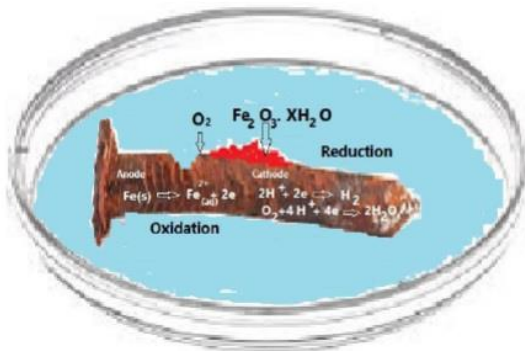

Fig. 1. Rusting of iron in acidic media.

When the pH rise, the electrolyte is in rich hydroxide ions, at the same time iron atoms transfer 2e⁻ and form Fe^{+2}, Figure -2, Eqs. (5,6):
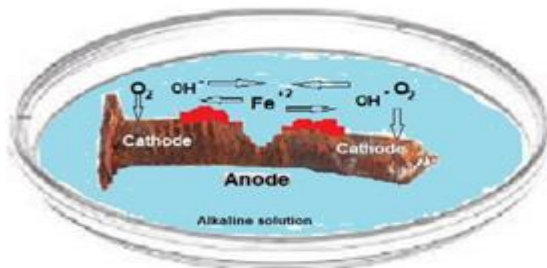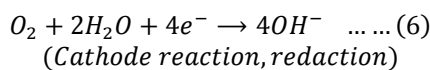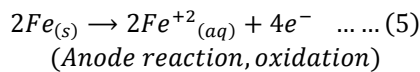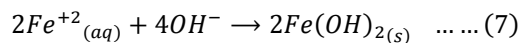

Fig. 2. Rusting of iron in alkaline media.

$$2Fe_{(s)} \longrightarrow 2Fe^{+2}{}_{(aq)} + 4e^- \quad ......(5)$$
$$(Anode\ reaction, oxidation)$$

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \quad ......(6)$$
$$(Cathode\ reaction, redaction)$$

Fe^{+2} move through the electrolytic solution towards the cathode to interact with the product of the reduction process and produce a solid reddish-brown color product (rust) as in the following equation Eq. (7):

$$2Fe^{+2}{}_{(aq)} + 4OH^- \longrightarrow 2Fe(OH)_{2(s)} \quad ......(7)$$

The reaction continues in presence of oxygen to produce rust. Iron hydroxide (III) undergoes a dehydration process that turns it into a red oxide (III) (Dehydration), Figure-3, according to the following equation, Eq. (8): [22]:

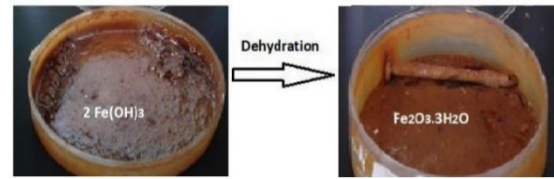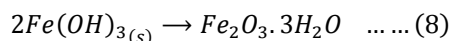$$2Fe(OH)_{3(s)} \longrightarrow Fe_2O_3 . 3H_2O \quad ......(8)$$

Fig. 3. Dehydration of iron rust.

3.2. Effect of immersion time on % corrosion

Corrosion is a natural process that occurs when a material's qualities deteriorate over time as a result of its interaction with the environment [23]. Cathodic protection is a corrosion control technique that involves making a metal surface the cathode of an electrochemical cell [24]. Tables (1,2 and 3) and Figures (4,5 and 6) show that as the immersion time increased, the % corrosion increased. For instance in pH = 1, the % corrosion of Fe without protection increased "19.3%, 43.88%, 92.26%" when immersion time increased (30, 60 and 90 days) respectively.

In the same manner, the % corrosion of Fe/Zn couple increased "5.24%, 15.35%, 21.82%" when immersion time increased (30, 60, and 90 days) respectively. Also for Fe/Cu couple, the % corrosion increased "12.67%, 43.88%, 49.84%" when immersion time increased (30, 60, and 90 days) respectively.
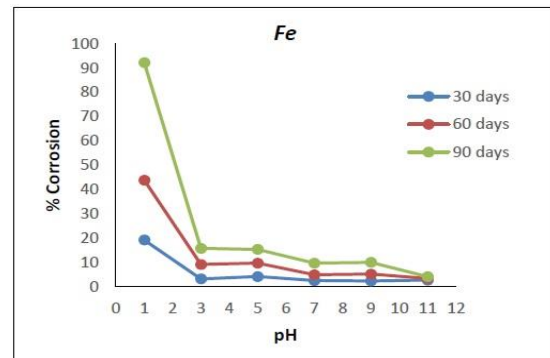

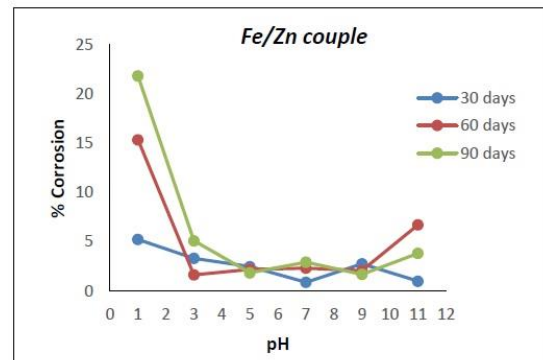Fig. 4. The effect of immersion time and pH on % corrosion for Fe without protection.

Fig. 5. The effect of immersion time and pH on % corrosion for Fe/Zn couple.

Table 1: Weight loss, %corrosion and CR of Fe without protection for different pH media and at differentimmersion times.

pH	Fe without protection								
	30 days			60 days			90 days		
	wt. loss gm.	% corrosion	CR (mpy)	wt. loss gm.	% corrosion	CR (mpy)	wt. loss gm.	% corrosion	CR (mpy)
1	0.691	19.3	64.47896	1.65	43.88	76.982839	3.29	92.26	102.3327434
3	0.118	3.3	11.010879	0.331	9.2	15.443224	0.568	15.83	17.66717272
5	0.138	4.26	12.877129	0.314	9.76	14.650068	0.493	15.43	15.33435942
7	0.093	2.6	8.6780655	0.243	4.97	11.337473	0.474	9.77	14.74338005
9	0.118	2.44	11.010879	0.253	5.25	11.804035	0.48	10.11	14.93000512
11	0.135	2.78	12.597192	0.167	3.45	7.7915964	0.227	4.18	7.060648253

Table 2 : Weight loss, %corrosion and CR of Fe/Zn couple for different pH media and at different immersion times.

pH	Fe/Zn couple								
	30 days			60 days			90 days		
	wt. loss gm.	% corrosion	CR (mpy)	wt. loss gm.	% corrosion	CR (mpy)	wt. loss gm.	% corrosion	CR (mpy)
1	0.104	5.24	9.7045033	0.303	15.35	14.136849	0.428	21.82	13.3125879
3	0.066	3.32	6.1586271	0.033	1.65	1.5396568	0.1	5.11	3.110417733
5	0.048	2.49	4.4790015	0.044	2.21	2.0528757	0.037	1.86	1.150854561
7	0.018	0.9	1.6796256	0.047	2.33	2.1928445	0.059	2.93	1.835146462
9	0.054	2.76	5.0388767	0.04	2.07	1.8662506	0.034	1.7	1.057542029
11	0.02	1	1.8662506	0.131	6.72	6.1119708	0.075	3.84	2.332813299

Table 3 :Weight loss, %corrosion and CR of Fe/Cu couple for different pH media and at different immersion times.

pH	Fe/Cu couple								
	30 days			60 days			90 days		
	wt. loss gm.	% corrosion	CR (mpy)	wt. loss gm.	% corrosion	CR (mpy)	wt. loss gm.	% corrosion	CR (mpy)
1	0.252	12.67	23.514758	0.625	31.4	29.160166	0.995	49.84	30.94865644
3	0.134	6.75	12.503879	0.301	15.46	14.043536	0.275	13.81	8.553648765
5	0.157	7.9	14.650068	0.25	12.69	11.664066	0.24	12.16	7.465002558
7	0.144	7.27	13.437005	0.279	14.12	13.017098	0.346	17.3	10.76204535
9	0.219	11.08	20.435445	0.361	18.44	16.842912	0.31	15.86	9.642294971
11	0.18	9.31	16.796256	0.228	11.5	10.637629	0.203	10.29	6.314147997

3.3. Effect of pH on the % Corrosion

When the concentration of corrosive acid media (low pH) is raised, the % corrosion increases as well. This is primarily owing to the fact that as the acid concentration rises, the amount of hydrogen ions, which are the active species, rises as well [25]. Figure – 7 reveals the effect of acidic and neutral media on % corrosion of iron after 90 days immersion times. It is observed that at pH=1,3,5 and 7, the % corrosion reached "92.26%, 15.83%, 15.43% and 9.77%" respectively.
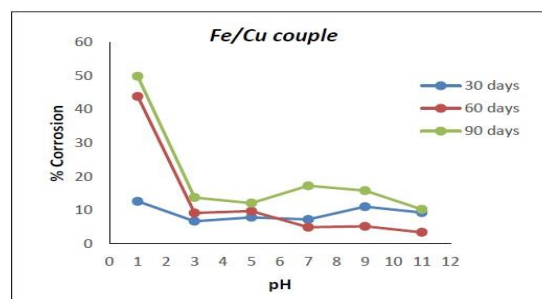

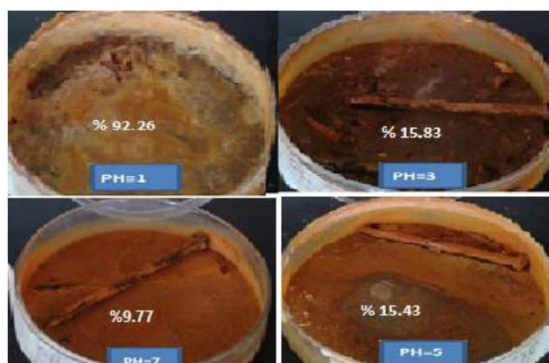Fig. 6. The effect of immersion time and pH on % corrosion for Fe/Cu couple.

Fig. 7. The % corrosion at acidic and nuetral media.

The % corrosion of iron after 90 days in alkaline media was studied, and it was revealed that iron corroded in these media but in a low rate. The % corrosion was reduced to 4.18 % as the concentration of corrosive alkaline media was increased (pH=11), Figures – 8. This is due to the creation of a Fe(OH)$_3$ layer (thin film and foam) on the surface of the iron specimen which decreases the % corrosion when the concentration of alkaline increases [26]. The graphical results in Figure - 4 show that the % corrosion of the Fe without protection, in acidic media, is higher than that of the neutral and alkaline media. For the protected specimen, Fe/Zn couple Figure - 5, there was a slight change in the % corrosion in some pH values and for certain exposure periods such as pH=3, 60 days. We suggest that there are some reasons that affected the % corrosion of the aforementioned cases, including leaving unprotected areas of samples and also forming membrane or layers of corrosive residues such as oxides and other compounds, in addition to the variation in dissolved oxygen levels in some corrosive media.
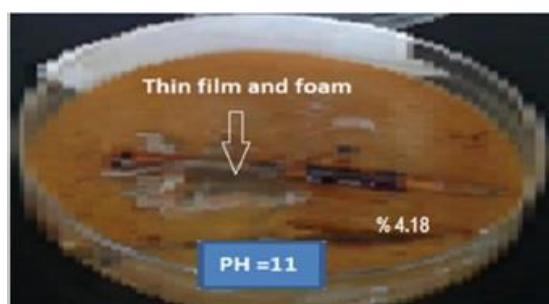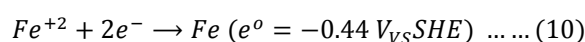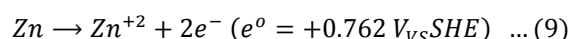

Fig. 8. The % corrosion at alkaline media.

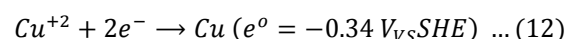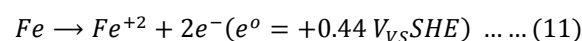### 3.4. Corrosion rate and Cathodic protection

The cathodic protection principle can be clarified as follows: when two metals are electrically linked and immersed in an electrolyte such as acid or alkaline, electrons flow from the more active metal to the less active metal due to changes in electrical potential—

which is the driving force. The more active metal, the anode, supplies current and dissolves gradually into ions in the electrolyte, while simultaneously producing electrons that the cathode (the less active) gets through the metallic connection (galvanic). As a result, the cathode becomes negatively polarized and corrosion-resistant [27].

At this present work, the iron nail was coupled with the more electropositive metal like zinc that acts as a sacrificial anode to protect the iron nail from corrosion. On the other hand, the iron nail was coupled with less electropositive metals like copper, so iron will act as a sacrificial anode to protect the copper from corrosion [1,20]. The reactions that occur in the Fe/Zn couple are as follows, Eqs. (9,10) [12]:

$$Zn \longrightarrow Zn^{+2} + 2e^- \ (e^o = +0.762 \ V_{VS}SHE) \ ...(9)$$

$$Fe^{+2} + 2e^- \longrightarrow Fe \ (e^o = -0.44 \ V_{VS}SHE) \ ......(10)$$

And the reactions that occur in the Fe/Cu couple are as follows, Eqs

$$Fe \longrightarrow Fe^{+2} + 2e^- (e^o = +0.44 \ V_{VS}SHE) \ ......(11)$$

$$Cu^{+2} + 2e^- \longrightarrow Cu \ (e^o = -0.34 \ V_{VS}SHE) \ ...(12)$$

The variation of CR for iron without protection, Fe/Zn couple and Fe/Cu couple that immersion in different pH corrosive media (1,3,5,7,9 and 11) for (30, 60 and 90 days) are shown in the Tables (1,2 and 3) and Figures (9,10 and 11). Results proved that the CR of iron without protection was declined, from 102.33 mpy to 13.31 mpy at pH=1 and after 90 days, when it coupled with Zn that acts as a sacrificial anode and corroded instead of it. Whereas, CR of Fe/Cu couple increased significantly from 13.31 mpy to 30.94 mpy at pH=1 and after 90 days when compared with CR of Fe/Zn couple because in Fe/Cu the iron acts as sacrificial anode and corroded instead of Cu. It was also found that the longer exposure time to the media, the higher the CR, with the continued increase in weight loss.
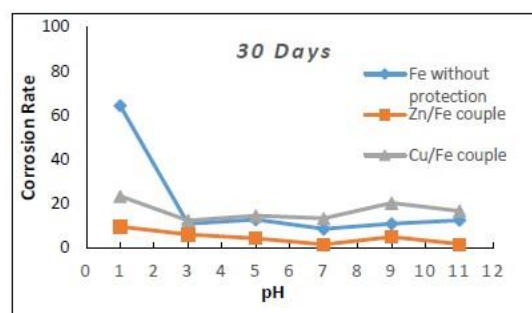

Fig. 9. The CR for Fe without protection, Fe/Zn couple and Fe/Cu couple that immersion in different pH corrosive media for 30 days
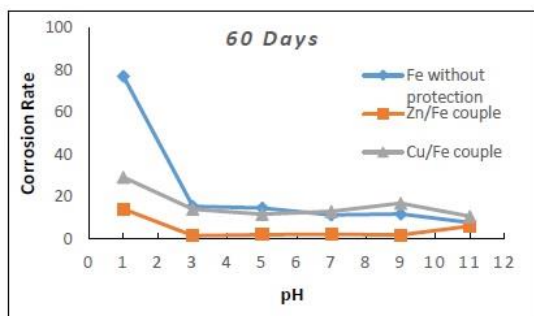
Fig. 10. The CR for Fe without protection, Fe/Zn couple and Fe/Cu couple that immersion in different pH corrosive media for 60 days
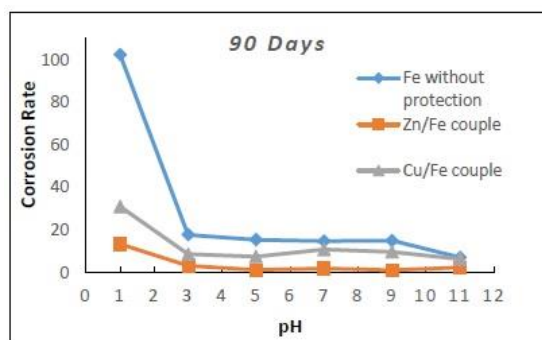

Fig. 11. The CR for Fe without protection, Fe/Zn couple and Fe/Cu couple that immersion in different pH corrosive media for 90 days

4. Conclusions

1. The % corrosion of iron without protection increased at pH=1 (acidic media) to reach 92.26% after 90 days. This indicates that in the presence of an acid, the corrosion was accelerated. While the % corrosion decreased to 4.18 % at pH=11 (alkaline media) after 90 days, this is due to the formation of a $Fe(OH)_3$ layer which decreases the % corrosion.

2. The principle of sacrificial anode became clear through the comparison of CR of iron without protection with CR of Fe/Zn couple and CR of Fe/Cu couple.

3. When iron and zinc were combined, the CR decreased from 102.33 mpy to 13.31 mpy at pH=1 and after 90 days. Because of its duty as a cathode, the iron is protected in this situation. By flowing electrons towards the iron, the sacrificed zinc should be corroded.

4. When copper is paired with iron, the CR of the iron increases significantly from 13.31 mpy to 30.94 mpy at pH=1 and after 90 days when compared with CR of Fe/Zn couple. Because of

its function as a cathode, copper is protected in this case. The electrons should move towards the copper, corroding the sacrificed iron.

5. The cathodic protection using zinc as a sacrificial has a positive effect on decreasing the % corrosion and CR of iron. It was observed that the minimal weight loss was 0.02 gm in pH=11 when iron coupled with zinc.

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