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LOCALIZED CORROSION OF ALUMINUM ALLOYS
FOR OTEC HEAT EXCHANGERS

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January 1979

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EXECUTIVE SUMMARY

Aluminum-magnesium alloy 5052 is one of the leading candidates for OTEC heat exchanger and condenser tubing. Existing field data show that alloy 5052 corrodes by pitting and crevice corrosion in seawater. These same data suggest that corrosion rates may be accelerated in certain deep Pacific Ocean waters similar to those that will be utilized in OTEC condensers.

This paper reports the results of a laboratory study undertaken to assess (1) whether accelerated corrosion of aluminum alloy 5052 in the deep ocean is a real possibility, (2) whether accelerated deep ocean corrosion will be of concern to an OTEC plant using aluminum alloy heat exchanger tubing, and (3) what deep ocean variables could be responsible for an increased corrosion rate. Accordingly, the corrosion behavior of both alloy 5052 and pure aluminum (which serves as a baseline material) has been measured in the laboratory under simulated deep ocean conditions. The effects of dissolved oxygen, pH, temperature and copper ion concentration of the seawater have been studied by both simple immersion and galvanic cell tests under controlled conditions and by electrochemical techniques.

Through this program, objectives (1) and (3) above have been completed. Objective (2) has been partially completed and the work necessary to finish it has been outlined and recommended. It is shown that a decrease in pH from 8.2 to 7.5 as found in the deep ocean both decreases the time for pits to initiate and increases their growth rate. A decrease in dissolved oxygen has the opposite effect, but when pH and dissolved oxygen are varied together as in the deep ocean, the pH effect predominates. The effects of a decrease in temperature with depth are to encourage rapid pit initiation and to slow down the pit growth rate. From the data in which oxygen, pH and temperature are all varied together, it is concluded that an increase in corrosion rate is indeed to be expected in many deep ocean waters, and that a combination of low pH and low temperature is responsible, rather than low oxygen as many had previously believed. The most corrosive set of conditions

encountered was low pH and temperature coupled with high oxygen. Fortunately for OTEC, such conditions are not found occurring together naturally in the ocean. The most corrosive set of real conditions was found to be in the midrange of all three variables where temperature and pH are low enough to give rapid corrosion initiation, and the dissolved oxygen is high enough to permit high growth rates. Such conditions are found at depths of 150 to 400 meters in the Pacific Ocean, while in the Atlantic they may be found at greater depths due to the higher overall levels of oxygen. For this reason, it is recommended that oxygen, pH and temperature profiles be measured at all potential OTEC sites before detailed design of a plant to be located at that site is begun. Using the hydrographic data along with the polarization techniques described in this report, the depths corresponding to the most corrosive conditions at that site can be identified, and the plant designed to avoid locating the cold and warm water intakes at these depths. For most locations it should be possible, using the techniques we have developed, to locate the warm water intake above and the cold water intake below the most corrosive depth.

It should be noted that although the most highly corrosive set of conditions identified by our experimental program do not occur together naturally, it may be possible to create them artificially inside an OTEC condenser taking in deep water having low pH, low temperature and low DO. The velocity of the water through the tubing may increase the transport of oxygen to the surface sufficiently to raise the effective DO and make the water very corrosive compared to surface water, especially if pits have already initiated during a prior shutdown period. A laboratory program to assess the danger of this possibility has been proposed, but not yet been funded.

It is shown that pit initiation times for alloy 5052, especially under quiescent low pH conditions, can be as short as half a day. This means that some pitting is almost inevitable during shutdown periods, and especially during the initial start-up period before corrosion product films have had a chance to build up. In this connection, it is recommended that heat exchangers be designed to avoid zero velocity conditions and to provide for complete drainage of the tubing during maintenance periods longer than one-half day. Due to the possibility of short initiation times, it is also recommended that OTEC consider either attempting to avoid pitting altogether

by a combination of cladding and maintenance of a continuous flow, or controlling the perforation of unclad tubing by inducing as high a pit density as possible and selecting the proper tube wall thickness. A methodology is outlined for combining existing corrosion data, laboratory electrochemical data such as given in this report and a knowledge of the number of pits on the surface, to predict corrosion rates at an OTEC site for which the proper hydrographic data have been measured, but for which there are no corrosion data. A design engineer would then use this information to choose the proper tube wall thickness to obtain the desired lifetime.

Data on the effects of Cu^{++} ions on both alloy 5052 and 99.99% aluminum are presented which show that Cu^{++} concentrations as low as 30 ppb may accelerate corrosion. Therefore, it is recommended that copper-nickel components upstream of aluminum alloy heat exchanger tubing be avoided if at all possible. In case it is decided that copper-nickel intake screening is necessary, an experimental program to determine the severity of the problem is suggested.

A final recommendation based on our results is that all proposed chemical cleaning techniques be examined carefully to see if they could lead to even a temporary (i.e., one-half hour or longer) combination of low pH and high DO on the seawater side of the tubing. Any cleaning procedure that has this potential should be rejected if aluminum tubing is chosen, as such conditions could lead to severe corrosion.

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ABSTRACT

The effects of dissolved oxygen, pH and temperature on the rate of initiation and growth of pitting and crevice corrosion of aluminum alloy 5052 and pure aluminum have been determined. Variations in pH and temperature rather than dissolved oxygen are shown to account for increased corrosion rates of 5000 series aluminum alloys that have been reported for deep ocean exposures. The impact of these results on the use of aluminum for OTEC heat exchanger tubing and on possible approaches to corrosion control are discussed.

I. INTRODUCTION

The long-term effectiveness of any Ocean Thermal Energy Conversion (OTEC) type power-generating plant depends critically on the performance of the material selected as heat exchanger tubing for the evaporator and condenser.¹ Several aluminum alloys are prime candidates for this application due to the high strength-to-weight ratio, resistance to general corrosion and high thermal conductivity.² Alloy 5052, a weldable, nonheat treatable aluminum-magnesium alloy, which is readily available in seamless tubing, has particularly been recommended for this service.³

The corrosion behavior of aluminum alloy 5052 in surface seawater²⁻¹⁴ and in desalination environments^{15,16} has been studied and is reasonably well characterized. Less is known about its behavior in deep ocean waters¹⁷⁻¹⁹ typical of those to which an OTEC installation will be subjected. The desalination data are encouraging because, although rapid initial corrosion rates were observed, the rate of penetration by pitting slowed with time and tended to become self-limiting.¹⁶ Caution should be exercised, however, when attempting to apply the desalination data to OTEC because the environments are different. The desalination environment typically involves temperatures from 65 to 120°C, dissolved oxygen concentrations below 0.1 ppm, pH in the acidic range from 4 to 7.6 and higher than ambient salinity.¹⁶

In contrast, the OTEC environment involves temperatures from 4 to 40°C, dissolved oxygen from 0.5 to 7.5 ppm, pH from 7.4 to 8.4 and ambient salinity.

The corrosion data that are available for 5000 series aluminum alloys at various depths in the Pacific Ocean show that these alloys may suffer accelerated rates of corrosion in the deep ocean when compared with those at the surface.^{8,19} The rates that were reported reached a maximum of three times those of the surface at a depth of 500 to 900 meters, then decreased again to twice the surface rate at 2000 meters. This is shown averaged over all alloys tested in Figure 1. This is of concern to the OTEC Program because the cold water inlet pipe of proposed OTEC plants may be taking in deep ocean water similar to that in which the above maximum corrosion rates were reported. Figure 2 shows the variation with depth of dissolved oxygen, pH, temperature and salinity at the sites from which the deep Pacific Ocean corrosion data were obtained.¹⁹ Note that the dissolved oxygen concentration reaches a minimum at the same 500 to 900-meter depth at which the maximum corrosion rate was reported. For this reason, it has usually been assumed that the low dissolved oxygen concentration was in some way responsible for the increased corrosion rate.^{8,19} The objectives of the research program, the results of which are given in this report, were to assess what threat, if any, an increase in corrosion rate of 5000 series aluminum alloys in the deep ocean may pose to the use of aluminum alloy heat exchanger tubing in OTEC installations and to determine whether or not decreased oxygen is the causal agent for the increased rate.

Other factors could also be important in determining the rate. For instance, the pH curve of Figure 2 has the same shape as that of the dissolved oxygen curve, and other data from the Pacific Ocean have shown²⁰ that the inorganic substances NO_3^- , SiO_3^{--} and PO_4^{3-} often reach maximum concentrations at the same 500 to 900-meter depth. Moreover, many of the individual 5000 series alloys behave quite differently²¹ from the average shown in Figure 1. It is known^{9,22} that aluminum and aluminum alloys suffer accelerated rates of attack at pH values above 10 and below 4, but no detailed data have been reported on the effects of pH within the normal range (7.4 to 8.2) of open ocean seawater. It has been reported¹⁶ that several aluminum alloys, including 5052, show little effect of dissolved oxygen in the range from 30 to 1000 ppb, while the same alloys are sensitive to pH changes between 3.8 and 7.4. In addition, aluminum and aluminum alloys, because of their active nature,

Figure 1. Apparent Relation between Average Pit Depths of 5000 Series Aluminum Alloys and the Oxygen Concentration of Pacific Ocean Seawater⁸

Figure 2. Hydrographic Data as a Function of Depth at the Site from which the Deep Pacific Ocean Corrosion Data Were Taken¹⁹

are known to scavenge heavy metals from aqueous solutions.²³⁻²⁵ Cupric ions in particular can cause pitting of aluminum alloys in freshwater if present in concentrations exceeding about 0.1 ppm.^{23,24} Since OTEC plants may be using copper-nickel intake screening upstream of the evaporator and perhaps the condenser as well, it is important to establish the lower threshold concentration of Cu^{++} apt to cause pitting of alloy 5052 and 99.99% aluminum in seawater.

Each of the variables discussed above can influence the overall corrosion rate by affecting (a) the induction time for pitting and crevice corrosion to initiate or (b) the rate of pit or crevice growth after initiation. The initiation of pits on a free surface is thought to occur only at potentials noble to a well-defined critical potential.²⁶ This potential represents that at which Cl^- ions succeed in disrupting the passive film at local sites, leading to a high rate of dissolution. A pit then nucleates at this site where passivity has broken down. Once initiation has been accomplished, the active anode inside the pit would be expected to supply current for polarizing the metal in the active direction, away from the critical potential. This expectation agrees with field observations that the 5000 series aluminum alloys undergo pitting while their corrosion potentials are several hundred millivolts active to the critical value.^{13,14}

If current theoretical concepts are correct, then the corrosion potential of the metal must rise to the critical value before pitting can initiate. The causal agent for the noble shift is clear if a source of Cu^{++} ions is present, but is uncertain in the absence of copper. One possibility is the rather large transient shifts in potential that are experienced upon initial immersion of any metal into an electrolyte. What is not known is how long the corrosion potential must remain at, or noble to, the critical value in order to nucleate stable pits. If transient potentials do play a role in meeting the requirement for a noble shift in corrosion potential, then the required duration of that noble potential must be brief, as transient potentials decay quickly. The question of duration of the noble potential is one that is not addressed by the experiments described in this report, but which should be the subject of future research. It should be emphasized here that it is only the initiation of pits that is believed to require a noble shift of the corrosion potential to the critical value. Subsequent propagation of the pits may occur at less noble potentials.

In contrast, crevice corrosion is not initiated at a specific potential.²⁷ It occurs at sites of restricted geometry where breakdown of passivity is induced by a localized reduction of oxygen concentration coupled with the accumulation of acid anodic corrosion products such as aluminum chloride. These changes may be brought about through the operation of differential oxygen concentration cells acting at crevices. In an OTEC heat exchanger, crevices may be present at the interfaces between tubes and the tube sheet, or they may be created by deposits of fouling organisms. Although the initiation of pitting and crevice corrosion takes place by different mechanisms as described above, the rate of corrosion subsequent to initiation is controlled in each case by the rate of oxygen reduction or hydrogen evolution at cathodic sites on the metal surface.²⁶

The first part of the experimental program described in the following sections was to establish the effects on the corrosion potential of dissolved oxygen, pH, temperature, and heavy metal ion concentrations when varied both independently and in combination. Next, effects on the critical pitting potential were determined. The critical potential is already known to be unaffected by dissolved oxygen and heavy metals.²⁵ Following this, effects on the initiation of pitting and crevice corrosion were determined by simple immersion tests under controlled conditions. Finally, the rate of corrosion after initiation was determined by measuring the current density upon cathodic polarization of an aluminum electrode either in a galvanic corrosion cell formed with a suitable anode or by potentiostatic methods. In this final set of experiments, an increase in cathodic current density upon changing the dissolved oxygen, pH, etc. from values characteristic of surface water to those of deep water was taken as a measure of increased pit and crevice growth rates under corresponding conditions in the deep ocean. Conversely, a decrease in current density was taken as an indication of decreased pit and crevice growth rates. Most of the data presented are concentrated on alloy 5052 because of the likelihood of its use in OTEC systems, while 99.99% aluminum serves as a comparative standard or control.

II. EXPERIMENTAL TECHNIQUES

The results reported in this paper were generated on cylindrical laboratory electrodes 2 to 5 cm long and 0.6 to 0.95 cm in diameter mounted with

a Teflon* compression gasket to avoid crevice effects. The 5052 alloy electrodes were either machined from 6.35-mm-thick rolled sheet with the rolling direction parallel to the axis of the cylinder or cut from 9.5-mm-diameter extruded rod, both supplied by Reynolds Metals Company. The 99.99% aluminum was purchased from Materials Research Corporation as 9.5-mm-diameter rod. Table I shows the analyses of these materials provided by the suppliers.

In order to obtain reproducible corrosion potentials, it was necessary to strictly control the specimen preparation procedure, and the following sequence was finally adopted. A uniform surface was provided for all electrodes by abrading through 600-grit emery paper followed by pickling for 20 minutes in 20% nitric acid at 50 to 60°C, dipping in 1N sodium hydroxide for 5 seconds at 50 to 60°C and rinsing in distilled water. After pickling, all electrodes were aged for one hour in distilled water before insertion into the test cell. After pickling and again after aging, all electrodes were examined at a magnification of 25X in a stereo microscope. Any electrode on which pits were found was recycled through the abrasion and pickling steps before using.

Three percent NaCl solutions were made from distilled water with a resistivity greater than 0.8 megohm and certified grade NaCl from Fisher Scientific Company. The seawater used was full strength (32 to 35‰ salinity) clean surface water brought to the laboratory in 55-liter polyethylene jugs from 40 to 100 miles east of the mouth of Delaware Bay at two to three-week intervals by the research vessel, Cape Henlopen. The seawater was kept in an air-conditioned compartment on the ship and arrived in the laboratory within 24 hours after removal from the ocean. Once in the laboratory, the water was passed through glass fiber and 0.2-μm membrane (Millipore) filters in series to remove detritus and most marine microorganisms and was kept aerated. The aluminum electrodes behaved consistently in this water for about 21 days, but the behavior often began to change during the fourth week.

Corrosion potentials of the test electrodes were measured against a saturated calomel reference electrode (SCE) using a high impedance Keithly Model 602 electrometer. The dissolved oxygen concentration was controlled between 0.6 ppm and air saturation by bubbling the proper air-nitrogen

* Trademark. E. I. duPont de Nemours & Company, Wilmington, DE 19898.

TABLE I
Composition of Alloys Used

Component	99.99% Aluminum* (ppm)	Alloy 5052+ (%)
Silicon	3.50	0.08
Iron	1.20	0.19
Copper	0.05	0.01
Manganese	NT	0.02
Magnesium	1.00	2.44
Chromium	0.25	0.20
Nickel	<0.30	0.02
Zinc	<0.18	0.01
Lead	<0.25	<0.01
Tin	<0.64	<0.01
Titanium	0.40	<0.01
Zirconium	0.95	NT
Sodium	<0.50	NT
Oxygen	10.00	NT
Nitrogen	<5.00	NT
Hydrogen	<1.00	NT
Aluminum	Balance	Balance

*Material and analysis supplied by Materials Research Corporation.

+Material and analysis supplied by Reynolds Metals Company.

NT - Indicates component not tested for.

mixture from a premixed compressed gas cylinder through the electrolyte. Oxygen concentrations were measured using a YSI Model 57 oxygen meter.

The pH of the electrolyte was controlled either by small additions of 0.1 N HCl or NaOH (0.01 N in 3% NaCl) or by varying the partial pressure of CO₂ in the air-nitrogen mixture described above using flow meters. Control was achievable by the acid-base method to better than ± 0.05 pH units, and by the CO₂ method to ± 0.02 pH units. The CO₂ method was nearly always used in seawater, while the acid-base method was frequently used in NaCl solutions. The temperature of the test cell was controlled by pumping precooled alcohol through a glass cooling coil inserted into the electrolyte. Pre-cooling was done with an FTS Systems Model MC260SV Cooling Unit. Control was achieved to better than 0.5°C over the temperature range from 4 to 25°C. In all cases where no specific temperature is given, the test was run at room temperature (22 to 25°C).

Pit and crevice initiation tests were run in wide mouth 500-ml Erlenmeyer flasks. For tests at air saturation these were left open to the atmosphere. Tests at lower values of dissolved oxygen were run by bubbling the proper air-nitrogen mixture through a flask fitted with a rubber stopper through which were inserted the electrode holder, a gas bubbler for the appropriate nitrogen-oxygen mixture, a salt bridge and a gas outlet tube. For long-term low oxygen tests, the cell was sealed off by closing a stopcock on the gas inlet tube and plugging the outlet with a closed end glass tube. The freshly pickled and aged electrode was immersed in the seawater after the dissolved oxygen reached equilibrium (usually about one hour). Smooth electrodes were used for pit initiation tests. Similar electrodes were used for the crevice tests with the crevice being formed by slipping a single rubber "O-ring" around each electrode.

Corrosion potentials of the test electrodes were measured at least daily on the SCE scale as described above. Each test was terminated as soon as the white aluminum hydroxide corrosion product was visible at a pit initiation site on the cylindrical surface of the electrode or adjacent to the rubber "O-ring" creating the test crevice. After the corrosion product was cleaned off by gently brushing under distilled water, corrosion was confirmed by examination in a stereo microscope.

Critical pitting potentials and cathodic polarization curves were measured with standard potentiostatic techniques^{28,29} in a 1000-ml six-neck polarization

flask containing natural seawater or 3% NaCl using either a Princeton Applied Research Model 173 or a Wenking Model 70TS1 potentiostat. The final value for the critical pitting potential was taken as the most noble potential that could be maintained for at least 12 hours with neither an increase in current density nor the development of pits on the electrode surface large enough to be observed at a magnification of 25X in a stereo microscope.

In the cathodic polarization experiments, the freshly pickled and aged electrode was allowed to come to steady state (usually about one hour after immersion) in seawater or 3% NaCl in which the pH and dissolved oxygen were being controlled as described above. No stirring was used during the test other than the mild agitation provided by the gas bubbler. The pH was continuously monitored during each run using a Fisher Accumet Digital pH meter with a combination pH electrode mounted through one of four outside necks of the flask. Polarization began from the steady-state corrosion potential in discrete steps of 25 mV every five minutes in the active direction until the cathodic current density reached about $10 \mu\text{A}/\text{cm}^2$. Sets of cathodic polarization curves at successively more acidic pH values were run in three different ways: (a) all on the same electrode without repickling between runs of a series, (b) using a freshly pickled and aged electrode for each new pH value, or (c) using a freshly pickled and aged electrode for each potential level within each curve.

Cathodic polarization was also achieved by the alternative method of connecting the test electrode to a more active metal in a galvanic cell. In these experiments, alloy 5052 was coupled to a zinc electrode through an external circuit. Dissolved oxygen and pH within the cell were controlled as described previously, and the steady-state cell current was measured using a zero resistance ammeter. The pH and/or dissolved oxygen of the test solution was then changed and a new steady-state current measured. A steady pH value was maintained by connecting the test flask to a gravity feed flow-through system having two large reservoirs, one adjusted to the initial and the other to the final pH desired. After measurements were made at the initial pH, a stopcock was turned to draw water from the other reservoir at the final pH.

The effects of heavy metal ion concentrations on both the corrosion potential and on pit initiation were measured by adding the proper concentration directly to the seawater in the test flask. Copper and iron were added as the sulfate salt, and iron was also introduced in one experiment by

allowing a piece of steel to corrode in the bottom of the test flask for 48 hours. The actual concentration of free Cu^{++} ions was not measured. Corrosion potentials were monitored as described previously, and the presence or absence of pits was confirmed by examination in a low-power microscope.

III. RESULTS

A. The Critical Pitting Potential

The critical pitting potential of alloy 5052 in seawater of salinity 32‰, pH 8.2 and 25°C, was measured by standard techniques and found to be -0.69 ± 0.01 V on the saturated calomel (SCE) scale. In seawater of salinity 35‰ or in 3.5% NaCl, the measured value was slightly more active at -0.72 ± 0.015 V SCE. Measurements were also made at pH values of 7.8 and 7.5 and at temperatures of 4 and 10°C, but any differences fell within the experimental error mentioned above. Therefore, since the critical pitting potential is not a function of dissolved oxygen,²⁵ pH or temperature, it will not vary with depth and can be eliminated from consideration as a factor responsible for increased corrosion rates of aluminum in the deep ocean.

B. The Corrosion Potential

Data illustrating how the corrosion potential of alloy 5052 varied with dissolved oxygen at pH 8.2 and with pH at air saturation over the range in which these variables are found in the open ocean are shown in Figure 3. Decreasing dissolved oxygen made the corrosion potential more active while decreasing pH made it more noble. The slope of the dissolved oxygen curve was always positive, the corrosion potential becoming more noble at the rate of 50 ± 5 mV for each ppm increase in dissolved oxygen. For pH, the slope was always negative with the corrosion potential becoming more active with rising pH at the rate of -37 ± 5 mV for each 0.1 pH unit down to pH 7.5. Below 7.5 the rate of change decreased because the corrosion potential began to approach the critical pitting potential. The vertical error bars shown in Figure 3, and throughout this report except where stated otherwise, represent the envelope of all data observed rather than the standard deviation.

Corrosion potential measurements were also made at the four combinations of pH and dissolved oxygen shown in Table II. The corrosion potential of 5052 Al as a function of these conditions is shown in Figure 4. The corrosion potential became more noble with the progression of decreasing pH and dissolved oxygen pairs shown in Table II. The data in Figure 4 are a composite of four

TABLE II

Approximate Ocean Depth Ranges Corresponding to
Experimental Combinations of pH and Dissolved Oxygen

pH	Temperature (°C)	DO (ppm)	Depth (m)
8.20	15.0	7.2-7.5	Surface
7.85	8.5	3.1	150 to 200
7.65	7.0 or 3.0	1.3	350 to 380 or 1060 to 1300
7.50	4.0-5.0	0.6	500 to 900

Figure 3. Effect of DO at pH 8.2 and of pH at Air Saturation on the Corrosion Potential of Alloy 5052 in Seawater

Figure 4. Effect of Combinations of pH and DO Found in the Deep Pacific Ocean (See Figure 2 and Table II) on the Corrosion Potential of Alloy 5052 in Seawater

individual runs, whose average corresponding to the curve drawn through the data is similar in shape to the pH curve of Figure 3. As is seen in Figure 3, the pH and DO effects were in opposition, but Figure 4 shows that the pH effect predominated when both were varied together. In these tests, the corrosion potential was always active to the critical pitting potential. This is in contrast to the case of decreasing the pH alone as shown in Figure 3, where the critical pitting potential was sometimes approached during the experiment.

The effect of decreasing temperature on the corrosion potential of alloy 5052 in air-saturated seawater at pH values of 7.7 and 8.2 is shown in Figure 5. As was the case for pH alone, a decrease in temperature, with all other factors held constant, causes the corrosion potential to shift in the noble direction. At air saturation, a decrease in temperature to 4°C is alone sufficient to raise the corrosion potential to within 20 mV of the critical pitting potential at pH 7.7, or to within 150 mV at pH 8.2. Decreasing the dissolved oxygen at the same time as temperature, however, reduces the amount of noble shift. The effect of a decrease in pH upon the corrosion potential of alloy 5052 in air-saturated 3% NaCl is shown in Figure 6. The shift in the noble direction with decreasing pH is about half that for natural seawater (see Figure 3) but does not disappear entirely. The corrosion potential at pH 8.2 is more noble than that in seawater at the same pH, while at pH 7.2 the corrosion potential is more active.

The corrosion potential of 99.99% aluminum in seawater as a function of pH at air saturation and dissolved oxygen at pH 8.2 is shown in Figure 7. The direction of potential shift with decreasing pH and dissolved oxygen was the same as for alloy 5052 but the effect was not as large. The slope of the pH curve for 99.99% aluminum was -18 ± 3 mV per 0.1 pH unit and that of the dissolved oxygen curve was $+12 \pm 3$ mV per ppm.

Several anions and cations were added to 3% NaCl in an attempt to make the corrosion potential in that solution behave as it does in natural seawater. Nitrates, silicates and phosphates were added as the sodium salt at concentrations up to 80 μ moles per liter of solution. These produced no reproducible effect that was not within the experimental error shown in Figure 6. Additions of 140 ppm HCO_3^- ion as the sodium salt, however, made the corrosion potential more noble at pH 7.2 and more active at pH 8.2. At all pH values between and including these two extremes, the corrosion

Figure 5. Effect of Temperature at Two pH Values on the Corrosion Potential of Alloy 5052 in Air-saturated Seawater

Figure 6. Effect of pH on the Corrosion Potential of Alloy 5052 in 3% NaCl

Figure 7. Effect of DO at pH 8.2 and of pH at Air Saturation on the Corrosion Potential of 99.99% Aluminum in Seawater

potential closely reproduced that for alloy 5052 in natural seawater (see Figure 3). Additions of calcium to 40 ppm and magnesium to 1270 ppm both as the chloride produced no effect on the corrosion potential when added singly. Neither did simultaneous additions of calcium and magnesium alter the effect of HCO_3^- .

C. Pit and Crevice Initiation

The length of exposure to natural seawater necessary to initiate pitting and crevice corrosion was measured as a function of pH and dissolved oxygen concentration of the seawater. For alloy 5052, both pitting and crevice corrosion initiated on some of the samples in less than 15 days at pH 8.2, and the initiation times became shorter and more consistent as the pH decreased from 8.2 to 7.4. This is illustrated in Figures 8a and 8b where the solid points represent the average of all pit or crevice initiation times for those electrodes on which corrosion began in less than 30 days at a given pH, and the error bars represent the standard deviation. As soon as pitting had initiated, white specks of corrosion product were visible to the naked eye on the electrode surface and small spherical pits were observable under a low-power stereo microscope. Each time pitting was visible on the surface, the potential of the electrode had shifted to -0.7 ± 0.02 V on the saturated calomel scale. This agrees closely with our measurements of the potentiostatic critical pitting potential of alloy 5052 under the same experimental conditions. All tests represented by Figure 8 were stopped after corrosion started or after 30 days, whichever was shorter. At pH 8.2, 70% of both the pit and crevice tests had not begun to corrode within 30 days. At pH 7.6, 12% of the pit initiation tests and one of the crevice initiation tests did not corrode within 30 days, but all tests, both pit and crevice, at pH 7.8 and 7.4 initiated within that time period. Several of the pit and crevice tests at pH 8.2 that survived the first 30 days without initiation were continued for longer times, and had still not begun to corrode after 12 months of continuous immersion.

Pit and crevice initiation times on alloy 5052 were prolonged at pH 8.2 and dissolved oxygen concentrations below air saturation. Corrosion did not initiate within the 30-day test period on any of the electrodes at dissolved oxygen concentrations of 3.1, 1.3, or 0.6 ppm. From these results, it is evident that decreased oxygen concentration in the deep ocean cannot be

Figure 8. Effect of pH on Initiation of Pitting and Crevice Corrosion of Alloy 5052 in Air-saturated Seawater. Horizontal error bars represent the standard deviation.

responsible for a decrease in pit or crevice initiation times, while a decrease in pH could produce that effect.

In contrast to the behavior of alloy 5052, 99.99% aluminum resisted pit initiation for more than 30 days at dissolved oxygen levels from air saturation to 0.6 ppm and at pH values from 8.2 to 7.4. The corrosion potentials of all 99.99% aluminum electrodes remained active at about -1.4 ± 0.05 V SCE, and the surface was found to be free of pits under a stereo microscope at a magnification of 25X. One test in air-saturated seawater at pH 8.2 was run for more than 18 months. A heavy oxide film built up but there is still no sign of either pitting or crevice attack.

Crevice initiation tests have been run on 99.99% aluminum at pH values of 8.2, 7.8, 7.6, and 7.4, and crevice initiation has not taken place within 30 days at pH values more basic than 7.6. One test out of five at pH 7.6 initiated in one day, and three tests out of six at pH 7.4 initiated in 1, 3, and 33 days, respectively.

D. Heavy Metal Sensitivity

In clean seawater with residual Cu^{++} concentration of about 0.2 ppb, as measured by atomic absorption spectrometry, alloy 5052 pitted within 15 days (Figure 8). Figure 9 shows that addition of as little as 30 ppb Cu^{++} as CuSO_4 will reduce pit initiation times even further, but this is probably not of engineering significance to OTEC. In contrast, 99.99% aluminum, which does not pit in clean seawater, can be made to pit in less than one day by the addition of 0.2 ppm Cu^{++} . The long-term lower threshold of Cu^{++} for pitting of 99.99% aluminum is not well defined by the data in Figure 9, but appears to be about 40 ppb. It is possible that the threshold may be even lower. A series of long-term tests in air-saturated seawater at pH 8.2 and Cu^{++} ion concentrations of 1, 4, and 10 ppb showed no pitting after 6 months but by 18 months some broad shallow pitting had developed sporadically at all three concentrations. These tests are inconclusive but they may indicate that even 1 ppb of copper is too much over a long-term immersion. These values are considerably lower than the 0.1 ppm that would have been predicted from work in fresh waters. These data may be significant if pure aluminum is considered as a cladding material for OTEC heat exchanger surfaces, or if it is decided to use 90-10 copper-nickel screening on the warm water intake. It was expected that Fe^{++} ions would also shift the corrosion potential in the noble direction and accelerate pit initiation.

Figure 9. Effect of Addition of Cu^{++} Ion to Seawater on the Time for Initiation of Pits on Alloy 5052 and 99.99% Aluminum. Solid points represent conditions under which pitting started, and open points, conditions under which no pitting occurred.

Addition of up to 5 ppm of Fe^{++} , both as the sulfate and from a piece of corroding steel, however, had no measurable effect on the corrosion potential of 99.99% Al over a period of three days. Effects of copper and iron on accelerating the growth rate of pitting have not yet been studied.

E. Pit and Crevice Growth

1. *Alloy 5052 in Seawater*

a. Effect of Dissolved Oxygen at pH 8.2. The cathodic polarization of alloy 5052 was measured at pH 8.2 as a function of dissolved oxygen concentration by both the galvanic couple (Figure 10) and cathodic polarization (Figure 11) techniques. In both Figures 10 and 11, it is evident that decreasing the dissolved oxygen while maintaining everything else constant leads to a decrease in the cathodic current density. Thus a decrease in dissolved oxygen in the deep ocean cannot be responsible for an acceleration of either pit or crevice propagation rates. In contrast to this behavior, is the effect of small changes in pH.

b. Effect of pH at Air Saturation. The effect of pH on the cathodic polarization of 5052 aluminum was determined by both the galvanic couple and potentiostatic methods. In the galvanic couple tests, the steady-state current density of alloy 5052 coupled to zinc in seawater was first determined at pH 8.2. The pH was then changed to a more acidic value, and a new steady-state current density was measured. Figure 12 shows the ratio of the current density at the test pH to that at pH 8.2 as a function of the test pH. Each point plotted is the average of several runs. Individual ratios varied from 1.12 to 5.29 but were always greater than one, and were steady over the one to two-hour time period over which each test was run. This result was independent of the direction of the pH change. If the test pH was established first, then a reduction in current density was observed upon changing the pH to 8.2.

In order to eliminate the possibility that the observed changes were taking place on the zinc electrode rather than on the aluminum, these experiments were run with an alumina thimble around the zinc electrode to isolate it from the pH change. The increase in current observed upon decreasing the pH from 8.2 to 7.6 is shown in Figure 13. The experiment was then repeated with the thimble around the aluminum electrode, and apart from a brief transient there was no lasting change in current upon decreasing the pH.

Figure 10. Effect of DO on the Cathodic Current Density on Alloy 5052 Coupled to Zinc in Seawater at pH 8.2

Figure 11. Effect of DO on the Cathodic Polarization of Alloy 5052 in Seawater at pH 8.2

Figure 12. Increase in Current Density with Decreasing pH on 5052 Aluminum Coupled to Zinc in Air-saturated Seawater. Numerals beside each point represent the number of runs for which that point is the average.

Figure 13. Influence of Sudden pH Change on the Current Density for an Alloy 5052-Zinc Galvanic Couple in Seawater with the Zn and Al Electrodes Alternately Shielded from the pH Change

The pH effect was also observed by the potentiostatic method. Figure 14 shows a series of cathodic polarization curves of alloy 5052 in natural seawater all run on the same electrode at successive pH values of 8.2, 7.8, 7.5, and 7.2 using HCl control. Note that as the pH is decreased, the corrosion potential shifts in the noble direction (in agreement with Figure 3), and that each curve is progressively shifted toward higher current densities for any given value of the potential. Figure 15 shows the experimental variability encountered when a freshly pickled electrode is used for each curve at pH values of 8.2 and 7.2. The error bars represent the scatter in potential that was observed over at least five curves run under the same conditions. Also shown on Figure 12 are data (open points) taken by using a freshly pickled and aged electrode for each potential level within each curve. These data fall within the experimental scatter for curves run on a single electrode. In comparing Figures 14 and 15, note that the curves for pH 7.2 and 8.2 converge slower when succeeding curves are all run on the same electrode. This effect is probably an experimental artifact produced as each pH condition effects the next curve in the sequence. For the most accurate and reproducible data, separate electrodes should be used for each curve as was done in Figure 15. The pH 7.2 curve was repeated using both HCl additions and CO₂ partial pressure to control the pH. At current densities less than about 4 $\mu\text{A cm}^{-2}$, the differences fell within experimental error (Figure 16) and either method of pH control can be used.

c. Synergistic Effects of Oxygen, pH and Temperature. The strong systematic effect of pH on the cathodic polarization behavior of alloy 5052 at air saturation was somewhat modified at lower dissolved oxygen concentrations. The effect of reducing the dissolved oxygen to 3.0 is shown in Figure 17, in which the shaded areas represent the envelope of the data from Figure 15 for comparison. The data at pH 7.2 are not altered by the dissolved oxygen decrease, but the corrosion potentials at pH 7.7 and 8.2 are made more active. As the dissolved oxygen decreased still further to 0.6 ppm, the corrosion potentials became even more active. In addition, the slopes of the cathodic polarization curves at low current densities and low pH values became steeper.

When temperature was included as a variable in the cathodic polarization experiments, the results shown in Figures 18 through 20 were obtained. At 7.2 ppm dissolved oxygen and 4°C, the corrosion potentials at all pH values became noble (Figure 18), as would be expected from Figure 5.

Figure 14. Influence of pH on Cathodic Polarization of Alloy 5052 in Air-saturated Seawater. All curves were run in succession on the same electrode.

Figure 15. Experimental Variability of the Influence of pH on Cathodic Polarization when Using (1) a Separate Electrode at Each pH Value or (2) a Separate Electrode at Each Potential Level within Each Curve (Open Points)

Figure 16. Comparison of Cathodic Polarization Data in Air-saturated Seawater at pH 7.2 as Controlled by HCl Additions and by CO₂ Partial Pressure

Figure 17. Effect of pH on Cathodic Polarization of Alloy 5052 in Seawater with 3 ppm DO at $23 \pm 2^\circ\text{C}$. Shaded area represents the envelope of data from Figure 15.

Figure 18. Effect of pH on Cathodic Polarization of Alloy 5052 in Seawater with 7.2 ppm DO at 4.0°C . Shaded area represents the envelope of data from Figure 15.

Figure 19. Effect of pH on Cathodic Polarization of Alloy 5052 in Seawater with 5.0 ppm DO at 15°C. Shaded area represents the envelope of data in Figure 15.

Figure 20. Effect of pH on Cathodic Polarization of Alloy 5052 in Seawater with 0.6 ppm DO at 4.0°C. Shaded area represents the envelope of data in Figure 15.

This proved to be a highly corrosive set of conditions, especially at low pH. The envelope of the data from Figure 15 is shown for comparison. While the curve at pH 7.2 is not changed by the low temperature, at pH 7.7 the combination of reduced pH and low temperature caused the corrosion potential to exceed the critical pitting potential. On every trial attempted at DO 7.2 ppm, pH 7.7 and 4°C, the corrosion potential rose to the critical value within one-half hour after immersion in the test cell, and pitting began on the cylindrical surface of the electrode before it had equilibrated sufficiently to begin polarization. It is not known why conditions were more corrosive at pH 7.7 than at pH 7.2.

Figure 19 shows the cathodic polarization data at intermediate values of temperature (15°C) and dissolved oxygen (5.0 ppm). This set of conditions was nearly as corrosive as that at pH 7.7 in Figure 18. The lower temperature compensated for the reduced dissolved oxygen, and again the corrosion potentials were near the critical pitting potential. At pH 7.2, the corrosion potential often reached the critical value causing pitting to occur before the run could be started as described above. The curve at pH 7.2 in Figure 19 appears to be anomalous. The corrosion potential is very noble, and one would expect the curve to show higher current densities at all potentials (that is, have a shallower slope) than that at pH 7.7. It is suggested that pitting began just as this run was started, and the current supplied by the active pit tended to polarize the electrode in the same direction as the potentiostat, thereby making the applied potentiostatic current artificially low. The data at both low temperature (4°C) and low oxygen (0.6 ppm) are shown in Figure 20. Such conditions appear to be less corrosive than those of Figures 18 and 19. The corrosion potentials are less noble due to the very low oxygen, and the curves at all pH values show rapid polarization.

Figure 21 summarizes cathodic polarization data approximating three of the open ocean conditions shown in Table II (see Figure 2) as well as the hypothetical 15°C, 5.0 ppm DO, pH 7.7 curve from Figure 19. Note that at any given potential, noble to -1100 mV SCE, the current density is highest for the two curves at the intermediate values of temperature, pH and oxygen.

In Table III is presented a summary of all the cathodic polarization data from Figures 15 through 21 plus several other DO, pH and

Figure 21. Cathodic Polarization of Alloy 5052 in Seawater at Combinations of pH, DO and Temperature in the Deep Ocean (See Figure 2 and Table II)

TABLE III

Summary of Polarization Data for Alloy 5052

Temperature ($^{\circ}\text{C}$)	DO (ppm)	pH	Corrosion Potential (mV SCE)	$i(\mu\text{A cm}^{-2})$ at -1080 mV
22	Air saturation	8.2	-1040	1.0
		7.7	- 850	2.3
		7.2	- 725	4.0
	5.0	8.2	-1140	0
		7.7	- 845	2.4
		7.2	- 735	2.4
	3.0	8.2	-1170	0
		7.7	- 820	1.3
		7.2	- 715	4.1
15	5.0	8.2	- 805	3.3
		7.7	- 750	4.4
		7.2	- 700 (Pitted)	(1.1)
	3.0	8.2	- 840	0.8
		7.7	- 805	1.4
		7.2	- 750	2.7
8.5	3.0	7.8	- 770	1.4
4.0	7.2	8.2	- 880	1.2
		7.7	- 700 (Pitted)	-
		7.2	- 725	3.9
	5.0	8.2	- 825	2.1
		7.7	- 775	1.4
		7.2	- 750	1.2
	3.0	8.2	- 860	1.3
		7.7	- 750	0.4
		7.2	- 740	0.6
	0.6	8.2	- 840	0.5
		7.7	- 770	0.8
		7.2	- 750	0.3

temperature combinations not shown graphically. Each curve is characterized by its corrosion potential and by the current density (i) at a potential of -1080 mV SCE. The rationale for choosing -1080 mV is discussed later in this report. The trend within any set combination of DO and temperature is for the corrosion potential to become more noble and the current density at -1080 mV to become larger with decreasing pH. At 4°C and DO $\leq$ 5 ppm the current densities become very small and the trend with decreasing pH is reversed.

2. Alloy 5052 in 3% NaCl

In 3% NaCl at room temperature and air saturation, the effect of pH on cathodic polarization (Figure 22) is smaller than in natural seawater, but is still present at current densities up to about $1.5 \mu\text{A cm}^{-2}$. At higher current densities there is no significant difference between polarization curves at pH 7.2 and 8.2. The vertical error bars represent the envelope of the data from at least five runs at each pH, each using a freshly pickled electrode.

3. Cathodic Polarization of 99.99% Aluminum

When cathodic polarization data were repeated for 99.99% aluminum in seawater at room temperature, the results shown in Figures 23 and 24 were obtained. Corrosion potentials were more active as expected, and the effects of dissolved oxygen (Figure 23) and pH (Figure 24) were in the same direction as on alloy 5052, but smaller. The pH effect, in particular, disappears at current densities greater than about $2 \mu\text{A cm}^{-2}$.

IV. DISCUSSION

The objectives of this research were to determine what factors may have been responsible for the accelerated deep ocean corrosion rates of 5000 series aluminum alloys that have sometimes been observed and to assess what an increased corrosion rate might mean to an OTEC installation using alloy 5052 heat exchanger and condenser tubing. It would be well, at this time, to keep in mind that it is only the average pit depth for all 5000 series alloys that has been shown¹⁹ to vary according to Figure 1. As was pointed out in the Introduction, in-situ data for individual 5000 series alloys in the deep ocean are widely scattered and may or may not follow the trend shown by the average.

Our laboratory data presented in Figures 3 through 24 are consistent with both the average trend and the individual scatter. Our data strongly support

Figure 22. Cathodic Polarization of Alloy 5052 in Air-saturated 3% NaCl at $23 \pm 2^\circ\text{C}$

Figure 23. Effect of DO on Cathodic Polarization of 99.99% Aluminum in Seawater at pH 8.2

Figure 24. Influence of pH on Cathodic Polarization of 99.99% Aluminum in Air-saturated Seawater

the possibility of increased deep ocean corrosion rates for alloy 5052, while at the same time, allowing us to better understand why a great deal of individual scatter has also been observed. It is significant to OTEC, however, that our data predict that if greater depth resolution were available in Figure 1, the maximum corrosion rate would not necessarily coincide with the depth of the dissolved oxygen minimum, but would be located at some lesser depth, at intermediate values of oxygen, temperature and pH. Let us now take a closer look at the data to see how these conclusions were reached.

Although our data are consistent with increased corrosion rates in the deep ocean, they are not consistent with the idea^{8,19} that low dissolved oxygen concentrations in the deep ocean are responsible. A decrease in dissolved oxygen, all other factors held constant, reduces rather than increases the rate of pit and crevice growth as measured by cathodic polarization (see Figures 10 and 11). In addition, the data on pit and crevice initiation indicate that a decrease in dissolved oxygen prolongs rather than decreases the induction time. This means that a decrease in dissolved oxygen with depth in the Pacific Ocean cannot be responsible for an increased corrosion rate. On the other hand, a decrease in pH (again all other factors held constant) from the 8.2 characteristic of surface seawater, to 7.5, typical of deep Pacific Ocean waters, both reduces the induction time for corrosion to start (Figure 8) and increases current density for a given potential at cathodic sites (i.e. decreases polarization, Figures 14 and 15). The cathodic current density controls and is proportional to the observed corrosion rate at anodic sites,²⁶ and this means higher pit and crevice growth rates at low pH. The effect of a decrease in temperature, when varied independently, was to increase the probability of pit and crevice initiation by making the corrosion potential more noble (Figure 5), but to decrease the growth rate by making cathodic polarization more rapid.

More important to OTEC than these individual variations is what happens when pH, oxygen and temperature are varied together as they do in the real ocean. The necessary information is contained in the cathodic polarization curves of Figures 17 through 21; however, in order to relate these data to an OTEC plant, we must first have a calibration point. That is, we must determine at what value of potential the curves should be compared. Once this is known, current densities can be read directly from the appropriate curves and

converted to predicted average corrosion rates using Faraday's law, which relates weight of metal corroded per unit time to current density.

The needed calibration point is most easily deduced from weight-loss data. Using Faraday's law, one can calculate the average current density necessary to account for a given weight loss over a given period of time. From Godard's weight-loss data⁹ for alloy 5052 in Halifax, Nova Scotia surface water and Reinhart's data¹⁹ in deep Pacific waters, it was calculated that the appropriate average current densities are approximately 0.3 to 1.0 $\mu\text{A cm}^{-2}$ in surface water and 1.0 to 2.0 $\mu\text{A cm}^{-2}$ in deep Pacific water. The higher numbers in each of these ranges are from short-term (one year or less) data and the lower numbers from longer term data, probably reflecting a decrease in corrosion rate with time as corrosion product films build up.⁹

Returning now to Figure 21, where pH, dissolved oxygen and temperature are varied together, the potential corresponding to a current density of 1 $\mu\text{A cm}^{-2}$ on the curve for surface-water conditions (pH 8.2, DO 7.2 ppm) is about -1080 mV SCE. Presumably, the active pits have polarized the metal to this potential after they initiated at the critical pitting potential. Assume now that regardless of the initial environmental conditions, an active pit or crevice will always polarize the electrode to about this same -1080 mV. The intersections of each curve with a horizontal line at this potential can then be used to predict the cathodic current density under conditions corresponding to the curve of interest. The approximate Pacific Ocean depths corresponding to the curves in Figure 21 were shown in Table II. The intersection of the horizontal line at -1080 mV with the curve corresponding to the DO-pH minimum is at 0.3 $\mu\text{A cm}^{-2}$. This predicts that pit and crevice growth rates will be slower here than at the surface. This does not necessarily mean lower overall corrosion rates than at the surface, however, because the corrosion potential at conditions corresponding to the DO-pH minimum is only about 50 mV active to the critical pitting potential. Such a noble corrosion potential may encourage more rapid pit initiation than in surface water where the corrosion potential is 300 mV more active. It is difficult to say in any given situation whether initiation or growth will be more important, and this uncertainty could account for some of the scatter that has been observed in the data from field tests.¹⁹

The two curves in Figure 21 that correspond to intermediate values of pH, DO and temperature both show current densities at -1080 mV higher than those for surface-water conditions. In addition, these two curves also start from noble corrosion potentials. Both initiation and growth will be accelerated under these conditions, therefore, and overall corrosion rates are expected to be larger than at the surface. This is the basis on which it was concluded that our data are consistent with increased corrosion rates in the deep ocean, but that the maximum rate should occur at a lesser depth than that of the dissolved oxygen minimum.

In general, the most corrosive conditions encountered in these experiments were ones combining low temperature and low pH with high dissolved oxygen. These conditions encourage both noble corrosion potentials, which can lead to rapid initiation, and increased cathodic current densities, which lead to higher growth rates. It is fortunate for OTEC that this most corrosive set of conditions is almost never found together in the real environment. Low dissolved oxygen and low pH are closely coupled in the ocean. The dissolved oxygen minimum is caused by biological decay of descending organic matter. This process not only consumes oxygen but also produces CO_2 , which simultaneously keeps the pH low.³⁰ In the Pacific Ocean, low temperature and low pH occur together but the oxygen is also low, which reduces the corrosivity. In the deep Atlantic Ocean, high oxygen can be found together with low temperature but now the pH, which is coupled to dissolved oxygen, will be high,³⁰ again reducing the corrosivity. Since the most corrosive combination of low pH and high DO does not occur naturally, Figure 21 predicts that the most corrosive natural conditions will be those in the midrange of all three variables. Here, the temperature and pH are both low enough to make the corrosion potential noble, but the DO is still high enough to permit reasonably high growth rates. In the Pacific Ocean (see Figure 2) these conditions are most usually found at depths of 150 to 400 meters, while in the Atlantic they may be found at greater depths due to the higher overall levels of DO.³⁰ The data strongly suggest that OTEC should avoid locating either warm or cold water intakes at such depths.

To summarize our discussions so far, then, the general effects of pH, DO and temperature are as follows. Low pH encourages the initiation of both pitting and crevice corrosion and increases the growth rate. Low dissolved oxygen does the opposite. It both suppresses initiation and decreases the

growth rate. The effect of low temperature is mixed. It increases the tendency for initiation by shifting the corrosion potential in the noble direction but decreases the growth rate. The most corrosive naturally occurring combination of these variables is in the midrange of all three. Thus, an obvious recommendation is that (a) profiles of DO, pH and temperature be obtained at all potential OTEC sites, and (b) cathodic polarization curves at all appropriate sets of conditions be run before the design depths of warm and cold water intakes are fixed for any future OTEC plant.

Recent results reported by Munier and Craig³¹ are encouraging in that they encountered no pitting or crevice attack on heat exchanger tubing of either alloy 5052 or the less resistant 6061-T6 in the St. Croix OTEC corrosion experiments over a 72-day test period. Munier and Craig are quick to point out, however, that their results were obtained under ideal OTEC conditions of continuous flow, 27 to 29°C, 4 to 5 µg-atm/liter of dissolved oxygen and pH 8.0 to 8.2. Our results confirm that these are, indeed, the least corrosive of naturally occurring seawater conditions. The benefit to OTEC of maintaining a continuous flow is also demonstrated by their data in that a number of their initial corrosion potentials were more noble than the critical pitting potential at their salinity (about -0.725 volts Ag-AgCl), and yet they experienced no pitting. This should be attributed to the inhibitive effect on pit initiation of a continuous flow. Our results indicate that pitting would have occurred had their noble potentials been encountered under quiescent conditions. This indicates the importance to OTEC of maintaining constant velocity conditions in the heat exchanger tubing. Times when the unit is shut down for maintenance will be particularly critical--especially the initial installation period before protective corrosion products films have a chance to build up. If aluminum tubing is eventually chosen for OTEC, our data indicate that operational procedures should be developed that will prevent zero velocity conditions in the tubing from persisting for more than about 10 minutes during initial startup or 10 hours during subsequent shut-down periods. Some provision for complete drainage of the aluminum tubing should be provided in the design to accommodate longer shut-down periods.

Although some pit initiation is probably inevitable, short initiation times may not be of critical concern to OTEC because the rate of penetration of aluminum alloys by pitting in aqueous media are usually found to decrease with time. Godard et al.⁹ report that the maximum pit depth of aluminum in

fresh waters, and frequently also in seawater, varies with the cube root of time. This cube root relationship can be derived by assuming that a mature pit is spherical in shape and that its volume, or the weight loss of the specimen, increases linearly with time, t (i.e. $V \propto t$). Since the volume varies with the radius, r , cubed, the pit depth, d is proportional to $V^{1/3}$; and it follows that $d = 2r = Kt^{1/3}$, where K is a proportionality constant dependent on the specific material and environment.

Let us now see how the cube root law can be combined with our cathodic polarization data to develop a procedure for predicting the rate of penetration of OTEC tubing by pitting corrosion. If one takes the surface seawater weight-loss data published by Godard⁹ for alloy 5052 at Halifax, Nova Scotia, and plots it against exposure time, a straight line is obtained as seen in Figure 25. Since the weight loss is linear with time, the cube root relationship holds, and one is justified in applying this relationship to Godard's data in order to calculate the pit depth (or tube wall thickness required) as a function of desired service lifetime. If the weight loss falls off with time rather than remaining linear, then the following procedure will overestimate the wall thickness required.

First notice that in Figure 25, a straight line drawn through Godard's data does not pass through the origin. Godard cleaned his coupons with 50% phosphoric acid before measuring weight loss, and it is speculated that this resulted in each measurement being too high by a constant factor. Therefore, the curve has been translated down to pass through the origin, and the weight-loss data for the ensuing calculations will be taken from the dotted line. Assuming that all pits initiate simultaneously upon immersion, are the same size and are spherical in shape, the pit depths can be calculated as follows. The weight loss from Figure 25, density of aluminum, and volume of the pit are related by the expression,

$$\frac{\text{weight loss}}{\text{density}} = \text{volume} = \frac{4}{3} \pi r^3 = \frac{4}{3} \pi \left(\frac{d}{2}\right)^3,$$

where r is the radius of the spherical pit, and d is the pit depth. Solving for d and taking the density of aluminum to be about 2.7 g/cc, pit depths can be calculated as a function of time and the number of pits per unit area of surface (the pit density). The results appear in Table IV. Lifetimes are shown from 1 to 20 years, and pit densities are expressed both as a hypothetical total number of pits on Godard's 2-ft² coupons and as the number of pits

TABLE IV*

Wall Thickness of Tubing Required for
Various Lifetimes and Pit Densities

No. of Pits on 2-ft ² Coupon	No. of Pits per cm ²	Pit Depth or Wall Thickness (mm) Required, at Indicated Lifetime					
		1 yr	2 yr	5 yr	10 yr	15 yr	20 yr
1	5.3×10^{-4}	9.63	12.12	16.50	20.73	23.70	26.12
10	5.3×10^{-3}	4.47	5.63	7.64	9.62	11.02	12.12
10 ²	5.3×10^{-2}	2.08	2.61	3.55	4.45	5.11	5.63
10 ³	5.3×10^{-1}	0.96	1.21	1.65	2.06	2.37	2.61
10 ⁴	5.3	0.45	0.56	0.76	0.96	1.10	1.21
10 ⁵	5.3×10^1	0.21	0.26	0.35	0.45	0.51	0.56
10 ⁶	5.3×10^2	0.10	0.12	0.16	0.21	0.24	0.26

* Based on data of Godard (1967) for Halifax surface water. Assumes all pits initiate upon immersion, are the same size and are spherical in shape. For hemispherical pits, multiply all depths by 0.4.

Figure 25. Corrosion Weight-loss Data for Alloy 5052 in Halifax Seawater (from Godard)

per square centimeter of surface. In the first row of the table, all the weight loss from Figure 25 is considered to be the result of one single pit. In each succeeding row, the number of pits over which the weight loss is distributed is increased by an order of magnitude. It is realized that Godard's data are not strictly applicable to OTEC conditions because his panels were fouled, whereas OTEC heat exchanger surfaces will be kept clean. Godard's data have been used here as an example of what can be done, and any new sets of data that were done under OTEC conditions could be treated in the same manner.

The general methodology for prediction will be to use data such as those in Table IV from a well known set of conditions together with our cathodic polarization data to predict the relative rate of penetration under a new set of conditions. To illustrate how this might be done, suppose it is desired to keep the heat exchanger or condenser tube wall thickness no larger than 1 mm. For a pit density of $0.5/\text{cm}^2$, the lifetime would be one year. If however, one could induce $5.3 \text{ pits}/\text{cm}^2$, a lifetime of 10 years could be obtained. That such pit densities are realistic is implied by Godard's weight-loss and maximum pit depth data for alloy 5052 in Halifax seawater. A two-year exposure resulted in a maximum pit depth of 20 mils (about 0.5 mm) and a weight loss of 2.5 g (Figure 25). Table IV indicates that for a uniform pit depth of 0.5 mm and a two-year exposure, a pit density of $5.3 \text{ pits}/\text{cm}^2$ would be required to account for the weight loss reported. This type of data comparison is valid only if the pits are approximately spherical in shape. If the pits are broad and shallow, lower numbers of them would be needed.

Use of the type of data found in Table IV also allows one to take into account other factors such as nonuniform distribution of pit depths. If, as may be the case in actual service, the pits are not all the same depth, then it is necessary to know how much deeper than average the deepest pit is. This factor could be used as a multiplier for the depths shown in Table IV.

In a similar manner, the intersections of a horizontal line at -1080 mV with the polarization curves in Figure 21 could be used as multiplying factors for Table IV to account for the effects of pH, DO and temperature in the deep ocean. Again, if this method were to actually be used for penetration-rate predictions, Godard's data would have to be replaced by equivalent data run under actual or simulated OTEC conditions, and our surface seawater curve

from Figure 21 would have to be redone under those same conditions. The present data, however, serve well enough to illustrate the method.

Two other variables will need to be included before predictions of actual tubing lifetimes can be attempted. These are the velocity of fluid flow and the pit density. Velocity is expected, like temperature, to have two competing effects. An increase in velocity should suppress pit initiation, but once a pit gets started, the increase in transport of oxygen to cathodic sites on the surface may accelerate pit growth. This possibility may be particularly serious under deep ocean conditions where increased transport of dissolved oxygen by the velocity in the OTEC tubing may artificially create the most corrosive combination of low pH, low temperature and high oxygen.

Pit density data for 5000 series alloys in the deep Pacific Ocean reported by Reinhart¹⁹ are scattered over one and one-half orders of magnitude. Figure 26 shows these data plotted against pH. The scatter looks about the same when the data are plotted directly as a function of depth. Godard⁹ does not give the pit density as such in his data on corrosion of 5000 series alloys in surface seawaters but it can be calculated approximately from the weight loss and average pit depth, which are reported. The results are no more consistent than those in Figure 26. Since the pit density data reported in the literature are so variable, it will probably be necessary for us to learn how to control it. An experimental program for doing this and for determining the effect of velocity on the cathodic polarization data has been proposed to OTEC by the present author, but has not yet been funded.

One additional factor remains to be discussed, and this is the concentration of heavy metal ions--especially cupric ion. Since initiation times for pitting of alloy 5052 in seawater without Cu^{++} additions are usually less than two weeks, shorter induction times in the presence of increased Cu^{++} are not of engineering significance. An increase in cupric ion concentration could, however, increase pit growth rates of alloy 5052 by creating a noble and more efficient cathodic surface for the reduction of dissolved oxygen. In the case of 99.99% aluminum, which is resistant to pitting in clean seawater, an increase in Cu^{++} could lead to both reduced induction times and to increased growth rates. This could be important if 99.99% aluminum or a similar alloy is used for cladding.

Figure 26. Pit-density Data Reported by Reinhart¹⁹ for Aluminum Alloys at the Pacific Ocean Test Site Plotted as a Function of Seawater pH.

Since it has been proposed to use 90-10 copper-nickel screening for the warm water intake, it is important that two things be established: (a) The threshold limit of copper below which pit and crevice growth rates of alloy 5052 and 99.99% aluminum will not be increased, and the pit initiation time for pure aluminum will not be decreased; and (b) The level of copper in the water passing through the evaporator resulting from use of a copper-nickel intake screen. If the threshold value in (a) is lower than the level of copper in (b) and if copper-nickel screening must still be used, then it will be necessary to measure a multiplying factor to use with Table IV in determining the proper tube wall thickness to withstand the accelerated growth rates. This can be done using present potentiostatic techniques.

In light of the above discussion, it is suggested that there are two alternative approaches to heat exchanger corrosion control for the OTEC project. These are (a) avoiding perforation of the tubing by inducing as many pits as possible and selecting the proper tube wall thickness as per the methodology outlined above, or (b) attempting to avoid pitting altogether by cladding and not allowing zero velocity conditions to develop. Based on our data, the chances of avoiding pitting altogether over a 10 or 20-year lifetime would seem rather slim. If this is true, then the pertinent engineering questions become (a) how thick does the tube wall need to be to withstand the most severe conditions at a given oceanic site as a function of pit density and desired lifetime, and (b) what can be done to induce a high density of pits or to control the pit density--especially on a structure the size of OTEC, and (c) what will be the effect of intermittent mechanical cleaning on pit initiation and propagation rates? Three general approaches that might be used to achieve a high and controllable pit density are (a) inducing pits by a timed pulse of applied anodic current, (b) application of a porous aluminum surface coating by electrolytic methods, spraying or powder metal technology, or (c) changing the conductivity or defect structure of the passive film by alloying. The solutions to these questions, put in context with economic considerations will determine whether or not alloy 5052 can successfully be used for OTEC heat exchanger tubing, and if so, whether the bare alloy can be used or a clad construction will be necessary.

V. CONCLUSIONS

1. The data presented are consistent with the increased corrosion rates reported in the literature for 5000 series aluminum alloys in the Pacific Ocean.
2. These increased rates are caused by a combination of decreasing pH and temperature with depth rather than by a lower dissolved oxygen concentration.
3. Decreasing the pH of seawater from 8.2 to 7.2 increases the corrosion rate of aluminum alloy 5052 by both encouraging pit initiation and increasing pit growth rates. Decreasing the dissolved oxygen concentration from air saturation to 0.6 ppm has the opposite but smaller effect. Limited data indicate that 99.99% aluminum behaves similarly but is affected to a lesser degree.
4. Polarization data predict that the maximum corrosion rate for aluminum alloy 5052 in the deep ocean may be greater than that reported by Reinhart and will occur at depths having intermediate values of DO, pH, and temperature (150 to 200 meters in the Northwestern Pacific).
5. The induction time for the initiation of pitting and crevice corrosion of alloy 5052 in clean seawater can be relatively short--on the order of days. For 99.99% aluminum, the induction times are longer, and there are indications that 99.99% aluminum may not corrode at all in the absence of heavy metals and at pH more basic than 7.6.
6. Due to the possibility of short induction times for corrosion initiation, in alloy 5052, it is suggested that OTEC consider the following alternatives: (a) avoiding pitting of the base metal altogether by cladding with 99.99% aluminum or an alloy that behaves similarly and designing to avoid zero velocity flow conditions, or (b) controlling perforation of unclad tubing by inducing as high a pit density as possible and selecting the proper wall thickness according to the procedure outlined in this report.

VI. RECOMMENDATIONS

1. Measure profiles and seasonal variabilities of DO, pH and temperature at all potential OTEC sites.
2. Obtain cathodic polarization data under all appropriate sets of conditions measured above before the cold and warm water intake design depths are fixed.

3. Using the polarization data above, avoid locating intakes at depths having the most corrosive sets of conditions. In most cases, it should be possible to locate the warm water intake above and the cold water intake below the most corrosive depth.

4. Fund the experiments already proposed on the effects of pit density and velocity so the predictive methodology can be ready to use when needed for design and location of large OTEC plants.

5. Fund experiments to determine the effect of intermittent mechanical cleaning on pitting.

6. Avoid copper-nickel components upstream of aluminum heat exchanger tubing if at all possible. If not possible, fund the experiments recommended in this report to determine whether increased corrosion will be a design consideration.

7. Design heat exchangers to avoid zero velocity flow conditions, and for complete drainage of the tubing in the event of shut-down periods longer than about half a day.

8. Carefully examine all proposed cleaning techniques, and when aluminum tubing is used, reject any that could lead to even a temporary combination of low pH and high DO on the seawater side of the tube.

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