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Influence of alternating, direct and superimposed alternating and direct current on the corrosion of mild steel in marine environments

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Abstract

The corrosion of mild steel in marine environments was studied with respect to induced alternating current (AC), direct current (DC) and the superimposed AC+DC sources. Corrosion rate determination at the different applied AC, DC and AC+DC current densities was carried out by conventional weight loss method for the exposure period of 24 h. The quantitative estimation of leaching of iron into solution was done by using inductively coupled plasma spectrometry (ICP). Mild steel specimens were subjected to surface examinations after treatment with various AC, DC and AC+DC current densities. Surface analysis was done by optical microscopy. The salient features of this investigation are AC source accelerate the corrosion of mild steel in the presence of marine environments, but the extent of corrosion was increased when it was superimposed with DC. Especially, upto the corrosion current density, the AC field is not a great threat for mild steel and uniform corrosion was observed, But after the corrosion current density, AC accelerate the pitting corrosion of mild steel in marine media. Surface micrographs showed severe pitting at the higher AC sources. The concentration of iron was increased above the corrosion current density. The electrochemical measurements coupled with surface examination and solution analysis proved to be a very effective tool by means of characterizing the AC corrosion effect of mild steel in marine environments.

Keywords: AC corrosion; Mild steel; Marine environments

1. Introduction

It is well known that unidirectional currents are involved during the process of metallic

corrosion. However, under certain conditions, alternating currents can also cause corrosion although at a lower rate than direct currents. A review of literature reveals that a number of investigations have been carried out on the AC

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corrosion of iron, lead, copper, aluminium and other metals [1–3]. Beside, the corrosion of metals the dissolution of metals by AC has also attracted the attention [4]. The accelerated corrosion of metallic structures due to the presence of stray AC currents has been reported by Kulman [5] and Chin [6].

In rapidly growing demand for energy requires the construction of an increasing number of high voltage, high power transmission lines and laying of high pressure pipelines of large diameters situated nearby marine environments. AC corrosion mechanism is not yet understood and reliable techniques for the determination of the corrosion risk are not yet available. It becomes more difficult to install metallic pipelines with adequate distance from overhead high-voltage AC power transmission lines and/or AC powered rail transit systems and also away from marine areas. Therefore the risk of AC corrosion is increasing on the pipelines. Actually, several cases of AC corrosion on buried steel pipelines due to induced AC arising from high voltage AC power transmission lines have been reported [7]. The AC corrosion could occur even when the instant-off potential satisfied the conventional “potential based” cathodic protection (CP) criteria such as the -0.85 V vs. Cu/CuSO₄ polarized potential criterion. A number of laboratory and field studies have been performed to investigate the influence of AC induced voltage on the corrosion behaviour of corroding systems. The influence of AC in acidic and sulfate solutions has been reported [8–14]. However, more research is essentially needed for the influence of AC on chloride environments, since the marine environments have a high concentration of chloride ions, it is expected that AC may accelerate the corrosion.

This investigation is a systematic and detailed study on the influence of AC induced corrosion of mild steel in natural seawater. Since the seawater used here contains 18,500 ppm of chloride, studies were also carried out in NaCl solution

containing the same amount of chloride. In order to realize the individual influence of AC alone, experiments were also conducted on DC and superimposed AC+DC simultaneously in both the media.

2. Experimental

2.1. Materials

Mild steel obtained from Dongil Industries Co., Ltd., South Korea was used and the composition in wt% is follows: C (0.43), Si (0.22), Mn (0.72), P (0.013), S (0.015), Ni (0.05), Cr (0.10), Cu (0.12) and Fe balance. The mild steel specimen of size 2 cm (l) × 2 cm (b) × 0.5 cm (thickness) was used. The total geometrical area of the specimen was 11 cm² but the actual exposed area was 5.5 cm² and the other areas were used for taking electrical connection and properly insulated from the corrosive environments. They were then mechanically polished and then successively with finer SiC papers (240, 400, 600, 800, 1200 grit). Before and after each immersion experiment, individual specimens were cleaned with solutions containing concentrated HCl, SnCl₂ and Sb₂O₃ followed by a rinse with de-ionized water and acetone. Finally, all the specimens were dried under stream of hot air. Natural seawater (Jinhae sea, South Korea) and AR grade NaCl (DC Chemicals Co Ltd.,) was used as aggressive solutions. Solutions were purged with nitrogen gas to remove the dissolved oxygen.

2.2. Methods

2.2.1. DC polarisation technique

A conventional three electrode cell assembly is used here. The working electrode was mild steel specimen. Platinum foil and a saturated calomel electrode served as the auxiliary and reference electrodes respectively. The area of the counter electrode is much larger than the area of

the working electrode. This will exert a uniform potential field on the working electrode. Potentiodynamic polarization studies were carried out both in 18,500 ppm NaCl solution and natural seawater environments. A constant quantity of the test solution was taken in the polarization cell. The working, counter and reference electrodes were assembled and connections were made. The test solution were continuously stirred using a magnetic stirrer to avoid the concentration polarization. A time interval of about 10 to 15 min was given for each system to attain a steady state. Both cathodic and anodic polarization curves were recorded potentiodynamically using a Solartron-1480 multi-channel electrochemical interphase controlled by computer with Corrware software. Procedures and parameters specified in ASTM standard G5-87 were followed and all the experiments were carried out at a room temperature of 25 ± 1 °C. From the Tafel curves, actual i_{corr} values for mild steel in NaCl solution and natural seawater were derived.

2.2.2. Corrosion rate determination by weight loss measurements

Immersion experiments were carried out to quantify the corrosion rate of mild steel in NaCl solution and natural seawater medium under the influence of AC, DC and superimposed AC+DC sources. The weight of the mild steel samples was taken before and after immersion using Ohaus Explorer 4-digit electronic balance for gravimetric weight loss measurements. The AC signal was applied between the working electrode (mild steel) and the counter electrode (platinum gauge). A Solartron 1480 Multistat electrochemical measurement unit coupled with a Solartron 1255-B frequency response analyzer and multimedia computer was used to supply the required AC waveform. An oscilloscope was used to adjust as well as to monitor the AC signal applied. Immersion studies were carried out at the corrosion current density in both the media for the duration

of 24 h. Two current density values were chosen on lower and higher sides from the actual corrosion current density value and the experiments were conducted under the influence of AC, DC and the superimposed AC + DC sources. Blank experiment without applying any current density was carried out in both the media under natural immersion corrosion condition. Experiments were carried out both in natural seawater and in 18,500 ppm NaCl at an ambient temperature of 25 ± 1 °C. The values obtained are reasonable and reproducible from the triplicate set of experiments for each AC source and the average corrosion rate was made in mpy. Corrosion rate in mpy was made by using difference in weight losses between initial and final weight of the specimens for the exposure period of 24 h.

2.2.3. Solution analysis

The solution analysis was carried out with an idea to quantify the leaching characteristics of mild steel. It is expected that during the immersion studies the metal dissolution expected releasing considerable amount of metal ions from the material. In this study, mild steel specimens were immersed in test solutions at various source current densities. The concentration of metal ions present in the test solution was determined after treatment with AC, DC and the superimposed AC+DC sources at a fixed duration of 24 h. A blank experiment was also performed in both the media. The solution analysis was carried out using an inductively coupled plasma-atomic emission spectrometry (ICP, Applied Research Laboratory, USA). Triplicate experiments were carried out for each system and the average values are noted.

2.2.4. Surface examination

An optical microscopy was used to examine the nature of corrosion on the mild steel surface before and after immersion in various test solutions. The mild steel specimens were immersed in

various solutions for a fixed duration of 24 h under the influence of AC, DC and superimposed AC+DC sources. At the end of 24 h the specimens were taken out from the solution, thoroughly washed with distilled water, cleaned with acetone and dried. Micrographs were recorded at the different applied current densities in NaCl solution and natural seawater environments. The representative micrographs for each current source at the i_{corr} were given. The microscopic examination of the specimen was carried out using an Olympus-GX 71 Inverted System metallographic microscope coupled with a computer. Micrographs were recorded uniformly at the magnification of 40 \times .

3. Results and discussion

3.1. DC polarization measurements

Fig. 1 shows the typical polarization curves for mild steel in NaCl solution and natural seawater medium. It shows that mild steel has no active/passive transition when immersed in a chloride solution and also a linear behaviour was obtained in the Tafel region. The analysis of these curves in Corrware software gives the corrosion

current density (i_{corr}). The i_{corr} values for mild steel in NaCl solution and natural seawater environment were found to be 1.22 mA/cm² and 0.94 mA/cm² respectively. With respect to i_{corr} , two current density values were chosen on the lower and higher sides. The blank experiment without applying any current density (i.e. natural immersion corrosion condition) is denoted as $i = 0$. Table 1 gives the applied source current density values in mA/cm² for NaCl solution and

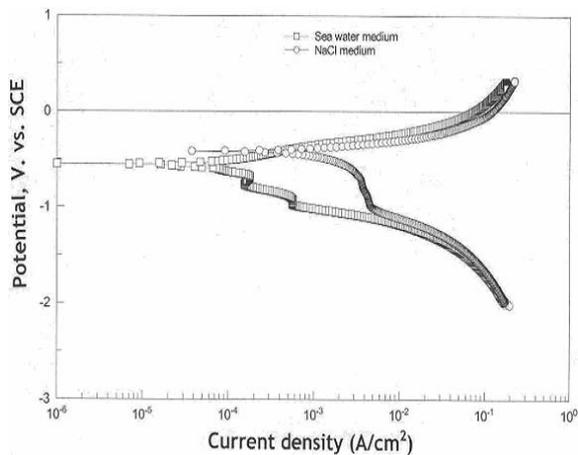


Fig. 1. Potentiodynamic polarization curves for mild steel in NaCl solution and natural seawater.

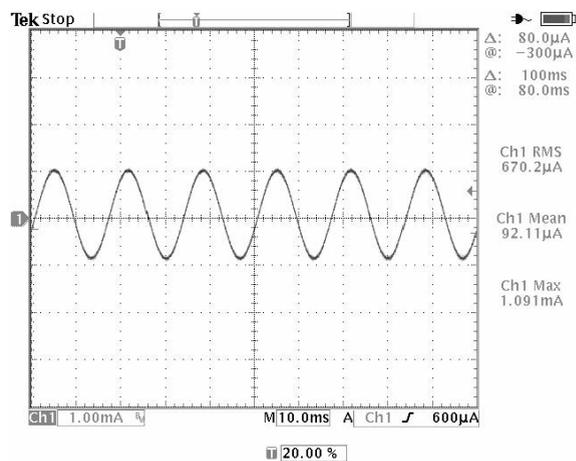


Fig. 2. Sinusoidal waveform of AC source applied at 60 Hz in NaCl solution.

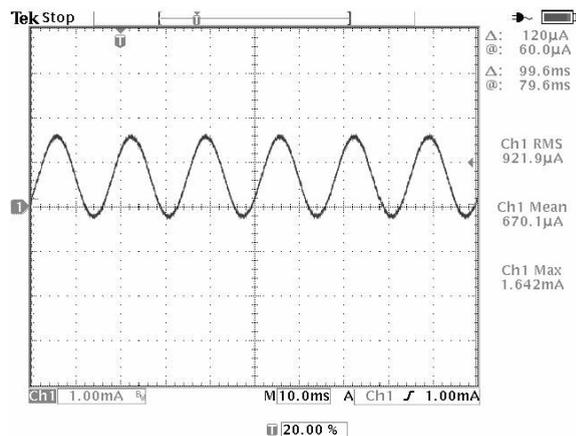


Fig. 3. Sinusoidal waveform of AC source applied at 60 Hz in natural seawater.

Table 1
Applied source current density values for mild steel in 18,500 ppm NaCl solution and natural seawater

S. no.	System studied	Details of applied current density	Source current density values (mA/cm ²)	
			NaCl	Seawater
1	Blank	No applied current density	0	0
2	$i \ll i_{\text{corr}}$	Applied current density far less than from the corrosion current density	0.0018	0.0018
3	$i < i_{\text{corr}}$	Applied current density less than from the corrosion current density	0.018	0.018
4	$i = i_{\text{corr}}$	Applied current density equal to the corrosion current density	1.220	0.940
5	$i > i_{\text{corr}}$	Applied current density greater than from corrosion current density	1.270	1.270
6	$i \gg i_{\text{corr}}$	Applied current density far greater than from the corrosion current density	1.810	1.810

natural seawater environments. In all the cases, the frequency of the AC modulation was held at 60 Hz. Figs. 2 and 3 show the sinusoidal waveform of AC source applied at 60 Hz across the cell in 18,500 ppm NaCl solution and in natural seawater respectively.

3.2. Influence of AC source on corrosion of mild steel in marine environments

3.2.1. Determination of corrosion rate

The influence of AC source on the corrosion of mild steel for the exposure period of 24 h in both the media is given in Table 2. It was found that the corrosion rate is increased as the AC source current density level is increased. It is interesting to note that, upto the four current density levels [$i = 0$, $i \ll i_{\text{corr}}$, $i < i_{\text{corr}}$ and $i = i_{\text{corr}}$], a steady increase in the corrosion rate was noticed. After that, i.e. above $i = i_{\text{corr}}$, a sudden steep increase in the corrosion rate is observed in NaCl solution. For example, the corrosion rate values up to the AC source level $i = i_{\text{corr}}$ is found to be 30 mpy only, but when the AC source level is increased beyond $i = i_{\text{corr}}$ (i.e., $i > i_{\text{corr}}$ and $i \gg i_{\text{corr}}$), the corrosion rate was found to be 92 mpy.

Here, it is noticed that there was a 3-fold increase in the corrosion rate values. It indicates that above the corrosion current density the AC induced corrosion is very a great threat for the mild steel in chloride environments. In seawater, there is a regular increase in the corrosion rate values as the current density is increased from 0 to $i \gg i_{\text{corr}}$. The corrosion rate values are found to be in the ranges from 10 mpy to 80 mpy, which is less when compared to the corrosion rate in NaCl solution. This may be due to the presence of other additional constituents in natural seawater which rendering the attacking anions inactive. Only chloride is taken care of when preparing 18,500 ppm NaCl solutions. But in natural seawater other additional constituents like Ca, Mg, K, S, Br etc., and few heavy elements inhibit the corrosion of mild steel and thereby showed less corrosion rate. The higher magnitude of corrosion rate for mild steel in both environments above the corrosion current densities may be due to the destabilization of the passive layer on the mild steel surface. The growth of the passive layer occurs as a result of electrochemical reaction and this passive layer is tends to depassivate at the higher current densities and accelerate the corrosion of mild steel [15].

Table 2

Corrosion rate (mpy) of mild steel in both the media under various electrical field from the immersion studies

Source	Current density					
	AC		DC		Super imposed AC + DC	
	NaCl	Seawater	NaCl	Seawater	NaCl	Seawater
$i = 0$	16±0.001	10±0.002	22±0.003	12±0.002	33±0.002	16±0.002
$i < i_{\text{corr}}$	17±0.003	11±0.002	33±0.007	28±0.003	50±0.003	32±0.007
$i < i_{\text{corr}}$	19±0.005	20±0.004	192±0.009	122±0.005	100±0.005	80±0.006
$i = i_{\text{corr}}$	30±0.005	28±0.006	362±0.001	320±0.007	566±0.006	482±0.007
$i > i_{\text{corr}}$	50±0.006	42±0.006	384±0.001	358±0.008	600±0.006	578±0.008
$i > i_{\text{corr}}$	92±0.001	80±0.006	486±0.002	443±0.008	833±0.008	803±0.007

3.2.2. Surface examination

Figs. 4a and b show micrographs for a mild steel surface in natural seawater and NaCl solution respectively at i_{corr} for the exposure period of 24 h under the influence of an AC source. Micrographs for mild steel in NaCl solution up to i_{corr} show the uniform corrosion on the mild steel surface. On the other hand, small numerous pits were observed at the higher AC source current densities. The changes in the surface morphology of mild steel by the AC source is indicating that AC sources have a strong influence on the corrosion kinetic parameter, i.e., corrosion current density. Recently Goidanich et al. reported that the AC affects the kinetic parameters such as Tafel slopes and exchange current densities for carbon steel, copper and zinc in 1 M sulphate solutions [16]. The initiation of pitting at the i_{corr} and above i_{corr} is due to the metal solution interface that could be altered by the AC signal and thereby affect the corrosion kinetics. Most probably both reversibility and faradaic rectification aspects have to be considered to understand the AC-induced corrosion [16]. Here the irreversibility of the chemical reactions occurring at the interface causes a change in the double layer compositions and a modification of the metal surface. But a definite trend was observed between AC corrosion immersion studies and surface morphology examinations.

3.2.3. Solution analysis by the ICP technique

The solution analysis by ICP technique was carried out to measure the exact leaching of Fe from mild steel in both the environments. The influence of AC source on the leaching of iron at various applied current densities in both the media is given in Fig. 5a. It was observed that the amount of leaching of Fe in NaCl solution is greater than natural seawater at all the current densities. The concentration of Fe at the i_{corr} was found to be 21 ppm for natural seawater and 23 ppm for the NaCl solution. In both the media, the amount of leaching was slightly increased when the current density is increased. The trend of reduction in the amount of leaching of Fe by various current densities follows the order:

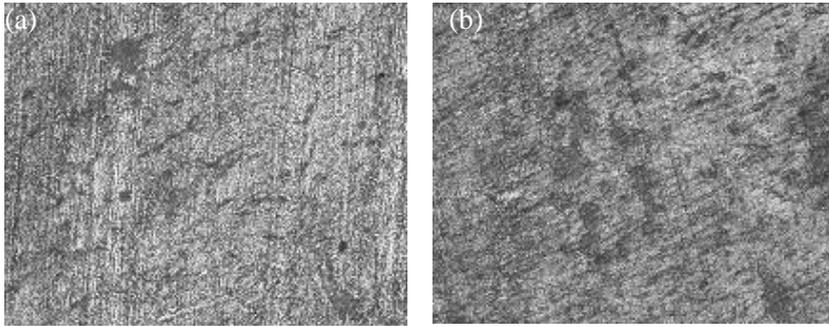
$$(i = 0) > (i < i_{\text{corr}}) > (i < i_{\text{corr}}) > (i = i_{\text{corr}}) > (i > i_{\text{corr}}) > (i > i_{\text{corr}})$$

The same order was already noticed in the immersion studies too.

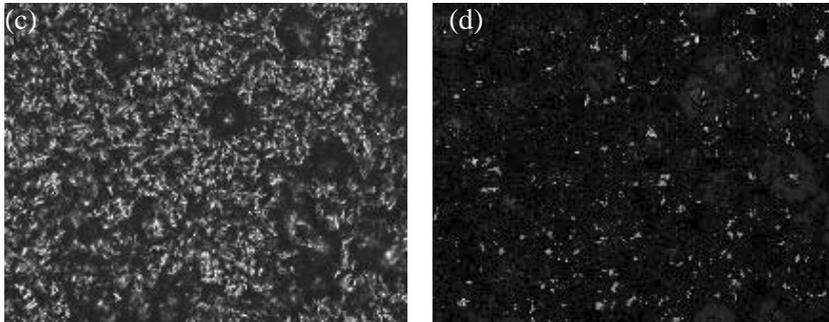
3.3. Influence of DC source on corrosion of mild steel in marine environments

3.3.1. Determination of corrosion rate

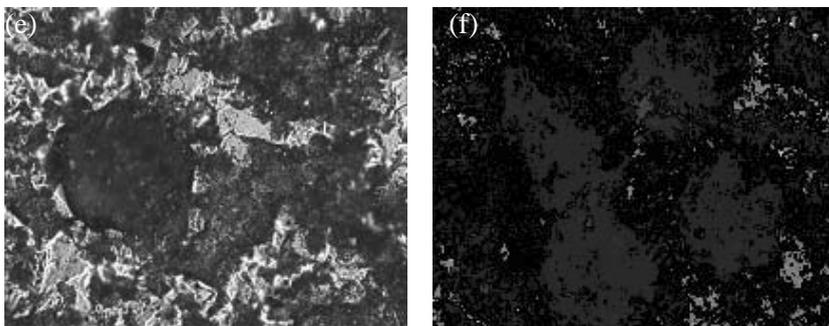
The influence of DC on the corrosion rate of mild steel in NaCl solution and natural seawater



Figs. 4a and b. Micrographs of mild steel for AC source at $i = i_{\text{corr}}$. 40 \times . (a) Natural seawater; (b) NaCl solution.



Figs. 4c and d. Micrographs of mild steel for DC source at $i = i_{\text{corr}}$. 40 \times . (a) Natural seawater; (b) NaCl solution.



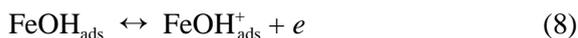
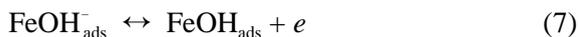
Figs. 4e and f. Micrographs of mild steel for AC+DC sources at $i = i_{\text{corr}}$. 40 \times . (a) Natural seawater; (b) NaCl solution.

medium is given in Table 2. The measured corrosion rates are directly proportional to the DC applied current densities in both the media. It was found that large variation in the corrosion rates between lower and higher current densities. Between the two solutions, NaCl showed more corrosion rate than natural seawater. For example the maximum corrosion rate for mild steel in natural seawater is 443 mpy but for NaCl solution is 486 mpy. Interestingly, the extent of corrosion by DC showed more than that of AC in both the solutions. Under the same experimental conditions and solutions, DC system showed a 12-fold

increase in the corrosion rate rather than AC system at i_{corr} . DC sources accelerate the corrosion in chloride solutions [17,18] in two ways as follows:



or



In either way, mild steel subjected to severe corrosion in the chloride environments in the presence of DC sources. The corrosion rate was found lower in seawater than NaCl solution. Salts such as carbonates, hydroxides, sulphates etc., of Ca^{2+} and Mg^{2+} are rather insoluble and would near to the metal surface and the presence of these ions therefore decrease the corrosion rate of mild steel in seawater.

3.3.2. Surface examination

Figs. 4c and d show micrographs for a mild steel surface in natural seawater and NaCl solution respectively at i_{corr} for the exposure period of 24 h under the influence of a DC source. When the DC current density applied at the electrode surface corresponds to i_{corr} , a pitting corrosion was started in both media. After that, the specimens underwent severe pitting and several pits grow with time. Later pits tend to merge and overlap each other showed larger pits on the mild steel surface. As evidenced from immersion studies, higher corrosion rates are noticed at the higher current densities, it is clearly reflected in the surface morphology also. So in DC corrosion studies also a definite trend was observed between immersion and surface morphology examination.

3.3.3. Solution analysis by the ICP technique

The amount of leaching of iron into the solution during the DC corrosion studies was carried out by ICP technique both in NaCl solution and

natural seawater environments and is given in Fig. 5b. It was found that the leaching of Fe in NaCl solution is found to be more than natural seawater at all the current densities. For example, the concentration of Fe at i_{corr} was found to be 480 ppm for natural seawater and 579 ppm for NaCl solution. The amount of leaching of Fe was almost doubled at the higher current densities. This is to be observed in both the media. The extent of leaching of Fe due to DC source was found more when compared to the AC source.

3.4. Influence of superimposed AC+DC source on corrosion of mild steel in marine environments

3.4.1. Determination of corrosion rate

The influence of superimposed AC + DC sources on the corrosion of mild steel for the exposure period of 24 h in both the media is given in Table 2. It is observed from Table 2 that the corrosion rate of mild steel in both the media were maximum at $i > i_{\text{corr}}$ and lower at $i < i_{\text{corr}}$. The influence of superimposed AC+DC source on the corrosion of mild steel was found to be very severe when compared to the individual influence of either AC or DC alone. Larger variation was observed in the corrosion rate values between superimposed AC upon DC and the individual AC or DC. For example at i_{corr} in NaCl solution, the corrosion rate values are found to be 566 mpy, 362 mpy and 30 mpy respectively for (AC+DC), DC and AC. Here it is concluded that the extent of corrosion of mild steel due to the superimposed AC+DC in NaCl solution is 1.5 times than DC and 18 times than AC. Tan and Chin [19] reported that superimposed AC + DC increased the corrosion of mild steel in aqueous Na_2SO_4 solution. In this study, the superimposed AC favoured the active dissolution potential region than the passive region. It appears that the passivity was destroyed in two ways. Firstly, the destruction of passivity of mild steel by superimposed AC + DC sources. Secondly the passive

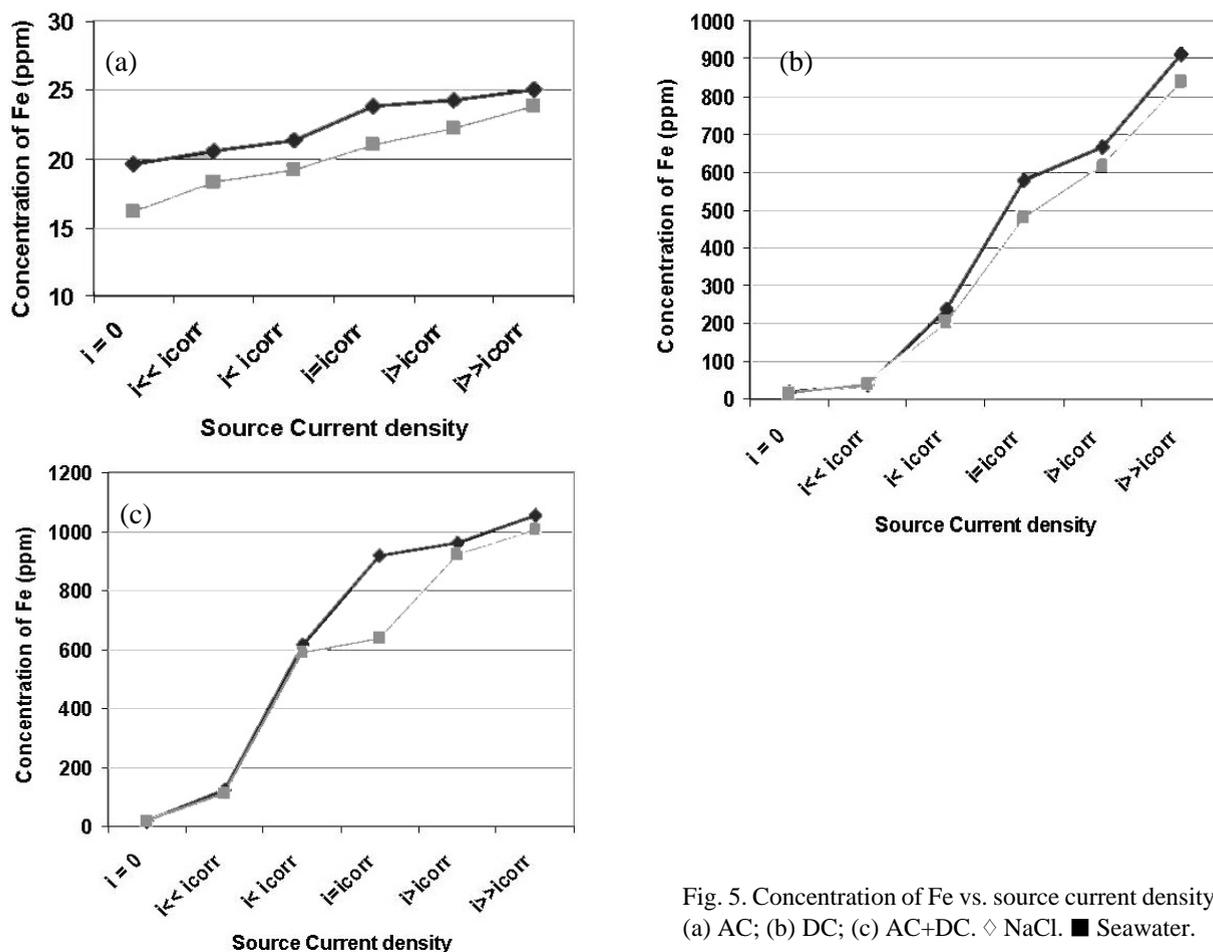


Fig. 5. Concentration of Fe vs. source current density. (a) AC; (b) DC; (c) AC+DC. \diamond NaCl. \blacksquare Seawater.

region was disappears completely due to the higher concentration of chloride ions in the solutions. The breakdown of passivity by chloride ions has been attributed to the ability of chloride ions to penetrate and to dissolve the passive oxide films on mild steel surface. This results in complex current fluctuations at the mild steel surface and thereby accelerating the corrosion vigorously. The trend in reduction of corrosion rate between the various types of sources in natural seawater environment follows the order: AC > DC > (AC + DC).

3.4.2. Surface examination

Figs. 4e and f show micrographs for mild steel surface in natural seawater and NaCl solution

respectively at i_{corr} for the exposure period of 24 h under the influence of superimposed AC + DC sources. The optical micrographs strongly suggest the significant evidence of severe pitting corrosion of mild steel surface in both the media. Here, micrographs strongly suggest that the superimposition of AC on DC influence the morphology of the specimens undergoing dissolution of metals. Superimposed AC + DC sources were applied especially at i_{corr} and above, an irregular shaped pits of various diameters and very deep were developed (Figs. 4e and f). The presence of chloride ions in solutions removed the passivity on localized areas on mild steel surfaces resulting pitting starts at higher current densities. In chloride solutions, the attack on mild steel behaved

like “etching” rather than “pitting”. As explained earlier in weight loss measurements, it is a fact that chloride ions had the ability to penetrate and disintegrate the oxide film on the metal surface and again superimposed AC+DC sources is applied, the protective film could be easily destroyed by perturbing the potential and virtually eliminated any oxide film and develops pitting corrosion at the mild steel surface. A close agreement was noticed between weight loss measurements and surface morphological studies in NaCl solutions and natural seawater environments.

3.4.3. Solution analysis by the ICP technique

The influence of superimposed AC + DC sources on the leaching of iron at various current densities in NaCl solution and natural seawater environments is given in Fig. 5c. As already observed in other cases, here also, the leaching of Fe into NaCl solution is more than natural seawater. As already evidenced from immersion studies and optical microscopic studies, in this technique also more leaching of Fe was noticed at higher source current density values and thereby indicating more corrosion rate values and accelerating pitting on the steel surface. The concentration of Fe at the corrosion current density level was found to be 639 ppm for natural seawater and 919 ppm for NaCl solution. The reduction of the amount of leaching by the different types of sources follows the order: AC > DC > (AC + DC). It is a fact that the amount of leaching of Fe is directly proportional to the corrosion rate, the superimposed AC+DC showed more corrosion rate than either AC or DC sources alone.

4. Proposed mechanism of action of AC corrosion at the various current densities

Below the corrosion current density ($i < i_{\text{corr}}$) — AC sources uniformly corrode the mild steel

in both the media. The corrosion rate was also found to be less at $i < i_{\text{corr}}$. Micrographs support the uniform corrosion at this current density in both the media. The schematic of the uniform corrosion of mild steel at the $i < i_{\text{corr}}$ is shown in Fig. 6(a). Uniform corrosion will tend to occur when some mild steel surface regions become anodic for a short period but at their location and that of the cathodic regions constantly change. General rusting of mild steel will take place when there is a uniform supply of oxygen available across the surface of the steel and there is a uniform distribution of defects in the oxide film. Therefore, overall attack takes place at a number of anodic sites whose positions may change leading to general rusting across the surface.

At the corrosion current density (i_{corr}) — When i_{appl} was held at i_{corr} , the dissolution rate and surface morphology of the mild steel in NaCl and seawater were significantly changed. Surface micrographs strongly suggest the possibility of pitting corrosion at i_{corr} . This is illustrated schematically in Fig.6(b). Here mild steel has undergone pitting in NaCl solution. Rapid dissolution occurs within the pit while oxygen reduction takes place on adjacent surfaces. This process is self-stimulating and self-propagating. The rapid dissolution of metal within the pit tends to produce an excess of positive charge in this area resulting in the migration of chloride ions to maintain electrical neutrality. Thus, in the pit there is a high concentration of FeCl_2 and as a result of hydrolysis, a high concentration of hydrogen ions. Both hydrogen and chloride ions stimulate the dissolution of most metals and alloys, and the entire process accelerates with time. Since the solubility of oxygen is virtually zero in concentrated solutions, no oxygen reduction occurs within a pit. The cathodic oxygen reduction on the surfaces adjacent to pits tends to suppress corrosion. In that case pits cathodically protect the rest of the metal surface.

Although Fig. 6(c) indicates how a pit grows through self-stimulation, it does not immediately

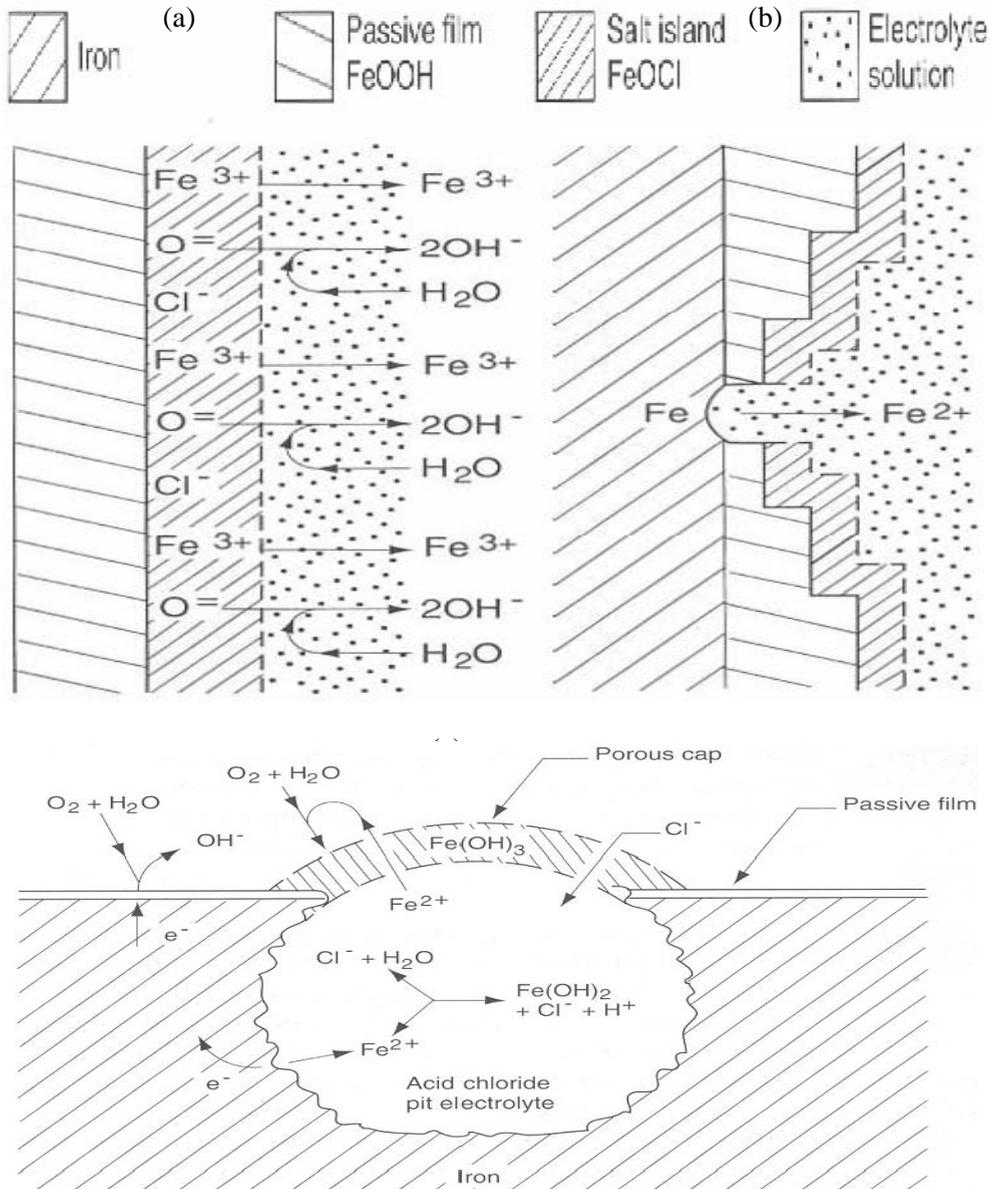


Fig. 6. Mechanism of action of AC corrosion at three stages. (a) $i < i_{corr}$; (b) $i = i_{corr}$; (c) $i > i_{corr}$.

suggest how this process is initiated. Micrographs (Figs. 4e and f) showed larger pits when immersed in NaCl solution in the presence of AC sources. At $i \gg i_{corr}$ the rate of metal dissolution is momentarily high at one particular point, chloride ions will migrate to this point. Since chloride stimulates metal dissolution, this change tends to

produce conditions that are favourable for further rapid dissolution at this point. Here pitting corrosion is predominantly taking place along with uniform corrosion.

Above the corrosion current density ($i > i_{corr}$) — Higher corrosion rates were observed when i_{appl} was held at beyond i_{corr} due to the fact that

pits once initiated on the mild steel surface at $i > i_{\text{corr}}$ the propagation is taking place as a result reduction of pH in the bulk solution.

In the case of pitting of iron in a slightly alkaline chloride solution a copious anodic production of positively charged Fe^{2+} attracts negative anions such as Cl^- followed by hydrolysis as below:



This will cause local pH reduction and, as a result, a self-propagating or autocatalytic nature of growth of pits. The acid chloride solution further accelerates anodic dissolution, which in turn further concentrates chloride in the pit. An insoluble $\text{Fe}(\text{OH})_3$ corrosion products collects at the pit mouth when Fe^{2+} diffuses out of the pit interior to the exterior where it is oxidized to Fe^{3+} and precipitates in the neutral bulk solution. The cap impedes easy escape of Fe^{2+} but is sufficiently porous to permit migration of Cl^- into the pit, thereby sustaining a high acid chloride concentration in the pit. Anodic polarization of the pit interior occurs by coupling to the exterior passive cathode surfaces. Cathodic reduction of a dissolved oxidizer such as oxygen consumes the electrons liberated by the anodic pit reaction.

The importance of the cathodic reaction to sustain pitting should be understood. Pit growth cannot continue without a cathodic reduction reaction to consume the electrons liberated by (i.e., to polarize anodically) the pit anodic reaction. Thus, pits are widely spaced in aerated salt solutions because oxygen has limited solubility, and a large surrounding area is needed to provide enough reduction capability to support the central pit anode. Any pit initiating within the cathodic area of a larger pit is suppressed by cathodic protection. The greater solubility of Fe^{3+} yields greater reduction rates on a smaller surface area, and pits can survive much closer to one another. In advanced stages, pits may become deep enough that reduction of H^+ on the pit walls near

the outer surface is possible, while the pit bottom still sustains anodic dissolution. Thus, hydrogen bubbles emanating from pits have been observed.

5. Conclusions

The following conclusions were drawn from the present investigation:

1. The extent of corrosion of mild steel in NaCl and in natural seawater environments was found to be less in AC when compared to the DC sources.

2. When alternating current (AC) signals are superimposed on a direct current (DC) at their respective corrosion current density ($i = i_{\text{corr}}$) or above the corrosion current density ($i > i_{\text{corr}}$), AC signal causes localized pits and simultaneously increase the corrosion rate. Similarly severe pitting on the surface was observed, especially superimposition of AC with DC at higher current density region ($i \gg i_{\text{corr}}$).

3. AC accelerates the corrosion of mild steel after the corrosion current density values whereas DC and (AC + DC) sources initiate the corrosion even below the corrosion current density values.

4. The electrochemical measurements coupled with surface examination and solution analysis proved to be a very effective tool to characterize the AC corrosion effect of mild steel in NaCl and natural seawater environments and a definite correlation was observed among these techniques.

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