

To the Graduate Council:

I am submitting herewith a thesis written by Lawretta C. Ononye entitled "Development of an Abiotic Laboratory Screening Test for Microbially Influenced Corrosion". I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Metallurgical Engineering.

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and Dean of the Graduate School

DEVELOPMENT OF AN ABIOTIC LABORATORY
SCREENING TEST FOR MICROBially
INFLUENCED CORROSION

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ABSTRACT

An abiotic laboratory screening test (ALST) was developed that replicated the major corrosion-causing characteristics of several natural biotic environments. The natural biotic environments replicated were a Delaware Bay seawater site, an Arizona well-water system and a Tennessee River fresh-water system. The ALST was designed to produce the following major microbial effects with respect to corrosion: (a) the high oxidizing power of the natural environment, (b) the chloride concentration of the natural environment, and (c) aerobic and anaerobic areas on the specimen surface, as produced by colonies of aerobic and anaerobic microorganisms in the natural biotic environment.

The ALST was evaluated by conducting corrosion tests on various materials (platinum electrodes, alloy 400, AL-6XN alloy, and 304L/316L stainless steels). The results obtained were compared with those obtained from the field studies at the natural biotic environment sites. It was found from polarization resistance measurements in the abiotic solution that alloy 400 had a corrosion rate that was in good agreement with that obtained in the Delaware Bay natural biotic water environment. Cathodic polarization behaviors were determined for platinum electrodes, alloy 400, and 304L stainless steel in the abiotic solution. Comparison of these results to those obtained in the field studies in the natural environments showed that the corrosion current densities were somewhat higher in the abiotic solution.

The open-circuit potentials (OCP) obtained for the materials in the abiotic solution were significantly higher than those obtained in the natural biotic environments.

The visual and microscopic results of the surfaces of the weldments after exposure in the ALST compared favorably with their counter-parts after exposure in the natural biotic water environments.

From the results, the developed ALST replicated the natural environments reasonably well. The higher ennoblement and corrosion current densities obtained in the ALST are indications that the developed ALST is a conservative test. If there is no significant accelerated corrosion in the ALST, there will not be significant accelerated corrosion in the natural biotic environment; but if there is significant accelerated corrosion in the ALST, there may or may not be significant accelerated corrosion in the natural biotic environment.

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CHAPTER 1

INTRODUCTION

Microbially influenced corrosion (MIC) is concerned with the effects that micro-organisms have on the corrosion behavior of materials. Micro-organisms inhabit natural water environments and have been studied intensely with respect to MIC. A major problem in the marine environment is corrosion; it is often the principal concern in the performance of ships, offshore structures and other equipment used in marine services. Interest in developing an abiotic laboratory-screening test for MIC is increasing because (i) the development of biotic laboratory-screening tests for MIC have met with little, if any, success, and (ii) an abiotic laboratory-screening test (ALST), relative to a biotic test, would be less expensive to perform, easier to perform, and less time consuming.

The realization of a low-cost test that would require no extraction of micro-organisms from their natural environment, no preservation of cultures, and no elaborate sterilization procedures in determining the corrosion behavior of materials hinges on the successful development of an abiotic laboratory-screening test for MIC that would be, ideally, feasible for any natural, biotic, aqueous environment.

Research at the University of Tennessee, sponsored by the Office of Naval Research (ONR), indicated that the development of biotic laboratory tests which replicated the microbially influenced corrosion observed at a Delaware Bay site was virtually impossible [1]. The biotic laboratory tests produced corrosion-potential and corrosion-rate results that bore little resemblance to the results of field studies conducted

in the natural biotic environment. The cultured microbial consortia simply did not replicate the natural environment.

In the present research, an abiotic laboratory-screening test was developed. The work consisted of two parts: (i) the replication of the principal corrosion-enhancing characteristics of the natural biotic water environments of interest, and (ii) measurement of corrosion behavior in the abiotic solution and comparison with corrosion behavior in the natural biotic environment.

It must be stressed that the natural biotic environment contains a multitude of micro-organisms, metabolic products of micro-organisms, organic species and inorganic species. The complexity of the natural environment makes it very difficult to replicate. The major corrosion-causing characteristics of the natural biotic environment replicated in the ALST included:

- (1) The high oxidizing power of the natural biotic environment,
- (2) The chloride concentration of the natural biotic environment, and
- (3) Aerobic and anaerobic areas on the specimen surface, as produced by colonies of aerobic and anaerobic micro-organisms in the natural biotic environment.

In natural biotic environments, multitudes of organic and inorganic species are formed. Especially important is the formation of manganic oxide, existing as a strong oxidizing agent, and peroxide, which is also a strong oxidizer. Their presence, as well as the possible presence of other oxidizers, bring about the ennoblement found in the natural biotic environments, i.e., an increase in the open-circuit potentials. Ferric ions (Fe^{3+}), a strong oxidizer, were employed in the abiotic solution, in the form of ferric

sulfate ($\text{Fe}_2(\text{SO}_4)_3$), to increase the oxidizing power of the abiotic solution. Chloride concentrations of the natural biotic environments, as measured from the field studies, were employed in the form of sodium chloride in a distilled-water-based solution for the abiotic solution. The special crevice geometry was employed to produce an anaerobic region (the crevice region) and an aerobic region (the non-crevice region) on the specimen surface.

The ALST was evaluated by conducting corrosion tests (polarization resistance measurements, cathodic and anodic polarization tests, open-circuit potential (OCP) measurements and immersion tests) on alloy 400, AL-6XN alloy, 304L/316L stainless steel and platinum electrodes in the abiotic solution. The results were compared to those of field studies in the natural biotic environments. The corrosion behaviors in the ALST were expected to agree with those obtained in the natural environments.

CHAPTER 2

LITERATURE REVIEW

2.1 MICROBIAALLY INFLUENCED CORROSION

Micro-organisms play an important role directly or indirectly in the corrosion of materials. Their activities may result in a range of consequences. Metals serve as colony sites for microbes in water environments resulting in the formation of biofilms. Biofilms are defined as microorganisms and extracellular products associated with a substratum (e.g., a metal surface) [11]. The process of biofilm formation starts as a result of organic deposits on the metal surface from the surrounding waters forming films. Micro-organisms then attach and colonize; biofilms develop and change as more deposits, debris, corrosion products and micro-organisms are collected. Moreover, factors such as temperature, the composition of the water, and surface roughness and geometry of the metal may enhance the formation of biofilms. Biofilms may affect the corrosion rates of the underlying materials which may result in unsatisfactory equipment performance or reduction in equipment lifetime.

It has been stressed that the identification of the corrosion causative organisms may be difficult since it often depends on the quantitative determination of numbers of each microbial type in a complex mixture, together with an assessment of its chemical and physical activities in that particular environment [7]. Nevertheless, micro-organisms such as algae, fungi and bacteria have been cited to play an important role with regard to

MIC [5]. Fungi and algae are capable of producing organic acids and can form large masses that trap other materials [5]. Bacteria have been studied intensively with respect to MIC, and among others are the sulfate-reducing bacteria (SRB), the sulfur-oxidizing bacteria (SOB), and the manganese-oxidizing bacteria (MOB). The sulfate-reducing bacteria can reduce sulfate to sulfide, which reacts with hydrogen to form hydrogen sulfide with the characteristic "rotten egg" smell. These bacteria are anaerobes. The sulfur-oxidizing bacteria are aerobic and are able to oxidize sulfur or sulfide to sulfate; an example of this is the *thiobacillus*, which can oxidize sulfur to sulfuric acid (H_2SO_4). Manganese-oxidizing bacteria are able to oxidize manganese to manganic oxide. An example of this bacteria is the genus *siderocapsa* [27].

Dexter and Gao [18] studied the corrosion of type 316 stainless steel in natural seawater and in filtered seawater. They found that the corrosion potentials of the stainless steel exposed in natural seawater were higher than in the filtered seawater. Scotto [16] also studied the corrosion of stainless steel in unfiltered seawater and filtered seawater. Potential ennoblement was observed in the unfiltered seawater relative to the filtered seawater. Observation of the cathodic behavior of stainless steel in natural seawater by Johnsen and Bardal [13] also showed ennoblement of the free corrosion potential.

Mollica and Trevis [12] studied marine corrosion and fouling. They showed that with increasing flow rate of water over the metal surfaces, the biofilm formation decreased and, hence, ennoblement decreased. Zhang and Dexter [20] found from their study on the effect of biofilms on crevice corrosion of stainless alloys in coastal seawater,

by using a remote-crevice-assembly technique, that marine biofilms slightly decreased the average initiation times of crevice corrosion for 316L and 317L stainless steel. They attributed the decrease of the initiation times by the biofilms as due to the ennoblement of the corrosion potential, E_{corr} . Also, from the same study, they found that biofilms increased the propagation rate of crevice corrosion on 316L, 317L and 904L stainless steels by one to three orders of magnitude. They attributed this increase to cathodic depolarization by the biofilms.

Mollica et al. [15] studied crevice corrosion resistance of stainless steels in natural seawater in the temperature range of 25°C to 40°C. They found that by raising the temperature to 40°C, ennoblement could be prevented. The corrosion of intermediate resistance stainless steels (317L and 904L) decreased by one to two orders of magnitude, but a low-resistance stainless steel (316L) was not affected by temperature. They attributed the difference at 25°C to the relative activities of micro-organisms in the biofilms.

Gallagher et al. [21] studied crevice corrosion of stainless steels in natural and artificial seawaters using a multiple-crevice-assembly device. Their results showed that in the artificial seawater, crevice corrosion was minimal for the range of steels tested as compared to that in the natural seawater. They attributed the difference to the presence of micro-organisms in the natural seawater.

Valen [14] studied the crevice corrosion of 316L stainless steel in natural and artificial seawater using a remote-crevice-assembly device. He found that the current density for 316L in natural seawater was higher than in artificial seawater by about two

orders of magnitude, but the cathodic-to-anodic area ratio was 20 times larger in the artificial seawater than the in natural seawater.

Buchanan et al. [24] studied microbially influenced corrosion of Fe-, Ni-, Cu-, and Ti-based weldments in natural Delaware Bay water and in laboratory control tests. They found that the microbial influence was significant in the corrosion of 304L, 316L, alloy 400 and 90-10 Cu-Ni weldments, with alloy 400 experiencing the greatest degree of acceleration. Also, the microbial influence produced accelerated corrosion for the creviced condition of AL-6XN weldments, but not for the non-creviced condition.

Therefore, biofilms bring about ennoblement of passive-metal corrosion potentials in natural biotic water environments. The changes in the chemistry of the metal surface due to bacterial metabolism are considered the reason for the potential ennoblement. Chandrasekaran and Dexter [19] studied the factors contributing to the ennoblement of passive metals due to biofilms in seawater. They found that only a combination of low oxygen, acidic pH and milli-molar concentrations of hydrogen peroxide produced the observed amount of ennoblement.

Chandrasekaran and Dexter [6] used platinum coupons to study the mechanisms of potential ennoblement in the presence of mature seawater biofilms. They concluded that the reduction in pH and production of hydrogen peroxide within biofilms are the primary contributors to ennoblement. Low pH alone was shown to be able to account for much, but not all, of the ennoblement observed on passive metals in marine and fresh water systems. Buchanan et al. [17] and Dexter and Lin [22] have discussed the fact that the oxygen equilibrium potential increases with decreasing pH, and that this effect could

be partly responsible for ennoblement associated with low-pH biofilms. The reduction of dissolved oxygen is an important cathodic reaction in the marine microbial environment.

Dickinson and Lewandowski [25] studied manganese biofouling of stainless steel, its deposition rates and its influence on corrosion processes, and concluded that ennoblement of 316L stainless steel in fresh river water was due to manganic oxide biofouling which indicated higher manganese-oxidizing bacteria activity in that study. They have also discussed the fact that under environmental conditions for which ennobled $E_{\text{corr}} < E_{\text{pit}}$, manganic oxide biofouling is not detrimental to passive metals and may serve to enhance passivity and that cathodic depolarization by MnO_2 shifts E_{corr} in the noble direction until the equilibrium potential is reached for the reaction:



If this potential is exceeded, MnO_2 will be stable with respect to reduction and increased cathodic current from continued MnO_2 deposition is offset by decreased current density at the individual deposits.

2.2 FUNDAMENTALS OF ELECTROCHEMICAL CORROSION

2.2.1 Open-Circuit Potential Measurements

In measuring the open-circuit potential (OCP), the working electrode (WE), a stable reference electrode (RE), and an electrometer (voltmeter with high input-impedance) are needed. Figure 2.1 shows the arrangement for measuring the OCP. The

WE is the material to be evaluated and it ranges from pure metals to complex alloys.

If the WE is an inert pure metal (such as platinum in many environments), the OCP measured is the reduction-oxidation (redox) potential of the environment. The redox potential is the equilibrium potential at which the oxidation and reduction reactions involving hydrogen ions, water, dissolved oxygen, or other species in the aqueous environment, take place at equilibrium. The OCP for platinum in a given environment can be used as a measure of the corrosivity of that environment. It varies with pH, oxygen concentration, and the types and concentrations of other species capable of undergoing oxidation/reduction reactions.

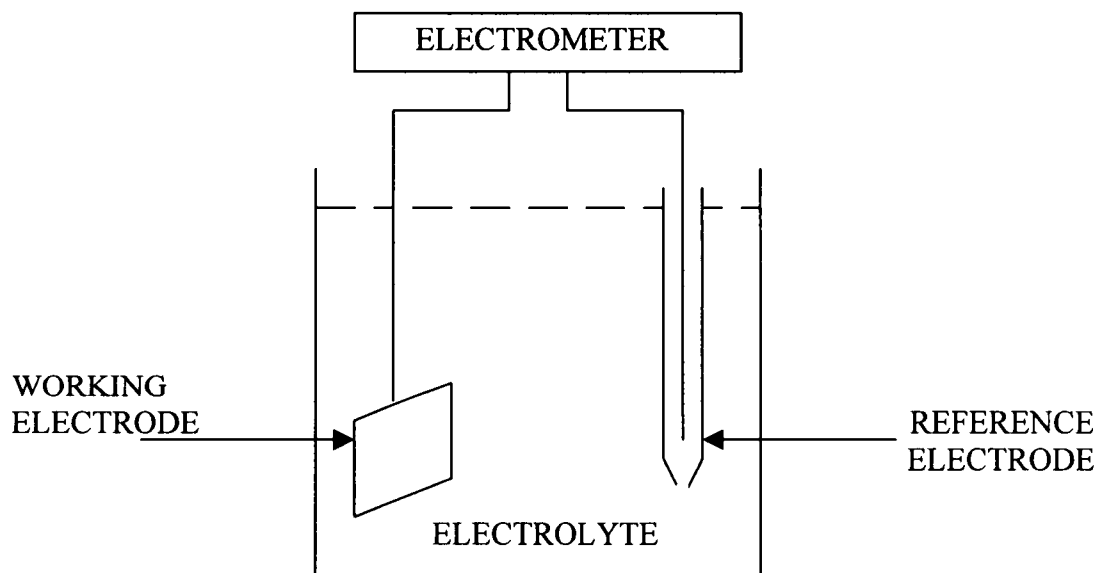


Figure 2.1: Arrangement used for open-circuit potential (OCP) measurements using an electrometer.

For metals and alloys undergoing corrosion, the OCP measured is the corrosion potential (E_{corr}), which is the steady-state potential at which the anodic reaction for the alloy is proceeding at the same rate as the cathodic reaction involving reduction of species in the environment (e.g., oxygen, hydrogen ions, water, etc.). The corrosion potential depends on variables such as the material to be evaluated, pH, the make-up of the electrolyte, etc., and provides little information on the corrosion behavior of the material. Since detailed information is required on the corrosion behavior of the material, there is need for other electrochemical corrosion tests.

The reference electrode is used to maintain a constant potential against which the potential of the WE is measured with an electrometer or high-impedance voltmeter. An electrometer is a potential-measuring instrument that has a sufficiently-high impedance ($> 10^{14}$ ohms) such that its measuring current is small enough so as not to affect the reference-electrode or working-electrode potentials.

2.2.2 Electrochemical Polarization Measurements

Electrochemical polarization measurements are used to determine the corrosion rates and behaviors of materials. They provide information on corrosion rates, charge-transfer or diffusion-controlled reactions, passivity, transpassivity and localized corrosion in a given environment. The instrument used to control and measure the electrochemical polarization behavior of materials is the potentiostat. The potentiostat is a special direct current (DC) power supply which will maintain the potential of the WE relative to the RE at a very constant (preset or set point) value even though the external circuit current, I_{ex} ,

may change over many orders of magnitude. The potentiostatic circuit includes the working electrode (WE), the counter or auxillary electrode (AE) and the reference electrode (RE). The counter electrode is made of a material that will support electrochemical oxidation or reduction reactions, but will not undergo corrosion (e.g., platinum). Hence, it will not contaminate the electrolyte. The working electrode is the corrosion sample, i.e., the material to be evaluated. The reference electrode supplies a constant potential against which the potential of the WE is measured with an electrometer (a high input impedance, greater than 10^{14} ohms, voltmeter). Only a negligibly, small current is allowed to pass through the RE so that the reference potential remains unchanged. A schematic diagram of the potentiostatic circuit is shown in Figure 2.2.

The polarization-resistance technique is employed for measuring corrosion rates of specimens. The technique provides rapid results in about ten minutes. Polarization resistance theory was developed by Stern and Geary [23]. The theoretical justification for this method is based on the expression for the external current, I_{ex} [26]. At any potential of the WE established by the potentiostat, the external current, I_{ex} , is the difference between the oxidation current (anodic current) at the metal surface, $I_{ox,m}$ and the reduction current (cathodic current) at the metal surface, $I_{red,x}$. i.e.,

$$I_{ex} = I_{ox,m} - I_{red,x} \quad 2.2$$

Upon dividing each term by the specimen area, A , to convert to current density, i ($i = I/A$),

equation 2.2 becomes

$$i_{ex} = i_{ox,m} - i_{red,x} \quad 2.3$$

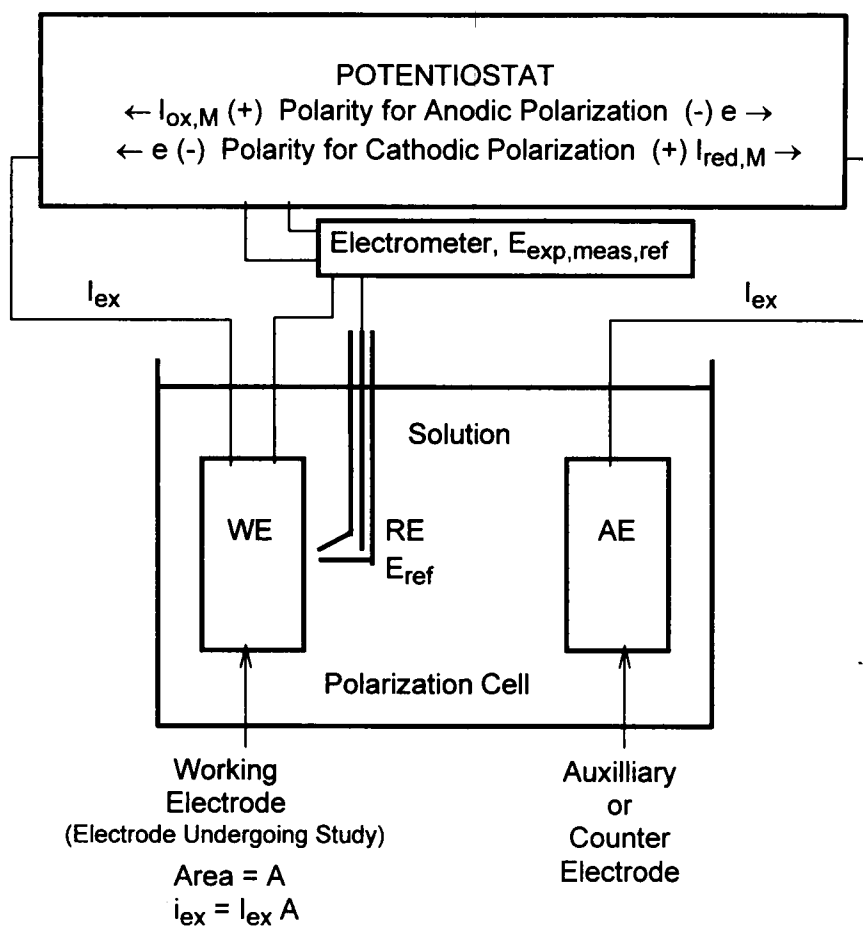


Figure 2.2: Potentiostatic circuit used to control and measure the electrochemical polarization behavior of materials.

where

$$i_{ox,m} = i_{o,m} e^{+2.30(E-E'm)/\beta_{ox,m}} \quad 2.4$$

$$i_{red,x} = i_{o,x} e^{-2.30(E-E'x)/\beta_{red,x}} \quad 2.5$$

In Equations 2.4 and 2.5, $i_{o,m}$ and $i_{o,x}$ are the exchange current densities for the metal and the cathodic-species reactions, respectively, E is the potential of the metal relative to the RE, E'_m and E'_x are the equilibrium potentials for the metal and cathodic-species reactions, respectively, and $\beta_{ox,m}$ and $\beta_{red,x}$ are the Tafel constants for anodic and cathodic reactions, respectively. Substitution of Equations 2.4 and 2.5 into Equation 2.3 yields:

$$i_{ex} = i_{o,m} e^{+2.30(E-E'm)/\beta_{ox,m}} - i_{o,x} e^{-2.30(E-E'x)/\beta_{red,x}} \quad 2.6$$

When the potential is equal to the corrosion potential ($E = E_{corr}$), $i_{ox,m}$ and $i_{red,x}$ are both equal to the corrosion current density, i_{corr} . Therefore, when $E = E_{corr}$,

$$i_{o,m} e^{+2.30(E_{corr}-E'm)/\beta_{ox,m}} = i_{o,x} e^{-2.30(E_{corr}-E'x)/\beta_{red,x}} = i_{corr} \quad 2.7$$

Division of Equation 2.6 by 2.7 yields:

$$i_{ex} / i_{corr} = e^{+2.30(E-E_{corr})/\beta_{ox,m}} - e^{-2.30(E-E_{corr})/\beta_{red,x}} \quad 2.8$$

Differentiation of Equation 2.8 with respect to E , evaluation at $E = E_{corr}$, and rearrangement produces:

$$\left(\frac{dE}{di_{ex}} \right)_{E_{corr}} = \beta_{ox,m} \beta_{red,x} / 2.3 i_{corr} (\beta_{ox,m} + \beta_{red,x}) = R_p \quad 2.9$$

where R_p is known as the polarization resistance. Experimentally, R_p is evaluated as the slope of the E versus i_{ex} curve at E_{corr} . Then, from known or assumed values for the Tafel constants (β s), the corrosion current density, i_{corr} , may be calculated. In the present research, the β values were each assumed to be 100 mV, which is a commonly applied and reasonably-accurate assumption.

Once i_{corr} is determined, Faraday's law be employed to calculate the average corrosion rate, as follows:

$$\text{Corrosion Rate (CR)} = 0.0129 (i_{corr}) \text{ Eq.Wt.} / \rho \quad 3.0$$

where the CR is in mils per year (mpy), i_{corr} in $\mu\text{A}/\text{cm}^2$, and density, ρ , in g/cm^3 . The equivalent weight (Eq. Wt.) is the atomic weight of the metal (g/mol) divided by the oxidation number (or valence number) of the metal ion.

Cathodic and anodic polarization measurements are obtained from potentiodynamic and cyclic polarization techniques. The potentiostat can be set to polarize the working electrode either in the cathodic or anodic direction. Figure 2.3 shows a schematic experimental polarization curve. If the working electrode is polarized anodically from E_{corr} , the net reaction at the working electrode surface is oxidation. This involves the removal of electrons from the surface of the WE resulting in more positive or noble potentials than E_{corr} . At these potentials, the number of electrons produced per unit time the reaction, $M \rightarrow M^{m+} + me$, is greater than the number consumed

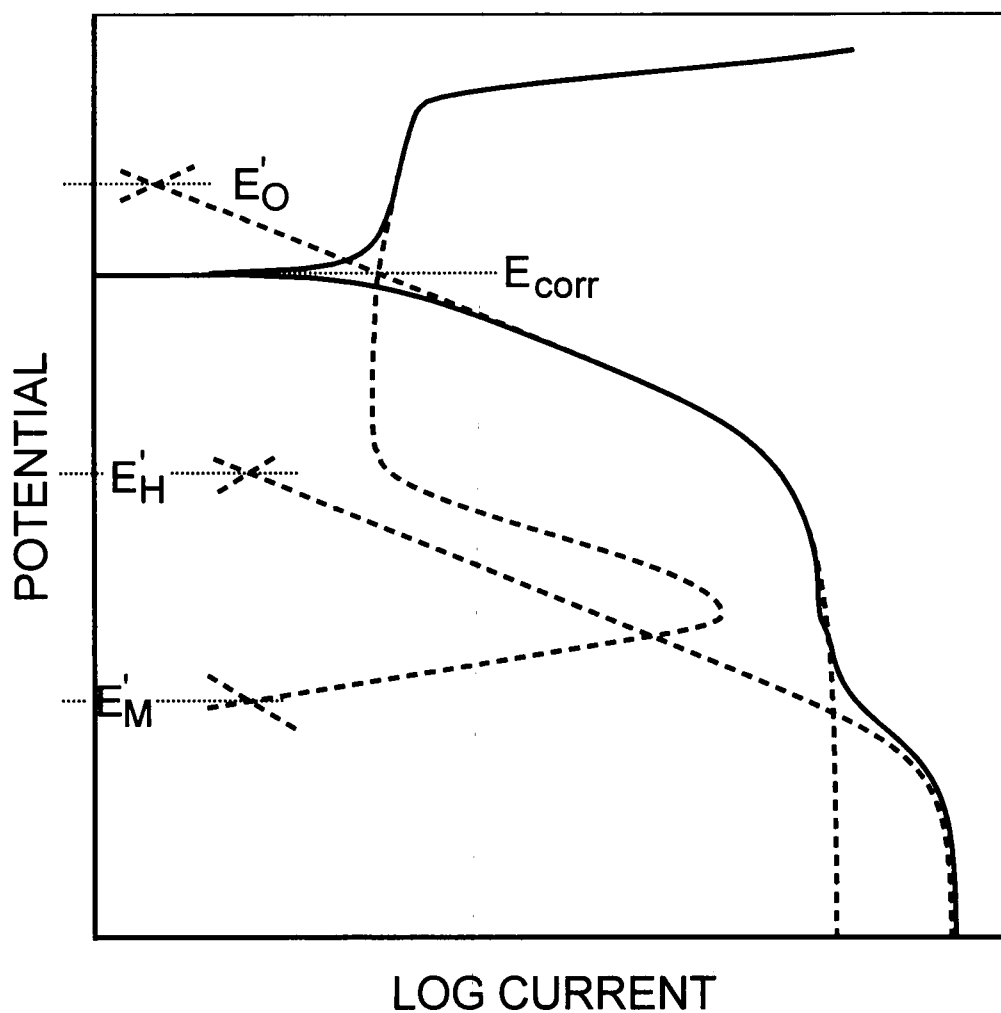


Figure 2.3: Schematic experimental polarization curves (solid curves) assuming active-passive behavior for the individual metal-oxidation curve and Tafel behavior plus limiting diffusion for the individual dissolved-oxygen and hydrogen-ion reduction curves (dashed curves). (Adapted from reference 26).

per unit time by the reduction reaction, $X^{x+} + xe \rightarrow X$. From Equation 2.2, I_{ex} , the external current, is positive when $I_{ox,m}$ is greater than $I_{red,x}$, and negative when $I_{red,x}$ is greater than $I_{ox,m}$. This change in sign takes place as I_{ex} passes through $I_{ex} = 0$. At this point, $E = E_{corr}$ and

$$I_{ox,m} = I_{red,x} = I_{corr}. \quad 2.11$$

If $E > E_{corr}$,

$$I_{ex} = I_{ex,a} > 0 \quad 2.12$$

where $I_{ex,a}$ is the external anodic current at which the anodic or oxidation reaction is dominant. For $E > E_{corr}$, the plot of potential versus the log of the external anodic current will be similar to the upper solid curve in Figure 2.3, the anodic part of the experimental polarization curve. If E is increased to the extent that $I_{red,x}$ is negligible, then,

$$I_{ex} = I_{ex,a} = I_{ox,m}. \quad 2.13$$

in this case, one is directly measuring the oxidation rate of the metal. As shown in Figure 2.3, the metal undergoes active-passive oxidation (anodic) behavior. E_{corr} is in the passive region.

If the working electrode is polarized cathodically from E_{corr} , the net reaction at the working electrode surface is reduction (the consumption of electrons at the surface of the WE). The potentials are more negative or more active than E_{corr} at the metal surface. At these potentials, the number of electrons consumed per unit time by the

reduction reaction, $X^{x+} + xe \rightarrow X$ is greater than the number produced per unit time by the oxidation reaction, $M \rightarrow M^{m+} + me$. Electrons are being supplied to WE by the external circuit. If $E < E_{\text{corr}}$,

$$I_{\text{ex}} = I_{\text{ex,c}} < 0 \quad 2.14$$

where $I_{\text{ex,c}}$ is the external cathodic current at which the cathodic or reduction reaction is dominant. For $E < E_{\text{corr}}$, a plot of potential versus the log of the external cathodic current will be similar to the lower solid curve in Figure 2.3, the cathodic part of the experimental polarization curve. If E is decreased to the extent that $I_{\text{ox,m}}$ is negligible, then,

$$I_{\text{ex}} = I_{\text{ex,c}} = -I_{\text{red,x}} \quad 2.15$$

in this case, one is directly measuring the cathodic reaction rate on the metal surface. Also shown in Figure 2.3 are the individual reduction curves assuming an aerated, acidic environment. The reduction curve showing Tafel behavior and a diffusion limit for dissolved oxygen begins at a higher potential than that for the reduction of hydrogen ions. The total reduction-rate experimental curve is shown as the solid curve.

Other characteristics of materials can be determined from electro-chemical polarization curves, such as the pitting potential, protection potential, etc. Usually, the surface condition of the material being evaluated is modified after employing these techniques because of the large potential excursions.

CHAPTER 3

MATERIALS AND EXPERIMENTAL PROCEDURES

3.1 MATERIALS

The materials evaluated in this study were weldments of alloy 400 (Monel 400), AL-6XN and 304L/316L stainless steel. Alloy 400 and AL-6XN were selected because they were among the weldments tested at the Delaware Bay site natural environment and they produced the most dramatic MIC effects [1]. Also, the choice of alloy 400 was made to represent nickel-based alloys used in marine services. It exhibits good performance in highly-aerated fast-moving seawater environments, and is used in heat exchangers, turbine blades, pump shafts and water boxes [4, 5]. AL-6XN is a high-nickel superaustenitic stainless steel. It is a high-performance stainless alloy with generally excellent corrosion resistance in chloride-rich environments. AL-6XN is an improvement over the alloy AL-6X with the designation of "N" for nitrogen additions. It is used in condenser tubing and heat exchangers. 304L and 316L are austenitic stainless steels. The chemical compositions of these materials are given in Table 3.1.

The weld specimens were bead-on-plate welds produced by the shielded-metal-arc welding process. After the welding, the plates were cut into specimens of size approximately 2.5 cm by 6.4 cm with the weld region centered on, and perpendicular to, the length of the specimen. The thickness of the specimens varied. The specimens used in this study were fabricated exactly the same as those tested in the natural biotic water

Table 3.1: Chemical compositions of the materials.

Material	Cr	Ni	Fe	Mo	Mn	Cu	Si	P	S	N	C
Alloy 400	-	Bal.	-	-	-	31.5	2	-	-	-	0.15
AL-6XN	20-22	23.5-25.5	Bal.	2.0	2.0	-	1.0	0.045	0.03	0.18-0.25	0.03
304L	18-20	8-12	Bal.	-	2.0	-	1.0	0.045	0.03	-	0.03
316L	16-18	10-14	Bal.	2-3	2.0	-	1.0	0.045	0.03	-	0.03

environment.

Also, the surface conditions of the materials were exactly the same as those tested in the natural environments. Alloy 400 was ground with a 80-grit SiC paper flapper wheel. AL-6XN weldments were tested in the as-welded condition and also in the as-welded and brushed (manual with stainless steel brush) condition. 304L/316L weldments were tested in the as-welded and in the as-welded and pickled conditions. The pickling solution consisted of 10% HNO₃ + 2% HF at a temperature of 110°F. Platinum electrodes, used for solution redox potential measurements, were mechanically cleaned with 9 µm Al₂O₃.

3.2 EXPERIMENTAL PROCEDURES

The development of an abiotic laboratory screening test (ALST) for MIC involved two parts: (i) replication of the major corrosion-causing characteristics of the natural biotic environments and (ii) measurements of corrosion behaviors in the abiotic solution and comparisons with corrosion behaviors in the natural biotic environments.

Three natural environments, the Delaware Bay site natural environment, Lewes, Delaware, the Arizona well-water system, Palo Verde Nuclear Generating Station and the Tennessee River fresh-water system, Fort Loudon Lake, Knoxville, Tennessee, were intended to be replicated by the ALST. These environments have different chloride contents as shown in Table 3.2. For each of the environments to be replicated, the chloride contents (28 ppt NaCl, 226 ppm chloride and 8 ppm chloride, respectively) were produced in the form of sodium chloride in a distilled-water-based solution. The oxidizing power of the abiotic solution was increased by adding ferric ions, Fe^{3+} , in the form of ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$). The exact concentration of ferric sulfate added was obtained by trial and error from the polarization resistance tests on alloy 400.

Four sets of experiments were performed. The first set, the polarization resistance measurements, were performed to determine the ferric sulfate concentration that produced the approximate corrosion rate for alloy 400 in the Delaware Bay site natural environment. The polarization resistance measurements were conducted using a EG&G 273 potentiostat. A platinum electrode was used for the counter electrode and a saturated calomel electrode (SCE) for the reference electrode. Nickel wires were spot-welded to the specimens and used for electrical connections. The part of the wire that

Table 3.2: The chloride contents as measured in the natural biotic environments.

Natural Environment	Chloride Content
Delaware Bay site	28 ppt NaCl
Arizona well water system	226 ppm chloride
Tennessee River fresh water system	8 ppm chloride

made contact with the electrolyte was coated with an epoxy (Americoat 90, manufactured by Ameron, 201 N Berry street, Brea, California) to prevent crevice corrosion at the wire/specimen interface.

Calculating the corrosion rates from the polarization resistance technique requires inputs such as the Tafel constants, the area of the specimen, densities and equivalent weights. 100 mV/decade was used for the Tafel constants. The specimen area was measured and entered. Also, densities and equivalent weights were obtained from the literature and are given in Table 3.3.

Following the polarization resistance measurements, cathodic polarization tests were performed on platinum electrodes, 304L stainless steel and alloy 400. 304L was mounted in Maraglass epoxy (Acme Division, New Haven, Connecticut) and then ground to 600-grit SiC surface finish. The cathodic behaviors of these materials were obtained

Table 3.3: Density and equivalent weight used in the corrosion rate calculations.

Specimen	Density	Equivalent weight
Alloy 400	8.83 g/cm ³	30.0

and the features were compared to their counterparts in the natural biotic environment. These measurements were accomplished with the EG&G 273, Princeton Applied Research, Potentiostat and a computer using PARC 342 software. The potential was scanned from 50mV above E_{corr} to -1000 mV with respect to the reference electrode (SCE), and a scan rate of 0.17 mV per second was used. The anodic polarization curve for alloy 400 was also obtained, and the corrosion predictions based on anodic and cathodic curves were compared to the corrosion rates obtained for this alloy.

Open-circuit potentials for the materials were obtained with an electrometer and a computer recording device. Saturated calomel electrodes were used for reference electrodes.

To further test the authenticity of the abiotic solution that replicated the natural environments, immersion tests were conducted. The specimens were exposed in crevice and non-crevice geometries. The assembly shown in Figure 3.1 was employed to impart a crevice along the length of the weldment. Backing plates, bolts, and nuts were fabricated from unalloyed titanium. For the crevice geometry, AL-6XN and 304L/316L stainless steel weldments were mounted in the crevice assembly with the weld surface

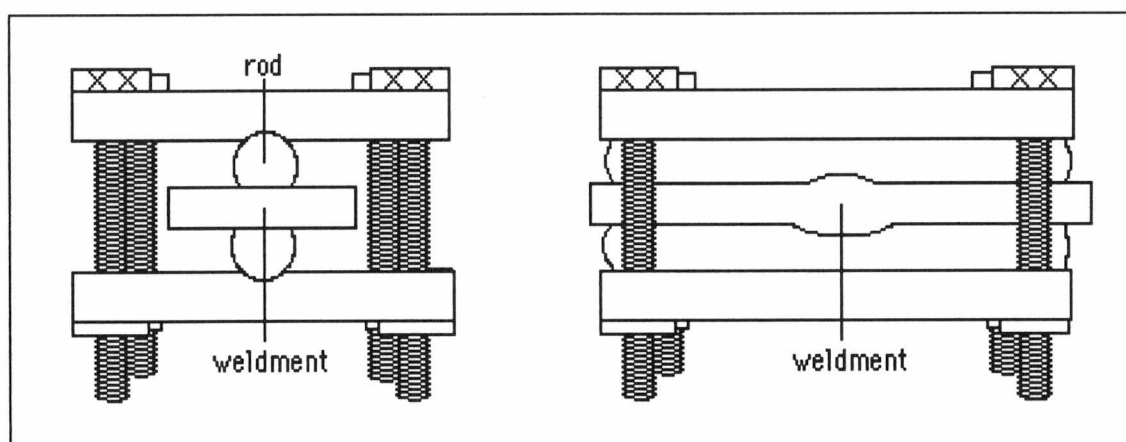


Figure 3.1: Assembly used to produce crevices on weldments.

facing upwards (ID surface for 304L/316L weldments). The weldments were creviced by two silicone rods that were cut to fit the crevice assembly after they were cleaned by boiling in distilled water for 30 minutes. The weldments were held in place by applying a torque of 2.0 in-lb to each of the four bolts. The crevice assemblies were placed in abiotic test cells intended to simulate MIC effects of the natural biotic environments. The exposure period was seven days.

AL-6XN weldments were exposed in (i) creviced, as-welded, (ii) creviced, brushed, (iii) non-creviced, as-welded, (iv) non-creviced, brushed, surface conditions in 28 ppt NaCl solution plus 0.001 M ferric sulfate, intended to replicate the Delaware Bay site natural environment. The pH of the solution was 3.3. 304L/316L weldments were exposed in (i) creviced, as-welded, (ii) creviced, pickled, (iii) non-creviced, as-welded, (iv) non-creviced, pickled, surface conditions in 226 ppm NaCl solution plus 0.001 M ferric sulfate, with a pH of 2.6 intended to replicate the Arizona well-water system, and in 8 ppm NaCl plus 0.001 M ferric sulfate with a pH of 2.6, intended to replicate the Tennessee River fresh-water system. Table 3.4 gives the pH of the abiotic solution replicating the natural environments intended to be simulated.

Following the exposures, the surfaces of the weldments were visually examined. Some of the specimens were also examined with the scanning electron microscope (SEM). The appearances and locations of corrosion, if any, were noted.

Table 3.4: pH values of the abiotic solutions replicating the natural environments.

Abiotic Solution	pH
28 ppt NaCl + 0.001 M ferric sulfate	3.3
226 ppm chloride + 0.001 M ferric sulfate	2.6
8 ppm chloride + 0.001 M ferric sulfate	2.6

CHAPTER 4

EXPERIMENTAL RESULTS

4.1. POLARIZATION RESISTANCE TESTS

Polarization resistance measurements were conducted to determine the corrosion rates for alloy 400 weldment specimens in an abiotic laboratory screening test (ALST) that simulated the Delaware Bay site natural biotic environment. Alloy 400 weldments, ground with an 80-grit paper flapper wheel, produced the most dramatic MIC effects in the field studies at the Delaware Bay site natural biotic water environment [1]. The measured sodium chloride (NaCl) content at the Delaware Bay site was 28 ppt [1]. This NaCl content was used in a distilled-water-based solution containing ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) to replicate the Delaware Bay site natural biotic environment. The exact concentration of ferric sulfate that simulated the MIC effects in the ALST was obtained by trial and error.

Figure 4.1 shows the corrosion rate as a function of time for alloy 400 weldment specimens. Curves 1, 2 and 3 were obtained in abiotic solutions containing 0.1 M, 0.01 M and 0.001 M ferric sulfate, respectively, in a distilled-water-based solution containing 28 ppt NaCl. Curve 4 was obtained in the control abiotic-test solution, consisting of 28 ppt NaCl only (i.e., without ferric sulfate). As reference, curves A and B of Figure 4.1 were obtained from the field studies at the Delaware Bay site natural biotic water environment. Curve A shows the surface average corrosion rate as a function of time in

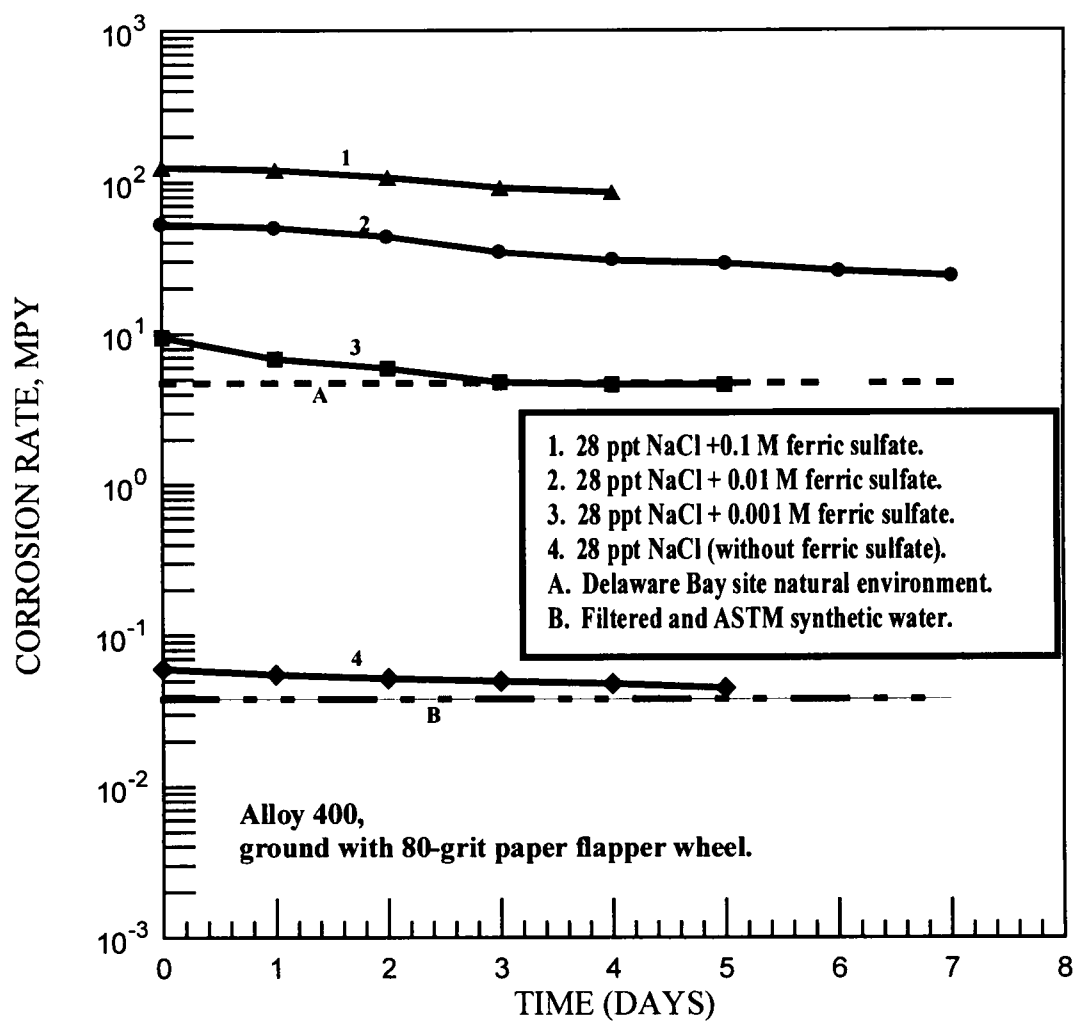


Figure 4.1: Corrosion rate as a function of time for alloy 400, ground with 80-grit paper flapper wheel.

the natural microbial environment at the Delaware Bay site; whereas, curve B is the corresponding control test depicting the surface average corrosion rate as a function of time in the filtered natural environment (minimal microorganisms) and in ASTM synthetic seawater (no microorganisms).

It is evident from Figure 4.1 that the surface average corrosion rate (5 mpy) for alloy 400 in the abiotic solution containing 28 ppt NaCl plus 0.001 M ferric sulfate (curve 3) replicated the corrosion rate (4.75 mpy) produced in the natural microbial environment (curve A) [1]. It is also apparent that the surface average corrosion rate in the control abiotic solution containing 28 ppt NaCl only (curve 4) had a value that was very close to the surface average corrosion rate obtained in the filtered natural environment and in ASTM synthetic seawater (curve B). The surface average corrosion rates (mpy) for alloy 400 weldment specimens, ground with 80-grit paper flapper wheel, as obtained from the Delaware Bay site field study [1] and from the present study (abiotic experiments), are summarized in Tables 4.1 and 4.2, respectively. From Figure 4.1 and Tables 4.1 and 4.2, it is evident that the concentration of ferric sulfate that best simulates the Delaware Bay microbial effects is 0.001 M.

4.2. CATHODIC POLARIZATION TESTS

Cathodic polarization tests were performed on platinum electrodes, 304L stainless steels and alloy 400 specimens in abiotic solutions in order to compare the results with the observed cathodic behaviors for these materials in the natural environments. These comparisons were made to further test the general validity of the ALST in terms of

Table 4.1: Surface average corrosion rates (mpy) for alloy 400, ground with 80 grit paper flapper wheel, obtained from polarization resistance tests at the Delaware Bay site [1].

Weldment Specimen	Natural Delaware Bay Water, Non-creviced*	Filtered Delaware Bay Water, Creviced**	ASTM Synthetic Water, Non-creviced***
Alloy 400	4.75	0.053	0.024

* Microorganisms present.

** Minimal microorganisms.

*** No microorganisms.

Table 4.2: Surface average corrosion rates (mpy) for alloy 400, ground with 80 grit paper flapper wheel, obtained from polarization resistance tests in abiotic experiments.

Weldment Specimen	28 ppt NaCl plus 0.001 M Ferric Sulfate, Non-creviced	28 ppt NaCl plus 0.01 M Ferric Sulfate, Non-creviced	28 ppt NaCl plus 0.1 M Ferric Sulfate, Non-creviced	28 ppt NaCl, Non-creviced*
Alloy 400	5.0	30	100	0.05

* Control test; no ferric sulfate.

replicating field test results in natural biotic environments.

4.2.1. Platinum Electrodes

The cathodic curves for platinum in the Delaware Bay seawater and in the abiotic solutions are presented in Figures 4.2 and 4.3, respectively. As shown in Figure 4.2, Chandrasekaran and Dexter [61] observed that the cathodic reaction shifted from predominantly oxygen reduction for bare platinum, to a combination of oxygen and peroxide reduction for biofilmed platinum, and to predominantly peroxide reduction as the biofilm matured. The biofilmed platinum cathodic curve coincided with that of the bare platinum at lower potentials due to depletion of peroxide in the biofilm. In Figure 4.3 for the abiotic solution, it is apparent that the cathodic reaction shifts from predominantly oxygen reduction (curve 4), to a combination of oxygen and ferric ion reduction (curve 3), to predominantly ferric ion reduction (curves 1 & 2) as the ferric sulfate concentration increases, for potentials higher than about -150 mV (SHE). It is also noticed that the cathodic curve for the platinum electrode in 28 ppt NaCl plus 0.001 M ferric sulfate (curve 3 of Figure 4.3) coincided with that of the platinum electrode in 28 ppt NaCl solution (without ferric sulfate) (curve 4 of Figure 4.3). This is due to the fact that the amount of ferric sulfate is small (0.001M), resulting in a diffusion limited current density for ferric-ion reduction (curve 3), which exactly coincides with that for oxygen reduction (curve 4).

It is, therefore, evident from Figures 4.2 and 4.3 that the abiotic solution

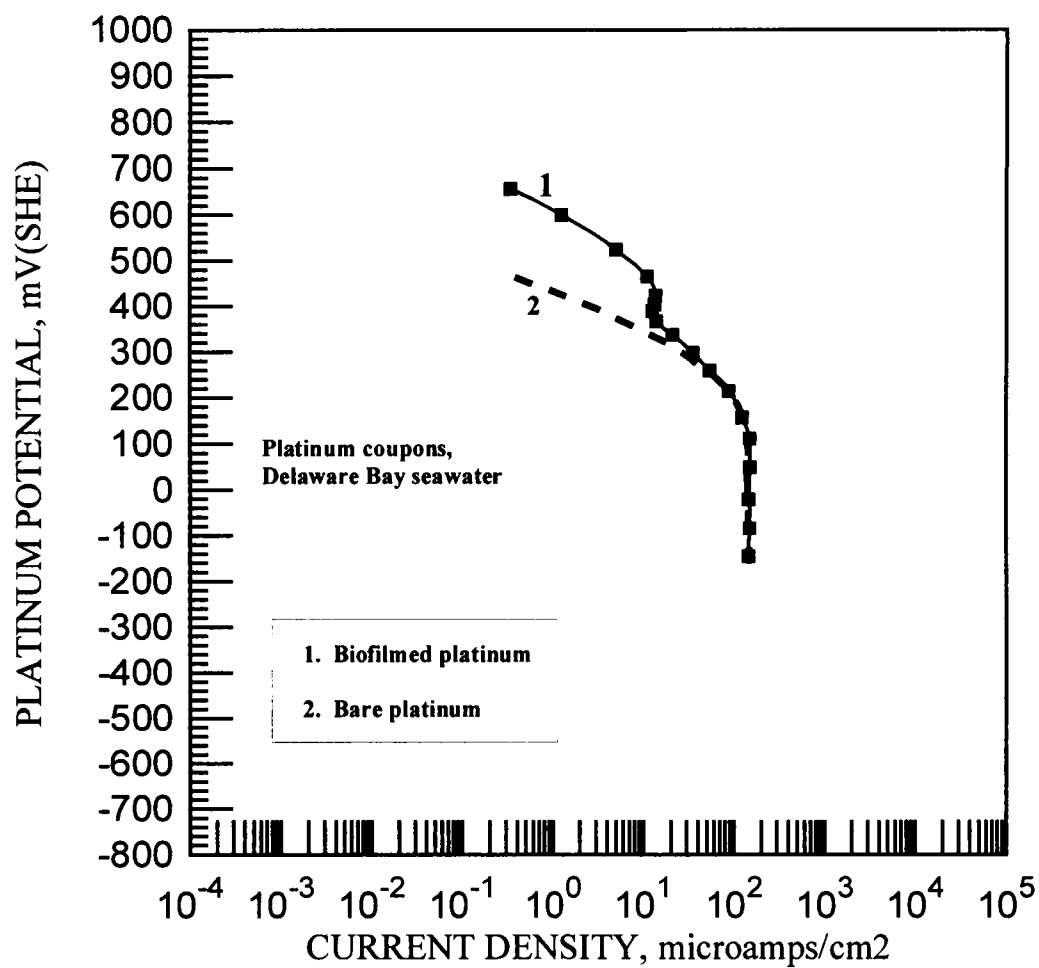


Figure 4.2 : Cathodic curves for platinum coupons (with and without biofilms) in Delaware Bay seawater. (Adapted from reference 3).

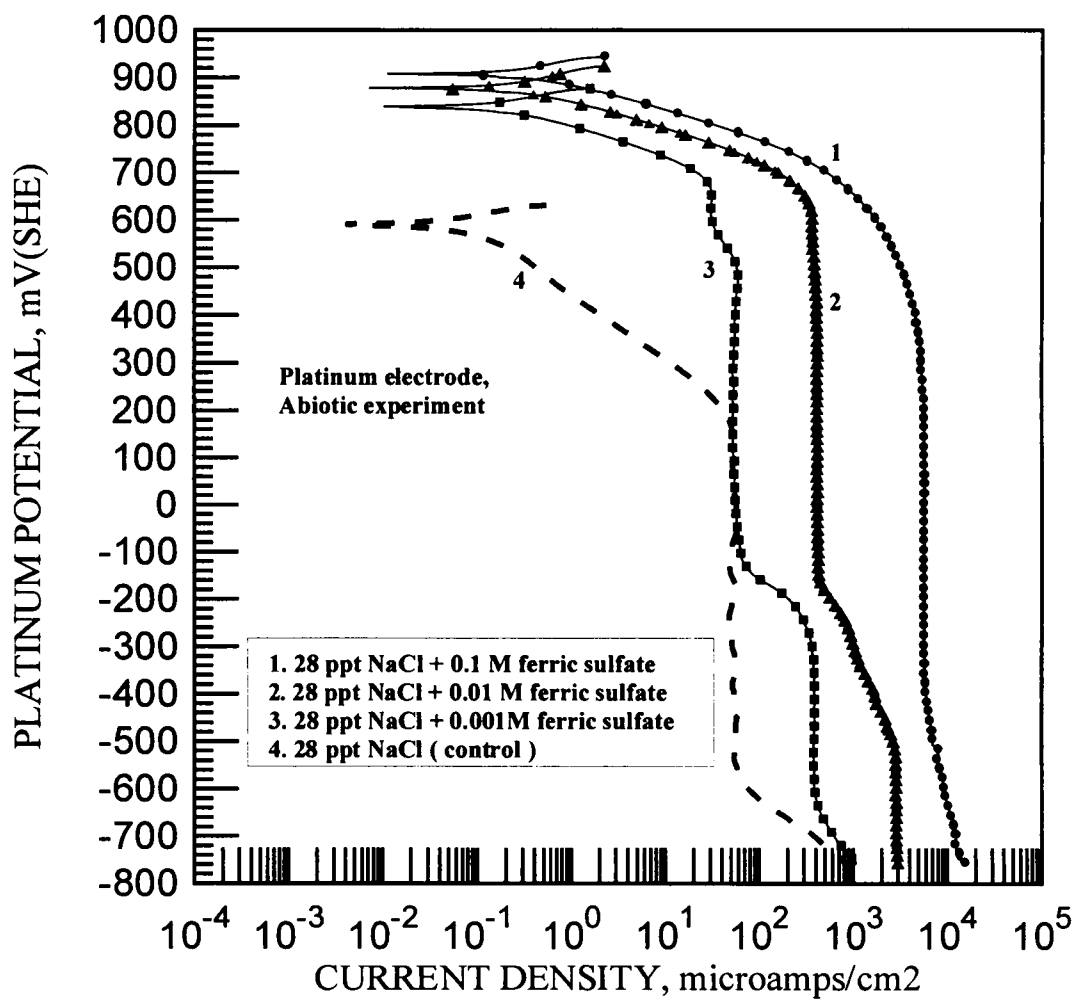


Figure 4.3: Cathodic curves for platinum electrode in abiotic solutions.

consisting of a distilled-water-based solution containing 28 ppt NaCl plus 0.001 M ferric sulfate, replicates the trends observed in the natural microbial environment at the Delaware Bay site. Hence, the 0.001M ferric sulfate solution of the ALST simulates the MIC effects of the natural biotic water environments. The higher potentials observed in the abiotic experiments might be attributed to the fact that ferric ions are strong oxidizers. Also, for potentials below -150 mV (SHE), there was an increase in current density due to the acidification associated with ferric-ion hydrolysis (Figure 4.3).

4.2.2. 304L Stainless Steel

To further verify that the ALST actually replicates the natural microbial environment, cathodic polarization tests were performed on 304L stainless steel in a fresh water system. The field study [9] in this environment (Tennessee River) showed a pronounced difference in the cathodic curves of 304L stainless steels in unfiltered (microorganisms present) and filtered (minimal microorganisms) river water.

Figure 4.4 presents the cathodic polarization curves for 304L stainless steel in the unfiltered and filtered Tennessee river water. Figure 4.5 shows the cathodic curves for 304L stainless steel in abiotic solutions intended to replicate the behaviors shown in Figure 4.4. It is apparent from Figure 4.5 (curve 1) that there are two reduction reactions, the reduction of ferric ions and reduction of dissolved oxygen. Also, curve 2 (Figure 4.5) has one reduction reaction, the reduction of dissolved oxygen. For the unfiltered Tennessee River water (curve 1 in Figure 4.4), there are two reduction reactions. The

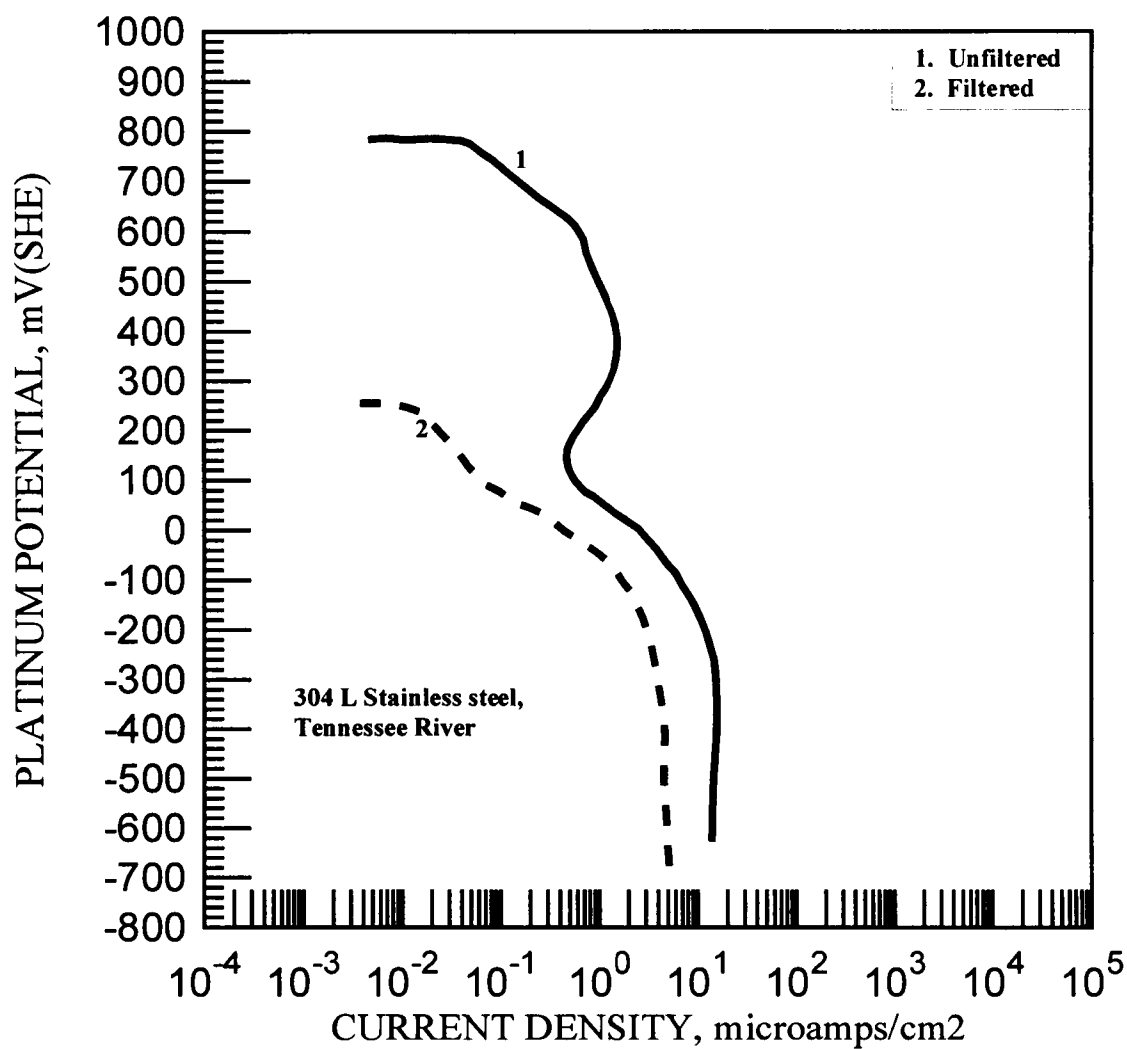


Figure 4.4 : Cathodic polarization curves for 304 L stainless steel in filtered and unfiltered Tennessee River water. (Adapted from reference 9).

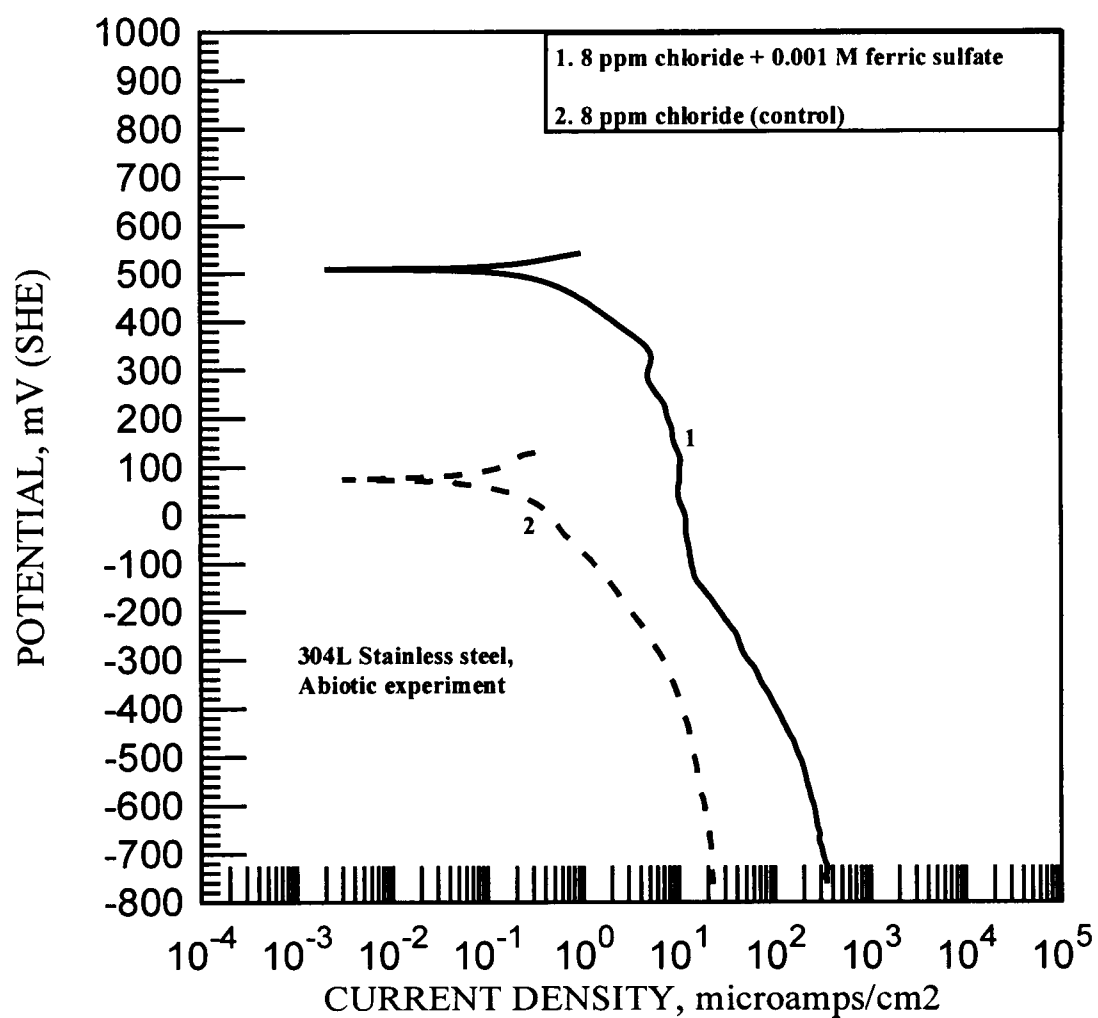


Figure 4.5 : Cathodic curves for 304L stainless steel in abiotic solutions.

species undergoing reduction in the higher-potential reaction is unknown; the lower potential reaction is the reduction of oxygen going into a diffusion limit. For the filtered water (curve 2 in Figure 4.4), two reduction reactions are observed instead of one (oxygen reduction); it is believed, therefore, that some microorganisms were still present in the filtered water.

Lower corrosion potentials are observed in the 304L stainless steel in the abiotic solutions (Figure 4.5), as compared to those in the unfiltered and filtered Tennessee River water (Figure 4.4). It is also noted that 304L stainless steel has a higher corrosion current density (corrosion rate) in the abiotic solution than in the natural environment.

4.2.2. Alloy 400 (Monel 400)

The cathodic polarization curves and an anodic curve for alloy 400 in abiotic solutions are shown in Figure 4.6. No comparison is made because no data of this type are available for this alloy in field studies of the natural biotic water environment. However, it was observed that in the abiotic solution containing 28 ppt NaCl plus 0.001 M ferric sulfate (curve 2), two reduction processes occurred, the reduction of ferric ions and dissolved oxygen, whereas, curve 3, which is the control test (without ferric sulfate) shows only the reduction of dissolved oxygen. Curves 2 & 3 in Figure 4.6, replicate unfiltered and filtered natural water environments respectively.

From the anodic and cathodic curves in Figure 4.6, the corrosion rates for alloy 400 were predicted to be 9.0 mpy and 0.06 mpy (curves 2 and 3, respectively) in the

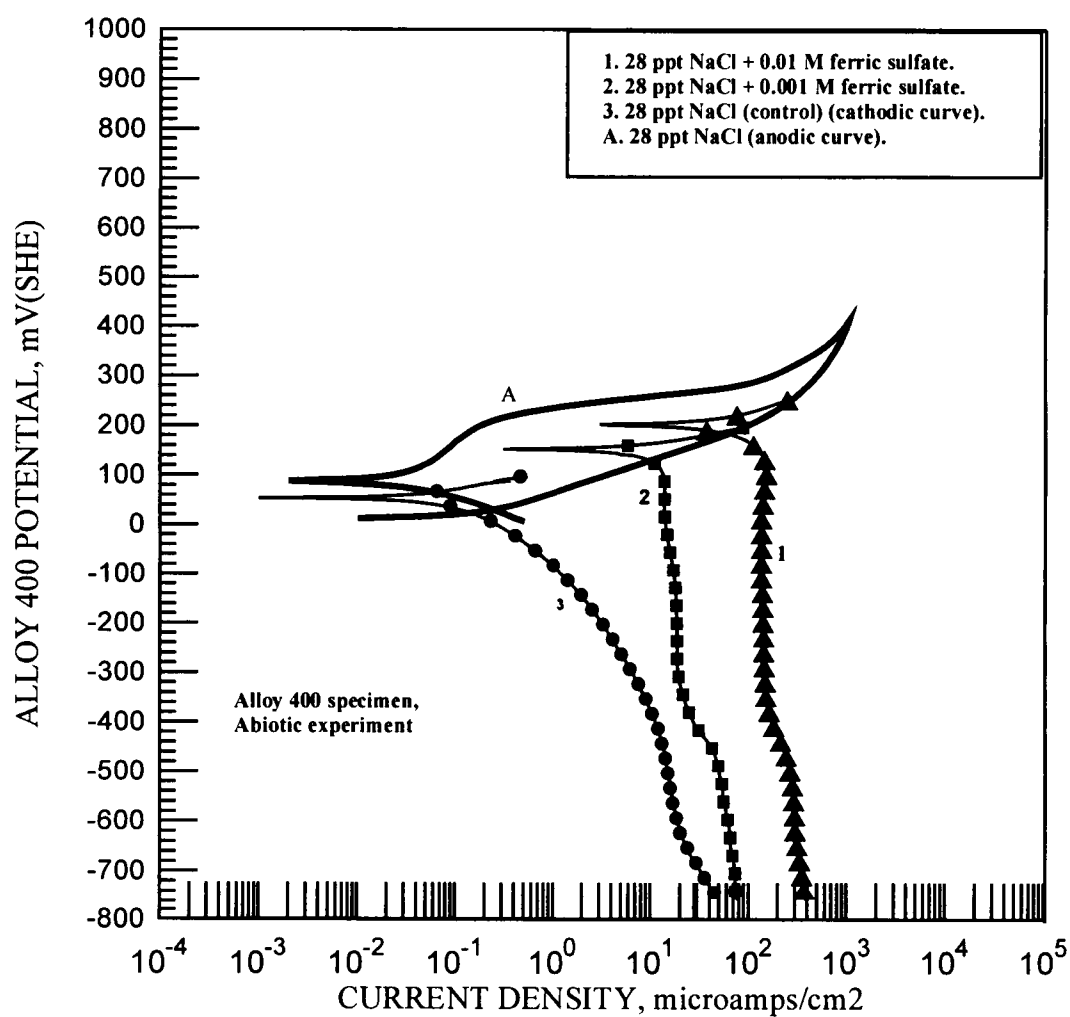


Figure 4.6: Cathodic curves(1, 2 & 3), and an anodic curve (A) for alloy 400 in abiotic solutions.

abiotic solution containing 28 ppt NaCl + 0.001 M ferric sulfate and in 28 ppt NaCl respectively. They compared favorable to those obtained from the polarization resistance tests.

4.3. OPEN-CIRCUIT POTENTIAL MEASUREMENTS

Open-circuit potential (OCP) measurements as a function of exposure time were obtained for platinum electrodes in abiotic solutions intended to replicate three different water environments: The Delaware Bay site, the Arizona well-water system and the Tennessee River fresh-water system. Also, OCP measurements were obtained for alloy 400 and AL-6XN in an abiotic solution intended to replicate the Delaware Bay natural biotic environment.

Figures 4.7, 4.9 and 4.11 show the OCP for platinum electrodes obtained from the field studies at the Delaware Bay, Arizona well-water system and Tennessee River fresh-water system, respectively. Figures 4.8, 4.10 and 4.12 show the OCP for platinum electrodes obtained from the abiotic experiments that simulated the Delaware Bay, the Arizona well-water system and the Tennessee River fresh-water system, respectively. It is observed (Figures 4.7 to 4.12) that the OCP in the abiotic experiments are higher than those obtained in the field tests at the natural biotic environments. This ennoblement might also be attributed to the fact that ferric ions are strong oxidizers. Figures 4.13 and 4.15 show the OCP for alloy 400 and AL-6XN respectively, in the natural Delaware Bay

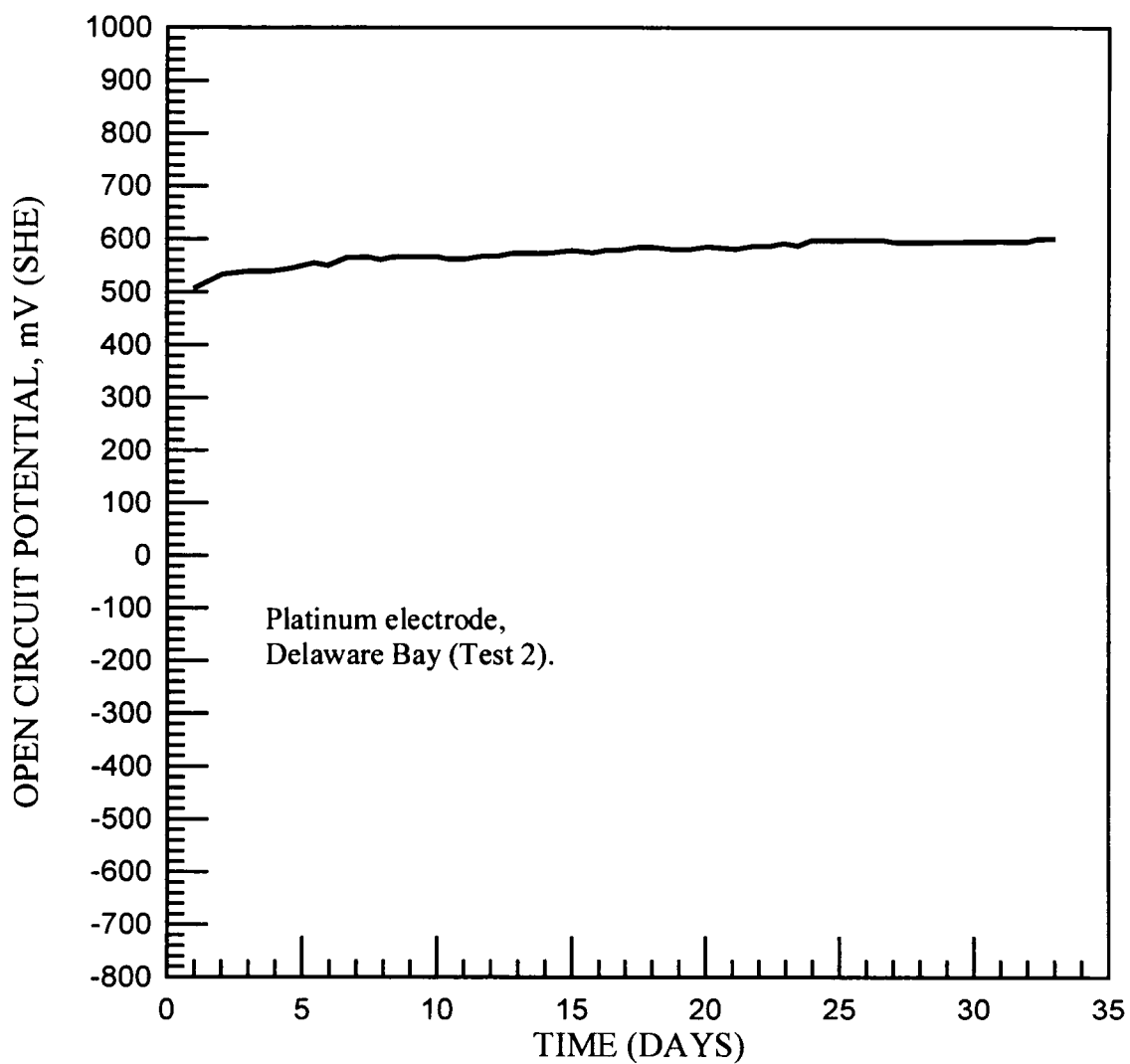


Figure 4.7: Open circuit potential for platinum electrode in the field studies at the Delaware Bay. (Adapted from reference 1).

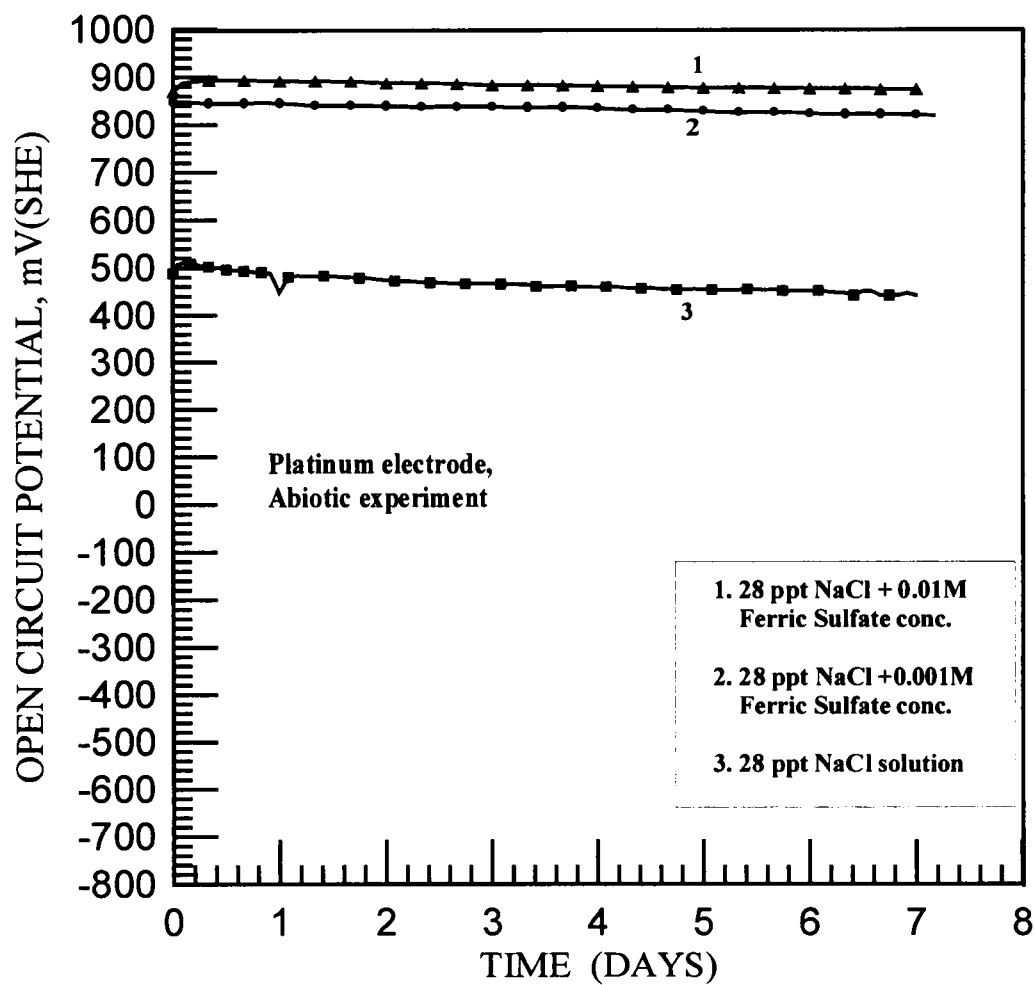


Figure 4.8: Open circuit potential versus time for platinum electrodes in abiotic solutions simulating the Delaware Bay site natural environment.

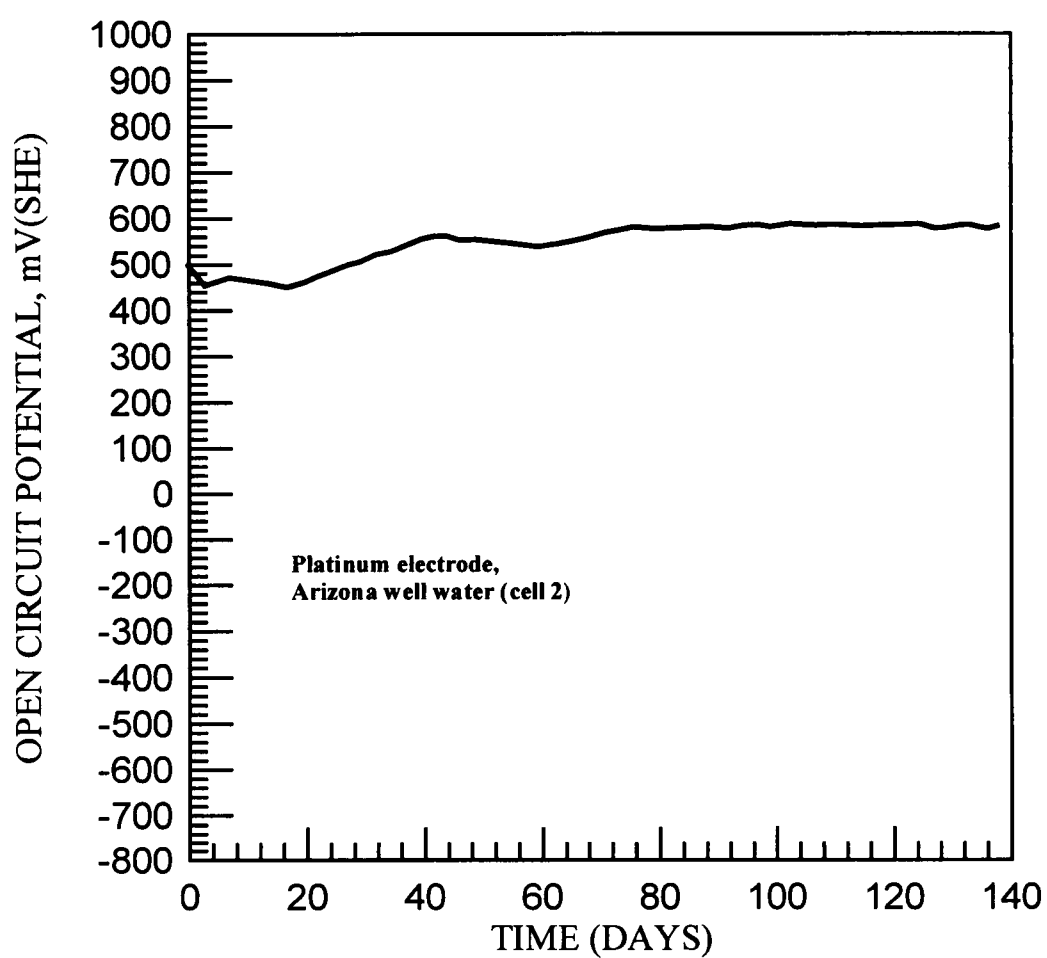


Figure 4.9 : Open circuit potential for platinum electrode in the field studies at the Arizona well water system. (Adapted from reference 8).

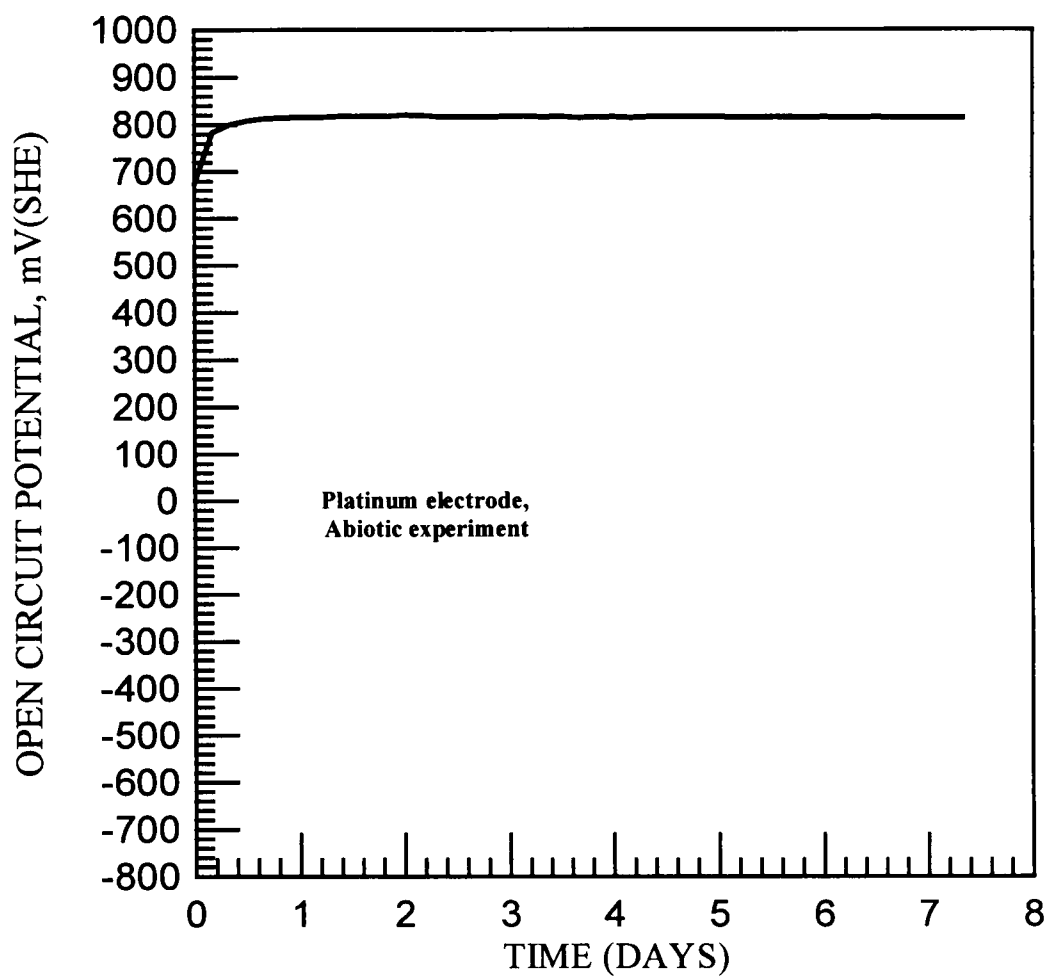


Figure 4.10: Open circuit potential for platinum electrode in abiotic solution (226 ppm Chloride + 0.001M ferric sulfate conc.) simulating the Arizona well water system.

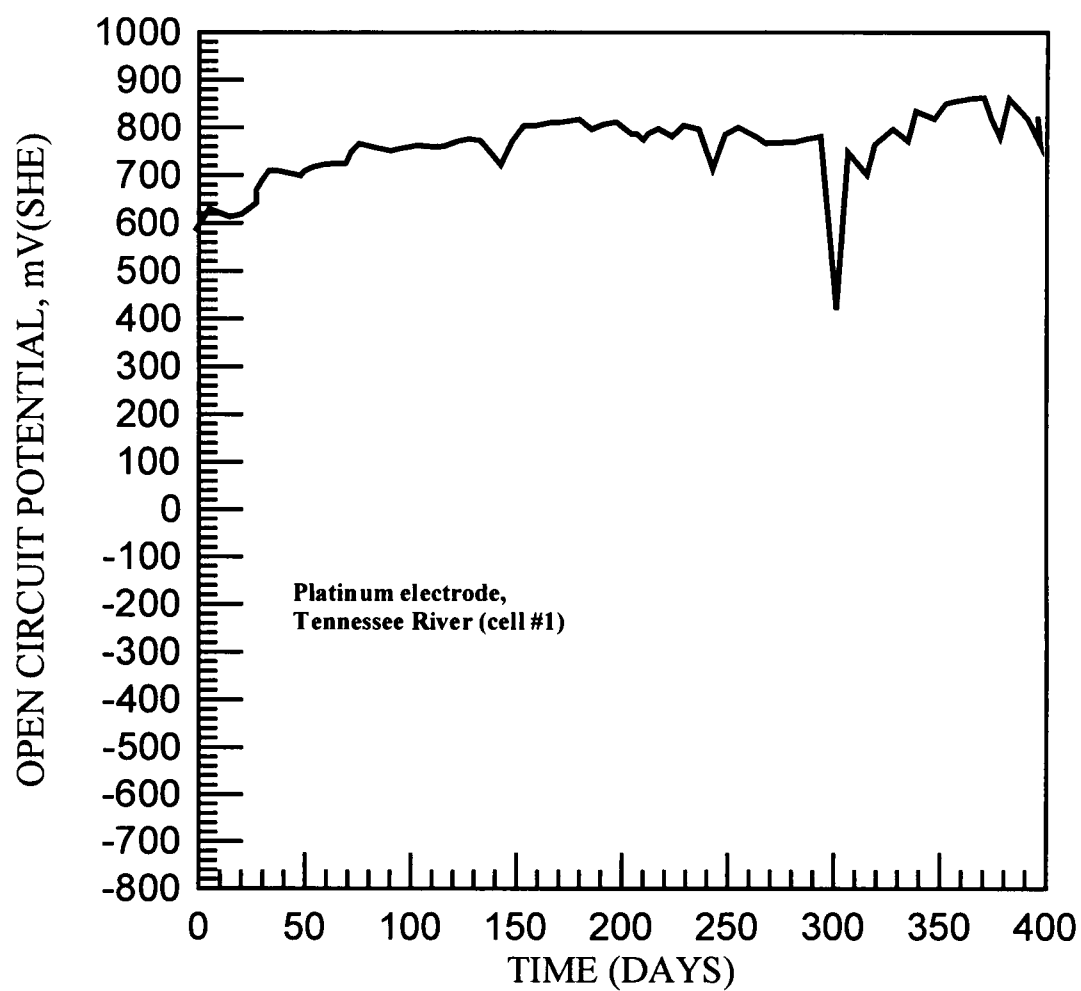


Figure 4.11: Open circuit potential for platinum electrode in the field studies at the Tennessee River. (Adapted from reference 9).

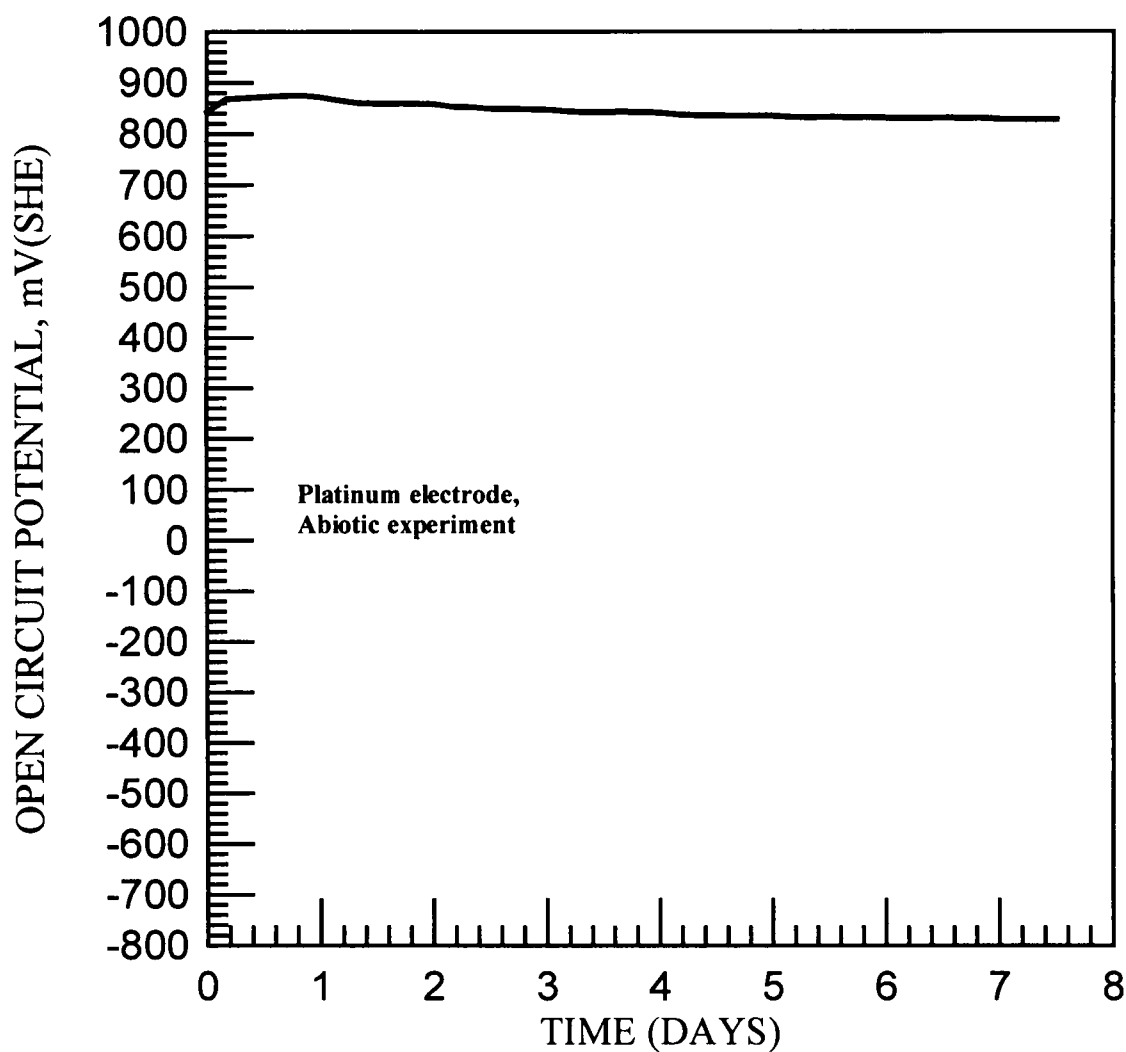


Figure 4.12: Open circuit potential for platinum electrode in abiotic solution (8 ppm Chloride + 0.001M Ferric Sulfate) simulating the Tennessee river fresh water system.

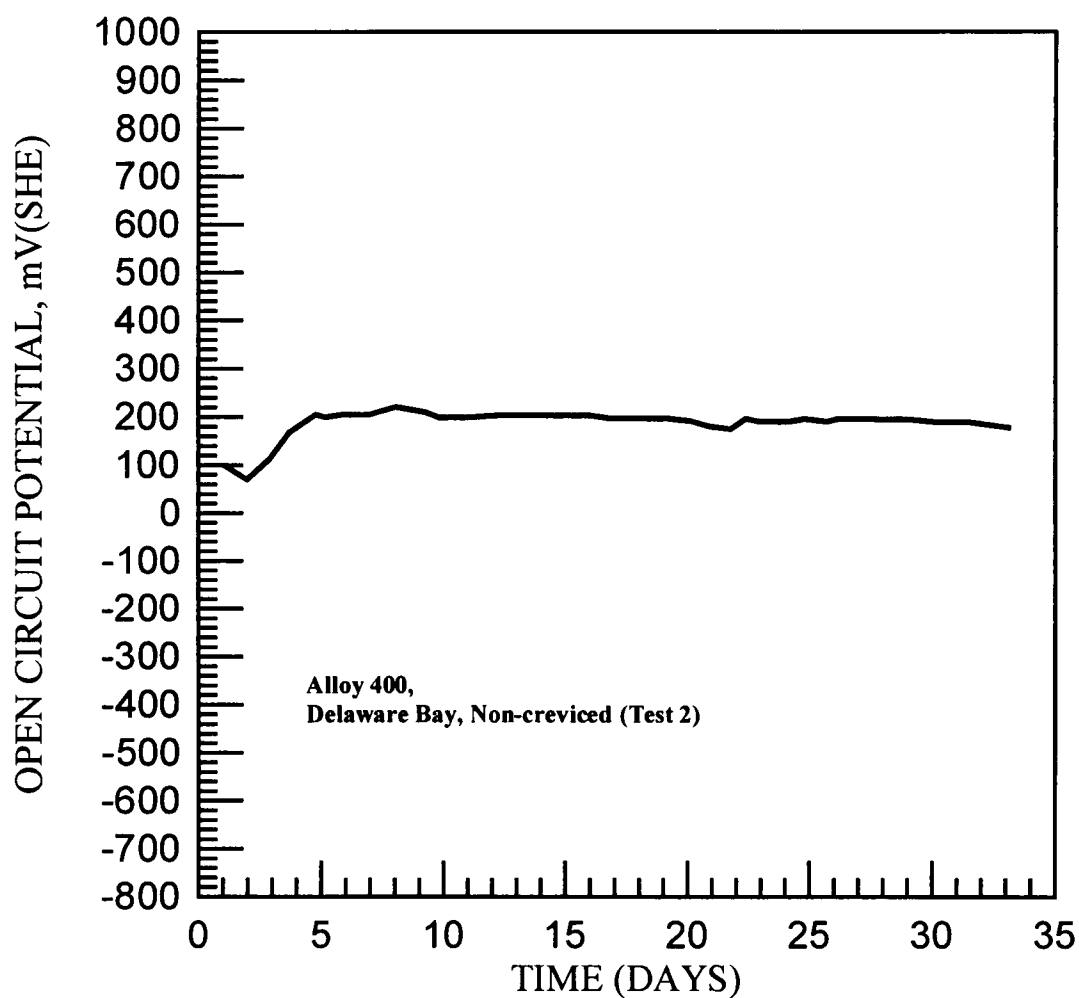


Figure 4.13: Open circuit potential for alloy 400 weldment, ground with 80 grit flapper wheel, in Delaware Bay, non-creviced. (Adapted from reference 1).

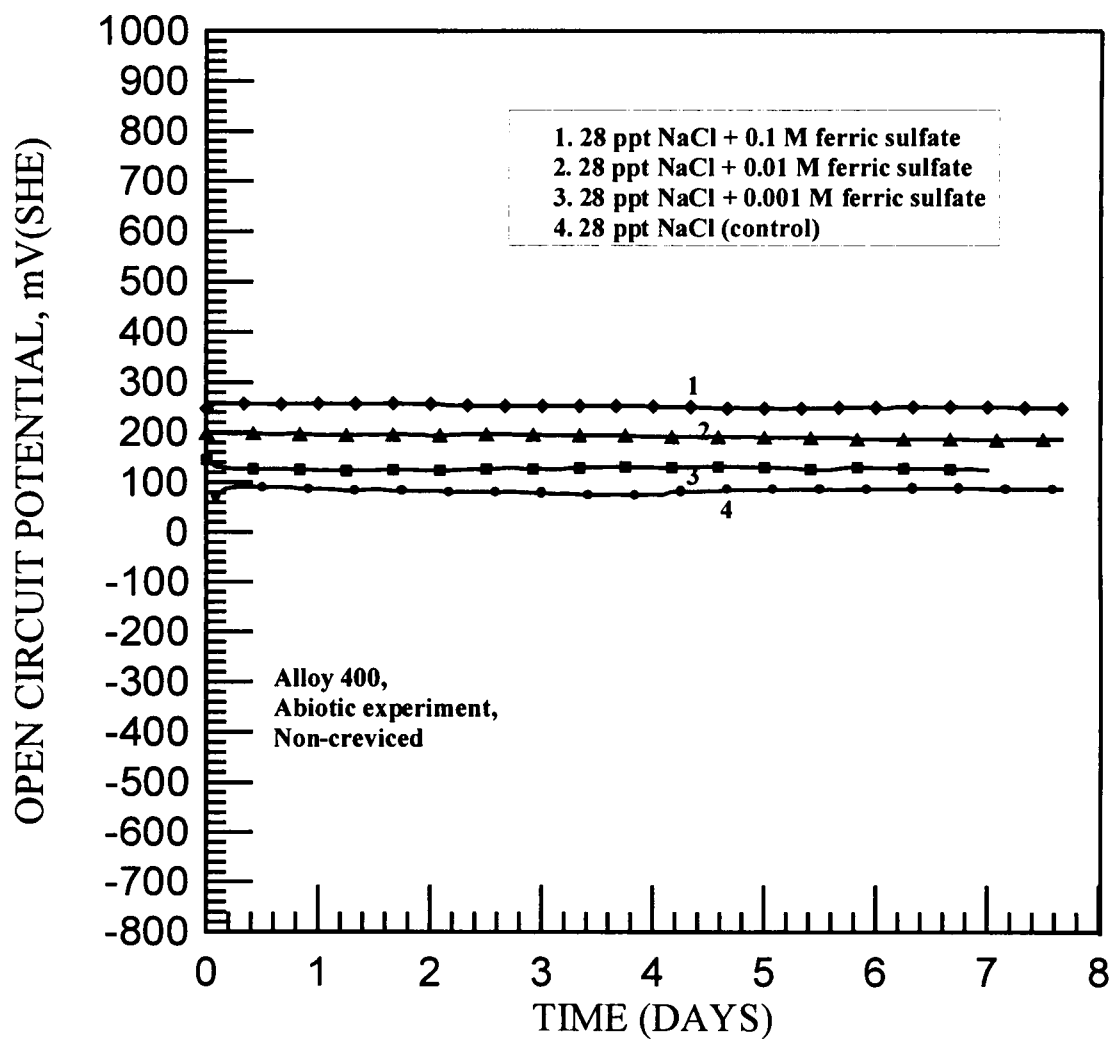


Figure 4.14: Open circuit potential for alloy 400, ground with 80 grit flapper wheel in abiotic solutions simulating the Delaware Bay.

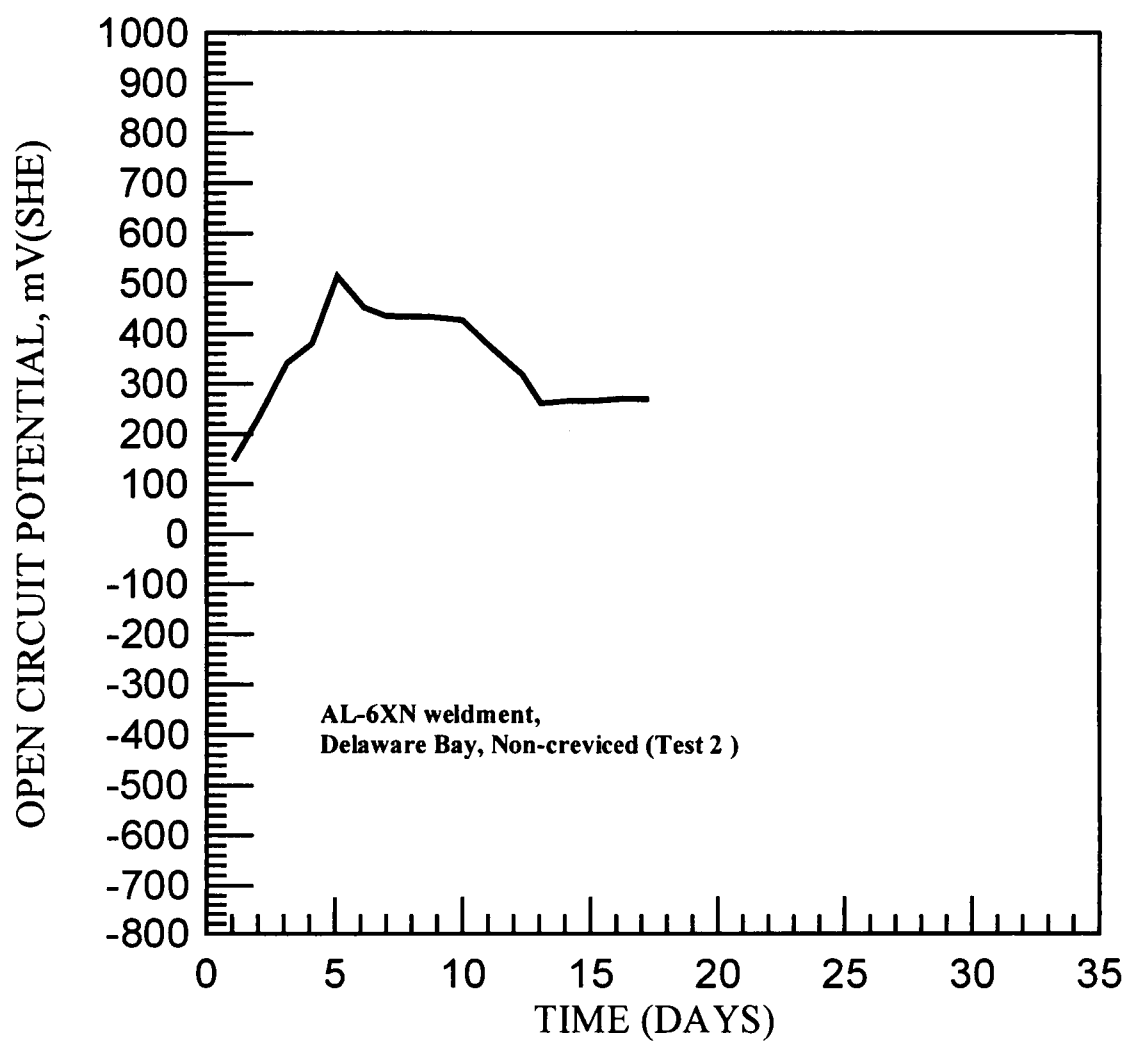


Figure 4.15: Open circuit potential for AL-6XN weldment, brushed, tested in Delaware Bay site. (Adapted from reference 1).

seawater, while Figures 4.14 and 4.16 show these materials in the abiotic solution that simulates the Delaware Bay seawater. The corrosion potentials for AL-6XN were higher in the abiotic solution than in the natural environment. Alloy 400 exhibited lower corrosion potentials in the abiotic solution.

4.4. SURFACE EXAMINATION

The surfaces of the specimens were examined after exposure in abiotic laboratory screening tests (ALST) for seven days. Visual and microscopic examination results were compared to those obtained from specimens exposed in the natural biotic microbial environments.

4.4.1. Exposure in ALST Replicating the Delaware Bay Site

The immersion tests on AL-6XN alloy in the abiotic solution (28 ppt NaCl + 0.001 M ferric sulfate) that replicated the major corrosion-enhancing characteristics of the Delaware Bay site water environment proved very encouraging. Buchanan et al. [1] studied the corrosion behavior of AL-6XN in the marine microbial environment at the Delaware Bay site. They found that the creviced AL-6XN specimens showed extensive corrosion preferentially at the weld region (heat tint area) underneath the silicone rods, but that the non-creviced specimens showed no evidence of accelerated corrosion. Some of their results are shown in Figures 4.17 and 4.18 [1].

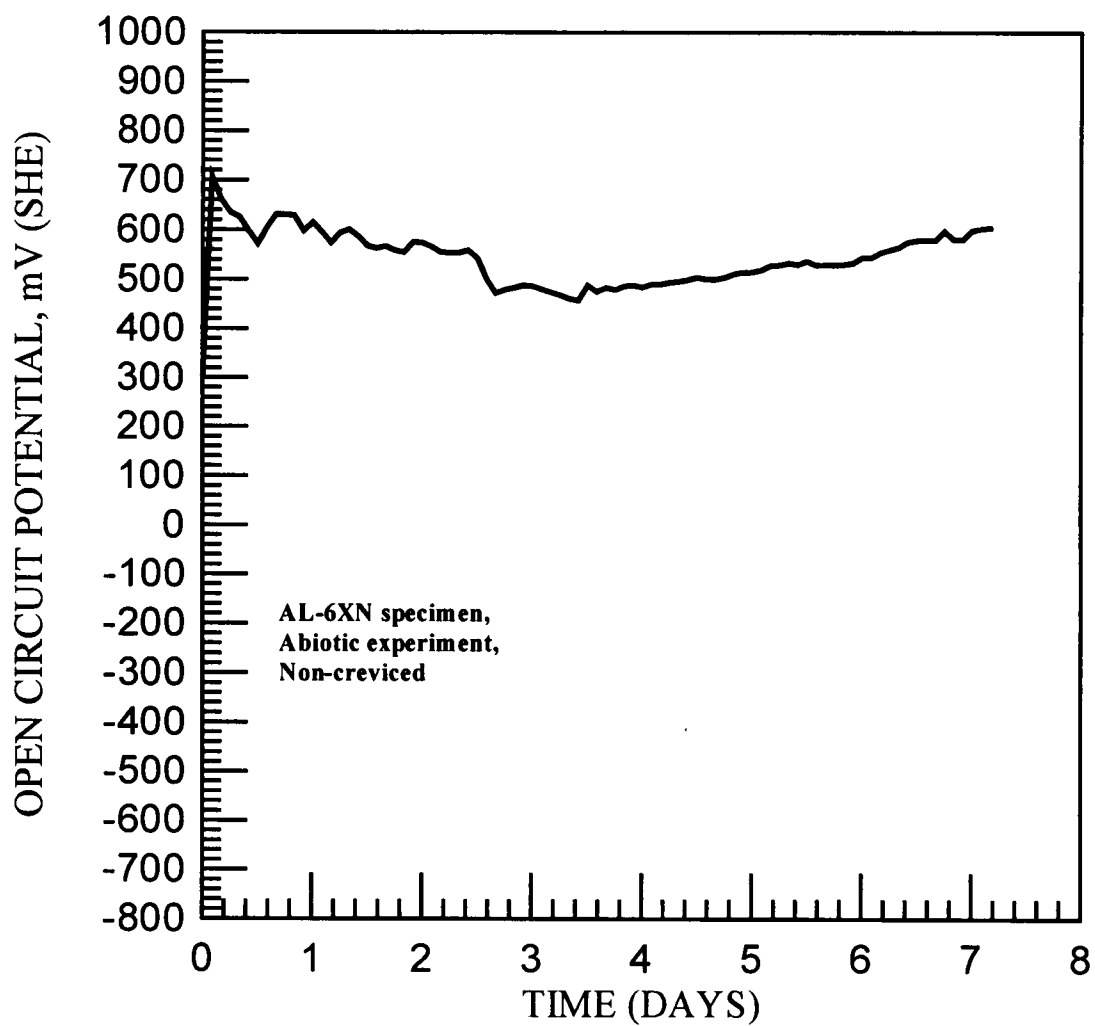
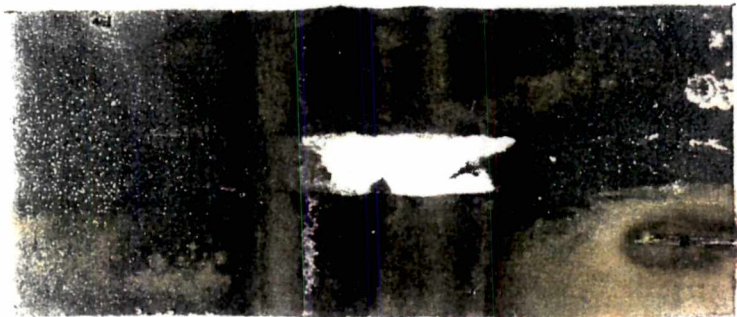


Figure 4.16: Open circuit potential for AL-6XN alloy (brushed) in 28 ppt NaCl + 0.001 M ferric sulfate conc.



Figures 4.17: Photograph showing corrosion of AL-6XN weldment, as-welded and creviced, exposed in Delaware Bay site natural water environment. (From reference 1).

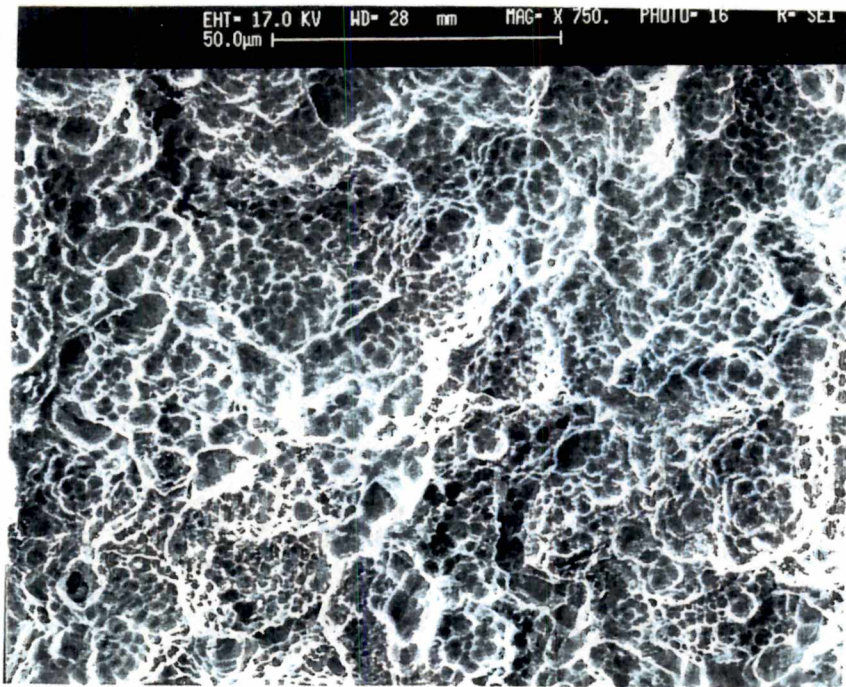


Figure 4.18: Scanning electron micrograph showing area in corroded region of Figure 4.17. (From reference 1)

Figures 4.19 to 4.22 show AL-6XN weldments after exposure in the ALST in the (i) creviced, no treatment, (ii) creviced, brushed, (iii) non-creviced, no treatment, and (iv) non-creviced, brushed, conditions, respectively. It was observed that only the creviced specimens showed extensive corrosion preferentially at the weld regions underneath the silicone rods, and no corrosion was found in the non-creviced specimens. Figure 4.23 shows the micrograph of the creviced, no treatment AL-6XN specimen, showing the area in the corroded region.

4.4.2. Exposure in ALST Replicating the Arizona Well Water System

The corrosion studies of stainless steel weldments at the Arizona well-water Site natural environment by Li et al. [8] showed that localized corrosion and nodules formed in the heat tint regions (weld regions) of the as-welded coupons, in the creviced geometry only, and that corrosion did not occur in the base-metal specimens, nor on creviced, pickled weldment coupons, nor on non-creviced, as-welded coupons. A 304L/316L stainless steel specimen (as-welded and creviced) after exposure for four months in the Arizona well water natural environment is shown in Figure 4.24 [8]. It is apparent from Figure 4.24 that there was corrosion nodule formation in the heat-tint region at the metal/epoxy interface due to the crevice geometry at the metal / epoxy interface.

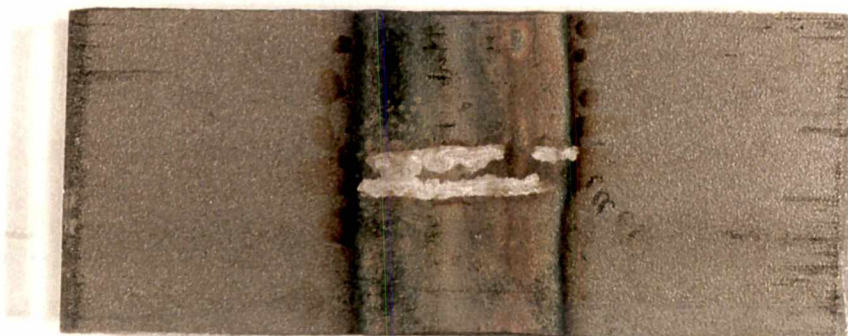


Figure 4.19: Photograph of AL-6XN weldment, as-welded and creviced. Tested in abiotic solution that simulates the Delaware Bay site water.

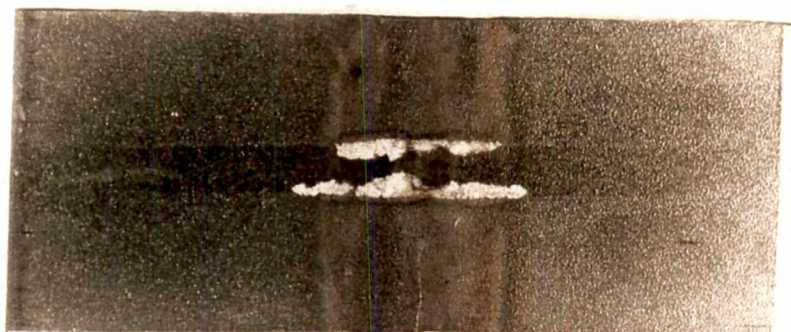


Figure 4.20: Photograph of AL-6XN weldment, brushed and creviced. Tested in abiotic solution that simulates the Delaware Bay site water.



Figure 4.21: Photograph of AL-6XN weldment, as-welded and non-creviced. Tested in abiotic solution that simulates the Delaware Bay site water.

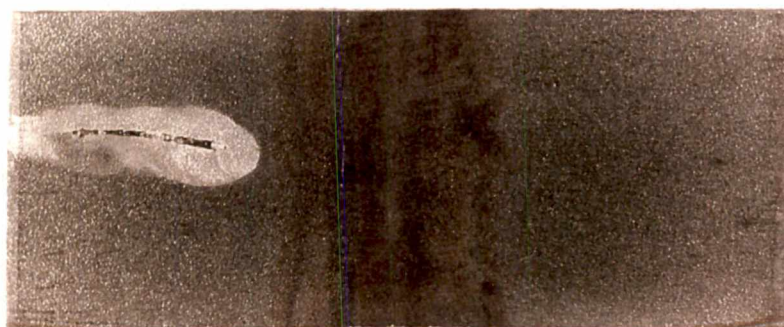


Figure 4.22: Photograph of AL-6XN weldment, brushed and non-creviced. Tested in abiotic solution that simulates the Delaware Bay site water.

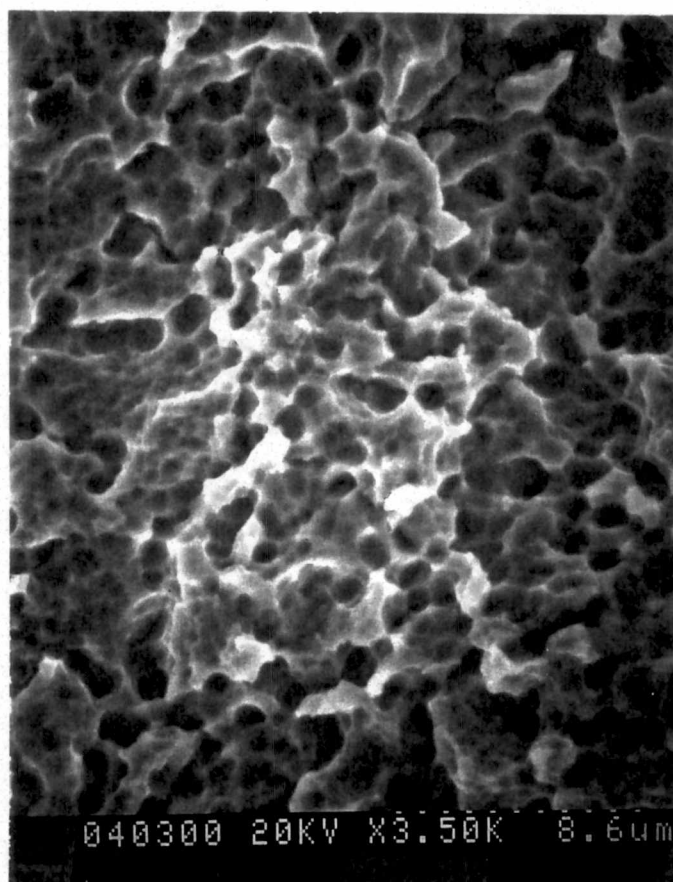


Figure 4.23: Scanning electron micrograph showing corroded region of Figure 4.19

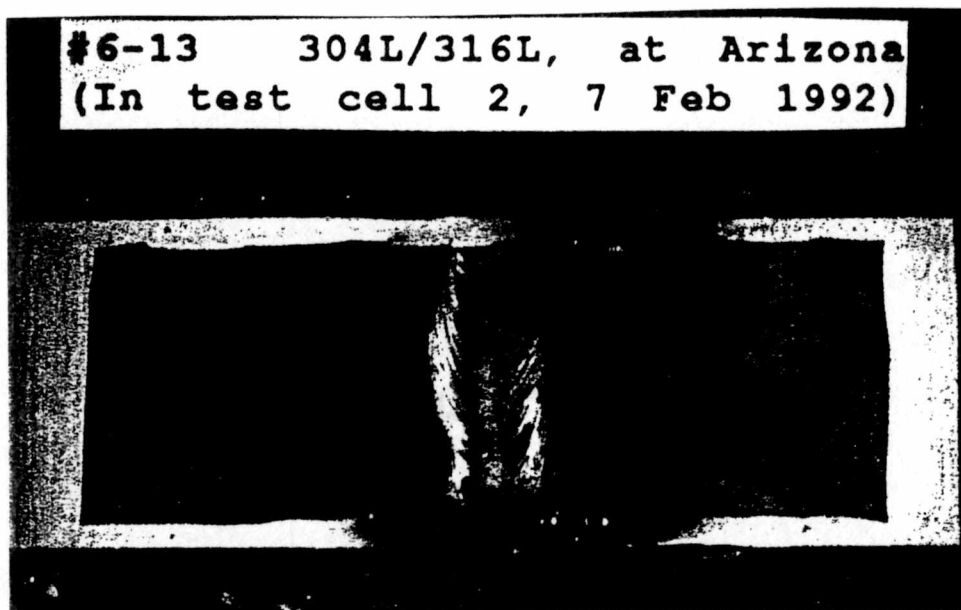


Figure 4.24: Photograph showing 304L/316L stainless steel specimen (as-welded, creviced) after exposure for four months in the Arizona natural well-water system. (From reference 8).

Figures 4.25 to 4.28 show 304L/316L stainless steel specimens in (i) as-welded, creviced, (ii) as welded, non-creviced, (iii) pickled, creviced, and (iv) pickled, non-creviced, conditions respectively, after exposure in the ALST containing 226 ppm chloride plus 0.001 M ferric sulfate, replicating the Arizona well-water system. It was found (Figure 4.25) that there was corrosion nodule formation in the heat-tint region (weld region) of the as-welded specimen, in the crevice geometry only; there was no corrosion in the base-metal specimen. Corrosion did not occur if the specimen was pickled or non-creviced (Figures 4.26 to 4.28). The present results are in good agreement with the field-test results at the natural biotic Arizona well-water system.

4.4.3 Exposure in ALST Replicating the Tennessee River Fresh-Water System

Figure 4.29 shows a 304L/316L stainless steel weldment (no treatment) after being exposed in the Tennessee River for a year and half. No visual corrosion-nodule formation had occurred. Figures 4.30 and 4.31 show the same weldments in the as-welded, creviced and in the as-welded, non-creviced conditions, respectively, after being exposed in the ALST containing 8 ppm chloride plus 0.001 M ferric sulfate that simulated the Tennessee River fresh-water system. From Figures 4.29, 4.30 and 4.31, some colorations were noted, but there was no identifiable corrosion of the weldments. Hence, there is a good agreement between the present study and that of the field-test results at the Tennessee River fresh-water system.

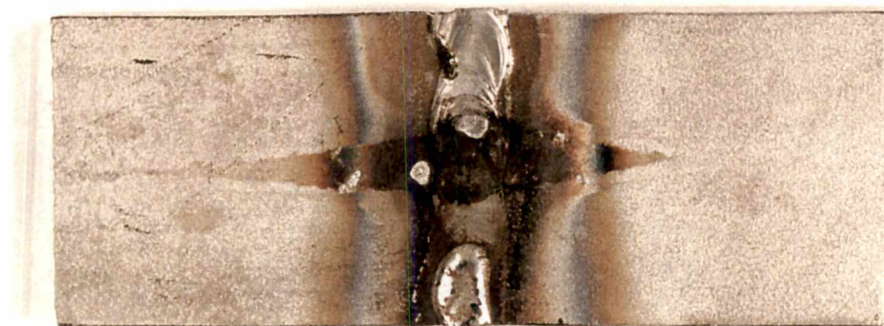


Figure 4.25: Photograph of 304L/316L weldment (as-welded, creviced). Tested in abiotic solution that simulates the Arizona well-water system.



Figure 4.26: Photograph of 304L/316L weldment (as-welded, non-creviced). Tested in abiotic solution that simulates the Arizona well-water system.

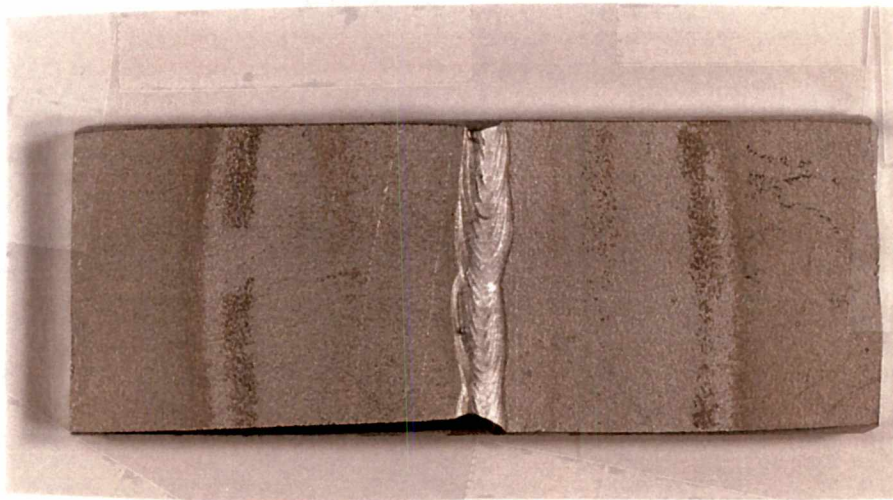


Figure 4.27: Photograph of 304L/316L weldment (pickled, creviced). Tested in abiotic solution that simulates the Arizona well-water system.

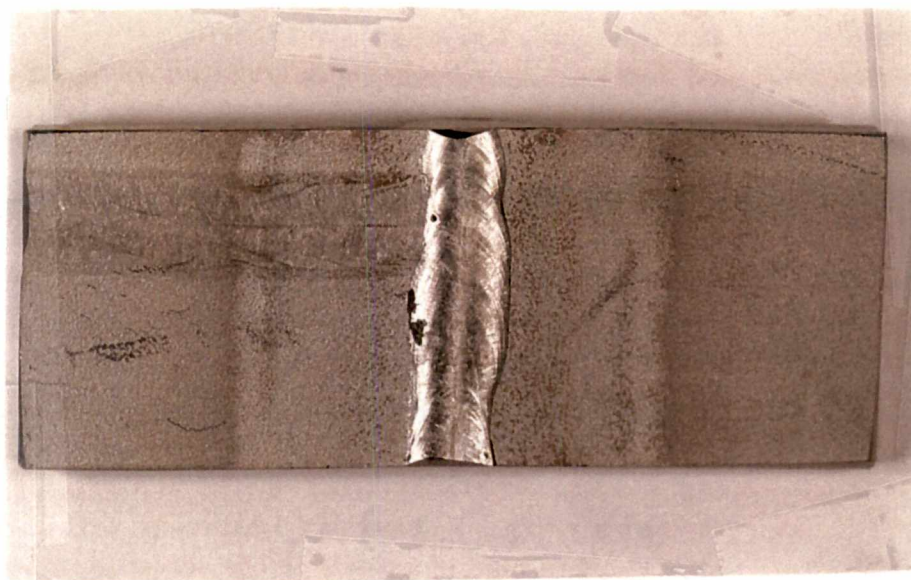


Figure 4.28: Photograph of 304L/316L weldment (pickled, non-creviced). Tested in abiotic solution that simulates the Arizona well-water system.

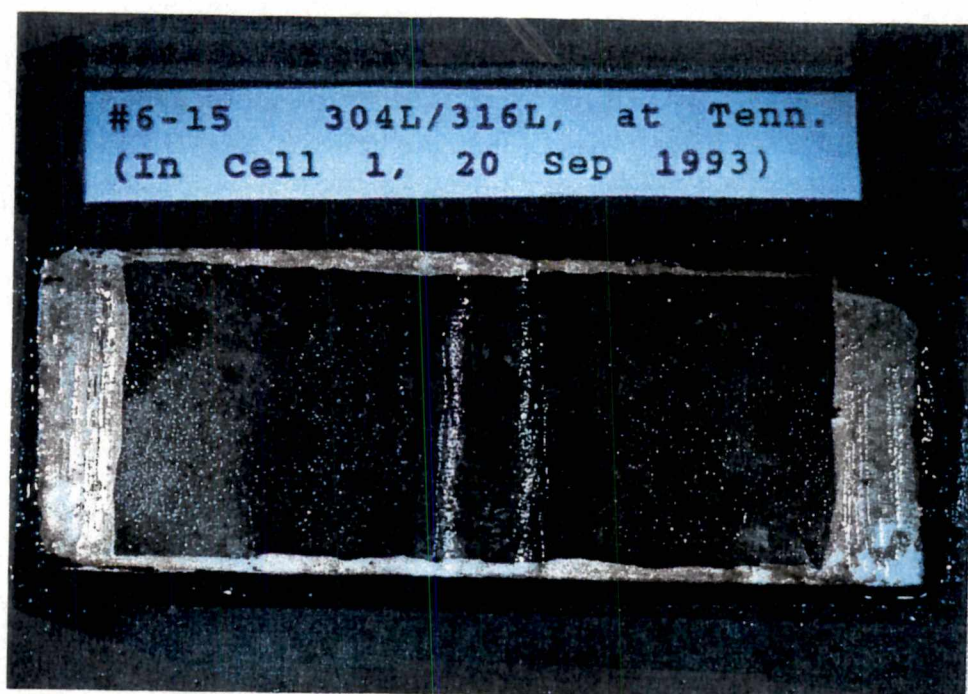


Figure 4.29: Photograph of 304L/316L weldment (as-welded, creviced). Tested in Tennessee River natural fresh-water system. (From reference 9).



Figure 4.30: Photograph of 304L/316L weldment (as-welded, creviced). Tested in abiotic solution that simulates the Tennessee River fresh-water system.



Figure 4.31: Photograph of 304L/316L weldment (as-welded, non-creviced). Tested in abiotic solution that simulates the Tennessee River fresh-water system.

CHAPTER 5

DISCUSSION OF RESULTS

The experimental results obtained in the abiotic laboratory screening test (ALST) exhibited both similar and distinctively characteristic phenomena when compared to those obtained in the natural biotic water environments.

From the polarization resistance measurements for alloy 400 weldments, in the abiotic solution containing 28 ppt NaCl plus 0.001 M ferric sulfate, intended to replicate the Delaware Bay seawater site, the corrosion rate obtained was in good agreement with that obtained in the field study at the Delaware Bay seawater site. The control test for this alloy in the abiotic solution containing 28 ppt NaCl (without ferric sulfate) also produced a corrosion rate that was very close to the surface average corrosion rate obtained in the filtered Delaware Bay natural environment and in ASTM synthetic seawater. These results were shown in Figure 4.1 and Tables 4.1 and 4.2.

The cathodic and anodic polarization curves (Figure 4.6) obtained for alloy 400 in the abiotic solutions were used to predict the corrosion rates for this alloy. The predictions were compared to the corrosion-rate results obtained from the polarization resistance measurements; they compared favorably.

The 28 ppt NaCl plus 0.001 M ferric sulfate abiotic solution replicated the "major" corrosion-causing characteristics of the Delaware Bay site natural environment. The microbial effects were, therefore, simulated with the 0.001 M ferric sulfate.

Furthermore, the validity of the ALST in terms of replicating field test results in natural biotic environments was verified from the cathodic behaviors of platinum electrodes and 304L stainless steel in abiotic solutions. The cathodic curves for platinum in 28 ppt NaCl and in 28 ppt NaCl plus 0.001 M ferric sulfate have one and two reduction reactions, respectively, for potentials higher than about -150 mV (SHE). This was observed in the cathodic curves obtained for bare and biofilmed platinum, respectively, in the field study at the Delaware Bay seawater site.

The cathodic curve for 304L stainless steel in the abiotic solution replicating the Tennessee River fresh-water system, containing 8 ppm chloride plus 0.001 M ferric sulfate, had two reduction reactions as observed for this alloy in the unfiltered Tennessee River fresh-water system. The cathodic curve for 304L stainless steel in the control abiotic solution, containing 8 ppm chloride (without ferric sulfate), had one reduction reaction, the reduction of dissolved oxygen. When compared to the cathodic curve obtained in the filtered Tennessee River fresh-water system, the latter seems to exhibit two reduction reactions, although the first reduction is not too pronounced. The second reduction is that of dissolved oxygen. The existence of the first reduction reaction is attributed to the fact that there might have been some micro-organisms still present after the filtration.

Surface examinations of the AL-6XN weldments after exposures in the abiotic solutions containing 28 ppt NaCl plus 0.001 M ferric sulfate revealed that there was extensive corrosion preferentially at the weld region (heat tint area) underneath the silicone rods only if the specimens were creviced. No corrosion was found in the non-creviced specimens. The results were in good agreement with the field-test results of

AL-6XN weldments exposed in Delaware Bay seawater site. The surface examinations of 304L/316L weldments exposed in the abiotic solution containing 226 ppm chloride plus 0.001 M ferric sulfate, intended to replicate the Arizona well-water system, showed that localized corrosion and nodule formation occurred in the heat-tint region (weld region) of the as-welded specimen in the creviced geometry only. There was no accelerated corrosion in the base-metal specimen. Also, accelerated corrosion did not occur if the specimen was pickled or non-creviced. These results replicated the field-test results for this alloy exposed in the Arizona well-water system. Moreover, surface examinations of 304L/316L weldments exposed in the abiotic solution containing 8 ppm NaCl plus 0.001 M ferric sulfate, replicating the Tennessee River fresh-water system, showed no identifiable corrosion. There was no identifiable corrosion for this weldment after exposure in the Tennessee River fresh-water system. There was, rather, some coloration found on the weldments. The results were also in agreement.

Based on the above successes in the results obtained in the ALST as compared to those obtained in field studies in natural biotic water environments, the conclusion is that the developed ALST works reasonably well. Although the developed ALST generally works, it exhibits some distinctive characteristics. There was a remarkable increase in the open circuit potentials for platinum electrodes in the ALST as compared to those in the natural environments. The ennoblement associated with the ALST was attributed to ferric ions being strong oxidizers. In addition, there was also an increase in the current densities for platinum electrodes and 304L stainless steel in the ALST relative to those in the natural biotic water environments.

The higher ennoblement and current densities obtained in ALST are indications that the developed ALST is a conservative test. It is conservative in the sense that if there is no accelerated corrosion of materials in the ALST, there will be no accelerated corrosion of materials in the natural environments; but if there is accelerated corrosion of materials in the ALST, there may or may not be accelerated corrosion in the natural environments.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

6.1 CONCLUSIONS

1. An abiotic laboratory-screening test (ALST) was developed. The developed ALST replicated the major corrosion-causing characteristics of natural biotic environments, such as the chloride contents, the high oxidizing power, and the aerobic and anaerobic areas on specimen surfaces as produced by aerobic and anaerobic microorganisms.
2. An abiotic solution containing 28 ppt NaCl plus 0.001 M ferric sulfate was employed in the ALST which replicated a Delaware Bay seawater site.
3. An abiotic solution containing 226 ppm NaCl plus 0.001 M ferric sulfate was employed in the ALST which replicated an Arizona well-water system.
4. An abiotic solution containing 8 ppm NaCl plus 0.001 M ferric sulfate was employed in the ALST for replication of a Tennessee River fresh-water system.

5. The 0.001 M ferric sulfate simulated the major MIC effects of the natural biotic water environments in the ALST.
6. The corrosion rates for alloy 400 in 28 ppt NaCl plus 0.001 M ferric sulfate were in good agreement with those obtained in the field studies in the Delaware Bay seawater site.
7. The reduction-reaction cathodic polarization behavior of a platinum electrode in 28 ppt NaCl plus 0.001 M ferric sulfate was similar to that obtained in the Delaware Bay seawater site. The cathodic curve for platinum in the abiotic solution had two reduction reactions, the reduction of ferric ions and dissolved oxygen. In the Delaware Bay seawater site, the cathodic curve for platinum exhibited two reduction reactions, the reduction of peroxide and dissolved oxygen.
8. The reduction-reaction cathodic polarization behavior for 304L in 8 ppm chloride plus 0.001 M ferric sulfate exhibited two reduction reactions, the reduction of ferric ions and dissolved oxygen. In the Tennessee River fresh-water system, the cathodic curve for 304L showed two reduction reactions, but the species undergoing reduction in the first, higher-potential reaction is not known. The second reduction is that of oxygen going into a diffusion limit.

9. The surface examinations of AL-6XN specimens after 7 days in 28 ppt NaCl plus 0.001 M ferric sulfate showed extensive corrosion preferentially at the weld regions underneath the silicone rods only in the creviced geometry. 304L/316L stainless steel specimens after 7 days in 226 ppm chloride plus 0.001 M ferric sulfate exhibited localized corrosion and nodule formation in the heat-tint region (weld region) of the as-welded and creviced specimen only. Corrosion did not occur if the specimen was pickled or non-creviced. 304L/316L specimens after 7 days in 8 ppm chloride plus 0.001 M ferric sulfate showed no identifiable corrosion in this abiotic solution. These results replicated their counter-parts in the natural environments.
10. The open-circuit potentials for platinum electrodes in the ALST were somewhat higher than in the natural environments. The ennoblement produced in the ALST was attributed to ferric ions being strong oxidizers.
11. The corrosion current densities for platinum electrodes and 304L stainless steel in abiotic solutions containing 28 ppt NaCl plus 0.001 M ferric sulfate, and 8 ppm chloride plus 0.001 M ferric sulfate, respectively, were significantly higher than those obtained in the natural environments.
12. The ennoblement and higher current densities obtained in the ALST were indications that the ALST is a conservative test. This implies that if there is

no accelerated corrosion in the ALST, there will not be accelerated corrosion in the natural biotic water environments; but if there is accelerated corrosion in the ALST, there may or may not be accelerated corrosion in the natural environments.

6.2 RECOMMENDATIONS FOR FUTURE RESEARCH

1. The developed abiotic laboratory-screening test (ALST) replicated three natural biotic water environments: a Delaware Bay seawater site, an Arizona well-water system and a Tennessee River fresh-water system representing high chloride, intermediate chloride and minimal chloride contents, respectively. It is recommended that more natural biotic environments be replicated in the ALST.
2. Ferric ions were employed in the form of ferric sulfate in the ALST to produce the high oxidizing power as found in the natural biotic environments. They produced, however, somewhat higher platinum potentials and lower corrosion potentials when compared to those found in the natural biotic water environments. Therefore, it is recommended that other oxidizers be tried. However, it has to be emphasized that in this work, hydrogen peroxide was initially employed but the results were not satisfactory.

3. In order to objectively develop an ALST, it was necessary to test materials that produced dramatic microbially-influenced-corrosion (MIC) effects in the natural biotic environments. It is recommended that a wide range of materials be tested in the ALST to more meaningfully determine the validity of the ALST.

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VITA

Lawretta Chineze Ononye was born in Lagos, Lagos State, Nigeria. She pursued her primary education in Kano and Onitsha. She attended Queen Elizabeth School, Ilorin (high school), and obtained her General Certificate for Education (GCE) (high school diploma) in 1983. Lawretta continued her education, and in 1990, she obtained Bachelor's degree in Physics, from Bendel State University, now called Edo State University, Ekpoma, Nigeria. She did national service for one year (1990-1991) at Army Day Secondary School, Odogbo, Ibadan, Nigeria, where she taught Physics. From 1991-1992, she was a teacher at Eleta high School. She came to USA in July 1992, and in 1994, she obtained another Bachelor's degree in Computer Science, from Knoxville college, Knoxville, Tennessee. Lawretta enrolled in the University of Tennessee in August of 1996, where she obtained her masters degree in Metallurgical Engineering in August of 1998. While at the University of Tennessee, she worked as a Graduate Teaching Assistant. Her thesis was "The Development of an Abiotic Laboratory Screening Test for Microbially Influenced Corrosion.