

Corrosion Testing

in Natural Waters

Second Volume

Robert M. Kain and Walter T. Young
editors



STP1300



STP 1300

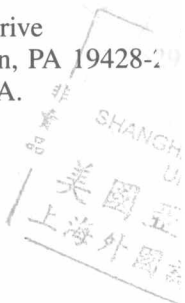
Corrosion Testing in Natural Waters: Second Volume

Robert M. Kain and Walter T. Young, Editors

ASTM Publication Code Number (PCN):
04-013000-27



ASTM
100 Barr Harbor Drive
West Conshohocken, PA 19428-29
Printed in the U.S.A.



Library of Congress

ISBN: 0-8031-2025-7

ASTM Publication Code Number (PCN): 04-013000-27

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To make technical information available as quickly as possible, the peer-reviewed papers in this publication were prepared "camera-ready" as submitted by the authors.

The quality of the papers in this publication reflects not only the obvious efforts of the authors and the technical editor(s), but also the work of these peer reviewers. The ASTM Committee on Publications acknowledges with appreciation their dedication and contribution of time and effort on behalf of ASTM.

Foreword

This publication, *Corrosion Testing in Natural Waters: Second Volume*, contains papers presented at the Second Symposium on Corrosion Testing in Natural Waters held 7 November 1995 in Norfolk, VA. This symposium was held in conjunction with the standards development meetings of Committee G1 on Corrosion of Metals, the symposium sponsor. Robert M. Kain, LaQue Center for Corrosion Technology, Inc., and Walter T. Young, Corpro Companies, Inc., served as co-chairmen of the symposium and editors of the resulting publication.

Overview

This is the second STP of the same title. The first volume, STP 1086, was published in 1990 and contained papers on seawater corrosivity, crevice corrosion resistance of stainless steels, corrosion fatigue testing, and corrosion in potable water. Since then, final results have become available from the worldwide study on corrosion behavior of metals in seawater, and additional studies have been performed that should be brought to the attention of the corrosion engineering community. The eight papers presented in this volume were presented at the ASTM symposium in Norfolk, Virginia on 7 November 1995. A brief description of each paper follows.

Monitoring Biofilm Formation in Power Plant Environments

Power plants experience severe general corrosion, pitting, underdeposit corrosion, and microbiologically influenced corrosion in cooling water systems. Corrosion results in significant reductions in plant operating efficiency and high costs of operation and maintenance. Microbiological corrosion (MIC) is a particularly difficult problem since alloys that should be corrosion resistant in the general environment often fail in a short period of time when microbiological mechanisms are also active.

This paper discusses a test procedure that can be used to monitor biological activity. The procedure is based on an electrochemical probe that can be placed on-line to provide early warning of biological activity so that early action can be taken.

Modeling of Marine Corrosion of Steel Specimens

A mathematical model would prove to be quite useful in predicting the corrosion performance of steel and other metals in seawater where detailed exposure data are not available. This paper considers the variables of temperature, marine growth, wave action, pollutants, dissolved oxygen, and salinity on the long-term general corrosion rate of steel. A conceptual mathematical model dealing with immersion corrosion, tidal corrosion, and atmospheric corrosion is presented in the first part of the paper. The model is applied to data in the literature for longer-term corrosion. The model is found to be incompatible with the standard non-linear model for atmospheric corrosion. The paper discusses the uncertainties of dealing with literature data.

Seawater Corrosivity Around the World: Results from Five Years of Testing

In 1980, ASTM Task Group G1.09.02.03 established a test program aimed at assessing seawater corrosivity worldwide. Fourteen locations in eight countries, where capabilities were available for testing in general compliance with ASTM Standard G52, "Recommended Practice of Conducting Surface Seawater Exposure Tests on Metals and Alloys," were selected. The task group also selected three baseline test materials to assess corrosivities at the designated test sites. The materials were aluminum alloys A95036, copper-nickel alloy C71500, and carbon steel alloy K01501.

The present report summarizes the five-year corrosivity results. It was concluded that experiments that rank or characterize test sites can be significantly affected by many variables. The paper reviews the variables that influenced the test results.

Twenty-Year Field Study of the Performance of Coatings in Seawater

The primary means of corrosion protection for steel immersed in seawater is the use of barrier coatings with or without cathodic protection. This paper presents the results of a study by the U.S. Army Construction Engineering Research Laboratories where steel H-piles were coated with various coatings and exposed to natural seawater in Cape Cod and LaCosta Island, Florida. The pilings were coated with epoxy, glass flake polyester, polyurethane, flame-sprayed zinc, and flame-sprayed aluminum coatings. Cathodic protection using sacrificial anodes was used on some of the uncoated and coated pilings. Evaluation was performed using electrochemical polarization and polarization decay techniques. Some of the piles were removed for measurement of corrosion.

Crevice Corrosion Testing of Austenitic, Superaustenitic, Superferritic, and Superduplex Stainless Steel Type Alloys in Seawater

In industry, many problems from corrosion occurring in crevices have been experienced and reported. These include the refining industry, offshore drilling platforms, nuclear power plants, chemical plants, and public utilities. The services are highly variable. Corrosion mechanisms and the results experienced are influenced by severe environments that can not always be avoided.

This paper provides the results of a series of crevice corrosion tests on a number of ferritic, austenitic, super austenitic, and duplex alloys in seawater. The test results are considered useful not in comparing materials, but also in selecting materials for design. The ultimate goal is to use materials that are superior to those currently in use. This will result in fewer outages, reduce repairs, and significantly lower costs.

Statistical Analysis of Pitting Corrosion in Condenser Tubes

Condenser tube failure by means of wall penetration allows cooling water to contaminate the working fluid (steam). Contamination, especially from brackish or seawater, lowers steam quality, and thus lowers overall plant efficiency. Because of the importance of minimizing leaks, power plant engineers are primarily concerned with the maximum localized corrosion in a unit rather than average corrosion values or rates. Extreme value statistical analysis is a useful tool for evaluating the chances of maximum corrosion rates based on relatively small data sizes. Extreme value statistical techniques allow the prediction of the most probable deepest pit in a given surface area based on data acquired from a smaller surface area. This paper describes the use of extreme value statistical methods as applied to pit depth analysis and presents examples of how it can be used.

Corrosion Coupon Testing in Natural Waters: A Case History Dealing with Reverse Osmosis Desalination of Seawater

Corrosion testing is generally intended to assess either the corrosion resistance of a material in a given environment and/or characterizing environmental corrosivity. This paper describes the tests conducted to evaluate the corrosivity of the environment and possible materials for use in a reverse osmosis plant to convert natural seawater to fresh water. The

tests were conducted according to ASTM Standard G4, "Standard Guide for Conducting Corrosion Coupon Tests in Field Applications," and ASTM Standard G78, "Standard Guide for Crevice Corrosion Testing of Iron-Base and Nickel-Base Stainless Alloys in Seawater and Other Chloride-Containing Waters." The paper focuses heavily on the experimental design of the program as it related to ASTM Standards G4 and G78.

Comparison of Current Reversal Chronopotentiometry (CRC) and Small Amplitude Cyclic Voltammetry (SACV) Method to Determine the Long-Term Corrosion Tendency of Copper-Nickel Alloys in Polluted and Unpolluted Seawater Under Jet-Impingement Conditions

This paper reports on tests using the technique of cyclic current reversal chronopotentiometry to measure the corrosion tendency of two copper-nickel alloys in sulfide polluted seawater. The results are compared to the polarization resistance method.

The symposium committee gratefully acknowledges the efforts of the authors and ASTM personnel that have made this publication possible.

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Robert M. Kain

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George J. Licina¹, George Nekoksa²

MONITORING BIOFILM FORMATION IN POWER PLANT ENVIRONMENTS

REFERENCE: Licina, G. J., Nekoksa, G., "Monitoring Biofilm Formation in Power Plant Environments," *Corrosion Testing in Natural Waters: Second Volume, ASTM STP 1300*, Robert M. Kain, Walter T. Young, Eds., American Society for Testing and Materials, 1997.

ABSTRACT: Power plants have experienced severe general corrosion, pitting, under deposit corrosion, and microbiologically influenced corrosion (MIC) in cooling water systems, resulting in decreased plant availability and significantly increased operations and maintenance costs. MIC has been a particularly difficult problem since corrosion resistant alloys in relatively benign environments have failed as a result of microbiological influences in short times. Copper base alloys, carbon steels and stainless steels have all been susceptible. In a number of instances, replacement of piping and heat exchangers has been required to alleviate corrosion-related problems.

Monitoring is a key element to improved corrosion control in cooling water systems. On-line methods provide evaluations of corrosion rates in real time and are sensitive to localized corrosion. Electrochemical methods of corrosion measurement are readily automated, both for acquisition of corrosion data and for process control. An electrochemical probe for on-line monitoring of biofilm activity has been shown to provide an early warning of biofilm formation and incipient MIC in fresh and saline waters.

KEYWORDS: monitoring, biofilm activity, microbiologically influenced corrosion, electrochemical methods

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BACKGROUND

Many industries, including nuclear and fossil-fueled power plants, oil and gas production, chemical processing, pulp and paper, transportation, and water distribution networks have experienced damage due to corrosion in natural waters. This damage results in increased downtime of equipment, increased operating costs, and can jeopardize the safe operation of plant equipment. These industries have recognized the importance of corrosion control on continued reliability and economic operation of their plants. In most circumstances, general corrosion has been adequately controlled or addressed during design. Localized corrosion due to pitting, crevice corrosion, underdeposit corrosion, or microbiologically influenced corrosion (MIC) has, of necessity, received greater attention during the 1980s and 1990s. Methods for control of localized-attack require a greater understanding of the types of local environments that can exist in power plant equipment. The power generation industry has devoted increasing attention to corrosion monitoring in cooling water environments. These environments range from "soft", fairly low conductivity fresh waters to scale-forming freshwater to brackish waters and seawater. Monitoring tools for a power plant must address the corrosion concerns associated with that plant's cooling water, including both the seasonal fluctuations that may be expected and the creation of local environments due to corrosion products, deposits, and microbiological growth.

On-line monitors must be:

- Simple to use. Installation and routine maintenance of the monitor(s) should not impact power plant operations.
- Simple to interpret. Results should be readily interpreted by operations personnel. Corrosion specialists should not need to be consulted routinely. Outputs should be amenable to automation (alarms, etc.).
- Rugged. The probes and equipment must be sufficiently rugged that frequent, unscheduled maintenance is avoided. Sensitivity to external noise (e.g., welding, the plant's turbine-generators) is unacceptable.
- Sensitive. Detectable electrochemical effects should appear on the probe before thick biofilms are established on plant components.
- Accurate. A monitoring device must provide reliable detection of biofilm activity with a minimum of false calls.
- Economical. Cost for installation, maintenance, and operation must be cost effective, as reflected by potential savings realized as a result of the improved monitoring capabilities.

The influence of MIC in power plant cooling waters has been a major source of problems as noted in a number of publications [1-4]. In many cases, corrosion resistant alloys have experienced rapid, through-wall penetration when exposed to potable waters from rivers, lakes, estuaries, and ponds; environments that would normally be considered benign. The influence of biofilms in establishing corrosion initiation sites and in providing conditions for the propagation of pits has been clearly demonstrated. Power plants have been required to modify, repair, or replace such lines in their entirety. A number of large, nuclear units have replaced their service water systems, at costs of the order of \$30,000,000 per plant.

Experience has shown that monitoring of corrosion and biofilm formation is best achieved in the plant's cooling water environment. The following discussion will describe the approach used for monitoring biofilm activity in several power plant and test installations using fresh and saline surface waters.

APPROACH

The BI \circ GEORGE³ probe (Figure 1) consists of two identical electrodes (where each electrode is made up of a stack of identical stainless steel discs), mounted on a threaded stainless steel body, and a simple control and data acquisition system. The electrode stacks are electrically isolated from each other and from the probe body. An epoxy resin fills the spaces between the electrode discs to provide a probe that is a smooth, right, circular cylinder. One set of discs is polarized relative to the other for a short time (one hour) each day. Polarity always remains the same. During the remaining 23 hours of the day, the electrodes are connected through a precision resistor. Currents (measured as the potential drop across the resistor) and potentials are monitored continuously.

The basis for the probe as an MIC monitor is that microbiologically influenced corrosion will not occur without a biofilm. If biofilm is controlled, MIC will be controlled. Interaction between the biofilm and metallic surfaces, which may also be affected by temperature and flow conditions must be understood and factored into plant control schemes.

The low level of polarization also simulates conditions conducive to microbial colonization such as those resulting from local anodic sites like inclusions or weldments.

³ BI \circ GEORGE is a trademark of Structural Integrity Associates, Inc., San Jose, California

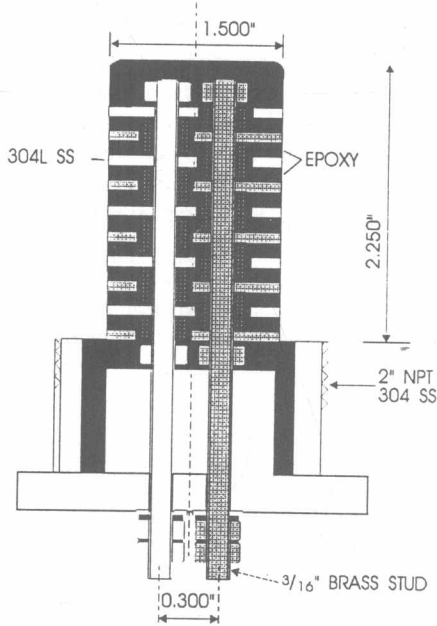


FIG. 1 -- Electrochemical Biofilm Probe

The "gentle" cathodic polarization can also encourage microbial colonization, similar to that observed on cathodically protected structures in biologically active environments as reported by Nekoksa and by Guezennec [5, 6] (Figure 2). Short polarization times also avoid shifting of the natural potential of the electrodes.

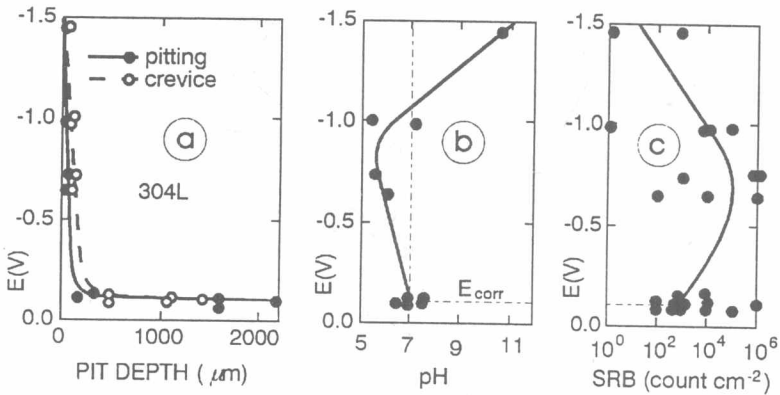


FIG. 2 -- Cathodic Protection Potential on Type 304L Stainless Steel versus (a) corrosion, (b) pH on the sample and (c) SRB count. E = potential (SCE); PD = pit depth (max.); CP = corrosion potential (From Reference 13)

The probe provides two methods for reliably monitoring biofilm activity on line. The **applied current**, the current required to achieve the pre-set potential applied between the two electrodes, remains fairly constant until a depolarizing influence, such as biofilm formation, occurs. Deposits such as biofilms produce a distinct increase in the applied current, consistent with a decrease in the polarization resistance. Generally, the applied current remains at an elevated level until the biofilm is removed or rendered inactive. For example, biofilms that catalyze the reduction of oxygen in aerated environments or which produce alternative cathodic reactions (e.g., the result of sulfate reducing bacteria or acid producing bacteria) are readily detectable, simply by observing changes in the current during the polarization cycle.

The **generated current**, the current that flows between the two nominally identical electrodes when no external potential is applied, provides an additional, usually more sensitive, indicator of biofilm activity. The generated current is determined by monitoring the potential drop across a precision resistor that connects the probe's positive and negative electrodes. Prior to formation of a biofilm, the generated current would be expected to be essentially zero; a reasonable assumption for two nominally identical electrodes exposed to the same environment. However, as a biofilm forms and the local environments on the discs of different polarity are changed, some current flow would be expected between the electrodes, even when no external potential is applied.

The probe was originally designed to monitor biofilm formation in fresh water cooled power plants, particularly in untreated waters. The early success in those environments prompted investigations into biofilm monitoring in saline waters. The primary concern with such waters was the potential for pitting or crevice corrosion of the stainless steel electrodes. Design modifications included the use of electrode materials that are commonly used in saline water service, such as commercially pure titanium and copper alloys (e.g., aluminum brass, 90-10 copper-nickel). Modified polarization schedules were also investigated to achieve the required levels of sensitivity and probe life.

The sensors described in this paper were installed in three different nuclear plants (Plants #1 thru 3), a large (>2000 MWe) fossil-fired station (Plant #4), and in a U.S. Navy test flume exposed to seawater from the Atlantic Ocean. Two of the three nuclear units are cooled by, "soft", scale-dissolving waters from a river or reservoir while the other nuclear facility uses a spray pond containing a scale-forming water. Exposure locations included a high pressure fire protection system line that served as the make-up source for the service water system and a treated essential equipment cooling water system line at Plant #1, a sidestream taken from the once-through service water system of another nuclear plant (Plant #2), an intermittent flow test stand exposed to the plant's emergency service water system spray pond (Plant #3), brackish water from the discharge canal at Plant #4, and the test flume. In addition to the site-to site variations, all of these installations also experience seasonal variability in water chemistry, influenced by seasonal differences in temperature and precipitation from year to year. The nature of the dissolved

and suspended solids and the microbiological character of the plants' cooling waters vary dramatically.

All of these plants have experienced general and localized corrosion of carbon steel piping, pitting of stainless steel components, or localized attack of heat exchanger tubes, including aluminum brass, admiralty, and copper-nickel alloys, due to localized corrosion. Many of the heat exchanger tube failures have been attributed to inlet end erosion, pitting, crevice corrosion, and MIC. The relative importance of MIC to the overall failure picture was not clear, however, all of the facilities were known to be in biologically active environments that had produced significant fouling of heat exchangers and offered the potential for MIC of structural materials. The probes were installed to evaluate their applicability as biofilm activity monitors for the particular water chemistry and operational philosophy and to assess the suitability of the probes for in-plant use.

In all of the exposures, the probes were exposed to the variations in flow rate, temperature, water chemistry, etc. inherent in the system. No attempts were made to control those parameters. Data collection was performed automatically using a data logger or chart recorder. In some installations, the probe was also interfaced to a personal computer. In all cases, analysis of the data was performed off-line.

Probes with stainless steel electrodes have been shown to be effective in monitoring biofilm activity in fresh water cooling systems [7-11]. Both stainless steel and titanium have been demonstrated to be compatible as biofilm monitoring electrodes in seawater [12]. For saline water exposures, probes with three different types of electrode materials were used. The standard probe with stainless steel electrodes (Type 304 and 304L in fresh waters; Type 316 in seawater) was polarized to 100 mV or 200 mV in all the fresh water installations and to 25 to 100 mV in saline waters. Copper base alloy electrodes, aluminum brass or 90-10 copper-nickel, were polarized to 60 or 200 mV in saline water environments. In order to optimize the signals from probes built with commercially pure titanium electrodes, a larger potential, 400 mV, was applied between the electrodes. Data were collected on a data logger or hybrid chart recorder. Plots were created from those data off-line using QuattroPro™ spreadsheet software.

RESULTS

Plant #1

The first probe was installed in the high pressure fire protection system in 1991. This plant had experienced significant corrosion of carbon steel piping and a build up of corrosion products on the pipe wall that effectively reduced the system's flow capacity. Attack beneath these deposits had been observed. The microbiological influences had not

been well characterized. The probe was installed directly into the flow stream. Normal fluid velocities past the probe were approximately 1.5 m/s.

The results from that probe are shown in Figure 3. Both the applied and generated currents exhibited a definite increase approximately 50 days into the exposure (December, 1991). In the Spring of 1992, the applied current increased to a value of more than 60 μA . At about the same time, the generated current actually changed sign, reaching levels of nearly $-40\mu\text{A}$ in the Summer of 1992. A very definite generated current of negative sign was maintained until the probe was replaced in October, 1993. Post-test examination of the probe revealed that the stainless steel electrodes were covered with a thick but patchy film consisting primarily of iron oxide. Microbiological characterization of the films, done at the site using MICKitsTM and from microscopic analyses performed by Bioindustrial Technologies, showed that the films contained both aerobic and anaerobic bacteria, acid producing bacteria (APB), and iron oxidizing bacteria only on the negative electrode. No sulfate reducing bacteria (SRB) were detected nor was any corrosion of the electrodes detected. Probably of greatest significance, the pH at the positive electrode was 4.9 vs. 8.3 at the negative electrode.

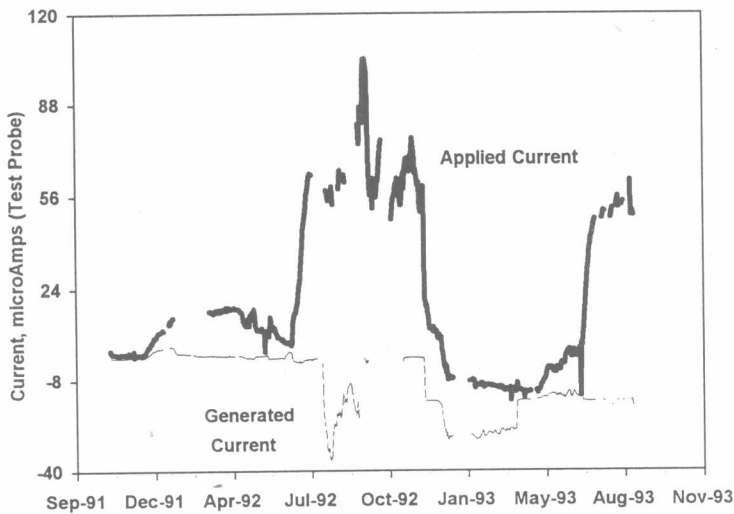


FIG. 3 -- Results from Plant #1 Fire Protection System

When the probe in the fire protection system was replaced in October, 1993, an additional probe was installed in the essential equipment cooling water (EECW) system. That probe gave no indication of any biofilm activity for the first ninety days of exposure (Figure 4). After about ninety days, a very definite generated current, with a negative sense, was observed. Since the generated current influenced the magnitude of the applied current, the arithmetic difference between the two currents (i.e., applied - generated) was used as the indicator of biofilm activity. That difference value reached a level of approximately 10 μA in April, 1994, then abruptly decreased to the baseline level of about 1.5 μA . The time that the abrupt decrease in the indicator variable occurred approximately two days after the plant's spring chlorination treatment, done to control Asiatic clams. The applied and generated currents (and their difference) began to increase again about one month later. In June, 1994, another abrupt decrease, again corresponding to a system chlorination, was observed. This cycle of indications of microbiological activity and destruction was repeated again. All probe tracking activities were turned over to the site in August, 1994.

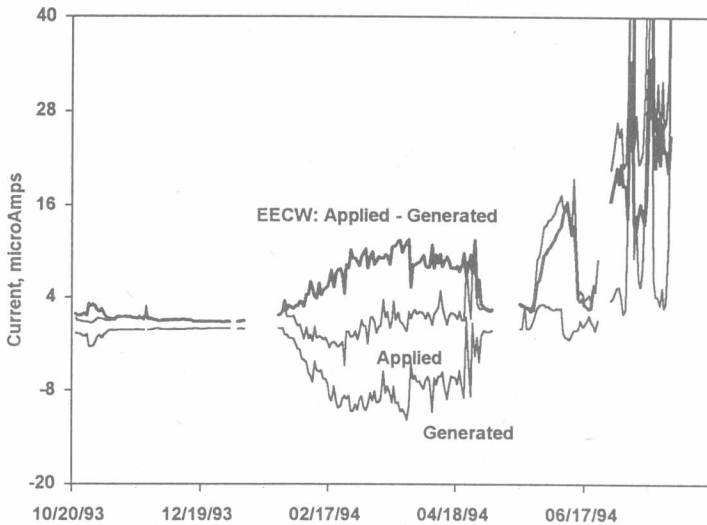


FIG. 4 -- Results from Plant #1 EECW

Plant #2

A probe was installed into a portable sidestream used to monitor fouling and the performance of biocides and other treatments in the once-through service water system of another large nuclear plant. The system was located immediately downstream of components that were known to be subject to fouling and corrosion. As shown in Figure 5, the probe fouled very rapidly, was effectively returned to the clean condition by chlorination, then fouled again. The applied current never responded to the chlorination (the abrupt decrease in applied current was the result of a mechanical cleaning of the probe), however, the generated current slowly decreased during and after the second chlorination. No post-test examination of the probe was performed.

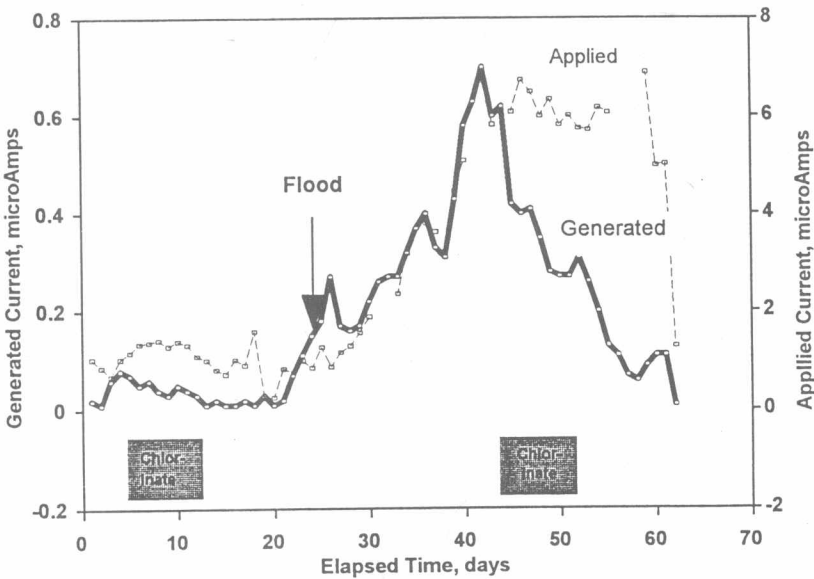


FIG. 5 -- Results from Plant #2