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Electrochemical studies of microbiologically influenced corrosion in natural freshwater system

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R. A. Buchanan, Major Professor

We have read this thesis and recommend its acceptance:

Eugene E. Stansbury, David C. White

Accepted for the Council:
Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

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Date Dec. 1991

ELECTROCHEMICAL STUDIES OF MICROBIOLOGICALLY INFLUENCED CORROSION IN NATURAL FRESHWATER SYSTEM

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Ping Li
December 1991

DEDICATION

This thesis is dedicated to my parents
Mr. Wenjie Li
and
Mrs. Pinying Qian

and to my brother
Mr. Qi Li

Without whom the completion of my
education would have been impossible

ACKNOWLEDGEMENTS

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ABSTRACT

An electrochemical field study of microbiologically influenced corrosion on carbon steel and stainless steel was conducted in a natural freshwater system. The specimens were exposed in filtered (0.2 µm) and unfiltered lake water respectively. The open-circuit potentials of corrosion specimens and platinum potentials were monitored during the exposures. The electrochemical impedance spectroscopy and polarization data were collected after exposures. The biofouling scraping after exposures was analyzed by microbiological approaches. The results show that the platinum potentials and corrosion potentials in the unfiltered lake water were significantly higher than in the filtered lake water. The ennoblement of the open-circuit potentials was thought to be due to an increase in the exchange current density for the oxygen reaction by the oxygen catalysis mechanism. The catalysis resulted from microbial effects, and was probably associated with the presence of algae.

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INTRODUCTION

Microbiologically influenced corrosion (MIC) is a new subject of science. It is currently a matter of great concern in all industrial and marine systems. However, microbially influenced corrosion did not bring to public attention 20 years ago. With a large quantity of case histories had been reported, people gradually believed that MIC was a matter fact and had been identified as a serious problem in the power-generation industry, petrochemical industry, gas transmission lines and naval systems etc. The early reviews of microbially influenced corrosion can be traced back to 20 years ago[1-6]. In recent years, MIC has received increased attention by corrosion scientists and engineers because it seems to be a major phenomenon of corrosion in natural environments. Since bacteria are omnipresent any construcural or functional materials made of metallic elements are capable of being subject to MIC attack to some extent in natural environment. Therefore, studies of microbially influenced corrosion become very significant and important to corrosion engineering. Due to its peculiar characteristics, MIC study is determined to be a cooperation of material scientists and microbiologists.

Microbially influenced corrosion is due to the presence of microorganisms on a metal surface which leads to changes in corrosion rates and also probably the types of the electrochemical reactions which are involved in corrosion processes. A great number of MIC failures belong to localized corrsion such as pitting or crevice corrosion. Microorganisms attached to metal surface usually form biofilms and create an occlusive geometry. That certainly impedes the mass transportation which occurs at normal site with absence of bacteria and results in inhomogeneous surface. In addition, bacteria secrete metabolites which often lead to lower the value of pH in local environments. All of them facilitate the development of localized corrosion. A lot of bacteria may alter electrochemical reaction, such as sulfate reducing bacteria (SRB) can remove hydrogen in cathodic site and results in cathodic depolarization. A lot of bacteria act as oxidizing or reducing agents which oxide or reduce metals back and forth so that they influence the corrosion of metals and alloys immersed in natural aqueous environments.

At the present state of knowledge, no working mechanism can account for general case of microbially influenced corrosion. One employed one case from which it is postulated can not interpret other cases. There is no doubt that bacteria are able to influence corrosion processes in terms of their characteristics. However, how bacteria make an impact on, what aspect contributes to more activity and which factor plays determined role are far to reach a clear understanding.

The laboratory studies in MIC render tremendous information to biocorrosion mechanism and characteristics of bacteria. The former investigations[7] carried out in the corrosion Lab, the University of Tennessee, concentrated on microbially influenced corrosion of stainless steels and as-deposited weld metal in a pure strain bacteria extracted out from a known MIC failure site in an industrial freshwater system. The bacterial strain was designated as A6F, and was characterized as rod shaped, gram negative, facultatively anaerobic, and acid producing. The good results were obtained and justified by a working mechanism that acidification occurred and induced localized corrosion during bacterial growth processes, which was postulated by former investigators. The A6F represents one of the typical kind of microbial corrosion. It has potential to account for what is going on at field study.

This thesis will present the electrochemical field studies of microbiologically influenced corrosion in a natural fresh water system. The experiments were conducted at the Singleton Facility on Fort Loudoun Lake, Tennessee River. The corrosion specimens were carbon steel, stainless steels and stainless steel weld metal. The open-circuit potentials of platinum and corrosion potentials of specimen were monitored as exposure time. The electrochemical impedance spectroscopy data were collected and the cathodic polarization behoviours were studied after exposure. The characteristics of microorganisms were examined incidental to the experiment.

Chapter 1. LITERATURE REVIEW

(1) Bacteria Characteristics

There is a great deal of literature on MIC in the last decade. It is dispersed in both the microbiology and corrosion fields. However, much of it deals with specific MIC attack or reports of case histories of observations incidental to the main study. Pope et al made a overall summary based on a report to the Chemical Process Industries in 1984[8]. They gave general remarks regarding the characteristics of microorganisms as they relate to MIC and a few type of metals or alloys subject to microbiological corrosion. In order to study the microbial corrosion, it is necessary to understand the bacteria characteristics.

Bacteria have a small size in magnitude of a micrometer. When they attach to the surfaces of metals, they can influence the reactions between the metals and the involved environments. Bacteria can produce extracellular polymeric substances (EPS) which frequently extend from the cell forming a tangled matrix of fibers which provide structure to the biofilm. Therefore, biofilms basically consist of microbial cells and their products. They sometimes provide a uniform coverage of the surface and in other locations may be quite patchy. Generally, most aquatic environments are short of nutrients, especially organic nutrients. However, a biofilm is a very adsorptive and porous structure. As a result, biofilms adsorb these materials, creating areas of relative plenty. Therefore, bacteria prefer to live on surfaces of substrates with biofilms. In addition, biofilms impede the mass transport between surfaces of metals and bulk environments. They create occlusive geometries in forms such as tubercles and nodules due to bacterial colonization, which usually are recognized to induce underdeposit localized corrosion. They can also form synergistic communities with other bacteria, fungi, algae, plants and animals. Such communities can accomplish things that the individuals alone can not perform.

The metabolism of bacteria is another important aspect associated with the corrosion process. In microorganisms the ratio of surface area to volume is very large. This high surface-to-volume ratio leads to extensive interactions with the environment. Heterotrophic bacteria utilize organic substances as carbon as an energy source. During the metabolic process of fermentation, they produce a wide variety of organic acids which may worsen the environments interaction with metals. Autotrophic bacteria may utilize oxygen, nitrate, sulfate, carbon dioxide and other inorganic compounds as the final electron acceptor in their respiratory metabolism. Light and other chemical substances may be involved in the process as the energy source to complete their metabolism. Some bacteria can oxidize or reduce metallic ions directly, e.g. iron bacteria can oxidize ferrous ions to ferric ions. The most important bacteria as far as MIC is concerned is the sulfate reducing bacteria (SRB). It is thought that most of the MIC attacks in the absence of oxygen are caused by such bacteria. In a moist atmosphere the following reactions take place:

(1) Iron oxidation:

$$4Fe + 8H^+ \Leftrightarrow 4Fe^{2+} + 4H_2$$

Normally, the iron is somewhat protected from further corrosion by the film of hydrogen. When sulfate and desulfurizing bacteria are present, they cause a cathodic depolarization, and the iron is oxidized even in the absence of oxygen:

(2) Sulfate reduction:

$$4H_2 + SO_4{}^{2-} \Leftrightarrow H_2S + 2H_2O + 2OH^-$$

(3) Precipitation of iron:

$$4Fe^{2+} + H_2S + 2OH^- + 4H_2O \Leftrightarrow FeS + 3Fe(OH)_2 + 6H^+$$

The sum of these three reactions:

$$4Fe + SO_4{}^{2-} + 2H_2O + 2H^+ \Leftrightarrow FeS + 3Fe(OH)_2$$

Considerable damage to pipelines is produced in this way[9].

Bacterial exopolymers not only contribute to the structural integrity of microbial films but also are thought to interact strongly with corroding metal surfaces[10]. In general, they are acidic and contain functional groups which readily bind metals[11]. The role of metal binding is related to corrosion in two ways: (1) If the concentrated metal is more noble than the ions in the surface lattice then dissolution of ions from the surface would be expected, and (2) If the surface ions are noble to the ions concentrated by the exopolymer, then that metal would oxidize in preference to the surface ions, thus preventing corrosion[12]. Furthermore, there are considerable differences in binding capacity between individual metal ions and specific exopolymers. The extent of the binding is dependent on environmental factors, such as pH, redox potential and competing ions[13].

(2) Electrochemical Corrosion Fundamentals

Corrosion Potential & Electrochemical Polarization

The open-circuit corrosion potential, E_{corr}, is the potential at steady state during which the anodic reaction for a metal is proceeding at the same rate as the cathodic reaction (usually oxygen or hydrogen reduction) in a given environment. The measurement of the corrosion potential requires a stable reference electrode, an electrometer or voltmeter with high input impedance, and in most of cases an appropriate recording device.

The corrosion potential is a function of many variables, such as the metal itself, the composition of the electrolyte, the pH value, etc. Thus it provides the least electrochemical information on the corrosion process. The measurement of the corrosion potential alone cannot account for the corrosion mechanisms without other electrochemical information. With respect to active materials (no passive films), the corrosion potential does not usually change very much with time because it is unlikely that the environment will polarize the material far away from the corrosion potential. However, with respect to passive materials, the corrosion potential sometimes can give direct information as to whether the materials are in the active or passive state. Large changes in potential can occur because a small corrosion current can polarize the materials out of their initial state.

Another potential measurement might be useful, a measurement of the reduction-oxidation (redox) potential of the environment. The redox potential is that potential associated with the equilibrium oxidation and reduction of hydrogen or oxygen (or maybe other redox species) in a corrosive environment. This is usually measured on an inert electrode such as platinum. It could be used as an indicator of the corrosivity of the environment, and in most cases it can provide the extent of change in oxygen concentration and pH value of the environment, provided proper calibration is made.

Electrochemical polarization is capable of providing an overview of the types of reactions which occur for a given corrosion system, such as charge transfer or diffusion controlled reactions, passivity, transpassivity and localized corrosion phenomena. It is a kinetic technique whereby the electrode under study is polarized in either the anodic or cathodic direction by application of an external current. The kinetic behaviors of expected or predicted reactions can be studied since the potential and external current are definitely functions of the electrochemical reactions. Other characteristics of materials also can be obtained from electrochemical polariztion curves, such as pitting potential, protection potential, susceptibility to localized corrosion, etc. The polarization technique, however, needs to scan the potential to a large extent, which leads to progressive modification of the surface conditions of the material.

Electrochemical Impedance Spectroscopy

Microbial corrosion is degradation of metals influenced by bacteria present on their surfaces. Bacteria themselves do not attack metals directly. Consequently, microbial corrosion is still an electrochemical process by nature. Therefore, any technique used in electrochemistry is valid in microbially influenced corrosion studies. Among the various electrochemical methods, electrochemical impedance spectroscopy promises to be a valuble technique in microbial corrosion studies.

Electrochemical impedance spectroscopy (EIS) is a new powerful technique which was introduced in corrosion applications in recent years. The power of EIS lies in the fact that it is essentially a steady-state technique that is capable of accessing relaxation phenomena covering a wide range of relaxation times. The steady-state character provides a means of attaining corrosion rate without destroying interfacial equilibrium, while study of relaxation permits a method for investigating interfacial reaction mechanisms.

Fundamentals

The general approach is to apply an electrical stimulus (a known voltage or current) to the electrodes and observe the response (the resulting current or voltage). The system must satisfy the following conditions:

Causality - The response of the system is due only to the perturbation applied and does not contain significant components from spurious sources.

Linearity - The perturbation/response of the system is described by a set of linear differential laws, or the system satisfies the superposition principle.

Stability - The system is stable in the sense that the properties of the system are time-invariant.

The response of any physical system to a perturbation of arbitrary form may be described by a transfer function:

$$H(s) = \frac{V(s)}{I(s)}$$

where s is the Laplace frequency, and V(s) and I(s) are the Laplace transforms of time-dependent voltage and current, respectively[14]. In terms of the sinusoidal frequency domain, the transfer function may be identified as an impedance:

$$Z(j\omega) = \frac{F\{V(t)\}}{F\{I(t)\}} = \frac{V(j\omega)}{I(j\omega)}$$

where F signifies the Fourier transform, and $V(j\omega)$ and $I(j\omega)$ are the sinusoidal voltage and current. It is noted that the original time variations of the applied voltage and the resulting current have disappeared, and the impedance is time-invariant, provided the interface is stable over the time of sampling.

Since the output may be changed in both amplitude and phase with respect to the input, we must express the impedance as a complex number:

$$Z(j\omega) = Z' + jZ''$$

where primed and double-primed variables refer to in-phase and quadrature components, respectively.

For nonlinear system, i.e., most real electrode material systems, EIS measurements are useful and meaningful only for signals of magnitude such that the response of system is electrically linear. This requires that the response to the sum of two separate input signals applied simultaneously be the sum of the responses of the signals applied separately. However, real electrochemical systems tend to show strong nonlinear behavior, especially in their interfacial response, when applied voltages or currents are large. But so long as the applied potential difference amplitude is less than the thermal voltage V_T:

$$V_T = \frac{RT}{F} = \frac{kT}{e}$$

about 25 mV at 25 $^{\circ}$c, it can be shown that the basic differential equations which govern the response of the system become linear to an excellent approximation. Here k is Boltzmann's constant, T the absolute temperature, e the proton charge, R the gas constant, and F the Faraday constant[15].

EIS Measuring Techniques

Basically, EIS measurements can be classified into two different techniques, i.e., in either frequency domain or time domain. Frequency domain impedance measurements are carried out using a small-amplitude sinusoidal excitation with frequency as the independent variable. A phase-sensitive detector (or lock-in amplifier) is a device that compares two sinusoidal signals to yield an output that can be used to obtain the phase difference between the signals and the ratio of peak amplitudes. Alternatively, the perturbation and response may be recorded in the time domain with time as the independent variable, and the impedance as a function of frequency can then be extracted by time-to-frequency conversion techniques such as Laplace or Fourier transformation. For instance, the Fast Fourier Transform (FFT) technique uses a computer algorithm to make a mixture of excitation waveforms of varying frequencies and then it is applied to the test system simultaneously. After the response is obtained, a Fourier transform operation is performed on this waveform to resolve it into discrete frequency data.

EIS Applications to the Corrosion of Materials

Electrochemical impedance spectroscopy is becoming increasingly popular in corrosion science and engineering. The early applications of EIS were in the measurement of corrosion rate because of its steady-state characteristic. The basis for the use of the EIS method is the Stern-Geary equation which provides a direct relationship between the steady state corrosion current and the polarization resistance:

$$i_{corr} = \frac{\beta a \beta c}{2.303(\beta a + \beta c)} \frac{1}{Rp}$$

Polarization resistance as related to EIS was proposed by Mansfeld[16], that it is given by the difference of the measured impedance in high and low frequencies due to the natures of capacitive, psuedoinductive and diffusional impedance:

$$R_P = \underset{\omega \to 0}{Z(j\omega)} - \underset{\omega \to \infty}{Z(j\omega)}$$

Polarization resistance by EIS measurement was compared with other electrochemical techniques such as small amplitude cyclic voltammetry and potential step[17]. The results showed it to be in good agreement.

The measurement of corrosion rate is not the only aspect of EIS as a powerful tool used in corrosion science. Many advances have been made in developing EIS for the analysis of electrochemical reaction mechanisms of corroding systems[18,19]. Since current in general is a function of potential and concentration of species, which is related to the perturbation throuth a transfer function, theoretically, measurement of the transfer function or impedance over a wide frequency range is able to provide a great deal of kinetic information on the electrochemical reaction processes.

Equivalent electrical circuits have been used extensively in interpreting EIS data. This method assumes electrical circuits have physical equivalence to the real components of electrochemical processes. Thus, it helps in the physical understanding of electrochemical processes. However, electrochemical reactions are active by nature and the same result can be obtained through different combinations of electrical circuits. The equivalent electrical circuits can not completely reflect the real corroding systems.

(3) Microbiologically Influenced Corrosion

The corrosion of metals in aqueous solutions is an electrochemical process. During electrochemical corrosion, an anodic reaction, or oxidation, proceeds concurrently with a cathodic reaction, or reduction. The quantity of electrons released from the metal by the anodic reaction is consumed equally by the cathodic reaction at the cathodic site. Metal ions dissolve into the solution while some other reactant is being reduced. Generally speaking, anything that leads to changes in these two processes will influence the electrochemical corrosion. Therefore, some factors that impede the electrochemical reaction are characteristically inhibitors and others that enhance it worsen the degradation of the metal. Microorganisms in aqueous solutions are known to significantly increase the corrosion rates of many metals and alloys and so the phenomenon is known as microbially influenced corrosion.

The mechanisms responsible for MIC are various and dependent on the specific metal, the bacteria species, the environment and the related conditions. It is very difficult to assess which factors have the major roles in the corrosion process. With the present knowledge, bacteria are able to cause electrochemical changes in anodic reactions, cathodic reactions, or both. It is observed that bacteria preferentially attack different phases in a metal, which is a good indicator that bacteria influence the anodic reaction. On the other hand, potential variations respondent to platinum electrodes prove that bacteria can modify cathodic reactions. Sometimes, the coupling between an anaerobic anode and an aerated cathode leads to rapid corrosion. Therefore, the study of the cathodic reaction in MIC is as important as the study of the anodic reaction.

One type of laboratory experiment in the study of MIC is the dual-cell or split-cell method[20]. The apparatus consists of two identical cells which are biologically isolated and electrolytically continuous. Two identical metal specimens immersed in the two cells respectively are coupled to a zero resistance ammeter. Bacteria are then inoculated into one of the two cells and the resulting galvanic current is recorded to provide a measure of the biological effect on the inoculated electrode with time dependence. If the reaction occurring at the surface of the working electrode is oxidation, an anodic current will be recorded; if it is reduction, a cathodic current results. In this work[20], bacteria on nickel 201 were responsible for an anodic corrosion current. It was also demenstrated that respiration and metabolic activities might be responsible for corrosion.

Laboratory studies of MIC provide tremendous insight into mechanisms. To study living biofilms, Fourier transform infrared spectroscopy (FT/IR) and gas chromatograph/mass spectroscopy (GC/MS) were developed by the Institute for Applied Microbiology group at the University of Tennessee, Knoxville. With these techniques, the biochemical properties of the cells and their extracellular products can be measured; the total community can be examined without the necessity of removing the microbes from surfaces, while the microstructure of multi-species consortia is preserved.

It is well known that sulfate reducing bacteria have a significant influence on MIC. Some other kinds of bacteria, however, also have contributions to MIC, such as the A6F bacteria extracted from a known MIC failure site in an industrial fresh water system. Broad studies of the A6F bacteria effects on five stainless steels (304L, 316L, 308 weld metal, 439 and AL-6XN^{TM}) were conducted by the corrosion group at the University of Tennessee[21]. The stainless steels were exposed in A6F bacterial solutions and sterile-control solutions respectively. Open-circuit potentials of the stainless steels and prepassived platinum electrodes were monitored during the 72-hour exposures. The anodic and cathodic polarization behaviours and the surface conditions after exposures were evaluated by various techniques. It was found that: (1) the A6F bacteria created a non-oxidizing, highly-deoxygenated, acidic environment at the specimen surfaces by decreasing the oxygen concentration and pH, and (2) significantly active corrosion in the form of crevice corrosion had occured at the metal/insulating-enamel junction sites. These results are consistent with most of the field observations that under-deposit corrosion is a major form of MIC failure for stainless steels.

Since laboratory studies can hardly mimic real environments, more attention is being placed on field studies of microbially influenced corrosion. According to Defranoux[22], the presence of a biofilm and its metabolic activity were intuitively thought to have an impact on the corrosion process. People have already observed, without giving its cause, that the corrosion rate in natural seawater is always higher than in artificial seawater. Mollica and Trevis[23] have experimentally confirmed this and showed two effects on the corrosion process. First, the bacterial slime film moved the free corrosion potential of stainless steel in the noble direction. Secondly, the film modified the cathodic reaction for oxygen by shifting the cathodic polarization curve toward higher current densities.

Scotto[24] observed the free corrosion potentials of stainless steel for up to 60 days. The noble movement in potential was obtained in unfiltered seawater, but not in filtered seawater. Furthermore, sodium azide, which inhibits the respiratory activity of bacteria, was added to the natural water after 60 days exposure. The noble corrosion potential in the presence of the bacterial film was restored to its value in filtered water. The point was that adding sodium azide decreased the bacterial activity, but did not remove the biofilms from the metal surfaces. It was concluded that since the uncorroded specimens had the same passivity currents in natural, artificial, and filter-sterilized seawater, the ennobling of the passive specimen potentials in natural seawater was due to a modification of the cathodic reaction caused by the microbiological slime on the metal surface. Since some enzymes, after adsorption on the surface of an electrode, can accelerate the trend of various electrochemical reactions according to hitherto little known bioelectro-catalytic mechanisms, the most likely explanation seems to be enzymic catalysis on the oxygen discharge. Therefore, this effect, on the one hand, could facilitate the initiation of localized corrosion for materials in the passive state, while on the other hand, it could accelerate the uniform corrosion rate for materials in the active state.

Johnsen and Bardal[25] investigated the cathodic behavior of stainless steel immersed in natural seawater by conducting cathodic polarization tests to specific potentials and then examining the changes in current density with time. The cathodic current density at constant potential as a function of time, after a constant value for the first few days, showed an increase and then a decrease. Ennoblement of the free corrosion potential was also observed. The authors concluded that bacteria built up a film on the metal surfaces and produced an extracellular slime. This production of slime resulted in accumulation of heavy metal ions in the slime. Since the exchange current density for the oxygen reaction is very sensitive to impurities in the electrolyte, i.e. some organic 4-coordinated metal complexes of Fe, Co and Ni have shown unusual catalytic properties in the oxygen reduction[26], the accumulation made the exchange current density of the cathodic reaction increase. This mechanism also explained the increase in the free corrosion potential with time. Although Johnsen and Bardal employed a different approach to study this phenomenon than Mollica and Scotto, from an essential point of view, the same conclusion was achieved, that the effect was caused by changes in the cathodic reaction as a result of microbiological activity on the metal surfaces.

Dexter and Gao[27] have reported free-corrosion potential and polarization data for 316 stainless steel exposed to natural seawater and filtered seawater. The authors confirmed that the corrosion potentials of stainless steels exposed to natural seawater move toward the noble direction, while the corrosion potentials of stainless steels immersed in filtered seawater do not. These results were consistent with those of previous authors. And again, the mechanism of the noble shift in potential in the presence of a bacterial film probably involved a change in the kinetics of the oxygen reaction. Finally, they concluded that natural seawater was more aggressive toward SS 316 than was the same water filtered to remove bacteria.

In summary, microbiologically influenced corrosion is a complicated process. Bacteria are able to enhance the corrosion of a metal and worsen the surrounding environment.

The mechanism responsible for MIC depends on the various conditions. There are no general rules to follow. The real mechanism remains far from complete understanding.

Chapter 2. EXPERIMENTAL PROCEDURES

(1) Experimental Specimens

Four kinds of specimens were employed in the field studies. They were C1018 carbon steel, AISI 304L and 316L stainless steel, and as-deposited ER308 stainless steel weld filler metal. The ER308 weld metal specimens were sectioned from heat exchanger pipes that had undergone fresh water MIC failures at a certain utility site. The chemical compositions of these materials are given in Table 2-1. The specimens were mounted in Maraglass epoxy and then ground to a 600-grit SiC finish. In order to prevent crevice corrosion[28], all the stainless steel specimens were prepassivated in 50% HNO_3 at 50 °C for 30 minutes. The epoxy/metal interface was bridged with insulating Glyptal 1201 Red Enamel. Finally, the exposed metal was ground again to 600-grit SiC finish to remove the passive film formed in HNO_3.

(2) Electrochemical Techniques Employed

Monitoring of the open-circuit corrosion potential of a specimen provides the most direct electrochemical information on corrosion processes. A computer/multiplexer/electrometer

Table 2-1.

Chemical Compositions of Materials Employed in the Field Study

Material	Composition (wt. %)					
	C	Cr	Ni	Mo	Mn	Others
C1018*	0.15-0.20	-	-	-	0.60-0.90	Si (0.10-0.20), P(0.04 max), S(0.05 max), Fe (balance)
304L	0.02	18.9	8.7	0.2	0.9	Si (1.0 max), Fe (balance)
316L	0.02	17.6	11.1	2.1	1.8	Si (1.0 max), Fe (balance)
308 WM	0.05	19.5	11.0	0.8	1.7	Si (0.38), Ti (0.01), Fe (balance)

*Composition ranges

system was constructed for this purpose. The system had 24 channels, and was capable of automatically scanning potentials on 24 coupons at any time interval and storing the data in a computer for later analyses. The field measurements were somewhat difficult because the electrolyte, i.e. the lake water, was electrically grounded. Any ground-loop currents or electromagnetic fields caused by power sources at the field site would have caused serious errors in the potential measurements. To eliminate this effect, a resistor/capacitor filter circuit was added to the measuring circuit, as shown in Figure 2-1.

Electrochemical impedance spectroscopy was used to study the kinetic mechanisms of the corrosion processes. The system consisted of an EG&G 273 Potentiostat, an EG&G 5208 Lock-In Amplifier and a computer. The lock-in amplifier generated sinusoidal wave frequencies from 5 Hz to 100 kHz. The computer, using an EG&G Fast Fourier Transform technique, produced the low frequencies from 50 μHz to 11 Hz. All frequencies in the low-frequency range were added and sent to the corrosion cell through the potentiostat.

And finally, cathodic polarization measurements were made to obtain the cathodic behaviors of the corrosion specimens. This was accomplished with the EG&G 273 Potentiostat and computer.

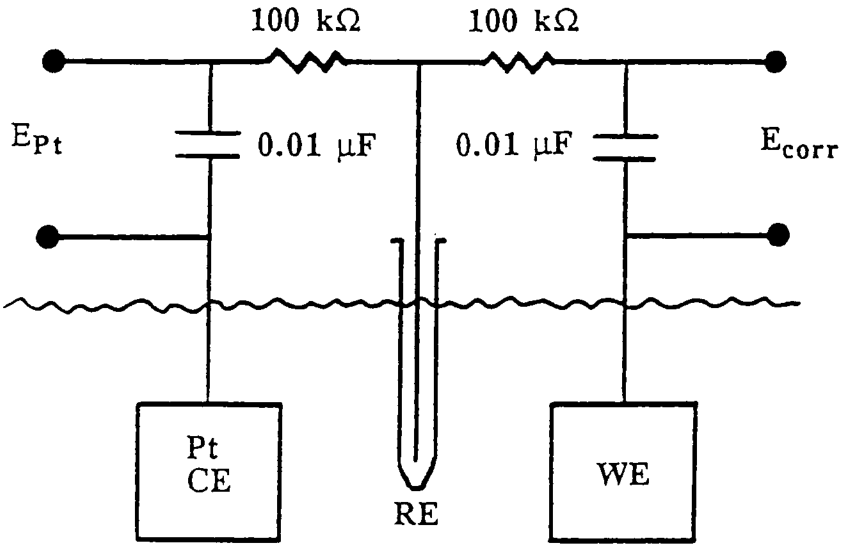


Figure 2-1. Resistor/Capacitor Filter Circuit.

(3) Electrochemical Measurement System

An electrochemical system was designed, constructed and installed at a Tennessee Valley Authority (TVA) site near Knoxville, Tennessee on Fort Loudoun Lake, Tennessee River. The system consisted of eight individual electrochemical cells, and was connected to a large water-storage tank to which the lake water was pumped once or twice per week. The lake water was continuously gravity-fed to the eight corrosion cells, with individual water inlet and outlet controls, and drained off to the Fort Loudoun Lake.

Each transparent (blue tint) 600 ml polyvinyl-chloride (PVC) cell contained a working electrode (corrosion sample), a prepassivated platinum electrode and a saturated Ag/AgCl reference electrode. The platinum electrode was prepassivated by immersion in 25% HNO_3 at 50 °C for 20 minutes. It was able to serve as a indicator, reflecting the environmental changes during open-circuit potential measurements, and as a counter electrode during electrochemical polarization measurements. The water-inlet valves were mounted on glass tubes which passed through rubber stoppers on the tops of the cells. The water-outlet valves were mounted on the upper walls of the cells, and were utilized to slow down the water flow rate to a controlled value such that fresh water and nutrients were continuously flowing through the cells.

Four of the eight electrochemical cells contained working electrodes of C1018 carbon steel, 304L and 316L stainless steel, and 308 stainless steel weld metal in filtered lake water. The inlet and outlet ports to each cell contained 0.2 µm filters to restrict or preclude the entrance of bacteria. The other four cells contained the same working electrode materials in unfiltered lake water. The water replacement rate through the filtered cells was 3 ml/hour, while the replacement rate through the unfiltered cells was adjusted to the same value.

Finally, all the working electrodes and platinum electrodes within the cells were connected to the computer/multiplexer/electrometer measurement system through the filter circuits in order to automatically monitor the open-circuit potentials during the entire exposure period. The complete system, except for the water-storage tank, was housed within a building heated in the winter but without air-conditioning in the summer. The system configuration is shown in Figure 2-2.

(4) Experimental Procedures

Three independent runs were conducted over different time periods: Run 1 (August 22 - October 26, 1989) was in the summer time; it lasted 63 days. Run 2 (January 17 - February

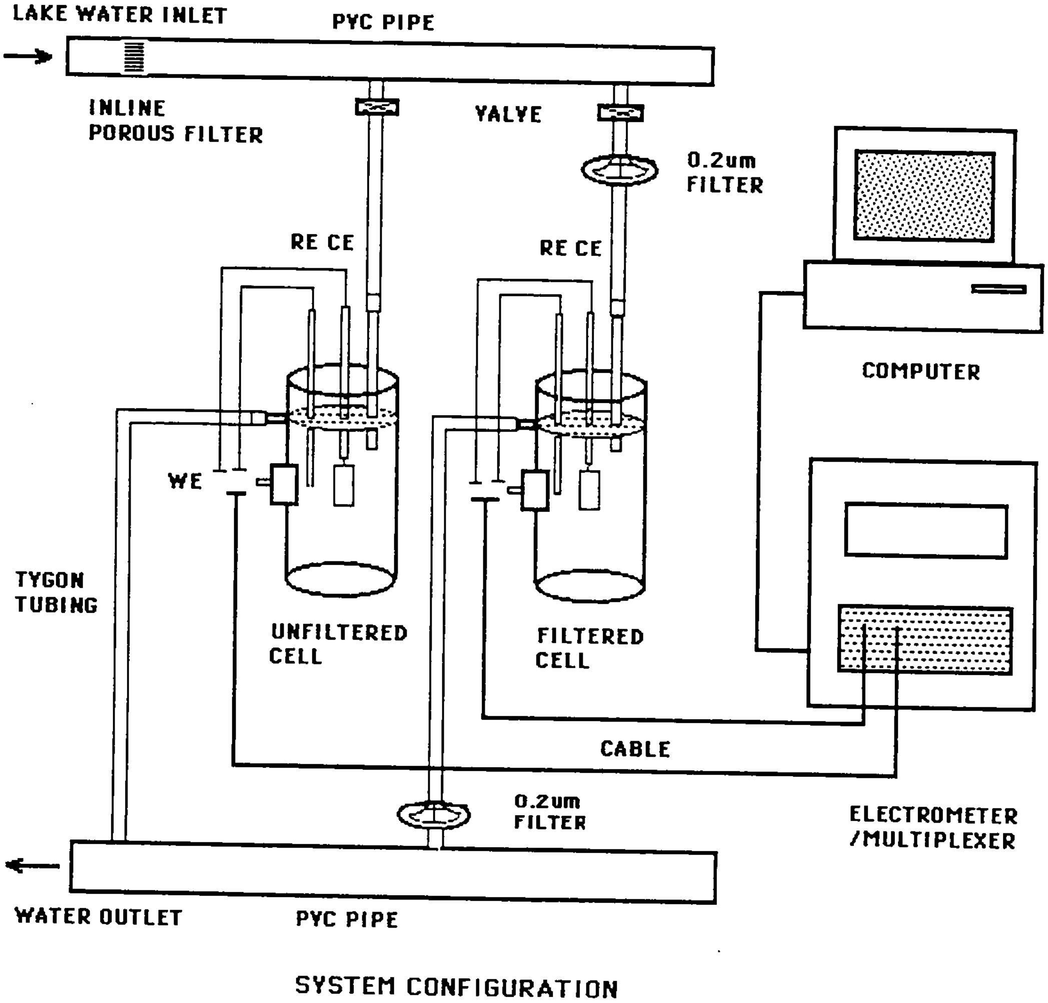


Figure 2-2. Electrochemical Measurement System

16, 1990) was in the winter time; it lasted 28 days. Run 3 (March 15 - May 23, 1990) was in the spring time; it lasted 70 days.

All components of the corrosion cells were combined in the laboratory, and then ethylene-oxide gas sterilized before beginning the field studies. The corrosion potentials of the working electrodes and the open-circuit potentials of the platinum electrodes were recorded in one hour intervals during the exposures for all three runs. At the ends of the exposure periods for Run 1 and Run 2, the cells were transported one-at-a-time to the laboratory, and immediately the electrochemical impedance spectroscopy data were collected over the frequency range from 1 mHz to 10 kHz. Then the cathodic polarization measurements were conducted on the corrosion specimens with a scan rate of 600 mV/hour. For Run 3, the same procedures were followed through the lake water exposure time, but the EIS and cathodic polarization data were not collected at the end of the exposure because the electrostatic field produced by a large potential polarization might have influenced the bacteria that resided at the surfaces of the corrosion coupons.

(5) Microbiological Analyses and Surface Examination

As an additional procedure in Run 3, separate coupons of matched materials were attached to the working electrode epoxy mounts. The coupons were not electrically connected to the monitoring system, but underwent the same filtered and unfiltered water exposures as the working electrode materials. At the end of the exposure, rather than taking EIS and cathodic polarization data, as in Run 1 and Run 2, a series of microbiological analyses and microscopic surface examinations were performed.

The biofouling material on the stainless steel 304L and carbon steel C1018 specimens, after exposure in both filtered and unfiltered water, was carefully scraped from the surface and then immediately injected into a mineral salts solution and a sulfate reducing bacteria (SRB) medium. These solutions were serially diluted from 10^{-1} to 10^{-6}. The serial solutions were spread on petri-dishes containing HACFU medium for aerobic bacteria and BHI medium for facultatively anaerobic bacteria, respectively. The bacteria in petri-dishes were allowed to grow for a few days. By the epifluorescent microscopy technique, the numbers of bacterial and algae cells were counted in the mineral-salts solution and the SRB medium, and the numbers of viable cells were counted in the HACFU and BHI growth media. Also, the characteristics of the bacteria were identified by the gram-stain approach. The metabolic behaviors of some bacteria were evaluated by determining whether or not they were acid producing.

Chapter 3. EXPERIMENTAL RESULTS

(1) Open-Circuit Potential and Cathodic Polarization

The open-circuit potentials of the prepassivated platinum electrodes (E_{Pt}) within the cells as a function of exposure time, the corrosion potentials of the corrosion specimens (E_{corr}) as a function of time, and the cathodic polarization curves of the specimens in the first two runs are shown in Figures 3-1 through 3-8. The platinum-potential and corrosion-potential variations with exposure time in Run 3 are given in Figures 3-9 through 3-12.

The open-circuit potential results exhibited several distinct phenomena. First, the open-circuit potentials of the platinum electrodes (E_{Pt}) in unfiltered lake water were always higher than in filtered lake water at the ends of the exposures. The potentials in unfiltered water varied from 600 to 750 mV(SHE), while in filtered water they were only within 300 to 600 mV(SHE). There were no abrupt and sustained changes in E_{Pt} with time, only relatively slow and continuous changes generally in the positive direction. Second, with the exception of 308 weld metal in Runs 2 and 3, the corrosion potentials (E_{corr}) for all materials were higher in the

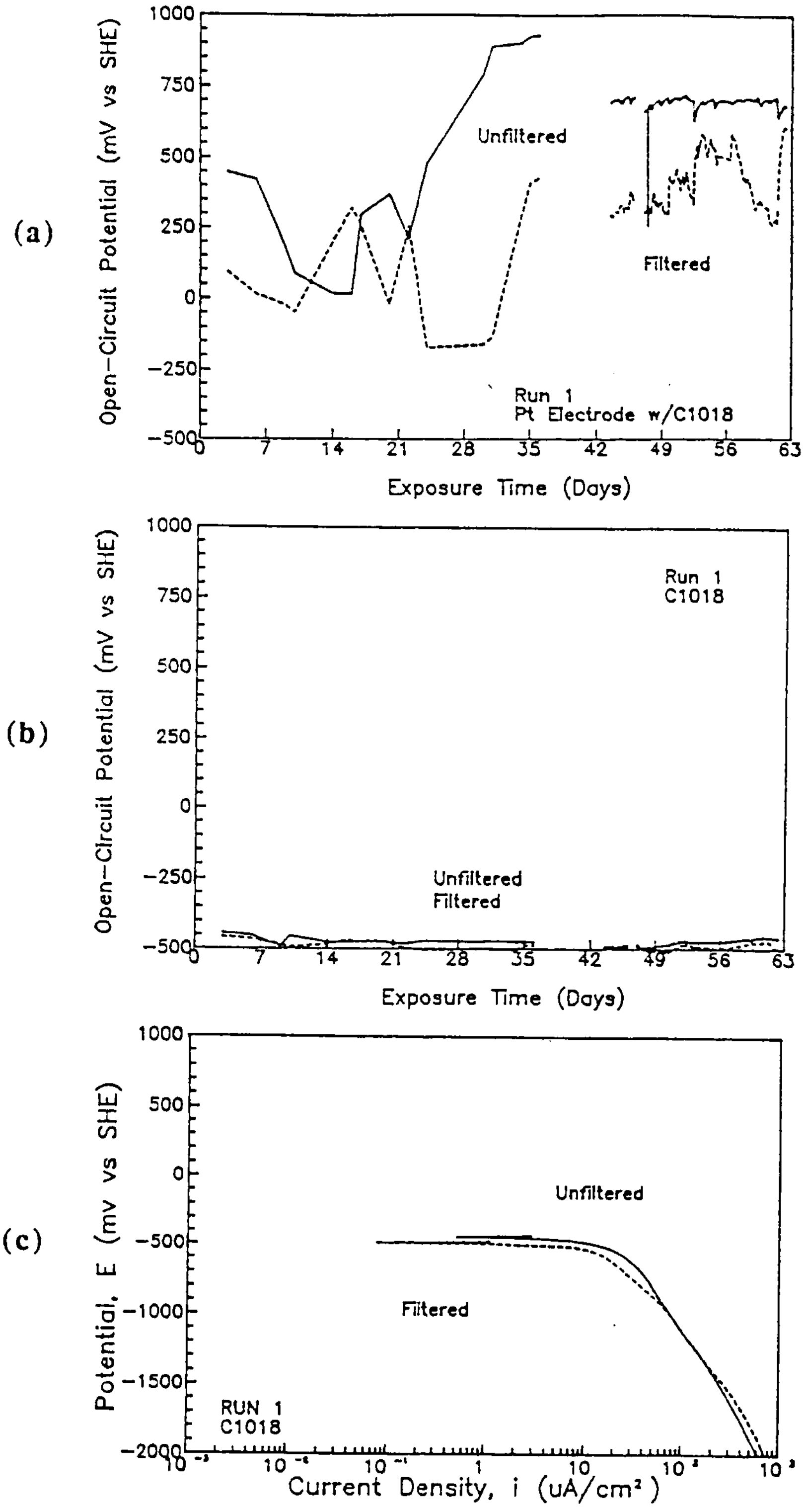


Figure 3-1. Field Electrochemical Results in Filtered and Unfiltered Lake Water, Run 1: (a) Pt Potential vs. Time, (b) Corrosion Potential for C1018 vs. Time, (c) Cathodic Polarization Curves for C1018 at Ends of Exposures.

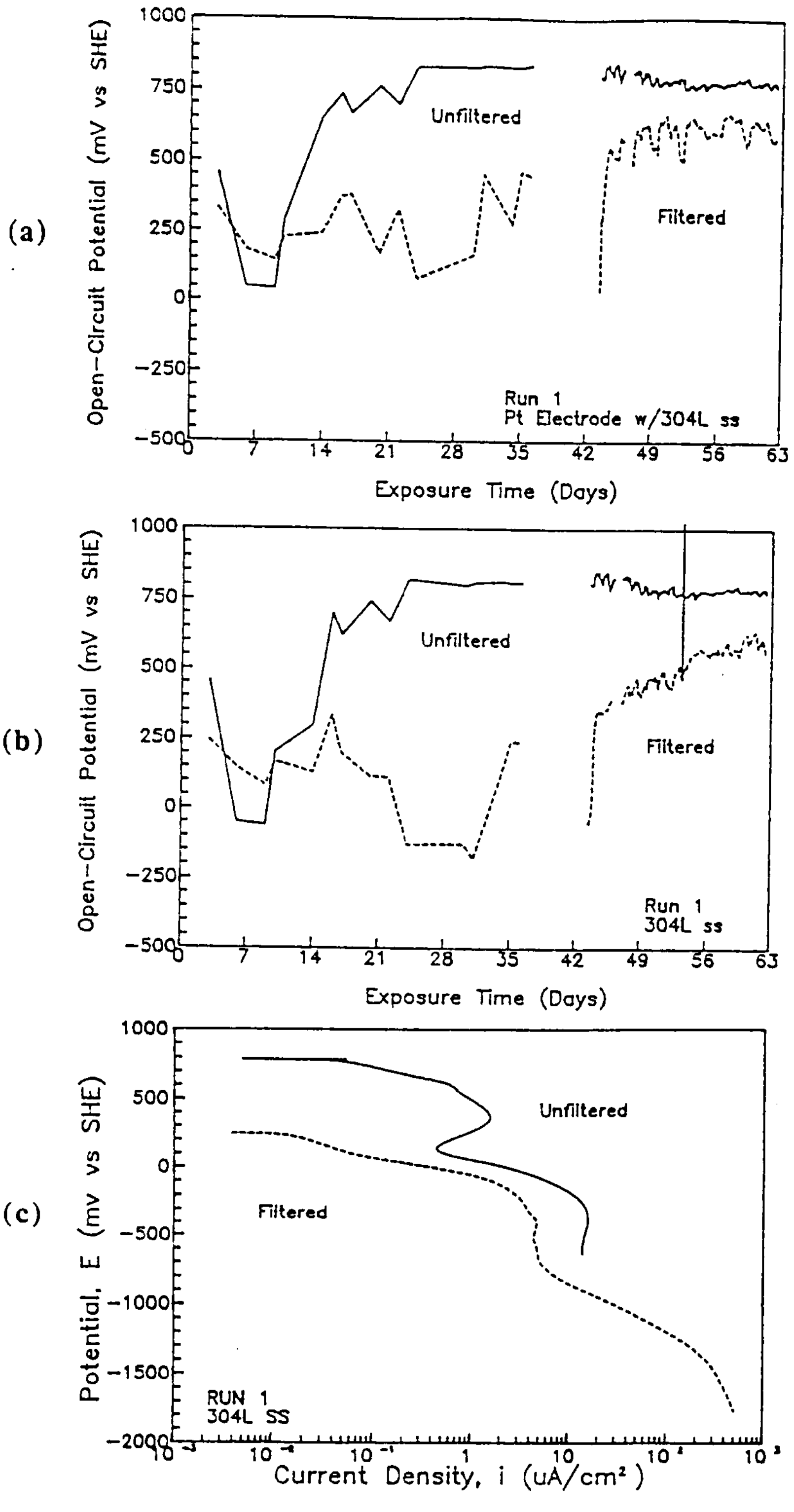


Figure 3-2. Field Electrochemical Results in Filtered and Unfiltered Lake Water, Run 1: (a) Pt Potential vs. Time, (b) Corrosion Potential for 304L vs. Time, (c) Cathodic Polarization Curves for 304L at Ends of Exposures.

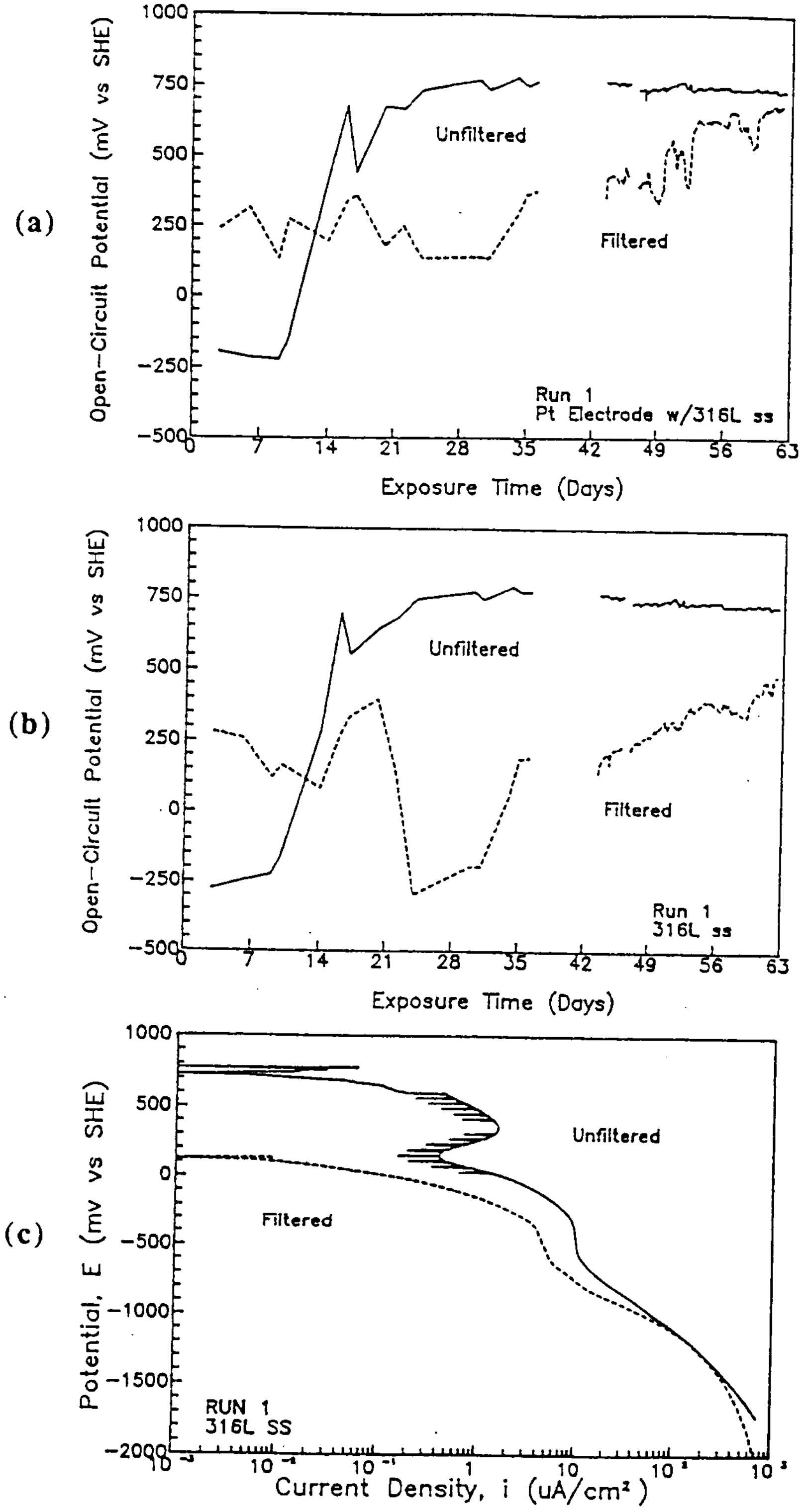


Figure 3-3. Field Electrochemical Results in Filtered and Unfiltered Lake Water, Run 1: (a) Pt Potential vs. Time, (b) Corrosion Potential for 316L vs. Time, (c) Cathodic Polarization Curves for 316L at Ends of Exposures.

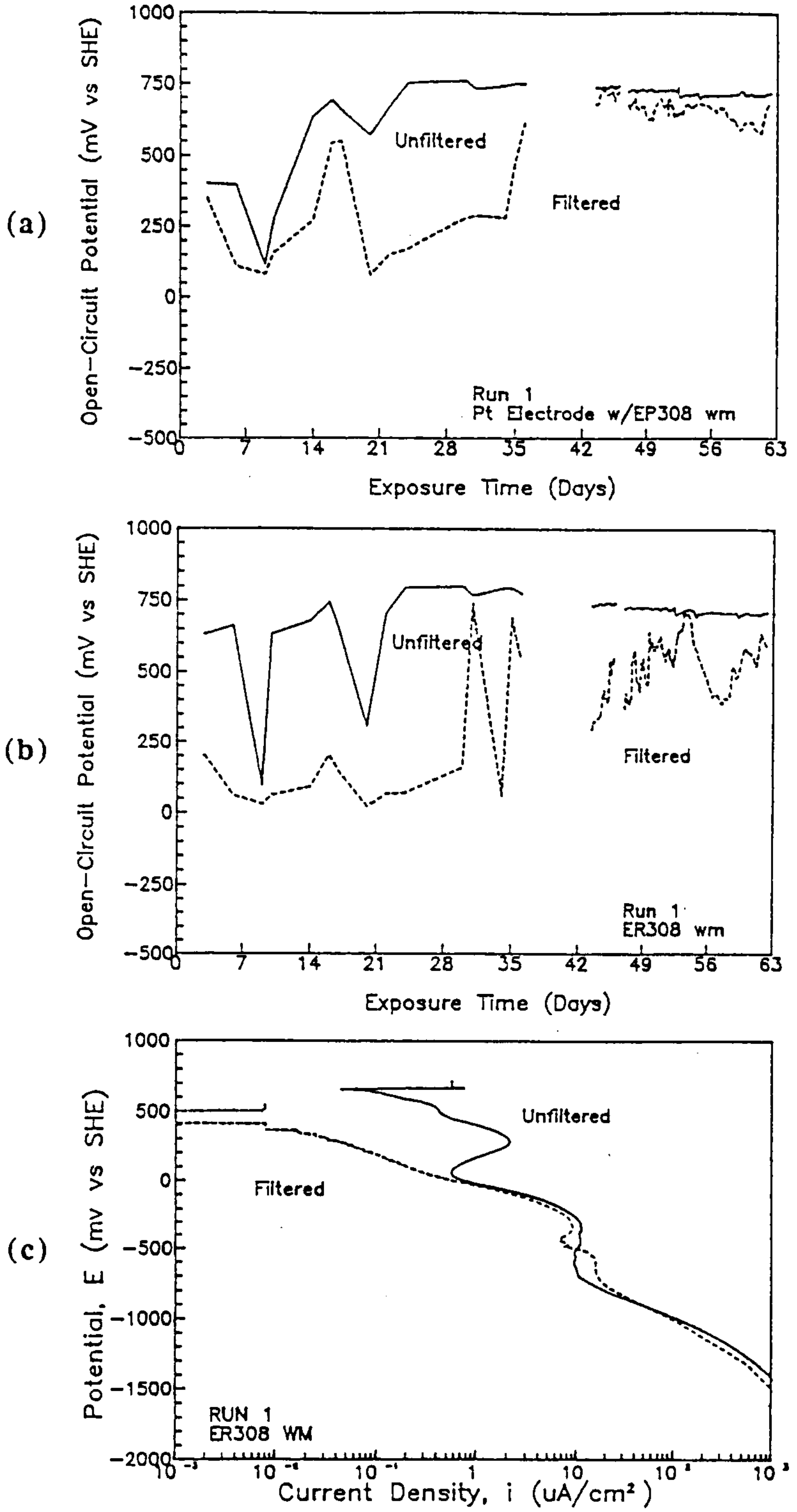


Figure 3-4. Field Electrochemical Results in Filtered and Unfiltered Lake Water, Run 1: (a) Pt Potential vs. Time, (b) Corrosion Potential for 308 Weld Metal vs. Time, (c) Cathodic Polarization Curves for 308 Weld Metal at Ends of Exposures.

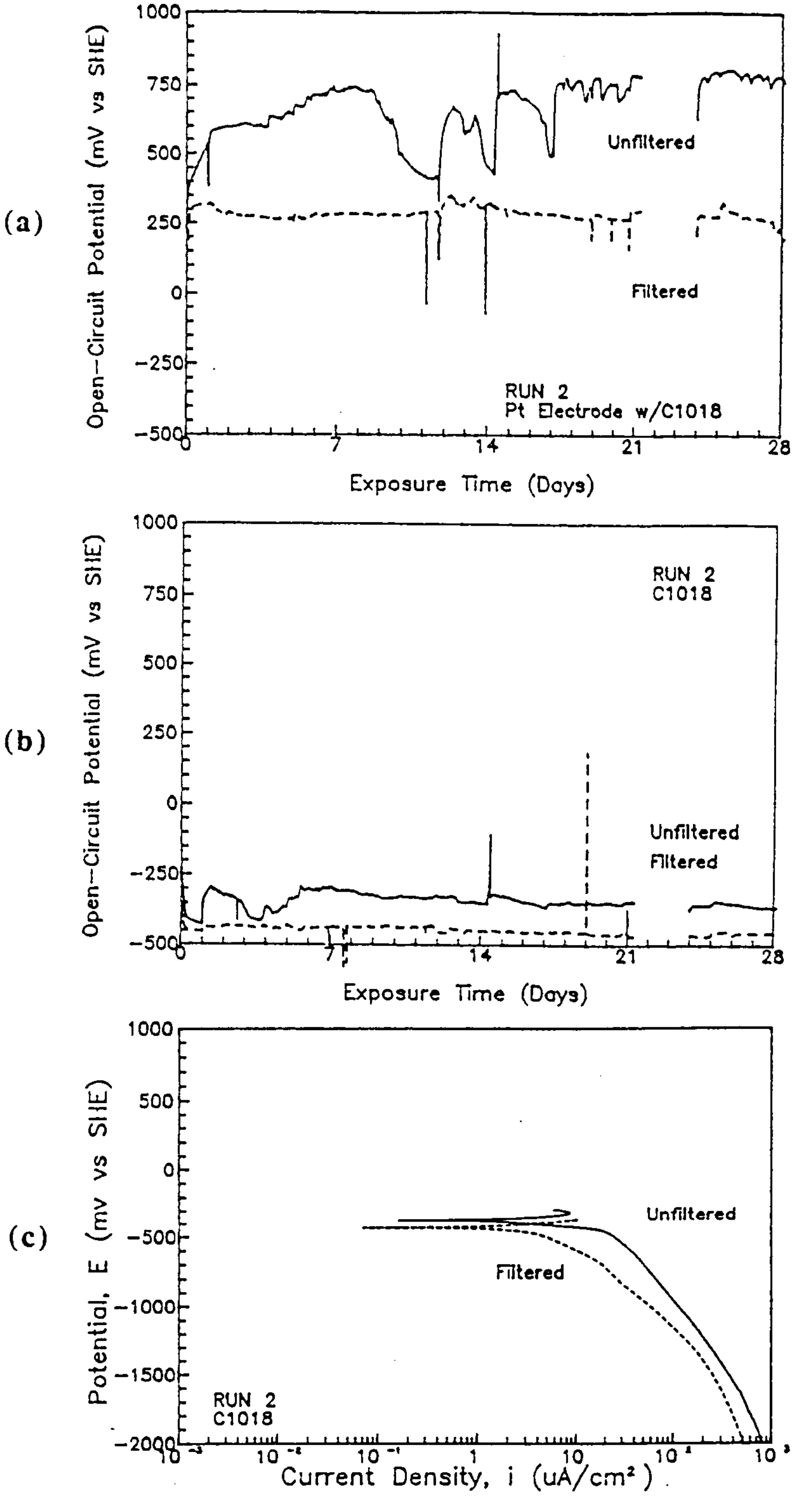


Figure 3-5. Field Electrochemical Results in Filtered and Unfiltered Lake Water, Run 2: (a) Pt Potential vs. Time, (b) Corrosion Potential for C1018 vs. Time, (c) Cathodic Polarization Curves for C1018 at Ends of Exposures.

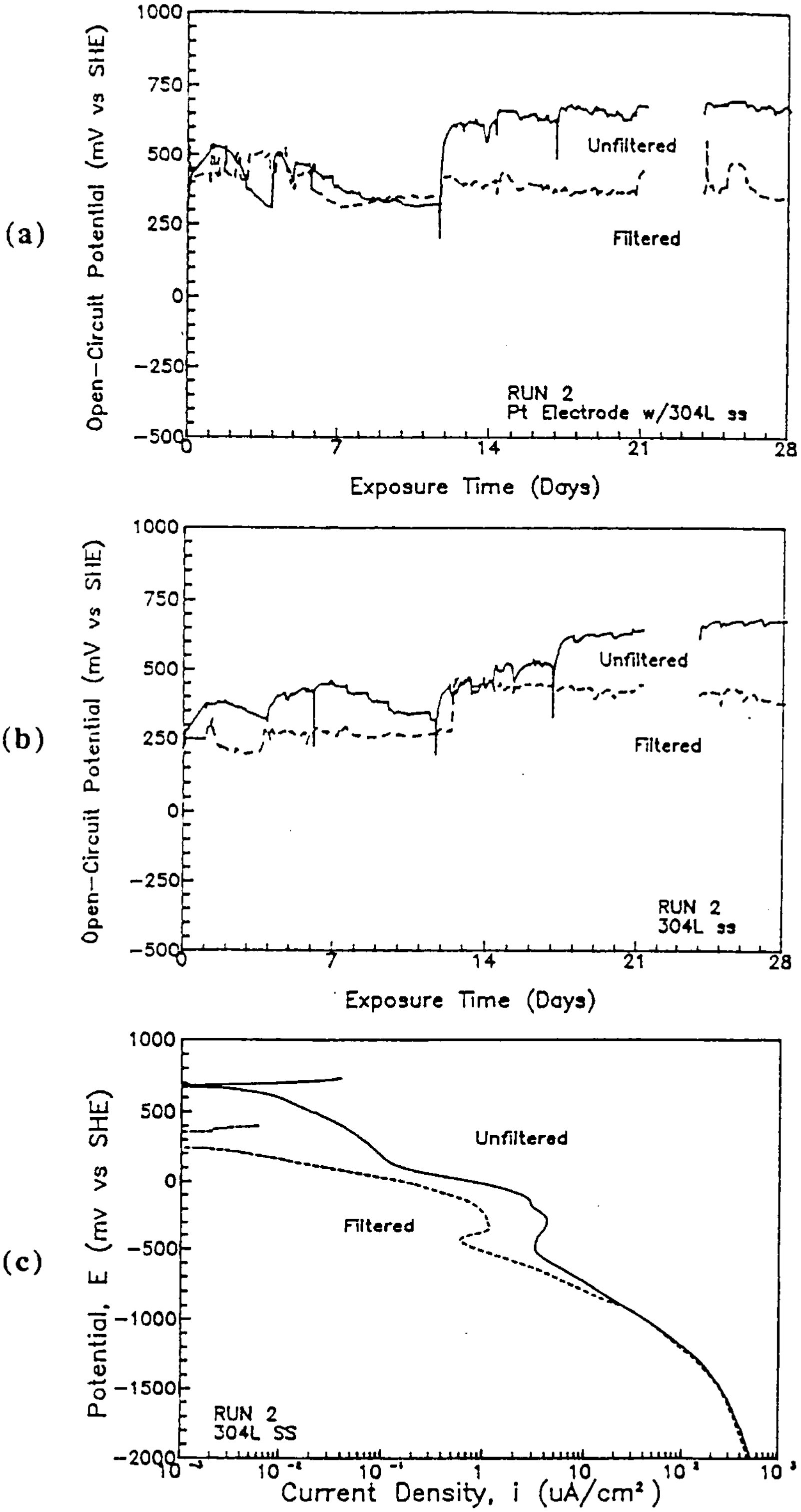


Figure 3-6. Field Electrochemical Results in Filtered and Unfiltered Lake, Run 2: (a) Pt Potential vs. Time, (b) Corrosion Potential for 304L vs. Time, (c) Cathodic Polarization Curves for 304L at Ends of Exposures.

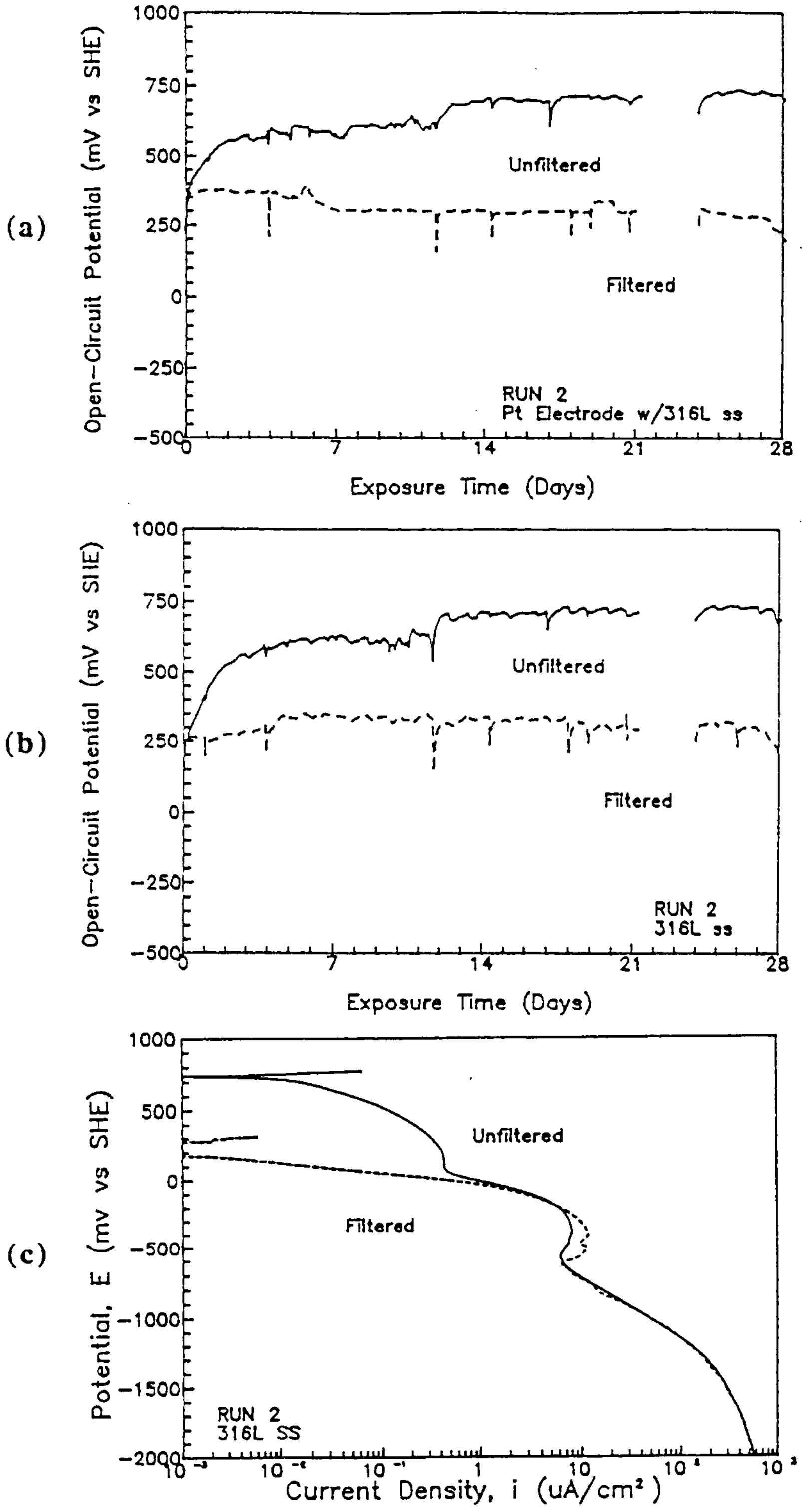


Figure 3-7. Field Electrochemical Results in Filtered and Unfiltered Lake Water, Run 2: (a) Pt Potential vs. Time, (b) Corrosion Potential for 316L vs. Time, (c) Cathodic Polarization Curves for 316L at Ends of Exposures.

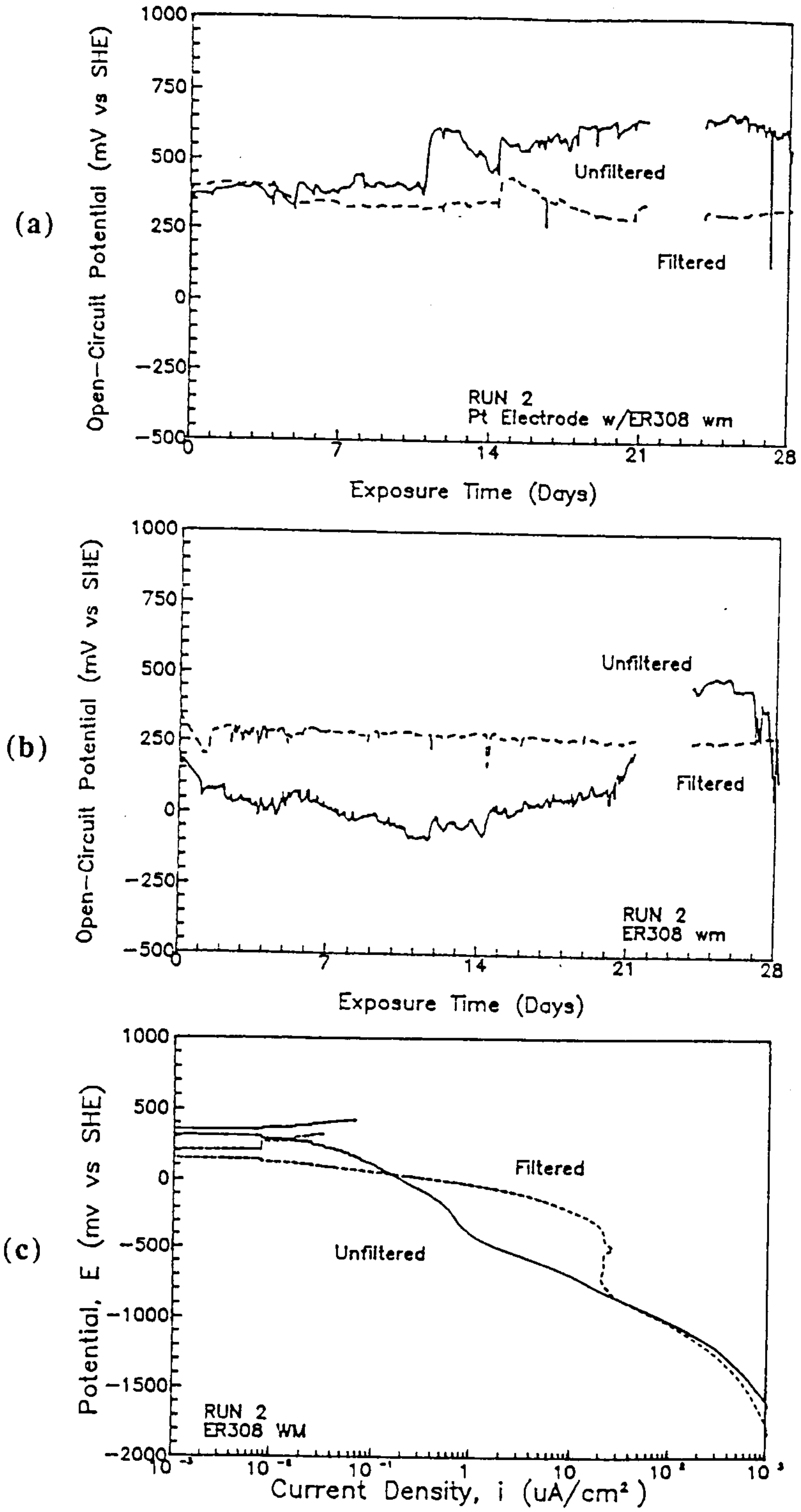


Figure 3-8. Field Electrochemical Results in Filtered and Unfiltered Lake Water, Run 2: (a) Pt Potential vs. Time, (b) Corrosion Potential for 308 Weld Metal vs. Time, (c) Cathodic Polarization Curves for 308 Weld Metal at Ends of Exposures.

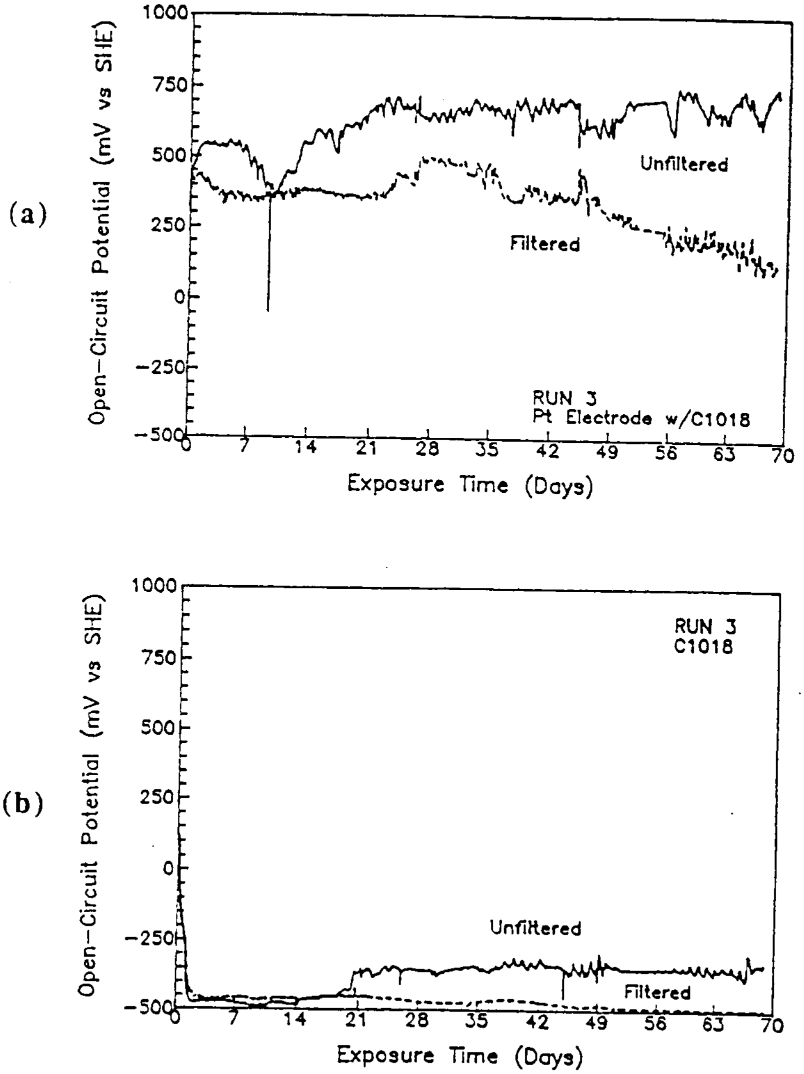
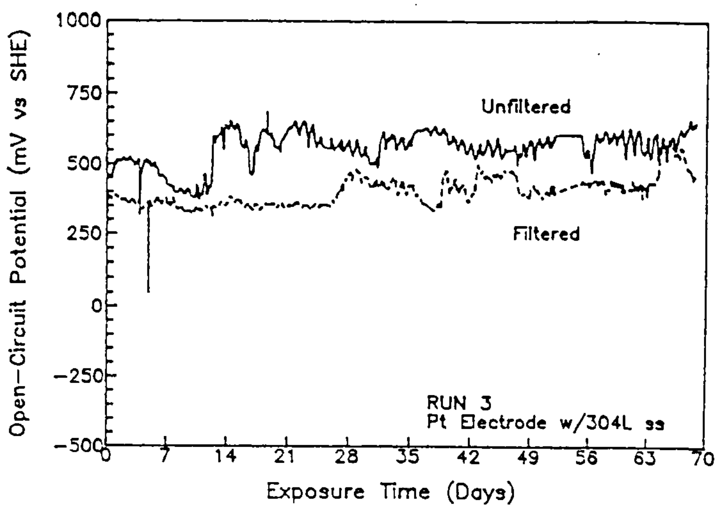


Figure 3-9. Field Electrochemical Results in Filtered and Unfiltered Lake Water, Run 3: (a) Pt Potential vs. Time, (b) Corrosion Potential for C1018 vs. Time.

(a)



(b)

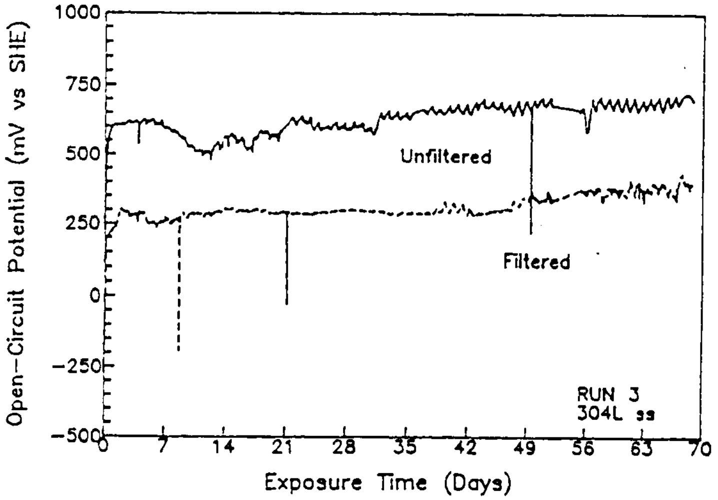


Figure 3-10. Field Electrochemical Results in Filtered and Unfiltered Lake Water, Run 3: (a) Pt Potential vs. Time, (b) Corrosion Potential for 304L vs. Time.

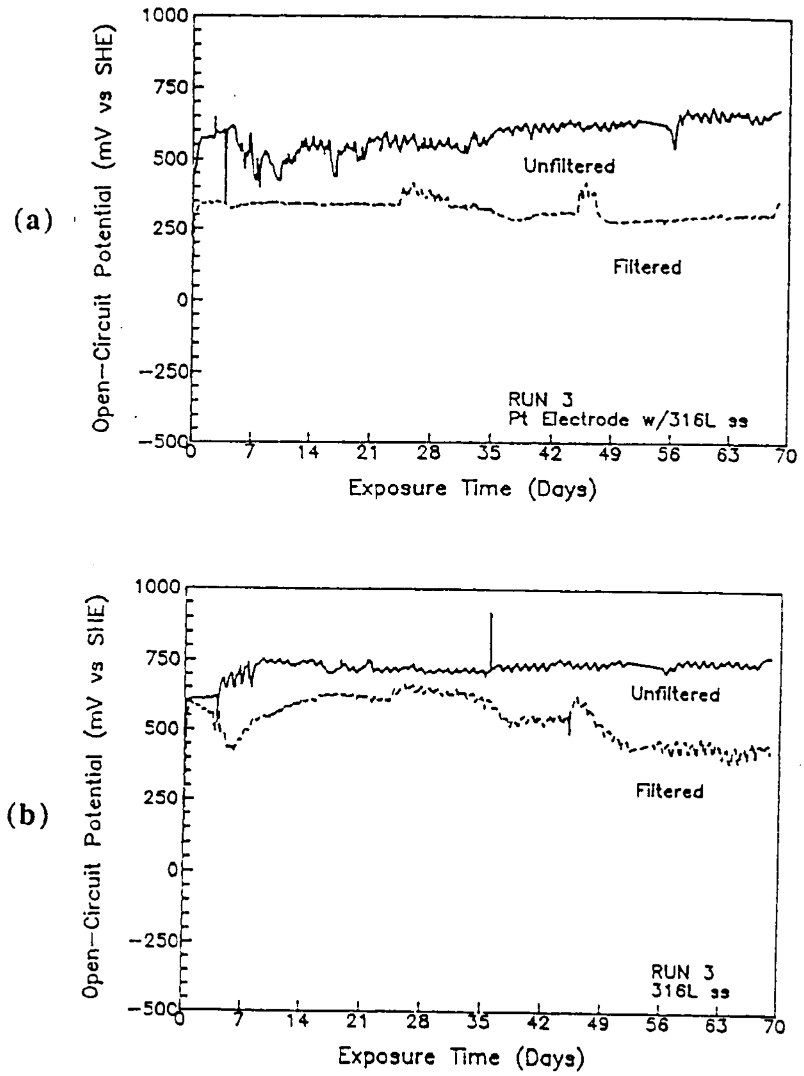


Figure 3-11. Field Electrochemcial Results in Filtered and Unfiltered Lake Water, Run 3: (a) Pt Potential vs. Time, (b) Corrosion Potential for 316L vs. Time.

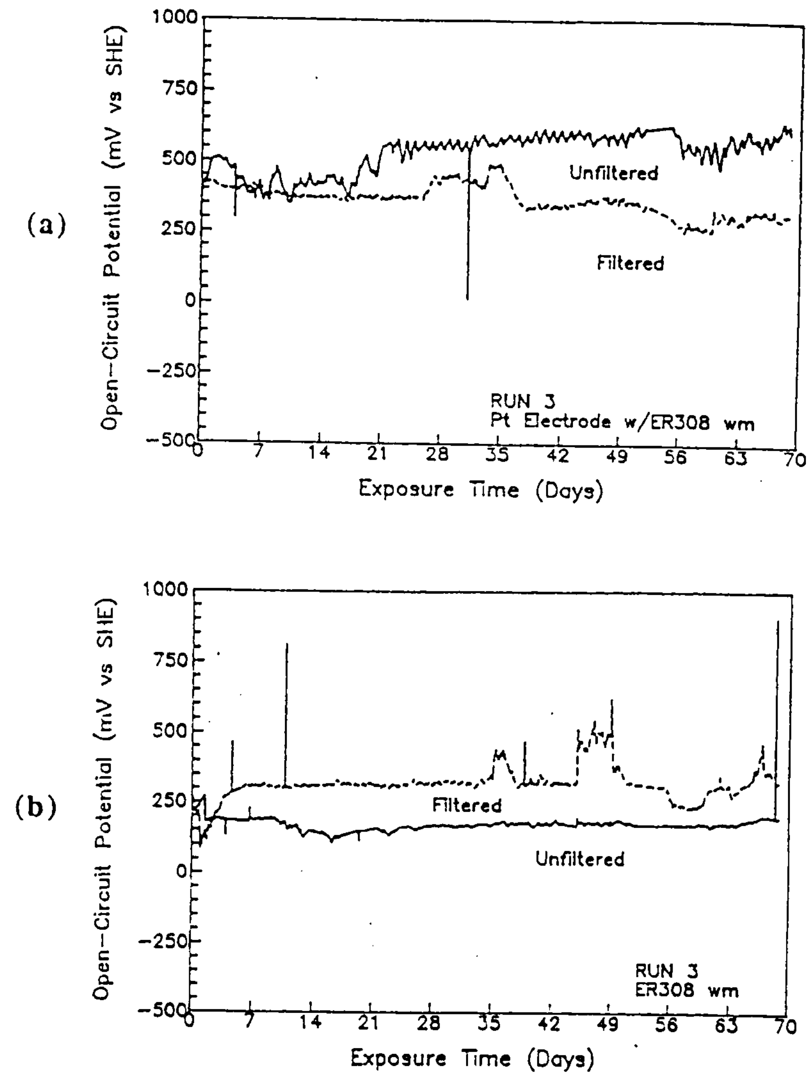


Figure 3-12. Field Electrochemcial Results in Filtered and Unfiltered Lake Water, Run 3: (a) Pt Potential vs. Time, (b) Corrosion Potential for 308 Weld Metal vs. Time.

unfiltered lake water. Among them, the E_{corr} values of the carbon steels were just slightly higher in unfiltered lake water, but the E_{corr} values of the stainless steels in unfiltered lake water were significantly higher than in filtered lake water. There were also no abrupt and sustained changes in E_{corr} with time, only relatively slow and continuous changes generally in the positive direction. Third, the open-circuit potentials of the platinum (E_{Pt}) and the corrosion potentials of the stainless steels (E_{corr}) had almost the same values in unfiltered and filtered lake water respectively.

The cathodic polarization curves at the ends of the exposures demonstrated distinctive differences in the unfiltered and filtered lake water. The most pronounced difference was for the stainless steels: in the potential range between the E_{corr} values for the filtered and unfiltered lake water, the unfiltered-lake-water curves demonstrated "cathodic peaks" (Run 1) or "apparent diffusion limits" (Run 2). These features indicated that different reduction processes occurred in the unfiltered as compared to the filtered lake water. For the carbon steels, active corrosion processes in both unfiltered and filtered lake water were apparently controlled by a cathodic diffusion process (as judged by reference to the cathodic polarization curves for the stainless steels).

(2) Electrochemical Impedance Spectroscopy

The results of the EIS data plotted in the Bode format are given in Figures 3-13 through 3-16 for Run 1 and in Figures 3-17 through 3-20 for Run 2. For Run 3, EIS data were not collected after the exposure. The log impedances and the phase shift angles are presented as a function of frequency. The EIS data in the low frequency range were scattered to some extent because of the use of relatively-high-resistance cracked-glass-bead type reference electrodes.

In Figures 3-13 through 3-20, all of the EIS data in the filtered lake water are plotted as open-square curves while the filtered-lake-water data are plotted as solid-square curves. Very high capacitive tendencies were shown in the EIS data for the stainless steels in the filtered lake water as evidenced by the large phase angles at the lowest frequencies in the phase-angle vs. log f plots. The high log impedances in the log Z vs. log f plots demonstrated that all the stainless steels in the filtered water were highly resistive and stayed passive. The phase-angle vs. log f curves exhibited only a single relaxation time. On the other hand, the EIS data for the stainless steels in the unfiltered lake water at the end of Run 1 exhibited an unique feature in that a second relaxation process occurred at higher frequencies. These characteristics were indicated by two distinct line segments in the mid-to-low frequency range of each log Z vs.

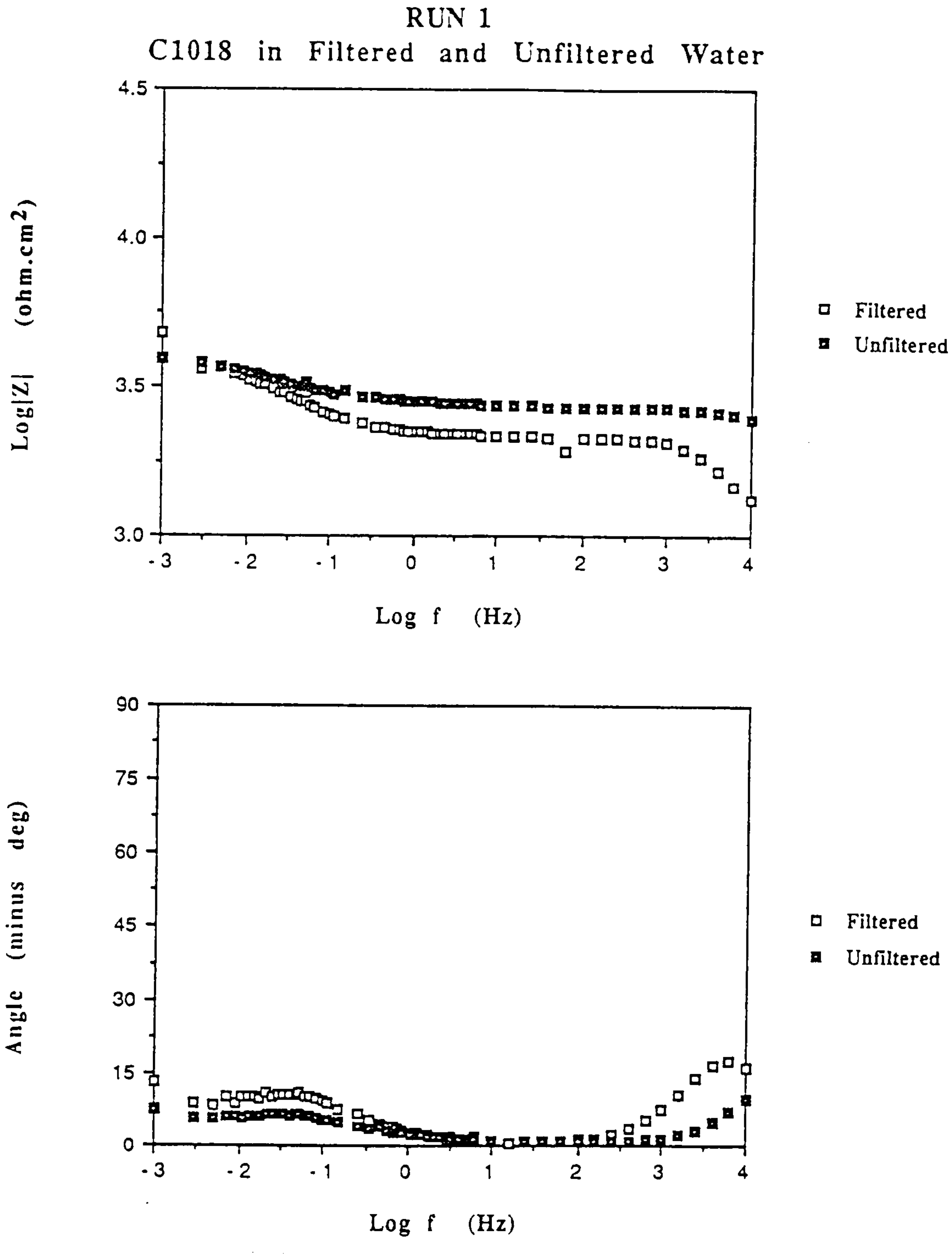


Figure 3-13. Electrochemical Impedance Spectroscopy Results at Ends of Exposures, Filtered and Unfiltered Lake Water, Run 1, C1018.

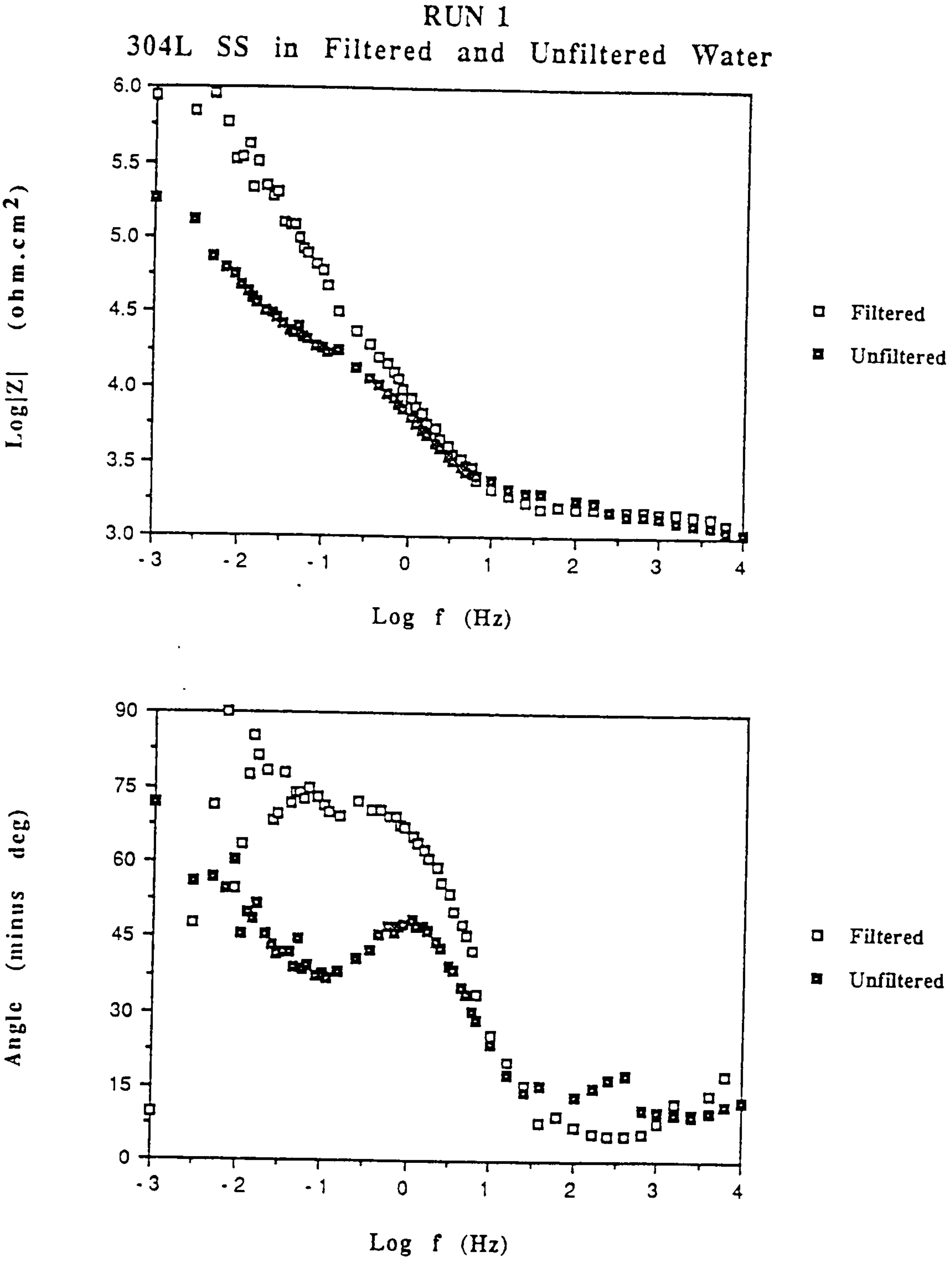


Figure 3-14. Electrochemical Impedance Spectroscopy Results at Ends of Exposures, Filtered and Unfiltered Lake Water, Run 1, 304L.

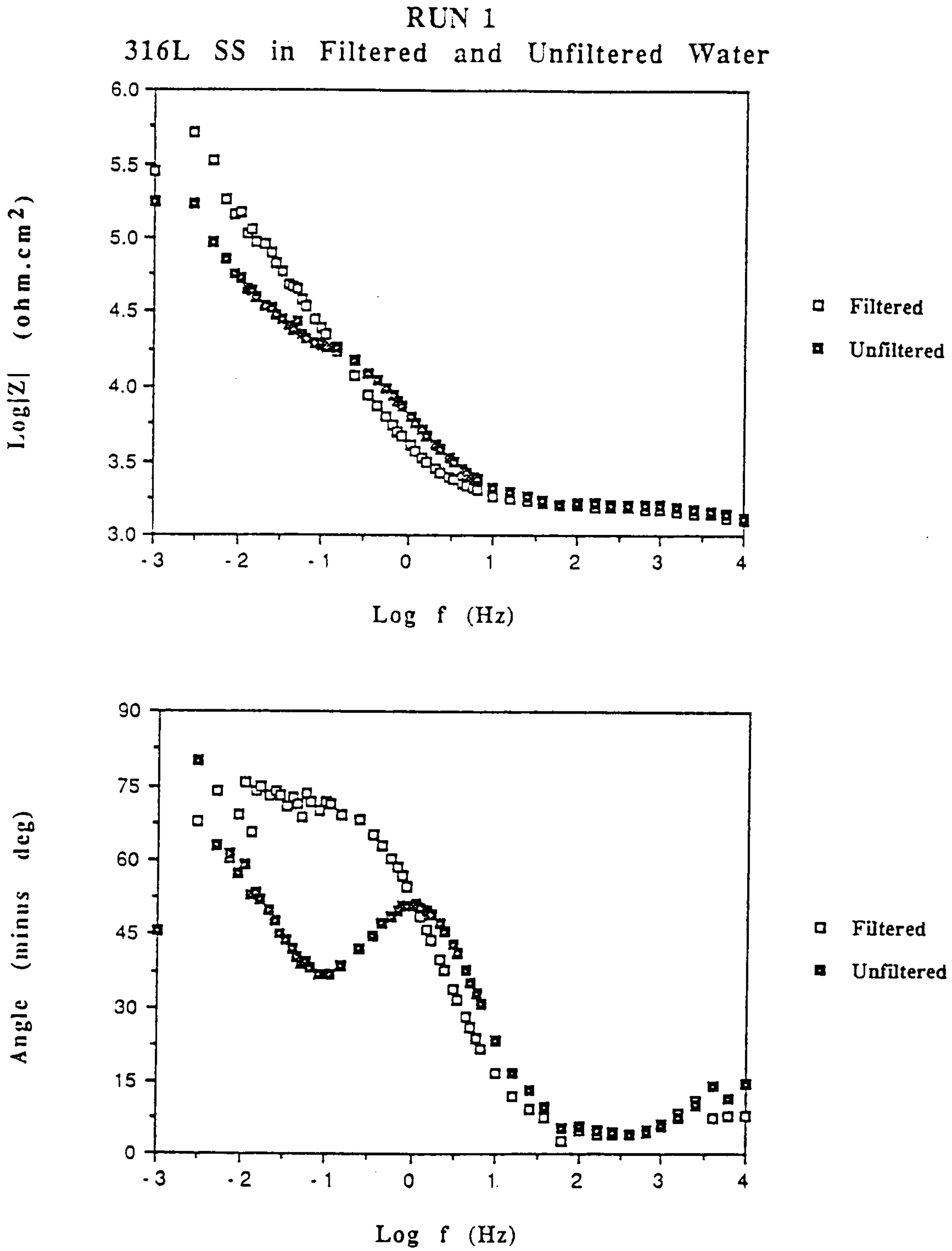

RUN 1
316L SS in Filtered and Unfiltered Water

Figure 3-15. Electrochemical Impedance Spectroscopy Results at Ends of Exposures, Filtered and Unfiltered Lake Water, Run 1, 316L.

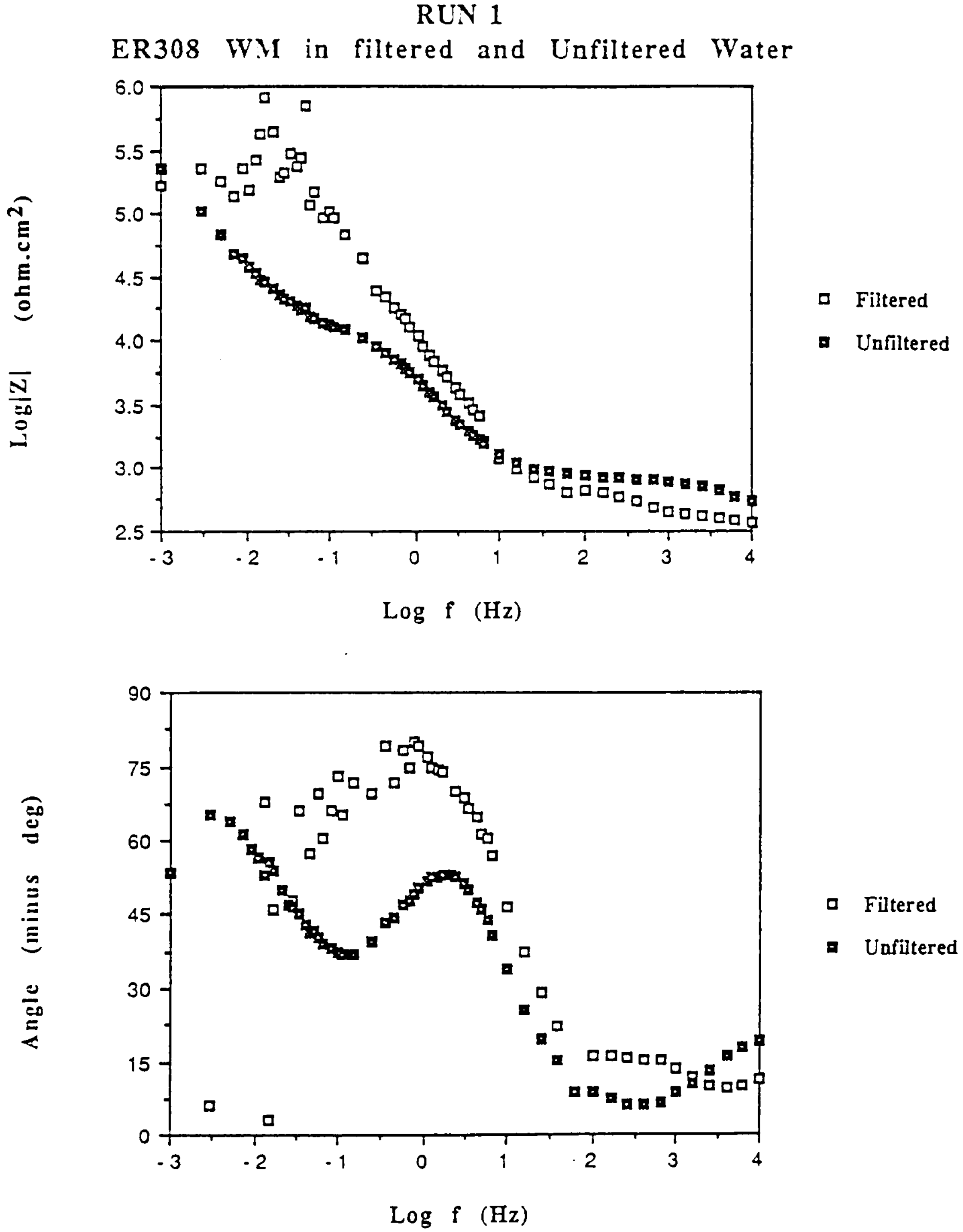


Figure 3-16. Electrochemical Impedance Spectroscopy Results at Ends of Exposures, Filtered and Unfiltered Lake Water, Run 1, 308 Weld Metal.

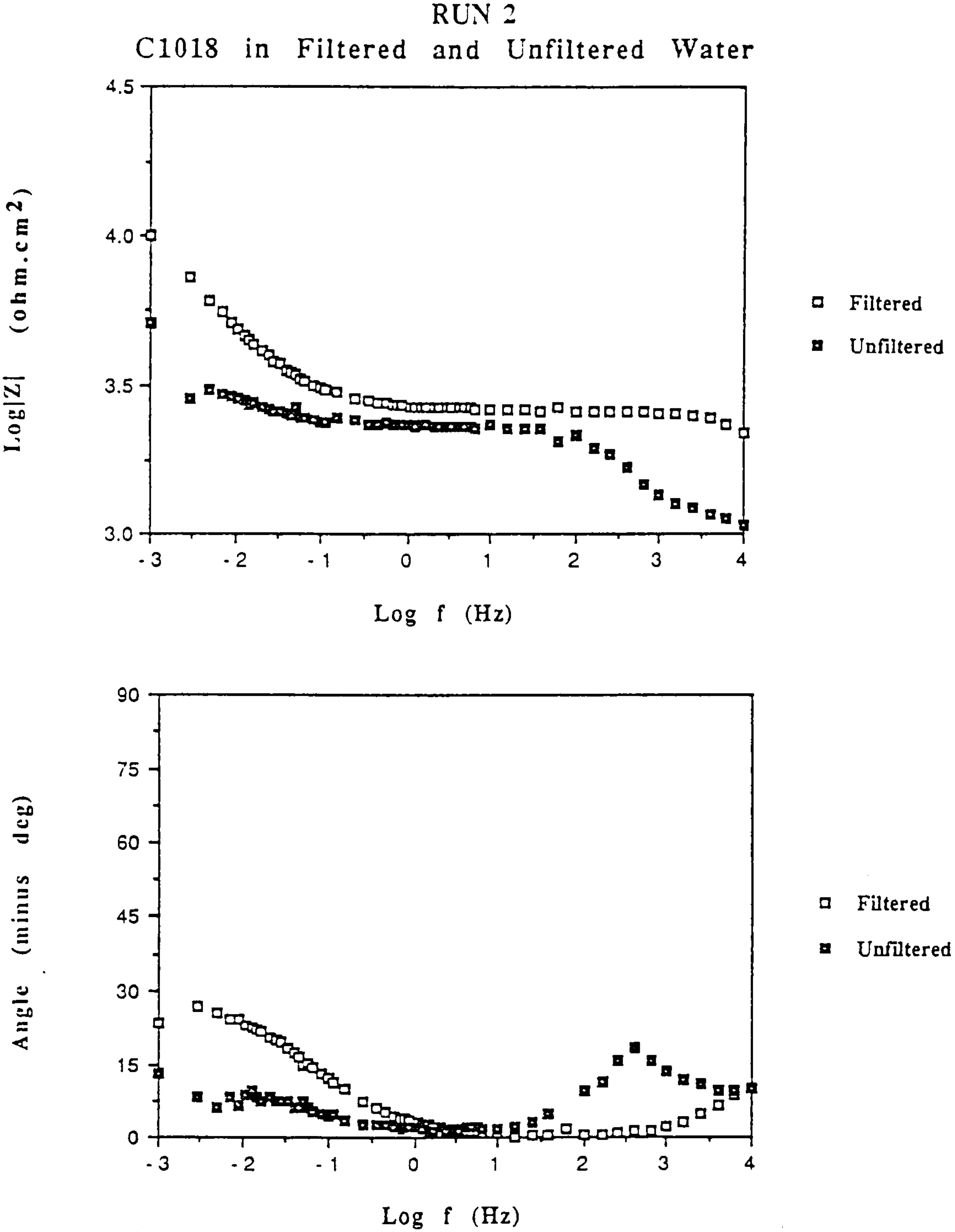


Figure 3-17. Electrochemical Impedance Spectroscopy Results at Ends of Exposures, Filtered and Unfiltered Lake Water, Run 2, C1018.

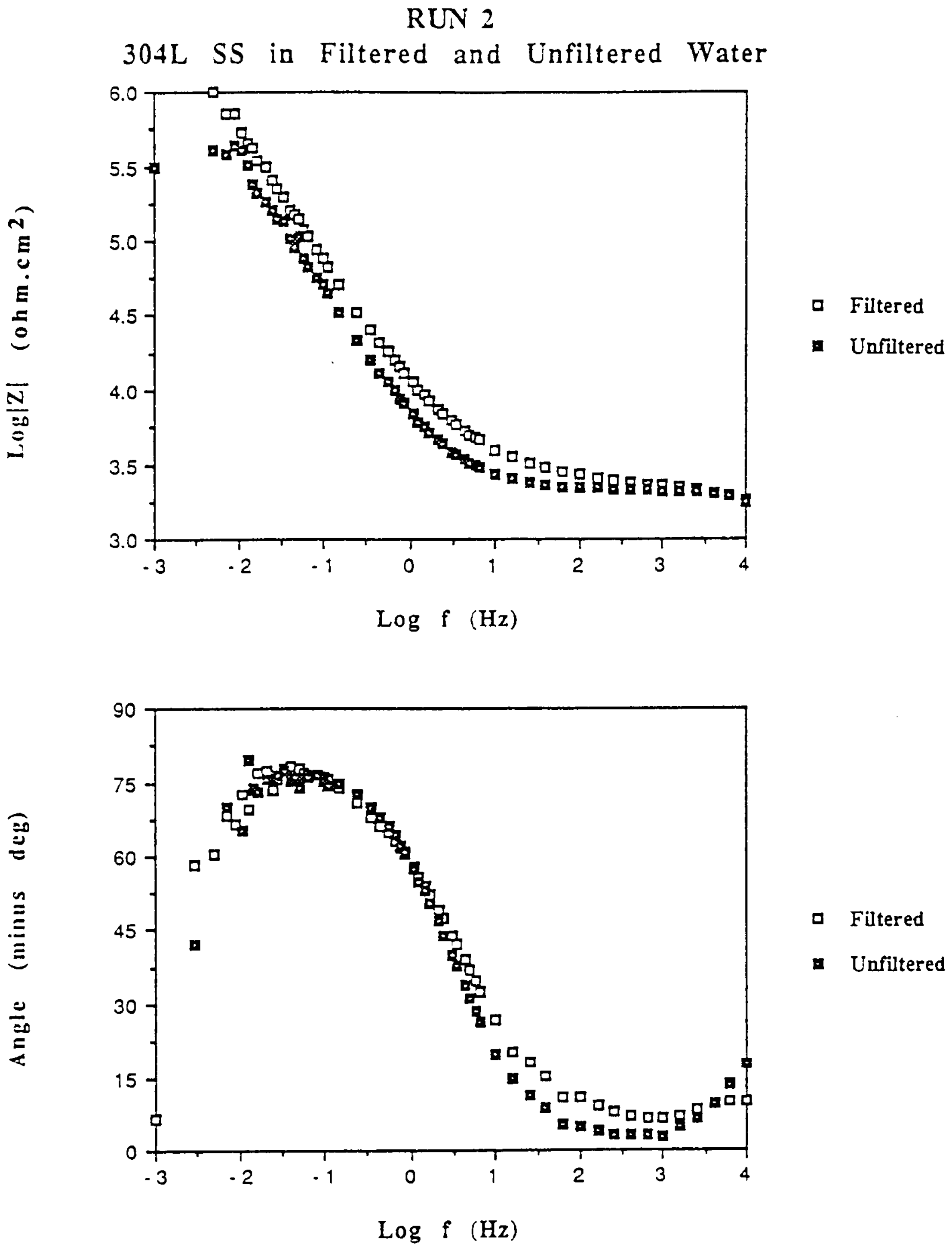


Figure 3-18. Electrochemical Impedance Spectroscopy Results at Ends of Exposures, Filtered and Unfiltered Lake Water, Run 2, 304L.

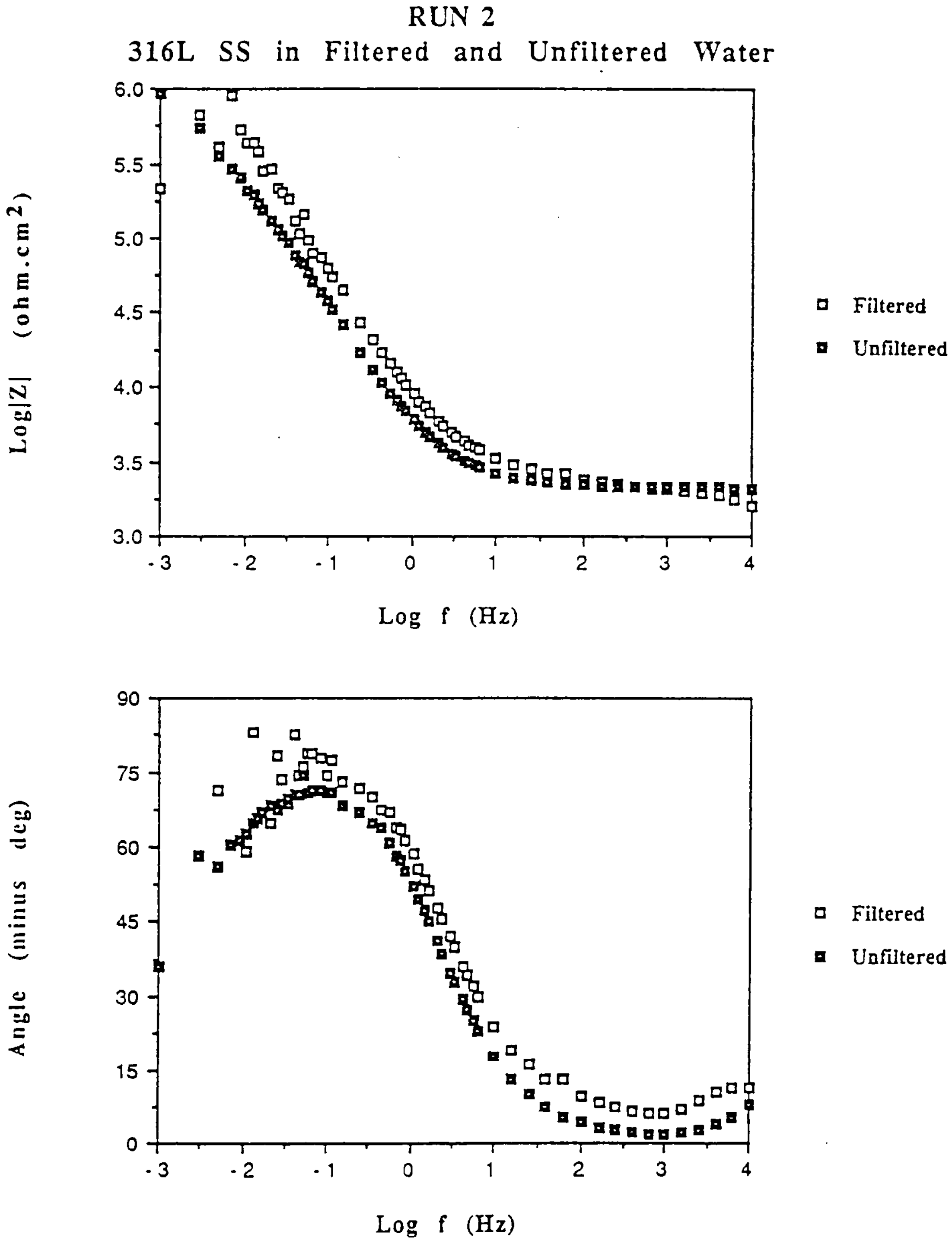


Figure 3-19. Electrochemical Impedance Spectroscopy Results at Ends of Exposures, Filtered and Unfiltered Lake Water, Run 2, 316L.

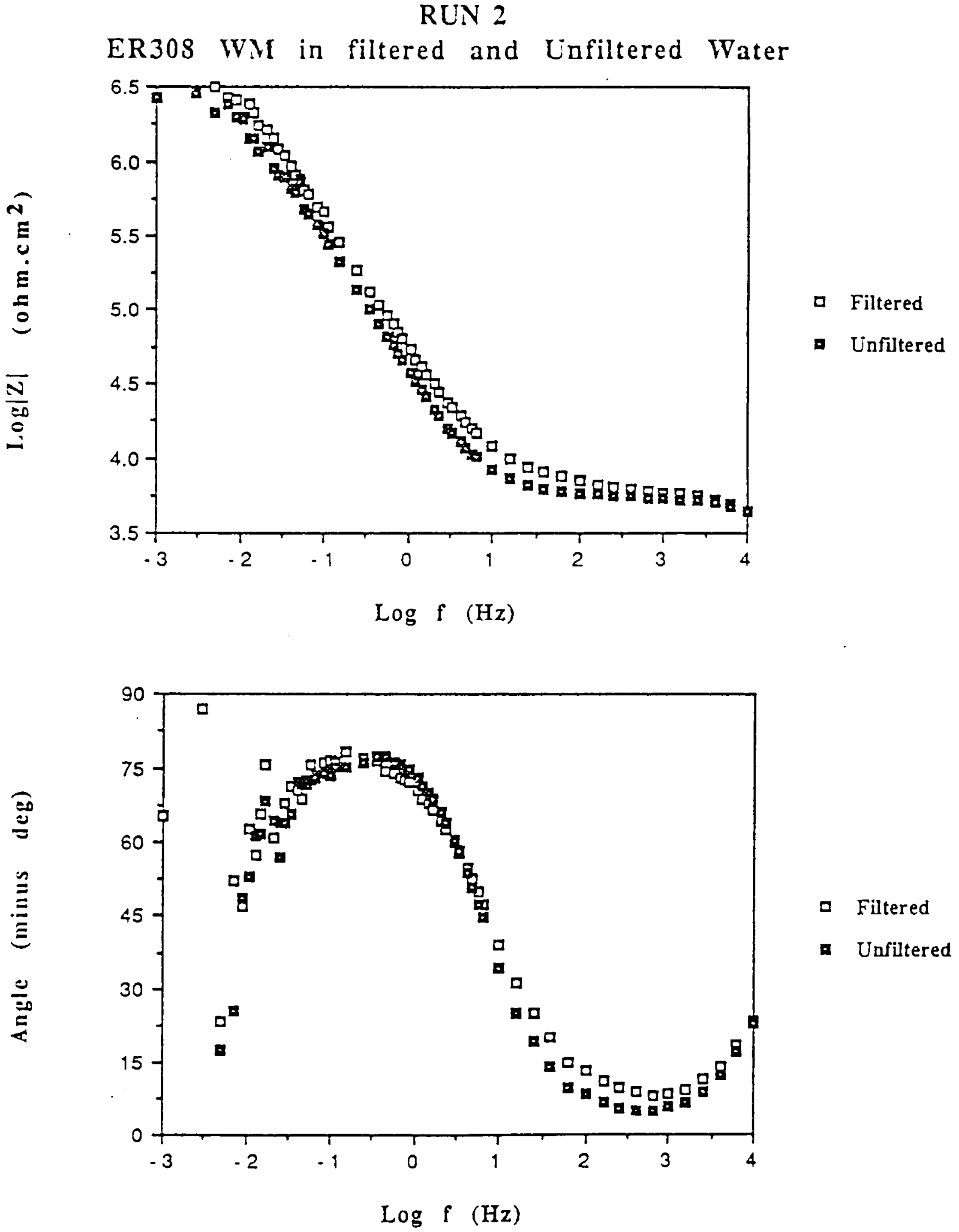


Figure 3-20. Electrochemical Impedance Spectroscopy Results at Ends of Exposures, Filtered and Unfiltered Lake Water, Run 2, 308.

log f plot. As far as impedances at 1 mHz were concerned, the impedances in the unfiltered lake water were much lower than in the filtered lake water. However, these major differences in features did not exist at the end of Run 2, at which the EIS data in the unfiltered lake water did not differentiate from the filtered water although the corrosion potentials and cathodic polarization curves characteristically differed between the filtered and unfiltered lake water.

The EIS results for the carbon steels in both the filtered and unfiltered lake water for Runs 1 and 2, as shown in Figures 13 and 17, indicated quite pure resistance tendencies. The phase angles were as low as 15 degrees. The impedance at the lowest frequency was lower for the unfiltered water (especially for Run 2). This result indicated a lower charge transfer resistance and a higher corrosion rate in the unfiltered water.

(3) Microbiological Analyses and Surface Examination

The results of the microbiological analyses of the biofouling material on the surfaces of the carbon steel and 304L stainless steel specimens at the end of Run 3 were as follows. As shown in Tables 3-1 and 3-2, bacteria were found on the surfaces exposed to both filtered and unfiltered water. This result came as a surprise since the purpose of the 0.2 μm in-line filters was to filter-sterilize the lake

Table 3-1.

Epifluorescent Cell Counts (No. Cells / cm^2)

COUPONS	BACTERIA 10^{-2} Dilution	 10^{-3} Dilution	ALGAE 10^{-2} Dilution	 10^{-3} Dilution
304L Filtered	$7.25x10^{7}$	$2.80x10^{7}$	---	---
304L Unfiltered	$1.18x10^{8}$	$1.50x10^{8}$	$6.43x10^{5}$	$2.20x10^{6}$
C1018 Filtered	$1.36x10^{8}$	$2.10x10^{8}$	---	---
C1018 Unfiltered	$9.65x10^{7}$	$9.00x10^{7}$	$9.69x10^{5}$	$1.78x10^{6}$

Table 3-2.

Viable Cell Counts (No. Cells / cm^2)

COUPONS	HACFU Medium (Aerobic Bacteria) 10^{-1} Dilution	 10^{-3} Dilution	BHI Medium (Facultatively Anaerobic Bacteria) 10^{-1} Dilution	 10^{-3} Dilution
304L Filtered	$1.61x10^{4}$	$4.24x10^{5}$	---	---
304L Unfiltered	$1.44x10^{3}$	$7.00x10^{3}$	$1.40x10^{2}$	---
C1018 Filtered	$2.06x10^{4}$	$4.20x10^{5}$	---	---
C1018 Unfiltered	$2.83x10^{3}$	$1.47x10^{6}$	confluent	$3.00x10^{3}$

water. On the filtered-water surfaces, only aerobic, gram negative, rod-shaped bacteria were observed. On the unfiltered-water surfaces, both aerobic and facultatively anaerobic, gram negative, rod-shaped bacteria were observed. In both cases, some of the bacteria were acid producing. Sulfate-reducing bacteria (SRB's) were not observed on either the filtered or unfiltered-water surfaces. A major difference between the filtered and unfiltered-water surfaces, as shown in Table 3-1, involved algae: algae were found on the surfaces exposed to unfiltered water but not on the surfaces exposed to filtered water. Therefore, in these experiments, it appeared that a major effect of the 0.2 μm filters was to filter out the algae, not the bacteria.

The results of the lake water analyses during Run 1 and 2 are presented in Table 3-3. Unfortunately, the water was not analyzed during Run 3. It is noted that the pH ranged from 6.9 to 7.2, the oxygen content from 3.9 to 8.9 ppm, and that the chloride levels were extremely low, 1.7-3.8 ppm.

As a result of the microbiological analyses at the end of Run 3, it was realized that algae effects may have been an important factor in these field studies. Therefore, it was determined that a perturbation on the microorganism consortium at the 316L specimen surfaces would be applied by eliminating light, since algae photosynthesizes oxygen when exposed to light. The electrochemical cells containing the

Table 3-3

Lake Water Analyses

	Analysis Date			
	8-25-89	9-20-89	10-31-89	1-22-90
Temperature (°C)	24	21	16	10
F (ppm)	0.094	0.122	0.065	0.119
Cl (ppm)	3.80	1.67	3.65	2.17
NO_3 (ppm)	1.50	2.58	1.50	2.99
PO_4 (ppm)	-	0.009	-	0.019
SO_4 (ppm)	7.16	5.97	7.10	6.82
Turbidity (NTU)	21	22	24	23
Dissolved O_2 (mg/L)	5.7	4.9	8.9	3.9
Hardness (mg/L)	91	49	54	92
Alkalinity (mg/L)	84	45	99	49
Fe (mg/L)	0.64	0.52	0.55	0.59
Total Solids (ppm)	123	131	149	140
Suspended Solids (ppm)	17	57	42	42
Dissolved Solids (ppm)	106	74	107	98
pH	7.0	6.92	7.02	7.20
Conductivity (micromhos/cm)	187.8	100.9	225	138.9

316L stainless steels in both the filtered and unfiltered lake water were covered with aluminum foil during part of an additional time of continuous exposure. The open-circuit potentials for the Pt electrodes and the 316L working electrodes during the additional exposure time (day 70 until day 117) are shown in Figure 3-21. The cells were covered from day 70 until day 112 and then uncovered from day 112 until the end of the exposure. As seen, both E_{Pt} and E_{corr} for the unfiltered-water cell decreased significantly over the initial period when no light was available, whereas E_{Pt} and E_{corr} for the filtered-water cell remained essentially unchanged. The decrease in E_{Pt} and E_{corr} for the unfiltered-water cell is believed to be due to the decreased activity of the algae and possibly to modification in the activities of the associated bacteria. At the intermediate time periods, E_{Pt} and E_{corr} for the unfiltered-water cell increased to high values and then decreased again for reasons not understood at the present time. At the last period of time, the cells were uncovered. The E_{Pt} and E_{corr} values in the unfiltered water rose to the high potential range and the potentials in the filtered water moved to the low potential range, which were consistent with the differences in potentials as previously measured in the uncovered condition. This result indicated that the algae and associated bacteria effects were activated and again in operation.

The E_{Pt} and E_{corr} values for the other filtered and

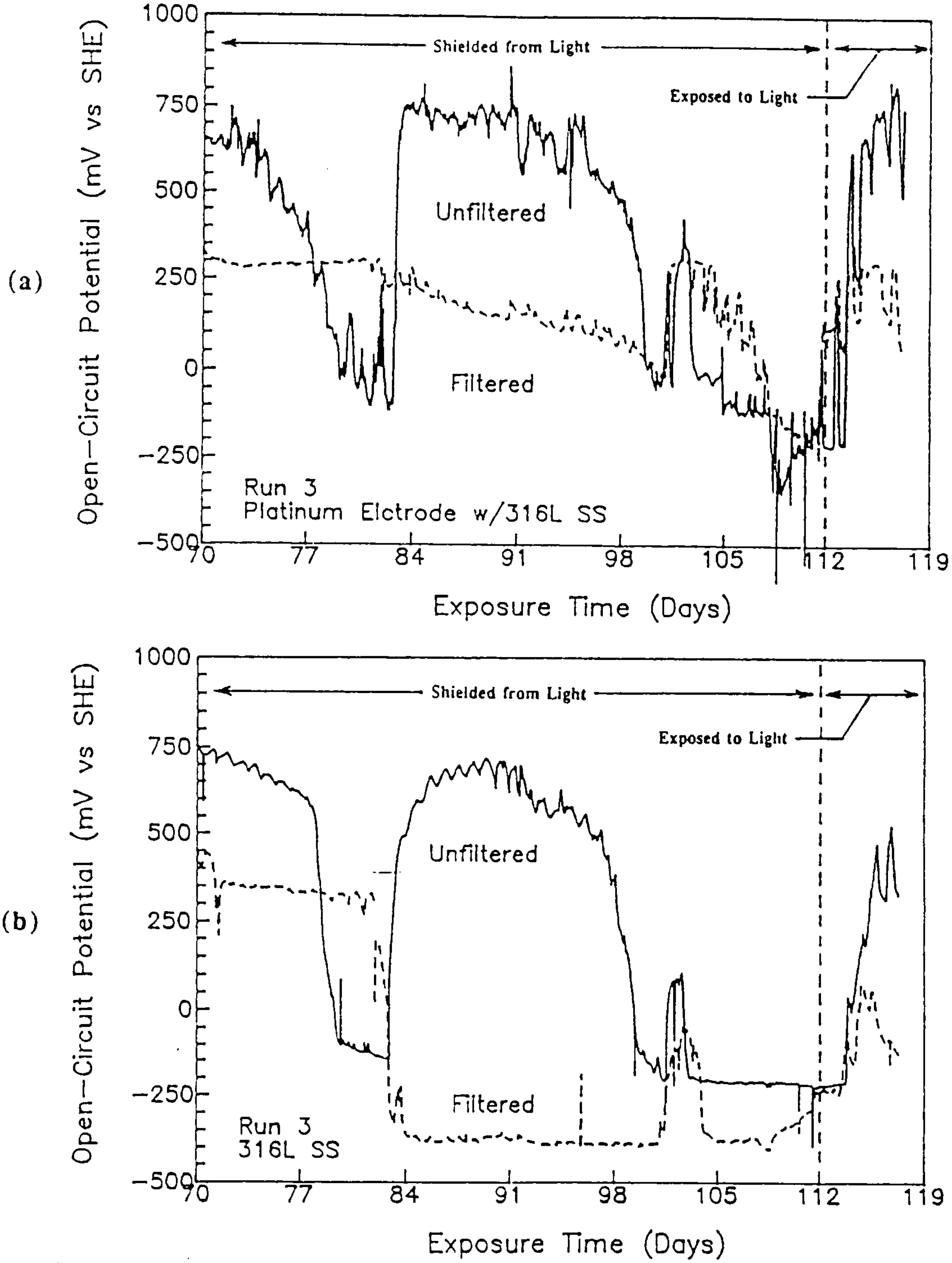


Figure 3-21. Platinum Potentials (a) and Corrosion Potentials (b) for 316L in Filtered and Unfiltered Lake Water During the Additional 47-Day Exposure after Run 3. Shielded from Light from Day 70 Until Day 112. Exposed to Light (Daylight Hours) from Day 112 until Day 117.

unfiltered-water cells containing 308 weld metal during the additional exposure time are shown in Figure 3-22. These cells were left uncovered and therefore were exposed to light during daylight hours. It is noted that both E_{Pt} and E_{corr} for the unfiltered-water condition showed oscillations with a 1-day period; the potentials increased during daylight hours and decreased at night. These results should be compared to the filtered-water condition, where no such oscillations occurred. It is reasonable to believe that the oscillations in potentials in the unfiltered water reflected the changes in algae activity and associated bacterial activity in response to light.

SEM micrographs of the 316L stainless steel in the filtered and unfiltered water after 117 days exposure are shown in Figures 3-23 and 3-24, respectively. The biofilm of the filtered-water surface was thinner and no algae were observed within the biofilm. The biofilm of the unfiltered-water surface for the stainless steel, however, was fairly thick and the algae dominated the specimen's surface. The predominating algae on the unfiltered-water surfaces belonged to the genus Amphora. Therefore, it was expected that the bacteria and the algae would have significant influences on the corrosion processes for the stainless steels in the unfiltered lake water.

After the biofouling materials were removed from the

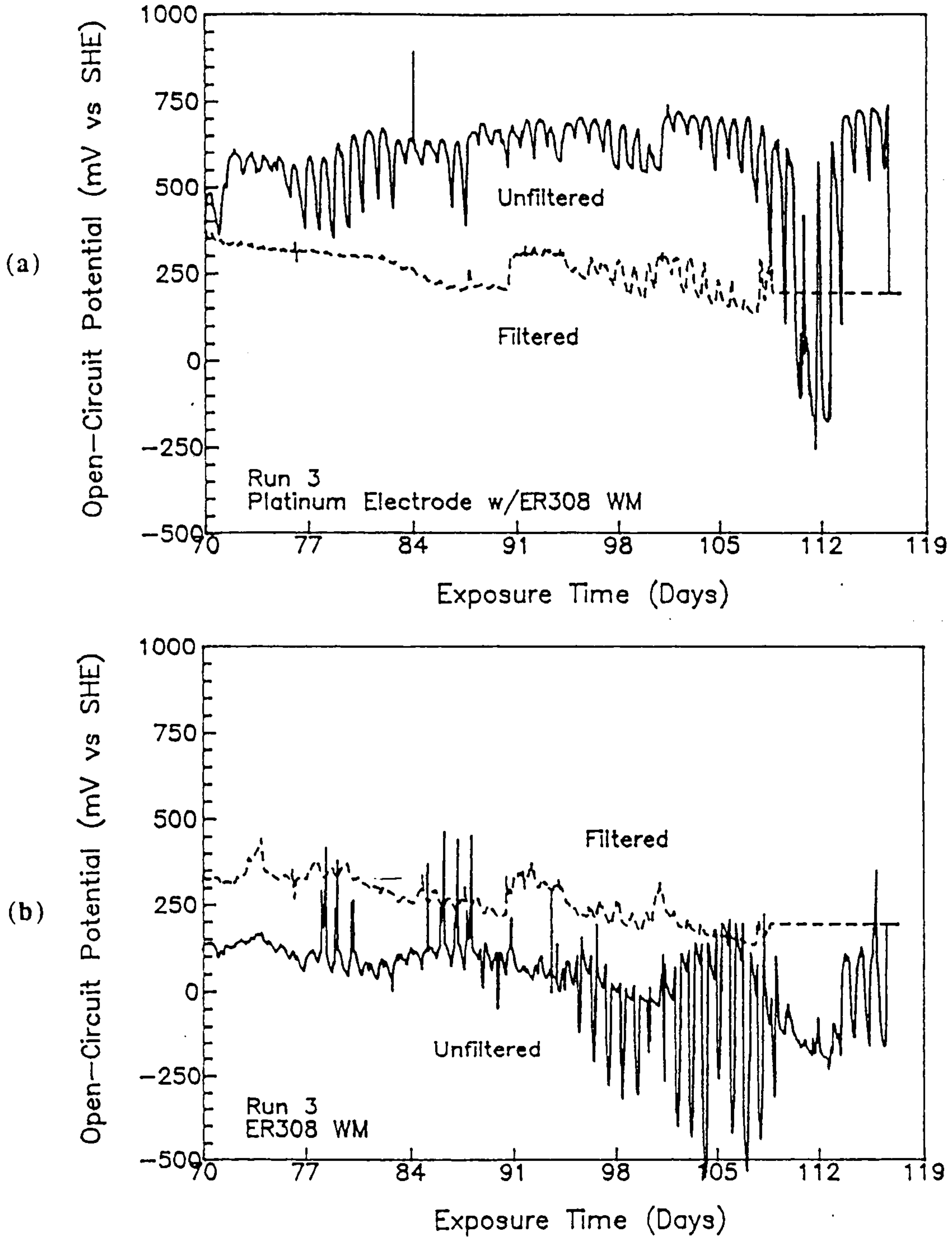


Figure 3-22. Platinum Potentials (a) and Corrosion Potentials (b) for 308 Weld Metal in Filtered and Unfiltered Lake Water During the Additional 47-Day Exposure After Run 3. Cells Were Not Shielded From Light.

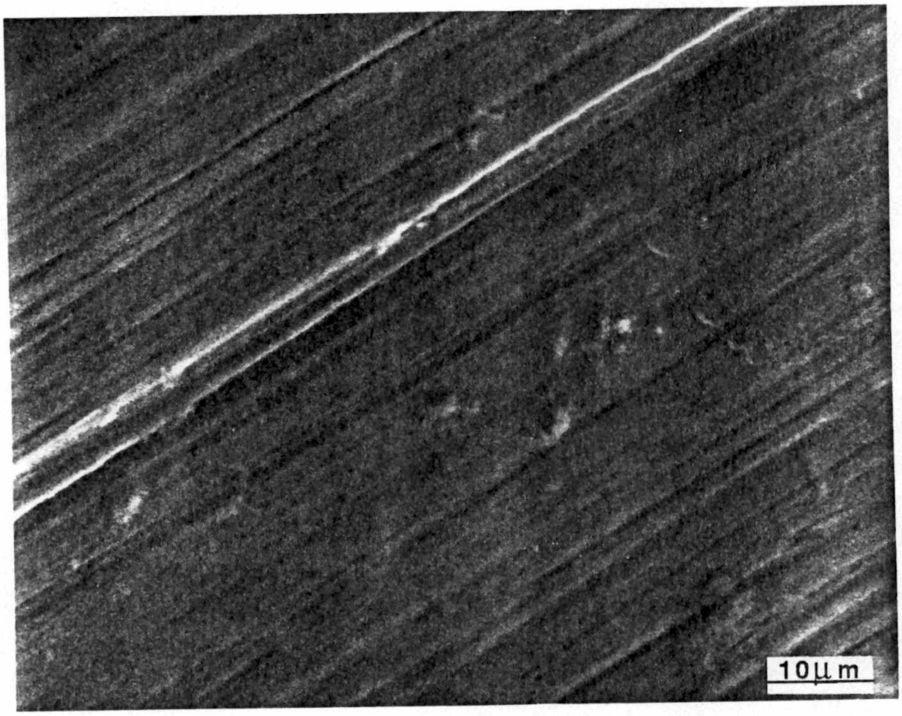


Figure 3-23. Scanning Electron Microscope Photograph Showing the Surface of 316L Stainless Steel After Exposure to Filtered Lake Water for 117 Days.

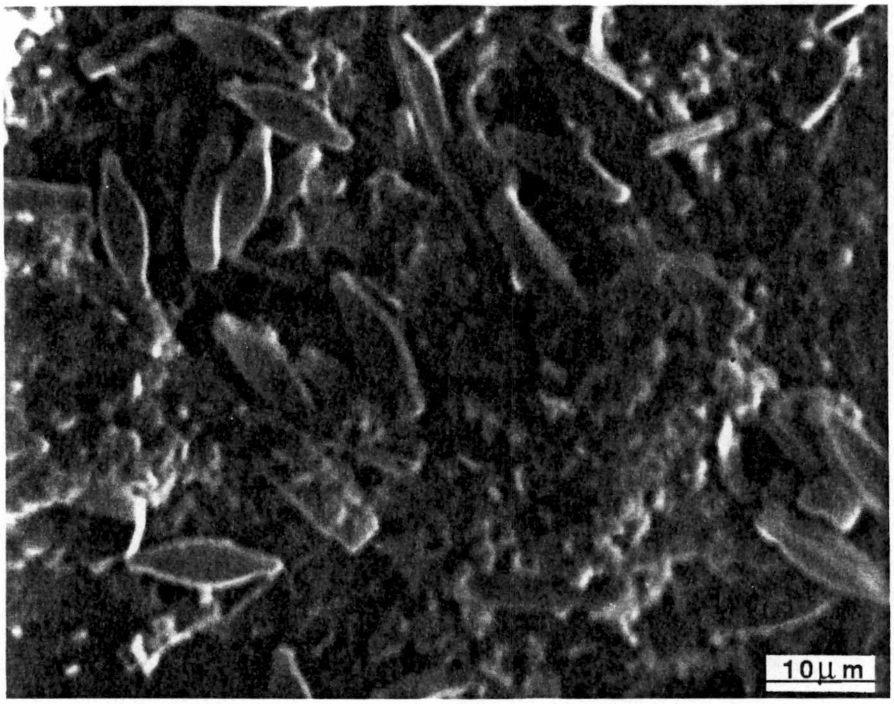


Figure 3-24. Scanning Electron Microscope Photograph Showing Algae on the Surface of 316L Stainless Steel After Exposure to Unfiltered Lake Water for 117 Days.

matched set of specimens attached to the epoxy mounts during Run 3 by ultrasonically cleaning in acetone, the specimens were examined by light microscopy. Essentially no differences in surface characteristics were observed between the filtered and unfiltered-water conditions for the C1018, 304L, 316L and 308 weld metal. No evidence of localized corrosion was found on any of the stainless steel specimen surfaces for either water condition.

Chapter 4. DISCUSSION

The experimental results in the unfiltered lake water exhibited several distinct phenomena, such as the higher platinum potentials and corrosion potentials, the novel cathodic polarization curves, the second relaxation process in the EIS data at the end of Run 1, and a great quantity of algae present on the surfaces of the specimens. All of these features were related to the tremendous differences in the filtered (0.2 µm) and unfiltered lake water from a microbiological point of view. The phenomena were especially reflected on the stainless steel specimens. Therefore, this discussion will start by describing the 316L stainless steel characteristics when exposed to the fresh lake water.

The following experiments were conducted in the laboratory with samples of fresh lake water. The 316L stainless steel specimens were exposed to the filtered and unfiltered solutions for 3 days in order to allow the specimens to stabilize electrochemically. It was expected that the 3-day exposures were not long enough to allow microbial influences to be developed in this part of the study. Filtration did not make difference in open-circuit potential. The platinum potentials (E_{Pt}) and corrosion potentials (E_{corr}) after 3-day exposures were about 500 and 300 mV(SHE) respectively. EIS data, and anodic and cathodic polarization data were collected at the ends of the 3 day exposure in unfiltered water, as shown in Figures 4-1 and 4-2. It is seen that the impedance of 316L exposed to the lake water was very high and the relaxation occurred at very low frequencies. The very-capacitive characteristics of the EIS data (Figure 4-1) indicated that capacitive current dominated the resulting current rather than faradaic current. Thus, the fresh lake water was not very aggressive. Figure 4-2 shows the anodic polarization curve of 316L stainless steel and the cathodic curve on 316L. The anodic curve exhibited a straight-line segment preceding the passive current density region. The line segment appeared not to be the normal region where anodic and cathodic current densities are generally comparable, because it existed over a range of more than 600 mV, so that it must have been a part of the anodic curve. This line segment will be used in a later discussion, which will discuss its intersection with the cathodic curve in the unfiltered water condition. These EIS and polarization curves presumably were not affected by microorganisms so that they might be used as a reference base for the later discussion.

As previously noted, the open-circuit potentials of the prepassivated platinum electrodes in the field studies were significantly higher in the unfiltered lake water as compared to the filtered lake water. It is reasonable to think that

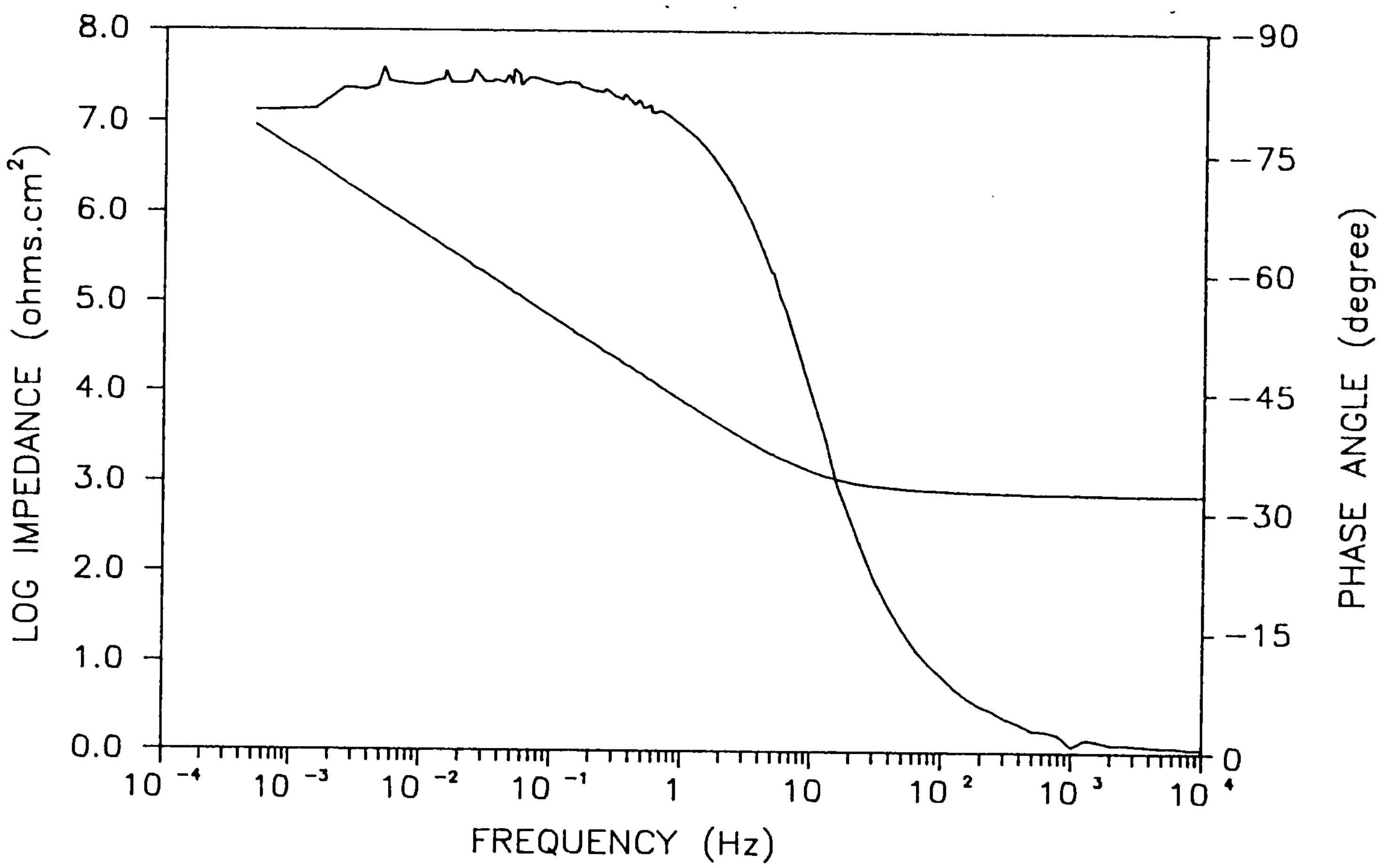


Figure 4-1. EIS Result of 316L Stainless Steel with Samples of Natural Lake Water After 3-day Exposure.

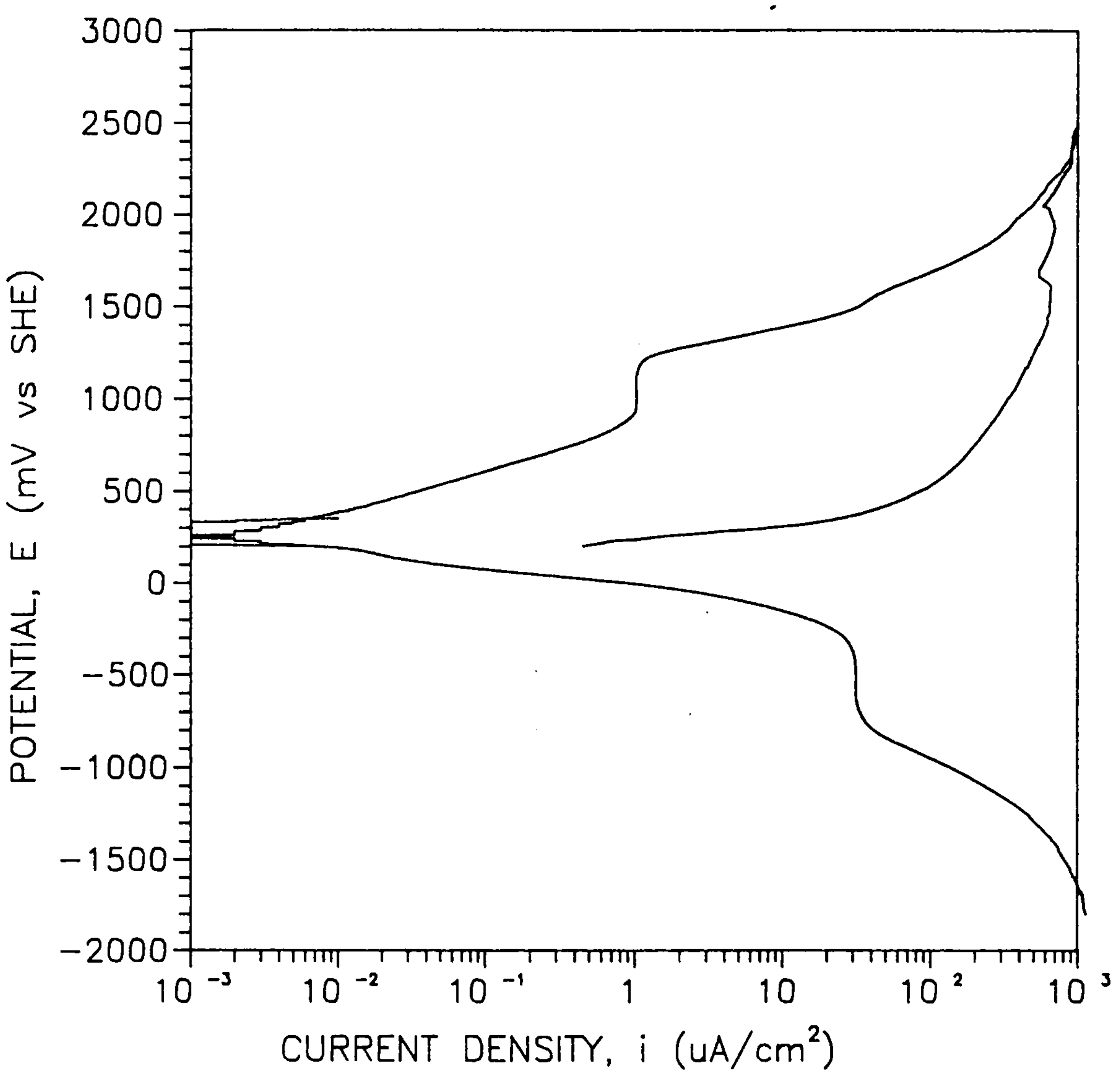


Figure 4-2. Anodic and Cathodic Polarization Curves of 316L Stainless Steel with Samples of Natural Lake Water After 3-day Exposure.

the large difference in platinum potential may be associated with the possible effects of pH, since microorganisms can produce organic acids during their metabolic processes. Relative to this consideration, the Nernst equation for the equilibrium potential of the oxygen reaction (normal aerated environment) is:

$$E'[\mathrm{mV(SHE)}] = 1{,}229 + 15 \log P_{O2} - 59 \mathrm{\ pH}$$

where P_{O2} is the partial pressure corresponding to the activity of dissolved oxygen. As the pH decreases, the equilibrium potential increases, with a change of 59 mV per pH unit. In this regard, it was envisioned that possibly the unfiltered-water biofilms became acidic, as well as highly oxygenated (the algae effect), relative to the filtered-water biofilms.

To experimentally evaluate the pH effect, first the open-circuit potential of the prepassivated platinum electrode (E_{Pt}) was measured in the laboratory as a function of pH with samples of natural lake water. The pH was adjusted through additions of H_2SO_4, with the lake water in both the aerated condition (air sparging) and the laboratory-deaerated condition (nitrogen sparging). The pH adjustments were started after 10 minute stabilizations in the aerated and deaerated lake water, and after a 3 day stabilization in the aerated lake water. The results are shown in Figure 4-3. As

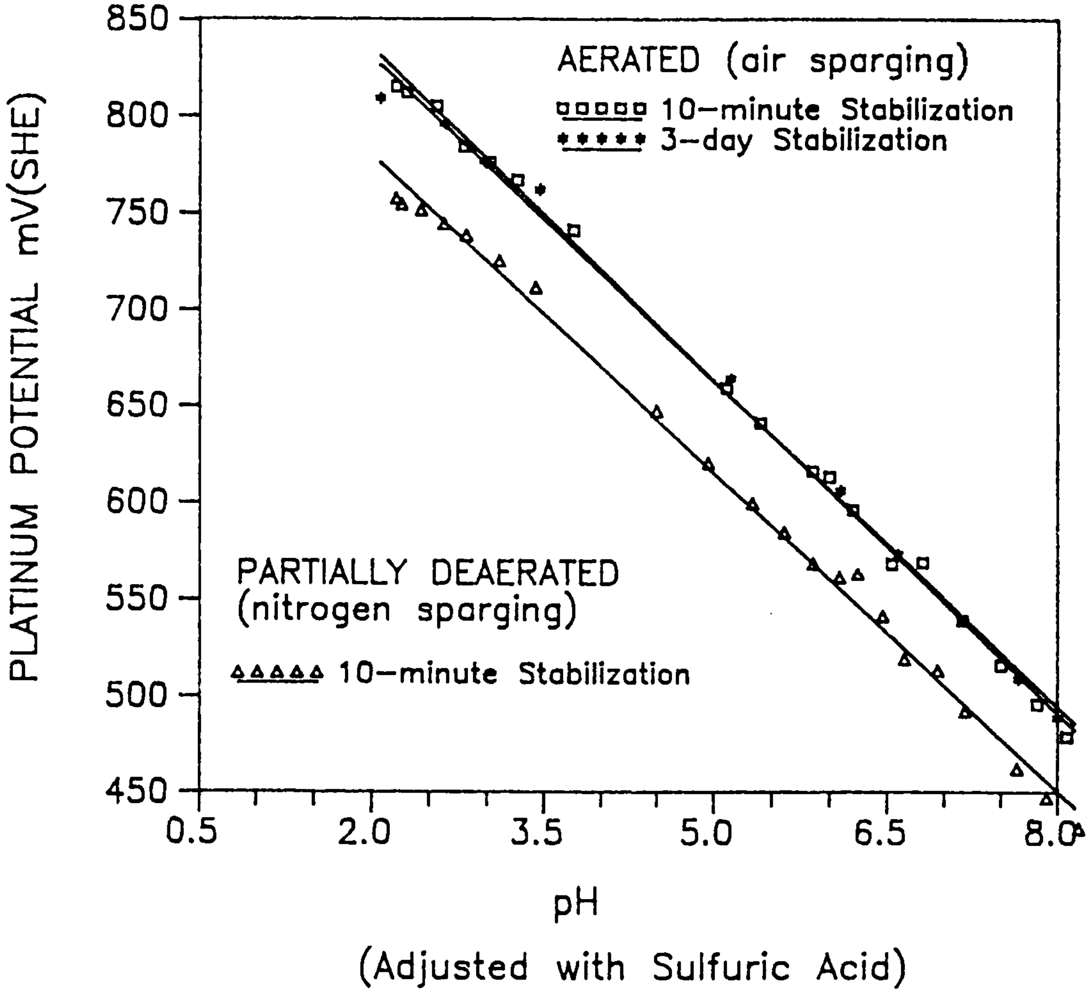


Figure 4-3. Platinum Potential (E_{Pt}) in Natural Lake Water with pH Adjusted by Additions of H_2SO_4.

expected, E_{Pt} increased with decreasing pH and was greater in the aerated condition than in the deaerated condition. Furthermore, the stabilization time in the aerated condition produced essentially no effect.

To further test the pH effect, the open-circuit corrosion potential (E_{corr}) of 316L stainless steel was measured in the laboratory as a function of pH with samples of natural lake water in the aerated condition (air sparging). The pH was adjusted through additions of H_2SO_4. The stainless steel with a 600-grit SiC surface finish was tested under three different conditions: (1) with a 10 minute stabilization period in the lake water before the pH adjustments were started, (2) with a 3 day stabilization period, and (3) with a prepassivation treatment in 50% NHO_3 at 50°C for 30 minutes, then a 3 day stabilization period. The results are shown in Figure 4-4. With the 10 minute stabilization period, E_{corr} initially increased with decreasing pH, but then at a pH of approximately 4.5 began to decrease, indicating the onset of passive-film instability. However, when the passive film was allowed to stabilize over 3 days, either in the nonprepassivated or prepassivated condition, E_{corr} continued to increase with decreasing pH down to a pH value of approximately 2.0. Therefore, these results indicated that in the low-chloride lake water of this study, the corrosion potential of 316L stainless steel can increase to quite high values at relatively low pH values.

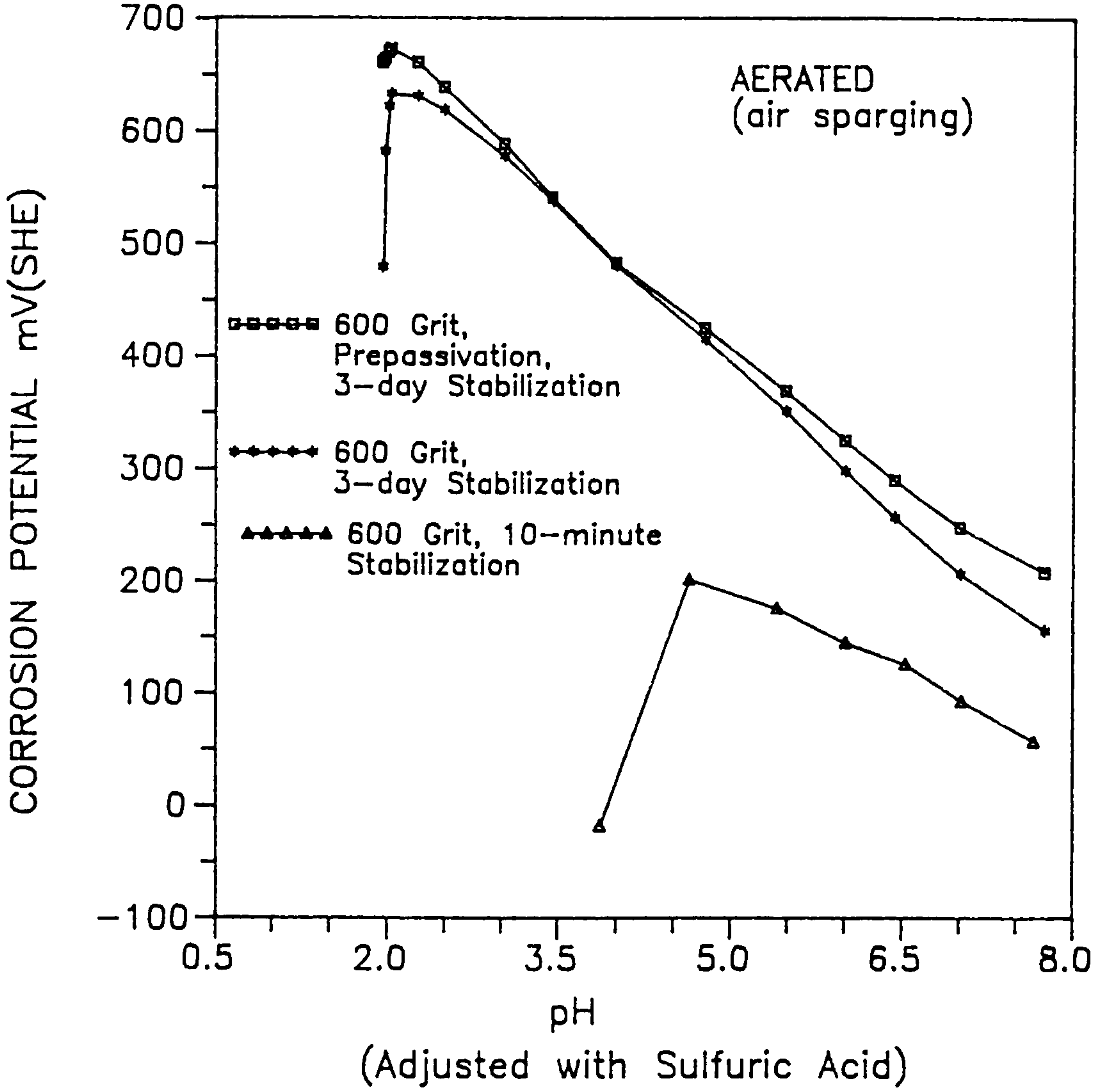


Figure 4-4. Corrosion Potential (E_{corr}) of 316L Stainless Steel in Natural Lake Water with pH Adjusted by Additions of H_2SO_4.

The results of the laboratory pH experiments exhibited two aspects which were not consistent with the field results of the present study. First, the corrosion potential of the stainless steel was not capable of reaching 700 mV(SHE) as the pH decreased, whereas the corrosion potentials of the stainless steels were usually above 700 mV(SHE) in the field results. Second, the large difference in potential between the platinum and stainless steel electrode did not diminish with pH adjustment in the laboratory experiments. The platinum potentials and the corrosion potentials for the stainless steels were almost the same in the field results. In addition, a very low pH value, less than 2, under the biofilms would be required to ennoble the corrosion potential of the stainless steel higher than 700 mV(SHE). Therefore, the pH-effect hypothesis involving significant acidification of the unfiltered-water biofilms appears unreasonable in terms of explaining the field results of the present study.

The microbiological analyses revealed that bacteria were found on the specimen surfaces in both the filtered and unfiltered lake water but that algae was found only in the unfiltered condition. The presence of algae was certainly related to the oxygen concentration under the biofilms because of the photosynthesis processes of algae. It is known that bacteria are able to catalyze the oxygen reaction, which consequently causes an increase of the exchange current density of the oxygen reaction[23,24,27]. The results of the field study involved some unique electrochemical features such as higher E_{Pt} and E_{corr} in the unfiltered lake water, abnormal cathodic behaviors in the unfiltered lake water, etc. These phenomena might be related to the presence of algae and possibly to a different consortium of bacteria compatible with the algae, which might lead to an increase in the exchange current density for the oxygen reaction in the unfiltered water condition.

A rough estimation of the corrosion current density can be made through the Stern-Geary equation with the present results of the EIS analyses. Tafel constants for the anodic reaction (βa=0.240 V/log i) and cathodic reaction (βc=0.075 V/log i) were obtained from the anodic and cathodic polarization curves of 316L stainless steel in Figure 4-2. The polarization resistance (R_p) of the 316L after a 3-day exposure (in Figure 4-1, assuming no microbial effects) and of the 304L after the 63 day exposure of Run 1 in unfiltered lake water (in Figure 3-14) were on the order of 10^7 and 10^5 (ohm.cm^2) magnitude, respectively. The R_p, βa and βc values were substituted into the Stern-Geary equation:

$$i_{corr} = \frac{\beta a \beta c}{2.303(\beta a + \beta c)} \frac{1}{R_p}$$

The corrosion current density (i_{corr}) with no microbial effects when exposed to the lake water was about 2.48×10^{-3}

($\mu A/cm^2$); whereas the corrosion current density in the unfiltered lake water after a 63 day exposure was 0.248 ($\mu A/cm^2$). If one reviews the anodic polarization curve in Figure 4-2, the i_{corr} value of 0.248 $\mu A/cm^2$ intersects the straight line segment of the anodic curve at a corrosion potential value of 720 mV(SHE); and the i_{corr} value of 2.48×10^{-3} $\mu A/cm^2$ intersects the anodic curve at a much lower corrosion potential value of 300 mV(SHE). In addition, if one considers that the E_{Pt} and E_{corr} values were about the same in the unfiltered condition, this observation suggests that the results of the field study might be associated with oxygen catalysis resulting in an increase of the exchange current density for the oxygen reaction.

To appreciate the oxygen catalysis mechanism, it will be considered in detail with reference to the schematic individual cathodic and anodic polarization curves in Figure 4-5. Anodic curves A1 and A2 represent the stainless steels and carbon steel, respectively, exposed to the natural lake water. The passive current density for the stainless steel is denoted as i_P. It is assumed that the anodic curves A1 and A2 did not change during the lake water exposures in either the filtered condition or unfiltered condition. The cathodic reactions involved oxygen reduction and then water reduction during further cathodic polarization. The pH is considered to be near neutral in all cases. Cathodic curves C1 and C2 are intended to represent oxygen reduction on stainless steel in

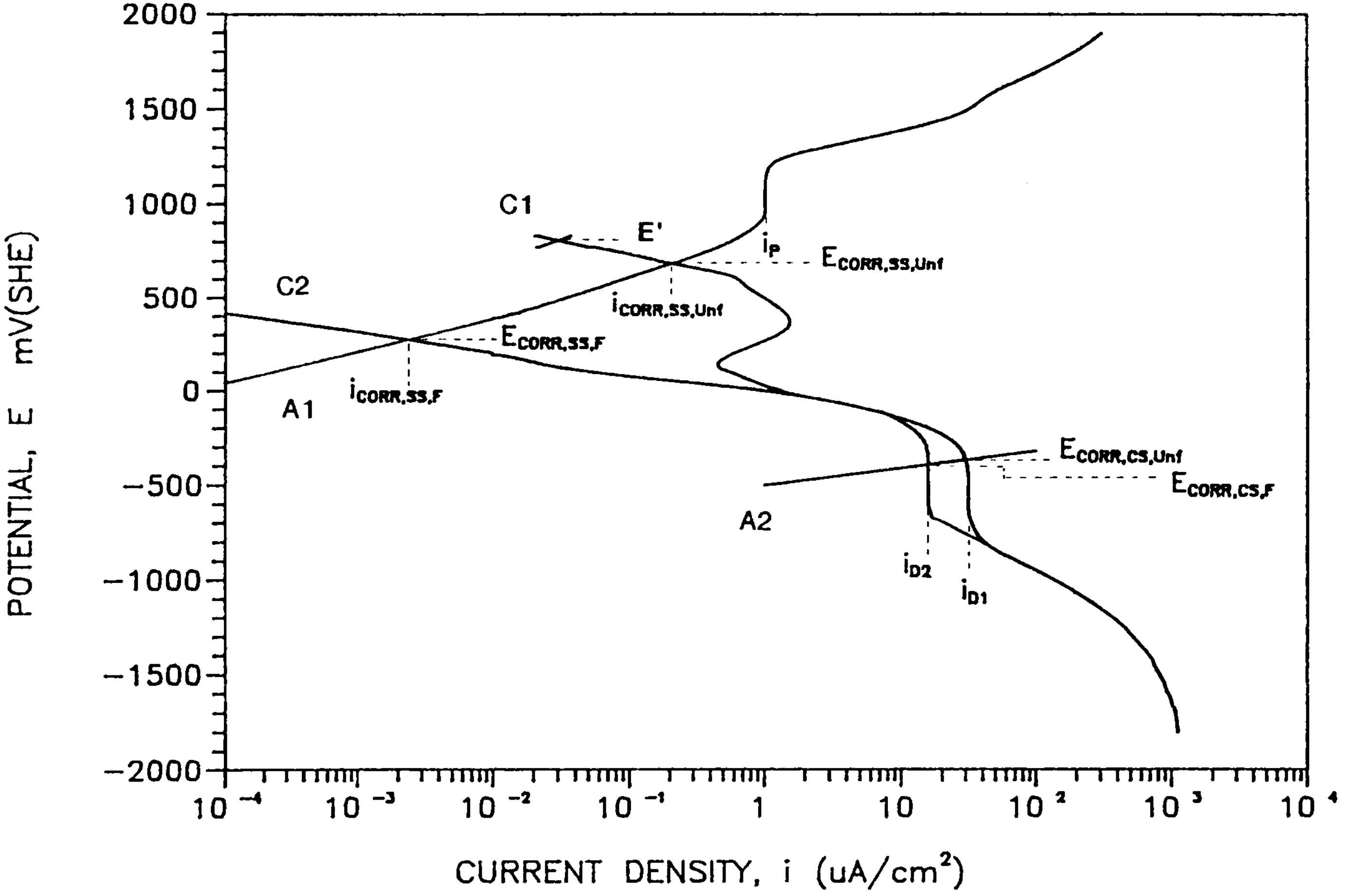


Figure 4-5. Schematic Individual Polarization Curves Based on the Oxygen-Catalysis Mechanism.

the unfiltered and filtered lake water, respectively. The oxygen-reduction diffusion limit is denoted as i_D.

Cathodic curve C2 is intended to reflect the filtered-lake-water field condition. The oxygen reduction on the stainless steels simply occurs and reaches the diffusion limit i_{D2} and then goes into water reduction during polarization. Curve C2 intersects with anodic curve A1 at a small corrosion current density ($i_{corr,SS,F}$) and produces the corrosion potential ($E_{corr,SS,F}$) which corresponds to the observed corrosion potential on stainless steel in the filtered lake water. Curve C2 intersects with anodic curve A2 at the diffusion current density (i_{D2}) and produces the corrosion potential ($E_{corr,CS,F}$) on carbon steel in the filtered water.

The more interesting phenomena occur in the unfiltered-water situation. Cathodic curve C1 is intended to represent the unfiltered-lake-water field condition. For water at pH = 7 and saturated with oxygen at atmospheric pressure (P_{O2} = 0.2 atm.), the Nernst equation yields an equilibrium potential of E'= 816 mV(SHE). It is considered that bacteria, probably in conjunction with compatible oxygen-producing algae, may accelerate the exchange current density for the oxygen reaction so that it translates the normal oxygen reduction curve to higher current density values. The oxygen equilibrium potential is denoted as E' corresponding the potential value of 816 mV(SHE). The cathodic curve C1 involving the oxygen-catalysis effect intersects the anodic curve A1 at a much higher corrosion potential ($E_{corr,SS,Unf}$), which is consistent with the observed corrosion potential of the stainless steel in the unfiltered lake water. Curve C1 is shown to reach an "apparent" diffusion limit, then produce a "cathodic peak," and finally merge with curve C2. The proposed behavior for curve C1 is rationalized as follows. Whatever specific mechanism is associated with the postulated catalysis of the oxygen-reduction reaction involves the biofilm per se, not the bulk water. The biofilm is of finite thickness and therefore limited in extent. During a polarization measurement, it is envisioned that the biofilm could undergo progressive degradation, and therefore the specific mechanism responsible for oxygen catalysis could also undergo degradation, such that the oxygen-reduction rate would ultimately be reduced to its normal value at a given potential. Based on this reasoning, in Figure 4-5, curve C1 is shown to go through a transition region (which could appear as an "apparent diffusion limit" or a "cathodic peak" depending on the nature of the transition) and ultimately merge with curve C2. Curve C1 reaches a higher diffusion current limit (i_{D1}) due to the oxygen-producing algae effect. It intersects curve A2 and produces the corrosion potential $E_{corr,CS,Unf}$ for carbon steel in the unfiltered water condition.

As previously described, the platinum potentials (E_{Pt}) and corrosion potentials (E_{corr}) for the stainless steel specimens in either the filtered water or unfiltered water had almost the same values. Theoretically, the E_{Pt} value should have represented the equilibrium potentials of the oxygen reaction in these cases. However, ideal equilibrium potential for the oxygen reaction have rarely been observed with platinum except for some specially purified solutions. In addition, the small exchange current density of the oxygen reaction on platinum makes the platinum electrode easily-polarizable. Under these conditions, the measured E_{Pt} values in the filtered lake water would undergo larger changes away from the equilibrium potential of the oxygen reaction as predicted by the Nernst equation, and exhibit lower potentials. On the other hand, the platinum electrodes in the unfiltered lake water possessed the higher exchange current density for the oxygen reaction because of the oxygen-catalysis due to microbiological effects. These platinum electrodes would be difficult to polarize due to the increase of the exchange current density. Therefore, the measured E_{Pt} values in the unfiltered water would undergo smaller changes, exhibit higher potentials, and approach the corrosion potentials for the stainless steels.

It is recalled that significant differences in EIS responses for the stainless steels were produced for the unfiltered-water and filtered-water conditions at the end of

Run 1, but not at the end of Run 2. Run 1 was longer in duration (63 vs. 28 days) and was conducted at a warmer time of year (August-October vs. January-February). Consequently, the conditions of Run 1 were such that thicker biomass deposits were created. Consistent with this hypothesis, the biomass deposits on the unfiltered-water specimens were visually observed to be greater than on the filtered-water specimens. This difference was especially obvious on the stainless-steel specimens since the corrosion products were much less. At the end of Run 1, for the stainless steels, the EIS data revealed two relaxation processes for the unfiltered-water specimens but only one relaxation process for the filtered-water specimens. Post-exposure microscopic examinations revealed no localized corrosion on any of these stainless steel specimens. It was determined that the stainless steel specimens stayed passive during the whole exposure. Surface events, including the faradaic processes, were slow and the rates of the charge transfer reaction were expected to be controlled by the resistance of the passive film. The Bode plane diagram (Figure 3-14) indicated that the lake water resistance was in the order of 1 (kOhm.cm^2); and the charge transfer resistance due to the passive film (Figure 4-1) was in excess of 10000 (kOhm.cm^2); while the resistance corresponding to the higher frequency relaxation in the unfiltered water (Figure 3-14) was just 10 (kOhm.cm^2), three orders of magnitude lower than the passive film resistance. Thus, the high frequency relaxation observed in the unfiltered water seems unlikely to be associated with the slow faradaic reaction processes associated with an intact passive film. Microscopic surface examination revealed no traces of active corrosion in either filtered or unfiltered systems. Since the high frequency relaxation coincided with a thick biofilm under which no corrosion was observed it was concluded that the biofilm acted as a semipermeable dielectric with both resistive and capacitive components that contributed to the interfacial impedance spectrum. Therefore, the differences in EIS responses were interpreted to only reflect the differences in biomass concentrations and distributions on the surfaces of the unfiltered-water and filtered-water stainless steel specimens.

SUMMARY AND CONCLUSIONS

The microbial corrosion field study in Fort Loudoun Lake, on the Tennessee River, of stainless steels and carbon steel resulted in some significant differences between the filtered water and unfiltered water conditions. It is believed that these significant differences were due to the microbial effects of the natural lake water. The results and relevant conclusions are summarized as follows:

> The platinum potentials (E_{Pt}) and corrosion potentials (E_{corr}) in the unfiltered lake water were significantly higher than in the filtered lake water. The ennoblement of the open-circuit potentials was thought to be due to an increase in the exchange current density for the oxygen reaction by the oxygen catalysis mechanism. The catalysis resulted from microbial effects, and was probably associated with the presence of algae.
>
> The oxygen-reduction cathodic polarization behavior for the stainless steel specimens in the unfiltered lake water exhibited a unique phenomenon in that a "diffusion limit" or "cathodic peak" was present during polarization. This characteristic of the reduction

process was related to the finite thickness of the biofilms which underwent degradation during large polarization such that the cathodic curves went through a transition region which appeared as either a "diffusion limit" or a "cathodic peak".

Microscopic examinations revealed that no localized corrosion occurred on the stainless steel specimens even though the corrosion potentials reached quite high values. Large quantities of algae were found on specimens in the unfiltered lake water after the longer exposures. All of the electrochemical, microbiological, and chemical results indicated that the Tennessee River water possessed a great number of algae, few sulfate reducing bacteria, and an extremely low chloride ion concentration (2-4 ppm).

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