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**EVALUATION OF ELECTROCHEMICAL CORROSION FOR MILD
STEEL EXPOSED TO DIFFERENT CHLORIDE MEDIA.**

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Abstract

The influence of different chloride media such as 3.5%NaCl, 10% NaCl, Väätänen nine salt solutions (VNSS) prepared as artificial seawater and natural seawater on the corrosion of mild steel (MS) has been studied using electrochemical polarization techniques. The effect of the addition of starch, glucose, yeast extract, peptone, and mixture of growth media on the corrosion behavior of mild steel has been also discussed. The order of the rate of decrease in oxide film thinning proceeds according to the following order of the type of the applied medium: 10%NaCl > seawater > VNSS > 3.5%NaCl. On the other hand in case of mild steel immersed in VNSS in presence of different nutrients the rate of oxide film thinning proceed according to the following order of the type of growth medium: Peptone < glucose < yeast extract < mixture of growth media \approx starch. Seawater was found to be less corrosive than VNSS. Addition of the growth media induced a decrease in both the cathodic and anodic currents and acted as a mixed type inhibitor. Cyclic polarization scans illustrate little decrease in the pitting tendency in the presence of growth media.

Keywords: mild steel, electrochemical polarization techniques, growth media, artificial seawater

1. Introduction

Seawater is the only electrolyte containing a relatively high concentration of salts that occurs commonly in nature, covering as it does over two-thirds of the earth as surface. It is both the most familiar and one of the most severe of natural corrosive agents [1] Seawater contains about 3.5% salt and is slightly alkaline, pH 8. It is a good electrolyte and can cause galvanic corrosion and crevice corrosion [2]. Corrosion of steel immersed in seawater is influenced by the interaction of several factors including temperature, salinity, dissolved oxygen, pH, carbon content, and hydrostatic pressure. F. Mansfeld et al present a critical review of the literature concerned with the application of electrochemical techniques in the study of corrosion of steel in seawater [3]. These electrochemical techniques include measurements of the corrosion potential, polarization resistance, electrochemical impedance, electrochemical noise, and the polarization curves including pitting scans. For each experimental technique, some discussion concerning experimental procedures, advantages, and disadvantages of the techniques were presented. The

effect of chloride media on the corrosion of mild steel and other alloys in the absence and presence of bacterial culture has been studied before [4-8]. Microbiologically Corrosion inhibition (MICI) was observed for these different alloys when exposed to VNSS in the presence of bacterial culture. The unexpected MICI brought the attention to study the effect of different factors that may interfere with the inhibition phenomena such as the presence of growth media [5 and 6].

2.Experimental Approach

2.1 Material and solutions

Mild steel specimens tested in the present study, are in the form of sheet, supplied by AL-EZZ Company in Alexandria. The designation and analysis of the material is given in Table (1). Before immersion in the test solution the mild steel electrode is prepared by polishing with SiC paper up to 1200 grade, washing with distilled water and then degreased with alcohol about 5 minutes, washed again with distilled water then dried it in air.

Table (1). Chemical composition of mild steel by weight percentage.

| Element | weight % |
|---------|----------|
| C | 0.175 |
| Si | 0.130 |
| Mn | 0.534 |
| P | 0.008 |
| S | 0.0094 |
| Cr | 0.0117 |
| Mo | 0.002 |
| Ni | 0.0188 |
| Al | 0.005 |
| Co | 0.0075 |
| Cu | 0.0047 |
| Nb | 0.003 |
| Ti | 0.002 |
| V | 0.005 |
| W | 0.172 |
| Fe | 99.07 |

Different chloride media were used in the present work such as, NaCl, Seawater, VNSS (Vätäänen nine salt solutions) prepared as artificial seawater with and without growth media [9]. The growth media that is required for the growth of different

bacterial cultures as described elsewhere consists of (starch 0.5g/L, glucose 0.5g/L, peptone 1g/L, and yeast extract 0.5g/L) [5].

2.2 Measurement methods

Electrochemical cell with three electrodes configuration has been used in potentiodynamic polarization studies using saturated Calomel electrode (SCE) as reference electrode and a cylindrical counter electrode of stainless steel 316 L. The exposed area of working electrode to solution was (1cm^2). Experiments which include open circuit $\{E_{\text{corr}}$ vs time $\}$, potentiodynamic polarization and cyclic polarization were carried out with model 352/252 corrosion measurement system, which consists of EG & G potentiostat/galvanostat model 273A driven by software from IBM computer. Measurements of polarizations curves were started after immersing the working electrode (mild steel) in the tested solutions for about 2 hours where the values of E_{corr} became stable. The anodic polarization data were measured from -15 mV to +1000 mV vs E_{corr} . The cathodic polarization was measured from +15 mV up to -1000 mV vs E_{corr} . The Tafel polarization was measured from -250 mV to +250 mV vs E_{corr} . The scan rate for polarization (anodic, cathodic) was 0.4 mV/S. However, in Tafel polarization the scan rate used was 0.3 mV/S.

3. Results and discussion.

3.1. Open Circuit Potential Measurements:

The open circuit potential measurements for mild steel as a function of time in VNSS, Seawater, 3.5% NaCl and 10% NaCl was studied and the results are illustrated in Fig.(1). It was found that there is a general tendency for open circuit potential (OCP) to shift towards more negative values, denoting the destruction of the pre-immersion oxide film, found on the surface of the mild steel and finally it reaches a steady state potential (E_{corr}). E_{corr} practically did not change during the following (15 days) of exposure to seawater and VNSS. However, a tendency to shift toward less negative values for the same time take place both in 3.5% and 10% NaCl solutions. The Cl^- ions promote corrosion and the extent of corrosion acceleration seems to depend on the concentration of the anion in solution.

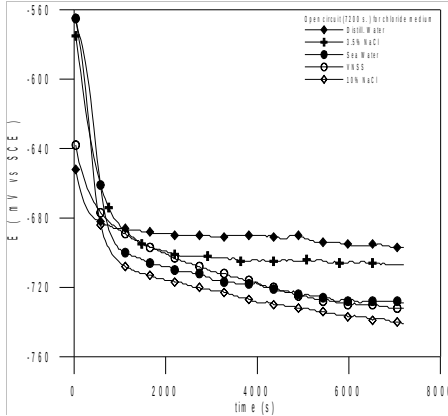


Fig. (1). potential-time curves for mild steel in different chloride media at room temperature

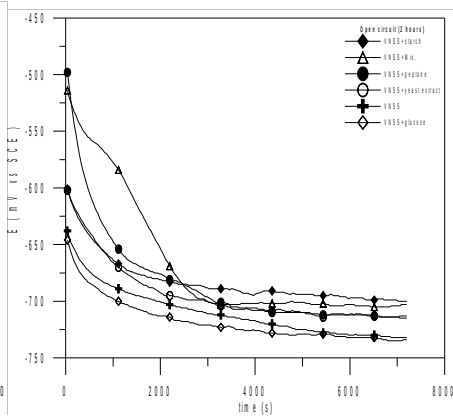


Fig. (2). potential-time curves for mild steel in VNSS in different nutrient medium.

Typical behavior of E_{corr} of mild steel during open circuit potential in VNSS solution, prior to and after addition of growth media is shown in Fig.(2). Upon different growth media, addition, slight ennoblement of E_{corr} occurred from -732 to -703 mV, indicating protection of the initially active mild steel electrode. This behavior indicates that the adsorbed growth media are attached to the most active anodic sites. E_{corr} practically did not change during the following 15 days of exposure.

3.2. Oxide Film Study

A theory for film thickening on the surface of metal and alloy based on open circuit potential measurements has been developed by Abd El-Kader and Shams El-Din [10]. The essence of the theory is based on the idea that the potential is determined by simultaneous anodic (film formation) and cathodic (oxygen reduction) couple, in which the anodic reaction is the rate limiting. By presenting the data in form of potential $-\log$ (time) curves, straight lines were obtained satisfying the relation (1) [10].

$$E = \text{constant} + 2.303 (\delta/\beta) \log t \dots\dots\dots (1)$$

Where (E) electrode potential with respect to a saturated calomel electrode, (t) is the time from the moment of immersion in solution, δ is the rate of oxide film thickening per decade of time and β is given by equation (2):

$$\beta = (nF / RT) \alpha \delta \dots\dots\dots (2)$$

Where (α) is a transference coefficient similar to that found in electrochemical kinetic rate expressions ($0.0 < \alpha < 1$), and (δ) is the width of the activation energy barrier to be traversed by the ion during oxide formation. The theory was applied to the cases of oxide growth on nickel, titanium [11], Fe-Cr alloys [12], and molybdenum steels [13].

It is evident from the curves in Figs. (3 and 4) that the relation between potential of the mild steel electrode versus the logarithm of the immersion time until potential reached steady state (E_{corr}) is confirmed. This behavior can be readily understood when one takes into consideration the physical properties of iron oxides, covering the metal surface. Consideration of the curves in Figs. (3 and 4) and the value of (δ) in table (2) allows the following conclusion to be drawn:

- (a) The rate of the pre immersion oxide film thinning (δ) for mild steel in different chloride solutions varies between (0.2385 – 0.3548 nm/log t).
- (b) For chloride solutions in the present study, the order of decrease the rate of oxide film thinning proceeds according to the following order of the type of the applied medium: 10%NaCl > seawater > VNSS > 3.5%NaCl
- (c) The order of the rate of oxide film thinning for mild steel immersed in VNSS in presence of different nutrient can follow the following order of the type of growth medium: peptone < glucose < yeast extract < growth media \approx starch

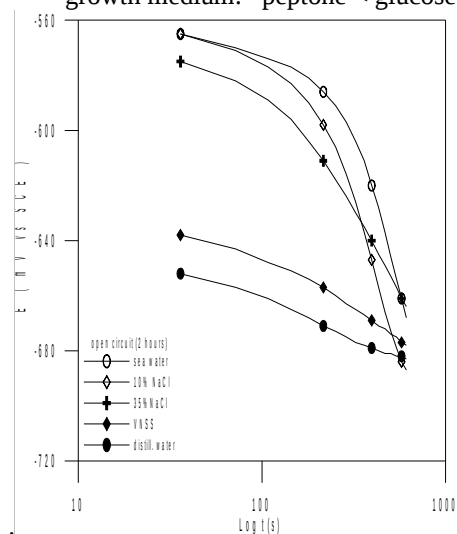


Fig. (3). potential-log time curves for mild steel in different chloride media at room temperature

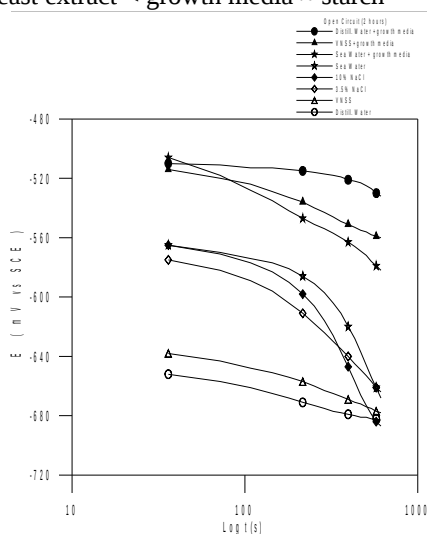


Fig. (4). potential-log time curves for mild steel in VNSS in different nutrient medium

Table (2). Values of slopes of E (mV) vs log t lines and the rate of oxide thinning (δ) (nm/log t) for mild steel in different test solutions.

| Test solution | Slope | Rate (nm/log t) δ |
|---------------------|---------|-------------------|
| Distilled water | 2.9520 | 0.0751 |
| 3.5%NaCl | 9.3750 | 0.2385 |
| 10%NaCl | 13.9416 | 0.3548 |
| Seawater | 11.0622 | 0.2815 |
| VNSS | 9.9666 | 0.2536 |
| VNSS+ starch | 4.6813 | 0.1191 |
| VNSS+ glucose | 4.0644 | 0.1034 |
| VNSS+ yeast extract | 4.3872 | 0.1116 |
| VNSS+ peptone | 1.2132 | 0.03087 |
| VNSS+ growth media | 4.6854 | 0.11922 |

3.3. Anodic, Cathodic, Linear and Tafel Polarizations.

Mild steel will corrode easily in seawater and a rust layer will be observed on its surface as soon as the mild steel is exposed to such very aggressive solutions. There have been many laboratory studies of the corrosion of mild steel in saline water but efforts to describe the rate of material loss with time have been limited, particularly for the early period of immersion [14]. Values of the corrosion rate in milli inches per year (mpy) were calculated from I_{corr} values as shown in equation (3) [1].

$$\text{The corrosion current (} I_{corr} \text{)} = \frac{\beta_A \beta_C}{3(Rp) (\beta_A + \beta_C)} \dots\dots\dots (3).$$

Once I_{corr} is determined, the corrosion rate can be calculated from the following equation :

$$\text{Corrosion rate (mpy)} = \frac{0.13 I_{corr} (E.W.)}{A. d} \dots\dots\dots(4)$$

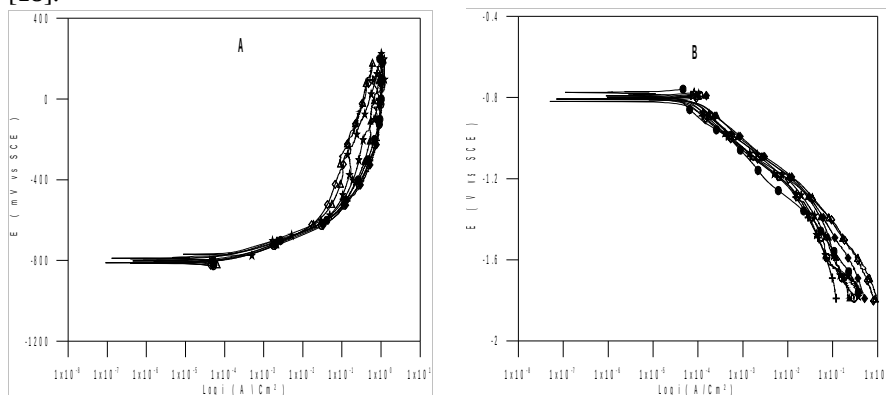
Where: E.W. = equivalent weight (in g. /eq.), A = area (in Cm²),d = density (g./Cm³), 0.13 =metric and time conversion factor.

Also the inhibitor efficiencies calculated from the polarization method using the equation (5) [15]:

$$I.E. \% = \frac{(C.R.)_{uninh.} - (C.R.)_{inh.}}{(C.R.)_{uninh.}} \times 100 \dots\dots\dots (5)$$

Where: $(C.R.)_{inh}$ and $(C.R.)_{uninh.}$ are the corrosion rate with and without inhibitor, respectively.

Corrosions made by linear, anodic, cathodic and Tafel plots polarization are illustrated in figs. (5 and 6) in the period of 15.00 days. It is clear from all figures that there is a very short period (<100 hours) during which there is initially a very high corrosion rate followed by a steady state. The corrosion rates then become approximately linear functions with period of exposure. A remarkable increase in the corrosion rate after 200 hours was observed for mild steel exposed to VNSS as compared with almost constant values in case of seawater. These results indicate that seawater is relatively less corrosive than VNSS for mild steel. No significant changes were observed in the cathodic polarization curves for mild steel exposed to VNSS or seawater figs. (7 and 8). Qualitatively the above observations are consistent with the suggestion of Terry and Edyvean [16] and Craig [17] and others that the period immediately after immersion involves rapid invasion of the establishment of anodic and cathodic regions on the corroding surface. However, whether these mechanisms are indeed the cause of the observed behavior is unclear since observations which produce results generally similar to those given in figs (5-6) have been made for mild steel under laboratory conditions. Such applied linear polarization techniques are similar to those obtained for Cu-Ni under similar conditions [18]. The usual interpretation is that from a theoretical perspective, the early (<100 hours) period is generally associated with activation control, and the period immediately after is the "concentration" control, the latter involving the limited diffusion of oxygen through the water flux adjacent to the corroding surface [18].



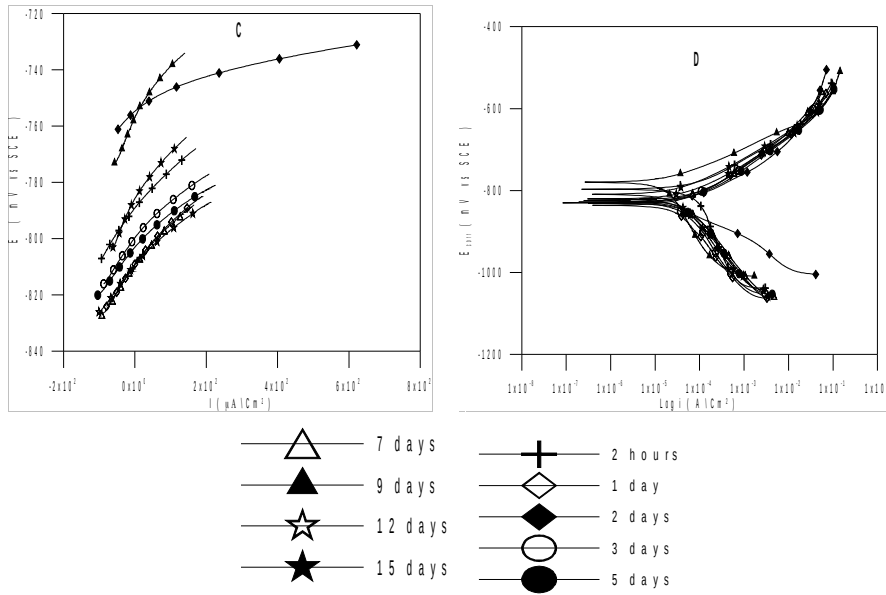
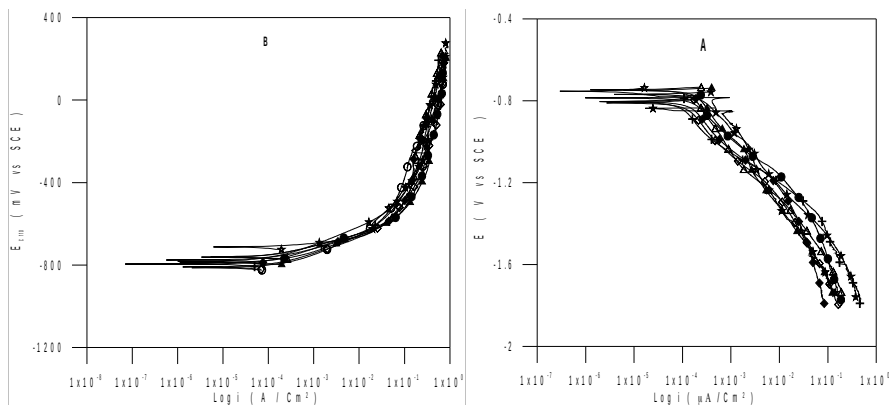


Fig.(5). Anodic (A), Cathodic (B), Linear (C) and Tafel plots (D) polarization curves of mild steel exposed to seawater for different times.



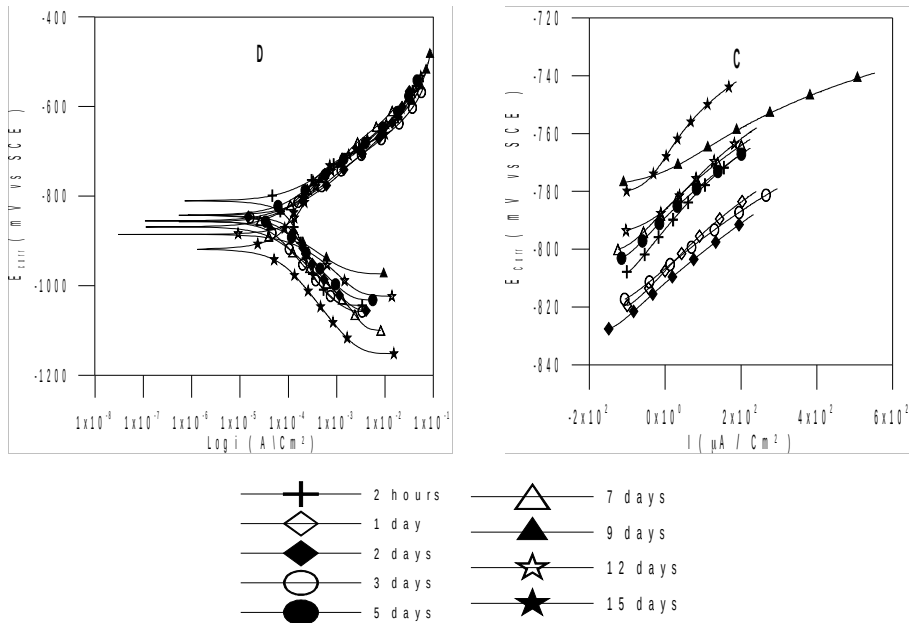


Fig. 6). Anodic (A), Cathodic (B), Linear (C) and Tafel plots (D) polarization curves of mild steel exposed to VNSS for different times.

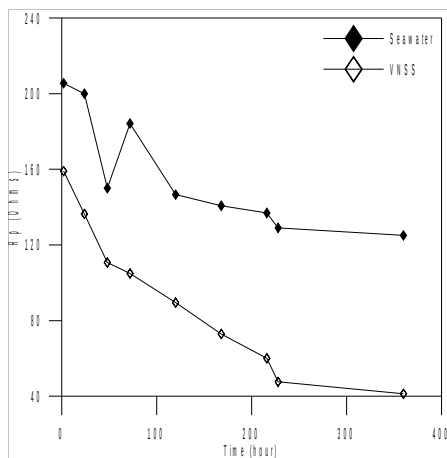


Fig. (7). Time dependence of polarization resistance for mild steel exposed to VNSS and seawater.

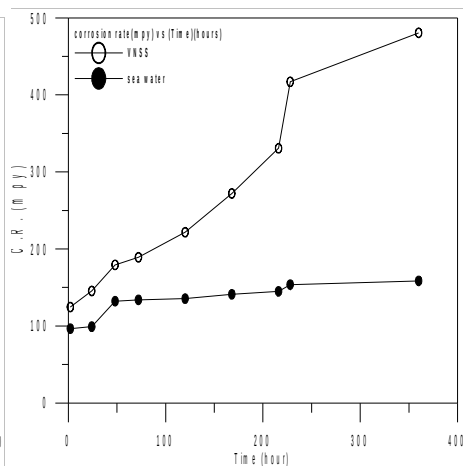
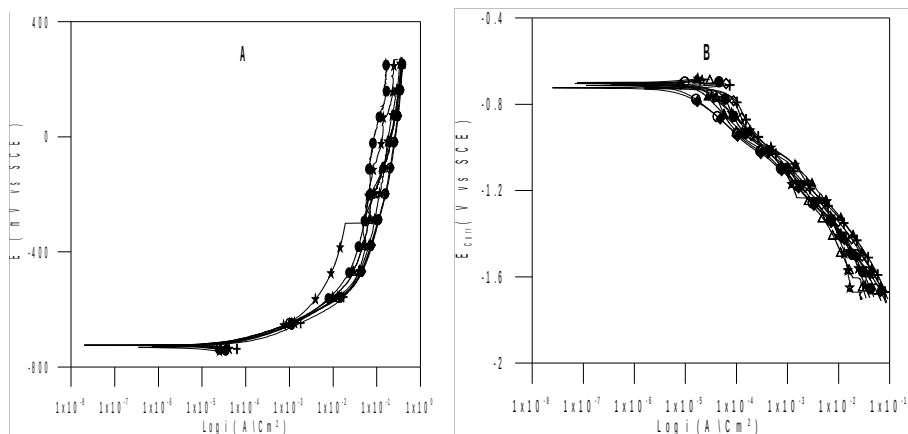


Fig. (8). Time dependence of corrosion rate for mild steel exposed to VNSS

The effect of different growth media on the corrosion behavior of mild steel studied in VNSS, gave results of the electrochemical parameters concerning the effect of the inhibition of the growth media in VNSS as shown in fig (9). In all cases, addition of the growth media (glucose, starch, peptone, yeast extract and their mixture) induced a large decrease in both the cathodic and anodic currents. These results, in addition to the clear overpotential in both cathodic and anodic curves, suggest the idea of the general adsorption of the growth media on the mild steel surfaces. Accordingly, the growth media are found to retard the dissolution of the metals and act as mixed- type inhibitors. The recorded results, illustrate the percentage corrosion inhibitor for mild steel by growth media in VNSS, where the rate increases with immersion time figs. (10 and 11). The inhibition efficiency proceeds according to the following order of the type of growth media after 15.00 days:

mixture of growth media (MGM)(98.7%) > yeast (91.52%) > starch (75.23%) > peptone (72.7%) > glucose (67.73%) Fig. (11).

It can be concluded from the obtained results that (MGM) has proven to be the efficient inhibitor for corrosion of mild steel in VNSS solutions. The inhibitive property may be argued to be due to the formation of a very low soluble layer and compact Fe-MGM complex film on the electrode surface. Further studies should be conducted to evaluate the physical properties of the obtained oxide layer.



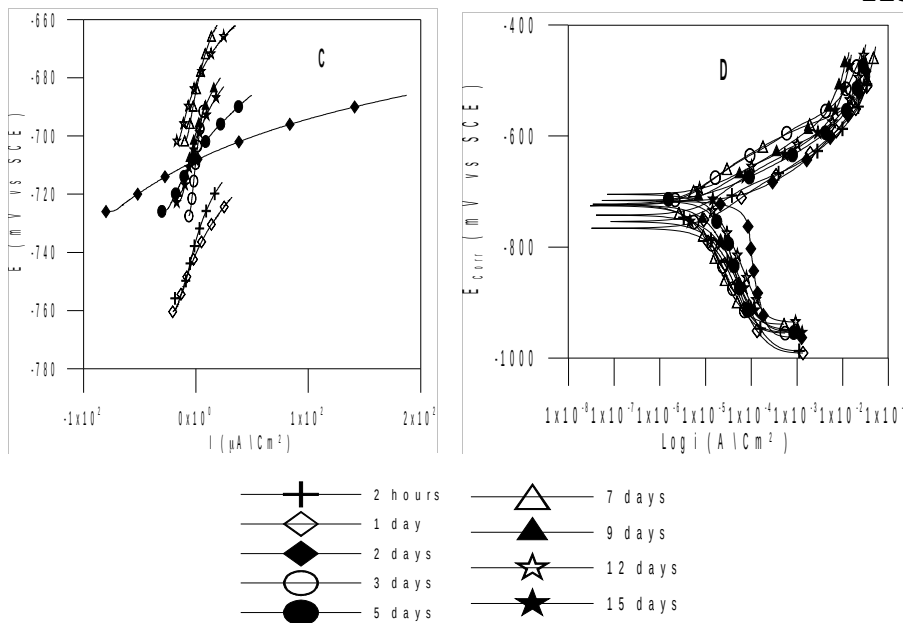


Fig. (9). Anodic (A), Cathodic (B), Linear (C) and Tafel plots (D) polarization curves of mild steel exposed to VNSS in mixture of growth media for different times.

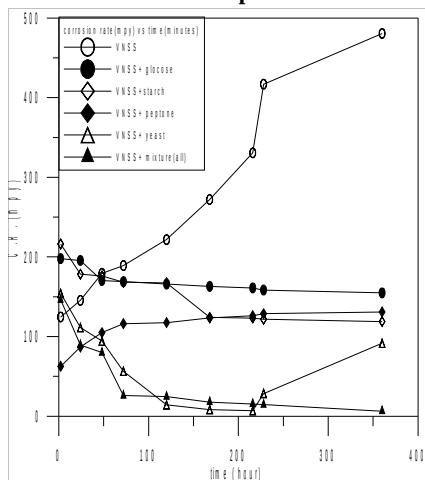


Fig. (10). Time dependence of corrosion rate for mild steel exposed to VNSS with and without of different growth media

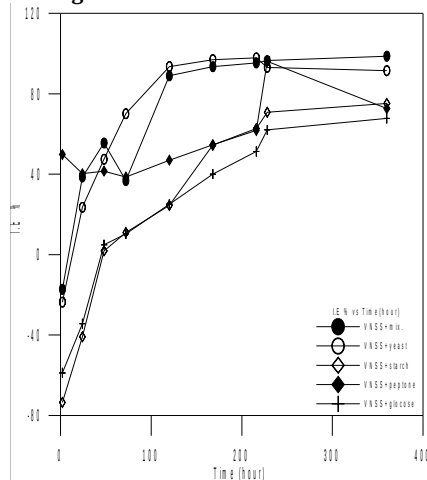


Fig. (11). Time dependence of the inhibition efficiency % for mild steel exposed to VNSS and different growth media

3.4. Cyclic Polarization

A cyclic polarization scan provides a qualitative view of pitting corrosion mechanisms. More specifically a pitting scan (another name for the technique) can determine the tendency of a metal to undergo surface pitting or crevicing when placed in a specific corrosive environment. Results of the cyclic polarization curves for mild steel in different studied media 3.5%NaCl, 10%NaCl, seawater, VNSS and distilled water are shown in Fig. (12). Moreover, the effect of the addition of different growth media on VNSS will also be reported in Fig. (13). When pitting occurs on the forward scan, the reverse scan will trace a hysteresis loop. Data given in table (3) show that the size of the pitting loop is a rough indication of pitting tendency, the larger the loop, the greater the tendency to pit. Increasing the area is found to proceed according to the following order of the medium:

$$10\%NaCl > 3.5\%NaCl > Seawater > VNSS \gg \gg Distilled\ water.$$

Accordingly, the recorded results shown in Fig (13) and table (3) illustrated decrease in pitting tendency in presence of different growth media.

Table (3). Cyclic polarization hysteresis loops areas for mild steel in different media.

| Corrosive media | | Area C/Cm ² |
|--------------------|-----------|------------------------|
| Distilled water | (2 hours) | 1.896 |
| Distilled water | (15 days) | 0.955 |
| 3.5%NaCl | (2 hours) | 188.2 |
| 3.5%NaCl | (15 days) | 97.13 |
| 10%NaCl | (2 hours) | 294.4 |
| 10%NaCl | (15 days) | 287.7 |
| Seawater | (2 hours) | 167.4 |
| Seawater | (15 days) | 182.0 |
| VNSS | (2 hours) | 114.8 |
| VNSS | (15 days) | 51.08 |
| VNSS+starch | (2 hours) | 103.5 |
| VNSS+glucose | (2 hours) | 110.6 |
| VNSS+yeast extract | (2 hours) | 66.97 |
| VNSS+peptone | (2 hours) | 75.60 |
| VNSS+growth media | (2 hours) | 99.87 |
| VNSS+G.M. | (15 days) | 62.07 |
| VNSS+starch | (2 hours) | 103.5 |
| VNSS+glucose | (2 hours) | 110.6 |
| VNSS+yeast extract | (2 hours) | 66.97 |

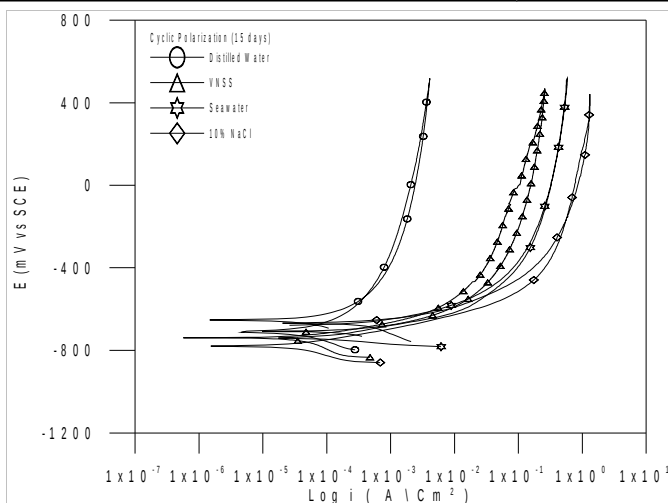
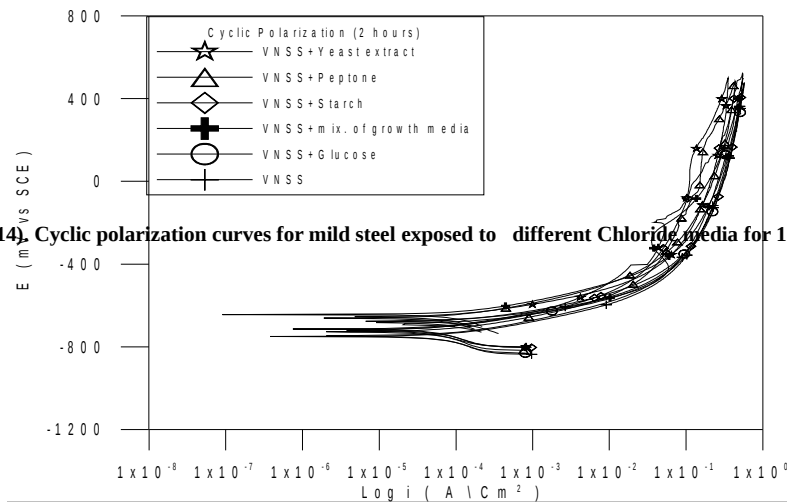


Fig. (13). Cyclic polarization curves for mild steel exposed to different Chloride media for 15 days.



.Fig. (14). Cyclic polarization curves for mild steel exposed to different Chloride media for 15 days

4. Conclusions

1- The obtained results show that in different chloride solutions there is always a general tendency for the steady state potential to shift towards more negative values, denoting destruction of the pre-immersion oxide film formed on the surface of the mild steel.

2- The Cl^- ion promotes corrosion and the extent of corrosion acceleration seems to depend on the contamination of anion in solution. In case of different growth media addition, slight ennoblement of E_{corr} occurred, indicating passivation of the initially active mild steel electrodes. In chloride solutions in the present study, the order of decrease the rate of oxide film thinning proceeds according to the following order of the type of the applied medium:

$$10\% \text{NaCl} > \text{seawater} > \text{VNSS} > 3.5\% \text{NaCl}$$

On the other hand in case of mild steel immersed in VNSS in presence of different nutrients the rate of oxide film thinning proceed according to the following order of the type of growth medium:

Peptone < glucose < yeast extract < mixture of growth media \approx starch

3- A remarkable increase in the corrosion rate was observed after 100 hours in case of VNSS as compared with the almost constant values in case of seawater. These results indicate that seawater is relatively less corrosive than VNSS for mild steel. The usual interpretation is that from a theoretical perspective, the early (<100 hours) period is generally associated with "activation" control, and the period immediately after that is the "concentration" control, the later involving the limited diffusion of oxygen through the water flux adjacent to the corroding surface.

4- A cyclic polarization scan provides a qualitative view of pitting corrosion mechanisms. The size of the pitting loop is a rough indication of the pitting tendency. The order of the values of the area of hysteresis loop proceeds according to the following order of the studied medium:

10%NaCl > 3.5%NaCl > seawater > VNSS.

The recorded results may illustrate little decrease in pitting tendency in presence of different growth media.

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