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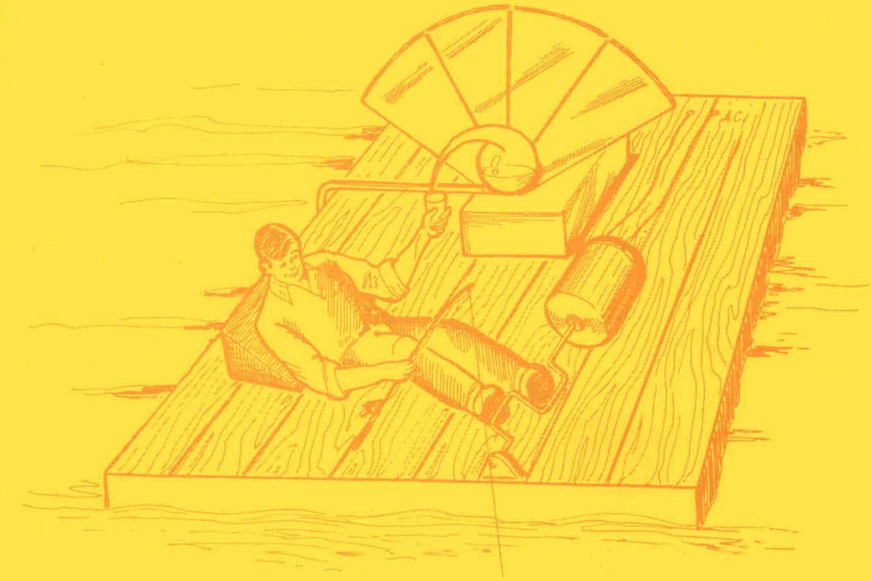
PROCEEDINGS OF THE OCEAN THERMAL ENERGY CONVERSION (OTEC) BIOFOULING, CORROSION, AND MATERIALS WORKSHOP

January 8-10, 1979

Rosslyn, Virginia



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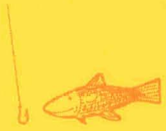

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ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

PROCEEDINGS OF THE OCEAN THERMAL ENERGY CONVERSION (OTEC) BIOLFOULING, CORROSION, AND MATERIALS WORKSHOP

January 8-10, 1979
Rosslyn, Virginia

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PREFACE

Argonne's OTEC Biofouling, Corrosion, and Materials (BCM) Project was established in March 1978. It soon became evident to us in the Project that there was by no means optimum communication among the twenty or so contractors working in the program and between them and the Department of Energy (DOE). For example, those doing ocean measurements in the Gulf of Mexico did not have a good opportunity to pass on what they were learning to those in Hawaii and vice versa. And, there was no easy way to pass on to those doing the R&D in the field the trends in the overall OTEC program so they could optimize their work in accordance with the needs. In addition, we could see an increasingly urgent need to develop a BCM program plan (1) to ensure that our projected program would be optimized in terms of OTEC needs and in terms of current detailed knowledge of fouling, the effectiveness of countermeasures, and corrosion, and (2) to provide material to justify DOE program decisions and to support requests for funding.

At first we planned to bring "our" people together in special sessions at the next (the sixth) annual OTEC conference. But when it became known that this meeting would not be held before June 1979, we decided to have our own Workshop in January 1979, to meet the needs for communication and to help develop a program plan. It was decided that the Workshop would not be closed to attendance by others, but that it would be focused to the needs of those in the BCM program and only limited numbers of others would be made welcome. With the support of the DOE BCM Program Manager Gene Kinelski and special program advisors Frank LaQue and Ralph Mitchell, we decided to structure the meeting into a presentation of current status of all program elements, together with plans for the future, followed by sessions on specific topics, focusing the discussions in each on answering two questions:

1. What do we know or have we done in comparison with the needs identified?

2. What are the remaining needs, what must be done and how long will it take?

The specific topics chosen to cover the subject and to minimize the loss of contribution by those desiring to participate simultaneously in more than one session were

A. 8:30-11:00 AM, Measurement of R_f and Analysis of Heat Transfer Data

B. 8:30-11:00 AM, Biology of Fouling

AB. 11:00 AM-12:15 PM, Fouling and Countermeasures

C. 8:30 AM-12:15 PM, Corrosion and the Application of Materials.

These Proceedings of the Workshop have been prepared from camera-ready copy provided by the authors and from summaries of the sessions on specific topics written by the three chairmen, Peter H. Benson, Joseph B. Darby, Jr., and Glenn F. Popper, the three Assistant Managers of Argonne's BCM Project. The order of presentation of the papers is not entirely that followed for the three-day Workshop, since some rearrangement has been done to group papers on similar topics under program headings.

J. E. Draley, Manager
OTEC Biofouling, Corrosion, and
Materials Project at
Argonne National Laboratory

OTEC OVERVIEWS

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THE REQUIREMENTS FOR BIOFOULING, CORROSION, AND MATERIALS IN THE OTEC PROGRAM

by

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ABSTRACT

Investigations in the OTEC Biofouling, Corrosion and Materials Program emphasize heat transfer as influenced by biofouling, corrosion, biofouling and its countermeasures, and materials selection. A review of the data reported indicates that a large number of unknowns still exist. The objective of this Workshop is to establish guidelines for satisfactory solutions.

I. INTRODUCTION

At this Workshop on Biofouling, Corrosion, and Materials, the format is organized differently than those previously used. We will spend the first two days in formal presentations of progress made in individual projects. These papers will serve to bring all of us up-to-date on the work being done and results that we hope to achieve during this fiscal year. The third day will be devoted to workshops on specific subjects of great importance to the OTEC program.

In my presentation to you this morning, I would like to outline where I think we are in our various major subject areas. I would also like to enumerate the areas of concern to us that need attention. During the Workshops on Wednesday, it is requested that these concern items be considered. Hopefully, the Workshop will produce guidelines for work that needs to be done, who will do it, how long it will take, and some idea of the cost of the experimentation or study.

II. OTEC SYSTEMS DEVELOPMENT

As an introduction to the specific areas of Biofouling, Corrosion, and Materials Development, Figures 1 and 2 will illustrate our milestone and interface goals. It is apparent that our efforts must be coordinated with those of the power system and ocean engineering groups under Ken Read and Bill Sherwood. Until design concepts are proposed by both Ken and Bill, we cannot get too deeply involved with Biofouling, Corrosion and Materials. However, to some degree, we have to anticipate areas that require long lead time experimentation to aid the designers of power system and ocean components. The critical interfaces, of course, are with the two major developments, OTEC-1 and OTEC-10.

OTEC SYSTEMS DEVELOPMENT

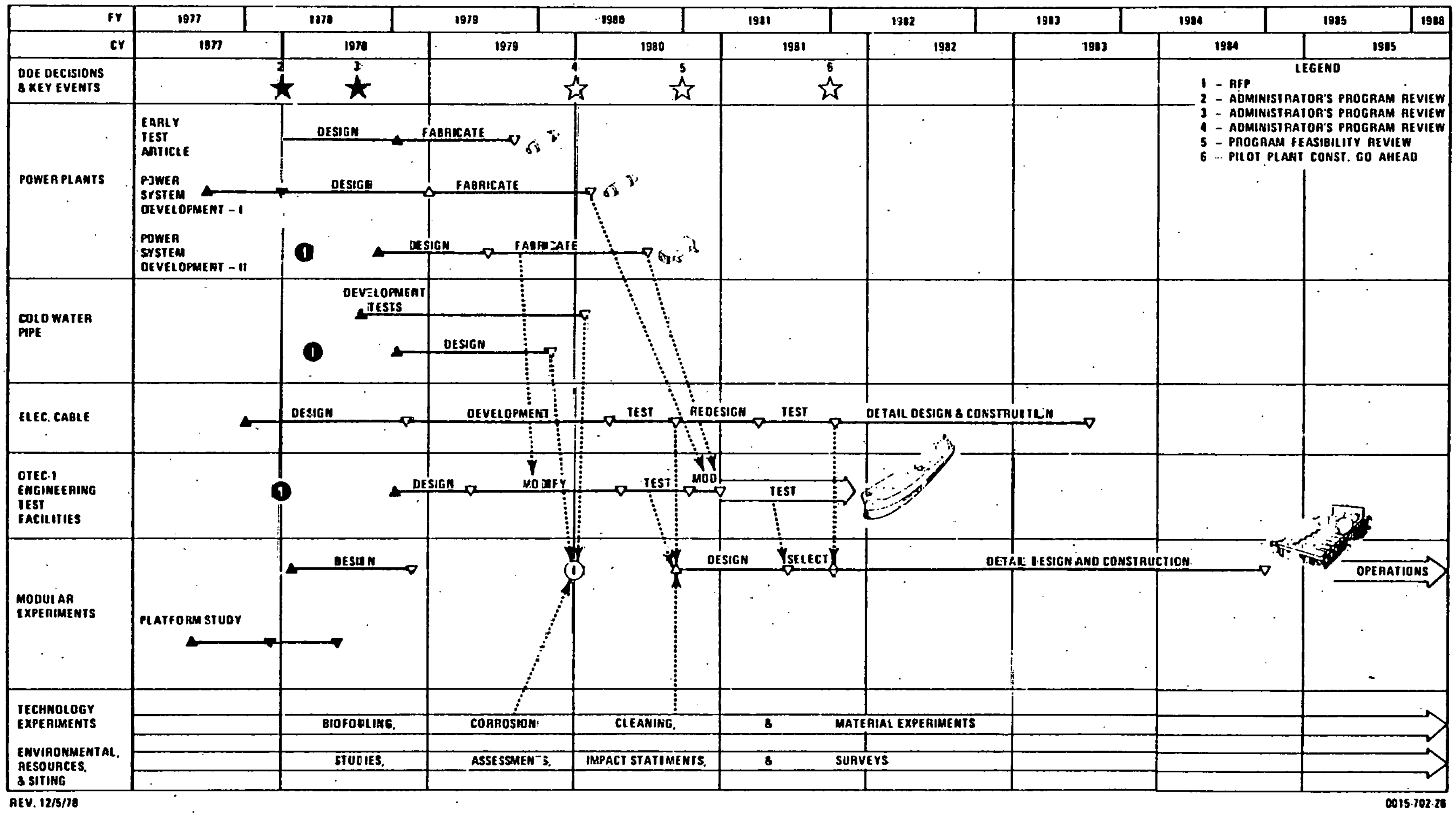

Figure 1

OTEC SYSTEMS DEVELOPMENT
BIFOULING, CORROSION, AND MATERIALS INTERFACE

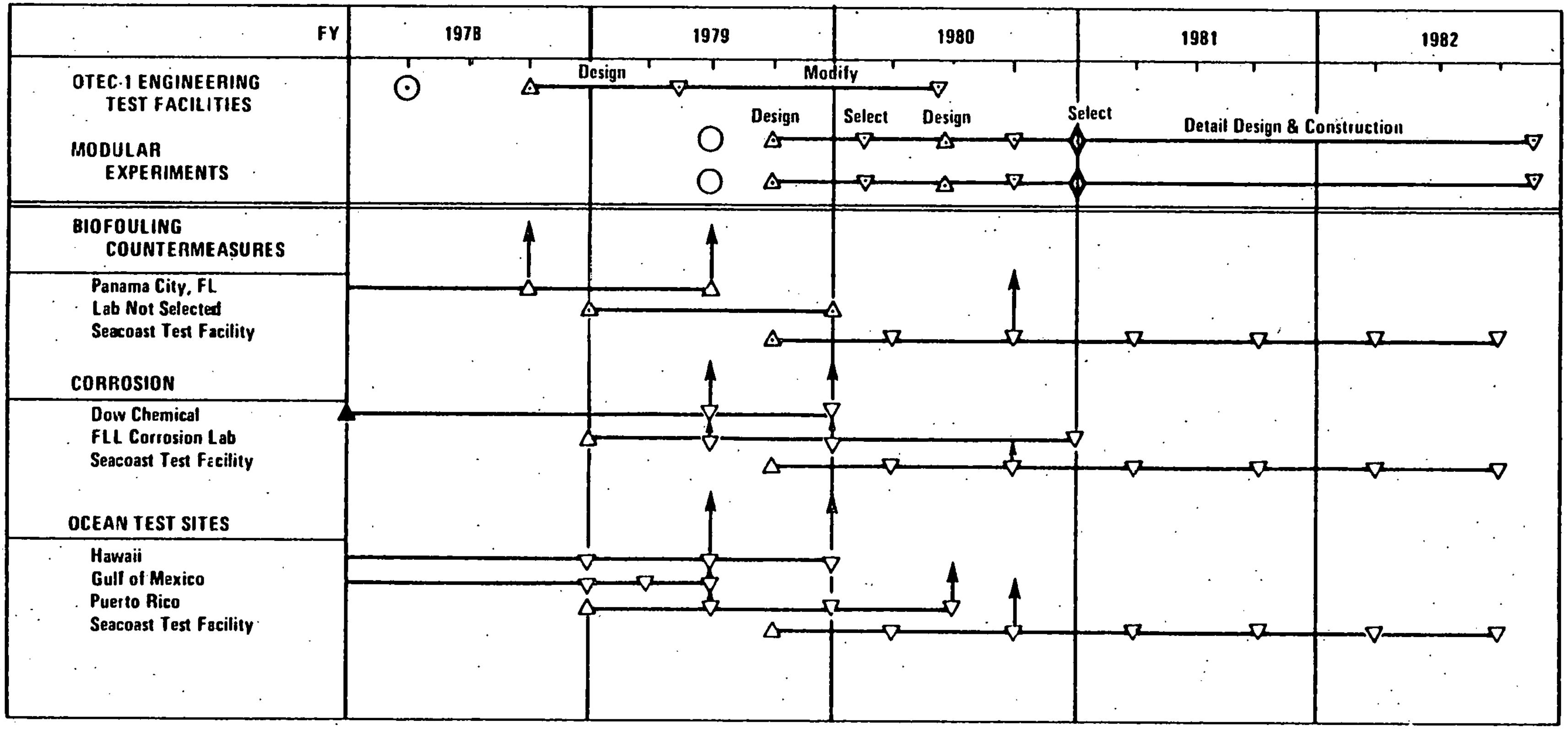

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Figure 2

In my presentation today, I would like to address the following subject areas:

Microbiofouling
Microbiofouling Countermeasures
Macrofouling Countermeasures
Heat Exchanger Corrosion and Materials Selection
Other Component Materials Problems.

In some of my remarks, I realize that some effort may be under way, but I will mention the problem area anyway to keep everyone informed.

A. MICROBIOFOULING

Programmatically, the emphasis in our biofouling control investigations has been on microbiofouling. However, both micro- and macrobiofouling are important -- micro for heat transfer surfaces and macro for all other wetted surfaces.

In microbiofouling, we have learned that the effect of the "conditioning" film on heat transfer surfaces is not important. However, it may be of importance in establishing the base for subsequent microbiofouling buildup. After mechanical cleaning, using M.A.N. brushes in CMU heat transfer devices in tests at Ke-ahole Point, Hawaii and the Naval Coastal Systems Center at Panama City, Florida, the rate of increase in R_f (resistance to heat transfer attributable to biofouling) is rapid and no conditioning time is available. In other words, the cleaning method did not remove the conditioning film,

There are a number of unknowns that influence microbiofouling such as,

1) What are the effects of seasonal variations?

2) What are the long-term effects of mechanically removing biofouling films on a periodic basis?

3) What explanation is there for the variation in the steep slopes of the R_f versus time plots? What causes the variations -- the season of the year, temperature, an influx of a new body of seawater either nutrient rich or poor, effect of mechanical cleaning, etc,?

4) What are the thicknesses of the microbiological films -- as related to the R_f or time? Are these thickness measurements significant? Could our understanding of the nature of the films be enhanced by thickness measurements?

5) What is the role of the conditioning film? Does it vary from OTEC site to site? If we knew more about this biological polymer layer, could we design better cleaning methods for its removal or prevention?

6) How does the corrosion product film, such as forms on aluminum alloys, influence the buildup of microbiofouling? If a calcareous deposit forms on the heat transfer surfaces, what is its effect on the buildup of microbiofouling?

7) What is the influence of the base metal -- whether it is aluminum, copper-nickel, stainless steel, or titanium -- on the microbiofouling?

8) Is microbiofouling influenced by OTEC potential site locations? Are certain species of biota more prevalent in one site?

B. MICROBIOFOULING COUNTERMEASURES

In order to maintain an R_f of less than 0.0001 hr-°F-ft^2/Btu, countermeasures to microbiofouling are important to OTEC heat exchangers. Based on extensive Technology Reviews, we have identified four basic types of countermeasures to fouling:

Amertap balls
M.A.N. brushes
Chlorination
Slurries

These methods are being evaluated (or will be shortly) at the Naval Coastal Systems Center, Panama City, Florida. The advantage of conducting such tests using warm, coastal Gulf of Mexico seawater is that rapid fouling occurs during most of the year, thus permitting us to obtain more data in a short period of time. Also, it is thought that if we can clean at Panama City, Florida, we should be able to do as well or better in clean, open ocean water. One important difference in the results of these tests is that the effect of a conditioning film is obscured by the rapid biota growth.

Preliminary tests using M.A.N. brushes on a cycle of two passes every 8 hours indicate that titanium pipes can be kept clean -- below an R_f of 0.0001 -- for a period of 70 days. Under similar conditions, Aluminum Alloy 5052 pipes could not be maintained below an R_f of 0.0001. Unfortunately, the pipes were not readily removable for detailed biological investigations. Therefore, the reason for the difference between aluminum and titanium is not known.

There are a number of unknowns that need further experimentation and/or research, such as,

1) What countermeasures are suitable for OTEC heat exchangers? The answers will be obtained in tests at the new Seacoast Test Facility and the OTEC-1 platform. OTEC-1 will be equipped to use Amertap balls and chlorination on the 1-MWe heat exchangers. (The reasons for these being selected could be discussed at one of the sessions devoted to that subject.)

2) Are there any metals that cannot be kept clean because of the influence of their corrosion product films?

3) What chlorination dosages keep R_f below 0.0001? Will mechanical cleaning be required, in addition to a chemical method? If chlorination is used, can the effluents meet the as yet unknown requirements of EPA in clean seawater? Will batch chlorination on one module at a time be a feasible method of cleaning? If the chlorination effluents are too high to comply with EPA regulations, can dilution be used to overcome this problem? (The effluent from one module could be pumped back into the cold or warm water pipe at a controlled rate.)

4) With mechanical cleaning, will erosion-corrosion occur? (Further coverage will be given under Corrosion.)

5) What are the long-term effects of cleaning, either mechanically alone or together with chlorination?

6) How will the tests at the Naval Coastal Systems Center, Panama City, Florida compare with tests in clean, open ocean water? Can tests be devised that could be conducted sooner than those planned for the Seacoast Test Facility and/or OTEC-1?

7) How do countermeasures compare with warm water versus cold water? The earliest tests planned for cold, deep ocean water will be at the Seacoast Test Facility.

C. MACROFOULING COUNTERMEASURES

The influence of macrofouling on OTEC components is viewed as a serious problem. If it can be overcome by means of chlorination, meeting the requirements of EPA, which have not been established as yet for open ocean conditions, then we will have a simple solution. If not, then we will need to rely on other means of keeping the components clean. Under consideration are the following countermeasures:

Slurry cleaning

Use of copper alloys with antifouling characteristics (provided aluminum is not used downstream of the copper)

Antifouling paints

Antifoulants impregnated into concrete and/or plastic.

Some of the unknowns in this area are as follows:

1) Will low dosage chlorination work?

2) How will we keep macrofouling off surfaces in Amertap ball handling systems, M.A.N. cages and brushes, screens, distribution piping, valves, pumps, tube sheets, water boxes, etc?

3) Will macrofouling be as much a problem in cold water components as it is anticipated to be in warm water?

4) If antifouling coatings are required, will we be forced to remove components, like heat exchangers, and recoat them at shore-based facilities? What will these costs amount to and what will be the effect on power production?

5) Can we use mechanical methods of cleaning, such as Scamp, controlled automatically?

D. HEAT EXCHANGER CORROSION AND MATERIALS SELECTION

After extensive Technology Reviews and much discussion, the selection of candidate OTEC heat exchanger alloys was made to include:

Titanium Grade 2

Aluminum alloy Alclad 3003 (3004) or Alloy 5052

Copper-nickel Alloy 706 (90 copper-10 nickel)

20Cr-24Ni-6Mo-Fe Alloys.

Since the Workshop discussion will involve these alloys, it is important in our overview to report the current status of our knowledge -- as it applies to OTEC heat exchangers.

1. Titanium

Titanium, Commercial grade 2, is believed to be an excellent choice for OTEC heat exchanger tubing and strip. Archival data are plentiful in justifying titanium as a very low risk option for a 30-year service life. It will withstand the potential corrosion of seawater as well as the working fluid, ammonia, environments. Based on OTEC design efforts, titanium tubing can be used with a 0.028-inch wall thickness.

When titanium cores are used, it is anticipated that a titanium clad tube sheet would be used with steel waterboxes and shells. If strip is used in compact heat exchangers, the thickness would be similar -- perhaps 0.028 or 0.032 inch. The supply of titanium in tube or strip has been of some concern to some people. If I may quote one of my friends, Don McCue of Timet, he has stated that

> "Even with the large quantities of material which will be required by OTEC, there is ample supply of titanium ore which ranks just below bauxite in availability. Therefore, if the demand is present, the industry will increase its sponge making and tube manufacturing facilities."

The question of the cost of titanium heat exchangers is an important factor. Although a 30-year life is expected, the cost overall must be compared with a lower cost material, like aluminum, which may have to be replaced every 8 or 10 years. OTEC design contractors have indicated that the lower cost material may be more cost effective.

2. Cr-Ni-Mo-Fe Alloys

In the past few years, the 20Cr-24Ni-6Mo-Fe alloys have found an increasing application for surface condensers in coastal power plants -- especially those that are forced to use polluted seawater. Extensive testing has shown that this alloy will resist crevice corrosion in seawater environments. This alloy has been found to resist pitting type corrosion as well in seawater.

In addition to the Cr-Ni-Mo-Fe alloy, the high purity, high chromium alloys containing from 1 to 4% molybdenum have performed well enough in evaluation tests to warrant further attention. As of now, however, there have not been enough trial or full-scale installations in condensers to give them a record of long-time service experience equivalent to that supporting the choice of the Cr-Ni-Mo-Fe alloy.

It is believed that the Ni-Cr-Mo-Fe alloy is a good candidate for OTEC heat exchanger tubes and strips. This low risk option is rather expensive, but the costs should be somewhat lower than titanium. The wall thickness for tubing and the thickness of strip would be similar to that used for titanium. Again, it is anticipated that a 30-year life could be achieved with this alloy.

3. Copper-Nickel

The copper alloys have been used for many years for surface condensers, at shore-based power plants and in ships. The copper-nickel alloys have been used where their resistance to high velocity water is desired and a greater degree of overall corrosion resistance is needed than could be achieved with the brasses or bronzes. In addition to the excellent properties of the copper-nickel alloys, the antifouling properties of the 90% copper-10% nickel Alloy 706 are attractive for use in keeping microbiofouling below an R_f of 0.0001. Recent data from the F. L. LaQue Corrosion Laboratory and Harvard University indicate that, in addition to preventing macrobiofouling, Alloy 706 prevents microbiofouling as well. This very exciting development will be substantiated in tests using the CMU heat transfer device at Hawaii and in the Gulf of Mexico. Even if the use of Alloy 706 does not, by itself, keep the microbiofouling under control, it is believed that the cleaning problem would be substantially reduced.

The use of Alloy 706, although it is suitable for the seawater environment, does present some unknowns with regard to the ammonia working fluid environment. Data are being obtained in tests at Dow Chemical Laboratory on the resistance of Alloy 706 to seawater contaminated with ammonia and ammonia contaminated with seawater. Until these data are available, the copper-nickels will be kept on the back burner. In the meantime, all OTEC ocean tests using the CMU heat transfer devices do include Alloy 706 pipe.

4. Aluminum

Aluminum alloys have been evaluated in the OTEC program since its inception because of the possibility of achieving a low-cost heat exchanger design. Also, the possibility of using extruded aluminum for tube enhancement has been attractive to designers. The archival data for aluminum in seawater environments are not applicable to OTEC conditions. The data from the desalination industry are not applicable because the seawater is pretreated using either deaeration or the addition of phosphates for carbonate control. The data on Alloy 5052 taken from test exposures in tidal flow coastal seawater are likewise not applicable to OTEC because the specimens were permitted to freely foul. It is our belief that the accumulation of heavy deposits of macrobiofouling essentially stifle pitting-type corrosion of aluminum. The specific missing factor in all previously reported data is that an OTEC heat transfer surface must be cleaned periodically and microbiofouling must be kept below an R_f of 0.0001.

One interesting bit of archival data, obtained from the Alcoa Clipper ship, was reported to us by Alcoa in their Technology Review papers. A seawater cooled, oil cooler had been built of Alclad 3003 with 10 mils of cladding alloy 7072. After a service life of 10 years, the loss of cladding was of the order of 1 mil per year.

Corrosion tests performed under the OTEC program have included Alloys 5052 and 6061-T6. Tests performed by Johns Hopkins University/Applied Physics Laboratory and supported by the Sea Grant Program used Alclad 3004. After only 10 weeks of test at Ke-ahole Point on a moored boat, the Noi'i, the Alloy 6061 pipe specimens had corroded intergranularly. After about four months of test, again at Ke-ahole Point, of the APL trombone heat exchanger with seawater flowing over the outside of the tubes at 3 feet/second, the Alclad alloy 3004 had about 40% of its cladding area corroded away. These tubes were welded from clad strip with 1 mil of cladding. Although the cladding was gone from the adjacent areas, the weld bead had corroded interdendritically.

At this point in the OTEC program, we do not have sufficient data to say that we can qualify aluminum for OTEC heat exchangers nor can we say that we cannot qualify aluminum. Some of the unknowns that we need to evaluate and test are as follows:

a) The aluminum protective oxide film is composed of two aluminum oxide layers. Adjacent to the metal is an amorphous (noncrystalline), nonporous, and protective barrier layer. An overlaying layer is a thicker, relatively porous, and less protective bulk layer with crystalline characteristics. If we need to use mechanical cleaning methods in our heat exchangers, will the oxide layers be eroded away, will the barrier layer remain protective if the bulk layer is abraded away, or will both layers resist the cleaning abrasive conditions? Also of concern with regard to the oxide corrosion layers is whether or not the bulk layer porous structure serves to trap or hold microbiofouling and thereby increase the resistance to heat transfer. Also, will the entrapped microorganisms be difficult to remove by the methods being considered for OTEC countermeasures to biofouling?

b) If our heat exchangers are maintained in a clean condition (R_f kept below 0.0001), will the aluminum exhibit more or less resistance to pitting corrosion?

c) Which alloy is most suitable for our heat exchangers, Alloy 5052 or Alclad 3003? If Alclad is to be preferred, should the cladding layer be a minimum of 10 mils? If Alclad is to be preferred, is Alloy 7072 the preferred coating alloy? Would a lower zinc alloy be preferred?

d) Since aluminum is subject to crevice corrosion, would Alclad 3003 be a preferred choice to Alloy 5052? If crevice corrosion is to be a serious problem with aluminum regardless of the alloy chosen, could designs be considered that eliminate faying edges?

e) Is as-welded aluminum tubing suitable for our heat exchangers or should we specify extruded tubing only?

f) Since compact heat exchangers are being designed under the PSD-II contracts, are there any precautions that should be observed in alloy selection or methods of joining?

5. Enhancement of Heat Transfer Surfaces

In OTEC design efforts for shell and tube heat exchangers as well as with the compact designs, it would be desirable to be able to provide an enhanced surface. Some designers have preferred enhancement on the water side and the working fluid side. However, others have not chosen to enhance the seawater side because of the potential problems of preventing or removing biofouling. At the present time, we are mainly concerned with enhancements that are an integral part of the heat exchanger surface, such as flutes, corrugations, scribe marks, flame sprayed coatings, etc.

If the alloy is readily extrudable, like aluminum, then the fins or flutes can be manufactured using a current technology. The selection of the proper alloy for corrosion resistance, such as Alloy 5052, may present problems in extrusion and/or subsequent machinability. If the alloy would be enhanced best by corrugating, such as titanium, the technology for using corrugated strip, rolling into a tube, and welding needs to be developed. The other methods of enhancement will need to be worked on when specific designs are implemented.

6. Steel Components

If aluminum cores are used in heat exchangers, the remaining components, such as tube sheets, shells, and water boxes, could be built of aluminum. With the other alloy candidates; titanium, Cr-Ni-Mo-Fe, or copper-nickel, the tube sheet could be a clad plate. The water box could be coated steel and the shell could remain as bare steel.

With the OTEC goal of a 30-year life, the coated steel components could present a serious problem. Most coatings on steel in seawater have a life limited to about 5 years. Some of the unknowns associated with using coated steel are as follows:

1) Which coating will give a service life of 5 years? Will any coating last 10, 15, or 30 years without a need for recoating?

2) If recoating is necessary every 5 years, how will it be done? Can it be recoated in place? Must the components be taken ashore for recoating?

3) Would bare steel be a suitable solution to the problem?

4) If lining or cladding of the steel components with alloys matching the tubes is the only way to ensure an adequate life, would the cost be prohibitive?

E. OTHER COMPONENT MATERIALS PROBLEMS

1. Turbine

Since an OTEC evaporator will be vaporizing ammonia into a gas with very little, if any, moisture content, there is a potential problem with stress-corrosion cracking (SCC) of normally used steel turbine alloys. In order to prevent SCC of steel containers used for transporting ammonia, it was learned that a moisture content of 0.2% was required as a corrosion inhibitor. Since there is no obvious way to ensure that the ammonia gas entering the turbine (or in contact with any other steel component) has the required 0.2% water content, we must investigate the possibility of using alloys other than turbine steel, such as Type 403 stainless steel, aluminum, etc. Rod Teel has prepared a talk on his findings in this area.

2. Polyethylene Pipe

Polyethylene pipe is being considered for a number of OTEC components. It is seriously being considered for the cold water pipes at our Seacoast Test Facility and on OTEC-1. Recently, Sea Grant funded research at MIT by Donnelly and Cohen has indicated that we may be in trouble with this plastic when used in flexure. (Our cold water pipe applications will be operating in flexure.) Strip specimens of low density polyethylene were tested in flexure from 1000 to 1 million cycles at a frequency of 1 Hz with an amplitude of 1 mm in air, tap water, and aquarium salt water. The crystallinity dropped from 50% in the plastic in air to a value of 38-40% in synthetic seawater after 1 million cycles. The modulus of elasticity and yield strength also dropped, but specific data were not made available by the authors. Surprisingly, similar tests conducted by Dupont-Canada, manufacturer of our 4-foot diameter pipe (Sclairpipe) for OTEC-1, showed that the crystallinity increased in flexure tests conducted in tap water.

Although these data may not be applicable directly to pipe sections under OTEC conditions, it does alert us to the possibility of premature, brittle failure of polyethylene, Tests should be started quickly to substantiate these data to come up with an alternate plastic material if necessary.

OVERVIEW OF BIOFOULING, CORROSION, AND MATERIALS PROGRAM

by

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ABSTRACT

The current and near future OTEC Biofouling, Corrosion, and Materials Program is described.

I. INTRODUCTION

My purpose in addressing you this morning is to identify the various parts of the Biofouling, Corrosion, and Materials Program. I believe the perspective this will give you will be useful during the sessions in which the various speakers are describing their programs and plans.

II. PROGRAM DESCRIPTION

We have categorized the program under eight headings. The first three are shown in Figure 1a. There have been a number of reviews of technology important in the BCM area, including some related to fouling, some to corrosion, and some to intake screens. In Figure 1a, the first three reviews, now in preparation, address the qualification of materials for use in OTEC heat exchangers. All will be done in the near future by Frank LaQue. The stress corrosion of steels in ammonia is being reviewed by Rod Teel; his results will be presented in this Workshop. Having heard of the embrittlement of some grades of polyethylene due to multiple flexing in seawater, we are examining this subject to evaluate its seriousness with respect to utilization of this material in cold water pipes. Dave Thomas has been studying current experience from water intake screens and will report this to you later.

Central to the measurement of the effect of microfouling on heat exchangers is the measurement of fouling resistance to a high degree of precision. A good laboratory research apparatus was developed by John Fetkovich a few years ago. In an effort to have an instrument more suitable for general field use, a new design has been developed and we expect to manufacture new devices soon. This work is being done at Argonne National Laboratory; Pete Gavin will tell you about it later.

At three sites we have been or expect to be measuring the development of fouling resistance, the corrosion behavior, and the biological character of the organic microfouling that develops. These sites are shown as Items 3B, 3C, and 3E in Figure 1a. Item 3A refers to an interpretation of fouling resistance data that is being carried out by John Fetkovich at Carnegie-Mellon University. Item 3D refers to a study that has been performed by NDBO related to the feasibility of doing ocean measurements at a site that might be suitable for a grazing OTEC plant.

As indicated in Figure 1b, there are or will be a number of activities related to fouling countermeasures. At Panama City, experiments are being performed on the cleaning of microbiofouling films, and a new contractor will be added soon to expand our capability. Biological support to these studies is provided by Dave White at Florida State University. Item 4D refers to a study of ultrasonic cleaning of the film that forms on the outside of 3-in.-diameter tubes during the Gulf of Mexico experiment. The measurement of R_f and the determination of the efficacy of ultrasonic cleaning of these tubes will be done by Freeman Hill of the Applied Physics Laboratory.

The Civil Engineering Laboratory is studying the performance of antifouling concrete, some of which was prepared for the first time in this program. At the University of Miami, John Morse is studying the factors important in the formation of calcareous scales and the importance of this deposition for OTEC. Finally, we expect to attempt to develop a method of measuring the thickness of films in situ. This contract has not been let.

In continuation of an older series, experiments will be performed to determine the corrosion behavior in seawater-ammonia mixtures (Item 5A) of four materials of major importance in the OTEC program (aluminum, titanium, a special stainless steel, and copper-nickel) by the Dow Chemical Company. In addition (Items 5B and 5C), corrosion tests will be run to determine the effects of cleaning tubes with M.A.N. brushes and to observe the susceptibility of the same materials to crevice corrosion. We have not yet determined whether corrosion experiments with small model heat exchangers will be carried out (Item 5D).

An important element in our program (Figure 1c) is the current design, and soon we hope construction, of the Seacoast Test Facility. This is being done by the Research Corporation of the University of Hawaii under a subcontract with Argonne National Laboratory. We are in the process of setting up the initial program of the facility and determining the experimental needs so that it will be possible to begin operation of the facility as soon as it is completed.

Biofouling, Corrosion and Materials interest on OTEC-1 is strong. Argonne is to provide monitors that will allow the sensitive determination of R_f and the measurement of corrosion and biological characteristics of the fouling deposits. These monitoring tests should simulate the behavior of the tubes in the actual heat exchangers that will be operating on OTEC-1.

Finally, the management of the program is carried out through a project at Argonne National Laboratory.

Review by J. E. Draley, BCM Project Manager

BIOFOULING, CORROSION, AND MATERIALS PROGRAM

1. Technology Reviews
    - A. Copper-Nickel Alloys
    - B. Stainless Steel
    - C. Aluminum Alloys
    - D. Stress Corrosion of Steels in Ammonia
    - E. Embrittlement of Plastics
    - F. Water Intake Screens

2. Instrumentation
    - A. Device Manufacture

3. Ocean Measurements
    - A. Interpretation of Fouling Resistance Data
    - B. Hawaii
    - C. Gulf of Mexico
    - D. Tropical Site Study
    - E. Puerto Rico

Figure 1a

BIOFOULING, CORROSION, AND MATERIALS PROGRAM
(Contd)

4. Fouling Countermeasures
   - A. Panama City
   - B. New Contractor
   - C. Biological Support
   - D. Ultrasonic Cleaning
   - E. Antifouling Concrete
   - F. Calcareous Scales
   - G. Film Thickness Measurement

5. Corrosion Studies
   - A. Ammonia-Seawater
   - B. Effects of Brushing
   - C. Crevice Corrosion
   - D. Model Heat Exchangers

Figure 1b

BIOFOULING, CORROSION, AND MATERIALS PROGRAM
(Contd)

6. Seacoast Test Facility
7. OTEC-I
8. Management

Figure 1c

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BIOFOULING

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INTERPRETATION AND IMPLICATIONS OF OTEC BIOFOULING DATA

by

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I. INTRODUCTION

In this paper we wish to discuss the nature of the biofouling data which have so far been obtained, and to consider its implications. It is important to try to obtain an understanding of the underlying phenomena which determine the fouling process. This is so for several reasons. First, it could lead us to devise effective means of inhibiting and removing fouling, as well as help us to avoid wasting effort on methods which clearly will not work. Second, it could help us to anticipate unexpected future problems. Third, it should enable us to know which are the critical experiments to do, and how they should be conducted.

The experimental apparatus and procedures have been discussed at length previously, and will not be described here. Similarly, the data have been described in detail elsewhere. We will therefore consider only its dominant qualitative aspects. Those who are not familiar with the apparatus and the data are referred to earlier reports.[1]

II. OBSERVATIONS

In studying the data, we consider, for the moment, only that portion of an experiment before any long-term ($\gtrsim$ 2 hrs) pump stoppages. (We consider the effect of such stoppages later.) When we do this, we find a remarkable simplicity in the results. The fouling thickness builds generally as shown in Fig. 1. In each case, starting with a new heat exchanger tube at t=0, we find the fouling building at rates which vary from experiment to experiment, and, within an experiment, from time to time. However, we find that invariably, once the fouling thickness reaches ~20 μm, the growth becomes linear with time. Furthermore, the rate of growth in the linear region is roughly independent of all parameters which have been studied so far. The ranges of variation of these parameters are indicated in Table I. It is worth emphasizing especially that the linear fouling rate is independent of flow velocity from 3-6 ft/sec, and of seawater bacterial levels from 10-20,000 per ml.

Next, we look at the effects of pump shut-downs. We first exclude all data coming after a long pump shut-down. The effect on fouling growth of short ($\lesssim$ 2 hrs) shut-downs is illustrated in Fig. 2. We find that short shut-downs do not significantly change the fouling phenomenon, except to increase slightly the rate of fouling. The increase is greater the greater is the fractional down time.

Long pump shut-downs ($\gtrsim$ 1 day) are found to lead to a new phenomenon: macrofouling. In all cases when there were no long pump shut-downs, we have found, upon disassembly of the apparatus, no evidence of macrofouling (e.g., barnacles). On the other hand, in every case when macrofouling has been found, it was after such a long shut-down.

Finally, of course, one of the most important observations made so far is that mechanical cleaning works. It is apparently easy to keep a tube nearly free of biofouling by at least one standard method of mechanical cleaning (M.A.N. brushes).

III. INTERPRETATION

As we will show, it appears that most of the observed characteristics of biofouling can be explained by a simple physical model of the process. Of course, one cannot say, just because the model is consonant with the data, that it is correct in all its details. Nevertheless, it works within the limits of the available data; it can be useful in planning and predicting; and it no doubt has at least some truth imbedded in it. For these reasons we present it here in spite of the very limited amount of data available.

In the initial period of the fouling of a clean surface, biologists believe, organisms do not attach effectively. It is apparently first necessary that a microscopic layer of non-living but organically derived material be adsorbed first. Only then can small organisms (such as bacteria) attach effectively.

In this initial period, often called the induction period, two processes are clearly important in fouling buildup: adsorption and multiplication (i.e., growth of organisms already attached). It is possible to write a mathematical expression, representing the physical and biological processes involved. However, the model is found to be dependent on many factors which we do not have enough data to evaluate at this stage. Therefore, we do not discuss the model quantitatively (however, see below), merely pointing out that at this stage, the rate of fouling buildup should depend on the character of the seawater, especially on its living and non-living organic content, on the flow velocity, and on many other factors.

At the end of the induction period the phase of linear fouling growth is initiated. This process is independent of most parameters, which implies it is a very simple and basic process, and one which should be amenable to quantitative understanding.

In developing a physical model, we again consider, as in the induction period, that adsorption and multiplication will be the important phenomena in the growth of the fouling layer. In general, of course, both will be happening simultaneously. However, to simplify the discussion, we will first consider each as if it were occurring alone. To simplify further, we will represent the variety of organisms involved by a single "average" one having characteristics (such as diameter, etc.) typical of the group. (These simplifications are not essential. However, it is not worthwhile here to consider the most general form of the model, especially in light of the small amount of available data.)

First consider adsorption. It is easy to show* that the fouling should, in this process, build up according to the relation:

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* We do not here present the detailed calculations leading to this and later results, in order not to complicate the discussion excessively. The complete details will appear in a paper now being prepared for publication. The author will be happy to supply these before publication to anyone interested.

$$F = b \, \ell n \left[\frac{\varepsilon_o}{\varepsilon_f} \; e^{t/\tau} + (1 - \frac{\varepsilon_o}{\varepsilon_f}) \right] \quad . \tag{1}$$

Here, F is the thickness of the fouling layer, b is the dimension of a typical fouling organism measured perpendicular to the wall. The factors ε_o and ε_f are, respectively, the "sticking factors" for a bare, and for a fouled surface. (That is, ε measures the likelihood that an organism striking the wall will stick. If ε=0, it never sticks; if ε=1 it always sticks. In general, $0 \le \varepsilon \le 1$, and $\varepsilon_f > \varepsilon_o$.) And τ is given by

$$\tau = D_p/0.024 \; ab \; \varepsilon_f \; Dn_b(Pr)(Re)^{0.8} \quad , \tag{2}$$

where D_p is the diameter of the pipe or tube being studied, a is the cross-sectional area of the pipe wall taken up by one fouling organism*, D is the diffusion constant of an organism through water, n_b is the volume concentration of organisms in the local water, Pr is the Prandtl number and Re is the Reynolds number of the flow.

We see that Eq.(1) is not a linear function of time. However, it is seen to become linear asymptotically, where it reduces to

$$F = (0.024 \; ab \; \varepsilon_f \; Dn_b/D_p)(Pr)(Re)^{0.8} t$$

$$+ \; b \; \ell n \; (\varepsilon_o/\varepsilon_f) \quad . \tag{3}$$

Of primary interest in this expression are the following observations. The rate of fouling in the linear region (i.e., the coefficient of t in Eq. (3)) depends on the characteristics of the responsible organisms through the factors a, b, ε_f, and D, none of which are very precisely known. Further, it is proportional to the volume concentration of organisms (n_b), and to the 0.8 power of the flow velocity (through the factor $(Re)^{0.8}$). These dependences are in direct contradiction to the observed results. We conclude therefore that, in the linear region of biofouling growth, adsorption of new organisms onto the wall is unimportant. The dominant mechanism of biofouling growth, then, must be multiplication, or growth, of those already attached.

Now we consider the multiplication of attached organisms. We assume that a typical organism will multiply with a generation time τ_2. We expect that, because of the availability of nutrients and the ability to be rid of waste products, the organisms nearest the surface will multiply fastest. The value of τ_2, then, will depend upon depth in the fouling film. Again, we simplify by assuming that all organisms within a depth d_m multiply with the same generation time τ_2, and all those at greater depth do not multiply at all.** This picture is of course appropriate only after the fouling

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* Note that the space taken up by one organism may be larger than its size as a result, e.g., of exudation of material.

** It is easy to see that not all the attached organisms can multiply at the same rate for this leads to an exponential growth contrary to what is observed.

thickness is greater than d_m; i.e., in the linear growth region. One easily determines then that the fouling will build according to the relation

$$F = d_m(1 + t/\tau_2) \quad . \tag{4}$$

This result has several important characteristics. Perhaps most importantly, it does not depend on n_b, the concentration of organisms in the water. Also, it will not depend upon flow velocity if τ_2 is not nutrient-limited at the lowest observed flow velocities. Equation (4) is clearly in agreement with the remarkable observation that the rate of fouling growth does not depend on any of the factors given in Table I.

To summarize, the observed data lead us to a model of biofouling in which we divide the process into two periods. In the first, the induction period, the clean surface is covered with living and non-living organic material up to a depth of at least d_m. The fouling rate during this time depends on many factors including the nature of the organisms, the nature of the surface, the concentration of organisms and the flow velocity. In the second, the linear period, the fouling rate becomes constant at a level which depends only on two factors: the depth, d_m, to which the organisms remain prolific (multiply), and their average generation time, τ_2.

We turn now to consider what we can deduce about biofouling under OTEC conditions using this model.

First, by comparing with the data we can obtain at least approximate values of the important numbers d_m and τ_2. The value of d_m must be of the order of the fouling thickness at the point of transition between the induction and linear periods. This is found to be (very roughly)

$$d_m \cong 20\ \mu m \quad .$$

Since the universal slope of the fouling curve is (very roughly) 10 μm/week, we conclude that the average generation time is

$$\tau_2 \cong 2\ \text{weeks}.$$

We reemphasize that this is an average generation time within the outer 20 μm of the fouling layer. At the top of the layer it is presumably much shorter than this, while it becomes very long deeper in.

We note that this model allows us to say something about the effective size* of the responsible organisms. A typical dimension must be less than 20 μm. If the actual size of the organisms is 20 μm, then the prolific layer is just one organism deep. On the other hand, they may be smaller. If for example, they are 2 μm in size, then the prolific layer is 10 organisms deep.

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* Here, "effective size" refers to the mean separation between organisms in the fouling layer. Because of exudations, possible water spaces, etc., this may be significantly larger than the "bare size" of the organism as it floats freely.

In fact, the preliminary microscopic observations[2] of the fouling layer are consistent with the dominant organisms being bacteria with typical bare sizes well below 20 μm.

We have already alluded to the fact that apparently macrofoulers, such as barnacles, do not attach to the wall as long as the water is flowing (at least at speeds greater than 3 ft/sec). How can we understand this? In fact, it is easy to understand this at least semiquantitatively through the application of some simple physical principles.

Next to the wall, the flow is laminar with a velocity profile approximately linear near the wall (with, of course, v=0 at the wall). The laminar layer is , for example, at a bulk flow velocity of 6 ft/sec, about 100 μm thick. When an organism attaches to the wall, the water exerts a drag force on it, parallel to the flow, of approximately

$$F_d = 6\pi r^2 \mu \frac{dv}{dy} , \qquad (5)$$

where r is a "typical radius" of the organism, μ is the viscosity of water, and $\frac{dv}{dy}$ is the velocity gradient at the wall. To counteract this, the wall will exert a force of adhesion on the organism. It is a reasonable guess that this force of adhesion is proportional to roughly the first power of r (think, for example, of stripping a piece of tape from a surface). So we write for the force of adhesion

$$F_a = sr . \qquad (6)$$

Here, s is a "stickiness factor" (not to be confused with the sticking factor, ε, defined earlier) which determines how tightly the organism can cling to the wall. The important thing is that if $F_d > F_a$, the organism will not stick. We get the limiting case then by considering $F_d = F_a$ which yields

$$\frac{dv}{dy} = \frac{s}{6\pi\mu r} . \qquad (7)$$

But we also have, from hydrodynamic theory,

$$\frac{dv}{dy} = e\, v_b^{1.8} , \qquad (8)$$

where e is a numerical constant depending on the properties of water, and v_b is the bulk flow velocity.

Combining Eq.(7) and (8), and using the appropriate numerical values, we get

$$\left(\frac{v_b}{10\ \text{ft/sec}}\right)^{1.8} = \frac{1}{4.18\times10^3\ \text{dynes/cm}^2}\ \frac{s}{r} . \qquad (9)$$

It is worthwhile, perhaps, to emphasize the significance of Eq.(9). It says that for a given organism (i.e.,given s and r), there is a critical flow velocity given by v_b in Eq.(9), such that, if the flow velocity exceeds v_b, the organism cannot stick, and if it is less than v_b, it will stick. Given, for example, barnacle larvae of known size r, and stickiness s, Eq.(9) could be used to calculate the highest velocity, v_b, at which barnacles could attach.

Of course, we do not know the stickiness of barnacle larvae. If we did the right experiments we could determine s. That is, for barnacle larvae of known size r, vary the velocity v_b until the critical value is found. Then Eq.(9) could be used to calculate s.

Or, we could look at Eq.(9) from another point of view. Consider a variety of organisms of various sizes r, all having roughly the same stickiness s. At a given flow velocity v_b, we could then solve Eq.(9) for the critical size, r. Organisms larger than this could not stick, while those smaller would. Thus, the fact that we have a continuous flow past the wall serves as a "size filter" for sticking organisms, much as an ordinary filter works: those smaller than the critical size pass (stick) while the larger ones do not.

The preceding discussion leads naturally to consideration of the observation that if the flow is interrupted (by pump shut-downs) for a sufficiently long time (much longer than an hour, less than 2-3 days), barnacles are observed to attach and grow. This is easily explained in terms of Eq.(9), since, when the pumps are off, $v_b=0$, which is obviously below the critical velocity for barnacle larvae whatever it may be.

On the other hand, we observe that some pump shut-downs do not lead to barnacle growth: namely, those which are short (e.g., $\lesssim$ 2 hrs). According to Eq.(9), barnacle larvae will surely attach at such times. The apparent anomaly is removed if we invoke a phenomenon well known to biologists. That is, that a barnacle (as well as other organisms) holds tighter to a surface the longer it has been attached. This is presumed to be due to exudates which serve to bind the organism to the surface. That is to say, in terms of Eq.(9), that the "stickiness",s, of an organism is a function of time:$s=s(t)$. It is interesting to note that we could measure this time dependence if we did the obvious experiments. All that we know from the limited data so far available is that if $v_b=0$ for a time less than 1-2 hrs, any attached barnacles are washed off when flow is resumed if $v_b \gtrsim 3$ ft/sec, while if $v_b=0$ for several days, they are not washed off afterwards if $v_b \lesssim 6$ ft/sec.

All of this clearly also relates to another phenomenon mentioned earlier. That is that the rate of fouling in the linear period increases with the fractional pump down-time, for short pump stoppages. Again, this can be understood in terms of Eq.(9). During the stoppage ($v_b=0$) all organisms can attach regardless of size. During the brief stoppage, their stickiness, s, can increase only a little. When the pumps are restarted, then, the very large organisms are washed off. But some, somewhat larger than those which normally attach, have sufficiently larger values of s, so that they remain even after the pumps are started. In effect, then, frequent short pump stoppages have the result that a greater fraction of the local organisms, in general larger ones, contribute to the overall fouling rate. The new population of organisms apparently either increases d_m, or decreases τ_2, or both. Why this happens is as yet unclear.

There have been suggestions in the past that chemotaxis might be important in the process of fouling in these tests. This now appears not to be so. We have seen that in the important period, when the fouling is growing linearly, adsorption is not important; the growth is dominantly by multiplication of those already attached. Even in the induction period, when adsorption is important, it is unlikely that chemotaxis plays a role. The reason for this is to be found in the dynamics of the motion of small objects (such as bacteria) through the laminar flow layer near the wall. Since the object finds itself in a shear field due to the velocity gradient, it will be rotating. The rate of rotation will be approximately

$$\omega = \frac{1}{2} \frac{dv}{dy} \quad . \tag{10}$$

We note that, at a bulk velocity of 6 ft/sec, for example, this corresponds to an angular speed of about 10,000 sec^{-1}. It would be remarkable if a bacterium spinning at this rate could tell where it was going, or do anything about it if it could.

IV. FUTURE PLANS

There are many experiments we would like to see done in order to test the model, to extend its range of validity, to refine it and to evaluate some of the unknown factors. Some of the more interesting, for example, would be to measure the stickiness s and its time dependence, to extend the range of velocity covered in the experiments, to study the temperature dependence of these phenomenon, and in general to learn more about the characteristics of the organisms involved, such as type, bare size, effective size, concentration in the water, etc. It should be noted that many of these experiments could be done more cheaply and easily, and with more controlled conditions, in the laboratory rather than in the field.

We will not discuss these experiments in detail here. Most in this audience are less interested in the model than in the problem of getting immediate design data for OTEC heat exchangers. We turn therefore to consider some potentially important problems for OTEC which are suggested by the data and by this picture.

It would be of interest to have data over a wider velocity range. The velocity/critical-size effect discussed here implies that there is a velocity above which even the very small organisms responsible for microfouling will not attach. If this velocity is not too high, it might be feasible to run heat exchangers above the critical velocity if, in the overall optimization, the increased costs of high velocity operation are counterbalanced by decreased costs of antifouling methods.

More information on the stickiness vs. time of barnacle larvae (and other macrofoulers) might be useful. We know that if flow is interrupted for less than about two hours, barnacles will not permanently attach, while if the interruption is longer than several days, they will. Operators of an OTEC plant will need guidelines to tell them how long is a safe shut-down before antimacrofouling measures must be instituted.

Studies at lower velocities might be important in order to determine the critical velocity for barnacles and other macrofoulers. This is so because there may be locations within a heat exchanger where, even at high nominal velocities, the actual local velocity may be very low. This would be so, for example at the downstream end of a heat exchanger tube if there is a sudden step in tube size. Barnacles attaching at such points could grow to sizes which would close the end of the tube. Measures such as

M.A.N. brushing are not likely to remove such large organisms. If the critical velocity is known, one could design the flow paths to avoid the dangerous regions. If this is not possible, then specific antimacrofouling measures may be needed in the affected areas.

There are related problems involved in using non-cylindrical heat exchanger geometries such as plate-fin. Depending on the geometry, there can be regions (e.g., in corners) where the shear stress in the flow becomes very low. If so, macrofoulers can attach and grow. This would obviously complicate the antifouling problem.

So far, we have no information at all on deep (cold) water biofouling. A popular opinion is that biofouling in the condenser will be minimal or non-existent because there are few organisms living at 1000 meters depth. However, the concentration of organisms affects only the rate of biofouling in the induction period. In the more important linear period, the fouling rate depends only on the generation time of the attached organisms, not on their concentration in local waters. Therefore the build up will likely be as fast as in the surface waters.

There are, of course, many other experiments which need to be done as well. Since most of these have been discussed previously, we need not dwell on them here.

V. CONCLUSION

We have seen that a simple physical model appears to explain most of the characteristics of OTEC heat exchanger biofouling. Naturally, with so little data in hand, we cannot have great confidence that all aspects of the model are correct. Still, it can serve as a useful guide in planning. It would be desirable to get some of the basic data necessary to test the model, and to refine it. It could help to save much effort and perhaps avoid future mistakes.

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TABLE I

PARAMETERS OF CMU OTEC BIOFOULING EXPERIMENTS

Expt.	Location	Date	Nominal Velocity (ft/sec)	Material	Pressure Change (ft of H_2O)	Bacterial Counts
NOI'I	Keahole Point	Jul-Sep 1976	3	Al 6061-T6	35	High*
NOI'I	Keahole Point	Aug-Sep 1976	6	Al 6061-T6	35	High*
BUOY SERIES I	Keahole Point	Feb-Jul 1977	3	Al 6061-T6	3	High**
BUOY SERIES I	Keahole Point	Feb-Jul 1977	6	Al 6061-T6	6	High**
BUOY SERIES I	Keahole Point	Feb-Apr 1977	6	Ti Grade 2	6	High**
ST. CROIX	St. Croix	Jul-Sep 1977	3	Al 6061-T6	75	Low+
ST. CROIX	St. Croix	Jul-Sep 1977	6	Al 6061-T6	75	Low+

* Harvey[2] reports approximately 20,000 bacteria/ml in addition to diatoms, glass fibers, and glass chips in water taken from near the intakes for the Noi'i experiments.

** No measurements have been reported for water from the vicinity of the buoy, but we expect the values to be similar to those found near Noi'i.

\+ Hirshman *et al.*[3] report bacterial populations of below 10/ml in the St. Croix intake water. See also Aftring *et al.*[4]

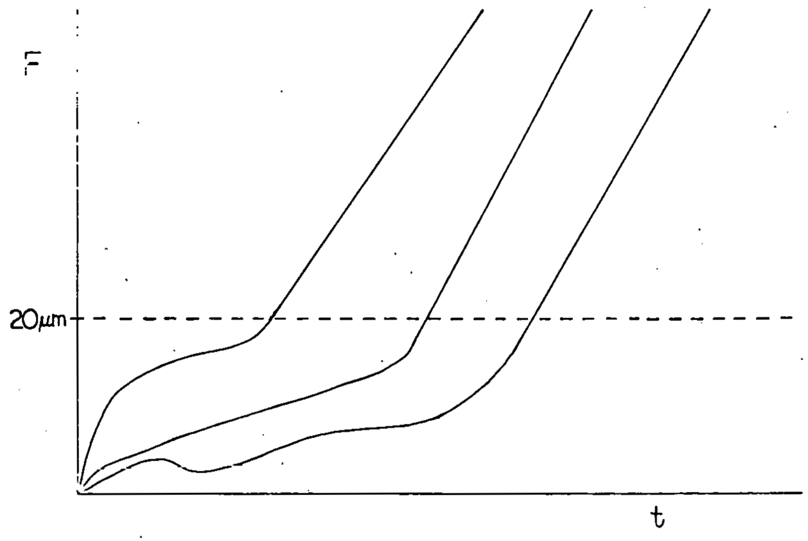

Fig. 1. A qualitative representation of typical biofouling data. F represents the apparent thickness of the biofilm, t is time. It is generally observed that the fouling grows at a rate which varies with conditions until it is about 20 μm thick. Thereafter the growth is approximately linear for as long as has so far been observed.

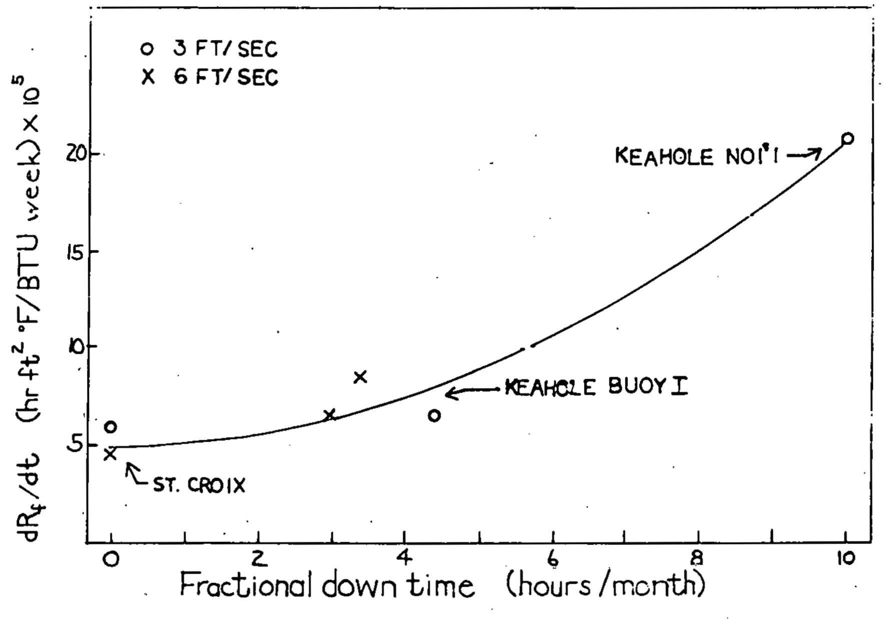

Fig. 2. The dependence of fouling rate on short (≤ 2 hr) pump stoppages. The ordinate, dR_f/dt, is the slope of the fouling growth curves in the linear region (corresponding to the parts of the curves above the dashed line in Fig. 1). The ordinate is the total pump down time per month. The experiments from which the data were taken are indicated. We see that the fouling rate increases with down time. However, as long as the pumps are down less than a total of 1-2 hrs/mo, the effect on the results is very small.

PRELIMINARY RESULTS FROM KE-AHOLE BUOY DEPLOYMENT #3

by

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INTRODUCTION

As reported by Fetkovich [1,2], previous biofouling and corrosion experiments at Ke-ahole Point have provided some knowledge of changes of heat transfer due to biofouling and corrosion on two types of test alloys, specifically aluminum and titanium. The purpose of this deployment is to increase our understanding of this phenomenon and comparatively examine two untried materials.

BACKGROUND

During deployment #1 (Fetkovich [1]) test sections of aluminum 6061-T6 and grade 2 titanium were deployed after cleaning with 100 strokes of a bristle brush and a commercial cleanser.

During deployment #2 (thus far unreported), two test sections of aluminum 5052 and two test sections of titanium grade 2 were cleaned prior to submersion using techniques described by Craig et al, 1978 [3].

Experimental Procedure

The test sections in the present deployment (#3) differ from those of the prior deployments in the following respects:

a. For the first time four different materials, at similar flow velocities, have been deployed simultaneously on the buoy. These are:

    1. Aluminum 5052 (5.7 ft/sec)
    2. Titanium SB-337 (7.7 ft/sec)
    3. Stainless Steel AL-6X (7.3 ft/sec)
    4. Copper-Nickel Alloy 90-10 (7.3 ft/sec)

b. All test sections were cleaned with neutral pH detergent soap (Liqui-Nox manufactured by Alkanox, Inc.), using 40 strokes of a M.A.N. brush designed specifically for 1" pipes.

c. After cleaning, the sections were rinsed with tap water for 20 minutes and then filled with deionized water and capped in preparation for installation on the buoy.

The instrumentation and pumps were deployed on 4 November 1978; however, unfavorable seas prevented divers from making the final hookups until 6 November when the instrumentation seals were removed and flow was started. The lower seals were removed approximately one hour prior to pump start-up while the upper stoppers remained in place until approximately five minutes before start-up.

At the start of the experiment all data appeared normal except for flowmeter signals which were fluctuating. By 8 November the flowmeter data had settled down and continued to function correctly until 15 November when all flowmeter signals were lost. On 9 November, a connector failed on a newly-designed pump while divers were on the buoy and Instrument A (aluminum 5052) was changed to a spare pump already mounted on the buoy. Total downtime for this instrument was less than 15 minutes. All systems continued to function normally with the exception of the electronic flowmeters until 20 December when, presumably due to generator problems, one pump (Inst. D AL-6X) was found to have shut down. The pump was restarted successfully and the experiment continued.

The present data acquisition techniques follow those described by Fetkovich [4] and the analysis of the data is being undertaken using detailed procedures developed and furnished by the CMU biofouling and corrosion group. Close coordination with the CMU biofouling group during the present deployment has been indispensable to the acquisition and preliminary analysis of data from the current deployment.

The inability to obtain electronic flowmeter data after 15 November necessitated the expediency of using the initially measured velocities as the basis for all subsequent velocity-dependent calculations. We recognize that this introduces an uncertainty into the data reduction which is difficult to quantify. However, efforts are underway to minimize this problem by using other velocity measurement techniques. Based on data gained from prior experience, we feel that the assumptions made as regards velocity do not materially detract from overall results presented.

Results. The data herein and their analysis are preliminary and are presented with this caveat. There was no rejection of any usable data. Two anomalous points (Nov. 30/Cu-Ni and Nov. 27/Al 5052) indicate that some, and thus far unknown, factor entered the system during this period. All data points represent the average value of 12-16 separate cooling curves taken on the same day, except for the last values which are the average of only two cooling curves.

Unit B titanium shows the characteristic "conditioning" period (Fetkovich [2]) showing little change in R_f for the first four weeks. From the fourth week on thermal resistance increases smoothly and at a rate nearly identical to the other materials.

Unit A aluminum appears to have a short "conditioning" period; afterwards it continues to foul at the expected rate.

Unit D stainless steel also shows a relatively short "conditioning" period; its fouling rate is also in general agreement with the other materials.

Unit C Copper-Nickel appears to have little if any "conditioning" period. Cursory S.E.M. examination (Berger, oral communication) indicates no evident biological activity through the first two weeks. The differences noticeable between materials at this state in the experiment appear to be associated with the duration of the conditioning period. However, the data suggest there may be other measurable differences.

We propose to continue this deployment and conduct the following experiments:

1. When a test unit reaches an R_f of .0002, clean the unit using a M.A.N. brush and techniques as described by Fetkovich [1], allow the unit to refoul to .0002 and repeat the cleaning procedure.

2. After the second cleaning, allow the thermal resistance to reach some steady state as anticipated by information obtained from Keahole buoy deployment #2 (unreported).

3. After insuring that a steady state has been reached, we will remove the pump flow restrictors increasing flow velocity to approximately 10 ft/sec to observe if this will have any effect on the accumulated fouling. This step is, of course, dependent upon our ability to obtain accurate flow velocities at the time.

4. At the conclusion of Item 3 above, a re-evaluation of the experimental direction will be made and additional operations planned.

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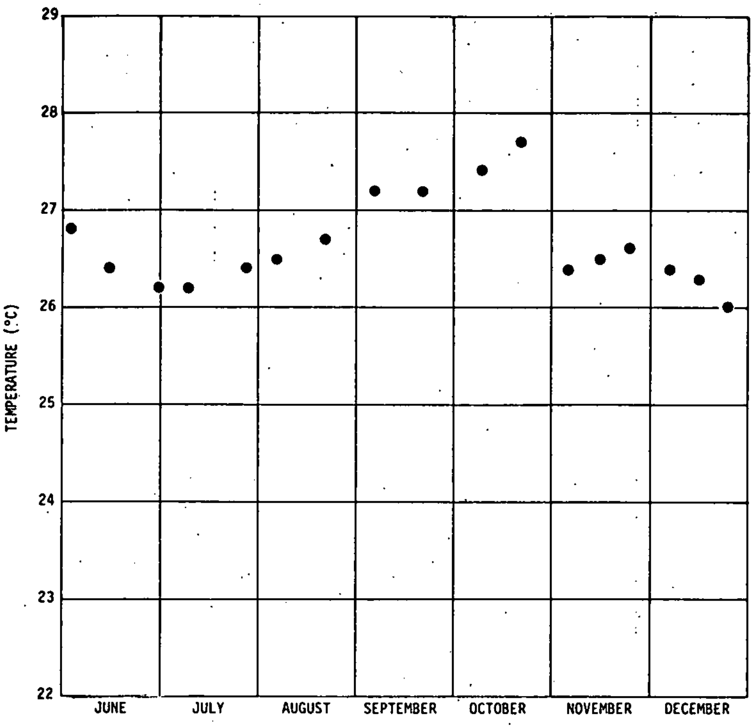
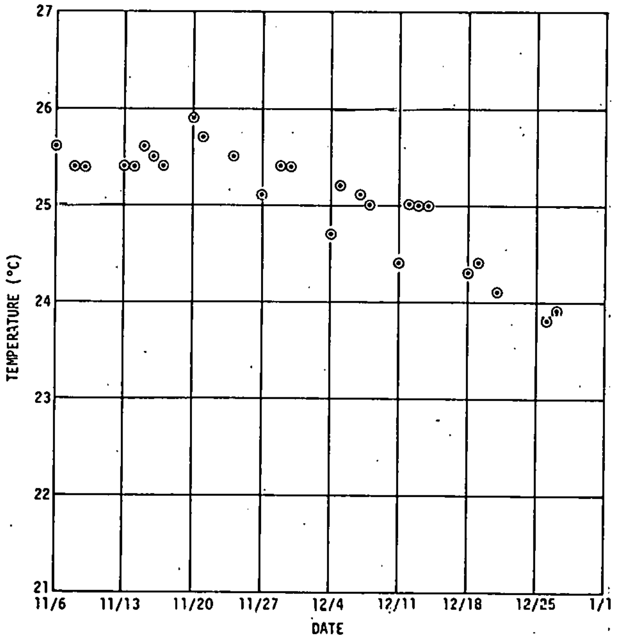


DIVER OBSERVED TEMPERATURES AT THE BUOY
FIGURE 1

TABLE I
KEAHOLE POINT BUOY TEMPERATURES
(June - December 1978)

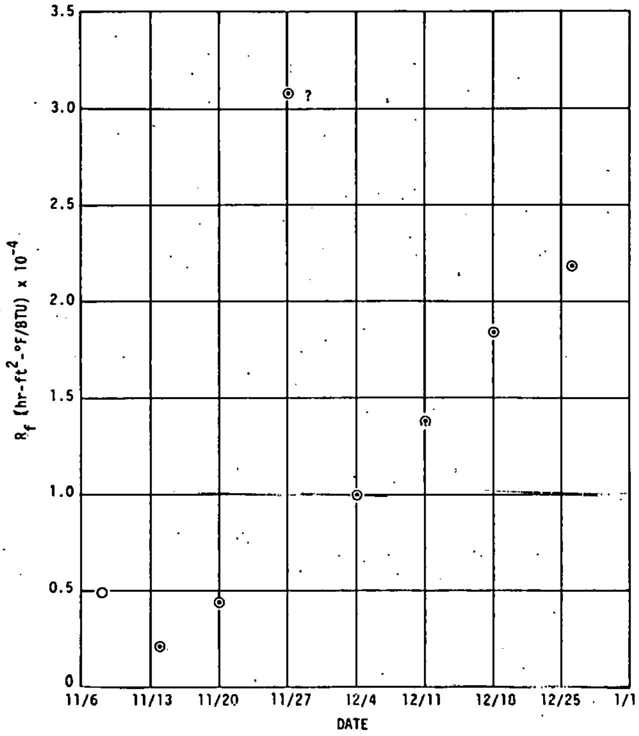
Date	Temperature (°C)	Time (AM)	Current (0-Strong)
6/2	26.8	10:00	
6/17	26.4	10:15	
6/30	26.2	9:45	
7/14	26.2	8:45	Mild
7/28	26.4	9:30	Slight
8/11	26.5	10:05	None
8/25	26.7	10:15	None
9/8	27.2	11:00	Medium
9/22	27.2	10:15	None
10/6	27.4	8:30	
10/20	27.7	10:00	
11/3	26.4	10:00	
11/10	26.5	10:00	
11/17	26.6	10:30	
12/1	26.4	9:30	
12/22	25.3	10:00	Slight
12/28	25.0	9:30	Medium



KP III DATA
THERMISTOR DERIVED TEMPERATURE
UNITS A thru D
FIGURE 2

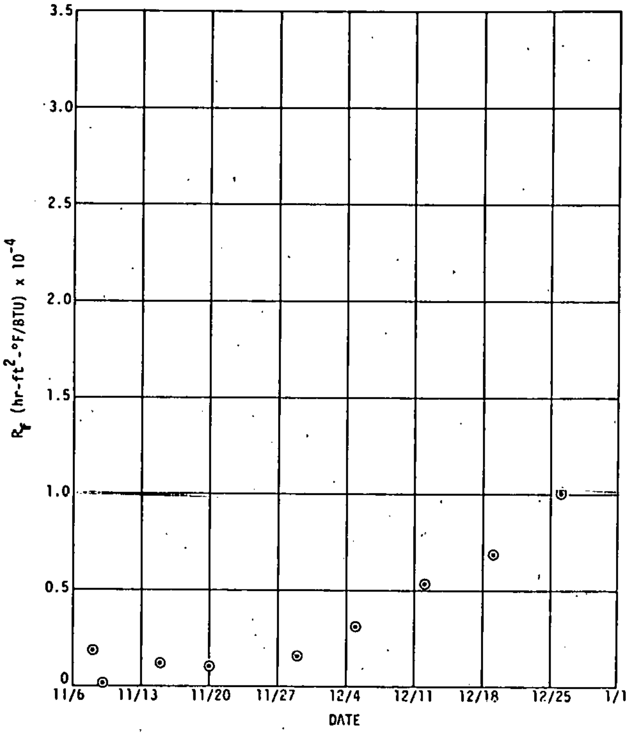
TABLE II
THERMISTOR TEMPERATURES

11/6	26.6°C	12/4	25.7°C
8	26.4	5	26.2
9	26.4	7	26.1
13	26.4	8	26.0
14	26.4	11	25.4
15	26.6	12	26.0
16	26.5	13	26.0
17	26.4	14	26.0
20	26.9	18	25.3
21	26.7	19	25.4
24	26.5	21	25.1
27	26.1	26	24.8
29	26.4	27	24.9
30	26.4		



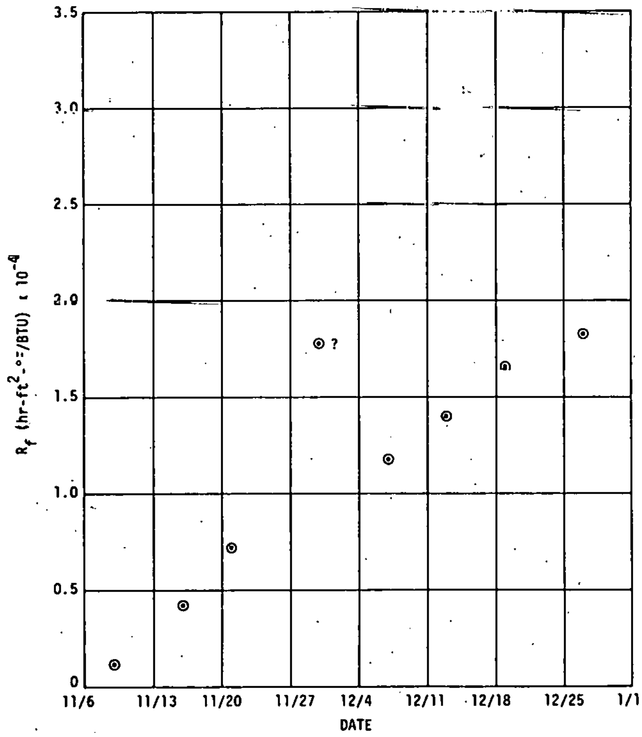
KP III DATA
AL #13
UNIT A

FIGURE 3.



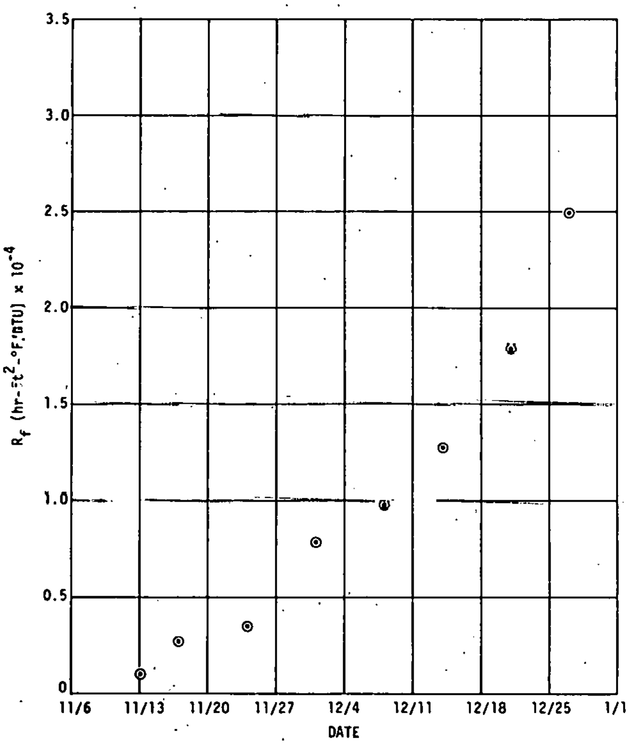
KP III DATA
TI #14
UNIT B

FIGURE 4



KP III DATA
C/N #15
UNIT C

FIGURE 5



KP III DATA
SS #16
UNIT D

FIGURE 6

TABLE III

CALCULATED R_f's

AL #13 - UNIT A

11/6	0
8	0.0000490
14	0.0000209
20	0.0000435
27	0.0003068
12/4	0.0000997
11	0.0001384
18	0.0001846
26	0.0002184

TI #14 - UNIT B

11/6	0
8	0.0000181
9	0.000016
15	0.0000122
20/21	0.0000101
29	0.0000153
12/5	0.0000307
12	0.0000534
19	0.0000693
26	0.0001005

C/N #15 - UNIT C

11/6	0
9	0.0000122
16	0.0000412
21	0.0000711
30	0.0001767
12/7	0.0001175
13	0.0001396
20	0.0001515
27	0.0001819

SS #16 - UNIT D

11/6	0
13	0.0000100
17	0.0000227
24	0.0000353
12/1	0.0000779
8	0.0000975
14	0.0001494
21	0.0001792
27	0.0002493

BIOFOULING ASSAYS FOR OTEC PIPES

by

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I. INTRODUCTION

We have been concerned with the early biofouling on the heat exchanger pipes in pilot OTEC projects at Keahole Point, Hawaii. Our task has been to "perform biofouling determinations on samples, coupons,..."

Microbiofouling begins on the immersion of a solid surface in seawater. Since the nature of events and their sequence are not fully understood, prevention of microbiofouling over a short period of time is (at this time) possible only with frequent drastic treatment of the surfaces with corrosive and toxic substances. Macrofouling invariably follows unless the primary fouling layers are physically removed from the surface in question. The fact is that unless the surface is maintained inimicable to microbial colonization, it will be colonized and microfouling processes will proceed.

Our immediate goal has been to find ways to measure quantitatively the nature and amount of early biofouling under simulated OTEC flow conditions. We have set out to develop or adapt a variety of analytical procedures endowed with the sensitivity which is required to measure the small amounts of fouling products which deposit on the pipe surfaces in the early stages and to determine the suitability of these methods for use as indices of the biofouling process.

This paper is a report of our progress. As an appendix we have added a summary of some of the experimental procedures. The following topics are considered:

a. Methods to remove biofilm from pipe surfaces for study
b. Chemical analyses
c. Physical measurements

II. METHODS AND RESULTS

A. Removal of biofilm from metal coupons:

Because of the small amounts of materials which constitute the biofouling layer in the early stages, recovery of the insoluble film must be efficient and reproducible. Different analyses pose special problems. The different pipe materials introduce further complications. Several general procedures have been tried. These fall into three classes:

a. wiping or scraping
b. ballistic or sonic treatment
c. direct chemical (or solvent) extraction
d. (no removal) direct examination of the surfaces

We have been unable to remove all of the organic layer from aluminum pipe without removing (in certain cases) significant amounts of aluminum and/or the hydrated aluminum oxide layer. This is because of aluminum's property of micropitting and of the oxide layer's propensity to absorb all sorts of materials. At the outset we tried to remove the film by wiping the pipe surface with slightly wetted all glass swabs (glass wool formed on glass rods). The film is readily released afterwards into an appropriate diluent for analysis. This method worked fairly well for surfaces where the fouling layer was macroscopic, that is (we estimate having a wet thickness of 0.05mm or more). However, all of the film is not removed and what is removed includes considerable amounts of insoluble aluminum metal and compounds. The procedure is better for titanium. It has not been tried with copper-nickel or stainless steel alloys. A razor blade or scalpel on some surfaces is equally effective although they tend to scrape deeper into soft metal surfaces. Rigid implements, however, are often unwieldy on small curved surfaces. In principle, the inorganic complement of the fouling layer could be dissolved in mineral acid leaving the organic matrix for analysis.

The most promising approach, to date, has been the use of a ballistic disintegrator, a device which oscillates rapidly enough to permit both cavitation of the aqueous solution and sheer forces of sufficient magnitude between suspended particles and the container wall to release material from the film. The device resembles in operation a highspeed paint-shaker. One-inch lengths of 1-inch pipe are capped with RTV-silicone rubber caps molded to fit snuggly the tube ends after placing 3 ml of water or buffer and 1 to 3 g of microscopic glass beads. (MMM "Superbrite" MMM Co used in reflective signs or Ballitini glass beads of comparable size) After shaking for 5 minutes at about 25hz the beads are allowed to settle and the liquid is removed. The suspended organic (and inorganic) matter can be decanted. This procedure can be repeated several times until significant amounts of material are no longer removed from the pipe surface. Table 1 shows the effectiveness of removing film under several conditions.

We did not find sonic treatment of the fouled pipe sections to be an effective way of removing the surface-bound organic matter. This may have been solely a limitation of the sonic device available, a laboratory probe type.

Certain components of the film cannot be treated in the above manners. They must be rapidly extracted from the pipe surface in such a way as to remove or prevent degradative enzymatic activity. In Hawaii we are faced by an experiment located 200 miles from the laboratory. For the moment we are freezing some pipe coupons at dry-ice-alcohol temperatures and holding the samples frozen until they can be processed in the laboratory.

TABLE 1. EXTRACTION OF PIPE FOULING MATERIAL USING A RECIPROCAL SHAKING DEVICE

SAMPLE	TREATMENT	ORGANIC IRON RELEASED (ng CATALASE)
1. Cleaned Pipe	3ml H_2O shaken 5 min.	0
	+ 3ml H_2O shaken 5 min more	0
2. Cleaned Pipe	3ml H_2O + 1g glass beads shaken 5 min.	0.14
	+ 3ml H_2O + 1g glass beads shaken 5 min more	0.04
3. 48-hr fouled pipe	3ml H_2O shaken 5 min.	0.21
	+ 3ml H_2O shaken 5 min more	0
4. 48-hr fouled pipe	3ml H_2O + 1g glass beads shaken 5 min.	1.03
	+ 3ml H_2O + 1g glass beads shaken 5 min. more	0.62

One-inch lengths of 1" ID aluminum pipe (either freshly scrubbed or which had been allowed to foul in a bucket which contained about 1.5 gallons of sea water recirculating at about 5 gal min^{-1}) were capped with RTV silicone rubber end pieces after the addition of 3ml water with or without 1g glass beads ("Superbright Glass Beads" MMM Co, Inc). The units were placed on a reciprocatingshaker which oscillated at approximately 25 hz for 5 min. After removal of the contents the procedure was repeated once with fresh reagents. The glass particles were sedimented and the suspension containing the material removed from the pipe was assayed for "organic iron" by the luminol procedure.

B. <u>CHEMICAL ANALYSES</u>

1. <u>Protein</u>: A fluorometric assay was used which is based on the methods of (1) and (2). The test depends on the reaction of phthalaldehyde with primary amines which have been generated by the alkaline hydrolysis of protein. The phthaldehyde--amine complex fluoresces. Figure <u>1</u> shows a standard curve run with a known mixture of proteins. In biofouling studies the fouling film can be collected on tared polycarbonate membrane filters which entirely dissolve during the alkali treatment after determination of dry weight, and/or "dry weight-minus-acid solubles."

2. Organic iron. This test is one of the simplest and most reproducible of the assays (3,4). It is based on the fact that iron-containing organic compounds such as cytochromes, catalase, ferredoxins catalyze light emission from luminol (5 amino-2,3-dihydro-1,4 phthalazinedione) under specified conditions. Since all cells contain some organically-bound iron, this reaction can be used as a measure of cell mass (living or dead). The test can be done by introducing suspension of biofouling material directly into the reaction mixture. Injection of the biofilm suspension initiates the reaction. A curve for a commercial catalase preparation is shown in Figure 10.

3. Bacterial biomass (muramate as D-lactate, and D-alanine) Primary microbial filming is believed to be due largely to bacteria. Two tests were originally proposed to estimate the contribution of the biofouling film which is bacterial in origin. They are based on the fact that bacteria contain in their cell walls a peptidoglycan complex. While this substance varies among bacterial species both in quantity and structure, it contains in all instances D-aminoacids and a derivative of muramic acid. These substances are not found in other cells. The assays for both D-alanine and muramic acid are complex and depend upon coupling with one or more enzyme systems. Muramic acid is freed from cells by acid hydrolysis; D-amino acids are also released in this manner. Alkaline hydrolysis of muramate releases D-lactate. This compound is then assayed using D-lactic dehydrogenase coupled with NAD.(4,5) The resulting NADH is estimated fluorometrically. The assay for D-lactate, itself works well (see figure 2). Using heterogeneous material of biological origin or even cells from pure cultures of bacteria as the sources of muramic acid, however, the hydrolyses produce interfering materials which fluoresce and mask the NADH when it is formed in the presence of lactate. We have not explored ways to eliminate this problem. Chromatographic procedures have been used but these are not practical for the routine test we hope to achieve.

D-alanine is measured using D-aminoacid oxidase which produces pyruvate. The resulting pyruvate is assayed by the oxidation of NADH, the reverse of the reaction above.

4. ATP and FMN Adenosinetriphosphate (ATP) and flavin mononucleotide (FMN) are two coenzymes found in all cells. Both are relatively unstable compounds; the former is readily hydrolyzed by phosphoric esterases (ATP-ases) which are widely distributed in both living and dying cells and extracellularly as the result of cell death. Thus ATP-disappears rapidly on the death of a cell; ATP can be used as a measure of "live biomass" (more or less). FMN is more stable than ATP though it is light sensitive and readily photooxidized. Both of these substances can be estimated by specific luciferase-catalyzed reactions. ATP is required for activity of the firefly-luciferin-luciferase system(6), reduced FMN is needed for that of luminescent marine bacteria(8,9,4). Using these light-emitting reactions the FMN or ATP in very small amounts of cell material can be detected. Figures 5 and 6 show standard curves for these compounds. For both types of assays, the essential substrate is extracted from the fouled layer with boiling buffer (see section on extraction).

Both these complex light-emitting reactions are sensitive to contamination by certain metal ions. We have encountered in some samples loss of activity following the extraction procedure which is attributed to metal ions present on the pipe sample. We are currently experimenting with EDTA as a chelating agent and cation exchange resins as means to overcome the metal inhibition. To date we have not done any tests with samples from the actual buoy OTEC experiment. These are being held frozen until the procedures are more reliable. We anticipate some difficulties with the Cu-Ni alloy pipes because of the biological toxicity of these metals.

5. Inorganic iron While the pipes in the UH-CMU OTEC project do not have significant deposits of iron oxide in the fouling layer, those of the recent APL project did. We, therefore, modified one of the colorimetric assays for iron (10) for use with the OTEC pipe studies. The test measures ferrous (iron-II); the iron is extracted from the film with mineral acid, reduced with hydroxylamine and reacted with the chromogen, o-phenanthroline. As used the sensitivity of the test is limited to samples containing about 100ng iron or more, see Figure 4.

6. Polygalacturonic acids Bacteria are among the first colonizers of surfaces. Some of them produce extracellular secretions which form films. In some organisms the film is composed largely of polygalacturonic acids (11). Several colorimetric tests exist to estimate polygalacturonic acid (12,13). However, because the amount of biofouling materials are extremely small during the first weeks of exposure to water, methods which are more sensitive than those cited above were deemed necessary. A search of the literature examination on the metabolism of galacturonic acid by bacteria showed that an NAD-linked galacturonate dehydrogenase was described in pseudomonads of phytopathogenic origin (14). Because of the sensitivity of assays based on the fluorescence of NADH, we believe a useful test could be developed using the galacturonate dehydrogenase. Several cultures of bacteria were readily obtained from galacturonate enrichments. Crude extracts from each of these showed galacturonate-NAD dehydrogenase activity. From one of these organisms a partially purified extract was made. A test was set up and the preliminary standard curve is given in Figure 3. This curve was obtained by conventional spectrophometric absorption of NADH at 340nm. The fluorometric version of the test should be 100 times more sensitive. The hydrolysis of polygalacturonates to the free sugar acid was tested using HCl (1 to 6N) for various times (1 to 24 h) at various temperatures (4 to 80C). In all cases decomposition of the galacturonate occurred in the acid medium. The percent loss was not assessed but it was evident that a nonconstant amount of substrate was destroyed depending in part on what other constituents were present in the hydrolysate. For this reason acid hydrolysis was abandoned. Instead, the use of the enzyme pectinase (Sigma #P4625) was adopted. It was possible to hydrolyze samples of polygalacturonate in about 2 hrs at pH4 at 35-40C. We have not tested pipe coupons from the OTEC project by this method to date. A disadvantage of the chemical acid hydrolysis procedure is that it releases compounds other than galacturonate.

These, catalyzed by other enzymes in the crude galacturonate dehydrogenase preparation would also cause in the reduction of NAD which might be erroneously interpreted as having been formed from the presence of galacturonate. With the enzymic digestion of the polymer, this type of interference is greatly reduced.

C. PHYSICAL MEASUREMENTS

1. Preparation of samples for SEM and X-ray fluorescence studies. Sections of experimental pipe are fixed with glutaraldehyde (4% in seawater) for about 1 minute. The pipe is dehydrated progressively starting with ethanol-sea water then ethanol-water mixture. For transportation to the laboratory and short-term storage, the samples are kept in aqueous 70 to 75% ethanol solutions. Samples are then taken through 95% and absolute ethanol and critical point dried from Freon 22. For X-ray fluorescence studies the samples are treated as above or simply air-dried from ethanol. Glutaraldehyde-treatment has no measurable effect on these analyses. Samples are mounted and for SEM use sputtered with a gold-palladium film. For x-ray fluorescence studies the specimens were coated preferably with a carbon film; this permits analysis for the elements of lower atomic number, e.g. nitrogen, sulfur, and phosphorus, which is not possible in the presence of gold or palladium.

Some recent observations made from scanning electron micrographs will be discussed by H. White in another report.

2. EDAX (Energy dispersive analysis of X-rays) studies. At the outset we proposed to measure the extent of biofouling by comparing the elemental distribution in the surface layer of the heat-exchanger pipes before and after exposure to flow. Two approaches were used.

A. Elemental distributions. X-rays emitted from atoms have quantum energies characteristic of the particular element. The array of X-rays which emanate from a specimen during SEM studies can be collected, their energies sorted in pulse-height analyzers and assigned to the element from which they came. In figures 7,8,9 are shown elemental distributions on aluminum, titanium and glass surfaces before and after fouling. The relative amount of each element is a function of the accelerating voltage employed, the thickness of the surface films (if any) and other factors. However, it can be noted that some significantly different distributions of elements are found in the unfouled and fouled surfaces.

B. Topographic distribution of elements by EDAX. It is also possible to present topographic maps of the elements detected by X-ray fluorescence. These can be displayed for each measured element. They can then be compared to each other and to a scanning electron micrograph of the same area. Some preliminary results of this type are shown in figure 11. In figure 11 an aluminum coupon was in seawater for 2 months. It can be seen that the atoms calcium, magnesium, silicon and iron are not uniformly distributed while those for copper and scandium are uniformly scattered in the fields. The former 4 elements can be associated with structures in the specimen; the latter apparently are randomly absorbed onto the surface irrespective of its discontinuous nature. The low magnesium content in the area of the crack in the fouled oxide layer and the complementary increase in the amount of aluminum should be noted. High aluminum content is to be expected because the pipe is aluminum. But the pipe is a Mg-Al alloy as is evident from Figure 7. The reason for the low Mg content is not known. It is possible that the Mg was differentially removed from the surface of the pipe.

From the examination of a number of surfaces, we conclude that x-ray fluorescence could be a useful tool to assess biofouling particularly after some period of immersion. It is also possible that under carefully controlled conditions some insight into the corrosion or leaching mechanisms of the metal surfaces could result.

III. APPENDIX: Procedures

A. FLUOROMETRIC DETERMINATION OF PROTEIN

Ref: (1) (2)

Principle: o-phthalaldehyde reacts with primary amines to make complexes which are fluorescent. Protein is hydrolyzed in alkali and reacted with the aldehyde.

Reagents:

1. NaOH, 1N for hydrolysis of protein
2. Boric acid buffer: H_3BO_3, 12.5g dissolved in 450ml glass-dist water; 0.45g BRIJ (polyoxyethylene, 23 lauryl ether) (or 1.5ml of 30% soln) and 1 ml 2-mercaptoethanol are added. Solid pellet KOH added to pH 10.4. Solution made to 500ml with g-d water. Yields 0.4M borate.
3. Particle-free water redistilled from glass
4. o-phthalaldehyde reagent. 25 mg recrystallized compound added to 0.5ml spectral-grade methanol and brought to 50ml in borate buffer.

Protein hydrolysis:

Protein(standards) containing 10mg/ml; 0.1ml (1 mg) is mixed in a pyrex tube with 1 ml 1N NaOH. Tube is maintained overnight at 110° allowing to evaporate to dryness. Biological samples placed on polycarbonate filters are treated in the same manner. Following hydrolysis, the residue in the tube is dissolved in 1 ml saturated boric acids (pH ends up at ca 8.0).

Assay procedure:

10 to 100 µl of hydrolyzed sample is placed in 10x75mm tube containing 2.5ml borate buffer; 0.5ml o-phthalaldehyde reagent is added. Tubes are sealed with parafilm, inverted twice. Tubes should be precleaned by ignition (500C, 2h) Reaction is read in fluorometer, Exc. at 339 nm; emis. at 444nm. Read 10 minutes after mixing. Procedure can be used with 6x50mm tubes by 5-fold reduction in volumes.

B. DETERMINATION OF BACTERIAL BIOMASS FROM D-ALANINE AND D-LACTATE

Ref: (4) (5)

Acid hydrolysis: This procedure liberates the glycopeptide components releasing free aminoacids and muramic acid. Place sample in 6N HCl in s-c tube at 105° for 4.5h. Cool sample and dry under reduced pressure at 55° over NaOH. Store at -20°.

Alkaline hydrolysis: This procedure liberates lactate from muramic acid. The acid hydrolysate is suspended in 1N NH_4OH at 38° 30 minutes in s-c tube.

1. D-Lactate analysis

Fluorometer: Exc. 368nm Emis. 480nm

Reagents:

1. 0.1M TRIS pH 8.5
2. D-lactate, 10mg/ml TRIS soln
3. 3-acetylpyridine-DPN, each tube to get 100 µl of 10mg/ml TRIS
4. D-LDH, made up to ca 0.4 units/µl TRIS

Cocktail: 1.8ml buffer
100µl 3-AP-DPN
20µl D-LDH
0-100µl sample

Incubate in 10x75mm tube for 15 minutes at 37° and read. Or reduce volumes 4X and use 6x50ml tube.

2. D-Alanine analysis

Fluorometer: as above

Reagents:

1. Buffer: 0.05M phosphate pH 7.5
2. Catalase buffer: above + 2.5 μg catalase per ml
3. Lactic dehydrogenase: (LDH) about 1 unit per μl buffer
4. D-aminoacid oxidase: about 0.2 units per μl
5. NADH: 0.04 mg per ml in buffer

Cocktail: 100μl NADH
20 μl LDH
20 μl D-AAO
0-80μl D-alanine
1.8ml catalase buffer

Place above in 10x75mm tube and put on water bath 37° for 15 minutes. Remove and read. For 6x50 tubes reduce proportions. Active dehydrogenases in bacterial sample may regenerate NADH which will interfere with the test.

C. COLORIMETRIC DETERMINATION OF IRON

Ref: (10)

Reagents:

1. 6N HCl
2. Hydroxylamine-HCl: 10g in 100ml g-d water
3. Sodium acetate, 100g in 400ml water
4. Phenanthroline; 100mg in 100ml water; add 2 drops concn HCl to dissolve.
5. Standard iron: 0.9245g $FeNH_4(SO_4)_2{=}12H_2O$ in 25ml water + 10ml H_2SO_4. Add $KMnO_4$ dropwise until faint pink (solution is oxidized). Dilute to 535ml. This will give a standard iron solution of 200μg per ml.

Procedure: Place iron-containing sample in 100ml flask
Add 1 ml Na acetate and 1 ml hydroxyl amine solutions.
Dilute to about 75 ml with water
Add 10 ml phenanthroline solution
Dilute to 100 ml with water
Let color develop for 15 minutes
Read at 510 nm
Method can be reduced in volumes of all components to a total of 2-3 ml or as required.

D. ASSAY FOR FMN

Ref: (4) (8) (9)

Principle: Cellular FMN is reduced with sodium borohydride and palladium chloride as catalysts. The resulting FMNH reacts with bacterial luciferase-aliphatic aldehyde complex and oxygen to give light.

Cocktail:
100μl TRIS-acetate buffer 0.4M pH 6.4
50 μl $PdCl_2$ (0.01mg/ml) in 0.1M TRIS-acetate buffer pH 6.4
100μl sample or standard diluted in TRIS-acetate 0.4M pH 6.4
50 μl $NaBH_4$ 74mg/5ml TRIS-acetate 0.1M pH 6.7. Reagent is perpared immediately before use
100μl luciferase-decanal-bisulfite addition product

Procedure:

1. A saturated solution of the decanal-bisulfite addition product is prepared 0.4M TRIS-acetate buffer pH6.4 and kept cold
2. Bacterial luciferase (Sigma Chemical #L-2379) 1.5mg per ml in the same buffer.
3. Just before beginning the run mix 4 ml of enzyme with 2 ml decanal-complex. Place in repeating Hamilton syringe set to inject 0.1 ml.
4. 6x50mm reaction tubes are filled with buffer, $PdCl_2$ and sample.
5. $NaBH_4$ solution is added to mixture while vortexing.
6. Place tube in photometer, wait 10 sec; inject enzyme complex.

Extraction of coupons: Coupons are placed in TRIS-acetate 0.13M pH6.4 buffer at 110°. Extract for 3 minutes. Cool in ice bath.

E. IRON-CONTAINING ORGANIC COMPOUNDS

Ref: (3) (4)

Reagents:

1. Standard: catalase, 10 mg per ml
2. Sodium perborate, 1.5g per 100ml water
3. Luminol (Sigma Chemical Co #A-8511), made up to 100ml in 0.75N NaOH 10.6mg luminol + 360 mg glucose
4. NaOH, 0.75N

<u>Cocktail</u>: 50 μl perborate solution
50 μl luminol solution
300 μl NaOH
100 μl sample

<u>Procedure</u>: All Reagents (except sample) are added to 6x50 ml tubes and placed in the photometer. Sample is loaded into syringe injected and light is measured. Cellular material does not need to be extracted since most cells lyse in the NaOH solution.

IV. ACKNOWLEDGEMENTS

We gratefully acknowledge the work of Gregg Ayakawa who helped to develop the galacturonate assay and the patience of Bill Showers in running the SEM and EDAX instruments. To all the others who directly or indirectly were instrumental in providing us with the OTEC samples, we say <u>mahalo nui</u>.

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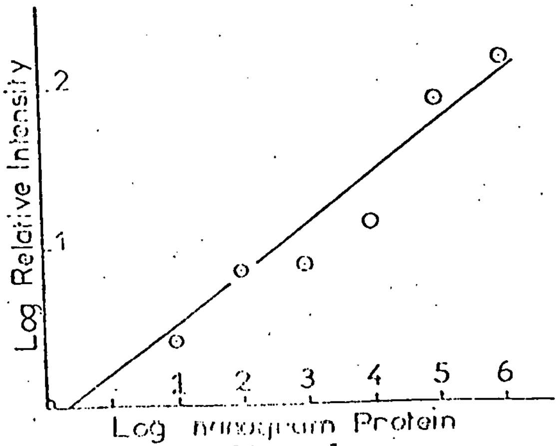
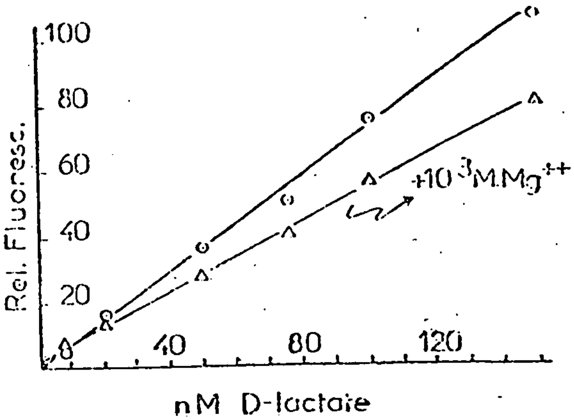


Figure 1



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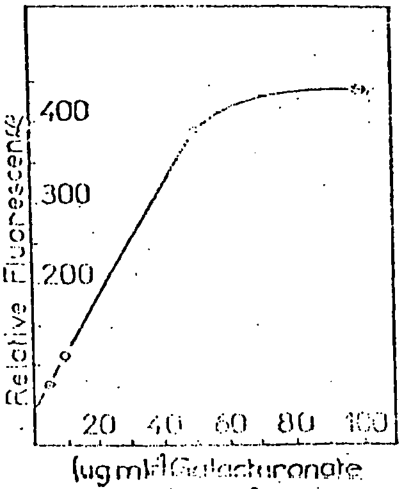

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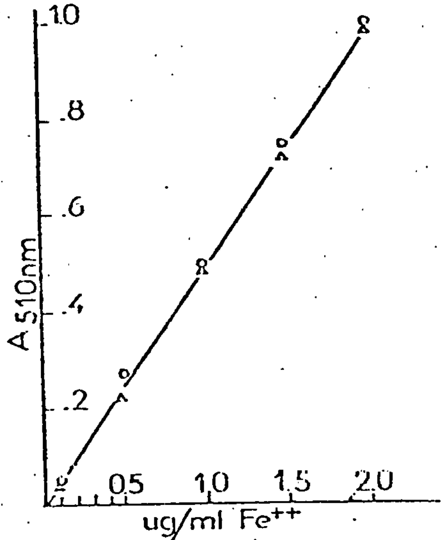


Figure 4

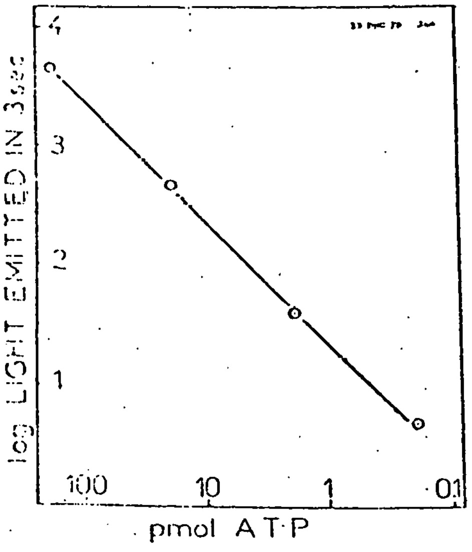


Figure 5

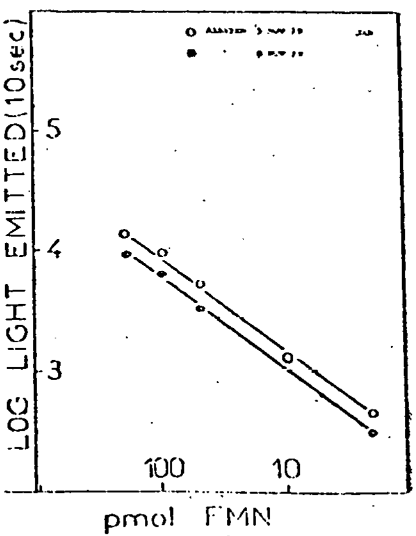
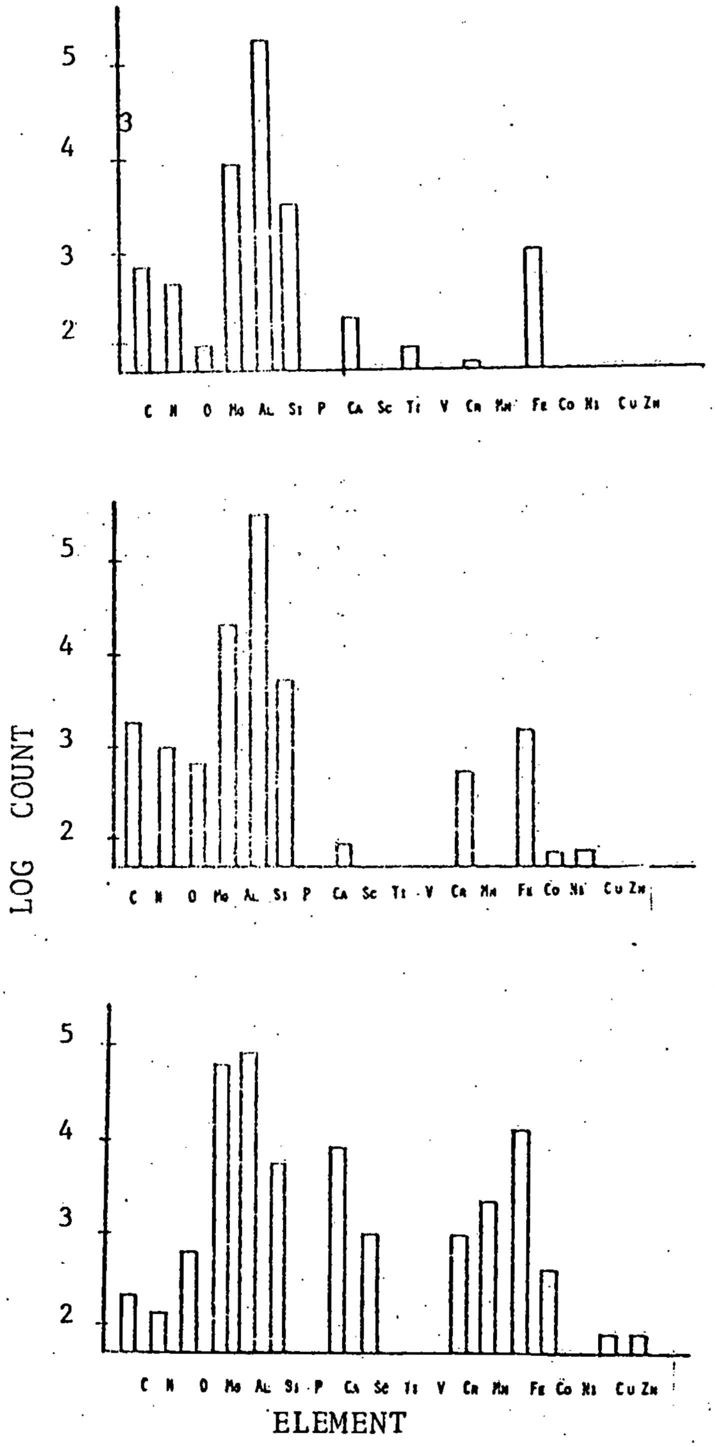


Figure 6

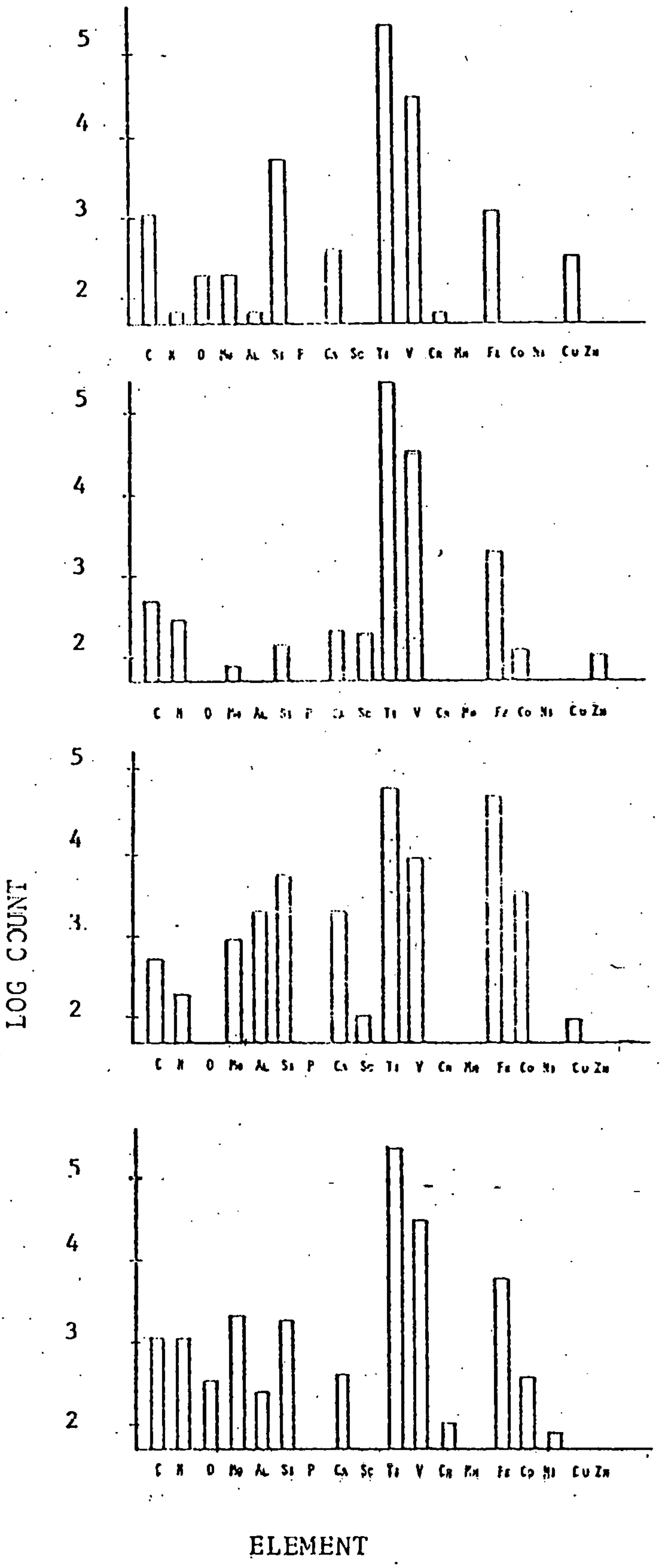


A. Cleaned but not immersed

B. Looking at a hole in the biofilm. 8-month immersion.

C. 8-month immersion: low magnification

Figure 7 Distribution of elements in Aluminum coupons: EDAX analysis



A. Cleaned but never immersed in sea water

B. Spot EDAX of the bottom of a crack through the biofilm of coupon immersed 30 days

C. 30 day immersion: low magnification

D. 8-month immersion: low magnification

Figure 8 Distribution of elements in Titanium coupons: EDAX analysis

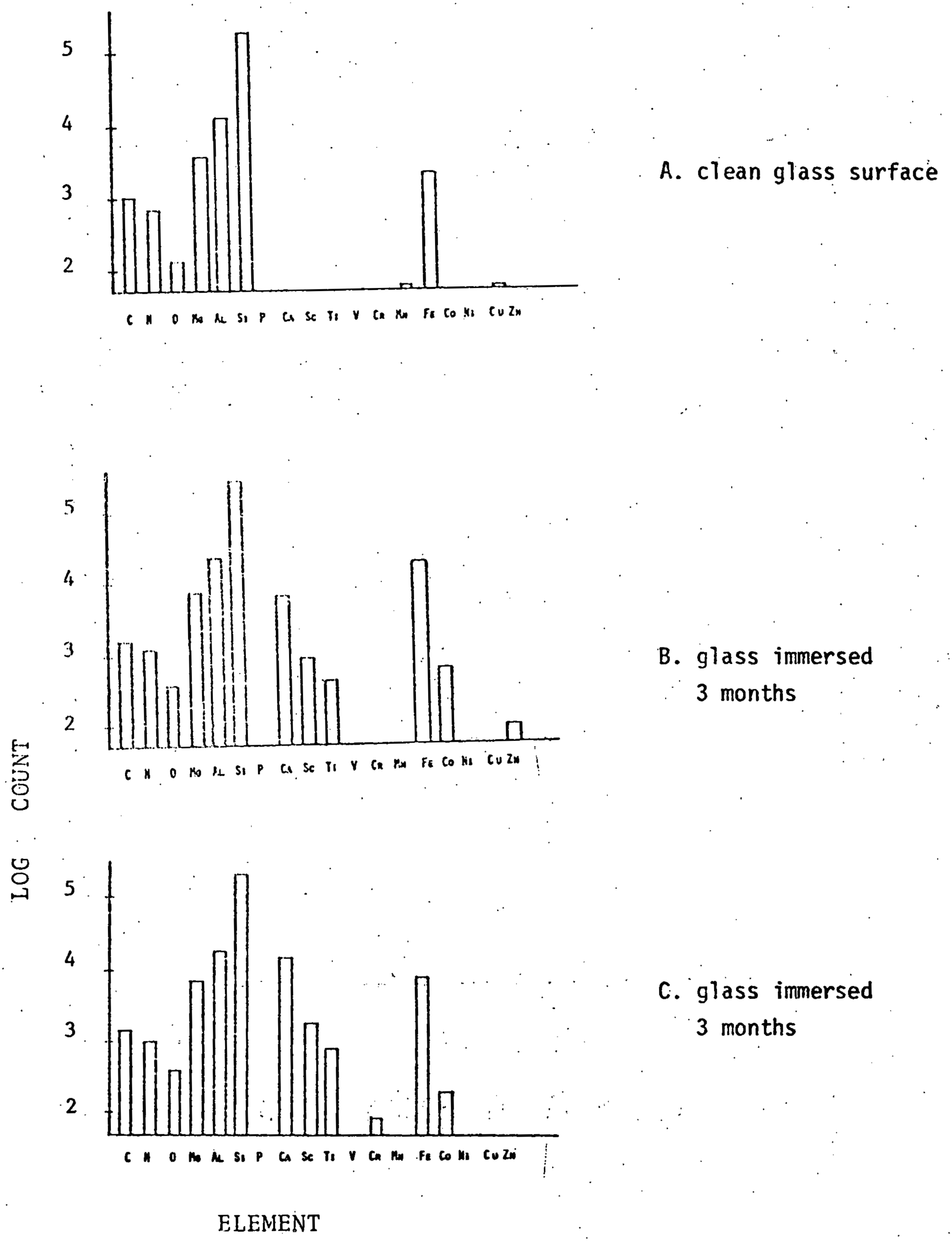
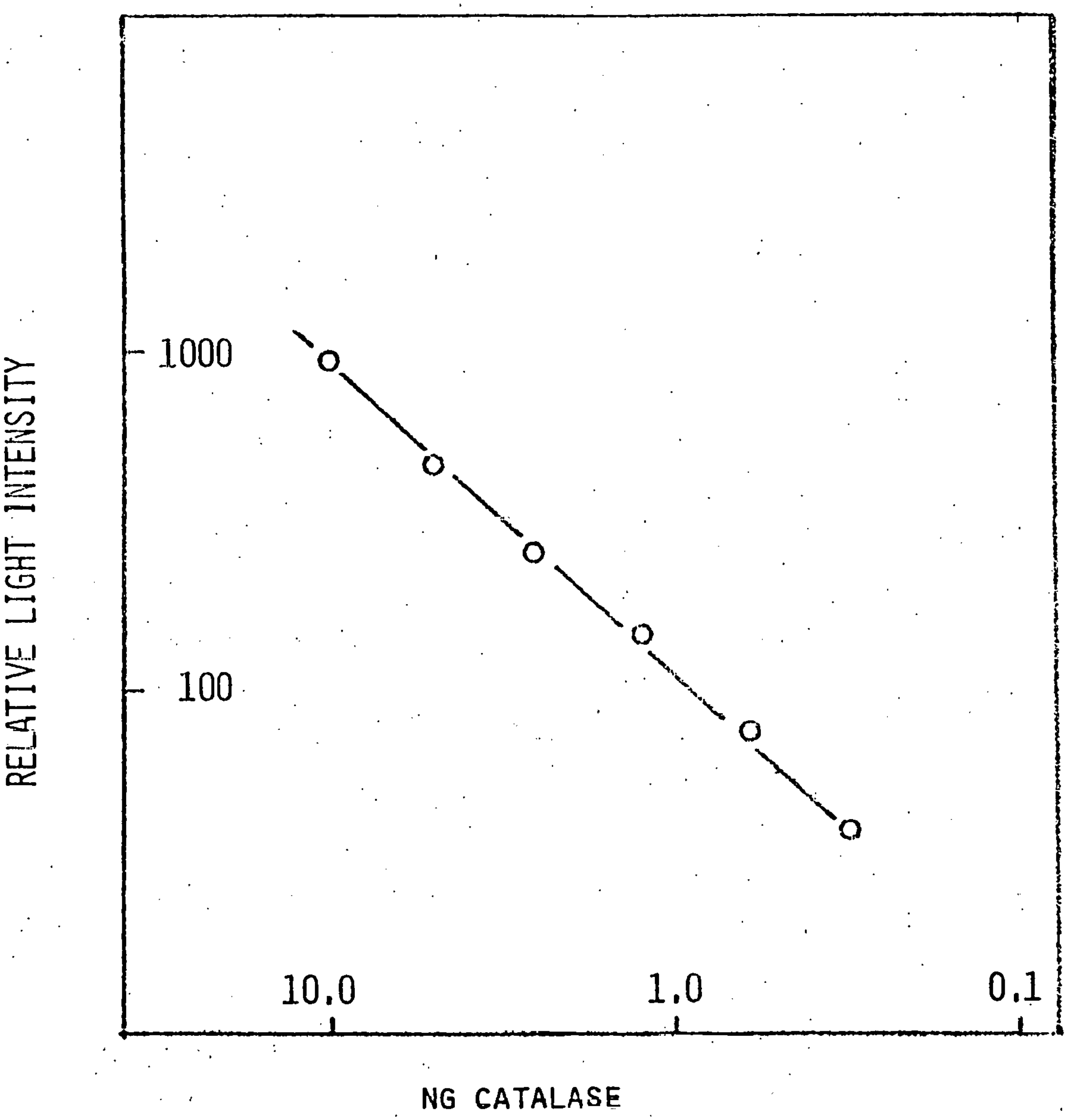
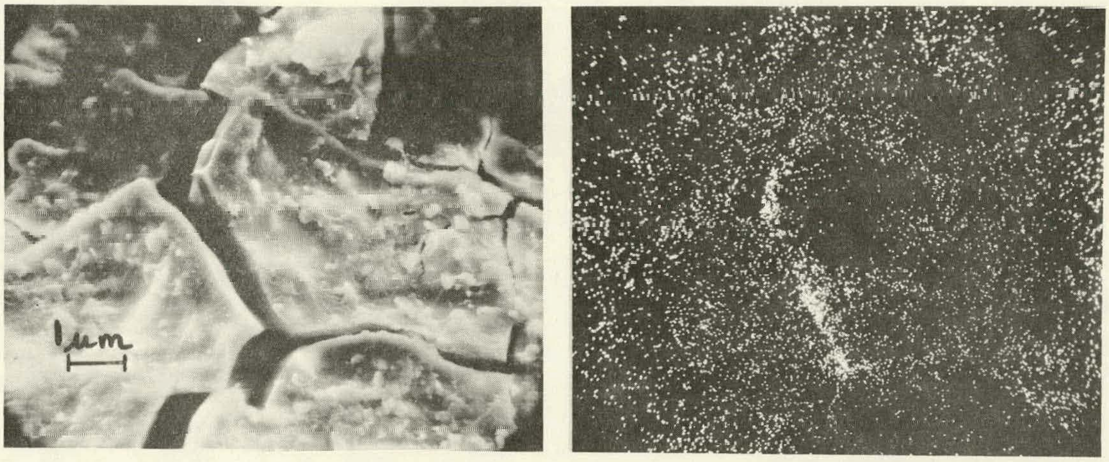


Figure 9 Distribution of elements on glass slides: EDAX analysis



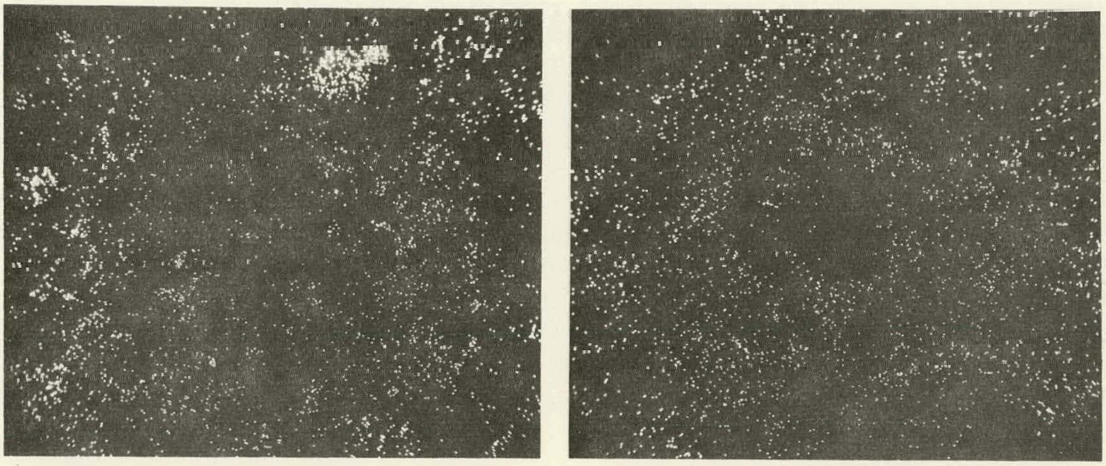
DETERMINATION OF ORGANIC IRON

Figure 10



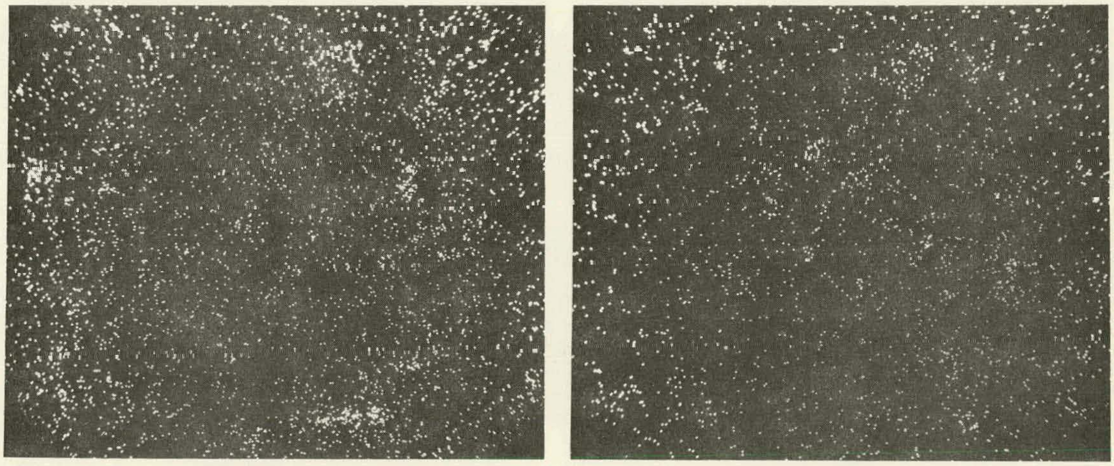
8 MO (BRUSHED AT 30 WKS)

ALUMINUM



SILICON

MAGNESIUM



CALCIUM

IRON

ALUMINUM COUPONS (2 MO. IN FLOW)

Figure 11

ANTI-FOULING MARINE CONCRETE

by

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INTRODUCTION

The ultimate objective of this project is to develop a long-lasting, environmentally safe, and structurally sound concrete with anti fouling and anti-pholad properties. It is intended that the concrete will be used to line the inner surface of seawater intake ducts and to form the basic floating structure of an OTEC plant.

This report deals with the techniques for incorporating antifouling chemical mixtures into concrete, the subsequent testing of the resulting concrete for compressive strength and shear strength, as well as antifouling properties. The rate of corrosion of reinforcing rods embedded in the concrete as well as a study of the outward diffusion of antifouling chemicals from concrete have been initiated. The minimum effective concentration of antifouling agents will be determined. To date concrete test cylinders have been exposed for periods of four months to one year at Port Hueneme, California, Key West, Florida, and Miami, Florida. The antifouling agents under test are Tributyltin oxide (TBTO), Cuprous Oxide (Cu_2O), Creosote and mixtures of these.

BACKGROUND

Incorporation of toxic chemicals into concrete was accomplished by Mr. James S. Muraoka[1] at CEL several years ago. His approach was to impregnate a porous aggregate with toxins and to use this impregnated aggregate to prepare the concrete. The toxins diffused out of the finished concrete slowly thereby preventing the settlement of fouling organisms. Many types of toxins were used in these investigations, and emphasis was placed on antifouling properties rather than on strength. This work was completed and a patent was issued to Mr. Muraoka in the mid-1970s.

With the advent of the concept of OTEC, antifouling concrete with a higher compressive strength than was achieved in the earlier work was required. The studies reported here are directed at this objective.

EXPERIMENTAL PROCEDURE AND RESULTS

Preparation of Concrete. Because many liquid antifouling agents are water immiscible, and therefore difficult to incorporate into concrete, a technique had to be developed to incorporate them in the finished concrete[2].

To accomplish this the following technique evolved. A porous aggregate, in lieu of gravel, is impregnated with various liquid antifouling agents by placing the aggregate in a container from which the air is removed. The liquid chemical is then admitted to cover the aggregate, and air is allowed to enter the container slowly to force the liquid into the pores. The treated aggregate is allowed to air dry for 24 hours, and then superficially washed with 90% acetone in water. The impregnated aggregate thus prepared was used in the usual manner to prepare concrete which ultimately had a compressive and shear strength approximately that of a concrete prepared using a similar composition but with unimpregnated aggregate.

Strength Tests. The compressive strengths of cylinders of a concrete composition with different antifouling additives were as follows:

Antifoulant	Compressive Strength (psi)
None	4660
TBTO	6010
Cu_2O	5330
TBTO + Cu_2O	5360
TBTO + Creosote	3730

Shear tests performed on concrete containing TBTO treated aggregate yielded a shear strength of 3400 lbs, whereas control concrete sheared at 3900 lbs.

Corrosion of Simulated Reinforcing Rods. In the following experiments 6d nails, simulating reinforcing rods were incorporated into test cylinders containing antifouling agents. Such test cylinders were exposed to constantly flowing sea water. No weight loss of metal was observed in these embedded nails. Other test cylinders with antifouling agents were crushed and placed in separate containers subject to flowing sea water. In this accelerated corrosion experiment nails were placed in intimate contact with the crushed concrete. After 131 days exposure the nails were removed, ultrasonically cleaned, rinsed with water, dried, and weighed. Measured weight losses were:

Sample	Weight Loss (grams)	%
Control	1.68	8.11
TBTO	1.32	6.42
TBTO + Creosote	1.10	5.34
TBTO + Cu_2O	1.50	7.29
Cu_2O	1.98	9.61

Diffusion of Antifoulant. Approximately 10,000 larvae of the red abalone *Haliotis rufescens* were placed in tanks containing cured concrete cylinders lacking TBTO and an equal number placed in a similar container containing cured concrete cylinders containing TBTO. After 16 hours all development of the larvae terminated at a multicellular level in both containers. In a similar container containing no cylinders development of the larvae continued in a normal manner through the trochophore stage. It is suggested that some biotoxic substances are released from the concrete to halt larvae growth.

Approximately 5,000 fertilized abalone eggs were placed in a container with antifoulant containing cylinders that had been leached in running sea water for 102 days. Eighteen hours after the introduction of eggs, the developmental stage was determined as follows:

Sample	Results
Control	Normal development
TBTO	Development terminated
TBTO + Creosote	Development terminated
Cu_2O	Development terminated
TBTO + Cu_2O	Development terminated

Pholad Resistance. Samples of the antifouling concretes have been placed in the water off Key West, Florida where pholads are known to be abundant. No pholad attack on the cylinders has been noted after six months. Further observations will be made.

Antifouling Properties. In earlier experiments concrete was impregnated with several different antifoulants (i.e., TBTO with creosote, malachite green, pentachlorophenol, nicotine, tributyltin fluoride (TBTF), copper naphthenate, and a quaternary ammonium compound). Seven years later (1977) the samples containing TBTO and creosote showed a remarkable freedom from fouling. Analysis of a representative TBTO-containing specimen exposed in the harbor for seven years showed the tin content of portions near the surface to be virtually the same as that at the interior. Acetone washed replicate samples contained but a tiny amount of tin, indicating the metal was still bound in an organic molecule.

The encouraging results of the earlier experiments led to an emphasis on the use of creosote and TBTO in the present experiments. At Port Hueneme weight increases of test cylinders after 8 months are: control 196 gm, TBTO 150 gm, and TBTO/creosote (60/40) 133 gm. Similarly treated cylinders exposed in Key Biscayne showed weight gains of: control 633 gm, TBTO 524 gm, TBTO/creosote 496 gm.

Cylinders containing TBTO and cuprous oxide exposed for a shorter period of time at Key West, Florida, appear to be yielding more promising results.

PLANS FOR THE FUTURE

Results from the current studies will continue to be evaluated. These include weight gain of test cylinders, simulated rebar corrosion, pholad resistance, compressive strength, and biotoxicity of antifoulants. Additional experimental cylinders will be prepared and exposed at different, particularly offshore, sites such as Keahole Point, Hawaii. These will contain newer promising materials such as chlorinated organic compounds and solid and polymerized organotin compounds.

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GULF OF MEXICO OCEAN THERMAL ENERGY CONVERSION (OTEC) BIOFOULING AND CORROSION EXPERIMENT

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I. INTRODUCTION

A model OTEC heat exchanger system containing 2 loops of 5052 aluminum, was mounted on a National Oceanographic and Atmospheric Administration (NOAA) 40-foot discus buoy. Water from an 80-foot depth was pumped through the loops at a flow rate of 6 ft/sec for approximately six weeks. Sections of the sample loops were removed periodically and the resulting fouling characterized by the following parameters: wet film thickness, film density, adenosine triphosphate (ATP) and total organic carbon. Scanning electron microscopy was used to describe the surface features of the pipe interiors and to identify the types of fouling organisms. Heat transfer was measured using a device developed by John Fetkovich[1] at Carnegie-Mellon University and the data reported as resistance due to fouling (R_f).

The objective of this experiment was to relate the character of the biofouling/corrosion film to the observed loss in heat transfer efficiency.

II. METHODS AND MATERIALS

A. HEAT TRANSFER EFFICIENCY

Heat transfer efficiency was measured using a 12-inch long copper heater cylinder clamped around the candidate heat exchanger tube with a 2-inch long copper reference cylinder similarly mounted. The heater cylinder was warmed by a Nichrome heater which was wrapped around it and which dissipated 254 watts under design conditions. The temperature of a radial point in the copper heater cylinder relative to the temperature of the flowing seawater was measured by means of a thermistor. The flow velocity of the water was measured by means of a Ramapo Mark V strain gauge flow meter. Heat exchange data were generated by applying voltage to the heater and monitoring the temperature rise of the heated cylinders. When a steady state condition was reached, the heater power was turned off and the temperature of the heated cylinder decayed exponentially. Accumulation of raw data began when the heater was turned off and extended for 12 time constants. A 10-time constant interval was required for the thermopile voltage to decay to its asymptotic value. By taking an average of the thermopile voltage during the final two time constant intervals, an asympototic value was obtained.[2] The resulting data were used by Battelle Northwest, Richland, Washington to determine the heat transfer coefficient between the tube and flowing water.

B. SAMPLE REMOVAL

Nine-inch sample sections were scheduled for removal at the following intervals: 0 hours (immediately after cleaning and before the flow of sea water through the pipes), one week, two weeks and at two-week intervals thereafter until the conclusion of the experiment. The original sample loops were 90" long (ten nine-inch samples). After removal of the first nine-inch section, a replacement nine-inch section was installed. After removal of the second nine-inch sample section, the nine-inch replacement section was also removed and the two were replaced by a single replacement section eighteen inches long. This process was repeated throughout the duration of the experiment so that the total length of the sample loop remained the same. In addition, since the replacement section increased in length each time, the loop was always composed of only two sections of pipe of differing exposure times. All pipe surfaces were cleaned as outlined by Craig, et al.[3] Cleaned replacement sections were kept dry and capped until the time of their installation.

To sample the pipe, the flow was diverted through a by-pass pipe, and the 9" sections were removed using a tubing cutter (figures 1 and 2). The removed sections were filled with membrane filtered (0.45 um pore size) sea water, capped and put on ice until they could be moved to the support ship for processing. There, they were secured vertically in a vise (still filled with sea water) and the necessary subsections were removed using a pipe cutter.

The first sections to be removed were four one-half inch rings from which ATP was immediately extracted. One-inch rings were removed for a determination of total organic carbon and for the inorganic analysis. The ring used for the inorganic scale analysis was rinsed in distilled water. These rings were placed in plastic bags and frozen immediately. (The methods used for characterizing the inorganic scale formation and the results obtained will be presented by John Morse, University of Florida). The specially-milled section (wall thickness 0.030 inch) was then removed and tin snips were used to make six coupons, each about 7mm square. The coupons were placed immediately into vials containing 4% V/V SEM grade glutaraldehyde in membrane filtered (0.45 um pore size) sea water and stored at $4^{o}C$.

The last section to be handled was the three-inch corrosion section which was rinsed in distilled water, allowed to air dry, packed in a plastic bag and prepared for shipment to the University of Miami.

C. ATP

The cut and outside edges of each one-half inch ring were wiped with a tissue saturated with 100% ETOH, the ring dipped in a beaker of filtered sea water and then dropped into 24 ml of ice cold 0.6N H_2SO_4, with a magnetic stirring bar placed in the center of the ring to provide agitation during the extraction. After approximately 20 min. (during which the other rings were cut from the pipe and processed) the rings were removed, and 4 ml of 0.060M EDTA in 0.05M Tris (pH7.8) were added, followed by 4 ml of

3N NaOH. Final pH was adjusted to 7.8 and the extract was frozen for later analysis. This extraction procedure is an adaptation of one reported by Karl and LaRock.[4] Extraction, neutralization and storage were all carried out in acid washed plastic vials to preclude transfer losses. After extraction, each ring was measured with a vernier caliper for the determination of sample area.

For analysis, each extract was brought to 45 ml with 0.05 M Tris at pH 7.8 and assayed using an Aminco Chem-Glow Photometer with integrator and Dupont luciferin - luciferase enzyme-substrate system. At least three determinations were made on each extract. Statistics of variation were computed using the Q test to eliminate spurious values[5] and Youden's methods for small sets of data.[6]

D. TOTAL ORGANIC CARBON

The one-inch frozen rings were allowed to come to room temperature, measured with a vernier caliper for area determination and then extracted. The extraction was accomplished using 10% phosphoric acid to which potassium persulfate (20g/1) had been added. One ml of the phosphoric acid mixture was pipetted into each of the rings which were slowly rotated for five minutes to bathe the entire inside surface. The ring interiors were rinsed with 9 ml of the 10% phosphoric acid/potassium persulfate mixture, and the entire extract transferred to a 10 ml precombusted glass ampule. Three individual, successive extractions were made for each ring. The value of the third extraction served as a procedural blank (since extractions of a ring beyond three times generally resulted in a low, fairly constant value) and was substracted from the values of the first and second extractions. The two corrected values thus obtained were added together to derive total organic carbon. The ampules were purged with oxygen at a flow rate of 80 ml/min to remove inorganic carbon and sealed. Duplicate rings were extracted for roughly half of the sections examined. After sealing the ampules, the conversion of organic carbon to carbon dioxide was accomplished in a pressure vessel maintained at a temperature of 175°C ± 5°C.

An Oceanography International Corporation non-dispersive infrared analyzer was used to determine the concentration of carbon dioxide resulting from the wet oxidation of the organic matter in each of the ampules.

E. SCANNING ELECTRON MICROSCOPY

Coupons fixed in 4% (V/V) glutaradehyde in 0.45 um pore size filtered sea water were transferred through several filtered sea water/distilled water washes, dehydrated in acetone and critical point dried using liquid CO_2 before being coated with Au-Pd in a Polaron sputter-coater and examined with an AMR-1000A scanning electron microscope operated at an accelerating voltage of 30KV.

F. LIGHT SECTION MICROSCOPY

Wet film thickness on 4% glutaraldehyde-fixed coupons was determined using a Carl Zeiss Light Section Microscope. This instrument measures the thickness of any transparent film --- such as aluminum oxide --- as the observed distance between the reflections of a razor thin band of light from the top and bottom surfaces of the film.[7] If the refractive index of the material is known, the true thickness can be very accurately determined from:

$$S' \sqrt{2N^2 -1}$$

where: S' = the distance between the reflected light bands

N = refractive index (1.60 for anodized aluminum)

Measurements were made by Dr. George Loeb at the Naval Research Laboratory, Washington, D.C.

G. FILM DENSITY

For the purpose of the present work, film density was defined as the dry film mass per wet film volume. Dry film weights were provided by Dr. Laurence Poteat, University of Miami and were determined by weighing the rings while coated, removing the film by chemical dissolution[8] and reweighing the rings. Length of the rings was measured with a vernier caliper and the surface area calculated. Wet film thicknesses measured by light section microscopy were multiplied by the area to determine the film volume. Densities are presented as 1x10^2mg/cm^3.

III. RESULTS

A. The sampling schedule is given in Table 1. A flow rate of 6 ft/sec was maintained in the two aluminum loops (3 and 5) for six weeks, at which time flow ceased in both loops. Flow in loop 3 could not be restarted and the pipe drained of water, but after 20 to 40 hours, the flow in loop 5 (which was filled with water but stagnant during this period) was resumed until the experiment was terminated after 67 days.

Although it has been well documented that surfaces become colonized by microorganisms within a few hours after exposure to seawater[9,10] the corrosion of submerged aluminum surfaces is so aggressive as to prevent the settlement of microorganisms for several days.[11] For this reason, the first sample collection was scheduled after a week of exposure time; adverse weather postponed this further to 11 days.

B. HEAT TRANSFER RESISTANCE

The heat transfer data are plotted as thermal resistance of the accumulated fouling layer, R_f(hr ft^2 ^oF/BTU). R_f is defined as the difference between 1/h (where h is the measured heat transfer coefficient at any given time) and the initial value of 1/h.[1] The value of h depends on the flow velocity as well as water temperature. For ease of comparison each value of h is normalized to the same temperature (70^{o}F) and flow velocity (6 ft/sec).

Heat transfer (R_f) data are presented for loops three and five in table 2 and figure 3.

R_f is the basic parameter of the experiment to which all the others are compared (note that the sampling intervals were not the same as for the other parameters). Although loops 3 and 5 were ostensibly duplicates, their R_f values began to diverge after the 18 day sample. Because of equipment failures, no data were received from loop 3 after 36 days.

C. FILM THICKNESS

Wet film thickness measurements are presented in figure 4. Precision of the measurement is $\pm$3um. In loop 3 the wet film thickness increased rapidly during the first 11 days to 18.4 um then leveled off at about 20 um for the duration of the experiment. Loop 5 increased even more rapidly during the first 11 days, but, unlike loop 3, then continued to increase after 18 days to another plateau of about 30 um.

D. FILM DENSITY

The variations of film density (dry weight of the scale per wet film volume) are presented in figure 11. The change in loop 3 approximated a constant relationship (regression coefficient r= 0.99) whereas that for loop 5 was essentially independent of exposure time after 18 days.

E. ORGANIC CARBON

Organic carbon data are presented for loops 3 and 5 in figures 9 and 10 respectively. The same pattern of a steady increase with time was seen for loop 3 while loop 5 again exhibited a less simple relationship.

F. ATP

The ATP data for samples taken from the original pipes and for the replacement sections are presented in figures 7 and 8, respectively. A constituent of living cells only, the ATP indicated that microorganisms were present in detectible quantities in all sample loops at 11 and 18 days. After this, the ATP values for the two aluminum pipes differed both in absolute amounts and in their phase: ATP values in loop 3 peaked after 32 days at 1300pg/cm^2 while those in loop 5 peaked after 45 days at 2300pg/cm^2. Concentrations of ATP decreased in both loops to almost their initial values after these spikes.

G. SCANNING ELECTRON MICROSCOPY

The SEM micrographs are arranged in appendix B to show the chronological development of fouling in the sample pipes. Plates 1 through 7 apply to loop 3, plates 8 through 15 to loop 5. The microscopic evidence generally supports and clarifies the trends of the chemical and physical data, especially with regard to the divergent development of the fouling in loops 3 and 5.

At time zero (immediately after cleaning) the pipe surfaces of loops 3 and 5 had similar appearances (plate 1). They were uniformly etched by the sodium hydroxide and nitric acid washes and were free of lubricant, extrusion lines, and oxide layer. After 11 days exposure, the surfaces of the aluminum pipes were covered with a corrosion film of about 20 um thickness and a density of about 250 mg/cm^3 (plates 2 & 3). The corrosion layer forms as a continuous gelatinous film. In the preparation for SEM the water of hydration is lost and the material shrinks, resulting in the "dried mud" appearance.[3] Both x-ray fluorescence examination[12] and chemical analysis[13] revealed this film to be composed primarily of aluminum salts, with significant amounts of magnesium, calcium, and iron.

At this point, no microorganisms could be found on samples from either loop.

By day 18, microscopically different fouling was evident in the two loops. Although the ATP and total organic carbon data indicated equivalent biomass and organic matter on the surfaces of the two loops, few cells could actually be located on the loop 3 coupons. These occurred in very widely separated patches. Loop 5, exhibited a surface slightly more heavily fouled with cells of two morphologies: one a smooth, 15-20 um filament having a swelling just before the attached end, and the other an ovoid rod (plate 8). Some of the latter were undergoing cell division, an indication that they were actually growing on this surface and not simply fortuitously adsorbing to it from the bulk water. In addition to these patches of bacteria, the surface of loop 5 appeared to be more heavily fouled with the amorphous masses, from 1 to 10 um in size, seen on the surfaces of both loops from day 11 onward (plates 6,10,13, 14). This material, composed of 0.1 to 0.2 um subunits, exhibited a high degree of "charging" (*i.e.* secondary electron emission), and contributed to surface roughness.

At day 32, the patches of bacteria on loop 5 were noticably smaller and less numerous (plate 9). A long rod type appeared (though not in large numbers) which was always flat on the surface of the corrosion film (plate 10). None of the filamentous type was seen, and the short ovoid rods predominated the flora. The same type of short rod predominated the surface of loop 3 as well, occuring in dense, isolated patches (plate 4).

At day 45, cells on loop 3 were difficult to find. The few that were visible were poorly defined, as if they were empty cell walls of autolysed cells or as if partly obscured by an overlying film. In loop 5, on the other hand, the filamentous type had reappeared and predominated. These cells occurred to some degree all over the surface, often in dense mats of intertwined filaments (plate 11).

At day 67, the filamentous type was still present in even larger numbers, along with at least two different types of rods (plates 12 & 13). This surface --- which experienced between 20 and 40 hours of stagnant conditions shortly after day 45 --- showed large amounts of organic film for the first time. This film trapped particulates from the water, as evidenced by the piece of diatom frustule in plate 14. It is obvious that, for loop 5 at least, the experiment terminated just as the biological film was becoming well established.

The replacement sections, which were always emplaced downstream of the original pipe sections (i.e. the loops were sampled from top to bottom - see figure 2), exhibited an accelerated and more diverse development of the microbiological fouling for both loops. All the morphological types seen on the original sections were also seen on the replacement sections, plus possibly one or two others (plates 5-7 15-19).

H. WATER QUALITY INDICATOR SYSTEM

The only parameter for which reliable data could be obtained from the Water Quality Indicator System was that of water temperature in ^{o}C presented in figure 14. The data show a general warming trend from April to June with a good deal of fluctuation during the experiment.

IV. DISCUSSION

A. PHYSICAL/CHEMICAL PARAMETERS

The objective of this experiment was to relate the character of the biofouling/corrosion film to the observed loss in heat transfer efficiency. Unfortunately, there are several aspects of the heat transfer data which make it doubtful that such comparisons would be useful.

The most apparent problem with the R_f values is the wide uncertainty limits, which are generally an order of magnitude greater than the R_f measurements themselves (table 2). The second problem is R_f increases very slowly initially (figure 3), whereas the thickness of the corrosion film grows very quickly (figure 4). During the first days of exposure the corrosion layer on the aluminum surfaces is being formed so aggressively that microorganisms can play little role in the film formation process, leaving the physics and chemistry of the inorganic film as the controlling factor. If this is the case, the R_f should exhibit the same rapid increase as the film thickness, then level off, reflecting the stabilization of the film. If film density (figure 11) rather than thickness is considered, the relationship should be generally the same, since the rate of R_f increase should level off as the film becomes more dense and conductive.

The R_f data deviate even more from theory if one imposes the limits calculated by Bell[14] on a plot of wet film thickness vs R_f (figure 5). Most of the data for both loops 3 and 5 fall well below the R_f which would be exhibited by an almost solid film (figure 6).

For these reasons, correlations between R_f and any of the measured parameters are not discussed in this report.

The salient feature of the results is the lack of replication between the "duplicate" aluminum sample loops during the early stages of microfouling. The differences between loops 3 and 5 are most obvious when their surfaces are visualized with the SEM. Loop 3 is characterized by low densities of amorphous particulates and of short, rod-shaped bacteria which are anchored close to the surface, while loop 5 is characterized by the early onset of consistently heavier concentrations of particulates, rods, and long, filamentous cells. It is obvious that the differences in film thickness (figure 4) and density (figure 11) between the two loops are due to physical/chemical processes in loop 3 and to biological effects on these processes in loop 5. These biological effects may be due to both the physical presence and the metabolism of the microorganisms.

Wet film thicknesses in both loops reach a plateau at a value of about 20 um between 11 and 18 days, but in loop 5 the thickness continues to increase an additional 10 to 12 um, directly reflecting the increase in the numbers of the long, filamentous cells (15-20um). At 45 days organic carbon (figure 10), which includes a cellular carbon component, ATP (figure 7), which is a measure of live biomass, and film thickness (figure 4) all reach peak values in loop 5. Microscopic and biochemical evidence (plates 11 through 14) substantiate the contribution by the microorganisms to the film thickness.

Film density, another property which would be expected to affect heat transfer efficiency, is also impacted by biofouling (figure 11). In contrast with loop 3 which reveals a steady increase in film density with time (correlation coefficient =1, P=0.05), a plot of density in loop 5 breaks sharply around the onset of biofouling. Presumably the corrosion film in loop 5 is also increasing in density, but that increase apparently is being offset by the accretion of low molecular weight, hydrated organic material in the form of cells and their polysaccharide secretions. This may, in fact, contribute to the apparent decoupling of film density vs organic carbon in loop 5 in contrast to loop 3 (figure 12) which has a linear correlation coefficient of .99 (P=.05). Another aspect of this decoupling is seen in (figure 13), showing the relationship between film density and thickness.

A higher film density will tend to decrease R_f, as demonstrated by Bell's calculations (figure 5) in which a non-porous material of a given thickness results in a lower R_f than a hydrated biological film of the same thickness.

B. BIOCHEMICAL PARAMETERS AND MICROSCOPY

One of the most useful parameters for gauging the impact of bacteria on the heat transfer efficiency across the film would perhaps be cell counts (areal densities of cells). Determining visual counts with the SEM is difficult during the early stages of biofouling, as is the situation in this experiment. The generally patchy distribution of the cells on the pipe surface requires that a prohibitively large number of fields must be counted for statistical validity. The measures of organic carbon & ATP are alternatives to the direct estimate of cell numbers. They also give additional information on the level of cellular metabolism which, for bacteria, is as important a parameter as cell number.

ATP is the only parameter which conveniently allows an estimate of the living microbial biomass (ATP is a cellular component which is degraded very rapidly upon the death of the cell). However, the amount of ATP per cell can vary within a factor of 10 among different species and even the ATP vs cell carbon ratio can vary within a factor of 4.[15,16] In addition, within a given species the amount of ATP in the cell varies over the growth cycle and with physiological state.[15, 17] For these reasons, no attempt has been made to relate cell numbers to the ATP values. The levels of ATP observed (figure 7) yield cellular carbon estimates[15] only 1/10 to 1/1000 the amount of organic carbon measured in this film. The bulk of the organic carbon values in the early stages can be attributed to adsorbed dissolved organic matter. As living and dead biomass and associated secretions increase, their contribution to the total organic carbon should increase to a significant level.

It has been demonstrated by LaMotta[18] that basal microorganisms (those within the forming film) will suffer substrate/oxygen starvation leading to the accumulation of dead organic matter in the layers of the film. The rapidly forming corrosion layer on aluminum surfaces tends to obscure microorganisms and its rapid deposition may further impair oxygen transfer.

The ATP results presented here are generally supported by the SEM observations. The data appear to illustrate the correlation of ATP with biomass, the variation between species, and the effect of physiological state.

ATP values indicate that a substantial amount of biomass is present through 18 days although none is detected with the SEM. A reasonable explanation for this may be that cells during this period are unable to maintain an irreversible contact with the surface and are rinsed off during the preparation of the sample for SEM. The initial stage of bacterial adhesion is termed the reversible sorption phase[19] and consists of that period when the electrostatic and hydrophobic forces are balanced against a double layer replusion force. In addition, at the 11 and 18-day exposure times the "areal dilution" effect will make it difficult to find any bacteria on the surface during this time. If one assumes a cellular ATP ratio of 2×10^{-15}g ATP/cell[15] a cell density on the order of 5×10^{4} cells/cm^2 would be predicted. At a magnification of 2000x (the minimum at which a single bacterium would be recognized as such on these surfaces) only one cell would be included in each field if the cells were evenly distributed. Obviously, microscopic detection of such low concentrations are strongly dependent on such factors as the character of the surface, state of preservation of the cells, and their spatial distribution.

The peak in ATP at 32 days in loop 3 corresponds to an increase in the cell density seen with the SEM. Irreversible attachment of bacteria to the aluminum surfaces can be demonstrated at this time in loop 3 and at 18 days in loop 5 (plates 4 and 8). This phase is that in which the cell is producing permanent attachments to "anchor" it to the surface.[19] Such attachment requires a specific type of surface on which to act[20] and this is supplied by a layer of organic material which has been shown to coat surfaces exposed to seawater.

Baier[21,22] described the attraction of non-living organic matter to surfaces exposed to seawater and considered that such glyco-protein "conditioning films" were a prerequisite to later adsorption of cellular material to solid substrates. Loeb & Neihof[23] found that such dissolved organic substances were present in all natural seawater. These organic films are postulated to reach a thickness of several hundred angstroms.[21] These thin films have no direct effect on heat transfer efficiency, but they do attract living bacterial cells[24] that ultimately colonize the surface.

The first observed colonies are composed of small, rod-shaped bacteria. The small rods have a selective advantage over other bacterial groups in this irreversible sorption.[25] Small rods are also able to reproduce at low nutrient levels and to produce extracellular polymeric fibrillar material.[26] Hendricks[27] reported that bacteria sorbed to surfaces appear to be metabolically more active than suspended ones. Both direct and indirect evidence have shown that irreversible attachment involves polymeric bridging of cells to substrata by extracellular secretions[28,29] as seen in plates 5 and 6. The fibrils may also be concentrated at the poles of the cells (plate 5), causing the latter to be orientated at right angles to the surface.[19]

The low ATP values of 32 days in loop 5 corresponds to an observed lack of microflora on the surface. Those seen were short rods occurring in scattered patches.

The enrichment of the surface with short rods and adsorbed nutrients provide concentrated food supplies for subsequent colonization by filamentous bacteria[30] as is seen in Loop 5 after 45 days and in loop 3 replacement sections. The peak in ATP in loop 5 at 45 days reflects the proliferation of the filamentous cells (plates 11).

From the ATP data it is apparent that the stagnant condition which occurred between days 45 and 67 in loop 5 had a catastrophic effect on the biofilm. The decrease in living biomass is corroborated by the SEM micrographs (plates 12 - 14) showing fewer cells. The copious production of slime after the shutdown in loop 5 (plates 12 - 14) was apparently the result of low oxygen or low nutrient stress during the stagnant conditions. Much faster accretion of particulates on the surface may be predicted as the result of such a shutdown, as evidenced by the diatom frustule seen in plate 14.

The slime film resulting from the secretion of polymer and the inclusion of dead cells provides a nutrient-rich substrate that is available for further colonization. The amount and diversity of biofouling after such a shut down would be expected to increase more extensively with no lag phase. The implications to a functioning OTEC plant are obvious.

Finally, it is apparent from the present work that downstream replacement sections foul more quickly than do sections of the original flow loop (plates 5 - 7, 15-19). Flow through the original pipe sections that have a biofilm formation innoculates the replacement sections so that they are colonized in a shorter period of time than were the original sections. In loop three, the 15 day replacement section was fouled to the same extent as the adjacent downstream 32-day exposed section. The fouling organisms were identical and the ATP values were similar (figure 8). The same is true of a 14-day replacement section downstream from a 45-day original section in loop 5. A similar observation was made in a biofouling experiment at St. Croix, Virgin Islands.[31]

The observed surface fouling during the period of time covered in this test was complex, dynamic and sensitive to changes in environmental conditions. It appears that the biology of the fouling film was just beginning to have significant effects upon the experiment. The results reinforce the fact that problems in microbial ecology must be described by several parameters and that those parameters must be evaluated for their synergistic effects if the system is to be understood.

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Appendix A

Table

Figure

SAMPLE SCHEDULE

TABLE 1

	Sample Date	Time Exposed	Samples Removed
t_0	2 April 1978	0 hours	3-11, 5-11 & 7-2
t_1	12 April 1978	11 days	3-12, 3-2, & 5-12 5-2 & 7-3
t_2	19 April 1978	18.5 days	3-3, 5-3 & 7-4
t_3	3 May 1978	32 days 15 days	3-4, 5-4 & 7-5 3-Spare & 5-Spare
t_4	17 May 1978	45 days 14 days	3-5, 5-5 & 7-6 3-13 A&B, 5-13 A&B
t_5	8 June 1978	67 days 22 days	5-6 & 7-7 5-14 A & C

Samples 3-spare, 5-spare, 3-12, 5-12, 3-13 A & B, 5-13 A & B and 5-14 A & C are all replacement sections. Replacement sections were not available for the titanium loop.

TABLE 2

HEAT TRANSFER RESULTS FROM THE NDBO OTEC-2 BIOFOULING AND CORROSION EXPERIMENT

	Week	Days	Date	H (Btu/hr ft^2 ^{o}F)	ΔH (Btu/hr ft^2 ^{o}F)	R_f (hrft^2 ^{o}F/Btu)	ΔR_f (hrft^2 ^{o}F/Btu)
Loop 3			3/30/78	1007	*		
	0		4/4/78	1076	*	0	
	2.3	16	4/20/78	1065	±88	0.00001	±0.00011
	3.0	21	4/25/78	1058	±64	0.00002	±0.00010
	4.0	28	5/2/78	1049	±74	0.00002	±0.00010
	5.1	36	5/10/78	1039	±22	0.00009	±0.00008
Loop 5			3/28/78	1003	±29		
	0		4/5/78	992	±54	0	
	2.3	16	4/21/78	986	±56	0.00001	±0.00008
	3.1	22	4/27/78	966	±100	0.00003	±0.00012
	4.1	29	5/4/78	950	±69	0.00004	±0.00009
	5.1	36	5/11/78	931	±46	0.00007	±0.00008
	6.1	43	5/18/78	888	±20	0.00012	±0.00006
	7.0	49	5/24/78	868	±32	0.00014	±0.00007
	8.0	56	5/31/78	854	±27	0.00016	±0.00007
Loop 7			3/29/78	1101	±32		
	0		4/6/78	1081	±33	0	
	2.3	16	4/22/78	1083	±34	0.00000	±0.00004

ΔH & ΔR are uncertainty estimates[32]

*Uncertainty estimates not available for these dates because of flowmeter malfunction.

Figure 1

Biofouling & Corrosion Sample Section

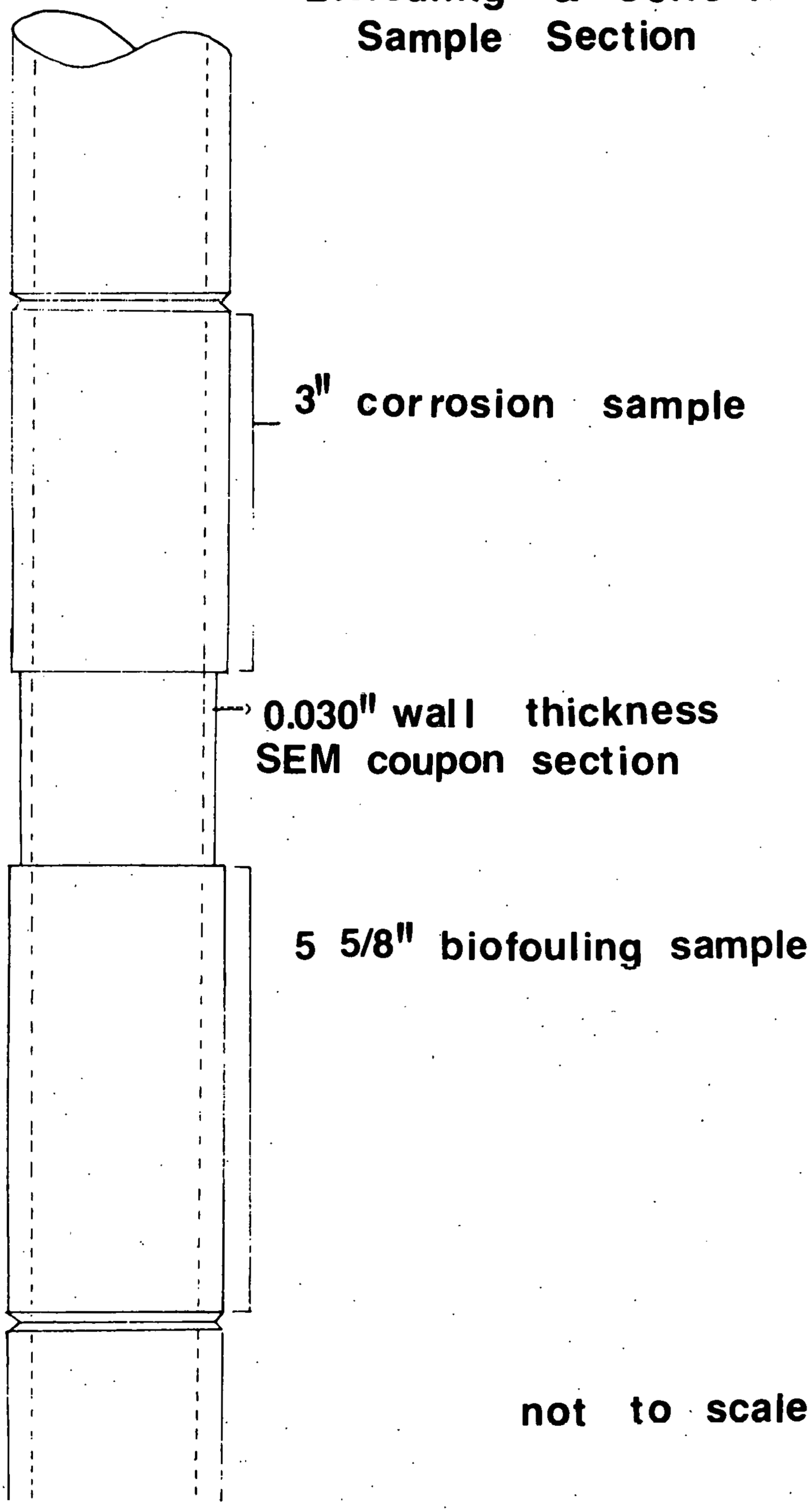


Figure 2 FLOW SCHEMATIC - HEAT TRANSFER MONITOR LOOPS

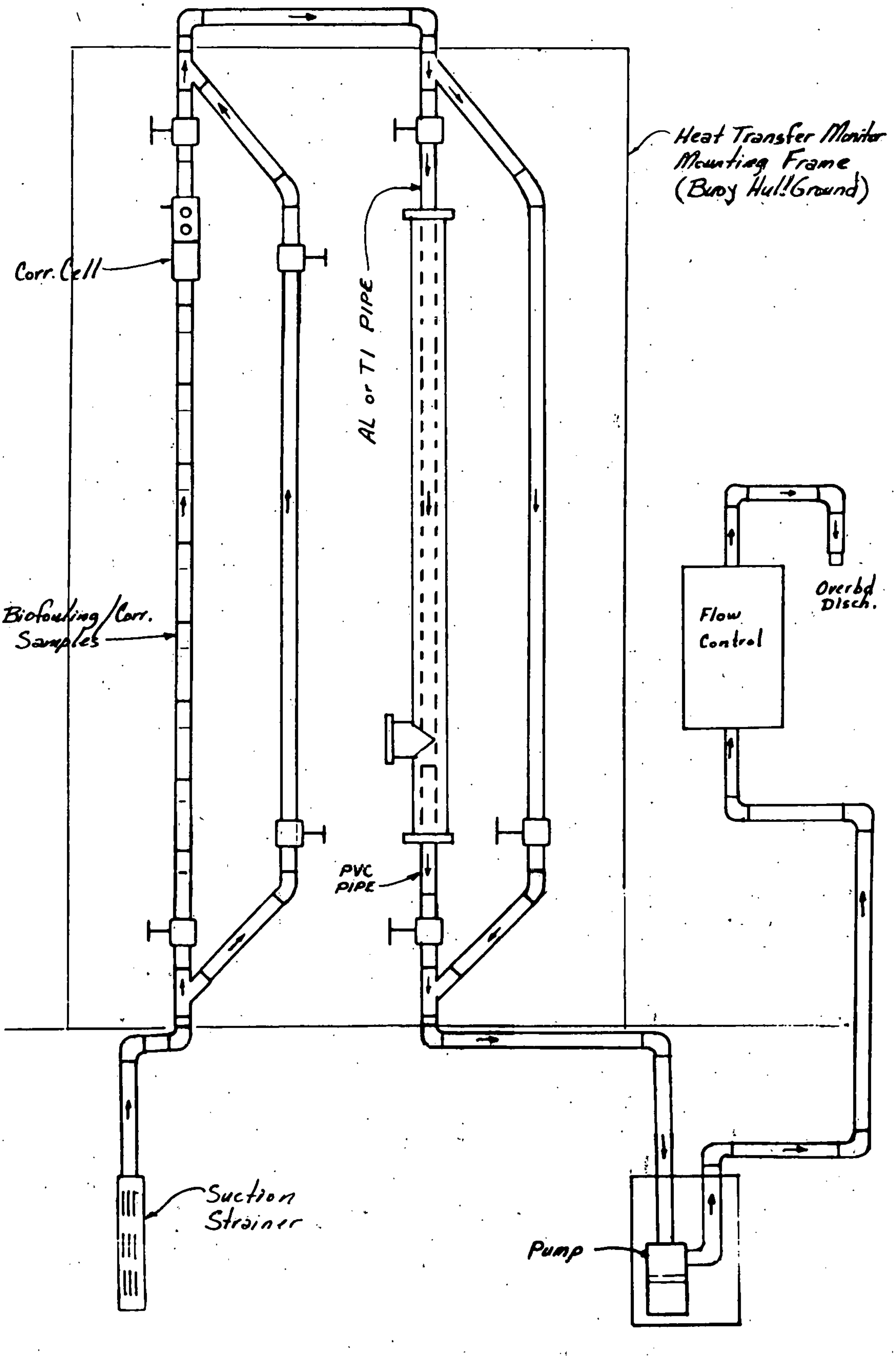
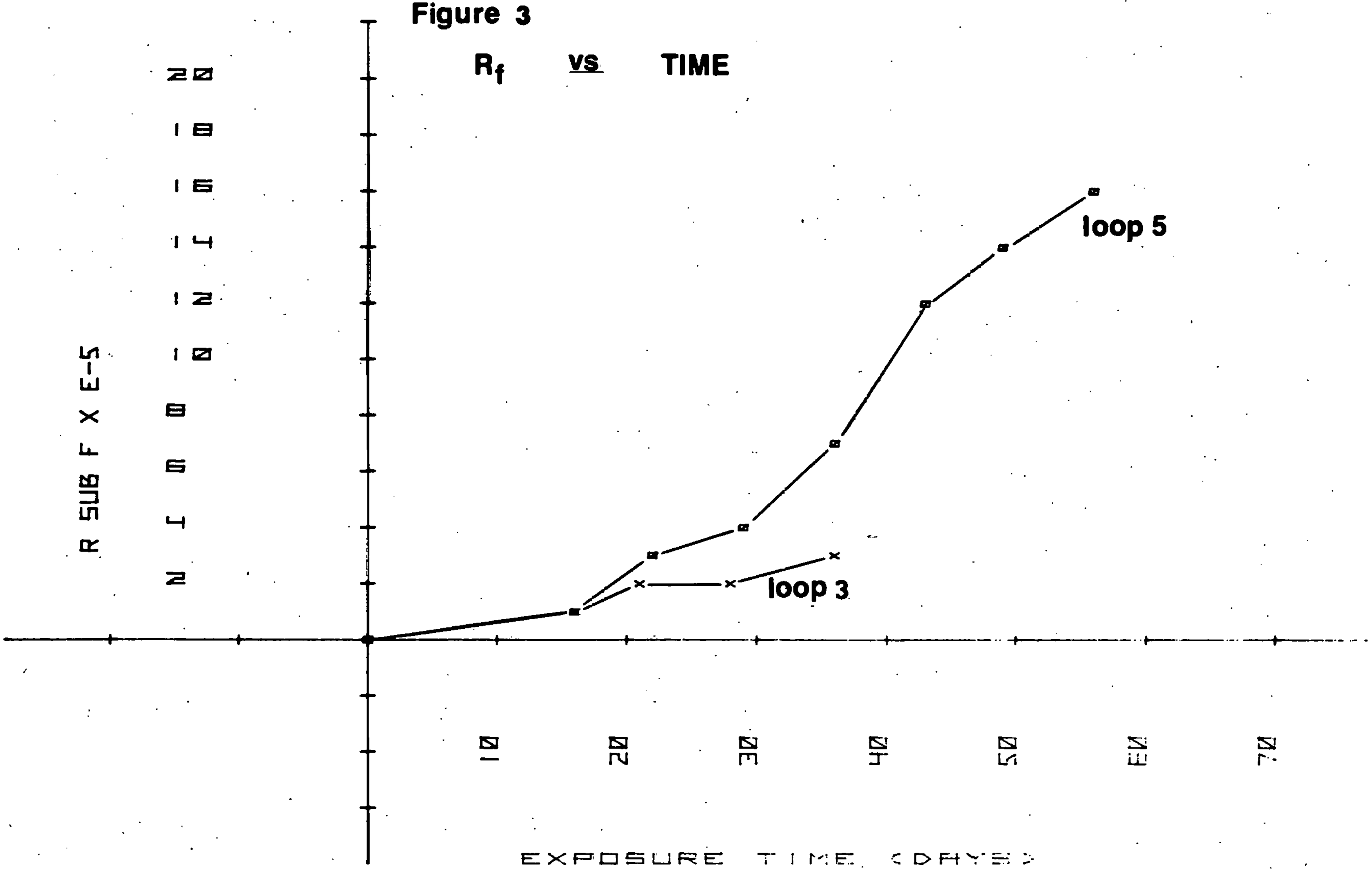


Figure 3

R_f vs TIME



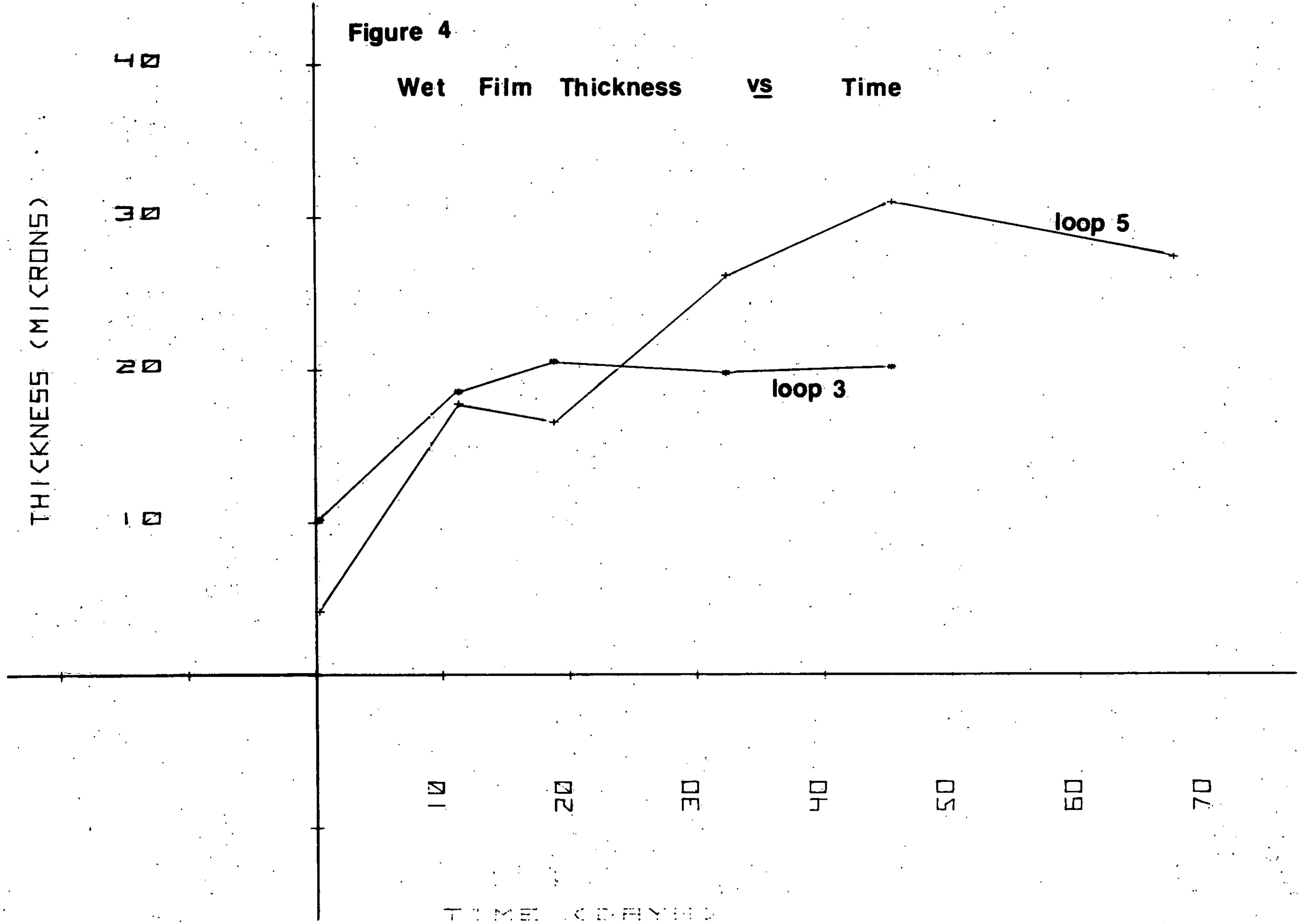
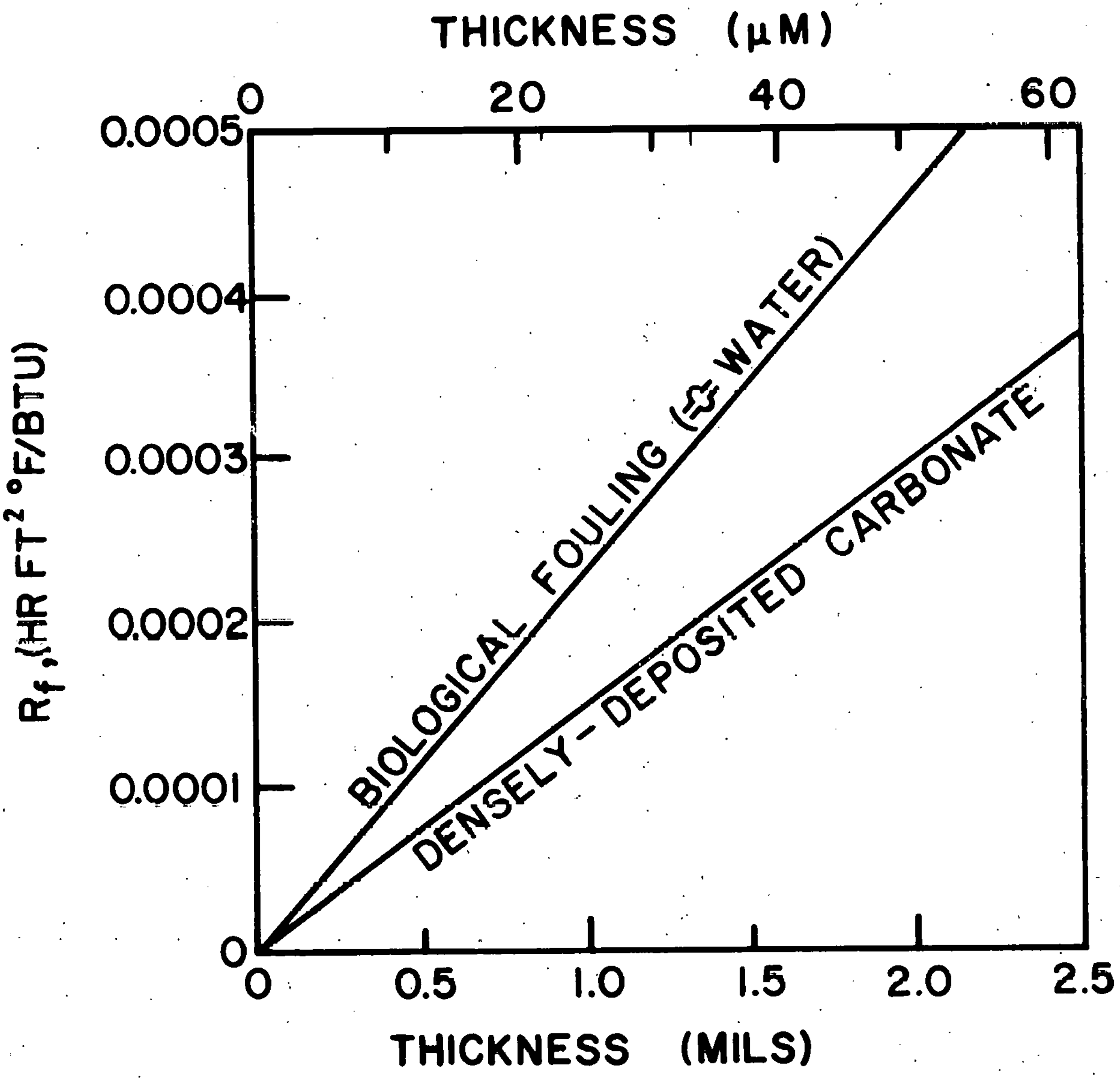


Figure 4

Wet Film Thickness vs Time

Figure 5

R_f vs THICKNESS



The relation between heat transfer, and the thickness of biofouling and solid calcium carbonate layers on heat exchanger surfaces (Bell, unpublished data from Morse _et al_, 1978).

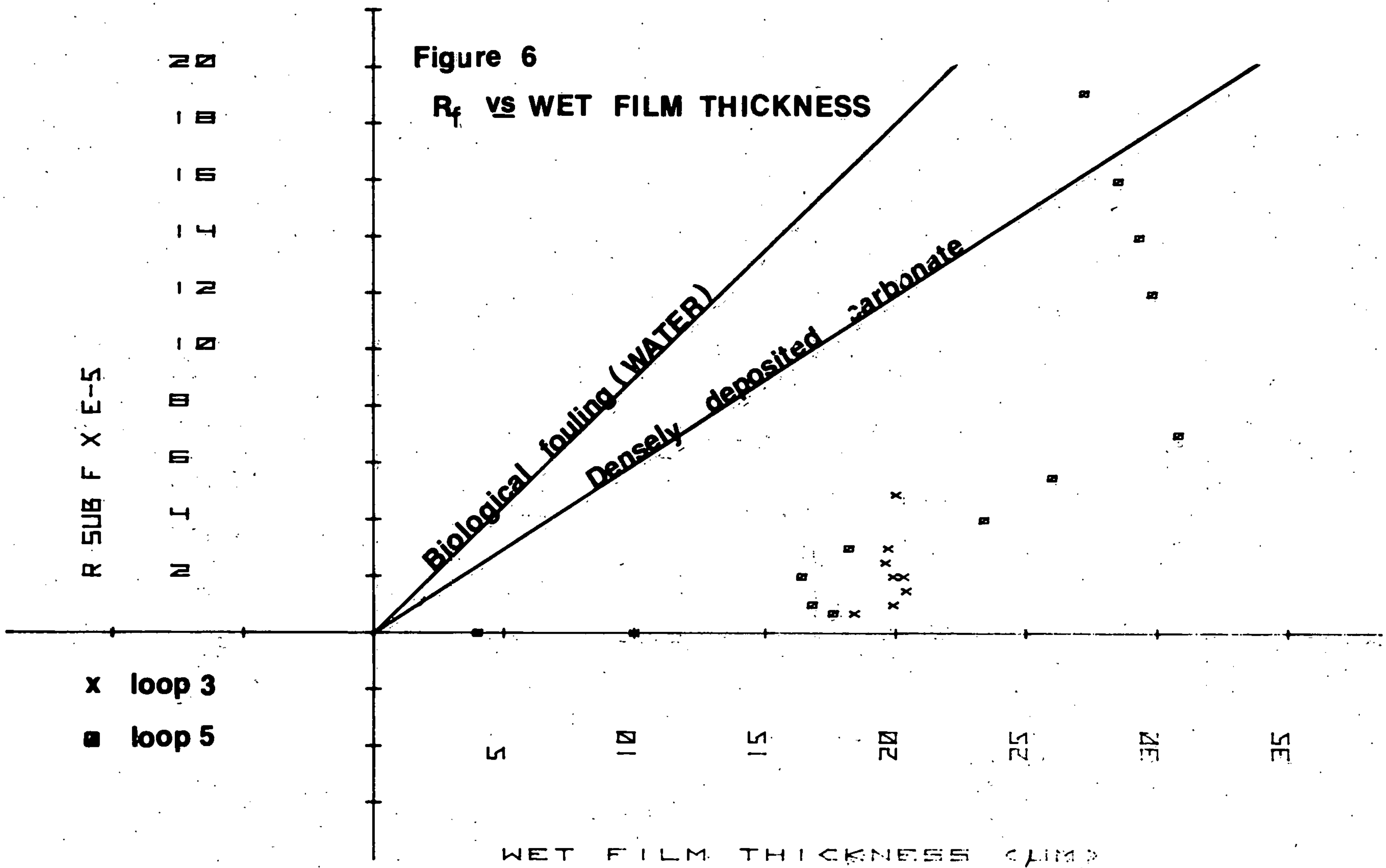


Figure 6

R_f vs WET FILM THICKNESS

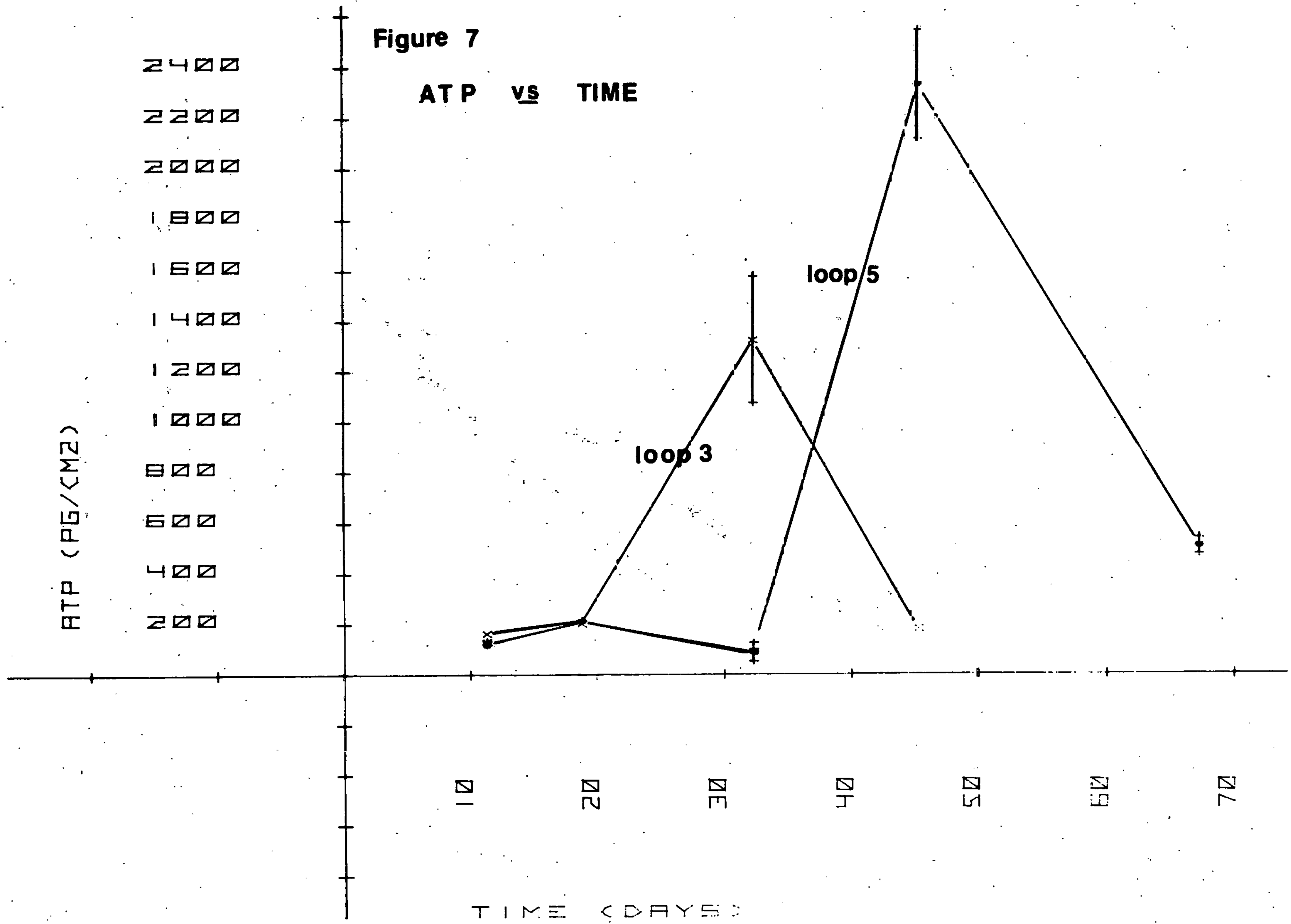


Figure 7

ATP vs TIME

Figure 8

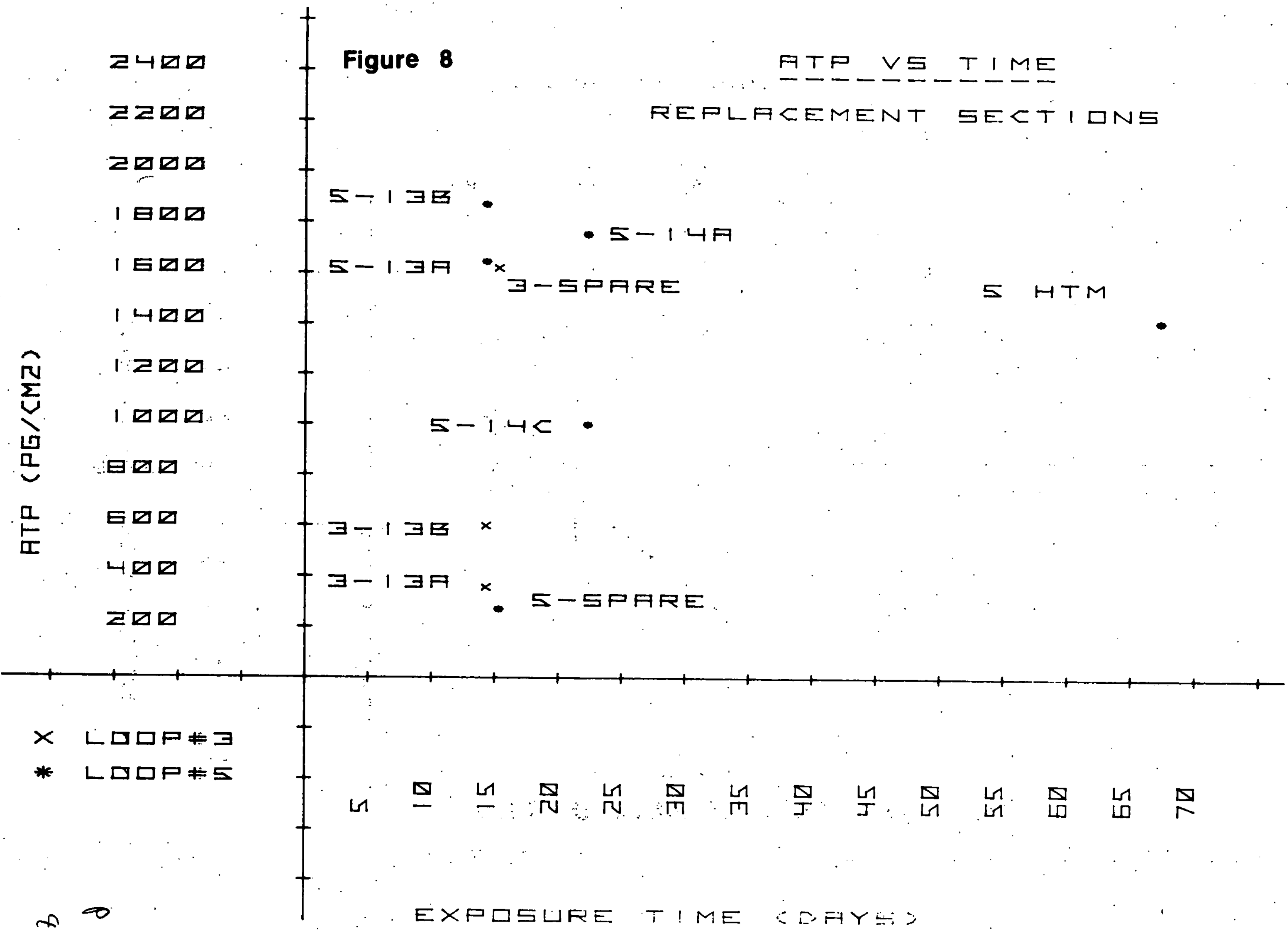
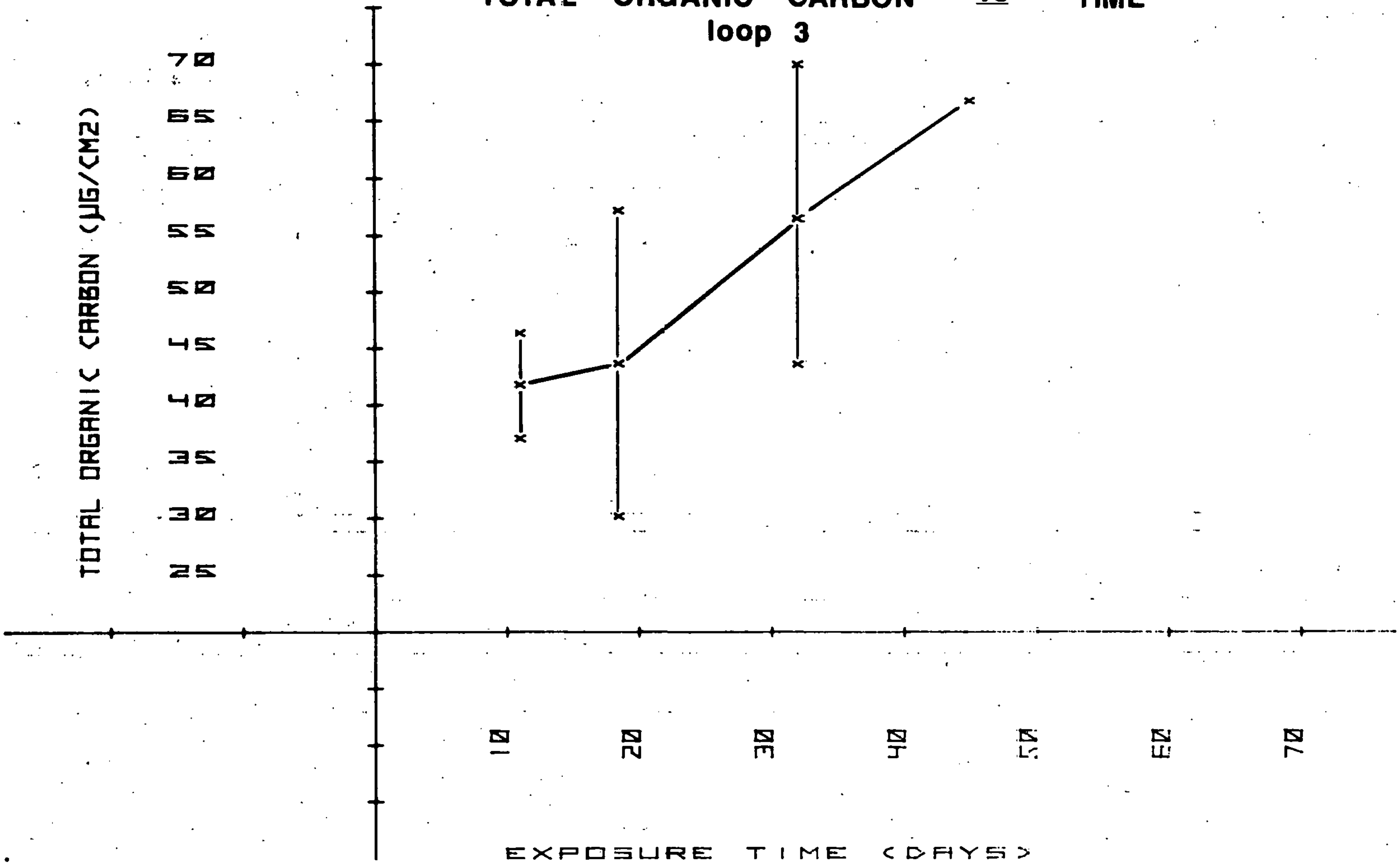

ATP VS TIME
REPLACEMENT SECTIONS
ATP (PG/CM2)
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
5-13B
5-14A
5-13A
3-SPARE
5 HTM
5-14C
3-13B
3-13A
5-SPARE
X LOOP#3
* LOOP#5
5
10
15
20
25
30
35
40
45
50
55
60
65
70
EXPOSURE TIME (DAYS)

Figure 9

TOTAL ORGANIC CARBON vs TIME
loop 3



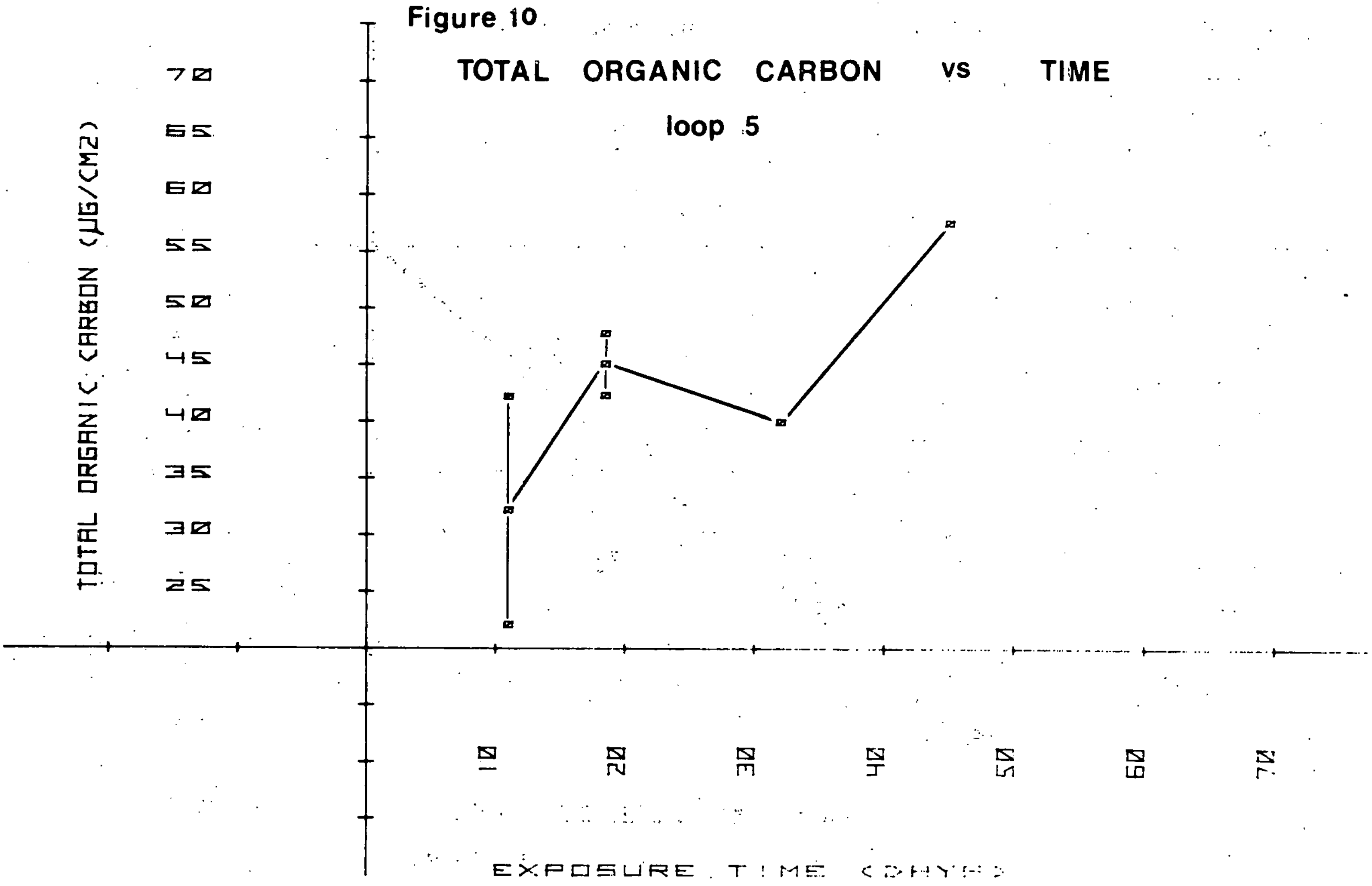


Figure 10

TOTAL ORGANIC CARBON vs TIME

loop 5

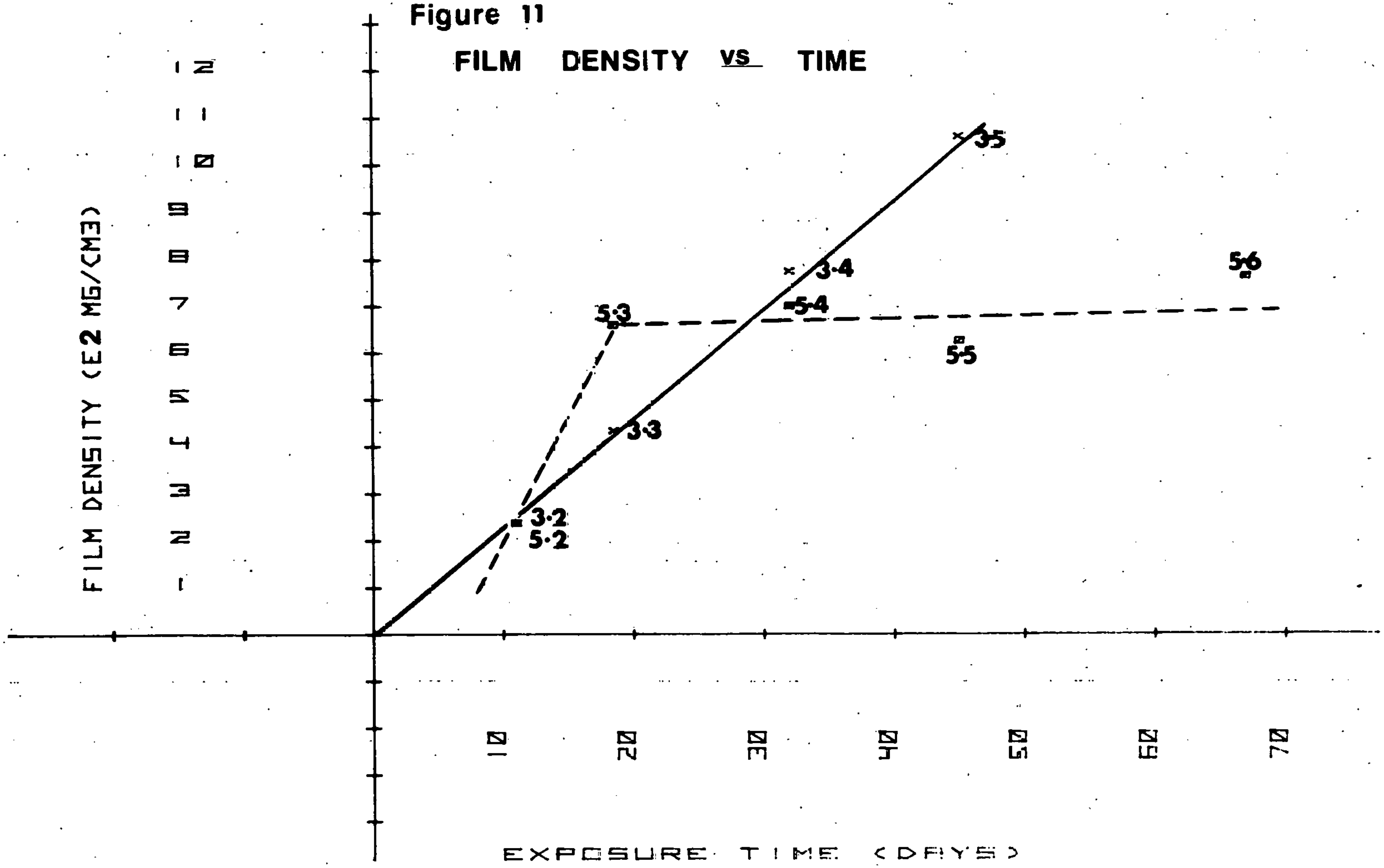
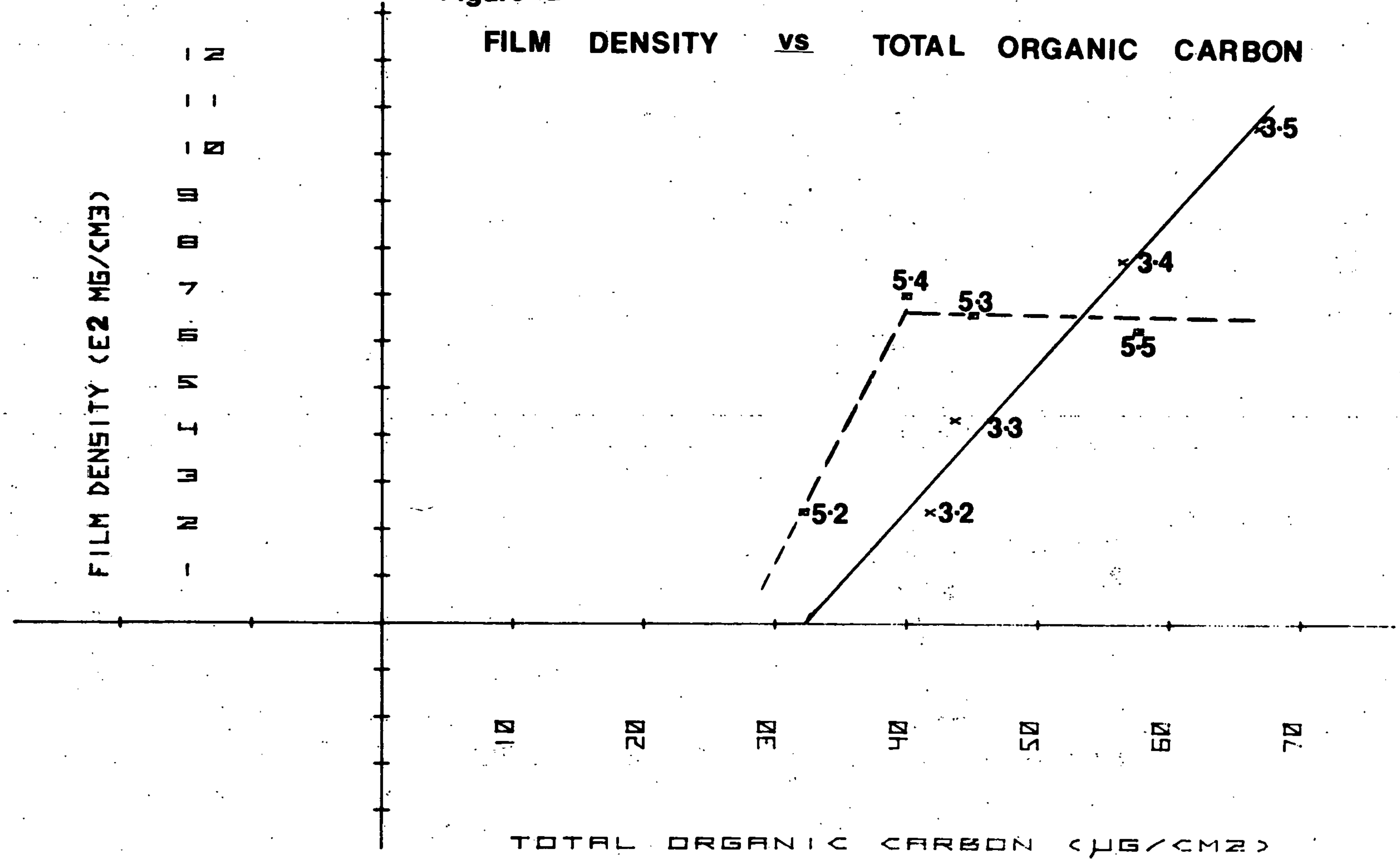


Figure 11

FILM DENSITY vs TIME

Figure 12

FILM DENSITY vs TOTAL ORGANIC CARBON



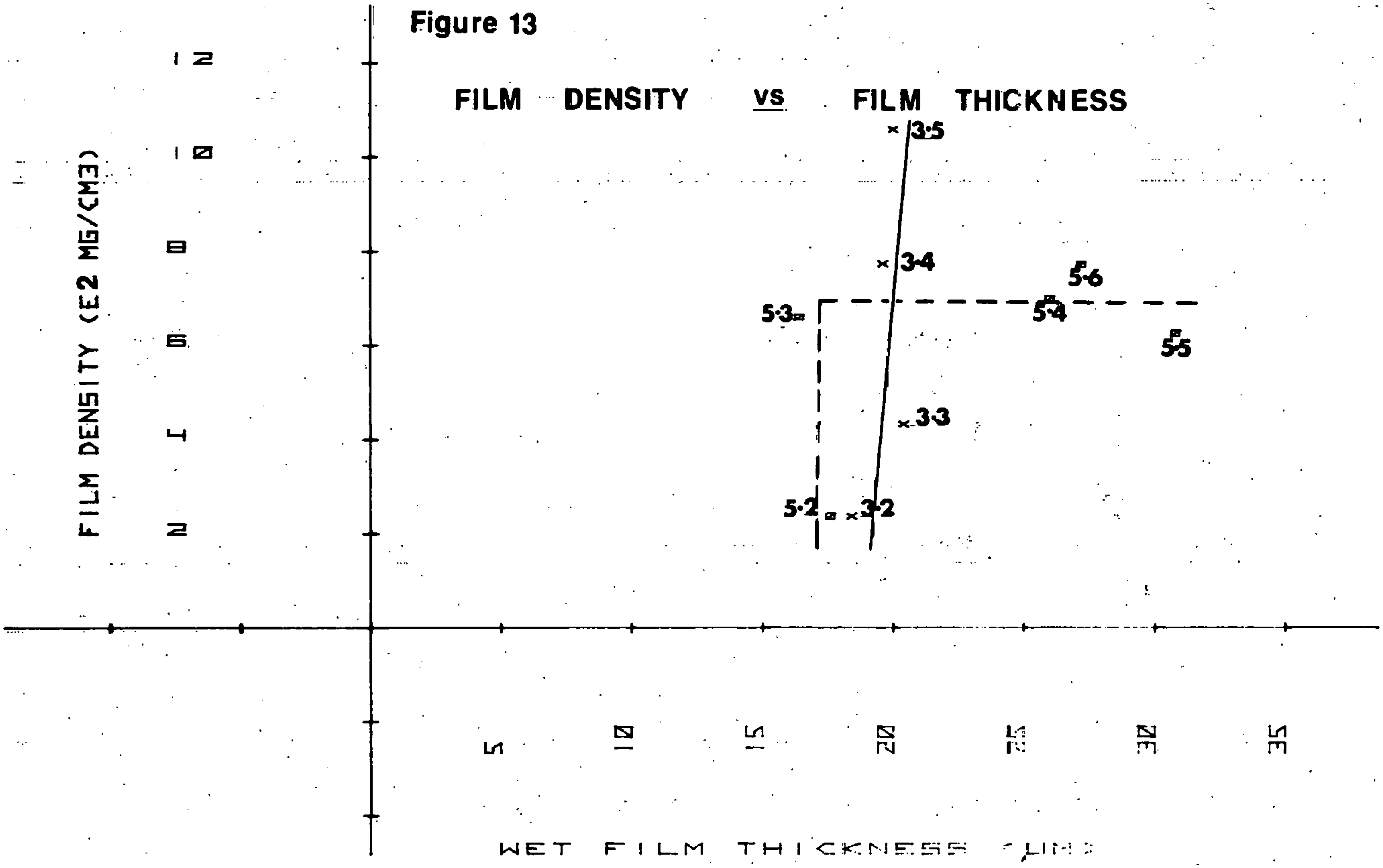


Figure 13

FILM DENSITY vs FILM THICKNESS

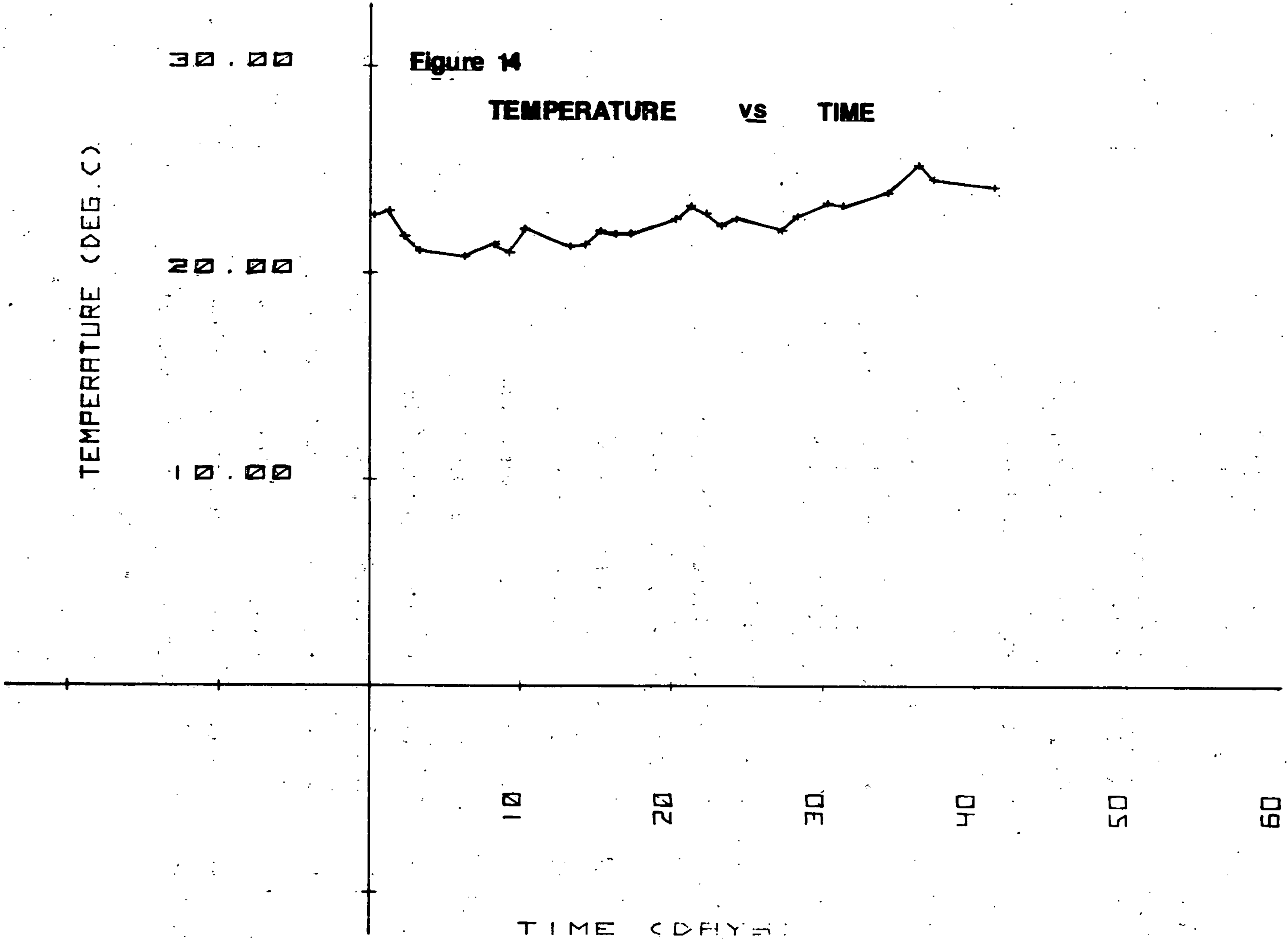


Figure 14

TEMPERATURE vs TIME

Appendix B

Plate

1 Clean 5052 Aluminum surface

Loop 3 5052 Aluminum

2 T_1 - 11 day exposure - original loop

3 T_2 - 11 day exposure - original loop

4 T_3 - 32 day exposure - original loop

5 T_3 - 15 day exposure - replacement section

6 T_3 - 15 day exposure - replacement section

7 T_3 - 15 day exposure - replacement section

Loop 5 5052 Aluminum

8 T_2 - 18.5 day exposure - original loop

9 T_3 - 32 day exposure - original loop

10 T_3 - 32 day exposure - original loop

11 T_4 - 45 day exposure - original loop

12 T_5 - 67 day exposure - original loop

13 T_5 - 67 day exposure - original loop

14 T_5 - 67 day exposure - original loop

15 T_4 - 14 day exposure - replacement section

16 T_4 - 14 day exposure - replacement section

17 T_4 - 14 day exposure - replacement section

18 T_4 - 14 day exposure - replacement section

19 T_4 - 14 day exposure - replacement section

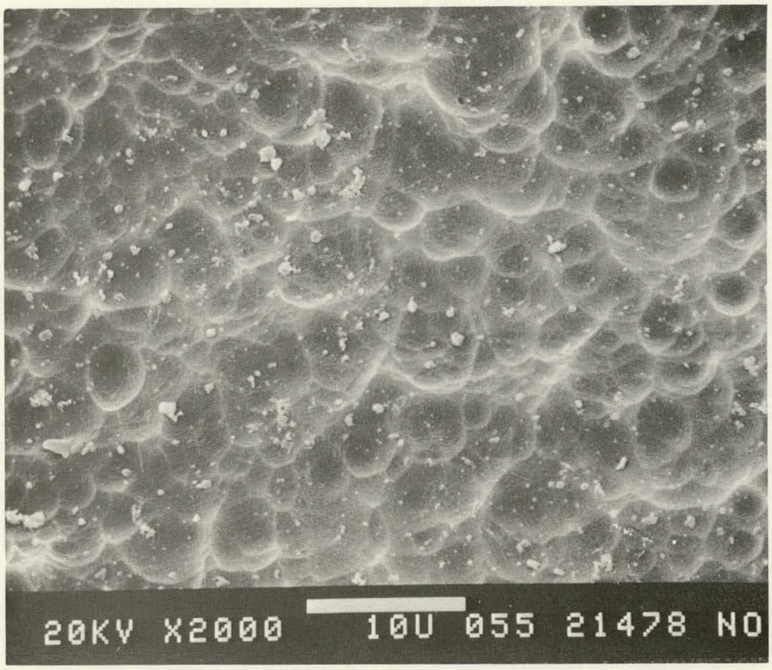


Plate 1 Magnification 2000x

Clean aluminum pipe surface. Surface is uniformly etched. Neither lubricant nor extrusion lines are apparent.

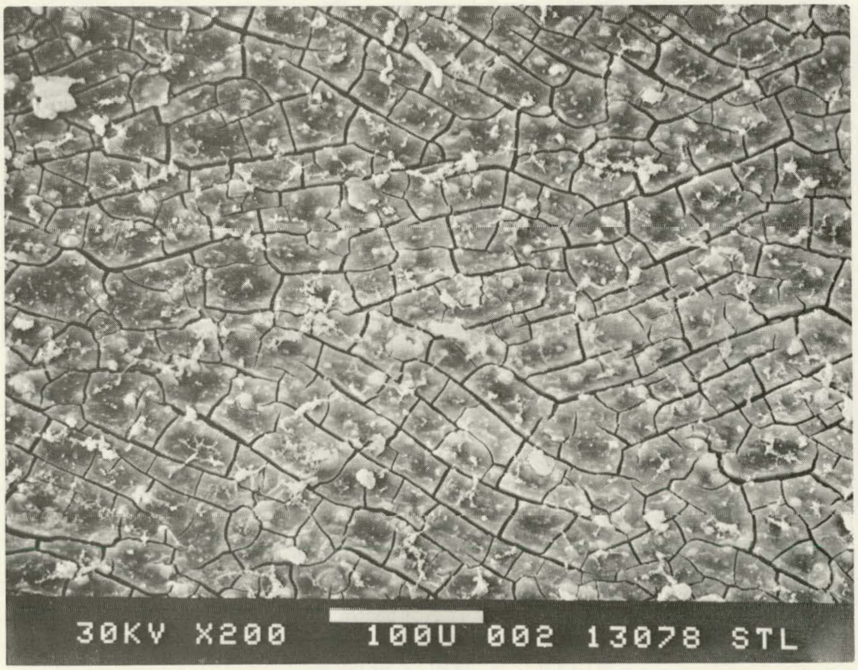


Plate 2 Magnification 200x

Aluminum pipe after 11 days exposure to flowing seawater. "Dried mud" appearance due to loss of water of hydration from gelatinous corrosion film.

Plate 3 Magnification 10000x

Aluminum pipe after 11 days exposure to flowing seawater. Dried film thickness 2.5um.

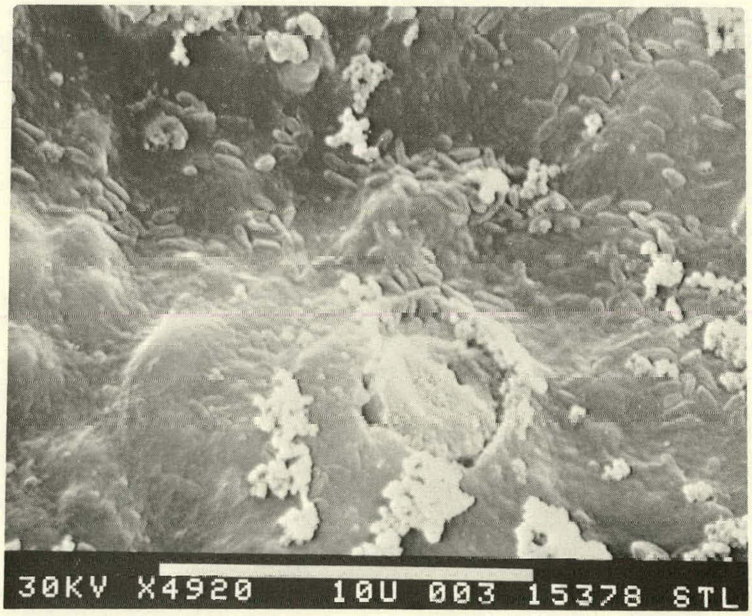


Plate 4 Magnification 4920x

Aluminum pipe after 32 days exposure to flowing seawater. Colonization of surface by short rods.

Plate 5 Magnification 20400x

Aluminum replacement section after 15 days exposure to flowing seawater. Replacement section downstream from 32 day exposure. Polymeric anchors bind cells to surface.

Plate 6 Magnification 10300x

Aluminum replacement section after 15 days exposure to flowing seawater. Replacement section downstream from 32 day exposure. Example of polymeric bridging of cells to metal surface.

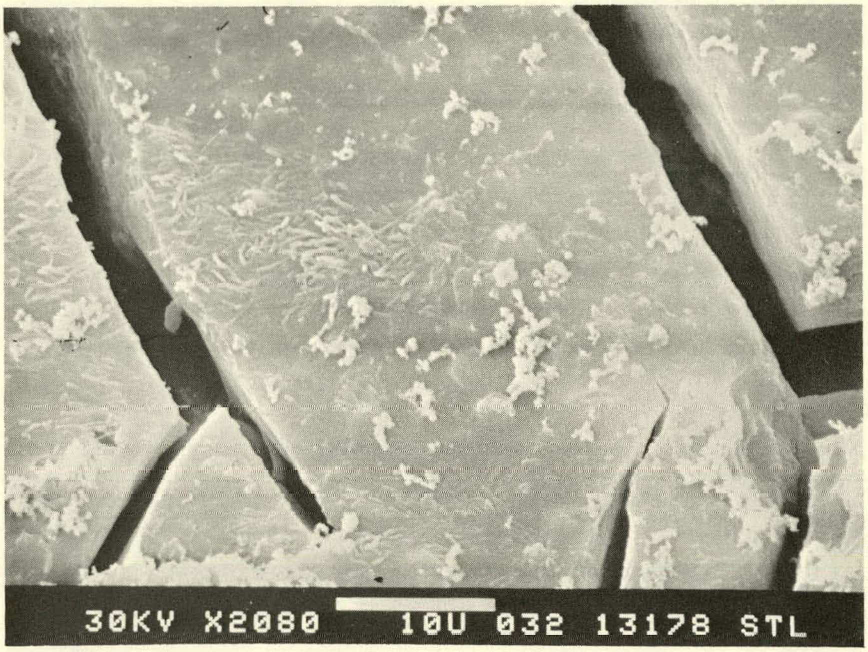


Plate 7 Magnification 2080x

Aluminum replacement section after 15 days exposure to flowing seawater. Replacement section downstream from 32 day exposure. Bacterial growth along the axis of hydraulic flow.

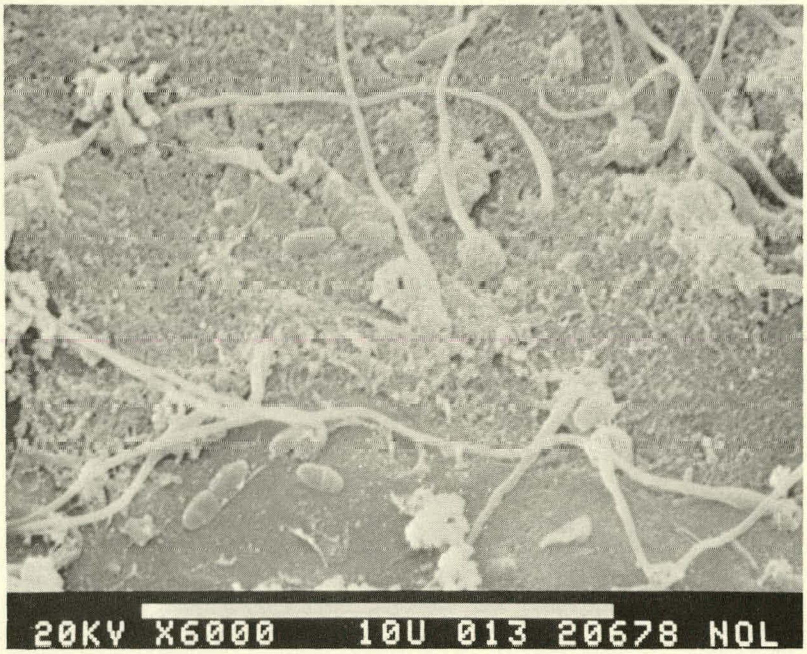


Plate 8 Magnification 6000x

Aluminum pipe after 18.5 day exposure to flowing seawater. Small rods assoicated with surface undergoing cell division. Few filamentous bacteria associated with surface.

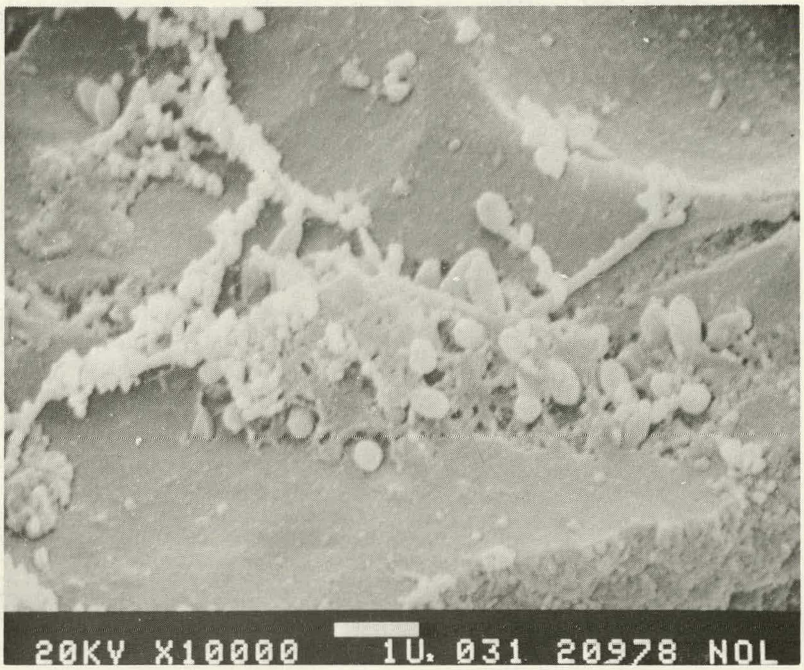


Plate 9 Magnification 10000x

Aluminum surface after 32 day exposure to flowing seawater. Short rods bound in a polymeric matrix.

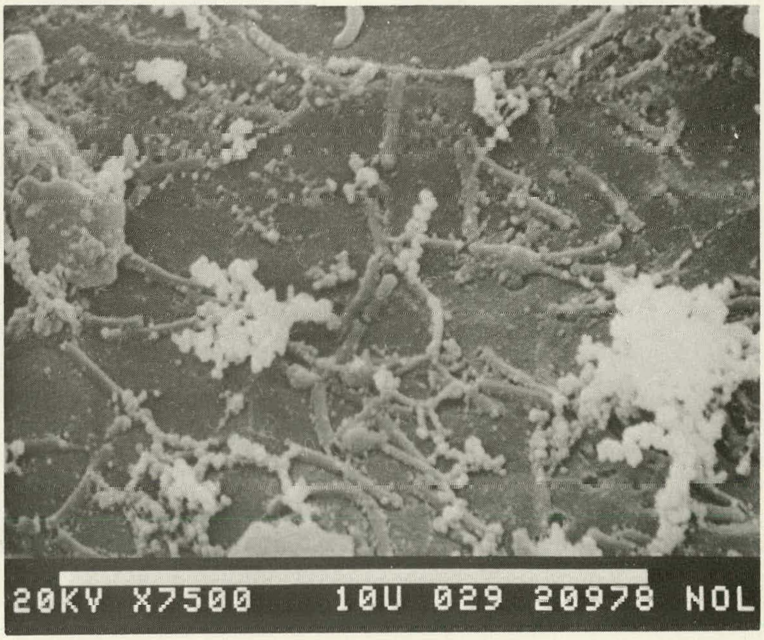


Plate 10 Magnification 7500x

Aluminum surface after 32 day exposure to flowing seawater. Long rods colonizing surface.

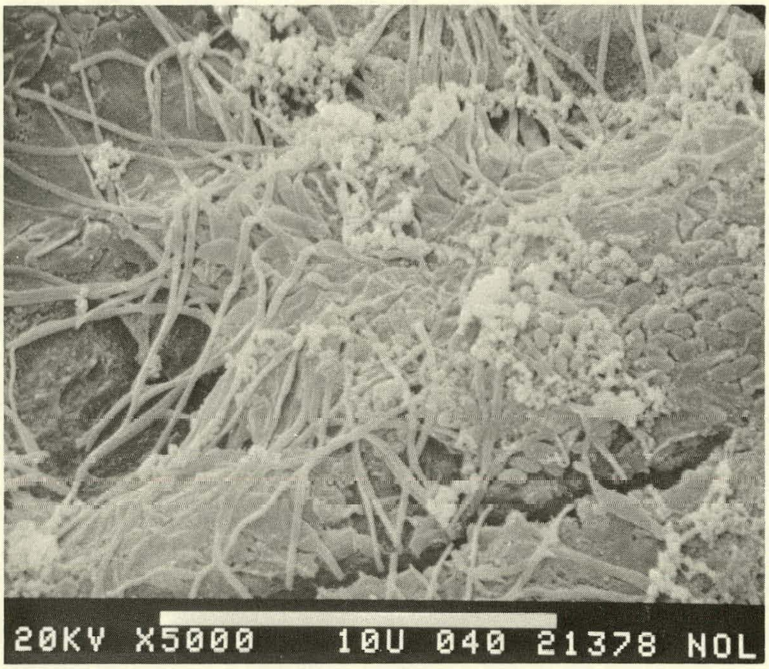


Plate 11 Magnification 5000x

Aluminum surface after 45 day exposure to flowing seawater. Filamentous bacteria colonizing surface. Filaments entwined.

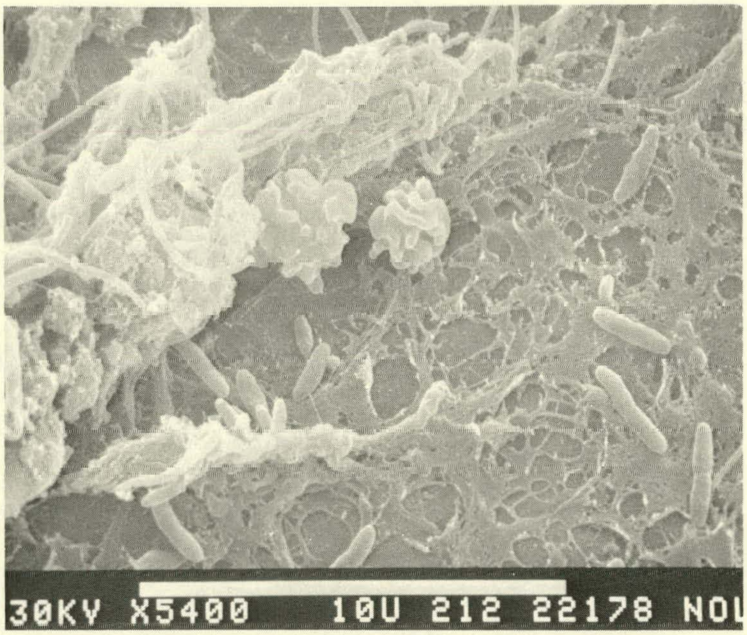


Plate 12 Magnification 5400x

Aluminum surface after 67 day exposure to flowing seawater. Flow interrupted for 20-40 hours at 45 days. Surface covered with slime layer. Rod-shaped bacteria on surface.

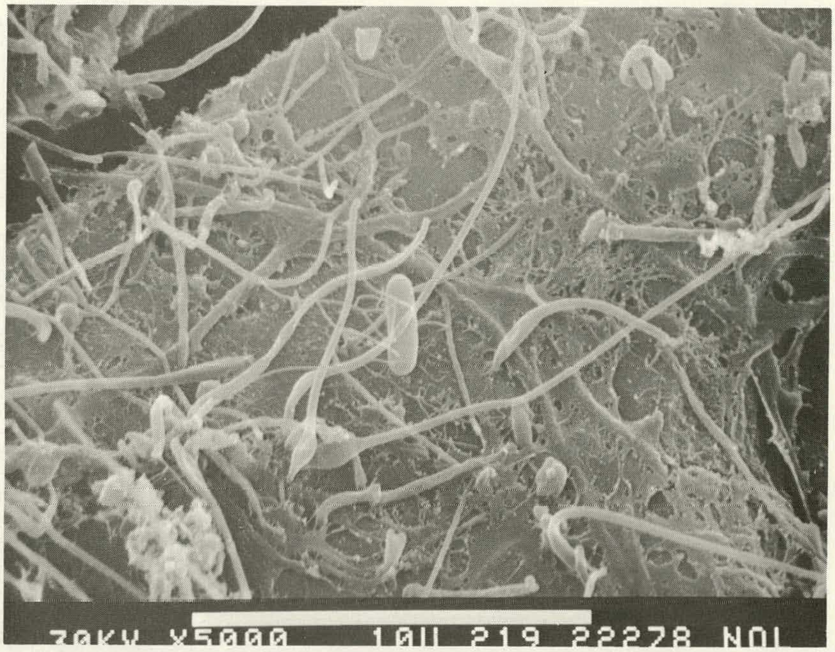


Plate 13 Magnification 5000x

Aluminum surface after 67 day exposure to flowing seawater. Flow interrupted for 20-40 hours at 45 days. Surface covered with slime layer. Filamentous bacteria attached to surface.

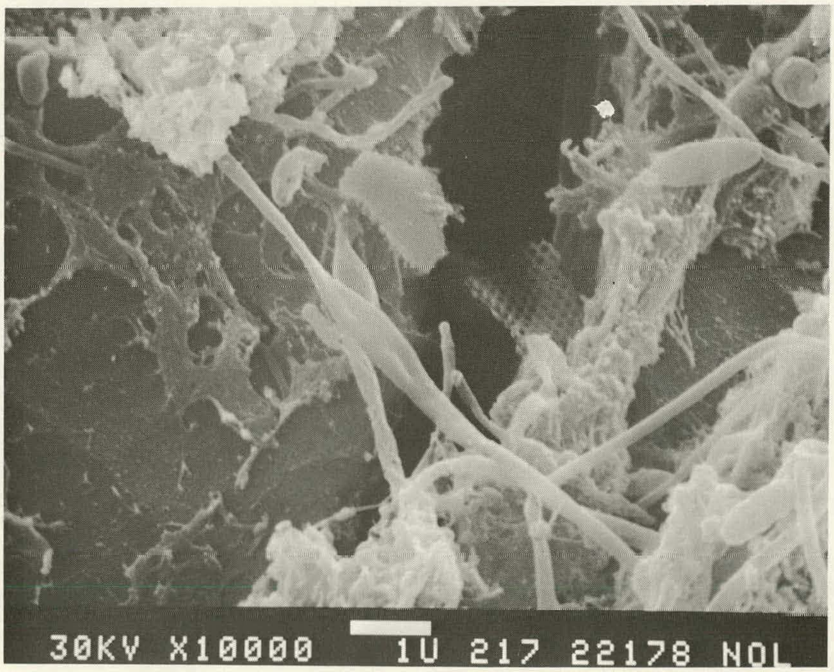


Plate 14 Magnification 10000x

Aluminum surface after 67 day exposure to flowing seawater. Flow interrupted for 20-40 hours at 45 days. Surface covered with slime film. Filamentous bacteria present. Diaton frustule fragment caught in slime.

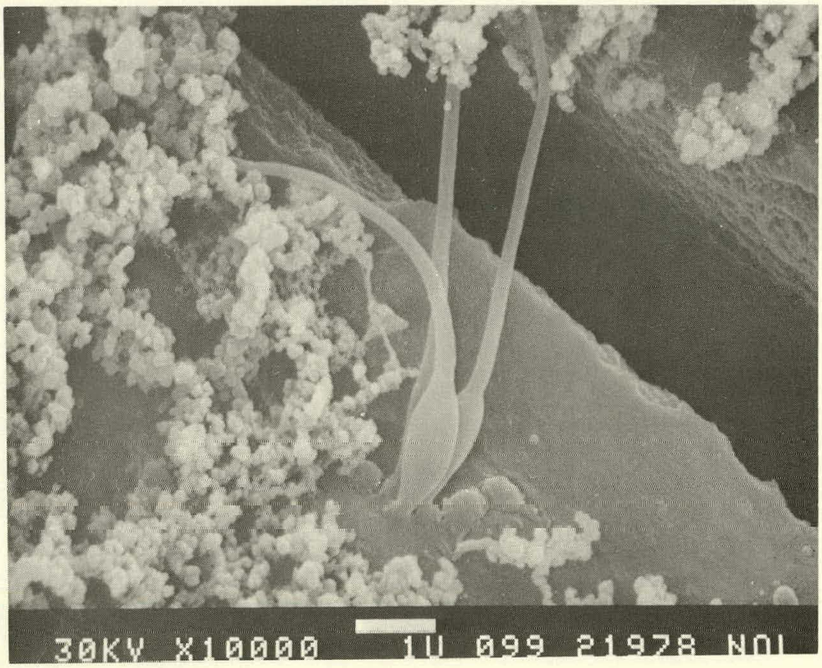


Plate 15 Magnification 10000x

Aluminum surface of replacement section exposed for 14 days of flowing seawater. Replacement section downstream from 45 day exposure. Colony of filamentous bacteria anchored to surface.

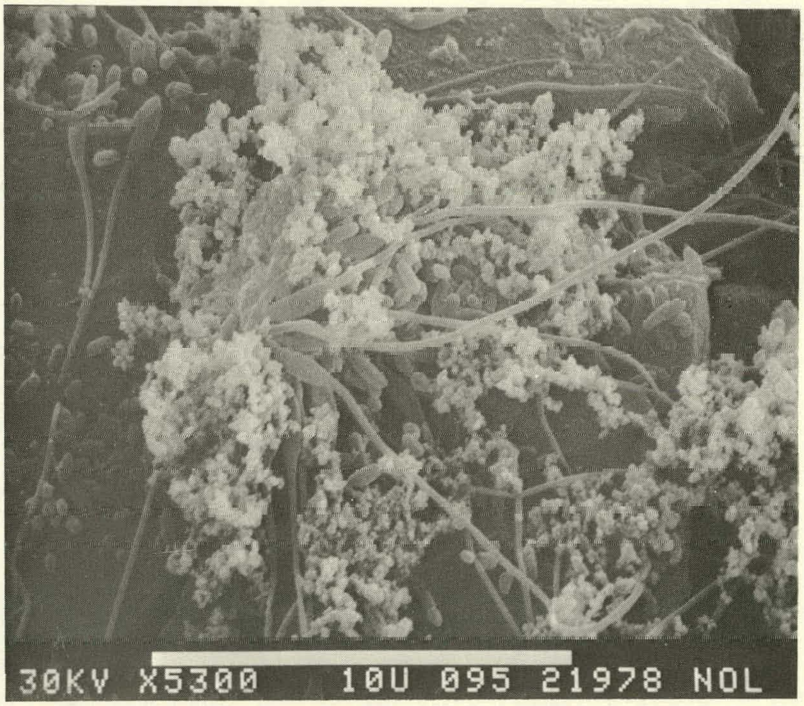


Plate 16 Magnification 5300x

Aluminum surface of replacement section exposed for 14 days to flowing seawater. Replacement section downstream from 45 day exposure. Filamentous bacteria on surface. Detrital material collected on surface.

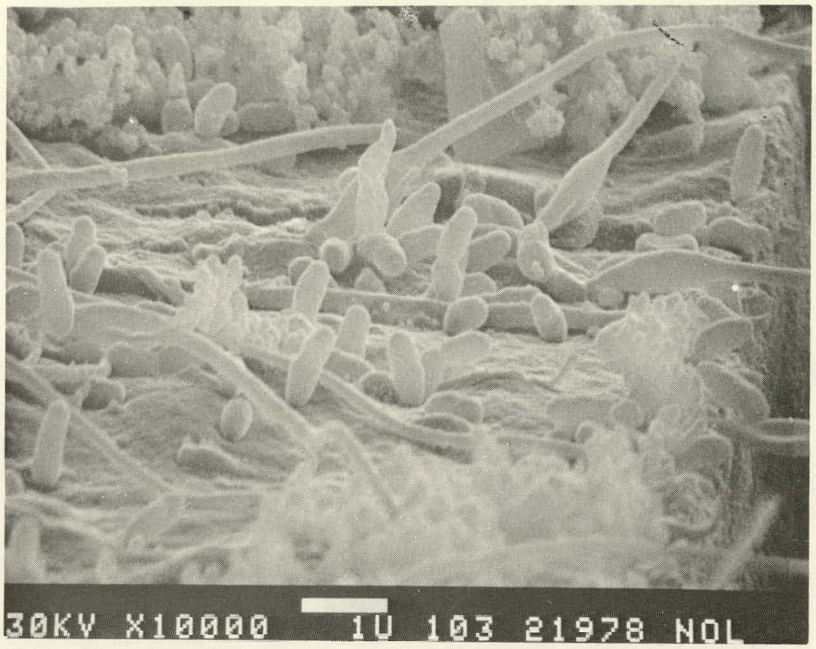


Plate 17 Magnification 10000x

Aluminum surface of replacement section exposed for 14 days to flowing seawater. Replacement section downstream from 45 day exposure. Extreme angle view.

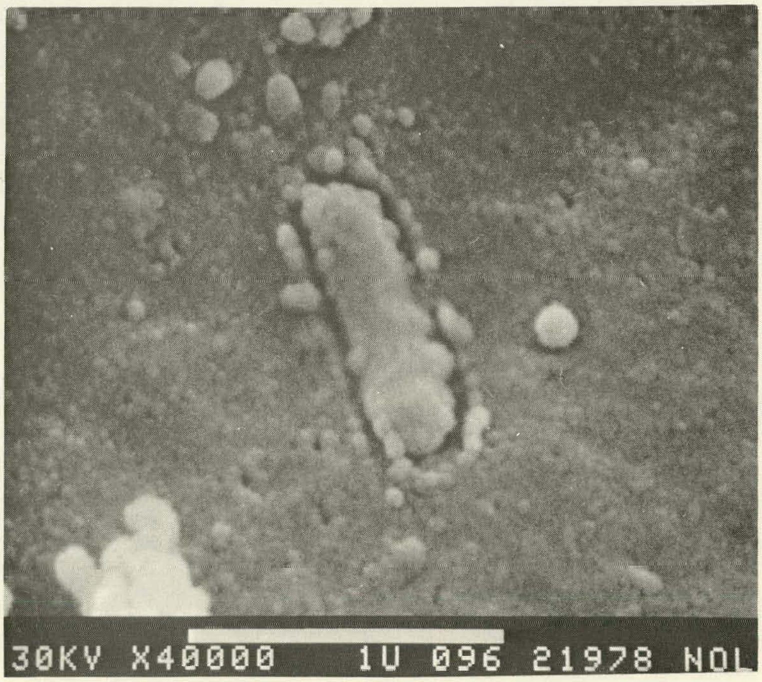


Plate 18 Magnification 40000x

Aluminum surface of replacement section exposed for 14 days to flowing seawater. Replacement section downstream from 45 day exposure. Acid-producing bacterium dissolving inorganic scale.

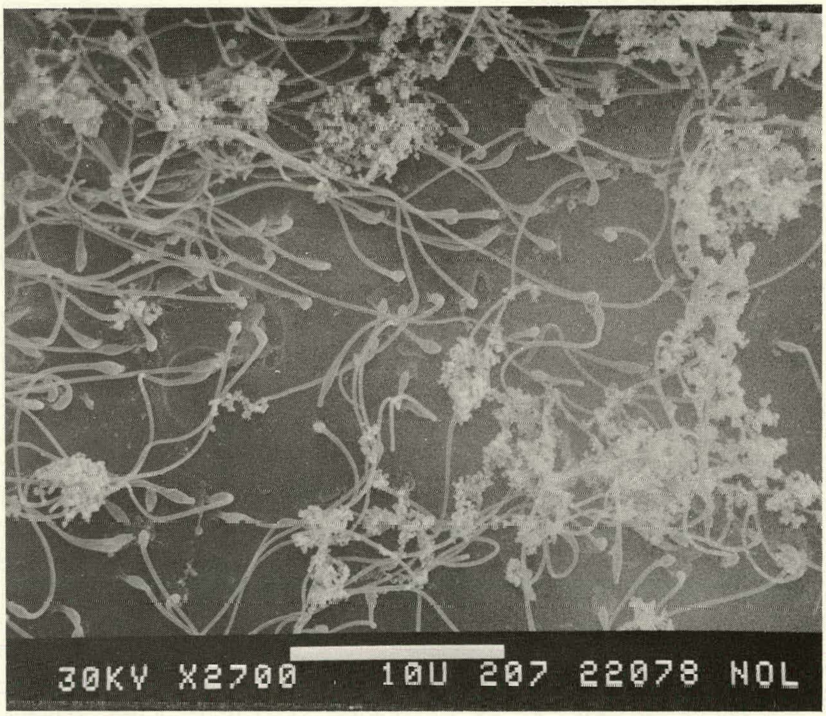


Plate 19 Magnification 2700x

Aluminum surface of replacement section exposed for 14 day to flowing seawater. Replacement section downstream from 45 day exposure. Surface colonized by filamentous bacteria. Filaments 20um long extending from the surface.

MEASUREMENT OF MICROFOULING MASS AND COMMUNITY STRUCTURE DURING SUCCESSION IN OTEC SIMULATORS - A PRELIMINARY REPORT

by

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I. INTRODUCTION

The initial task of this laboratory is to develop microassays for the biomass, physiological state and population structure of the microfouling community in the Naval Coastal Systems Center OTEC simulation system. These methods involve the measurement of biochemical parameters that characterize different components of the community or more or less specifically indicate the metabolic status of the population.

A. BACKGROUND

We are developing a relatively standardized analysis scheme to characterize the status of the microfouling community that is based on the use of biochemical "hallmarks" to identify various portions of the community.

Samples are first extracted by the Bligh and Dyer method (1-3). The aqueous phase has been shown to contain 80 to 92% of the adenosine nucleotides. These are concentrated, quantitatively converted into the fluorescent 1, ^{6}N ethylenoadenosine nucleotide derivatives, separated by high resolution liquid chromatography and determined fluorometrically. From this the energy charge, total adenosine nucleotides and the ATP/ADP ratios - measures of the physiological status - can be determined. The chloroform phase contains the lipids. These are subjected to acid methanolysis creating fatty acid methyl esters, free aldehydes, sphingamines and sterols, plus water-soluble components. The lipid soluble components are separated by one-dimensional thin layer chromatography. The hydrocarbon band at the front has not been examined. It is readily contaminated with anthropogenic products - difficult to distinguish from natural components without using ^{14}C incorporation. The next band contains the fatty acid methyl esters and fatty aldehydes. Both these components can be recovered quantitatively. Hydroxy fatty acid esters are recovered from bands below this. The steroids are found in a band below the hydroxy fatty acid esters. The sphingamines derived from the sphingolipids, ethers, and other charged non-methanolizable lipids remain at the origin.

The water soluble lipid methanolysate will be analyzed for phosphate and phosphonate. The remainder will be methylated, reduced in the presence of sodium to alditols, separated from amino-containing components on Dowex 50, both fractions peracetylated and analyzed by gas liquid chromatography. In the neutral "sugar" portion will be acetylated ethylene glycol (a measure of protozoa), glycerol (total lipid), the alditols of the sugar and inositol, The presence of lipids containing carbohydrates has great taxonomic significance in monocultures (4).

1. Fatty Acid Methyl Esters.

We have just received a state-of-the-art capillary (open tubular capillary column) automated Varian 3700 gas chromatograph, which with a 60-meter OV-101 column will give us 190,000 theoretical plates of separative power, increased sensitivity (with splitless injection) and more rapid analysis than the standard packed column. In addition to the fatty acids, the free fatty aldehydes will be in this fraction (we hydrolyze any dimethyl or monomethyl acetals formed prior to the thin layer chromatography by exposure to HCl vapor).

We have already seen on 12-meter packed columns multiple overlaps, indicating a great complexity of fatty acids and aldehydes is present. Indeed, in our previous work with monocultures, we defined no less than 64 fatty acids in Staphylococcus aureus (5).

We are particularly interested in separating and identifying positional isomers of the branched, the branched and unsaturated, and the unsaturated isomers.

Significance. Fatty acids may well prove to be the ideal measures of population structure as certain components of the microbial population are enriched in particular fatty acids.

Short (13-21 carbon) iso- and anteiso-branched fatty acids are characteristic of gram positive bacteria (6, 7) with few exceptions (8). Protozoa and fungi form significant amounts of these branched fatty acids when supplied with branched precursors in their growth milieu (9-11). Their presence correlates with the bacterial colonization of dead Spartina marsh grass (12).

Cyclopropane fatty acids in bacteria are restricted to certain lipids since they are formed from monoenoic fatty acids only when they are esterified with certain lipids (13). They are restricted to certain classes of bacteria (largely gram-negative) (6, 14), and to the kinetosomes of some protozoa (11). Terrestrial plants also contain these fatty acids. In some bacterial species the cyclopropane fatty acids accumulate in the stationary phase (15-17) or with adverse growth conditions (18), resulting in a decrease in 18-carbon mono-unsaturated fatty acids and an increase in 19-carbon cyclopropane fatty acids. With prolonged incubation this increases the proportion of branched-chain fatty acids (19).

In general the branched chain fatty acids are associated with gram-positive bacteria. Gram-negative bacteria contain higher proportions of mono-unsaturated and cyclopropane fatty acids. The exceptions seem to be Lactobacilli and Clostridia, which are gram-positive, but have fatty acid composition more like the gram-negative species (14, 15, 20).

It is possible to infer community structure from the position of the double bond in hexadecanoic monounsaturated fatty acids. The aerobic system that is widespread in bacteria (21) results in cis vaccenic acid (16:1Δ7ω9) (9).

Polyenoic fatty acids are not found in bacteria (6, 9, 14, 15). An exception is a conjugated dienoic fatty acid found in a bacterium under unnatural growth conditions (22). Certain complex blue-green algae contain 18 carbon trienoic fatty acids (9, 23-25), but no polyenoics longer than 18 carbon atoms. Polyenoics longer than 18 carbons are typical of eukaryotes, especially photosynthetic eukaryotes (9, 14). By noting the positions of the unsaturations in these fatty acids phylogenetic associations and further differentiation of the populations are possible (9, 26, 27).

In preliminary experiments we have shown that the biomass, relative dominance, number of species, species richness of animals attracted to detritus-containing baskets was not related significantly to gross measures of microbial biomass such as total extractible ATP, oxygen utilization, extractible lipid phosphate or poly-β-hydroxy butyrate at the significant level of 0.05 in regressions run between the animal parameter and the microbial parameter. These were experiments run in Apalachicola Bay for 3 months consisting of 20 samples taken after 2 and 4 weeks of incubation. However when the animal composition and biomass was related to the relative proportions of fatty acid methyl esters derived from the microflora on the detritus, the significance of the microbial population structure was readily apparent. From this study, correlation between the proportion of fatty acid methyl esters and measures of water quality, microbial biomass and the macrofaunal mass and population structure that was attracted to the detritus have been defined.

The detrital microbial population structure shows correlation between pH and 18:0 (18 carbon saturated ester), a weakly suggestive correlation between salinity and 17 cyclo and 18:0, and negative correlation between temperature, 17 cyclo and 18:0 esters. The microbial biomass and activity measured as oxygen uptake and lipid phosphate shows a strong negative correlation and a weak correlation with the proportion of 15 Br. The PHB level correlates with the 16:0 (10 carbon monoenoic ester) and weakly with 18:1 content of the population.

Most interesting is the excellent correlation between macrofaunal biomass and 17 cyclo, 16:1 and 15 Br. The 15 Br content correlates with the number of species, the Margalef richness and biomass.

The high positive correlation of 15 Br fatty acids with the number of species, the Margalef richness and biomass of the detrital macrofauna clearly shows a selectivity by these animals for areas rich in bacteria, especially gram-positive bacteria in the microflora. The strong negative correlation with the rate of oxygen utilization suggests that the 15 Br fatty acids were largely in anaerobic or facultatively anaerobic bacteria.

Cyclopropane fatty acids are restricted to certain lipids, since they are formed from monoenoic fatty acids only when they are esterified with certain lipids (13). They are restricted largely to gram-negative bacteria plus the gram-positive Clostridia and Lactobacter (6, 14), the kinetosomes of some protozoa (11) and terrestrial plants. Cyclopropane fatty acids accumulate in stationary growth phase (15-17) or with adverse growth conditions (18). The negative correlation between temperature and proportion of 17 cyclo ester may indicate a faster turnover at higher temperature with less accumulation of cyclopropane fatty acids.

Again there is an excellent positive correlation between high proportion of 17 cyclo in the microbial population and the biomass and Shannon diversity of the detritivore macrofauna.

Monounsaturated fatty acids are found in gram-negative bacteria (and the Lactobacter) and in microeukaryotes (9).

The excellent negative correlation of the proportions of 16:1 with the number of detritus-associated macrofaunal animals, coupled with the positive correlation with detrital animal biomass may reflect the presence of the fatty acid in both the prokaryotes and microeukaryotes. The positive correlation of PHB content with the proportion of 16 and 18 carbon monoenoic fatty acids may reflect the high association of PHB formation with gram negativity in the detrital bacteria.

The 18 carbon saturated fatty acid ester is found universally in microeukaryotes and prokaryotes and shows correlation not with the detrital macroflora but with the temperature, salinity and pH. This may reflect a correlation of the total microbial biomass with the physical parameters just as shown by the detrital macrofauna (see below).

In a second experiment performed by Dr. Roy Robertson at Sapelo Island, Georgia, the effects of caging snails compared with areas where they were excluded showed:

1. a decrease in lipid phosphate (decrease in microbial biomass (3, 28).

2. a great decrease in polyenoic fatty acids (a decrease in algae and nematodes - eukaryotes).

3. a relative increase in 15 branched fatty acids (an increase in bacteria).

4. a decrease in cyclopropane fatty acids - a decrease in stationary phase bacteria (they are growing faster) - which will be checked by measuring rates of DNA synthesis and rates of muramic acid turnover.

In a third set of experiments we have shifted detritus (Teflon strips incubated in the estuary) from a fungus "heaven" (pH 5.5, enriched with sucrose, nutrient broth and antibiotics, penicillin and streptomycin) to "hell" (pH 7.8, plus cyclohexamide, glutamine and sodium phosphate). There are clear differences in morphology by scanning electron microscopy - filamentous organisms in "heaven", bacteria-looking organisms in "hell". The incorporation of thymidine relative to uridine with DNA is much lower in "hell" than "heaven", as expected from the lack of salvage pathways in fungi. The steroids are greater in "heaven" as are the polyenoic fatty acids, the proportion of phosphatidyl serine, the carbohydrate diglycerides, the phosphatidyl inositol and triglyceride and the sphingolipids. When coupled with the steroid analysis (see below) these patterns should be very helpful in the analysis of population structure.

In a similar type of experiment the effect of adding nutrients to the detrital microflora showed an increase in biomass (ATP increased 20-fold; lipid phosphate 20-fold; DNA synthesis 3-fold; oxygen utilization, 20-fold). With a decrease in the phosphatidyl serine to phosphatidyl glycerol ratio, a 10-fold increase in 15 branched, 17 and 19 cyclopropane fatty acids (indicating a great increase in bacteria paralleled by the muramic acid increase) but a 2-4-fold increase in 16:1, 18:1, 18:2, 20:4 and 20:5, and a 4-fold increase in phosphatidyl inositol indicating an increase in eukaryotes. The steroids have not been analyzed as yet. These data appear to be compatible with the scanning electron microscopy morphologic changes.

In experiments performed in collaboration with Dr. Jean Nickels at Sapelo Island, the presence and activity of nematodes in the mud is correlated with increases in steroids and certain polyenoic fatty acids that correspond to those found in the isolated worms. We hope by following the structures of the polyenoic fatty acids and using isotopes we can determine the extent of the synthesis or modification of polyenoic fatty acids by nematodes, and then use them to help define their food sources. The steroids will also be useful in this regard. With the ability to separate the isomers of the unsaturated fatty acids by capillary gas chromatography, as well as the structural definition by the electron impact -produced fragmentation pattern of the mass spectrum, we can more readily define the details of the population structure. For example, the oomycetes contain both the alpha and gamma linolenic derivatives. Omega 3 (20:5, 22:6) and omega 6 (18:3, 20:4); Chyridomycetes contain omega 3 (18:3, 18:4, 20:5), and omega 6 (18:3, 20:4); the zygomycetes contain only omega 6 (18:3, 20:4), the Basidiomycetes ascomycetes omega 3 (18:3) and the yeasts omega 3 (18:3) (9).

2. Fatty Aldehydes

Fatty aldehydes are derived from the plasmalogens by mild acid hydrolysis. Plasmalogens are found in specific parts of eukaryotes and in anaerobic bacteria, specifically Clostridia, Bacteroides, Propionibacterium, Selenomonas, Peptostreptococcus, Desulphovibrio (29, 30). They are found rarely in plants (31), fish amd mollusks (32, 33).

Significance. We have shown an excellent correlation between the presence of the acid labile plasmalogen bond and the recovery of long-chain fatty aldehydes in sediments, and the striking finding that the anaerobes are concentrated in micronotches in the aerobic portion of the sediment! We would expect to show high concentrations of cis vaccenic acid (18:1Δ11) made by the anaerobic pathway involving β-hydroxy decanoyl-S-ACP rather than the 18:1Δ9 oleic acid formed by eukaryotic and microbial aerobic pathways.

3. Hydroxy fatty acids.

In microbes, hydroxy fatty acids are found in the lipids of a few microbes, Arthrobacter(34), Rhodomicrobium (35, 36), Pseudomonas (37), as well as Nocardias (38).

As described above, β-hydroxy fatty acids are found in the lipid extracted residue after acid hydrolysis where they are covalently bound to the lipopolysaccharide (39, 40). β-hydroxy fatty acids are found in the hydrolized residues of detritus extracted of its lipids. In these experiments hydroxy fatty acids are extracted from acid hydrolysate of the residue after lipid extraction. The fatty acids are extracted in chloroform, transferred to saturated sodium bicarbonate, methylated, separated from other lipids on thin layer plates, recovered and defined by the changes in their retention volume before and after reaction with trifluoroacetic anhydride. Their structure can be readily proved by GC/MS.

4. Steroids.

Fungal steroids are well-suited for defining the population of a detrital or sedimentary sample. The steroids of fungi can be complex and in some cases specific. Their destruction has been tabulated conveniently in recent reviews (41-43).

Significance We have established that the thin layer method of separating the acid methanolysis of the lipid extract yields steroids at 0.2-0.3 and that cholesterol can be quantitatively recovered. As expected, when the detrital microflora are incubated under conditions promoting fungal growth the proportion of steroids increases relative to the phospholipids.

We have been able to separate trimethyl silinated ergosterol and cholesterol using SP-1200, which is probably too polar to use as a capillary column combined with MS. Support coated open tubular columns (SCOT) (44) or long capillary columns with OV-101 (our fatty acid column) readily separate steroids (45) and give excellent EI-MS.

In collaboration with Randle Hicks, a doctoral graduate student in the Institute of Ecology at the University of Georgia, we are examining the lipid composition of morphologically definable dominant estuarine fungi grown under conditions to mimic the natural environment. We are examining two presently, Alternaria maritima and what he has identified as Dendryphiella salina, which are major fungi on dead Spartina at Sapelo Island. We will look for unique lipids and then see if we can detect them in nature.

In experiments in collaboration with Dr. Jean Nickels at Sapelo, we have shown in preliminary experiments that the nematode content correlates with the cholesterol recovered from muds.

5. Sphingamines.

Acid methanolysis of the lipids remaining on the origin of the thin layer plates contain the aliphatic amines - the sphingosine base - derived from the sphingolipids. These are found primarily in eukaryotes with the C_{17} sphingosine and dehydrosphingosine; the phytosphingosines C_{20} sphingosine are found in macroplants, protozoa, yeasts, fungi and mammals (46).

Unsaturated sphingosines and branched sphingosine have been detected in scorpions, oysters and their structure characterized by GC/MS (47, 48). The determination of the double bonds required osmium tetroxide treatment of the N-acetylated sphingamine, then trimethyl silation before GC/MS.

Significance. Sphingolipids are exceedingly rare in bacteria, but they have been detected in anaerobic gram-negative spore formers and defined as C_{18},

C_{16}, and C_{19} branched derivatives by GC/MS in work we did with monocultures of Bacteriodes melaninogenicus (49). We have not had an opportunity to examine the environmental samples as yet.

6. Lipid Carbohydrates, Amino Acids and Glycerol.

We will acetylate the water phase from the acid methanolysis of the lipid and use gas-liquid chromatography to assay the acetylated glycerol and ethylene glycol to measure the total glycerol lipid (the glycerol to lipid phosphorous ratio should be high in organisms with high triglycerides - the eukaryotes) and the proportion of ethylene glycol-containing lipids which are a measure of some protozoa.

Significance. Certain lipids contain carbohydrates and amino acids. In preliminary work we have detected seven alditols of neutral sugars after methanolic hydrolysis, reduction with sodium, separation of amino sugars and amino acids on microcolumns of Dowex 50, acetylation, then chromatography on SP-2230. We have shown changes in the lipid carbohydrate composition with depth in the sediment. We are presently establishing which lipid-derived sugars contain ^{14}C from detritus and the verification of their structures by GC/MS would be very helpful in defining the population structure.

Amino sugars, particularly glucosamine, have been detected in microbial (Bacilli and Pseudomonas) phospholipids (6, 50), the lipoamino acids (primarily alanine, lysine, ornithine) have been found in Clostridia, and gram-positive organisms (9, 51). These are amino acid esters of phosphatidyl glycerol.

The amino sugars and amino acids after the Na^+ reduction would be amino alcohols which after acetylation are separable by GC. The GC/MS would be very helpful in their identification. The phospholipids on acid methanolysis will yield di-, mono- and ethanolamine which we have separated on GLC (52). We have not been able as yet to derivitize choline, so it is easily run on GC.

II. EXPERIMENTAL PROCEDURE

A. RESULTS

1. Methods Development.

The following reports our initial experience in the development of the methodology:

a. Alkaline Phosphatase. The assay of alkaline phosphatase has been shown to give excellent correspondence to the extractible ATP, respiratory activity and the rate of incorporation of $H_3{}^{32}PO_4$ into the phospholipids of the detrital microflora, all of which measure parameters related to the microbial biomass (53). The release of this enzyme from its periplasmic localization in many bacteria is facilitated by damage to the cell wall - membrane complex - as exemplified by the marked increase in activity of the fouling community after exposure to ultrasonic vibration. Consequently it was felt it might be a useful assay. The enzyme is inducible but synthesis is not repressed at phosphate concentrations in the water column of less than $1 \times 10^{-5}M$ in our experiments.

The initial experiments in the current series involved determination of the kinetics, reproducibility and effects of freezing of a microfouling community on the alkaline phosphatase activity. Freezing, and return to the laboratory for assay, under conditions where the temperature and mixing can be more carefully controlled than in experiments performed at the site, results in significant decreases in the standard deviation of the measure (Table 1). Freezing has no significant effect on the mean value of alkaline phosphatase activity if incubation is longer than 20 minutes (Fig. 1).

b. Assay of Adenine Nucleotides. Because of the difficulties of extracting ATP reproducibly with acid from metallic surfaces, the problems of inhibition of the enzyme luciferase by metallic ions, and the inability to easily measure AMP, cyclic AMP and ADP, from the limited samples available in a cleaned OTEC simulator tube, we have devoted a major effort into developing methods and instrumentation to detect these nucleotides without using the luciferase system. The method involves solvent extraction, derivatization and chromatographic separation.

A procedure which quantitatively converts the three nucleotides AMP (as well as cyclic AMP), ADP and ATP into 1-^{6}N ethenoadenosine nucleotides has been developed. The reactions are complete in 2 hours at 60°C and the yield is quantitative (Fig. 2). The derivatives have excellent fluorescent properties with maximal excitation at 280 nm and emission at 410 nm (Fig. 3). A gradient system using high pressure liquid chromatography and a Whatman pellicular SAX ion exchange column readily separates the nucleotides in a system that can be automated.

Our fluorescence detector is still not optimal (the ultraviolet source needs redesigning and the proper emission filters are back-ordered), but we can easily detect 10^{-7} g of adenosine nucleotides. With the fluorochrome detector requested in the application for continuation, we should be in the 10^{-9} or 10^{-10} range, which is adequate for all OTEC samples.

The fact that we have eliminated the problem of inhibition of luciferase enzyme system lets us modify the extraction system. We can use the remarkable power of lipid solvents to liberate ATP. At the present state we can recover 92% of added ATP from muds.

Preliminary analysis of aluminum pipe exposed as described in Table 1 shows essentially no difference between fresh or frozen samples to compare with other OTEC samples the total adenosine nucleotides were 14.2 ± 1.9 x 10^{-9}g (fresh) and 13.96 ± 1.5 x 10^{-9}g (frozen) per cm^2 of fouled surface.

c. Lipid Analysis. An initial requirement for extraction and subsequent analysis of the lipid composition of the microfouling community was the development of a closure that formed a chloroform-tight seal at each end of the pipe section. John Highsmith of the Florida State University Biological Science instrument shop designed a stainless steel core that is pulled against a Teflon ring by a screw that effectively seals the pipes. The only requirement is that the ends be deburred after cutting and that the tube not be far from round. We now can extract the lipids and use the water phase of the extract for the adenosine nucleotide measurements reported in Table 2. The lipid analysis is not completed at the time of this report. However the methodology is developing well. The overall scheme is diagrammed in Fig. 4.

The water phase from the acid methanolysis contains water-soluble portions of the lipids. Phosphates and phosphonates are readily determined after digestion (3). Glycerol and ethylene glycol are readily determined after acetylation and separation by gas liquid chromatography (Fig. 5). More complex carbohydrates are methylated, reduced to alditols in the presence of sodium, separated from the amino sugars and acids on Dowex 50 microcolumns, peracetylated and analyzed by gas liquid chromatography. The separation of the neutral carbohydrates from a detrital sample (from a polyethylene surface) is illustrated in Fig. 6. The amino sugars and acids (reduced now to amino alcohols) are readily separated and detected by GLC.

The lipid soluble portion of the acid methanolysis is first fractionated by thin layer chromatography. We have established that recovery of authentic methyl esters of fatty acids 16:0, 16:1, 18:0, 18:1, 18:2, 18:3, 20:5 and stearaldehyde, from the uppermost fraction, 7-hydroxy methyl stearate, from the next highest, and cholesterol from the lowest is quantitative with packed columns. The reproducibility of separation of fatty acid methyl esters shows errors of less than 10% in the proportion (54). With our new GLC with capillary column with the increase in theoretical plates from 3,000 to 190,000, the increased sensitivity of the new detectors with subsequent improved resolution, and the use of the autosampler requested in the ongoing budget for reproducibility and automation, the accuracy should be substantially increased to the level necessary for sampling OTEC pipes.

2. Analysis of Microfouling Succession.

The first 8-week cycle of sampling from the Naval Coastal Systems Center OTEC site has been completed and the analysis partially completed. Both aluminum and titanium pipes were utilized. Analytical data are summarized in Table 3.

The total organic carbon shows variability, but that the initial build-up is slower on the titanium surface. These pipes were originally cleaned with acid. The ATP analysis by the acid extraction - luciferin method (OTEC standard) shows variability that does not always parallel the total organic carbon.

Analysis of the scanning electron microscopic morphology shows a number of interesting features:

a) build-up can be seen in low power views in the first two weeks to high levels in both the aluminum and titanium pipes;

b) the population after one week has a diverse morphology, suggesting the presence of both eukaryotes and prokaryotes, which should yield interesting lipid analysis.

c) aluminum as early as one week shows fissuring and corrosion. These pipes were acid treated before the start of the experiment. Titanium shows no fissuring. In the experiment running currently, the pipes were not acid-washed.

B. PLANS FOR CONTINUATION

With delivery of equipment and the development of analytical methods, the analysis of the community structure can begin in earnest. These experiments in succession can be repeated as controls to test cleaning effectiveness. We plan to continue development and application of these methods to study effects of chlorination, Amertap, and M.A.N. brushing cleaning systems in the hope of developing biological prediction effectiveness, i.e., if the population structure and physiological status are altered in any way the rate of fouling or the cleaning frequency for effective heat transfer could be predicted. Questions we hope to address in Tallahassee in the next year are:

Does repeated cleaning result in a selection of a resistant population? A typical experimental design is set up as diagrammed in Fig. 7. Do different cleaning methods select for different populations? This will then be correlated with heat transfer data in our cooperative efforts with NCSC.

As it stands in our preliminary investigation, the best correlation between a measure of the biological fouling community activity and the R_f has been the total organic carbon, but not with measures of living biomass such as ATP. This suggests that it is the polymers excreted by the microflora that are critical. We will attempt to measure the ratio of polymer to viable cell mass and try to induce polymer formation with stress so we can see what carbohydrates might be developed into a reasonable measure.

C. RECOMMENDATIONS FOR FUTURE WORK.

This work should be coordinated with a physical method of measuring the fouling thickness, preferably while the system is running.

D. CONCLUSIONS AND RECOMMENDATIONS.

It looks as if freezing pipes immediately after removal from the stream is not prejudicial to the ATP analysis and may be helpful to the alkaline phosphatase. The effect on lipid composition remains to be examined.

Clearly titanium is much less rapidly fouled than aluminum and shows no evidence of corrosion in six weeks in our single completed study.

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TABLE 1

ALKALINE PHOSPHATASE ACTIVITIES OF THE MICROFOULING COMMUNITY AFTER EXPOSURE FOR 3 WEEKS TO SEA WATER FLOWING AT A RATE OF 30 LITERS/h. 22-24°C, IN 1" INTERNAL DIAMETER ALUMINUM PIPES AT THE FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLORIDA IN NOVEMBER - DECEMBER 1978.

Time Minutes[a]	Fresh	Frozen
	µmoles PNP/1" pipe section	
0	11.9 ± 0.46	15.5 ± 0.50
10	21.5 ± 4.11	15.1 ± 3.1
20	35.8 ± 2.7	27.8 ± 2.7
30	38.9 ± 7.1	39.4 ± 4.7
40	53.9 ± 8.2	49.7 ± 5.5
50	66.2 ±17.5	60.0 ± 8.9
60	67.7 ±14.2	66.4 ± 5.3

[a] 3 replicates measured at the incubation times indicated (30 min represents 10 samples) of samples measured immediately after removal from the sea water stream (fresh) or after being held for 3 weeks at -20°C. Incubations were at 30°C.

TABLE 2

THE EFFECT OF FREEZING ON THE RECOVERY OF TOTAL ADENOSINE NUCLEOTIDES FROM 10" ALUMINUM PIPE SECTIONS BY CHLOROFORM METHANOL EXTRACTION, FLUORESCENT DERIVATIZATION, CHROMATOGRAPHIC SEPARATION AND FLUORESCENT DETECTION. CONDITIONS WERE THOSE DESCRIBED IN TABLE 1.

Fresh	Frozen
22.8	24.9
22.3	25.8
22.4	27.0
26.5	20.1
30.2	24.4
-	21.5
24.4 ± 3.3	23.97 ± 2.64

TABLE 3

ANALYTICAL DATA FROM THE 8-WEEK MICROFOULING SUCCESSION EXPERIMENT AT NAVAL COASTAL SYSTEMS CENTER, OCTOBER - NOVEMBER 1978

Week	Total organic carbon mg/cm^2				Alkaline phosphatase µmoles PNP/cm^2				ATP (Acid extract - Luciferin) g x 10^{-9}/cm^2			
	Al		Ti		Al		Ti		Al		Ti	
1	1.3	5.0	0.41	0.1	2.44	2.62	2.19	0.25				
2	3.1	3.4	1.6	1.3	2.63	2.63	0.69	0.87				
3	3.6	4.2	3.3	3.8	1.45	2.42	0.78	0.57				
4	1.1	3.4	4.2	4.5	0.83	-	1.10	1.44				
5	6.8	5.2	7.0	8.4	2.22	2.47	1.91	1.29	5.9	5.9	6.7	6.5
6	4.9	2.9	10.0	8.0	2.36	2.56	2.88	3.94	-	39.6	33	3.4
7	7.5	7.2	14.2	13.5	2.52	2.09	2.54	2.25	220	117	158	71
8	9.0	5.1	5.5	2.6	3.07	2.47	2.74	2.32	194	107	110	106
Control	0.04		0.05		-		-		0.0004		0.0005	

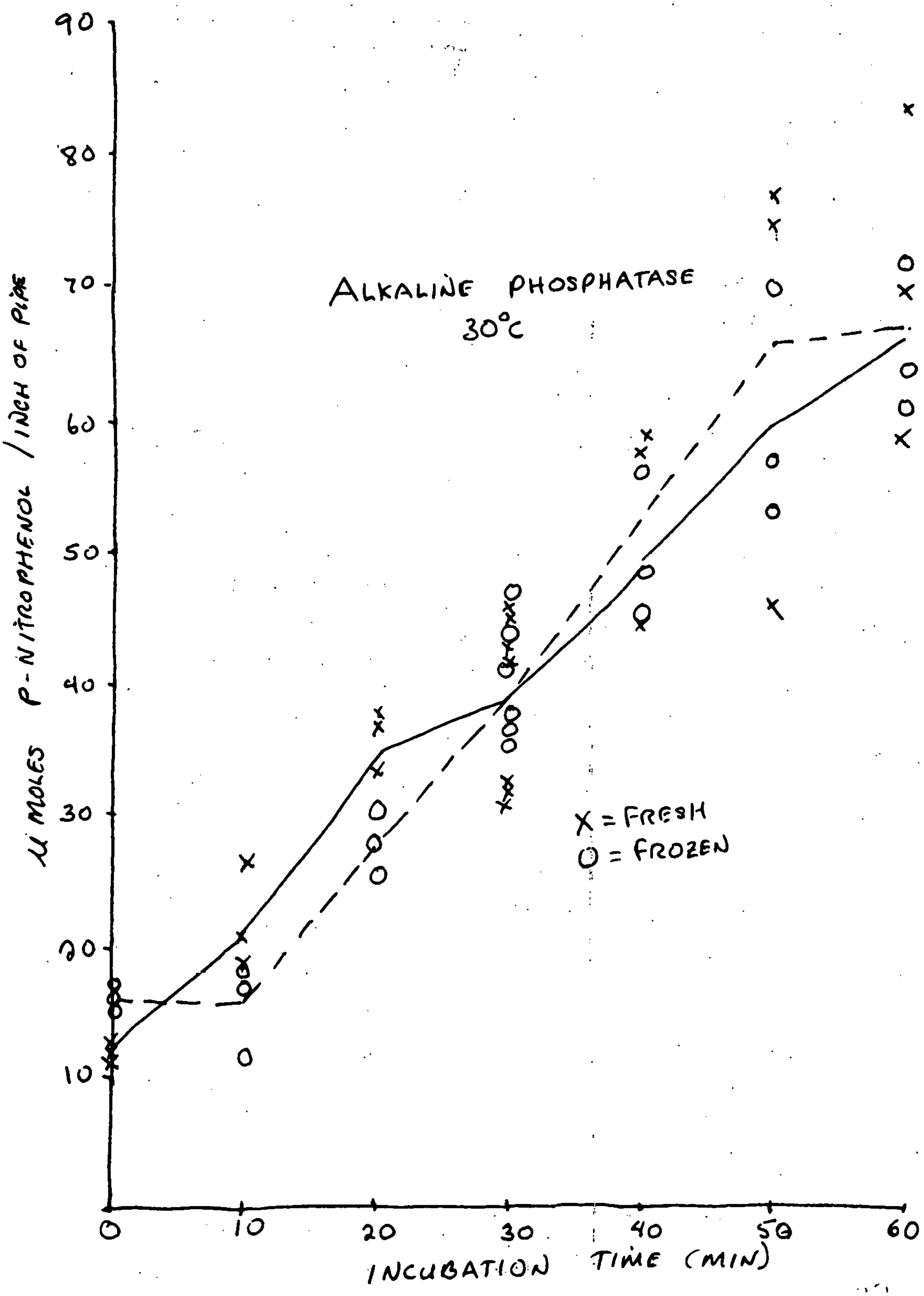

Fig. 1. Effect of freezing on the alkaline phosphatase activity of the microfouling community in aluminum pipes. Experiments performed as described in Table 1.

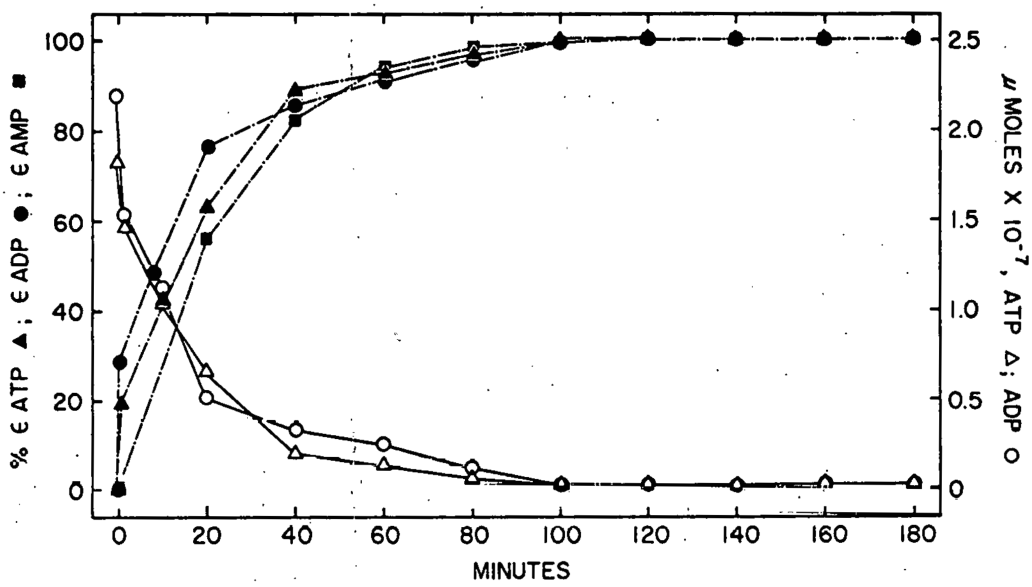

Fig. 2. Kinetics of the formation of the 1, ^{6}N ethyleno adenosine nucleotides (indicated as ε) from AMP, ADP, and ATP during incubation at pH 6.1 at 60°C in the presence of freshly distilled chloroacetaldehyde. The ε nucleotides were detected by their fluorescence and the underivatized nucleotides by their absorbance at 260 nm after separation by ion exchange high pressure liquid chromatography. εAMP and AMP did not separate under these conditions.

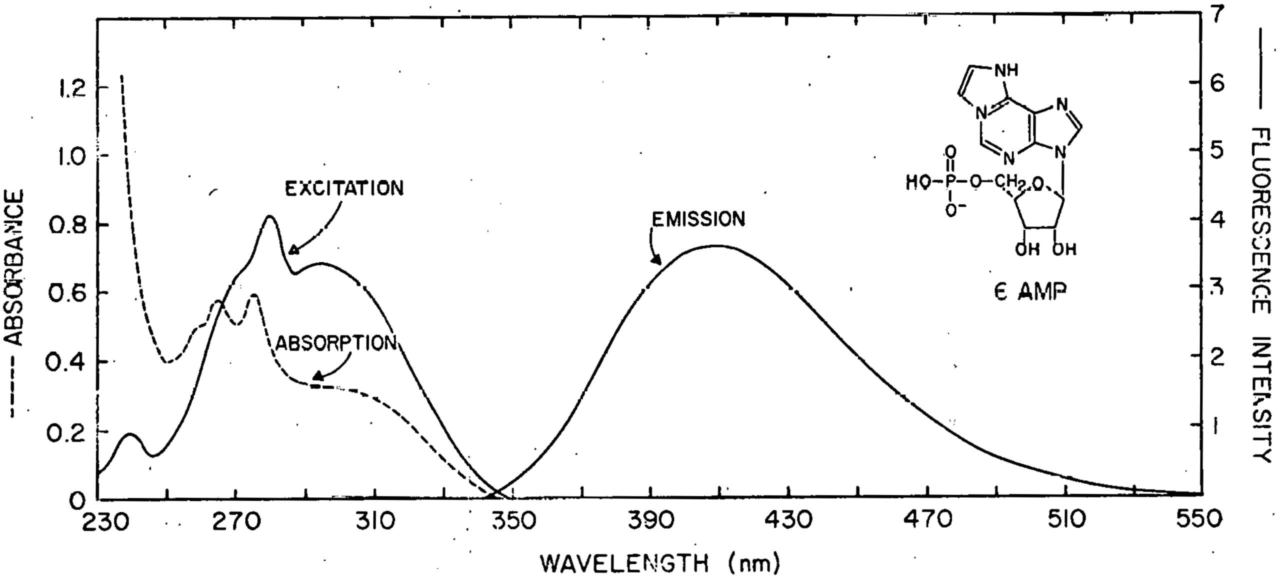

Fig. 3. The ultraviolet absorbance spectra and the fluorescence excitation and emission spectra of εAMP measured at pH 4.6 at an ionic strength of 0.01 M (conditions of elution). The spectra of εADP and εATP are essentially similar, but with the expected lower molar yields.

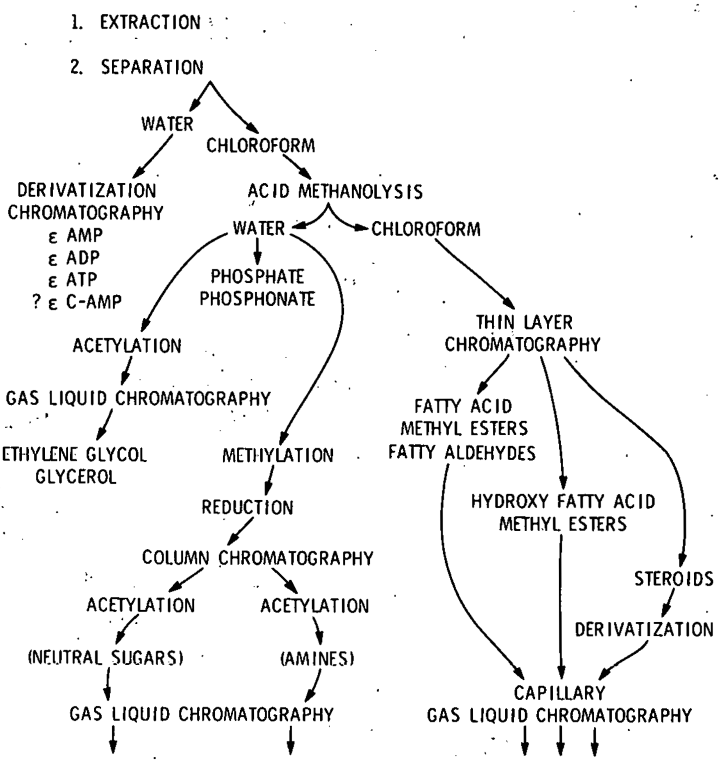

Fig. 4. The analysis scheme for the samples from OTEC samples.

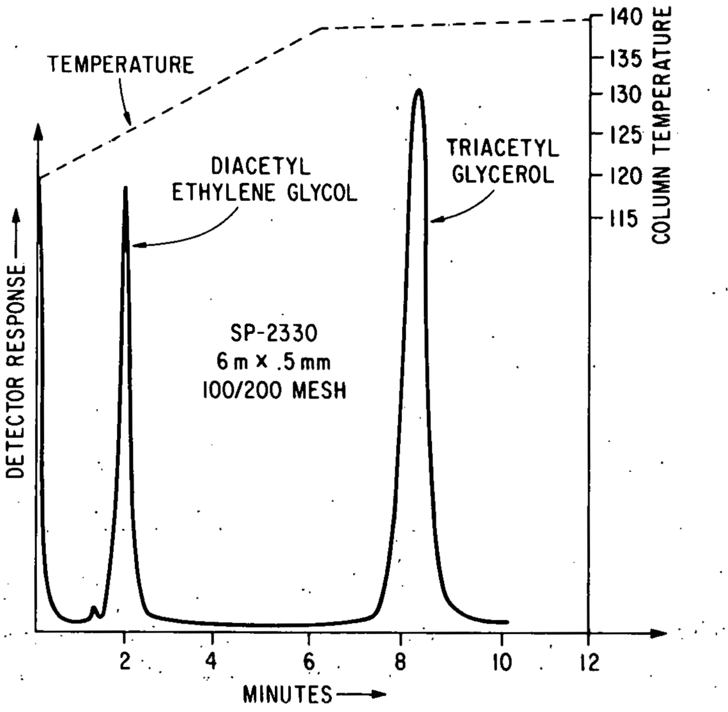

Fig. 5. Tracing of the GLC separation of glycerol triacetate and ethylene glycol diacetate from the lipids.

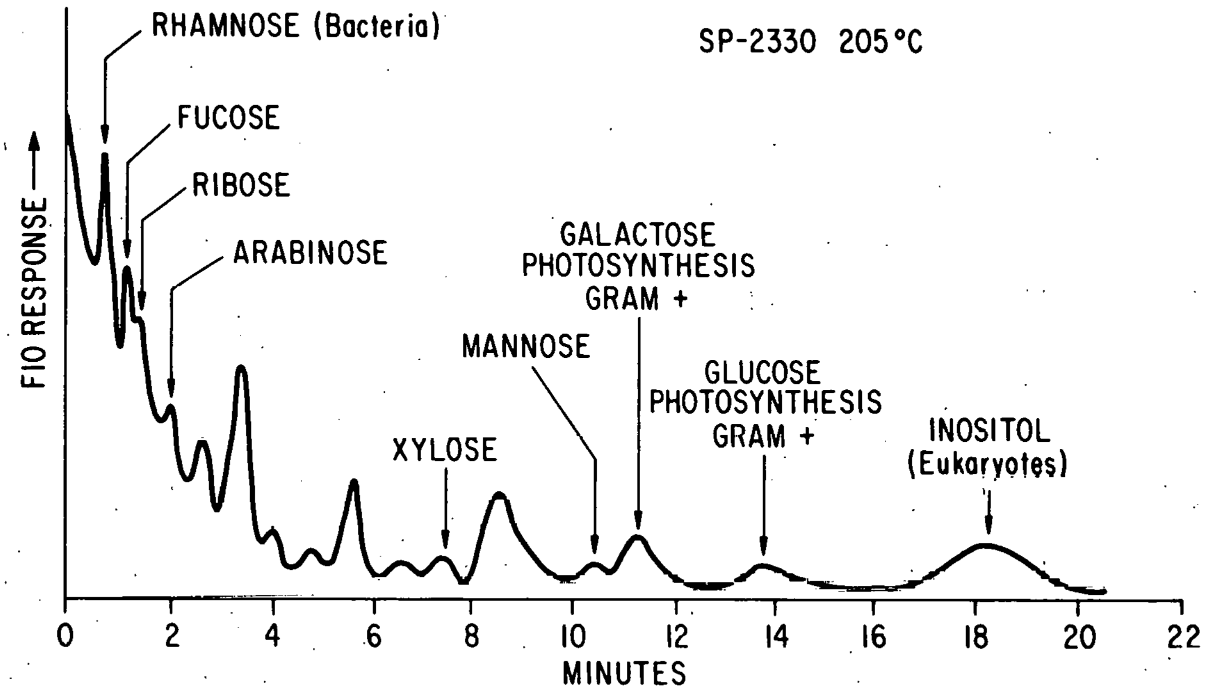

Fig. 6. Tracing of the GLC separation of neutral sugar derivatives derived from the detrital microflora found on a plastic surface exposed to sea water for 3 weeks.

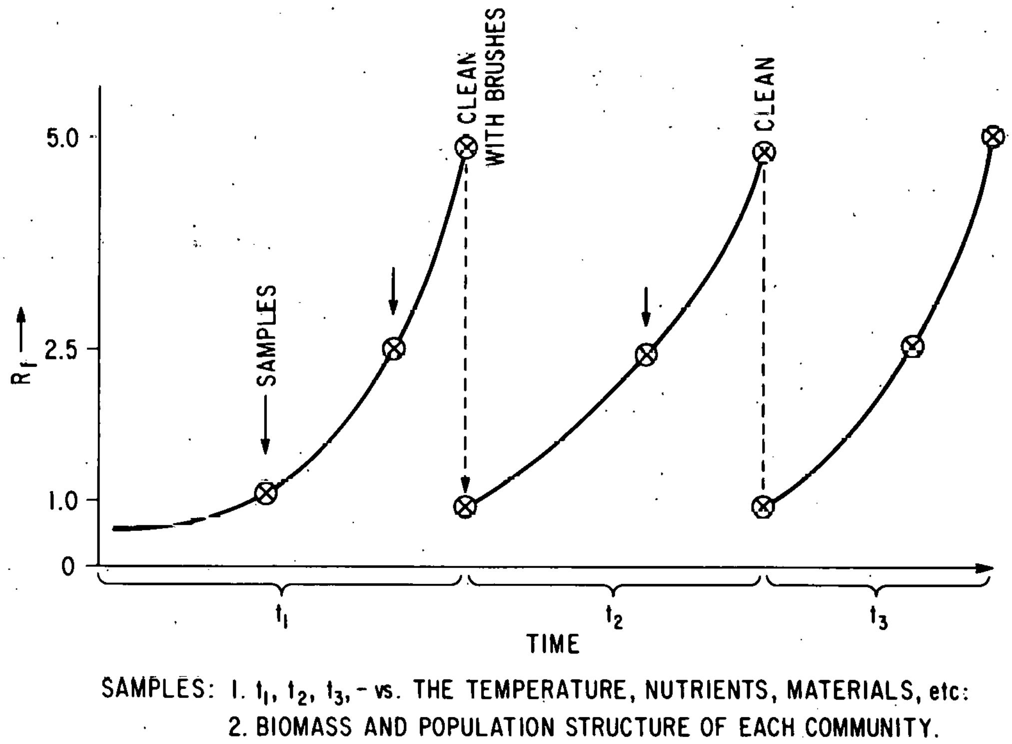

Fig. 7. Proposed experimental tests in which the application of the methods developed as outlined above would be used to follow the selection of a microfouling community after cleaning with brushes.

MACROFOULING AT THE GULF OF MEXICO OTEC SITE

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We are in the process of sampling the macrofouling communities in the Gulf of Mexico and at OTEC sites in Puerto Rico and Hawaii, to determine the kinds of macrofouling and boring organisms that will be encountered at these locations, their rates of accumulation, and their vertical distribution.

Open sea macrofoulers are collected by exposing wood/asbestos test panels at several depths for long periods of time. In the Gulf of Mexico, at the OTEC site 160 miles west of Tampa Florida, there are 22 sets of test panels attached to a buoy mooring line at regular intervals from the surface to a depth of 970 m. At other OTEC sites, 5 test panels each are being exposed at regular intervals to 150 m.

Most of these test panels are scheduled for recovery in the spring of 1979, after from 6 months to a year of continuous exposure. However, we have recovered and analyzed one series of panels that were exposed for 84 days in the upper 22 meters of water at the Gulf of Mexico site. The macrofouling species attached to these panels, and there vertical distribution, are shown in the enclosed table.

We found no unexpected organisms or unusual distribution of species attached to the test panels, and the accumulation of biomass was, as expected, modest by nearshore standards. Marine borers were, however, surprisingly abundant this far from shore.

After examining this initial series of test panels from the Gulf of Mexico OTEC site, we are still forecasting a persistent but slow buildup of both hardshelled and softbodied macrofoulers on the hull of the Gulf of Mexico OTEC power plant (and on other "blue water" power plants as well), and a lesser amount of only softbodied organisms on the cold water pipe and mooring system, that will cause no hydrodynamic or weight problems over the life of the structure, no matter what materials or design are used. We are also forecasting that there will be little or no attachment, and therefore no significant problems from macrofouling, on the inside of the cold water pipe or on the condensors. There will, however, be attachment of substantial numbers of macrofouling organisms in the warm water flow system (screens, conduits, water boxes, etc.). If a 6-10 cm. blanket of calcareous organisms cannot be tolerated, some method of biofouling control will be required.

There will be enough of the right kinds of marine borers, at least in the upper layers, to seriously damage susceptible materials. Critical materials should have an accelerated screening to ascertain marine borer resistance.

Organisms	Vertical Distribution					
	Surf.	6m	10m	15m	20m	22m
Obelia flabellata	x	x	x	x	x	x
Lepas anatifera	x	x	x	x	x	x
Balanus reticularis	x	x	x	x	x	x
Balanus eburneus	x	x	-	-	x	x
Balanus tintinnabulum	x	x	-	-	-	x
Balanus trigonus	x	-	-	-	-	x
Conchoderma virgatum	x	x	-	-	-	-
Pinna carnea	-	x	-	-	-	x
Pinctada imbricata	x	-	-	-	-	-
Membranipora tuberculata	x	-	-	-	-	-
Hydroides elegans	x	-	-	-	-	-
Bankia carinata		x	x	x	x	x
Bankia fimbriatula		x	-	x	-	x
Teredora malleolus		x	-	x	x	-
Martesia striata		x	-	-	x	-
Lyrodus floridanus		x	x	x	x	-
Dry wgt. of macrofoulers (gms/m^2)	710	110	56	45	56	56
Borers per m^2 of wood surface		1,274	998	500	862	155

Macrofouling organisms collected on test panels exposed for 84 days at various depths at the Gulf of Mexico OTEC site.

THE OTEC GULF OF MEXICO EXPERIMENT (GOME)

by

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I. BACKGROUND

A. PREPARATION FOR PHASE I

In response to a Department of Energy (DOE) request for the development of an OTEC-GOME project, the National Oceanic and Atmospheric Administration (NOAA) Data Buoy Office (NDBO) initiated action to organize the project. NDBO established a project management team for the OTEC buoy project. NDBO and Battelle Northwest, the Energy Research and Development Agency (ERDA)/OTEC biofouling and corrosion contractor, discussed in early 1977 the possibility of using a 40-foot discus buoy in the NDBO inventory as a platform for an OTEC experiment. By May 1977, NDBO and Battelle Northwest had concluded a contract to perform the task with the proposed buoy. A preliminary design for the OTEC-GOME was developed by NDBO.

Because the planned time of performance called for only 6 months, it was deemed advisable to contract tasking to the best qualified companies on a sole-source basis. By mid-June 1977, both Southwest Research Institute (SWRI) and Magnavox were under contract to NDBO. SWRI performed the final design and fabrication of the hydraulic and power system. Magnavox provided the data and control system. The integration and end-to-end testing of the system was performed at NSTL. The Phase I OTEC buoy, designated OTEC-2, was deployed during March 1978 in the Gulf of Mexico at 27°33' N and 85°31' W, or approximately 180 miles west of Tampa, Florida.

B. PHASE I

During the Phase I deployment, four experiments were operational. Three of these had provisions for experimental data to be collected on biological fouling, corrosion, and heat exchange rate monitoring, and the fourth provided measurements principally for water quality.

While the experiment was operational, heat exchange degradation data was collected by an electronically controlled automatic system and transmitted via an HF link to NSTL. Also, data samples were collected on microbiology, macrobiology, and corrosion rates at 2-week intervals.

C. PREPARATION FOR PHASE II

On 24 May 1978, NDBO directed that the OTEC-GOME buoy be retrieved for refurbishment and reconfiguration for the Phase II experiment. It had been determined in early May 1978 that a major reconfiguration would be required to correct known mechanical problems and to further enhance operational reliability. Consequently, the pumping system was redesigned to provide a pressure system rather than the suction system which had formerly been installed. A parallel redundant pump system with two pumps was installed, with a third pump on inactive standby to improve the flow system reliability. In addition, the suction hose and suction hose support systems were redesigned to improve the survivability. The plumbing was extensively redesigned to accept the pressure system. The experimental sections retained the same basic design, but were reworked. A new experiment, the Johns Hopkins water box, was added for Phase II. This new experiment was designed to provide data on biofouling effects of the flow of sea water over the exterior surfaces of aluminum heat exchanger tubes, as opposed to sea water flowing through the tubes. The water quality instrumentation was removed and water quality data will be sampled during each buoy visit.

II. PHASE II OTEC-GOME

A. OTEC-GOME OBJECTIVES

The purpose of the OTEC-GOME project is to obtain in situ experimental data on the biofouling, corrosion, and heat transfer characteristics of tubes of four different metals (aluminum, titanium, stainless steel A1-6x, and 90-10 copper-nickel) in test sections by drawing sea water from a depth of approximately 75 feet. The heat transfer monitor experiment will provide a fundamental understanding of the mechanism of biofouling microfilm buildup on tube walls and its critical relationship to heat transfer efficiency. The Johns Hopkins water box experiment will provide data on corrosion and biofouling on the exterior exposed surface of aluminum tubes at heat exchanger flow rates of sea water. The water box data will be used to develop tube cleaning techniques. Additional objectives of the overall project are as follows:

- To place test panels, or coupons, of various metals and materials at several depths to study the effect of depth on biofouling and corrosion.
- To collect marine borers on wood test panels at several depths and classify them. The effect of different species on various plastics and other nonmetallic materials is already known. This study is aimed at being better able to recommend materials for construction of future OTEC apparatus where nonmetallics are possible candidates.
- To study the effects of macrofouling on buoy structure and inlet water pipes and mooring. This is of interest from the following standpoints:
  - Buoy and mooring hydrodynamics
  - Cleaning techniques and frequency
  - Avoidance of inlet water pipe plugging
  - The integrity of materials of construction.
- To gain experience with the problems of supporting and servicing an offshore OTEC experiment.

The experiment is configured as shown in Figure 1. The various systems and components of the OTEC-GOME are described in the following paragraphs.

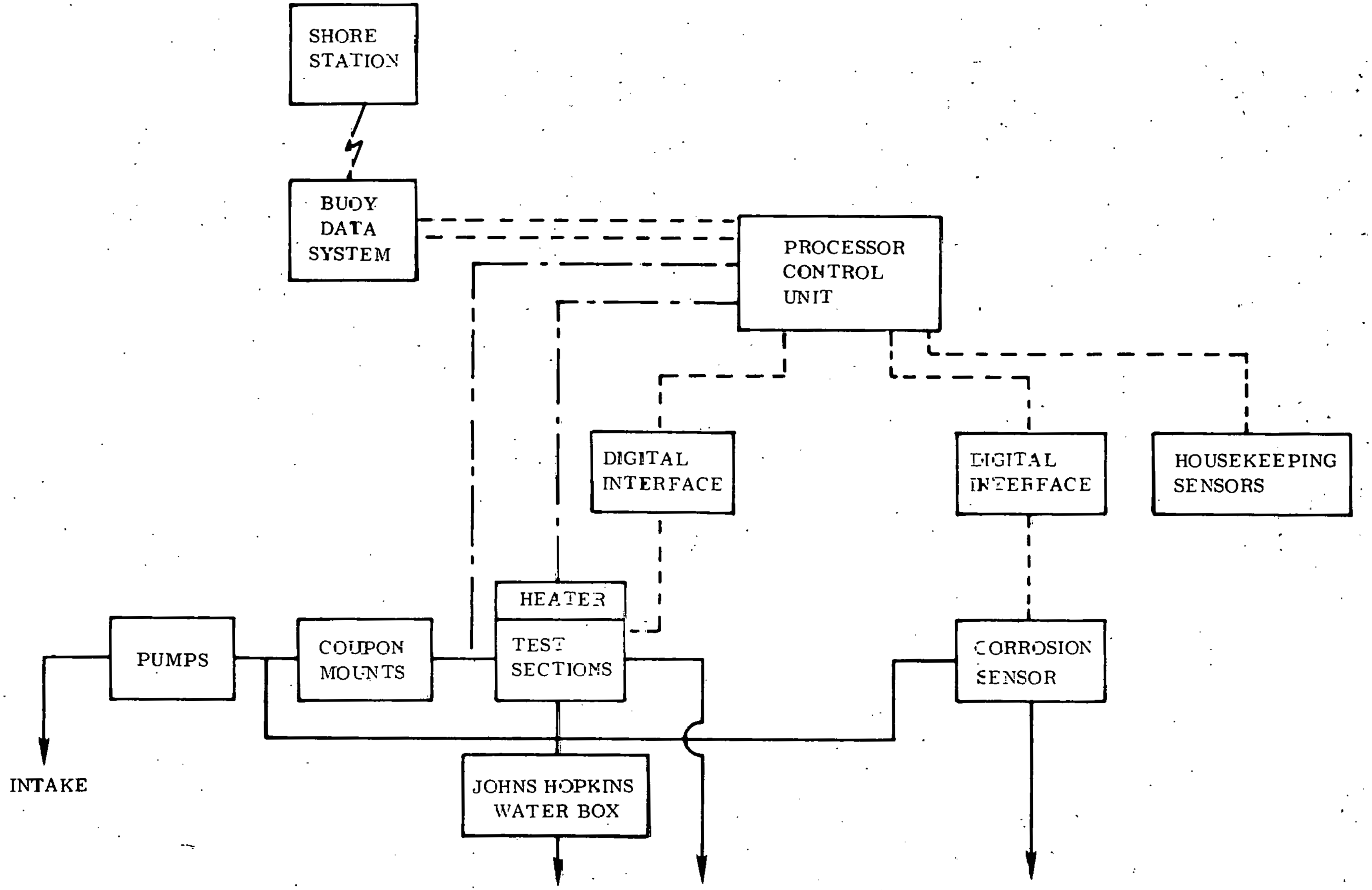


Figure 1. CTEC-GOME Configuration.

B. DESCRIPTION OF THE PROJECT SYSTEM DESIGN

1. Hull and Superstructure

The OTEC-GOME apparatus is installed on a 40-foot discus steel hull buoy which has a draft of 7' 6". There are three compartments, one 8' x 16' and two 8' x 8'. There are 16 peripheral tanks, of which four are foam-filled and four are diesel fuel tanks. Two of the normally void compartments are utilized to house the OTEC-GOME below-deck piping and pumps. Each compartment has either a hatch or a manhole. The buoy is capable of surviving extreme weather conditions in deep oceans. The buoy also has an HF antenna system and two diesel generators with long, uninterrupted operating capability.

2. Mooring

The OTEC-GOME is moored, as depicted in Figure 2, at 27°33' N and 85°31' W at a depth of approximately 4740 feet. Two 90-foot shots of chain are connected to the lower central part of the buoy. A swivel is placed between the two shots of chain to prevent twisting. Attached to the upper chain are five standoffs which prevent the 75-foot inlet suction hose from becoming entangled with the mooring chain.

3. Pressure Water System

The purpose of the pressure water system is to pump water from 75 feet below the surface and pass it, at controlled constant velocity, through biofouling and corrosion sample tubing and through heat transfer monitors. A continuous, constant-pressure flow of water through the Johns Hopkins water box is also maintained (see Figure 3). The pressure water system is made up of the following elements:

- Suction strainer (1)
- Suction hose (1)
- Suction hose attachment assembly
- Main pumps (three 3-hp pumps, two operating and one on standby)
- Biofouling and corrosion experiment and bypass valves (4)
- HTM experiment and bypass valves (4)
- Flow control and measuring systems (5)
- Johns Hopkins water box experiment
- Discharge piping.

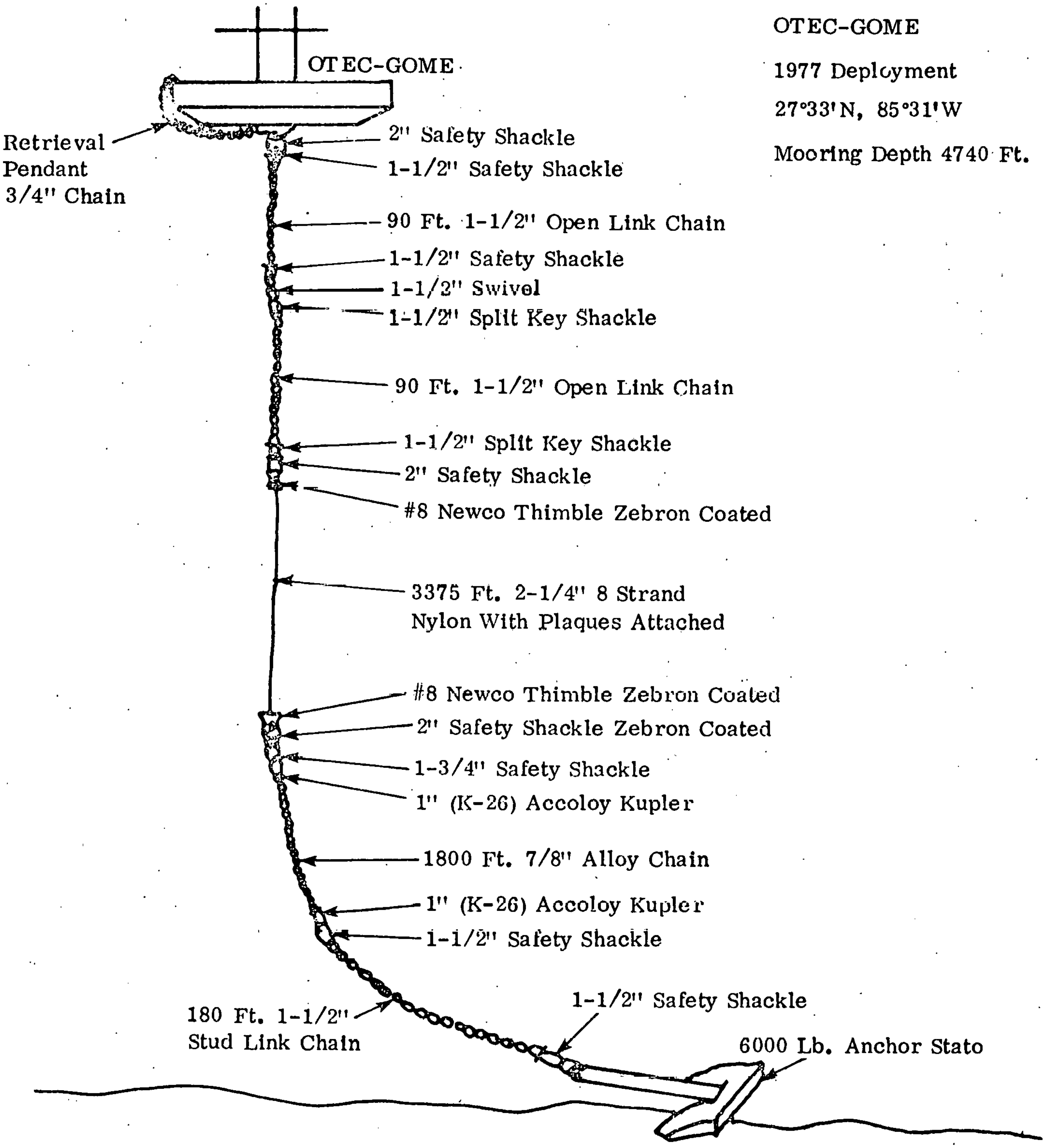


Figure 2. OTEC-GOME Mooring System.

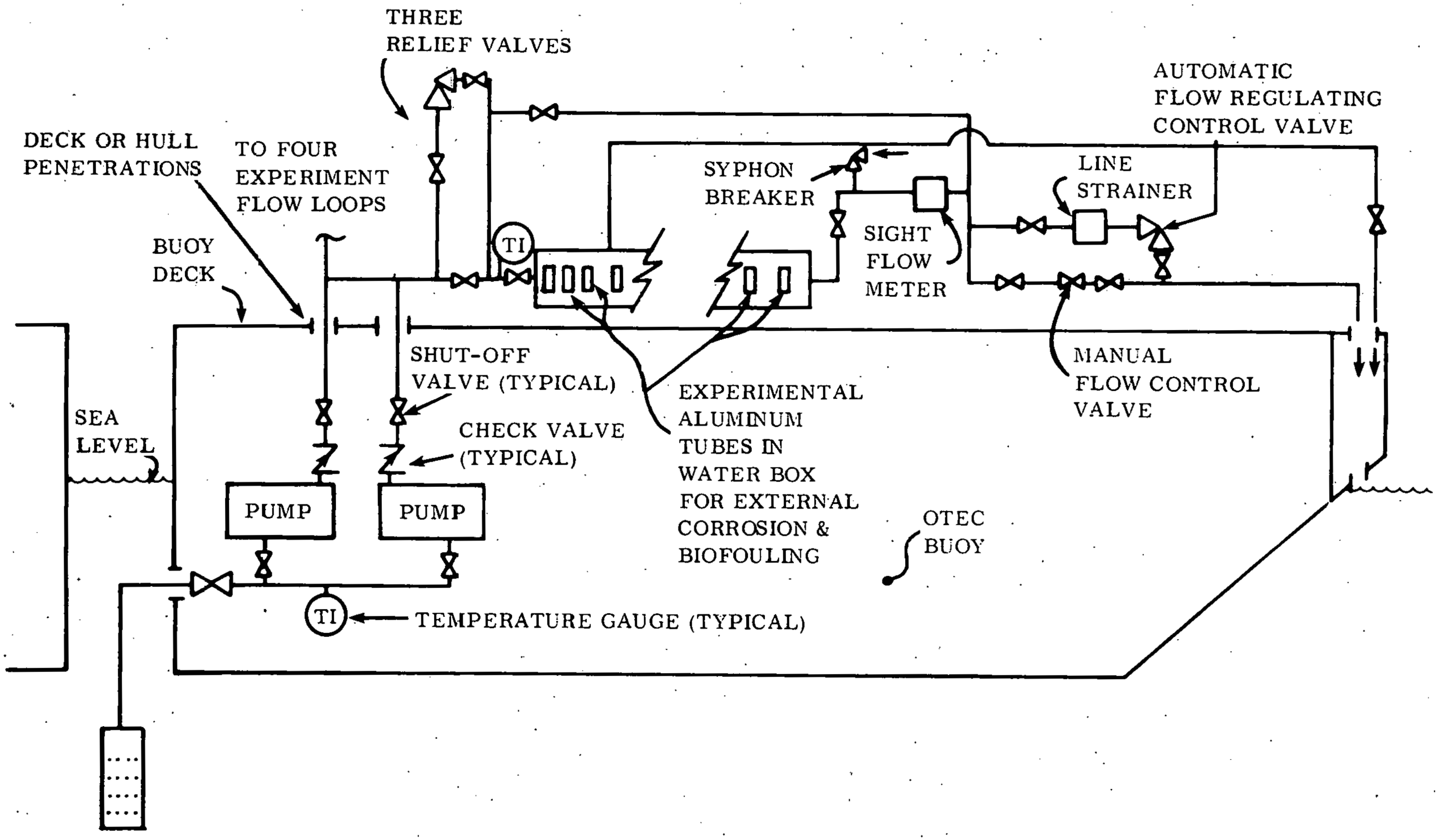


Figure 3. Pressure Water System.

The pressure water system has three primary experiment loops, one secondary (sacrificial) experiment loop, and one water box loop. Each of the four experiment loops will provide biofouling, corrosion, and decay of heat transfer rate data on tubes of 90% copper/10% nickel, 5000 series (5052-0) aluminum, A1-6x stainless steel, and titanium. The stainless steel experiment will be secondary. The length of time to reach the critical OTEC heat transfer rate, as well as corrosion effects, at this Gulf of Mexico location will be determined on these various metallic tubes.

The Johns Hopkins water box loop is designed to allow the study of biological growth on exterior tube surfaces as opposed to the interior of heat exchanger type tubes. The tube samples in the water box are sections of 3-inch aluminum tubing with the same properties that may be used in operational heat exchangers. They are being subjected to a pressure head greater than 3 feet and a flow rate of approximately 2.5 feet per second. The tubes are spaced approximately 1.25 inches between adjacent tube surfaces. The water box experiment was designed and constructed by Southwest Research Institute.

The pressure water system has three pumps installed. A fourth pump is being retained at NSTL for immediate shipment to and installation on the buoy at sea if required. Two of the three pumps aboard the buoy are operating at all times. Each of the two operating pumps can individually support the primary experiments. The third pump will not be operating, but will be connected into the system. In order to bring the third pump into the pumping system, it is necessary for someone to go to the buoy, secure the defective pump, and actuate the third pump. All three pumps are accessible for removal and replacement at sea. It should be noted that a single pump may not be able to support the primary experiments, the secondary experiment, and the water box. Accordingly, if one of the two normally operating pumps should fail, the secondary (stainless steel) loop will automatically be isolated from the experiment. The remaining pump will support the primary loops and the water box until such time as the reserve pump can be actuated for additional pumping capacity.

All three pumps on board the OTEC buoy are located below deck, with their suction inlets below the level of the buoy waterline. Each pump draws water through a common all-plastic suction strainer. The suction hose is a 6-inch diameter 75-foot long SBR rubber hose. Thermistors monitor the temperature of the pumps to detect overheating. Each pump is driven with a close-coupled, totally enclosed, fan-cooled motor. The electric motors are 115-volt single-phase and develop approximately 3 horsepower each. Current requirement is for approximately 18 to 20 amps for each pump motor when they are throttled back to provide normal system pressure flow. All pump components in contact with sea water are polyvinylchloride (PVC) or equivalent inert material. Seals are Viton or equal. All materials of construction subject to contact with the sea water being supplied to the experiment are PVC or equivalent. No metallic ions are introduced into the experiment by system components. The discharge line of each pump has a check valve to prevent backflow as well as the necessary block valves to enable removal of an inoperative pump. A pressure indicator is provided on the manifold on the discharge side of the pumps. A vacuum gage on the suction inlet manifold enables detection of an obstruction.

The pipe and valves are oversized to minimize system pressure losses, thus enabling the maximum number of experiments to be performed within the constraints of buoy electrical power generating capability. The pump discharge head is stabilized by allowing the experiment discharge to manifold into a common header.

The pressure water system uses Kates flow-control valves which employ a mechanical variable orifice to maintain a constant flow rate regardless of upstream or downstream pressure changes. The flow-control valve is provided with a mesh strainer immediately upstream of the valve. The strainer will be serviced during each service visit. A sight glass flowmeter is provided downstream of the experiments to visually observe the fluid flow from each experiment as well as measure the flow rate. Bypasses are provided to maintain the required flow rates while servicing the flow-control strainer or flow-control valve itself. Spare flow-control valves, as well as other components, are stored on the buoy. The strainer, the flow-control valve, or the sight flowmeter can be replaced easily if there is even the slightest indication of biological growth that might affect the flow rate through the experiment. The discharge lines empty over the edge of the buoy.

In the event of alternator or other power failure, the biofouling, corrosion, and heat exchange monitor sections will remain filled with water. Static-head loops and vacuum breaker valves at the top of these loops will keep the samples wet until a service party can reach the buoy.

4. Power System

The primary power is obtained from two diesel-powered alternators. Alternator outputs are 115-volt, 60-Hertz, 39-amp capacity each.

Each pump motor is on a separate breaker and powered by separate alternators. A total of three pump motors are wired in, but only two can run at one time. A switch arrangement will select the diesel alternator that will drive the motors. One pump motor will operate from alternator number 1 and the other motor will operate from generator number 2. This arrangement supplies a second level of redundancy, since one pump can supply all primary flow water requirements.

A bilge pump and float switch are installed in each pump compartment to remove any condensation or seepage. Pump compartment lighting and electrical outlets have been installed to aid in maintenance and service to the pumps and motors.

The measure of housekeeping alternator current serves as an indication that the pump motors are functioning properly.

A solenoid valve shuts off flow to experiment number 4 in the event of a pump failure. A reduction in alternator current signals the loss of a pump.

5. Corrosion and Biofouling Sampling Systems

Corrosion and biofouling experiment systems are located both above and below the water surface. In series with each heat transfer monitor experiment, a sample tube made of the same material as the heat transfer monitor tube is included. Below the surface, mounted on the standoffs and the mooring line, various samples for biofouling are attached. Figure 4 shows the locations of the various samples.

a. Corrosion Sampling System. A corrosion rate monitor system, which was developed at the University of Miami, has been installed in the OTEC-GOME. This instrument has two parts, a sensor and the electronic components. The sensor has the outward appearance of a PVC coupon ring holder. Instead of two rings inside, it has one ring which serves as a working electrode and a semi-cylindrical piece of platinum-clad titanium wire mesh which serves as the counter electrode oriented transverse to the flow path. There is also a reference electrode in this sensor. Four electrical leads are required; two for voltage sensing between the reference electrode and the working electrode, and two to carry the polarizing current between the counter electrode and the working electrode. This unit monitors corrosion potential. A shift in potential gives evidence of the onset of localized corrosion. The corrosion rate monitor is located in the downstream side of test loop number 4. It is subject to maintenance requirements at sea, and a spare sensor as well as certain other spare parts (electrodes) are available.

The corrosion sensor provides one of the inputs to the corrosion monitor. Corrosion potential and polarization current data are acquired each time a corrosion measurement is made on command. This information is transmitted to shore, processed, and sent to the principal investigator. In addition to the corrosion cell, there will be one cell per loop (after the first service visit) that can be read manually during subsequent service visits to the buoy. These additional cells will be installed during the first service visit. These loops all have corrosion sensors which are not monitored by corrosion rate monitors, but are installed and used as weight loss sensors.

b. Biofouling Sampling System. Each of the four experiment loops on the pressure side of the pumps has sea water from a depth of 75 feet pumped through the sample tube. The sample section is equipped with bypass piping for sample removal. The sample tube has machined notches. The notches facilitate removing sections at sea with a tubing cutter and replacing them with a tube and rubber hose connecting links. The water flows out through the top of the sample coupon tube and down into the top of the vertically mounted heat transfer monitor experiment section, flowing inside the inner tube. The water flows out the bottom of the heat transfer section, goes through a flow-control system, and then overboard. There are four experiment loops as described in section II, B, 3.

A schematic diagram of a test loop is shown in Figure 5. The test coupon tube is mounted vertically so that 9-inch sections can be periodically removed at sea with a tubing cutter, starting always at the top of the tube (original) portion so water will remain in the portion below the cut and protect the biofouling film.

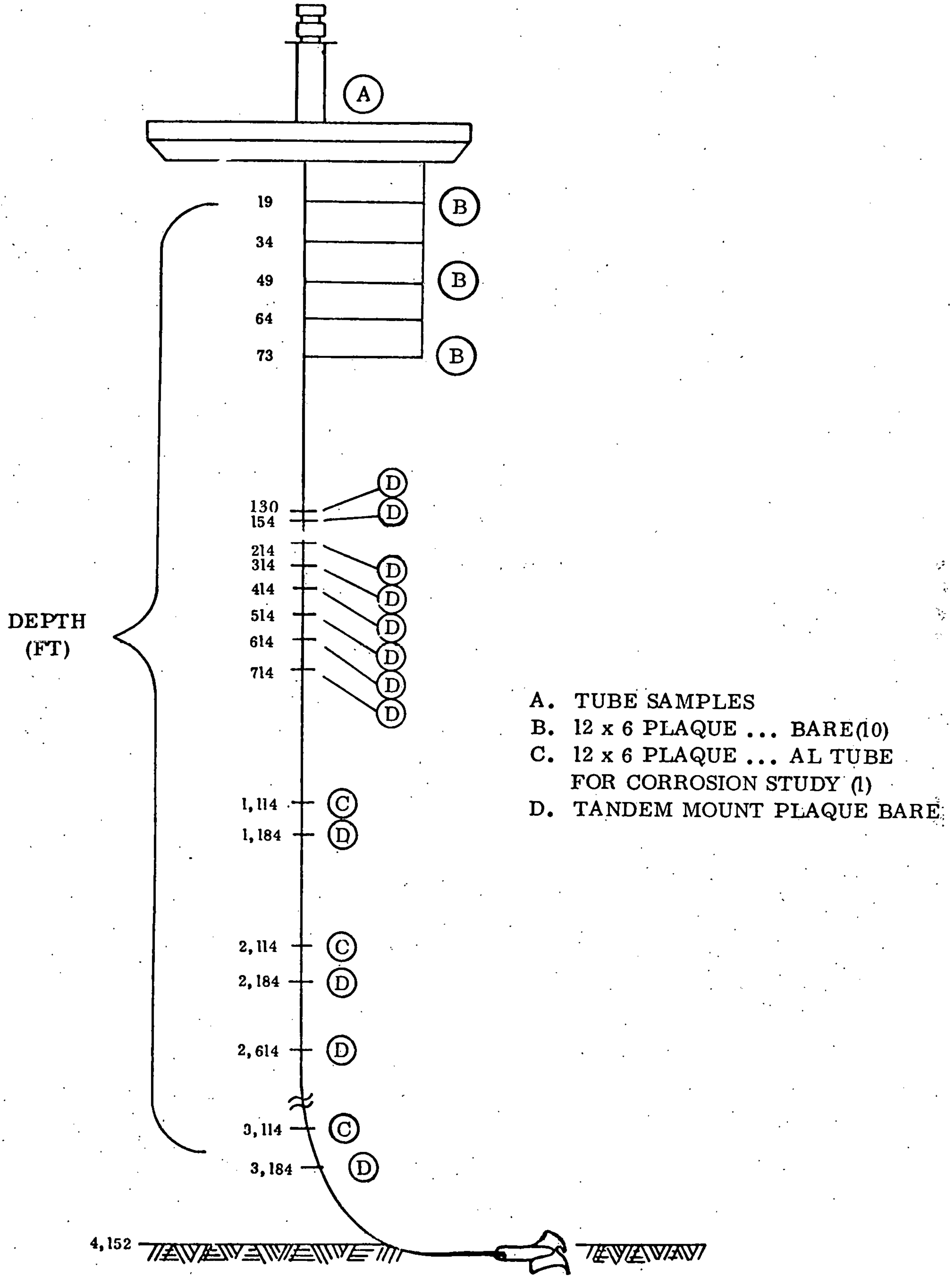


Figure 4. Sample Locations.

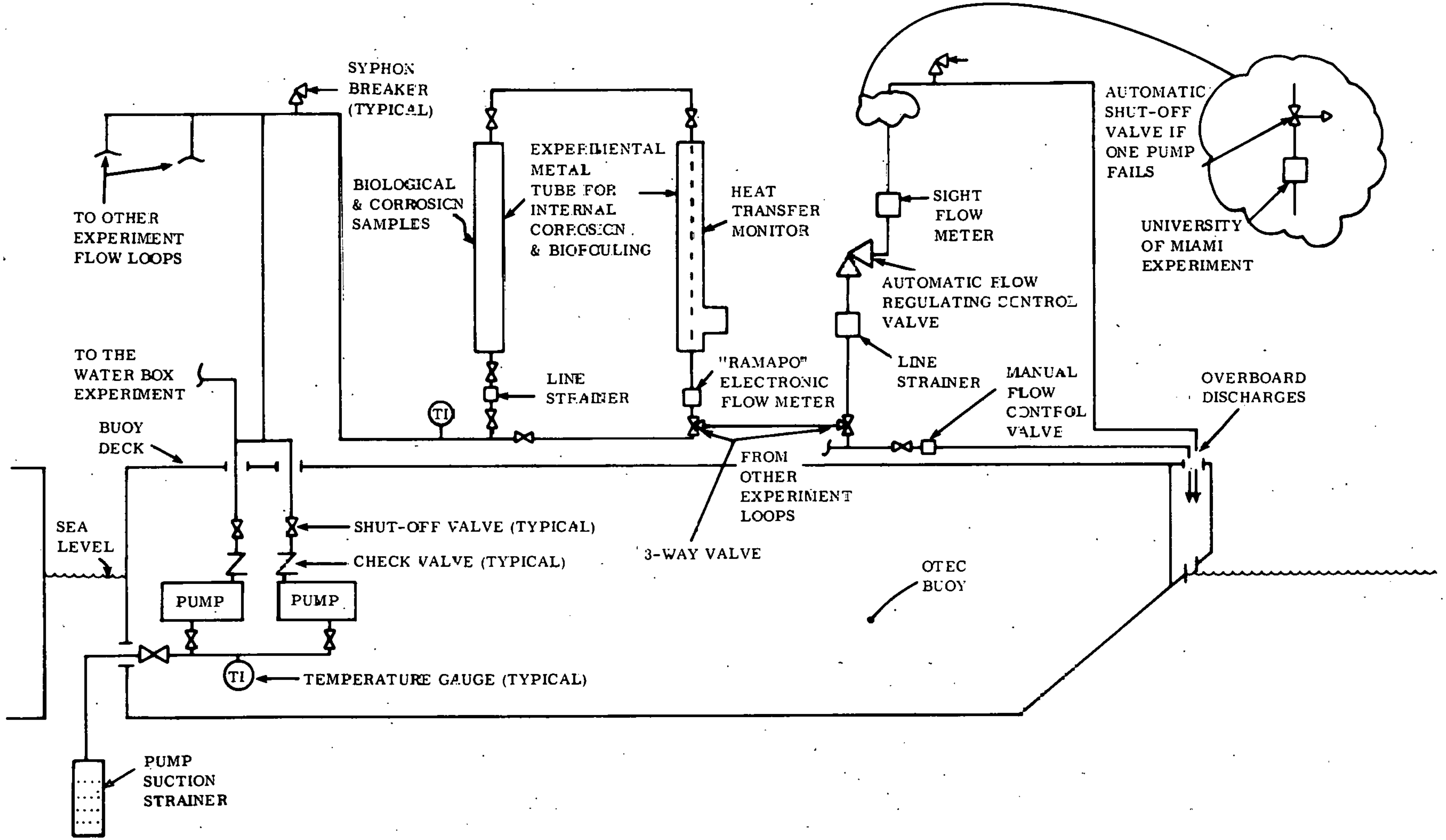


Figure 5. Biofouling/Corrosion - Heat Transfer Experiment Flow Loop.

The piping is PVC with the exception of the test coupon tubes and HTM tubes, which are both of the metal alloy being tested. All four experiment loops have the same water velocity, 6 feet per second, throughout the duration of the 3- to 4-month experiment.

The small length of tube, the sample coupon, that is brought in for laboratory examination is subjected to careful handling and treatment procedures. Biological growth film thickness is measured, and the biological and chemical composition of the film as well as the mode of attachment of the various kinds of organisms and their growth patterns are determined. A coupon cut from the tube is sent to the Argonne National Laboratories (ANL) for corrosion studies. A 3-inch portion of the 9-inch tube and small pre-weighed coupon rings, which were held in a PVC holder, are also forwarded to ANL for determining corrosion rate by weight loss.

Test panels and sections of metal are attached under the buoy and at several depths. These serve the following purposes:

- Metal Tubes - micro-biofouling and corrosion
- Wood Panels - to collect marine borers
- Cement Asbestos Panels - to collect macrofouling.

6. Heat Transfer Monitor Experiment

The heat transfer monitor experiment is based on Newton's law of cooling.(1) On command, an electrically heated ring, clamped on the outside of the metallic tube being tested, heats the tube to 1.8° C above the water temperature or applies heat for 10 time constants, and then cuts off. The time series of the temperature difference between the tube wall and water is used to accurately establish a time constant. Reference 1 discusses the corrections, based on water temperature and flow rate, used to calculate the heat transfer coefficient and fouling factor.

Five sampling modes are available for obtaining points on the curve: adaptive and 2-, 4-, 8-, or 16-second intervals. The adaptive mode selects sampling rates which depend on the previously calculated approximate time constant. The heating collar is positioned ~96 inches from the upstream end of the test pipe. The temperature is determined some distance from the center of the pipe and compared to the inlet water temperature 12 inches upstream. Ten seconds after the heat is turned off, data collection begins. As the biofouling film forms, the cooling time will increase up to a point where the heat transfer efficiency is critical. Macrofouling (visible barnacles, etc.) will not yet have formed. This amount of biofouling cannot be tolerated on the heat transfer surfaces. Cleaning methods for removing the biofouling microfilm and reestablishing efficient heat transfer are not included in the OTEC-GOME requirements.

The heat exchanger shell is PVC and has foam casing insulation. This combination provides insulation and protection from salt water. It also provides physical protection for the metal tube and its electronic instrumentation. There is no liquid in the annulus.

The primary flow measurement is obtained with a (RAMAPO) strain-gage-type electronic flowmeter located below the heat exchanger monitor downstream of the heat transfer measurement system. The flow controlling system is located downstream of the experiments. The flow is controlled by a mechanical flow-control valve (Kates). Six-feet-per-second linear flow is the target velocity.

7. Johns Hopkins Water Box

The Johns Hopkins water box was added to the Phase II deployment to provide scientific data on biofouling effects of the flow of sea water over the exposed surfaces of aluminum heat-exchanger type tubes. The information acquired will provide data that may be used to develop cleaning techniques. This apparatus was designed and constructed by SWRI.

The water box was designed to operate as a pressure vessel in the primary mode of operation. The alternative or secondary mode of operation utilizes static head pressure. Sample tubes are installed in a row in such a manner that they may be removed during service visits. These sample tubes are 3 inches in diameter, 3 inches long, and spaced 1-1/4 inches apart to allow the flow of sea water over the exposed surfaces. The sea water flow rate is 2.5 feet per second in both the pressure and static modes.

The water box contains 12 tubes, half of which will be used for biofouling/corrosion analysis and the other half for heat transfer and cleaning tests. The biofouling/corrosion tubes will be segmented and will undergo close examination of the accumulated material on the outer surface. By reusing the sample tubes after they are cleaned at various time periods, additional data can be obtained as to how biofouling accumulates on initially clean surfaces versus those that have been previously subjected to fouling and cleaning.

8. Electronics

The experiment is controlled remotely via commands over an HF link. Three frequencies are available, one in each of the 4-, 6-, and 8-MHz bands. Frequency shift keying modulation is used with a data rate of 75 bits per second.

The processor control unit (PCU) for OTEC-GOME receives 5-bit instructions from the Phase II DPM and acts upon the instructions.

The PCU recognizes three types of commands as follows:

- Set parameter or mode for sampling rate
- Initiate or continue data collection
- Report data.

The basic Magnavox electronic payload used on OTEC-GOME consists of three subsystems: HF communications, data processing module, and power regulation module. Standard Magnavox electronic payload system components are installed for measuring wind speed and direction, barometric pressure, air temperature, and ocean temperature. The met package is tied to the data processor module through the primary sensor processor.

The OTEC housekeeping system is controlled by the PCU. Ac volts, ac amps, engine oil temperature, engine cylinder head temperature, three compartment temperatures, and three pump motor case temperatures are reported as housekeeping data.

The Shore Collection Station (SCS), located in the S-II Building at NSTL, is the point from which OTEC-GOME is controlled. Commands sent to OTEC-GOME to initiate experiments, set up parameters, continue experiments, and transmit data originate at the SCS. (See Figure 6 for schedule.) Data received at the NSTL SCS is filed in mass storage. Quick-look results are printed out immediately to permit evaluation of data quality before the experiment continues. A data tape is produced for Argonne National Laboratories. Figure 7 shows a functional block diagram of the OTEC-GOME data and control system.

III. SYSTEM TESTS AND DEPLOYED RESULTS

A. BURN-IN

1. Power System

Early in the burn-in period, it was discovered that the Lister diesel engines were inadequate for the load demanded by the OTEC-GOME systems. Two Deitz diesels of higher power rating were installed. No manfunctions were noted with about 10 weeks of accrued burn-in time.

One of the battery charger power supplies experienced a failure, which was subsequently repaired. No other power system malfunctions were noted during the 10 weeks of burn-in.

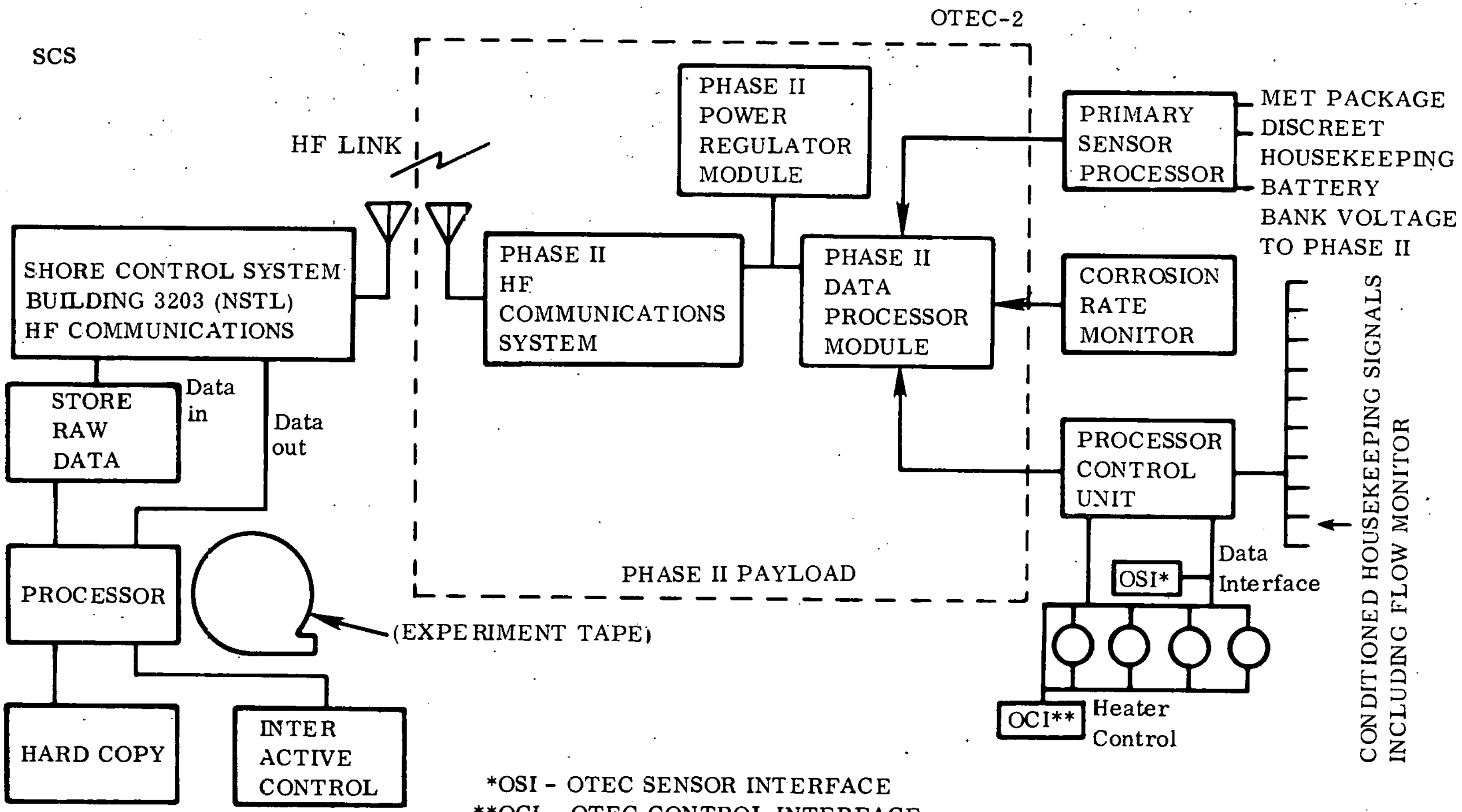
2. Pump System

Two types of pump failures were uncovered during burn-in. One failure mode was diagnosed as impeller misalignment with the sidewall, which caused scoring of the sidewall and increased power to drive the pump. This eventually led to circuit breaker operation. Proper shimming and torquing of the pumps' bases relieved this problem.

The second failure mode noted was that the impeller-to-shaft machine screw retainer backed out. This was fixed by using a compound on the mating threads. Although long periods of uninterrupted operation were not achieved, it was felt that the problems had been solved.

REQUIRED WEEKLY DATA					
	M	T	W	T	F
EXPERIMENT 1					
OTEC Data					
16 Frames		X			
EXPERIMENT 2					
OTEC Data					
16 Frames			X		
EXPERIMENT 3					
OTEC Data					
16 Frames				X	
EXPERIMENT 4					
OTEC Data					
16 Frames					X
SYNOPTIC					
Housekeeping (1 Frame)	X	X	X	X	X
MET (1 Frame)	X	X	X	X	X
Corrosion (1 Frame)	X	X	X	X	X

Figure 6. OTEC-GOME Phase II Report Schedule.



*OSI - OTEC SENSOR INTERFACE
**OCI - OTEC CONTROL INTERFACE

Figure 7. OTEC-GOME Data and Control System.

3. Data System and Instrumentation

The data system has been working flawlessly since the beginning of the burn-in test. A test which caused the system to operate in all of its modes was performed during burn-in, and simulated deployed data acquisition was performed.

Some minor start-up problems were experienced with the instrumentation wiring from the HTM electronics to the connector. A repair to a problem of this nature was made during deployment.

The biggest problem experienced with the HTM system was a poor fit of the HTM collars on the pipes. After proper torquing was performed and the systems tested, three out of four systems produced time constants which were much longer than expected. The problem was resolved by using the HTM collars from OTEC-2 and O-TUG.

4. Wilson Tests

After the problems were resolved in the HTMs, a Wilson test was performed on each loop. Dr. Mahalingham, from Carnegie-Mellon University, was at NSTL to analyze the data as it became available. The Wilson plots are shown in Figures 8, 9, 10, and 11.

B. DEPLOYMENT AND RESULTS

The OTEC-GOME buoy was deployed on 2 December 1978 at the same location as OTEC-2 (27°33' N, 85°31' W). The USCGC BLACKTHORN towed OTEC-GOME to the site and the mooring was accomplished. The MOBY-II, a privately owned vessel under contract to CSC, supported the start-up operations.

All tasks were accomplished. Only the repair required on experiment 4 mentioned previously slowed down an otherwise efficient operation.

All data scheduled to be taken has been successfully reported to shore. Minor problems are being experienced because of noise on the HF link. Parity errors are frequently present in the data, requiring retransmittal of data and merging to obtain errorless data frames. As of 27 December 1978, three groups of approximately 16 frames of data for each experiment have been transmitted to Argonne Labs on tape. Hard copies of the corrosion data are also available (one frame per day) and will be transmitted to Argonne for analysis.

The first service visit is scheduled for the week of January 14, 1979. Coupon samples will be taken from each flow loop and the weight loss corrosion monitor will be installed in the space vacated by the first samples. Two additional visits will be made during the projected 8- to 10-week deployment.

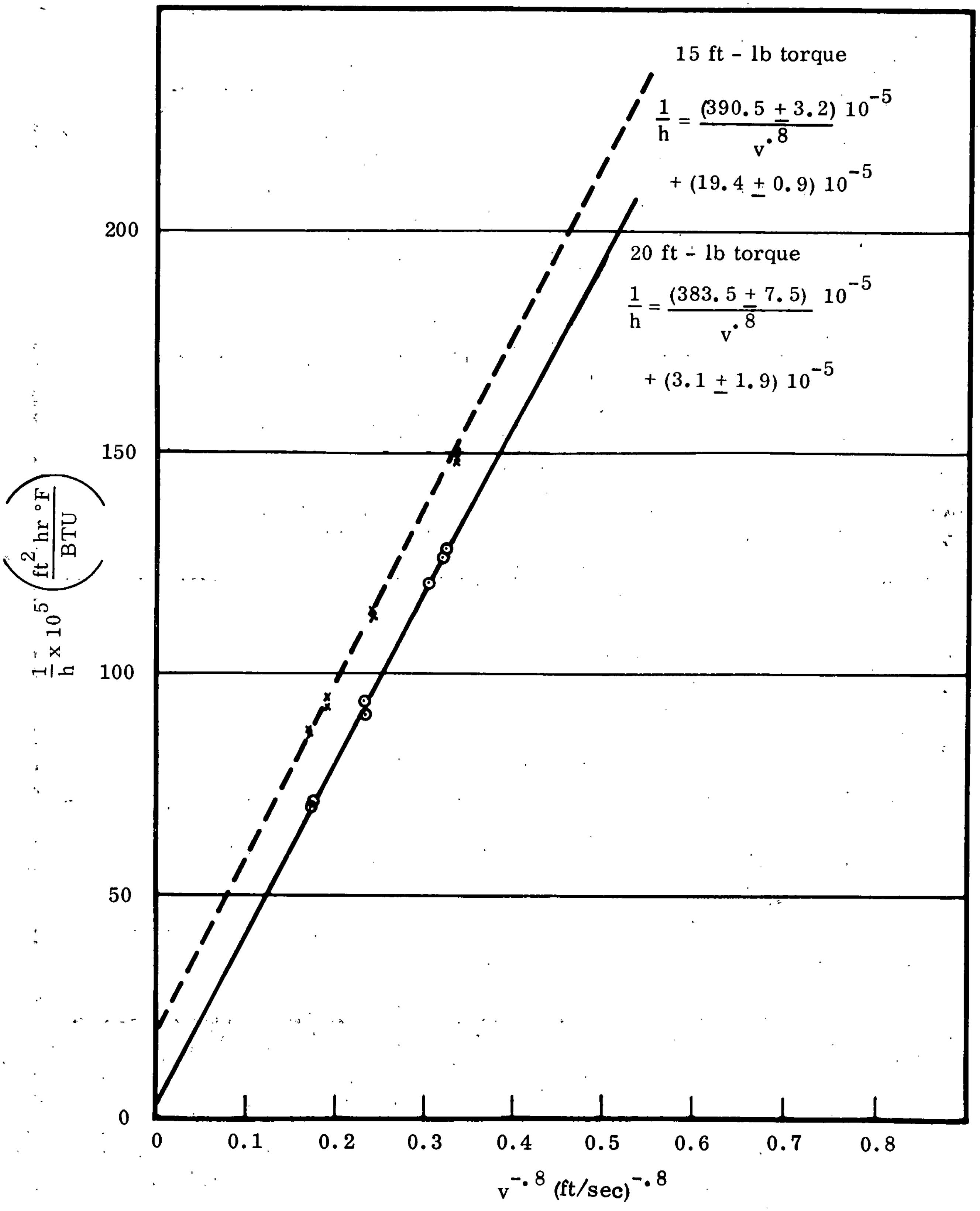


Figure 8. Wilson Plot for Aluminum 5052.

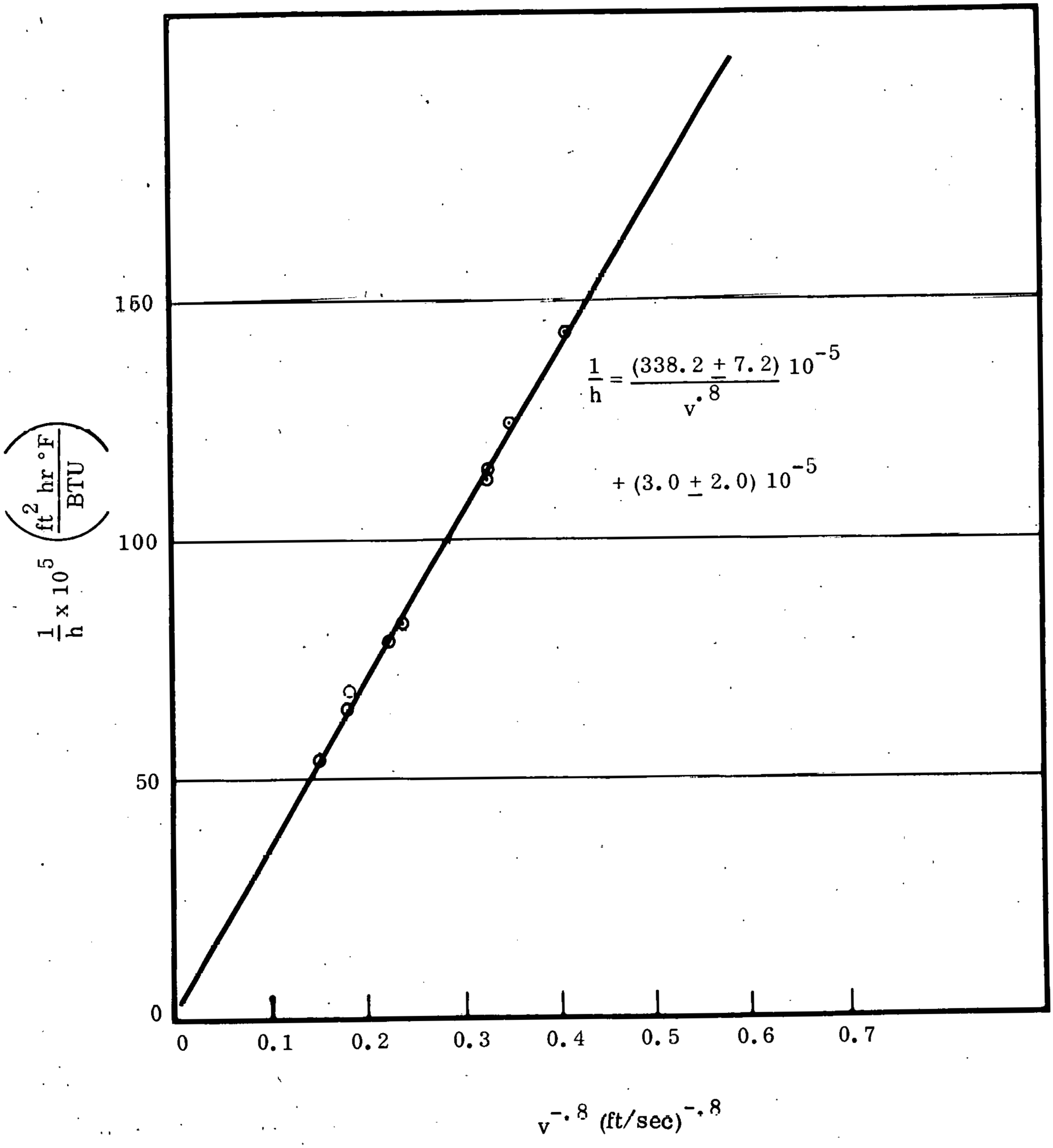


Figure 9. Wilson Plot for Titanium (Grade 2) - Preliminary Analysis.

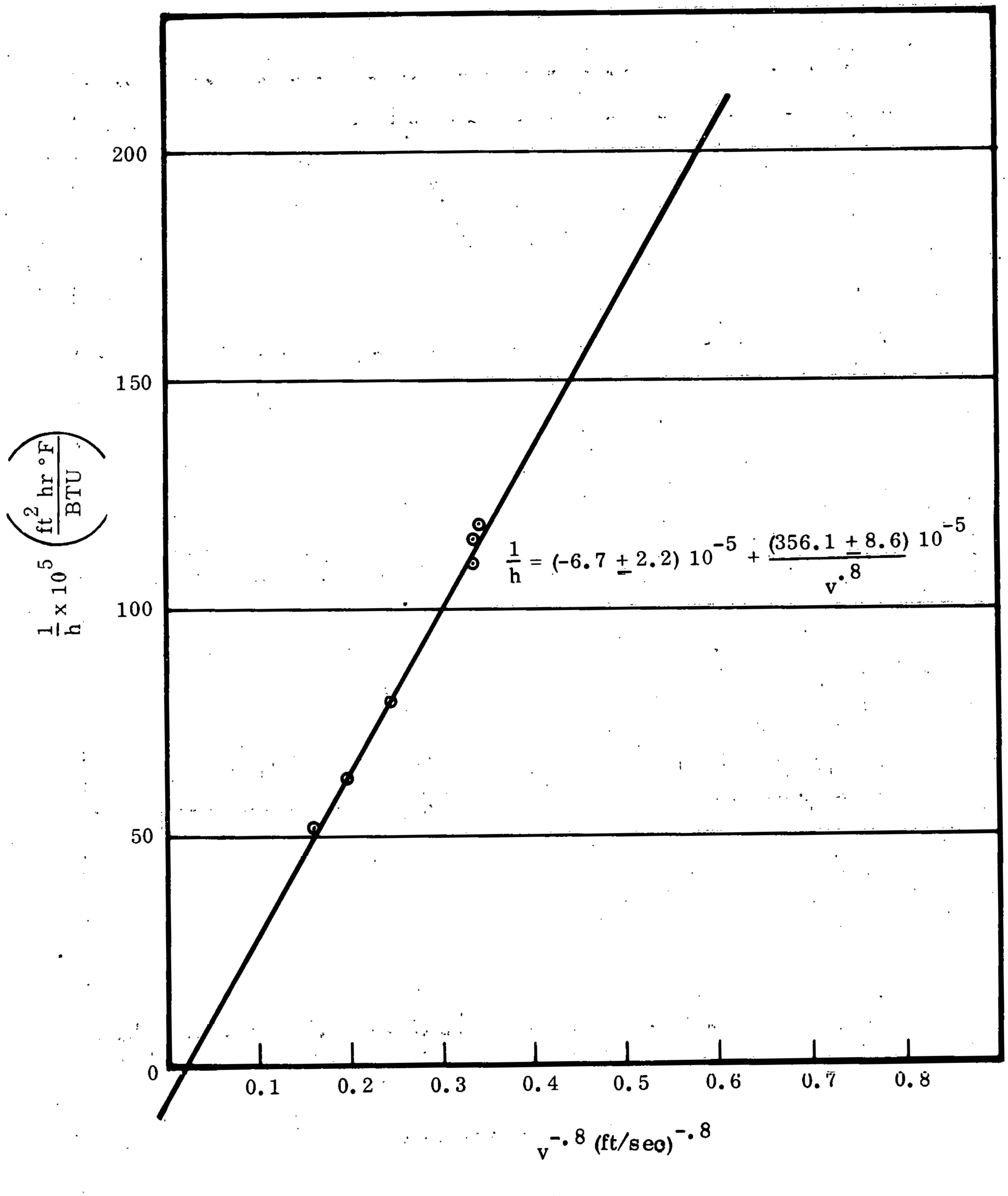


Figure 10. Wilson Plot for Cu/Ni (90/10).

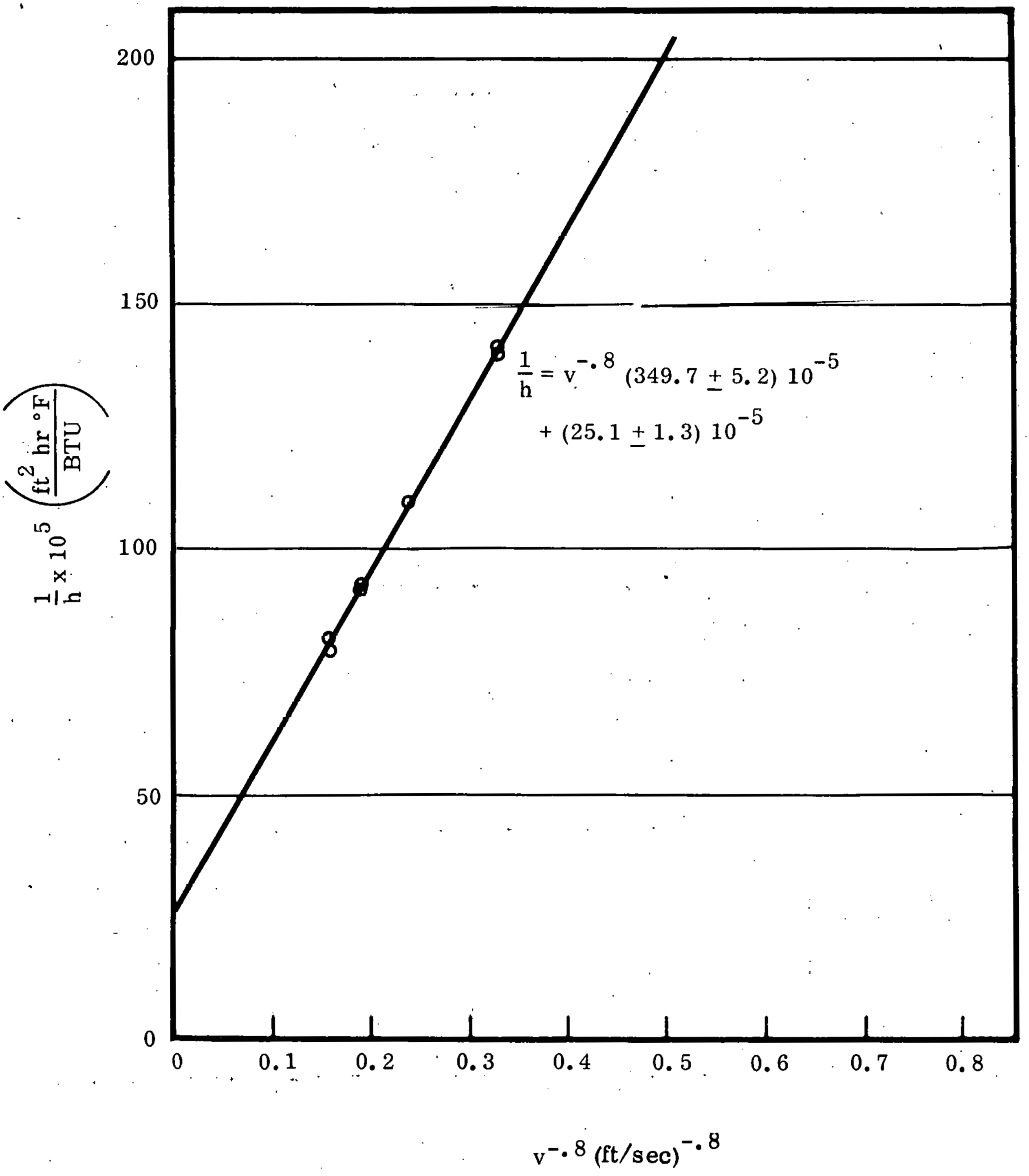


Figure 11. Wilson Plot for Al-6x Stainless Steel.

ACKNOWLEDGEMENTS

The integration contractor personnel supplied much of the information contained in this report. In addition to the efforts of Bobbie Hammet, a coauthor, George Prine of Computer Sciences Corporation is due thanks for his untiring efforts in the systems integration, tests, and deployment.

Sperry personnel in the shore control station, Bobbie Redmon, Mike Basoco, and V. L. Clark deserve a special note of thanks for the many long hours spent in extracting data from the OTEC-GOME system.

Dr. Mahalingham of Carnegie-Mellon University also deserves recognition for his valuable contribution in the preliminary testing of the HTMs and his on-the-spot analysis of the Wilson test data.

REFERENCE

1. J. G. Fetkovich, et al., "A System for Measuring the Effect of Fouling and Corrosion on Heat Transfer Under Simulated OTEC Conditions," Carnegie-Mellon University, Pittsburgh, PA, for DOE Contract E (1101) 4041, December 1976.

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PRELIMINARY EVALUATION OF FLOW-DRIVEN BRUSHES FOR REMOVAL OF SOFT BIOFOULING FROM HEAT EXCHANGER TUBES IN OTEC POWER PLANTS

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ABSTRACT

Preliminary investigation of flow-driven brushes for removal of soft biofouling accumulations (primary slimes) from the internal surfaces of seawater cooled heat exchanger tubes has been completed. The cleaning ability of a commercial system was measured with single tube heat transfer monitors. The evaluation indicates that flow-driven brushing every 8 hours will maintain an acceptably low fouling resistance (less than 0.0005 $\frac{\text{ft}^2\text{-hr-}^\circ\text{F}}{\text{BTU}}$) in cylindrical titanium tubes but not in aluminum alloy tubes of the same configuration. Plans for an evaluation of chlorination as well as continued investigation of mechanical cleaning techniques are discussed.

INTRODUCTION

Due to the low temperature difference between seawater and the working fluid in OTEC heat exchangers, a large heat transfer coefficient must be maintained. It has been estimated[1] that only fouling resistances smaller than 0.0005 $\frac{\text{ft}^2\text{-hr-}^\circ\text{F}}{\text{BTU}}$ can be tolerated before the economic advantage of the OTEC plant would be lost. Cleanliness of the heat exchanger tubes is, therefore, a critical operational requirement of the OTEC concept.

Among the various cleaning techniques that have been recommended for maintaining the required level of cleanliness[2] are three methods which are presently being investigated in Panama City, Florida. These are: flow-driven brushes, recirculating sponge balls, and chlorination. Although each technique has its problems, they share the principal advantage of being in situ systems which require limited maintenance. This paper reports the results of a preliminary evaluation of one of the mechanical cleaning methods: flow-driven brushes.

TEST SITE CHARACTERIZATION

Panama City and the Naval Coastal Systems Center (NCSC) test site are located on the shores of St. Andrew Bay, a modest stream-fed estuary which empties into the Gulf of Mexico approximately 230 nautical miles (420 km) east of New Orleans. The Bay was formed during the Holocene Transgression (3000 to 20,000 years ago) when seas rose to their present level and flooded the tributary valleys of the local stream system. Greatest depths are thus generally found within meandering channels located along the central axis of each of the three arms of the Bay. The central portion of the Bay upon which the test site is located varies from 35 to 50 feet (10.6 to 15.2 m) in depth. This unusual depth is one unique characteristic of the St. Andrew Bay System among all bays on the Gulf Coast[3].

Another unique feature of the Bay is its limited freshwater feed source which contributes to the unusually high salinities recorded at the test site. Other water quality parameters of the Bay were described in 1972[4] and 1975[5]. More recently, Salsman and Ciesluk[6] reported on environmental conditions in coastal waters near Panama City.

Data from the test site itself have been recorded for the past 5 years by Braswell and Lott[7]. During the course of this study, site characterization was undertaken by NCSC contractors (see Acknowledgements).

Measurements of selected water quality parameters are presented for the study period in Table 1. For future studies, measurements of these same parameters are continuing under the direction of Dr. David C. White of Florida State University. Upon completion of biological analyses, tests of correlation between site characteristics, biological analyses, and fouling resistances will be possible.

Presently, these data describe near-oceanic conditions typical of a well-flushed, deep water estuary. Salinities average above 30 o/oo, and turbidities are very low for inshore waters. Dissolved oxygen levels, biochemical oxygen demands, and nutrient values (nitrates and phosphates) indicate a nonpolluted test area. Measurements of total carbon, ATP (adenosine triphosphate), and bacterial counts are moderate, indicating a nonpolluted near-ocean environment with a healthy microbial community.

Predictably, primary film formation is rapid at the test site. Bacterial films will begin to form within a few hours on static panels exposed at the site for a few hours, and progress to a noticeable layer within a few days. Taxonomic studies of bacteria from film samples on static panels exposed at the site have been conducted by O'Neill[8].

PLANNING AND DESIGN OF EXPERIMENTS

Evaluation of the effectiveness of various mechanical cleaning techniques, including flow-driven brushes, was planned by engineers of the David W. Taylor Naval Ship Research and Development Center at Annapolis (see Acknowledgements). Plans for the evaluation and details of the test apparatus have been thoroughly reviewed by Fritsch et al.[1] Methods of measuring the filmside heat transfer coefficient which were developed at Carnegie Mellon University (CMU) were modified to achieve improved performance. Although the modifications were designed to enhance studies with both smooth and extended surface tubes, only smooth-walled tubes have been tested to date.

Seawater is supplied to test sections from an intake depth of approximately 7 feet. To eliminate tidal and temperature fluctuations, a two stage pumping system first supplies a 750 gallon (2839 1) fiberglass feed tank. From the feed tank, seawater is pumped to a main header which supplies the individual heat transfer units.

FLOW-DRIVEN BRUSH CLEANING SYSTEM

Each tube is supplied with a brush approximately 2 inches in length and slightly larger in diameter than the tube inside diameter. As the brush passes through the tube a shearing force is exerted against fouling material

Table 1. Site Characterization Data for OTEC Heat Exchanger Cleaning Tests

PARAMETER	MEAN VALUE (X)			
	September	October	November	December
Conductivity (mmhos/cm)	42.81	44.54	44.82	39.31
Salinity (ppt)	26.54	30.75	31.88	30.99
Temperature (°C)	28.19	22.94	21.32	16.05
Acidity (pH)	7.6	7.9	7.6	7.8
Turbidity (NTU)	1.7	1.7	1.3	0.93
Dissolved Oxygen (PPM)	4.7	6.9	6.6	7.3
Biochemical Oxygen Demand (PPM)	2.08	2.97	3.4	3.2
Nitrogen, Ammonia (mg N-NH_3/L)	0.012	0.005	0.010	0.013
Nitrogen, Nitrate (mg N-NO_3/L)	0.002	0.004	0.003	0.003
Phosphate, Phosphorus (mg P-PO_4/L)	0.034	0.040	0.008	0.059
Total Organic Carbon (mg C/L)	521	442	615	2806*
Adenosine Triphosphate (mg ATP/L)	3.334×10^{-3}	8.732×10^{-4}	1.147×10^{-3}	4.86×10^{-4}
Total Bacteria (cfu/mL)	3076	5973	554	1382

*A single high value (7300 mg/L) recorded on 12/12 resulted in this unusually high mean. Excluding this value gives a mean of 558 which is consistent with other values shown.

on the tube wall. The brush is propelled through the tube by seawater from the main header. Flow may occur in either the forward or reverse direction depending upon the position of a three-way ball valve. To allow flow reversal, a variable timer simultaneously actuates motors controlling two of these valves.

At each end of the tube, a nylon basket traps and holds the brush until flow is reversed. A flowmeter to monitor seawater velocity and a modified CMU device to monitor heat transfer coefficients feed data to a DEC 1134 computer, the test control unit.

Cleaning Schedule

Manufacturer's recommended cleaning schedules were followed for these experiments. Flow was reversed every 8 hours in the flow-driven brush system. A double reversal was effected on this schedule, allowing the brushes to pass down the tubes and return at the end of each 8-hour interval. Plexiglas viewports at each end of the system allowed operators to verify motion of the brushes. The experiments were conducted over a period of 3 months from mid-September to mid-December 1978. One aluminum (alloy 5052) and one titanium pipe were cleaned during this period.

Controls

Four control units were fed simultaneously from the same seawater header. Each unit consisted of an aluminum or titanium pipe equipped with a flowmeter and modified CMU device. One aluminum and one titanium control unit were cleaned daily, while a second pair of the same metals were allowed to foul freely.

Cleaning was effected by 20 passes of a nylon-bristle bottle brush on an extended handle. The brush was designed to tightly fill the tubes being cleaned, hence a considerable shear force was exerted on the tube walls. Daily cleaning was calculated to ensure that the fouling layer thermal resistance in the controls did not exceed 0.0005 ft^2-hr-°F/BTU (0.0001 hr-m^2-°C/K_{cal}).

Biological Test Sections

Biological test sections were placed immediately downstream of the free-fouling controls. These consisted of identical aluminum and titanium piping which was pre-scored on the exterior to facilitate removal of samples for tests. Tests included sections for lipid analyses, ATP (adenosine triphosphate) assays, alkaline phosphatase measurements, and scanning electron microscopy. Details of these biochemical and biological tests will be presented elsewhere.[9]

RESULTS

Test units were labeled Tube 1 through Tube 6:

Tube 1	Control, cleaned daily (6061 Aluminum)
Tube 2	Control, cleaned daily (Titanium)
Tube 3	Control, not cleaned (5052 Aluminum)
Tube 4	Control, not cleaned (Titanium)

Tube 5 Flow-driven brush system (5052 Aluminum)
Tube 6 Flow-driven brush system (Titanium)

Results of fouling resistance measurements for each tube are presented in Figures 1 through 6. These graphs include data from the entire 3-month test period. However, during this period, problems with computer software and retrieval of information from magnetic storage discs resulted in the loss of some data points. The total data recorded consisted of measurements each 30 minutes, or 48 data points per day for the 3-month period. The portion of total data available to construct these graphs yielded an abundance of points for unbiased estimates of the fouling resistance over that period of time.

Although values in these graphs may occasionally drop below zero, the strongly negative results shown in Figure 1 are not considered meaningful (see Discussion).

DISCUSSION AND CONCLUSIONS

Thermal resistance between the seawater flowing through the tubes and the temperature sensor in the tube wall is estimated from a Wilson plot[10]. The method is generally accurate, but it has certain limitations for fouling studies. In addition to the problems cited by Fritsch et al.,[1] initial formulation of the plot may suffer from the amount and accuracy of data available.

The strongly negative values shown in Figure 1 for Control Tube 1 are believed to result in part from inadequate Wilson plot parameters. In addition, the vigorous daily cleaning to which this aluminum tube was subjected may have removed oxide layers from the tube wall. This repeated scouring of the pipe surface may have resulted in an actual decrease in the thermal resistance of the pipe after the Wilson plot was taken. Hence values based upon the original plot may become negative.

Cleaning of Tube 1 was abandoned late in the test period to study the problem resulting in negative data for the tube. The fouling resistance values then increased to a considerable degree, but remained negative throughout the study. This evidence indicates that both wall scouring and a faulty Wilson plot were responsible for offsetting Figure 1 to yield negative values. Calculations are continuing in an effort to better understand the data and correct the offset in this graph.

Conversely, Figure 2 (the companion control for the titanium pipe) shows the results expected for a tube cleaned daily. The fouling resistance of this tube was maintained near 0.0001 ft^2-hr-°F/BTU for most of the study period. This was well within the range sought for this experimental control (<0.0005 ft^2-hr-°F/BTU). Removal of an oxide layer, which is believed to be partially responsible for the negative data for aluminum Tube 1, apparently was insignificant in the vigorously cleaned titanium tube.

It is significant that a fouling resistance indicative of a small thermally resistant layer was maintained despite the vigorous cleaning. The nature of this layer was not determined. The pipe wall appeared clean upon visual inspection and in borescope photographs taken after the test. The authors feel that the material was most likely inorganic since it is unlikely that much biological material could have remained after such rigorous cleaning.

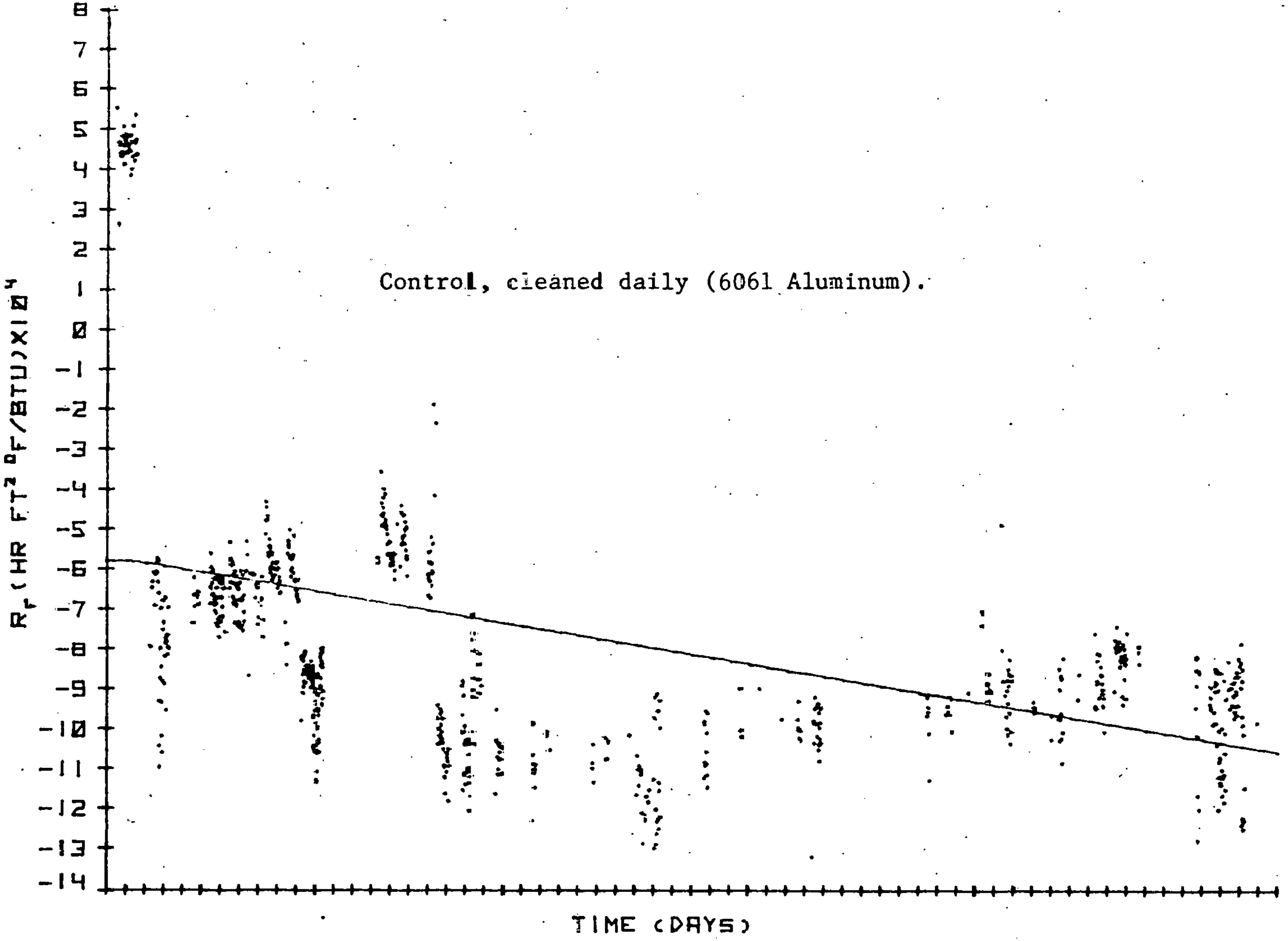
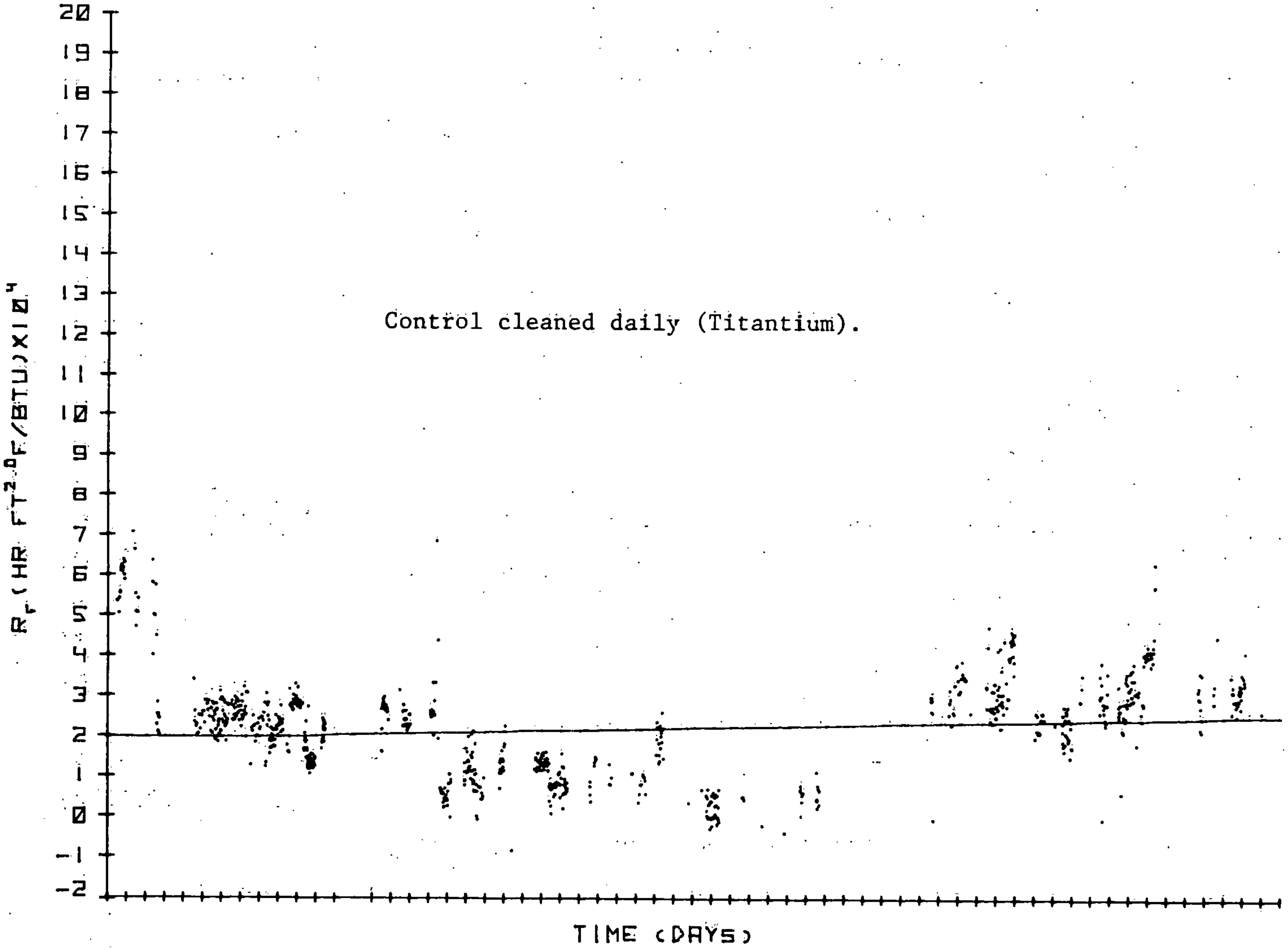
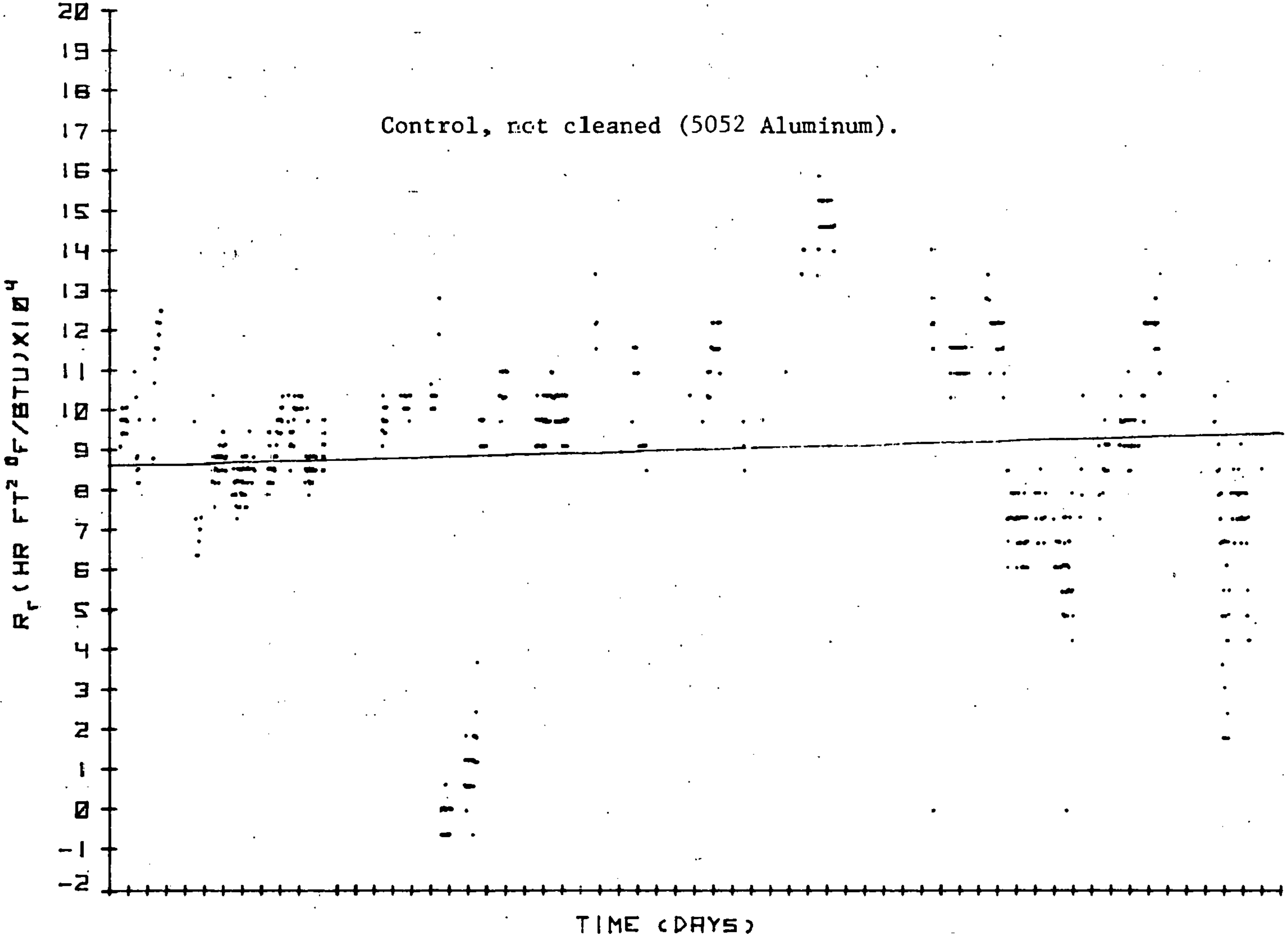


Figure 1 - Thermal Resistance (R_f) vs Time for Tube 1



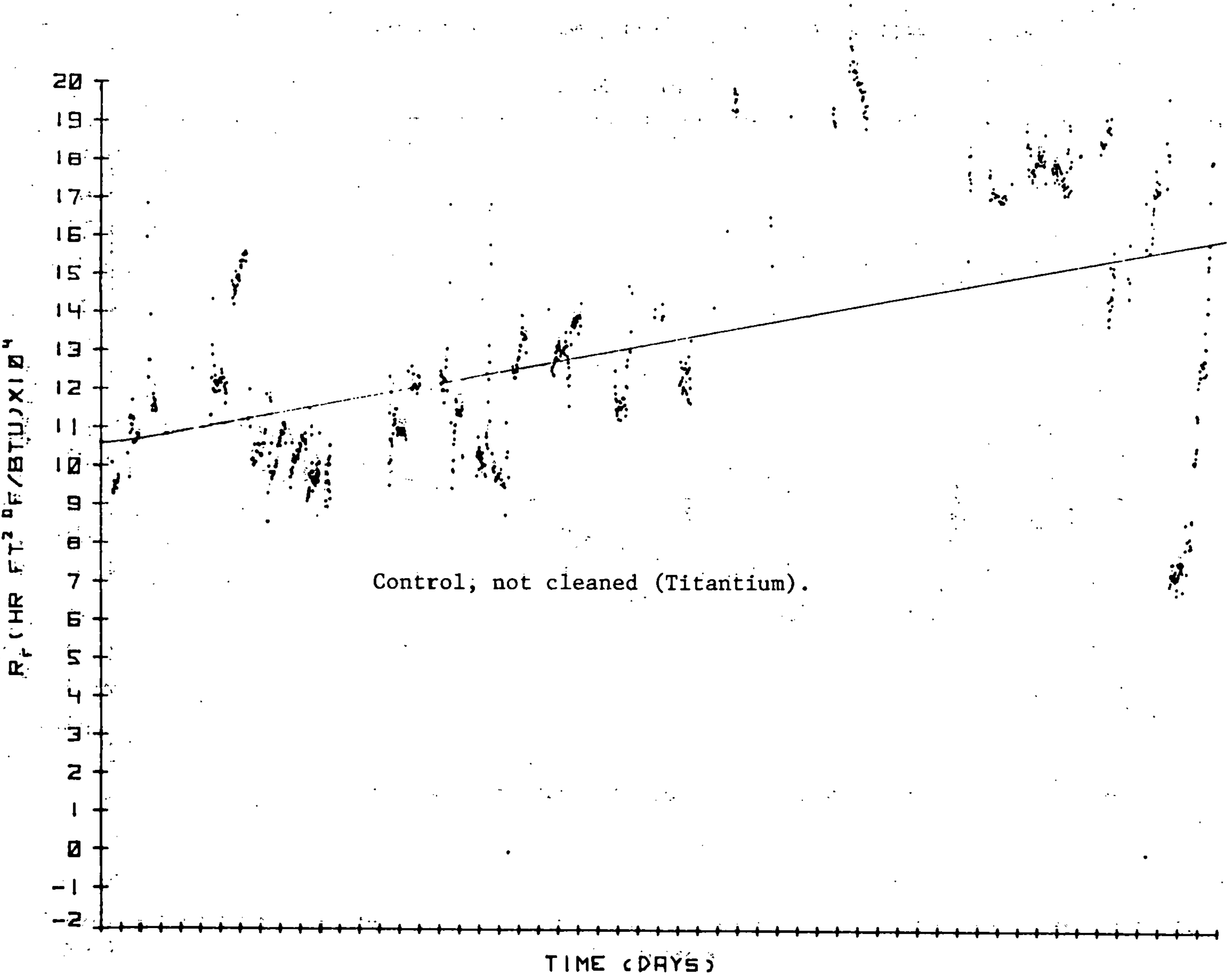
Control cleaned daily (Titantium).

Figure 2 - Thermal Resistance (R_f) vs Time for Tube 2



Control, not cleaned (5052 Aluminum).

Figure 3 - Thermal Resistance (R_f) vs Time for Tube 3



Control, not cleaned (Titantium).

Figure 4 - Thermal Resistance (R_f) vs Time for Tube 4

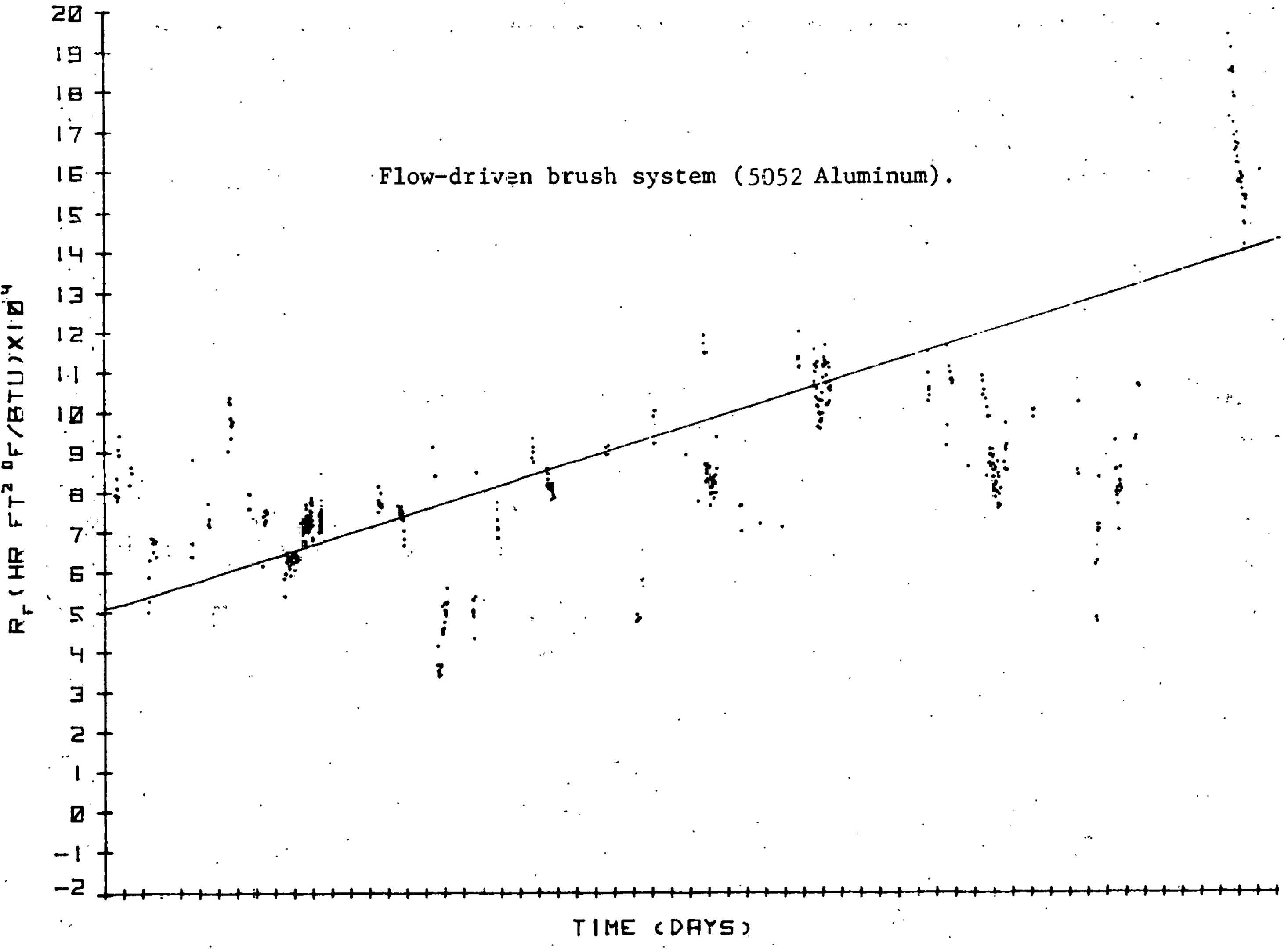
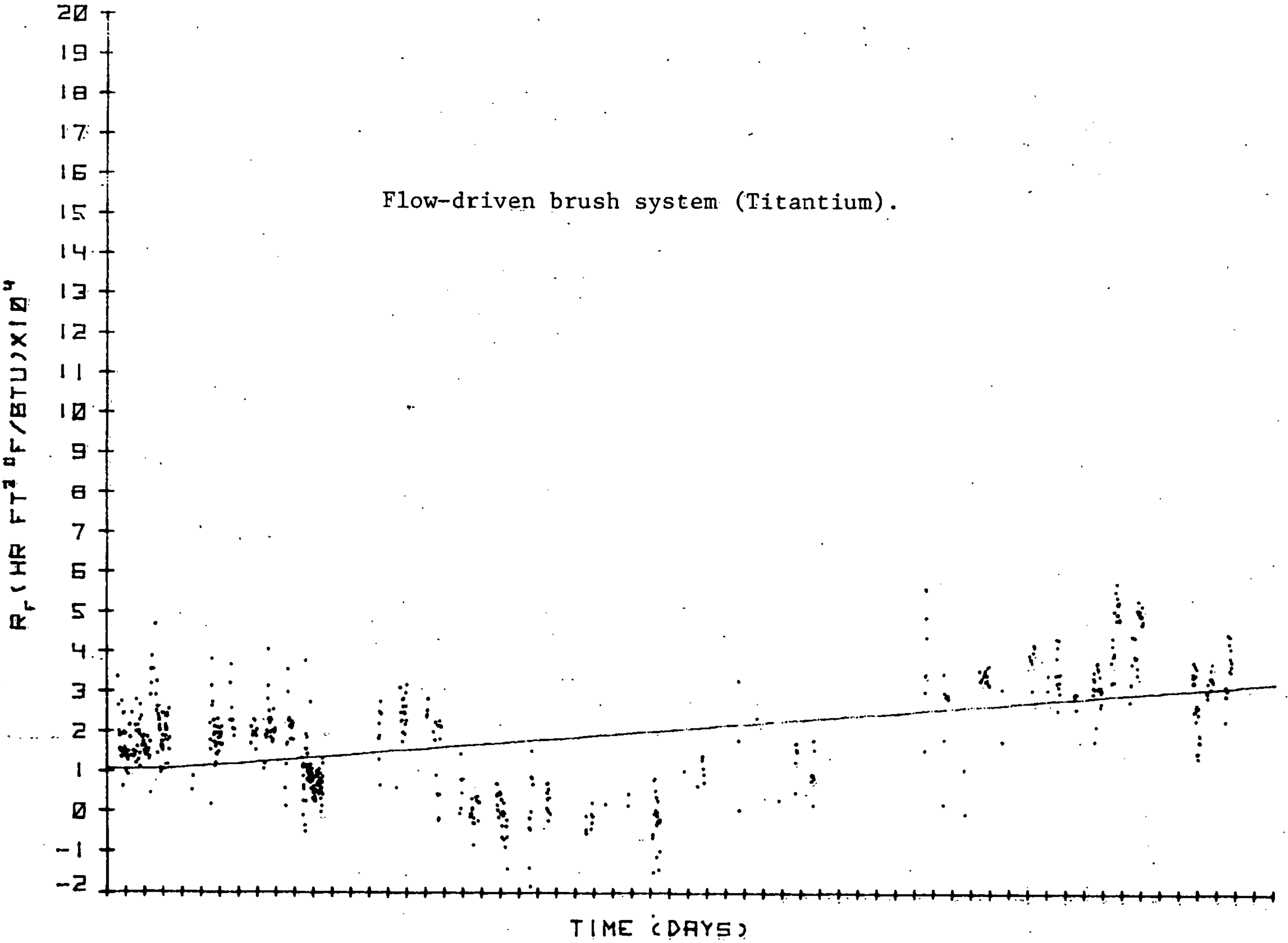


Figure 5 - Thermal Resistance (R_f) vs Time for Tube 5



Flow-driven brush system (Titantium).

Figure 6 - Thermal Resistance (R_f) vs Time for Tube 6

Figures 3 and 4 (Tubes 3 and 4, the free-fouling controls) also showed results which were close to those anticipated. The fouling resistance increased to high levels, and a thermally resistant layer was maintained throughout the test period. Variations in the fouling resistance occurred suddenly, and appeared to indicate occasional sloughing off of portions of the fouling film.

Comparison of Tubes 3 and 4 is of interest since it appears that titanium fouls more rapidly and to a greater extent that does aluminum. This observation is confirmed by the biological data as well as the measurements of thermal resistance. Results obtained over the 3-month period generally indicate higher values for alkaline phosphatase, TOC (total organic carbon), and ATP (adenosine triphosphate) from titanium pipe sections. At the conclusion of the test, substantial soft fouling layer could be seen in each pipe (Tube 3 and 4) and appeared on borescope photographs.

Tubes 5 and 6, cleaned by the flow-driven brush systems, were, of course, the units of greatest interest in these experiments. Although the experimental procedure was reviewed and approved by the manufacturer before and after the tests, several factors which may not be involved in an evaluation for OTEC applications were noted. First, both the types and quantity of fouling organisms at the test site may differ significantly from the flora and fauna of a potential OTEC site. Presumably bacterial genera which constitute the primary film formers at these flowrates (6 ft/sec) do not differ significantly.[8] However, the concentration of these microorganisms is much greater at this shallow-water, inshore test site than at a potential OTEC deep-water intake. Secondly, the design of the test apparatus created low velocity areas near the test pipe. In these areas, such as the viewports surrounding the nylon cages at the ends of the pipes, substantial macrofouling could occur. These communities directly affected the operation of the brush cages, and also contributed to the volume and composition of debris passing through the tubes. Though some low velocity areas will inevitably occur in the design of an OTEC plant, their proximity to, and influence upon, the heat exchanger tubes would predictably be less dramatic than the oyster-dominated communities in the NCSC test apparatus.

The buildup of debris from these communities completely stopped the movement and cleaning action of the brush in Tube 5 (the aluminum pipe). Fortunately, the obstruction of this brush occurred near the end of the experiment, and valid results were obtained for a suitably long test period (approximately 2-months). However, both brushes exhibited an accumulation of debris that would not be expected in a normal OTEC operation.

Despite the accumulation of foreign material in the brushes, both systems showed a substantial degree of cleaning effectiveness. In Tube 6, the titanium tube, the flow-driven brush satisfied the manufacturers claim, and maintained a fouling resistance near 0.0001 ft^2-hr-°F/BTU throughout most of the test period. Visual inspection and borescope observations of this pipe at the end of the 3-month test period confirmed that Tube 6 was shiny and clean on the interior.

The system was somewhat less effective for the aluminum pipe (Tube 5). Even before the brush became stuck in its nylon cage, fouling resistance in

Tube 5 began to exceed the acceptable limit (0.0005 ft^2-hr-°F/BTU). Visual inspection and borescope observations of this tube revealed a noticeable film at the end of the test. Even after hand brushing and chemical cleaning (sodium hydroxide followed by nitric acid) the interior of this tube exhibited a hard scale. This residue may indicate that the fouling resistance in this aluminum tube was due primarily to inorganic deposits.

Although the flow-driven brush system performed well in this evaluation, there was some evidence of brush fatigue even at the end of this relatively short test period. Measurements of bristle length before and after the test indicated an average decrease of 0.014 inches (0.34 mm) in bristle length. Microscopic examination revealed a distinct flattening of the bristle ends due to wear. Over the extended life of an OTEC plant, bristle wear may become a significant factor in the effectiveness of this brushing system.

FUTURE WORK

Further tests of flow-driven brushes for removal of soft fouling from OTEC heat exchangers are being planned. In addition, evaluation of a recirculating sponge-ball cleaning system has been scheduled. Both techniques will be conducted on smooth-walled cylindrical pipes of titanium and aluminum. Low levels of chlorination will be evaluated in combination with each cleaning technique. If time permits, the tests will be expanded to include stainless steel and copper-nickel alloys as possible heat exchanger materials.

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A REVIEW OF WATER INTAKE SCREENING OPTIONS FOR COASTAL WATER USERS WITH RECOMMENDATIONS FOR OCEAN THERMAL ENERGY CONVERSION (OTEC) PLANTS

by

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ABSTRACT

The large volumes of water withdrawn at both the warm and cold water intakes of an OTEC plant must be screened to remove organisms and debris which could clog the heat exchangers. This paper reviews the recent literature on screening technology. In addition, various screen manufacturers and coastal facilities which use large volumes of seawater were visited to determine the operating experience with present screen technology. Static screens (particularly the Johnson Division, UOP profile wire screen and the Royce Equipment Company carrousel screen) have the potential advantage for OTEC of operating in a completely submerged state and of being cheaper to operate and maintain than traveling screens. However, there is no operational history with these static screens for large intake systems. The most promising traveling screen options for OTEC are the dual flow screens. They offer more screening surface and less head loss than through flow screens of similar size. They also have been operated in seawater for large intake systems. More detailed designs of potential OTEC plants, particularly screen wells, conduit and surge tank construction and head losses need to be determined before the best alternative intake screen can be selected.

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I. INTRODUCTION

Ocean Thermal Energy Conversion (OTEC) plants will require large volumes of water to generate electrical power. The projected water demand for OTEC-1 (a 1-MWe test unit) is 4,290 liters/sec or 68,000 gpm (gallons per minute) for the condenser and 3,785 liters/sec (60,000 gpm) for the evaporator. A Lockheed design for a 92-MWe module requires 384,858 liters/sec (6.1 million gpm) for the condenser and 410,094 liters/sec (6.5 million gpm) for the evaporator. Warm seawater (26.7-29.4 C) for the evaporator will be extracted at a depth of 6.1 to 30.5 m (20 to 100 ft); cold seawater (3.3-4.4 C) for the condenser will be taken at approximately 975 m (3,200 ft; Gilbert/Commonwealth[1]).

The large volumes of water withdrawn at both the warm and cold water intakes of an OTEC plant must be screened to remove materials which could clog the heat exchangers. The screens should also be designed to minimize the impact to marine organisms which may collect on the screens (impingement) or pass through the plant (entrainment). Both entrainment and impingement are a function of the screen mesh size, volume of water withdrawn and intake location although impingement is also a function of intake water velocity.

Most coastal electric generating stations employ vertical traveling screens, which use wire mesh openings of 9.5 mm (3/8 inch). They are generally operated on an intermittent basis. Fish and debris frequently are collected on site and then disposed of off site. Recent environmental regulations including the Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500) require cooling water intake structures to reflect the best technology available for minimizing adverse environmental impact. Section 316(b) of this act outlines requirements for a document to be submitted to the Environmental Protection Agency (EPA) which discusses the extent and significance of losses due to entrainment and impingement by an industrial water user. As a result of these regulations new screening techniques may have to be developed or older systems improved to provide environmental protection and good operational performance in new generating stations. This is also true for OTEC plants which require much larger water volumes than conventional generating stations.

This paper includes information on static and traveling water intake screen technology. Reviews of present screening options for power plants were presented by Riesbol and Gear[2]; Sonnichsen et al.[3]; Hanson, White and Li[4]; Richards[5]; O'Keefe[6]; and Mussalli, Taft, and Hofmann[7]. The recent literature on screening technology as related to OTEC was also reviewed and included papers by Thomas and Bason[8]; Gilbert/Commonwealth[1]; Nath et al.[9]; and Hansen[10]. Thomas and Bason[8] reviewed static screen options for water intakes and their applicability to OTEC. Nath et al[9] and Hansen[10] presented an overview of projected biological problems at potential OTEC sites, reviewed various screening systems and made cost estimates for some. In addition to the literature review, various screen manufacturers and coastal facilities which use large volumes of seawater were visited to determine present available screen technology and actual operating experience. Information from the above sources was used to discuss potential options for OTEC test modules and a commercial plant.

II. STATIC SCREEN OPTIONS FOR WATER INTAKES

Static screen options for water intakes were discussed by Thomas and Bason[8] and included fixed wire-mesh screens, perforated pipes and plates, various filtering systems such as the radial well intake, Johnson Division, UOP profile wire screens, and the Royce Equipment Company carrousel screen.

Static screens have the potential advantage for OTEC of operating in a completely submerged state and of being cheaper to operate and maintain than traveling screens. They have the disadvantage of being difficult to service while submerged and the potential for collapse if they cannot be effectively backwashed and cleaned of organisms and debris. They also do not have an operating history with large volumes of seawater.

A problem with all screen systems is that larvae of macrofouling organisms pass through the mesh and then settle on the intake conduit and elsewhere in the water system. With static screens the screen surface also becomes fouled and the inner surface of the screen may be particularly difficult to clean.

Fixed wire-mesh screens are used at some electric generating stations. They require periodic removal for manual cleaning and maintenance, and most impinged organisms are killed. When removed, material and organisms in the water can enter the plant and potentially clog the condensers. Ansuini et al.[11] discussed the use of fouling resistant copper screens for OTEC, based on technology and components previously developed for aquaculture containment systems.

The perforated pipe intake consists of a submerged pipe with numerous small holes or slots through which water is drawn. One drawback is that the more openings or the greater the area of openings the weaker the pipe becomes structurally.

The Johnson profile wire screen is fabricated in cylindrical form by helically winding and welding V-shaped profile wire to evenly spaced support rods (Fig. 1). This construction results in a smooth external screen surface with a continuous slot which enlarges inwardly (Thomas and Bason[8]). This smooth, curved external surface allows debris and small organisms to be washed off the surface by ambient currents (Fig. 2). Heavy macrofouling growth must be mechanically removed from both the outside and inside screen surface to prevent clogging. Loosely impinged material is cleaned off by backflushing with air or water (Hanson et al.[12]).

Air backflushing can be accomplished by the release of compressed air into the screen. Both this system and backflushing with water require that the pumps be shut down or the water flow reversed. If the MAN brushes are used for cleaning of the condenser tubes then flow reversal could be used to clean both the condensers and the intake screens. Recent research has and is being conducted on Johnson screens and they are being considered for a number of electric generating stations.

The Royce carrousel screen represents another static screen option. This screen is also circular and the wire mesh is made of "Smooth-Tex", a woven mesh which has a smooth external surface to facilitate removal of fish and debris. Vanes within the screen and a bypass system where water is pumped past the screens will create a current vector along the wire mesh surface which should remove organisms and debris. This screen is still in the development stage and research with it is just beginning.

The Johnson profile screen is considered the most promising of the static screen options (Thomas and Bason[8]). It is potentially the most environmentally sound screening system. However, both this screen and the carrousel screen need testing with relatively large volumes of intake water before they could be recommended for use in a commercial OTEC plant.

III. TRAVELING WATER SCREEN OPTIONS FOR WATER INTAKES

A. VERTICAL TRAVELING SCREENS

Four traveling screen manufacturers were visited: Envirex, FMC-Link Belt, Royce Equipment Company, and Passavant Corporation. All make screens for electric utilities, chemical plants, waste treatment facilities (microscreens and filtration systems), paper mills, and other water users.

Most manufacturers provide primarily the conventional (through-flow) traveling screens. These screens are perpendicular to the water flow and water passes through both the ascending and descending screen panels. Fish and debris are lifted from the water on the ascending side and are washed into one or two troughs on either the front or back side of the screen (Fig. 3).

These manufacturers also provide dual flow (double entry, single exit) traveling screens, particularly for the overseas market. These screens are placed parallel to the screen well walls and to the incoming water (similar to the Passavant screens). However, water flows inward through both the ascending and descending screen panels toward the center of the screen and then out the rear to the pumps (Fig. 4). A modification to this screen system is FMC's No-Well screen (Fig. 5). This screen is suspended in the water from a platform, and is free on the sides and bottom.

Passavant provides a single entry, double exit, screen (centerflow screen). Water enters the center of the screen and then exits through both the ascending and descending screens (Fig. 6). This system has the baskets parallel to the walls of the screen well and to the incoming water flow.

B. MATERIALS AND CONSTRUCTION CONSIDERATIONS FOR TRAVELING SCREENS

The above manufacturers use a variety of screen materials. Most use a screen mesh material of 304 or 316 stainless steel of 9.5 mm (3/8 inch) diameter opening; monel wire is used extensively in salt water. Passavant has used primarily a polyester, nylon, or nytex weave of 0.5 - 1 mm (0.02 - 0.04 inch) mesh opening. Other materials used include copper-nickel and PVC.

The screen frames are made of materials including mild steel, stainless steels, and aluminum-bronze. In salt water many exposed metal surfaces are covered with a coal tar epoxy coating. Sacrificial anodes are used on many screen panels, and some plants use induced current for corrosion protection.

Screen size is variable and depends on the particular needs of each plant. A standard through-flow screen might be 2.4 - 3.05 m (8 - 10 ft) in width and 6.1 - 12.2 m (20 - 40 ft) deep. Screens are available up to 4.3 m (14 ft) in width but problems due to the screen weight plus detrital loading have occurred with this size screen. Most manufacturers prefer their screens to be 3.05 m (10 ft) or less in width. Depth is less important and some screens over 30.5 m (100 ft) deep have been manufactured. These are usually made for riverine locations where water depth is highly variable.

A clean screen will normally have a head loss of only 5.1 - 7.6 cm (2 - 3 inches). Most screens are designed to withstand a head differential of 1.5 - 3.05 m (5 - 10 ft). The recent trend is toward bigger, wider, and stronger screens. Some screens now are designed for a head differential of up to 4.6 m (15 ft) and require that the whole screen be reinforced and have heavy duty parts. As with many other features of screens, there is a wide latitude in design.

Traveling screens may run intermittently (either on a timer or when the head differential across the screen reaches a certain level) or continuously. Continuous operation is usually used when debris loading is heavy or with some fish protection systems. Most screens have a dual drive mechanism and will operate at either low, 0.6 - 1.5 m/min (2 - 5 ft/min), or high, 3.05 - 9.1 m/min (10 - 30 ft/min), speeds.

Traveling screens are cleaned by water sprays. Those screens with a fish protection system usually have a light 13.8-69 kN/m^2 (kilometer per square meter; 2 - 10 psi) spray for fish and a heavy (413.8 - 758.6 kN/m^2; 60 - 110 psi) spray for debris. The through-flow screens have the spray header on the inside and wash debris either to the front or to the rear. The Passavant screen system has the header above the screen and washes materials into a trough which runs down the center of the screen (Fig. 6).

The volume of water withdrawn through an individual screen varies greatly. One of the largest flows per individual screen is with the Passavant system at a generating station in Europe: 20,820 liter/sec (330,000 gpm) through a screen with 62 panels. A typical through-flow screen at a large coastal facility might draw approximately 6309 liter/sec (100,000 gpm) per screen.

The number of screens used and the volume of water withdrawn per screen depends, in part, on the intake velocity. Most plants have intake velocities which range between 0.15 and 0.6 mps (meters per sec; 0.5 and 2.0 fps). In Europe, screens are designed for 0.9 to 1.2 mps (3 to 4 fps) velocities. In recent years, the EPA has recommended intake velocities of about 0.15 mps (0.5 fps) for fish protection, but in many situations velocities of 0.3 to 0.5 mps (1.0 to 1.5 fps) have proved adequate for fish protection. Velocities at a power plant intake usually vary widely between screens and over the surface of each screen.

The cost and delivery schedule for various screen systems depend on variables including screen size (width and depth which is dependent in part on low water depth), number of screens, screen materials, and intake volume and velocity.

C. OPERATIONAL EXPERIENCE WITH TRAVELING SCREENS AT COASTAL WATER INTAKE SYSTEMS

Three plants located on estuarine waters adjacent to the Gulf of Mexico were visited. They are large water users (over 63,091 liter/sec or 1 million gpm) and have numerous through-flow traveling screens to filter water.

All three plants have had their screens clog due to jellyfish, ctenophores, or fishes (particularly large schools of the Gulf menhaden, <u>Brevoortia patronus</u>). In one instance, an estimated 49,900 kg (55 tons) of menhaden were impinged in a 24-hr period; 53 screen panels had to be replaced. At one plant the water spray was not strong enough to remove large jellyfish which then had to be removed by hand.

These traveling screens were designed to run intermittently, either automatically by pressure differential or manually once an 8-hr shift. Steel portions of the screens were generally protected by coal tar epoxy paint. Sacrificial anodes were used to protect the screen mesh and other metal surfaces exposed to saltwater. The greatest biofouling problem at one plant was with colonial hydroids which at times grew so thick on the trash bars that the bars had to be mechanically cleaned once a week.

One coastal plant in Texas uses Passavant center flow screens. Each of the two, 325 MW units have two screens which pass a total of 21,451 to 22,713 liter/sec (340,000 to 360,000 gpm). Each screen has 53 panels. The screen mesh material originally was 0.5-mm (0.02 inch) polyester dacron but was recently converted to 1-mm (0.04 inch) nylon or nytex material. The screens rotate continuously at 4.3 to 8.5 mpm (meters per minute, 14 to 28 fpm) depending on debris loading.

This plant is located on high salinity water (30 - 55 ppt salinity) and exposed metal is protected cathodically. Some fouling occurred on the screen frames but in general biofouling has not been a problem. The major problem at this power station has been clogging of the screens and condenser tubes by marine grasses. The fine mesh screens were used to remove these fine grasses. They have an additional advantage because survival of impinged organisms is high.

A station on estuarine water in Florida uses the FMC No-Well screen. Each screen and pump provided 7571 liter/sec (120,000 gpm) of water. Two screens and two pumps are located on a single platform above the water and provide circulating water for each units condenser. The screens are about 2.1 m (7 ft) wide and 5.3 m (17.5 ft) deep. The pump is close to the screens and is connected to the screen wall by a few feet of suction pipe. The intake velocity averages about 0.3 mps (1 fps) but is highest near the bottom of the screen at the depth of the intake pipe to the pump.

The screen mesh is stainless steel and the lip of the screen panels is carbon steel. The system is cathodically protected. Occassional problems exist with heavy barnacle growth on the lip of the screen panels and with oysters which either grow or somehow pass to the inside of the screens. In addition, marine grasses and jellyfish have clogged the screens. The screens are run intermittently either once or twice during an 8-hr shift. Only minimal maintenance of the screens has been necessary although the screens are removed once a year for maintenance.

It is difficult to generalize from the operational experience at one industrial water user to what might be expected at another. The location of intakes, water quality, biofouling, detritus and nekton loadings on the screens, and frequency of rotation and maintenance vary from one plant to another. In many cases where a screen system has failed it is often due to its location in the water body or to improper maintenance. Most large coastal water users expend considerable man-hours each year maintaining their intake screening system. At times of heavy detrital or nekton loading on the screen, this may be a full-time job for a number of plant personnel.

IV. FISH PROTECTION SYSTEMS

A. MODIFICATIONS TO STANDARD TRAVELING SCREENS

Most traveling screens are designed to protect the plant of the industrial water user but not fish and other aquatic organisms. The screens are generally run intermittently sometimes only once or twice a day. Fish that are impinged on the screens may suffocate or they may fall off the screens and become reimpinged. Those which remain on the screens are usually removed by a high pressure (690 to 828 kN/m^2 or 100 to 120 psi) spray and along with debris are either collected for disposal or returned to the environment. Even with a fish return system, many organisms are killed by the screen operation described above or die shortly thereafter due to latent effects.

Important environmental modifications to the standard vertical traveling screen and its operation were made at the Virginia Electric and Power Company Surry Power Station in May 1974 (White and Brehmer[13]). These modified screens, made by Envirex, are known as the Ristroph traveling fish screens. Each screen had 47 screen panels which were each 4.27 m (14 ft) wide by 0.6 (2 ft) high. To the base of each panel was attached a trough which was 50.8 mm (2 inches) deep by 139.7 mm (5.5 inches) wide. This trough held water as the screen rotated upward and carried impinged organisms. The screen was run continuously usually at 3.05 m/min (10 ft/min). As the screen panels rotated over the top of the screen two low pressure sprays, 103 to 138 kN/m^2 (15 to 20 psi), one inside and another located outside the rotating screen, washed organisms into the collection trough. This trough contained water and returned the organisms to the water away from the intake. A high pressure spray can be incorporated below the fish trough which washes all the remaining materials into a debris trough. Materials from this trough may then be collected and dumped or they may be returned to the environment.

The advantages of these modifications to impinged organisms are many. Because the screens rotate continuously, organisms are impinged for minutes rather than hours. The troughs on the screen panels keep the organisms in water as the screen ascends and help prevent organisms from falling off the screen and becoming reimpinged. The low pressure sprays gently remove the organisms from the screens into the fish trough. At the Surry Power Station, the average survival of all species of fish for the first 18 months of operation was 93.3% (White and Brehmer[13]).

Other screen manufacturers also provide various fish protection and return systems. Some provide fine mesh screens (0.5 - 3 mm openings) so that some of the larger "entrainable" forms can also be removed in the fish return systems. Additional modifications have and will continue to be made on existing screen systems to reduce mortalities to impinged organisms. In most cases, each industrial water user makes modifications unique to their particular intake situation.

B. FISH GUIDANCE AND DIVERSION

Presently, most screens designed for fish guidance and diversion are experimental. However, they may have application in the warm water intake for OTEC. Important variables for fish guidance and diversion include screen or louver angle to flow; ambient, intake, and bypass velocities; and turbulence in front of the screens. Common ones that have been tried include the horizontal traveling screen, angled louvers, angled screens, and fish deterrent systems such as air bubble curtains, water and air jets, electricity, hanging rods or chains, loud sounds, and lights.

V. DESIGN AND OPERATIONAL CONSIDERATIONS FOR OTEC

A general overview of the OTEC concept and various proposed plant configurations is given by Griffin[14] and Avery[15]. Because detailed designs are lacking for the various OTEC plant configurations, it is difficult to make specific recommendations on the intake screening system. Hansen[10] stated that details of the screen well, conduit and surge tank construction, and head loss would need to be determined before the best intake screen could be selected.

The OTEC concept provides unique water-intake screening problems. The floating plant will have large submerged intakes that require large volumes of water. Most conventional power plants with large water requirements use vertical traveling screens at their intakes. The tops of these screens are out of the water where they can be serviced and cleaned. Those power plants and ships which use submerged intakes usually require relatively small volumes of water with low intake velocities. In the latter cases, a perforated pipe or fixed bar screen is usually adequate.

At present, the Department of Energy proposes to use sumps in the OTEC plant which will be located between both the warm and cold water inlets and the heat exchangers. These sumps would provide an air-water interface where conventional screening could be used. Hansen[10] recommended that an air-water surface be incorporated within the path of flow of both the cold and warm water systems so that state-of-the-art traveling screens could be used. He concluded that a coarse bar screen (trash rack) of 0.15-m (0.5-ft) openings would be needed at each intake and that either a through-flow or dual-flow vertical traveling screen of 9.5-mm (3/8 inch) mesh size, a through screen velocity of 0.46 m/sec (1.5 ft/sec), and water depth of 15.2 to 30.5 m (50 to 100 ft) be used in the sumps. A fish collection and return system would be needed for the warm water screen system to attempt to return impinged organisms alive to the environment. Most organisms in the cold-water system will be dead because of rapid pressure changes encountered in their transit up the pipe and their subsequent impingement on the screens.

Hansen[10] made annual cost computations for each screen arrangement (principally through-flow and dual-flow vertical traveling screens and Johnson profile wire screens) based on a 100-MWe OTEC plant with warm and cold water flows of 7075 m^3/sec (15,000 ft^3/s) each. At all intake depths the principle components of the total cost were the initial cost, head loss, and operational maintenance costs. For traveling screens, the most economical screen width was 3.05 m (10 ft) and total cost was optimized at an intake velocity of 0.46 m/sec (1.5 ft/sec). Many assumptions (i.e. pump sizes, head losses, impingement rates) were made to arrive at these costs and as more detailed designs become available, revised cost estimates should be made. The space requirements and cost estimates for very large sumps or surge tanks will have to be calculated along with the added weight of standing water and traveling screens internal to the plant.

State-of-the-art traveling screens were recommended for OTEC plants by Hansen[10]. He stated that there was little operational data on dual-flow screens. However, his dual-flow screens were No-Well screens; he did not discuss the Passavant center flow screen (single entry, double exit screen) which has an extensive operational history in Europe. Because head losses may be critical in cost considerations for OTEC, a dual-flow screen may be the most practical traveling screen to use.

Thomas and Bason[8] discussed static screen options for OTEC. They stated that the Johnson profile wire screens offered the best option among static screening alternatives for OTEC. If these screens are effective at the external inlets to the warm and/or cold water intakes they would eliminate the need for trash racks, internal sumps, traveling screens, and a fish and debris return system. They would also provide the most environmentally acceptable screening system by eliminating impingement and reducing entrainment of most nektonic organisms. The Royce carrousel screen might also be very effective. It could be made with woven copper or copper-nickel mesh to reduce fouling and should be lighter than the Johnson screen.

The OTEC-1 barge will require 3786 and 4290 liter/sec (60,000 and 68,000 gpm) for the warm and cold water system, respectively. For the proposed OTEC Seacoast Test Facility, about 606 and 404 liter/sec (9600 and 6400 gpm) would be required for the warm and cold water systems, respectively. It would not be worthwhile testing various traveling screens for these low volumes of water as all are presently being used in salt water for much larger flows. Static screen options, such as the Johnson profile wire screen and Royce carrousel screen should be tested because they could provide substantial cost savings over the life of an OTEC plant and would be environmentally acceptable.

VI. SUMMARY AND CONCLUSIONS

The large volumes of water withdrawn at both the warm and cold intakes of an OTEC plant must be screened to remove materials which could clog the heat exchangers. The screens should also be designed to minimize the impact to marine organisms which may collect on the screens (impingement) or pass through the plant (entrainment). New screening techniques may have to be developed or older systems improved to provide environmental protection and good operational performance in new generating stations such as OTEC.

Present screening options for water intake systems include a variety of static and traveling screens which were discussed in the paper. Static screens have the potential advantage for OTEC of operating in a completely submerged state and of being cheaper to operate and maintain than traveling screens. However, they do not have an operating history with large volumes of seawater.

Of the static screen options the Johnson Divison, UOP profile wire screen and the Royce Equipment Company carrousel screen have the best potential for OTEC. Recent research has and is being conducted on Johnson screens and they are being considered for a number of electric generating stations. The Royce carrousel screen is still in the development stage and research with it is just beginning.

The most promising of the traveling screen options for OTEC are the dual flow screens, particularly the Passavant Corp. traveling band screen and the FMC "No-Well" screen. Both offer more screening surface and less head loss than through-flow screens of similar size. They have also been operated in seawater for large intake systems.

Construction considerations for traveling screens and their operational experience at coastal water intake systems were discussed. A variety of screen sizes and materials are provided by screen manufacturers to meet a particular customers needs. Biofouling and corrosion cause some problems at coastal power plants. However, the greatest problem seems to be from the heavy loading of the screens by detrital material and aquatic organisms. Occassionally screen systems have collapsed in these situations.

Because water intake systems must reflect the best technology available for minimizing environmental damage various fish protection systems must be considered. If traveling screens are used a system should be incorporated which will return organisms impinged on the screens to the environment. The advantage of some of the static screen options is that if they are properly designed they may almost eliminate the impingement of organisms and can also reduce entrainment.

It is recommended that for OTEC-1 and the Seacoast Test Facility that one or more of the static screen options be used. Because these screens offer potential cost savings over the life of an OTEC plant and are environmentally acceptable they should be tested to determine their potential suitability for a commercial OTEC plant. The various traveling water screen options are presently being used at large coastal facilities and most have an extensive operational history. Little additional information would be gained by testing them for relatively small water intake systems.

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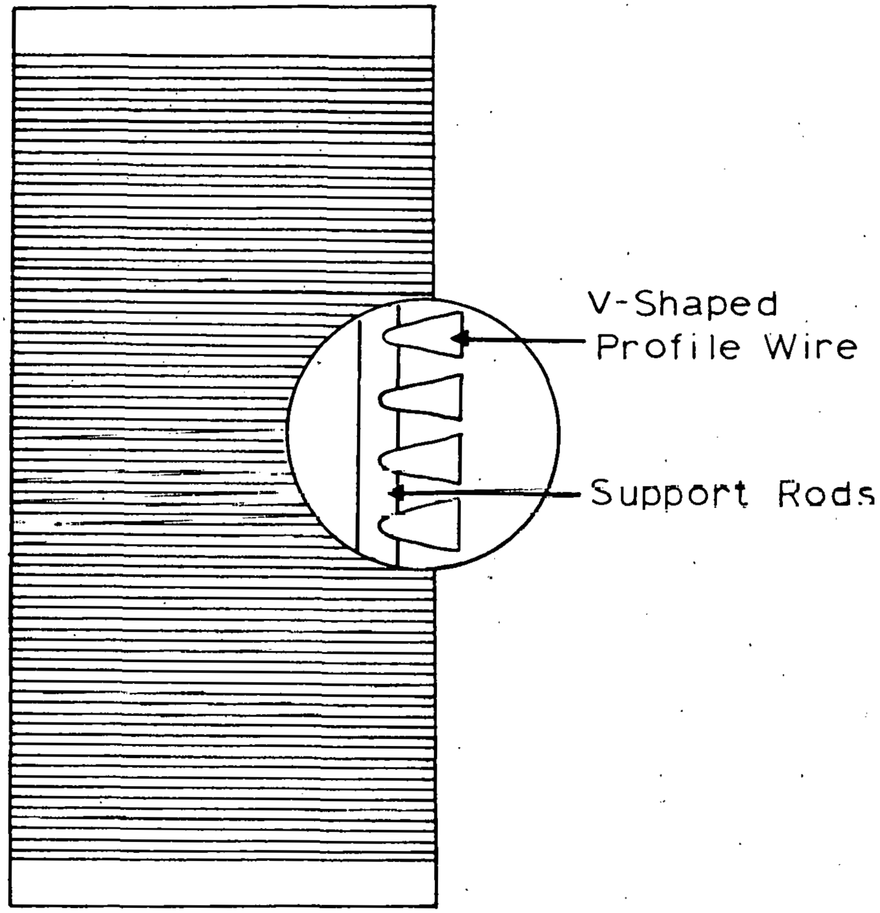
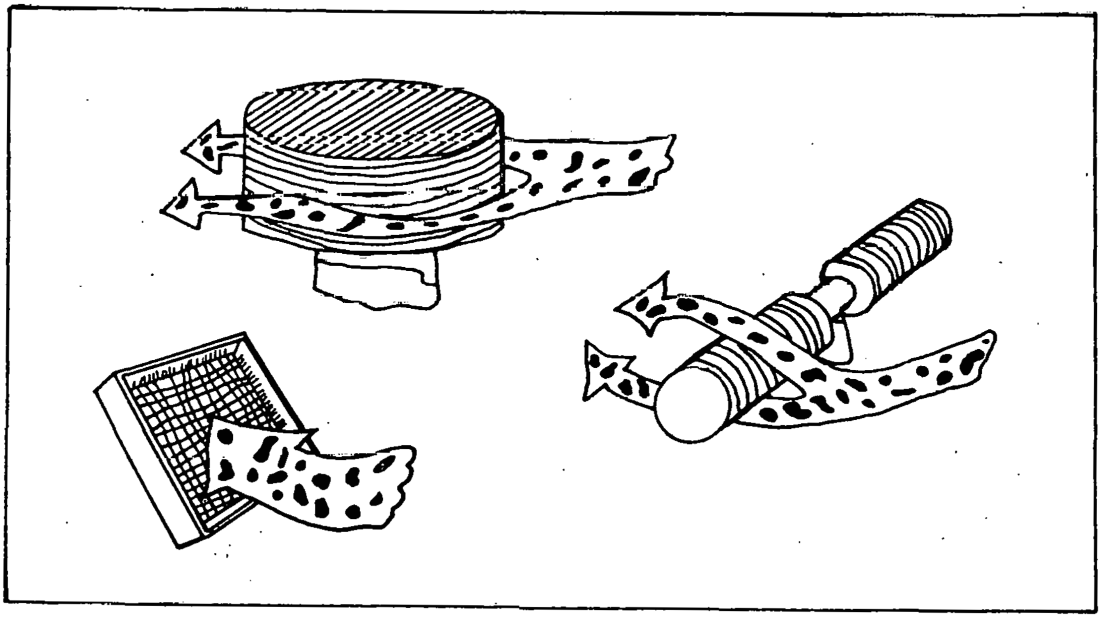
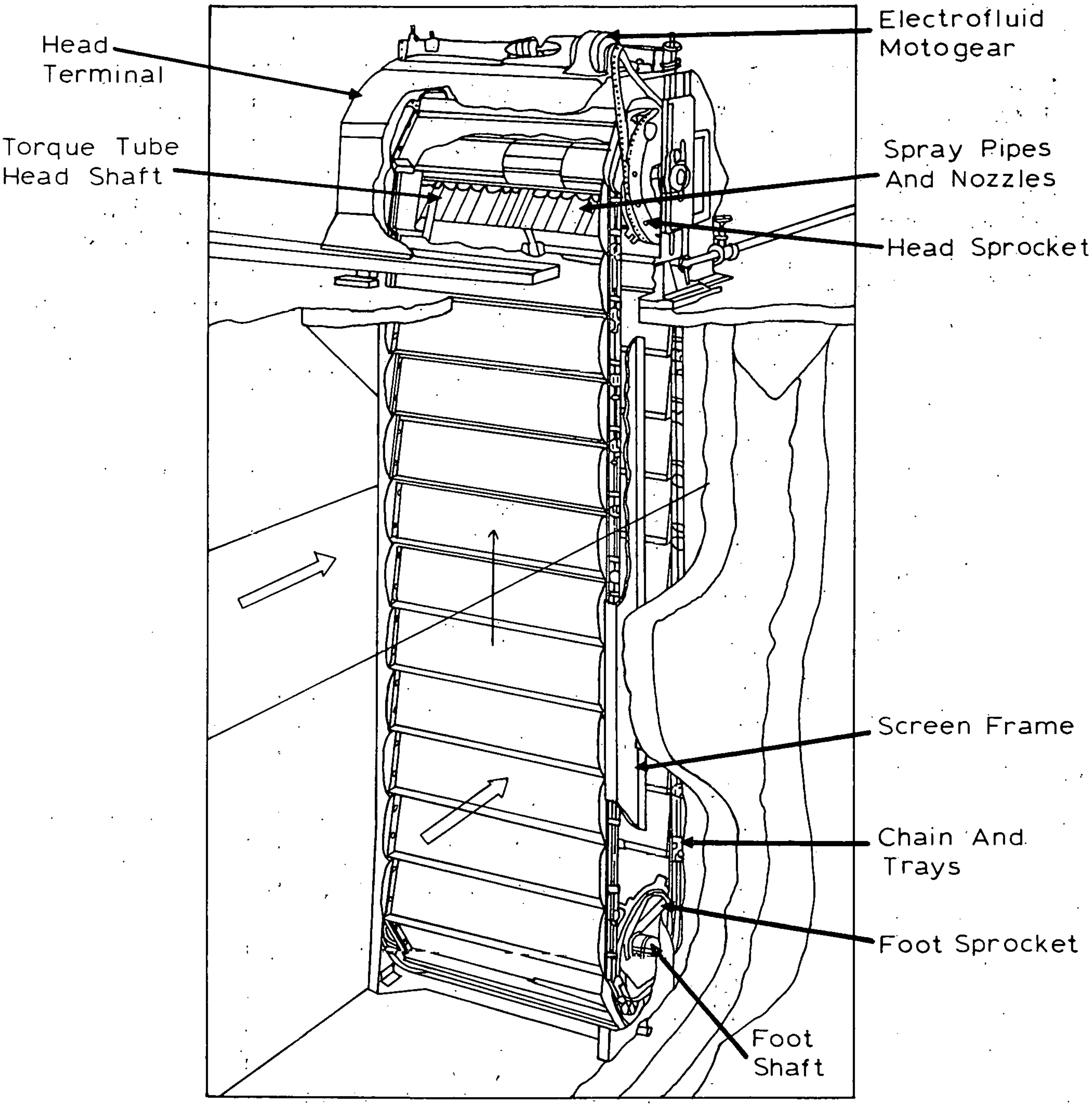


Cylindrical Johnson Profile-Wire Screen
(Hanson et al. 1978)
FIGURE 1



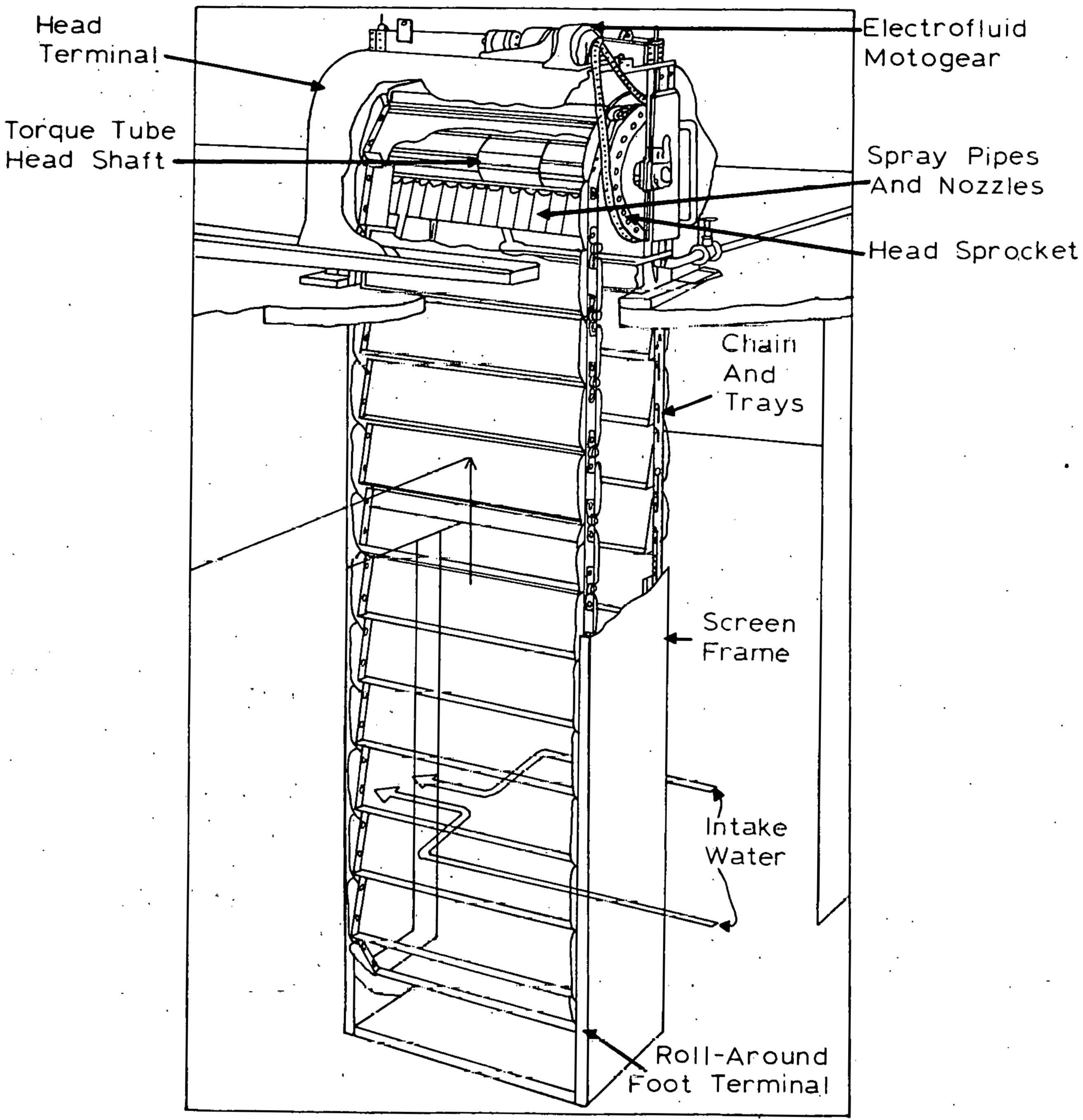
Johnson Intake Screens
(Johnson Div., UOP Inc.)
FIGURE 2



Thru Flow Traveling Screen

(FMC Corp.)

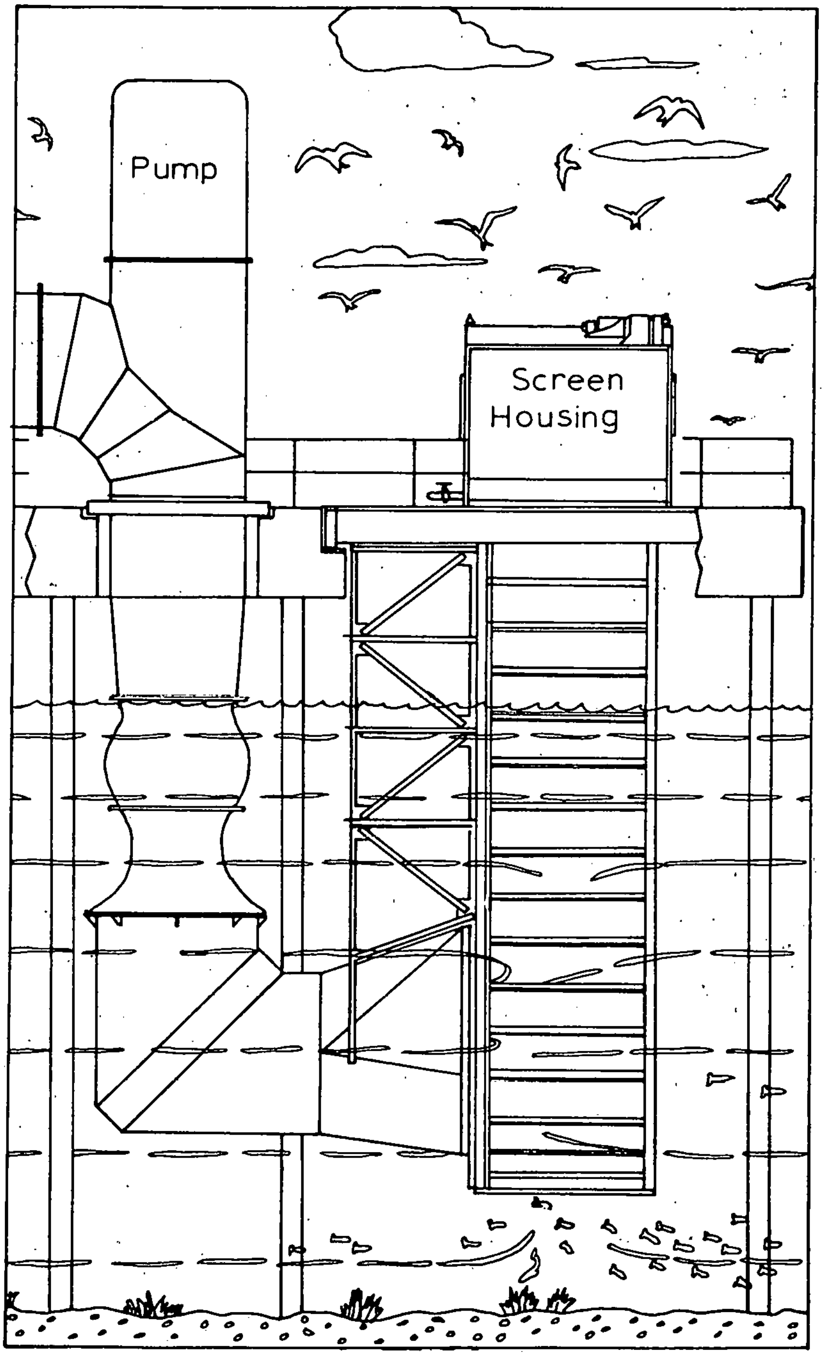
FIGURE 3



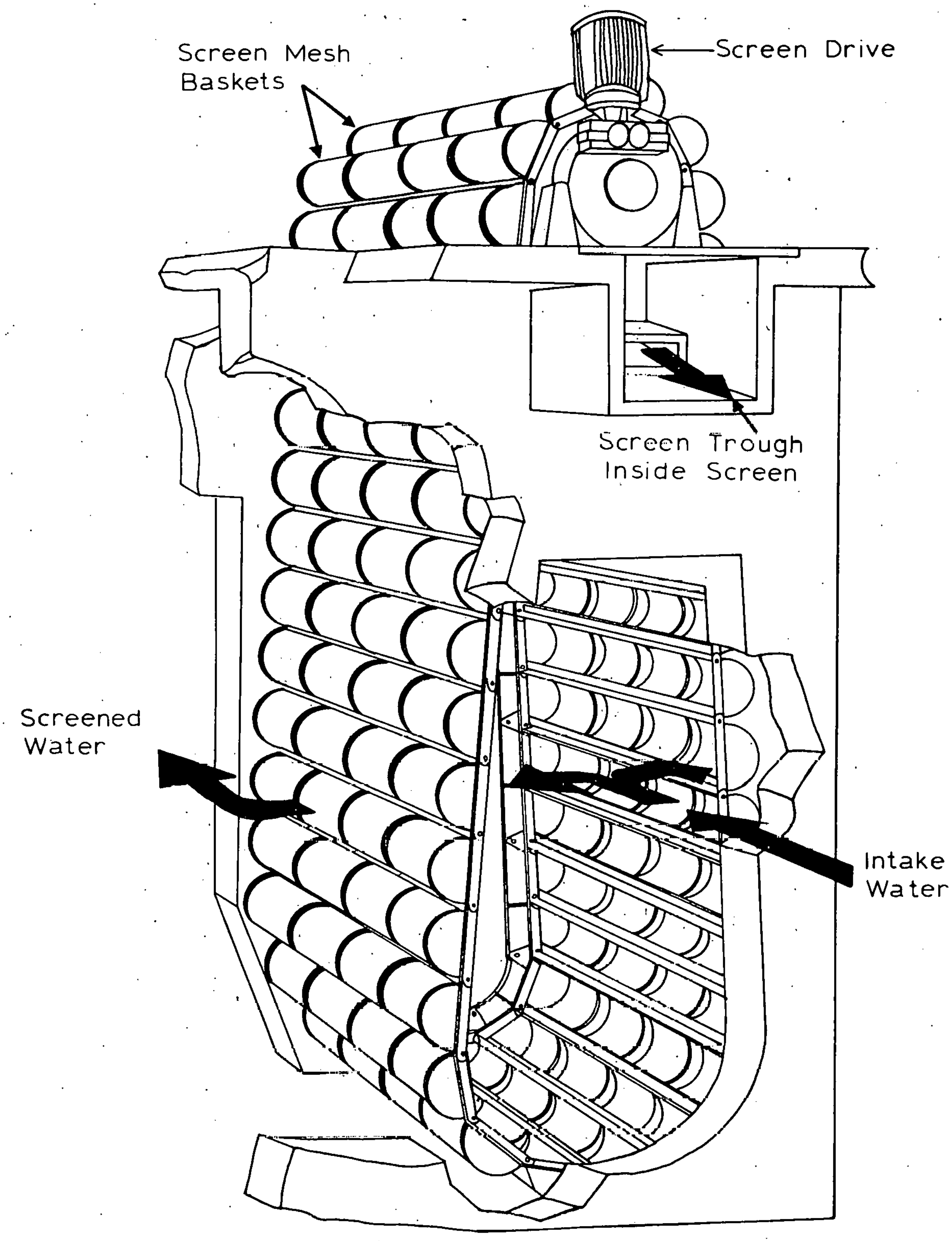
Dual-Flow Traveling Screen

(FMC Corp.)

FIGURE 4



FMC No-Well Screen
FIGURE 5



Passavant Center Flow Traveling Band Screen

FIGURE 6

NONBIOGENIC DEPOSITS AT THE OTEC HEAT EXCHANGER-SEAWATER INTERFACE

by

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I. INTRODUCTION

The economic feasibility of ocean thermal energy conversion to electrical power is strongly dependent on the efficiency of heat transfer between seawater and the working fluid. The efficiency of heat transfer depends primarily on three design factors. The first is the ratio of fluid volumes to their interfacial area. The second is the residence time of the fluids in the heat exchangers. The third is the thermal resistivity of the barrier (heat exchanger tubes) used to separate the seawater and working fluid. Ideally, this resistivity is dependent on the thermal conductivity of the materials from which the heat exchanger tubes are constructed and their thickness. All of these design factors can be dealt with in a relatively straightforward manner to achieve optimal cost to efficiency ratios. The situation is, however, complicated by the fact that deposits are expected to form at the interfaces between the heat exchanger tubes and the fluids. These deposits will increase resistance to heat transfer between the working fluid and seawater. A knowledge of the rate of formation, thermal resistivity and resistance to cleaning procedures of such deposits is, therefore, critical to the overall OTEC plant design, and to the success of the OTEC program.

The deposits, which may form on OTEC heat exchangers, can be divided into three major catagories; corrosion products, precipitates from fluids, and living organisms and their products (biofouling). Only corrosion products and precipitates are likely to form at the working fluid-heat exchanger interface. All three major types of deposits are likely to form at the seawater-heat exchanger interface, and they can be expected to be interrelated in a complex manner. In this paper, a brief discussion is presented of the status of our knowledge about nonbiogenic deposits at the seawater-heat exchanger interface and recommendations are made for further tests.

II. CURRENT STATUS OF KNOWLEDGE

The only studies which have been made so far of the chemistry of the nonbiogenic deposits forming at test heat exchanger tubing-seawater interfaces are an extraction procedure study on samples from the St. Croix biofouling and corrosion experiment (Craig, Munier and Morse, 1978), and a detailed study on samples of aluminum and titanium pipe from the first Gulf of Mexico biofouling and corrosion experiment (Morse, 1978). The chemistry of the deposits on the aluminum tubing was found to be similar in both tests. Consequently, this paper will concentrate on the results of the Gulf of Mexico tests for which there are more data.

A. ALUMINUM TUBING

Aluminum, probably present as a hydroxide, generally accounts for approximately 75 percent of the inorganic scale. Magnesium, also probably present as a hydroxide, frequently makes up about 20 percent of the inorganic scale. Calcium, possibly present as a carbonate, usually accounts for only about 2 to 4 percent of the inorganic scale. The only samples which exhibited a significant calcium enrichment, perhaps indicative of calcium carbonate deposition, were pitted samples from the St. Croix tests. Copper is strongly depleted in the scale relative to the 5052 aluminum alloy when normalized against aluminum, with approximately 99 percent of the copper generally being lost. The behavior of iron is more complex (see Figure 1). During the rapid inorganic scale growth phase iron is strongly enriched in the scale relative to the 5052 aluminum alloy when normalized against the host aluminum alloy. After the rate of growth slows, there is a rapid loss of iron from the scale. The rate of iron loss decreases with time. A possible explanation for this observation is that the redox potential in the interstitial solution of the scale drops, causing a reduction of the iron exposed to the interstitial solution from a +3 state to the more soluble +2 state. The migration of the iron out of the scale indicates that the scale must be both porous and permeable. The samples which were emplaced near the end of the tests exhibit depleted concentrations of iron even though their exposure time was relatively short.

The rate of inorganic scale deposition on aluminum tubing is highest during the first few days of exposure, during which no data was collected. Approximately half of the inorganic scale, which was deposited during the 67 days of exposure, was present after 11 days (time of first sampling). After this initial period the growth of the inorganic deposits was relatively slow and steady (see Figure 2, note that the thicknesses are based on zero porosity). The residual sea salt values within the surface deposits were used to make estimates of scale porosity. These estimates indicate that the deposits have a high water content with early values approaching 90% water by volume. Thicknesses of wet scale calculated by this method agree well with direct measurments of scale thickness (personal communication, Brenda Little, Miami, Florida, December 11, 1978). Based on these calculations the steady state growth rate of the nonbiogenic scale component is on the order of 0.4 μm per day or about 10 μm per month.

At present, thereis no information on the rate of aluminum loss during the early period of exposure. However, a very speculative calculation can be made to get an idea how long it would take to dissolve an aluminum heat exchange 1 mm in thickness, if cleaning resulted in nearly total removal of any deposits. Only two simple and perhaps offsetting assumptions must be made. The first is that 75% of the aluminum found in the scale after 11 days was deposited during the first day. The second is that no aluminum is lost to solution during the corrosion process. The rate of thinning calculated by these assumptions is approximately 0.2 mm per yr. This would lead to a lifetime expectancy for aluminum heat exchangers of about 5 years, which is certainly not acceptable. While this calculation should not be given great significance because of its speculative nature, it certainly points up the critical need to obtain information about corrosion rates under simulated cleaning conditions.

B. TITANIUM TUBING

Only a small amount of inorganic scale (less than 0.2 μm) was deposited on the titanium pipes. With the exception of the samples from the long titanium pipe at the bottom of the loop which had significantly smaller inorganic deposits (less than 0.08 μm), there are no major discernable differences in the amount or character of the inorganic scale on samples through which seawater flow was continuous and those in which seawater stagnated. Aluminum, not titanium, was the major inorganic scale component in all samples. The source of this aluminum is presently a mystery. Calcium was enriched relative to magnesium on all samples through which the seawater flow had been continuous and the samples from the long titanium pipe from the bottom of the test loop. This may be indicative of calcium carbonate formation. Magnesium was enriched relative to calcium on the other samples.

III. TESTS CURRENTLY UNDERWAY

Four types of tests are currently being conducted at the University of Miami to gain a better understanding of nonbiogenic deposits which may be formed at the heat exchanger-seawater interface. These tests are being conducted on aluminum, titanium, stainless steel and copper-nickel alloys. The primary emphasis of the tests is on the conditions which may result in calcium carbonate deposition. These tests are: 1) determination of the inorganic chemistry of deposits formed on tubing samples during the second Gulf of Mexico biofouling and corrosion experiment, 2) measurement of the growth rate of calcite and aragonite powders in seawater samples of different chemical composition, 3) determination of the chemistry of tubing surfaces after exposure to stagnant seawater at different temperatures and initial saturation states with respect to calcium carbonate, and 4) determination of the influence of liquid ammonia leakage into tubes through which surface seawater is flowing at 6 feet per second.

The first two tests have not yet been conducted. Most of the exposures to seawater have been completed on the second two tests, but detailed analyses of the deposits formed are only partially complete. Until these analyses are completed it is judged unwise to present results as they may be misleading.

IV. RECOMMENDATIONS FOR FURTHER TESTS

Tests which have been or are currently being conducted have suffered from several weaknesses which need to be corrected in future tests. One major weakness has been the use of test aluminum tubes of different thickness produced by different manufacturing processes. Inadequate attention has been paid to the exact method of tubing production, the state of tubing surfaces at the time of delivery and the chemistry of the tubing surfaces after cleaning. No data presently exists regarding the rate of formation and the chemistry of inorganic scale production during the early stages of exposure, when the rate of inorganic scale formation is most rapid. The influences of initial surface chemistry and the chemistry of the seawater passing through the tubes are totally unknown. It is unfortunate that there has been no effort to carefully monitor the chemistry and biology of the seawater passing through the test tubing samples. This lack of information makes it impossible to attempt to explain differences in results between different tests. The use of data collected at different times and locations from those of the tests is scientifically unsound, due to the high temporal and spacial variability of seawater. Exposure times have been far too short. Very often the most interesting information starts to be produced only near the termination of the tests. The lack of careful intercalibration, of different techniques for characterizing test heat exchanger tubing surfaces before and after exposure to seawater with each other and R_f measurements has severely complicated the interpretation of test results.

Perhaps the most pressing need for information about the depositional processes occurring at the test heat exchanger tubing-seawater interface is with regard to the influence of cleaning procedures and the behavior of the interface when exposed to cold deep seawater. The true seriousness of biofouling and scale formation can only be evaluated under simulated cleaning procedures conducted during tests of much longer duration than those which have been made so far.

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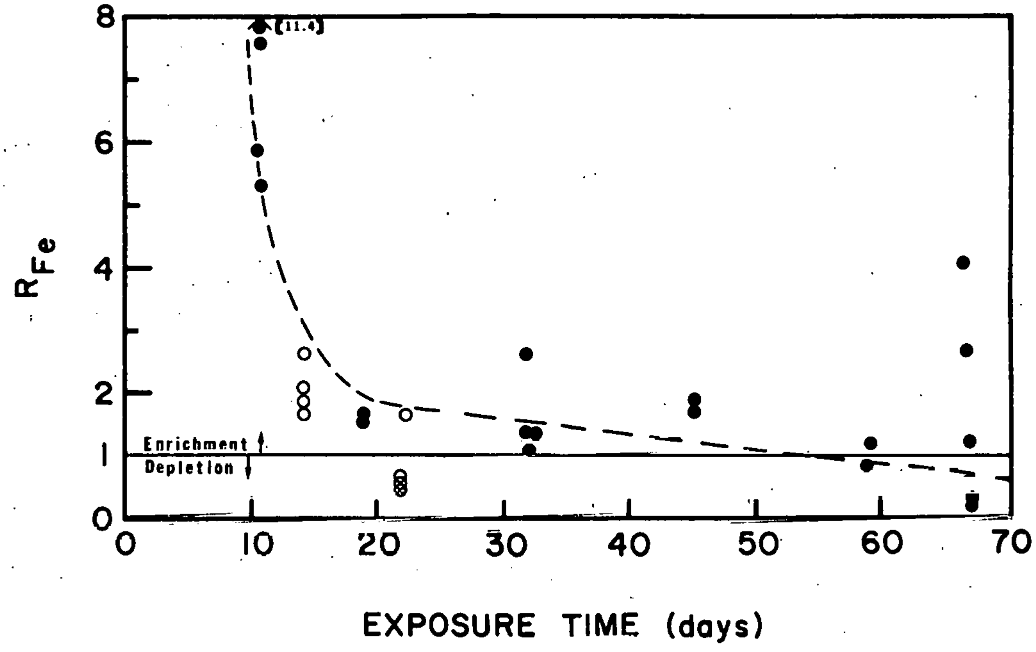
8
6
4
2
1
0
R_{Fe}
[11.4]
Enrichment ↑
Depletion ↓
0
10
20
30
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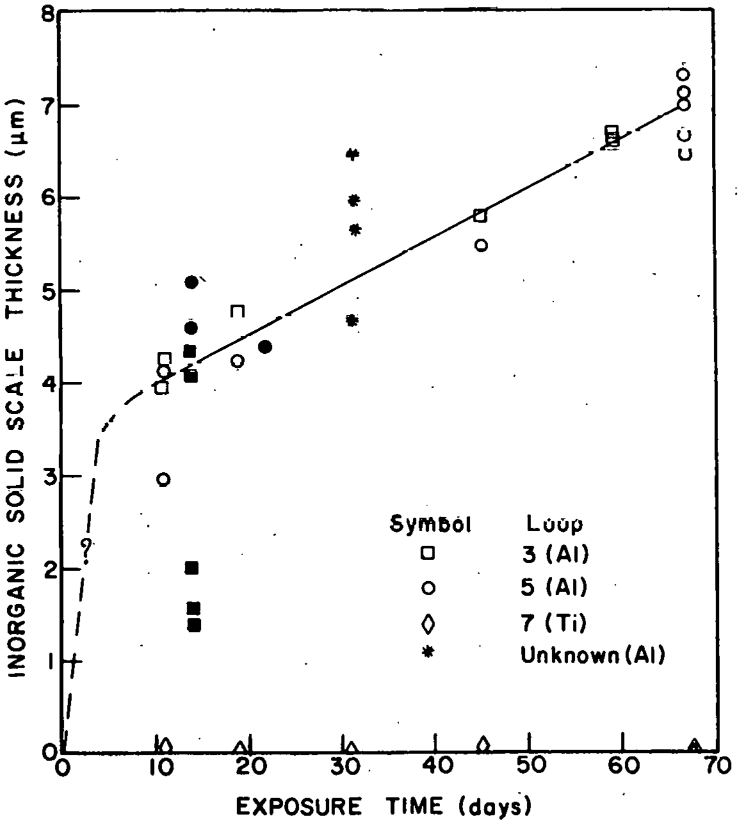
50
60
70
EXPOSURE TIME (days)


8
7
6
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3
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INORGANIC SOLID SCALE THICKNESS (μm)
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Symbol
Loop
□ 3 (Al)
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50
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70
EXPOSURE TIME (days)

CORROSION

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CORROSION OF ALUMINUM AND TITANIUM AT KEAHOLE POINT OVER AN EIGHT MONTH PERIOD

by

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ABSTRACT

Aluminum and titanium samples were exposed to flowing seawater on an underwater buoy off Keahole Point, Hawaii. Samples were periodically removed to determine the nature and amount of both the biofouling and corrosion products. This paper is concerned only with the corrosion aspect. The results over an 8 month period indicate that whereas the titanium samples were unaffected, the corrosion product film of the aluminum samples increased in thickness parabolically with time. No evidence of pitting was found on any of the samples examined. The results indicate that if the corrosion product film is not removed by brushing or dissolution, then a corrosion loss of only 100μm (4 mils) is predicted over a 30 year lifetime.

INTRODUCTION

The successful design of an OTEC plant requires information on the corrosion behavior of materials used in the heat exchanger modules. Leading candidates for this application include 5052-H34 aluminum and titanium alloys. Aluminum is attractive on the basis of its relatively low cost and ease of fabrication as well as an acceptably low corrosion rate. Titanium would clearly be the preferred material because of its inert behavior under OTEC conditions if the costs of the raw material and subsequent manufacturing operations were comparable to that of aluminum.

The purpose of this investigation was to attempt to determine the corrosion mechanism of the candidate materials in seawater, especially at early times, and thereby allow a prediction of the potential lifetime in OTEC applications.

The corrosion behavior of a number of aluminum and titanium samples were studied over a wide range of exposure times from November 1977 to July 1978 to determine their suitability for OTEC applications.

EXPERIMENTAL PROCEDURES

Split ring coupons 2" long were machined from 1" diameter 5052-H34 (strain hardened and stabilized) aluminum and titanium pipe. Aluminum samples were cleaned by a NaOH/HNO_3 treatment according to the method of Craig, *et al.* [1]. Titanium samples were cleaned with a 5% HNO_3-1% HF mixture. The coupons were placed down stream from the CMU heat transfer apparatus in the underwater buoy off Keahole Point and exposed to flowing seawater in the range of 1 to 2 m/s for times ranging from 3 hours to 8 months. None of the coupons were disturbed after installation.

In addition to the split ring coupons, brushed and unbrushed samples were obtained from the 8½ ft long aluminum and titanium pipes used in the heat transfer instrument. These were brushed at the end of 13, 22, and 29 weeks exposure to flowing seawater using 20 passes of a MAN brush after the fouling resistance reached predetermined values.

Coupons were removed periodically and immersed in seawater containing 2.5% glutaraldehyde to preserve the biofouling products. After biological examination the samples were scrubbed with a sponge under flowing tap water to remove the biofouling layer. After mounting on SEM holders the dried samples were transferred directly to the SEM without the application of a sputtered conducting film.

EXPERIMENTAL RESULTS

Titanium Titanium samples removed from the buoy confirmed the excellent corrosion resistance of titanium in flowing seawater. No detectible change in the surface morphology of the titanium samples was found for either the brushed or unbrushed sections. The surface of an 8 month brushed titanium sample is shown in Fig. 1. The rough, grooved surface shown here is typical of the other titanium samples and is undoubtably due to the manufacturing process used to produce the pipe sections. These surface irregularities are considerably larger than those found for the aluminum samples. The microscopically rough areas may present a rather attractive surface for the attachment of biofouling organisms.

Aluminum The surface of an aluminum sample immersed in seawater and then immediately preserved in the glutaraldehyde-seawater solution ("0-hour") is shown in Fig. 2. Extrusion lines, as well as numerous surface depressions presumably due to the cleaning procedure, are evident in addition to a number of particles randomly dispersed over the surface, which are assumed to be salt crystals.

After 8 months exposure the surface had a cracked "dried mud" appearance over a large area, as shown in Fig. 3. This morphology is similar to that found by Craig, *et al.* [2] for 6061-T6 aluminum. They concluded that a continuous gelatinous film of aluminum oxide trihydrate was formed on exposure to seawater which fractured when dried. The dried corrosion product film of samples taken from the unbrushed region of the heat transfer section tended to flake off very easily, whereas the brushed samples had a much more tightly adhering film.

After examination of the long term exposures (8 months), a series of short-time samples were examined in an effort to determine the initial kinetics of film formation. The exposure times were 3 hours, 6 hours, 12 hours, 24 hours, 48 hours, 72 hours, 1 week, 2 weeks, and 3 weeks.

After only 6 hours, surface cracks were just visible at 800X magnification, indicating the presence of a corrosion product film. This is in agreement with that found by Craig, *et al.* [2] who found that polarization occurred after 45 to 75 minutes. It could not be determined by SEM techniques if the 3 hour coupon also had a passivating film present.

After 12 hours, the entire surface area was covered by a cracked, but continuous, film, as shown in Fig. 4. Higher magnification revealed that there were occasionally pieces missing from the continuous dried film. An estimate of the dried film thickness could be made in these areas. As the exposure time increased it was found that the thickness, as well as the average diameter of the cracked corrosion film platelets, steadily increased.

The 2 week sample is shown in Fig. 5. The hole in the film probably resulted from the drying process and is not believed to be a corrosion pit in the underlying aluminum surface. In fact, no evidence of pitting was found in any of the samples examined. This lack of pitting is presumably due to both the low copper concentration in the 5052 alloy as well as the caustic/acid cleaning procedure, which would presumably passivate any iron particles present on the surface.

These results of increasing film thickness with time differ from those of Craig, *et al.* [2]. They found that the corrosion product film of 6061-T6 aluminum showed no trend to be either heavier of lighter (per unit area) as exposure time increased. This constant film thickness was attributed to the steady-state dissolution of the hydrated aluminum oxide film. Their limiting film thickness was estimated to be of the order of 1.8 to 6.4 μm, which is an order of magnitude thinner than that estimated by Fetkovich from the heat transfer results.

DISCUSSION

Although the corrosion resistance of titanium in flowing seawater is excellent, its rough, irregular surface could result in increased rates of biofouling, compared to a "smooth" surface. Some thought should be given to determining the effects of surface roughness on biofouling rates on titanium in the future.

Little and Lavoie [3] measured the wet film thickness by light section microscopy as a function of exposure time. Their results indicate that the growth rate was initially much larger than at later times. Morse [4] determined the dry film thickness by measuring the residual sea salt values within the surface deposits. Again, the film thickness increased rapidly in the beginning, after which the growth was relatively slow and steady.

When aluminum is in contact with seawater under these conditions, a gelatinous corrosion product of aluminum oxide trihydrate forms at the metal/oxide interface [1]. If growth of the film is controlled by diffusion of some species through the film (e.g. water molecules), and the film is continuous, then the growth rate should follow the parabolic rate law in which the film thickness is proportional to the square root of time.

The aluminum oxide trihydrate film is expected to be continuous since the Pilling-Bedworth ratio (volume of the corrosion product to that of the metal) is about 3.22, which is greater than the critical value of unity required for a continuous film.

It has been estimated that nearly 90% of the initial film thickness is water of hydration [4]. Examination of corrosion products by SEM techniques, however, results in a nearly complete dehydration of the wet film. Therefore, correlation of actual film thickness under operating conditions with dry film thickness measured by other techniques, such as SEM, must be done with caution.

It was noticed that the platelets seen in the SEM steadily increased in size as the length of exposure time increased.

It is expected that the platelet size, which is easy to measure in the SEM, is related to the wet film thickness for the following reasons.

As the film dehydrates, there are no restrictions as to how much it may shrink normal to the surface, but since it remains firmly attached to the substrate, a tensile stress large enough to produce the familiar "mud-cracked" pattern, observed in all samples, is induced in the dehydrated film.

Since the film is constrained from shrinking laterally due to coherency with the substrate, the resulting platelet size should be of the same size as that of the film thickness when hydrated. Therefore, assuming that the growth rate of the wet film is diffusion controlled, if the average platelet diameter, d, is plotted vs the square root of time, a linear relation should be obtained.

The average platelet diameter was determined by the line intersection method [5] and is given in Table 1 for the exposure times indicated. As shown in Fig. 6, d does, in fact, increase parabolically with time for exposure times at least less than three weeks. The relationship between d (μm) and time, t (hours), is given by:

$$d = 1.44\ \mu m + 0.66\ t^{1/2}\ . \qquad (1)$$

The fact that d does not extrapolate to zero as time decreases can be explained if the minimum crack size is required to be about the same as the initial grain size of the underlying aluminum. Craig, *et al.* [1] found that the crack network is of the same order of magnitude as the grain size.

The only measurements of wet film thickness available, at the present time, are those of Little and Lavoie [3]. Their results, along with their estimates of error (±3μm), are shown in Fig. 7. The average platelet diameter, based on Eqn. 1, is shown to agree favorably with wet film thickness over the time span indicated, lending further support to d being a good estimate of the wet film thickness. The deviation of the wet film thickness from that predicted at the early times of exposure may be due to a much less dense wet film initially [3], which would result in a larger film thickness than expected.

Assuming that the wet film thickness (d) is 3.22 times the reduction in aluminum thickness due to corrosion (based on an assumed wet film density of 2.423 g/cm^3 [2]), the corrosion loss, $\Delta x(\mu m)$, can be predicted from Eqn. 1:

$$\Delta x = 0.20\ t^{1/2}\ . \qquad (2)$$

(The time independent term, 0.45 μm, is neglected since Δx must approach zero as exposure time decreases.)

If the attack is uniform and the corrosion product film is not removed by brushing or dissolution, then the corrosion loss should only be 100 μm (4 mils) over a 30 year lifetime.

The film thickness growth rate, $\dot{G}$, as well as the corrosion rate, $\dot{C}$, (μm/yr) can be obtained by differentiating Eqn. 1 and 2 with respect to time:

$$\dot{G} = 2900\ t^{-1/2} \qquad (3)$$

$$\dot{C} = 900\ t^{-1/2} \qquad (4)$$

where time is, again, given in hours. These predicted rates are shown in Fig. 8 over a 12 month period.

At very early times, the rates are very large but decrease rapidly with time. There is no steady-state growth or corrosion rate predicted. If the corrosion product film is completely removed when the aluminum surface is brushed to reduce the fouling resistance (R_f), then the corrosion rate would again be very large. Assuming the aluminum heat exchangers were brushed once a month, and this resulted in complete removal of the corrosion product film, then the total corrosion loss over a period of 30 years is given by

$$\Delta x = 30 \times 12 \times 0.20(730)^{1/2} \simeq 2000\ \mu m \simeq 75\ \text{mils}\ ,$$

a loss of thickness that could be tolerated.

In fact, the results from the 8 month exposure sample predict that the corrosion product film is not removed by the brushing procedure used in this experiment. The measured platelet diameter for the 8 month brushed sample was found to be 51 μm. If this is indeed the same as the wet film thickness before dehydration, and the film was removed by brushing, then a larger d would be predicted by Eqn. 1, because the film would reform after the three brushing operations. However, the predicted d is 52 μm, in excellent agreement with the measured d. Therefore, two conclusions can be made. First, the film continues to increase in thickness, and the aluminum continues to decrease in thickness, parabolically with time over the entire 8-month period. Second, the effect of brushing on film removal appears to be negligible.

The absence of pitting of 5052-H34 aluminum in flowing seawater over an 8-month period, as well as the low predicted corrosion rate recommends this alloy for serious consideration for OTEC applications.

Work is continuing on the underwater buoy at Keahole Point at the present time. There are now four different metals being exposed to flowing seawater. These include the previous 5052-H34 aluminum and titanium alloys as well as AL-6X stainless steel and a CA-706 copper-nickel alloy.

In addition to the above metals, a number of amorphous metals and their crystalline counterparts, are being exposed to the same flowing seawater under a grant from the NSF. Amorphous metals are attractive because of their inert behavior even under highly oxidizing conditions, their high hardness and surface finish, and their resistance to pitting. The major drawback to the application of amorphous metals for OTEC purposes, at the present time, is their limited fabrication shapes. Presently, only ribbon-like, or perhaps sheet, is available. However, if plate-type heat exchangers are considered, or if the amorphous strip can be joined into a tube configuration, then amorphous metals might be expected to seriously challenge both the corrosion resistance of titanium as well as the cost of aluminum.

ACKNOWLEDGMENTS

The author would like to thank Hank White, Brenda Little, John Morse, and Glen Zeman for helpful discussions. The photographic work of Nirmal Devnani is greatly appreciated.

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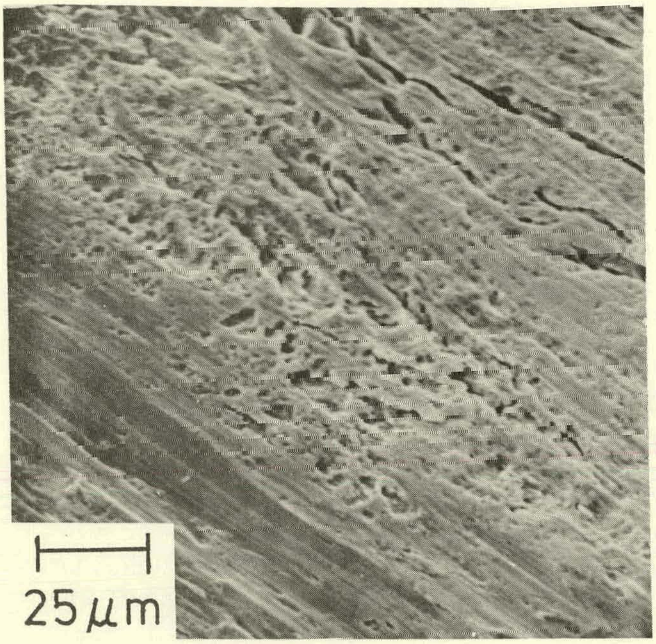


Fig. 1 SEM photograph of a periodically brushed titanium pipe after 8 months exposure to flowing seawater.

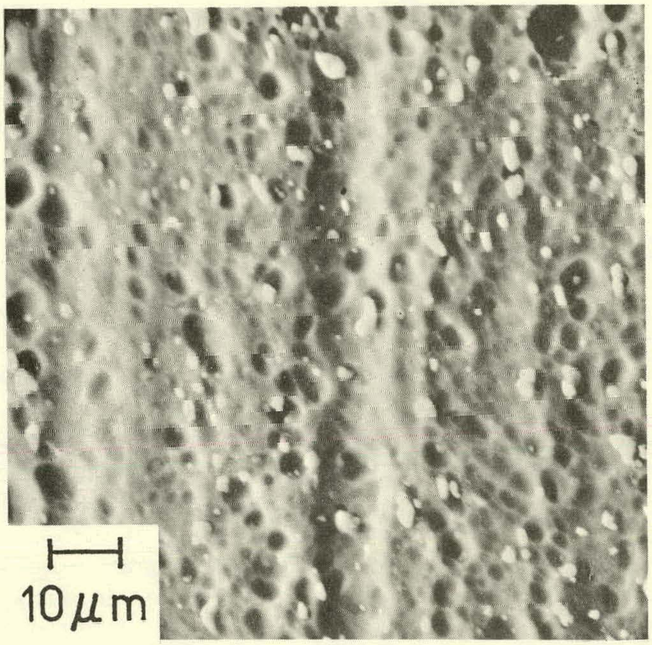


Fig. 2 SEM photograph of a "0-hour" alumisample briefly exposed to seawater and then immediately immersed in a seawater 2.5% glutaraldehyde solution.

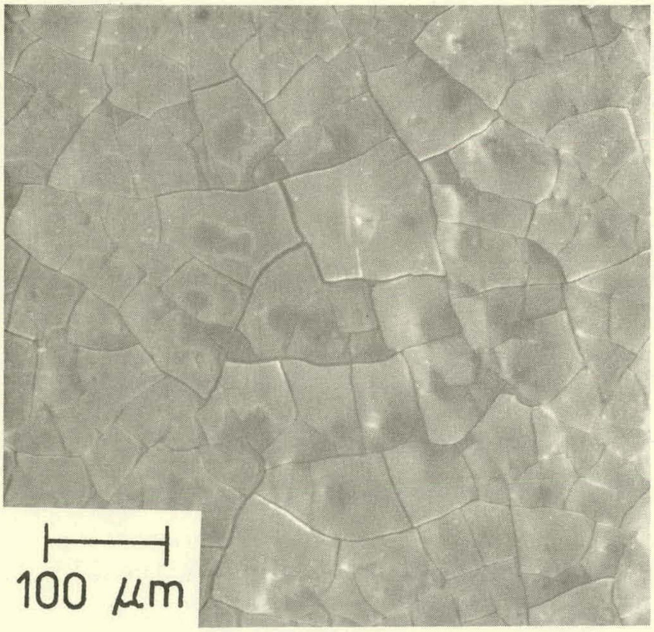


Fig. 3 SEM photograph of a brushed aluminum pipe after 8 months exposure to flowing seawater.

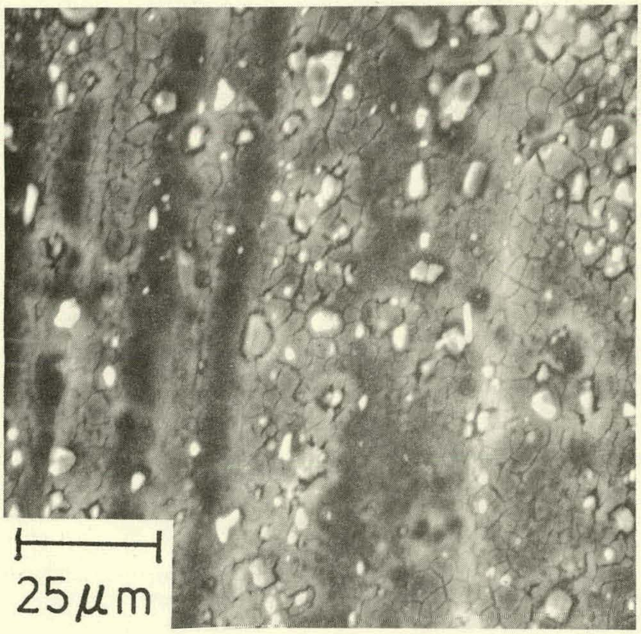


Fig. 4 SEM photograph of an unbrushed aluminum coupon after 12 hours exposure to flowing seawater. A cracked, but continuous, corrosion product film is clearly evident.

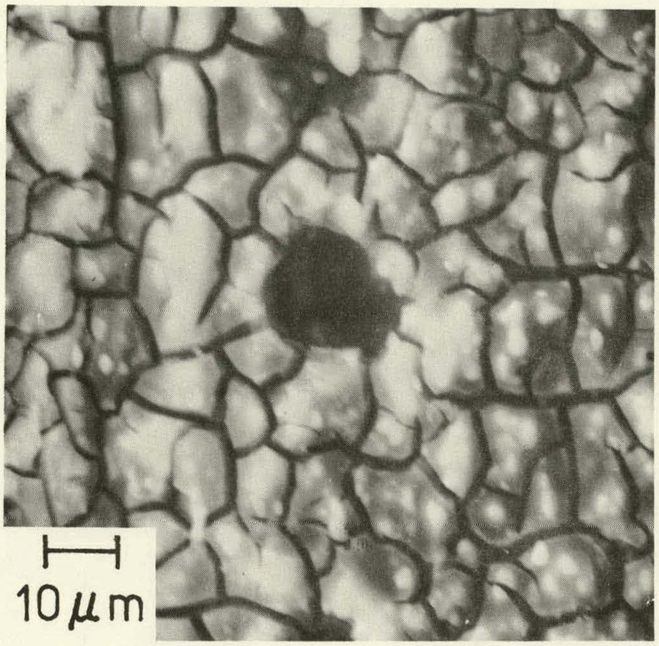


Fig. 5 SEM photograph of an unbrushed aluminum coupon after 2 weeks exposure to flowing seawater. The hole in the corrosion product film is believed to have formed after drying of the film.

Table 1

MEASURED PLATELET DIAMETER (d) AND PREDICTED CORROSION RATE (Δx) AT EARLY TIMES

t (hours)	$t^{1/2}$ (hours)$^{1/2}$	d (μm)	Δx (μm)
12	3.46	3.4	0.69
24	4.90	4.4	0.98
48	6.93	6.5	1.39
72	8.49	7.0	1.70
168	12.96	10.7	2.59
336	18.33	12.6	3.67
504	22.45	17.0	4.49
504	22.45	15.7	4.49

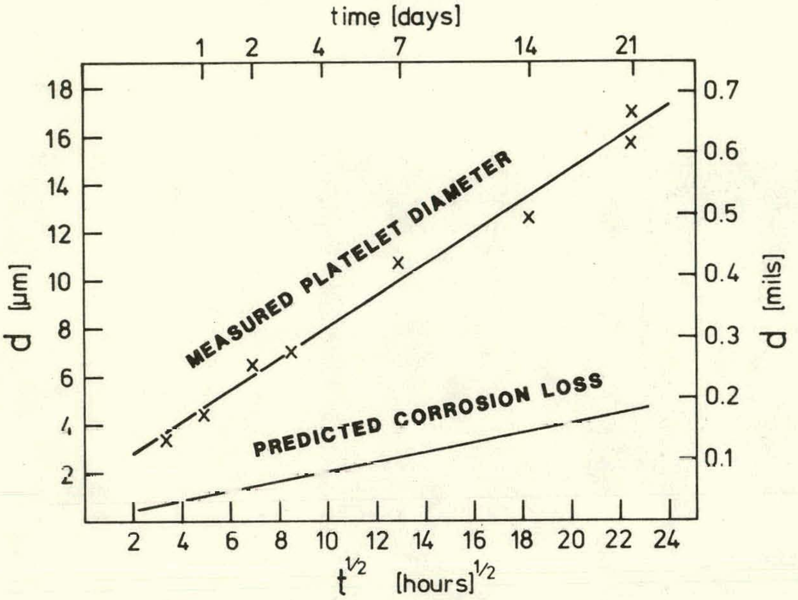
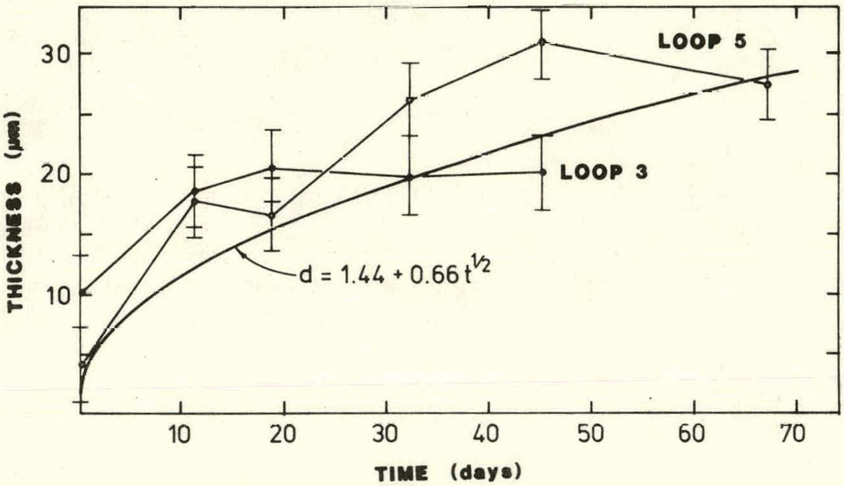


Fig. 6

Measured platelet diameter, d, as a function of the square root of time as well as the predicted corrosion loss, Δx, of 5052-H34 aluminum.

Fig. 7

Wet film thickness vs time as determined by light-section microscopy [3]. Predicted wet film thickness from the equation $d = 1.44 + 0.66\ t^{1/2}$.



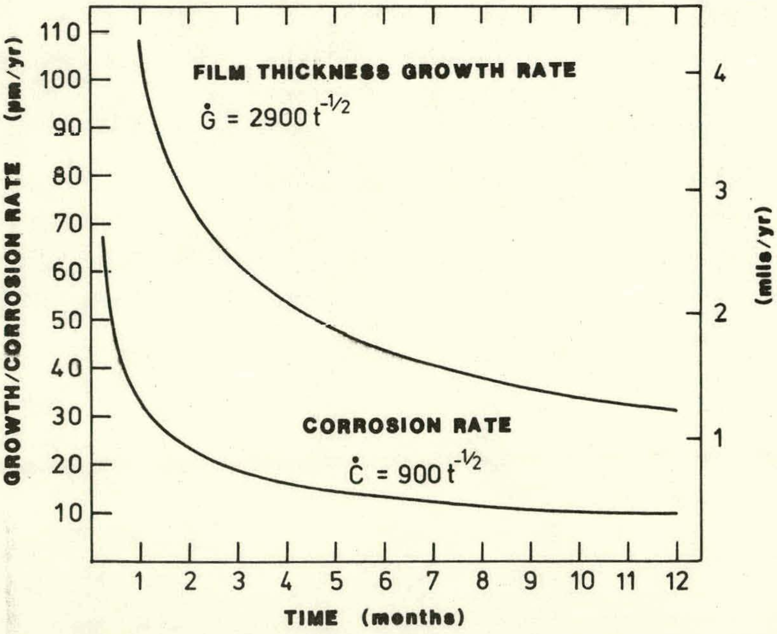


Fig. 8

Film thickness growth rate, G, and corrosion rate, C, (μm/year) predicted from the parabolic rate law.

CORROSION OF ALUMINUM AND TITANIUM DURING THE FIRST GULF OF MEXICO BUOY DEPLOYMENT

by

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I. INTRODUCTION

The OTEC Buoy was deployed in the Gulf of Mexico from March 16, 1978 thru June 7, 1978. During this time the University of Miami conducted the corrosion assessment study to evaluate the aluminum and titanium pipes used for the experiment. The specific tasks for this study were to develop field procedures and requirements for the acquisition of corrosion data on the pipes used on the buoy.

II. EXPERIMENTAL PROCEDURE

A. CORROSION TESTS

To accomplish these tasks, an instrument, developed at the University of Miami, was used on the buoy to automatically measure corrosion data and feed the data into the buoy system for transmission to the shore station. A duplicate system was used in the laboratory to help evaluate the results of the data from the buoy. Specimens from the buoy were examined to identify type, rate, severity, and corrosion product composition of the corrosion on the test samples. Weight loss specimens and submerged plaques were used to verify the corrosion rate as determined by the corrosion rate meter.

The weight loss specimens and the corrosion samples were located in several loops with the Heat Transfer Units. A typical loop is shown in Figure 1 with the flow of sea water thru the pipe as shown. The corrosion samples were removed with the Bio-samples at selected times during the test. Corrosion sample 3, as a typical sample, is shown in Figure 2. After removal, the corrosion samples were rinsed in distilled water, dried, and sent to the laboratory for study. Each loop held two weight loss specimens and a silver-silver chloride cell for measuring corrosion potential during the operation of the buoy.

B. CORROSION RATE METER

The Remotely Controlled Corrosion Rate Meter (RCCRM) was constructed in two parts - the sensor and the meter. The sensor was located in the water quality loop shown in Figure 3. The corrosion rate sensor consisted of an aluminum ring 1 inch in diameter and 1 inch long, a silver-silver chloride cell and a platinum screen all assembled in a PVC holder. The corrosion rate sensor is shown in Figure 4.

The corrosion rate meter is located inside of the buoy and is connected to the sensor by shielded cable. The meter is a micro-processor controlled device for electronically measuring the corrosion rates of metals in an electrolyte. The instrument has six main divisions as shown in Figure 5. The first section is the power section. The power source is a 28 volt supply from the

Phase II payload system. There is a 5 volt voltage regulator which has constant output. This part of the power supply drives the micro-processor part of the instrument. The current drawn from the 28 volt supply is only 17 ma. The other part of the power section is a switchable DC/DC converter, which has ± 15 volt output. These ± 15 volt outputs have ± 5 volt voltage regulators on them. These are the voltages necessary to drive the analog section of the board. To conserve power the analog section is only turned on during actual data acquisition periods. The power needed from the 28 volt supply with the DC/DC converter on is 170 ma.

The second section of the instrument is the 12 bit A/D converter with it's associated output buffer and input multiplexer. The inputs to the multiplexer are several op amps and the D/A converter. The multiplexer and the A/D converter are controlled by output from the micro-processor.

The third section is the 12 bit D/A converter. There is a 12 bit buffer to hold the input to the D/A converter.

The fourth section has the analog switches and control line buffers. The analog switches control the application of current during the corrosion rate measuring process, and the routing of signals throughout the analog section.

The fifth section is the data output port and the control lines. This section interfaces with the DPM of the Phase II Payload System.

The last section is the micro-processor. This section also contains the EPROM which contains the program, the RAM which holds the data, and all the associated address decoding and control logic. All of the chips in this section are CMOS which accounts for the low power consumption. A detailed schematic of the RCCRM is shown in Figure 6.

A loop of flowing sea water set up at the University of Miami duplicated the loop on the buoy. The laboratory loop had a corrosion sensor identical to those on the buoy. The meter used in the laboratory was electrically the same as that used on the buoy but it was not automatic. It was manually operated and read directly.

The RCCRM operates on a principle proposed by Stern and Geary*. The principle states that the corrosion current can be calculated from the polarization current with a known displacement from the corrosion potential.

The Stern-Geary equation is:

$$i_{corr} = \frac{1}{2.3} \frac{I_{app}}{\Delta E\ A} \frac{Bc\ Ba}{Bc + Ba}$$

where

i_{corr} = corrosion current density

I_{app} = applied current

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* M. Stern & A. L. Geary, J. Electrochemical Society 104 56, (1957).

ΔE = potential displacement

A = area of sensor

Bc, Ba = Tafel slope of cathode, anode for aluminum

The Tafel slopes for aluminum were assumed to be equal and to have a value of 0.06. The sensor area was 20.3 cm^2.

To evaluate the meter and the assumptions above, tests were made on aluminum specimens in the laboratory loop. After stabilization of the samples, two tests with the corrosion rate meter gave calculated corrosion rates of 1.44 mpy and 1.39 mpy. Weight loss specimen gave a value of 1.32 mpy. This was considered to be satisfactory agreement for the conditions imposed.

C. CORROSION FILM THICKNESS

A standard technique used to determine corrosion film thicknesses on aluminum is by calculating the film thickness from the weight loss of a specimen when the film is removed chemically. This technique, based on ASTM specification G-1, the chemical dissolution method for the removal of corrosion products, assumes that the corrosion product is $Al(OH)_3$ with a density of 2.473 gr/cm^3. This technique was used throughout the study to determine the corrosion film thickness.

There are several factors which can affect the accuracy of this method such as damage to the specimen, non uniform film, and the possibility that the film is not $Al(OH)_3$. To check the validity of these measurements, other methods were used. Metallographic techniques have been used to measure thicknesses of aluminum oxide (Al_2O_3) films on aluminum. The technique used is to plate the oxide with a layer of nickel by electroless nickel plating. After plating, the aluminum specimen is sectioned and the oxide layer is measured with the aid of a microscope. Attempts to coat the corrosion films with nickel was not successful. A reaction between the corrosion film and the solution destroyed the film. Electroplating was tried but it was also unsuccessful. Vacuum plating a thin layer of metal directly on the specimen clearly outlined the corrosion film. A one micron thick layer of chromium metal vacuum plated on the film gave the best results and was used for the metallographic technique of film thickness measurement.

D. CORROSION PRODUCT EVALUATION

In addition to the film thickness determination, the characteristics and the elements found in the corrosion product was determined. The film surface was studied using a Scanning Electron Microscope. An X-ray analysis attachment (EDAX) to the SEM was used to analyse the film.

To study the general corrosion of these alloys plaques containing three pipe samples were placed in the sea water outside the University of Miami laboratory and under the buoy. A diagram of the plaques is shown in Figure 7.

III. RESULTS

A. CORROSION RATE METER

The early results of the corrosion meter from the Laboratory Loop and from the buoy is shown in Figure 8. This plot of corrosion potential vs corrosion current density is shown for aluminum alloy 5052 for both meters. It should be noted that the laboratory data starts from time zero but the buoy data starts on the 17th day. The laboratory data shows a decrease in the potential for the first eight days and then a decrease in the corrosion current with an increase in the potential. The slope of this part of the curve is almost identical to the results of an investigation by Craig in 1970 as shown in the insert. The buoy data shows a similar slope for the data between the 17th day and the 29th day. Weight loss of the aluminum is calculated from the corrosion current density. The corrosion rate in mils per year is shown for the laboratory and the buoy specimens in Figure 9. While the two rates show some displacement, they both appear to level off at about 0.10 to 0.15 mils per year. Plots of metal loss in mils vs time for the two loops are shown in Figure 10. The loss rate from the lab specimen is almost leveled after forty days, whereas it is a constant rate for the buoy specimen after twenty days. The loss calculated for buoy specimen is different than that of lab's due to the fact that the corrosion rate for the first seventeen days of the buoy specimen is taken to be the rate measured on the 17th day which is lower than the previous rates. Since the metal loss is an accumulative measure and is directly proportional to the corrosion rate the loss is under-estimated. This can be corrected by extrapolating the corrosion rate for the first two weeks from the available data and then calculating the metal loss.

A plot of corrosion potential vs time is shown in Figure 11. Both plots are very similar (except for the missing days on the buoy) until the 36th day. At this time the corrosion potential on the buoy started increasing and by the 39th day the potential was about 0.75 volts. A plot of current vs potential for the buoy, Figure 12, shows a change in the slope on the 36th day. The sudden change in the potential indicates that something has happened to the corrosion mechanism occurring in the sample and that uniform corrosion is no longer occurring. As the corrosion rate calculations are based on uniform corrosion, these rates may not be valid after the 36th day.

After the buoy experiment was completed, the corrosion rate sensor was removed. Examination of the sensor showed severe pitting on one end. The cause of the pitting is not known but it was probably the result of the crevice between the rubber ring which held the aluminum ring in position. The ring with the corrosion is shown in Figure 13. Inspection of the ring shows discoloration on the bottom 80% of the ring as shown in Figure 14. This could have been caused by air trapped in the top of the horizontal ring while the loop was running or when the loop was shut down and left with stagnant water in the ring. It was noted that the pitting appeared to start at the interface between the water and the air. No other pitting on any of the buoy samples was observed. It should be noted that the corrosion pipes were vertical and that the meter sensor was in a horizontal leg thus it was the only aluminum specimen which could be exposed to stagnant water.

B. CORROSION FILM THICKNESS

The corrosion film thickness was determined by two methods - the chemical dissolution method and the metallographic method. The results are shown in Figure 15 as a plot of film thickness in microns vs days on the buoy. The results of thickness determined by the chemical method shows considerable scatter. Data for both pipes 3 and 5 are shown and both appeared to be in the same range. The scatter in the data is probably due to damage during cutting which caused loss of part of the film. The assumed density of the film is also in question. The data shows a gradual increase in film thickness to an average of a micron in 57 days.

The film thickness determined by metallographic technique shows less scatter but was based on fewer specimens. This data shows a rapid increase in film thickness to about eight microns in eleven days and then a slow rate of growth to about 12 microns in 46 days. Laboratory tests show that the eight micron thickness may be reached as early as eight days after start of water flow.

The corrosion films as observed at 1000X magnification are shown in Figure 16. The film outlined by a thin layer of chromium can be measured directly. From these photos and from the SEM photos a shrinkage of the film of 7 to 10% can be seen. Of importance to heat transfer is the thickness of the film while the sea water was flowing thru the pipe. If we assume that the cracks in the film occurred during drying after the water flow stopped, the film thickness should be up to 10% thicker than that measured. This would indicate that the film thickness during operation was about 13 microns.

C. EXAMINATION OF CORROSION PRODUCTS

1. Sea Water Pipes

The corrosion samples were removed from the sea water loops and returned to the laboratory as scheduled. Each sample was sectioned and one section was used for film thickness measurements and one used for Scanning Electron Microscope examination. Three loops were used on the buoy; loop 3 and loop 5 had aluminum alloy 5052-0 pipes and loop 7 had titanium. Examination of the corrosion products of the aluminum pipes were made by light microscope and SEM. The corrosion film on the aluminum is shown in Figure 17 at 100X and at 1000X. All of the aluminum samples removed from the buoy had a similar appearance. The mud cake or cracked appearance of the film is a result of shrinkage of the film during drying after removal from the water. There was no observed difference in the film between specimen in loop 3 and in loop 5. One unusual film was noticed in loop 5 specimen 12 which was removed after 11 days flow of water. This film seen in Figure 18 at 1000X and 10,000X appears to be in two layers. Both layers show shrinkage cracks.

The appearance of the titanium samples from loop 7 is shown in Figure 19 at 1000X. The film is thin and transparent and does not effect the appearance of the metal. Film thickness is shown in Figure 20 at 1000X and 10,000X by the SEM.

The oxide films were analyzed on the SEM by X-ray dispersion techniques. The elements which were detected on the aluminum pipes were primarily aluminum with magnesium, silicon, calcium, chromium, and iron, with trace amounts of sodium, chlorine and sulphur. The analysis of the titanium specimen indicated only titanium.

2. Underwater Plaques and Weight Loss Specimen

Unfortunately the weight loss specimen and the plaques were not retrieved from the buoy and thus exact weight loss data was not available. The aluminum pipes exposed to sea water at the laboratory were completely covered by marine growth. Pitting was observed on the surface of the aluminum and under the fasteners. The titanium pipe did not show any corrosion.

IV. CONCLUSIONS

From the study of corrosion of aluminum and titanium during the first Gulf of Mexico OTEC buoy deployment the following conclusions were made.

(1) The remotely controlled corrosion rate meter operated successfully to monitor corrosion in the aluminum pipes. The indication by the meter of change in mode of corrosion from uniform to pitting was confirmed by observation of pitting in the sensor after removal from the system. The corrosion rates indicated by the meter could not be confirmed due to loss of the weight loss specimen.

(2) After an initial rapid rate of corrosion the corrosion rate of aluminum drops to a rate of 0.10 to 0.15 mpy.

(3) No pitting corrosion was found in any pipe loops except for that found in the meter sensor. This pitting was probably due to stagnant water in the pipe or to the rubber sealing ring.

(4) The corrosion product film on both aluminum and titanium pipes on the buoy were similar in appearance and properties to products produced as a result of test in the laboratory and to the products obtained during other sea water studies.

(5) The metallographic technique developed for study of film thickness is better than the chemical method and indicated a maximum film thickness of 13 micron in 46 days.

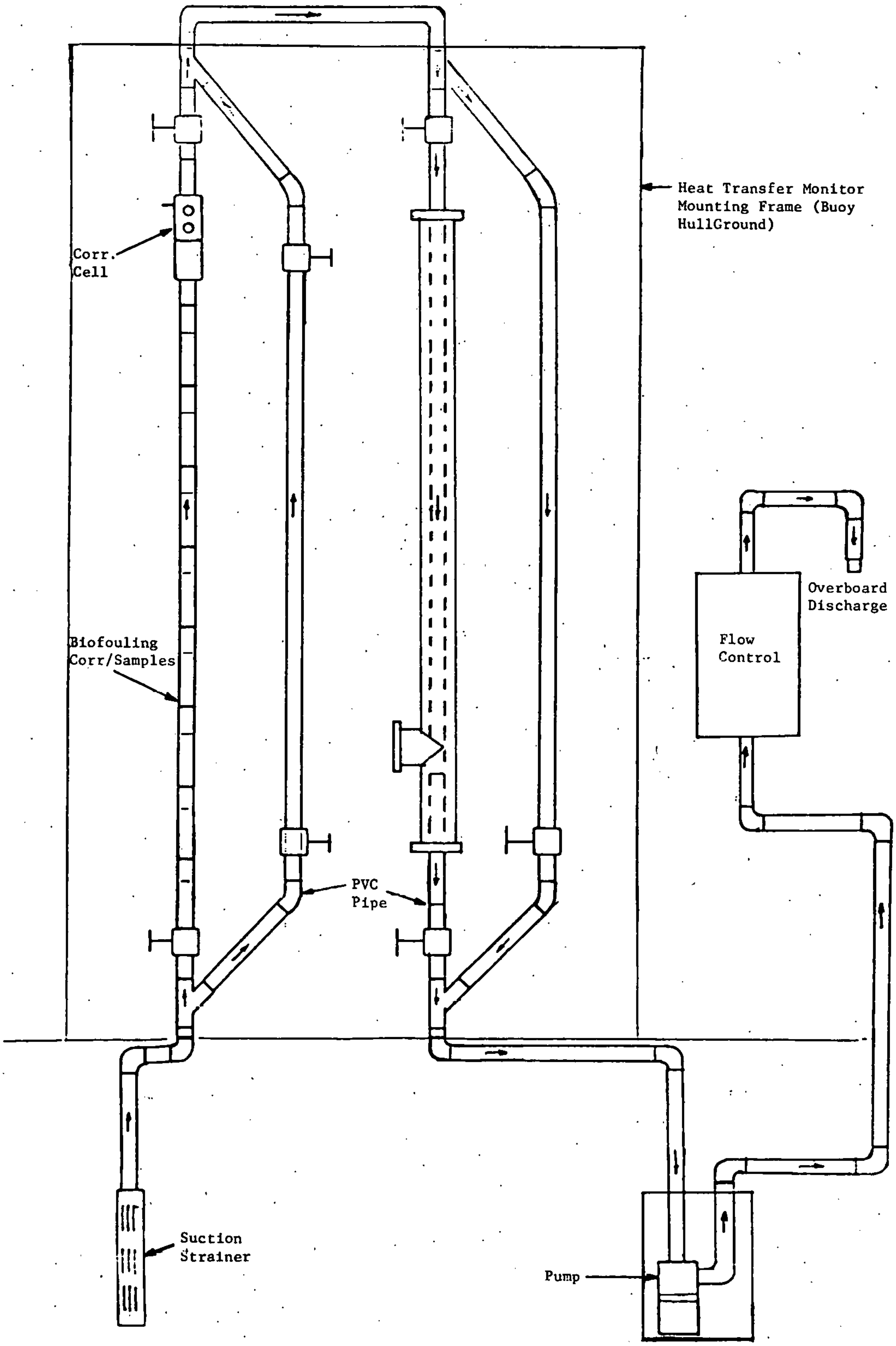

Figure 1 Corrosion and Heat Transfer Loops on Buoy

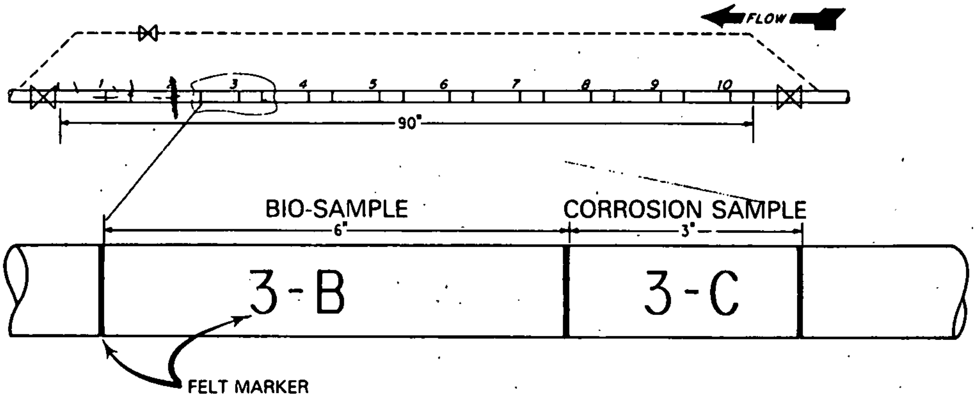

Figure 2

Location of Corrosion Sample

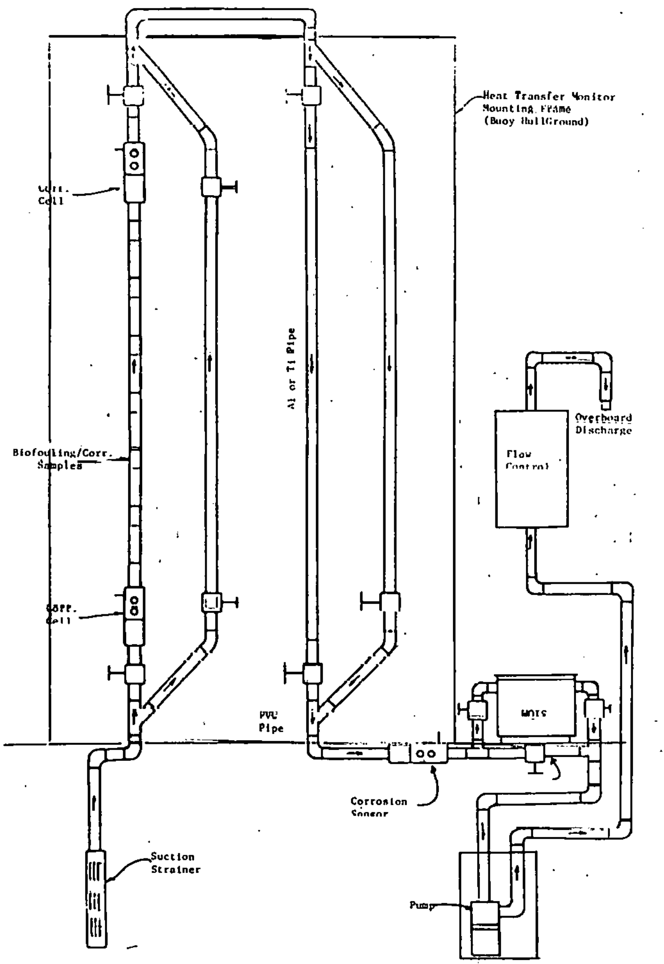

Figure 3

Location of Corrosion Sensor on WQIS Loop

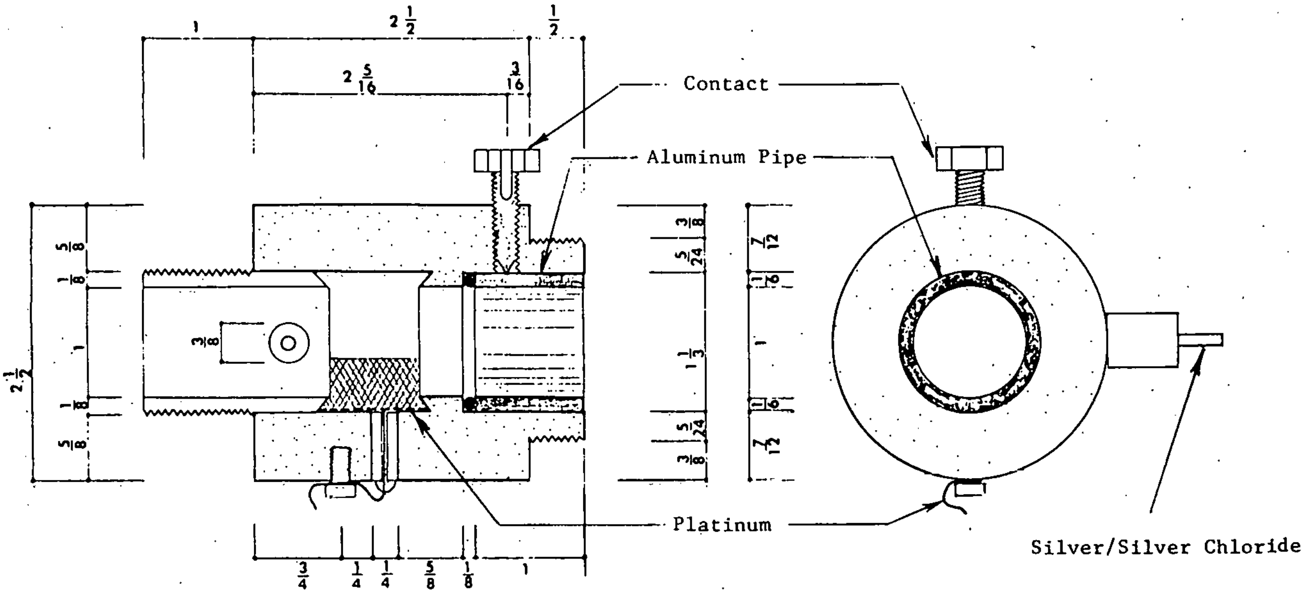

Figure 4 Corrosion Rate Sensor

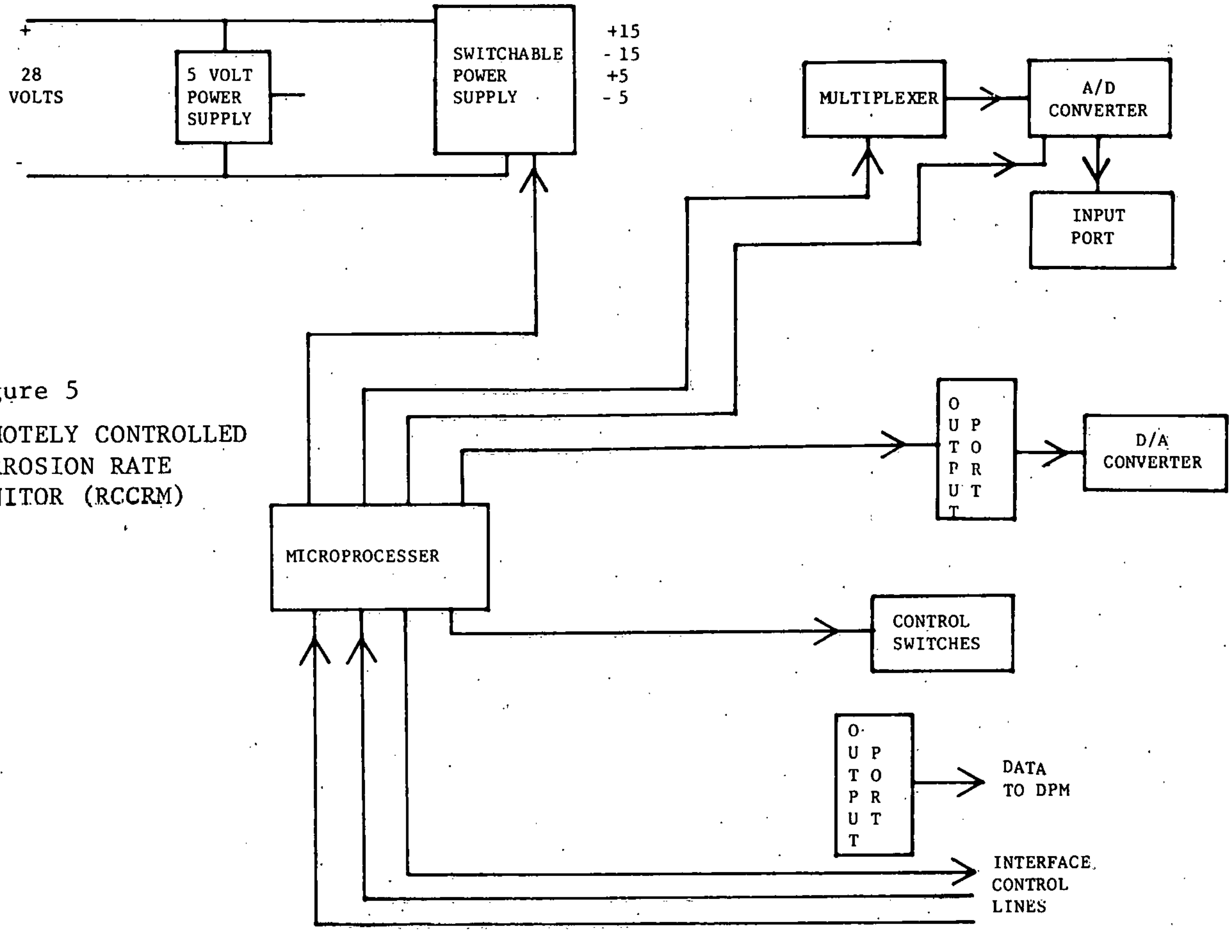

Figure 5

REMOTELY CONTROLLED CORROSION RATE MONITOR (RCCRM)

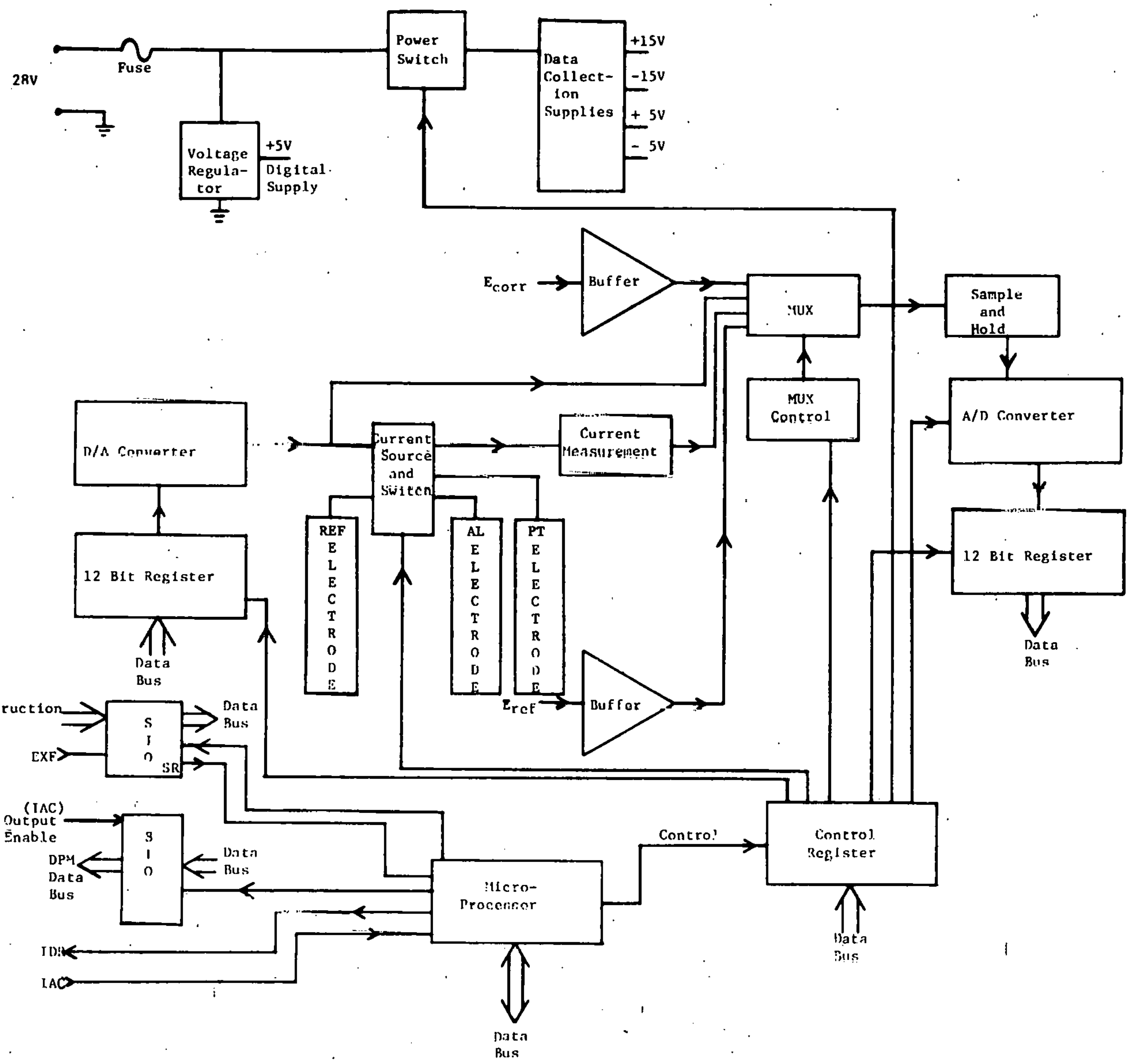

Figure 6 Schematic of Corrosion Meter

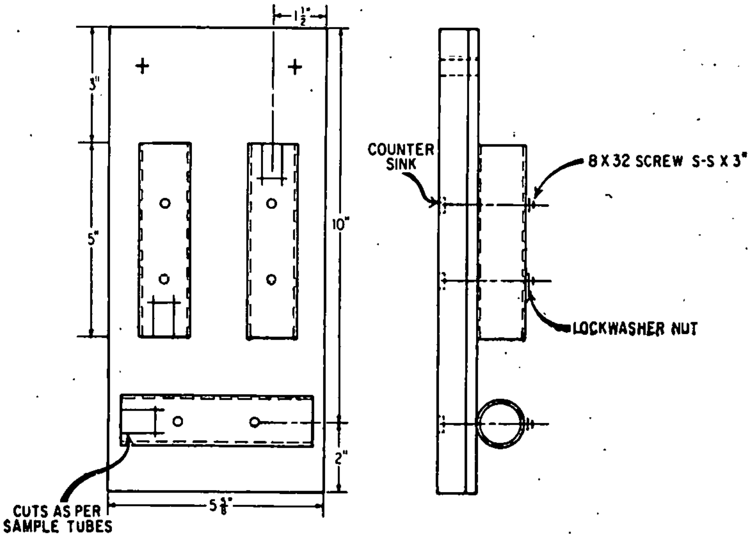

Figure 7

Plaque for Under Sea Corrosion Tests

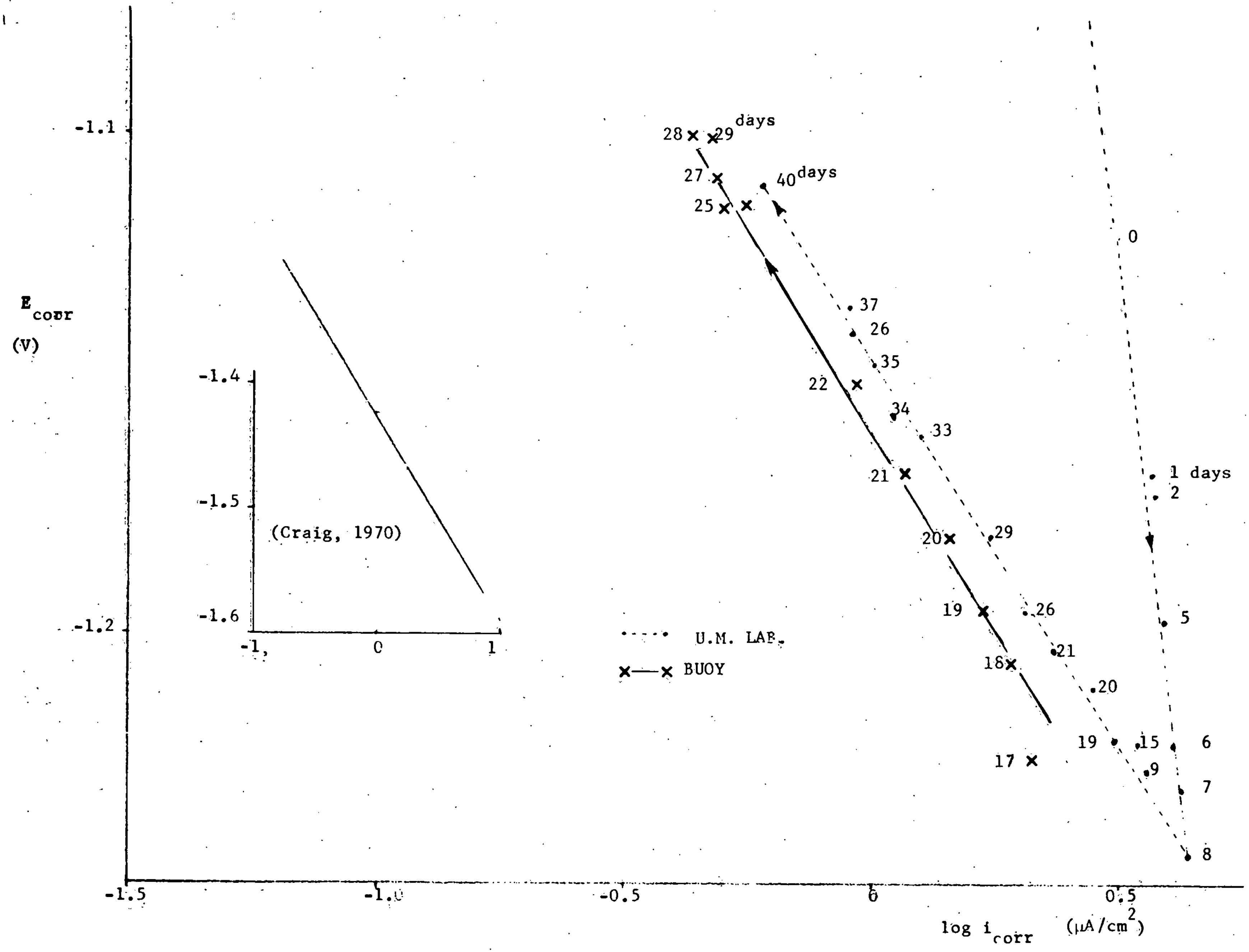

Figure 8 Corrosion Potential E_{corr} vs Log Corrosion Current

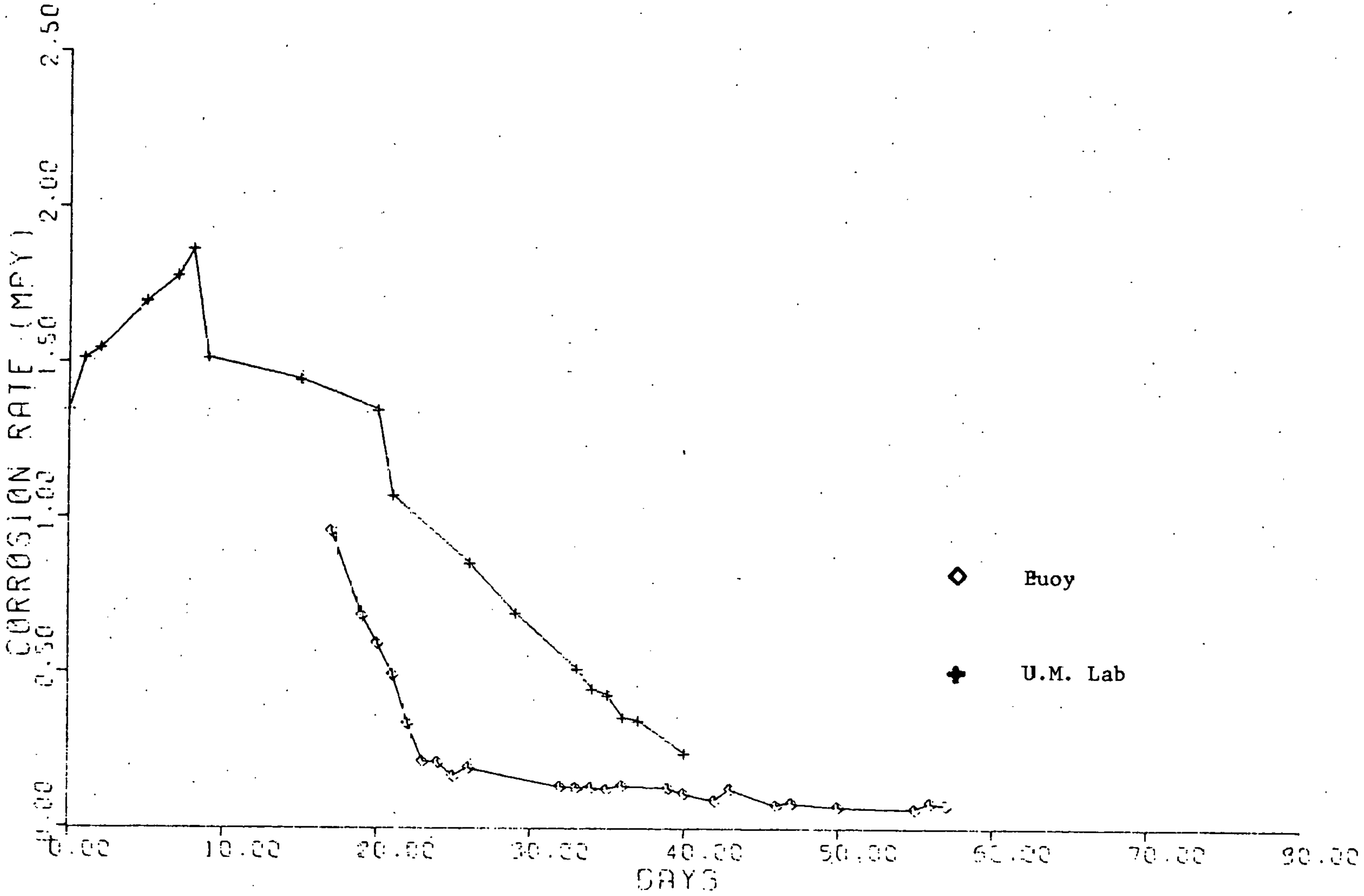

Figure 9 Corrosion Rate in Mils per Years vs Time in Days

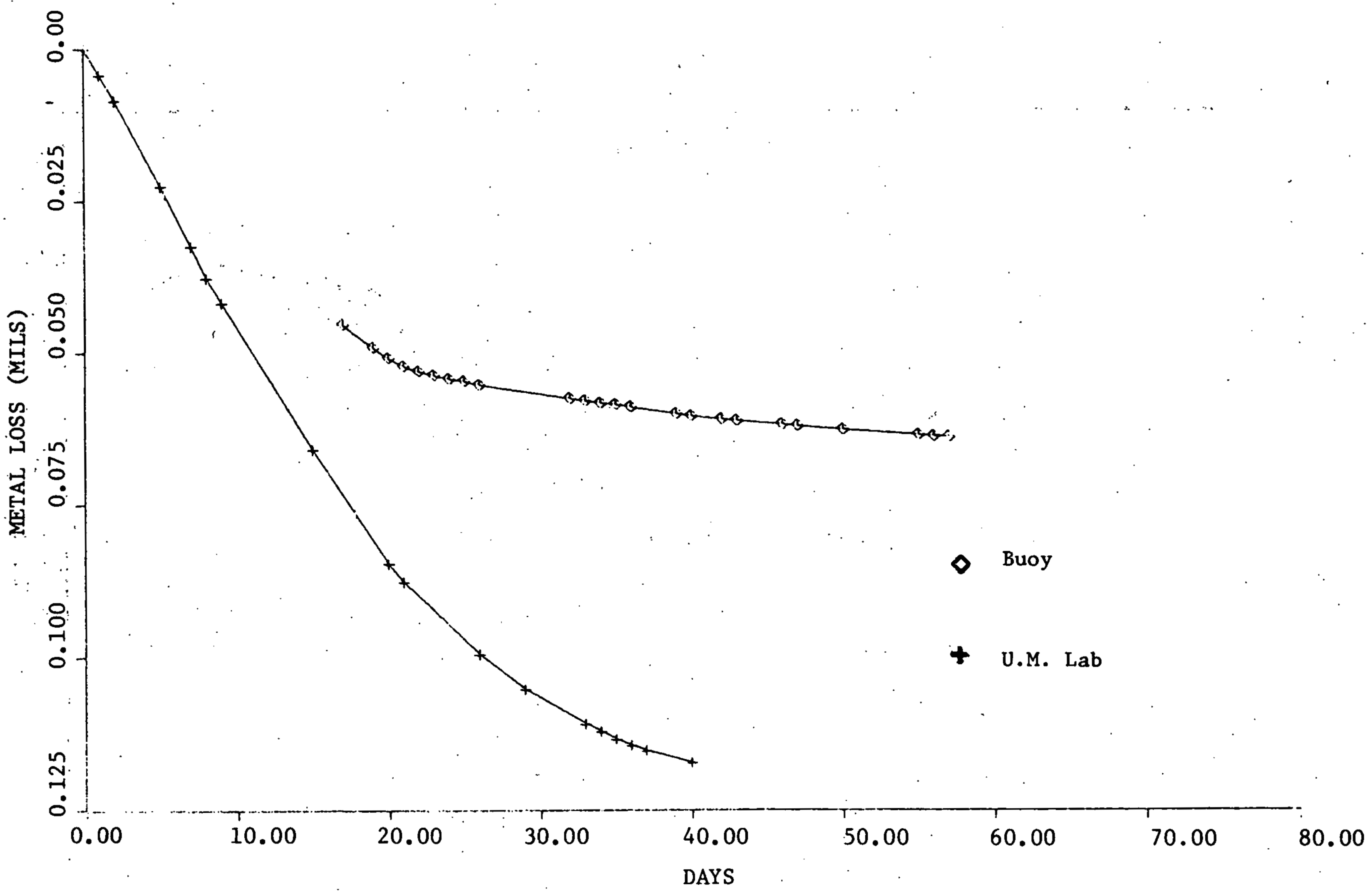

Figure 10 Metal Loss in Mils vs Time in Days

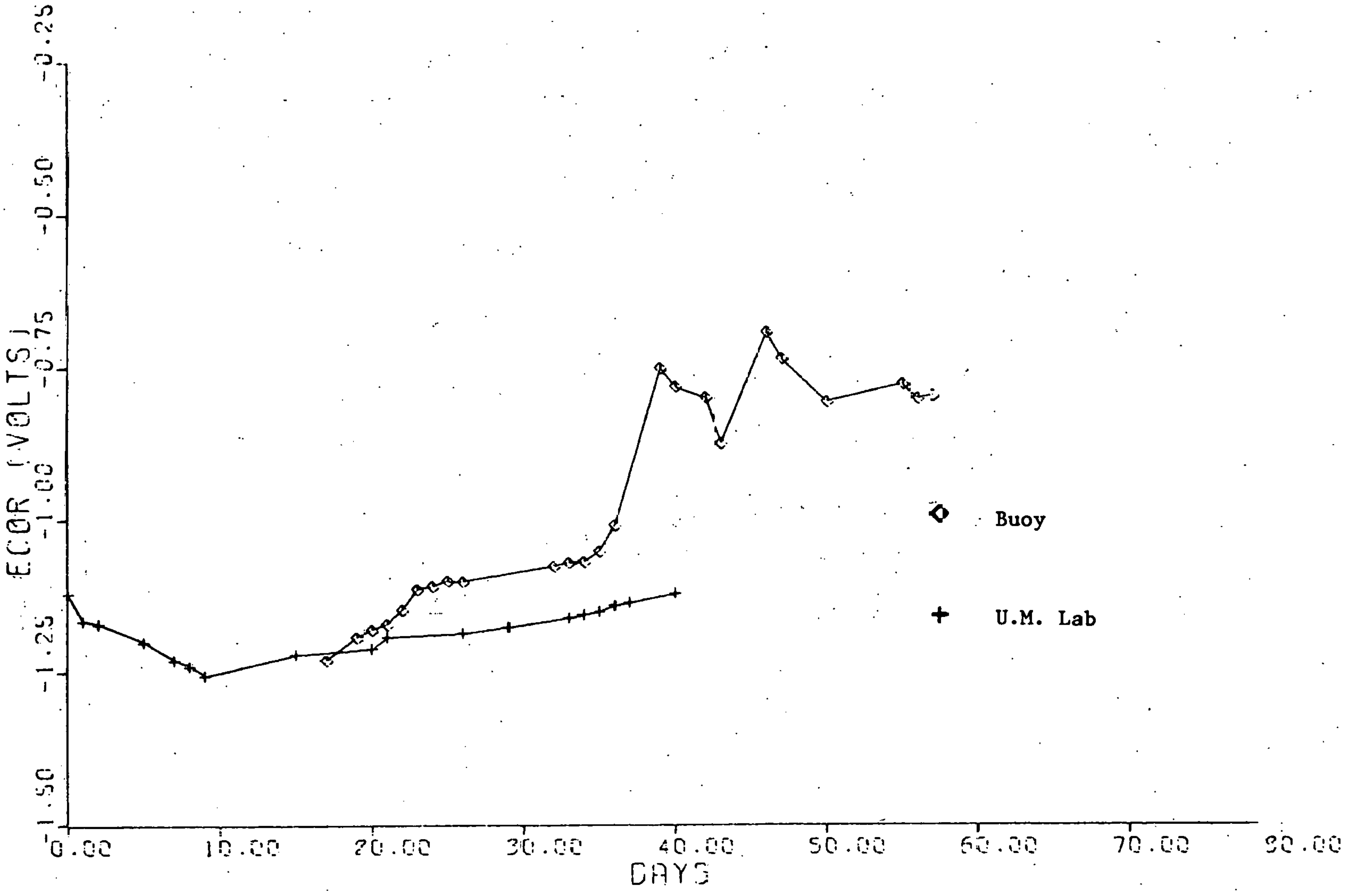

Figure 11 Corrosion Potential in Volts vs Time for 5052 Aluminum

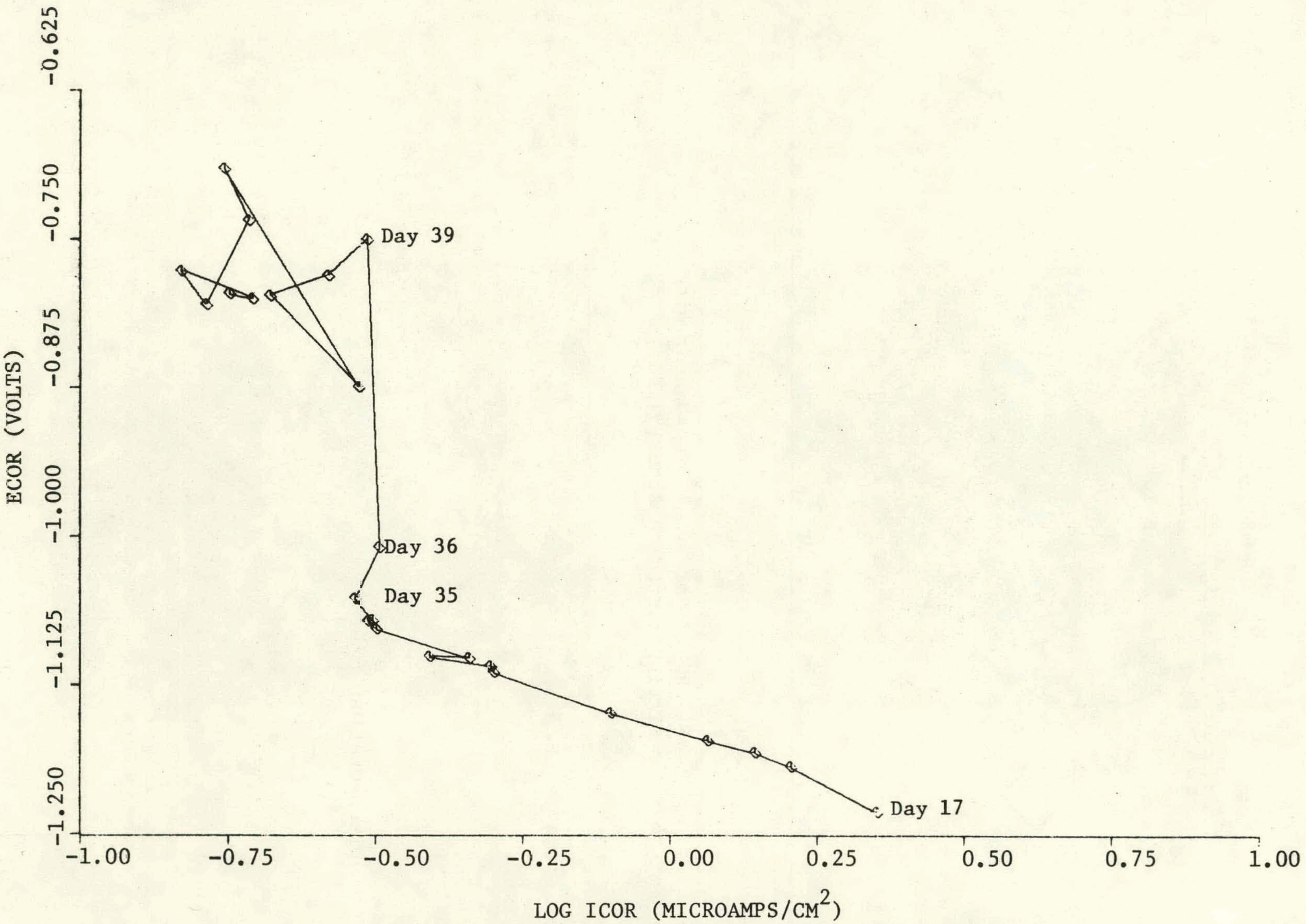

Figure 12 Corrosion Potential vs Log Corrosion Current for Buoy Specimen from Day 17 thru Day 57

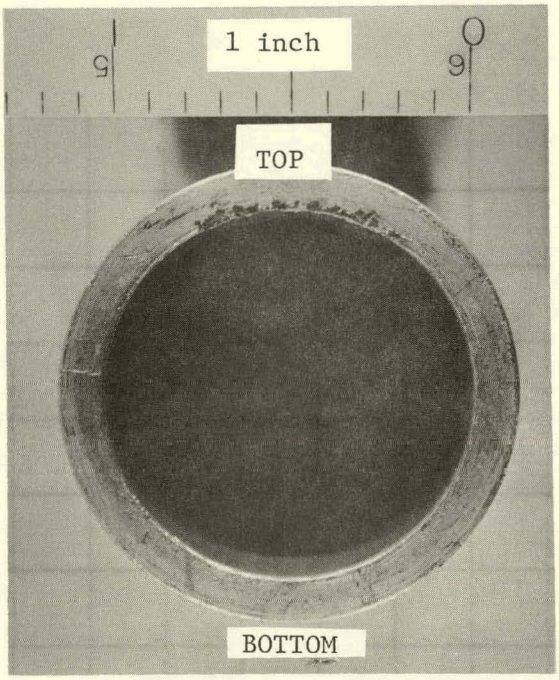

FIGURE 13 Aluminum Ring Sensor with Pitting Corrosion After 57 Days on Buoy

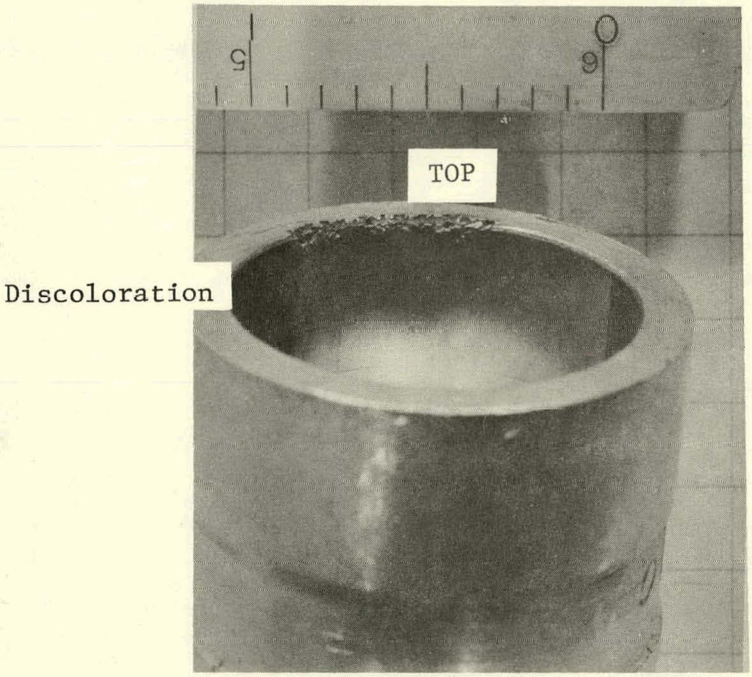

FIGURE 14 Ring Showing Pitting and Discoloration Except at Top of Ring

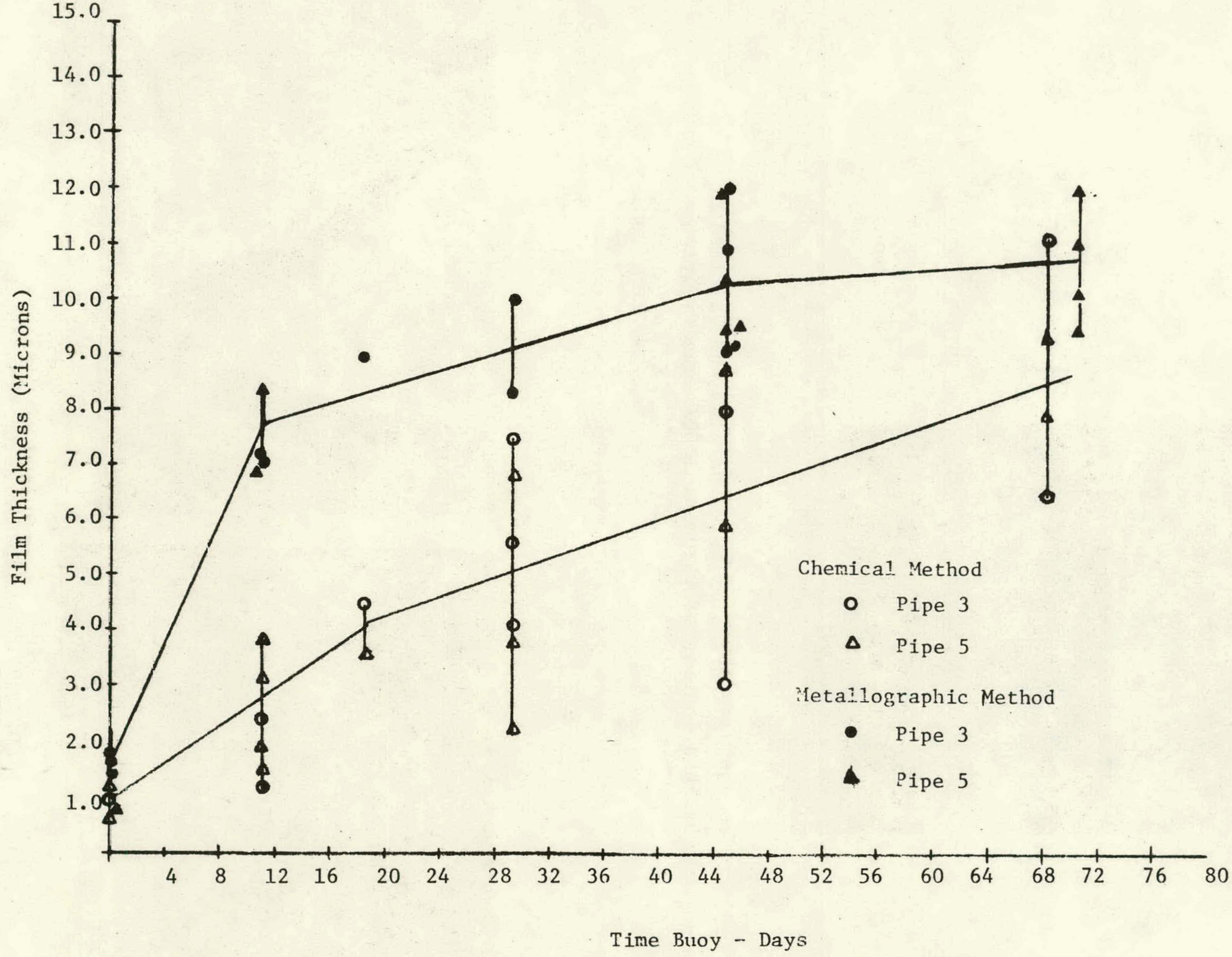

Figure 15 Film Thickness by Two Methods vs Time on Buoy

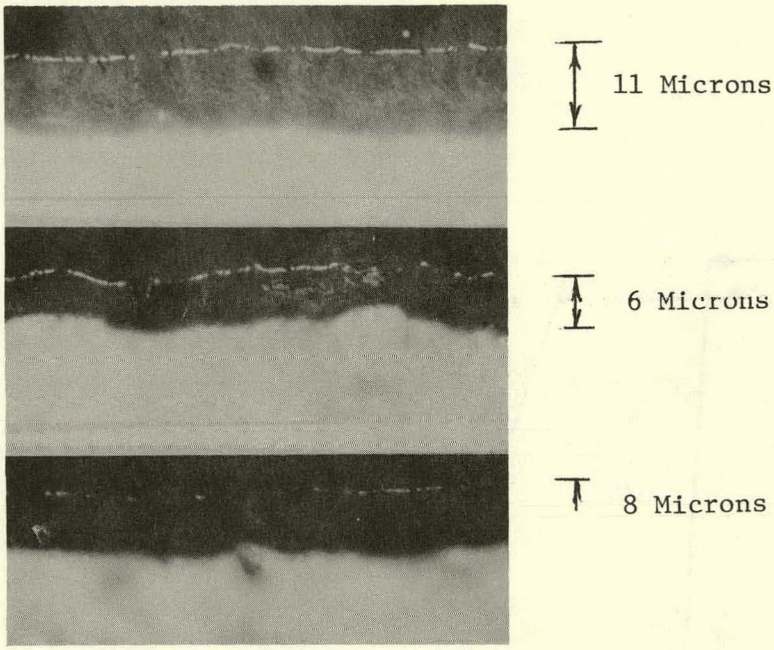

FIGURE 16 Corrosion Films on Aluminum Outlined by Thin Coating of Chromium 1000X Magnification

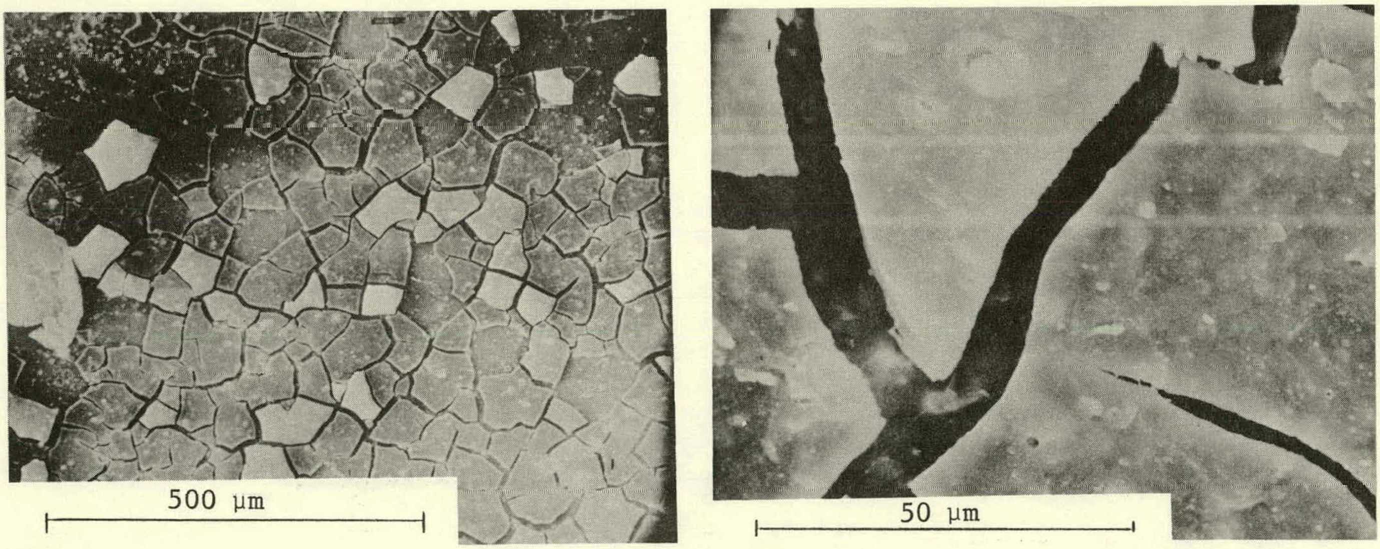

FIGURE 17 Typical Corrosion Product at 100X (left) and at 1000X (right)

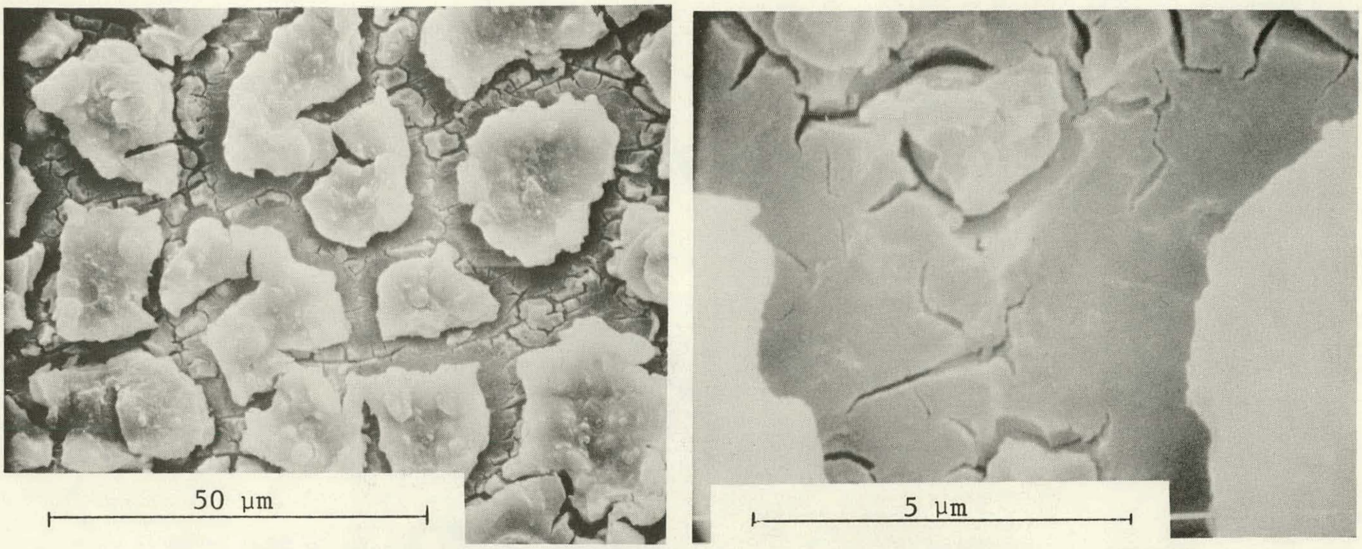

FIGURE 18 Aluminum Pipe
with Two Corrosion Films

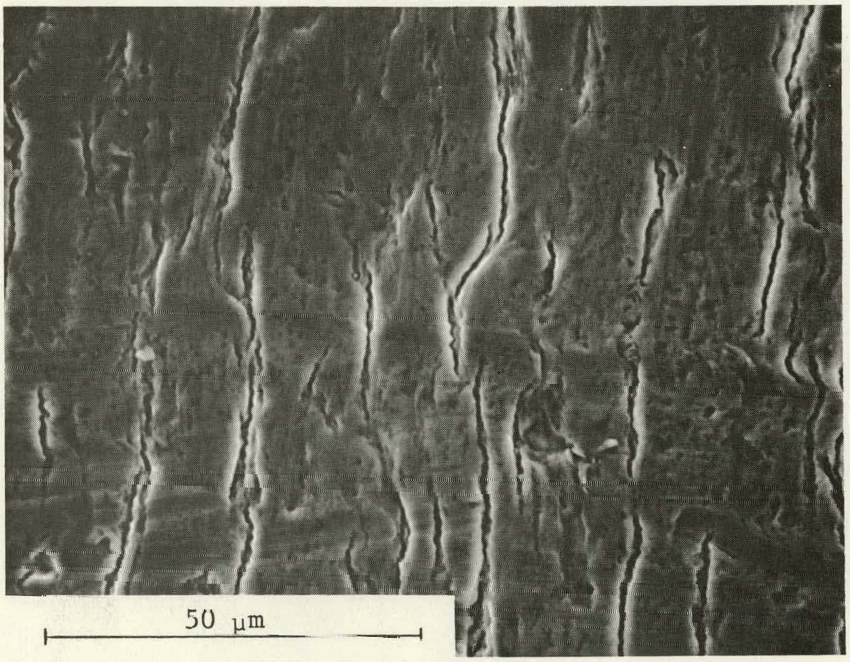

FIGURE 19 Titanium Surface
after Exposure to Sea Water

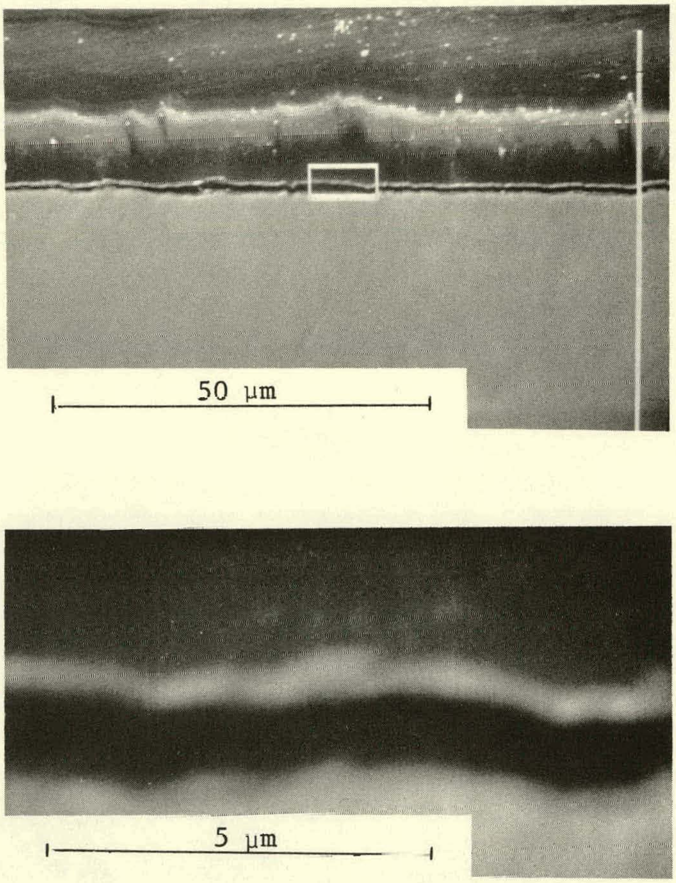

Figure 20 Titanium Corrosion Film at 1000X (upper) and 10,000X (lower) by SEM

RESISTANCE OF OTEC HEAT EXCHANGER ALLOYS TO MARINE EXPOSURES UNDER CONDITIONS OF CREVICE CORROSION AND CORROSION ACCELERATED BY MECHANICAL ABRASION

by

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INTRODUCTION

That seawater is a corrosive environment to most engineering materials of construction is a recognized fact. Characterization of the processes by which materials corrode in seawater and the environmental factors which affect these processes has been pursued by many researchers over the years. However, advancements in technology have led to development of new generations of materials and application of these materials to more and more challenging environmental conditions. The concept of ocean thermal energy conversion offers, in many ways, some of these challenging applications. The mere size of a fully operational OTEC system and the economic requirement of continuous operation will present corrosion-related problems for which an existing data base does not now exist.

BACKGROUND

The two specific corrosion areas of primary interest to OTEC involve development of engineering support data on crevice corrosion and corrosion accelerated by mechanical abrasion.

Experimental Procedure

All evaluations will utilize full-strength, air-saturated natural seawater. The nominal chemistry of seawater at the F. L. LaQue Corrosion Laboratory is shown in Table I and the seasonal variation of some of these parameters is shown in Figure 1. Characterization of the seawater chemistry is performed on a routine basis to assure the integrity of the corrosion data.

The alloys or metals utilized in this evaluation will be fully certified for chemistry and mechanical properties. These properties will meet any required ASTM or MIL specifications and, where possible, one primary heat of each material will be utilized for all evaluations. The materials will be evaluated with an as-received surface finish and will undergo only a degreasing surface treatment prior to exposure in seawater. Upon removal from the test exposures, materials will be cleaned to remove corrosion products in general accord with ASTM G-1 - Standard Recommended Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens.[1]

The evaluation of test specimens after seawater exposure will include assessment of the type and extent of corrosive phenomena as well as evidence of any biological fouling. Photographic documentation of these phenomena will be performed on a macro and micro scale as appropriate. Documentation of the corrosion data will be in a form compatible with generally accepted scientific techniques, e.g., gravimetric analyses, depths of attack.

Phase I - Crevice Corrosion and Metal Ion Concentration Cell Study

The purpose of this investigative phase is to assess the susceptibility of candidate OTEC heat exchanger materials to localized corrosion phenomena. Seven candidate alloys have been specified and a control alloy for comparative baseline purposes is recommended. These are listed in Table II with their nominal compositions.

Duplicate specimens of each material will be fitted with a non-metallic multiple crevice assembly (MCA).[2] These assemblies have 20 grooves and plateaus creating 20 crevice sites on each side of a test specimen (a total of 40 sites per specimen). Crevice assemblies are secured to the specimens with an insulated, corrosion resistant fastener and tightened to a torque of 10 newton-meters. The ratio of cathodic (bold) area to anodic (crevice) area is dictated by overall specimen dimensions. Area ratios of 150:1 and 300:1 will be utilized with specimens of dimensions 150 X 125 mm and 150 X 250 mm, respectively. A typically assembled crevice specimen is shown in Figure 2 and Figure 3 shows the pattern of attack typical for some stainless steels in seawater.

All specimen edges will be machined in a fashion to minimize the presence of cold-work deformed microstructures. Failure to do so may result in localized corrosion of these edges, particularly with stainless steels. This factor can influence the corrosion behavior at the MCA crevice sites to varying extents.[3] Except for specimen edges, all materials will be evaluated with the "mill finish" to approximate the condition in which materials will be utilized in OTEC systems. The surfaces will be degreased with acetone and a light scrub with pumice.

Ambient temperature, once-through seawater at a nominal velocity of 0.6 m/s will be utilized. All specimens will be exposed vertically in the seawater trough in a sequence to avoid metal ion contamination effects (e.g., aluminum alloys upstream of copper alloys). The test duration will be for a period of six months, during which time there will be a tendency for biofouling of some alloys. To minimize this element of interference in the controlled multiple crevice assembly evaluations, specimens will be periodically cleaned of any biofouling. This will be achieved by light scrubbing of the bold area of the specimens while they remain in seawater. The frequency of this cleaning will be dictated by the propensity of the fouling organisms to attach.

At the end of the exposure period, the crevice assemblies will be removed and the specimens probed for any incipient attack either at the MCA sites or on the bold areas. Specimens will be cleaned and depths of crevice attack measured to the nearest 0.01 mm. For passive alloys, the extent of crevice corrosion will be reported in terms of percent of crevice sites attacked and range and maximum depth of penetration. For other alloys, the extent of metal ion concentration cell corrosion will be reported in terms of approximate area of corrosive attack and maximum depth of penetration.

The resulting data from this program will be expected to form a baseline assessment of localized corrosion performance of these candidate OTEC heat exchanger materials. Since it is expected that chlorination for biofouling control may be utilized in OTEC and ammonia interleakage may occur within the system, localized corrosion behavior in these environments would be a logical follow-on program. It is recommended that any further evaluations accessing environmental variables (e.g., seawater temperature, pH, dissolved oxygen, chlorine or ammonia additions) and any evaluations assessing material variables (e.g., processing conditions) should be performed on specimens with a common surface finish. It has been shown[3] that specimen surface preparation (e.g., mill pickling, surface roughness, mechanical damage) can affect the response of some materials to crevice corrosion initiation. A uniformally ground surface generally results in more reproducible data and would allow a clearer assessment of effects of any minor environmental and material variables.

Phase II - Mechanical Abrasion Effects on Corrosion of Candidate OTEC Heat Exchanger Materials

The purpose of this investigative phase is to assess the effects of mechanical cleaning for heat transfer efficiency on the corrosion behavior of candidate OTEC heat exchanger materials. Five candidate alloys have been identified and are listed in Table III. Duplicate specimens of thin wall, 25 mm nominal diameter tubing (150 mm length) will be evaluated for each test condition. Exposure durations of 3, 7 and 12 months will be utilized with each alloy exposed in a separate test loop.

Recirculated, unfiltered seawater will be utilized in these test loops. The loops will be designed to contain a seawater volume allowing for a minimum of 0.35 liters of seawater for each 5.0 cm^2 of metal specimen surface area. The refreshment rate of seawater in these loops will be a minimum of one liter per minute. Analyses of oxygen and chloride levels, pH and metal ion concentrations will be performed to insure that no deviations from the raw seawater chemistry occur during the test duration.

The seawater will be maintained at a temperature of 30C and the loops will operate at a seawater velocity of 1.8 m/s. Seawater will be circulated through the tube I.D. while the O.D. will be protected from the marine environment by an inert coating.

Three environmental conditions will be assessed: 1) untreated seawater, 2) untreated seawater with mechanical cleaning, and 3) chlorinated seawater with mechanical cleaning. The untreated seawater condition will form the baseline from which to assess the effects of mechanical cleaning.

Mechanical cleaning will be evaluated by the use of a MAN ® brush system. Utilizing an automatically controlled seawater flow reversal system, the brush will be moved through the tube I.D. at a frequency of twice every eight hours. Appropriate brushes will be selected for each material and will be replaced with the recommended frequency. To assess galvanic effects, which might occur as a result of incomplete cleaning in an OTEC system, additional specimens will be included for a 7 month duration. These specimens will be exposed in the test loops such that one specimen is mechanically cleaned while the second specimen remains uncleaned. Galvanic coupling via external electrical connections will allow galvanic current measurements.

A final condition will utilize the above MAN ® brush system but will also include a residual chlorine level of 0.1 mg/l in the seawater. The chlorination will be achieved by metered injection of chlorinated seawater into the seawater stream from a reservoir of electrolyzed seawater maintained at a constant stock concentration (e.g., 100 mg/l). This system should provide more stability in the chlorine level than either batch treated water or electrolyzing the primary flow in the test loop. The general appearance of these test loops is schematically shown in Figure 4.

At the end of each exposure duration, the environmental effects on the tube materials will be assessed by chronogravimetric analyses and, after tube splitting, photographic documentation. To obtain both weight loss data as well as before cleaning appearance of the extent of any fouling, one tube will be acid cleaned before splitting while the replicate tube will be split before acid cleaning. Both the nature of any corrosive attack and the depth of penetration will also be determined.

REFERENCES

1. 1978 Annual Book of ASTM Standards, Part 10.
2. D. B. Anderson, "Statistical Aspects of Crevice Corrosion in Seawater", ASTM STP 576 - Galvanic and Pitting Corrosion - Field and Laboratory Studies, 1976.
3. R. M. Kain, "Crevice Corrosion Resistance of Austenitic Stainless Steels in Ambient and Elevated Temperature Seawater", to be presented at CORROSION/79.

TABLE I

Nominal Composition of Seawater at the F. L. LaQue Corrosion Laboratory

Major Variables

	Maximum	Minimum	Average
pH	8.1	7.8	8.0
T, °C	29	6	18
Cl-, g/L	19.8	18.1	19.0
O_2, mg/L	9.3	5.0	6.4

Average Analysis, mg/l

Cations		Anions	
Na	10,006	SO_4	2510
Ca	398	HCO_3	133
Mg	1204	NO_3	1.2
K	369	PO_4	0.01
Cu	0.015	F	1.5
Fe	0.200	Br	61
Zn	0.012	I	0.16
		Cl	19,000

TABLE II

Materials for Localized Corrosion Evaluations

CA 706	Cu-10Ni-1.4Fe
CA 722	Cu-15Ni-0.5Cr
Spinodal CuNiSn	Cu-10Ni-8Sn
Grade 5052 Al	Al-2.5Mg-0.25Cr
Alclad Aluminum	7072 (Al-1.0Zn) clad 3003 (Al-1.2Mn)
Titanium, C.P.	Ti
Al-6X Stainless Steel	Fe-24Ni-20Cr-6Mo
Type 316 Stainless Steel	Fe-18Cr-10Ni-2Mo

TABLE III

Materials for Corrosion Accelerated by Mechanical Abrasion

CA 706	Cu-10Ni-1.4Fe
Grade 5052 Al	Al-2.5Mg-0.25Cr
Al clad Aluminum	7072 (Al-1.0Zn) clad 3003 (Al-1.2Mn)
Titanium, C.P.	Ti
Al-6X Stainless Steel	Fe-24Ni-20Cr-6Mo

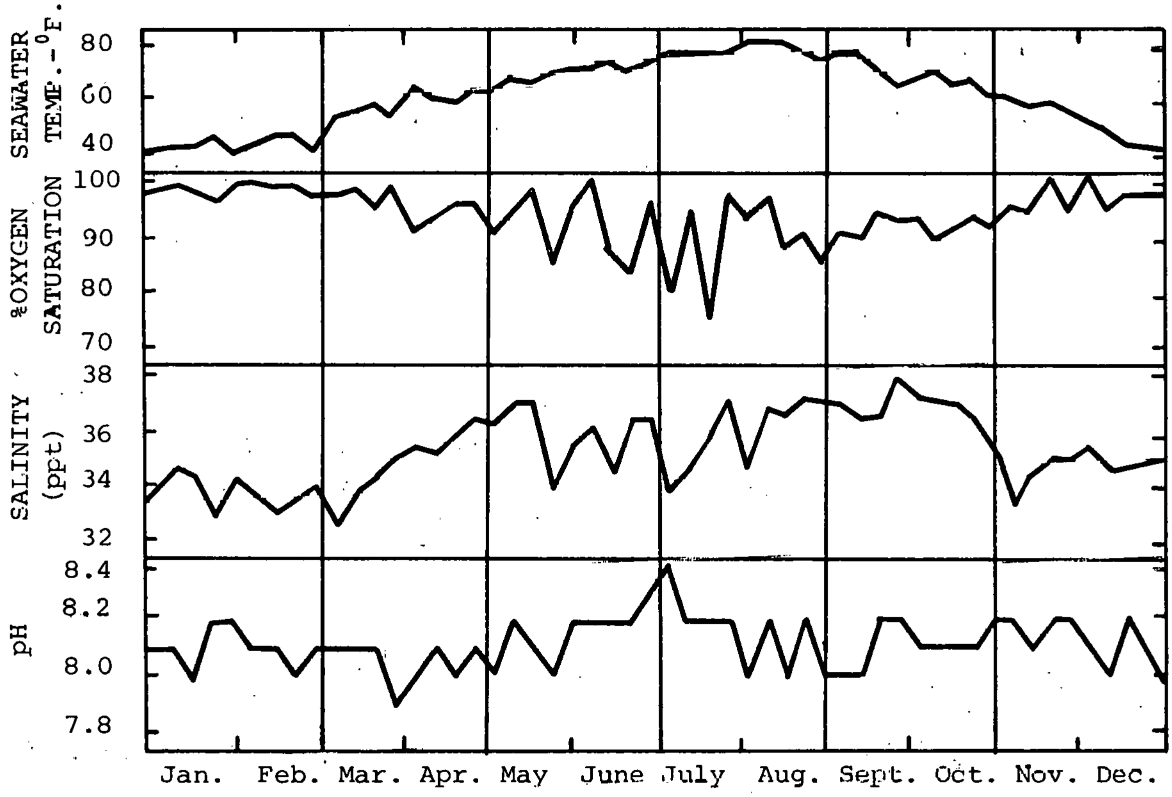

Figure 1. Typical seawater hydrology at FLLCL

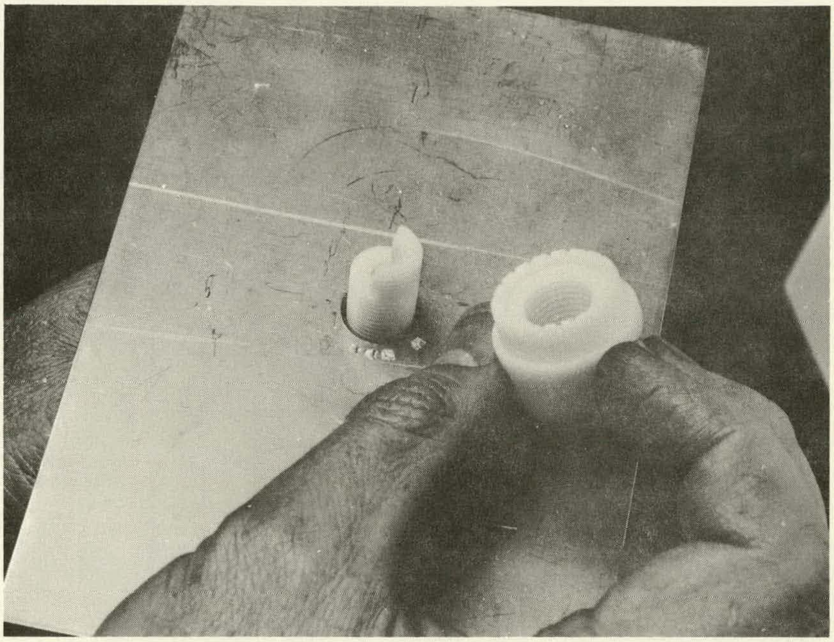

Figure 2 - Test specimen with a non-metallic multiple crevice assembly

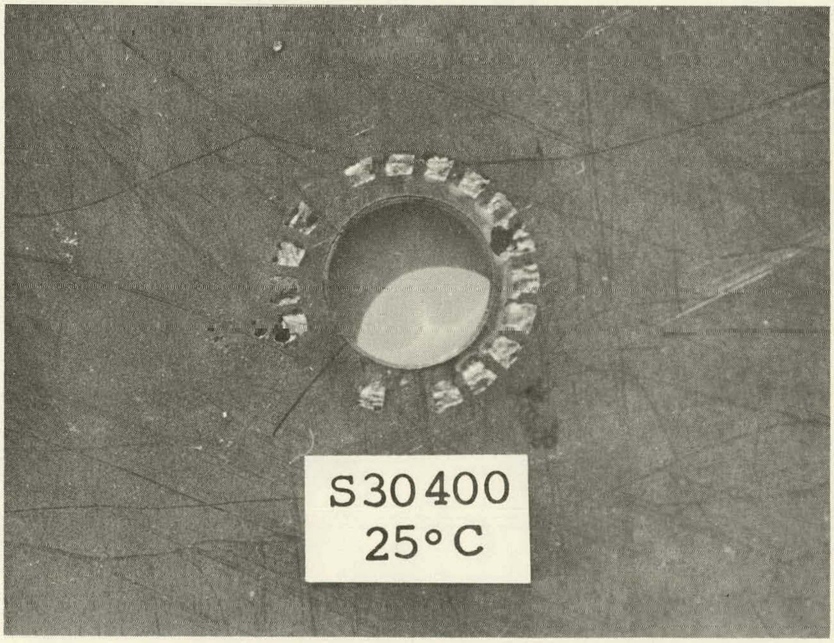

Figure 3. Typical pattern of crevice corrosion for some stainless steels exposed in ambient temperature seawater with the MCA.

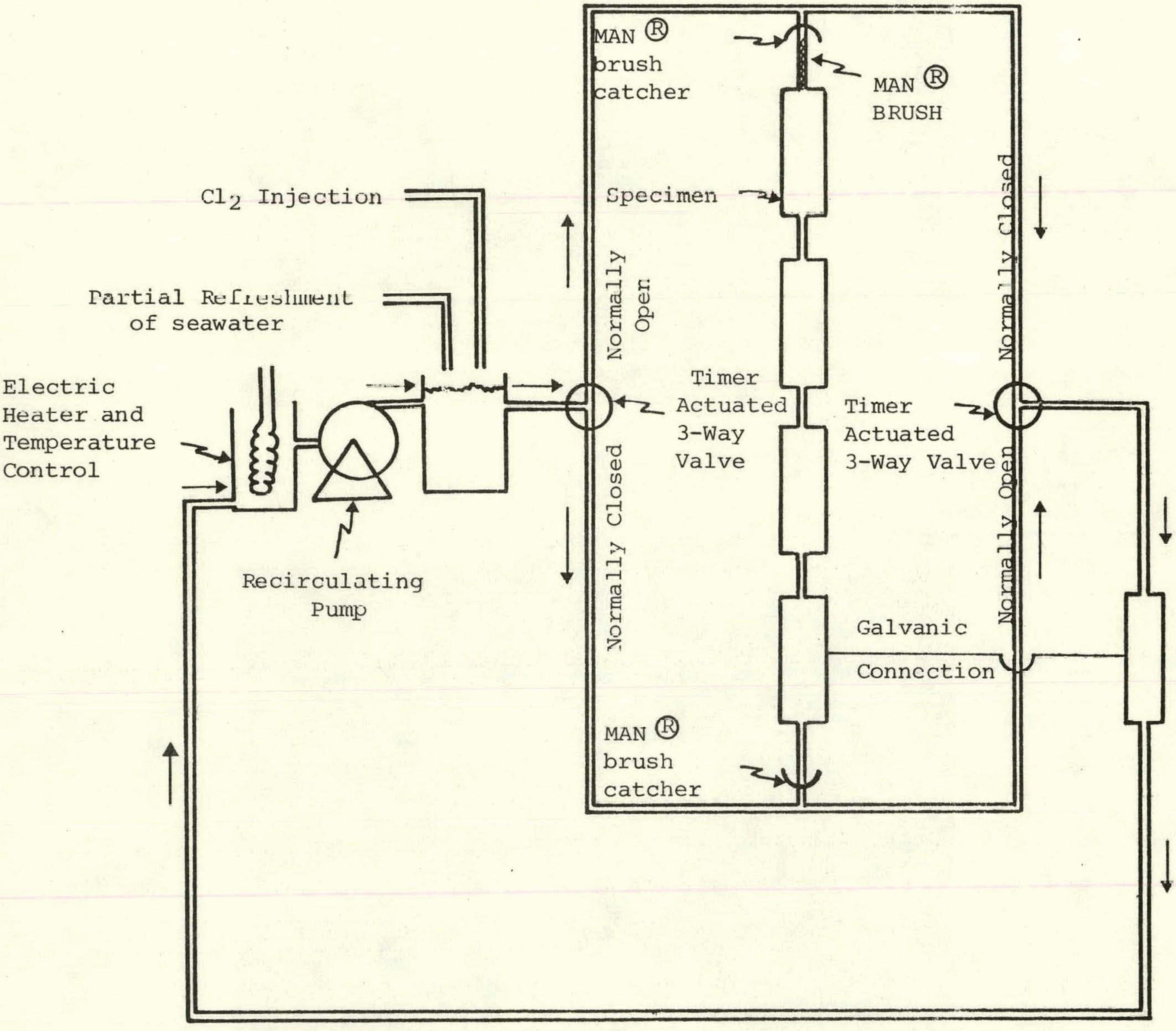

Figure 4. Schematic of MAN ® brush cleaning system with partial seawater refreshment, chlorination and temperature control.

INTERLEAKAGE OF AMMONIA AND SEAWATER IN OTEC HEAT EXCHANGERS -- EFFECTS ON CORROSION AND SCALE FORMATION

by

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I. INTRODUCTION

A principal Ocean Thermal Energy Conversion (OTEC) concept under consideration is based upon the use of an ammonia-cycle generator system powered by small thermal differences available between surface and deep ocean waters. The purpose of this contractual effort was to assess the influence of seawater-ammonia mixtures on proposed OTEC heat exchanger materials at environmental conditions simulating an OTEC plant exposure.

Testing was to remain on a coupon test scale, and relevant information sought included degree and definition of chemical scaling, general corrosion rates, pitting, crevice corrosion, and influence of intermittent but sequential chemical and mechanical cleaning. Heat exchanger materials, as proposed by the Department of Energy, included commercially pure (CP) titanium, and aluminum alloys 3003, 5052, and 5086. Additionally, specimens of aluminum alloy 5052 pretreated in boiling deionized water were included in all exposures.

The possibility of either an ammonia or seawater intrusion (leak) in either the OTEC evaporator or condenser, constituted the stimulus for this research on candidate OTEC heat exchanger materials. The concern was that low concentrations of ammonia in seawater, and conversely, low concentrations of seawater in ammonia, may act to seriously impair material performance.

This paper summarizes the results of the experimental testing program carried on at Freeport from September 1977 until January 1979, under contract to Battelle Pacific Northwest Laboratories and Argonne National Laboratory. A description of the experimental testing program begun in December 1978 under contract to Argonne National Laboratory is also contained herein.

II. SUMMARY

Exposures were completed for nominal 8, 30, 80, and 800 ppm additions of ammonia to seawater at 5°C and 30°C. The change in pH resulting from the ammonia addition has resulted in scaling at all ammonia concentrations, with calcite formation followed by aragonite and then brucite as concentrations increased. It is anticipated that a continuous cleaning process could control scale at 8 ppm, 30°C and 5°C, and at 30 ppm, 5°C, but that scaling at 80 ppm and 800 ppm additions is not economically controllable. Corrosion has been minimal except for measureable pitting on Al 3003, Al 5052, Al 5086 at 8 ppm, 30°C, and on Al 5052 at 8 ppm, 5°C. Ambient temperature seawater controls show general corrosion attack but insignificant pit attack.

Exposures were also completed for 0, 0.1, 1.0, and 2.5% nominal seawater additions to commercially pure ammonia at 5°C. Both corrosion and scaling have been minimal for these exposures.

The exposures reported herein indicate that CP titanium will give superior performance in an OTEC heat exchanger followed by pretreated aluminum alloy 5052.

III. EXPERIMENTAL

A. PROCEDURES

1. Test Units

Four test units were constructed to meet the requirements of the corrosion test program. The exposure conditions required included seawater with small additions of ammonia at 5°C and 30°C, anhydrous ammonia with small additions of seawater at 5°C, and once-through ambient temperature seawater.

Two test units were designed and constructed to test the subject alloys in seawater with small concentrations of ammonia using recirculating seawater-ammonia mixtures with a continuous blowdown, as depicted in the generalized schematic in Figure 1. One unit operated at 30°C and the other at 5°C. The low temperature unit employed an external chiller circuit with heat removal from the loop by means of a cold glycol-water solution. Units are constructed of plastic-lined steel (polypropylene, Saran®, Teflon®, and Kynar®) and Alloy 20 stainless steel.

To insure adequate mixing, the two units receive ammonia solution downstream of the recirculating pump. Concentrations of ammonia in seawater are routinely obtained by analysis of the system blowdown. Both units contain all instruments necessary for automatic control and failsafe shutdown to prevent specimens from experiencing excessive ammonia concentrations.

A third test unit to operate at 5°C using mixtures of anhydrous ammonia with low concentrations of seawater was constructed according to the generalized schematic in Figure 2. Construction material is welded stainless steel 304 alloy, Teflon-lined steel, and Alloy 20 stainless steel. The loop contains a suitable pump, temperature detectors, flow control and monitoring devices, as well as all automatic controls necessary for failsafe system operation. A chiller is incorporated in the circuit to maintain a 5°C environment within the test loop.

The test loop is designed to contain 100 lbs. of anhydrous ammonia to reach a volume-to-specimen area ratio believed to simulate proposed OTEC conditions.

A fourth unit for testing of cleaning procedures was constructed, as depicted in Figure 3. It is a once-through seawater loop with automatic flow control. Cleaning test specimens were exposed to unfiltered seawater and temperature is not controlled.

Seawater utilized in these tests is from the Gulf of Mexico intake basin located at the Dow Chemical Texas Division industrial site "A" at Freeport, Texas. After large incoming debris is screened out at the Dow intake basin, the seawater is transferred through flumes (canals) to a second smaller sedimentation basin near the OTEC test facility. The seawater is then transferred through a system of copper-free piping to the test units where (with the exception of the cleaning test specimens) the seawater is filtered to contain a maximum particle size of 25 microns.

2. Specimens

Preparation and handling procedures of the metal specimens were more elaborate than would be the case for tubes entering an actual OTEC heat exchanger, but conducted within the recommendations of the National Association of Corrosion Engineers.

The alloys specified for use in these tests include aluminum alloys 3003, 5052, and 5086, and CP titanium.

A sample series of aluminum alloy 5052 pretreated in boiling deionized water for eight hours was added to the test because one of the findings of the Office of Saline Water desalination materials test programs indicated that the higher general and pitting corrosion attack of aluminum which occurs during the initial few weeks can be effectively reduced or eliminated by such pretreatment.

General and pitting corrosion rate determinations utilized (6" x 3/4" x (0.06-0.08)") nominal size coupons. These specimens were held in Teflon-lined spools of the test units. Fluid velocity past the specimens was accurately fixed by knowledge of the flow rate and available cross sectional area in the holder. Figure 4 shows a separate coupon holder assembly.

Crevice corrosion determinations utilized (3" x 3" x (0.06-0.08)") nominal size specimens with a centered (1/2" diameter) hole. These specimens were mounted on a rod holder and individually separated by special crevice contactors. These contacts were specifically designed to form eight crevice areas on each side of the specimen faces with fluid stagnation points between the crevice areas. Contact pressure between the separators and specimens was applied from each end of the crevice assembly. All portions of the assembly were fabricated of glass-filled Teflon. Mounting of the assembly in the test environment is accomplished through connections at the rod ends. Figure 5 shows a crevice specimen assembly.

Upon removal from the test environment, photographs were made of the fouled/scaled specimens, thickness of the scale determined, and specimens submitted for analysis of surface deposits. Specimens were then acid-cleaned using an ultrasonic cleaner, degreased and weighed. Weight losses were determined for calculation of general corrosion rates.

Weight loss and microscopic data was resolved into general corrosion rate, projected general corrosion rate, maximum pit depth, and approximate pit density.

General corrosion rate was calculated as suggested by NACE standard TM-01-69 (1972 Revision). However, passivating alloys often experience a high initial weight loss which is not indicative of long-term alloy performance. In assessing long-term performance of such alloys, the projected corrosion rate is more indicative of the true alloy performance. Therefore, projected corrosion rate determinations were also made based upon time and weight loss difference calculated for the final specimen pulls. Pit and crevice attack were also assessed.

3. Cleaning Tests

The purpose of this test is to compare the influence on corrosion of mechanical and chemical cleaning techniques.

The mechanical cleaning technique employed consisted of a simulated M.A.N.® brush system. Cleaning was performed under flowing tap water.

Chemical cleaning chosen utilized a non-proprietary mix that can be foamed. Four chemical solutions were screened and harsh acid cleaning using a 10% H_2SO_4, 2% chromic acid solution provided the best results.

B. CORROSION

Experience with the use of aluminum has indicated that this metal can be sensitive to pit attack in alkaline media. As seawater is slightly alkaline, and seawater plus ammonia is more alkaline, it was necessary to perform preliminary screening tests to evaluate specified aluminum alloys under simulated OTEC conditions. Titanium, another contender for OTEC heat exchanger use, was also tested.

1. Seawater Controls

Corrosion control tests were conducted using ambient temperature seawater at 5.0 fps and a once-through system. These control tests were run at periods coinciding with the 8, 30, and 800 ppm ammonia in seawater exposures.

Corrosion on the seawater controls was marked by general, uniform surface attack and the absence of significant pitting. Aluminum alloys 3003, 5052, and 5086 all show projected corrosion rates of 2.2-2.6 mpy, with aluminum alloy 5086 giving the most consistent performance of the three untreated alloys. Treated aluminum alloy 5052 was superior to all aluminum tested with a projected corrosion rate of 0.60 mpy. CP titanium showed negligible attack and was generally superior to all metals on test.

2. Ammonia in Seawater

The results are summarized in Figure 6 for the 5°C exposure and Figure 7 for the 30°C exposure. At 30°C, with 8 ppm ammonia aggressive pit attack was noted on aluminum alloys 3003, 5052, and 5086. At 5°C, aggressive pit attack was noted on aluminum alloy 5052. Parallel ambient temperature seawater controls showed greater general corrosion rates but only insignificant pit attack on these same alloys. Performance of the crevice test specimens was generally superior to that of the weight loss coupons. CP titanium showed negligible pit attack and constituted the superior metal at these exposures followed by pretreated aluminum alloy 5052.

At 30°C, with 30 ppm ammonia, one or two pits 1-2 mils deep were noted on aluminum alloys 3003, 5052, and 5086. At 5°C no significant pit attack occurred. Crevice corrosion was not observed at the 30°C temperature exposure. At 5°C, 1-2 mils crevice attack penetration was noted on aluminum alloys 3003, 5052, and 5086. CP titanium gave the best corrosion performance of any metal tested at this exposure followed by pretreated aluminum alloy 5052.

Exposures at 5°C and 30°C with 80 ppm ammonia, were completed with pulls at 10, 30, and 51 days. The proposed 60-day exposures were cut short because of extensive calcareous scaling within the units. Projected general corrosion rates at 30°C were generally 50-100% of the projected ambient temperature seawater corrosion rate for the aluminum alloys while those at 5°C were minimal. Maximum observed pit depth on any specimen was estimated at less than 1 mil penetration. No significant crevice attack was noted on either test after 50 days although some slight impressions were present at the lower temperature. Again CP titanium and pretreated aluminum alloy 5052 showed overall superior performance.

The 5°C and 30°C exposures at 800 ppm ammonia in seawater were terminated at 10 days because of excessive scaling. Both projected general corrosion rates and pitting were negligible, a factor probably related to the rapid scaling.

3. Seawater in Ammonia

Simulation of a seawater leak into the ammonia side of an OTEC heat exchanger was performed at 5°C, condenser temperature, and at simulated leak severities of a nominal 0, 0.1, 1.0, 2.5% seawater. Scale was not observed to form within the test unit over the range of seawater concentrations investigated. Pit and projected general corrosion rates for these test exposures are summarized in Figure 8.

Corrosion tests in 5°C commercially pure anhydrous ammonia (151 ppm water) were terminated after 10 and 38 day specimen exposures. Pit, crevice, and general corrosion attack were minimal on all alloys tested. Initially high general corrosion rates were observed for pretreated aluminum alloy 5052. However, these rates decreased with time such that at the conclusion of the test all aluminum alloy rates were comparable. CP titanium demonstrated corrosion resistance superior to that of any metal tested, followed in order by pretreated aluminum alloy 5052 and aluminum alloys 5052, 3003, and 5086.

Pitting and crevice attack was negligible for all alloys tested in anhydrous ammonia with 0.1% seawater at 5°C. Projected corrosion rates for aluminum alloys 3003, 5052, and 5086 are less than 0.12 mpy at 2.5 fps and 0.43-0.69 mpy at 5.6 fps; thus indicating a significant velocity effect at this exposure. Initially high corrosion rates for pretreated aluminum alloy 5052 give a projected corrosion rate at 24 days which is negligible. The superior metals at this exposure are CP titanium and pretreated aluminum alloy 5052.

Pitting and crevice attack was negligible except for one pit observed on aluminum alloy 5052 at 5.6 fps when 1.0% seawater was added to ammonia at 5°C. Initially high corrosion rates on pretreated aluminum alloy 5052 declined such that after 59 days exposure this alloy showed negligible additional corrosion attack. CP titanium constituted the superior metal at this exposure followed by pretreated aluminum alloy 5052.

Pit and crevice attack were negligible in anhydrous ammonia with 2.5% seawater at 5°C although projected corrosion rates for aluminum alloys 3003, 5052, and 5086 were greater than for ammonia exposures with lower seawater percentages. Initially high general corrosion rates for pretreated aluminum alloy 5052 declined to much more reasonable rates after 53 days exposure. CP titanium again was superior metal for this exposure followed by pretreated aluminum alloy 5052.

C. SCALE FORMATION

Mixing of ammonia and water will result in hydrolysis of the ammonia to form ammonium and hydroxyl ions. The resulting solution is thus more alkaline, and in seawater an increase in alkalinity enhances calcium carbonate and magnesium hydroxide precipitate formation. Precipitates so formed may then nucleate and form scales on heat exchanger surfaces in a manner which will seriously impair heat transfer.

1. Effect of the presence of seawater ions

This set of problems is due to the nature of the hydrolysis of ammonia and to the formation of hydroxyl ion:

$$NH_3^0 + HOH \rightarrow NH_4^+ + OH^-$$

As a result of the hydroxyl ion formation, solutions of ammonia in water are very basic with a pH of 14 easily attainable. In seawater the hydroxyl ion reacts with bicarbonate (the predominant ionic form of carbon dioxide) to produce carbonate ion:

$$HCO_3^- + OH^- \rightarrow CO_3^= + HOH$$

which in turn will react with calcium present to precipitate calcium carbonate:

$$Ca^{++} + CO_3^= \rightarrow CaCO_3\downarrow$$

Or, alternately, the hydroxyl ion produced by the hydrolysis of ammonia can react directly with the magnesium present in seawater to precipitate magnesium hydroxide:

$$Mg^{++} + 2OH^- \rightarrow Mg(OH)_2\downarrow$$

In general, if sufficient ammonia is present, the sequence of chemical events would be:

1. conversion of HCO_3^- to $CO_3^=$
2. precipitation of $CaCO_3$
3. precipitation of $Mg(OH)_2$
4. elevation of solution pH

At the point of leakage, it is likely that all of these chemical events will occur. In Figure 9 is shown a possible set of results of ammonia leakage into seawater. If seawater is trapped by scale in the vicinity of the leak, it is possible that catastrophic attack on aluminum can occur.

2. Leakage of seawater into ammonia

The other type of possible leakage is shown in Figure 10, where seawater is leaking into ammonia. In this case, as the ammonia hydrolyzes, the alkaline components of the seawater will precipitate. In addition, some water will be abstracted from the seawater into the ammonia. The remaining aqueous solution will become concentrated and the solubilities of some compounds other than the scale will be exceeded. In actuality, crystalline NH_4Cl has been found in our testing. The remaining solution will not only be concentrated electrolytically, but will be high in Na^+ and OH^- ions at a pH of 14. The same kind of metallic attack may occur on the ammonia side as was possible on the seawater side.

Ammonia ionizes as does water to form the equivalent of acids and bases:

			Acid		Base
Water	HOH	→	H^+	+	OH^-
Ammonia	NH_3	→	NH_4^+	+	NH_2^-

Some salts are soluble in ammonia, NH_4Cl for example, which would be produced by the leakage of seawater into ammonia. The protonated NH_4^+ in ammonia would act as the H^+ equivalent in water and NH_4Cl in ammonia would be equivalent to HCl in water. There would be an excess of protonated species (increase in acidity) and an increase in conductivity, both likely to lead to attack of aluminum wherever it is contacted by ammonia solution. This kind of behavior has been observed on the aluminum surfaces exposed to ammonia contaminated by water and electrolytes.

3. Encountered scales and scaling rates

In these tests ammonia was added to the recirculating seawater loop (with continuous refreshment) as ammonium hydroxide, ammonia already hydrolyzed to its product ions. Levels of addition were as previously stated. The results, summarized in Figure 11, indicate greater rates of scale/fouling growth at higher temperatures and concentrations of ammonia. Figure 12 is presented to indicate the corresponding increase in pH. Not indicated is a slight difference observed in initial scale nucleation rates for the subject alloys, in which CP titanium and pretreated aluminum alloy 5052-H14 were observed to very slightly retard initial scale growth.

Crystalline components of the scale were determined using X-ray diffraction, energy dispersive X-ray, and infrared spectral analysis. Scale composition development followed the pattern expected, with calcite forming initially followed by aragonite and brucite at higher ammonia concentrations and temperatures. At zero and 8 ppm ammonia in seawater the primary constituent of the surface deposit are amorphous muds and organic materials.

Observations indicated that fouling/scale formation may be controllable at 8 ppm ammonia in seawater, 5°C and 30°C, and 30 ppm ammonia in seawater, 5°C, if a continuous cleaning process is employed. It is believed, however, that concentrations of ammonia in seawater above 80 ppm would not be economically controllable. Of the subject alloys tested, fouling appeared to be more easily removed from CP titanium and pretreated aluminum alloy 5052-H14. Figure 13 shows the scale at 10 days for the 800 ppm exposure.

D. SPECIAL CLEANING TESTS

Cleaning test specimens were continuously exposed to ambient temperature, unfiltered seawater for a total of 10 months with specimen cleaning pulls at 1, 2, 3, and 7 months. Additionally, an extra set of specimens (Group 2) was entered and specimen cleaning pulls conducted at 1½, 6, and 9 month intervals. Mechanical (M.A.N.® Brush) and chemical (sulfuric/chromic acid) cleaning procedures were employed as previously outlined. In addition, a set of uncleaned corrosion control blanks were inserted in the test. At 10 months all specimens were ultrasonically acid cleaned to permit determination of specimen corrosion rate.

Results of this testing are summarized in Figure 14. Uncleaned corrosion control specimens gave the best corrosion performance, closely followed by specimens cleaned using the simulated M.A.N.® brush system. Film buildup on the uncleaned controls was severe, however, and it is believed that the resulting loss of heat transfer could not be tolerated in an OTEC plant. Further, corrosion rates which might be attributed to the daily use of a M.A.N.® brush system cannot accurately be extrapolated from these tests. However, based on these cursory results, a mechanical cleaning system is the preferred mechanism of fouling control for the aluminum alloys tested.

The performance of CP titanium was independent of cleaning techniques employed, showing overall excellent performance. Pretreated aluminum 5052 provided the lowest general corrosion rate of any aluminum alloy; however this material was subject to very severe pit attack under debris which would accumulate at the upstream specimen end. Severe pit attack was not noted on aluminum alloys 3003, 5052, and 5086, although very broad but shallow pit depressions would again occur at the upstream specimen end. For the uncleaned corrosion controls, aluminum alloy 5086 was followed in corrosion performance by aluminum alloys 5052 and 3003, although mechanically cleaned specimens of these same alloys gave almost identical corrosion rates.

IV. FUTURE EXPERIMENTAL PROGRAM

The objective of the continued 14-month testing program is to further develop information on the corrosion scaling and fouling of candidate alloys, especially under conditions of controlled exposure to ammonia leakage into once-through seawater, and to low concentrations of seawater and water in ammonia.

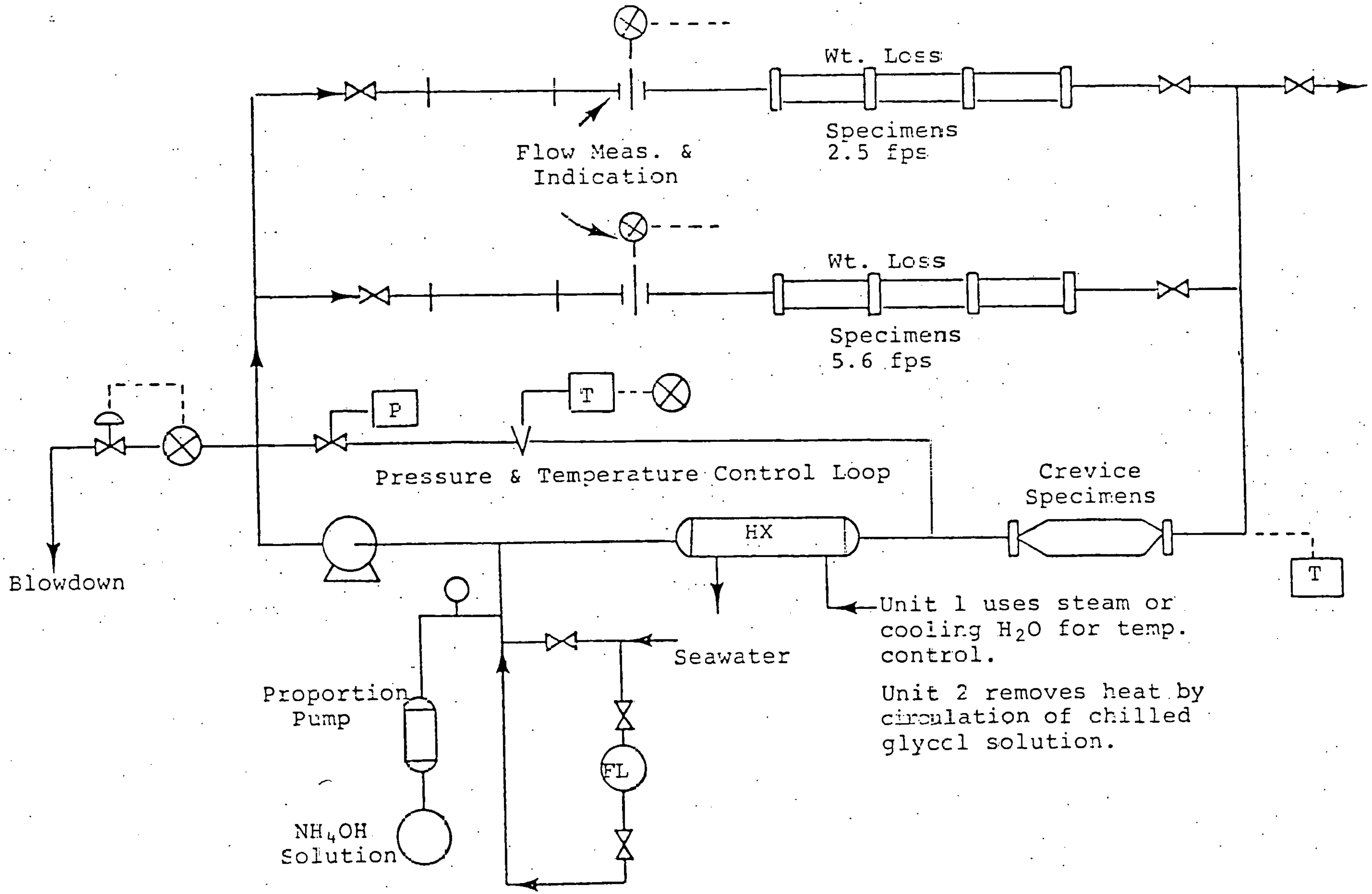
Of particular significance is exposure of the test alloys (Al 5052, Stainless Al6X, CP titanium and Copper Alloy 706) in the form of tubes to seawater flowing at 5 feet per second and at 30°C to which ammonia has been introduced through drilled holes simulating leaks. Four nominal 1-inch tubes of each alloy will be initially tested for each of two leak diameters. Half of the tubes will be removed and examined after 4.5 months of exposure. These tubes will be replaced by similar tubing for a similar exposure period. The remaining tubes will undergo a 9-month exposure. A process flowsheet is shown in Figure 15.

In addition, test alloys in the form of coupons and short tube sections will be exposed to flowing seawater at 30°C and at 6 fps in which ammonia concentrations of 5, 10, and 20 ppm are maintained. Control test alloy coupons will be exposed to ambient seawater at 6 fps for a period of one year.

Duplicate coupons of the test alloys will be exposed to flowing, recirculating ammonia at 6 fps and 30°C with water concentrations of 150 ppm deionized water and 1.0% seawater plus 150 ppm deionized water. Visual and microscopic examinations and ion and crystallographic analyses will be made after 0.5- and 2-month exposure periods.

Figure 1

SIMPLIFIED FLOWSHEET OF CORROSION TEST UNITS TO DETERMINE EFFECT OF LOW CONC. OF NH_3 IN SEAWATER (UNITS 1 & 2)



Unit 1 uses steam or cooling H_2O for temp. control.

Unit 2 removes heat by circulation of chilled glycol solution.

Figure 2

SIMPLIFIED FLOWSHEET OF CORROSION TEST UNIT TO DETERMINE EFFECT OF LOW CONC. OF SEAWATER IN AMMONIA (UNIT 3)

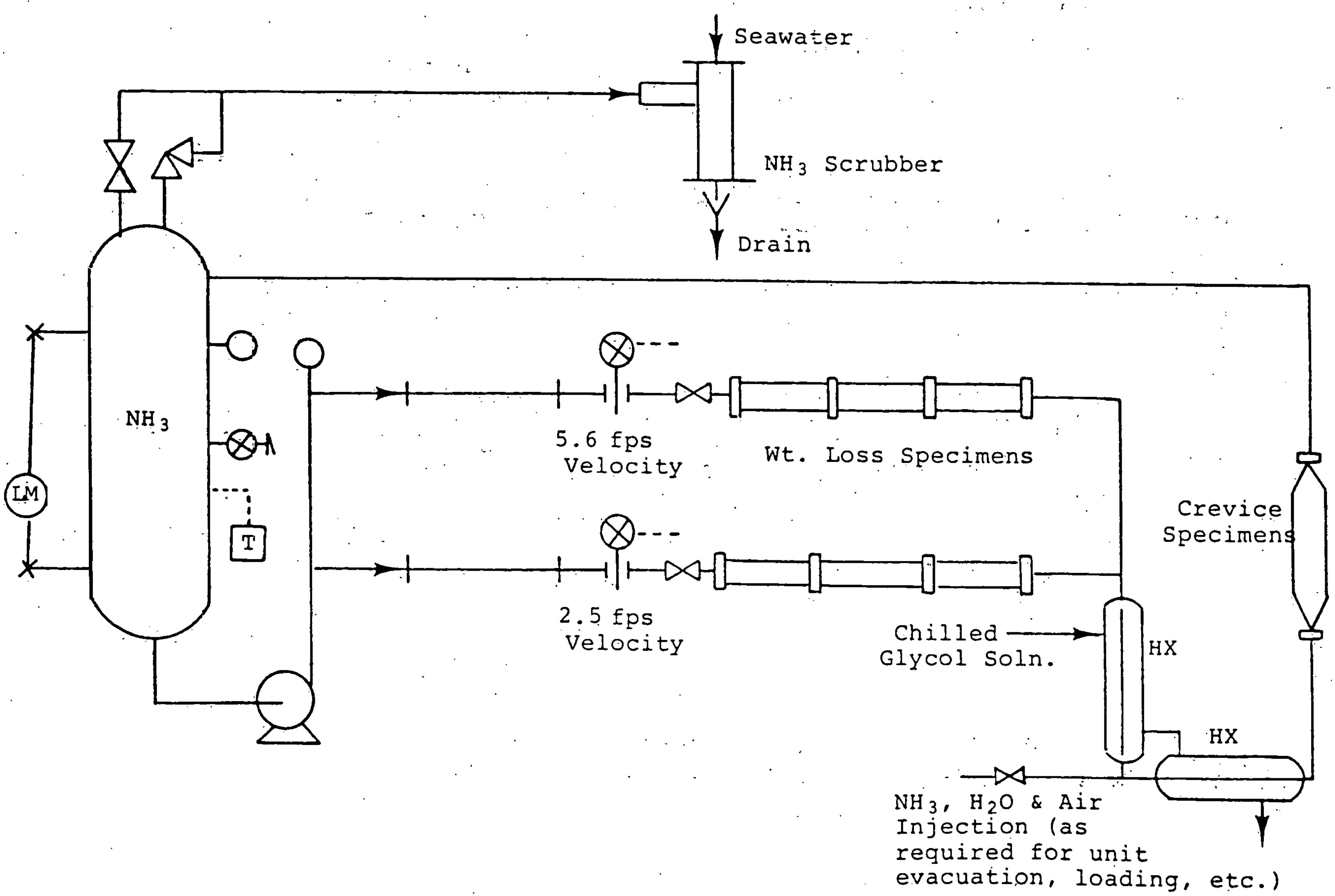
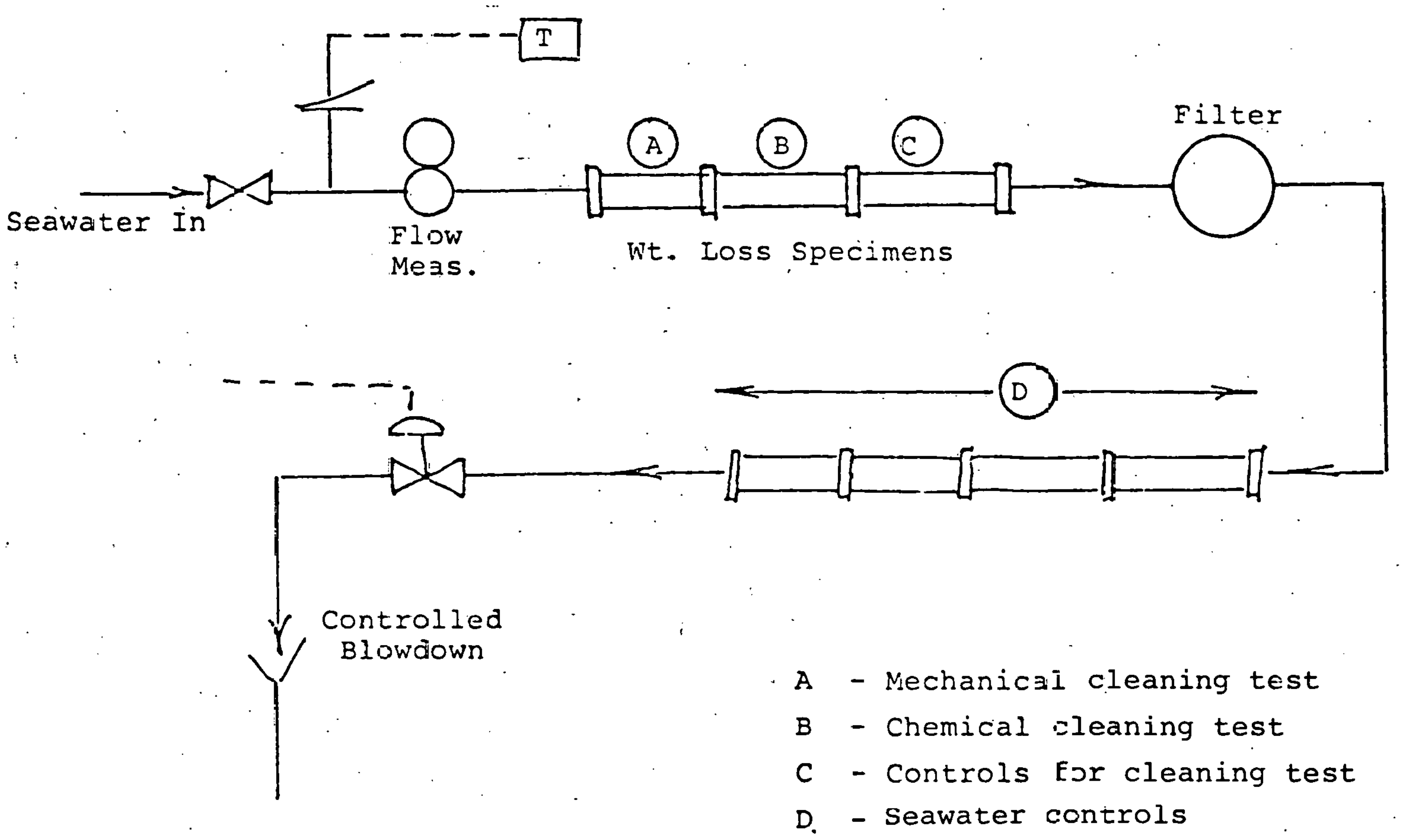


Figure 3

FLOWSHEET FOR INSTALLATION OF CLEANING LOSS SPECIMENS AND UNCONTAMINATED CORROSION-SCALING CONTROLS



A - Mechanical cleaning test
B - Chemical cleaning test
C - Controls for cleaning test
D - Seawater controls

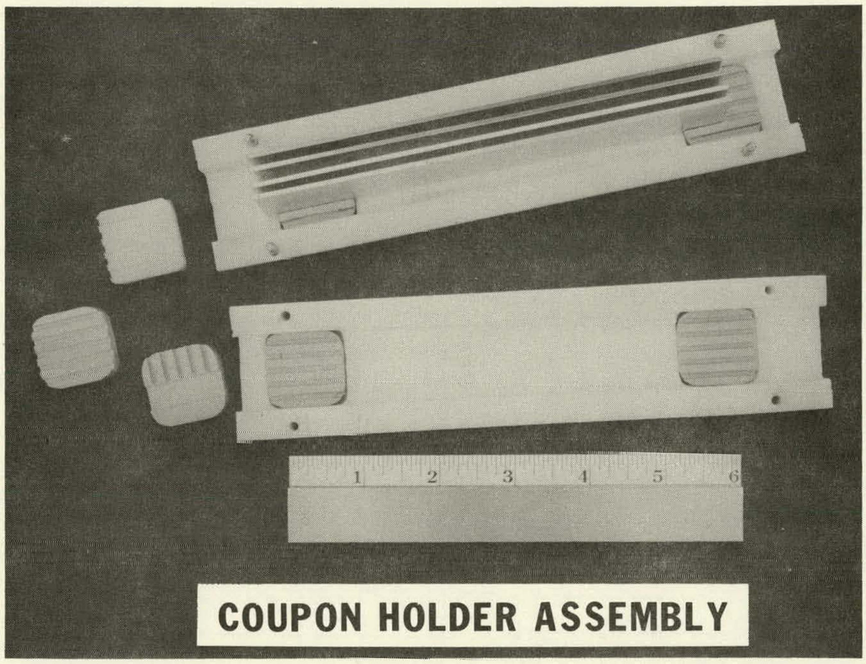


Figure 4

TEFLON WEIGHT-LOSS AND PITTING SPECIMEN HOLDER

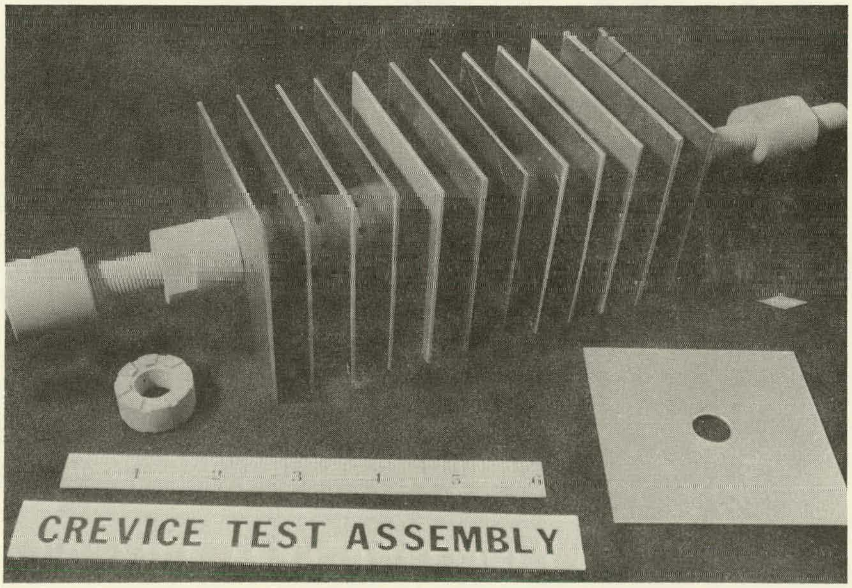


Figure 5

CREVICE CORROSION SPECIMEN ASSEMBLY

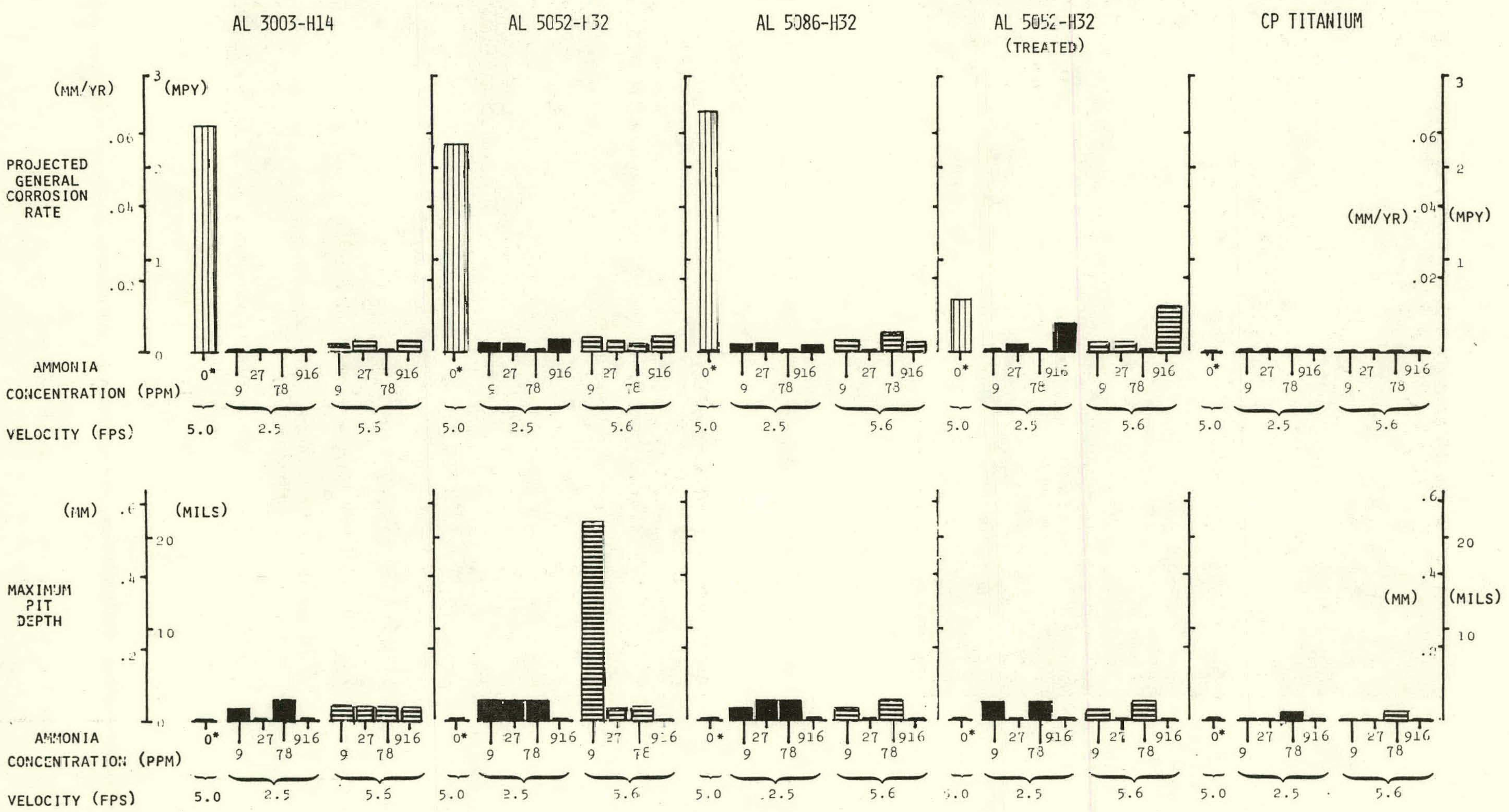
FIGURE 6

CORROSION SUMMARY: PROJECTED GENERAL CORROSION RATE AND MAXIMUM PIT DEPTH

SEAWATER MIXED WITH AMMONIA*

CONDENSER: 5° C

KEY	▥	■	▤
FPS.	5.0*	2.5	5.6



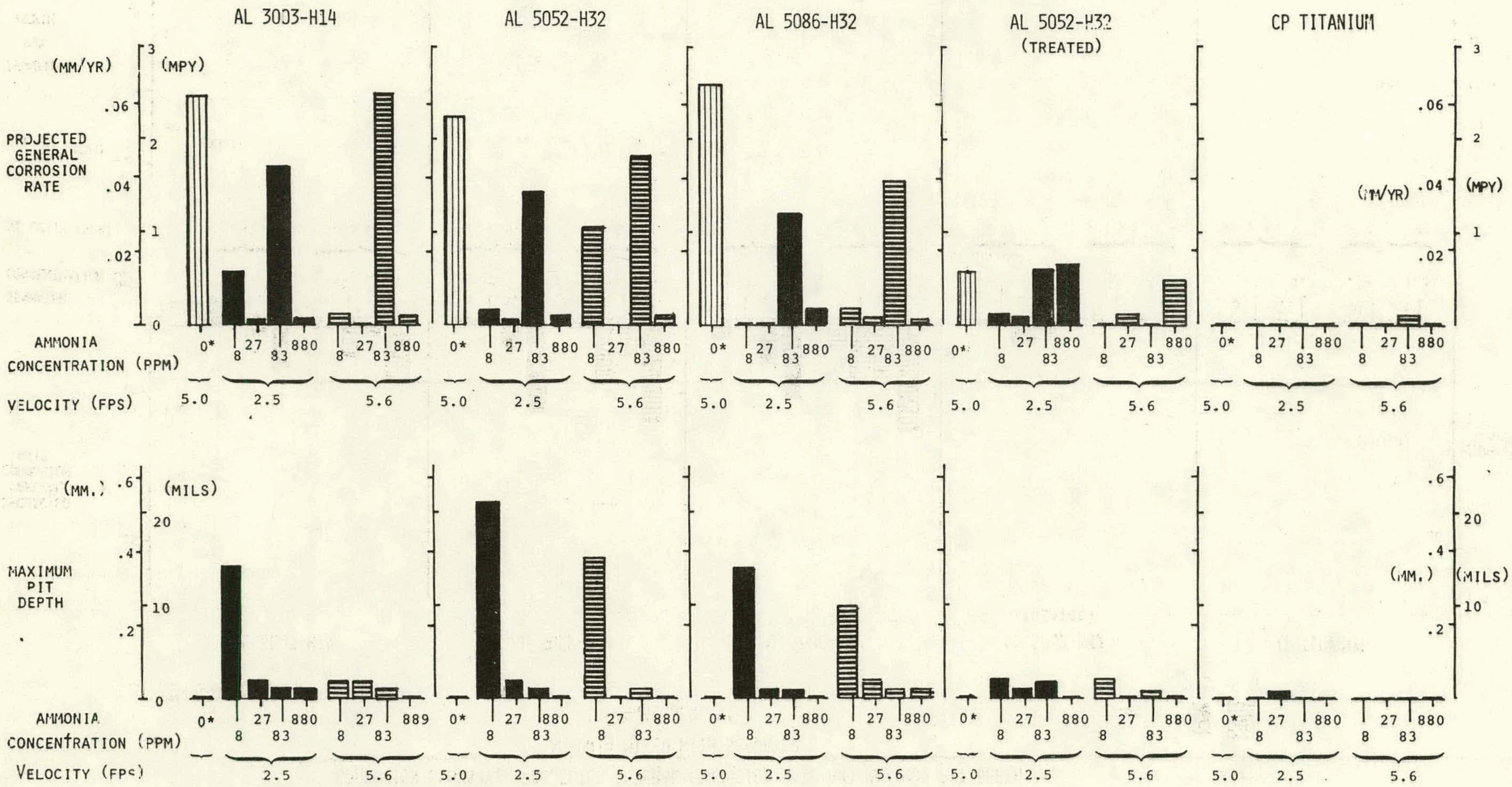
* INCLUDES AMBIENT TEMPERATURE CONTROLS (~23° C)

FIGURE 7

CORROSION SUMMARY: PROJECTED GENERAL CORROSION RATE AND MAXIMUM PIT DEPTH

SEAWATER MIXED WITH AMMONIA

EVAPORATOR: 30°C*



* INCLUDES AMBIENT TEMPERATURE SEAWATER CONTROLS (~23°C)

FIGURE 8

CORROSION SUMMARY: PROJECTED GENERAL CORROSION RATE AND MAXIMUM PIT DEPTH

AMMONIA MIXED WITH SEAWATER

CONDENSER: 5° C

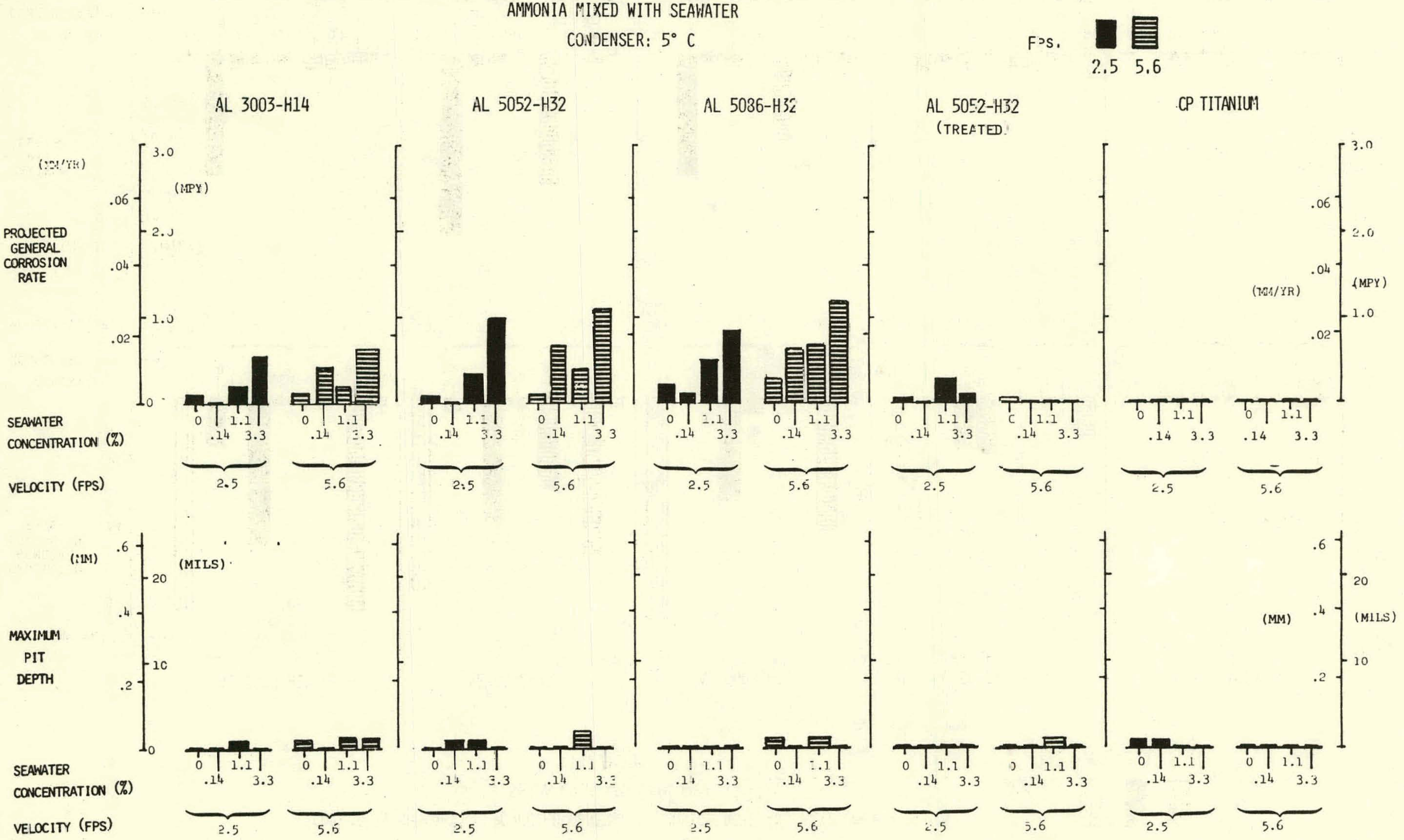


Figure 9

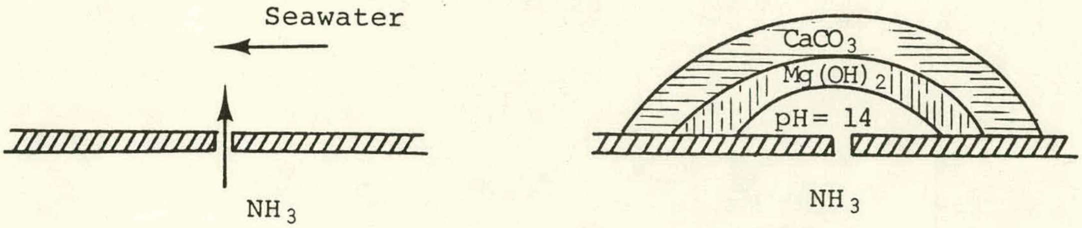


Figure 10

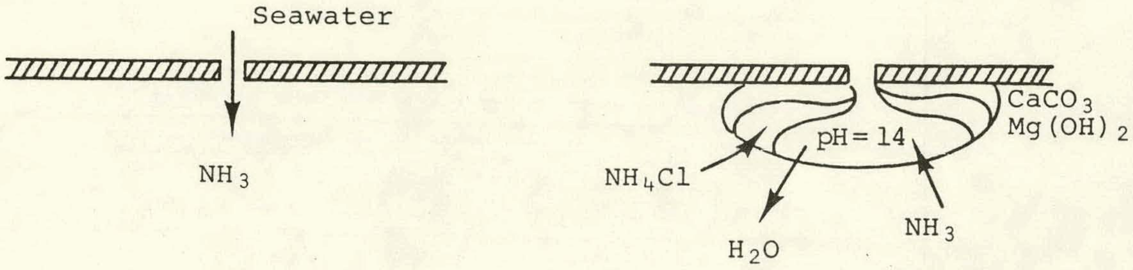
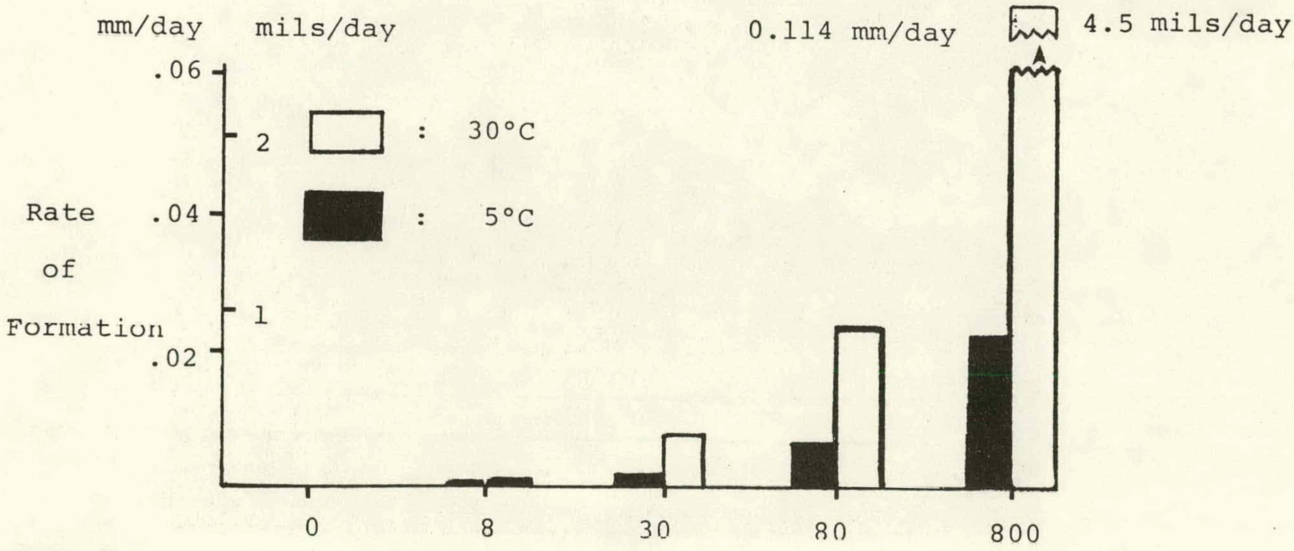


FIGURE 11

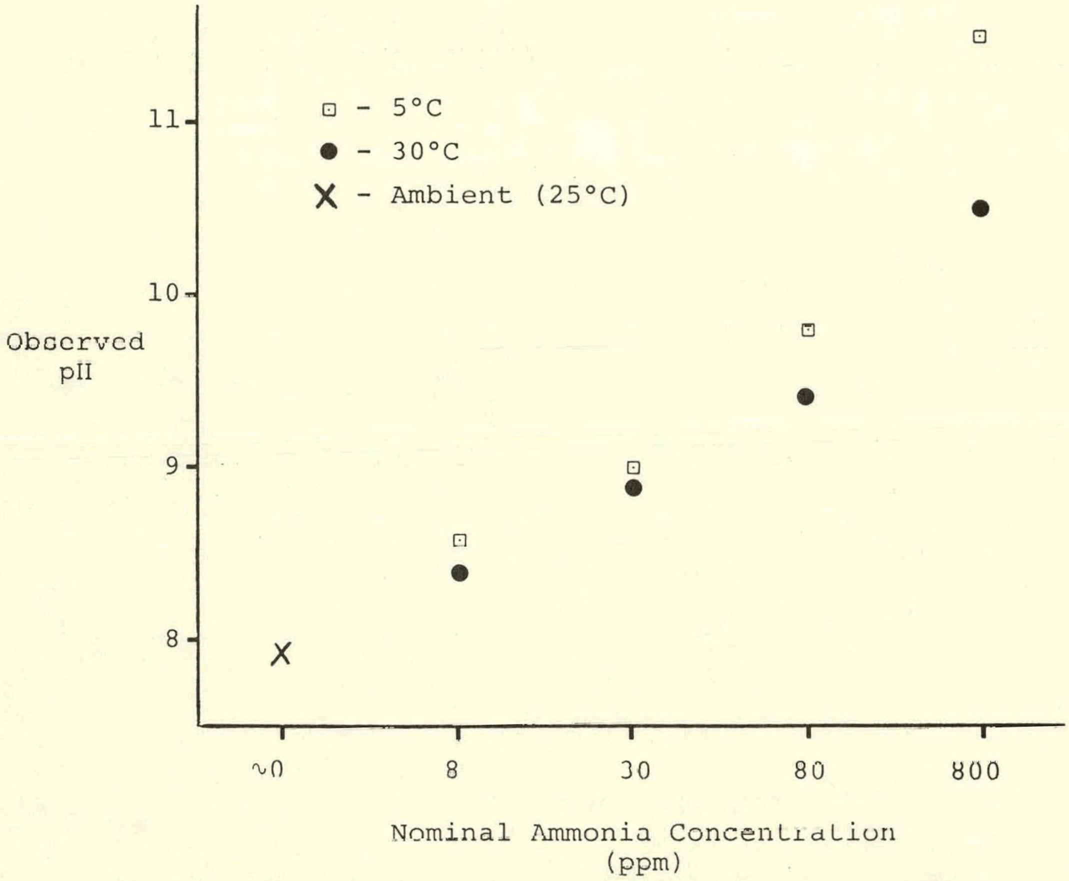
FOULING FORMATION *



* As formed on Crevice Test Assembly (∿0.26 fps)

FIGURE 12

AMMONIA CONCENTRATION VS pH



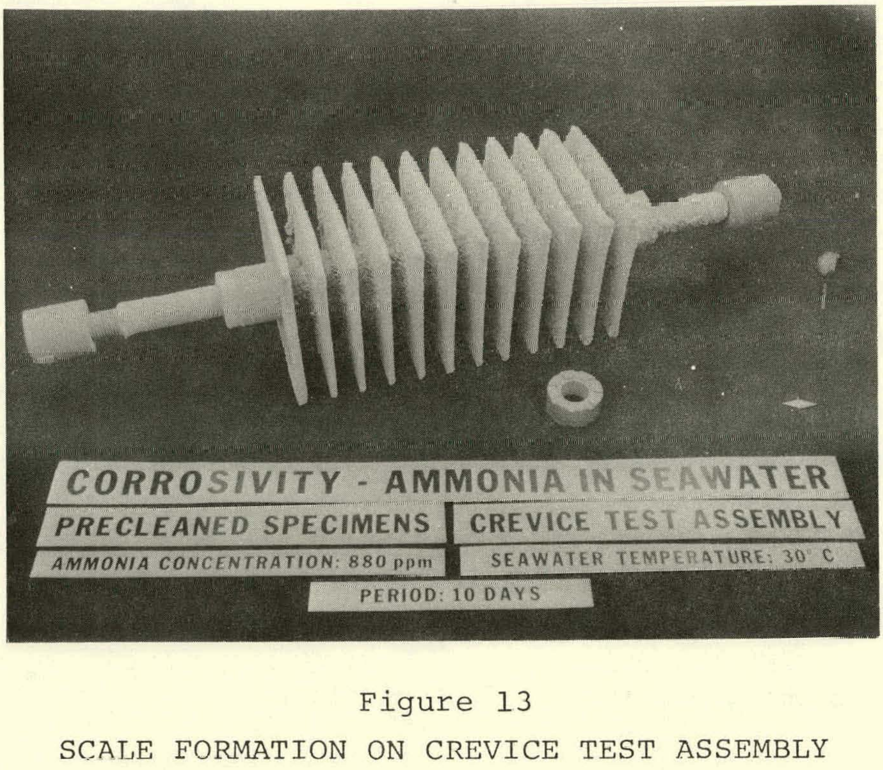


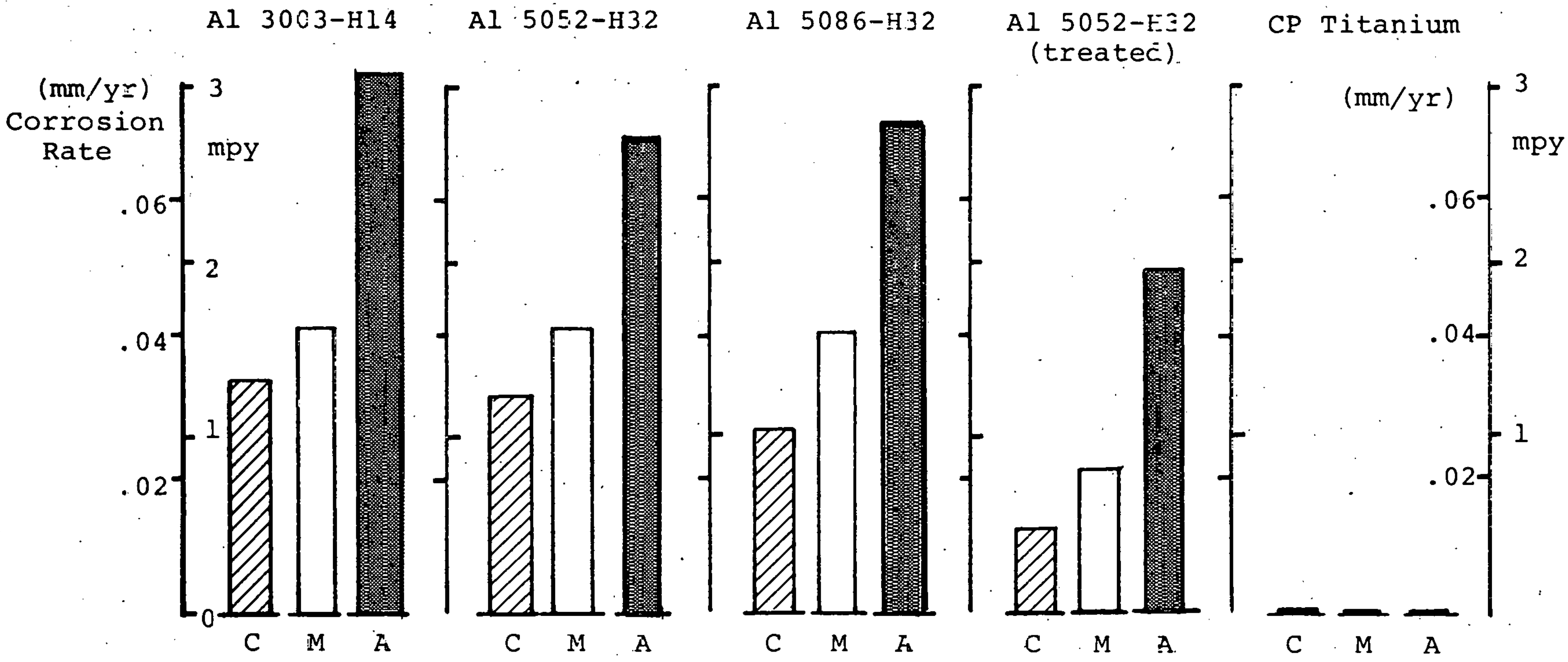
Figure 13

SCALE FORMATION ON CREVICE TEST ASSEMBLY

880 ppm AMMONIA IN SEAWATER AT 30°C

FIGURE 14

GENERAL CORROSION RATE VS CLEANING METHOD*



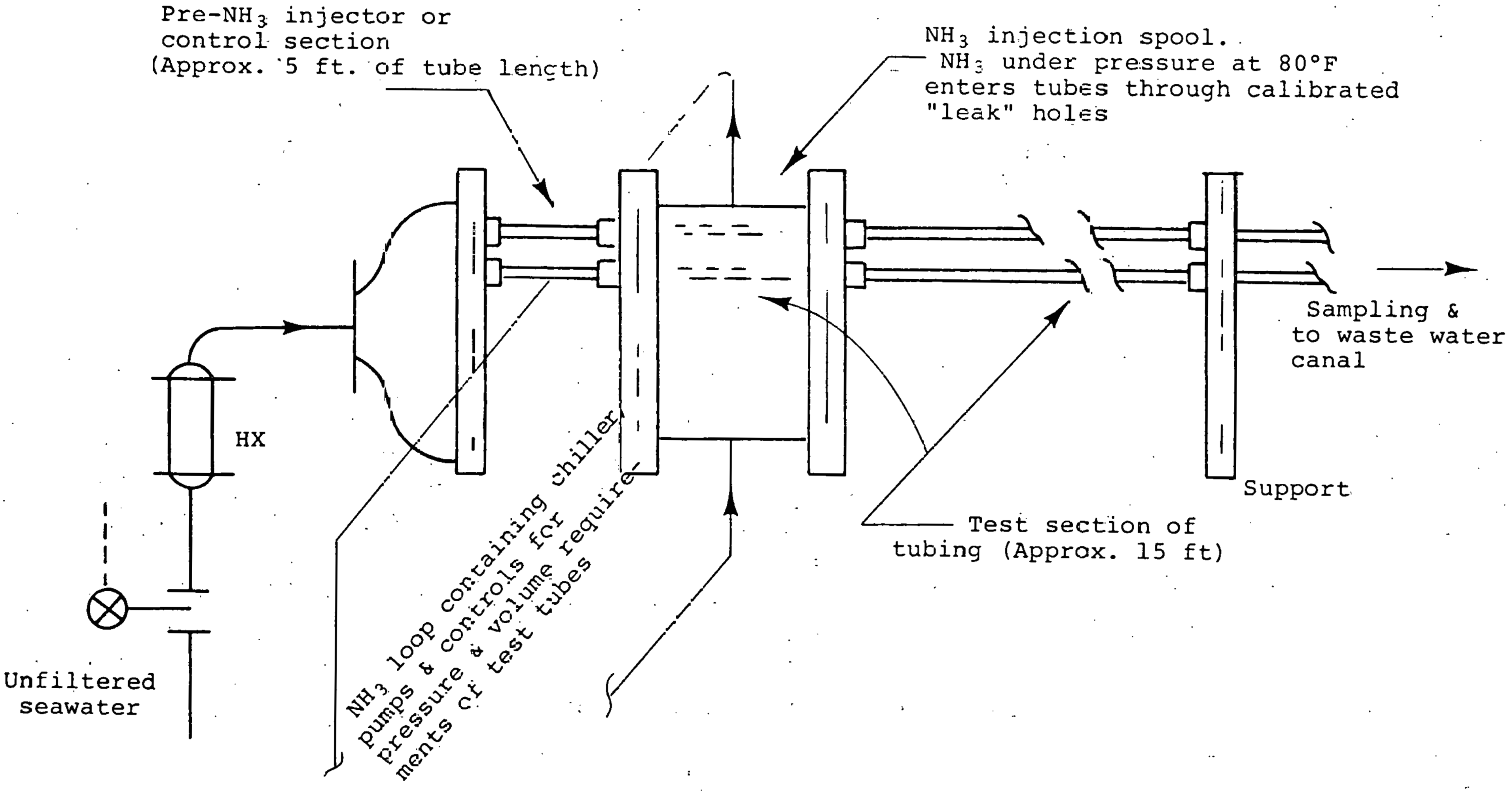
Cleaning Method:

- ▨ C : Uncleaned Controls
- ☐ M : Mechanical (MAN Brush)
- ■ A : Acid Chemical Cleaning

*Bar "C" is representative of a 10-month exposure without intermediate cleaning. Bars "M" and "A" represent 3-5 sequential cleaning experiences over 9-10 months. Final cleaning was standard laboratory practice.

Figure 15

HIGHLY SIMPLIFIED FLOWSHEET OF TUBULAR TEST UNIT
TO DETERMINE FFECT OF AMMONIA LEAKAGE INTO SEAWATER



THE QUALIFICATION OF METALS AND ALLOYS FOR OTEC HEAT EXCHANGERS -- PRESENT STATUS

by

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I. INTRODUCTION

My remarks to you today constitute a summarization of two papers on the Qualification of Stainless Steel and Aluminum for OTEC Heat Exchangers. The complete papers will be presented at the OTEC Conference in June 1979 and will subsequently be published in the Proceedings of the meeting and elsewhere.

II. AL-6X ALLOY

Qualification of the AL-6X alloy as a candidate for use as tubing in Ocean Thermal Energy Conversion (OTEC) heat exchangers is based on results of accelerated tests using ferric chloride for resistance to crevice corrosion and pitting, long-time crevice corrosion and pitting tests in natural sea water and anticipated resistance to attack by ammonia and mixtures of ammonia and sea water.

Since the alloy has no natural resistance to fouling by marine organisms, it will be able to accommodate action to prevent fouling by chlorination or to remove it by mechanical cleaning techniques or appropriate chemical cleaning methods.

The satisfactory behavior indicated by the various accelerated and long-time corrosion tests has been confirmed by excellent performance of several million feet of tubing in condensers in coastal power plants.

Early evaluation tests demonstrated the need for proper heat treatment to avoid the presence of a sigma phase, which resulted in severe pitting of some, but not all, specimens in tests in natural sea water.

The available data qualify the AL-6X alloy as being a satisfactory alternate to titanium for tubes in OTEC heat exchangers.

III. ALUMINUM

Aluminum can neither be qualified nor disqualified for use as tubes in OTEC heat exchangers on the basis of already available data on resistance to corrosion especially by pitting or corrosion in crevices. Alloys identified as being worthy of further studies under conditions properly related to OTEC service are Alclad (7072) 3003 or 3004 and Al5052. In view of the thin walls of heat exchanger tubes, the prime requirement is resistance to penetration by pitting. This suggests Alclad would have a considerable advantage, based on the ability of the cladding to arrest penetration of the core alloy, so long as a substantial area of cladding is able to survive.

A principal target of further testing should be to establish whether periodic cleaning will increase the loss of cladding above the approximately 1 mil per year indicated by behavior in the absence of any effects of cleaning. Available data suggest a possible life of about 10 years for Alclad tubes with 10 mils of cladding. This assumes the development of effective cleaning treatments that would not seriously impair resistance to corrosion.

Corrosion testing programs that will clarify the suitability of aluminum for OTEC heat exchanger tubes are being or will be carried out in Hawaii, Puerto Rico, Gulf of Mexico, Harbor Island, North Carolina, and possibly at other locations. These tests on the Alclad 3003 and 5052 alloys will be under conditions of flow, cleaning to remove fouling, and treatments to prevent fouling that may be encountered in OTEC heat exchangers.

The danger of crevice corrosion will have to be taken into account in connection with the use of aluminum in designs where crevices cannot be avoided, such as plate-type heat exchangers, or may be difficult to seal as at tube supports in heat exchangers with water outside the tubes. Crevice corrosion seems likely to be more severe in condensers handling water from great depths.

A design velocity of flow of water below 8 ft/sec is not expected to result in intolerable erosion of aluminum. Crevice corrosion is accelerated by movement of water. This could be more of a problem in plate-type heat exchangers and in those with water outside the tubes.

The vulnerability of aluminum to acceleration of corrosion by galvanic action in contact with most other metals needed for OTEC system components, and by effects of heavy metals (copper) from corrosion upstream of aluminum, will limit choices of materials for such components.

This could increase costs of such components and limit means of avoiding fouling in piping, screens and water boxes by use of copper alloys naturally resistant to fouling by barnacles, etc.

Electrical insulation of dissimilar metals, while desirable, is less important than elimination of heavy metal corrosion products. In this context, avoidance of sources of copper is likely to be more important than avoidance of sources of iron.

The fear of possible effects of leakage of ammonia in accelerating corrosion of aluminum has been found to be less significant than a more drastic effect of ammonia leakage in triggering intolerable deposition of carbonate scale from water likely to be supersaturated with calcium carbonate. This, plus the economic penalty of loss of ammonia by leakage, will require extraordinary steps to prevent, detect, and correct even slight leakage of ammonia in OTEC heat exchangers, irrespective of the metal to be used.

The danger of scaling associated with leakage of ammonia will be much greater in plate-type heat exchangers. Leakage through a single plate could trigger deposition of scale on the surfaces of many plates downstream of the original source of a nucleating precipitate.

There is also the possibility that scale deposition could be triggered by nuclei carried into the main body of water by brushes or balls used for mechanical cleaning.

There is what may be no more than a temporary impediment to the use of aluminum in contact with ammonia. Such use is prohibited currently by U.S. Coast Guard Regulation CG-257. However, aluminum is permitted by a pending IMCO (Inter-Governmental Maritime Consultative Organization) Standard. The latter may be taken into account, along with new data showing aluminum to be satisfactorily resistant to attack by ammonia, in action that may be taken by the Coast Guard to waive their prohibition of aluminum as applied to OTEC systems.

The relatively low corrosion fatigue strength of aluminum suggests the need for special attention to assessment of the danger of encountering harmful vibration and consideration of whatever steps may be indicated to control such vibration. Even more attention may be required in designs to avoid fretting corrosion at tube supports such as has been experienced as a result of vibration of aluminum tubes in heat exchangers.

Records of service appropriately related to OTEC heat exchangers are not sufficient to either qualify or disqualify aluminum for this use. They do qualify Alclad 3003 or 3004 and the 5052 alloy as candidates worthy of continuing evaluation. Of the two, the performance records for Alclad give it an advantage over the 5052 alloy for shell and tube heat exchangers.

The situation with respect to plate-type heat exchangers is clouded by reported failures of aluminum by crevice corrosion in desalination service and by experience reported by manufacturers of this type of heat exchanger. Alclad would appear to be the better choice in any further efforts to qualify aluminum for this application. Special attention should be paid to the choice of adhesive to seal crevices under gaskets.

There should be no problem of stress-corrosion cracking of aluminum in either seawater or ammonia.

There is no problem of supply of aluminum ore and of aluminum metal that would restrain the use of aluminum in any probable scale of OTEC operations. There may be restrictions on the extended surface configurations available in Alclad or 5052 alloy especially in the form of welded tubing.

OTEC CORROSION/BIOFOULING STUDIES

by

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I. INTRODUCTION

During the past four years, Lockheed Ocean Systems Group has had government contracts related to the Ocean Thermal Energy Conversion (OTEC) Program. In support of these contracts, Lockheed Ocean Systems has expended company development funds to study heat transfer, biofouling and corrosion problems as they are related to OTEC. This paper describes some of the results of a few of the Lockheed Ocean Systems OTEC development programs.

A. BACKGROUND

OTEC heat exchangers have been identified as representing approximately 50% of an OTEC plant capital cost. It has also been ascertained that OTEC heat exchangers must be kept relatively clean to maintain a high heat transfer coefficient. In 1976, work was initiated to gather information on biofouling and how it is controlled in the power industry.

At the same time in 1976, design concepts for a heat transfer measurement device that would evaluate biofouling effects were pursued. This work resulted in a contract in 1977 from Battelle-Pacific Northwest Laboratories to design, build and test such a heat transfer device.

Design of the device was completed but the Department of Energy determined that the device was not needed since it already had a working heat transfer measurement device developed by Carnegie-Mellon University.

Two other problem areas associated with the heat exchangers that needed investigation were biofouling control methods and determination of the lowest life-cycle cost material for the heat exchanger tubing.

1. Experimental Procedure

In an effort to solve some of the previously described problems, a heat transfer measurement device, two (2) biofouling corrosion test loops, and a closed loop M.A.N. brush test were designed, built and put into operation during 1978.

a. <u>Biofouling and Corrosion Test Loops</u>. Two test loops were installed in early 1978 at San Diego (Fig. 1). Evaluation of biofouling on aluminum alloy 5052 tubing with and without chlorination via microscopy was not satisfactory except from a qualitative standpoint. It was decided that a heat transfer measurement device was needed so it was designed, built, and tested in the fall of 1978.

After solving a number of problems, a second generation design was built using 6061 aluminum tubing (3 units) and 90-10 copper nickel (1 unit). These four units went into test in January 1979.

Heat transfer measurements from the prototype and second generation units will be presented in the paper "A Measurement Technique for Condenser Tube Biofouling" by P. C. Springer and W. L. Owens at the Condenser Biofouling Control Symposium in Atlanta on the 26th of March. Although the results to date are for a few months of operation during the winter months, there is an indication that low level chlorination such as .1 ppm is effective. The design and operation of the prototype and second unit will also be presented in the paper mentioned above.

To obtain corrosion data on the candidate materials for the heat exchanger tubing, anodized and unanodized aluminum alloy 5052 tubes 10 feet long were placed in test during June of 1978. These test sections have now been exposed to seawater flowing at 6 ft/sec for 142 and 127 days.

Samples one inch to six inches long have been removed every 40 to 60 days to determine extent of corrosion attack. To date there is no evidence of pitting corrosion based on examination at 30X magnification of the anodized or unanodized aluminum alloy 5052 tubing after 142 days and 127 days (respectively) exposure (Table 1).

During November of 1978, a second corrosion loop separate from the biofouling heat transfer measurement loop was built. This loop had aluminum alloy Alclad 3003 and stainless steel AL-6X tubing placed in test in early December. Aluminum alloy 3004, Alclad 3004, and welded 5052 tubing will be placed in this loop in March. Specimens will be removed and examined for evidence of corrosion after 60, 120, 180 and 360 days of continuous exposure to 6 ft/sec seawater.

b. <u>M.A.N. Brush Test.</u> A closed seawater loop was designed and built as shown in Figure 2 to determine if the M.A.N. brush would cause excessive wear of aluminum tubing or if the nylon bristles of the brush would wear down and become ineffective as a cleaning method after a relatively short number of cycles. A 12" long, 1.5 inch outside diameter aluminum alloy 5052-0 tube was installed in the loop with a simulated plexiglass water box 6 inches in diameter at each end.

M.A.N. brush cages were installed at each end of the aluminum tube and the brush was driven through the tube every 30 seconds by alternately starting and stopping a pump at each end of the aluminum tube. After 23,480 trips through the aluminum 5052-0 tube, the wall thickness was measured at seven different locations within one inch of each end. As can be seen from the measurements shown in Table I, there was no wear of the aluminum 5052-0 tube wall.

Additional brush cycles were completed on other tube materials to measure brush wear. The M.A.N. brush was cycled through a 12" long tube a total of 194,276 times. The bristle wear loss was approximately .035" to

.050" based on at least five measurements taken at each of the 0° - 180° and 90° - 270° diameters. These measurements were made from 4X magnification photographs of the brush after each wear test.

The brush had roughly the same resistance to travel through the tube, which was significant, after 194,347 cycles as it did after 113,637 cycles. This implies that wear of the brush bristles had essentially stopped. This was verified by measurements which showed approximately .010" to .015" bristle wear from 113,637 cycles to 194,347 cycles.

Assuming a M.A.N. brush cycle of once a day in a 50 foot long OTEC heat exchanger tube, the 194,347 cycles represent 5.3 years of service.

This test confirmed the writer's opinion the M.A.N. bristle brush would not cause wear of aluminum tubing and that the brush life would be at least three years.

II. SUMMARY

Lockheed Ocean Systems will continue the above described test programs through 1980. The heat transfer measurement device will be used on 4 to 6 different materials. Three different biofouling control methods will be evaluated by the heat transfer measurement device. Nine different tubular materials and at least three different plate materials will be corrosion tested.

TABLE 1

LOCKHEED - OCEAN SYSTEMS
OTEC - TESTS

CORROSION

		IN - TEST		
ALUMINUM	CONDITIONS	LOCATION	DATE	RESULTS
o 5052 - ANODIZED TEFLON SEAL	6 FT/SEC	S. DIEGO	6-6-78	142 DAYS - NO FITTING
o 5052 - ANODIZED CHROMATE SEAL	"	"	6-6-78	" " " "
o 5052	"	"	6-21-78	127 " " "
o ALCLAD 3003	"	"	12-7-78	

MAN BRUSH TESTS

- o TEST DESCRIPTION - CLOSED CYCLE W/NATURAL SEAWATER
- o TUBE SIZE - 1.5" O.D. X .06" WALL X 12" LONG
- o TOTAL NUMBER OF CYCLES - 194,376
- o TUBE WEAR - ALUMINUM ALLOY 5052-0 - VISUAL - NONE (23,480 CYCLES)

- DIMENSIONAL - NONE - TUBE WALL BEFORE - .0639"
TUBE WALL AFTER - .0642"
AVERAGE OF 7 MEASUREMENTS

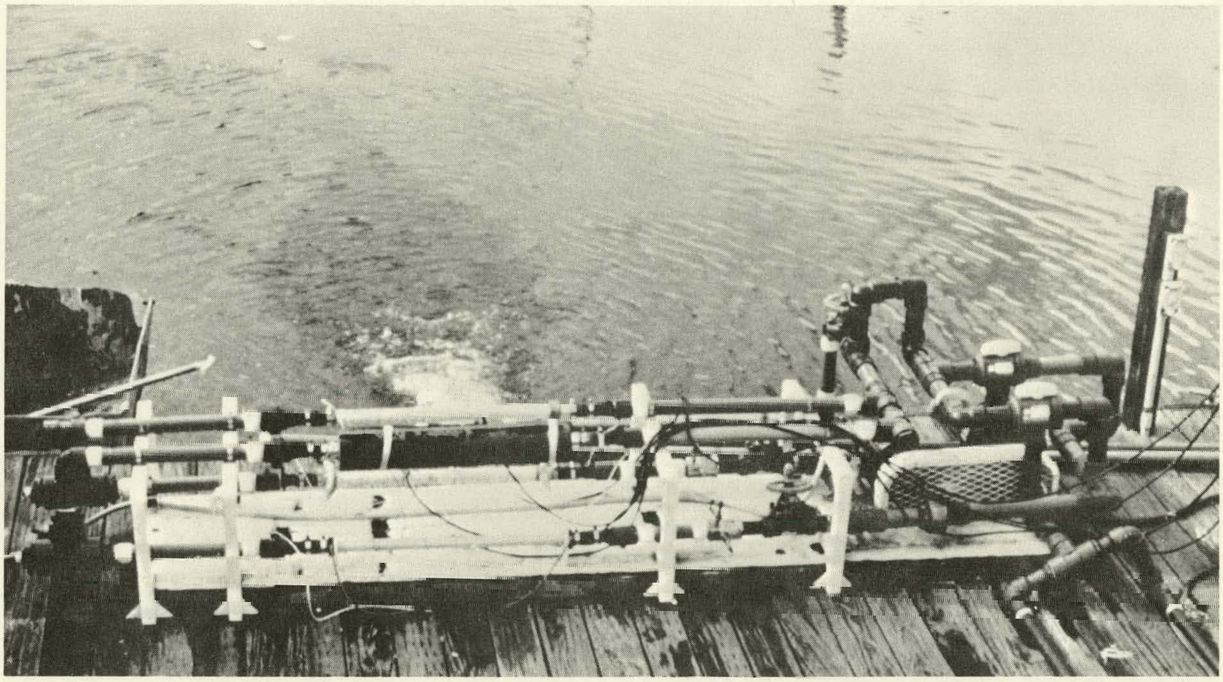

Fig. 1. Biofouling-Corrosion Loops with Prototype Heat Transfer Measurement Device

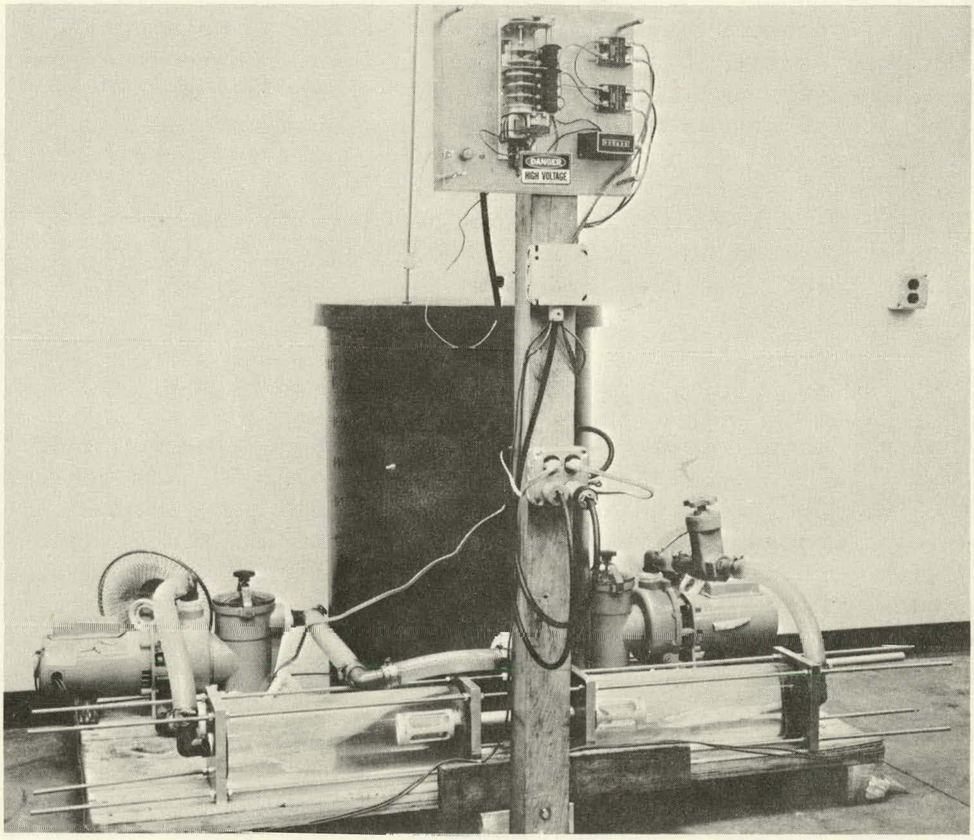

Fig. 2. M.A.N. Brush Wear Test Loop

THE STRESS-CORROSION CRACKING OF STEELS IN AMMONIA -- A SURVEY

by

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ABSTRACT

Carbon steel and higher strength, quenched and tempered steel, when cold formed and/or welded, are subject to stress-corrosion cracking (SCC) in air-contaminated dry ammonia. The constituents in air responsible for SCC are oxygen and combinations of oxygen and nitrogen. Neither nitrogen nor carbon dioxide alone or combined contribute to this type failure. Water has been shown to be an effective inhibitor of SCC when present in the amount of 0.08 to 0.2% (wt) (800 to 2000 ppm). Hydrazine (N_2H_4) has also been shown to be an effective inhibitor of SCC when present at about the same concentration.

A galvanic series for metals in ammonia has been established that shows metals to be arranged in a similar relative position as observed for metals in sea water. Little is known of galvanic effects in ammonia between steel and more noble metals such as titanium and stainless alloys. Where water has proven effective as an inhibitor of SCC in an "all steel" system, it may not be adequate in a mixed-metal system such as would be found in an OTEC plant using shell and tube heat exchangers. Additional research is required to determine the severity of the coupling effect, especially regarding the possibility of accelerated SCC failures of steel. [It should be noted that this is a preliminary report. A more comprehensive document is in preparation.]

I. INTRODUCTION

Various grades of steel have been in ammonia service for over fifty years. During the early years, beginning in the 1920's, low-strength carbon steels were found to be adequate for liquid ammonia manufacture and storage. Reciprocating compressors were used, and, undoubtedly, the ammonia was contaminated with both oil and water. Since most ammonia was used at the point of manufacture, there was little need for over-the-road transport. Therefore, the need to construct light-weight tanks of higher strength steel suitable for road transporation did not exist.

Stress-corrosion cracking (SCC) of carbon and alloy steels in ammonia service has occurred spasmodically worldwide since about 1950. Countries where tank failures have been noted include South Africa, Finland, Denmark, Ireland, England and the United States. During the 1950-1960 period, there was an increase in the use of anhydrous ammonia for agricultural use. This led to a demand for more tanks.

Light-weight, high-strength steels were developed in order to maximize truck hauling efficiency and minimize transport weight. Thus, increasing quantities of both low-strength carbon steel and higher strength, quenched and tempered steel appeared in reactors, storage tanks, agricultural nurse and applicator tanks, pipe lines and over-the-road tanks on trucks. As time progressed, more frequent SCC failures of steel in ammonia service were noted.

Collectively, it can be stated that, although some tank failures were observed in the early years, the problems associated with SCC were relatively few before 1956. From 1956 to 1960, approximately 3% of the containers in ammonia service were failing after three (3) years of service. Failures occurred on the interior surfaces of tanks, principally on the heads adjacent to the shell-to-head weld area. Investigators found that, although the tanks which failed had been built to ASME code, they had not been stress-relief annealed after welding. These failures brought forth a large industrial and scientific effort on a worldwide scale aimed at inspecting existing tanks, determining the cause of failure and assessing what action might be undertaken to solve the problem. (At this time it should be recognized that, although failures were occurring throughout the world, practices for handling ammonia were probably quite different in each country.) As a result of these actions, it was agreed that ammonia, steel and environmental factors should be investigated.

II. AMMONIA

A. PURITY

The purity of ammonia depends on the grade. During the early years of manufacture, only one grade was needed, and, although considered "pure," it contained water as well as oil; the presence of oil was due to lubricants used for the compressors. The interior surfaces of ammonia storage tanks used during the 1920-1930 period were observed to be covered with a film of oil. With the development of controlled atmosphere annealing for metallurgical processing, a higher purity metallurgical grade of ammonia was developed. Refrigeration-grade ammonia, whose need was also developing at the time, could tolerate more impurities and, finally, the least pure ammonia was identified as commercial grade. Specifications were developed for each grade.

1. Metallurgical Grade*

The purity of this grade of ammonia is 99.995%, based on oil and water content. A typical analysis is as follows: H_2O, 18 ppm; oil, 0.9 ppm; noncondensable gases, 35 ppm (volume); Fe(CO), 0.8 ppm; Cl^-, 0.12 ppm; and

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*Steels used for handling these two grades of ammonia require a mandatory postweld stress-relief anneal and exclusive use of lower strength nonquenched and tempered steel.

H_2S, not determined (N.D.). It should be noted that this grade of ammonia is not sufficiently pure to avoid the possibility of SCC of steel in the absence of water (inhibitor).

2. Refrigeration Grade*

The NH_3 content is guaranteed not less than 99.98%, when determined as the difference between 100% and total residue. Of this total residue, the nonbasic gas above the anhydrous liquid does not exceed 0.20 ml per gram ammonia; moisture content is less than 0.01 ml per 100 ml of ammonia; no residue in excess of one part in 6000 by weight is found on evaporation at atmospheric pressure, and no pyridine is present. (Information source: Allied Chemical Co., Nitrogen Division.)

3. Commercial Grade

The NH_3 content is guaranteed not less than 99.50%. (Information source: Allied Chemical Co., Nitrogen Division.)

Agricultural ammonia, which is considered a commercial grade, has a specification calling for NH_3, 99.5% (minimum by weight); water, 0.2% (minimum by weight); oil, 4 ppm (maximum); and inerts, 0.5 cc/g (maximum).

NOTE: In a number of laboratory tests conducted on various grades of steel after 1956, it should be recognized that not all sources of ammonia gas caused SCC; but 50-70% did. This suggests that the mode of ammonia manufacture may play a part in SCC, i.e., that air, which includes oxygen and other "inert" gases, may contaminate the ammonia.

B. CONTAMINANTS

The contaminants in ammonia that were found to cause SCC of steel were (a) air, (b) oxygen and (c) oxygen and nitrogen combined.

It has also been determined that neither carbon dioxide nor nitrogen will cause SCC of steel. Early investigative work attributed some SCC failures to the presence of carbon dioxide in ammonia, but this was later proved incorrect. Nitrogen in combination with oxygen is not as damaging as oxygen alone, but takes a close second place. Other contaminants that were investigated included compressor oil (1%), ethyl mercaptan (0.005%), sodium cyanide (0.01%), sodium chloride (1.0%) and copper sulfate (0.1%). In the absence of air and water (refrigeration-grade ammonia), one specimen out of four failed as a result of compressor oil and sodium cyanide, and two out of four because of the presence of copper sulfate. With the same grade of ammonia and in the presence of air (oxygen) but no water, one specimen out of four failed in sodium cyanide and copper sulfate. Again, in the same grade of ammonia and in the presence of air and 0.5% (wt) water, none of the four specimens failed in each contaminant. All of the foregoing results were obtained with T-1 steel (high strength) and AISI 4130 alloy steel tuning-fork specimens (Figure 1) in the cold-worked, welded, and

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*See footnote on previous page.

stressed condition. Test duration was 115 weeks. It should be appreciated that this represents a very severe test for SCC susceptibility and illustrates the tremendous advantage of having water present as an inhibitor. Other tests on these steels included refrigeration-grade ammonia in the presence of air with water additions of 0.5, 1.0, 2.0 and 4.0% (wt). No failures occurred at any of these water concentrations.

C. INHIBITORS

As described above, water has been shown to be an effective inhibitor of SCC susceptibility of steel in air (oxygen)-contaminated ammonia. The beneficial effects of the presence of water have been demonstrated under field conditions as well as in laboratory experiments involving the use of tuning-fork specimens and in the more recently used slow-strain rate test. The most effective range of water as an inhibitor of SCC of steel in air-contaminated ammonia appears to be from 0.08 to 0.2% by weight.

Of interest, is the fact that hydrazine has also been found to serve as an effective inhibitor, its concentration being on the same order as water. It is believed that hydrazine (N_2H_4) acts to scavenge oxygen, thereby removing it from the system, i.e.,

$$O_2 + N_2H_4 \rightarrow 2H_2O + N_2.$$

The equation suggests the possibility of a dual function, removing oxygen and, interestingly, supplying water to the system. To this writer's knowledge, hydrazine has not been used in ammonia service on a commercial basis simply because water has been less costly. However, the value of hydrazine in preventing SCC of steel in air-contaminated ammonia has been demonstrated a number of times in laboratory tests.

III. STEEL

Numerous steels have been investigated for failure by SCC in ammonia, both in the field and in laboratory tests using tuning-fork specimens and the previously mentioned slow strain-rate test. Steels that have been found to fail in air-contaminated ammonia are as follows:

A 202B (base metal and heat-affected zone)
A 212
ASME Case 1056 Steel
A 204B
4130
A 515 Grade 70
Si-Mn-Al Fine Grain (Denmark)
T-1
A 517 Grade F
A 285
Spring Steel (high carbon)
Line Pipe Steel API x 42*
Line Pipe Steel API x 46*
Line Pipe Steel API x 52*
Line Pipe Steel API x 60*

(Water not present under these services or test conditions.)

Typical SCC failures in the various grades of steel are shown in Figures 2 through 9.

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*Welded and annealed.

A. STRENGTH

Laboratory investigations on a number of these steels showed that the most severe SCC occurred with steels in the cold-worked, welded and stressed condition, in which the steel is at a very high stress level and a heat-affected zone is present. The next most severe condition was the cold-worked and stressed condition, while the least severe was the stressed only condition. The severity of cracking generally decreased with stress level with nonspring steels. It is apparent from all of this work that there is a distinct advantage in using steel with the lowest strength possible consistent with engineering design and economic requirements.

B. COMPOSITION

Investigative work on the effect of composition of steel on SCC susceptibility in air-contaminated ammonia has not been extensive. Copper in steel was looked at and found to be innocuous at low concentration levels.

C. METALLURGICAL FACTORS

Fine-grain steels appear to offer an advantage over coarse-grain steels in resisting SCC in air-contaminated ammonia.

D. HEAT TREATMENT

Where the size of the vessel will permit, a full anneal is desirable, particularly if cold-formed heads have been used in conjunction with welded construction. The use of hot-formed heads is preferred, and the welds can be stress-relieved locally after fabrication. If 0.2% (wt) water is present in the ammonia as an inhibitor, tanks can be constructed with hot-formed heads with no stress relief after welding. This applies to carbon steel construction. Higher strength quenched and tempered steels with hot-formed heads should be stress-relieved after welding and water should be present as an inhibitor.

E. WELDING

Recommended welding practices for each grade of steel used should be followed. Welding should be kept to a minimum. External tank welds for the attachment of various items should be treated the same as internal welds, as SCC failures can occur at heat-affected zones.

The beneficial effect of a postweld heat treatment in an A 517 steel is shown in Figure 10. Note the tremendous improvement in hardness following the heat treatment - such treatments significantly reduce stress.

IV. ENVIRONMENTAL FACTORS

A. TEMPERATURE

Warm temperatures appear to enhance the SCC susceptibility of steel in air-contaminated ammonia, whereas cold temperatures are beneficial. Care, however, should be taken in the selection of the steel to be used in cold conditions to avoid the possibility of brittle failure.

B. DEW POINTS

Stressed steel in air-contaminated ammonia vapor, even with 0.2% (wt) water present in the liquid ammonia, is more likely to fail by SCC under condensing conditions, i.e., when the steel is cooler than the liquid, than when the steel is warmer than the liquid. This is best illustrated in an article by Ludwigsen and Arup. They assume a large pressurized storage tank half-filled with ammonia, as shown in Figure 11. Assuming the ammonia contains sufficient oxygen to cause SCC with no water present, the composition of the ammonia liquid and vapor would be as shown in Table I. Quoting this article, "the distribution coefficients of these constituents between liquid and vapor are not very well known, but if we assume one likely set of coefficients, the corresponding composition of the vapor would be that given in the second column in Table I. It is seen that the vapor contains 600 times more oxygen and only one third of the water as compared with the liquid."

"At uniform temperature, the top inner surface of the tank will be wetted by a thin (10 to 100 molecular layers) film of adsorbed liquid ammonia, and under equilibrium conditions this should be of the same composition as the bulk liquid."

"In reality, the temperature of the tank top will vary considerably between day and night, and in consequence the tank top will shift between being dry and wet. During a cold night, copious condensation will occur, liquid ammonia will run down the walls, and the composition of this liquid has no time to reach equilibrium, but its composition shifts towards the composition of the vapor. It can safely be argued, that it will always contain more oxygen and less water than the bulk liquid, and therefore, be more likely to promote SCC."

Considering that effective inhibition to SCC of stressed steel in air-contaminated ammonia has been achieved with 0.08 to 0.2% (wt) water and this represents 800 and 2000 ppm, respectively, it will be noted, in referring to Table I, that insufficient water is present in the vapor to prevent SCC.

V. OTHER FACTORS TO CONSIDER IN OTEC DESIGN

So far, we have discussed rather simple systems, a relatively large area of steel as represented by the tank and minor amounts of more cathodic metals such as stainless steel valves or valve trim that might be coupled to the tank. In such a situation, the large area of steel predominates and the presence of the cathodic metal is hardly noted from a galvanic standpoint.

OTEC design is much more complex. Heat exchanger tube surface area should equal or exceed the steel shell surface area and thus exert considerable galvanic effect. An electrochemical galvanic series for metals in ammonia has been established in uncontaminated liquid ammonia and air-contaminated liquid ammonia, as shown in Figures 12 and 13. In uncontaminated liquid ammonia, carbon steel is shown to be anodic to the stainless steels and titanium (Figure 12). In air-contaminated liquid ammonia, aluminum is shown to be anodic to titanium, the stainless steels and carbon steel. Since on occasion OTEC ammonia tanks will be subject to air during filling and draining, these potential differences are of interest. Of more importance is the anodic condition of steel in relation to titanium, stainless steel and, although not shown, probably copper-nickel, as shown in Figure 12. This galvanic effect may be an accelerating factor as regards the SCC susceptibility of steel and should be investigated further. In some OTEC designs, titanium and stainless alloy tube surfaces are to be coated with an aluminum oxide coating for surface enhancement. This coating may serve another advantage - that of removing the noble (to steel) titanium and stainless surface from the system. Also, in the case of copper-nickel tubes, a bimetal tube is being considered that will place steel on the ammonia side and copper-nickel on the seawater side, to the advantage of both metal systems.

VI. GENERAL CORROSION RESISTANCE OF ALLOYS TO AMMONIA

A number of alloys have been exposed to metallurgical-grade ammonia for one (1) and eight (8) months. Results are given in Table II.

From this it will be noted that all metals listed, except zinc, are satisfactorily resistant to general corrosion in ammonia.

VII. RESEARCH NEEDS

1. Study the effect of galvanically coupled dissimilar metals in both liquid and gaseous ammonia.

   a. Metals should include titanium, grade 2, coupled to steel; CA-706 and CA-722 coupled to steel; Alclad aluminum and 5052 aluminum coupled to steel; and "20-24-6" stainless alloy coupled to steel. Area ratios should be varied; the steel should be with and without stress and welds.

   b. The liquid and gaseous ammonia should be with and without water and with and without chlorides in the presence of water.

   c. The effectiveness of hydrazine and other likely inhibitors should also be investigated under all conditions.

2. Develop an instrument that will read oxygen levels in the presence of ammonia, to ppb, with a high degree of accuracy and reliability. (The gas chromatograph is only good to 4 ppm O_2.)

3. Investigate the feasibility of metallizing welds in steel plate with aluminum in order to circumvent the need of stress-relieving welds, particularly in the vapor area (condenser) where the availability of water as an inhibitor of SCC may be limited.

4. Develop an inhibitor that will carry through the turbine and be effective in small amounts in all components of the OTEC cycle, both with and without the presence of water. (Can water and hydrazine [N_2H_4] be used jointly to avoid the need for postweld heat treatments?)

5. What effect does the weldment have on SCC? (C-Mn, C-1/2Mo, etc.)

6. Do minor elements in steels, such as Sn, Zn or others, contribute to SCC-type of failure in ammonia? Compositional limits in steels and their effect on SCC have not been defined.

7. Determine the effectiveness of low quantities (<0.08%) of water in the vapor; with and without the presence of varying quantities of hydrazine as an SCC inhibitor of fabricated steel.

8. Determine if hydrazine will carry over from the evaporator to the condenser, through the compressor, more efficiently than water.

9. Determine the partition coefficient of contaminants and inhibitors in liquid and gaseous ammonia under OTEC conditions.

10. The effect of temperature on SCC of steel should be studied.

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APPENDIX

ASSOCIATIONS AND SPECIFYING ORGANIZATIONS DEALING WITH AMMONIA

Compressed Gas Association

New York, N. Y.

Bulletins:	(a)	TB-2	Guidelines for Inspection & Repair of MC-330 and MC-331 Cargo Tanks
	(b)	G-2	Anhydrous Ammonia
		G-2.1	American National Standard Safety Requirements for the Storage and Handling of Anhydrous Ammonia, K61.1
		G-2.2T	Tentative Standard Method for Determining Minimum of 0.2% Water in Anhydrous Ammonia

The Fertilizer Institute

1015 18th Street, N.W.
Washington, D. C. 20036

Mr. Carl Johnson
Telephone: 202/466-2700

(Formerly, Agricultural Ammonia Institute Combined with The National Plant Food Institute)

(Formerly, Agricultural Ammonia Institute)

(Formerly, Agricultural Nitrogen Institute)

a. Document: "Safety Requirements for Storage and Handling of Anhydrous Ammonia."

b. Report: "Stress Corrosion Cracking of Steel In Agricultural Ammonia," (a report from The Research Committee of the Agricultural Ammonia Institute).

c. Has a device for low level NH_3 gas sensing.

d. Has a study underway at A. D. Little ($1 million) jointly funded by The Fertilizer Institute, the U.S.C.G. and ANSI on ammonia spills. Tests are being conducted at The Naval Weapons Center, China Lake, CA.

e. Worked jointly with NACE Committee T5E-10 (1971-1972) to establish guidelines for ammonia containers. The preliminary working group to this Committee suggested the following after a 1956 study:

1. Tanks for ammonia service should have either:

    (a) Hot-formed heads

    (b) Stress-relieved cold-formed heads, or

    (c) Full stress relief of the entire tank following fabrication.

2. Tanks over 36 inches in diameter should be either fully stress relieved or fabricated with heads that are hot-formed or stress-relieved. Service experience has indicated that ammonia applicator tanks with a diameter <36 inches are relatively insensitive to cracking.

3. Extreme care should be taken to eliminate air from agricultural ammonia systems.

4. Agricultural ammonia should contain water to inhibit SCC, with minimum water at 0.2% (by wt). [Distilled water, deionized water, or steam condensate.]

International Institute of Ammonia Refrigeration

Chicago, Ill.

Brochure: "Equipment Design and Installation of Ammonia Mechanical Refrigeration Systems"

American National Standards Institute (ANSI)

New York, N. Y.

Document: "American National Standard Safety Requirements for the Storage and Handling of Anhydrous Ammonia" (K 61.1-1972). This standard applies to ANSI and The Fertilizer Institute. Both of these Societies work with The Compressed Gas Association through Committee.

The ANSI Guide: Applies to the design, construction, location installation and operation of anhydrous ammonia systems. The STD does not apply to:

a. Ammonia manufacturing plants

b. Refrigeration plants

c. Ammonia transportation pipelines.

1. Containers exceeding 36 inches in diameter or 250-gallon capacity shall be stress-relieved after fabrication or cold-formed heads, when used, shall be stress-relieved or hot-formed heads shall be used.

2. Welding to the shell, head or any other part of the container subject to internal pressure shall be done in compliance with the code under which the container was fabricated. Other welding is permited only on saddle plates, lugs, or brackets attached to the container by the container manufacturer.

3. All containers except refrigerated storage tanks with a design pressure of less than 15 psig and containers constructed in accordance with specifications of the DOT, shall be inspected by a person having a current certificate of competency from The National Board of Boiler and Pressure Vessel Inspectors.

4. Piping used on nonrefrigerated systems shall be at least ASTM A-53 Grade B. Electric Resistance Welded and Electric Flash Welded or equal. Such pipe shall be at least Schedule 40 when joints are welded, or welded and flanged. Such pipe shall be at least Schedule 80 when joints are threaded. Brass, copper, or galvanized steel pipe or tubing shall not be used.

5. Cast iron fittings shall not be used but this shall not prohibit the use of fittings made specifically for ammonia service of malleable or nodular iron such as Specification ASTM A 47 or ASTM A 395.

6. After assembly, all piping and tubing shall be tested and proved to be free from leaks at a pressure not less than the normal operating pressure of the system.

7. The shell or head thickness of any container shall not be less than 3/16 inch.

American Institute of Chemical Engineers (AIChE)

Publishes: Monograph entitled, "Safety In Air and Ammonia Plants" (The Proceedings of The Annual Symposia on Safety in Ammonia Plants - Fall AIChE meetings held each year)
Ammonia Plant Safety Series:

Ammonia Plant Safety and Related Facilities, Vol. 20 (1978)

T-59 Ammonia Plant Safety and Related Facilities, Vol. 19 (1977)

T-56 Ammonia Plant and Safety, Vol. 18 (1976)

T-52 Ammonia Plant and Safety, Vol. 17 (1975)

T-48 Ammonia Plant and Safety, Vol. 16 (1974)

T-45	Ammonia Plant and Safety, Vol. 15 (1973)
T-42	Ammonia Plant and Safety, Vol. 14 (1972)
T-38	Ammonia Plant and Safety, Vol. 13 (1971)
T-35	Ammonia Plant and Safety, Vol. 12 (1970)
-	Ammonia Plant and Safety, Vol. 11 (1969)

Manufacturing Chemists Association

Washington, D. C.

Brochure: Chemical Safety Data
(Not presently available - under revision)

U. S. Department of Transportation (ICC)

Washington, D. C.

Hazardous Materials Regulation - Title 49 - Transportation, Code of Federal Regulations - Parts 171-190. Also, see DOT Report - No. DOT-FH-11-8568.

The DOT adopted the NACE Committee T-5E-10 recommendations:

1. Stress-relieve tanks over 36 inches in diameter. These must be stress-relieved as a unit or must be fabricated with hot-formed or stress-relieved heads.

2. Remove all air from the system.

3. In handling agricultural-grade ammonia, vessels fabricated from Q and T steels should contain a minimum of 0.2% (by wt) water.

4. Cargo tanks made to Specifications MC-330 and MC-331, constructed of Q and T steels may be used only for ammonia having a minimum water content of 0.2% or for ammonia of at least 99.995% purity. Other grades of ammonia would have to be moved in tanks other than Non-Q and T steel.

5. Tanks that have been open shall be purged of air before loading.

6. Inspection by wet fluorescent magnetic particle method for all Q and T steels in ammonia service. This includes all internal welds and areas extending 2 inches in from such welds and similar areas opposite all exterior welds

as well as the interior surface of tank heads. If any crack whatsoever is found, the entire interior surface of the tank must also be inspected by the wet fluorescent magnetic particle method.

7. DOT requires a pressure test every five years. All Q and T steel must be pressure tested.

American Society of Mechanical Engineers (ASME)

Reference: None presently available.

Associations Who Do Not Specify Materials For Ammonia

American Iron and Steel Institute (AISI)

American Petroleum Institute (API)

National Association of Corrosion Engineers (NACE)

TABLE I. DISTRIBUTION OF OXYGEN AND WATER BETWEEN LIQUID AND VAPOR IN AMMONIA STORAGE. THE TOTAL AMOUNTS HAVE BEEN CALCULATED FOR THE TANK SHOWN IN FIGURE 11

	Composition		Total Amounts	
			1500 Tons	15 Tons
	Liquid (ppm)	Vapor (ppm)	Liquid (kg)	Vapor (kg)
Oxygen	10	6000	15	90
Water	2000	600	3000	9

(From Ludwigsen and Arup.)

TABLE II. GENERAL CORROSION PERFORMANCE OF VARIOUS MATERIALS IN LIQUID AMMONIA

Alloy Designation	Weight Change (mg/dm^2)	
	1 Month Exposure	8 Month Exposure
Type 304 SS	0	+3.0
Type 316 SS	0	+3.4
Type 430 SS	0	+3.8
Type 410 SS	-7.52	+0.75
Al-3003	+7.52	+1.9
Al-5454	+12.8	+1.12
Titanium	0	+3.0
Monel	-1.5	-3.4
Inconel 600	-1.5	+2.6
Zinc	-47.0	-21.0
Iron	-2.25	-1.5
Carbon Steel	-3.76	-0.75
Hastelloy C	-1.13	+0.75
ASTM 517 Grade F Steel	-3.0	-0.75

Note: + means weight gain, and - means weight loss. (From Jones and Wilde.)

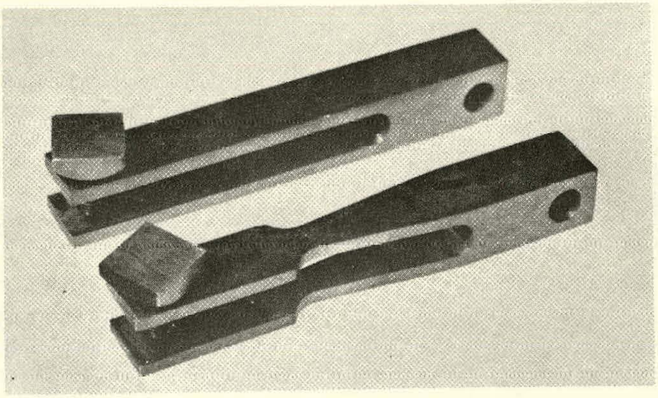


Figure 1

Tuning-fork specimens used in stress-corrosion studies. Approximately actual size. (From Loginow and Phelps.)

Figure 2

Crack in ASTM A517 steel tank after anhydrous ammonia service. Etched in nital. (From Loginow.)

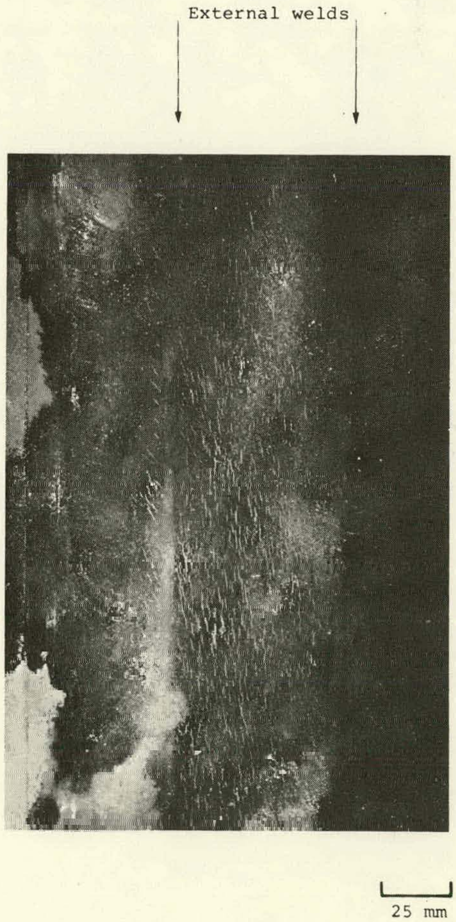


Figure 3

Cracking in the head of an ammonia tank opposite an external doubler plate revealed by the wet fluorescent magnetic particle method. The cracks are located both between and outside parallel external welds. (From Loginow.)

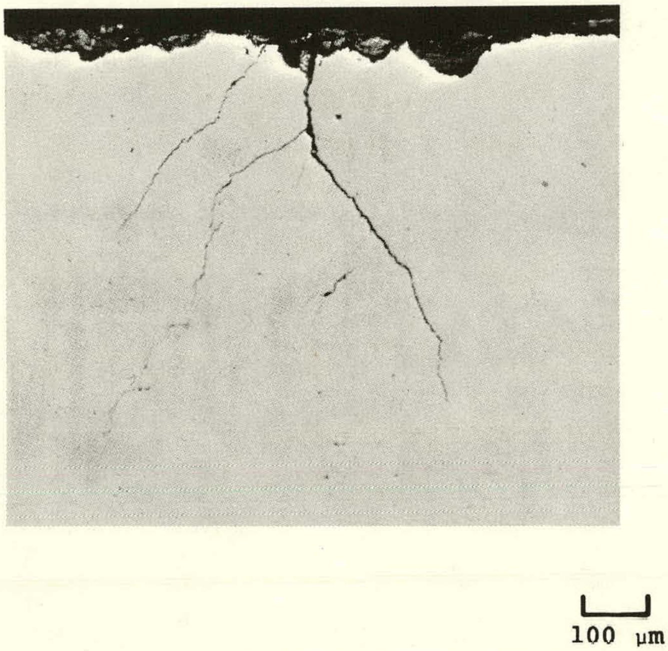


Figure 4

Cross section of ASTM A517 steel tank head that cracked in anhydrous ammonia service. Not etched. (From Loginow.)

Figure 5

Cracks in A517 steel tank after anhydrous ammonia service. Etched in nital. (From Loginow.)

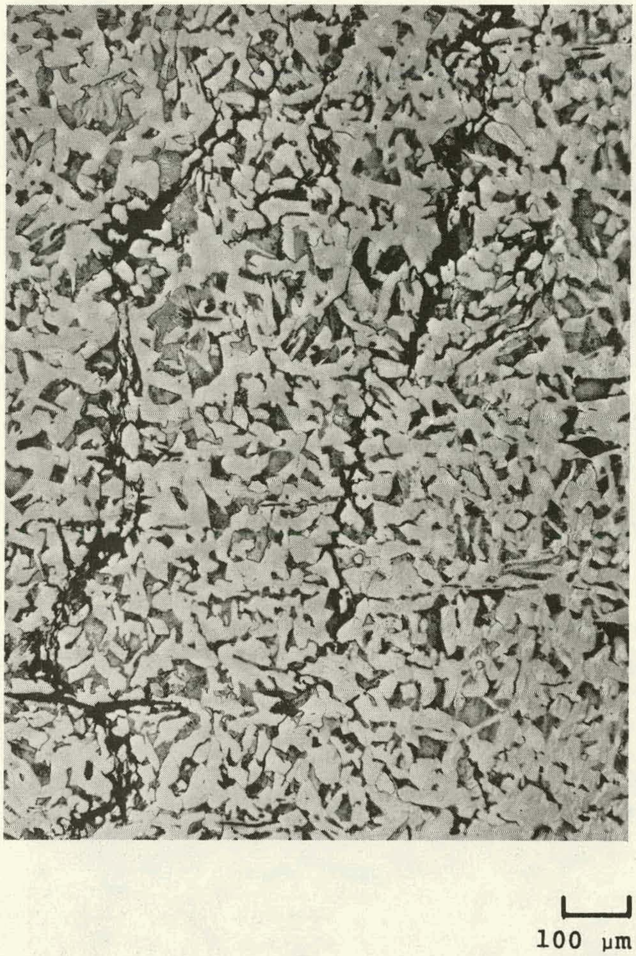
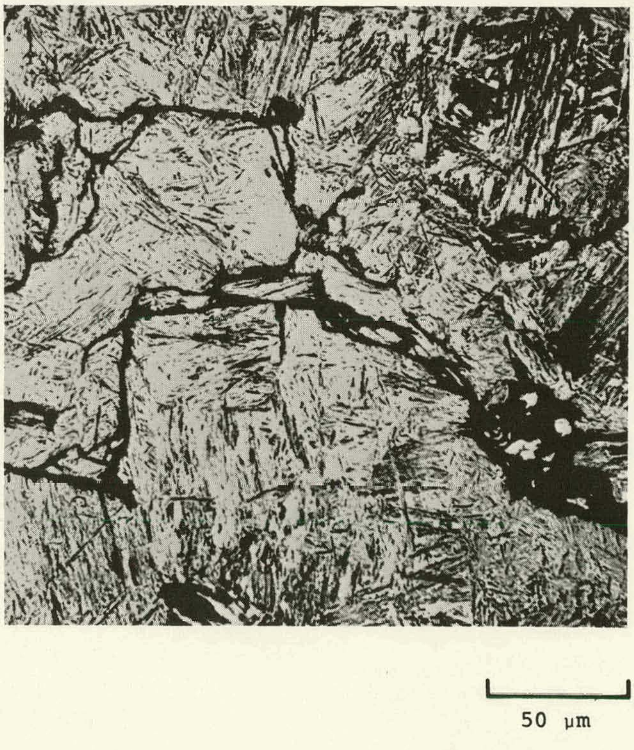


Figure 6

Cross section of a cold formed ASTM A515 Grade 70 steel tank head that cracked in anhydrous ammonia service. Etched in nital. (From Loginow.)

Figure 7

Stress corrosion cracks in heat affected zone of ASTM A202 steel caused by anhydrous ammonia. Etched in picral. (From Loginow.)



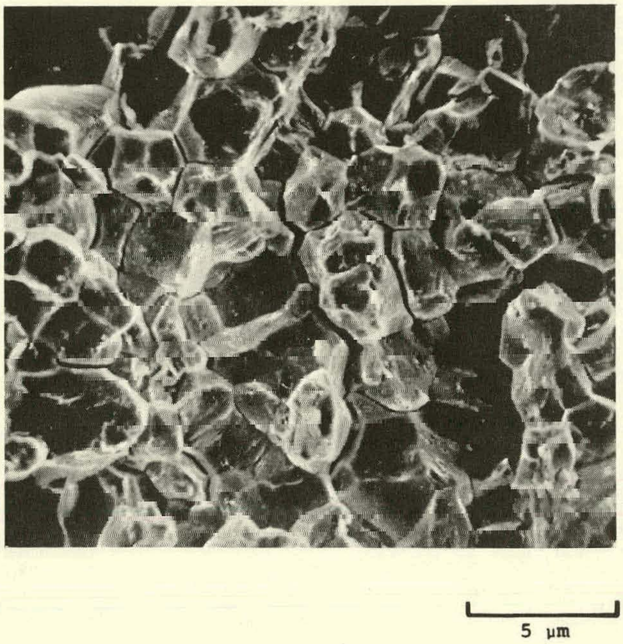


Figure 8

SEM fractograph of an ammonia stress corrosion crack in HAZ of ASTM A517 steel. (From Loginow.)

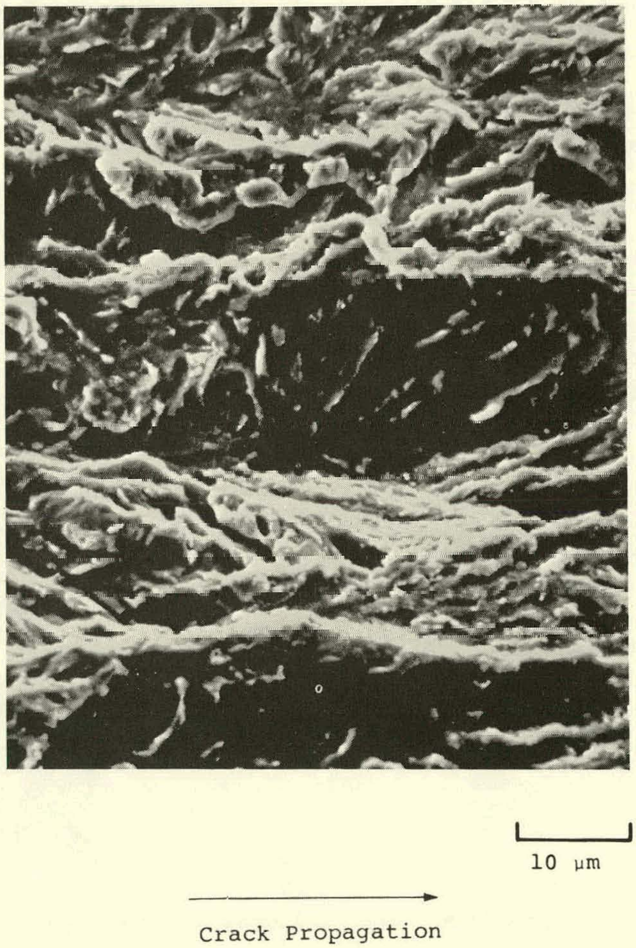


Figure 9

SEM fractograph of a stress corrosion crack in AISI 4130 steel. (From Loginow.)

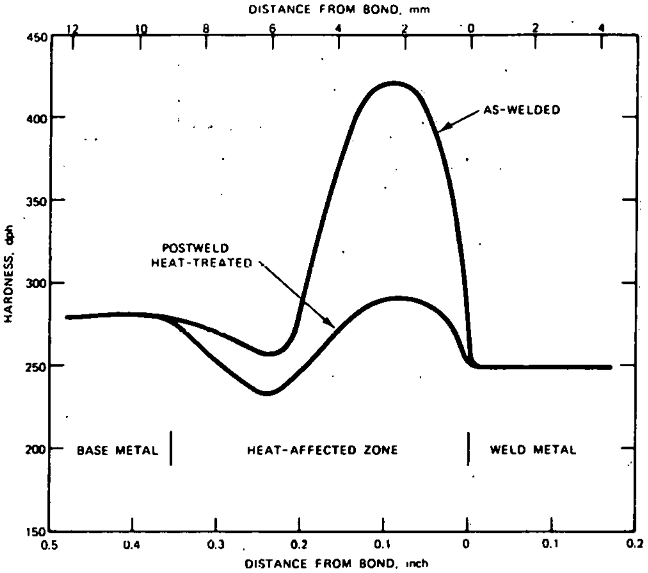
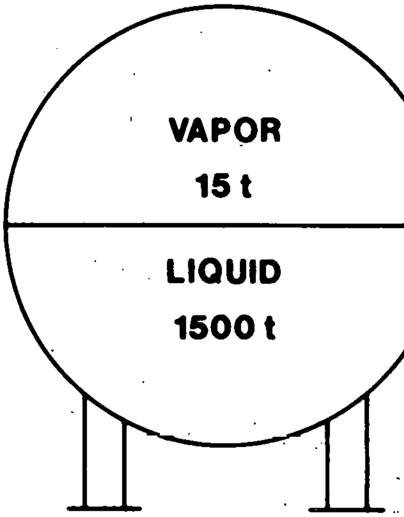


Figure 10

Typical hardness traverses in weldments of ASTM A517 steel. (From Loginow.)

Figure 11

5000 m^3 steel sphere for liquid ammonia. The tank is shown half filled with liquid ammonia at 17 C where the saturated vapors exert a pressure of 8 kg/cm^2 above the atmospheric pressure. (From Ludwigsen and Arup.)



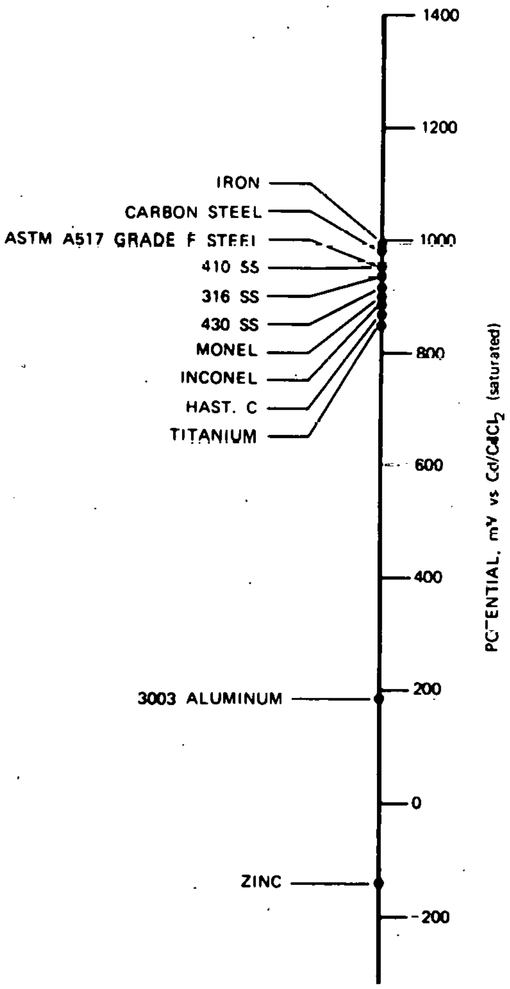


Figure 12

Galvanic series in uncontaminated liquid ammonia. (From Jones and Wilde.)

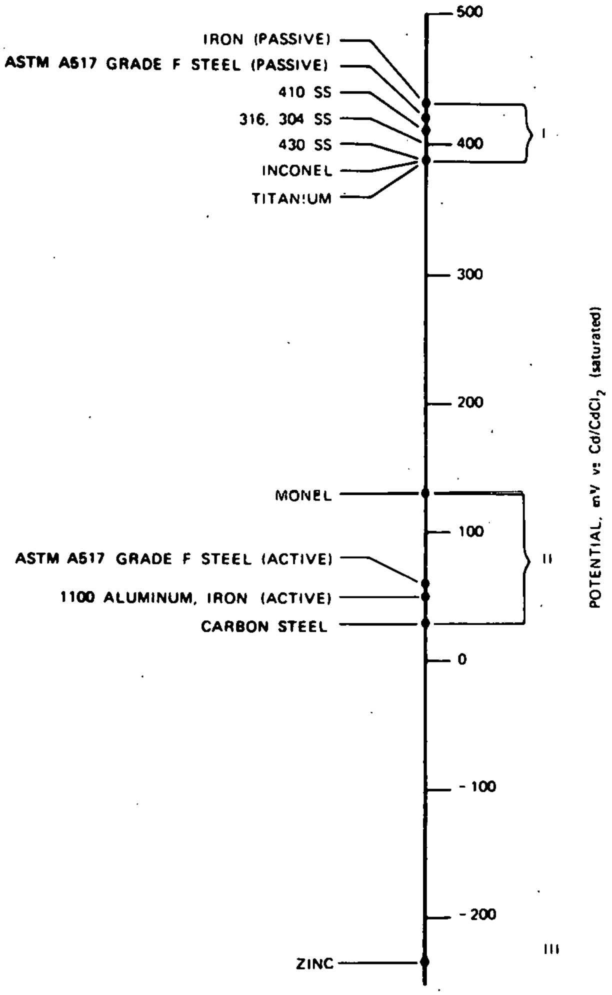


Figure 13

Galvanic series in air contaminated liquid ammonia. (From Jones and Wilde.)

NEW DEVELOPMENTS

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CONCEPTUAL PLAN FOR A "SEACOAST TEST FACILITY" AT KE-AHOLE POINT, KONA, HAWAII

by

Hank White and Edward Noda
University of Hawaii

Ever since the OTEC concept of power generation began to receive serious consideration as a viable alternative energy source, there has been a general consensus that a Seacoast Test Facility would provide an ideal environment for the studies needed to evaluate OTEC power cycle configurations. A critical requirement of such a facility is to bring together, on a laboratory scale but under realistic operating conditions, the necessary ocean thermal resources, that is, the warm surface water and the deep cold waters. While elements such as site, facilities, and the warm surface water are relatively easy to provide using standard engineering practices, to obtain the deep cold water is a more difficult problem. Initial estimates for traditional steel-and-concrete pipes of the type presently used in the offshore oil fields and present state of the art in deploying this type of pipe indicated that the costs of installation to depths of 2000 feet or more would be prohibitive, particularly along a 30° ocean bottom slope as encountered at Ke-ahole Point, Hawaii.

Beginning in late 1976 preliminary discussions were held at the University of Hawaii seeking a new, innovative approach to the cold water pipe problem, which would significantly reduce deployment risks but that at the same time would be technically viable with an acceptable level of deployment risk. After a number of concepts had been studied, Makai Ocean Engineering of Honolulu, Hawaii, was engaged in November 1977 to develop a conceptual design of such a cold water pipe system. The results of this effort indicated that based on the bathymetry at Ke-ahole Point [Noda: "Site Selection Bathymetry Survey, Ke-ahole, Hawaii, in Conjunction with Ocean Thermal Energy Conversion Facilities, Dec. 1977," Look Laboratory, 78-43], such an approach should be considered seriously.

Fundamentally, the system proposed was to use a "floating" high molecular weight polyethylene pipe suspended above the ocean bottom by "tethers" on 19 ft. centers. It was also suggested that a submerged pumping station should be used to reduce suction on the deep pipe and to minimize the possibility of cavitation and resultant impeller wear. The initial capacity of this system was arbitrarily established at 3000 G.P.M. with an anticipated three-year service life. When a Request for Proposal (RFP) for a Seacoast Test Facility was advertised by Argonne National Laboratory (ANL), the State of Hawaii submitted a proposal based on this floating pipe concept.

The RFP from ANL mandated several criteria which necessitated modification of the prior conceptual design. Principal among these was the requirement for 6400 G.P.M. for the cold water side, and 9600 G.P.M. for the warm water side. A ten-year service life was also stipulated in the RFP, far in excess of the three-year service life originally envisioned. Makai Ocean Engineering responded to these changes with a revised conceptual design that would provide the total seawater delivery specified. The State of Hawaii undertook the planning and construction of the onshore facilities. It is this proposal which resulted in a two-phase contractual award from ANL. The first phase is for detailed designs and plans based on the previous design concept and the second phase is for construction.

We are currently in the design phase and although several elements are under re-evaluation, we will address today the proposed STF as it is described in the conceptual design envisioned in our proposal, "Design and Construction Proposal OTEC Seacoast Test Facility, June 1978."

For convenience, the overall project may be divided into two distinct areas: the onshore facilities which consists of the more or less "normal" elements of any test facility, warehouses, offices, laboratories, etc., and the offshore facilities which contain the "unusual" elements necessary to deliver the specified quantities and types of seawater to the test site.

The onshore support facilities consist of a 4800 sq. ft. warehouse containing a machine shop and a carpentry shop, an office building (2000 sq. ft.) containing an electronics shop, and on top of this a resident manager's quarters. An emergency power generating plant of 750 KW capacity is also provided to insure continuity of operations in the event of a power failure from the normal commercial sources.

The onshore facilities for experimentation and testing consist of a 2625 sq. ft. laboratory building which is designed for general use and a simple 60' x 100' concrete pad to be used for various experimental apparatus configurations associated with OTEC research. This approach was adopted to provide the maximum flexibility for the various large component layouts which may have to be accommodated during the testing period. The benign climate of Ke-ahole Point makes such a simple approach feasible. All of the onshore facilities are designed for expansion to at least double their present size, should future needs dictate such developments. The offshore system is, of course, the heart of the test facility, and it is this element that presents the greatest challenge.

The cold water pipe descends to a depth of 2100 feet, thereby assuring a minimum temperature difference of 18.7°C in March and a maximum of 21.3°C during August-September. The calculated increase in temperature for the cold water during its transition from inlet to outlet is approximately 0.2°C. The approximate dimensions of this pipe are 28" o.d. with a wall thickness varying from .864' to 1.848'. The total effective length of the pipe from inlet through pumps to the test site is approximately 6800 feet. The pipe inlet is approximately 37 feet above the bottom; at the 2100 feet level; its end is blocked, and for 20 feet shoreward the wall is perforated with approximately 1000 two-inch diameter holes, thus preventing the ingestion of animals large enough to cause pump damage. Supplemental filtration is also provided at the header tank. The proposed polyethylene pipe has approximately five pounds of positive buoyancy per lineal foot; this buoyancy is used to suspend the pipe above its bottom mooring system which consists of clump anchors connected with chain. Analyses indicate that although the current velocity imposed on the pipe at right angles may reach 1.75 knots the pipe will remain at least 8 feet above the nominal bottom contour. This technique was adopted so that the pipe would not be subjected to wear on the irregular bottom, as might occur with normal pipe-laying techniques. Additionally, since the bottom slope from the

500 feet level downward is approximately 30°, this configuration allows most of the tensile stresses to be borne primarily by the bottom mooring system. The tethers have a chain lower element in those areas where tether abrasion is considered likely. This chain is supported by a buoyant float so that it does not subtract from the pipe's net buoyancy. Any worn tethers are designed to be replaced from a manned submersible, and four adjacent tethers must fail before a "zipper" effect becomes likely. Deployment of this system is to be accomplished by controlled flooding starting from the shoreward side.

As the pipe reaches 200 feet depth, there is a steep rubble slope rising to the 60 feet level; here the pipe is coupled to another similar pipe which is nested inside a 40-inch I.D. concrete-coated cylinder steel pipe. The annulus thus formed is used to discharge the cold water effluent returning from the test site.

This configuration is continued up the slope to the proposed pumping station where the water passes through two pumps and the pipe system is manifolded in such a way that a spare third pump can be remotely brought into service, should one of the regular pumps fail or require repair. The annular flow configuration is preserved from the pumping station through the interface zone at the coastline. This configuration not only provides armoring for the relatively delicate polyethylene pipe in the nearshore surf zone and on the surface, but also tends to minimize the exchange of heat of the incoming cold water during its transition from the 200 feet level to an area where conventional insulating techniques may be used. The cold water pipe terminates at a gravity header tank that is approximately 20 feet above the test site and has an overflow capability designed to accommodate full pump capacity and, additionally, it provides an opportunity to filter fine material from the seawater prior to its entrance into the experimental apparatus.

The warm water pipe system has a buoyed screened inlet accessible to divers at approximately 100 feet just below the pump station. Except for the additional one-third increase in capacity and its effluent discharge at the water's edge, the warm water system is identical to the cold water system.

We would like to note that the pump location is currently undergoing re-evaluation based on the long-term maintenance costs versus the installation costs and, as of this date, there is a strong indication that the final design will be a free surface submerged pump system located well back from the normal coastline. Other design elements are also undergoing re-evaluation to minimize risk and increase cost effectiveness.

The goals established for this design were to provide OTEC investigators a shoreside facility that would provide the seawater resources necessary to study on a small scale the essential elements needed for an operable OTEC power cycle system. This onshore location and its close proximity to a major airfield and deep cold water harbor will maximize the flexibility of the investigator to make configuration or component changes with minimum of inconvenience and cost.

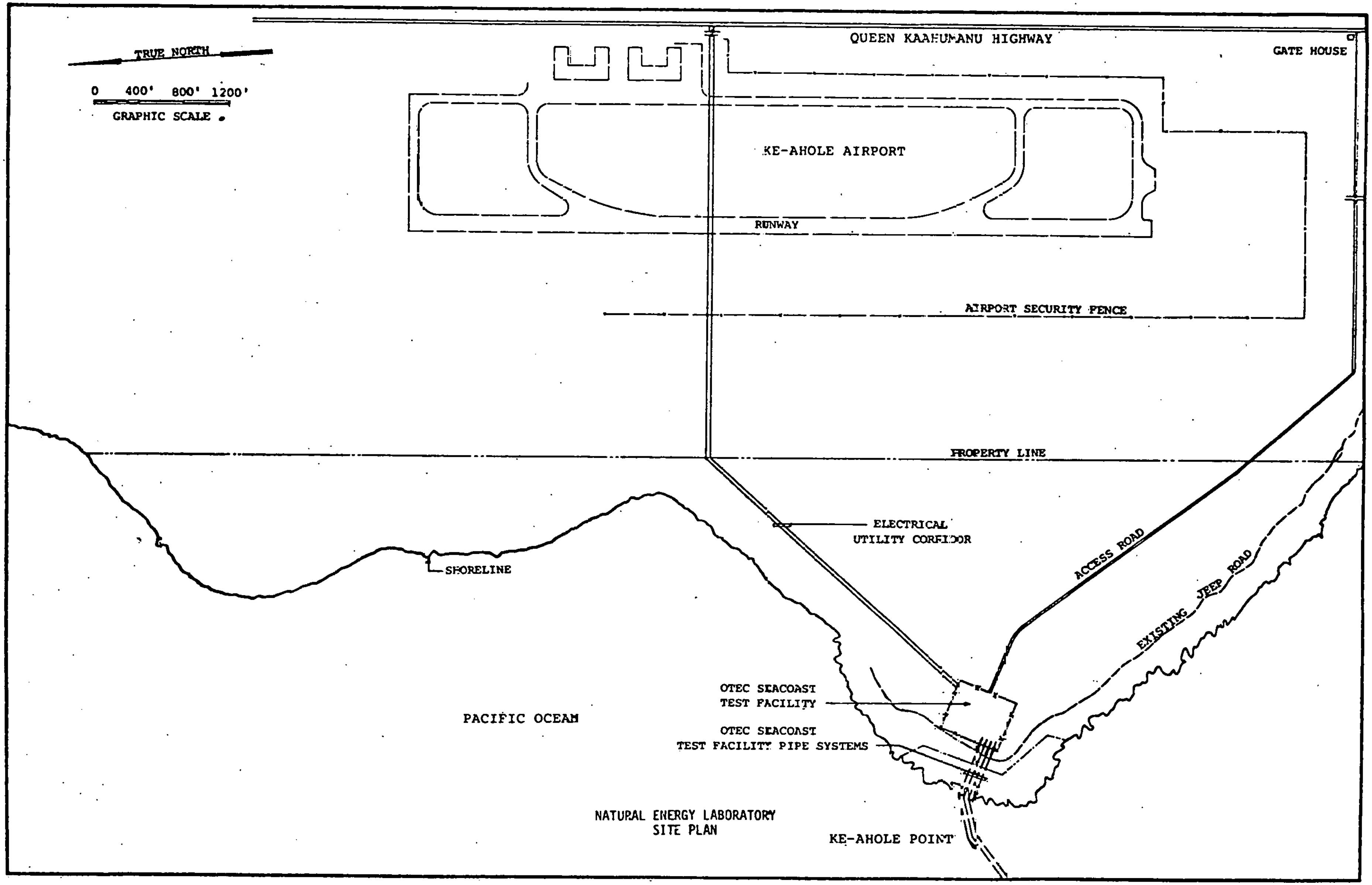

TRUE NORTH
0 400' 800' 1200'
GRAPHIC SCALE
QUEEN KAAHUMANU HIGHWAY
GATE HOUSE
KE-AHOLE AIRPORT
RUNWAY
AIRPORT SECURITY FENCE
PROPERTY LINE
ELECTRICAL UTILITY CORRIDOR
ACCESS ROAD
EXISTING JEEP ROAD
SHORELINE
PACIFIC OCEAN
OTEC SEACOAST TEST FACILITY
OTEC SEACOAST TEST FACILITY PIPE SYSTEMS
NATURAL ENERGY LABORATORY SITE PLAN
KE-AHOLE POINT

FIGURE 1

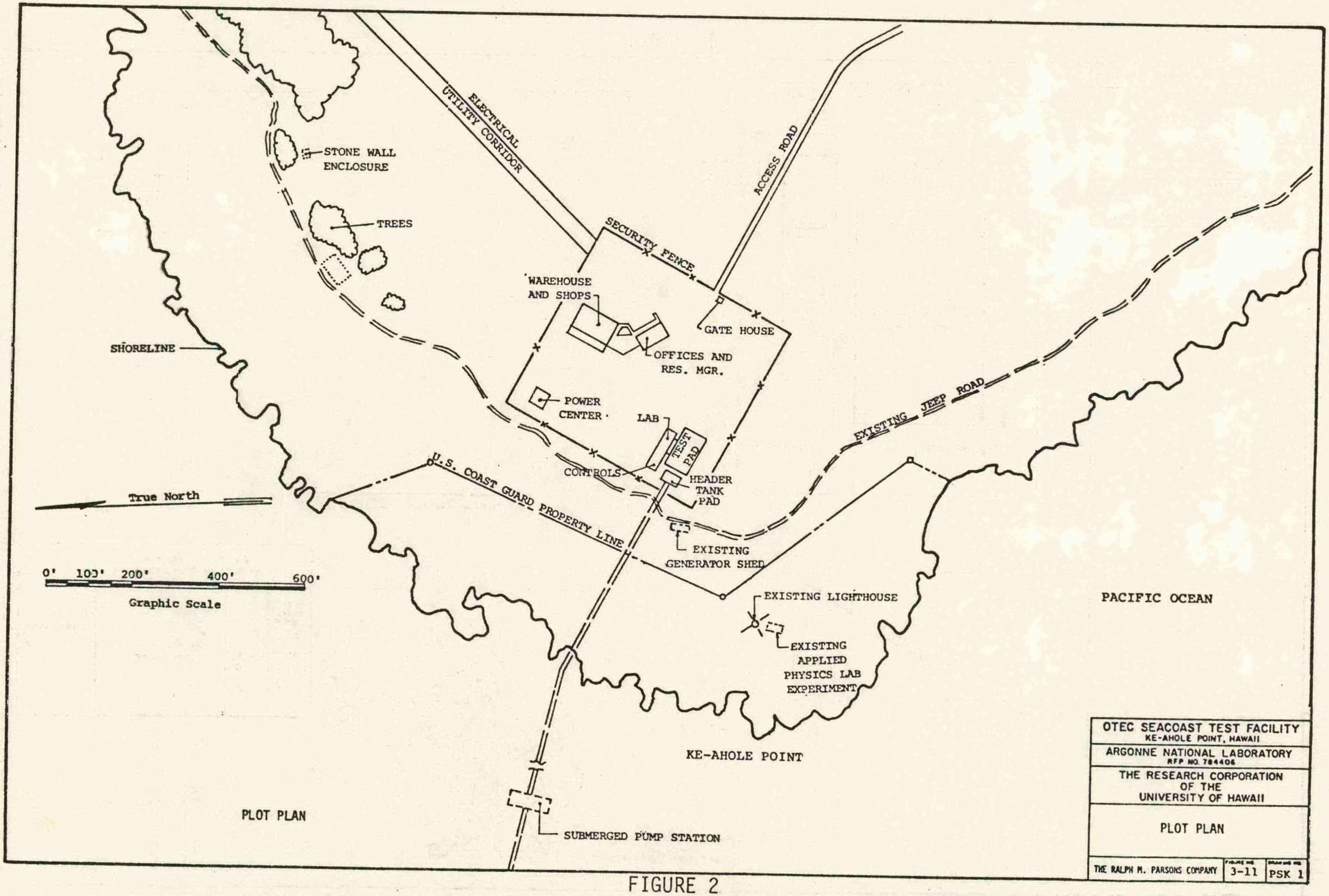

ELECTRICAL UTILITY CORRIDOR
ACCESS ROAD
STONE WALL ENCLOSURE
TREES
SECURITY FENCE
WAREHOUSE AND SHOPS
GATE HOUSE
OFFICES AND RES. MGR.
SHORELINE
POWER CENTER
LAB
TEST PAD
EXISTING JEEP ROAD
CONTROLS
HEADER TANK PAD
U.S. COAST GUARD PROPERTY LINE
True North
EXISTING GENERATOR SHED
0' 100' 200' 400' 600'
Graphic Scale
EXISTING LIGHTHOUSE
PACIFIC OCEAN
EXISTING APPLIED PHYSICS LAB EXPERIMENT
KE-AHOLE POINT
PLOT PLAN
SUBMERGED PUMP STATION
OTEC SEACOAST TEST FACILITY
KE-AHOLE POINT, HAWAII
ARGONNE NATIONAL LABORATORY
RFP NO. 784406
THE RESEARCH CORPORATION OF THE UNIVERSITY OF HAWAII
PLOT PLAN
THE RALPH M. PARSONS COMPANY
3-11
PSK 1

FIGURE 2

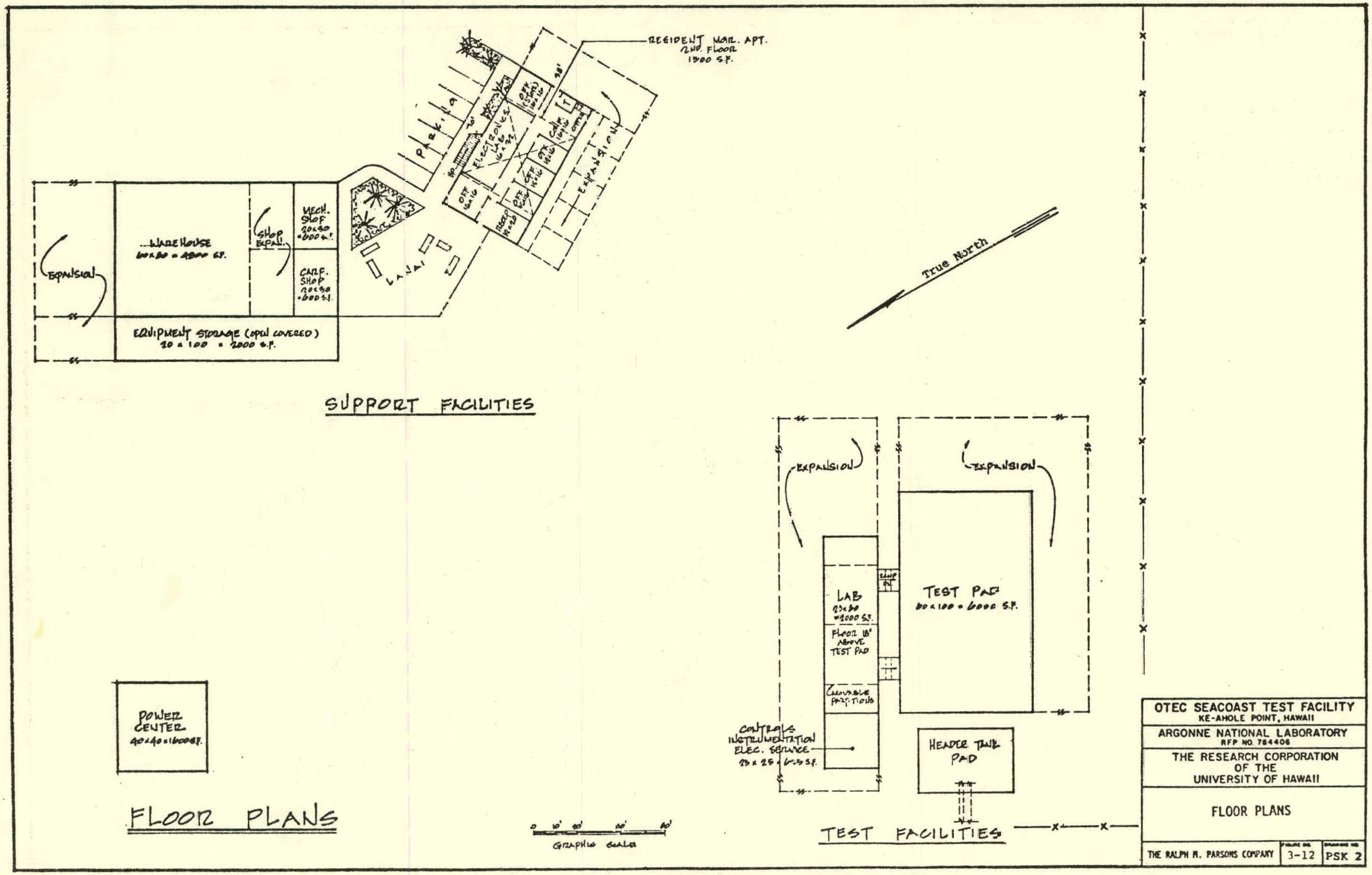
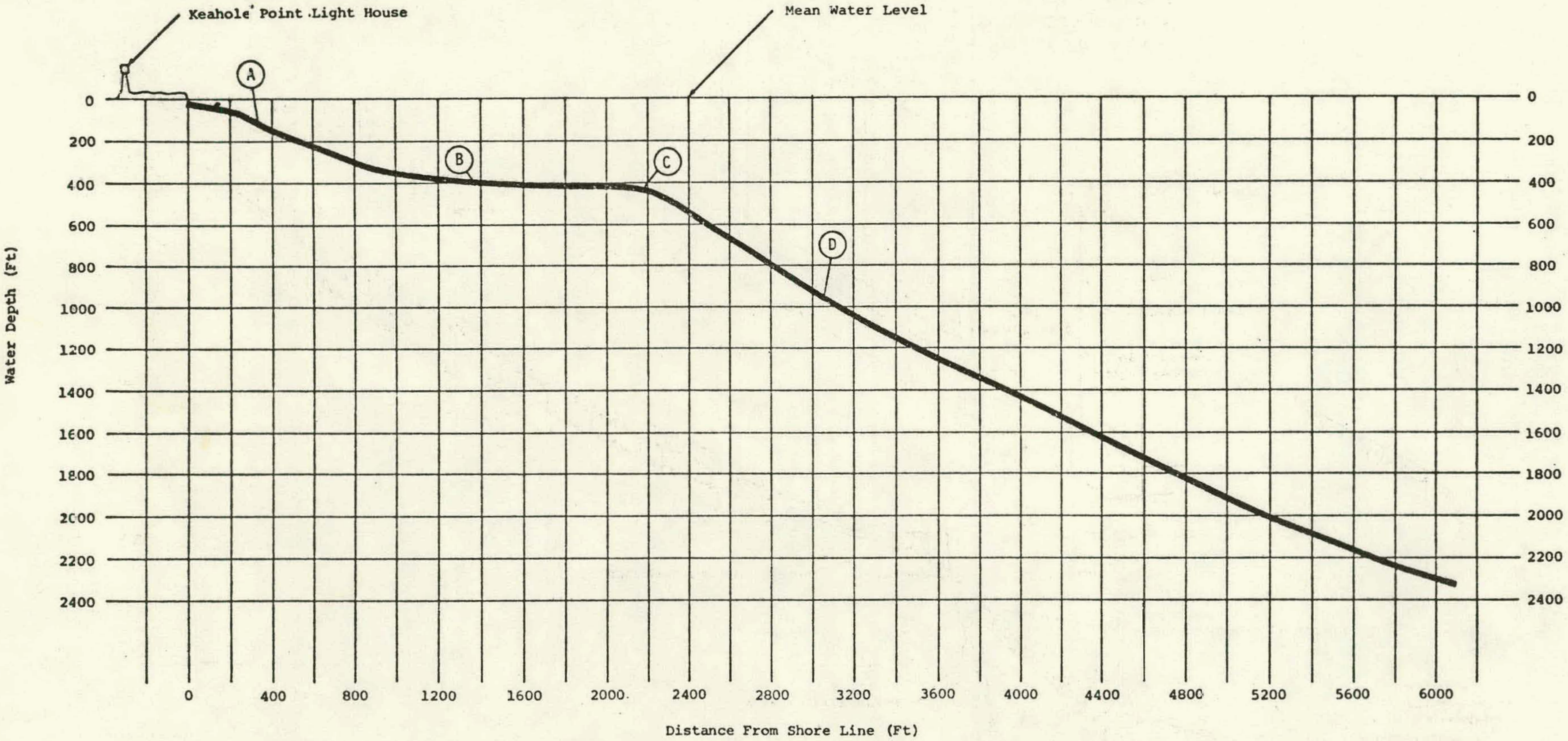

RESIDENT MGR. APT.
2ND. FLOOR
1300 S.F.
PARKING
ELECTRONICS LAB 16 x 32
OFF. (STOR.) 10 x 16
OFF. 10 x 16
CONF. 10 x 16
OFFICE
T
RECEP 16 x 20
LANAI
EXPANSION
38'
70'
WAREHOUSE
60 x 80 = 4800 S.F.
SHOP EXPAN.
MECH. SHOP 20 x 30 = 600 S.F.
CARP. SHOP 20 x 30 = 600 S.F.
EXPANSION
EQUIPMENT STORAGE (OPEN COVERED)
20 x 100 = 2000 S.F.
SUPPORT FACILITIES
True North
EXPANSION
EXPANSION
LAB
25 x 80
= 2000 S.F.
FLOOR 18' ABOVE TEST PAD
MOVABLE PARTITIONS
RAMP UP
TEST PAD
60 x 100 = 6000 S.F.
CONTROLS
INSTRUMENTATION
ELEC. SERVICE
25 x 25 = 625 S.F.
HEADER TANK PAD
TEST FACILITIES
POWER CENTER
40 x 40 = 1600 S.F.
FLOOR PLANS
0 10' 20' 40' 80'
GRAPHIC SCALE
OTEC SEACOAST TEST FACILITY
KE-AHOLE POINT, HAWAII
ARGONNE NATIONAL LABORATORY
RFP NO. 784406
THE RESEARCH CORPORATION
OF THE
UNIVERSITY OF HAWAII
FLOOR PLANS
THE RALPH M. PARSONS COMPANY
FIGURE NO. 3-12
DRAWING NO. PSK 2

FIGURE 3



CROSS SECTION VIEW OF BOTTOM PROFILE AT KE-AHOLE POINT, HAWAII
ORIENTED 245 °T FROM KE-AHOLE POINT LIGHT HOUSE.

KE-AHOLE POINT BOTTOM PROFILE

FIGURE 4

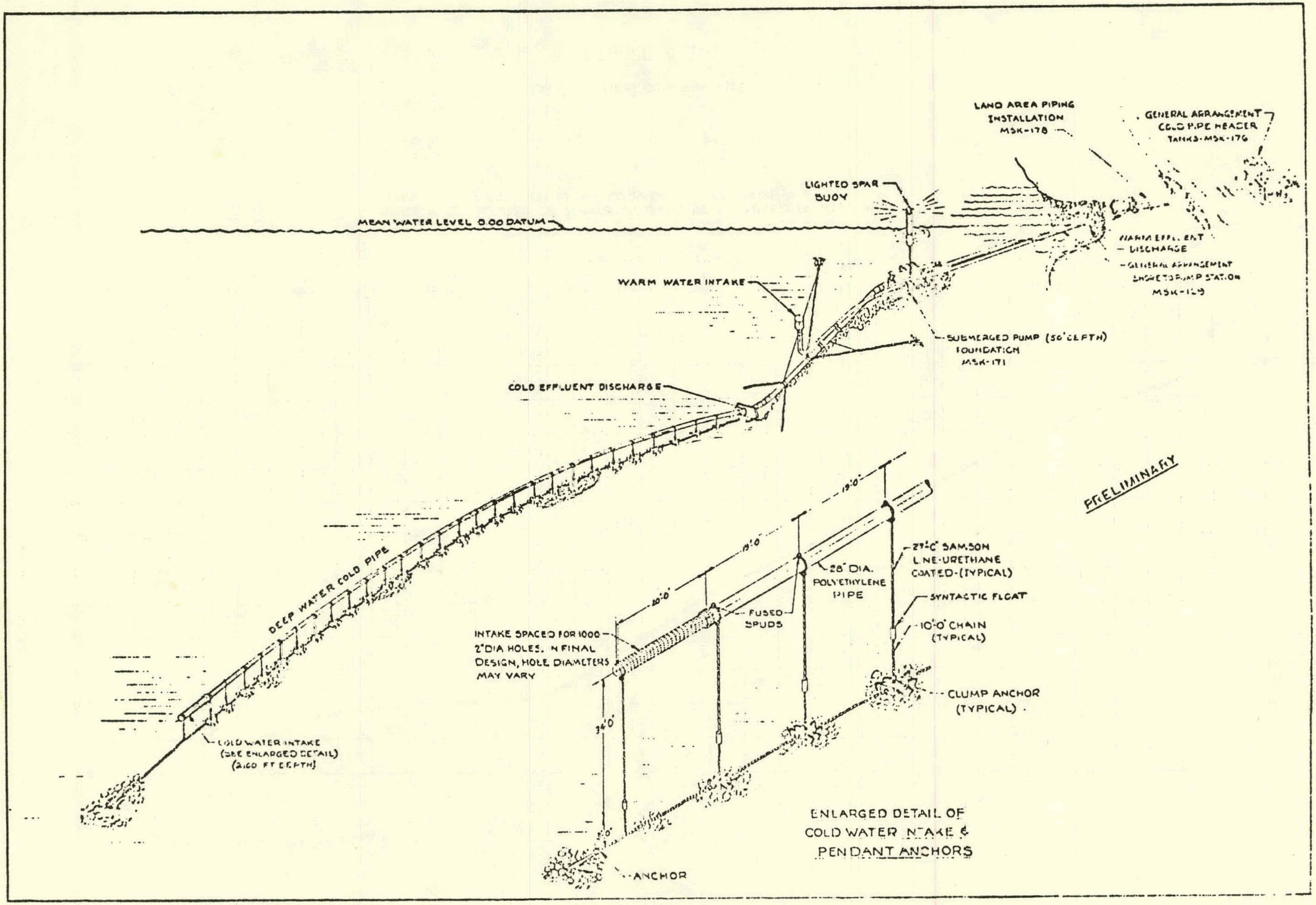

LAND AREA PIPING
INSTALLATION
MSK-178
GENERAL ARRANGEMENT
COLD PIPE HEADER
TANKS-MSK-176
LIGHTED SPAR
BUOY
MEAN WATER LEVEL 0.00 DATUM
WARM EFFLUENT
DISCHARGE
GENERAL ARRANGEMENT
SHORE PUMP STATION
MSK-129
WARM WATER INTAKE
SUBMERGED PUMP (50' DEPTH)
FOUNDATION
MSK-171
COLD EFFLUENT DISCHARGE
PRELIMINARY
DEEP WATER COLD PIPE
19'0"
19'0"
20'0"
27'-0" SAMSON
LINE-URETHANE
COATED-(TYPICAL)
28" DIA.
POLYETHYLENE
PIPE
FUSED
SPUDS
SYNTACTIC FLOAT
10'-0" CHAIN
(TYPICAL)
INTAKE SPACED FOR 1000
2" DIA HOLES. IN FINAL
DESIGN, HOLE DIAMETERS
MAY VARY
34'0"
CLUMP ANCHOR
(TYPICAL)
COLD WATER INTAKE
(SEE ENLARGED DETAIL)
(2.60 FT DEPTH)
ENLARGED DETAIL OF
COLD WATER INTAKE &
PENDANT ANCHORS
ANCHOR

FIGURE 5

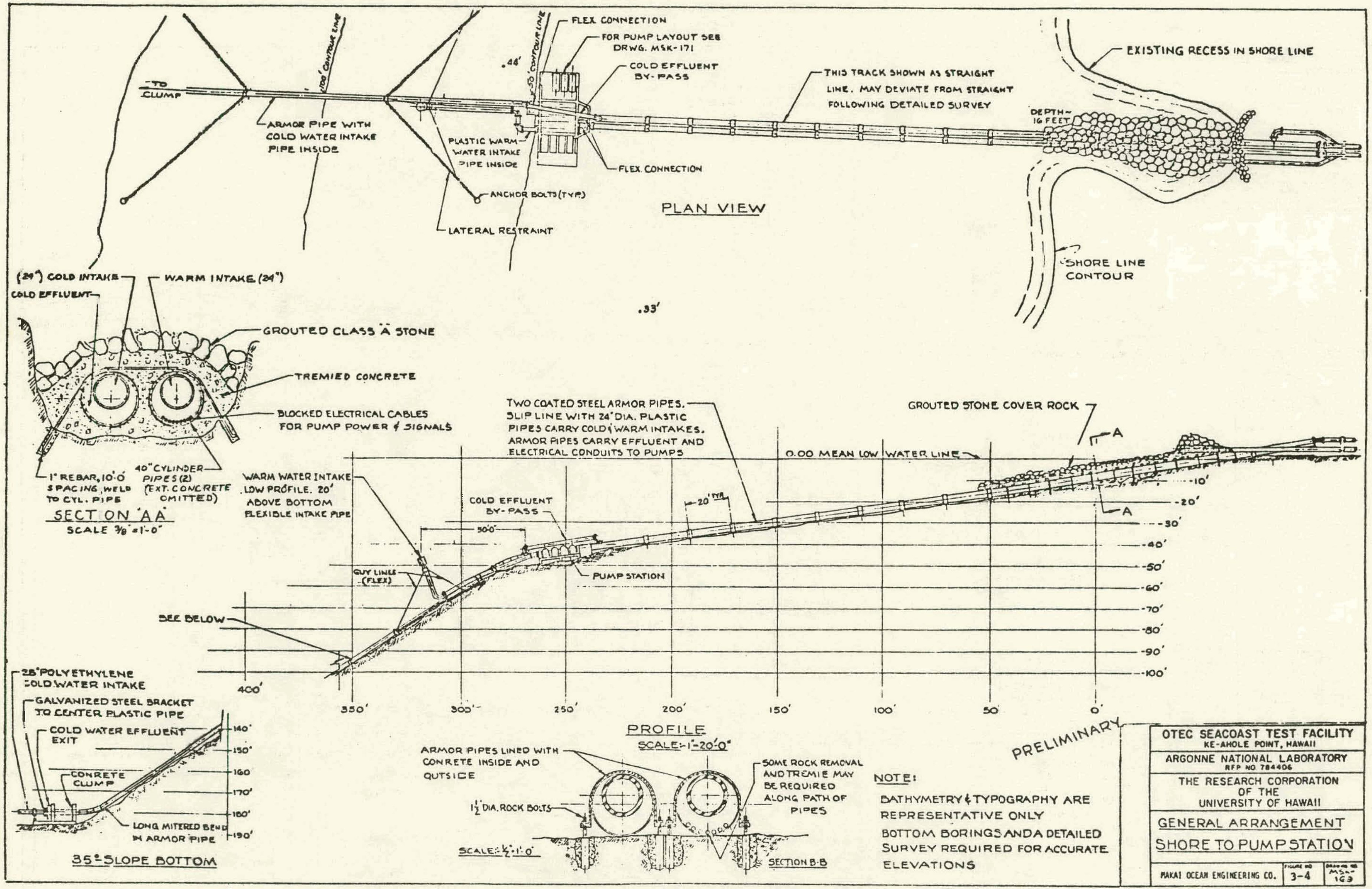

TO CLUMP
100' CONTOUR LINE
ARMOR PIPE WITH COLD WATER INTAKE PIPE INSIDE
.44'
50' CONTOUR LINE
FLEX CONNECTION
FOR PUMP LAYOUT SEE DRWG. MSK-171
COLD EFFLUENT BY-PASS
PLASTIC WARM WATER INTAKE PIPE INSIDE
FLEX. CONNECTION
ANCHOR BOLTS (TYP)
LATERAL RESTRAINT
THIS TRACK SHOWN AS STRAIGHT LINE. MAY DEVIATE FROM STRAIGHT FOLLOWING DETAILED SURVEY
DEPTH-16 FEET
EXISTING RECESS IN SHORE LINE
SHORE LINE CONTOUR
PLAN VIEW
.33'
(24") COLD INTAKE
WARM INTAKE (24")
COLD EFFLUENT
GROUTED CLASS "A" STONE
TREMIED CONCRETE
BLOCKED ELECTRICAL CABLES FOR PUMP POWER & SIGNALS
1" REBAR, 10'-0" SPACING, WELD TO CYL. PIPE
40" CYLINDER PIPES (2) (EXT. CONCRETE OMITTED)
SECTION "AA"
SCALE 3/8"=1'-0"
TWO COATED STEEL ARMOR PIPES. SLIP LINE WITH 24" DIA. PLASTIC PIPES CARRY COLD & WARM INTAKES. ARMOR PIPES CARRY EFFLUENT AND ELECTRICAL CONDUITS TO PUMPS
GROUTED STONE COVER ROCK
0.00 MEAN LOW WATER LINE
A
A
WARM WATER INTAKE LOW PROFILE. 20' ABOVE BOTTOM FLEXIBLE INTAKE PIPE
COLD EFFLUENT BY-PASS
50'-0"
20' TYP
GUY LINES (FLEX)
PUMP STATION
SEE BELOW
-10'
-20'
-30'
-40'
-50'
-60'
-70'
-80'
-90'
-100'
400'
350'
300'
250'
200'
150'
100'
50'
0'
PROFILE
SCALE 1"=20'-0"
PRELIMINARY
28" POLYETHYLENE COLD WATER INTAKE
GALVANIZED STEEL BRACKET TO CENTER PLASTIC PIPE
COLD WATER EFFLUENT EXIT
CONRETE CLUMP
LONG MITERED BEND IN ARMOR PIPE
140'
150'
160'
170'
180'
190'
35° SLOPE BOTTOM
ARMOR PIPES LINED WITH CONRETE INSIDE AND OUTSIDE
1½" DIA. ROCK BOLTS
SOME ROCK REMOVAL AND TREMIE MAY BE REQUIRED ALONG PATH OF PIPES
SCALE: ½"=1'-0"
SECTION B-B
NOTE:
BATHYMETRY & TYPOGRAPHY ARE REPRESENTATIVE ONLY
BOTTOM BORINGS AND A DETAILED SURVEY REQUIRED FOR ACCURATE ELEVATIONS
OTEC SEACOAST TEST FACILITY
KE-AHOLE POINT, HAWAII
ARGONNE NATIONAL LABORATORY
RFP NO 784406
THE RESEARCH CORPORATION OF THE UNIVERSITY OF HAWAII
GENERAL ARRANGEMENT
SHORE TO PUMP STATION
MAKAI OCEAN ENGINEERING CO.
FIGURE NO 3-4
DRAWING NO MSK-163

FIGURE 6

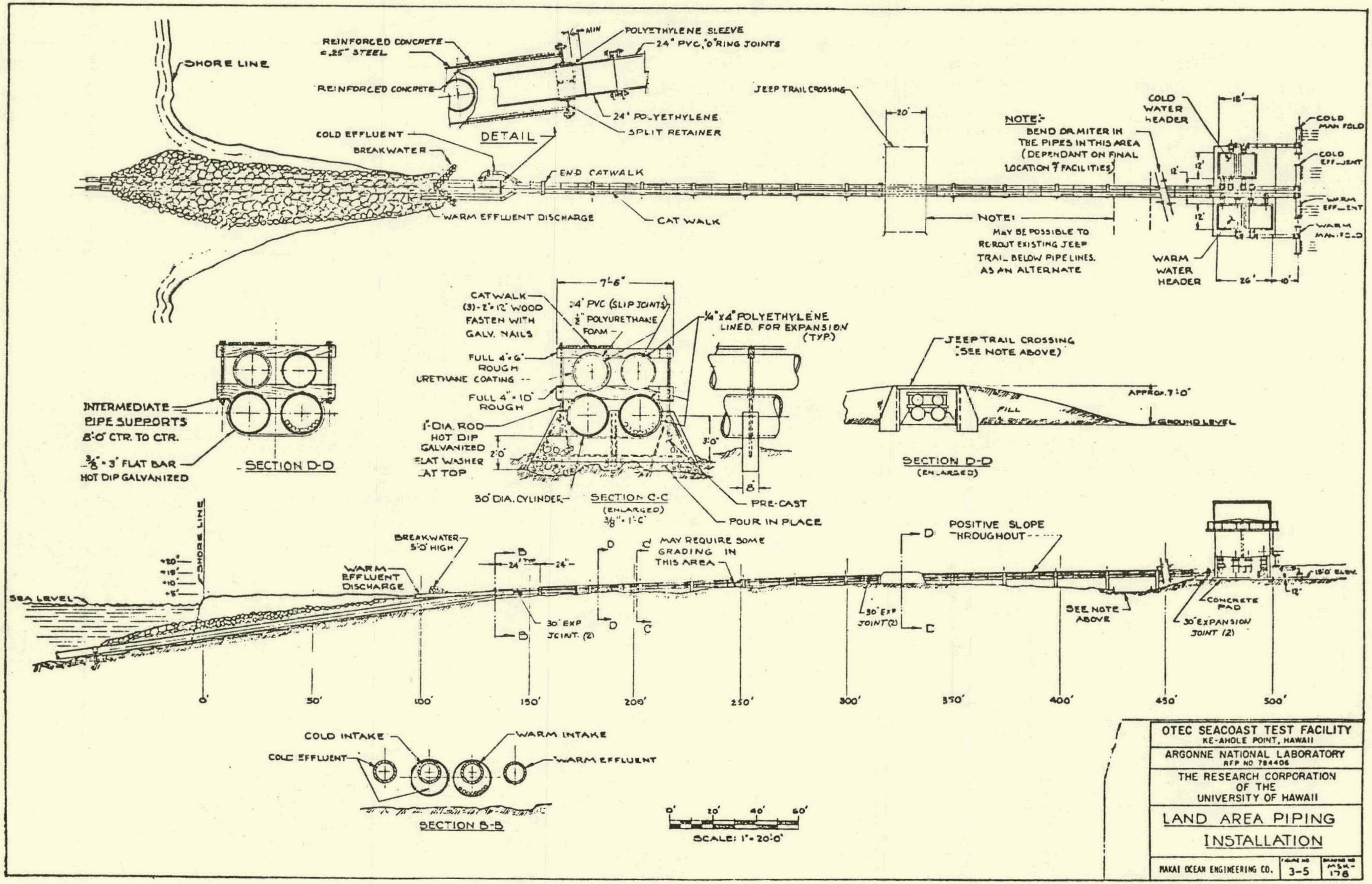
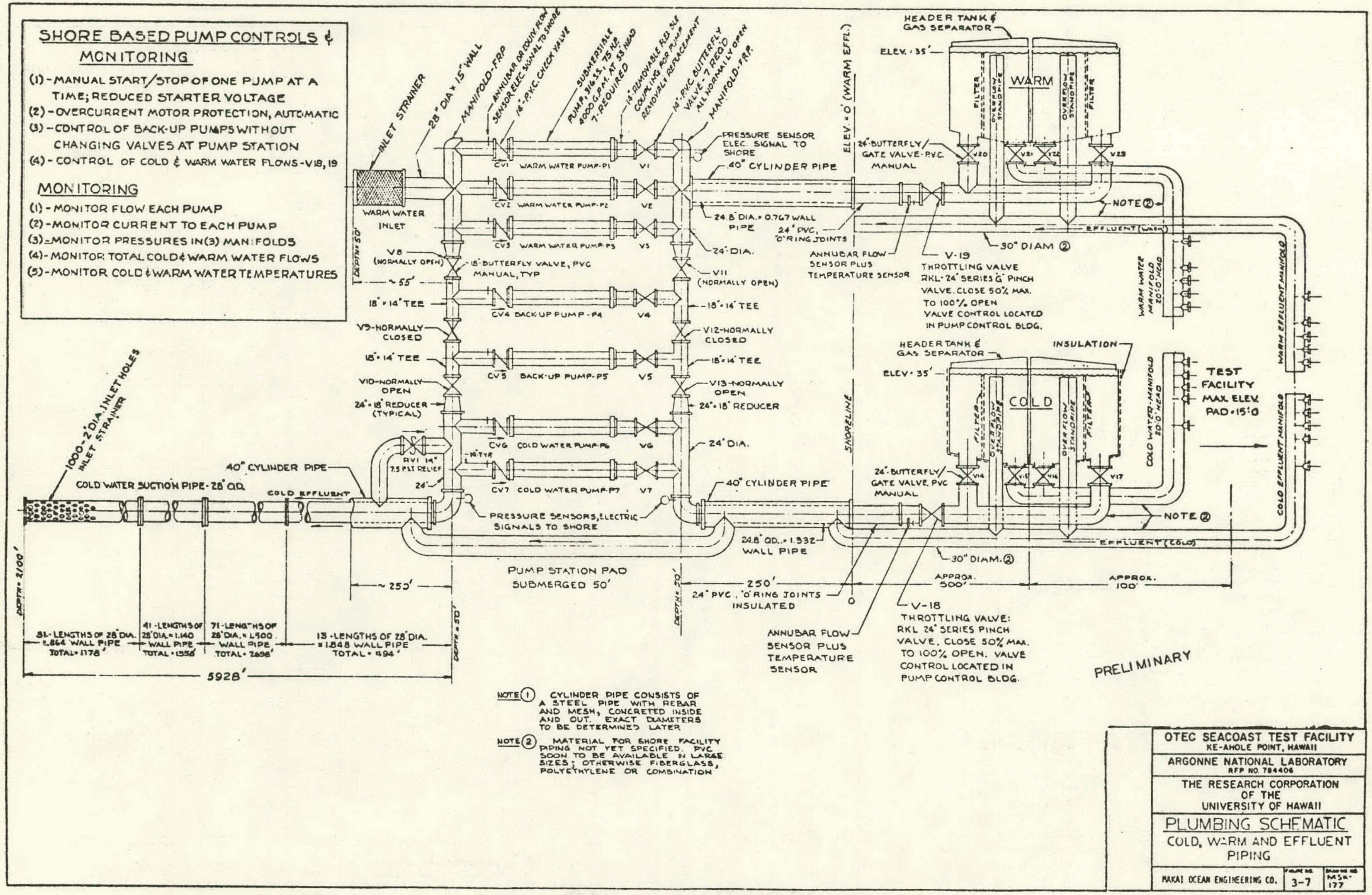

SHORE LINE
REINFORCED CONCRETE c.25" STEEL
REINFORCED CONCRETE
6" MIN
POLYETHYLENE SLEEVE
24" PVC, "O" RING JOINTS
24" POLYETHYLENE
SPLIT RETAINER
DETAIL
COLD EFFLUENT
BREAKWATER
END CATWALK
WARM EFFLUENT DISCHARGE
CAT WALK
JEEP TRAIL CROSSING
20'
NOTE:- BEND OR MITER IN THE PIPES IN THIS AREA (DEPENDANT ON FINAL LOCATION OF FACILITIES)
NOTE: MAY BE POSSIBLE TO REROUT EXISTING JEEP TRAIL BELOW PIPE LINES. AS AN ALTERNATE
COLD WATER HEADER
18'
12'
12'
12'
COLD MANIFOLD
COLD EFFLUENT
WARM EFFLUENT
WARM MANIFOLD
WARM WATER HEADER
26'
10'
INTERMEDIATE PIPE SUPPORTS 8'-0" CTR. TO CTR.
3/8" × 3" FLAT BAR HOT DIP GALVANIZED
SECTION D-D
7'-6"
CATWALK (3)-2"×12" WOOD FASTEN WITH GALV. NAILS
24" PVC (SLIP JOINTS)
1/2" POLYURETHANE FOAM
1/4"×4" POLYETHYLENE LINED. FOR EXPANSION (TYP.)
FULL 4"×6" ROUGH
URETHANE COATING
FULL 4"×10" ROUGH
1"-DIA. ROD HOT DIP GALVANIZED FLAT WASHER AT TOP
2'-0"
3'-0"
8"
30" DIA. CYLINDER
SECTION C-C (ENLARGED) 3/8" = 1'-0"
PRE-CAST
POUR IN PLACE
JEEP TRAIL CROSSING (SEE NOTE ABOVE)
APPROX. 7'-0"
FILL
GROUND LEVEL
SECTION D-D (ENLARGED)
SHORE LINE
+20'
+15'
+10'
+5'
SEA LEVEL
BREAKWATER 5'-0" HIGH
WARM EFFLUENT DISCHARGE
B
24' TYP.
24'
B
30' EXP JOINT (2)
D
D
C
C
MAY REQUIRE SOME GRADING IN THIS AREA
D
D
30' EXP JOINT (2)
POSITIVE SLOPE THROUGHOUT
SEE NOTE ABOVE
CONCRETE PAD
30' EXPANSION JOINT (2)
15'0" ELEV.
12'
0'
50'
100'
150'
200'
250'
300'
350'
400'
450'
500'
COLD INTAKE
WARM INTAKE
COLD EFFLUENT
WARM EFFLUENT
SECTION B-B
0'
20'
40'
60'
SCALE: 1" = 20'-0"
OTEC SEACOAST TEST FACILITY
KE-AHOLE POINT, HAWAII
ARGONNE NATIONAL LABORATORY
RFP NO 784406
THE RESEARCH CORPORATION OF THE UNIVERSITY OF HAWAII
LAND AREA PIPING INSTALLATION
MAKAI OCEAN ENGINEERING CO.
FIGURE NO 3-5
DRAWING NO MSK-178

FIGURE 7



SHORE BASED PUMP CONTROLS & MONITORING

(1) - MANUAL START/STOP OF ONE PUMP AT A TIME; REDUCED STARTER VOLTAGE
(2) - OVERCURRENT MOTOR PROTECTION, AUTOMATIC
(3) - CONTROL OF BACK-UP PUMPS WITHOUT CHANGING VALVES AT PUMP STATION
(4) - CONTROL OF COLD & WARM WATER FLOWS - V18, 19

MONITORING

(1) - MONITOR FLOW EACH PUMP
(2) - MONITOR CURRENT TO EACH PUMP
(3) - MONITOR PRESSURES IN (3) MANIFOLDS
(4) - MONITOR TOTAL COLD & WARM WATER FLOWS
(5) - MONITOR COLD & WARM WATER TEMPERATURES

NOTE ① CYLINDER PIPE CONSISTS OF A STEEL PIPE WITH REBAR AND MESH, CONCRETED INSIDE AND OUT. EXACT DIAMETERS TO BE DETERMINED LATER

NOTE ② MATERIAL FOR SHORE FACILITY PIPING NOT YET SPECIFIED. PVC SOON TO BE AVAILABLE IN LARGE SIZES; OTHERWISE FIBERGLASS, POLYETHYLENE OR COMBINATION

OTEC SEACOAST TEST FACILITY
KE-AHOLE POINT, HAWAII
ARGONNE NATIONAL LABORATORY
RFP NO. 784406
THE RESEARCH CORPORATION OF THE UNIVERSITY OF HAWAII
PLUMBING SCHEMATIC
COLD, WARM AND EFFLUENT PIPING
MAKAI OCEAN ENGINEERING CO.
3-7
MSK-177

FIGURE 8

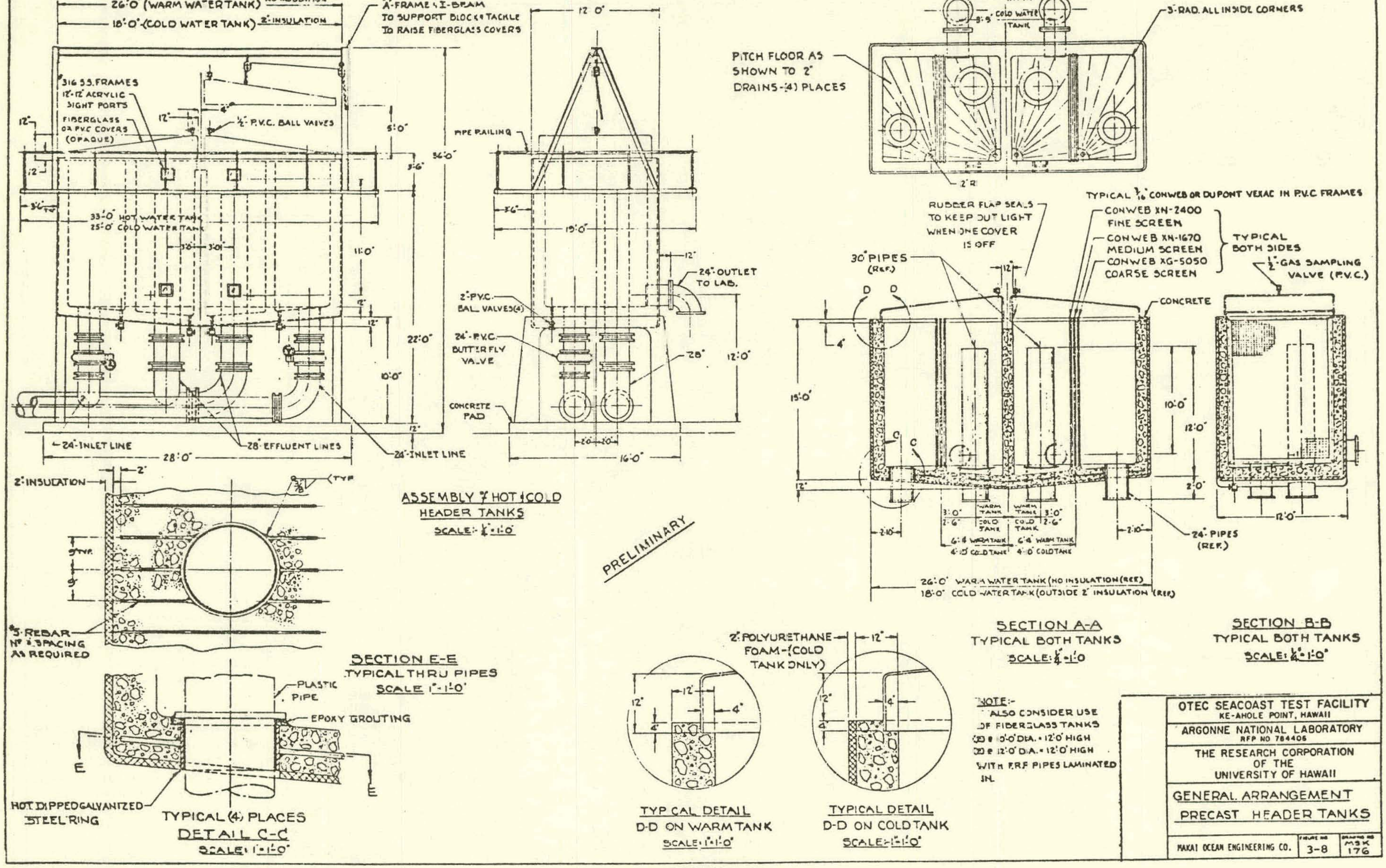

26'-0" (WARM WATER TANK) NO INSULATION
18'-0" (COLD WATER TANK) 2" INSULATION
"A"-FRAME & I-BEAM TO SUPPORT BLOCK & TACKLE TO RAISE FIBERGLASS COVERS
316 S.S. FRAMES
12"-12" ACRYLIC SIGHT PORTS
FIBERGLASS OR P.V.C. COVERS (OPAQUE)
1/2" P.V.C. BALL VALVES
33'-0" HOT WATER TANK
25'-0" COLD WATER TANK
5'-0"
3'-6"
36'-0"
11'-0"
22'-0"
10'-0"
24" INLET LINE
28" EFFLUENT LINES
24" INLET LINE
28'-0"
ASSEMBLY OF HOT & COLD HEADER TANKS
SCALE: 1/4" = 1'-0"
12'-0"
PIPE RAILING
2" P.V.C. BALL VALVES (4)
24" P.V.C. BUTTERFLY VALVE
CONCRETE PAD
24" OUTLET TO LAB.
28"
12'-0"
15'-0"
16'-0"
PITCH FLOOR AS SHOWN TO 2" DRAINS-(4) PLACES
9'-0" WARM WATER TANK
8'-9" COLD WATER TANK
3" RAD. ALL INSIDE CORNERS
2" R
RUBBER FLAP SEALS TO KEEP OUT LIGHT WHEN ONE COVER IS OFF
TYPICAL 3/16" CONWEB OR DUPONT VEXAR IN P.V.C. FRAMES
CONWEB XN-2400 FINE SCREEN
CONWEB XN-1670 MEDIUM SCREEN
CONWEB XG-5050 COARSE SCREEN
TYPICAL BOTH SIDES
1/2" GAS SAMPLING VALVE (P.V.C.)
30" PIPES (REF.)
CONCRETE
D D
C C
15'-0"
10'-0"
12'-0"
2'-0"
3'-0" WARM TANK
2'-6" COLD TANK
6'-4" WARM TANK
4'-0" COLD TANK
2'-10"
24" PIPES (REF.)
26'-0" WARM WATER TANK (NO INSULATION (REF)
18'-0" COLD WATER TANK (OUTSIDE 2" INSULATION (REF)
SECTION A-A
TYPICAL BOTH TANKS
SCALE: 1/4" = 1'-0
SECTION B-B
TYPICAL BOTH TANKS
SCALE: 1/4" = 1'-0"
PRELIMINARY
2" INSULATION
2"
3/8" TYP
9" TYP.
#5 REBAR NO. & SPACING AS REQUIRED
SECTION E-E
TYPICAL THRU PIPES
SCALE 1" = 1'-0"
PLASTIC PIPE
EPOXY GROUTING
E
E
HOT DIPPED GALVANIZED STEEL RING
TYPICAL (4) PLACES
DETAIL C-C
SCALE: 1" = 1'-0"
2" POLYURETHANE FOAM-(COLD TANK ONLY)
12"
4"
TYPICAL DETAIL
D-D ON WARM TANK
SCALE: 1" = 1'-0"
TYPICAL DETAIL
D-D ON COLD TANK
SCALE: 1" = 1'-0"
NOTE:-
ALSO CONSIDER USE OF FIBERGLASS TANKS
(2) @ 10'-0" DIA. × 12'-0" HIGH
(2) @ 12'-0" DIA. × 12'-0" HIGH
WITH F.R.P. PIPES LAMINATED IN.
OTEC SEACOAST TEST FACILITY
KE-AHOLE POINT, HAWAII
ARGONNE NATIONAL LABORATORY
RFP NO 784405
THE RESEARCH CORPORATION OF THE UNIVERSITY OF HAWAII
GENERAL ARRANGEMENT
PRECAST HEADER TANKS
MAKAI OCEAN ENGINEERING CO.
FIGURE NO 3-8
DRAWING NO MSK 176

FIGURE 9

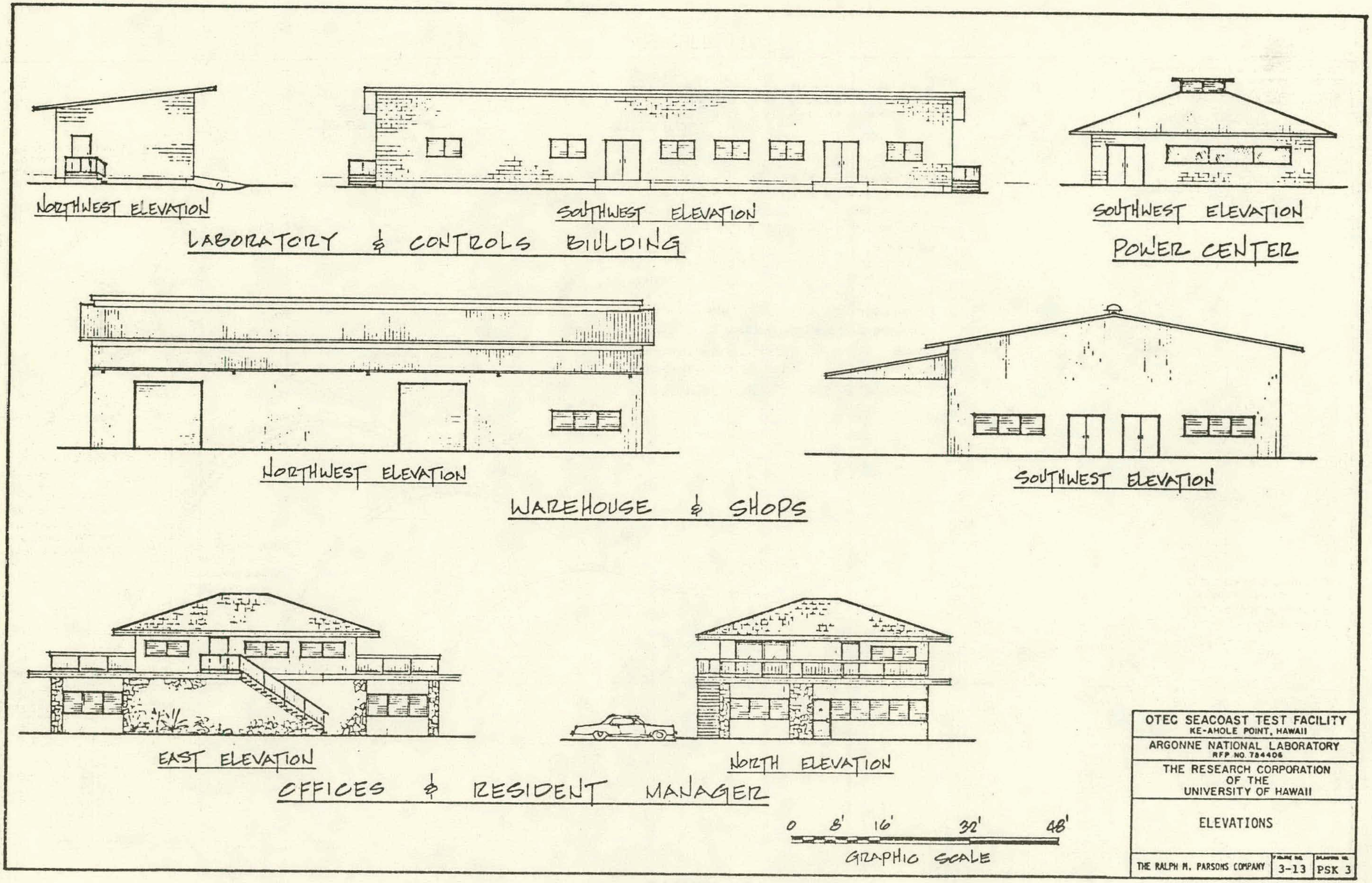
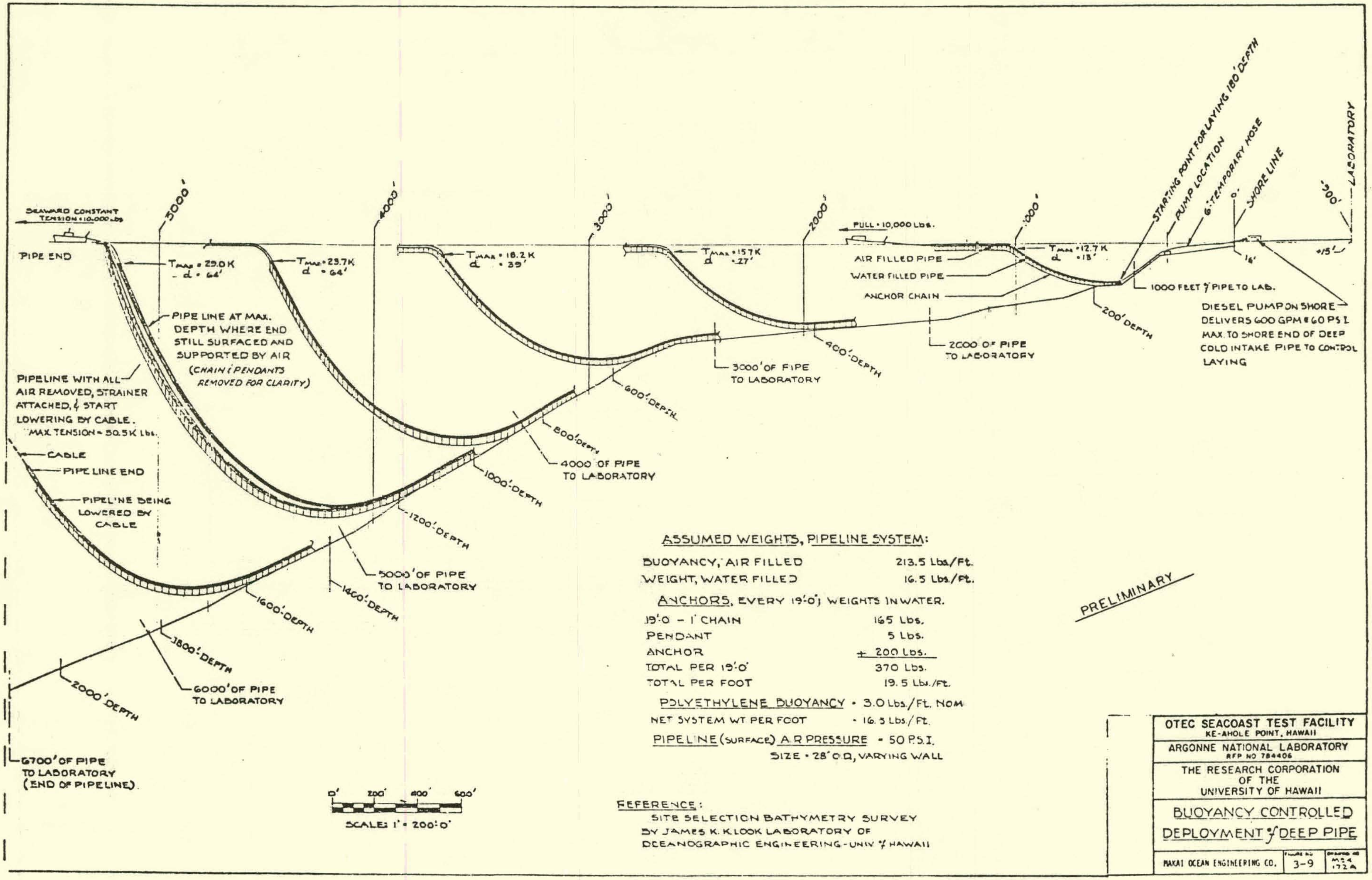

NORTHWEST ELEVATION
SOUTHWEST ELEVATION
LABORATORY & CONTROLS BUILDING
SOUTHWEST ELEVATION
POWER CENTER
NORTHWEST ELEVATION
SOUTHWEST ELEVATION
WAREHOUSE & SHOPS
EAST ELEVATION
NORTH ELEVATION
OFFICES & RESIDENT MANAGER
0 8' 16' 32' 48'
GRAPHIC SCALE
OTEC SEACOAST TEST FACILITY
KE-AHOLE POINT, HAWAII
ARGONNE NATIONAL LABORATORY
RFP NO. 784406
THE RESEARCH CORPORATION OF THE UNIVERSITY OF HAWAII
ELEVATIONS
THE RALPH M. PARSONS COMPANY
3-13
PSK 3

FIGURE 10



ASSUMED WEIGHTS, PIPELINE SYSTEM:

BUOYANCY, AIR FILLED	213.5 Lbs./Ft.
WEIGHT, WATER FILLED	16.5 Lbs./Ft.

ANCHORS, EVERY 19'-0"; WEIGHTS IN WATER.

19'-0 - 1" CHAIN	165 Lbs.
PENDANT	5 Lbs.
ANCHOR	+ 200 Lbs.
TOTAL PER 19'-0"	370 Lbs.
TOTAL PER FOOT	19.5 Lbs./Ft.

POLYETHYLENE BUOYANCY • 3.0 Lbs./Ft. NOM

NET SYSTEM WT PER FOOT • 16.5 Lbs./Ft.

PIPELINE (SURFACE) AIR PRESSURE • 50 P.S.I.

SIZE • 28" O.D., VARYING WALL

REFERENCE:
SITE SELECTION BATHYMETRY SURVEY
BY JAMES K. K. LOOK LABORATORY OF
OCEANOGRAPHIC ENGINEERING - UNIV. of HAWAII

OTEC SEACOAST TEST FACILITY
KE-AHOLE POINT, HAWAII

ARGONNE NATIONAL LABORATORY
RFP NO 784406

THE RESEARCH CORPORATION
OF THE
UNIVERSITY OF HAWAII

BUOYANCY CONTROLLED
DEPLOYMENT of DEEP PIPE

MAKAI OCEAN ENGINEERING CO. | FIGURE NO 3-9 | DRAWING NO M84 172A

FIGURE 11

OTEC BIOFOULING, CORROSION, AND MATERIALS STUDY FROM A MOORED PLATFORM AT PUNTA TUNA, PUERTO RICO: DESIGN PHASE

by

D.S. Sasscer, T.R. Tosteson, K.B. Pedersen,
F. Rosa and F.L. Benitez
Center for Energy and Environment Research
University of Puerto Rico
Mayaguez, Puerto Rico, 00708

INTRODUCTION

Puerto Rico's need for large quantities of additional electrical power in the near future, combined with the excellent thermal resources available, make Puerto Rico the most promising U.S. location for cost effective OTEC power plants. However, before an OTEC power plant can be placed in Caribbean waters, or at any other location, it will be necessary to better understand the phenomenon of fouling in OTEC heat exchangers, and the relationships which exist between biogrowth, corrosion, cleaning procedures, materials, site location, and heat transfer.

The objectives of this investigation, therefore, are:

1) Obtain a better understanding of the nature of the fouling that can be expected to occur in OTEC heat exchangers by a replicated, multi-seasonal determination of the effect of biogrowth, corrosion, and materials on the heat transfer coefficient.

2) Determine the compatibility of Caribbean open ocean surface water with OTEC at a site where the local electrical utility has expressed an interest in cooperating with DOE in OTEC power plant development.

3) Investigate OTEC fouling on a versatile, permanently moored research platform which can be used for continued and/or expanded testing with surface water, and which can serve as a prototype for an OTEC test facility using both, surface and deep ocean water.

BACKGROUND

A contract was awarded to the Center for Energy and Environment Research, (CEER), during November, 1978 for the Design Phase of a three phase project (Design, Construction and Operation) to conduct an OTEC biofouling, corrosion and materials study from a moored platform at Punta Tuna, Puerto Rico. Southwest Research Institute of San Antonio, Texas is

CEER'S subcontractor for the design of the experimental water system. A single point, tension moored buoy has been layed at the proposed site of the study. A vessel, the LCU-1470, has been obtained for the experiment and is now in the Barbour Boat Works, New Bern North Carolina awaiting overhaul.

The experimental facility will be constructed at SwRI, shipped to New Bern and installed onboard the vessel during overhaul. It is estimated that the vessel will be sailed to Puerto Rico and moored to the buoy at the Punta Tuna site, ready for data acquisition, during June, 1979.

Experimental Proceedures

The experiment will correlate biogrowth, corrosion and heat transfer change in simulated aluminum and titanium heat exchanger tubes. During the first part of the study, emphasis will be given to understanding the biogrowth phenomena. For this reason weekly R_f determination will be made and coupon samples for biogrowth study will be collected approximately once a week, from six aluminum and six titanium tubes during a three month period. Between three and six of the coupons of each material will be analyzed each week for biogrowth and one sample will be analyzed for corrosion. Both biogrowth and corrosion will be correlated with R_f.

Biogrowth Selected samples of heat exchanger tubing will be examined in the course of this study in order to determine the rate at which these surfaces are fouled by materials present in ambient seawater and acquire adherent marine micro-organisms. A series of 10 samples (approximately 6 replicas of each) of heat exchanger tubing will be taken over a period of 90 days exposure to ambient seawater at the proposed OTEC site. Four major aspects will be examined concerning the accumulation of materials on the test surfaces.

1. Film Thickness: The wet film thickness found on the test surface will be determined microscopically and the volume per unit area calculated. Segments of the exposed surfaces will be preserved in a hydrated condition, transported to the laboratory and examined by reflectance microscopy.
2. Film Density: The film density will be calculated on the basis of film volume described above, and a determination made of the total amount of solute accumulated on the test surfaces. Samples of exposed surfaces will be foiled (aluminum foil) and frozen (liquid nitrogen) at the sampling site. These surfaces will be transported to the laboratory in a frozen condition and subsequently freeze dried. The total amount of material accumulated will be removed from the test surface and weighed.
3. Chemical Composition of the Film: The solute materials accumulating on the test surfaces, isolated as described in #2 above, will be analyzed for organic carbon content and for the presence of selected inorganics (Ca^{++}, Mg^{++}, $SO_4^=$ and $PO_4^=$). These analyses will be contracted to an analytical laboratory. The ATP and Chlorophyll "a" contents of the isolated materials will also be determined by the contracted analytical facility.
4. Scanning Electron Microscopy of Exposed Surfaces: The condition of the exposed surfaces will be visualized using SEM. Such facilities

appear to be available at the University of Puerto Rico, Mayaguez. Samples of exposed surfaces will be frozen at the OTEC site (as described in #2 above), and transported to the laboratory. The subsequent drying and coating of the sample in preparation for the SEM will have to be assessed with the specific material or sample at hand. This procedure will be analyzed prior to the field experiment, employing typically "fouled" surfaces of the heat exchanger tubes.

Additional studies will be conducted on selected samples of solute materials that accumulate on the surfaces employed in this study. The high molecular weight components accumulated will be examined with high pressure liquid chromatography (HPLC). These materials will be fractionated on HPLC cationic exchange columns and the resulting materials (fractions) examined for their ability to enhance the adhesion of micro-organisms to the test surfaces.

Heat Transfer To measure changes in heat transfer properties of the tubes as a result of biofouling and/or corrosion, a device developed at Carnegie-Mellon University (CMU) will be mounted on one tube in each four tube experimental module (Figure 5). The CMU device, (Figure 3), consistes of a copper heater cylinder and a copper referecnce cylinder, both of which are clamped to the tube and have temperature sensing devices, a thermister attached directly to the tube, and a flow meter. A small amount of heat is applied to the outer surface of the heater cylinder, and when the temperature of the cylinder reaches a steady state, the heat is turned off. Measurements of water temperature, flow velocity, and the temperatures of the heater and reference cylinders are taken at six second intervals until the temperature of the heater cylinder again reaches a steady state. Using these data, the CMU group has developed a program to calculate a mean conductance coefficient and the standard deviation of the mean. This program will be used for our data reduction along with the uncertainty analysis developed by Battele PNL as a subroutine to the CMU program. During the 3 months of the experiment, heat transfer data will be collected weekly.

Major sources of variation in characteristics and sources of error with plans of how these will be avoided or at least minimized are as follows:

1) Pump Stoppage It is essential to maintain a steady flow of water through the experimental tubes. Once the flow has been interrupted, all subsequent data are of questionable value. The LCU will have a full-time crew of three people. The crew will be responsible for checking the pumps at hourly intervals to make sure they are functioning properly. Each pair of modules will be provided with a spare pump which can be activated if one of the primary pumps fails.

2) Flowmeter Fouling Since the heat transfer coefficient is a function of water velocity, among other factors, it is important to measure the flow rate accurately. The CMU device uses an intrusion-type flowmeter, and

biofouling of the sensor may alter its calibration. Therefore, the flowmeter will be calibrated before and after each run.

3) Flow Rate Fluctuations When the experimental equipment is mounted on a platform, rolling and pitching of the platform due to wave action results in fluctuations in the flow rate. To minimize this effect, both intake and outlet hoses for each system will be passed through a hole in the bottom, located close to the center of action, of the LCU.

4) Rapid Variation of Sea Water Temperature Measurements of the heat transfer coefficient will be influenced by the water temperature. This is sensitive to fluctuations as small as 0.1°C. Errors resulting from variations of sea water temperature can be minimized by making several measurements (~16 on the same day). Erratic values caused by temperature changes can then be eliminated on statistical grounds.

5) Contact Resistance between Heater Cylinder and Tube With the CMU device, it is assumed that the contact resistance between the heater and reference cylinders and the heat transfer tube remains constant throughout all of the experiments. The thermal conductivity will be tested between the tube and the device prior to the experiment and again at the termination of the experiment.

Corrosion During the initial three month experiment it is not expected that significant corrosion will occur, however, for completness, one sample each of aluminum and titanium will be collected and analyzed each week. Starting with the evaluation of a cleaned set of control samples, samples progressively removed from the test pipes will be examined for the type, rate, severity of corrosion and the composition of corrosion products and scale which are found on the pipes. Corrosion potentials and corrosion rates will be measured both at the test pipes and using a sensor located at the water quality indicator system. These data will be correlated with the data from the biofouling and heat exchanger experiments.

Corrosion data will include: corrosion potentials, polarization currents, and physical samples representing corrosion phenomena.

Examination of samples will include visual observation of type of attack, including any pitting, description of the corrosion product film. microscopic examination and recording of the film thickness and texture, and elemental analysis using SEM Microprobe analysis.

Experimental Design

Site The study will be conducted approximately three kilometers southeast of Punta Tuna, which is located in the southeast corner of Puerto Rico, where the water depth is approximately 1200 meters. Figure 1 shows the site of the experiment.

Experimental Modules The experiment will be conducted with four independent modules. Each module will be self contained with motors and pumps and will consist of one CMU instrumented tube for heat transfer measurements and three uninstrumented coupon tubes for biogrowth and corrosion samples. A block diagram for experiment is shown in figure 2, figure 3 is a sketch of the CMU heat transfer measurement device and figure 4 shows an uninstrumented coupon tube.

As is indicated in figure 5, the water flow for each module has a common inlet and then passes through the experimental tubes in parallel paths. This system enables an independent analysis to be made of the relation between biogrowth, corrosion and heat transfer for each tube. The flow loop assembly of figure 6 and the pump assembly of figure 7 show the arrangement of modules and the redundency of pumps.

A block diagram showing the power distribution from the two 50 KW diesel generators to the experiment is shown in figure 8 and the flow control system is given in figure 9.

Experimental Platform The experiment will be conducted from the deck of an LCU moored to a buoy at the site. The LCU is of the 1466 class and will be modified so as to allow the inlet and exhaust water hoses to be run through an 18 inch diameter well which will be installed through the bottom of the vessel. Figure 10 and figure 11 give an outboard profile and plan view of the vessel showing the location of the hose well, the two diesel generators, the experimental modules, the data acquisition house, and the canvas canopy to be constructed over the experimental working area. It can be noted that less than half of the open deck area of the vessel will be utilized by this experiment which will allow ample room for later modification or expansion of the research facility.

Conclusion The design phase of this experiment will be completed during the first week of February 1979. The experimental flow system is being designed by Southwest Research Institute (SwRI). This system will be built in modular form and tested at SwRI. After testing, the system along with a data acquisition "shack", will be transported to, and installed onboard the research vessel during vessel overhaul. It is estimated that the vessel will be sailed to Puerto Rico and moored at the test site during June 1979 and that data collection will start during July 1979.

References:

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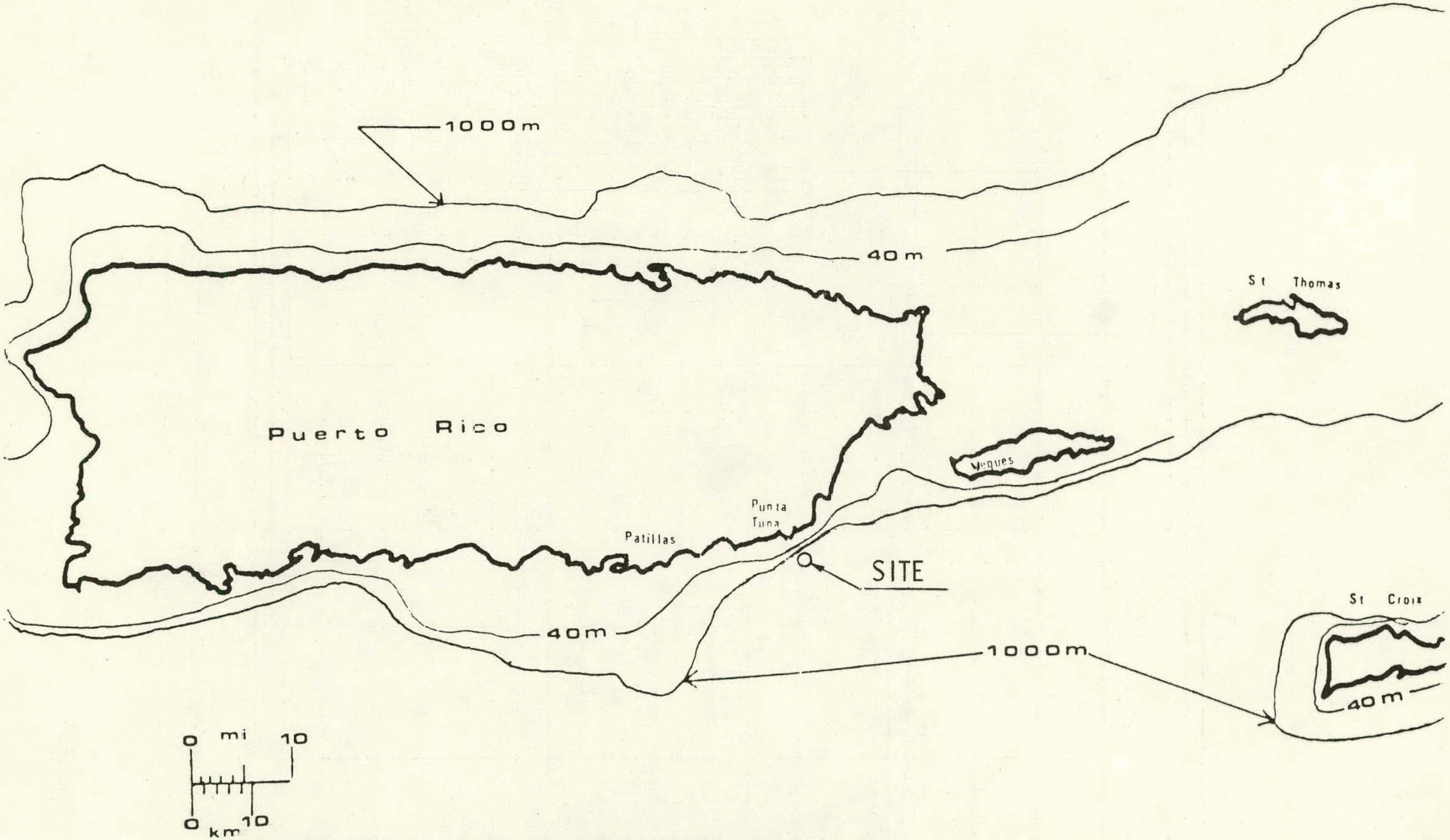
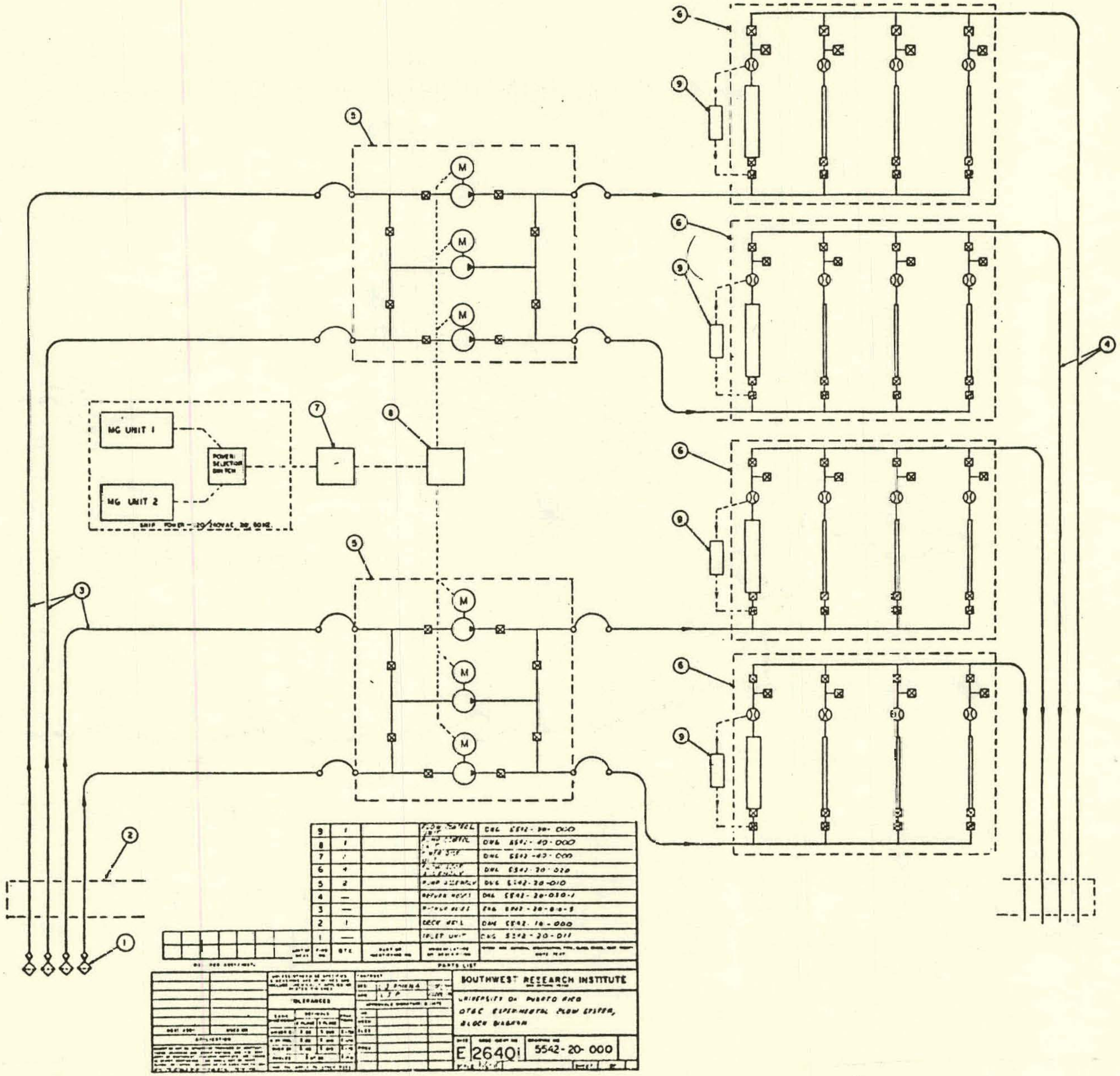


FIGURE 1. SITE OF EXPERIMENTAL WORK



MG UNIT 1
MG UNIT 2
POWER SELECTION SWITCH
M
1
2
3
4
5
6
7
8
9
PUMP ASSEMBLY
DWG 5542-20-010
DECK WELL
DWG 5542-10-000
INLET UNIT
PARTS LIST
TOLERANCES
SOUTHWEST RESEARCH INSTITUTE
UNIVERSITY OF PUERTO RICO
OTEC EXPERIMENTAL FLOW SYSTEM,
BLOCK DIAGRAM
E
26401
5542-20-000

FIGURE. 2

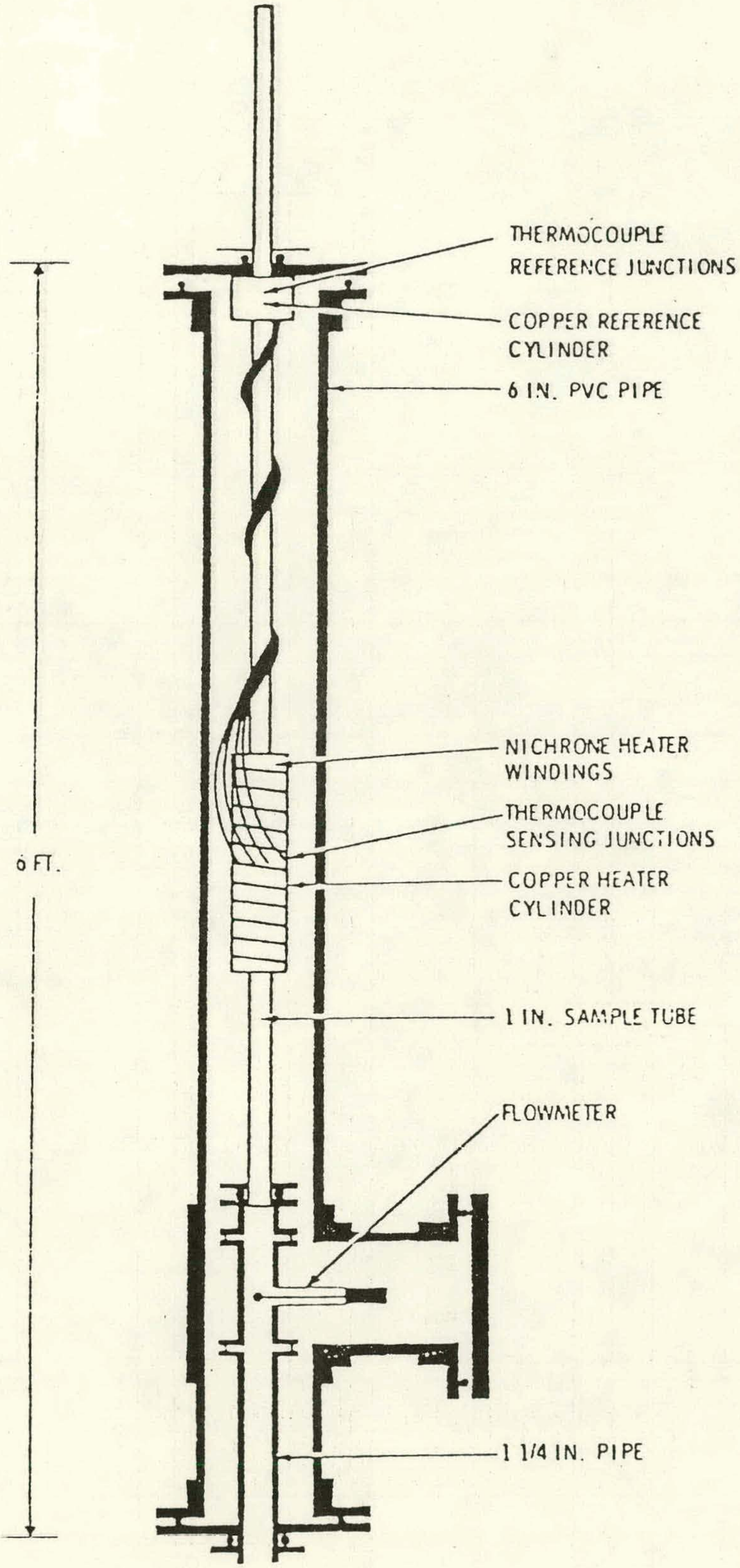


Fig. 3. CMU Heat Transfer Measurement Device

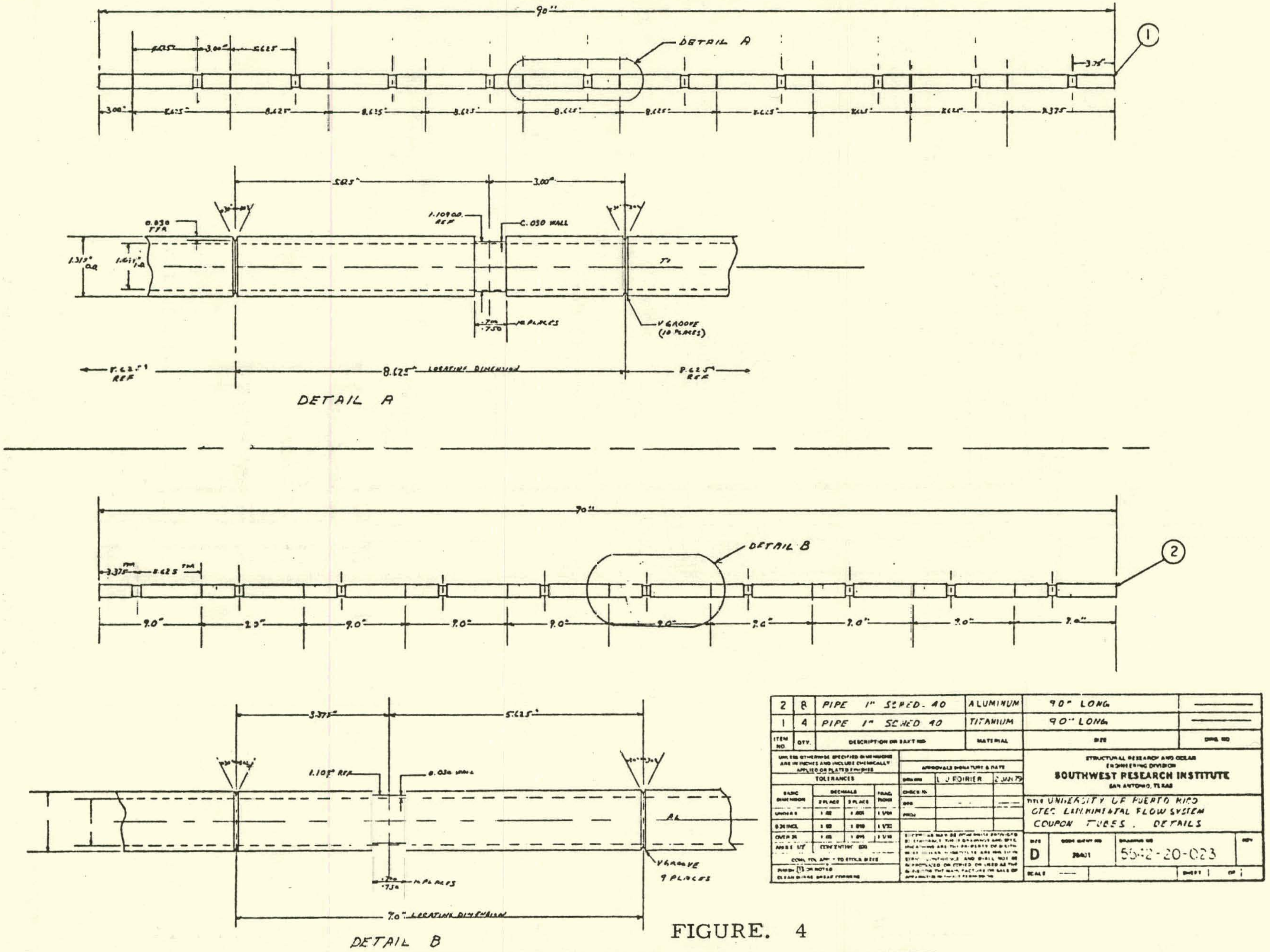

90"
DETAIL A
①
3.00"
5.625"
8.625"
3.375
1.315" O.D.
1.049" I.D.
0.030 TYP.
1.109 O.D. REF
0.030 WALL
.700 / .750 10 PLACES
V GROOVE (10 PLACES)
8.625" REF
8.625" LOCATING DIMENSION
Ti
DETAIL A
90"
DETAIL B
②
9.0"
1.105" REF
0.030 WALL
.700 / .750 10 PLACES
V GROOVE 9 PLACES
9.0" LOCATING DIMENSION
AL
DETAIL B
2 | 8 | PIPE 1" SCHED. 40 | ALUMINUM | 90" LONG
1 | 4 | PIPE 1" SCHED 40 | TITANIUM | 90" LONG
ITEM NO. | QTY. | DESCRIPTION OR PART NO. | MATERIAL | SIZE | DWG. NO.
TOLERANCES
APPROVALS SIGNATURE & DATE
DRAWN L J POIRIER 2 JAN 79
STRUCTURAL RESEARCH AND OCEAN ENGINEERING DIVISION
SOUTHWEST RESEARCH INSTITUTE
SAN ANTONIO, TEXAS
TITLE UNIVERSITY OF PUERTO RICO OTEC EXPERIMENTAL FLOW SYSTEM COUPON TUBES, DETAILS
SIZE D
55-2-20-023
SHEET 1 OF 1

FIGURE. 4

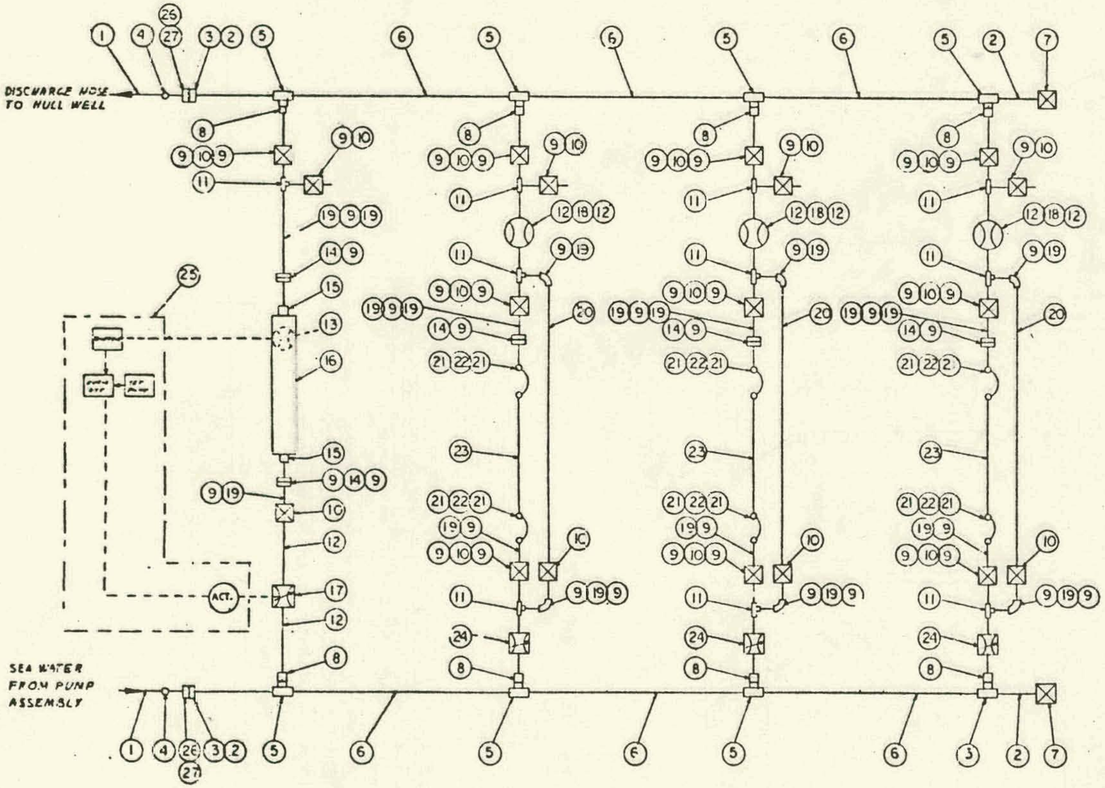


FIGURE. 5

NOTES.

1. FOUR ASSEMBLIES REQUIRED

ITEM NO	QTY.	DESCRIPTION OR PART NO.	MATERIAL	SIZE	DWG NO.
27	1	½ UNION, USP 27300	PVC	2" PIPE, THREADED	
26	2	NIPPLE SHORT USP 27096	PVC	2" PIPE SCH 80	
25	1	FLOW CONTROL UNIT	—	6 FPS	5542-30-000
24	3	DIAPHRAGM VALVE, GF IND,	PVC	1", GF 161.313.063	—
23	3	COUPON TUBE	Ti or ALUM.	1" SPONSOR FURNISHED	5542-20-023
22	6	HOSE	PVC	1"	—
21	12	HOSE CLAMP	STAINLESS	1"	—
20	A/R	PIPE	PVC	1" SCH 40	—
19	18	ELBOW, USP. 28057	PVC	1"	—
18	3	FLOWMETER RCM1'-72-VDC-200	MONEL	1" 0-20 GPM	—
17	1	FLOW CONTROL VALVE, GF IND	PVC	1", GF 150.111.508	—
16	1	HEAT EXCHANGER	STAINLESS	SPONSOR FURNISHED	D-402
15	2	FEM ADAPTER, USP 27262	PVC	1"	—
14	5	UNION, USP. 28063	PVC.	1"	—
13	1	FLOWMETER	STAINLESS	PART OF HEAT EXCHANGER PKG.	D-402
12	8	NIPPLE	PVC	1" SCH 80 THREADED 1 END	—
11	10	TEE, USP 28059	PVC	1"	—
10	18	BALL VALVE, USP 27323	PVC	1"	—
9	47	NIPPLE, CLOSE	PVC	1" SCH. 40	—
8	8	REDUCING BUSHING, USP 26058	PVC	2" to 1" PIPE	—
7	2	BALL VALVE, USP. 27366	PVC	2"	—
6	A/R	PIPE	PVC	2" SCH 40	—
5	8	TEE, USP. 28104	PVC	2"	—
4	2	HOSE CLAMP USP 29238	STAINLESS	2"	—
3	1	½ UNION USP 28108	PVC	2", SOCKET	—
2	4	NIPPLE, CLOSE	PVC	2", SCH. 40	—
1	A/R	HOSE, GOODYEAR 1000	PVC	2" DIA.	—

UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES AND INCLUDE CHEMICALLY APPLIED OR PLATED FINISHES

TOLERANCES

APPROVALS SIGNATURE & DATE

DRAWN [illegible]

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DES. [illegible]

PROJ

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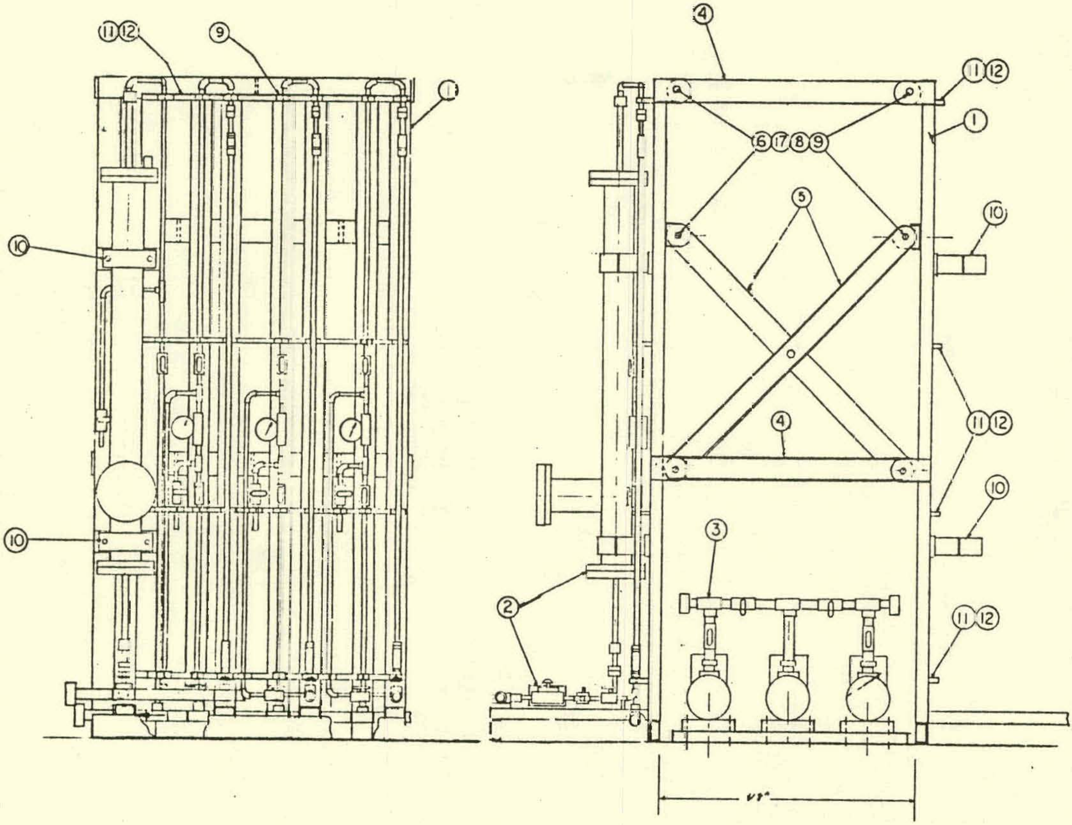
SAN ANTONIO TEXAS

TITLE UNIVERSITY OF PUERTO RICO
OTEC EXPERIMENTAL FLOW SYSTEM
FLOW LOOP ASSEMBLY SCHEMATIC

SIZE D
CODE IDENT NO 28401
DRAWING NO. 5542-20-020
REV

SCALE NONE
SHEET 1 OF 1



NOTES:

1. FOUR FLOW LOOPS REQUIRED, TWO LOOPS PER ASSEMBLY
2. MATCH DRILL 1⅛ HOLES IN ITEMS 4 & 5 ON ASSEMBLY
3. PARTS QUANTITY LISTED BELOW ARE FOR ONE ASSEMBLY OF TWO LOOPS BACK TO BACK.

ITEM NO	QTY.	DESCRIPTION OR PART NO.	MATERIAL	SIZE	DWG NO
12	74	PIPE CLAMPS HYDRAZORB 100100	——	1" PIPE	——
11	8	CHANNEL HYDRA-ZORB 111048	——	48" LONG	——
10	4	PIPE CLAMP STAUFF SPAL	POLY PRO.	6" SPAL 9168-S-PP-AS	——
9	22	HEX NUT	STEEL	1"-NC	——
8	22	LOCK WASHER	STEEL	1"	
7	44	FLAT WASHER	STEEL	1"	——
6	22	HEX HEAD MACHINE BOLT	STEEL	1"-NC	——
5	4	CHANNEL C4 X 7.25	A-36	4"W X 65" LONG	——
4	6	CHANNEL C4 X 7.25	A-36	4"W X 48" LONG	——
3	1	PUMP ASSEMBLY	——	—— ——	5542-20-020
2	2	FLOW LOOP COMPONENTS	——	—— ——	5542-20-020
1	2	FRAME ASSEMBLY	——	—— ——	5542-20-022

UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES AND INCLUDE CHEMICALLY APPLIED OR PLATED FINISHES

TOLERANCES

BASIC DIMENSION	DECIMALS 2 PLACE	DECIMALS 3 PLACE	FRACTIONS
UNDER 6	± .02	± .005	± 1/64
6-24 INCL	± .03	± .010	± 1/32
OVER 24	± .06	± .015	± 1/16
ANGLE ± 1/2°	CONCENTRIC .010		

CONC TOL APPLY TO STOCK SIZES

FINISH ∇ UNLESS NOTED

CLEAN BURRS BREAK CORNERS

APPROVALS SIGNATURE & DATE

DRAWN	[illegible]	[illegible]
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DES	[illegible]	[illegible]
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SAN ANTONIO TEXAS

TITLE UNIVERSITY OF PUERTO RICO
OTEC EXPERIMENTAL FLOW SYSTEM
FLOW LOOP ASSEMBLY. LAYOUT

SIZE	CODE IDENT NO.	DRAWING NO.	REV
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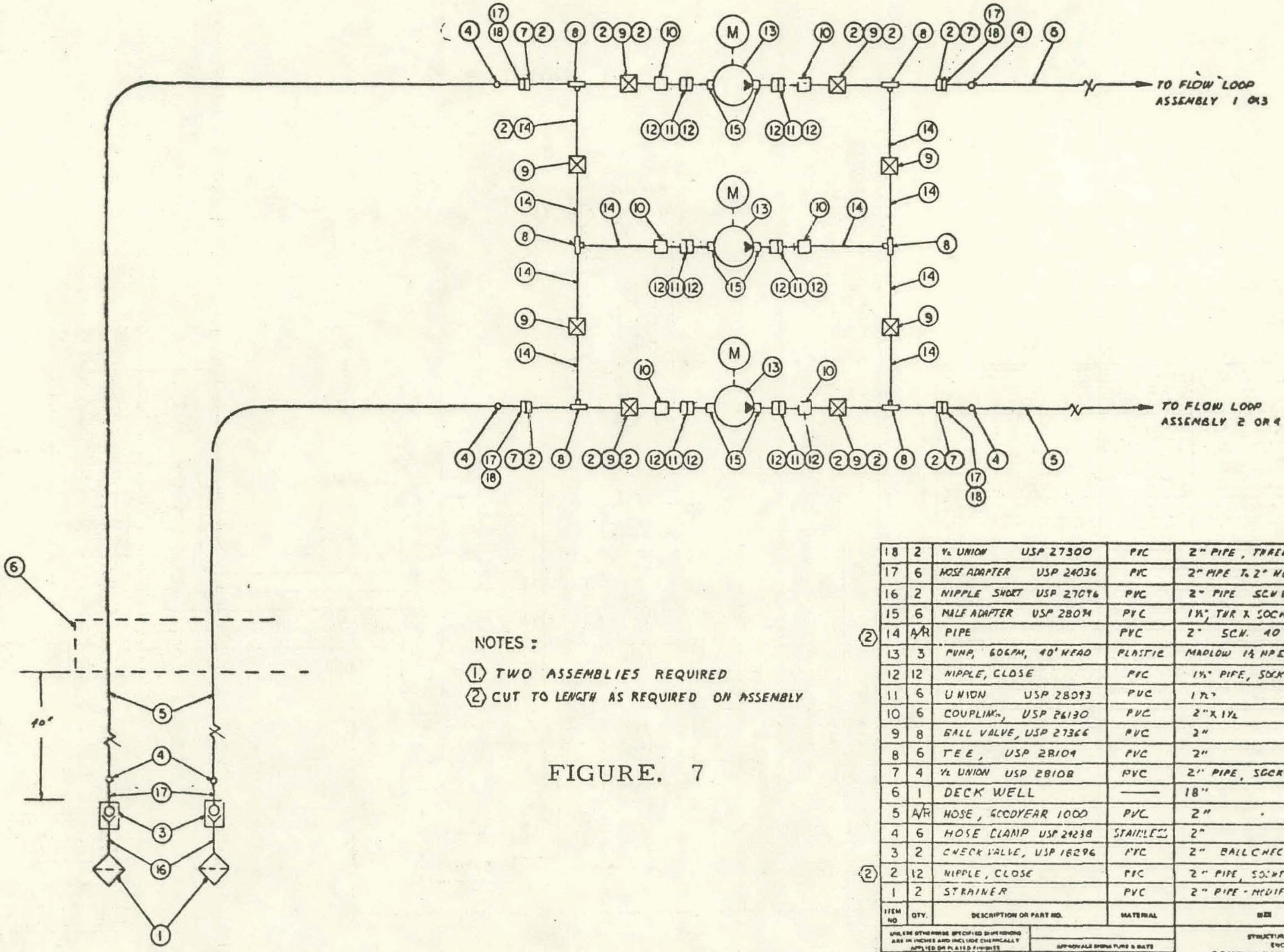
SCALE 1/10		SHEET 1 OF 1	

FIGURE. 6



NOTES :

① TWO ASSEMBLIES REQUIRED

② CUT TO LENGTH AS REQUIRED ON ASSEMBLY

FIGURE. 7

	18	2	½ UNION USP 27300	PVC	2" PIPE , THREADED	
	17	6	HOSE ADAPTER USP 24036	PVC	2" PIPE To 2" HOSE	———
	16	2	NIPPLE SHORT USP 27096	PVC	2" PIPE SCH 80	———
	15	6	MALE ADAPTER USP 28074	PVC	1½" THR X SOCKET	———
②	14	A/R	PIPE	PVC	2" SCH. 40	———
	13	3	PUMP, 60GPM, 40' HEAD	PLASTIC	MARLOW 1½ HP ELX-B3	———
	12	12	NIPPLE, CLOSE	PVC	1½" PIPE, SOCKET, SCH. 40	———
	11	6	UNION USP 28093	PVC	1½"	———
	10	6	COUPLING, USP 26130	PVC	2" X 1½	———
	9	8	BALL VALVE, USP 27366	PVC	2"	———
	8	6	TEE, USP 28104	PVC	2"	———
	7	4	½ UNION USP 28108	PVC	2" PIPE, SOCKET	———
	6	1	DECK WELL	———	18"	5542-10-000
	5	A/R	HOSE , GOODYEAR 1000	PVC	2"	———
	4	6	HOSE CLAMP USP 24238	STAINLESS	2"	———
	3	2	CHECK VALVE, USP 16296	PVC	2" BALL CHECK	———
②	2	12	NIPPLE , CLOSE	PVC	2" PIPE, SOCKET, SCH 40	———
	1	2	STRAINER	PVC	2" PIPE - MODIFIED	5542-20-011
	ITEM NO	QTY.	DESCRIPTION OR PART NO.	MATERIAL	SIZE	DWG. NO.

UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES AND INCLUDE CHEMICALLY APPLIED OR PLATED FINISHES

TOLERANCES

BASIC DIMENSION	DECIMALS 2 PLACE	DECIMALS 3 PLACE	FRACTIONS
UNDER 6	±.02	±.005	±1/64
6-24 INCL	±.03	±.010	±1/32
OVER 24	±.06	±.015	±1/16
ANGLE ±½°	CONCENTRIC .030		

[illegible] TOL APPLY TO STOCK SIZES

FINISH [illegible] OR NOTED
CLEAN BURRS, BREAK CORNERS

APPROVALS SIGNATURE & DATE

DRAWN	L. J. [illegible]	[illegible]
CHECKED		
DES.	[illegible]	[illegible]
PROJ		

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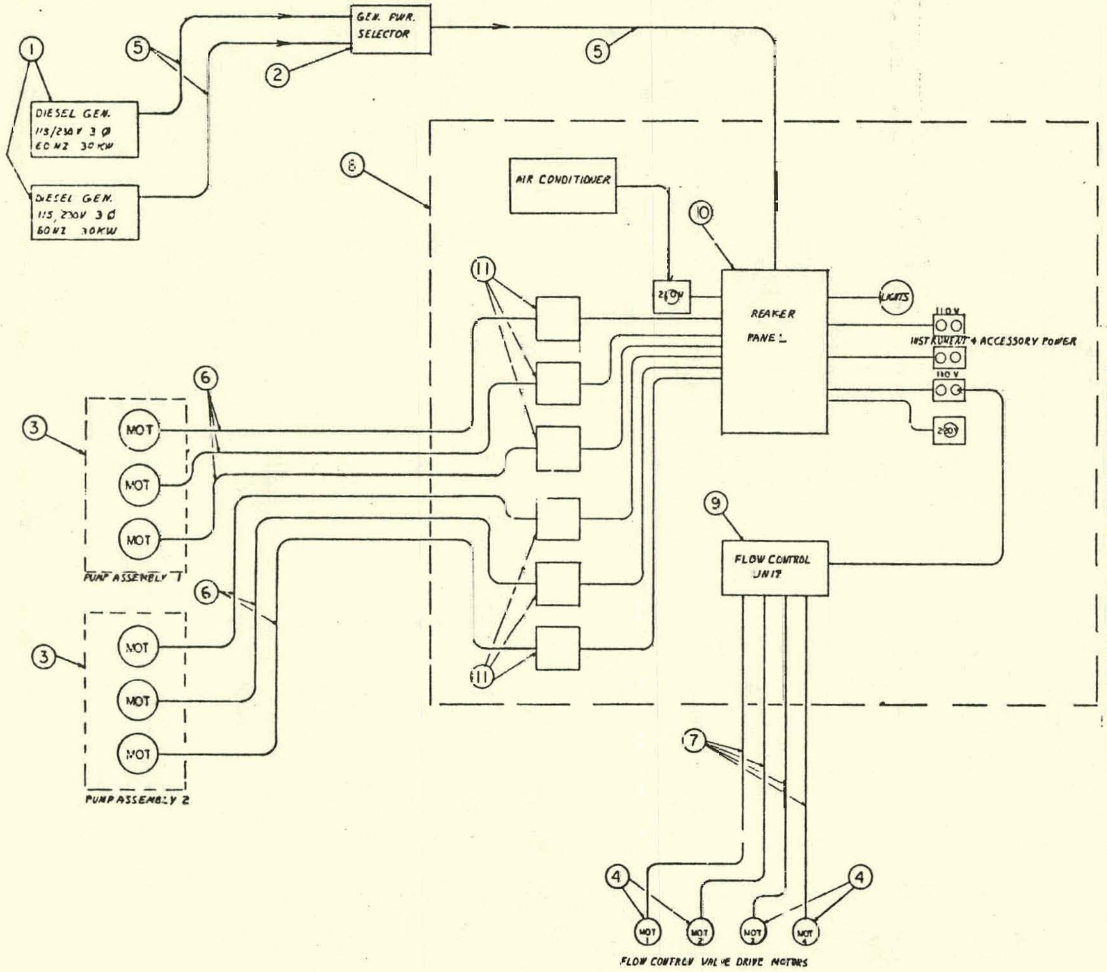
STRUCTURAL RESEARCH AND OCEAN ENGINEERING DIVISION
SOUTHWEST RESEARCH INSTITUTE
SAN ANTONIO, TEXAS

TITLE UNIVERSITY OF PUERTO RICO
OTEC EXPERIMENTAL FLOW SYSTEM
PUMP ASSEMBLY, SCHEMATIC

SIZE	CODE IDENT NO.	DRAWING NO.	REV
D	26401	5542-20-010	

SCALE NONE SHEET 1 OF 1



ITEM NO	QTY.	DESCRIPTION OR PART NO	MATERIAL	SIZE	DWG NO
11	6	MOTOR STARTER, MANUAL, ALLEN BRADLEY 609-AJW	——	SIZE 0, 220V, 3 Ø	——
10	1	LOAD CENTER & BREAKER PANEL WESTINGHOUSE QICP-309-MV	——	100 AMP 30 POS & MAIN FIXR, 7-3P220V, 2-2P220V, 5-1PHSE, 15A	——
9	1	FLOW CONTROL UNIT	——	——	5542-30-000
8	1	DECK HOUSE, INSTRUMENT	FIBERGLASS	8' X 12' X 8'	——
7	A/R	POWER CABLE, ARMORED, TTSA-7A	——	3 COND 20AWG OR EQUIV	——
6	A/R	POWER CABLE, ARMORED, FGSB-3	——	4 COND 14AWG OR EQUIV	——
5	A/R	POWER CABLE ARMORED FGSB-50	——	4 COND. 7AWG OR EQUIV.	——
4	4	FLOW CONTROL VALVE ASSEMBLY		115V SINGLE PHASE PER DRIVE	5542-20-020-1
3	2	PUMP UNIT ASSEMBLY	——	1½ HP, 3 Ø, 230 VOLT, TEFC DRIVE	5542-20-010
2	1	POWER SELECTOR SWITCH	——	220V [illegible]	[illegible]
1	2	DIESEL ELECTRIC GENERATOR	——	115/220V, 3PHASE, 60HZ, 30KW [illegible]	[illegible]

UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES AND INCLUDE CHEMICALLY APPLIED OR PLATED FINISHES

TOLERANCES

BASIC DIMENSION	DECIMALS 2 PLACE	DECIMALS 3 PLACE	FRACTIONS
UNDER 6	±.02	±.005	±1/64
6-24 INCL	±.03	±.010	±1/32
OVER 24	±.05	±.015	±1/16

ANGLE ±1/2° CONCENTRIC: .020

CONTL TOL APPLY TO STOCK SIZES

FINISH [illegible] OR NOTED

CLEAN BURRS, BREAK CORNERS

APPROVALS SIGNATURE & DATE

DRAWN	L J PORTER	27 DEC 75
CHECKED		
DES.	[illegible]	[illegible]
PROJ		

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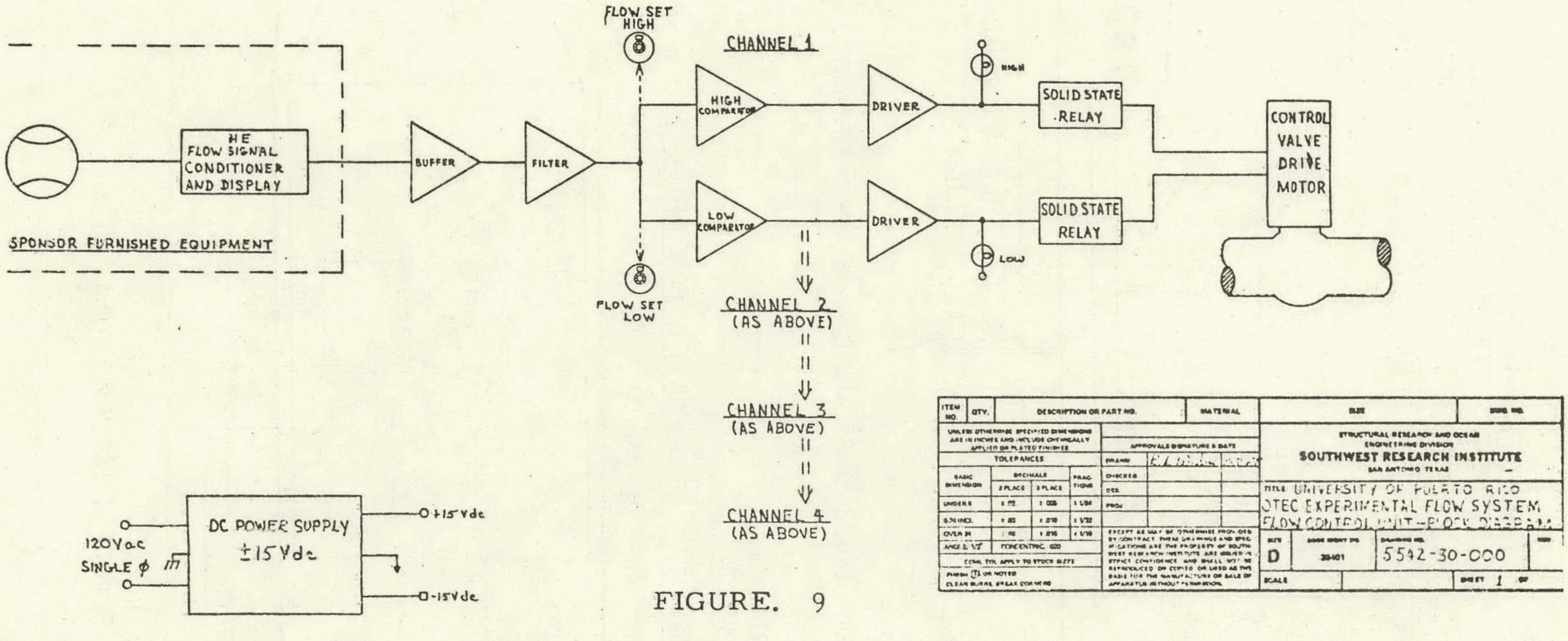
STRUCTURAL RESEARCH AND OCEAN ENGINEERING DIVISION
SOUTHWEST RESEARCH INSTITUTE
SAN ANTONIO, TEXAS

TITLE UNIVERSITY OF PUERTO RICO
OTEC EXPERIMENTAL FLOW SYSTEM
POWER DISTRIBUTION DIAGRAM

SIZE D
CODE IDENT NO. 20401
DRAWING NO. 5542-40-000
REV
SCALE NONE
SHEET 1 OF 1

FIGURE. 8



FLOW SET HIGH
CHANNEL 1
HE FLOW SIGNAL CONDITIONER AND DISPLAY
BUFFER
FILTER
HIGH COMPARATOR
LOW COMPARATOR
DRIVER
DRIVER
HIGH
LOW
SOLID STATE RELAY
SOLID STATE RELAY
CONTROL VALVE DRIVE MOTOR
SPONSOR FURNISHED EQUIPMENT
FLOW SET LOW
CHANNEL 2 (AS ABOVE)
CHANNEL 3 (AS ABOVE)
CHANNEL 4 (AS ABOVE)
120Vac SINGLE ϕ
DC POWER SUPPLY ±15Vdc
+15Vdc
-15Vdc
ITEM NO.
QTY.
DESCRIPTION OR PART NO.
MATERIAL
UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES AND INCLUDE CHEMICALLY APPLIED OR PLATED FINISHES
TOLERANCES
APPROVALS SIGNATURE & DATE
DRAWN
CHECKED
PROJ
STRUCTURAL RESEARCH AND OCEAN ENGINEERING DIVISION
SOUTHWEST RESEARCH INSTITUTE
SAN ANTONIO TEXAS
TITLE UNIVERSITY OF PUERTO RICO OTEC EXPERIMENTAL FLOW SYSTEM FLOW CONTROL UNIT—BLOCK DIAGRAM
SIZE D
30401
DRAWING NO. 5542-30-000
SCALE
SHEET 1 OF

FIGURE. 9

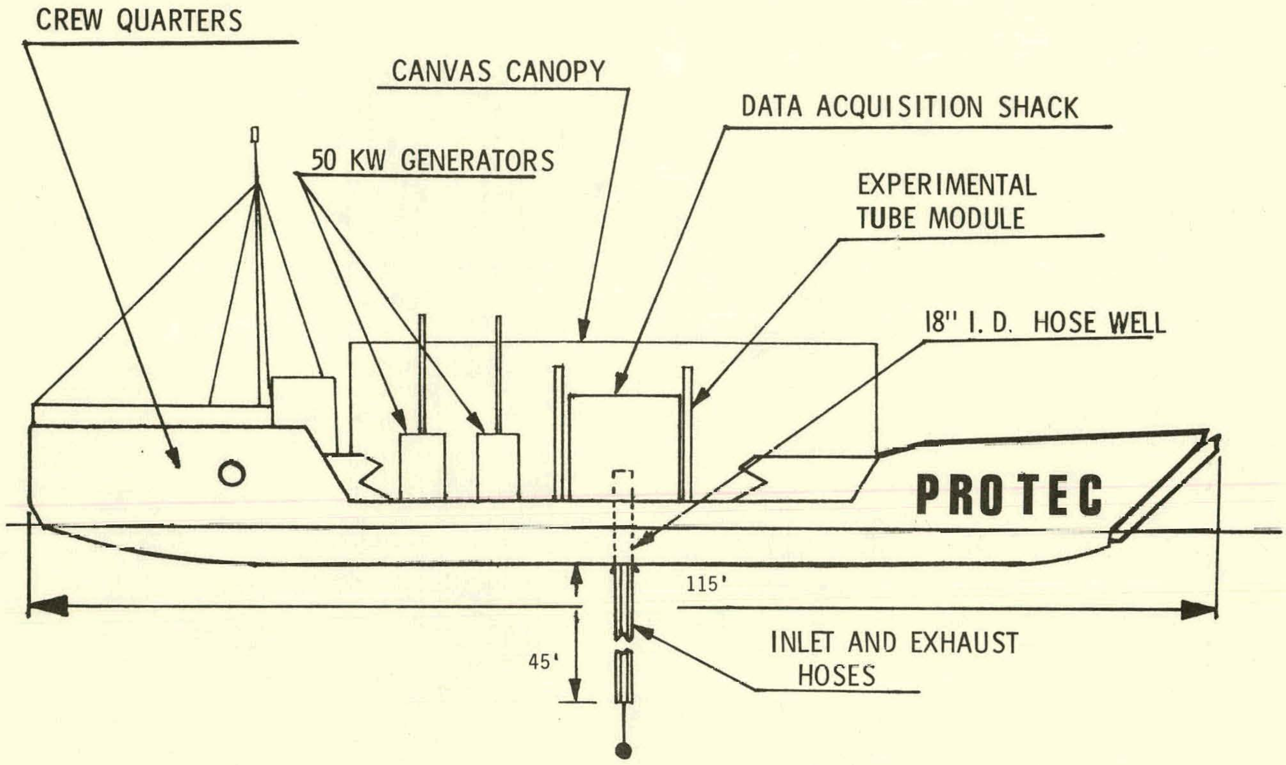


FIGURE 10. OUTBOARD PROFILE OF RESEARCH PLATFORM (LCU-1470)

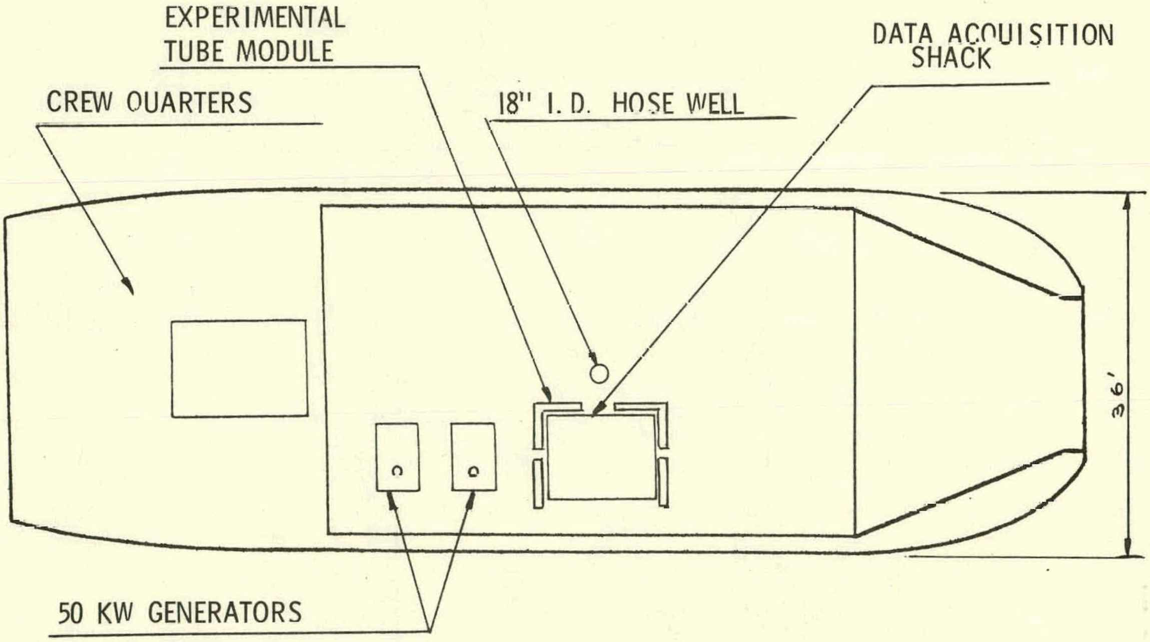


FIGURE 11. PLAN OF RESEARCH PLATFORM (LCU-1470)

A MODULE FOR MEASURING R_f AND COLLECTING BIOLOGICAL AND CORROSION SPECIMENS

by

A. P. Gavin, M. Rodin and G. F. Popper

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I. INTRODUCTION

Experiments for the OTEC Biofouling, Corrosion and Materials program are presently being conducted at several locations by different contractors and the future OTEC program envisions the involvement of several new sites and operators. The experiments normally performed at these sites usually include the determination of the change in heat transfer coefficient due to fouling of the heat transfer tube surface (R_f) and the evaluation with respect to the biofouling and corrosion of these tubes which have been exposed to the seawater. Experience to date has shown that if meaningful data which can be correlated between sites is to be obtained, it is essential that as far as possible equipment and procedures used by the contractors at the various sites be standardized. To accomplish this, the Argonne National Laboratory (ANL) Components Technology (CT) Division has been assigned the task of designing and assuring the availability of standard OTEC experiment modules to other projects. Each module is to contain a redesigned Heat Transfer Monitor (HTM), sufficient tubing sections to provide the required biofouling and corrosion samples and all of the pipe, valves, and auxiliary equipment required to evaluate a specific fouling countermeasures technique. Standard instruments, data acquisition and analysis systems are also to be developed along with standard procedures for the installation and operation of these modules.

HEAT TRANSFER MONITORS

Measurements of changes in the heat transfer coefficient due to fouling, R_f, using the Heat Transfer Monitor (HTM) apparatus developed by Fetkovich at Carnegie-Mellon University have been made by several organizations in various locations. Variations of the basic apparatus and in the data acquisition and reduction systems make correlation of the results between these locations difficult. Differences in the operating procedures and the physical arrangement of the systems also lead to uncertainties in the interpretation of these results. The HTM units now being used are direct copies of the original design by CMU intended for laboratory evaluation of the device. Field experience has indicated that, while this design can be used to produce satisfactory data, modifications to improve the measurement of some parameters, to facilitate the assembly and installation, and to simplify shipping and handling are desirable.

In order to achieve these objectives, ANL is designing a modified HTM that will be a standard unit to be used by all future OTEC installations. Standardization of the instrument and data handling techniques are also a part of this task.

The redesign of the Fetkovich HTM device was initiated at a workshop held at the David W. Taylor Naval Ship Research and Development Center in Annapolis, Maryland, on August 22 and 23, 1978. This workshop was attended by representatives of organizations which have been involved with the manufacture and use of the device. The attendees agreed on a list of modifications to be incorporated in the redesigned device. ANL then proceeded to produce a set of drawings which depicted a device with the recommended changes. These preliminary drawings were distributed to the organizations involved with the use of the devices for comment on December 4, 1978. Comments received from this distribution have been evaluated and the suggested changes have been incorporated into the design where feasible.

Figure 1 depicts the design which is the result of this development process. A prototype unit of this design will be manufactured and tested at ANL together with a unit manufactured to the original CMU design to establish the ability of the redesigned device to produce results which can be correlated with the data obtained to date using the CMU device.

The major changes incorporated into the ANL unit are:

1. Modified the unit for use with 1 in. O.D. tubing.
2. Changed the heater blocks to a three (3) part, ring clamped design.
3. Made the heater, guard heater, and reference blocks identical.
4. Changed the location of the reference block.
5. Incorporated a nonintrusive flowmeter in a separate housing.
6. Reduced the thermopile from 11 to 6 sets of junctions.
7. Included an internal gas temperature thermister.
8. Changed the housing design to reduce weight and bulk.
9. Incorporated external thermal insulation.

The use of 1 in. O.D. tubing in place of 1 in. schedule 40 pipe for the flow tubes not only is more prototypic of the tubes to be used in the actual OTEC heat exchangers but also facilitates a reduction in the overall size and weight of the units.

The design of the copper heater and reference block was changed to reduce difficulties with the assembly of the blocks onto the flow tubes. The surfaces of the tube and the inside of the copper blocks are highly polished to provide good thermal contact at the interface and scratching of these surfaces during assembly reduces the effectiveness of this preparation. The heaters for these blocks will be of the etched foil, Kaptan laminated, type with self adhesive backing. Each segment of the heater, guard heaters and reference block will have identical heaters applied to the outer surface.

Since much of the discrepancy in the fouling factor data seems to be associated with the flow data, the incorporation of a more reliable flowmeter was indicated. The use of a nonintrusive type of meter is required if cleaning systems (brush or ball) are to be evaluated. Our evaluation of available flowmeters has resulted in the choice of the Controlotron ultrasonic flowmeter. This choice is based on the use of several (up to 10) sets of clamp-on transducers with a multiplexer unit and one readout unit. The flowmeter transducers for each unit are located in a separate detachable housing. Since the transducers are designed specifically for use on a given pipe size, material, and wall thickness, all units will employ a flowmeter tube of 1 in. schedule 80 PVC pipe attached to the HTM flow tube by a special coupling with "O" ring seals.

To reduce the difficulties with assembly and installation of the thermopile, the assembly specified will be composed of six hot and six cold junctions. Two junctions will be located in symmetrically located wells in each segment of the heater and reference blocks. The individual junctions will be metal sheathed and the wires between junctions will be one continuous length to eliminate the possibility of external junctions formed by slight variations in materials. The complete thermopile units will be purchased from a commercial vendor. If initial experience with the assemblies employing the six junction thermopiles indicates that halving the number of junctions seriously affects the reliability of the temperature difference data, the number can easily be restored to the original 12 by placing a second commercial six junction assembly in series with the first and installing two junctions in each well in the heater and reference blocks.

The original HTM units were designed to operate with the entire housing submerged and thus a near constant temperature of the air inside the housing was assured. Units operated on shore or above water on buoys experience greater variation in internal air temperature due to ambient air temperature variations and to radiant heating due to exposure to the sun. In order to allow an evaluation of these temperature variations and for a correction to be applied by the data reduction system, if required, an internal gas temperature thermister has been included in the redesign. To reduce the magnitude of these internal temperature fluctuations a one inch thick layer of rigid thermal insulation with a white PVC outer jacket has been specified.

A standard electronics package containing amplifiers to supply signals to the data acquisition system from the thermopile, and the water and air temperature thermisters will be included with each HTM unit.

If fabrication and assembly of the initial prototype unit at ANL reveals that additional minor changes in design details are desirable, they will be incorporated before production of additional units is initiated. During the assembly and testing of the prototype unit, standard procedures will be developed for the assembly, installation, and operation of the HTM's.

BIOFOULING AND CORROSION SPECIMENS

In order to provide the required specimens for periodic evaluation of biofouling and corrosion of the tube surfaces each module will contain two sample tubes each at least 90 inches long of the same size and material as the HTM flow tube. The module piping will route the flow from the HTM through these tubes in a series arrangement and will provide for bypass of this flow during the time when the tubes are being sampled. Since the tubes will be 1 in. O.D. with relatively thin walls, samples will be cut with a tubing cutter and the interior of the cut end will be expanded to its original I.D. by means of a special swagging tool. Sections removed will be replaced with lengths of the original tubing held in place by hose sections and tube clamps. The piping arrangement and handling procedures will be designed to assure that the tubes are never allowed to become dry and to minimize the exposure at stagnant or low velocity flow.

CLEANING SYSTEMS

Proposed mechanical cleaning for OTEC heat exchangers include flow driven brushes, recirculating balls and slurry systems. Chlorination or other chemical systems alone or in combination with mechanical systems are also to be investigated. The basic test modules will be designed to provide space and piping adaptable to the inclusion of necessary equipment to clean the HTM and the biofouling and corrosion tubes in accordance with a selected cleaning system. The cleaning system incorporated in a given module will depend on the specific purpose of the test to be run and on the availability of cleaning system requirements at the installation site.

Some modules will be used to monitor conditions in operating test heat exchangers while others will be used to evaluate basic fouling and corrosive tendencies of the seawater at specific test sites or to evaluate the effectiveness of the fouling countermeasure techniques. Figure 2 illustrates the makeup of a typical module. This drawing is a schematic layout of a module that will contain an Amertap ball cleaning system for installation on OTEC-1 to monitor conditions in the heat exchanger tubes in either the condensor or evaporator if Amertap balls are selected as the cleaning method for these exchangers.

GENERAL DESIGN CRITERIA

The following general criteria will be observed in the design of the test modules.

1. All materials which contact the seawater will be either plastic or type 316 stainless steel.
2. Pipe other than that in the HTM and sample tubes will be 1 1/4 in. Schedule 80 PVC or plastic hose.
3. In as far as possible there will be no components in the system which contain stagnant or low velocity seawater.

DATA ACQUISITION AND ANALYSIS

As mentioned above, each HTM unit will include an amplifier package to provide standard high level signals from the thermopile, the water temperature thermister, and the air temperature thermister to a data acquisition system (DAS). The flow signal will be provided to the DAS from a set of transducers on each unit through a multiplexer and a common readout unit. A standard specification for the computer hardware and software will be developed.

SUMMARY

The development of a standard module for measuring R_f and for collecting biological and corrosion specimens as described in this paper is expected to result in an improvement in the quality of data being collected at each OTEC site and to facilitate the correlation of information between sites.

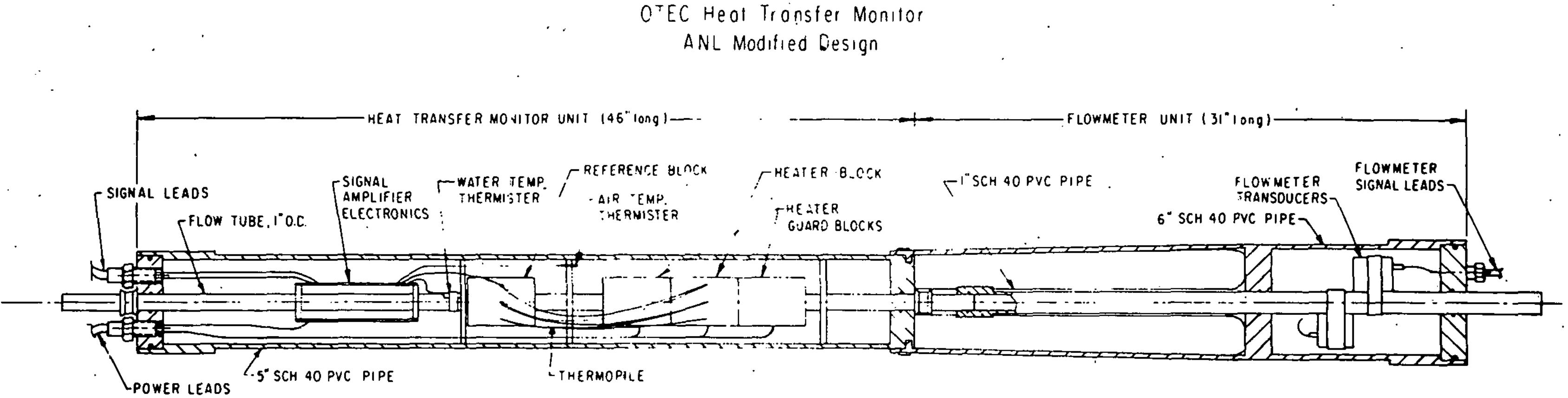

Figure 1

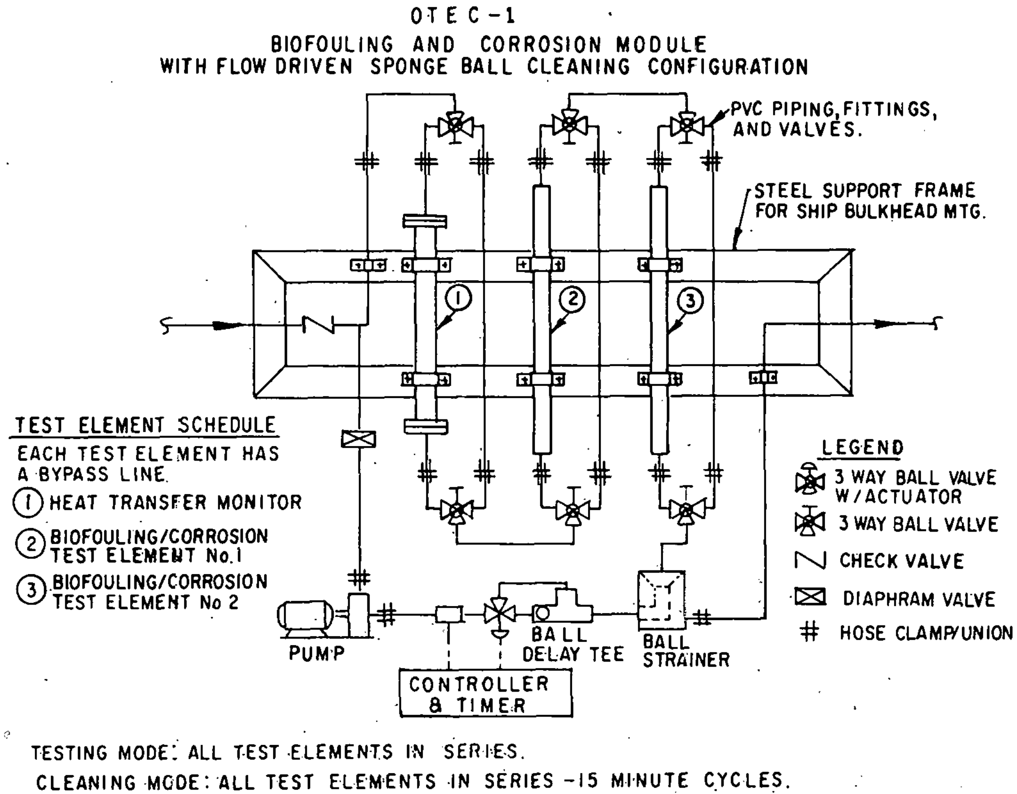

Figure 2

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MEASUREMENT OF R_f AND ANALYSIS OF HEAT TRANSFER DATA: SUMMARY

Chairman: Glenn F. Popper
January 10, 1979

The purpose of this session of the Workshop was to bring together the cognizant OTEC organizations and individuals to discuss the instruments used to measure the changes in heat transfer rates (R_f) and the techniques to analyze the data from these instruments.

The attendees concluded that there are a number of different versions of the basic Carnegie-Mellon University (CMU) heat transfer monitor (HTM) instrument being used to measure changes in heat transfer rate as described in CMU Report COO-4041-10. These variations in HTM design and in the data analysis techniques used may lead to incorrect or inconsistant results. The development of a standarized instrument and data analysis system was encouraged.

The ANL-redesigned CMU HTM was believed to be a significant step toward achieving a field-operable instrument that would achieve consistent results. The redesigned HTM is shown in Figure 1 and was described in a meeting paper.

This reference design incorporates the modifications suggested by the participants of the Workshop held at the David Taylor Naval Ship Research and Development Center (NSRDC) at Annapolis, Maryland on August 22 and 23, 1978.

The major modifications to the CMU device are as follows:

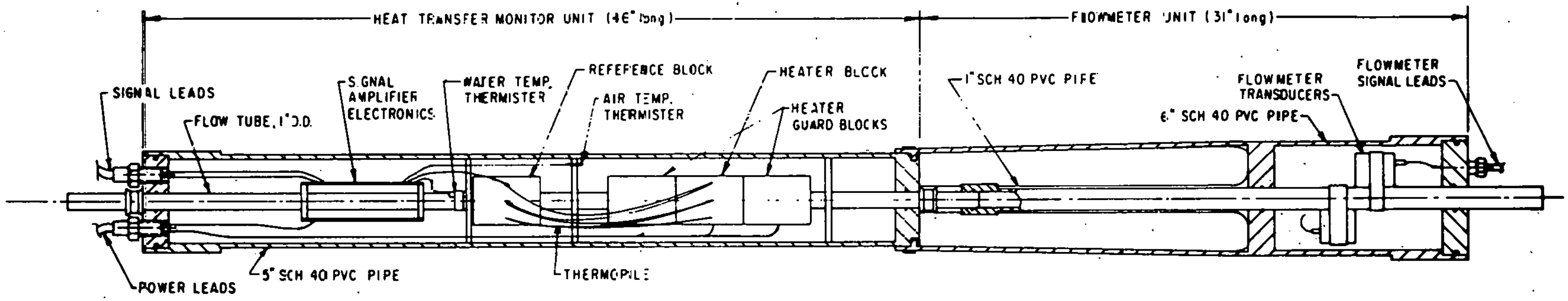
1. Modified for use on 1-in.-OD tubing.
2. Changed heater blocks to three-part, ring-clamped design.
3. Made heater, heater guards and reference block the same size.
4. Changed location of reference block.
5. Incorporated nonintrusive flowmeter in separate housing.
6. Reduced thermopile from 11 to 6 sets of junctions.
7. Included internal gas temperature thermister.
8. Changed housing design to reduce weight and bulk.
9. Incorporated external thermal insulation.

ANL is in the process of fabricating a prototype unit and will test the redesigned HTM to compare its performance with that of a standard CMU instrument.

The redesigned HTM was discussed by the participants. Several additional modifications were suggested for consideration. These included easy access to the electronic modules and a possible increase in the number of junctions used in the thermopile.

The present HTM design was judged to be sensitive and sufficiently accurate to make the needed measurements, and the accuracy and uncertainty in the measurement were assessed. The participants believed that R_f could be measured with an inaccuracy of less than ± 20% based upon measuring the heat transfer coefficient with an inaccuracy less than ± 2%. The absolute variation in measurement of an R_f of 0.0001 would therefore be expected to be $\leq \pm 0.00002$.

OTEC Heat Transfer Monitor
ANL Modified Design



The participants suggested that the effects of tube surface finish, temperature gradients, water temperature, and pump stoppage on R_f be studied. The correction factors used in the various HTM configurations should also be checked and verified.

A complete standardized system should be developed to measure R_f, including the data-acquisition system and methods of data analysis. A centralized depot for the data and data analysis should be established so that results from the various sites can be compared and interpretations of the data presented.

QUESTIONS AND WRITTEN COMMENTS

1. What do we know or have we done in comparison with the needs identified?
2. What are the remaining needs, what must be done and how long will it take?

George A. Cypher, International Copper Research Association

We suggest that a direct comparison of the Fetkovich (CMU) device with the heat transfer research institute (HTRI) device be made at the same time and placed on the same materials. The latter device has been used for many years by the chemical process industry and many of these devices are in operation around the USA. We have an HTRI unit and would be glad to cooperate with DOE on such a test and we have discussed this with them. We reported on the HTRI unit and gave typical results at the Seattle meeting.

An error analysis of the HTRI device has been made and is available, I believe, from HTRI, since G. Suitor of HTRI discussed this at the Seattle meeting.

LIST OF ATTENDEES

MEASUREMENT OF R_f AND ANALYSIS OF HEAT TRANSFER DATA: SUMMARY

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Honolulu, HI 96822

BIOLOGY OF FOULING: SUMMARY

Chairman: Peter H. Benson
January 10, 1979

The purpose of this session of the Workshop was to bring together OTEC investigators and interested parties to establish the present status of the fouling programs and determine what should be done with regard to identified needs. Although interrelated and difficult to separate, discussions on the measurement of R_f and cleaning techniques were not the intent of this session but were to be addressed in other sessions.

The following tentative agenda was adopted to facilitate discussions and utilize the limited time more effectively. No additional areas for discussions were proposed, and the subject of macrofouling was only briefly touched upon.

- Microfouling
  - Generic Issues
    1. Seasonal and geographic variation
    2. Materials effects
    3. Flow-rate effects
    4. The effect of periodic shutdown
    5. Cause and effect relationships (correlations)
  - Methodology
    1. Standardization
       - a. Sample preparation and procedures
       - b. Analytical procedures
         - 1) Film thickness
         - 2) Film density
         - 3) Film characterization
  - What is Needed?
- Macrofouling
  - Cold water pipe and system
  - Warm water pipe and system
  - Platform and associated structures

Although the title of this session was limited to biology, the role of inorganic film components could not be ignored, since measurements of heat transfer resistance (R_f) include both the inorganic and organic constituents of a fouling film.

It was agreed that the R_f curves exhibit similar shapes, a lag phase usually of a few weeks followed by a linear growth phase, regardless of season, location, or material. The importance of understanding the lag phase was emphasized, since once the growth phase is entered cleaning becomes imperative.

Results indicate that the length of the lag phase varies geographically by season and substrate. This variability, the effect of cleaning on R_f curves, and the role of "conditioning" films after cleaning require additional study.

A simple relationship between R_f and film characteristics, such as film thickness, although often assumed, has not been demonstrated. Studies to date have failed to demonstrate correlation of the observed heat transfer loss (R_f) with any film characteristic, with the possible exception of total organic carbon.

It was the consensus that long-term studies (18-month duration) with adequate replication at three test sites would yield a reliable data base from which the generic issues outlined could be resolved. To obtain such quantitative data, it was recommended that fewer materials be tested with greater intensity. Following such baseline studies, emphasis could be placed on one site to resolve more specific issues such as plant shutdown.

A reoccurring theme throughout the entire discussion was the need to standardize methods. To assure consistent results, it was proposed that similar materials and sample preparation be employed by all investigators. A simple degreasing procedure was recommended for all sample preparation.

The problems of vertical versus horizontal tube configuration was touched upon. In near-shore horizontal arrays, the bottoms of tubes are scoured by suspended sediment, etc., which leads to a discontinuous growth pattern of the fouling film. This problem can be avoided and sample collection is facilitated if tubes are maintained vertically. It was felt that the composition of microfouling species would not vary greatly between configurations; however, this has not been demonstrated. Accordingly, most investigators felt that the vertical configuration should be maintained, although scouring problems probably would not be encountered at an open ocean site.

It was recommended that a common suite of analyses be performed on samples from all test sites and emphasis be placed on correlating these analyses to environmental parameters as well as R_f.

The following analyses were suggested:

1. Film thickness (possibly with light microscopy)
2. Film density
3. ATP (although some results are conflicting)
4. Total organic carbon
5. Scanning electron microscopy (with less emphasis).

New methods for characterizing fouling films, now being developed in the laboratory, should be integrated into the basic list. Frictional resistance was suggested as a potential new measurement technique. Interlaboratory calibrations should be conducted, and, during cleaning experiments, tubes should be cleaned at the same value of R_f at all test sites.

Macrofouling was barely touched upon, although it was recognized as a major problem on the warm water side of OTEC, particularly on intake structures. There was general agreement that macrofouling problems on the platform and cold water side will be minimal.

SUMMARY RECOMMENDATIONS

1. Long-term experiments (18-month duration) with replicate sampling should be conducted at three study sites to resolve generic issues. After this quantitative baseline is established, emphasis can be shifted to the resolution of specific problems at one site.
2. Fewer materials should be tested with greater intensity to ensure adequate replication.
3. Emphasis should be placed upon the lag phase in film development, including the role of "conditioning" films.
4. Standardization of methods should be stressed. The following should be included:
    a. Sample preparation -- a simple degreasing technique was recommended.
    b. Similar sample materials should be used at all test sites.
    c. Similar configurations in experimental test arrays should be maintained at all sites. A vertical configuration was preferred for near-shore studies.
    d. The following suite of analyses should be common to all test sites:
        1) Film thickness
        2) Film density
        3) ATP
        4) TOC
        5) SEM.
5. A target R_f should be established for all cleaning experiments.
6. Water quality parameters should be monitored at all test sites as follows:

$$\left.\begin{array}{l}\text{Dissolved organic carbon}\\ \text{Particulate organic carbon}\end{array}\right\rangle \quad \text{Total organic carbon}$$

DO, salinity, temperature and pH
Total nitrogen and phosphorus
Heavy metals
Ammonia

LIST OF ATTENDEES

BIOLOGY OF FOULING: SUMMARY

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CORROSION AND THE APPLICATION OF MATERIALS

Chairman: Joseph B. Darby, Jr.
January 10, 1979

I. INTRODUCTION

The Chairman opened the session by defining the objective to be the development of guidelines for research and development necessary to meet OTEC requirements in the area of corrosion as well as materials applications.

The agenda for this meeting provided for work needs relative to five OTEC hardware components:

Heat Exchangers
Turbines
Cold Water Pipe
Screens
Other Components

The Chairman also announced that ANL intends to maintain a stockpile of materials for all OTEC participants. This will result in materials standardization among OTEC investigators and minimization of differences in test material characterization such as composition and surface finish.

II. HEAT EXCHANGERS

Material selection and corrosion problems associated with heat exchanger surfaces were identified as the most critical areas for technical activity. Heat exchanger designs under consideration include the conventional shell and tube configuration and plate type. The problems, in general, fall into two categories: (a) to select a heat exchanger material from candidate alloy types presently being considered for qualification, and (b) to establish the effect of cleaning on the corrosion resistance and life of components that serve as heat exchanger surfaces. The discussion of heat exchanger materials was carried out in terms of each candidate alloy type.

A. TITANIUM ALLOYS

The OTEC candidate from this family is commercially pure or unalloyed titanium, which is basically 99.0-99.2% titanium with a variety of impurity elements.

A question was raised as to whether the prime candidate, Grade 2, is satisfactory for OTEC requirements. Discussion revealed that overlap exists in specification requirements for Grades 1, 2 and 3. It was pointed out that ductility is an important property for the fabrication of plate-type heat exchangers and expansion of the tube at the tube sheet. Therefore, preference should be given to the low end of the Grade 2 specification. No difficulty was foreseen in applying the Linde coating to the outside surface of the tube for surface enhancement.

It was agreed that the most economical titanium tubing would be roll-formed from strip and welded; a rolled weld bead would be more likely than a scarfed weld. Although TIG-welded tubing meets OTEC requirements, tubing might also be produced by the Thermatool technique.

Other comments pertaining to titanium tubing were
(a) Titanium tubing might be improved by better end preparation to facilitate rolling.
(b) Tool wear was cited as a problem in providing patterned (enhanced) tubing.
(c) The question was raised as to who decides the preferred enhanced surface design.
(d) Best heat transfer is achieved with fluted tubes. Enhancement forces a greater tube wall thickness.
(e) The surface finish of titanium tubing needs improvement. Observations have been made that the titanium tube surface has cracks to 12-18 microinches in depth, which leads to fast biofouling buildup; deposits as thick as 20 microns were noted. Some individuals present thought that surface improvement was impractical and others disagreed. Some thought that surface improvement would double the cost. It was suggested that perhaps Industry can address this subject and advise what can be supplied economically.

It was agreed that titanium purchased to ASTM specification qualifies as an OTEC heat exchanger material with an expected life in excess of 30 years.

B. Cr-Ni-Mo ALLOYS

The specific alloy that has been qualified for OTEC heat exchanger applications is AL-6X*. In his evaluation, F. L. LaQue was able to qualify this alloy on the basis of short-term and long-term laboratory tests and, more importantly, because of application of "a million feet of tubing" in power plants using seawater for cooling. In the Workshop discussions, it was recognized that the designation represents a specific alloy product of Allegheny Ludlum Steel Corporation. E. H. Kinelski, DOE, suggested the use of a more general designation for this family of alloys, such as 20Cr-24Ni-6Mo-Fe. It was pointed out that many alloys fall in this category, and, at some point, specification limits will have to be defined for alloy qualification. In this regard, it was recommended that the contracted effort with INCO for marine corrosion studies be amended to accommodate the exposure of alloy compositions, other than AL-6X, in the crevice corrosion phase of the program. It was further suggested that these alloys be included in other OTEC programs where corrosion exposure specimen tests are being performed. There was general agreement to the foregoing.

Other likely candidate materials that might be described as "20-24-6" alloys are
(a) Custom 748 -- alloy being developed by Car Tech (not commercial as yet).
(b) 6M -- alloy being developed by Crucible Steel Corporation (not commercial as yet). It was also suggested by the Crucible representative that the new ferritic high-chromium molybdenum steels be considered.

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*Trade name, Allegheny Ludlum Steel Corporation, Pittsburgh, Pa.

Uddeholm alloy (20Cr-24Ni-4 1/2Mo-1 1/2Cu) was mentioned, but then rejected with the statement that it is not recommended for thin gauge tubes. It was stated that Sandvik Steel Company has two compositions, both are available in thin gauge and resistant to ammonia, which might be considered for OTEC use. An Allegheny Ludlum Steel Corporation representative suggested that the ferritic high-chromium molybdenum steels, such as (a) 26Cr-1Mo, (b) 29Cr-4Ni-2Mo, and (c) SC-1 (26Cr-3Mo), be considered. He also stated that he foresees no problem with corrosion or expansion of these welded tube ends.

A representative of Colt Industries, Trent Tube Division, mentioned their new alloy Sea Cure (composition: 26Cr-2.5Ni-3Mo-0.3Ti-0.02C-0.3Si balance Fe) as an OTEC candidate material.

It was suggested that all of these alloys might meet the first qualifying steps by using the matrix data developed by F. L. LaQue for AL-6X as a guide to their suitability and acceptability. A crevice corrosion study performed on coupon-type specimens would be a part of the qualification test. Once qualified as to crevice and pitting resistance, cleaning or fouling tests would be unnecessary.

It was agreed that any proposal for work on AL-6X should be amended to include other qualifying Cr-Mo alloys.

In general, Workshop participants agreed with F. L. LaQue's qualification of AL-6X and the projected 30-year life expectancy. AL-6X is not a proprietary composition. Specifications for the composition are being developed by ASTM Committee E44.11 and ASME.

C. COPPER ALLOYS

Copper-nickel alloy CA 706 is the prime candidate from the copper-base alloy family. No copper-base alloy, however, has been qualified to date because of two questions relating to performance in OTEC heat exchangers. The first involves the performance of CA 706 and other copper alloys in seawater/ammonia mixtures. There was a general feeling that performance in seawater contaminated with small amounts of ammonia would present no serious problems, based on Dow Chemical Company tests reported at this meeting. On the other hand, the corrosion behavior of copper alloys in ammonia containing seawater contaminants is unknown. (It was observed that CA 706 has been successfully used in handling steam condensate known to have 1000-2000 ppm NH_3 present.) Results from the next phase of the Dow program should provide clarification. It was brought out that ammonia refrigeration units of Cu-Ni were manufactured by Borg Warner for use on banana boats. E. H. Kinelski requested the copper industry to provide information on the performance of materials in shipboard refrigeration systems that utilize ammonia as the working fluid. It was pointed out that G. J. Danek, ANL Consultant, will be conducting an experience survey on the subject and would be the person to contact.

A suggested approach for circumventing corrosion problems of CA 706 in seawater-contaminated ammonia was the use of a duplex material, copper-nickel clad steel. It was pointed out that manufacturing technology is well developed and many manufacturers have the capability to fabricate duplex tubing and plate, e.g. Bridgeport Tube Company, Anaconda, and others. Improved heat transfer was attributed to Cu-Ni clad steel vis-a-vis copper-nickel. Copper-nickel surfaces were said to be free of macrofouling in seawater exposure.

The second question relating to the performance of copper-base alloys in OTEC heat exchangers concerns the corrosion-erosion resistance of CA 706. It is recognized that certain plate-type heat exchanger configurations, currently under consideration for OTEC, produce turbulence which may be too severe for CA 706. If this proves to be the case, an alternate chromium-containing candidate, CA 722, has been proposed. It was pointed out that CA 722 has the erosion resistance of CA 715 plus the added advantage of fouling resistance. In this regard, it will be necessary to design velocity-response experiments that relate to the application. It will also be necessary to determine the influence of crevices that are inherent in the plate-type configuration. With regard to this problem, E. H. Kinelski suggested that J. F. Rynewicz of Lockheed, Corporation talk to Alfa-Laval about the possibility of making one of the scheduled plate-type units of CA 722. (Earlier, Alfa-Laval had stated that CA 706 was not suitable for use in plate-type heat exchangers.) CA 722 is manufactured by Olin and Wolverine. J. E. Rynewicz indicated that he would talk to Alfa-Laval and the Copper Development Association (CDA) about performing some specimen tests with both materials. F. L. LaQue suggested that model plate-type test units be used in experimental work rather than subjecting the material to high-velocity testing. Mention was made of the fact that Lockheed is working with Alfa-Laval on plate-type heat exchangers. Mechanical Equipment Company was also mentioned as having the capability to make plate-type heat exchangers of CA 706. Initially, a problem was encountered with graphite-containing gasket material, but this has been rectified.

Finally, additional questions were raised. Do copper-base alloys offer a major advantage from the standpoint of antifouling? Will these alloys be easier to clean than other candidates? It was mentioned that CMU heat transfer tests should include Cu-Ni alloys at the first opportunity. These points should be addressed in upcoming heat transfer and cleaning experiments planned in various OTEC programs. (Olin said that they would be willing to furnish Cu-Ni tubes for such experiments.)

D. ALUMINUM ALLOYS

The prime candidate aluminum materials, Alclad 3004 and alloy 5052, have not been qualified for OTEC in the LaQue study. However, F. L. LaQue led off the discussion with an assertion designed to stimulate thinking: "If I had to build an OTEC plant tomorrow with aluminum heat exchangers, I would use Alclad and assume a 10-year life." It was projected by LaQue that the clad coating would corrode at 1 mil/yr. Discussions followed that addressed areas of uncertainty with regard to the use of aluminum alloys in OTEC heat exchangers. A critical area requiring additional work was identified to be the determination of the effect of cleaning on protective oxide films. Also, in the case of Alclad, will cleaning result in more or less pitting resistance? A suggestion was made during the discussion that, in conducting cleaning or tube-exposure experiments, artificial defects should be introduced to simulate pitting of cladding material. Mention was made that, in effect, defects were already present, e. g., in roll-formed/welded tubing, the weld line would be free of cladding. J. E. Draley, ANL, indicated that the defect suggestion would be taken under advisement. In connection with this discussion, a judgment was put forth that, if the problem is related to pitting and since cladding controls pitting, program efforts should emphasize the study of cladding material. It was agreed that experiments are currently being planned that will address the critical question of the effect of cleaning in INCO and other programs. Another question raised was whether we can anticipate that Alclad will have more resistance to crevice corrosion that the unclad alloy. Representatives of both Reynolds Metals and Alcoa agreed that as long as cladding exists, it should protect the core material.

There was a period of discussion addressed to the question of whether 7072 is the optimum cladding to use for the OTEC application. Also, what is the practical thickness limit for cladding material? The aluminum industry stated that 5% cladding is the usual industry practice. In the case of OTEC, a 10-mil clad thickness was suggested as being more suitable. Alclad on the inside of a tube is not standard nor readily available. The clad coating is usually softer than the base alloy; however, it is not a firm requirement. Surface finish was stated to be independent of the hardness of the cladding. J. E. Draley asked the Alcoa representative to estimate the time and cost required to identify the optimum cladding alloy. To this the Reynolds representative responded that a program is needed to optimize cladding material, core material, and cladding thickness. J. E. Draley indicated that this subject would be discussed seriously in the near future with The Aluminum Association and/or the producers. Given a fixed amount of dollars to spend, the Alcoa representative stated that an Alclad tube with a 10-mil cladding would be preferred over a solid alloy. It was stated that Alclad tubing is 20% less costly than 5052 alloy. Alcoa stated that they do not manufacture welded tubing. (Strip is manufactured that is capable of being roll-formed and welded by others.) Kaiser manufactures a welded aluminum tube. Aluminum company representatives stated that aluminum pipe and tubing are manufactured by similar methods.

A brief discussion on the possible effect of copper ions from screens on the corrosion behavior of aluminum led to the judgment that copper-ion concentration would be expected to be quite low, perhaps lower than the seawater background level, and, thus, the influence should be negligible. In this regard, F. L. LaQue urged that "somebody" do the necessary arithmetic to estimate the copper-ion concentration to which heat exchangers would be exposed.

In summary, aluminum alloys have not been qualified for OTEC because of information gaps in critical areas. However, on the basis of present knowledge, a high probability exists that aluminum alloys, and particularly Alclad, will be satisfactory for OTEC heat exchangers with an anticipated minimum life of 10 years.

E. SURFACE PROPERTIES

Two topics on heat exchangers, not material specific, are summarized separately.

A strong plea was made by F. L. LaQue to "zero in" on the OTEC heat exchanger configuration, particularly as to whether there will be conjugated surface enhancement on the seawater and working fluid sides. It was pointed out that design, manufacture, and corrosion considerations are difficult to address without this information. For example, what can be done with ends of tubes that have modified configurations? In this connection, E. H. Kinelski expressed the opinion that designers would probably prefer longitudinal enhancement. The most critical problem anticipated is that all of the experimental work now under way on the cleaning of smooth-surface tubes would be of limited usefulness if an enhanced configuration were to be selected. Concern was expressed as to whether cleaning methods would be effective on enhanced surfaces.

The second general topic related to heat exchangers is the importance of surface finish in terms of scale build up. Opinions were expressed that improved surface finish on heat exchanger surfaces would promote a cleaner surface, and therefore improved performance. On the other hand, reference was made to the Dow experiments that indicate, after a short period of time, the performance of heat exchangers is the same regardless of starting surface finish condition. However, proponents of clean surfaces countered by pointing out that, because of cleaning procedures, we are interested in only the early stages of film development. The consensus was that it would not be economically practical to specify surfaces of improved quality, since manufacturers would require extraordinary measures to improve the currently available as-fabricated finish.

III. TURBINES

Steels presently used in turbines, 403 and 410 stainless steel, are candidate materials for OTEC turbines where the working fluid is ammonia of low moisture content. It has been shown in industrial studies that a moisture content of 0.2% by weight must be maintained to circumvent stress-corrosion problems of these materials. Since there is no way to ensure this level of moisture, alternate material suggestions were solicited. It was generally agreed that a suitable material could be selected from the 400 series stainless steels. However, M. J. Mann of General Electric Company, Schenectady, N. Y., indicated that these alloys are also susceptible to stress-corrosion cracking in ammonia. He agreed to provide details to R. B. Teel, ANL Consultant, at a later date. It was also suggested that information on turbine materials might be obtained from EPRI. A suggestion was made that corrosion-fatigue properties should be determined for candidate alloys.

IV. COLD WATER PIPE

Candidate materials for this component include reinforced concrete and high density polyethylene. With respect to concrete, it was suggested that OTEC follow the petroleum industry technology for aggregate mix. However, potential corrosion problems related to reinforcement should not be ignored. Reinforcement can be cathodic because it is surrounded by the alkaline concrete mixture and thereby could accelerate the corrosion of other more active materials boldly exposed to seawater. This was not seen to be a problem on OTEC systems except for possibly mooring lines. To avoid such a problem, the line can be insulated from the cold water pipe. It was also pointed out that performance improvement can be achieved by using nickel coated reinforcement, for which 17-year marine exposure data are available, or reinforcement manufactured from a corrosion-resistant material. Nonmetallics for reinforcement were suggested, and Concrete Technology Company is investigating this area at Tacoma, Washington.

Polyethylene is a candidate pipe material on OTEC-1 and mini-OTEC where the cold water pipe is relatively small in diameter. It was pointed out in the discussion that, in full-scale OTEC designs, the pipe size is beyond state-of-the-art manufacturing capability. Recent work at MIT indicated a potential fatigue problem with low-density polyethylene when cyclically stressed in seawater. J. F. Rynewicz indicated that fatigue studies have been performed but he was not certain of the environment. He will provide details to G. J. Danek, who is preparing a survey on the subject.

V. SCREENS

In connection with screens, E. W. Thiele of CDA reported that he is working with the Johnson Division of Universal Oil Products, Incorporated, a manufacturer of industrial water filtering screens and related equipment. They are investigating three alloys: CA 706, CA 715 and silicon bronze. It is recognized that the latter material is velocity limited to about 2 ft/sec. Also, crevices may be a problem with bronze. Testing will be performed at 1/2 ft/sec to determine whether this flow is sufficient to provide the necessary fouling control. CDA has also been contacted by Royce Company to look at their design. A suggestion was made to look at No-Foul* rubber coatings for screens. D. L. Thomas of Radiation Management Corporation reported that he had made inquiries and found that the No-Foul material is available only in sheet form, usually 1/2-in. thick, and, thus, could not be applied to screening as a coating. J. F. Rynewicz stated that Goodyear Tire & Rubber Company has a thinner sheet material, about 1/16 in. The suggestion was made that these manufacturers might be encouraged to develop a material that could be applied by standard coating technology.

R. B. Teel suggested that wire size for screen use was critical from a corrosion standpoint. Optimum wire gauge for screen use might be an area of investigation.

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*Trade name, B. F. Goodrich Company, Akron, Ohio.

VI. OTHER COMPONENTS

Included in this category are pumps, valves, heat exchanger shell materials and baffles. The limited descussion indicated that no serious material problems are anticipated. F. L. LaQue suggested that his book, Marine Corrosion, be used as a reference for suitable pump materials. A comment regarding materials in contact with ammonia was to use high fracture toughness steel, such as SA 516, cited as a fine-grain C-Mn steel.

QUESTIONS AND WRITTEN COMMENTS

1. What do we know or have we done in comparison with the needs identified?

2. What are the remaining needs, what must be done and how long will it take?

Robert S. C. Munier, Tracor Marine

I suggest that there still remains a need to standardize the ongoing and planned field measurement programs (Keahole Point, Gulf of Mexico, Puerto Rico). The R_f, fouling, and corrosion data collected to date at the different sites has not been effectively comparable.

Robert Zawierucha, Union Carbide Corporation, Linde Division

I appreciate the effort that went into the OTEC Workshop held in Washington during the period, January 8-10, 1979. The exchange of views which it permitted was an important benefit to all of the individuals who attended.

Towards the end of the OTEC Workshop written comments were solicited on a number of subjects. Areas which I would like to comment on are as follows:

1) Testing of Alclad Aluminum Alloys
2) Cladding and Substrate Compositions For Optimization
3) Strength Level Of Titanium Alloys For OTEC
4) Stainless Steels For OTEC Service
5) Stress Corrosion Of Ferrous Alloys In Ammonia

I. Testing of Alclad

Union Carbide's position has been that the Alclad alloys 3003 or 3004 are the most viable aluminum alloys for seawater exposure. On the basis of our own experience, it must be acknowledged that the corrosion testing of Alclad alloys must be approached with caution. When mixes of aluminum alloys are used in test heat exchangers it is entirely possible that the cladding at tube inlets will be dissipated needlessly as the cladding will be protecting other unclad tubes, tube sheets and shells. This cladding loss will result in inlet end erosion of Alclad tubes. Thus, careful consideration of cladding throwing power and careful designs must be factored into the experiment.

II. Optimization of Cladding and Substrate Compositions

On the basis of work by Bonewitz, some concern exists as to whether the 7072 alloy is the best cladding alloy for both surface and deepwater service. By the same token, 5052 clad with 7072 has been theorized as being an optimum OTEC material. Experiments to clarify these positions are recommended.

III. Titanium Strength Level

Questions were raised about the strength level of titanium to be utilized for OTEC. From the standpoint of fabrication it is always desirable to use the titanium grade with the lowest possible strength level. Titanium is a potent scavenger of interstitial elements such as oxygen and nitrogen but especially the former. This scavenging takes place in welding even under shielding conditions which might, for most materials, be quite adequate. Many welding engineers, to minimize the possibility of embrittlement, use titanium welding wire that is of lower strength than the material to be welded. This is done on the basis that contamination by interstitials will occur and the strength level of the weld metal will increase. Thus, titanium wire equivalent to Grade 1 might be utilized for welding titanium tubing equivalent to SB-338 Grade 2, for example.

Commercially, pure titanium alloy of the type known as SB-338 Grade 2 is generally considered to be immune to seawater stress corrosion cracking. It should be known that high strength titanium alloys are subject to a variant of stress corrosion cracking known as "accelerated crack propagation" or "reduced fracture toughness." In this SCC variant, the environment, in this case seawater, is not corrosive enough to initiate stress corrosion cracks but in the susceptible alloys it is able to propagate flaws and cracks easily.

The corrosion literature of the 1962 to 1970 period has numerous references to accelerated crack propagation in high strength titanium alloys exposed to seawater. Much of the work was conducted by the U. S. Navy for its Deep Submergence Search and Rescue Vehicle (DSSRV). While much of the work concentrated on the higher strength "super alpha" or "alpha-beta" alloys there was some attention paid to the commercially pure titanium alloys.

J. L. Cavallero of the U. S. Navy Marine Engineering Laboratory indicated that a critical minimum oxygen content of 0.250% was the threshold level for "accelerated crack propagation" in commercially pure Ti alloy subjected to seawater. The 0.250% oxygen content happens to be the upper limit for oxygen for titanium tubing per ASME specification SB-338 Grade 2. I believe that the applicable report is Marine Engineering Laboratory Report 2483 entitled "Embrittlement of Titanium In Sea Water" and it is dated October, 1963. A maximum oxygen content of 0.35% is allowed for titanium per ASME specification SB-338 Grade 3. While there have been no known "accelerated crack propagation" problems with titanium condenser tubes in seawater which have been supplied to SB-338 Grade 2 it may be desirable not to push for higher strength titanium grades in OTEC service.

It should also be noted that contamination of SB-338 Grade 2 material which has a relatively high strength level due to the presence of oxygen may occur in subsequent welding/heat treatment procedures. Since titanium is a veritable "sponge" where oxygen is concerned, the additional oxygen contamination may make the original tubing susceptible to "accelerated crack propagation." The UCC policy is to attempt to obtain titanium material at the low end of the strength range for SB-338 Grade 2 to provide tolerance for possible contamination. The use of low strength Grade 1 material is desirable. Unfortunately, this grade is in short supply and probably prohibitively expensive.

IV. Stainless Steels For OTEC Service

Alloy AL-6X (2Cr-25Ni-6Mo) has been suggested as an equivalent to titanium for seawater service because of its performance in trails at numerous sites. Potential savings in fabrication costs make such alloys attractive. Sandvik alloy 2RK65 (20Cr-25Ni-4.5Mo-1.5Cu) reportedly also has performed well in numerous coastal applications including ammonia/area plants cooled with seawater. Numerous foreign specifications exist for the alloy. ASTM specification B-625 covers plate and sheet forms of these materials. Seawater experience with Sandvik alloy 2RE69 (25Cr-22Ni-2.1Mo-.12N) is less well developed. It is suggested that consideration be given to utilization of these materials in OTEC experiments and thinking.

V. Stress Corrosion Of Ferrous Alloys In Ammonia

The Linde Division of Union Carbide Corporation has experienced stress corrosion failures of alloy steels in anhydrous ammonia. Internally, measures to limit reoccurrences have been taken. Refer to a paper by Deegan, Wilde and Staehle entitled "Some Electrochemical Aspects Of SCC Of Steels In Liquid Ammonia Environments" which appeared in the April 1976 edition of Corrosion magazine. It suggests that contamination of anhydrous ammonia, by as little as 0.3 ppm oxygen and 4 ppm nitrogen, will cause stress corrosion cracking of ferrous alloys. The model proposed in this reference suggests that both oxygen and nitrogen are required, although at the OTEC workshop it was suggested that only oxygen contamination was necessary. The levels of oxygen and nitrogen which were cited are quite low.

Realistically, the following should be accepted:

1) In a process application it may be extremely difficult to eliminate contamination of anhydrous ammonia by low levels of oxygen and nitrogen.

2) Inhibition may not always be effective under all conditions.

3) Residual stresses due to fabrication will probably be more significant than actual operating stresses. Sources of the residual stresses will be welding processes and metal deformation during fabrication or setup.

4) Irrespective of potential ammonia SCC problems; alloy steels are still attractive for OTEC.

If the above are accepted, it would, therefore, be advisable to adopt a "fail safe policy" and use materials with excellent toughness and resistance to crack propagation. Fine grained steels with excellent toughness, such as those included in ASME specification SA-516, are suggested. These were used by UCC for the Argonne OTEC vessels and are used extensively in chemical process applications requiring toughness at temperatures as low as -50°F.

The preference would be for the lowest strength grade, i.e. Grade 55, but this may not be realistic for very large vessels. Local stress relief of welds is also suggested for large vessels. For small vessels the entire vessel should be stress relieved at temperatures not exceeding 1200°F. Of course, coatings and judicious use of sacrificial anodes are other alternatives.

It was indicated in the OTEC workshop that stress corrosion cracking of martensitic stainless steels had been reported in contaminated anhydrous ammonia. The author is not aware of any such instances in UCC process applications or elsewhere. In view of the fact that high strength heat treatable stainless steels are potential turbine material candidates for OTEC, it would seem reasonable to run compatibility tests of potential materials in contaminated ammonia known to cause SCC in ferrous alloys. Corrosion fatigue tests in addition to stress corrosion tests are strongly recommended as fatigue is a serious failure mode in turbine applications.

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FOULING AND COUNTERMEASURES: SUMMARY

Chairmen: Glenn F. Popper and Peter H. Benson
January 10, 1979

This session was held with approximately the combined attendance of the two preceding sessions held on the Measurement of R_f and Analysis of Heat Transfer Data and the Biology of Fouling. The purpose of this session was to attempt to determine the current status of the OTEC Fouling and Countermeasures programs and what should the programs be in the future to answer the identified needs.

The attendees were asked to address the following types of questions. What fouling countermeasures are suitable for OTEC systems? What chlorine dosages will keep R_f below 0.0001 in heat exchanger tubes? If chlorination is used, can the effluents meet the as yet unknown requirements of the EPA in clean ocean water?

The general conclusion was that, although a number of fouling and countermeasures programs and experiments are being conducted, the above types of questions could not be specifically answered at this time. It will be important to know the effects of chlorination on both macro- and microbiofouling. There are procedures to obtain variations in EPA requirements, and therefore chlorination should now be considered a viable fouling countermeasure option. Mechanical countermeasures must be studied in depth to determine their effectiveness.

A two-phase fouling countermeasures program is anticipated. The first phase is being conducted in locations where accelerated fouling occurs, such as Panama City, Florida. This Phase 1 program, requiring a large number of tests, will be used as a sorting and selection process to determine the most appropriate techniques and technique variables. For instance with M.A.N. brushes, the optimum type of bristle, length and stiffness of bristle, and length of brush would be determined. Subsequently, confirmation of the best cleaning parameters will be made in OTEC-type water at the Seacoast Test Facility.

It was suggested that the effects of an Amertap ball carrying calcium carbonate from an ammonia leak through a clean system be studied. The replication of data from a given site and system is needed. The utility of ultrasonic cleaning was discussed with some pros and cons being presented. Again no firm statements were made on either fouling or fouling countermeasures.

QUESTIONS AND WRITTEN COMMENTS

1. What do we know or have we done in comparison with the needs identified?

John A. Braswell, Naval Coastal Systems Center

Preliminary investigation of flow-driven brushes for removal of soft biofouling accumulations (primary slimes) from the internal surfaces of seawater-cooled heat exchanger tubes has been completed. The cleaning ability of a commercial system was measured with single tube, heat transfer monitors. The evaluation indicates that flow-driven brushing every eight hours will maintain an acceptably low fouling resistance (less than 0.005 ft^2-hr-°F/Btu) in cylindrical titanium tubes but not in aluminum alloy tubes of the same configuration.

2. What are the remaining needs, what must be done, and how long will it take?

John A. Braswell, Naval Coastal Systems Center

Further tests of flow-driven brushes for removal of soft fouling from OTEC heat exchangers are being planned. In addition, evaluation of a recirculating sponge-ball cleaning system has been scheduled. Both techniques will be conducted on smooth-walled cylindrical pipes of titanium and aluminum. Low levels of chlorination will be evaluated in combination with each cleaning technique. If time permits, the tests should be expanded to include stainless steel and copper-nickel alloys as possible heat exchanger materials. The scheduled tests will begin within the month, and should be completed by the end of the calendar year.

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CLOSING REMARKS

Workshop Chairman: Joseph E. Draley
January 10, 1979

After considering the events of the past three days, I believe it is accurate to say that participants in the OTEC BCM Program now know each other and each knows what the others have been and plan to be doing. Each has been updated concerning the overall plans for the OTEC Program and each has been challenged to upgrade his ability to obtain useful data and to develop the understanding that hopefully will lead to success in the OTEC undertaking. There has been good opportunity to discuss with the most knowledgeable and involved investigators the problems and details that must be considered to make the best progress.

The summaries of the sessions on specific topics, as presented by the three chairmen, have made it clear that participants have been thinking hard in their efforts to guide the program elements along the route required to answer some of the most difficult and most essential problems faced by OTEC designers. It is going to be necessary, they say, (a) to know enough about fouling to identify fouling-related problems and provide the background needed for development of successful countermeasures, (b) to establish and optimize the efficacy of available countermeasures and possibly to develop new ones, and (c) to utilize the materials that offer the greatest chance of technological success -- reliable power production at an acceptable price -- if we are to succeed, for the materials challenge is severe.

As measured by the criteria set up for this Workshop, the past three days have been most successful; for me at least they have also been most rewarding, and I thank you all for your contributions and for your efforts, on our own behalf and on behalf of the Department of Energy.

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