

**GEORGIA INSTITUTE OF TECHNOLOGY**  
**OFFICE OF CONTRACT ADMINISTRATION**  
**SPONSORED PROJECT INITIATION**

Date: April 25, 1980

Project Title: Electrochemical Conditions Within Stress Corrosion Cracks

Project No: E-19-612

Project Director: Dr. Miroslav Marek

Sponsor: U.S. Army Research Office; Research Triangle Park, NC 27709

Agreement Period: From April 1, 1980 Until March 31, 1981 (R&D Perf. Period)

Type Agreement: Contract No. DAAG29-80-C-0098

Amount: \$47,145

Reports Required: Semi-Annual Progress Report; Final Technical Report

Sponsor Contact Person (s):

Technical Matters

Dr. P. A. Parrish  
Metallurgy & Material Science Division  
P. O. Box 12211  
Research Triangle Park, NC 27709

Contractual Matters

(thru OCA)

Mr. A. J. Van Hall (All administrative  
no-fund actions)  
Mr. H.T. Throckmorton (All funding  
actions)  
U.S. Army Research Office  
P.O. Box 12211  
Research Triangle Park, NC 27709  
Mr. Thomas A. Bryant, ONR RR-Ga. Tech  
(Property Administration, Closing duties  
etc.)

Defense Priority Rating: None

Assigned to: Chemical Engineering (School/~~Laboratory~~)

COPIES TO:

Project Director  
Division Chief (EES)  
School/Laboratory Director  
Dean/Director-EES  
Accounting Office  
Procurement Office  
Security Coordinator (OCA)  
✓ Reports Coordinator (OCA)

Library, Technical Reports Section  
EES Information Office  
EES Reports & Procedures  
Project File (OCA)  
Project Code (GTRI)  
Other C. E. Smith

SPONSORED PROJECT TERMINATION SHEET

Date 9/9/81

Project Title: Electrochemical Conditions Within Stress Corrosion Cracks

Project No: E-19-612 (Subproject is A-2661/Hubbard-EMSL)

Project Director: Dr. Miroslav Marek

Sponsor: U.S. Army Research Office

Effective Termination Date: 6/30/81

Clearance of Accounting Charges: 8/31/81 (reporting)

Grant/Contract Closeout Actions Remaining:

- ☒ Final Invoice and Closing Documents
- ☐ Final Fiscal Report
- ☒ Final Report of Inventions
- ☒ Govt. Property Inventory & Related Certificate
- ☐ Classified Material Certificate
- ☐ Other \_\_\_\_\_

Assigned to: ChE (School/~~Laboratory~~)

COPIES TO:

Administrative Coordinator  
Research Property Management  
Accounting  
Procurement/EES Supply Services

Research Security Services  
~~Reports Coordinator (OCA)~~  
Legal Services (OCA)  
Library

EES Public Relations (2)  
Computer Input  
Project File  
Other \_\_\_\_\_

## PROGRESS REPORT

(TWENTY COPIES REQUIRED)

1. ARO PROPOSAL NUMBER: \_\_\_\_\_
2. PERIOD COVERED BY REPORT: 4/1/80 - 12/31/80
3. TITLE OF PROPOSAL: Electrochemical Conditions Within Stress  
Corrosion Cracks
4. CONTRACT OR GRANT NUMBER: DAAG29-80-C-0098
5. NAME OF INSTITUTION: Georgia Institute of Technology
6. AUTHOR(S) OF REPORT: Miroslav Marek, Ph.D.
7. LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED UNDER ARO SPONSORSHIP  
DURING THIS PERIOD, INCLUDING JOURNAL REFERENCES:

None

8. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED  
DURING THIS REPORTING PERIOD:

Miroslav Marek, Ph.D., Associate Professor (Principal Investigator)  
James Hubbard, Sr. Research Scientist  
John Rinker, Research Engineer  
Amal Chatterjee, Student Assistant

Dr. M. Marek                      17082-MS  
Georgia Institute of Technology  
School of Chemical Engineering  
Atlanta, GA 30332

## BRIEF OUTLINE OF RESEARCH FINDINGS

### OBJECTIVE

The objective of the program in the first year is to develop improved techniques of determination of electrochemical conditions within stress corrosion cracks. The parameters to be determined include acidity (pH), chloride ion concentration, concentration of cations (ions of alloying elements), and electrode potential. Standard techniques of analysis of corrosion products and fracture surfaces are expected to be used in the later phases of the program.

### RESULTS

Table 1 shows a list of the techniques which have been selected for exploration and development, and summarizes the progress which has been made to date. Table 2 shows the schedule of the individual tasks which have been performed, as well as the plan for the remaining part of the first year. All tests were made on type 7079 aluminum alloy using 3.5% NaCl solution. Specimens were of double cantilever type, bolt or wedge loaded.

### DISCUSSION

All the techniques selected for exploration have been examined to some extent. Depending on the success to date they have been divided in three groups, as follows:

- Group 1. Successful techniques, which will be further improved and used in the research;
- Group 2. Unsuccessful techniques, which will be abandoned, at least for the near future;
- Group 3. Promising techniques which have not been fully successful and need further development.

Following is a brief review of the techniques and comments regarding their success or lack of it.



Group 1. The techniques in this group include potential measurements with an implanted reference probe, and pH and potential measurements with probes positioned along the crack trace on the side of the specimen. It is recognized that the latter technique does not allow measurement of pH near the tip of the crack; however, the results provide reference points against which data from other tests can be checked.

The preliminary data on the potential variation along the crack length are consistent with the results from the implanted electrode. Together they show the potential drop from the mouth of the crack to the leading edge which will be possible to correlate with the theoretical predictions.

Group 2. The techniques which have been explored and abandoned include the use of indicators on the fracture surface, which was found to have low resolution, and the techniques based on the pickup of the solution from the fracture surface with microcapillaries following freezing. Because of the extremely thin film of the solution at the fracture surface the technique did not yield enough solution for analysis.

Group 3. The techniques explored and selected for further testing include the following:

Analysis of the solution absorbed in a special membrane attached to the side of the specimen. To date the efforts have been unsuccessful because no suitable membrane material was found. Further effort will be made to find a material which will not allow excessive spread of the solution.

Techniques based on pickup of the solution with capillaries from the side of the specimen. The efforts using commercial microcapillaries (down to 0.1  $\mu\text{l}$ ) have not been successful. Further effort will be made using special microcapillaries with extremely fine tips. The success will depend on the availability of the capillaries and the design of a setup which will make possible extremely accurate positioning of the capillaries in the crack.

Techniques based on pickup of the solution in capillaries implanted in the specimen. To date only a small fraction of tests yielded useable samples. The efforts will continue till the end of the year.

A technique which has not been included in either group is the freeze-drying method followed by replication and microprobe analysis. The development of this technique has been delayed by the unavailability of a suitable vacuum system and other technical difficulties. A vacuum system for this purpose is now being assembled. To make possible the development of this technique a no-cost extension of the project through 6/30/81 will be requested.

Table 1  
Summary of Techniques Explored in the Program

| Sampling Technique   | Parameter                                      | Analytical Technique                                     | Progress To Date  | Group*   |
|--|--|--|---|----------|
| Freezing, Application of Indicators on the Fracture Surface        | pH   | Visual Observation of Color Changes                      | Working, but little promise of new information                | II       |
| Capillary Pickup from Fracture Surfaces after Freezing and Thawing | pH<br>(Cl <sup>-</sup> )<br>(Me <sup>+</sup> ) | Micro pH Electrode<br>Ion-selective El.<br>AA            | No success  | II       |
| Capillary Pickup from the Crack at the Surface                     | pH<br>(Cl <sup>-</sup> )<br>(Me <sup>+</sup> ) | Micro pH Electrode<br>Ion-selective El.<br>AA            | No success with commercial capillaries. Promise with fine tip | III      |
| Miroelectrode Measurement in the Crack at the Surface              | pH<br>E  | Direct Measurement<br>Direct Measurement                 | Successfully away from tip                                    | I        |
| Implanted Microelectrode   | E<br>pH  | Direct Measurement<br>Direct Measurement                 | Successfull<br>no attempt                                     | I<br>III |
| Implanted Microcapillary   | pH<br>(Cl <sup>-</sup> )<br>(Me <sup>+</sup> ) | Micro pH Electrode<br>Ion-selective El.<br>AA            | Little success  | III      |
| Absorbing Membrane on Specimen Surface                             | pH<br>(Cl <sup>-</sup> )<br>(Me <sup>+</sup> ) | Indicators<br>Indicators or Probe<br>Indicators or Probe | No success with membranes available to date                   | III      |
| Freeze-drying and replicating                                      | (Cl <sup>-</sup> )<br>(Me <sup>+</sup> )       | Electron Microprobe                                      | Work delayed  |          |

Groups    I. Ready for application  
           II. Abandoned  
           III. Shows some promise but requires further development

Table 2  
Work Record and Program

| Week No. | Week of | Design of Work        | Preparations for Tests                               | Testing and Data Processing                    |
|----------|---------|-----------------------|--|--|
| 1        | 4/7     |                       |  |  |
| 2        | 4/14    |                       |  |  |
| 3        | 4/21    |                       |  |  |
| 4        | 4/28    |                       |  |  |
| 5        | 5/5     | Program of tests      |  |  |
| 6        | 5/12    | Specimen Design       |  |  |
| 7        | 5/19    | Search for Indicators | Machining: Specimen Set I. Preparation of Indicators |  |
| 8        | 5/26    |                       |  |  |
| 9        | 6/2     |                       |  | Tests: pH Indicators on Fracture Surfaces      |
| 10       | 6/9     |                       |  |  |
| 11       | 6/16    | VACATION              |  |  |
| 12       | 6/23    |                       |  | Tests: Capillary Pickup from Fracture Surfaces |
| 13       | 6/30    | Vacuum System         |  |  |
| 14       | 7/7     | Microelectrodes       |  |  |
| 15       | 7/14    | Micromanipulator      | Machining: Specimen Set II                           |  |
| 16       | 7/21    |                       |  |  |
| 17       | 7/28    |                       | Loading Grips  | Tests: Implanted Capillary                     |
| 18       | 8/4     |                       | Micromanipulator Adaptation                          |  |
| 19       | 8/11    |                       |  | Tests: Microprobes on specimen side            |
| 20       | 8/18    |                       |  |  |
| 21       | 8/25    | Membranes             |  |  |
| 22       | 9/1     | Dr. Scully's visit    |  |  |
| 23       | 9/8     |                       |  | Tests with membranes                           |
| 24       | 9/15    |                       |  |  |
| 25       | 9/22    |                       |  | Capillary on side                              |
| 26       | 9/29    | Supplies              |  |  |
| 27       | 10/6    | ABSENCE               |  |  |
| 28       | 10/13   | ABSENCE               |  |  |
| 29       | 10/20   | Vacuum system         | Machining: Specimen Set III                          |  |
| 30       | 10/27   |                       |  | Probes on side                                 |

Table 2  
(continued)

| Week No | Week of | Design of Work     | Preparations for Tests | Testing and Data Processing |
|---------|---------|--------------------|------------------------|-----------------------------|
| 31      | 11/3    |                    | Vacuum System          |                             |
| 32      | 11/10   |                    |                        |                             |
| 33      | 11/17   | Supplies           |                        | Tests: Membranes            |
| 34      | 11/24   | Experiments        | Vacuum system          |                             |
| 35      | 12/1    | Vacuum system      |                        |                             |
| 36      | 12/8    |                    |                        | Tests: Capillary            |
| 37      | 12/15   |                    |                        | pickup on side              |
| 38      | 12/22   | CHRISTMAS HOLIDAYS |                        |                             |
| 39      | 12/29   | CHRISTMAS HOLIDAYS |                        |                             |
| 40      | 1/5     | Supplies           | Potential Tests        |                             |
| 41      | 1/12    |                    |                        | Tests: Implanted            |
| 42      | 1/19    |                    |                        | Electrode                   |
| 43      | 1/26    |                    |                        |                             |
| 44      | 2/1     |                    | Vacuum system          |                             |
| 45      | 2/9     |                    | Freeze-drying          |                             |
| 46      | 2/16    |                    | facilities             |                             |
| 47      | 2/23    |                    |                        |                             |
| 48      | 3/2     |                    |                        | Freeze-dry tests            |
| 49      | 3/9     |                    |                        |                             |
| 50      | 3/16    |                    |                        |                             |
| 51      | 3/23    |                    |                        |                             |



ELECTROCHEMICAL CONDITIONS WITHIN  
STRESS CORROSION CRACKS  
(Experimental Techniques)

by

Miroslav Marek, Ph.D.  
School of Chemical Engineering  
Metallurgy Program

GEORGIA INSTITUTE OF TECHNOLOGY  
Atlanta, Georgia 30332

Final Report  
Contract No. DAAG29-80-C-0098

Prepared for  
Army Research Office  
Research Triangle Park, NC 27709

## TABLE OF CONTENTS

PAGE

|  |     |
|--|-----|
| FOREWARD . . . . .                                     | i   |
| LIST OF FIGURES . . . . .                              | ii  |
| LIST OF TABLES . . . . .                               | iii |
| Chapter  |     |
| I. INTRODUCTION . . . . .                              | 1   |
| II. BACKGROUND . . . . .                               | 2   |
| III. STRESS CORROSION SPECIMENS . . . . .              | 4   |
| IV. COLLECTION OF LIQUID SAMPLES FROM CRACKS . . . . . | 5   |
| V. VACUUM FREEZE-DRYING OF THE SOLUTION . . . . .      | 7   |
| VI. DETERMINATION OF ACIDITY . . . . .                 | 9   |
| VI-1 pH Indicators                                     |     |
| VI-2 Analysis of the Solution Drawn from Cracks        |     |
| VI-3 Direct Electrode Measurement                      |     |
| VI-4 Results   |     |
| VII. ANALYSIS FOR CHLORIDES . . . . .                  | 12  |
| VII-1 Analysis of the Solution Drawn from Cracks       |     |
| VII-2 Direct Electrode Measurement                     |     |
| VII-3 Vacuum Freeze-dry Technique                      |     |
| VII-4 Results  |     |
| VIII. ANALYSIS FOR METALLIC IONS . . . . .             | 14  |
| VIII-1 Analysis of the Solution Drawn from Cracks      |     |
| VIII-2 Vacuum Freeze-dry Technique                     |     |
| VIII-3 Results   |     |
| IX. CRACK TIP POTENTIAL MEASUREMENTS . . . . .         | 16  |
| IX-1 Implanted Reference Electrode                     |     |
| IX-2 Results   |     |
| X. OTHER TECHNIQUES . . . . .                          | 18  |
| XI. DISCUSSION . . . . .                               | 19  |
| XII. CONCLUSIONS AND RECOMMENDATIONS . . . . .         | 22  |
| References . . . . .                                   | 24  |

## FOREWORD

This final report was prepared by Miroslav Marek, Ph.D., of the School of Chemical Engineering, Metallurgy Program, Georgia Institute of Technology, Atlanta, Georgia 30332, in fulfillment of the requirements of ARO Contract No. DAAG29-80-C-0098, Research Project No. E-19-612 and subproject A-2661. The R & D Performance Period is 1 April 1980 to 30 June 1981 and the Contract Period is 1 April 1980 to 31 August 1981. Participating scientific personnel include Miroslav Marek, Ph.D., Associate Professor in the School of Chemical Engineering, Metallurgy Program, (Principal Investigator) and James L. Hubbard, Senior Research Scientist in the Engineering Experiment Station, Georgia Institute of Technology.

## LIST OF FIGURES

- Fig. 1. SCC Specimen for the Determination of Electrochemical Conditions within Cracks.
- Fig. 2. Microcapillary Probe for Collection of Liquid Samples from Cracks.
- Fig. 3. Experimental Setup for Application of Microprobes in Cracks.
- Fig. 4. Experimental Setup for Application of Microprobes in Cracks (Detail).
- Fig. 5. Vacuum Chamber Used for Freeze-Drying of the Electrolyte.
- Fig. 6. Thermoelectrically Cooled Stage and Carbon Evaporator Used in the Freeze-Dry Technique.
- Fig. 7. Schematic Illustration of the Location of Indicator Strips for Determination of Crack Tip Acidity.
- Fig. 8. Setup for pH Analysis of Microliter Samples Using an Inverted pH Electrode.
- Fig. 9. Results of pH Measurements Using Various Techniques.
- Fig. 10. Results of Analyses for Chlorides.
- Fig. 11. Results of Analyses for Aluminum Ions.
- Fig. 12. Results of Analyses for Zinc Ions.
- Fig. 13. Setup for Measurement of the Potential at the Crack Tip Using an Implanted Electrode.
- Fig. 14. Potential Variation vs. Time as Measured by the Implanted Electrode and an Electrode in the Notch.

## LIST OF TABLES

Table 1. Parameters of the AA Analysis

Table 2. Results of the AA Analysis of Extraction Replicas

Table 3. Results of the Crack Tip Potential Measurements



## I. INTRODUCTION

The objective of this investigation was to determine the electrochemical conditions in propagating stress corrosion cracks. In the first phase of the project, which is the subject of this report, the aim was to develop improved techniques of the measurement of the solution chemistry and potential within the cracks. While many techniques were explored only the most promising ones were selected for actual analyses of conditions within cracks. Chapter IV describes the technique of collection of liquid samples of the solution from cracks, and Chapter V the development of the vacuum freeze-drying technique as a modification of the freezing technique developed by Brown.<sup>(1)</sup> Chapters VI to VII then describe the experimental procedures developed for the determination of acidity, concentration of chlorides, and concentration of metal ions. The experimental technique used for the measurement of the electrode potential at the crack tip is reported in Chapter IX. A short description of various other techniques which were explored is presented in Chapter X, Discussion in Chapter XI, and Conclusions and Recommendations in Chapter XII.

In the investigation described in this report the main purpose of the measurements was to gain experience in the application of the various techniques, and exploration of the limits of usefulness of each one of them. The limited time did not allow collection of systematic and comprehensive data or a study of the effects of alloy composition, heat treatment, or mechanical parameters on the electrochemical conditions within the cracks.

## II. BACKGROUND

Electrochemical conditions within cracks in materials susceptible to stress corrosion cracking (SCC) are, on one hand, the evidence of the electrochemical processes which take place during crack propagation. For instance, the presence of metal ions indicates dissolution; acidified electrolyte is the evidence of hydrolysis; highly negative electrode potential at the tip shows that fresh metal surface is being exposed and a voltage drop exists along the length of the crack, etc. On the other hand, detailed information on the conditions within the cracks helps to make a choice between the various hypotheses of the mechanism of environment-assisted cracking. For instance, the values of acidity and potential at the crack tip show if the reduction of hydrogen ions can take place and possibly result in hydrogen embrittlement; the chemistry of the crack tip environment may or may not support the formation of particular surface films, etc. Thus the determination of the conditions within propagating cracks assists in both the inductive and deductive part of the scientific process.

Experimental determination of the composition of the electrolyte in propagating cracks is difficult because of the small volume of the solution in narrow cracks and inaccessibility by standard techniques of sample collection. The measurement of the potential at the crack tip presents additional problem because the probe must be introduced close to the crack tip. The pioneering work on the solution chemistry in propagating stress corrosion cracks was done by B. F. Brown and his co-workers<sup>(1-4)</sup>; their original technique included freezing of the solution, mechanical opening of the crack, and subsequent analysis of the electrolyte using indicators or colorimetry. Another technique, reported by Brown<sup>(3)</sup> and Smith et al<sup>(4)</sup> involved the use of a pH microelectrode placed on the side of the specimen in the path of the propagating crack on a

small piece of filter paper; a small amount of the solution would be drawn by capillary action into the filter paper and produce the electrode response. Leidheiser and Kissinger<sup>(5)</sup> used the basic freezing technique combined with a spectrophotometric analysis of the solution from cracks in brass which was collected from the fracture surfaces in either fiber paper or fine glass capillaries.

The use of microprobes placed inside the crack was pioneered by Davis.<sup>(6)</sup> Specially prepared microelectrodes were placed into the mouth of the crack to determine pH and potential variation as a function of stress intensity and applied potential in aluminum alloys. Only very short cracks could be explored because of the narrowness of the cracks.

In the previous research at Georgia Institute of Technology the freezing technique and indicators were used to determine the pH at the tip of stress corrosion cracks in Type 316 stainless steel.<sup>(7)</sup> In a later study the freezing technique was modified to allow quantitative determination of the concentration of metal and chloride ions in the crack as a function of the distance from the crack tip.<sup>(8)</sup> Implantation of capillaries in the specimen also was attempted. In addition, studies were made on the simulation of crack conditions in macrocells,<sup>(9)</sup> and on the chemistry of the solution in crevices.<sup>(8,10)</sup> These studies provided the experience on which the current study was based.

### III. STRESS CORROSION SPECIMENS

All tests were made using aluminum alloy 7079 in T6 condition. This alloy was selected because of the high susceptibility to SCC and fast crack propagation rate. The specimens were machined from a 1 in. thick plate. Cracks were induced in the short transverse direction. Specimens were of the double cantilever type with machined chevron notches, and they were loaded by bolts in the opening mode. The bolts were machined from the same material as the specimens to avoid galvanic effects. The shape and dimensions are shown in Figure 1. The thickness of the specimens (3/4 in.) ensured plane strain conditions along the major part of the crack front.

Cracks were initiated by tightening the bolts to the point of mechanical overload ("pop-in crack"). The notch was then partially sealed with a transparent adhesive tape and filled with the corrosive solution, which was a 3.5%, aqueous solution of sodium chloride. The progress of cracking was monitored optically on the polished sides of the specimens using a low power optical stereo microscope. The analyses were made (or the test terminated) when the crack was between 1.7 in. and 2.0 in. long (as measured from the load line).



#### IV. COLLECTION OF LIQUID SAMPLES FROM CRACKS

Initially attempts were made to collect solution samples from propagating cracks by drawing the solution by capillary action into commercial straight microcapillaries either from the fracture surface, using the freezing technique, or from the crack opening at the side of the specimen. These attempts were generally unsuccessful; although occasionally a small amount of solution was collected, the technique was unreliable.

A more successful technique was developed using a capillary microprobe into which the solution was drawn by an application of vacuum using a syringe. The capillary microprobe was a glass tube with a microcapillary tip about  $0.05\text{ }\mu\text{m}$  in diameter; it was made from a commercial potassium ion electrode used for the analysis of the electrolyte in biological cells. (Model MI-331, Microelectrodes, Inc.) The electrode was emptied and the silver wire removed, and the glass probe was connected by plastic tubing to a microsyringe (Hamilton Co., various models). The assembled probe is shown in Figure 2. The experimental setup included a micromanipulator and a stereo-microscope. The setup is shown in Figures 3 and 4 (different probe is shown).

The sample collection procedure was as follows: The specimen with a propagating crack was placed horizontally under the micromanipulator in which the capillary microprobe was installed. Observing the movement of the probe through the microscope the probe tip was inserted in the opening of the crack on the side of the specimen. Using the plunger of the microsyringe to create vacuum a small amount of the solution was drawn into the tip of the capillary. The probe was removed from the manipulator and the solution was expelled and analyzed. Since the syringe was calibrated the amount of the solution collected for analysis was known. With a microsyringe of  $1\text{ }\mu\text{l}$  total capacity solution samples as small as  $0.1\text{ }\mu\text{l}$  were successfully collected.



The main drawback of this technique is that in specimens with narrow cracks the opening of the crack near the tip is too narrow for the insertion of the probe tip. In the aluminum alloy specimens used in this investigation the smallest distance from the crack front at which samples could be collected was about 3 mm (at stress intensities in the plateau region of the  $\dot{v}$  vs.  $K$  curve). Occasionally, a small droplet of the solution formed near the tip of the crack trace and allowed the collection of a sample at a shorter distance from the tip; these events, however, could not be relied upon.

The samples drawn from the crack opening using this techniques were analyzed for acidity, chloride ion concentration, and metal ion concentration using the methods described in Chapters VI, VII, and VIII.

## V. VACUUM FREEZE-DRYING OF THE SOLUTION

In the original freezing technique developed by Brown<sup>(1-4)</sup> the solution within the propagating crack was frozen, the specimen was fractured to open the crack, and the electrolyte was analyzed upon thawing. This procedure limited the analytical techniques to the use of indicators if variation of chemistry with the distance from the crack tip was to be determined. The solution could also be analyzed after washing from the fracture surface, but the results then showed only average values of the composition.<sup>(2)</sup> In specimen with relatively wide cracks it is possible to collect the solution from the fracture surfaces upon thawing into capillaries,<sup>(5)</sup> but the procedure was unsuccessful in this investigation because of the extremely small amounts of the solution in the narrow cracks.

To overcome some of the drawbacks of the freezing technique a modified technique was designed<sup>(8)</sup> which involves vacuum freeze-drying of the solution on the fracture surfaces. The procedure includes the following main steps: The specimen containing a propagating crack is rapidly cooled to freeze the electrolyte within the crack, usually by immersion in liquid nitrogen. The specimen is fractured by a mechanical overload, and the two halves are placed in a vacuum chamber. Under vacuum the solution dries by sublimation of water without thawing and the dissolved species remain on the fracture surface as a dry residue distributed in the same way as in the liquid electrolyte. This residue can be analyzed either directly on the fracture surfaces, or after stripping with an extraction replica. Electron microprobe analysis or other suitable techniques can be used to obtain quantitative data of the amounts of elements as a function of the distance from the crack tip.

Several obstacles had to be overcome to make the technique practical. When exposed to the laboratory air the specimen cooled to liquid nitrogen

temperature becomes quickly covered with frozen condensed moisture; therefore, the specimen had to be handled in a glove box with controlled, dry atmosphere. The specimen must not be allowed to warm up to the melting temperature of the solution before it is completely dried up; therefore, a cooling stage was needed in the vacuum system. Following the drying the specimen has to be transferred to the analytical instrument, such as the electron microprobe, often to a considerable distance, or handled during the replication. The residue of the electrolyte, however, could easily be dislodged. Therefore, it was desirable to fix the residue on the fracture surface as soon as possible by a thin deposit of carbon which did not interfere with the subsequent analysis.

Since no vacuum system was available for this project which would have allowed the aforementioned procedure, a dedicated system was built using some parts of an old vacuum evaporator. The bell jar was enclosed in a glove box made of polycarbonate plastic. A thermoelectric cooling stage and carbon rod evaporator were designed and built. The setup is shown in Figures 5 and 6.

Because of the time it took to obtain the vacuum components, to design and make the parts, and to assemble the system, little time was left during this project period for the use of the system in the analysis. The limited data obtained are presented in Chapters VII and VIII.

## VI. DETERMINATION OF ACIDITY

### VI-1. pH Indicators

Indicators of acidity were used in three different ways, as follows:

- a. Congo-red tests strips (commercial, Fisher Scientific Cat. No. 14-861) were applied on the fracture surfaces following freezing in liquid nitrogen and mechanical opening of the specimen. The tests were made in a glove box in a dry air atmosphere to prevent condensation of water vapor on the cold metal surfaces. The color change (from red in neutral to blue in acidic solution) was observed using a magnifying glass when the frozen solution on the fracture surfaces melted and compared with the changes produced by standard solutions. This techniques was described by Brown et al (1).
- b. Congo-red test paper (commerical, as above), was cut into narrow, about 1 mm wide strips, and attached using an adhesive tape on the side of the specimen in the path of the propagating crack. The strips were oriented  $90^{\circ}$  with respect to the direction of the crack, as shown in Figure 7. When the crack reached the test strip a small amount of the solution was drawn into the strip and provided an indication of the acidity near the crack tip.
- c. Fluorescent pH indicator added to the electrolyte. Erythrosin B (Fisher Scientific, Cat. No. E-513) was used in various concentrations (1-10%); this indicator shows yellow fluorecence at about pH3.6. After the crack has propagated the trace of the crack was observed under black light (ultraviolet) illumination using a magnifying lens. Several specimens were also frozen and opened and the fracture surfaces observed in black light as the electrolyte melted.



#### VI-2. Analysis of the Solution Drawn from Cracks.

The technique described in Chapter IV was used to collect the liquid samples. The sample in the microcapillary probe was expelled into an inverted pH electrode (cup electrode), touched with a micro-reference probe, as shown in Figure 8, and pH was measured with a commercial pH meter (Orion Research Model 801A). About 0.5  $\mu$ l of the solution was needed for the measurement.

#### VI-3. Direct Electrode Measurement.

A microelectrode with a pH-sensitive glass tip of about 2  $\mu$ m in diameter (Model MI-102, Microelectrodes, Inc.) was inserted into the crack opening on the specimen side using the setup shown in Figures 3 and 4. The tip of a reference microelectrode (Model MI-401, Microelectrodes, Inc.) was placed in the electrolyte in the notch, and pH was measured with a commercial pH meter (Orion Research Model 801A). Because the pH electrode tip had to be immersed about 50  $\mu$ m in the solution for reliable measurement the technique was limited to distances from the crack front larger than about 6 mm.

#### VI-4. Results

The results of the pH measurements are summarized in Figure 9 for a crack length of about 1.7 in. The results of direct electrode measurement and analysis of the solution drawn in the capillary are in good agreement and show acceptable scatter at distance larger than 5 mm from the crack front. Closer to the crack tip few direct measurements were made because of the difficulty of the procedure. Reliable data for acidity near the crack tip were obtained only using the test strips applied to the side of the specimens; these determinations did not allow, however, a pH measurement as a function of the distance from the crack tip, and the pH values were only estimates based on the visual comparison of the color changes with strips exposed to pH standards.



The technique was, however, more reliable than the application of indicators on the fracture surfaces using the freezing technique. The fluorescent pH indicator showed response in the regions where the test strips indicated pH values around 3.5 - 4, but did not provide sufficient resolution and showed little advantage in this application over conventional color pH indicators.

## VII. ANALYSIS FOR CHLORIDES

### VII-1. Analysis of the Solution Drawn from Cracks.

The procedures of the collection of the electrolyte samples for the analysis was described in Chapter IV. The solution from the capillary was diluted with distilled water to obtain a sample volume of 10  $\mu$ l or more. The samples were then analyzed using a chloride-ion selective combination electrode (Orion Model 96-17) and Confined Spot test papers (Yagoda, S & S No. 211-Y, Carl Schleicher & Schuell Co.). Because of the limitations described in Chapter IV no data were obtained at distances closer than 4mm from the crack front.

### VII-2. Direct Electrode Measurement.

A chloride-ion sensitive microelectrode with a tip radius of about 0.5  $\mu$ m, made for intracellular measurements (Model MI-332, Microelectrodes, Inc.) was used as a probe inserted into the crack opening on the side of the specimen, using the setup described generally in Chapter IV and shown in Figures 3 and 4. The tip of a reference microelectrode (Model MI-401, Microelectrodes, Inc.) was immersed in the solution in the notch, and the response was measured using a commercial pH/ion meter (Orion Model 801A). The electrode was calibrated using commercial chloride standards. Because of the small size of the electrode tip it was possible to make measurements as close as 4 mm from the crack front.

### VII-3. Vacuum Freeze-dry Technique.

The technique is described in general in Chapter V. For the determination of the chlorides the procedure was as follows: the specimen with a propagating crack was cooled in liquid nitrogen to freeze the solution in the crack; the vessel with the specimen immersed in liquid nitrogen was placed in a glove box in which the atmosphere was dry air; the specimen was removed from liquid

nitrogen, broken mechanically by tightening the bolts, and placed on the thermoelectric cool plate; the bell jar was placed over the cool plate and the air was pumped out; the specimen was kept in vacuum and at sub-freezing temperatures until the electrolyte was completely freeze-dried; the evaporator was energized to coat the fracture surfaces with a thin layer of carbon; the specimen was allowed to warm-up to room temperature and air was slowly admitted to the chamber; the specimen was taken off the stage and was ready for the analysis by the electron microprobe.

#### VII-4. Results

The results of the analysis of the solution samples drawn from the crack and the direct electrode measurements are shown in Figure 10. The two sets of results are in good agreement, the direct measurements showing less scatter. Two specimens were prepared using the vacuum freeze-dry technique and a preliminary measurement using the electron microprobe indicated the presence of chlorine-containing residue on the fracture surfaces and a concentration build-up in a region close to the crack front. A detailed measurement, which requires mapping of chlorine on both fracture surfaces, was not finished by the end of the project period.

## VIII. ANALYSIS FOR METALLIC IONS

### VIII-1. Analysis of the Solution Drawn from the Crack.

The trial analysis was made for Al and Zn ions. Because of the high concentrations of these ions in the crack solution the small sample, volumes (0.1  $\mu$ l) obtained using this technique were not an obstacle to the determination; the main drawback was the inability to collect samples from regions closer than about 4 mm from the crack front.

Following the drawing of the solution sample from the crack the sample was diluted with ultra-pure hydrochloric acid diluted to 10%. The usual dilution of the sample ranged from 100 to 1,000 for Al and 50 to 500 for Zn. The diluted solution was analyzed by atomic absorption spectrophotometry using carbon furnace atomization. The equipment included Varian Model 1200 spectrophotometer, Varian Model 90 carbon rod atomizer, and Model BC6 Background Correction Unit. The volume of each individual analyzed sample was 5  $\mu$ l. Since typically about 0.1  $\mu$ l was drawn from the crack and diluted 250 times, about 5 analyses could be made from each collection. The data of the absorbance were evaluated with respect to absorbance vs. concentration data obtained using AA solution standards. In this exploratory phase of the program no effort was made to improve the accuracy of the analysis by matching more closely the matrix of the standards with that of the samples. The analytical parameters and other data are presented in Table 1.

### VIII-2. Vacuum Freeze-dry Technique.

The technique is described in general in Chapter V. For the determination of metallic ions the procedure provided two halves of the fractured specimen which contained the dry residue of the crack electrolyte remaining on the fracture surfaces and stabilized by the film of the deposited carbon. Since

the substrate contained the elements of interest the residue could not be analyzed directly using the electron microscope; instead, the residue of the solution was lifted from the surface using a replicating tape and coated again with carbon.

Although the use of the electron microprobe is most advantageous in analyzing the residue obtained by the freeze-drying technique, a less expensive procedure was used in this phase of the program. The replicating tape, stripped from the fracture surface and containing the residue was cut into small strips, and about 0.2 mm wide, and 5 mm long, parallel to the crack front. The strips were then analyzed by atomic absorption analysis using carbon furnace atomization. The analytical parameters were generally similar to those shown in Table 1, however, instead of the carbon tubes used for liquid samples, carbon cups were used. The plastic of the replicating tape was ashed before the analysis for the metal ions.

### VIII-3. Results

The results of the analyses of samples drawn from the crack are shown in Figures 11 and 12. The data show large scatter and a larger number of analyses would be needed to obtain statistically significant results.

The results of the preliminary AA analysis of the extraction replica are presented in Table 2. The data have been processed to show concentration of the elements per unit area of the fracture surface. The results, however, have not been processed to take into account the changing width of the crack as a function of the distance from the crack tip.



## IX. CRACK TIP POTENTIAL MEASUREMENTS

### IX-1. Implanted Reference Electrode.

The standard SCC specimen, described in Chapter III was modified by drilling a hole 0.085 in. in diameter from the bottom of the specimen, towards the notch, as shown in Figure 1. A flexible barrel reference electrode (Model MI-402, Microelectrodes, Inc.) was inserted in the hole. A small amount of cotton slightly moistened with a potassium chloride-saturated gel provided the conductive path between the liquid junction of the electrode and the metal surface at the end of the hole. The specimen was precracked and the notch filled with the electrolyte, and a microreference electrode (Model MI-401, Microelectrodes, Inc.) was placed in the solution in the notch. The setup is shown in Figure 13. The electrode potential differences between each electrode and the specimen were measured using two electrometers and recorded on a two-pen strip chart recorder. Before each test the potential of each electrode was measured with respect to a standard calomel electrode, and the potential data were corrected accordingly.

In the initial phase of the experiment, before the crack reached the probe, the implanted electrode measured the electrode potential of the surface at the end of the hole which was in contact with the moistened cotton, and the recorded potential values were of no importance. When the crack reached the hole and the crack tip solution came in contact with the salt bridge formed by the cotton the potential difference measured by the implanted electrode changed instantaneously, as shown in Figure 14. As the crack propagated further the potential measured by the implanted electrode approached that of the electrode in the notch.

## IX-2. Results

When the crack reached the probe the implanted electrode measured a mixed potential resulting from the presence of two conductive paths from the liquid junction of the electrode: to the solution and surfaces within the crack, and to the metal surface at the end of the hole. Therefore, the potential values provided by the implanted electrode contained an error due to the mixed character of the potential measurement. Since the potential changed to a more negative value when the crack reached the electrode the actual crack tip potential was more negative than shown by the data, which are presented in Table 3. The error is expected to be relatively small, because the metal surface inside the hole was polarized cathodically, and was easily polarizable in this direction. However, further effort needs to be made to minimize the error, possibly by using an insulating brittle coating on the surfaces within the hole.

## X. OTHER TECHNIQUES

In addition to the techniques described in Chapters IV to IX several other alternatives were explored. An attempt was made to collect samples from the fracture surfaces using microcapillaries, as described by Leidheiser and Kissinger;<sup>(5)</sup> the attempts were generally unsuccessful because of the very thin layer of the electrolyte in the narrow cracks in the aluminum alloy. Collection of the solution from the opening of the crack on the specimen side into a strip of fiber paper or membrane, which then could be analyzed, was unsuccessful because a suitable material was not found which would not allow the lateral spreading of the solution. Equally unsuccessful was the implantation of capillaries and pH electrodes in the specimen in the path of the propagating crack. Solution was collected in implanted capillaries, but it could not be positively determined if the electrolyte was drawn from the crack tip region or from the crack after the front has passed the tip of the capillary. Also, the amount collected (0.5  $\mu$ l) in capillaries which could be practically implanted was too large to be representative of only the crack tip region.

One technique which was promising but was not adequately explored was the potential measurement on the side of the specimen which would provide a map of the potential distribution around the crack opening near the tip. The technique required building or purchase of a special stage which would allow accurate monitoring of the position of the probe; this was found not to be feasible during this project period.

## XI. DISCUSSION

Determination of the electrochemical conditions within cracks is a difficult experimental problem mainly because of the inaccessibility of the region near the crack front. Basically, either the measurements are made in situ, using various types of microprobes, or samples are collected and the analysis is made elsewhere. The freezing technique is a variation which facilitates either the in situ measurement, or the collection of samples.

For in situ measurements the microprobes, such as pH, reference, or ion-selective microelectrodes, must be placed within the region of interest in the crack. The most important region exists near the crack front where the crack, in most materials, is only a few micrometers wide, at most. The probe can be inserted in three different ways: a) from the mouth of the crack, perpendicular to the crack front; b) from the opening of the crack on the specimen side, parallel to the crack front or at an angle; c) implanted in the specimen and reached by the crack as it propagates. The insertion from the mouth of the crack, as used by Davis,<sup>(6)</sup> is practical only if the crack is very short, i.e., shortly after initiation, and the crack tip conditions may not be representative of the conditions in longer, propagating cracks. The insertion from the side of the crack, which was used in this investigation, is open to the objection that the solution chemistry may be different from that deeper below the surface. The main drawback, however, was the inability to make the measurements very close to the crack front. Although calculations of the crack width based on the theoretical deflection of beams indicate that a probe with a 0.5  $\mu\text{m}$  tip diameter (the chloride ion electrode used in this study) could be placed as close as 2 mm or less from the crack front, the closest distance found possible in this work was about 4 mm. The larger pH probe could not be placed closer than about 6 mm from the front. This makes



the technique unsuitable for the examination of the conditions in the region at the tip, which seems to extend about 2-3 mm from the crack front, as shown by the indicators applied on the fracture surfaces using the freezing technique. On the other hand, the measurements made in the opening of the crack on the specimen side are not useless; since they are direct quantitative measurements yielding values of concentration, they can be used to verify the data obtained by other indirect techniques.

The use of implanted probes was found practical only for the measurement of the crack tip potential. The technique appears to be sound, although further improvement needs to be made to minimize the error caused by the exposure of other surfaces at the electrode tip.

Sampling of the solution from the opening of the crack on the specimen side proved to be feasible, but suffered from the same drawback as the direct electrode measurement, i.e., the inability to make the sampling very close to the crack tip. Another problem concerns the sample volume. In this investigation it was found possible and practical to draw samples of 0.1  $\mu$ l. This sample volume represents, however, an area of several millimeters square within narrow cracks which are several micrometers wide. Therefore, it is impossible to achieve a good spatial resolution unless smaller sample volumes can be collected and analyzed. This is possible but it would require further sophistication of the procedure.

The freezing technique substantially facilitates the solution chemistry determination and its full potential probably has not been reached. In its original form, combined with the use of indicators, it yields only semi-quantitative data. Collection of liquid samples from the fracture surfaces upon thawing, as used by Leidheiser and Kissinger<sup>(5)</sup>, was found impractical for very narrow cracks studied in this work.



The vacuum freeze-dry technique of preservation of the components of the electrolyte seems capable of yielding more accurate quantitative data for chlorides and metallic ions, with good spatial resolution. Unfortunately, the necessity to build a special, dedicated vacuum system did not leave enough time for the practical application of the technique by the end of the project period.

Although the determination of the crack tip pH values was successfully made in the very first experimental study of this subject<sup>(1)</sup>, further sophistication of the measurement in terms of accuracy and spatial resolution seems to be more difficult than for the other parameters of the solution chemistry. Since the vacuum freeze-dry technique is not applicable, the measurements in longer cracks have to be made either on the side of the specimen, or with the use of the basic freezing technique. In this study the use of indicators on the specimen side was found feasible, but the results did not provide more information than the data reported previously. An advance in this task remains as a challenge for future work.

The objective of this phase of the project was to explore and develop the techniques of analysis, not to collect significant data. The results of the measurements are presented in this report as an illustration of the capabilities of the techniques rather than a contribution to the knowledge of the conditions in the cracks. Essentially, the data confirm the previous findings: a region of high acidity at the crack tip, an increase in chloride ion concentration towards the tip, and high concentration of metallic ions in the crack tip region. The crack tip potential data show a definite, but relatively small potential drop between the mouth of the crack and the more negative crack tip.

## XII. CONCLUSIONS AND RECOMMENDATIONS

The study has shown that quantitative, more detailed data than previously reported can be obtained for the electrochemical conditions within stress corrosion cracks by an application of careful sampling techniques, the use of microelectrodes, and modifications of the techniques used in the past. The determination of the solution chemistry within the cracks by direct measurements within the crack and by analyzing liquid samples drawn from the crack provides data which can be evaluated without complicated processing based on assumptions concerning the width of the crack. The main drawback of these techniques is the inability to analyze the electrolyte close to the crack front. The preservation of the dissolved species by freezing and vacuum freeze-drying remains a promising technique for the determination of chlorides and metallic ions in the immediate vicinity of the crack front. The data have to be processed using measurements or assumptions of the crack width. The technique has not been fully evaluated in this study because of the lack of time.

The direct measurement of the potential at the crack tip remains a difficult experimental problem. The measurement with an implanted electrode provides reproducible data, but further effort will have to be made to make sure that the measured values do not contain a substantial experimental error. Measurement of the potential at the crack opening on the specimen surface, which was not explored in this study, is a promising alternative.

The following recommendations are made for future work in this area:

- a. To use the vacuum freeze-dry technique and compare the results with those obtained by direct measurements in the regions where both techniques can be used.

- b. To improve the measurement of crack tip potential using the implanted electrode by minimizing the exposure of surfaces other than those in the crack. This may be accomplished by the use of an insulating coating at the tip of the probe.
- c. To explore the measurement of the crack tip potential by a probe located at the opening of the crack on the specimen surface.

### References

1. B. F. Brown, C. T. Fujii, and E. P. Dahlberg, J. Electrochem. Soc., 116, 218 (1969).
2. G. Sandoz, C. T. Fujii, and B. F. Brown, Corr. Sci., 10, 839 (1970).
3. B. F. Brown: "Solution Chemistry within Stress Corrosion Cracks in Titanium 8-1-1 Alloy." Paper presented at the International Symposium on Stress Corrosion Mechanism of Titanium Alloys, Georgia Institute of Technology, Atlanta, Georgia 1971.
4. J. A. Smith, M. H. Peterson, and B. F. Brown, Corrosion, 26, 539 (1970).
5. H. Leidheiser and R. Kissinger, Corrosion, 28, 218 (1972).
6. J. A. Davis, Localized Corrosion, B. F. Brown, J. Kruger, R. W. Staehle, eds., NACE, p. 168 (1974).
7. M. Marek and R. F. Hochman, Corrosion, 26, 5 (1970).
8. M. Marek, J. G. Rinker, and R. F. Hochman: "Solution Chemistry in Crevices and Stress Corrosion Cracks." Paper presented at the 6th International Congress on Metallic Corrosion, Sydney, 1975.
9. R. Piccinini, M. Marek, R. F. Hochman, and A. J.E. Pourbaix, Localized Corrosion. B. F. Brown, J. Kruger, R. W. Staehle, eds., NACE, p. 179 (1974).
10. M. Marek and R. F. Hochman, A Study of Localized Corrosion Cell Reactions. Paper presented at the NACE Corrosion Research Conference, Anaheim, Calif. 1973.

Table 1

PARAMETERS OF THE AA ANALYSIS

Aluminum:

|                          |                      |
|--------------------------|----------------------|
| Wavelength:              | 309.3 nm             |
| Lamp current:            | 5 mA                 |
| Atomization temperature: | 2,500 <sup>o</sup> C |
| Ramp:                    | 400 <sup>o</sup> C/s |
| Hold time:               | 2 s                  |

Zinc:

|                          |                      |
|--------------------------|----------------------|
| Wavelength:              | 307.6 nm             |
| Lamp current:            | 5 mA                 |
| Atomization temperature: | 1,400 <sup>o</sup> C |
| Ramp:                    | 300 <sup>o</sup> C/s |
| Hold time:               | 3 s                  |



Table 2

## RESULTS OF THE AA ANALYSIS OF EXTRACTION REPLICAS

| Distance from<br>the crack front<br>(mm) | Aluminum<br>( $\mu\text{g}/\text{cm}^2$ )<br>(1) | Zinc<br>( $\mu\text{g}/\text{cm}^2$ )<br>(1) |
|--|--|--|
| 0.5                                      | 0.2  | < 0.03                                       |
| 1.0                                      | 0.8  | < 0.03                                       |
| 1.5                                      | 1.5  | 0.05   |
| 2.0                                      | 2.3  | 0.06   |
| 3.0                                      | 0.6  | 0.05   |
| 4.0                                      | 0.35   | 0.08   |
| 5.0                                      | 0.003 (2)  | 0.006 (2)                                    |

## Notes:

- (1) Cumulative values from matching areas on both fracture surfaces.
- (2) Data obtained using large replica samples.

Table 3

RESULTS OF THE CRACK TIP POTENTIAL MEASUREMENTS

| Test No. | $E_N$ (V, SCE) | $E_{CT}$ (V, SCE) |
|----------|----------------|-------------------|
| 1        | -0.912         | -0.980            |
| 2        | -0.905         | -0.968            |
| 3        | -0.908         | -0.952            |
| 4        | -0.915         | -0.974            |
| 5        | -0.910         | -0.966            |

$E_N$  . . . Electrode potential measured by the electrode in the notch, at the time of the crack emergence at the implanted probe.

$E_{CT}$  . . Electrode potential measured by the implanted electrode at the instant of crack emergence.

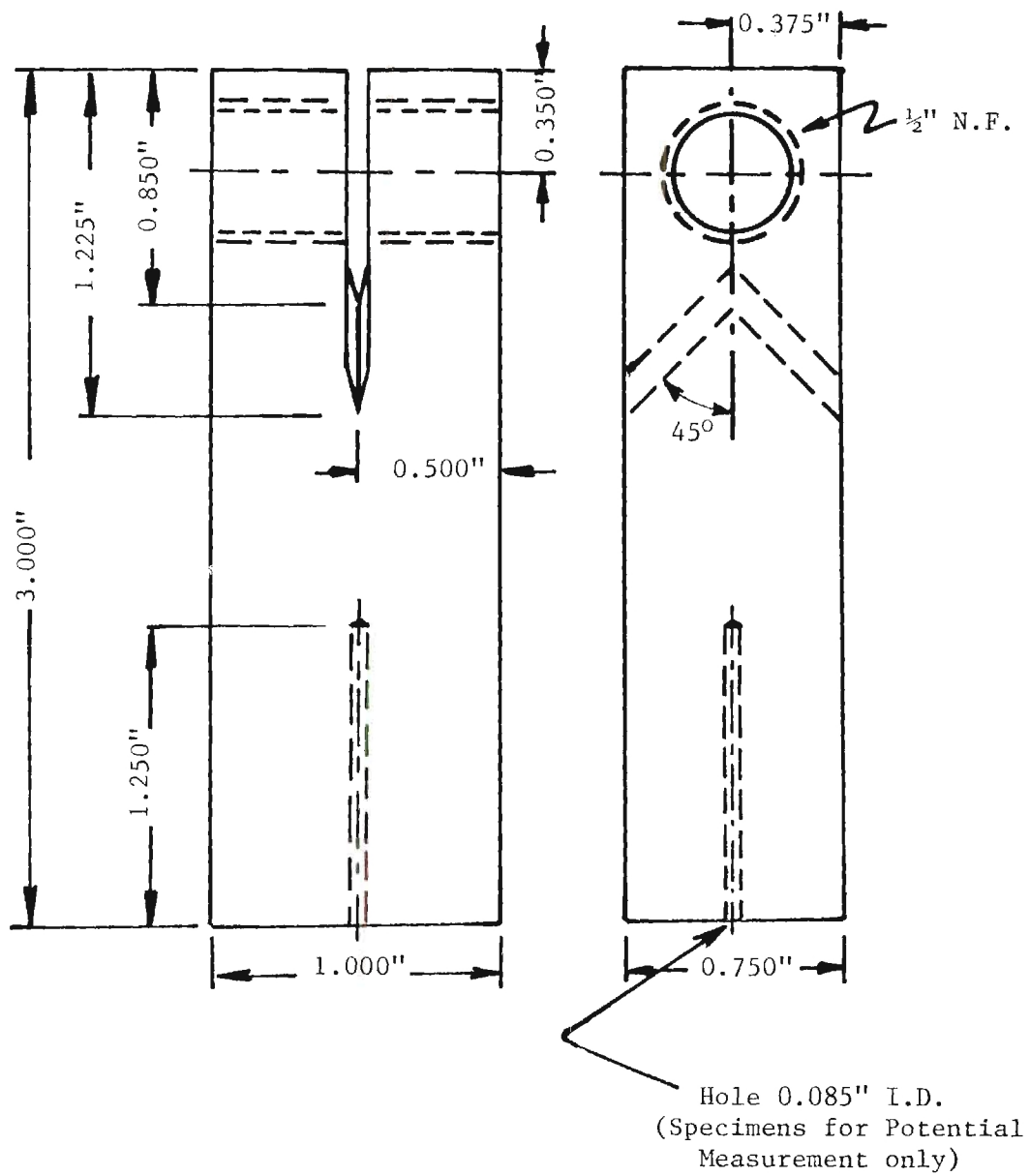


Fig. 1. SCC Specimen for the Determination of Electrochemical Conditions within cracks.

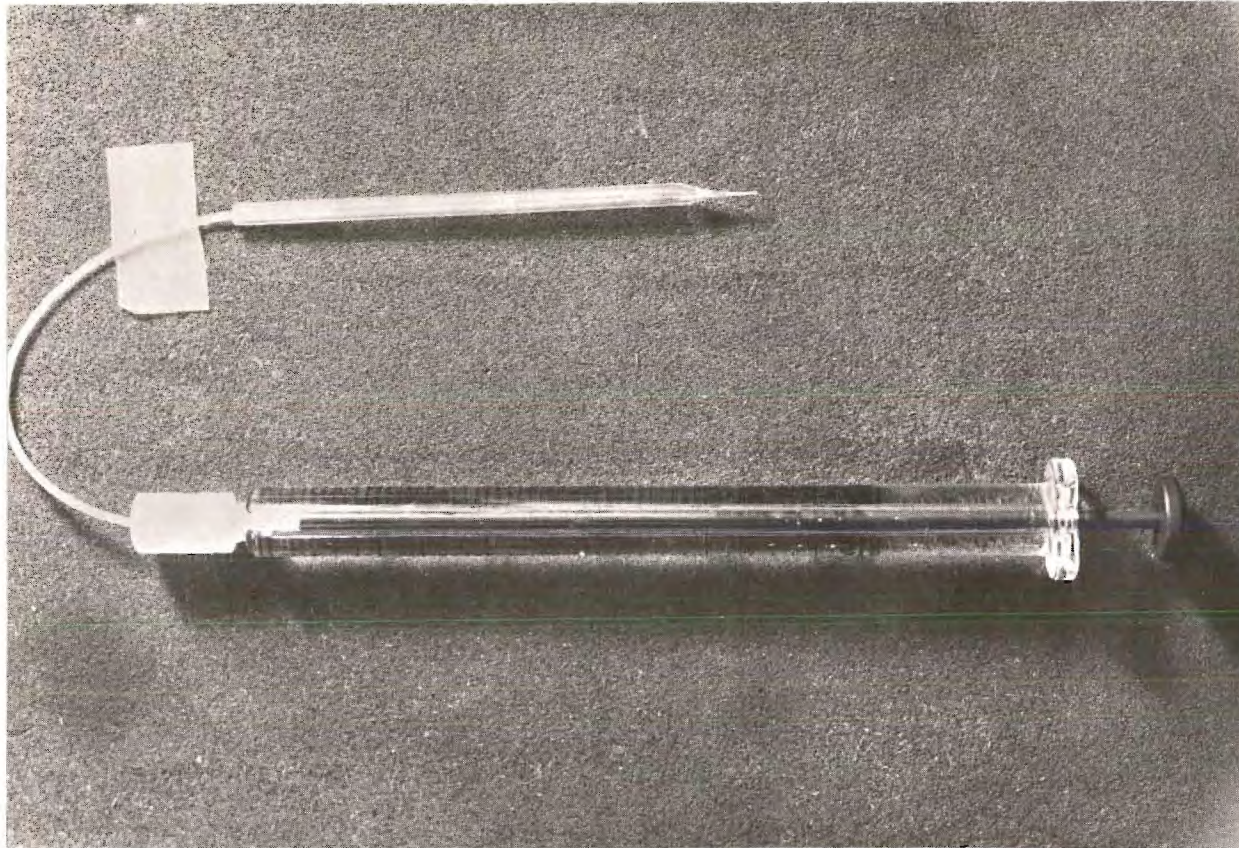


Fig. 2. Microcapillary Probe for Collection of Liquid Samples from Cracks.



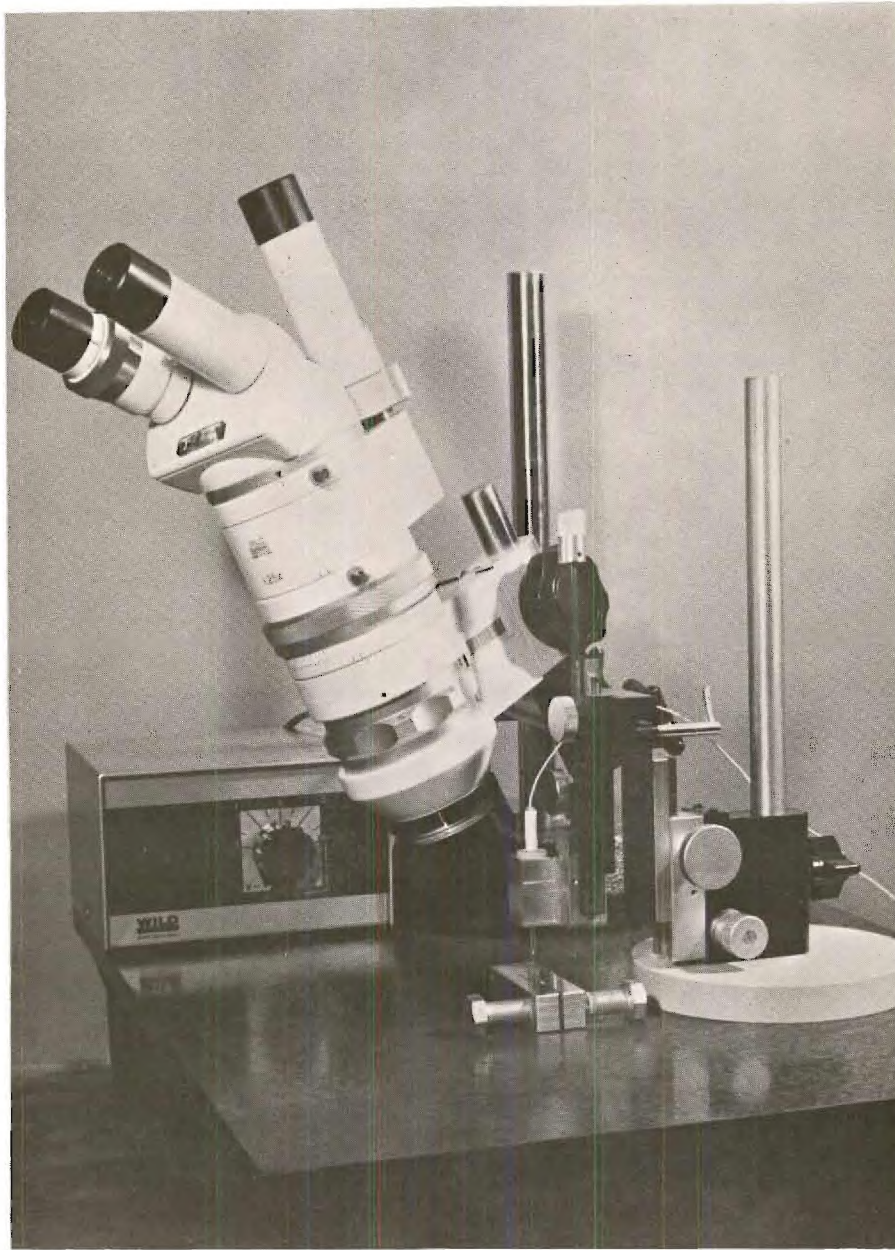


Fig. 3. Experimental Setup for Application of Microprobes in Cracks.



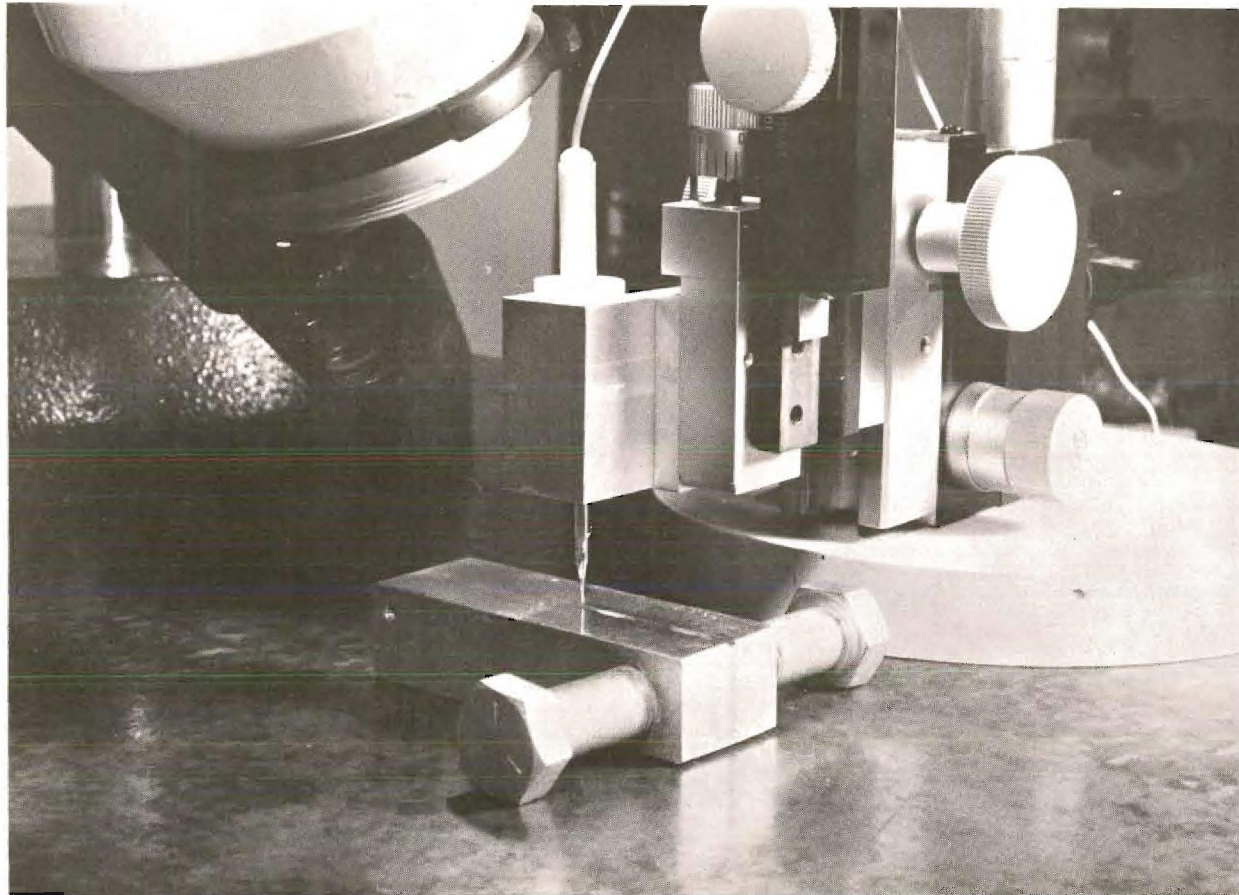


Fig. 4. Experimental Setup for Application of Microprobes in Cracks (Detail).

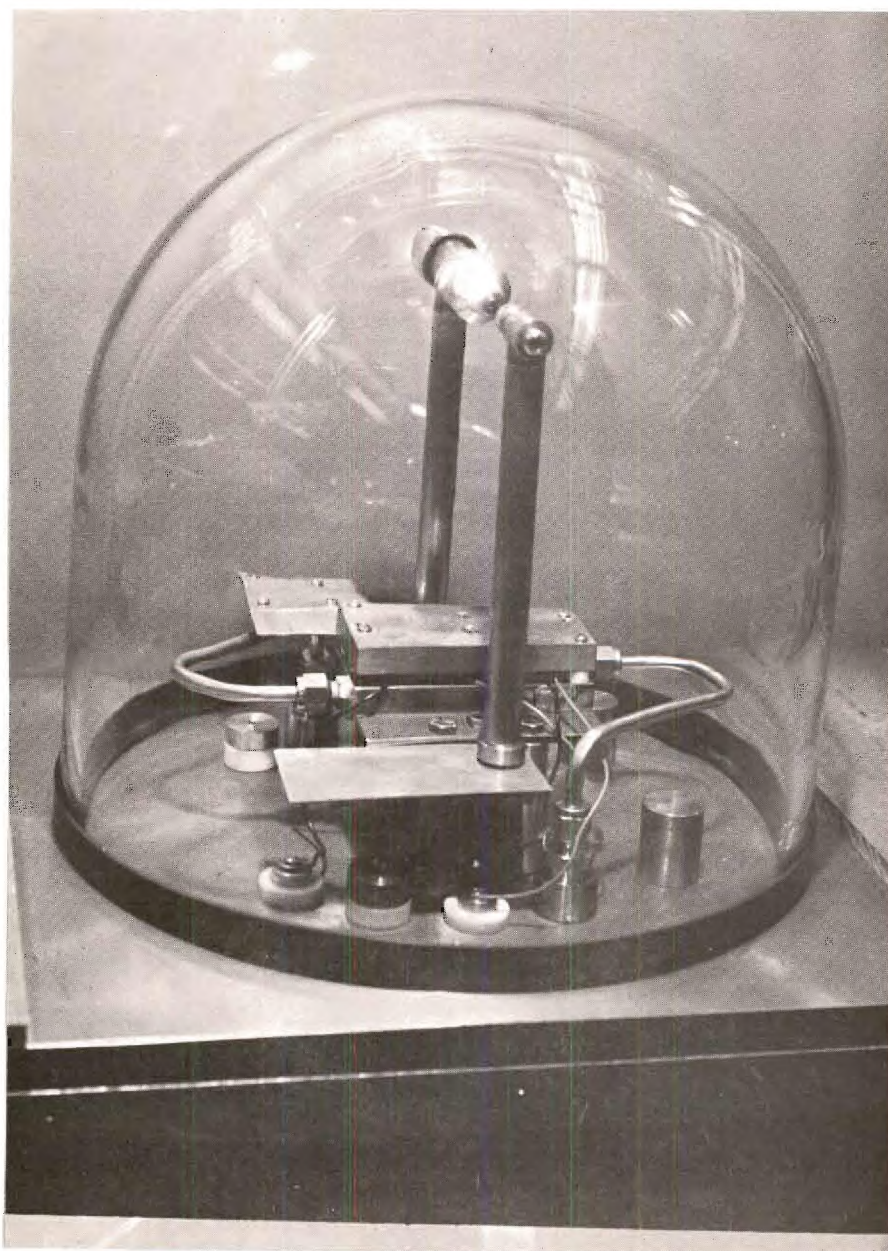


Fig. 5. Vacuum Chamber Used for Freeze-Drying  
of the Electrolyte.



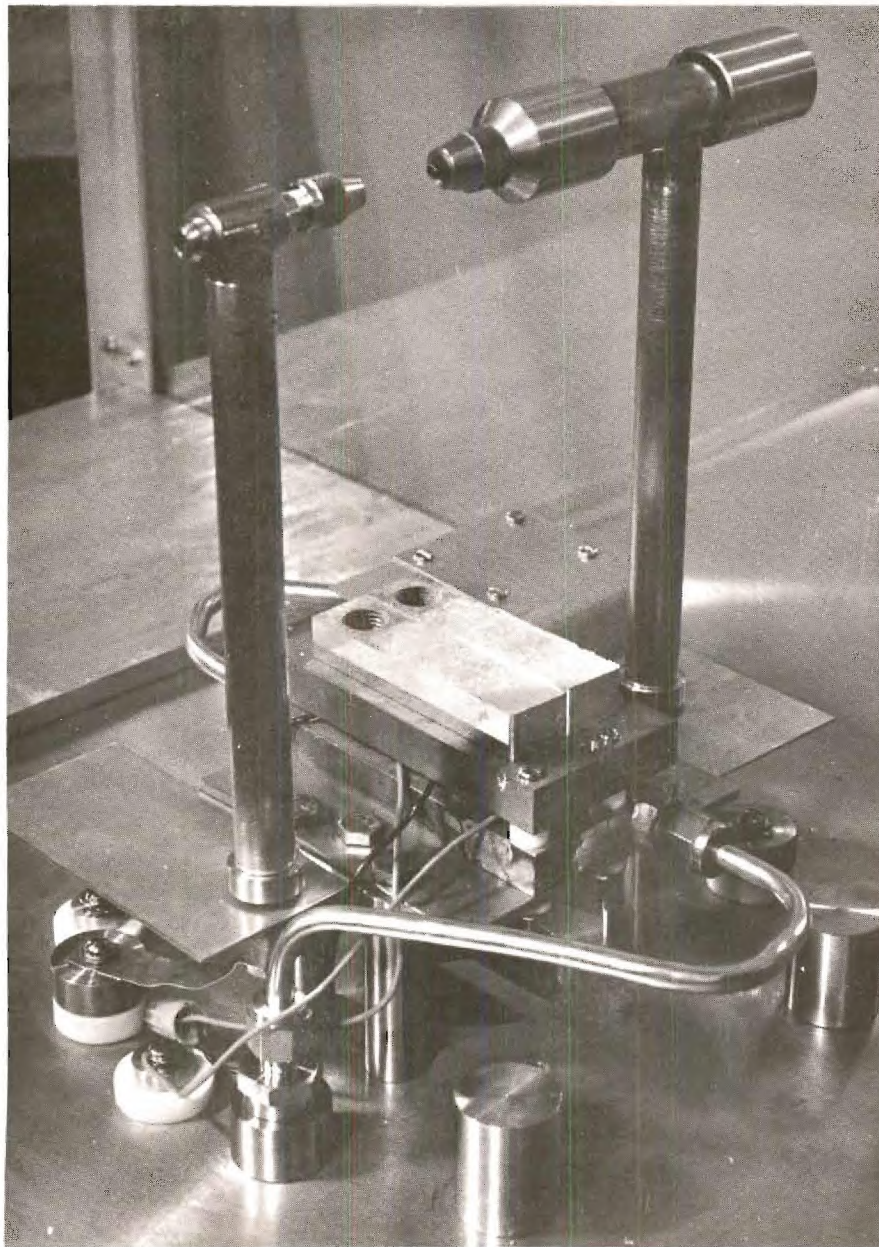


Fig. 6. Thermoelectrically Cooled Stage and Carbon Evaporator Used in the Freeze-Dry Technique.

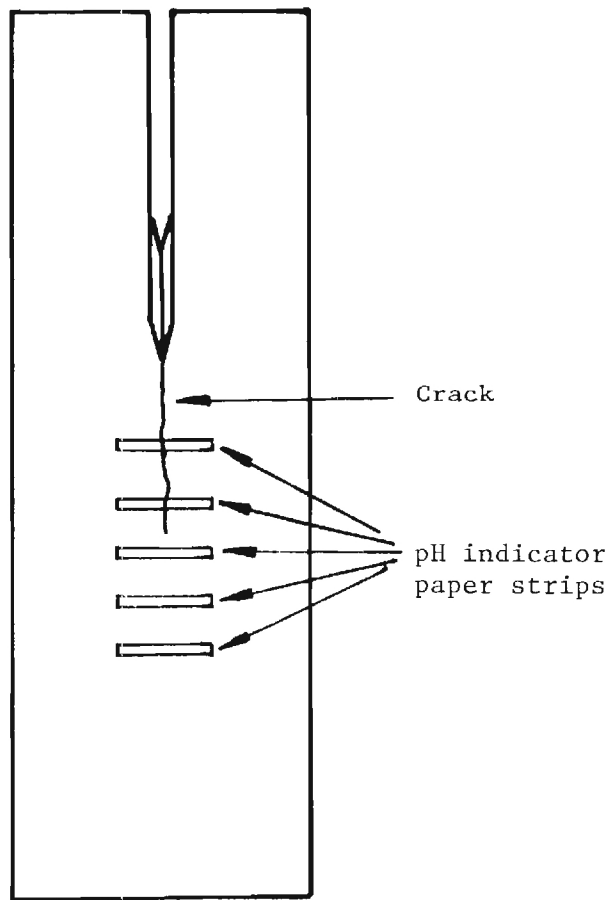


Fig. 7. Schematic Illustration of the Location of Indicator Strips for Determination of Crack Tip Acidity.

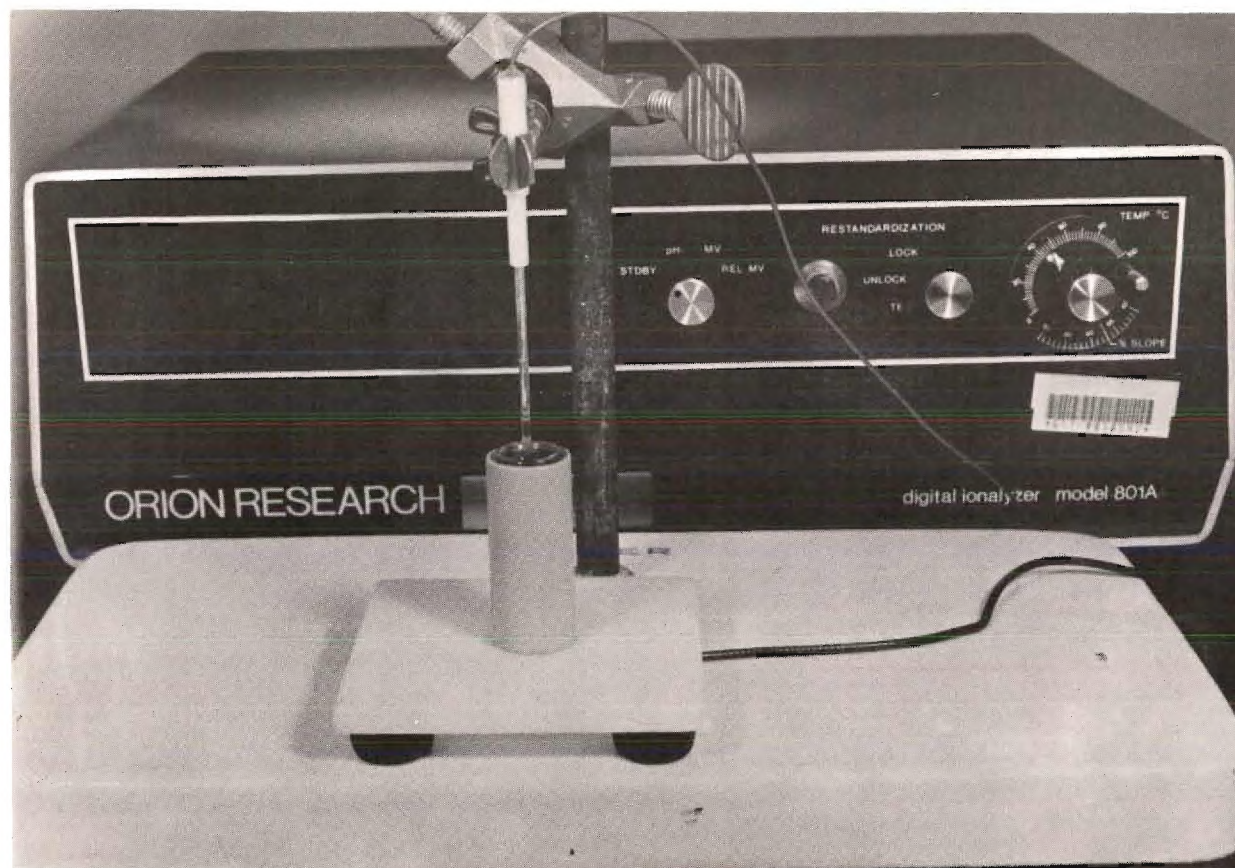


Fig. 8. Setup for pH Analysis of Microliter Samples Using an Inverted pH Electrode.



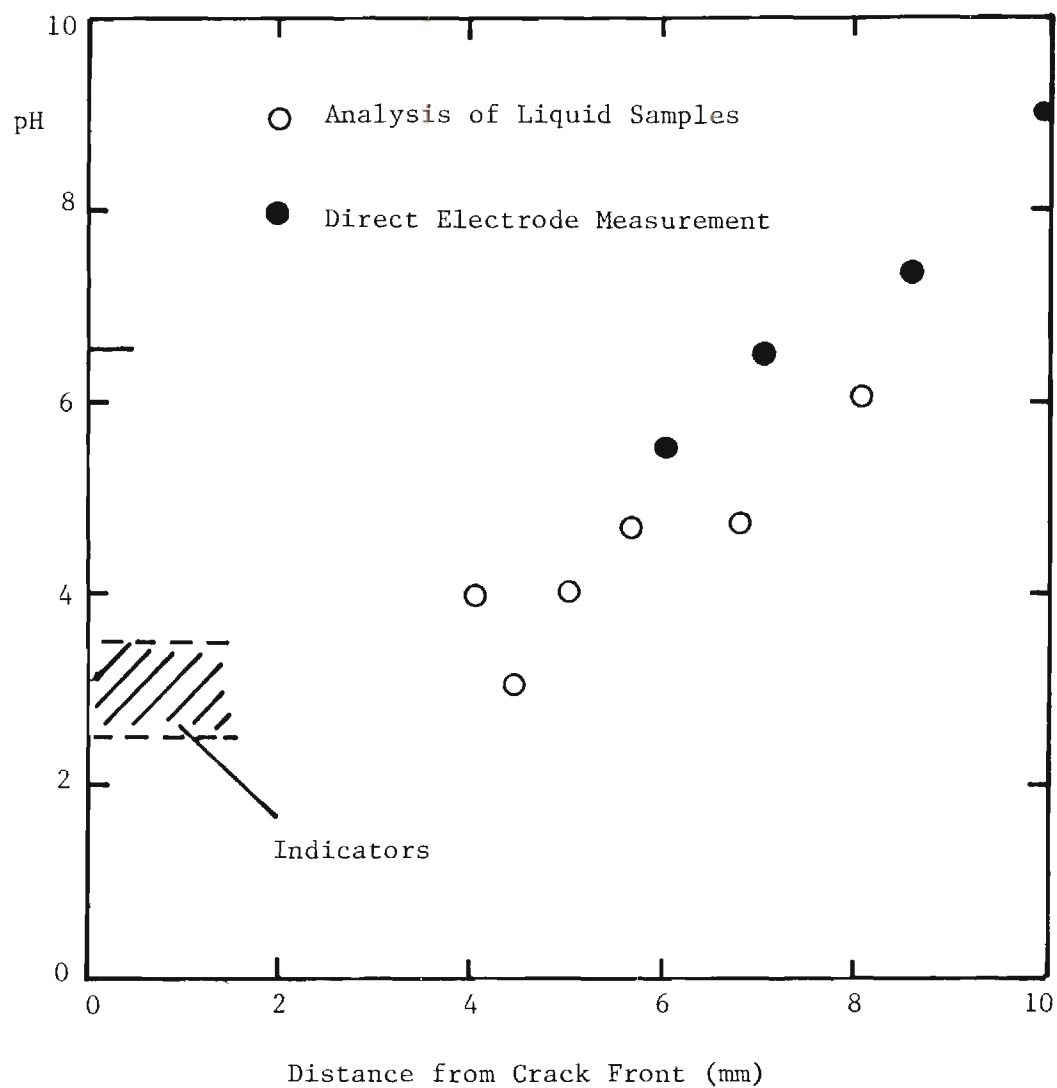


Fig. 9. Results of pH Measurements Using Various Techniques.

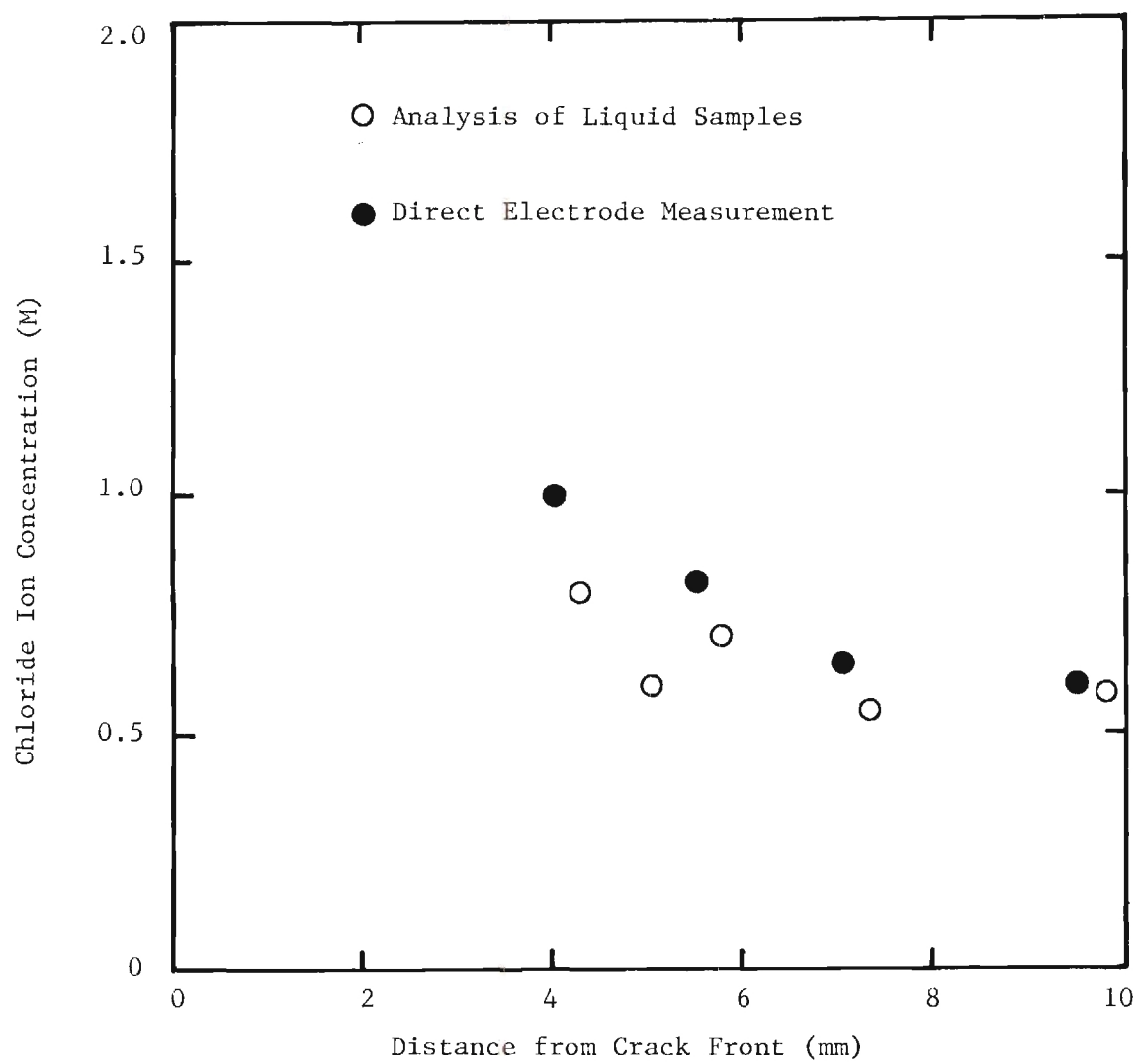


Fig. 10. Results of Analyses for Chlorides.

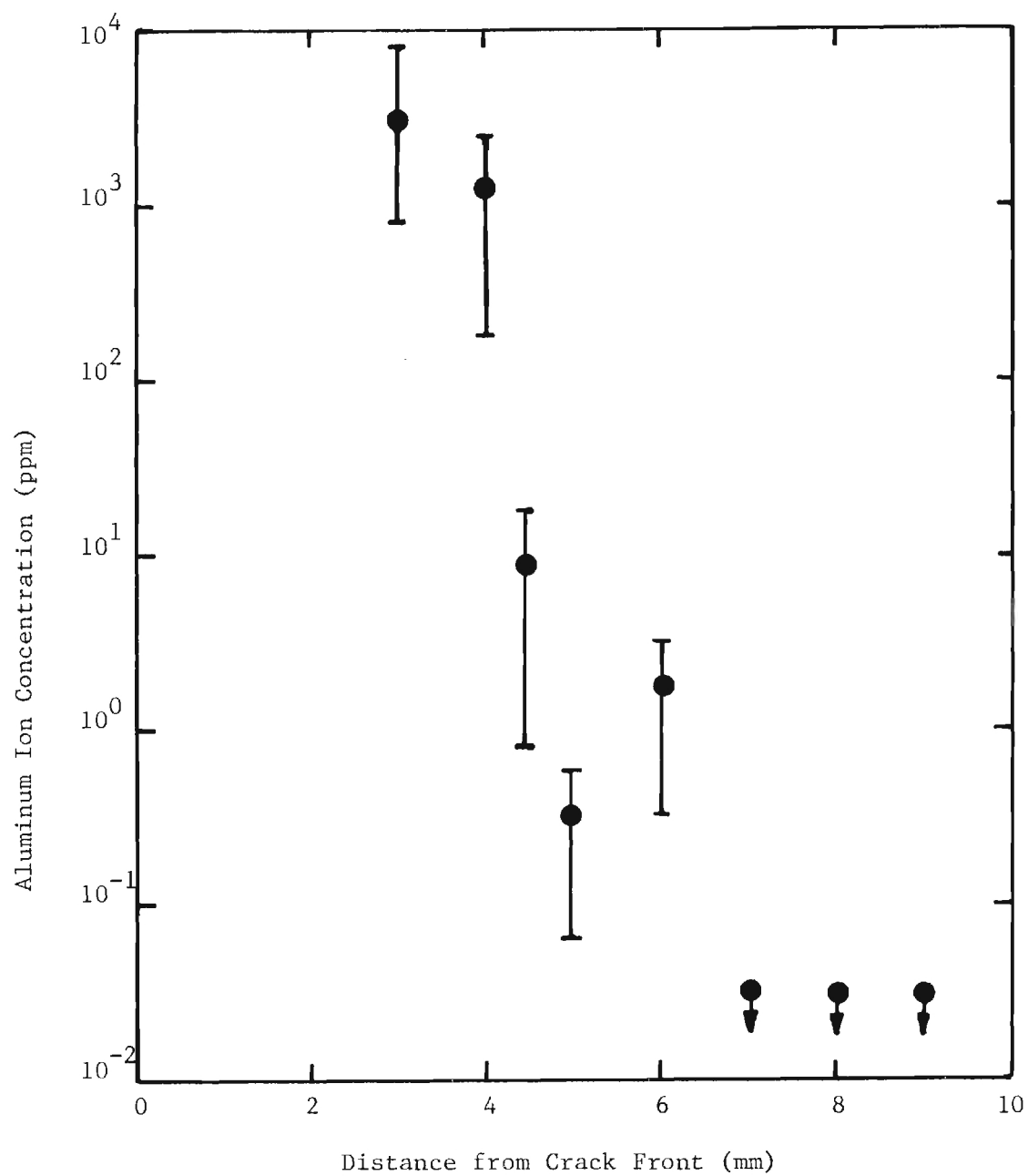


Fig. 11. Results of Analyses for Aluminum Ions.

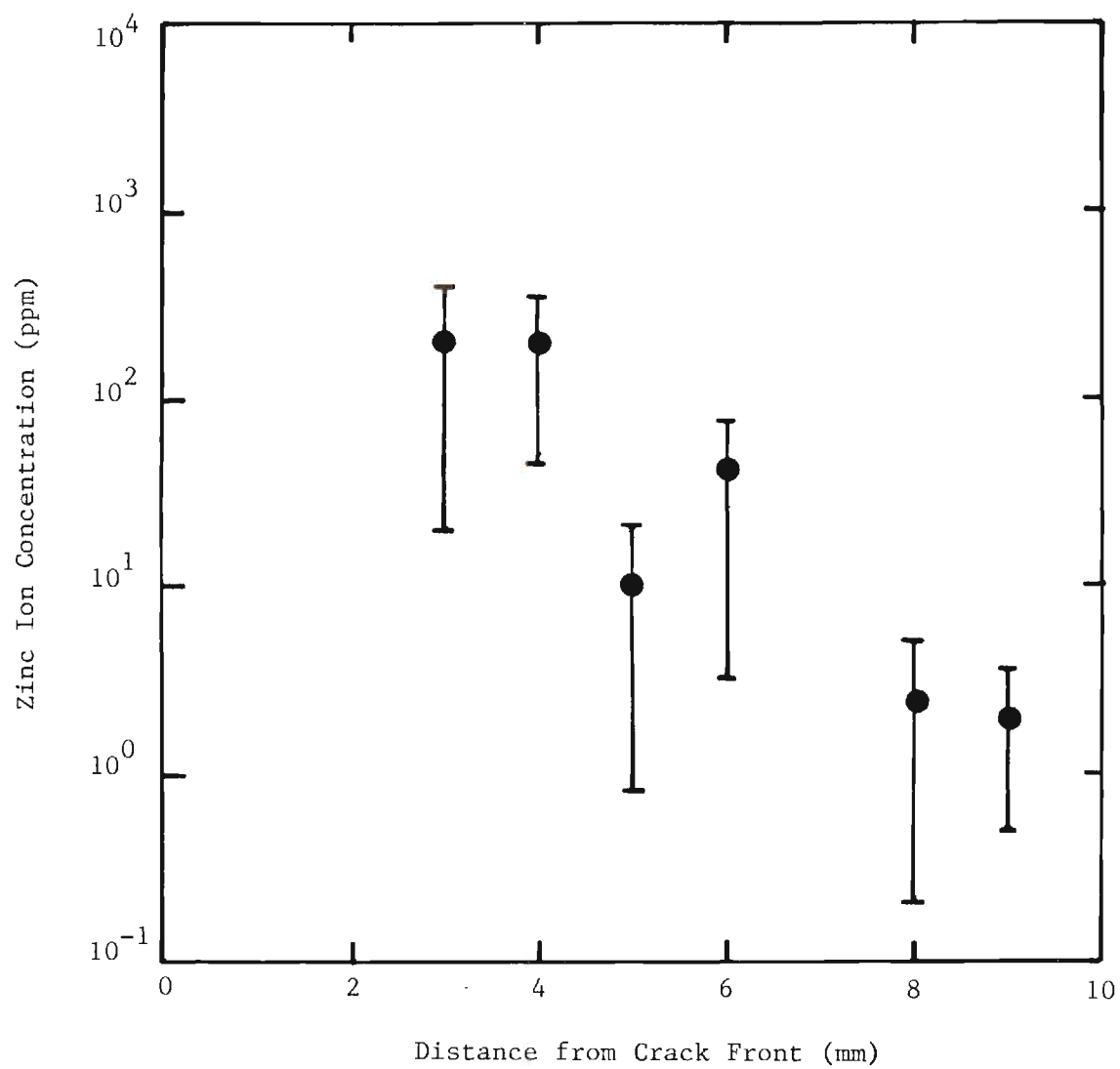


Fig. 12. Results of Analyses for Zinc Ions.

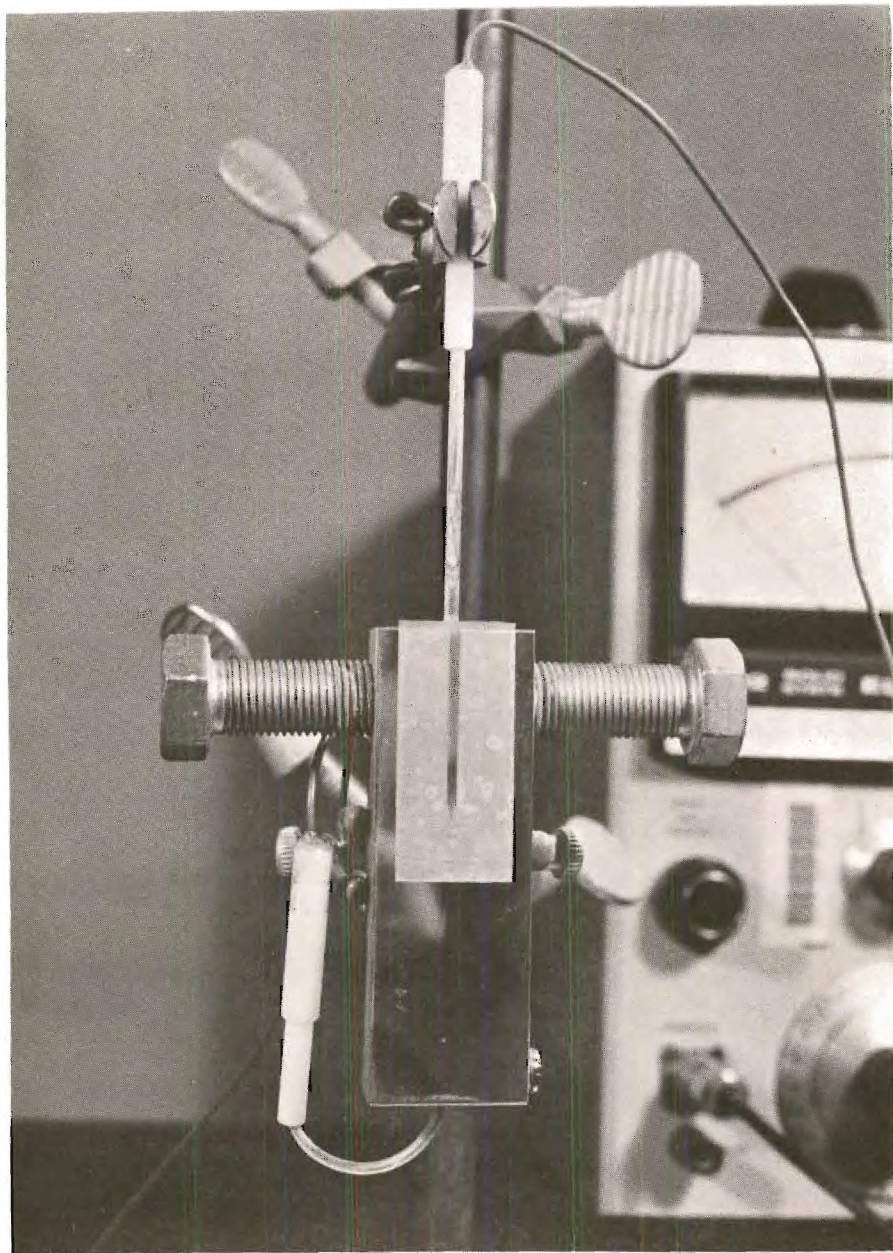


Fig. 13. Setup for Measurement of the Potential at the Crack Tip Using an Implanted Electrode.



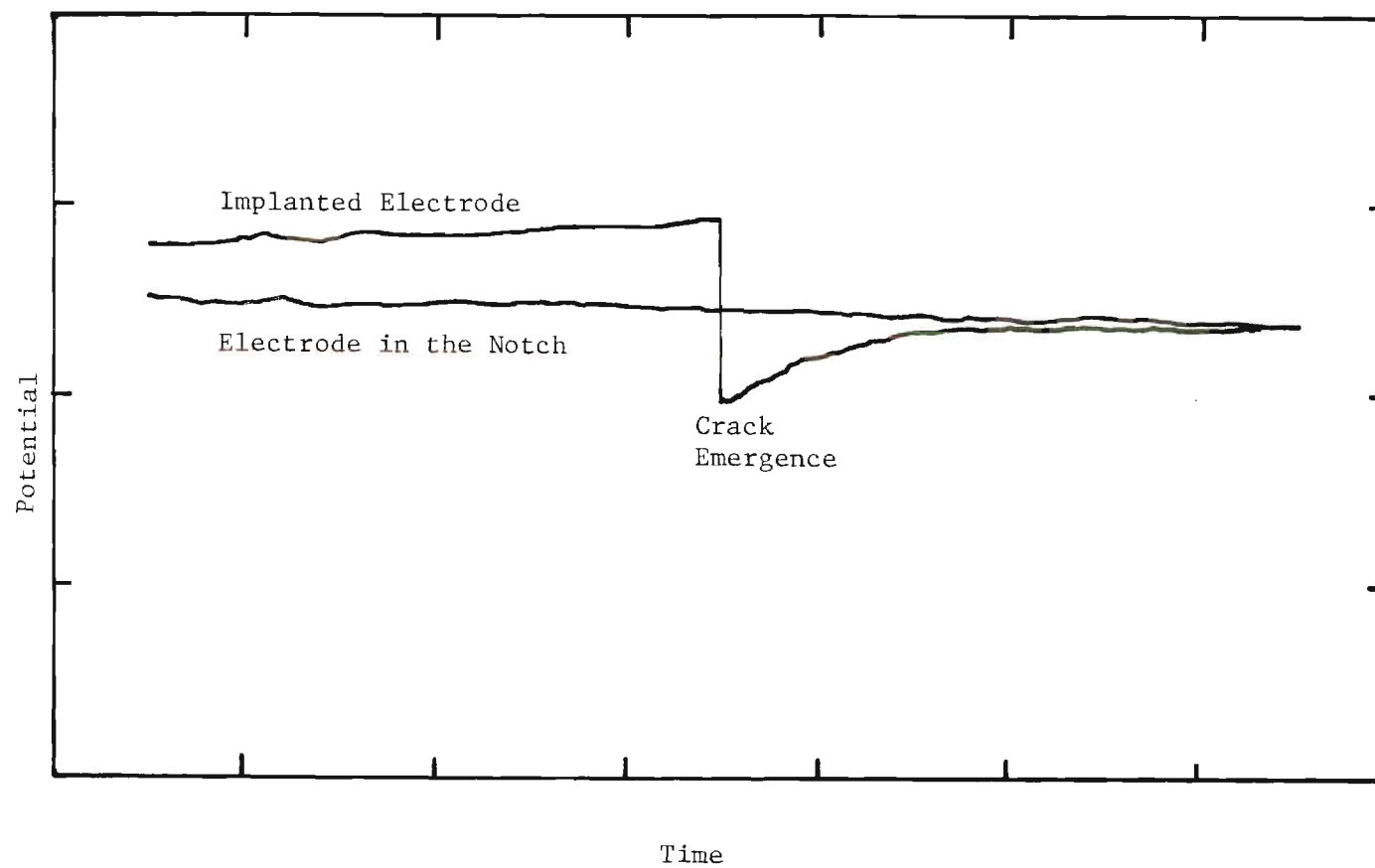


Fig. 14. Potential Variation vs. Time as Measured by the Implanted Electrode and an Electrode in the Notch.