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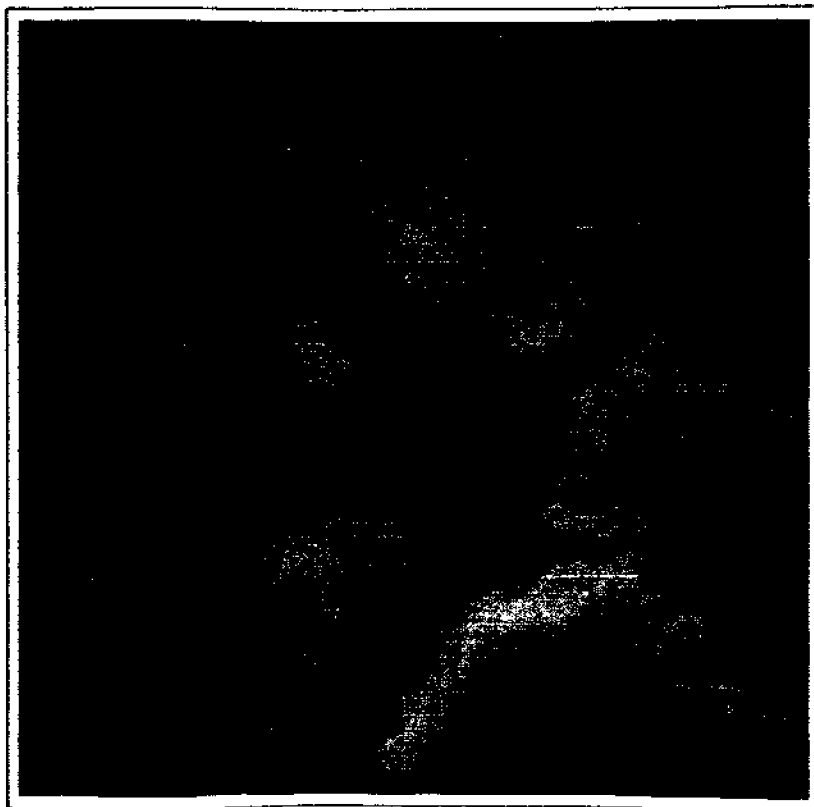
Sea Grant Program on Marine Corrosion FINAL REPORT

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Sea Grant Depos

Volume One — Technical Summary

Edited by
S. C. Dexter
and
W. H. Hartr

NATIONAL SEA GRANT DEPOSITORY
P.O. BOX 1100
URI, NORTHERN AVENUE, 06320
NANTUCKET, MA 01904



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NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
UNITED STATES DEPARTMENT OF COMMERCE

AUGUST 1984
UNIVERSITY OF DELAWARE
Sea Grant College Program
LEWES, DELAWARE 19958

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Sea Grant

SEA GRANT PROGRAM ON MARINE CORROSION
FINAL REPORT

VOLUME ONE - TECHNICAL SUMMARY

Submitted to
The Office of Sea Grant Programs
National Oceanic and Atmospheric Administration
United States Department of Commerce

Marine Corrosion Program Principal Investigators:

Stephen C. Dexter, University of Delaware
Overall Program Leader and
Localized Corrosion Project Leader

William H. Hartt, Florida Atlantic University
Calcareous Deposits Project Leader

John Ambrose, University of Florida

Charles H. Culberson, University of Delaware

Ronald M. Latanision, Massachusetts Institute of Technology

Thad S. Lee, LaQue Center for Corrosion Technology

Samuel W. Smith, Florida Atlantic University

Michael A. Streicher, University of Delaware

August 1984
University of Delaware
Sea Grant College Program
Lewes, Delaware 19958
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NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
U.S. DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20540

PREFACE

The Sea Grant Program on Marine Corrosion began in the fall of 1980 as a cooperative research project involving eight principal investigators from both academia and industry. An important component of the Program was the establishment of an Industrial Advisory Panel, whose primary functions were to keep the investigators aware of developing industrial problems in the area of marine corrosion, and to assist the investigators in technology transfer.

The Program was to last for three years, and was viewed by both the National Sea Grant Office and by the investigators themselves as an experiment in forging closer ties between a substantial academic research effort and its ultimate beneficiaries in industry.

This report, in four volumes, will serve, not only to document the technical results from three years of work by the eight principal investigators with their associates and students, but also to evaluate the success of that experiment, and to recommend whether the structure of the Program should be continued, and perhaps used as a model in other fields of research.

Volume One of the report is a stand-alone document, summarizing and evaluating the results of the entire program, while Volumes Two through Four present the technical details for each of the major segments of the program. Volume One is intended to be readable for the general educated public, whereas Volumes Two, Three and Four are intended to be reference volumes for those interested in specific areas of marine corrosion research and engineering.

Stephen C. Dexter
Overall Program Leader

Sea Grant Program on
Marine Corrosion

FINAL REPORT

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VOLUME FOUR Supporting Data - Localized Corrosion, Stainless Alloys

I. EXECUTIVE SUMMARY (S. C. Dexter, Program Leader)

A. Description of the Program

The Sea Grant Program on Marine Corrosion began as a three year endeavor in October of 1980. Its intention was to unite the expertise and resources of marine oriented materials scientists from five universities and one independent industrial research laboratory into a coordinated effort to address selected marine corrosion problems of both practical and scientific importance.

The overall objectives of the Marine Corrosion Program were to: focus the expertise and resources of widely scattered marine materials scientists, encourage a multidisciplinary approach in marine corrosion research, and provide a mechanism for rapid technology transfer and exchange of ideas between the academic and industrial research sectors.

One of the key components of the Program, and a major contributor to its eventual success, was the establishment of an Industrial Advisory Panel. Members of the Panel were chosen both for their expertise and direct involvement in marine corrosion research, and for their ability to represent the interests and needs of a broad sector of marine industry, rather than just their own company. Industries represented by the Panel members included: the aluminum, nickel, steel and stainless steel producers and fabricators; the marine electronics and instrumentation industries; the offshore oil and gas industries; the cathodic protection industry and the electric power industry.

Two problems were selected for attention during the three year program. These were: 1) the nature of calcareous deposits and their relation to cathodic protection of steel in seawater, and 2) the localized corrosion of aluminum and stainless alloys. Leadership for the research on these two problems was provided by W. H. Hartt of the Department of Ocean Engineering, Florida Atlantic University, and S. C. Dexter of the College of Marine Studies, University of Delaware, respectively. Overall leadership of the Marine Corrosion Program was provided by Dexter.

B. Summary of Technical Results

B.1. Calcareous Deposits

The team of principal investigators in this project was: W. H. Hartt, Project Leader, John Ambrose of the University of Florida, Charles Culberson of the University of Delaware, and Samuel Smith of Florida Atlantic University. The project objectives were to: develop a more fundamental understanding of how calcareous deposits form on cathodic surfaces in seawater, to determine what role they play in the process of cracking due to corrosion fatigue, to determine the practical significance of structure-property relationships of the deposit and to model the process of deposition with respect to seawater exposure conditions.

The applied current density necessary to maintain a given level of cathodic protection on a steel surface immersed in seawater decreases as a calcareous deposit forms. That current density was used in the experiments as an inverse indicator of the ease with which the deposit forms under a given set of conditions. It was found that the current density increased by up to 30% with decrease in pH from 8.2 to 7.2, thus signifying an inhibition in deposit formation at the lower pH. Likewise, the current increased as the temperature dropped from 25 to 3 C. In contrast, the amount of deposit formed and the current density both decreased with decrease in dissolved oxygen concentration of the water. This latter effect was due to a decrease in the rate of the cathodic reaction (reduction of oxygen to hydroxide ions) rather than to a direct inhibition of deposit formation.

The two main components of the calcareous deposit are calcium carbonate (calcite and/or aragonite) and magnesium hydroxide (brucite). It was found that the magnesium dissolved in seawater has a negative influence on the quality of the deposit because the magnesium hydroxide that forms is less protective than calcium carbonate. Hydrodynamics of flow around the electrode also influenced the deposit. Prior to formation of a substantial deposit, the current density for a given level of protection increased with increase in flow velocity. Current density was found to correlate best with the magnitude of hydrodynamic shear rather than with nominal electrolyte velocity.

According to the above results, the lower temperature, pH and oxygen often found together in deep water should act together to inhibit deposit formation. Moreover, the solubilities of both calcium and magnesium components of the film increase with pressure, making it less likely that a deposit will form in the deep water. Thus, the results of this work indicate that higher current densities should be required for cathodic protection in cold, deep water. This agrees with experience in the offshore industry, where it has been found that calcareous deposits form slowly, if at all, in deep water.

With regard to the role of calcareous deposits in the process of corrosion fatigue, it has previously been observed that such deposits form within corrosion fatigue cracks, and that their effect is usually to reduce crack growth rate by mechanically interfering with crack closure, thus, reducing the stress intensity range. During the course of the present investigation, it was expected that calcareous deposit formation inside the crack would be influenced by the time variable geometry and altered seawater chemistry of the crack interior, and by mass transport of reactants and products due to the pumping action of crack opening and closing. It was observed that the chemistry of the deposit within simulated fatigue cracks was basically the same as that on the boldly exposed surface, except that $\text{Mg}(\text{OH})_2$ was somewhat more prevalent inside the crack, and the density of the deposit was slightly less. The morphology of the deposit inside the crack was influenced by the hydrodynamics of electrolyte flow. The electrochemical potential profile, measured as a function of depth into the crack, was relatively flat, indicating that the interior surface of the crack was easily polarized. Additional research on the electrochemical characteristics of the crack interior and on the influence of hydrodynamics will be required in order to fully understand the role of calcareous deposits in corrosion fatigue.

An important step in coming to an understanding of how calcareous deposits form on cathodically protected surfaces is the formulating of a computer based mathematical model of the process. Toward this end, a finite element model has been constructed to predict deposition rates and deposit properties, given the proper information about substrate,

hydrodynamics and seawater chemistry. The basic model is in place, and its predictions have been shown to fit the experimental data with reasonable accuracy. Further development is being done to include the effects of factors such as pressure and hydrodynamics.

B.2. Localized Corrosion

The team of investigators in this project was: S. C. Dexter, Project Leader; R. M. Latanision of the Massachusetts Institute of Technology; M. A. Streicher of the University of Delaware and T. S. Lee of the LaQue Center for Corrosion Technology, Inc. The objectives of the Project were to: 1) identify the rate controlling chemical, electrochemical, mechanical, physical and metallurgical processes for localized corrosion of aluminum and stainless alloys; 2) use that information in the mathematical modeling of localized corrosion in those two alloy systems; and 3) develop accelerated tests to act as an interface between the electrochemical laboratory work, data from natural seawater testing and service experience.

B.2.a. Aluminum Alloys

Dexter and Latanision were the principal investigators in the work on aluminum alloys. The work focused first on clarifying the mechanism of the previously observed effects of magnesium and copper on the cathodic reaction (which is often rate controlling) on pure aluminum and aluminum alloys in aerated seawater. Next, the work turned to determining the effect of electrolyte flow velocity on the cathodic reaction. Finally, the work also resulted in a major improvement in the utility of the scanning potential microprobe (SPM) as an instrument for studying pitting corrosion of metallic surfaces.

In an earlier project, Dexter had demonstrated the effect of magnesium on the cathodic reaction kinetics of aluminum in seawater. In the present investigation, it was shown that 200 ppm of magnesium in the water was enough to cause the effect, that other divalent cations (calcium and strontium) dissolved in seawater did not produce the same effect and that the magnesium had to be present in the water. Magnesium from the water became incorporated into the passive film, as shown by scanning Auger analysis. In contrast, magnesium present as an alloying element in the metal was not incorporated into the film and did not

alter the cathodic kinetics. Computer modeling indicated that magnesium was incorporated into the film by an adsorption reaction, rather than by the precipitation of $\text{Mg}(\text{OH})_2$.

The Scanning Potential Microprobe (SPM) is an electrochemical instrument capable of monitoring pit initiation and growth on the surface of a metal sample while it is exposed to the electrolyte. The surface of the metal is scanned by a microelectrode, which senses potential gradients in the electrolyte due to current flow in the solution between local anodes and cathodes. The SPM generates an electrochemical map of the surface on an X-Y recorder, showing pits as "hills" and cathodic sites as "valleys". During the work on aluminum alloys, the basic SPM design by Ishikawa and Isaacs was modified to increase spatial resolution so that incipient pits could be mapped. The computer controlled instrument was fitted with a platinum tipped microelectrode held 100 microns above the surface and vibrated by a piezoelectric crystal. The signal was then processed by a frequency-specific amplifier connected to the computer. Spatial resolution on the order of tens of microns was achieved. Sites of anodic activity on the SPM map were identified with pits on the polished aluminum surface, then the surface chemistry of the region surrounding the pit was analyzed by the scanning Auger microprobe. It was verified by these techniques that excess magnesium exists on the surface when magnesium is present in the electrolyte. It was also found that most of the excess magnesium was within 4 to 5 microns of the pit sites.

These findings were all consistent with the earlier hypothesis by Roland and Dexter that the role of magnesium was to act as a specific catalyst for the reduction of percarbonic acid at the cathode surface, thus increasing the rate of the overall cathode reaction by adding another reduction current to that of dissolved oxygen. The long-term practical significance of the magnesium effect in the corrosion of aluminum alloys in seawater was called into question, however, when it was also shown that the magnesium effect disappears within about 24 hours of immersion of the sample into the electrolyte. The reason for this is not known, although it was determined that it was not the result of a depletion of magnesium from the test solution. Thus, while it

seems likely that magnesium has an effect on the initial corrosion rate while the passive film is reaching an equilibrium with the electrolyte, its long-term effect is probably much less significant than that of the chloride ion.

It has been known for a long time that copper deposits on aluminum surfaces and greatly increases the corrosion rate. Present results from both laboratory experiments and computer modeling indicated that the mechanism of copper deposition was reduction of copper ions to the metallic state, rather than adsorption. Moreover, the results indicated that all the copper present in seawater will be reduced, rather than just the "free" copper ions. Thus, the total analytical copper concentration is the proper variable to be concerned with when dealing with aluminum corrosion.

Variations in the velocity of flow from zero to about 100 cm/sec are typical for open ocean flow conditions. An increase in flow speed within that range always had two competing effects on the cathodic reaction on aluminum. The first effect was to shift the corrosion potential in the active (negative) direction, away from the pitting potential. The second effect was to depolarize the cathode by decreasing the slope of the cathodic polarization curve. At a surface water pH of 8.2, the effect on the corrosion potential predominated at all current densities, so that the net effect was to polarize the cathode and reduce the tendency to initiate pitting. At a pH of 7.2, however, the depolarization effect predominated at current densities greater than 3 microamperes/sq cm. There was some concern that this might cause a super corrosive condition in oxygen deficient deep ocean water under flow conditions such as would be encountered in heat exchanger tubing. Separate laboratory tests did not confirm the development of such a super corrosive condition under a simulated deep ocean combination of low pH, temperature and dissolved oxygen. This was probably because the slow reaction kinetics at the low temperature kept the cathodic current density below 3 microamperes/sq cm. Additional work should still be done at intermediate values of temperature, pH and oxygen.

B.2.b. Stainless Alloys

Lee and Streicher were the principal investigators in the stainless alloys part of the Localized Corrosion Project. This work proceeded along several different lines in parallel. Multiple crevice and remote crevice assembly techniques were used to investigate the effect of geometrical, metallurgical, environmental and electrochemical factors in initiation and growth of crevice corrosion. This information was used for improving and verifying a mathematical model of crevice corrosion, particularly in the propagation phase. A limited amount of work was done on the role of bacteria in crevice corrosion initiation. Finally, a substantial effort was made to develop new accelerated test methods for evaluating the resistance of old and new stainless alloys to crevice corrosion.

Much of the variability of crevice corrosion test data can be attributed to variations in crevice geometry. During the course of this research, a number of methods for improving the reproducibility of initial crevice geometry have been investigated. These methods include: using a variety of metallic, polymeric and ceramic materials as the crevice former in the multiple crevice assembly test; specifying an initial torque on the loading bolts of the crevice former; and applying the load to the crevice former by means of a hydraulic piston.

Multiple and remote crevice assembly data have been used to document the effects of environmental variables such as: pH, dissolved oxygen and chloride concentrations, temperature and velocity of flow. It was found that these factors do not always affect initiation and propagation of crevice corrosion in the same way. A dramatic example is the reduction in crevice propagation rates at temperatures between 45° and 70°C as compared to that at lower temperatures. Multiple and remote crevice assembly tests have also been used to clarify the mechanism and conditions under which carbon steel can be used as a sacrificial anode to reduce or prevent crevice corrosion of stainless alloys.

The mathematical crevice corrosion model of Oldfield and Sutton has been used to complement the multiple and remote crevice assembly testing. The data from these experiments has been used as an aid in extending the model to cover the propagation phase of crevice corrosion.

Using the preliminary propagation model it has been concluded that:

1) there is a critical cathode to anode area ratio, which is somewhat dependent on solution velocity, necessary to sustain crevice corrosion by the cathodic reduction of dissolved oxygen; and 2) the role of crevice geometry, particularly the initial crevice gap, may be different in the propagation phase than it was for initiation. Cases were found among the alloys having a relatively poor resistance to propagation that the rate of propagation increased with increasing crevice gap, quite the opposite of the effect on initiation. The effect of crevice gap, however, was often found to be counteracted by the effects of mass transport on the crevice solution composition and pH, and the opposite tendencies were often found among the alloys more resistant to crevice propagation.

The initiation phase of the Oldfield and Sutton model is based on the assumption that crevice corrosion initiates when the dissolved oxygen in the crevice solution is depleted by electrochemical reduction to hydroxyl ions at the metal surface. It has recently been asked whether bacteria in the crevice solution could play an important role in the oxygen depletion process. In an experiment done in Dexter's laboratory, the potential of a platinum electrode was used to measure the rate of oxygen depletion in a series of special test cells. It was found that, while bacterial oxygen utilization is a factor, the electrochemical mechanism for oxygen depletion was favored by more than 150 to one. It was also predicted from the experimental data that the electrochemical mechanism would deplete the oxygen in a typical crevice within about 10 minutes. This value was in excellent agreement with, and justifies the assumption of the Oldfield and Sutton model.

The goal of the accelerated testing portion of the Localized Corrosion Project was to develop a rapid laboratory test that could be used both to rank stainless alloys for alloy selection in service applications and as a tool in new alloy development work. Most of the effort was spent on developing the critical crevice temperature test utilizing the Swedish made Santron 400 potentiostat. In this test an alloy specimen with crevice former is immersed in the test solution at a controlled temperature. A preselected potential is applied to the specimen while the temperature of the test solution is automatically

increased at regular intervals. Crevice initiation is detected by the onset of a current flow from the specimen. The temperature at which this occurs is recorded as the critical crevice corrosion temperature for the given alloy, crevice device, solution composition and test procedure. This has proved to be a versatile and reproducible test, whose results can be correlated with those from ferric chloride and natural seawater tests. There are several critical crevice temperature test parameters that can be adjusted on the Santron potentiostat. Among these are: the measuring time at each temperature step, the current level selected to represent initiation, the impressed potential level and the size of the temperature interval. In addition, certain test procedures can be varied. For instance, one can apply the test potential continuously, or intermittently, disconnecting it during those time intervals while the temperature is being raised. Much work on the effects of these factors has already been done. But it is hoped that such versatility will eventually allow the test to be "tuned" to the specific crevice conditions for common applications in industrial service.

To date, two different approaches to ranking stainless alloys have been taken by the investigators involved in this Project. Streicher has analyzed a large volume of the existing natural seawater crevice corrosion data and has devised a "crevice corrosion index", which combines parameters concerned with initiation and propagation. Forty-six alloys were ranked on the basis of this "index", and the rankings made it possible to derive conclusions on the roles of alloying elements, surface finish and test parameters. Lee and his colleagues prefer to rank alloys according to their separate tendencies for initiation and propagation, due to the observation that the same environmental factors may effect initiation and propagation differently. Useful conclusions have been generated during this work by both approaches to ranking. It remains to be seen which of the two approaches (or, perhaps a combination of them) will prove to be of the most practical long-term benefit.

C. Evaluation by Industrial Advisory Panel Chairman

An independent assessment of the Program from the point of view of the Industrial Advisory Panel has been written by Panel Chairman, W. W. Kirk, of the LaQue Center for Corrosion Technology, Inc. That assessment is presented below.

"Members of the Industrial Advisory Panel benefited significantly from the opportunity to interact with both principal investigators and Sea Grant coordinators in this Program on Marine Corrosion. The objectives of the Panel stated in Section II-B were to uphold high standards of quality research and improve industry/academia communications such that results will be beneficial to all concerned. We are convinced that these objectives have been met and, furthermore, that this program serves as a model for future cooperative research of all types sponsored by both government and the private sector.

Semi-annual meetings with the investigators accomplished all of the primary objectives. In many cases these meetings included or resulted in later one-on-one type discussions, correspondence and visits to review data, supply materials and recommend courses of action. This mechanism kept panelists aware of the progress of research and the planning process, while bringing an awareness of industry problems and opportunities continually before the investigators.

We are favorably impressed with the greatly improved understanding of seawater chemistry as it affects corrosion and cathodic protection processes. Appreciation of the role of carbon and organics in surface film and calcareous deposit chemistry helps to better define and confirm the greater corrosivity of natural seawater vs. synthetic chloride solutions. Likewise, a better understanding of calcareous deposit chemistry and morphology can assist in achieving more economical design of cathodic protection systems. Great strides have been made toward modeling and predicting the nature of surface deposits in a given environment/material situation. Through coaching by industrial advisors, investigators confirmed the inhibition of calcareous product formation in deep ocean water, which helps explain the higher current densities necessary to achieve cathodic protection of working structures on the ocean bottom versus the requirements at the shallow depths.

In the studies of aluminum alloys, a much better understanding of the relationship between microstructure and corrosion has been achieved. The role of magnesium, its origin, level and mechanism of entry into the corrosion film, has been found significant in understanding or predicting the performance of aluminum alloys in seawater. A particularly useful research tool, the scanning potential microprobe, was developed for use in investigating the initiation of pitting corrosion in alloys 5052 and 3003 in saltwater and seawater. All of these results should provide a useful base for using aluminum alloys in such applications as OTEC condensers and heat exchangers.

Predictive modeling of the initiation phase of crevice corrosion in stainless steels is now being utilized in industry as one important result of this program. Understanding the relative importance of metallurgical, environmental and geometric variables enables an improved base upon which to select the appropriate stainless steel for a given application. The inverse relationship between temperature and crevice corrosion susceptibility, within practical limits, is surprising but important. Furthermore, the ease of galvanic protection by coupling with carbon steel can explain and enable much successful use of stainless steels in seawater. This expanded data base is very useful toward confident selection of stainless steels for seawater handling systems, for example, in coastal utilities industries.

The panelists support the public presentation and publication of results from this program, providing a very useful reference base for marine corrosion engineering. Significant progress has been made toward convincing the engineer that methods exist to enable selection of the right material to produce the most effective combination of corrosion resistance and economics in the fields addressed here.

Finally, we must state our appreciation of the excellent cooperation toward high quality results achieved during times when industry throughout the world was suffering one of the worst economic recessions in history. Sincere thanks are due the National Sea Grant Program for their financial support and personal encouragement throughout this three year effort."

II. REVIEW OF PROGRAM ORGANIZATION AND OBJECTIVES (S. C. Dexter)

A. Scientific

The Sea Grant Program on Marine Corrosion began as a three-year endeavor on 1 October 1980. Its intention was to unite the expertise and resources of marine oriented materials scientists from five universities and one independent research center into a coordinated effort to solve selected marine corrosion problems of both practical and scientific importance.

Two broad problem areas were selected to receive our initial attention. Problem selection was based on: a) practical significance to marine-related industries, and b) our capability of addressing the problem with expertise and equipment currently available. The two problems selected were: 1) the relation between calcareous deposits and cathodic protection of structural steel, and 2) the localized corrosion of aluminum and stainless alloys.

The general approach to each of the above problem areas was to combine natural seawater testing, electrochemical science, surface science, mathematical modeling, and accelerated laboratory testing in order to develop a better understanding of the basic processes involved, and to generate data useful in design.

The Sea Grant Program on Marine Corrosion consisted of a series of coordinated research projects on those two broad topics as shown in the organizational chart of Figure 1. Overall scientific and engineering coordination and management for the program were the responsibility of the Overall Project Leader, Stephen C. Dexter, from the University of Delaware's College of Marine Studies.

Project I on the role of calcareous deposition in cathodic protection was coordinated by Dr. William Hartt of the Florida Atlantic University with co-principal investigators as shown in Figure 2. Project II on localized corrosion of aluminum and stainless alloys was led by Dr. Stephen Dexter of the University of Delaware with co-principal investigators as shown in Figure 3.

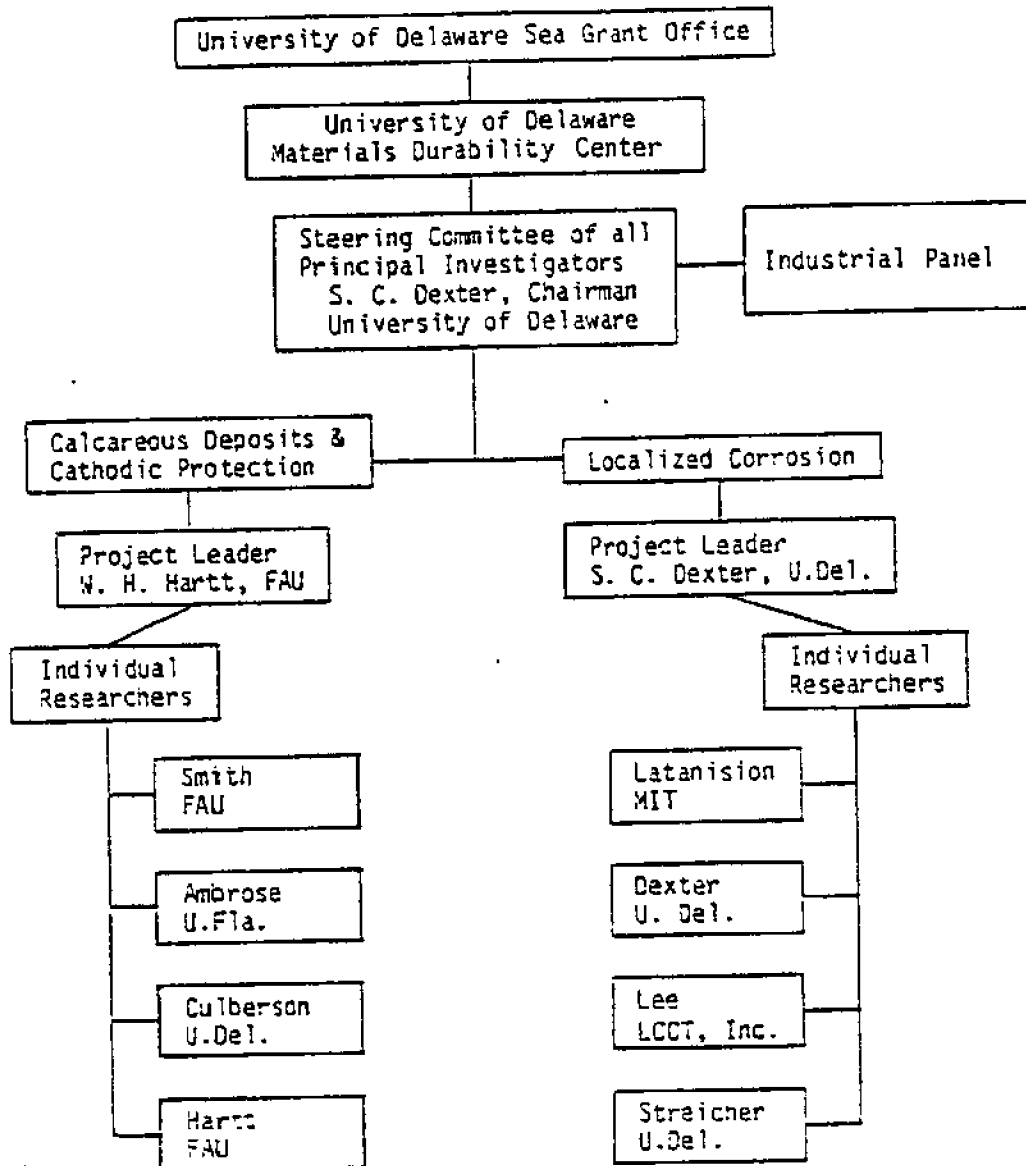


Figure 1

Figure 2
PROJECT I PRINCIPAL INVESTIGATORS

Dr. William H. Hartt, Project Leader
Professor
Department of Ocean Engineering
Florida Atlantic University
Boca Raton, FL 33431

Dr. John Ambrose
Associate Professor
Department of Materials Science
and Engineering
University of Florida
Gainesville, FL 32611

Dr. Charles Culberson
Associate Professor
College of Marine Studies
University of Delaware
Newark, DE 19716

Dr. Samuel W. Smith
Assistant Professor
Department of Ocean Engineering
Florida Atlantic University
Boca Raton, FL 33431

Figure 3
PROJECT II PRINCIPAL INVESTIGATORS

Dr. Stephen C. Dexter, Project Leader
Associate Professor
College of Marine Studies
University of Delaware
Lewes, DE 19958

Dr. Ronald Latanision
Professor
Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

Mr. Thad S. Lee
Vice President, Research and Engineering
LaQue Center for Corrosion Technology, Inc.
P.O. Box 656
Wrightsville Beach, NC 28480

Dr. Michael A. Streicher
Research Professor
Department of Chemical Engineering
University of Delaware
Newark, DE 19716

The overall objectives of the Marine Corrosion Program were to:

1. Focus the expertise and resources of marine oriented materials scientists into a coordinated effort to solve selected marine corrosion problems of both practical and scientific importance.
2. Encourage the integration of natural seawater testing, accelerated testing, and electrochemical science into a unified approach toward developing a better understanding of basic corrosion processes, and translating such knowledge into useful design criteria.
3. Provide a mechanism for cross-fertilization of ideas from both universities and industry on the solution to marine corrosion problems.

The first two of these overall objectives were met through the two technical projects whose results are summarized in the remainder of this volume. The third overall objective was accomplished through an Industrial Advisory Panel which was established during the first year, and with whom the Investigators had excellent interactions throughout the three years of the program.

B. Industrial Advisory Panel

The twelve members of the Advisory panel and their professional affiliations are shown in Figure 4, followed on the next page by a copy of the Charter for the panel giving its functions and purposes. There were seven formal meetings between the Industrial Panel and the Principal Investigators. These meetings are summarized in Figure 5. From the investigator's point of view, interactions with the panel were excellent. The panel members were enthusiastic and helpful, and several of them were instrumental in providing us with experimental alloys to test, chemical analyses of these alloys, and with data from service experience for comparison to our laboratory results.

The discussions at our group meetings were detailed and meaningful. We were particularly pleased to see several panel members asking questions and offering insights outside of their main area of expertise. During meetings in the second year, time was provided for small group

Figure 4
SEA GRANT PROGRAM ON MARINE CORROSION
INDUSTRIAL PANEL MEMBERSHIP

Mr. W. W. Kirk, Panel Chairman
LaQue Center for Corrosion Technology
Wrightsville Beach, NC

Dr. Robert Baboian
Texas Instruments, NACE, ASTM
Attleboro, MA

Mr. Seymour Coburn
U.S. Steel Corporation
Pittsburgh, PA

Mr. Terry Debold
Carpenter Technology, Inc.
Reading, PA

Mr. Al Goolsby & Mr. Bart Ellison
Shell Development Company
Houston, TX

Dr. Ivan Franson & Mr. Harry Deverell
Allegheny-Ludlum Steel Corp.
Brackenridge, PA

Mr. Ralph Horst
Alcoa Laboratories
Alcoa Center, PA

Mr. Curtis W. Kovach
Crucible Research Center
Pittsburgh, PA

Mr. Joseph A. Lehmann
Cathodic Protection Services, Inc.
Houston, TX

Dr. Barry C. Syrett
Electric Power Research Inst.
Palo Alto, CA

Mr. Ray Lindberg, Ex-Officio
Reynolds Metals Co. (Retired)
Richmond, VA

A CHARTER
 for the
INDUSTRIAL ADVISORY PANEL
 of the
SEA GRANT PROGRAM ON MARINE CORROSION

The functions and purposes for the Industrial Advisory Panel of the Sea Grant Program on Marine Corrosion shall be as follows:

- o To represent, through interactions with the principal investigators, the industrial viewpoint on, and to keep the principal investigators aware of developing practical marine corrosion problems.
- o To assist the principal investigators in technology transfer, especially in the presentation of design criteria in a format directly useful to professional corrosion engineers.
- o To meet periodically with the principal investigators for a review of their progress toward objectives from an industrial point of view. (It is intended that this industrial panel review will be separate from the peer review system through which the Sea Grant office will make decisions about continued funding of the program.)
- o To assist, if required, in the procurement of special alloys or other material necessary for the research program.
- o To provide practical guidance in matters relating to availability, fabricability, and cost of the alloys under investigation.

The formulation of an Industrial Advisory Panel represents a new approach to National Sea Grant Programs. The suggestion from the Sea Grant Office that such a panel be activated was based on the growing recognition that there is a distinct need to improve the interaction between university and industrial research organizations. It is expected that through such interactions, the transfer of technology will occur more smoothly and efficiently. Since corrosion has been selected as one of the prime technical problems for investigation using Federal funds, this program may well serve as a model for future cooperative efforts of this type.

Figure 5
SUMMARY OF
INVESTIGATOR/INDUSTRIAL PANEL MEETINGS

Date & Location	Purpose & Time Allotted	Attendance		Comments
		Investigators	Panel	
6 April 1981 Toronto	Organizational 7:00-10:00 p.m.	8	8	Foundation built for subsequent discussions.
19 August 1981 Washington, DC	Technical & Site Visit--9:00 a.m.- 12:30 p.m. & 2:00-3:00 p.m.	7	5	Good discussions on Project I.
22 March 1982 Houston	Technical 7:00-10:00 p.m.	7	9	Three hours was too short for full discussion of all aspects.
5-6 August 1982 Wrightsville Beach, NC	Technical 2:00-5:00 p.m., 7:00-10:00 p.m., & 9:00 a.m.- 12:00 p.m.	7	5	Plenty of time. Small group and one-on-one dis- cussions encouraged and beginning to happen, especially in Project II.
18-19 April 1983 Anaheim, CA	Technical Symposium 1:00-5:30 p.m. each of two days	8	9	Each Principal Investigator pre- sented a paper on Sea Grant Work at the CORROSION/83 Seawater Corrosion Symposium
19 April 1983 Anaheim, CA	Discussion 5:30-7:00 p.m.	7	8	Discussion of final report format, tech- nology transfer and future funding.
10 January 1984 Lewes, DE	Review Final Report Draft 1:00-4:00 p.m.	6		

and one-on-one discussions between investigators and panel members. We feel that these discussions were particularly fruitful. They led to the type of detailed questioning and frank discussion for which the big national meetings we usually attend provide neither the time nor the proper atmosphere.

Out of these meetings came a number of valuable suggestions from both individual panel members and from the panel collectively. A few examples of these suggestions are:

- a) That Project I concentrate on modeling the calcareous deposit itself rather than the cathodic protection system or the structure, and that they focus part of their effort on deposition under the deep, cold water conditions toward which the offshore industry is moving.
- b) That the aluminum part of Project II pay more attention than originally planned to the effect of impurity levels on marine corrosion resistance. Such data will help the industry in making management decisions about maximum permissible impurity levels in recycled aluminum products.
- c) That the results of the stainless alloys part of Project II will be most useful if they can begin to provide a sound basis on which to select from among the newer stainless alloys the one with the most effective combination of corrosion resistance and cost for a given application.

During the third year of the program the small group and individual discussions of year two continued, and we had hoped to encourage visits of the academic investigators to selected industrial facilities and of panel members to the universities. Time and financial constraints, however, limited these activities more than was intended. Also in year three, all principal investigators presented papers on the Sea Grant Work during the Seawater Corrosion Symposium at CORROSION/83 in Anaheim, California. This symposium was chaired by Dr. Dexter and was intended to serve as the technical part of the Advisory panel meeting. After the symposium, there was a supplementary evening meeting with the panel for the purpose of discussing technology transfer, the final report format and the desirability and feasibility of continuing this coordinated

effort beyond the third year. Finally, in January of 1984, a workshop was held in Lewes, Delaware for the purpose of planning future marine corrosion research and reviewing the draft Final Report.

III. SUMMARY OF TECHNICAL RESULTS AND THEIR SIGNIFICANCE

A. Project I - Calcareous Deposits and Cathodic Protection

A.1. Project Goals and Objectives (W. H. Hartt)

This activity has been organized into three subdivisions, termed Efforts I-III, and these are listed and defined in Figure 6. Thus, the overall objective of Project I has been to develop a more fundamental understanding of calcareous deposits, as these form on cathodic metal surfaces in sea water, to rationalize the practical significance of structure-property relationships of calcareous deposits and to make initial progress in predicting current-potential-time interrelationships of cathodic surfaces under conditions of sea water exposure. Correspondingly, Figure 7 presents the research plan for these activities as they were conceived at the beginning of the Program.

A.2. Background Information (W. H. Hartt)

The reactions which typically occur on cathodic metal surfaces in aqueous electrolytes involve the hydroxyl ion as reaction product. Thus, pH of the electrolyte adjacent to the metal surface may increase relative to the bulk value. For the case of sea water exposure this may result in precipitation of compounds such as CaCO_3 , $\text{Mg}(\text{OH})_2$ and others, since these are typically near saturation or supersaturated under ambient conditions. These precipitates form a film upon cathodic surfaces in such a way that the effectiveness, efficiency and economics of cathodic protection are all enhanced. Despite this, however, there has been only a limited amount of previous research on the fundamental properties of calcareous deposits. This is in spite of the fact that sea water chemistry, temperature and velocity are thought to have an important influence upon deposit properties.

Calcareous deposits have also been projected to influence fatigue of metals. In this regard these films have been observed to precipitate within cracks and to interfere with the normal closure processes. Consequently, the effective stress intensity range is lowered, and crack

EFFORT	EFFORT OBJECTIVE
EFFORT I - Nature and Properties of Calcareous Deposits.	To maximize efficiency and effectiveness of cathodic protection systems by determining fundamental properties of calcareous deposits as a function of electrochemical, chemical and physical variables of exposure.
EFFORT II - Calcareous Deposit Formation within Corrosion Fatigue Cracks.	To investigate preferential formation of calcareous deposits within corrosion fatigue cracks in cathodically protected steel and to determine how such deposit occurrence might contribute to enhanced structural reliability for situations involving dynamic loading in sea water.
EFFORT III - Modeling of Calcareous Deposit Formation	To develop mathematical models for formation of calcareous deposits.

Figure 6

Efforts in Project I - Calcareous Deposits and Cathodic Protection

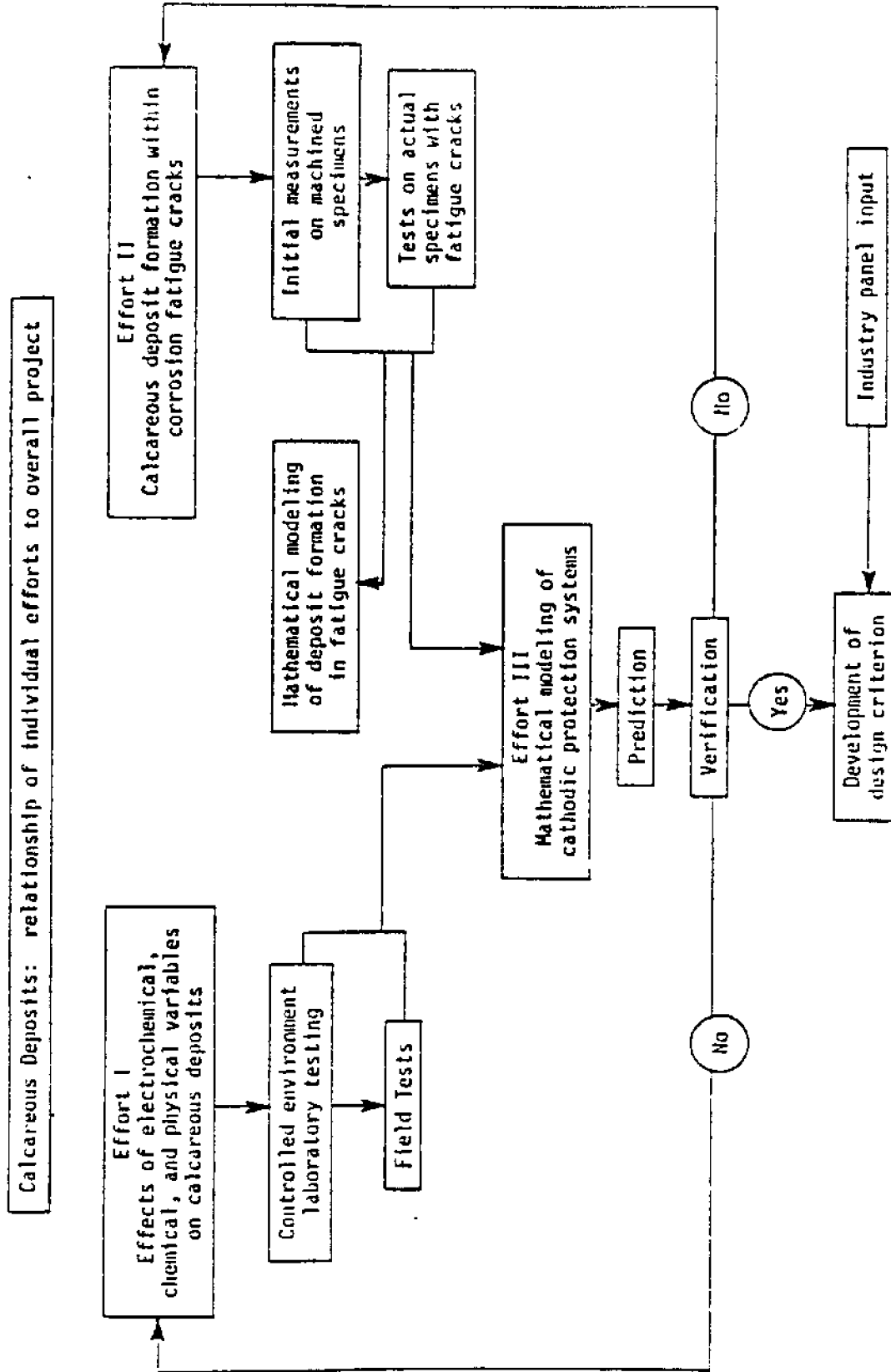


Figure 7 Research Plan for Project I.

growth rate may be either reduced or arrested altogether. However, no information has historically been available with regard to what chemical, electrochemical, physical and geometrical conditions promote formation of calcareous material within fatigue cracks.

An assessment of the major findings of this Program with regard to the nature of calcareous deposits, their relation to seawater chemistry and their interactions with the process of Corrosion Fatigue will be presented in summary form in the next three sections.

A.3. Critical Assessment and Conclusions (W. H. Hartt)

The technical investigation itself focused on a number of issues and variables pertaining to formation of calcareous deposits upon cathodically polarized steel surfaces in sea water. Included as primary variables pertaining to calcareous deposits per se (Effort I - see Figure 6) were sea water chemistry, hydrodynamics, temperature and substrate. Based upon these and also a limited number of high pressure experiments, projections are also made pertaining to the influence of water depth upon calcareous deposits. In the case of calcareous deposit formation within fatigue cracks (Effort II) the factors addressed in Effort I may be applied to the unique and time variable geometry which occurs in association with such cracks. Of particular importance are sea water chemistry modifications within corrosion fatigue cracks and mass transport of reactants and products. Within the modeling activity (Effort III) progress has been made in developing a time variable representation of the potential-current behavior of metal surfaces upon which calcareous deposits form, taking into account the variables listed above. The following is a summary of conclusions which have been reached.

A.3.a. Effort I - Nature and Properties of Calcareous Deposits

(W. H. Hartt with C. H. Culberson, J. Ambrose and S. W. Smith)

(1) Sea Water Chemistry

- (a) Experiments indicate that pH variations within the ambient sea water range can alter current density for polarization to a given potential by as much as 30%. This is due to the influence of pH upon carbonate ion concentration.

- (b) The current density to maintain a prescribed potential in the presence of a calcareous deposit increased with increasing oxygen concentration but at a less than linear rate. Since oxygen concentration influences the current density to maintain a particular potential, it is projected that deposit properties are a function of oxygen concentration of the electrolyte. In low oxygen sea water it may be reasoned that for relatively small amounts of cathodic protection, hydroxide ion production rate and pH at the metal-electrolyte interface may be sufficiently low that little or no deposit forms.
- (c) The magnesium ion has a negative influence upon calcareous deposit formation. Development of a technique for forming the initial deposit under a low magnesium ion concentration condition, such as by application of a calcium rich conversion coating, could enhance the protective nature of the deposit.
- (d) The kinetics of calcareous deposit formation were different for ASTM synthetic sea water, recirculated natural sea water and once through natural sea water. The apparent steady state current density (after 48 hours) was least for the once through natural sea water. The fact that calcium carbonate precipitation kinetics have been shown to be a function of organic content of the electrolyte was also thought to be influential.

(2) Temperature

Current density for polarization to a given potential in NaCl distilled water or in a calcium ion free synthetic sea water was greater at 25 than for 3°C. For natural sea water, where calcareous deposits may form, current density was less at 25°C. This was apparently due to the lower temperature having an inhibiting effect upon calcareous deposit formation.

(3) Hydrodynamics

- (a) The present experiments confirm earlier research results by showing that the current density for cathodic protection increased with increasing velocity.

- (b) In early stages of cathodic polarization (prior to calcareous deposit formation) current density to maintain a prescribed potential best correlated with the magnitude of hydrodynamic shear and not necessarily with nominal electrolyte velocity. Subsequent to calcareous deposit formation the dependence of current density upon hydrodynamic flow parameters was reduced in comparison to the pre-film period.
- (c) Morphology and chemistry of calcareous deposits which formed early in the cathodic polarization process was a function of hydrodynamic parameters. It may be reasoned that the properties of deposits formed during this period (early in the process) may be influential thereafter. On this basis the hydrodynamic flow character may have a long-term influence upon polarization characteristics.

(4) Water Depth

The low temperature and sea water chemistry results (see above) may be used to project cathodic protection requirements under deep ocean exposure conditions. Thus, the lower temperature, pH and oxygen concentrations, often found with increasing depth should have a negative influence upon calcareous deposit formation. In addition, increasing pressure should result in enhanced calcium carbonate and magnesium carbonate solubility. Hence, it is anticipated that higher current densities are necessary for cathodic protection under these conditions.

(5) Substrate

Variations in data were obvious that could only be explained on the basis of an influence of substrate chemistry and/or microstructure upon calcareous deposit formation. These variations were reproducible and could be eliminated by either cleaning and reusing the same specimen or by using specimens sectioned from the same rod.

As summarizing remarks it is concluded that the roll of temperature, electrolyte hydrodynamics and variables related to sea water chemistry which influence calcareous deposit occurrence and formation have been quantitatively disclosed. Additional research is necessary:

- (a) To more comprehensively investigate the roll of the above variables.

- (b) To better define the rate controlling step or steps.
- (c) To investigate interactive effects.
- (d) To investigate the roll of other variables that could be of major importance (pressure and organics, for example).

A.3.b. Effort II - Calcareous Deposit Formation Within Corrosion Fatigue Cracks (W. H. Hartt)

- (1) The chemistry of calcareous deposits which form within simulated fatigue cracks was basically that of the external deposit except that areas of brucite (Mg(OH)_2) are more commonly encountered.
- (2) Morphology of deposits within simulate fatigue cracks was variable depending upon location and mechanical factors which influence crack electrolyte flow and, hence, mass transport conditions (reactant availability and product dissipation).
- (3) The density of calcareous material that deposited upon simulated fatigue crack surfaces appeared to be less than for the boldly exposed surfaces. This may have been due to reduced reactant availability or relatively high velocity during the ingestion-ejection process or both.
- (4) Potential profile within simulated fatigue cracks and under the conditions investigated was relatively flat and indicative of ready polarization down the length of the crack. This has been related to oxygen concentration polarization and to the protective character of the calcareous deposit which formed.
- (5) pH within the simulated crack was high and pH profile away from the crack surface may have been more modest than for the boldly exposed surface. This was probably influential with regard to the deposit morphology differences between these two areas.
- (6) Aspects of this problem which require further attention include a) electrical current profile within cracks and b) hydrodynamics and mass transport within cracks.

A.3.c. Effort III - Modeling (S. W. Smith)

In the past most models of calcareous deposit formation have been based on experimental data. The approach used in this modeling effort emphasizes electrochemical theory, rather than empirical results. This report has shown that the computer model fits the experimental data with reasonable accuracy.

By the approach taken the model cannot deal with actual offshore structures; however, this was not the intent. The techniques employed should be applicable to most finite element programs and are more general than empirical models. The main area of the model which needs more work is the hydrodynamic component. The present model is based on a flat plate and a more general hydrodynamic approach is needed.

The model can be easily expanded to incorporate new information as it becomes available. For example, it would be relatively easy to include any kinetic effects due to pressure by adding an algorithm to the rate constant equation. For these reasons the model developed is a significant step forward in the modeling of calcareous deposits.

B. Project II - Localized Corrosion

B.1. Project Organization and Objectives (S. C. Dexter)

The overall flow of Project II is shown in the block diagram of Figure 8. The four research elements in the Project were: 1) identification of rate controlling variables and processes by electrochemical laboratory work, 2) development and evaluation of accelerated laboratory test procedures, 3) mathematical modeling, and 4) natural seawater testing.

The specific objectives of Project II were to:

1. Clarify the roles of magnesium, copper, organic films and velocity of flow on the pitting corrosion of aluminum-magnesium alloys in seawater so that these variables can be included in the modeling and predictive steps.
2. Determine the effects of key factors such as: crevice geometry, surface finish, cathode-to-anode area ratio, seawater temperature and seawater velocity on crevice corrosion of a series of stainless alloys. Use this experimental information to complement the modeling process and ultimately to improve predictive capabilities.

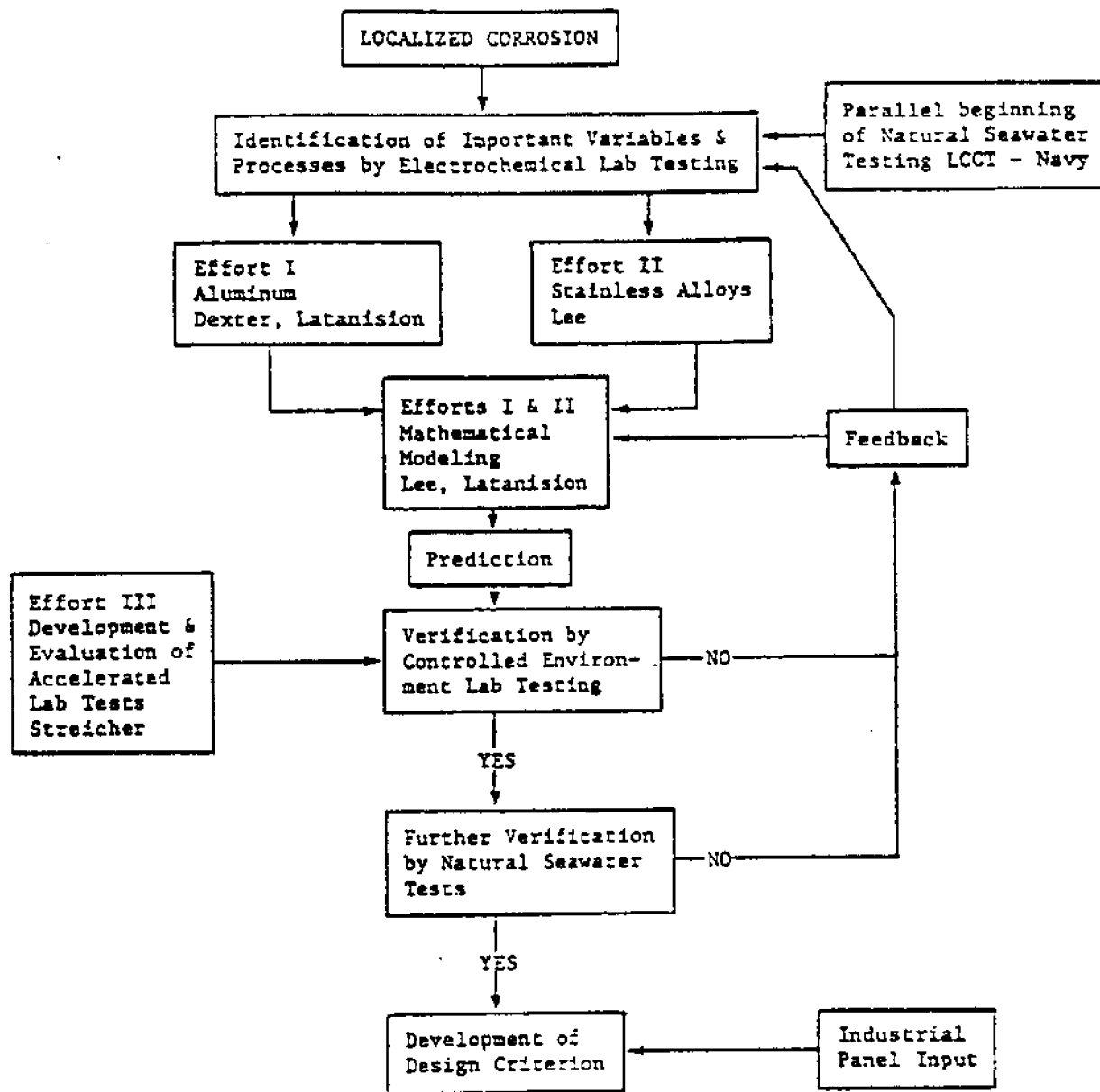


Figure 8 Research Plan for Project II

3. Evaluate and develop two types of accelerated laboratory tests for use in the first verification step of Figure 8 for stainless alloys and for further seawater alloy development activities. The two accelerated tests chosen were the Ferric Chloride Crevice Test and the Critical Crevice Temperature Test involving application of controlled anodic currents at a series of increasing temperatures.

B.2. Aluminum Alloys (S. C. Dexter and R. M. Latanision)

B.2.a. Background Information

It is now well established that the corrosion processes which occur on aluminum in natural seawater are more complex than those which occur in salt water of equivalent chloride content. The differences have been documented by both electrochemical and surface analytical techniques (1-3). One of the important differences between seawater and salt water is the presence of the magnesium cation in natural seawater. Dexter (2, 4) has shown that the presence of magnesium, either in the alloy or in the electrolyte, has a significant effect on the cathodic kinetics of the corrosion reaction. It has also been shown that large concentrations of magnesium are present on unalloyed aluminum surfaces corroded in seawater (3). It was, therefore, important to understand how and why magnesium appears on aluminum surfaces corroded in seawater. Several important questions to be answered were:

- 1) What is the source of the excess magnesium in the surface film. Does it come from the metal, the water or both, and what is the reaction by which it is deposited;
- 2) How much magnesium in the water or the alloy is needed to effect the cathode kinetics; and
- 3) Do other divalent cations present in seawater produce an effect similar to that of Mg?

Another factor that can be important in both laboratory saline solutions and natural seawater is the concentration of dissolved copper. Concentrations of copper as low as 10 to 30 ppb in the electrolyte can have a deleterious effect on the corrosion of aluminum due to an exchange reaction, which results in depolarization of the cathode (4). Unpolluted natural seawater generally contains less than 1 ppb copper, and less than 1% of that is present as Cu^{2+} , the majority being present

as dissolved $\text{Cu}(\text{OH})_2$ and CuCO_3 (5). Higher concentrations of copper can be present if there are local sources of input available. Copper alloy piping and cuprous oxide antifouling paints are two common sources.

Thus it was an important part of the Project to determine:

- 1) whether or not all of the above copper species would react with the aluminum surface, and
- 2) if there is a minimum concentration of copper below which the exchange reaction will not occur.

The final variable we wished to address was that of velocity of flow. Laboratory tests are often done under quiescent conditions, whereas natural seawater is usually in motion due to the action of wind driven waves or tidal currents and usually at velocities less than 1 meter per second. While much work had been done at velocities from 1 to 30 m/sec, very little had been done on the effects of lower velocities. We set out to determine:

- 1) If velocities in the 0 to 100 cm/sec range would have a significant effect on the cathodic kinetics already documented (1-4), and
- 2) If an increase in velocity under deep ocean conditions of low temperatures, oxygen and pH could lead to a significant increase in corrosion rate.

B.2.b. Effect of Magnesium and Other Divalent Cations

In this study, a combination of electrochemical experiments, surface analytical experiments and modeling techniques were used to investigate aluminum surfaces corroding in seawater and in artificial saline solutions.

The major divalent cations and their approximate concentrations in full strength natural seawater are: magnesium at 1290 ppm, calcium at 412 ppm and strontium at 8 ppm. A series of cathodic polarization experiments were done on 99.99% Al in a 3% NaCl + 140 ppm HCO_3 solution to which varying concentrations of the above cations had been added. These experiments clearly showed that 150 to 200 ppm of magnesium added as the chloride salt was sufficient to cause the observed depolarizing effect on cathode kinetics (6). This is far less magnesium than is present in full strength seawater, and shows that magnesium in the water

can have an influence on corrosion of aluminum in brackish waters of salinity as low as 4 to 5 parts per thousand. It was also discovered, however, that the magnesium effect disappeared after the electrode had been immersed for about 24 hours. The reason for this is not known, but it was confirmed by careful experimentation that it was not due to a depletion of magnesium in the test solution over that time period. Further experiments showed that additions of calcium and strontium in amounts up to their full strength seawater concentrations had no measurable effect on cathode kinetics (6).

In order to determine if magnesium in the alloy could produce the same effect on cathodic kinetics that it does in the water, a series of binary Al-Mg alloys were made for us by Alcoa Laboratories. Mr. Horst from the Industrial Advisory Panel was most helpful in the procurement of these special alloys. The alloys were produced on a 99.99% Al base with up to 2.5% Mg, corresponding to the concentration of Mg in commercial alloy 5052. It was found that the cathodic kinetics in 3% NaCl + HCO_3 solution were not affected by the presence of magnesium in the alloy.

That unexpected result was confirmed by another series of experiments (11) in which samples of alloy 5052 were exposed to both 3.5% NaCl solution and to natural seawater. After exposure, Auger spectra were taken at several sites on each specimen. The aluminum alloy 5052 exposed to a 3.5% NaCl showed no excess surface magnesium although the alloy contains 2.5% Mg. In contrast, the 5052 specimens exposed to natural seawater showed Mg concentrations in the barrier film comparable to those seen with pure aluminum (11).

A theoretical study employing a computer model based on thermodynamics was used (11) to investigate various chemical hypotheses for the mechanism of incorporation of magnesium into the surface film. The two mechanisms considered were: precipitation of magnesium hydroxide due to an increase in cathodic surface pH resulting from reduction of oxygen to OH^- ions, and physical adsorption.

The computer program used, MINEQL (7), with the Stanford Adsorption Package (8), allowed chemical speciation, precipitation, and adsorption to be investigated. For the computer modeling experiment, the surface

oxide was assumed to be γ -alumina. This was done for convenience because constants for the adsorption of Cu, Pb, Cd, Na, Cl and Zn on γ -alumina were obtainable from publications by Davis et al. (9, 10).

Experimental data on surface concentrations of Mg for comparison to the computer model predictions were obtained by immersing samples of aluminum alloys 1100 and 5052 to natural seawater, whose pH was controlled at various values within the seawater range of 7.2 to 8.1 by varying the amount of dissolved carbon dioxide in the water. Surface concentrations of Mg after exposure were determined by surface chemical analysis using a Scanning Auger Microprobe (SAM).

The pH values versus adsorbed Mg predicted by the computer model agreed with the experimentally determined surface coverages on the specimens exposed to natural seawater with organics present. At pH 8.1, the model predicted a surface composition of 8.5% Mg, while surface coverage determined by SAM was 7.8% (standard deviation 2.7%).

The possibility that the magnesium present on the aluminum surface was a result of the precipitation of magnesium hydroxide due to an increase in the pH resulting from cathodic activity was considered. The computer model showed that $\text{Mg}(\text{OH})_2$ is not predicted to precipitate until a pH of around 9.0. At low current densities on freely corroding surfaces, the pH is probably below 9.0. In addition, pure alumina colloids show magnesium on their surfaces with no cathodic reactions occurring (12). For these reasons, it was thought unlikely that precipitation of $\text{Mg}(\text{OH})_2$ is the major source of magnesium on aluminum surfaces during seawater exposure.

These studies showed that the surface films of aluminum corroded in seawater are different than those formed in simple salt solutions. The major difference was the presence of magnesium on the surface. Adsorption chemistry predicted the correct relation between surface magnesium concentration and pH and gave reasonable results for surface concentrations of other cations. Moreover, an adsorption process would not require the large changes in surface pH that would be required if the magnesium were due to precipitated magnesium hydroxide. When magnesium was present as an alloying addition, it did not appear on the

surface after exposure to a 3.5% NaCl solution. Rather, it seems that only magnesium in the electrolyte will appear as a surface species after corrosion has occurred.

These results are consistent with Rowland and Dexter's hypothesis (2) that magnesium acts as a catalyst for reduction of percarbonic acid. That mechanism would require free Mg^{2+} ions to be present in the water immediately adjacent to the surface. Since the reaction is specific to magnesium, the hypothesis predicted the result that other divalent cations would not have the same effect. The percarbonic acid reduction current, in the presence of magnesium, was hypothesized to add to that of the oxygen reduction reaction in depolarizing the cathode.

The discovery that the magnesium effect disappears with time over 24 hours leads to the conclusion that the effect is less important than was originally believed. Magnesium certainly has an effect on both cathode kinetics and film formation for short-term immersions. The presence of abundant magnesium in seawater is also seen as one contributing factor to the difference between the corrosion behavior of aluminum and its alloys in natural seawater and in saline solutions. Magnesium, along with bicarbonates, should be added to such solutions when they are being used to simulate natural seawater. The long-term effect of magnesium, however, is probably slight. Magnesium obviously plays a much less important role than that of the chloride ion.

B.2.c. Effect of Copper

Aluminum coupons were immersed in natural seawater purposely contaminated with various amounts of copper sulfate, and the surface concentrations of copper after exposure were measured by SAM analysis (11). In parallel with this work further investigations were done using the computer model for adsorption described in the previous section. The predicted surface concentration of copper due to adsorption was less than 10^{-10} moles per square meter for a seawater solution with 300 ppb copper. That surface concentration of copper would be undetectable by SAM analysis and would probably be insignificant to corrosion. However, copper could still be detected on the surface by SAM at solution concentrations as low as 100 ppb, and Dexter's earlier results (4) had shown a consistent effect on corrosion behavior at solution concentrations as low as 30 ppb, with sporadic effects at concentrations as low

as 1 ppb. Therefore, adsorption was ruled out as a mechanism for the interaction of copper with aluminum in seawater. The expected mechanism of copper deposition was reduction of copper ions to the metallic state at the aluminum surface (3, 4). This mechanism was investigated with the computer model by examining changes in speciation of the copper as a function of electrochemical potential of the aluminum surface. At the concentration of chloride found in full strength seawater and a potential of -0.537 V SHE (the critical pitting potential of aluminum in seawater) the model predicts, in agreement with thermodynamics (13), that all the copper will be reduced to the metallic state. This was true even though less than 0.1% of the copper was predicted to be present as free copper ions with the majority present initially as $\text{Cu}(\text{OH})_2$ and CuCO_3 . Further calculations for lower concentrations of copper indicated that copper will be present in the reduced state when in contact with pitting aluminum even at much less than 1 ppb. However, the model was based strictly on thermodynamics, and a kinetic barrier, such as one due to a nucleation energy barrier for deposition was not considered. Since, this could be a significant factor at very low concentrations of copper, the question as to whether there is a minimum concentration of copper below which the exchange reaction will not take place has yet to be answered.

This study confirmed that: 1) the presence of copper on aluminum surfaces is due to reduction to metallic copper, rather than adsorption, and 2) all the copper in solution can react with the aluminum surface, not just the free copper ions. This being the case, it is apparent that the detailed speciation of copper in seawater as a function of pH, temperature and pressure is of no consequence to the corrosion of aluminum.

B.2.d. Effect of Flow Velocity (S. C. Dexter and W. Rigby)

The effect of flow speed of the electrolyte on the corrosion behavior of aluminum alloy 5052 was investigated by use of a specially constructed flow through system in which the flow speed could be controlled from 0.5 to 75 cm/sec. The test section in the flow through system consisted of a tubular alloy 5052 electrode held at each end in machined teflon holders.

An increase in the speed of water flowing past the electrode surface in these tests always had two effects. The first effect was to shift the corrosion potential in the active (or negative) direction. At a seawater pH of 7.5, the corrosion potential changed linearly with the logarithm of the flow speed over the range from 1 to 70 cm/sec. The shift was 80 mv in the active direction for each tenfold increase in flow speed within that range. The second effect was to depolarize the cathode by decreasing the slope of the cathodic polarization curve. The data are summarized for a seawater pH of 8.2 in Figure 9, and for pH 7.5 in Figure 10. Each of the shaded bands in these figures represents the envelope of all the polarization curves measured for a particular set of velocity and pH conditions. Note that at pH 8.2, the active shift in the corrosion potential is always larger than the decrease in slope, with the net result that an increase in flow velocity always increases polarization of the cathode.

At the lower pH, however, the decrease in slope at the higher flow speeds more than compensates for the active shift in corrosion potential, with the net result being a depolarization of the cathode at current densities greater than 3 $\mu\text{A}/\text{sq cm}$.

There was some concern that this net depolarization of the cathode at the low pH might create a super corrosive condition in the deep ocean. Dexter had shown previously that the low temperature and low pH of the deep ocean combine to make the corrosion potential very noble, which encourages pit initiation. When these conditions were coupled with high dissolved oxygen in the laboratory, both initiation and growth of pits were rapid. In the real ocean, the pH and dissolved oxygen are always coupled. When the pH is low, the oxygen is also low. There was concern, however, that in an application such as Ocean Thermal Energy Conversion, in which cold, deep ocean water is pumped through aluminum tubing, the increase in mass transport of oxygen to the tube wall induced by the flow might artificially create the highly corrosive condition. When the combination of low pH, low temperature and low dissolved oxygen was tried in the laboratory at different flow speeds, however, the super corrosive condition did not materialize. There was no systematic effect of an increase in flow speed in these tests. This lack of response to flow speed was attributed to sluggish reaction

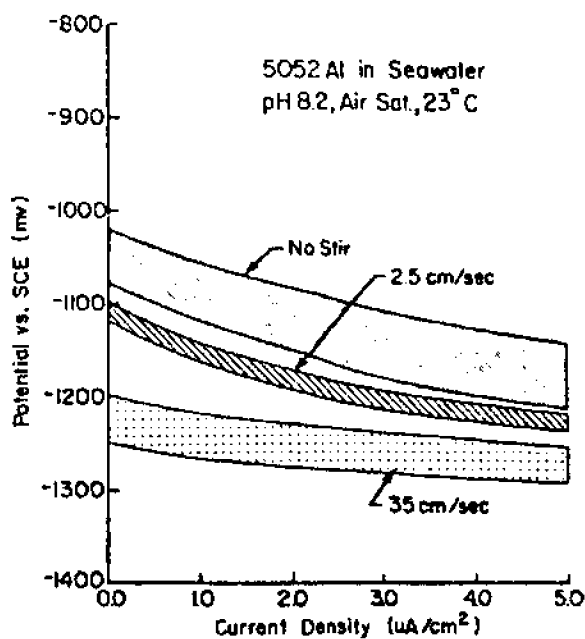


Fig. 9 - Cathodic polarization of alloy 5052 in pH 8.2 seawater in the flow through system as a function of flow rate.

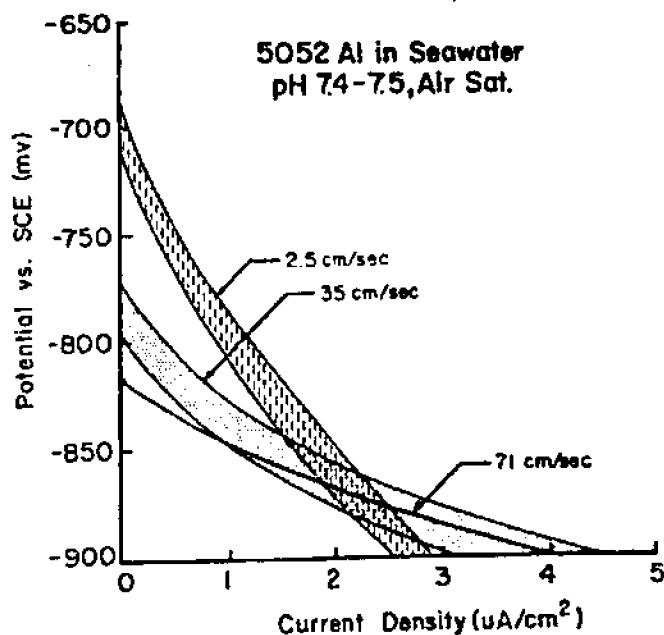


Fig. 10 - Cathodic polarization of alloy 5052 in pH 7.5 seawater in the flow through system as a function of flow rate.

kinetics at the low temperature. The results mean that one should not expect to find an immediate increase in the corrosivity of deep ocean water toward 5052 aluminum tubing just because the water is in motion. The laboratory tests, however, were run for short periods of time (less than 24 hours) compared to the 10 to 20 year desired lifetimes for commercial OTEC heat exchanger tubing. Thus, there may still be cause for concern about the corrosivity of cold, deep waters over long time periods, or at intermediate temperature and oxygen conditions.

B.2.e. Scanning Potential Microprobe Study of Pit Initiation on Aluminum (R. M. Latanision)

The Scanning Potential Microprobe (SPM) has been designed and built to study localized corrosion in situ. When examining specimens which have been exposed to salt water or seawater using Scanning Auger Microscopy, it is difficult to distinguish pits which were active at the time of removal from the electrolyte from pits which had passivated. Also, sites of cathodic activity cannot be easily identified. The SPM was developed to address these problems. With this apparatus, pit initiation and growth can be monitored on the metal sample surface while exposed to the electrolyte. The mapping of incipient pits was accomplished by scanning the surface with a vibrating metal microelectrode held 100 μm above the sample surface (See Figure 11). The vibration of the probe by a piezoelectric crystal allows the use of a frequency-specific amplifier for recording a more noise-free signal from the sensitive platinum microprobe tip. The advantage of using a metal microelectrode is that it has low resistance even with a small diameter, in contrast to a glass capillary electrode filled with a salt solution (14). The probe motion and data collection are computer-controlled for flexibility and storage.

The microelectrode senses potential gradients in the electrolyte due to current flow through the solution from an anode to a cathode site. An auxillary microelectrode several centimeters from the surface measures the overall solution potential, which is subtracted from the local potential. In this way, deviations from the overall potential are detected. The SPM generates a quasi-three-dimensional map of the surface on an X-Y recorder, showing anodic sites (pits) as "hills" and cathodic sites as "valleys". The SPM was based on the design of Ishikawa and

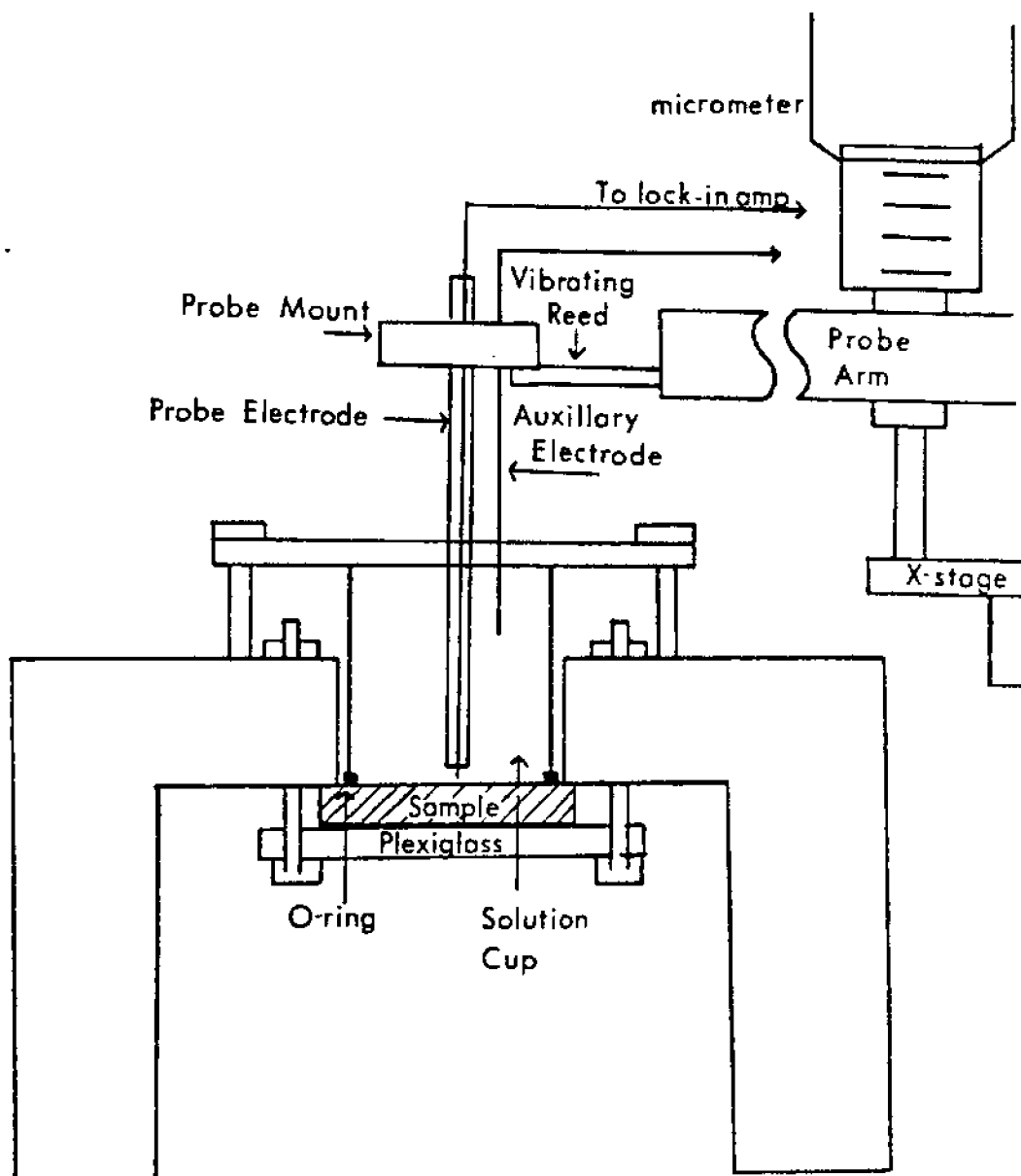


Fig. 11 Detail of electrodes and sample stage.

Isaacs (15) but was modified to optimize spatial resolution so that the location of newly initiated pits could be mapped. Spatial resolution on the order of tens of microns was achieved. This level of resolution was proven by correlating SPM maps showing pit sites with SEM photomicrographs of the surface. Two experimental parameters were found to be most important for high resolution. The conductivity of the solution must be relatively low (specific conductivity less than $10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$), and the probe tip must be small so that the probe can be held very close to the surface. This is because the potential gradients drop off very quickly due to the conductivity of the electrolyte. Therefore, a special sample stage was designed to keep the probe traveling parallel to the polished sample surface.

The SPM was used to locate active pit sites on the surface of aluminum alloys 5052 and 3003 exposed to an electrolyte containing NaCl, MgCl_2 and Na_2SO_4 . Seawater could not be used due to its high conductivity. The electrolytes used were based on the three major components of ASTM synthetic seawater so that the influence of magnesium could be studied. After an SPM map was completed, an SEM photograph of the surface was made. Sites of anodic activity on the SPM map were correlated with pits on the aluminum alloy surface. Then, the surface region around these pits was analyzed using the SAM. Excess surface concentrations of magnesium were found within 4 to 5 μm of the pit sites, as had been found in previous work with pure aluminum in seawater.

The SPM study has confirmed the presence of significant magnesium concentrations on aluminum alloy surfaces after exposure to Mg-containing electrolytes, particularly near pit sites. The level of resolution achieved with this version of the SPM represents a significant advance over previous implementations of this technique. It will hopefully be used in the future to identify cathodic sites on pitted aluminum in order to increase understanding of the cathodic processes associated with aluminum corrosion in seawater.

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B.3. Stainless Alloys (T. S. Lee and M. A. Streicher)

B.3.a. Multiple and Remote Crevice Assembly Tests (T. S. Lee and R. M. Cain)

Two test methodologies have been employed in the natural environment crevice corrosion tests conducted at the LaQue Center for Corrosion Technology, Inc. Both test techniques, the multiple crevice assembly and remote crevice assembly, are applicable in natural seawater and require no artificial or external stimulus to result in spontaneous crevice corrosion of a number of iron and nickel base alloys. The methods differ somewhat, however, in that the multiple crevice assembly is primarily of use as a screening tool to evaluate alloy susceptibility to crevice corrosion initiation with limited information on crevice propagation behavior. By contrast, the remote crevice assembly provides a quantitative indication of both time to initiation of crevice corrosion as well as rate of crevice corrosion propagation. Both of the methods have been used in studies to investigate effects of various factors on crevice corrosion.

(1) Effect of Crevice Geometry

The multiple crevice assembly has been frequently used to evaluate crevice corrosion behavior in seawater as well as in other chloride-containing environments. Many of the test programs have resulted in variability between seemingly replicate tests. This can be attributed to many factors, but one of the most significant factors is crevice geometry.

Actual crevice gaps which initially exist on crevice test assemblies have been characterized by scanning electron microscopy. These analyses have shown that a wide range in crevice gap can exist on a single crevice former. Gaps ranging from $< 0.1 \mu\text{m}$ to $2-3 \mu\text{m}$ in width have been documented. These data have provided input into mathematical model analyses which demonstrate the impact of this variation on crevice corrosion initiation. These analyses have also guided proper use and understanding of the experimental methods in crevice corrosion research.

Providing and defining a practical, consistent initial crevice gap has been a goal of this research. With the multiple and remote crevice assembly, the use of a specified initial tightening torque for securing the loading bolts on the crevice formers has enhanced reproducibility

while maintaining a practical experimental method useful for screening purposes. A more elaborate approach of applying a constant load on the crevice former through the use of a hydraulic piston has also been developed. While this maintains a constant crevice geometry until initiation of crevice corrosion occurs, the effective gap will be altered as soon as propagation commences.

One further development of this research on crevice geometry effects has been the implementation of a modified remote crevice assembly. This method, termed a compartmentalized cell, removes crevice geometry as a variable by utilizing an "anode" specimen in a simulated crevice solution coupled to a "cathode" specimen in the natural, bulk environment. In concert with the mathematical model, this tool allows studies on the effect of crevice solution composition on both the initiation phase and, more importantly, the propagation phase of crevice corrosion.

(2) Effect of Metallurgical Factors

Both the multiple and remote crevice assemblies have been used to characterize relative alloy behavior. The resultant data have been employed to evaluate the initiation and propagation behavior of numerous alloys as will be discussed in a later section.

The methods have also been applied to investigate effects of surface treatment on alloy crevice corrosion behavior. It has been observed that, in general, a surface ground finish will promote a more rapid occurrence and a greater degree of crevice initiation than will a "mill-finish" surface. This has been attributed to either the establishment of a more uniform surface which would promote a more consistently tight crevice, or to the exposure at the surface of inclusions resulting from removal of the mill finish.

(3) Effect of Environmental Factors

Among the environmental factors which will influence crevice corrosion behavior are:

- the pH and chloride level of both the crevice environment and the bulk environment
- the temperature of the environment
- the velocity of the seawater
- the level of dissolved oxygen in the bulk environment

Multiple and remote crevice assembly data have demonstrated that a decrease in bulk environment chloride level will decrease the extent of crevice corrosion. A more significant factor, however, is the nature of the environment. Specifically, it has been documented that the degree of crevice corrosion incurred in ambient temperature natural seawater is at least an order of magnitude greater than in comparable chloride containing solutions of synthetic seawater or sodium chloride (Figure 12).

Compartmentalized cell tests have shown that an increased acidity and chloride content of the crevice solution will increase the rate of propagation. These data have also been correlated with anodic polarization characteristics to explain observed crevice corrosion behavior.

Increasing seawater temperature has been shown to have a unique effect on crevice corrosion behavior in that a dramatic reduction in propagation rate occurs when temperatures exceed 45°C. This reduced propagation behavior extends at least to 70°C. Increased temperature obviously reduced oxygen solubility and compartmentalized cell tests have demonstrated the effect of bulk environment oxygen level on crevice corrosion (Figure 13). However, the magnitude of this effect is not sufficient by itself to explain the observed behavior in natural seawater. Further studies will be required to fully understand this phenomenon.

A final environmental factor of interest is seawater velocity. Velocity is a particularly important parameter in seawater systems in that low design velocities can allow settlement of debris or fouling organisms which form crevice sites. Conversely, higher velocities may prevent this settlement and flush solution out of other crevices such that a detrimental acid-chloride solution may not form. While remote crevice assembly tests were inconclusive in defining effects of solution velocity on crevice propagation rates, other immersion tests have shown that increased velocity will increase the extent of crevice corrosion under certain conditions. These can be related to the available boldly exposed cathode area available to sustain anodic reactions within the crevice.

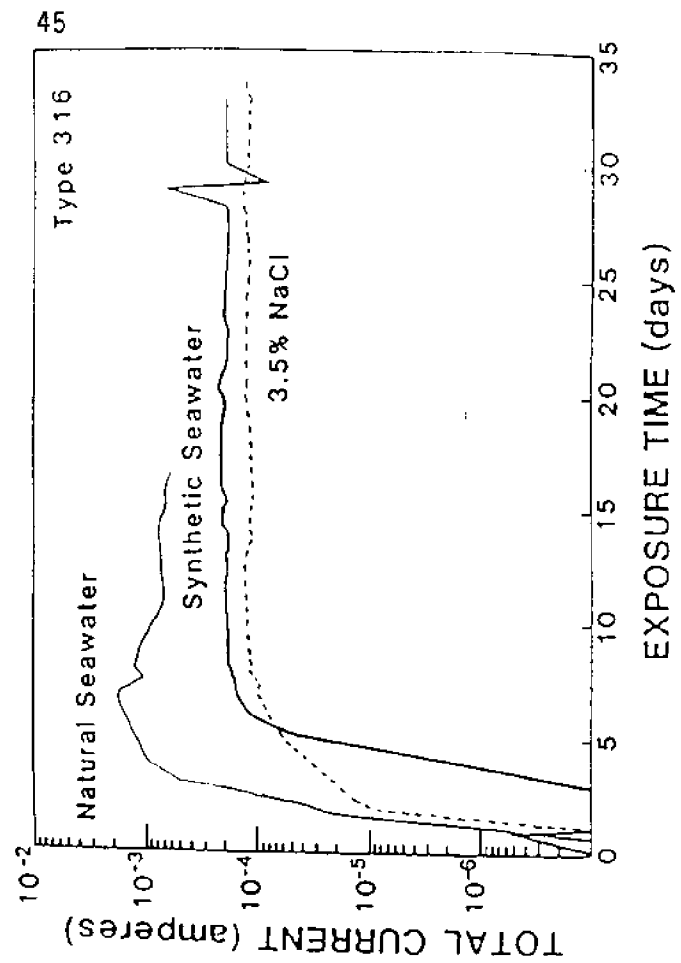
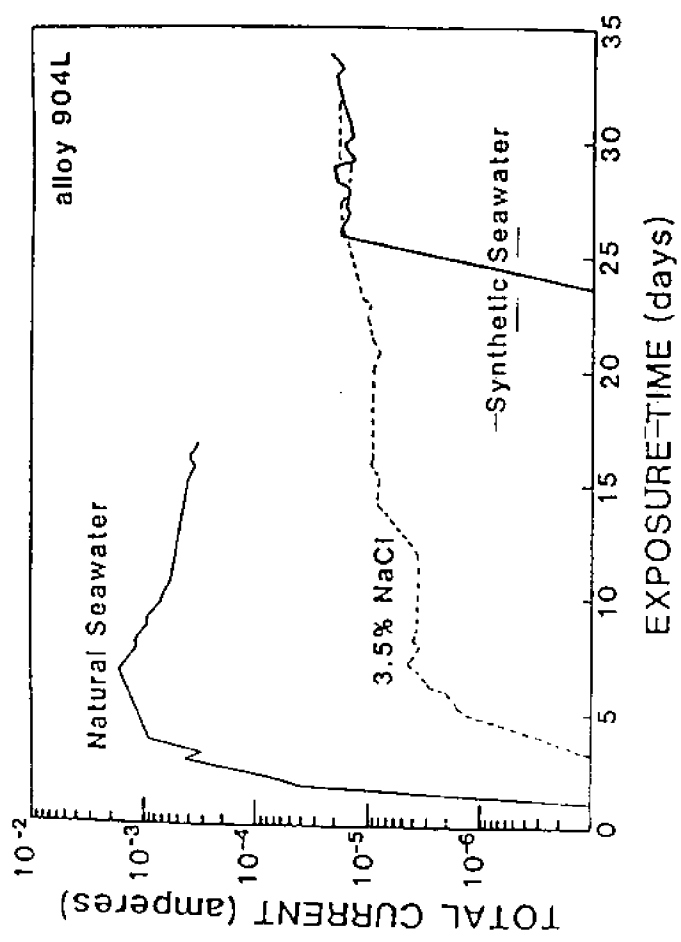
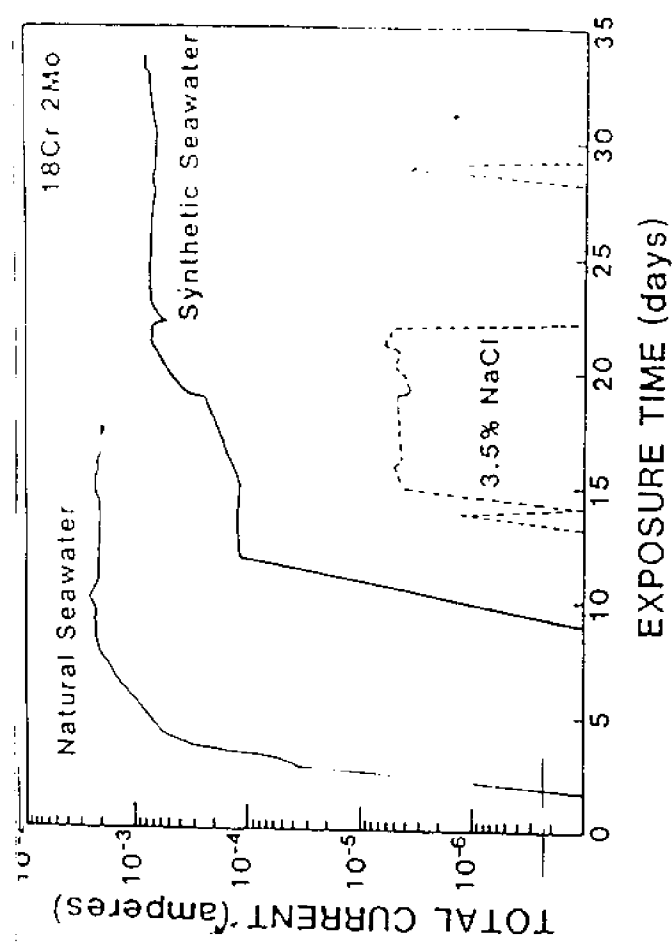
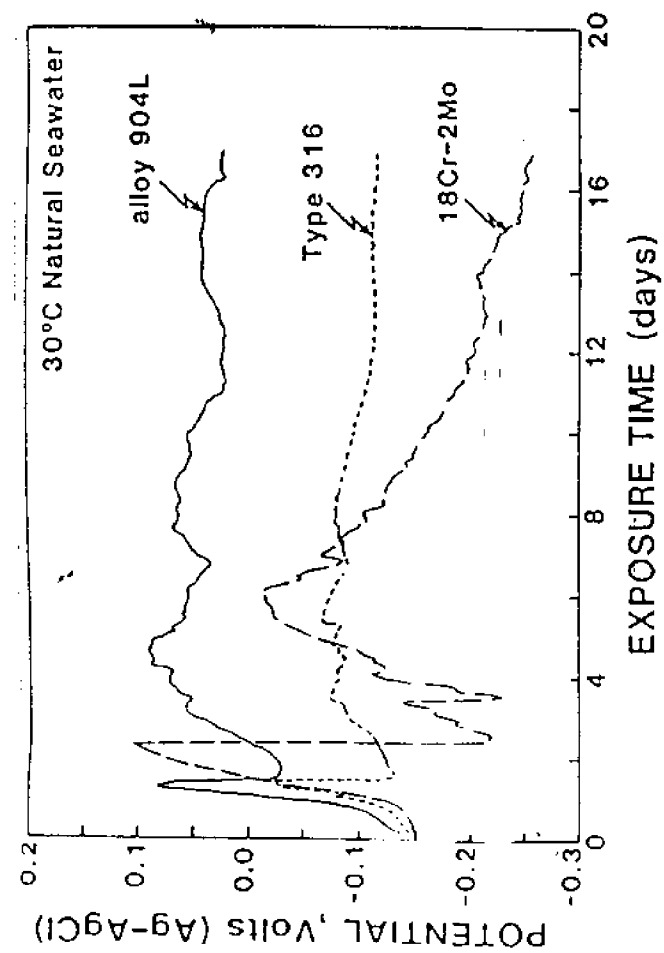


Figure 12 Remote crevice assembly test data describing the effects of alloy content and bulk environment on crevice corrosion resistance of stainless steels. Greater currents measured in natural seawater tests are indicative of higher crevice corrosion rates.

(4) Effect of Electrochemical Factors

Galvanic coupling with steel has been previously recognized as a viable means of affording protection to stainless steel. Carbon steel anodes which are 1/10 and 1/100 the area of the stainless steel surface area have been shown to prevent crevice corrosion of Type 316 in 28 day tests in low velocity seawater at 14°C. Unprotected samples corroded to a depth of up to 1.27 mm. Similar tests conducted in somewhat warmer seawater (i.e., 22-28°C) were also successful in controlling crevice corrosion for stainless steel to steel area ratios of 50:1. While some initiation of corrosion and slight penetration (0.02 mm maximum in 30 days) were measured at the 50:1 area ratio, the extent of penetration was more than two orders of magnitude less than that reported for uncoupled specimens.

Potential data reported for the 14°C seawater test show that values for unprotected specimens ($-0.030 \text{ V}_{\text{SCE}}$) approximate potentials for Type 316 undergoing crevice corrosion. Coupling with carbon steel resulted in an expected shift to more active potentials (-0.400 to -0.490 V). Increasing the stainless steel area reduced the degree of polarization (Figure 14a).

These couple potentials are more active to, or closely approximate, the corrosion potential for Type 316 exposed in deaerated, simulated crevice solutions (25°C) in the pH range 0.8 to 1.5. Any polarization resulting in potentials more negative than about -0.4 V would cathodically protect Type 316 in an aggressive crevice solution (Figure 14b). If the potential within a crevice is in the active potential regime (i.e., -0.3 to -0.4 V , approximately) or is more noble than the break-through potentials (-0.15 V in this case), then crevice corrosion propagation would be expected.

In cases where polarization due to coupling with carbon steel is not sufficient to adjust the potential of the stainless steel to the cathodic region, reduction in crevice corrosion propagation is still possible. This could result should the crevice potential be maintained in the passive region or at low currents associated with potentials active to the anodic peak. This was apparently the case where some slight penetration was observed in the warm seawater tests at the 50:1 stainless steel to steel area ratio.

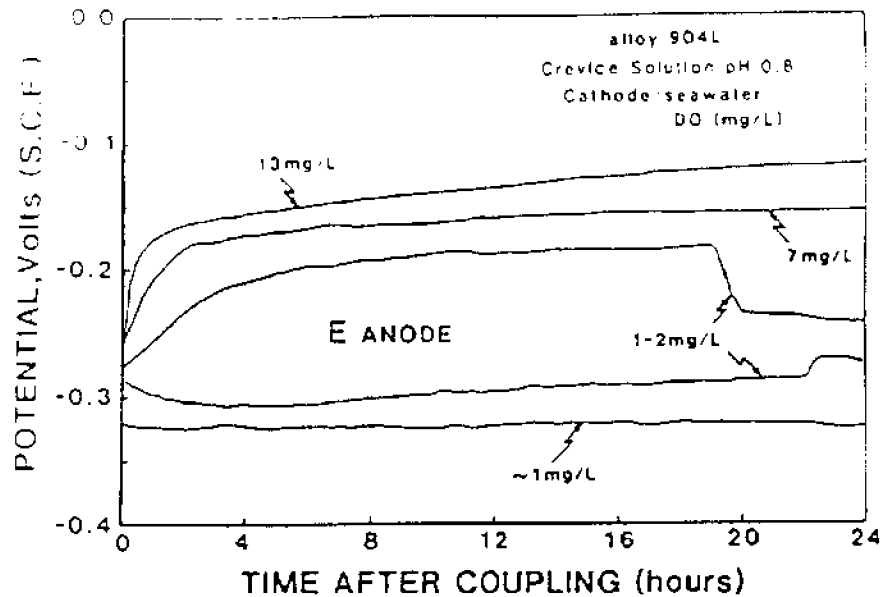


Figure 13 Compartmentalized cell test results describing the effect of bulk seawater oxygen concentration on polarization behavior of the anode member in a deaerated, simulated crevice solution. The differences in oxygen concentration, along with variations in cathode:anode areas, can cause a shift in the anode from one potential regime to another.

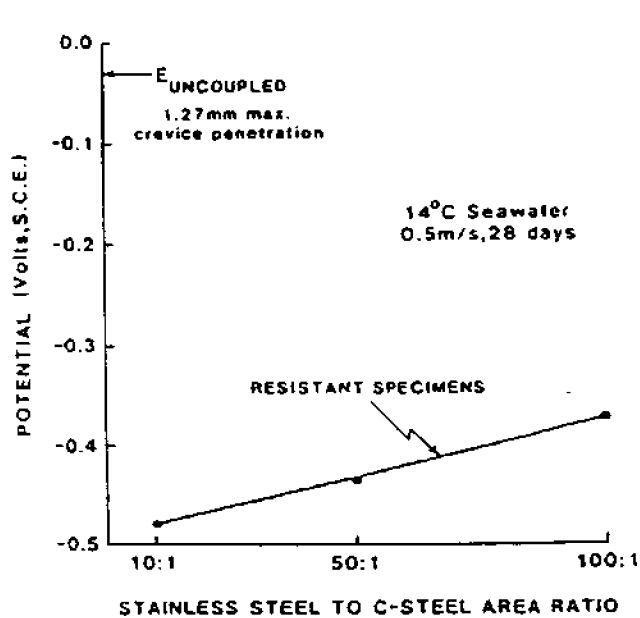


Figure 14a Potentials for coupled and uncoupled Type 316 stainless steel with multiple crevice assemblies.

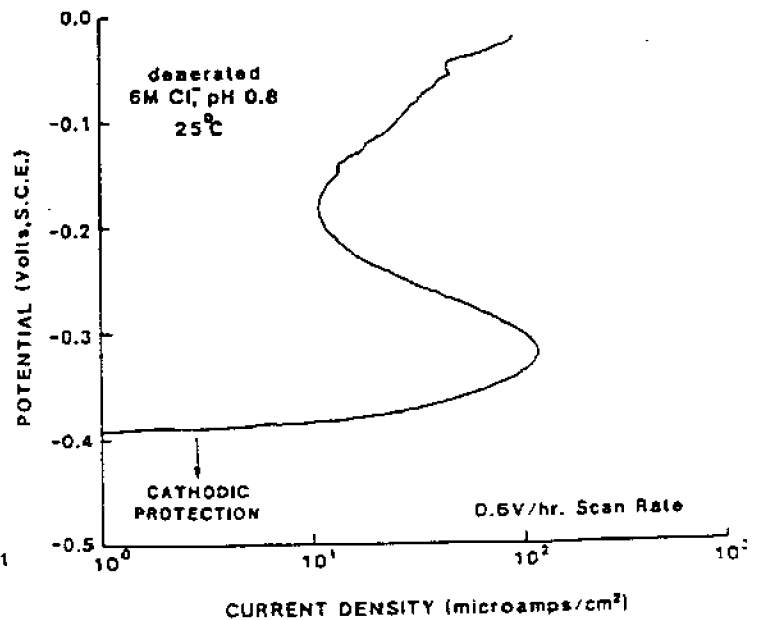


Figure 14b Anodic polarization curve for Type 316 stainless steel in simulated crevice solution. Cathodic protection is possible at potentials more active to -0.4 Volts.

B.3.b. Progress in Mathematical Modeling

A mathematical model of crevice corrosion, originally developed by J. W. Oldfield and W. H. Sutton, has been utilized to complement the multiple and remote crevice assembly testing. This computer model is based on the commonly accepted mechanism of crevice corrosion of stainless alloys involving deaeration, acidification and concentration of chlorides, breakdown of passivity and, finally, propagation. Crevice corrosion initiation resistance can be predicted upon input of values for a number of environmental, geometric, metallurgical and electrochemical parameters.

While some inputs represent known factors for a given situation, e.g., bulk environment and alloy composition, others such as crevice geometry are variable and may be assumed or measured. The model also requires inputs of a theoretical nature (chemical equilibria) and information based on electrochemical experimentation to identify critical crevice solution concentrations.

The initiation model is valuable in differentiating the times to predicted breakdown of passivity for a variety of alloy compositions/crevice geometry combinations. At present, the model does not provide an accurate prediction of the performance for the new super-ferritic alloys relative to observed excellent crevice corrosion resistance. On the other hand, the utility of the initial model has been further enhanced by the quantifications of crevice gap dimensions for a variety of crevice formers used in research and field applications.

Recent refinements and extension of the model have been directed at incorporation of the propagation stage of crevice corrosion. The propagation model considers crevice corrosion propagation in terms of an electrochemical cell with an anode, the actively dissolving alloy within the crevice, and a cathode, usually sustaining oxygen reduction outside the crevice and/or hydrogen evolution within the crevice. This model has shown the importance of additional parameters such as the corrosion cell voltage and the electrochemical response of an alloy in acid-chloride solutions on crevice corrosion of stainless steels. Among

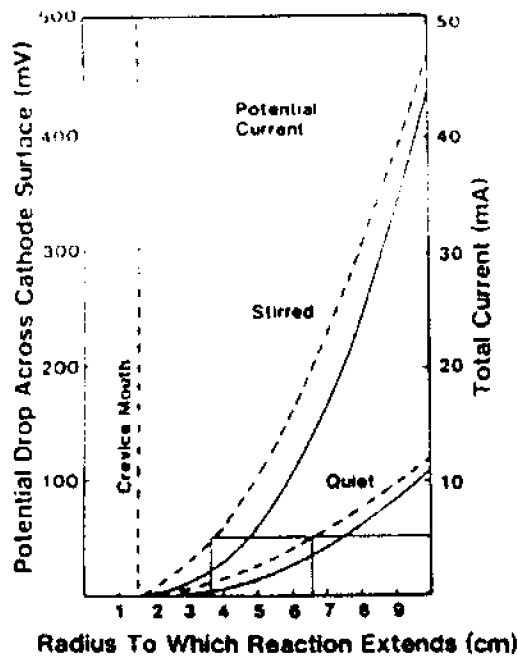
the conclusions which can be drawn from use of the preliminary propagation model are:

- the role of oxygen reduction on cathode surfaces can be modeled to demonstrate critical cathode to anode area ratios required to sustain crevice corrosion (Figure 15a and 15b). This can also be related to effects of solution velocity on cathodic oxygen reduction. These results were found to correlate well with actual immersion test results involving different size test panels exposed in quiescent and low velocity seawater.
- the role of crevice geometry, particularly the initial gap dimension, may have different effects on propagation for different alloys. In addition, the effect, in some cases, may be opposite to that governing the initiation phase of crevice corrosion.

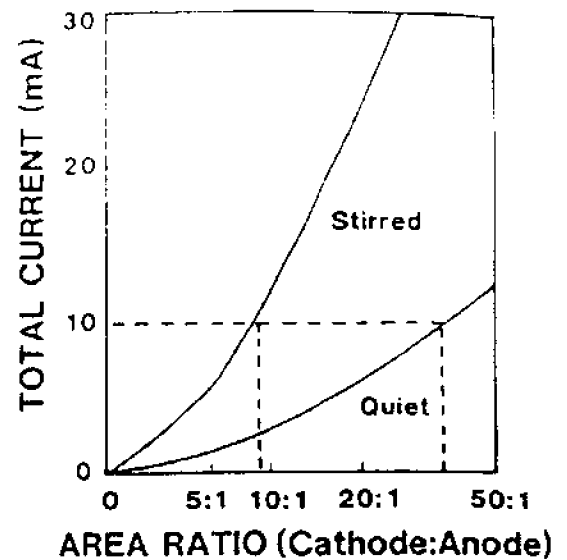
Figure 16a represents behavior of an alloy which demonstrates relatively "poor" resistance to propagation of crevice corrosion as evidenced by the rapid increase in propagation current as the pH in the crevice decreases. The horizontal lines reflect limiting propagation rates which would result from IR restrictions. Limiting rates for three different assumed crevice gaps are shown.

The data show that the propagation rate in this IR limited condition increases with increasing crevice gap. This is opposite to the effect of crevice geometry on crevice initiation where a tighter crevice is more severe. In this particular case, however, the large gap results in a large volume of electrolyte in the crevice and, hence, a lower resistance. This lower resistance results in a higher allowable maximum current for propagation.

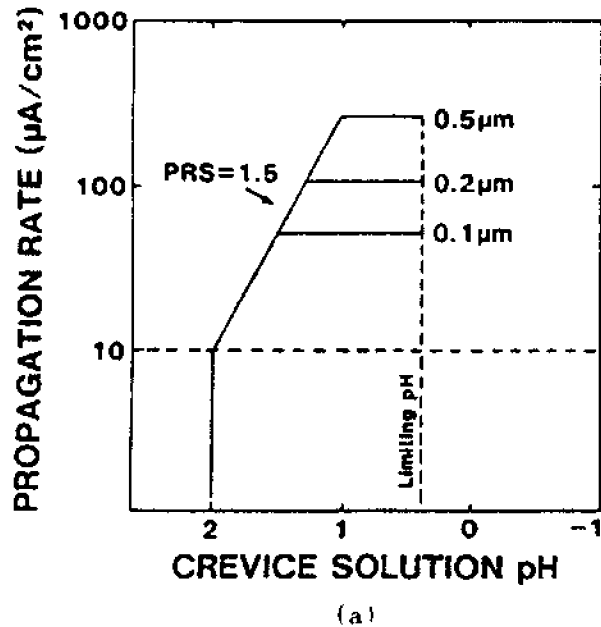
This particular effect of increasing gap allowing a higher propagation rate is often counteracted, however, by the effect of mass transport on the crevice solution composition. As the effective crevice gap is increased, either in original design or as a result of ongoing crevice corrosion, an increase in propagation rate can be expected only to the point where diffusion of chloride and hydrogen ions from the crevice confines is enhanced. At that point, the pH within the crevice



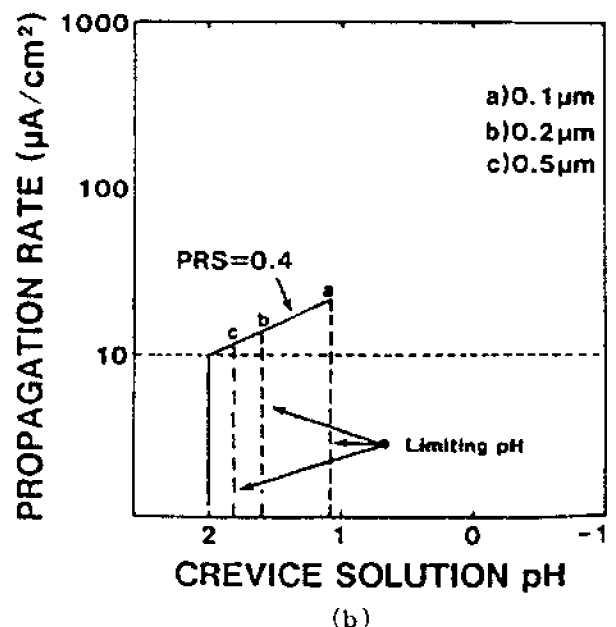
15a: Plot of potential drop across the cathode and total oxygen reduction current in quiet and stirred seawater as a function of distance from the crevice mouth.



15b: Predicted limits for crevice corrosion propagation due to limiting cathodic reduction currents. Area ratio function converted from radial distance.



(a)



(b)

Figure 16. Predicted crevice corrosion propagation rates as a function of crevice gap (degree of tightness) for stainless steels with low resistance (a) and better resistance (b). While both materials will initiate at pH=2, differences in the propagation rate slope (PRS) can effect the extent of corrosion.

may increase with the net result of a decrease in overall propagation current. This can be seen in Figure 16a where an order of magnitude decrease in propagation rate is observed with an increase in crevice solution pH of less than one unit.

An opposite effect of crevice gap is shown in Figure 16b which demonstrates the same type of data for a stainless steel with the same initiation resistance as before but with a more shallow log propagation current peak versus pH slope (by definition, a greater resistance to propagation than in the previous case). With this alloy, the IR limited conditions are not reached for the gaps considered and the limiting crevice solution pH is reached as a result of mass transfer restrictions. In this situation, the tighter crevices result in the development of a lower pH crevice solution and a resultant higher propagation rate. Referring to the experimental data shown in Figure 17 (in section 3e), it can be seen that the maximum depth of attack was decreased for alloys G, 6X and 20 mod when the less tight crevice gaps created by the lower assembly torque of 2.8 Nm were used. For all three alloys, propagation resistance behavior, as depicted in Figure 16b, has been measured.

B.3.c. Role of Bacteria in Crevice Corrosion Initiation (S. C. Dexter)

The initial step in the nucleation of crevice corrosion is depletion of dissolved oxygen in the crevice water. One critical input to the Oldfield model of crevice corrosion is the calculation of the time for oxygen depletion. The mechanism of depletion has usually been assumed to be electrochemical wastage of the metal within the crevice at the passive current density, i_p , but the question has been raised as to whether marine bacteria in the crevice water could make a significant contribution to the depletion process.

The Oldfield model predicts that the electrochemical mechanism alone is capable of depleting the oxygen in less than 15 minutes. Therefore, it may not matter in a practical sense whether or not microorganisms in the crevice water contribute much to the overall rate of oxygen utilization. However, it is important to our understanding of the mechanism of crevice corrosion to measure the relative contributions of the two mechanisms.

The well-known active shift in corrosion potential of a platinum electrode with decreasing dissolved oxygen concentration has been utilized to make the desired measurements using special cells constructed of either AISI type 316 stainless steel or polytetrafluoroethylene (TFE). The platinum electrode, along with a silver-silver chloride reference electrode, was mounted in the cap of the cell. The seawater in the cell was either left natural or sterilized. Thus, the following sets of conditions could be achieved: 1) electrochemical oxygen utilization alone using sterile water in the stainless steel cell, 2) biological utilization alone using natural seawater in the TFE cell, 3) electrochemical and biological utilization together using natural seawater in the stainless cell, or 4) no mechanism for utilization at all (other than passive wasting on the platinum and reference electrodes) using the TFE cell with sterile seawater.

The results indicated that the electrochemical and biological mechanisms produce roughly equivalent rates of oxygen utilization in our test cells. It should be remembered, however, that the biological mechanism is a volume effect, while the electrochemical mechanism is a surface effect. The surface-to-volume ratio in our cells was about 5 cm^{-1} , while that in a typical crevice is over 750 cm^{-1} . When the results were adjusted for this difference in surface-to-volume ratio, the electrochemical mechanism was favored by more than 150 to one.

For our cell geometry, it took about 24 hours for either of the two mechanisms to bring the dissolved oxygen all the way to zero. When translating those results to a crevice geometry, one would expect that the biological mechanism, being a volume effect, would not change much if the concentration of bacterial cells in the water was not changed. On the other hand, the electrochemical mechanism should be accelerated by a factor of about 150 due to the increase in the surface-to-volume ratio. Thus, our results predict that electrochemical oxygen depletion in the crevice should be complete in about $(24)/(150) = 0.16$ hours, or about 10 minutes. This value is in excellent agreement with predictions from the Oldfield model.

We have concluded that:

- (1) For clean stainless steel surfaces and natural seawater, the rates of electrochemical and biological utilization of dissolved oxygen are about equal for the geometry of the cells used in these experiments, that is, when the surface-to-volume ratio is less than about 10.
- (2) When the surface-to-volume ratio is 500 to 1000, as is probably typical for crevices in marine service, the electrochemical mechanism for oxygen utilization dominates by a factor of about 150.
- (3) The estimated time for oxygen depletion by electrochemical reduction, as predicted from our data corrected for crevice geometry, is in excellent agreement with predictions from the mathematical model of Oldfield.

B.3.d. Accelerated Testing (M. A. Streicher and N. Nagaswami)

The research at the University of Delaware on crevice corrosion of stainless alloys in chloride environments was undertaken to meet the need for a rapid laboratory crevice corrosion test which can be used a) to rank metals and alloys for service in marine environments, b) to investigate the effect of alloying and residual elements in crevice corrosion, c) to develop new, more economical alloy compositions having improved resistance in such environments, and d) to investigate the mechanism of crevice corrosion.

Under programs sponsored by the Navy and by the Ocean Thermal Energy (OTEC) program at the LaQue Center for Corrosion Technology, Inc., Wrightsville Beach, North Carolina a total of 46 different stainless alloys had been tested for their resistance to crevice corrosion in natural, filtered sea water at 30°C for periods up to 90 days. The data from these tests, as well as the metals used for these tests, were made available for our efforts to develop and use accelerated laboratory test methods.

In order to compare the results of various rapid laboratory test methods with the results of the long-time sea water tests, it was necessary to analyse the results of the seawater data for the effect of alloy composition (Cr, Mo, Ni, Mn, Cu, Nb, Ti) surface finish and such

test variables as length of testing, time and torque on the plastic crevice devices. A method for ranking alloys, based on a Crevice Corrosion Index (CCI), was developed. $CCI = S \times D$, where S is the number of panel faces showing crevice attack in a group of at least 3 panels (6 faces), and D is the maximum depth of attack measured on these faces. S is a measure of initiation and D a measure of growth of crevice corrosion.

The 46 alloys were ranked on the basis of this Index and the rankings made it possible to derive conclusions on the roles of alloying elements, surface finish and test parameters. Proposals for further sea water tests and for test procedures were also derived from this analysis. A detailed description of this effort is given in Volume IV of this report. A preprint was prepared for the NACE meeting at Anaheim, California, April, 1983. Also, a presentation on this paper was made at this conference and the paper has been published in Materials Performance, May, 1983, pp. 37-50, "Analysis of Crevice Corrosion Data from Two Sea Water Exposure Tests on Stainless Alloys".

The first part of the experimental work consisted of crevice corrosion tests in 10% ferric chloride solution. This solution has been widely used and was included in this investigation in order to provide a link with the extensive literature on the performance of stainless alloys. By progressively increasing the temperature of the solution for a given test alloy, a critical crevice corrosion temperature is determined above which that alloy will begin to corrode in a given length of time. The higher this temperature is found to be in this concentrated chloride solution the greater is the resistance of the alloy to crevice attack. Ten percent ferric chloride has a natural pH of 1.6 and is highly oxidizing with a redox and corrosion potential of +0.6 vs. SCE.

A second, more versatile and more rapid method was sought in order to vary the electrode potential and the solution composition. For this approach, a recently developed instrument, the Santron 400, made in Sweden, was used. In this test the specimen with crevice devices on it is immersed in a chloride solution of choice, such as sodium chloride, synthetic or natural seawater, with control of concentration, aeration (or purging with carbon dioxide) and pH. By connecting the specimen to

the Santron 400 potentiostat, and a counter electrode, a preselected potential can be applied to the specimen while the temperature of the test solution is automatically increased at regular intervals, e.g. 5°C. The onset of current flow, a sign of crevice attack, is monitored to establish the critical crevice corrosion temperature for the given alloy, crevice device, solution composition and test procedure.

Our results to date (see Volume IV) show that this method is very versatile, reproducible and can provide data which can be correlated with the results obtained in natural sea water and ferric chloride tests. The effect of various crevice devices such as: rubber bands and Teflon blocks, serrated Delrin and alumina insulators, have been studied, as well as a range of testing techniques, heating rates and times, applied potentials, sequences of applied potentials and criteria for interpreting the observed currents. Results in tests with the Santron 400 instrument indicate that the ceramic crevice washers yield the most consistent results and are less prone to relaxation effects as compared to the Delrin washers. Similar tests made by simple immersion in 10% ferric chloride solution showed that the critical crevice corrosion temperature increases in the following order: Delrin serrated washers, Teflon-block-rubber band crevices and alumina washers.

Studies were made to determine the effects of several Santron test parameters and to define procedures for conducting electrochemical tests.

- (1) Effect of Measuring Time (Time of current monitoring under applied potential at each temperature step).

Critical temperatures (at a maximum current of 1000 μ A) were determined for a set of alloys using measuring times of 20 min., 1 hour, 4 hours and 24 hours.

In the continuous potential application mode longer measuring times yielded lower critical temperatures. This is similar to longer term potentiostatic tests yielding lower pitting potentials.

In the intermittent potential application mode, where the pre-selected potential is applied only during times of constant temperature, and the specimen potential is decontrolled during the heating period, longer measuring times of up to 4 hours also yielded lower critical

temperatures. Increasing the measuring time to 24 hours did not significantly reduce the critical temperature provided sufficient time (1 - 4 hours) was allowed between temperature steps for the specimen to equilibrate to its corrosion potential.

- (2) Equilibration of specimens prior to start of test and prior to reapplication of the preselected potential at each temperature step.

Specimens must be allowed to equilibrate for 1 to 4 hours prior to starting the test (Corrosion Potential variation \pm mv/hr). Furthermore, in the intermittent mode of potential application, the specimen potential must be allowed to equilibrate (\pm mv/hr) prior to application of the preselected potential at the next test temperature. In the present instrument this is attainable by using very slow heating rates between test temperatures. However, it would be preferable to equilibrate the specimen at the next test temperature prior to reapplication of the selected potential.

This equilibration of specimens between test temperatures is seen to minimize any variation in critical temperatures determined due to selection of test starting temperature and measuring times. Furthermore, this procedure yields current spikes of equal magnitude upon reapplication of the preset potential as long as there is not initiation of crevice corrosion.

The magnitude of the current spikes is proportional to the difference between the specimen corrosion potential (prior to potential application) and the preselected applied potential. Upon initiation of crevice corrosion, the specimen corrosion potential shifts in the active direction and increases the potential difference between e_{corr} and e_{applied} and hence the magnitude of the current spike.

- (3) Critical current level representative of initiation of crevice corrosion and corresponding trends in free corrosion potentials of the specimen.

In most tests to date a critical current level of 1000 μ A, for the given specimen-crevice geometry, was utilized to define the critical temperature. This high current level provided for reproducible critical temperatures (as compared to 400, 800 μ A) and provided evidence of crevice attack upon visual inspection on the 120 grit finished samples

after the test. Recent tests indicate that a much lower current level, namely 50-100 μA , provides a finer definition of crevice corrosion initiation, and is corroborated by a shift in the specimen corrosion potential (upon removal of the applied potential) to values considerably more active than its original corrosion potential. Tests conducted on specimens with finer finishes 600 grit, 1 μ , will help define the critical current level for this test procedure. The results of our work have been published in Preprint #71 at the 1983 NACE meeting, as well as in a talk at that meeting. The work has also led to several suggestions for making the Santron instrument even more versatile, and to an extensive research proposal for new work.

B.3.e. Conclusions and Perspectives on Ranking of Stainless Alloys (T. S. Lee and R. M. Cain)

One of the most important aspects of any corrosion test is the criteria selected for proper evaluation of the test results. Because the crevice corrosion process is clearly separated into initiation and propagation phases, test data should be analyzed to determine relative alloy resistance to each of these stages of the process. The separate treatment of the two phases is theoretically credible since the mechanisms of crevice corrosion initiation and propagation are different. As such, various factors can be expected to influence each process differently (such as the previously discussed effects of initial crevice gap).

This clear separation of the crevice corrosion initiation and propagation behavior of alloys is particularly important from a practical viewpoint. It can allow a designer or engineer to select an alloy which may be subject to crevice corrosion initiation under certain conditions but for which an acceptably low degree of propagation will exist. Any treatment of data, such as the crevice corrosion index described in the previous section, which combines the two phases, allows no such delineation of alloy behavior and literally forces an engineer into a go/no-go decision on materials selection.

When faced with a materials selection decision for which no previous experience base exists, an engineer must initially consider screening tests such as the multiple crevice assembly test to narrow the

field of candidate alloys. Analyses of multiple crevice assembly data have clearly ranked alloy crevice corrosion initiation resistance based on number of crevice sites initiated as well as alloy resistance to propagation based on maximum depth of crevice corrosion (Figure 17). More important, the analyses indicate the effects of various factors on crevice corrosion behavior for each alloy.

It is this latter point which provides the most practical approach to alloy ranking and ultimate materials selection decisions. With the multiplicity of factors affecting crevice corrosion and the complex interactions of these factors, any simplified approach to alloy ranking will be misleading. The recent publication in Materials Performance Journal (Vol. 22(5), p. 37, 1983) of a "Crevice Corrosion Index" by our Sea Grant Corrosion Program Co-investigator at the University of Delaware is considered to be an oversimplification of the crevice corrosion process. This index treats the initiation and propagation stages as being equally affected by the same factors. Additionally, the multiple crevice test data used to establish this index do not consistently show a direct dependent relationship between the chosen initiation (sites attacked) and propagation (maximum depth of attack) parameters.

By delineating the crevice corrosion behavior of an alloy as a function of changes in the various geometrical, metallurgical, environmental and electrochemical factors, ultimately the limits of utility of the alloy can be defined. This can lead to practical design data for a system to allow use of a given material or, conversely, will identify the proper alloy for a specified set of system constraints. Further research and correlation of test data with service experience will be required in order to determine which approach to ranking of stainless alloys (crevice corrosion index, or that represented by Figure 17, or some combination thereof) will be of the most practical benefit.

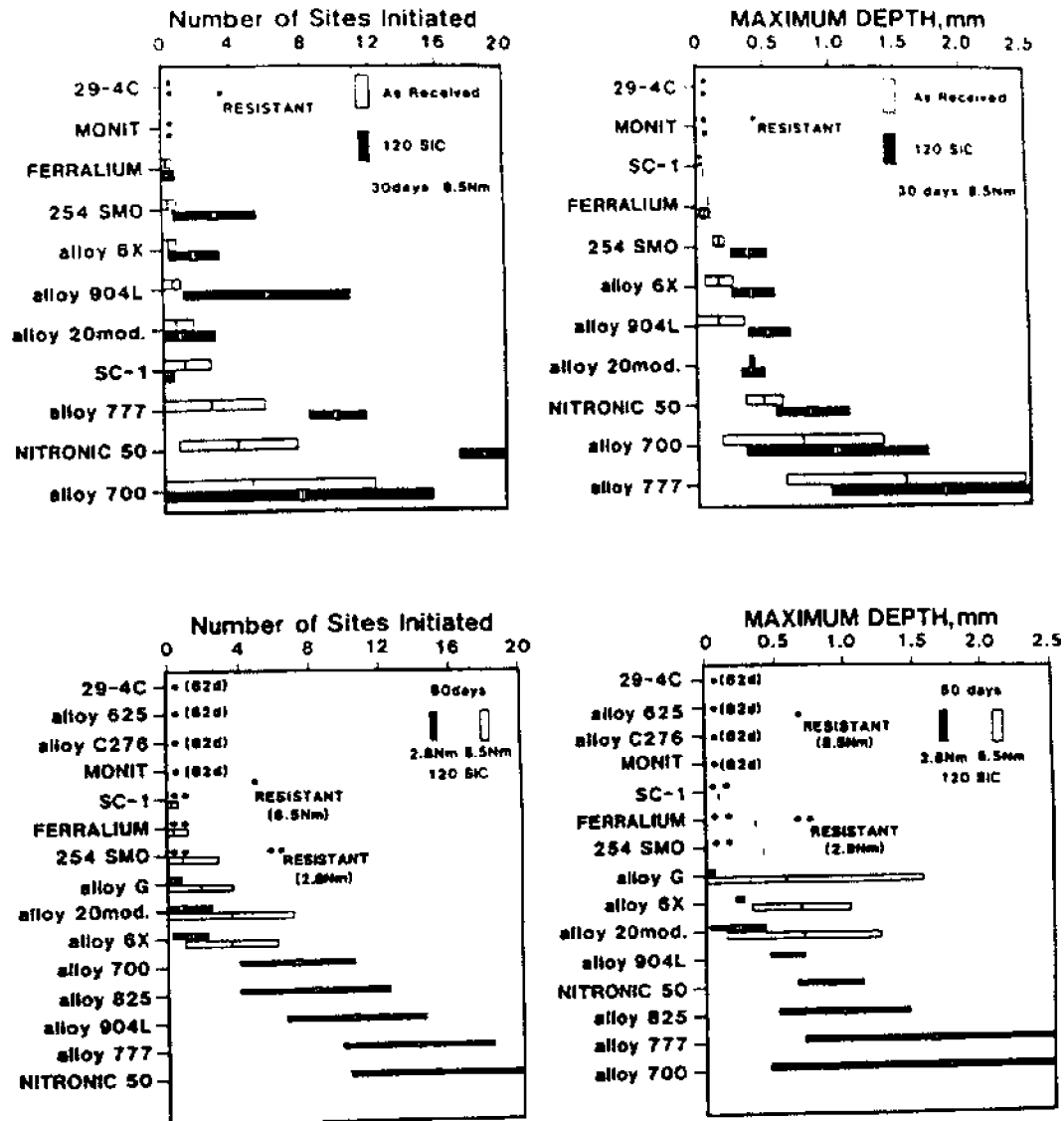


Figure 17.

Analysis of multiple crevice assembly test data describing the effects of surface finish (top) and initial assembly torque level (bottom) on initiation and penetration resistance. Bar graphs represent the mean values (plus and minus one standard deviation) for replicate tests at 30 days and 60 or 82 days, respectively.