"Characterization of Microbially-Influenced Corrosion (MIC) Under Cathodic Protection Conditions"

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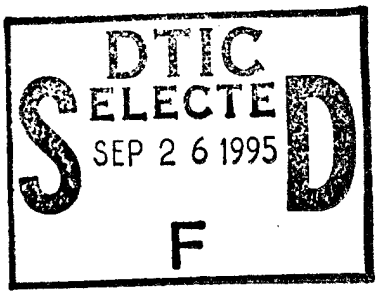

Progress Report

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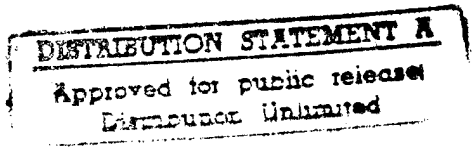

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INTRODUCTION

The corrosion of carbon steel due to the metabolic activity of bacteria, specifically sulfate-reducing bacteria (SRB), is known as Microbially-Influenced Corrosion (MIC). This type of corrosion usually results in a form of localized corrosion, e.g., crevice corrosion. The present research is intended to explore the effectiveness of cathodic protection in eliminating or limiting the destructive effects of MIC. Cathodic protection involves the application of a significantly negative voltage to prevent corrosion of the substrate. However, the problem lies in the fact that the value of this 'significantly negative voltage ' is unknown, and it is uncertain how effectively the current can be projected beneath tubercles that are formed by the bacterial colonies on the metal surface. By monitoring current and potential at a surface beneath SRB tubercles and/or developing realistic models for the electrical characteristics of surfaces covered with tubercles, it should be possible to determine what potentials can be imposed to such a surface, and whether these potentials are capable of providing cathodic protection.

EXPERIMENTAL

The experimental setup consists of the equipment and materials that are summarized in the Appendix. A three electrode configuration has been designed [FIG 1], of which the 2-inch diameter carbon steel samples function as the crevices, or the working electrodes (WE), and therefore undergo the corrosion. The 4-inch diameter carbon steel ring functions as the external steel surface and the reference electrode (RE) is a saturated calomel electrode (SCE) placed at the mouth of the crevice. For the simulated cathodic protection experiments, a platinum wire around the periphery of the cell functions as the counter electrode (CE) and a power supply will polarize the working electrode in the negative potential direction.. In order to monitor the pH and potential at the surface of the working electrode, Ag/AgCl combination pH/reference microelectrode probes are

supported by a Plexiglas former at a distance of 0.5 mm above the surface of the working electrode.

The entire setup is inside a 190mm x 100mm petri dish. The 6-inch diameter Plexiglas ring essentially serves as the base for the base (the 5-inch diameter piece of Plexiglas). This is done because the bottom of the petri dish is not perfectly flat, and using the 5-inch diameter piece of Plexiglas as the sole base would cause it to be unstable. Thus, the Plexiglas ring is epoxied to the petri dish bottom and the Plexiglas disc is epoxied on top of the ring. The carbon steel ring, serving as the external steel surface, has been epoxied on top of this base setup. The WE rests in the center of the carbon steel ring, separated by a thin strip of polyester epoxied to the inner ring so as to prevent electron flow between the two electrodes. The distance between the WE and the inner ring of the external steel surface is extremely small, providing a nearly perfect fit, so as to reduce the IR drop between the two electrodes. The WE and external surface are electrically connected to a zero-resistance ammeter via thin strands of plastic-coated copper wire. One wire has been soldered to the bottom center of the WE and the other to the edge of the carbon steel ring. Any exposed wire and solder connections have been coated with Microstop lacquer in order to prevent reactions between the wire and the electrolyte.

The 3-inch diameter piece of Plexiglas that forms the upper surface of the crevice is transparent and serves as the support to the Ag/AgCl combination pH/reference microelectrode probes. Teflon screws serve to raise the former, and hence the microelectrode probes, from the WE surface by extending a distance of 0.5 mm from the bottom of the Plexiglas former and resting on the carbon steel ring. The transparent nature of the Plexiglas former allows for direct observation of the changing crevice environment. The Plexiglas former has holes spaced at various distances along its diameter and one 3 mm diameter hole at its center. These holes have been placed in this manner so as to allow for potential and pH measurements at various distances into the crevice. The microelectrode probes are inserted into these holes, one at a time, and

potential and pH measurements will be recorded. Although this does not allow for simultaneous data acquisition, the time between measurements is relatively short, allowing for the collection of valid data. The central hole is for the pump tubing from which will flow, initially, sodium sulfides, and eventually, a solution inoculated with sulfate-reducing bacteria.

The bulk solution is neutral simulated seawater, essentially a NaCl solution. The tubing is attached to a peristaltic pump, which is regulated so that the fluid flowing from the pump flows at a rate of 3 ml/hr. The initial use of the sodium sulfides is intended to simulate the metabolic end-products of sulfate-reducing bacteria (SRB). These initial experiments are being run open to the atmosphere, although sulfate-reducing bacteria are obligatory anaerobes, meaning they thrive, reproduce, and grow in an atmosphere depleted of oxygen. Therefore, further experiments involving either the sodium sulfides or strains of SRB injected into the simulated seawater, will be run under anaerobic conditions. An anaerobic chamber, in which nitrogen or argon gas may be bubbled into the solution to deprive it of oxygen, or a glove box will be designed and utilized for such experiments.

The previously described experimental design is complete and intends to simulate the conditions at the interface of a 1080 carbon steel substrate and a tubercle containing sulfate-reducing bacteria, the principal bacteria implicated in anaerobic Microbially-Influenced Corrosion. The initial experiments are being run under open circuit, freely corroding conditions, where the current flow between the crevice and the steel substrate is being monitored. As noted above, we are initially using a sodium sulfide solution, but the experiments will eventually be done using a solution inoculated with sulfate-reducing bacteria, once they have been cultured. Subsequent experiments will also employ impressed current to simulate cathodic protection, using both galvanostatic and potentiostatic control.

MODEL DEVELOPMENT

Work has begun on developing a transmission line electrical analog for the crevice, which will be utilized to interpret electrochemical impedance data generated from the Frequency Response Analyzer. From FIG 2, it can be seen that the penetration length of the applied signal depends on the frequency of the perturbation. Using the equation $Z = (1/j\omega c)$, where Z is the impedance and ω is a function of frequency, it can be seen that by raising or lowering the frequency, the impedance across the metal/solution interface will be lowered or raised, respectively. The same argument holds for a more complicated electrical analog for the steel/solution interface. For our model, the resistance, R, is dependent on the concentration of ions in the electrolyte, and the impedance, Z, is dependent on the corrosion rate. When impedance is low and the resistance, R, is high, the current, I, drops off a short distance into the crevice. When impedance is high and the resistance, R is low, the current, I, can be injected further into the crevice. In this way, it is possible to interrogate the crevice to different depths, and hence to determine the effectiveness of cathodic protection at tubercle dimensions.

The transmission line model[1] for the test cell employs radial symmetry, which is the simplest geometrical description of a tubercle. The radius of the crevice will be denoted r_c. It is assumed that the potential of the metal phase is constant, while the potential in the solution phase is r-dependent, V(r). Applying both Ohm's and Kirchoff's laws to any circular ring above the disk-shaped crevice, of internal radius r and external radius r+dr, equations for the potential V(r) and the current i(r) are obtained as follows:

$$V-(V+dV) = R_S i(r), \text{ where } R_S = \rho dr/2\pi rh$$

$$\text{rearranging, } dV(r)/dr = -\rho i(r)/2\pi rh \qquad (1)$$

$$\text{Similarly, } 0-V = Z_e di/dr, \text{ where } Z_e = Z_1/2\pi r$$

$$\text{rearranging, } di(r)/dr = -2\pi r V(r)/Z_1 \qquad (2)$$

In the above equations, R_S is the resistance of an element dr above the crevice, ρ is the solution resistivity, Z_e is the impedance in units of ohm*cm, and Z_1 is the normal impedance of the metal/solution interphase in units of ohm*cm^2. By differentiating equation (1),

$$\begin{aligned} d^2V(r)/dr^2 &= -(\rho/2\pi h)[(rdi(r)-i(r))r^2] \\ &= -(\rho/2\pi h)[(-2\pi r^2V(r)/Z_1 + 2\pi rhdV(r)/\rho dr)/r^2] \\ &= -dV(r)/rdr + \rho V(r)/hZ_1 \end{aligned} \quad (3)$$

By differentiating equation (2),

$$\begin{aligned} d^2i(r)/dr^2 &= -(2\pi/Z_1)[rdV(r)/dr + V(r)] \\ &= -(2\pi/Z_1)[-r\rho i(r)/2\pi rh - Z_1 di(r)/2\pi rdr] \\ &= di(r)/rdr + \rho i(r)/Z_1 h \end{aligned} \quad (4)$$

By making the transformation $x = r\rho/Z_1h$, these equations can now be written as

$$f''(x) = -f'(x)/x + f(x) \quad (5)$$

where f is either V or i. This corresponds to the modified Bessel Equation with solutions given by

$$f(x) = AI_0(x) + BK_0(x) \quad (6)$$

where $I_0(x)$ and $K_0(x)$ are the modified Bessel functions of zero-order. The integration constants A and B are given by the boundary conditions for V and i:

$$I(x_c) = I_{applied} \qquad I(0) = 0 \quad (7)$$

$$(dV(x)/dx)_{x=0} = 0 \qquad (dV(x)/dx)_{x=x_c} = -I(x_c)\rho/2\pi x_c h \quad (8)$$

where x_c is the value of x corresponding to r_c. The total impedance of the metal surface can now be given by:

$$Z_T = (V(x_c)/I(x_c))_{x=x_c} \quad (9)$$

Through application of the boundary conditions,

$$Z_T = -[\rho/2\pi x_c h][(I_0(x_c)K_1(0)+I_1(0)K_0(x_c))/(I_1(x_c)K_1(0)-I_1(0)K_1(x_c)] \quad (10)$$

where I_1 and K_1 are the modified Bessel functions of first order.

By determining a value for Z_T, it is possible to compare experimental data to calculated data and compare, modifying the mathematical model accordingly. In this way, it will be possible to develop an optimization technique through our model.

MICROBIOLOGICAL ASPECTS

The modification of a New Brunswick Scientific Bioflow 30C chemostat is currently being carried out. The chemostat is a continuous flow reactor that will allow the growth conditions and residence time of cells to be controlled and varied as needed. Control of bacteria growth conditions is important for several reasons. First, it allows for precise control of the conditions of growth for the bacteria enhancing reproducibility and clarity of results. Additionally, the chemostat will allow the growth conditions to be modified to resemble either nutrient rich or poor conditions. The C:N:P ratio and substrate concentration in the medium can affect the production and quantity of bacterial exopolymers, a necessary component of biofilm formation.

It is anticipated that the physiological state of the bacteria is an important variable in the initiation of Microbially-Influenced Corrosion. The growth rate of the organism involved must be known and tested at several values. The chemostat will permit the culture of both sulfate-reducing and non sulfate-reducing bacteria for inoculation of the corrosion cell at known kinetic characteristics of the respective bacteria. We are interested in the capability of both hydrogenase-positive and negative, acetate utilizing and

non utilizing, and reduced sulfur species utilizing bacteria. Finally, the chemostat will be used to supply cells continuously to the experimental system.

The chemostat is being modified to have a continuous flow of O_2 free N_2:CO_2 (95%:5%), in an effort to maintain anaerobiosis. The chemostat was not designed with provisions for anaerobic operation so certain modifications and additions are being performed. The chemostat has and will be modified to have the ability to control several other variables. pH control will be necessary for those bacterial activities which alter the pH from an acceptable range. A pH controller will be employed for this purpose. The chemostat will also be maintained under constant temperature in a temperature controlled room.

A variety of bacterial strains, including non sulfate-reducing and sulfate-reducing bacteria (SRBs) are to be tested for their abilities to affect corrosion. These bacteria will be selected based on their physiological characteristics. The careful selection of bacterial strains will allow the determination of variables anticipated to affect proposed mechanisms of Microbially-Influenced Corrosion (MIC). Currently, the literature is being reviewed in order to select organisms that will allow the various mechanisms of MIC to be evaluated. The strains studied will, if possible, all be isolated from marine environments, some of which will be capable of forming exopolymers. Exopolymer formation is desirable in pure culture experiments, but, organisms deficient in this ability are still important. Such organisms could be part of a biofilm in which other organisms are responsible for producing the exopolymer matrix

Non sulfate-reducing bacteria may be important as either biofilm formers or as active participants in MIC. These non sulfate-reducing bacteria may affect corrosion by several mechanisms. A comparison of SRB and other biofilm bacteria may prove extremely useful in isolating some of the mechanisms of MIC. Bacteria are currently being evaluated for use in the experiments. Careful selection and control of growth conditions are necessary for determining the role of different mechanisms in MIC. A brief outline of

the various mechanisms of MIC, and characteristics of organisms useful for their study are being considered and is presented below. This list is not exhaustive, but represents some of the areas that need to be addressed. Preliminary experimentation will guide which areas are investigated most heavily.

Cathodic Depolarization

The consumption of hydrogen is considered an important mechanism of MIC[2]. A number of genera of bacteria possess hydrogenase enzymes for this transformation. Comparison of physiologically similar species, which are deficient in hydrogenase and possess hydrogenase, will be used to evaluate the contribution of this mechanism to the overall corrosion rate. Because of the variety of other mechanisms of MIC, several physiologically distinct types of organisms may have to be tested to understand the relative contribution of hydrogen utilization on the overall rate of corrosion. Biofilm cells should be more significant in corrosion compared to planktonic cell if hydrogenase activity is the rate controlling process due to the decreased diffusion distance foe hydrogen[3]. The effects of a number of environmental variables on the activity of hydrogen utilizers could be tested if hydrogen utilization proves to be a critical mechanism of MIC.

Two genera of bacteria containing hydrogenase positive members and commonly associated with MIC are *Clostridium* and *Desulfovibrio*[2]. A marine sulfate-reducer, *Desulfovibrio* has a high affinity for H_2, making it a good candidate for affecting cathodic depolarization. Many *Desulfovibrio* species can grow, sometimes very rapidly, on hydrogen[4]. V_{max} values for *Desulfovibrio vulgaris* have been recorded at greater than 5,000 $\mu mol\ g^{-1}\ h^{-1}$, and having a yield coefficient, Y, of 4.2 (g dry cell per mol H_2 dissimulated)[4].

Effects of Polymers on Metal Integrity

Exopolymers produced by bacteria "are usually acidic and contain functional groups that readily bind metal ions"[2]. Metals binding with polymers may affect the

stability of the metal surface[2]. The binding of metals and polymers varies by polymer type, metal type, and environmental conditions[2]. Exopolymer type structure is affected by growth conditions. By selecting different bacteria and manipulating their growth conditions, the type and amount of exopolymeric material can be altered. The effects of these changes on the corrosion rate will help to determine the effects of polymer production and type in the overall corrosion rate.

Acid Production

Bacterially produced acids are directly corrosive[2]. Among the secreted products of bacterial metabolism are a number of low molecular weight organic acids[5]. Sulfate-reducing bacteria are among the bacteria that produce and consume these acids. The production of acids represents a rather direct mechanism by which bacteria can increase the rate of corrosion in the immediate microenvironment. Biofilms can affect the contribution of acid production as a mechanism of MIC. Biofilms may serve to limit the diffusion rate of these acids away from the metal surface, increasing the pH gradient between certain areas. Biofilms may also contain bacteria that consume small organic acids, thereby offsetting the production of these same acids by other bacteria within the biofilm consortia. In order to experimentally examine the effects of biogenic acid production on reaction rate, work must begin with carefully chosen and well characterized pure cultures. By selecting bacteria that secrete organic acids under certain conditions, the significance of this mechanism of MIC may be evaluated. To further understand the role of these acids in corrosion, populations capable of utilizing these acids could be grown with acid producers. Such a system would be more representative of natural biofilms.

Creation of Microenvironments

Biofilms represent a barrier to the diffusion of corrosion products, and biologically produce molecules away from the metal surface. They also represent a barrier to transport

from the bulk solution to the organisms within the biofilm and on the metal surface. The physical barrier presented by the biofilm is analogous to other abiotic causes of heterogeneity at the metal surface[6]. The permeability of biofilms is affected by many variables. Through the use of experiments with bacteria that are biofilm formers, that do not conduct other reactions, and that are suspected to affect the rate of corrosion, the role of biofilms as barriers may be further understood.

The mechanisms listed above represent a few of the key factors biofilms and bacteria may demonstrate in increasing the rate of corrosion.

FUTURE WORK

As previously mentioned, the initial experiments involving the monitoring of current between the crevice and steel substrate are underway. The results of these experiments, as well as the results of the simulated cathodic protection experiments, will be provided in subsequent technical reports. Future work involves the culture and growth of SRBs and the incorporation of these bacteria into our test cell. We expect the attachment and growth of the SRB on the metal substrate surface, leading to the formation of a biofilm. Once this has been accomplished, we hope to determine the effect of growth rate on our impedance measurements.

Further work involves the fabrication of a Scanning Reference Electrode Probe in order to explore areas of high SRB-induced corrosion activity on a metal surface. This probe functions essentially to map current densities over the substrate exposed to MIC. An extensive product search has been conducted for the components of the probe and its construction will begin shortly. Through application of the probe to the impedance measurements, it is hoped that we can determine the chemical and electrochemical environments at the metal/tubercle interface, and consequently assess the effectiveness of cathodically protecting a surface exposed to MIC. A concern of which we will be aware is the possibility of injecting hydrogen into the substrate, during cathodic protection, to a

level which will embrittle the substrate. If this is the case, measures will be taken to analyze and study the damage due to hydrogen embrittlement.

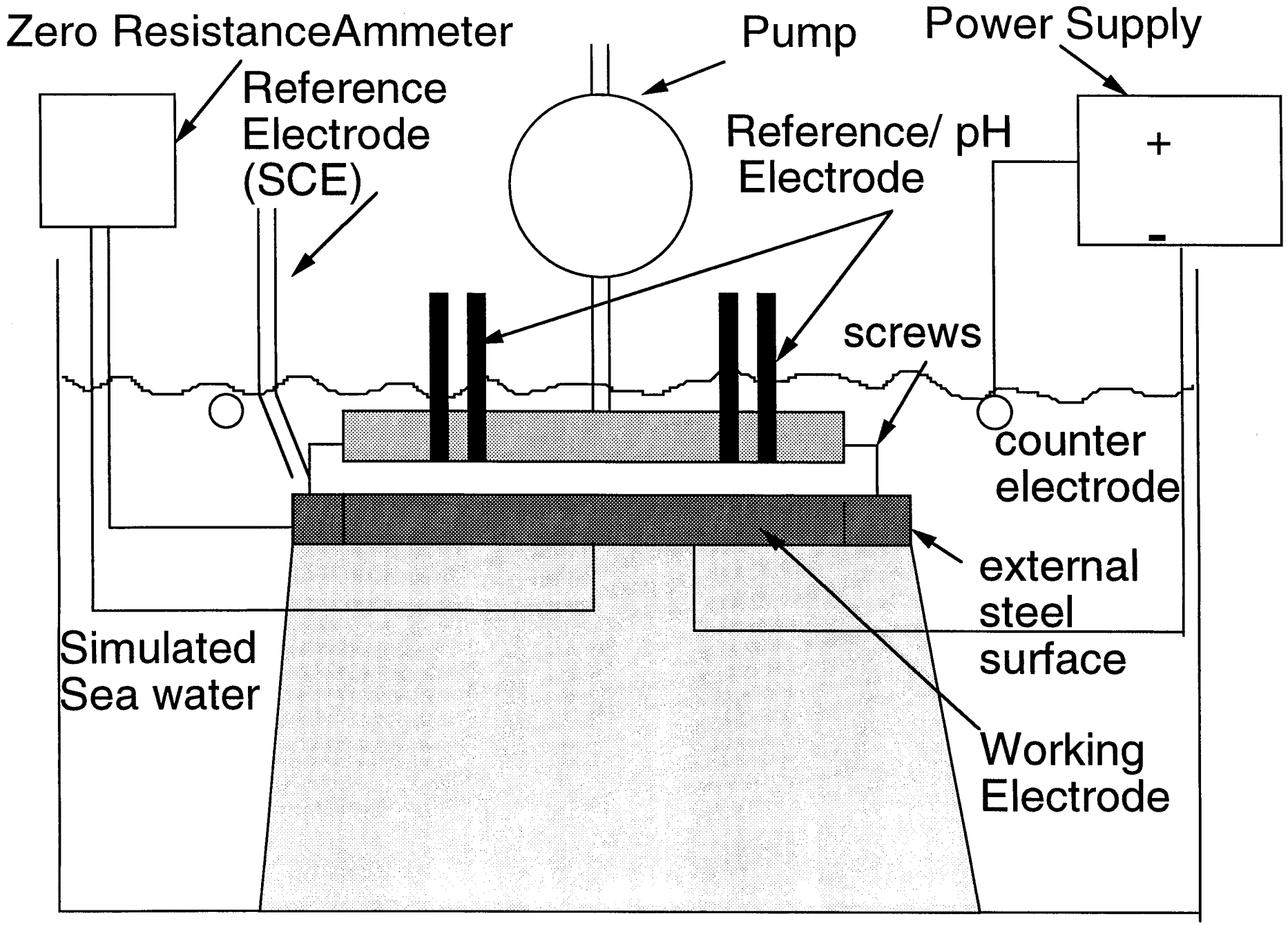

FIG 1: DIAGRAM OF EXPERIMENTAL CELL

$$Z = 1/jwc$$

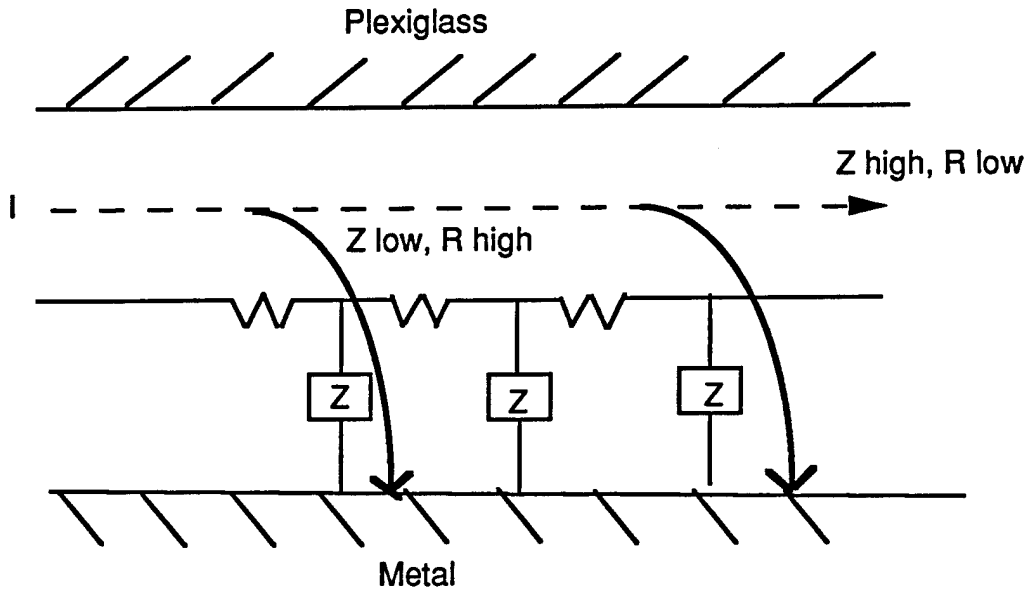

FIG 2: DETAILED TRANSMISSION LINE OF CREVICE

* interrrogate crevice to different depths
* Impedance (Z) is the relationship between applied potential and resulting current

APPENDIX

EQUIPMENT PURCHASES

* 1 Frequency Response Analyzer.....**$5950** (Equipment)

Voltech, Inc.
200 Butterfield Drive
Ashland, MA 01721
TEL: (508)881-7329
FAX: (508)879-8669

* 2 PC3 Potentiostat Board Sets w/ Cell & A/D Cables...**$3600 ea.** (Equipment)
* 1 CMS100B Electrochemical Corrosion Measurement System Software ...**$2160** (Equipment)
* 1 990-00064 PC3 to FRA Cable Kit w/ Adapters.....**$110** (Supplies & Mat'ls)

Gamry Instruments, Inc.
607-C1 Easton Rd.
Willow Grove, PA 19090
TEL: (215)830-9886
FAX:(215)830-9877

* 2 MI-410 Micro-Combination pH Probes.....**$185 ea.** (Supplies & Materials)

Microelectrodes, Inc.
298 Rockingham Road
Londonderry, NH 03053 USA
TEL: (603)668-0692
FAX: (603)668-7926

* 1 25411-162 190mm x 100mm Pyrex Crystallizing Dish...**$29.39** (S & M)

VWR Scientific
4717 Hinckley Indust. Pkwy.
Cleveland, OH 44109
TEL: (800)252-1234

* 1 13-875-200 2-Channel Peristaltic Pump.....**$660** (Supplies & Materials)
* 1 13-875-215D 8-Pack Silicone Rubber Pumping Tubing.....**$40.25** (S & M)
* 2 502021803 Tubing Assembly (washers & fittings).....**$17.38 ea.** (S & M)
* 1 13-641-241 Model 250A pH/mV/Celsius Meter w/ Starter Kit....**$735** (S&M)

Fisher Scientific
711 Forbes Avenue
Pittsburgh, PA 15219-4785
TEL: (412)562-8300
FAX: 1-800-926-1166

***6** 2-inch diameter, 0.125 inch thick 1080 carbon steel samples
***1** 4-inch diameter, 0.125 inch thick 1080 carbon steel ring w/ 2.009-inch diameter hole
***1** 3-inch diameter, 1-inch thick Plexiglas former with an array of 6 mm diameter holes for microelectrodes and one (1) 3 mm diameter hole for pump tubing
***1** 5-inch diameter, 0.75 inch thick piece of Plexiglas
***1** 6-inch diameter, 0.375 inch thick Plexiglas ring w/ 3.5-inch diameter hole

TOTAL: $132.98 (S&M)

Penn State University, Metal Machine Shop
Steidle Building Basement
State College, PA 16802

* Misc. Supplies and Materials.....**approx. $20** (S&M)

O.W. Houts & Son Inc.
West College Avenue & Buckout
State College, PA 16802

***1** 500 g Crystalline Sodium Sulfide.....**$19.20** (S&M)

Alfa/Johnson Matthey
P.O. Box 8247
Ward Hill, MA 01835-0747
TEL:(800) 343-0660
FAX:(800) 322-4757

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