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STUDY OF CORROSION AND ITS CONTROL IN ALUMINUM SOLAR COLLECTORS

Annual Report, June 1, 1977—July 31, 1978

By
D. Wong
F. H. Cocks
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August 1978

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Giner, Incorporated
Waltham, Massachusetts

U.S. Department of Energy

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ABSTRACT

The use of aluminum solar heat collectors with aqueous glycol solution as the heat transfer medium is potentially attractive but for the critical problem of corrosion. Such a corrosion problem must be resolved to prevent catastrophic plant failure. The goal of this program is then to develop and ascertain the requisite conditions under which such systems will survive a reasonable period of time.

In Phase I (June 1, 1976 - May 31, 1977) we have developed a non-destructive electrochemical technique (the linear polarization resistance method) to determine the overall aluminum corrosion rate under a wide range of conditions relevant to the operation of existing solar collector systems. Baseline aluminum corrosion data was obtained in 35 vol % aqueous ethylene glycol solutions at temperatures from ∿ 25 to ∿ 100°C. The effects of other parameters such as hydrodynamics, alloy compositions, impurities, dissolved oxygen and ethylene glycol decomposition products were also investigated. We have also collected and analyzed pitting data under laboratory conditions. Probable time to failure of a full size plant due to pitting perforation can be estimated by fitting the laboratory data into a cube root pit growth law and using Gaussian statistics.

It was concluded that aluminum and its alloys (1100 and 3003 series) possess marginal corrosion resistance in *pure* ethylene glycol solutions. When common contaminants (e.g. Cu^{+2}, Fe^{+3} and Cl^{-} ions) are present, the corrosion of aluminum surges to an *intolerable* level. Other parameters (such as hydrodynamics, dissolved oxygen and ethylene glycol decomposition products) did not seem to affect aluminum corrosion significantly. Aqueous ethylene glycol solutions cannot be used in aluminum solar collectors unless proper corrosion control methods (e.g. inhibitors) are used.

Phase II (June 1, 1977 - July 31, 1978) has been devoted primarily to the development of corrosion control methods for aluminum solar collectors using

ethylene glycol heat transfer fluids. Corrosion inhibitors and impurity scavengers have been tested and evaluated at temperatures up to 160°C under various laboratory conditions. A new corrosion rate measurement technique based on the use of thin foil samples was developed and adopted in this program to provide accelerated (yet undistorted) results.

In addition to the development of corrosion control methods, we have also extended the acquisition of baseline corrosion data to the aluminum/*propylene* glycol combination. Propylene glycol was chosen primarily because of its low toxicity. Aluminum corrosion characteristics were determined in 50, 85 and 100% propylene glycol solutions at temperatures between 25 to 160°C.

Corrosion behavior of aluminum in more concentrated *ethylene* glycol solutions (up to 100%) at higher temperatures (up to 160°C) was also obtained in order to broaden the baseline. The cube root pit growth law was also verified experimentally. All the parameters needed to predict the time to plant failure due to pitting perforation were also determined in the second phase of this program.

With regard to the aluminum/propylene glycol combination, aluminum alloys were found to be about ten times more corrosion resistant in propylene glycol than in ethylene glycol solutions under similar conditions. However, the presence of impurities such as Cu^{+2}, Fe^{+3} and Cl^{-} still causes rapid and serious corrosion attack unless proper corrosion control methods are implemented. The corrosion resistance of aluminum was also found to increase as the concentration of ethylene (or propylene) glycol solution increases.

An extensive literature review showed that phosphates, borates, nitrates and silicates and sodium mercaptobenzothiazole are effective corrosion inhibitors which are compatible with glycol solutions. It was determined that most inhibitor formulas, whether proprietary or prepared in-house, can reduce the overall aluminum corrosion rate to below 1 mpy *at temperatures below 100°C*, even when chloride, cupric and ferric ions are simultaneously present. Pitting corrosion is also completely suppressed. A preferred inhibitor composition (in g/liter) was found to be (4.5) $Na_3PO_4 \cdot 12\ H_2O$, (2.0) $NaNO_3$, (10.0) $Na_2B_4O_7 \cdot 5H_2O$, (1.5) $Na_2SiO_3 \cdot 9H_2O$, and (5.5) $C_7H_4NS_2Na$ for ethylene glycol. It was also recommended to add NaOH at 2.0 g/liter for pH adjustment purpose. This is known as Inhibitor Formula II in this program.

As the operating *temperature increases to 130°C*, several inhibited commercial solar collector heat transfer fluids began to fail. A surge in overall corrosion rate and the reappearance of pits were observed. Only Inhibitor Formula II and two other commercial automotive coolants remained effective at this temperature. At ∿ 160°C the overall aluminum corrosion rate exceeds the 1 mpy safety limit, even when exposed to 100% glycol (ethylene and propylene).

Both aluminum and zinc were selected as heavy metal ion scavengers. Aluminum powder was found to be less effective in the removal of cupric and ferric ions from glycol solutions than zinc. Both 1100 and 3003 series aluminum alloys were found to be free of any type of corrosion damage in uninhibited and contaminated (with Cu and/or Fe) glycol (ethylene and propylene) solutions at temperatures up to 130°C when zinc powder is added. Even at 160°C the aluminum corrosion resistance in such solutions still seems to be acceptable (although marginally so).

In addition to being an effective heavy metal ion scavenger, *zinc powder* was also found to protect aluminum from corrosion attack in ethylene and propylene glycol solutions with NaCl present. This is attributed to a cathodic protection type of mechanism rendered by the floating zinc powder in solution.

We have determined that zinc powder (2000 ppm) can be safely added to Inhibitor Formula II. The combined use of inhibitors and scavengers was found to provide *excellent corrosion protection* to aluminum. The corrosion rate was found to be less than 0.2 mpy at 130°C with Cu^{+2}, Fe^{+3} and Cl^- present.

I. INTRODUCTION AND SUMMARY

Solar thermal energy collector systems using aluminum roll-bond panels with aqueous ethylene glycol heat transfer fluids appear to have considerable economical advantages vis-a-vis other combinations of collector materials and heat transfer media. These advantages include low cost, low density, high thermal conductivity, and ease of fabrication of aluminum alloys, as well as the low cost, ready availability and the combined antifreezing and antiboiling properties of the glycol solutions. However, aluminum and its alloys are known to be susceptible to various types of corrosion in an aqueous environment once its protective oxide film is disrupted. Localized pitting corrosion is often to blame for early plant failure, especially in light gauge aluminum systems such as roll-bond aluminum panels (wall thickness is normally 30 mils).

An extensive review of open literature showed that very little information is available on aluminum corrosion in ethylene glycol solutions under conditions relevant to the operation of a solar collector system. It is, therefore, imperative to obtain such corrosion data in order to determine the extent of aluminum corrosion problems encountered in each case; corrosion control methods will then be developed and evaluated. The goal of this program is to clearly define the requisite conditions for obtaining satisfactory aluminum corrosion resistance in aqueous glycol solutions.

The initially proposed program was divided into two phases. Phase I (June 1, 1976-May 31, 1977) was addressed to the study of the corrosion of aluminum alloys in aqueous ethylene glycol solutions *without* the use of any corrosion control methods. Phase II (June 1, 1977-July 31, 1978) was primarily devoted to the development and evaluation of various corrosion control methods which are applied to the aluminum-glycol system.

A. Summary of Phase I

The corrosion characteristics of aluminum and some selected aluminum alloys in 35 vol % aqueous ethylene glycol solutions have been obtained experimentally using a non-destructive electrochemical technique (linear polarization resistance method). Pit depth was assessed via a quantitative metallographic measurement. The scope of this investigation covered the following range of conditions:

(1) four different aluminum compositions (i.e. 99.9% pure, 1100, 3003, and 3004 series aluminum);

(2) $\sim 25 - \sim 100^{\circ}C$;

(3) stagnant solutions, laminar and turbulent flows;

(4) aerated and de-aerated solutions;

(5) presence of common contaminants (e.g. Cl^-, Cu^{+2} and Fe^{+3} ions); and

(6) effects of ethylene glycol decomposition products.

In addition, the extent of galvanic attack and the susceptibility to stress corrosion cracking were also investigated for the aluminum ethylene glycol solution combination.

The significant findings are summarized as follows:

1. All four aluminum alloy compositions tested showed satisfactory corrosion resistance to uniform corrosion and *marginal* tolerance to pitting corrosion in *pure* aqueous ethylene glycol solution.

2. Cu^{+2} and Cl^- ions cause severe pitting damage, and Fe^{+3} ions accelerate uniform corrosion by a significant amount. The simultaneous presence of all species in solution will lead to catastrophic plant failure rapidly.

3. The temperature dependence of the measured corrosion rate is relatively small, with $\Delta H < 5$ Kcal/mole.

4. The presence of dissolved oxygen was not found to increase corrosion damage significantly. Hydrodynamic conditions and ethylene glycol decomposition products did not seem to affect the measured corrosion rates.

5. Stress corrosion cracking in aluminum solar collector panels made of relatively low yield strength alloys (e.g. 1100 and 3003 series aluminum alloy) does not appear to be a problem.

6. Galvanic attack on aluminum due to direct electrical contact with copper was found to be attributed to localized deposition corrosion. The corrosion rate depends on the anode (aluminum) to cathode (copper) surface area ratio, as well as the electrical conductivity of the solution. In *pure* ethylene glycol solution ($\sigma = 3.0 \times 10^{-6}$ mho/cm) such attack is negligible, even at 100°C; however, in the presence of impurities the corrosion rate increases rapidly and damage would be severe.

7. An aluminum alloy galvanic series in aqueous ethylene glycol solutions at 35% by volume has been established.

B. Summary of Phase II

We have prepared two inhibited ethylene glycol solutions (Inhibitor Formulas I and II) in the laboratory using the inhibitors developed primarily for automotive cooling systems. Nitrates, silicates, borates, phosphates and sodium mercaptobenzothiazole are used as corrosion inhibitors in these solutions. The pH of one of the solutions (Inhibitor Formula II) was adjusted to more alkaline to offset any detrimental effects from ethylene glycol decomposition products. This type of inhibited solution was found to provide satisfactory corrosion protection to aluminum alloys, even with all three species of contaminants present, at temperatures up to ∿ 100°C. Inhibitor Formula I was found to be undesirable due to the formation of a gel-like precipitate at high temperatures. Inhibitor Formula II with the following composition (g/liter): (4.5)$Na_3PO_4 \cdot 12H_2O$, (2.0)$NaNO_3$, (10.0)$Na_2B_4O_7 \cdot 5H_2O$, (1.5)$Na_2SiO_3 \cdot 9H_2O$, (5.5)$C_7H_4NS_2Na$ 50% solution, and (2.0)NaOH, was found to be effective at temperatures up to 130°C. At ∿ 160°C the corrosion rate of aluminum surges back up to above 1 mpy, and pitting corrosion (which was suppressed before) begins to reappear. Similar results were obtained using two commercial inhibited automotive coolants (ethylene glycol based).

After a careful evaluation of some commercially available glycol based "inhibited" solar collector heat transfer fluids (referred to as Inhibitors S1 and S2) we reached the conclusion that they can only be used at temperatures *below* 100°C.

This means that these solutions are probably "safe" when the collector fluid is in circulation. However, the fluid temperature can be expected to exceed 150°C at stagnation. At that temperature these fluids are extremely corrosive to aluminum. A concentrated inhibitor formula (Inhibitor C) was also found to be ineffective in preventing aluminum corrosion in glycol solutions. These commercial products are not recommended to be adopted to existing solar collector systems.

The use of a scavenger to remove deleterious contaminants from solution has been studied. The corrosiveness of the solution is expected to decrease as a consequence of the scavenging process. However, aluminum was found to be extremely susceptible to deposition type of pitting corrosion when cupric ions are present. In solutions with 0.2 ppm of Cu^{+2}, pits as deep as 90 μ were still observed on aluminum in two weeks. Zinc metal is an effective heavy metal ion scavenger. When used in powder form, it also protects aluminum from pitting despite the fact that chloride ions are present. This is attributed to a cathodic protection mechanism since zinc powder does come in electrical contact with aluminum in the corrosion cell. Zinc powder alone (in both ethylene glycol and propylene glycol) was found to be sufficient to protect aluminum alloys at temperatures up to 160°C.

Finally, a combination of corrosion inhibitors and zinc (Inhibitor Formula II and 2000 ppm zinc powder) was found to render excellent corrosion protection to aluminum at 130°C. The functions of corrosion inhibitors and that of the scavenger are complementing each other, which leads to a longer lifetime.

During Phase II we have also completed the study of corrosion behavior of aluminum in both pure and contaminated *propylene* glycol solutions. Pure propylene glycol solutions were found to be *less* corrosive to aluminum alloys. This is most probably attributed to the high solution pH which was measured at between 8 and 9. The presence of chloride and copper ions causes pitting corrosion, and ferric ions accelerate a more uniform type of attack on aluminum. The results are very similar to what we found for aluminum in aqueous ethylene glycol solutions. Although the extent of the corrosion problems in these cases were noted to be *one order of* *magnitude lower* than the ones in ethylene glycol solutions; the corrosion resistance of aluminum is still *not* sufficient for any light gauge aluminum structure to survive a reasonable duration.

Verification of the cube root pit growth has been completed. Results indicate the cube root law for pit growth is reasonably obeyed. The parameter a used to predict plant lifetime was also experimentally determined to be 0.14 (see equation 3).

II. EXPERIMENTAL METHODS

A. Linear Polarization Resistance Measurement

The method that is being used to determine the overall corrosion rate is an electrochemical measurement of linear polarization resistance. This is a non-destructive and more sensitive method for determining low corrosion rates than either weight loss or gas collection methods. Corrosion processes are mixed electrode reactions with the corrosion potential determined by both an anodic reaction (metal oxidation) and a cathodic reduction reaction on the metal surface. In the specific case of aluminum corrosion, the anodic reaction is aluminum dissolution, and the cathodic reaction is water reduction to hydrogen in total absence of oxygen or oxygen reduction when oxygen is present in sufficient amounts.

As a consequence of the action of the anodic and cathodic reactions, the corrosion potential adopts a value which is more positive than the thermodynamic potential of the metal oxidation reaction and more negative than that of the cathodic reduction reaction. In the case of aluminum corrosion, the potential is slightly more negative than the hydrogen electrode potential in de-aerated solutions and considerably more positive than this potential in aerated solutions.

The measurements are performed in a three-electrode cell containing the glycol/water solution. A small amount of current (sufficient to polarize the aluminum to a maximum of 10 mV about its corrosion potential) is passed between the aluminum and a counter electrode of pure graphite. The potential of the aluminum sample is measured versus a reference electrode, which can be any electrode that remains constant during the measurement and does not contaminate the solution.

A plot of applied current versus potential difference, at low polarization, yields a straight line, the slope of which ($\Delta E/\Delta i$) is defined as the linear polarization resistance. The overall corrosion current density can then be derived from the Stern-Geary equation(1):

$$i_{corr} = \frac{\beta_a \beta_c}{2.3 \frac{\Delta E}{\Delta i} (\beta_a + \beta_c)} \qquad (1)$$

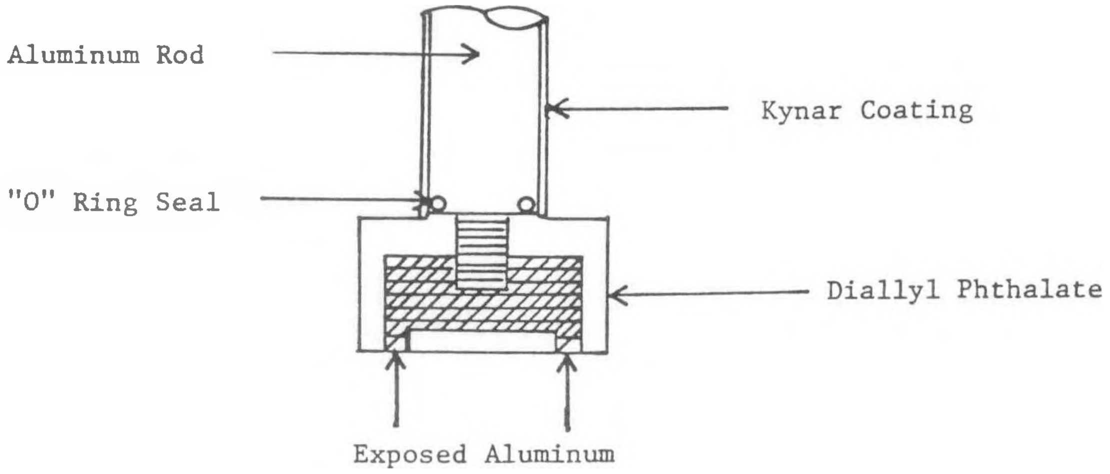
i_{corr}, the corrosion current density, can then be converted to corrosion penetration rate in mils/year or other convenient units. The Tafel parameters, β_a and β_c, are the slopes of the logarithmic local anodic and cathodic polarization curves, respectively. The values of β_a and β_c can also be determined experimentally using the same set-up. This electrochemical method of measuring the corrosion rate has been used successfully by several investigators to study aluminum corrosion in various media(2) including aqueous ethylene glycol solutions(3,4). The derivation(5) and validity(6) of the Stern-Geary equation have been fully discussed and reported in previous reports.

Similar sample (Figure 1) and cell (Figure 2) configurations as used in Phase I are adopted here. The same multi-station rotating electrode system (Figure 3) is used to generate corrosion data under different flow conditions. All aluminum samples are annealed according to Aluminum Association specifications to relieve machining stress and polished with 320 and 600 grit SiC paper.

The test period for all samples is at least seven days. Daily linear polarization resistance measurement is made for all samples. The linear polarization resistance is found to increase during the first few days until finally a stabilized value is reached after the establishment of steady state conditions at the metal/solution interface(3). This technique is not only used to generate baseline corrosion data but also to evaluate the effectiveness of the various inhibitors.

B. Determination of Tafel Slopes

The Tafel parameters, β_a and β_c, are directly determined experimentally rather than estimated from the literature. This measurement is similar to the linear polarization resistance determination. The difference is in polarizing the working electrode beyond the linear region up to about 100 mV more anodic or



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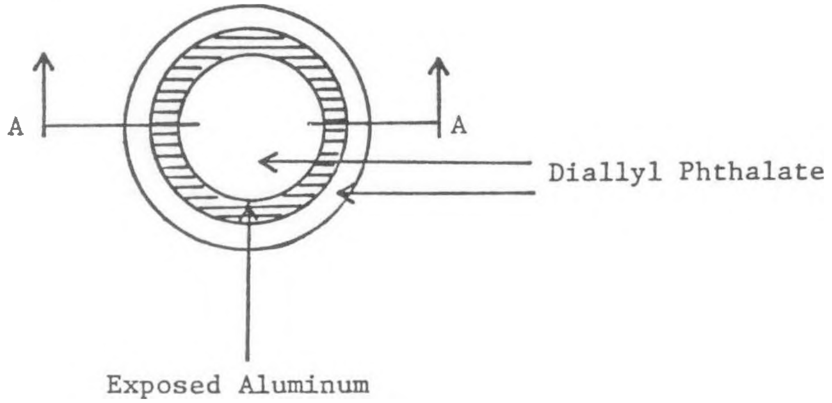
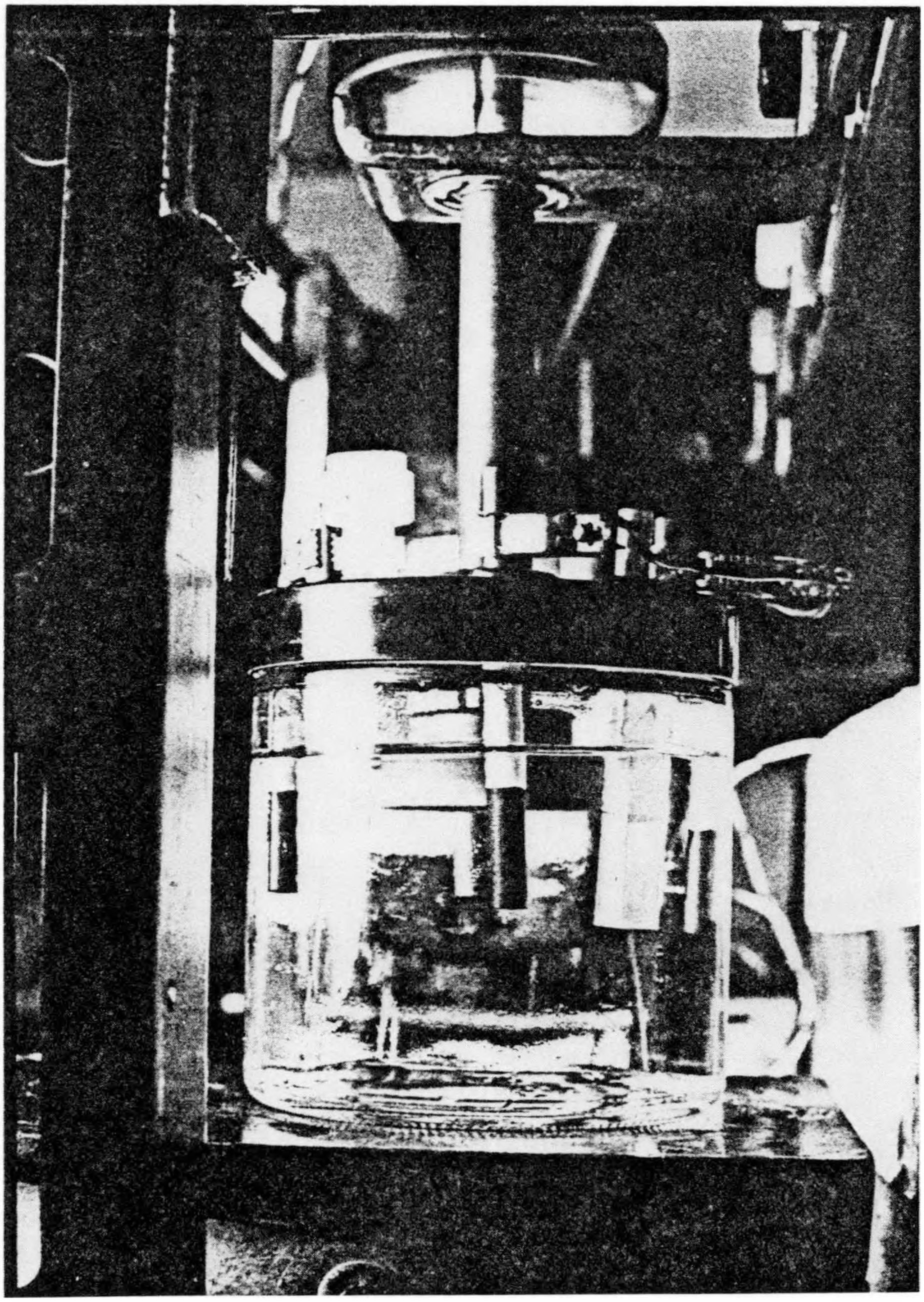
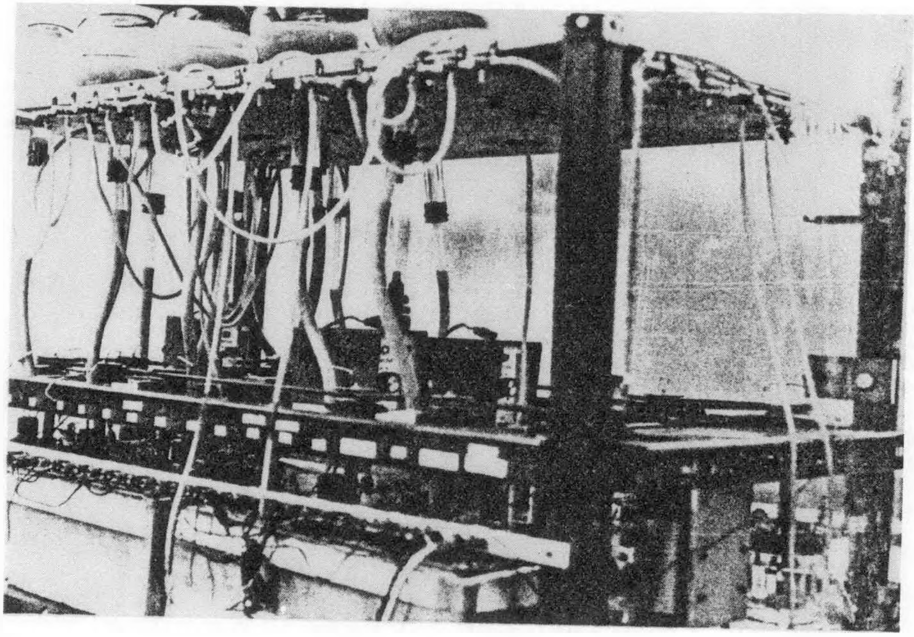


Figure 1. Configuration of Rotating Sample.



THE ELECTROCHEMICAL CELL
FOR LINEAR POLARIZATRION
MEASUREMENT

Figure 2.



MULTI-STATION VARIABLE SPEED ROTATION SYSTEM

Figure 3.

cathodic than the corrosion potential. This overvoltage is then plotted against the current density on a semilog scale. The two slopes of the curves obtained in the most anodic and cathodic regions (Tafel regions) are β_a and β_c, respectively.

C. Measurement of Pitting Corrosion

The pitting corrosion of selected aluminum alloys has been studied by measuring the maximum pit depth and pit density on each samples used in the electrochemical corrosion measurement under various conditions. The pit growth constant, k, is determined by the following equation(7):

$$D = k\, t^{1/3} \tag{2}$$

where D is the measured pit depth in a sample and t is the exposure time.

Pitting analysis is done by a quantitative metallographic examination of the surface of the aluminum sample after timed exposure to the ethylene glycol/water solution under various conditions of temperature, hydrodynamic flow, gas atmosphere and contaminants. At high magnification (500X) the instrument is first focused on the surface of the aluminum and then on the bottom of various pits to establish pit depth. Pit density and diameter are determined at the same time. Under flow conditions the mounted samples for linear polarization resistance measurements are used for pitting analysis also. Larger surface area samples are used for stagnant cases. In both cases pitted samples are cleaned according to ASTM standards(8) before making the measurements.

Since pit depth follows a Gaussian distribution with respect to exposed wetted surface area, the following equation is adopted to estimate the maximum pit depth expected in a real plant with wetted surface of A times larger than that of a laboratory sample(9).

$$p = k\, t^{1/3}\, A^{a} \tag{3}$$

Where p is the maximum probable pit penetration depth to be found on the exposed surface of such a plant, k and t are the same as defined in Eq. (2), and a is a parameter which has been determined experimentally. During the first quarter of

Phase II, we have exposed aluminum sheet samples of relatively large surface area in corrosive aqueous ethylene glycol environments to induce severe pitting corrosion. The exposed surface was then divided arbitrarily into N equal sections. The maximum pit depth D for each section was measured. The maximum and minimum values of D are designated as D_{max} and D_{min}, respectively. The parameter a is then derived from:

$$a = \frac{\log (D_{max}/D_{min})}{\log N} \qquad (4)$$

D. High Temperature Performance Test

Ethylene and propylene glycol solutions, with or without added contaminants and/or corrosion inhibitors, are also subject to a high temperature performance test at ∿ 160°C (320°F). These solutions are contained in glass beakers which are placed in an electric pressure cooker with a thermostatic temperature control. Aluminum samples are also immersed in these solutions to generate corrosion data at this temperature via the conventional weight loss technique. The exposure period is normally scheduled for 10 - 14 days. Both the change in the solution pH (before and after the high temperature test) and the weight loss are used to evaluate the performance of each inhibitor formula. Pitting measurement is also made on samples with pits after the exposure.

E. Thin Foil Sample Test

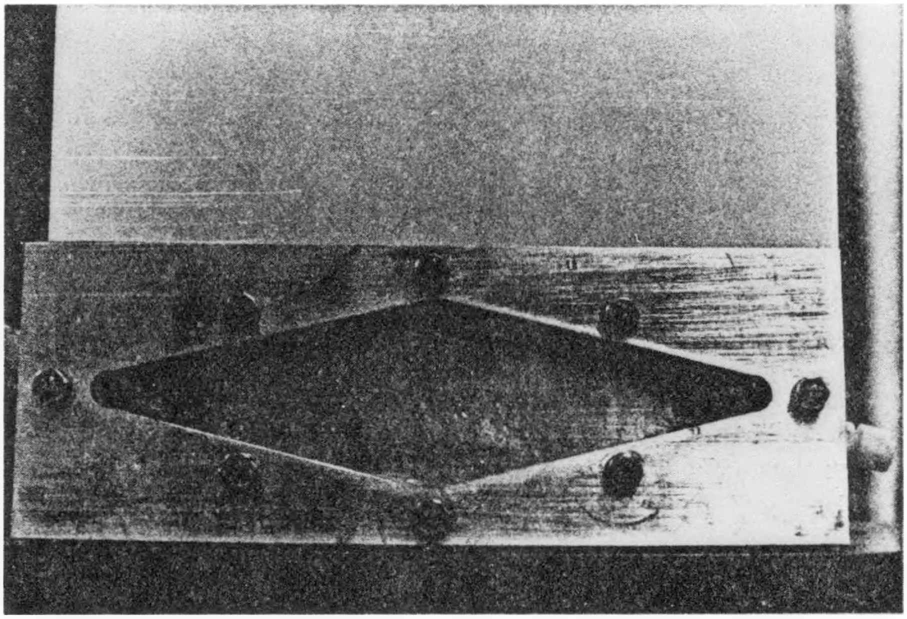
Samples made of very thin aluminum foils can in principle bring about accelerated and undistorted corrosion information. The overall corrosion rate can either be derived from the linear polarization resistance technique or the ohmic resistance method, or even a conventional weight loss measurement. Thin foil sample is especially attractive when a gravimetric method is used to determine the corrosion rate because of its high surface area to mass ratio.

When pitting corrosion is a problem, the 1 mil thick samples are expected to perforate in a matter of days or even hours. Perforation time can be obtained by visually examining the sample at regular time intervals. With the help of Equation (3), this measurable quantity can provide estimated plant lifetime.

We have used this newly developed method to obtain additional corrosion data in order to verify the major findings. So far, only the weight loss and visual examination methods were adopted in this program.

F. Circulation Panel

An aluminum circulation panel (Figure 4) was designed and fabricated to simulate the situation of an aluminum solar heat collector in which the temperature gradient is from the aluminum surface to the heat transfer fluid. It consists of an aluminum back panel, together with an inert transparent cover plate and a Teflon flow chamber. The aluminum panel is heated from behind, and the heat transfer fluid is circulated through the flow chamber to cool down a heat rejecting surface. During the second phase of the program, we have assembled the circulation panel and tested its operation at elevated temperatures. This panel will eventually be used to double check, under simulated operating conditions, the long term effectiveness of various inhibitors developed in this program. We will be able to perform: (a) linear polarization resistance measurement, (b) pit depth and density analysis, and (c) time lapse photography with heat transfer fluid in circulation.



CIRCULATION PANEL

Figure 4.

III. RESULTS AND DISCUSSION

A. Extended Baseline Information on Aluminum Corrosion in Uninhibited Ethylene Glycol Solutions

The baseline data on aluminum corrosion in uninhibited ethylene glycol solutions was broadened beyond the range of conditions covered in Phase I. We have obtained aluminum corrosion data in more concentrated uninhibited ethylene glycol solutions (up to 100%) at temperatures up to 160°C under stagnant conditions. The overall corrosion rate was determined using a weight loss method instead of the linear polarization resistance technique. In addition, the parameter a in Equation (3) was determined experimentally. The cube root pit growth law, adopted in this program, was also verified.

1. Determination of "a"

In Phase I we have taken the statistical nature of pitting corrosion by adopting Equation (3). This parameter "a" was chosen to be 0.2 for aluminum based on published data(9). We have performed our own experiment to determine the proper value of "a". Large 1100 series aluminum samples (3" x 4") were prepared and immersed in contaminated ethylene glycol solutions. Two 85 vol % ethylene glycol solutions, one with 200 ppm $CuSO_4$ and the other with 200 ppm each of $CuSO_4$, $Fe_2(SO_4)_3$ and NaCl were used for these tests. The samples were exposed for 21 days at 130°C. Each sample was then cleaned and divided into 24, 1" square sections. The maximum pit depth (D) for each section was determined. The two extremes of these "D" values obtained from each sample are designated as D_{max} and D_{min}, respectively. The parameter "a" can then be derived from Equation (5):

$$a = \frac{\log(D_{max}/D_{min})}{\log 24} \qquad (5)$$

The "a" values obtained from the two samples are reported in Table I. We found that "a" should be about 0.14 instead of 0.2. This new value was then adopted throughout the entirety of Phase II.

TABLE I

DETERMINATION OF "a"

SOLUTION	D_{max} (μ)	D_{min} (μ)	a
85 vol % E.G. Cu^{+2} (200 ppm)	135	85	0.15
85 vol % E.G. $Cu^{+2} + Fe^{+3} + Cl^{-}$ (200 ppm each)	115	75	0.13

2. Verification of Cube Root Law For Pit Growth

In Phase I a cube root law for pit propagation has been adopted and applied without reservation. We have established the validity of this law experimentally. Two simultaneous experiments were set up with several sets of aluminum samples exposed to 85 vol % ethylene glycol solutions with 200 ppm $CuSO_4$ and $CuSO_4$, NaCl and $Fe_2(SO_4)_3$ at 200 ppm each added. The solution temperature was set at 130°C. One set of samples was taken out at the end of a certain time period for pitting analysis. We have obtained pitting data on samples immersed for 1, 2, 3, 4, 6, 8, 12, 20 and 32 weeks. The results are reported in Table II. If the cube root law is followed, a plot of D versus time on a log-log scale should yield a straight line with its slope approximately equal to 0.3 and its intercept equal to log k.

We have analyzed our data accordingly and have established that the propagation of pitting penetration depth indeed obeys the cube root law for both 1100 and 3003 series aluminum in contaminated ethylene glycol solutions.

These results have fully demonstrated the validity of Equation (3) which was used to interpret our pitting data.

3. Extended Baseline Information on Aluminum Corrosion in Pure Ethylene Glycol Solutions

Since in Phase I most of the work has been done in 35 vol % ethylene glycol solutions at temperatures below 100°C, it is desirable to obtain additional aluminum corrosion characteristics in more concentrated solutions at higher temperatures to broaden our baseline. Corrosion measurement on aluminum samples exposed to more concentrated (up to 100%) ethylene glycol solutions at temperatures up to 160°C. The corrosion rate was obtained using a weight loss method, and both overall corrosion and pitting corrosion data are shown in Table III.

Pitting perforation remains to be the cause of corrosion failure even in 85 vol % pure ethylene glycol solutions. At 160°C the overall aluminum corrosion

TABLE II

VERIFICATION OF CUBE ROOT LAW FOR PIT PROPAGATION

	85% E.G. + Cu^{+2} (200 ppm				85% E.G. + Cu^{+2} + Cl^{-} + Fe^{+3} (200 ppm ea.)			
	1100 Alloy		3003 Alloy		1100 Alloy		3003 Alloy	
t (Days)	D (μ)	K (μ/day$^{1/3}$)	D (μ)	K (μ/day$^{1/3}$)	D (μ)	K (μ/day$^{1/3}$)	D (μ)	K (μ/day$^{1/3}$)
7	95	50	100	52	100	52	100	52
14	120	50	130	54	120	50	120	50
21	125	45	120	44	85	31	105	38
28	170	56	155	51	230	76	190	63
42	280	81	170	49	320	92	200	56
56	270	74	205	56	290	80	225	62
84	-	-	-	-	180	41	160	37
140	-	-	-	-	140	27	150	29
224	-	-	-	-	270	45	360	59
	S* = 0.38		S* = 0.24		S* = 0.35		S* = 0.37	

---

*Slope of log D vs. log t plot.

TABLE III

EXTENDED BASELINE DATA OF ALUMINUM CORROSION IN UNINHIBITED ETHYLENE GLYCOL SOLUTIONS

Solution	Additive(s)*	Temp. (°C)	Alloy	R^{a}_{corr} (mpy)	P(mils)+
85% E.G.	None	130	1100	0.1	24
			1100(foil)	0.1	-
			3003	0.1	15
100% E.G.	None	160	1100	0.6	-
85% E.G.	$Cu^{+2} + Fe^{+3} + Cl^-$	130	1100	-	65
			3003	-	55
50% E.G.	$Cu^{+2} + Fe^{+3} + Cl^-$		1100	-	100
			3003	-	120
35% E.G.	$Cu^{+2} + Fe^{+3} + Cl^-$		1100	-	90
			3003	-	100
85% E.G.	$Cu^{+2} + Fe^{+3} + Cl^-$ + NH_4Cl (10 ppm)		1100	-	52
			3003	-	55
100 % E.G.	$Cu^{+2} + Fe^{+3} + Cl^-$	160	1100	9.3	110

---

[*] 200 ppm each, unless otherwise specified.

[+] Probable penetration depth on a life size plant with a wetted surface area of $1.5 \times 10^5 cm^2$.

[a] Obtained via a weight loss measurement.

rate was found to increase significantly (by a factor of 6) compared to the one obtained at 130°C.

4. Extended Baseline Information on Aluminum Corrosion in Contaminated Ethylene Glycol Solutions

Similar aluminum corrosion tests were carried out in uninhibited ethylene glycol solutions with added impurities. The results are also shown in Table III. At 130°C pitting data were obtained in 35, 50 and 85 vol % ethylene glycol solutions contaminated with 200 ppm each of NaCl, $CuSO_4$ and $Fe_2(SO_4)_3$. With the same amount of impurities present, pits were shallower on samples exposed to the 85 vol % solution. It was also noted that the pit density on samples exposed to the 85 vol % solution is almost ten times higher than those immersed in the 35 and 50 vol % solutions. The average pit diameter was found to be at less than 10 mils on samples in the 85 vol % ethylene glycol solution, while pits on the other samples are larger in size (up to 50 mils in diameter). It is then more advantageous to use the concentrated ethylene glycol solution as the heat transfer fluid in an aluminum solar collector system. Pitting of aluminum remains to be a serious problem even in 100% ethylene glycol at 160°C when impurities are present (see Table III).

5. Effect of Cupric Ion Concentration on the Pitting Corrosion of Aluminum Alloys

An investigation was carried out to determine the effect of cupric ion concentration on the pitting corrosion of aluminum alloys since severe pitting activities on aluminum were partially attributed to the presence of cupric ions in solution. The ultimate goal was to determine a "critical" (threshold) concentration, if any, below which pitting does not occur.

Aluminum sheet samples were exposed to 50 vol % uninhibited ethylene glycol solutions with $CuSO_4$ added 200, 20, 2 and 0.2 for two weeks at 100°C to induce pits. The results are reported in Table IV. Although pit density was found to decrease with decreasing cupric ion concentration, the maximum pit depth was not

TABLE IV

EFFECT OF CUPRIC ION CONCENTRATION ON THE PITTING CORROSION OF ALUMINUM ALLOYS IN 50 VOL % ETHYLENE GLYCOL SOLUTIONS

(T = 100°C, 2 weeks, sample area = 102.3 cm^2)

$[Cu^+]$ (ppm)	Alloy	D(μ)	K(μ/$day^{1/3}$)	P(mils)*
200	1100	125	52	110
	3003	120	50	106
20	1100	110	46	97
	3003	110	46	97
2	1100	100	41	87
	3003	90	37	78
.2	1100	95	39	83
	3003	60	25	53
.2 + 200 ppm Na_2SO_4	1100	210	87	180
	3003	160	66	140

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*Probable penetration depth on a life size plant with 1.5 x $10^5 cm^2$ exposed surface area in 20 years.

affected appreciably by this change. 0.2 ppm of $CuSO_4$ in solution still poses a serious threat to aluminum. Pits as deep as 95 μ were found on those samples after two weeks of exposure. Samples were also immersed in a 50 vol % ethylene glycol solution with 0.2 ppm $CuSO_4$ and 200 ppm Na_2SO_4 (the latter was added just to increase the electrical conductivity), and pitting propagation was found to be more rapid in this solution. Any chemical scavenger will thus have to be able to reduce the copper ion concentration to below 0.2 ppm unless proper corrosion inhibitors are also incorporated in the corrosion control methods.

B. Laboratory Study of Corrosion of Aluminum Alloys in Uninhibited Propylene Glycol Solutions

Since propylene glycol possesses similar antifreezing and antiboiling properties as ethylene glycol and is far less toxic, it is probably more desirable to use it as the heat transfer fluid in aluminum solar collectors. However, similar aluminum corrosion problems are expected to be encountered in propylene glycol solutions as in ethylene glycol solutions. It is then mandatory to obtain baseline corrosion information for this fluid before any recommendations can be made in this regard.

It was decided at an earlier stage to devote part of the effort of the second phase of the program to the further understanding of aluminum corrosion in glycol/water solutions under various conditions relevant to the operation of a solar thermal energy collector system. The first target was to determine the corrosion characteristics of aluminum and its alloys in pure and contaminated *propylene* glycol/water solutions without the presence of corrosion inhibitors.

Baseline aluminum corrosion data were acquired in 50 vol % propylene glycol solutions under laminar flow and stagnant conditions at temperatures ranging from ∿ 25 to 100°C using linear polarization resistance and pit depth measurement techniques.

Additional aluminum corrosion data were obtained at higher temperatures (up to 160°C) in more concentrated stagnant propylene glycol solutions (up to 100%)

using weight loss and pit depth measurements. The results are presented as follows:

1. Corrosion Characteristics of Aluminum Alloys in Pure Uninhibited Propylene Glycol Solutions

Linear polarization resistance measurements of 1100 and 3003 series aluminum samples in a 50 vol % propylene glycol solution were made under laminar flow conditions within a temperature range from ∿ 25 to 100°C. At ambient temperature the pH and the electrical conductivity of this solution was measured to be 8.49 and 5.0 x 10^{-7} mho/cm, respectively. The Tafel slopes, β_a and β_c, were also determined experimentally. $\beta_a\beta_c/(\beta_a + \beta_c)$ was found to be ∿ 0.07V/decade under all conditions.

It was found that aluminum alloys possess excellent corrosion resistance in this medium with a maximum corrosion rate of ∿ 0.06 mpy at 100°C. The results are shown in Table V. A slight temperature dependence with an activation energy estimated at ∿ 4 Kcal/mole was noted.

All rotating samples were examined for signs of pitting corrosion, however, no pitting was observed. Sheet aluminum samples (total area > 200 cm^2) made of 1100 and 3003 series alloys were also prepared and immersed in a stagnant 50 vol % propylene glycol solution at 100°C for two weeks, and there was no sign of pitting corrosion either.

1100 and 3003 series aluminum samples (2" x 2" sheets) were also exposed to an 85 vol % pure propylene glycol solution at 130°C for six weeks. Very shallow pits (less than 10 μ) did appear under such conditions. Both the weight loss and the pitting data are presented in Table VI. The probable pitting penetration depth after 20 years was estimated to be less than 4 mils based on statistics.

At 160°C in 100% propylene glycol solution, aluminum corrosion still appeared to be insignificant based on weight loss data. However, pitting began to be more severe. Maximum pit depth of 35 μ was measured on 1100 series aluminum sample exposed for 14 days.

TABLE V

LINEAR POLARIZATION RESISTANCE OF ALUMINUM ALLOYS IN PURE UNINHIBITED PROPYLENE GLYCOL SOLUTIONS (50 VOL %) UNDER LAMINAR FLOW

Temp. (°C)	Alloy	$\frac{\Delta E}{\Delta i}$ (Ω/cm^2)	R^*_{corr} (mpy)
100	3003	3.3×10^5	0.039
100	1100	2.2×10^5	0.059
75	1100	5.0×10^5	0.026
25	1100	9.3×10^5	0.014

$^*\beta_a\beta_c/(\beta_a + \beta_c)$ = 0.07 V/decade

TABLE VI

BASELINE CORROSION DATA OF ALUMINUM IN PURE PROPYLENE GLYCOL SOLUTIONS

Solution	Temp. (°C)	Alloy	R_{corr} (mpy)	K (μ/day$^{1/3}$)	Sample Area (cm^2)	P* (mils)
85 vol % P.G.	130	1100	0.1	1.4	103.2	3.0
		3003	0.1	2.0	103.2	4.2
100% P.G.	160	1100	0.4	14.5	25.8	37

---

*Probable penetration depth in 20 years on a life size plant with wetted surface area of 1.5×10^5 cm^2.

These results lead to the conclusion that aluminum alloys are *more corrosion resistant* in propylene glycol solutions than in ethylene glycol solutions. Pitting corrosion was not observed at all at temperatures below 100°C. This is most probably due to the high pH of propylene glycol solutions, since aluminum alloys are known to be more corrosion resistant (especially to pitting attack) in slightly alkaline environment$^{(10)}$.

The corrosion resistance of aluminum was still found to be satisfactory, even at temperatures up to 130°C. However, light gauge aluminum structures can no longer be safely exposed to pure uninhibited propylene glycol solutions at 160°C.

2. Corrosion Characteristics of Aluminum Alloys in Contaminated Propylene Glycol Solutions

The linear polarization resistance of aluminum alloys in 50 vol % contaminated propylene glycol solutions have also been measured experimentally, and the results are reported in Table VII. The value of $\beta_a\beta_c/(\beta_a + \beta_c)$ was found to be $\sim$ 0.07 V/decade under all conditions. As we expected, the presence of chloride or cupric ions (at 200 ppm) in propylene glycol solutions caused a significant reduction in the corrosion resistance of aluminum. Severe pitting was observed (especially with Cu^{+2} present). Fe^{+3} ions (at 200 ppm) are responsible for an acceleration of the uniform corrosion rate to $\sim$ 10 mpy. The simultaneous presence of these three species in solar collector heat transfer fluid will lead to rapid plant failure. The corrosion rate was again found to be slightly temperature dependent with an activation energy estimated at less than 5 Kcal/mole.

The samples used in the linear polarization resistance experiment were then examined metallographically to determine pit depth. The pit constants and the probable pitting penetration depth p are also reported in Table VII.

TABLE VII

BASELINE CORROSION DATA OF ALUMINUM ALLOYS IN CONTAMINATED PROPYLENE GLYCOL SOLUTIONS

Base Solution	Additive(s)[*]	Alloy	Temp. (^{o}C)	Flow	R_{corr}[a] (mpy)	P[+] (mils)
50 vol % P.G.	Cl^-	1100	100	laminar	3.2	400
		"	75	"	1.9	370
		"	25	"	.06	290
	Cu^{+2}	1100	100	laminar	1.3	250
		3003	"	"	0.8	83
	Fe^{+3}	1100	100	laminar	7.2	0
	$Cu^{+2} + Fe^{+3} + Cl^-$	1100	100	laminar	16	160
		3003	"	"	11	590
		1100	"	stagnant	23	250
		"	75	"	21	-
		"	25	"	3.9	180
85 vol % P.G.	Cu^{+2}	1100	130	stagnant	-	11
		3003	"	"	-	11
	$Cu^{+2} + Fe^{+3} + Cl^-$	1100	130	stagnant	-	66
		3003	"	"	-	72
100 % P.G.	Cl^-	1100	160	stagnant	5.8	75
	Cu^{+2}	"	"	"	14	-
	Fe^{+3}	"	"	"	-	5
	$Cu^{+2} + Fe^{+2} + Cl^-$	"	"	"	14	100

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[*] 200 ppm each.

[+] Probable penetration depth on a plant with a wetted surface area of $1.5 \times 10^5 cm^2$ in 2

[a] Based on linear polarization resistance measurements at temperatures below $100^{o}C$ At temperatures above $100^{o}C$, weight loss method was used.

Additional corrosion data were generated by exposing 2" x 2" aluminum sheet samples in stagnant 85 vol % propylene glycol solutions at 130°C and also in 100% propylene glycol at 160°C. These results are also shown in Table VII.

Based on these results, we noted the following:

(1) Similar to what we have established for the aluminum-ethylene glycol systems, the corrosion resistance of aluminum is significantly reduced when chloride, cupric and ferric ions are present. Severe pitting corrosion can be induced by either chloride or cupric ion, and ferric ions were found to accelerate uniform corrosion.

(2) The corrosion resistance of aluminum was found to be higher (by about one order of magnitude) in propylene glycol than in ethylene glycol solutions under similar conditions. This is probably due to the fact that the pH of propylene glycol solutions are more alkaline. However, it is still at an intolerable level for light gauge aluminum structures to survive a reasonable period (say 20 years).

(3) The corrosion resistance of aluminum appeared to be higher in more concentrated solutions of propylene glycol. Pitting corrosion was found to be far less severe in 85 vol % solutions at 130°C than in 50 vol % solutions at 100°C. This added corrosion resistance may be attributed to the higher resistivity of the electrolyte (aqueous propylene glycol solution).

Since pitting corrosion is less severe in propylene glycol solutions at concentrations higher than 50 vol %, it is advisable to use more concentrated propylene glycol solutions as the heat transfer fluids in aluminum solar collectors from the corrosion point of view.

(4) The high temperature test performed at 160°C showed that pitting is still a major corrosion problem in 100% propylene glycol. Plant failure is imminent with chloride ions alone in solution.

C. Development and Evaluation of Corrosion Inhibitors for the Aluminum-Glycol/Water System

Based on the results presented so far in this report, it is clear that the use of *uninhibited* glycol/water solutions (either ethylene or propylene glycol) in aluminum solar heat collectors carries a high risk of catastrophic plant failure, especially when common contaminants are present. It is thus imperative to develop effective and economically feasible methods to control corrosion activities. One of the commonly used approaches is to incorporate corrosion inhibitors to the heat transfer fluids.

Inhibited ethylene glycol based antifreeze has been used successfully as an engine coolant in the automobile industry for over half a century. Effective corrosion inhibitors compatible with the system have been developed and used to protect various kinds of metals exposed to this heat transfer medium. A solar collector system is, in many ways, analogous to an automotive cooling system. They both consist of dissimilar metals exposed constantly to the heat transfer solution. The major differences are that the continuous operating hours for solar collectors are much longer, and the collector panel fluid may be at higher temperature (more than 150°C at stagnation) than in automotive application.

As a result of literature searching, we found that phosphates, borates, nitrates, silicates and sodium mercaptobenzothiazole (NaMBT) are the common inhibitory additives(11,12) used in the commercial coolants, although the exact formulas used in any given commercial product are invariably proprietary.

It is then the aim of this work to determine the optimum composition of these materials to be added to glycol/water solutions to reduce corrosion activities on aluminum under conditions directly relevant to the operation of actual solar heat collector systems. In addition, attempts were made to determine the stability as well as the effective lifetime of such *inhibited* glycol solutions.

Furthermore, we have also evaluated the effectiveness of a few commercially available inhibited heat transfer fluids, including some specifically developed for aluminum solar collectors.

1. Preparation of Inhibited Ethylene Glycol Solutions

Two inhibited ethylene glycol solutions (Formulas I and II) were prepared according to the compositions shown in Table VIII. It is important that proper mixing procedures be followed to minimize the formation of insolubles. The adopted procedure is to dissolve the borate in ethylene glycol with stirring; then dissolve the nitrate, silicate and phosphate in a separate portion of distilled water with mild heating before adding to the glycol borate solution; and finally, add the NaMBT solution. The water content is kept below 2 wt %.

The pH's and electrical conductivities of 85 vol % of both inhibited ethylene glycol solutions (Formulas I and II) were measured at ambient temperature, and the results are also shown in Table VIII. Sodium hydroxide was added to Formula II primarily to adjust the solution pH to more alkaline in order to offset the effect of possible organic acid formation due to ethylene glycol decomposition at high temperatures.

In addition to the two inhibited ethylene glycol solutions prepared in the laboratory, several commercially available coolants were also obtained and evaluated experimentally. This includes two inhibited automotive coolants (A1 and A2), two inhibited heat transfer fluids specifically designed for aluminum solar collectors (S1 and S2), and an inhibitor concentrate (C). A1 and A2 contain more than 95% ethylene glycol. Inhibitor S1 is an inhibited 50 vol % ethylene glycol solution, while S2 is a 50 vol % propylene glycol based inhibited heat transfer fluid. Inhibitor C is an aluminum corrosion inhibitor concentrate which can be added to pure ethylene glycol at concentrations ranging from 0.1 to 1.0 wt %.

2. Aluminum Corrosion in Inhibited Glycol Solutions

Aluminum corrosion characteristics in inhibited glycol solutions (ethylene and propylene) have been obtained in order to evaluate the performance of each formula. Overall corrosion rate was determined using the linear polarization

TABLE VIII

FUNCTIONS AND CONCENTRATIONS OF CORROSION INHIBITORS USED IN ETHYLENE GLYCOL SOLUTIONS

Inhibitor	Concentration (g/liter) Formula I	Concentration (g/liter) Formula II	Function
Sodium Orthophosphate $Na_3PO_4 \cdot 12H_2O$	4.5	4.5	Protects aluminum & steel
Sodium Nitrate $NaNO_3$	2.5	2.0	Protects aluminum & iron
Sodium Tetraborate $Na_2B_4O_7 \cdot 5H_2O$	11.2	10.0	Strong buffering agent, also protects steel
Sodium Metasilicate $Na_2SiO_3 \cdot 9H_2O$	2.0	1.5	Protects all metals
Sodium Mercaptobenzothiazole $C_7H_4NS_2Na$ 50% solution	1.8	5.5	Protects brass and copper
Sodium Hydroxide $NaOH$	-	2.0	Adjusts the solution pH
	pH = 6.86 $\sigma = 1.7\times10^{-3}$ mho/cm	pH = 11.0 $\sigma = 2.5 \times 10^{-3}$ mho/cm	

resistance technique at temperatures below 100°C. A weight loss method was used when solution temperature exceeded 100°C (up to 160°C). Pitting analysis was also performed, and the results are presented in terms of probable penetration depth $\underline{p}$ on a plant (1.5×10^5 cm^2 in surface area) in 20 years.

a. Aluminum Corrosion in Pure Inhibited Glycol Solutions

Aluminum corrosion characteristics have been studied in these inhibited glycol/water mixtures in the absence of any deleterious species. The linear polarization resistance measurements were performed at ∿ 100°C (∿ 210°F) under laminar flow conditions. These results are shown in Table IX. The pH and electrical conductivity of each inhibited glycol solution is also reported. In general we found that the inhibited solutions are much more conductive (by about three orders of magnitude) than the pure glycol/water solution. In most cases the pH of the inhibited solution is adjusted to slightly alkaline. The measured corrosion rates shown in Table IX are actually *higher* than the ones obtained in the pure *uninhibited* solutions. However, most of the rates were found to be within the tolerable range (less than 1.0 mpy). This increase is most probably due to the high solution conductivity. Inhibitor Formula I was found to form a gel-like layer around the exposed aluminum sample. This film probably provides corrosion protection; however, the same film most certainly will hinder the heat transfer efficiency and may eventually block the fluid passage in the collector panel.

These inhibited glycol solutions were then tested at higher temperatures. The weight loss of each aluminum coupon and the change of solution pH due to exposure at high temperatures were determined. The results are summarized in Table X and XI. As expected, the overall corrosion rate of aluminum was found to increase with temperature even in 100% inhibited glycol solutions. The corrosion rate, however, is still within the tolerable range (less than 1 mpy). The solution pH was found to decrease as a result of the high temperature exposure. A sharp drop of as much as 5 pH units was observed for solutions with Inhibitor C.

TABLE IX

LINEAR POLARIZATION RESISTANCE OF ALUMINUM ALLOYS IN INHIBITED AQUEOUS GLYCOL SOLUTIONS UNDER LAMINAR FLOW

Solution	pH+	σ(mho/cm)+	Alloy	Temp. (°C)	$\frac{\Delta E}{\Delta i}(\Omega/cm^2)$	R_{corr}^* (mpy)
35 Vol % Inhibitor A1	10.0	2.1×10^{-3}	3003	100	9.0×10^4	0.32
			1100	100	1.6×10^5	0.19
			1100	75	1.9×10^5	0.16
			1100	25	4.6×10^5	0.07
50 Vol % Inhibitor A2	8.85	3.1×10^{-3}	3003	100	1.0×10^5	0.30
			1100	100	1.0×10^5	0.30
85 Vol % Formula I	6.86	1.7×10^{-3}	3003	100	7.5×10^4	0.40
			1100	100	4.0×10^4	0.74
50 Vol % Formula II	10.9	3.0×10^{-3}	1100	100	1.5×10^5	0.20
			1100	50	1.8×10^5	0.16
			1100	25	5.5×10^5	0.05
Inhibitor S1	7.6	7.4×10^{-4}	1100	100	2.5×10^4	1.2
Inhibitor S2	7.3	4.6×10^{-4}	1100	100	2.7×10^5	0.05

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*$\beta_a\beta_c/(\beta_a + \beta_c)$ was assumed at 0.16 V/decade and 0.07 V/decade for ethylene and propylene glycol based solution, respectively.

+Measured at ambient temperature.

TABLE X

ALUMINUM CORROSION IN INHIBITED GLYCOL SOLUTIONS

WITHOUT CONTAMINANTS

Solution	T(^{o}C)	pH Before	pH After	Test Period (days)	Alloy	R^{*}_{corr}(mpy)	$^{+}$P(mil)
85% Inhibitor A1	130	-	-	28	1100	0.30	0
85% Inhibitor A2	130	9.4	8.4	28	1100	0.20	0
					3003	0.30	0
85% Formula II	130	11.0	7.5	14	1100	0.10	0
					3003	0.05	0
Inhibitor S1	130	7.6	6.8	28	1100	-	0
					3003	-	0
Inhibitor S2	130	7.3	6.9	28	1100	0.15	0
					3003	0.17	0
50% (E.G. + .1% Inhibitor C)	110	7.1	3.6	28	1100	0.20	59
					3003	0.30	63

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[*] Revised corrosion rates obtained via weight loss measurement.

[+] Probable pit penetration depth on a plant with 1.5 x 10^5cm^2 wetted surface area in 20 years.

TABLE XI

CORROSION OF ALUMINUM IN INHIBITED GLYCOL SOLUTIONS AT 160°C WITHOUT CONTAMINANTS

Solution	pH Before	pH After	Duration (days)	R^{*}_{corr} (mpy)
100% Inhibitor A1	10.0	8.5	11	1.0
100% Inhibitor A2	9.4	7.9	10	1.2
100% Formula II	11.1	7.2	11	1.0
E.G. +.1% Inhibitor C	8.1	2.5	10	0.9
E.G. + 1% Inhibitor C	7.8	2.4	10	0.6

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[*] Corrected corrosion rates after taking the effects of sample cleaning solution into account.

Pitting corrosion was not observed in most cases even at temperatures as high as 160°C. The only exception was Inhibitor C. Deep pits were found on aluminum samples (both 1100 and 3003 series alloys) exposed to a 50 vol % ethylene glycol solution with 0.05% Inhibitor C at 110°C. The relevant data is reported in Table X. A 90 μ deep pit found on a sample with a surface area of 103.2 cm^2 corresponds to a 60 mil penetration on a life size plant with a surface area of 1.5×10^5 cm^2 in 20 years. Since the wall thickness of a roll-bond aluminum panel is 30 mils, it is intolerable.

Based on these results, we can be certain that Inhibitor C and Formula I are not the proper heat transfer fluids to be used in aluminum solar collectors. The former fails to provide adequate pitting corrosion resistance while the latter forms a gel-like precipitate which is undesirable.

b. Aluminum Corrosion in Inhibited Glycol Solutions With Deleterious Contaminants

The performance of inhibited glycol solutions was further evaluated under conditions where chloride, copper and iron are present. The tests were performed first at temperatures below 100°C using the linear polarization resistance technique. At higher temperatures (up to 160°C), a conventional weight loss method was used to determine the corrosion rates. Maximum pit depth in each sample was also measured using a quantitative metallographic technique.

i. Results Obtained at Temperatures Below 100°C

We have obtained the linear polarization resistance of 1100 and 3003 series aluminum alloys in various inhibited glycol solutions with different added contaminants. Most of the measurements were performed under laminar flow conditions within a temperature range from ∿ 25 to ∿ 100°C. The results are shown in Table XII. We noted that most of these inhibited solutions rendered excellent corrosion protection within the range of experimental conditions ($T < 100°C$). These inhibitors can effectively reduce the corrosion attack on aluminum to less than 1 mpy for most cases, even when all three major contaminants

TABLE XII

LINEAR POLARIZATION RESISTANCE OF ALUMINUM IN INHIBITED GLYCOL SOLUTIONS WITH CONTAMINANTS

Additive(s)*	Base Solution+	Alloy	Temp. (^{o}C)	Flow	$\frac{\Delta E}{\Delta i}$($\Omega$/cm^2)	R_{corr}(mpy)
Cl^-	35% Inhibitor A1	1100	100	laminar	6.4×10^4	0.46
	50% Inhibitor A1	1100	100	laminar	1.2×10^5	0.25
	50% Inhibitor A2	1100	100	laminar	5.0×10^4	0.59
		3003	100	laminar	4.3×10^4	0.69
	50% Formula II	1100	100	laminar	1.2×10^5	0.25
		1100	75	laminar	1.7×10^5	0.17
		1100	25	laminar	2.2×10^5	0.13
Cu^{+2}	35% Inhibitor A1	1100	100	laminar	4.1×10^4	0.72
	50% Inhibitor A2	1100	100	laminar	4.5×10^4	0.66
	50% Formula II	1100	100	laminar	7.0×10^4	0.42
Fe^{+3}	35% Inhibitor A1	1100	100	laminar	1.0×10^5	0.30
$Cu^{+2} + Fe^{+3} + Cl^-$	50% Inhibitor A2	1100	100	stagnant	5.9×10^4	0.50
	85% Formula I	1100	100	laminar	7.6×10^4	0.39
		3003	100	laminar	5.2×10^4	0.57
	50% Formula II	1100	100	stagnant	1.7×10^4	1.7
		1100	75	stagnant	4.0×10^4	0.74
		1100	25	stagnant	6.0×10^4	0.49
	Inhibitor S1	1100	100	laminar	4.0×10^4	0.74
	Inhibitor S2	1100	100	laminar	2.0×10^4	0.65

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*At 200 ppm each.

+Percent by volume.

are present. However, we did observe the formation of insoluble precipitates in most solutions examined in this work. This effect most probably will hinder the heat transfer properties and may even cause crevice corrosion in solar collectors.

All samples used in the linear polarization resistance measurements have been subject to metallographic pitting examination, and no pitting was observed.

These encouraging results lead to the conclusion that Inhibitors A1, A2, S1, S2 and Formula II, all work effectively in preventing aluminum corrosion under the conditions investigated so far. Inhibitor Formula I was found to form the same gel-like precipitate as reported in Section III.C.2. However, we must emphasize that the inhibitor level must be maintained. Depletion of inhibitors will most probably result in a rapid surge of corrosion attack which leads to catastrophic plant failure.

ii. Results Obtained at Temperatures Above 100°C

The performance of inhibited glycol solutions (contaminated) was further evaluated at temperatures above 100°C. We have obtained aluminum corrosion data at 110 , 130, and 160°C, and they are shown in Tables XIII, XIV and XV, respectively. In certain cases, NH_4Cl (10 ppm) was added to simulate contaminants from residual solder in the system in addition to the common contaminants investigated in III.C.3. At 110°C we found that aluminum alloys are corroding at $\sim$ 1 mpy in inhibited solutions S1 and S2 with chloride and heavy metal ions present. A thin foil sample exposed to inhibitor S2 was perforated due to pitting corrosion. These results indicate that both S1 and S2 are no longer effective at this temperature (110°C).

Inhibitors A1, A2 and Formula II appeared to inhibit aluminum corrosion successfully at temperatures up to 130°C. The presence of NaCl, $CuSO_4$, $Fe_2(SO_4)_3$, and NH_4Cl do not effect the effectiveness of these inhibitors. Preliminary tests also showed that crevice corrosion and galvanic corrosion are not of any concern in these solutions. Pitting corrosion was completely surpassed under these

TABLE XIII

ALUMINUM CORROSION IN INHIBITED GLYCOL SOLUTIONS

USING THIN FOIL SAMPLES

T = 110°C Period = 15 days Sample Area = 3 in^2

Solution	Additive(s)*	Δm(mg)	R_{corr}(mpy)	Remarks
50% Inhibitor A1	Cl^-	0.7	0.12	
	Cu^{+2}	2.2	0.40	
	Fe^{+3}	0.7	0.12	
	$Cu^{+2} + Fe^{+3} + Cl^-$	3.8	0.70	
Inhibitor S1	$Cu^{+2} + Fe^{+3} + Cl^-$	5.4	1.0	
Inhibitor S2	$Cu^{+2} + Fe^{+3} + Cl^-$	6.3	1.2	Pitted

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*At 200 ppm each.

TABLE XIV

ALUMINUM CORROSION IN INHIBITED GLYCOL SOLUTIONS

WITH ADDED IMPURITIES AT 130°C

Base Solution	Additive(s)*	Before	After	Test Period (days)	Alloy	R_{corr}(mpy)	P(mils)
85% Inhibitor A1	$Cl^-+Fe^{+3}+Cu^{+2}$	9.7	7.2	42	1100	0.11	0
					3003	0.11	0
					1100(foil)	0.16	0
	$Cl^-+Fe^{+3}+Cu^{+2}$ $+NH_4Cl$ (10 ppm)	9.3	8.2	35	1100	-	0
					3003	-	0
85% Inhibitor A2	$Cl^-+Fe^{+3}+Cu^{+2}$	10.2	7.5	42	1100	0.13	0
					3003	0.14	0
					1100(foil)	0.20	0
	$Cl^-+Fe^{+3}+Cu^{+2}$ $+NH_4Cl$ (10 ppm)	8.5	8.4	35	1100	-	0
					3003	-	0
85% Inhibitor Formula I	$Cu^{+2}+Fe^{+3}+Cl^-$	-	-	14	1100	-	1.9
					3003	-	0.9
	$Cu^{+2}+Fe^{+3}+Cl^-$ $+NH_4Cl$ (10 ppm)	-	-	14	1100	-	0.3
					3003	-	2.6
85% Inhibitor Formula II	$Cl^-Fe^{+3}+Cu^{+2}$	11.4	6.4	42	1100	0.10	0
					3003	0.11	0
					1100(foil)	0.10	0
	$Cl^-+Fe^{+3}+Cu^{+2}$ $+NH_4Cl$ (10 ppm)	10.2	9.2	35	1100	-	0
					3003	-	0
85% (E.G. + 1% Inhibitor C)	$Cl^-+Fe^{+3}+Cu^{+2}$ $+NH_4Cl$ (10 ppm)	7.4	5.1	35	1100	-	58
					3003	-	94
50% (E.G. + .1% Inhibitor C)	Cl^-	-	-	28	1100	-	150
					3003	-	120
	Cu^{+2}	-	-	28	1100	-	120
					3003	-	170
	Fe^{+3}	-	-	28	1100	-	44
					3003	-	17
	$Cu^{+2}+Fe^{+3}+Cl^-$	-	-	28	1100	-	240
					3003	-	230
Inhibitor S2	Cl^-	-	-	28	1100	-	7
					3003	-	3
	Cu^{+2}	-	-	28	1100	-	0
					3003	-	3
	Fe^{+3}	-	-	28	1100	-	17
					3003	-	21
	$Cu^{+2}+Fe^{+3}+Cl^-$	-	-	28	1100	-	49
					3003	-	38

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*At 200 ppm each, except for NH_4Cl.

TABLE XV

ALUMINUM CORROSION IN INHIBITED GLYCOL WITH CONTAMINANTS* AT 160°C

Base Solution	pH Before	pH After	Time (days)	R_{corr}^{+} (mpy)
Inhibitor A1	9.9	8.1	11	1.3
Inhibitor A2	9.3	7.8	10	1.1
Formula II	11.2	7.0	11	1.0
E.G. + 0.1% Inhibitor C	5.0	4.0	10	2.2
E.G. + 1% Inhibitor C	7.6	2.0	11	2.3

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*$CuSO_4$, NaCl and $Fe_2(SO_4)_3$ at 200 ppm each.

+Revised corrosion rates after taking the effects of sample changing solution into account.

conditions. However, the corrosion rate surges back to above 1 mpy as temperature rises to 160°C. Shallow pits started to reappear on laboratory aluminum samples; indicative of the beginning of the breakdown of the corrosion inhibition mechanism.

With impurities present, Inhibitor Formula I was found to be unable to suppress pitting corrosion at 130°C. Very shallow pits began to appear on those aluminum samples exposed to it. As for Inhibitor S2, it was confirmed again that it failed to render enough protection to aluminum alloys at temperatures above 100°C. Pitting corrosion was observed on samples exposed to this inhibited solution with contaminants present. Probable pit depth of as high as 49 mils in 20 years was predicted based on laboratory pitting data obtained at 130°C. It is recommended that these commercially available "inhibited" aluminum solar collector heat transfer fluids be critically evaluated before putting them into existing systems. It was also concluded that Inhibitor C, even at 1%, is ineffective in protecting aluminum from corrosion under any condition.

Contamination due to residual of solder in the system does not seem to affect the effectiveness of corrosion inhibitors. It is also advisable to use more concentrated inhibited glycol solution from the corrosion control point of view.

D. Development and Study of the Effects of Chemical Scavengers For Contaminants

The use of chemical scavengers to remove deleterious impurities from the heat transfer medium is considered to be a viable approach to reduce the corrosiveness of such fluids. In this program we have examined two possible heavy metal ion scavenging agents (Al and Zn) both are metals more electrochemically active than copper and iron. Aluminum was selected because it is compatible with the solar collector systems. Zinc was chosen, instead of magnesium, due to the fact that zinc will not cause a rapid increase in solution pH and hence make the environment too corrosive for aluminum.

Aluminum corrosion characteristics were obtained in both uninhibited and inhibited glycol (ethylene and propylene) solutions with scavenging agents added. The amount of scavenger used depended upon the total impurity concentration in solution. The corrosion data was obtained from 1100 and 3003 series aluminum samples in both sheet and foil forms at temperatures ranging from 100 to 160°C.

1. Using Aluminum Powder as the Scavenger

Aluminum itself was selected as a heavy metal ion scavenger in this program because it is naturally compatible with the system. Fine aluminum powder (-150 mesh) was added to various uninhibited contaminated glycol solutions at concentrations several orders of magnitude higher than that of the total contaminants. Aluminum corrosion data was obtained in 85 vol % ethylene and propylene glycol solutions at 100°C. A scavenger to total impurity concentration ratio of 1000:1 was used. The results are shown in Table XVI. We noted that at such a high concentration ratio (1000:1), aluminum powder did not seem to be able to remove all the cupric ions from solution. Pitting is still a major mode of corrosion failure in solutions with cupric ions contamination, even with a huge amount of aluminum powder present. As we have demonstrated in Section III.A.5, the Cu^{+2} ions at 0.2 ppm still pose serious threats to aluminum. The scavenging mechanism seems to have effectively removed ferric ions and thus reduced the overall corrosion rate to below 1 mpy. Since the results are not very promising, no further test was performed at higher temperature using this particular grade of aluminum powder as a scavenger.

One possible explanation for the unsuccessful attempt to use such fine aluminum powder as a heavy metal scavenger in glycol solutions is that the fine powder used in the experiment has been passivated by the presence of an oxide film. In order to reassure ourselves of this conclusion, another set of aluminum corrosion data was obtained in contaminated glycol solutions with freshly supplied aluminum powder (-20 mesh) added as the scavenger. These results are shown in Table XVII. All samples were pitted, despite the fact that the corrosion rates appeared to be acceptable. In conclusion, aluminum can only be used as a scavenger to *reduce* the corrosiveness brought about by the presence of heavy

TABLE XVI

SCAVENGING EFFECTS OF FINE ALUMINUM POWDER (-150 mesh)

T = 100°C   t = 14 days   Sample Area = 51.6 cm^2 [Al] : [impurities] = 1000:1

Solution	Additive(s)[*]	Alloy	R_{corr}[+] (mpy)	p(mils)[#]	Remark
85% E.G.	Cu^{+2}	1100	0.64	44	
		3003	0.66	39	
	Fe^{+3}	1100	0.48	0	
		3003	0.58	0	
	$Cl^- + Cu^{+2} + Fe^{+3}$	1100	0.67	34	
		3003	0.67	34	
85% P.G.	Cu^{+2}	1100	1.20	-	Severely pitted
		3003	0.96	-	
	Fe^{+3}	1100	0.44	-	A few small pits
		3003	0.51	-	
	$Cl^- + Cu^{+2} + Fe^{+3}$	1100	1.54	-	Severely pitted
		3003	1.29	-	

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[*] 200 ppm each.

[+] Obtained from weight loss data.

[#] Maximum probable pit penetration depth of a life size plant (1.5 x 10^5 cm^2) in 20 years.

TABLE XVII

SCAVENGING EFFECT OF FRESH ALUMINUM POWDER (-20 mesh)

[Al] : [impurities] = 1000:1 T = 130°C t = 14 days Sample Area = 51.6 cm^2

Base Solution	Additive(s)*	Alloy	R_{corr} (mpy)	p(mils)+
85% E.G.	Cl^-	1100	0.20	67
		3003	0.20	10
	Cu^{+2}	1100	0.28	29
		3003	0.21	19
	$Cu^{+2} + Fe^{+3} + Cl^-$	1100	0.75	48
		3003	0.47	34

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*200 ppm each.

+Maximum probable pit penetration depth of a life size plant (1.5×10^5 cm^2) in 20 years.

metal ions in solution, however, without further development it is not quite effective to provide satisfactory corrosion protection on its own.

2. Using Zinc as the Scavenger

Due to the unsatisfactory scavenging effect obtained from aluminum powder, we extended this investigation to using zinc as a possible contaminant scavenger in glycol solutions. Preliminary investigation was carried out at 100°C with technical grade fine zinc powder (-150 mesh) as the scavenger. Aluminum corrosion data was obtained, and the results are shown in Table XVIII. At a 1000:1 Zn to total impurity concentration ratio, aluminum alloys were found to behave very well and to corrode uniformly (without any sign of pits) at the low rate of ∿ .4 mpy in contaminated ethylene and propylene glycol solutions. Most encouragingly, pitting was suppressed even when chloride ions are in solution. When the zinc powder concentration was reduced to 300:1, no significant change was observed. At this point it must be concluded that zinc is a much more efficient heavy metal ion scavenger in glycol solutions than is aluminum.

We have replaced zinc powder with zinc ribbons and performed a similar experiment as described above. The results are also shown in Table XVIII. These zinc ribbons were not in contact with the aluminum directly. We found that although the corrosion rates obtained via weight loss measurements remained more or less the same, pits started to appear on all samples. This may possibly be attributed to the reduction in active surface area when we switch from powder to ribbon. This investigation was then extended to higher temperatures. Aluminum corrosion data was obtained at 130°C with zinc to impurity concentration ratios at 1:1, 10:1, 100:1 and 1000:1. These results are presented in Table XIX. We noted that at 10:1 the presence of zinc powder has already changed the aluminum corrosion resistance in these contaminated glycol solutions from intolerable to a "marginally acceptable" level. As zinc concentration increased to 100:1 versus total impurities present, the corrosiveness of these solutions to aluminum was further reduced. Although pitting is not completely suppressed, the penetration

TABLE XVIII

SCAVENGING EFFECT OF ZINC AT 100°C

Solution	Additive(s)[1]	[Zn]:[Impurities]	Alloy	R_{corr}[2] (mpy)	
85% E.G.	Cu^{+2}	1000:1 (powder)	1100	0.35	
			3003	0.41	
	Fe^{+3}		1100	0.37	
			3003	0.39	
	$Cl^{-}+Cu^{+2}+Fe^{+3}$		1100	0.32	
			3003	0.41	
85% P.G.	Cu^{+2}		1100	0.30	
			3003	0.35	
	Fe^{+3}		1100	0.34	
			3003	0.37	
	$Cl^{-}+Cu^{+2}+Fe^{+3}$		1100	0.36	
			3003	0.41	
85% E.G.	Cu^{+2}	300:1 (powder)	1100	0.33	
			3003	0.37	
	Fe^{+3}		1100	0.33	
			3003	0.33	
	$Cl^{-}+Cu^{+2}+Fe^{+3}$		1100	0.31	
			3003	0.34	
	Cu^{+2}	∿500:1 (ribbon)	1100	0.34	
			3003	0.26	All samples pitted.
	Fe^{+3}		1100	0.37	
			3003	0.37	
	$Cl^{-}+Cu^{+2}+Fe^{+3}$		1100	0.42	
			3003	0.35	

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1 - 200 ppm each
2 - Obtained from weight loss

TABLE XIX

EFFECTS OF ZINC SCAVENGING AT HIGH TEMPERATURES

Solution	Additive(s)*	[Zn]:[Imp.]	Alloy	Temp (°C)	R_{corr}[+] (mpy)	p(mils)#
85% E.G.	Cl^-	1:1	1100	130	0.14	8
			3003		0.46	8
	Cu^{+2}		1100		1.07	27
			3003		1.00	23
	Fe^{+3}		1100		0.16	11
			3003		0.19	4
	$Cl^- + Cu^{+2} + Fe^{+3}$		1100		0.82	38
			3003		0.80	35
	Cl^-	10:1	1100		0.18	4
			3003		0.16	0
	Cu^{+2}		1100		0.37	15
			3003		0.25	8
	Fe^{+3}		1100		0.12	23
			3003		0.10	11
	$Cl^- + Cu^{+2} + Fe^{+3}$		1100		0.30	27
			3003		0.26	15
	Cl^-	100:1	1100		0.34	0
			3003		0.28	0
	Cu^{+2}		1100		0.11	8
			3003		0.09	4
	Fe^{+3}		1100		0.09	15
			3003		0.10	0
	$Cl^- + Cu^{+2} + Fe^{+3}$		1100		0.15	11
			3003		0.14	4
	Cl^-	1000:1	1100		0.63	0
			3003		0.69	0
100% E.G.	Cu^{+2}	200:1	1100	160	0.37	37
	$Cl^- + Cu^{+2} + Fe^{+3}$		1100		0.33	21
100% P.G.	Cu^{+2}	200:1	1100		0.33	0
	$Cl^- + Cu^{+2} + Fe^{+3}$		1100		0.46	11
50/50% E.G./P.G.	Cu^{+2}	200:1	1100		0.35	5
	$Cl^- + Cu^{+2} + Fe^{+3}$		1100		0.33	0
	$Cl^- + Cu^{+2} + Fe^{+3}$	1000:1	1100		0.27	0

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[*] 200 ppm each/[+] Obtained from weight loss./[#] Max. probable pit penetration depth of a life size plant ($1.5 \times 10^5 cm^2$) in 20 years.

depth is considered to be too shallow to cause any catastrophic corrosion failure. 3003 series alloys showed consistently better pitting corrosion resistance under these conditions.

Again, we noted that in addition to the effective removal of cupric and ferric ions from solution, zinc powder seemed to have effectively reduced aluminum corrosion in solution containing chloride ions. This encouraging phenomenon was further studied and will be discussed later.

Additional aluminum corrosion information was obtained at 160°C in ethylene glycol, propylene glycol and a 50:50 mixture of ethylene and propylene glycol. The results are also presented in Table XIX. Satisfactory corrosion resistance can be obtained by adding zinc powder to the glycols at concentration ratios greater than 200:1.

3. Mechanisms of Corrosion Protection Rendered by Zinc Powder

The fact that zinc powder in solution effectively reduced aluminum corrosion in uninhibited glycol solution when chloride ions are present is certainly worth further investigation. It is beyond doubt that zinc powder acts as a powerful scavenger for cupric and ferric ions. However, we do not expect zinc to be a chloride ion scavenger. The corrosion protection may either be rendered via a cathodic protection mechanism (zinc powder does come in electrical contact with aluminum samples) or a pH change of the solution, or a protective complex formation involving Zn^{+2} ions similar to the case of Ca^{+2} ions and hydroxylated organic functions(13,14). A simple pH effect was ruled out due to the fact that solution pH was measured at ∿ 7, and pitting has been reported in chloride containing glycol solutions in this program.

In order to gain clear understanding of this phenomenon, a series of experiments was performed to obtain aluminum corrosion data in Zn^{+2} ion containing glycol solutions. Three zinc compounds (i.e. zinc oxide, zinc chloride and zinc sulfate) were used in this study. They were added to contaminated glycol solutions, and aluminum corrosion data were obtained. The results are shown in Table XX.

TABLE XX

EFFECTS OF Zn^{+2} IONS ON ALUMINUM CORROSION IN GLYCOL SOLUTIONS

T = 130°C t = 14 days Sample Area = 51.6 cm^2

[Zn] : [Impurities] = 100:1

Solution	Additive(s)*	Scavenger	Alloy	R^{+}_{corr} (mpy)	p(mils)#
85% E.G.	Cl^-	ZnO	1100	0.43	58
			3003	0.44	29
	Cu^{+2}		1100	2.01	97
			3003	2.05	68
	$Cl^- + Cu^{+2} + Fe^{+3}$		1100	2.08	120
			3003	1.87	87
	Cl^-	$ZnCl_2$	1100	1.68	24
			3003	1.74	19
	Cu^{+2}		1100	1.32	24
			3003	1.68	24
	Cl^-	$ZnSO_4$	1100	0.88	29
			3003	1.10	10
	Cu^{+2}		1100	0.56	120
			3003	0.57	140
	$Cl^- + Cu^{+2} + Fe^{+3}$		1100	0.72	48
			3003	0.81	48

---

*200 ppm each.

+Obtained from weight loss data.

#Maximum probable pit penetration depth of a life size plant (1.5 x $10^5 cm^2$) in 20 years.

All samples were severely pitted, and the corrosion rates were found to be intolerably high for most cases.

Since we have obtained evidence which ruled out both a pH and the Zn^{+2} ion effects, the only logical explanation is that a cathodic protection type of mechanism keeps the electrochemical potential of aluminum below its critical pitting potential. This type of cathodic protection has been confirmed by Uhlig, *et al.*(15) in the laboratory, and it is a widely acknowledged corrosion control technique. Zinc powder floating in glycol solutions does come in electrical contact with aluminum and thus lowers the potential of aluminum. Additional proof was obtained with the following set of experiments. Contaminated ethylene glycol solutions (85 vol %) were pretreated with zinc powder at 300:1 concentration ratio (zinc versus total impurities). The zinc powder was subsequently filtered out, and these pretreated solutions were used to generate aluminum corrosion data at 100°C. The results are shown in Table XXI. The two solutions containing Cu^{+2} and Fe^{+3} ions to begin with did not cause any pitting corrosion. The overall corrosion rates are well within the tolerable range. These results strongly indicate that zinc powder has effectively removed Cu^{+2} and Fe^{+3} ions which cause aluminum to corrode in one form or another. As for samples exposed to the third solution, pitting corrosion was observed. Without zinc powder in solution, despite the fact that Cu^{+2} and Fe^{+3} are removed, chloride ions still induce pitting.

In conclusion, based on experimental evidence, we have determined that zinc is a more effective heavy metal ion scavenger than aluminum. When zinc is used in powder form, it acts as a floating sacrificial anode which also cathodically protects aluminum from pitting even in chloride ion containing solutions.

E. Combined Use of Inhibitors and Scavengers to Control Aluminum Corrosion

The combined effects of corrosion inhibitors and scavengers on aluminum corrosion in glycol/water solutions were investigated. An 85 vol % inhibited ethylene glycol solution (Inhibitor Formula II) was prepared. In

TABLE XXI

ALUMINUM CORROSION DATA IN CONTAMINATED GLYCOL SOLUTION

PRETREATED WITH ZINC POWDER

T = 100°C   t = 14 days   Sample Area = 51.6 cm^2

Solution	Additive(s)*	[Zn]:[Imp.]	Alloy	R^{+}_{corr} (mpy)	p(mils)#
85% E.G.	Cu^{+2}	300:1	1100	0.40	0
			3003	0.35	0
	Fe^{+3}		1100	0.34	0
			3003	0.20	0
	$Cl^{-} + Cu^{+2} + Fe^{+3}$		1100	0.17	24
			3003	0.18	19

---

*200 ppm added.

+Obtained from weight loss.

#Maximum probable pit penetration depth of a life size plant (1.5×10^{5} cm^2) in 20 years.

addition to all the inhibitors listed in Table VIII, 2000 ppm of Zn powder was also added. Aluminum corrosion data was obtained using samples made of 1100 and 3003 series alloys in sheet and foil form at 130°C. The relevant corrosion data is shown in Table XXII, together with solution pH changes due to such exposures. We noted that the corrosion rate is kept very low (below 0.2 mpy) even with all three major contaminants present. No pit was observed in all cases. The corrosion rates obtained from the sheet samples are in good agreement with the ones from the foil sample. More encouragingly, we found that the solution pH was not significantly affected after exposure to high temperature after two weeks. This indicates that the presence of zinc powder is not accelerating the degradation of ethylene glycol solutions.

TABLE XXII

ALUMINUM CORROSION IN ETHYLENE GLYCOL SOLUTIONS WITH Zn POWDER AND INHIBITORS

t = 14 days T = 130°C

Solution	Additive(s)*	Sample	Alloy	R^{+}_{corr} (mpy)	pH Before	pH After
85 Vol % Inhibitor Formula II + 2000 ppm Zn Powder	Cl^-	Sheet (25.8 cm^2)	1100	0.12	11.1	10.7
	Cu^{+2}			0.12	11.1	10.5
	Fe^{+3}			0.12	11.0	10.6
	$Cl^- + Cu^{+2}$			0.12	11.1	10.5
	$Cl^- + Fe^{+3}$			0.12	11.0	10.5
	$Cu^{+2} + Fe^{+3}$			0.12	11.0	10.5
	$Cl^- + Cu^{+2} + Fe^{+3}$			0.12	11.0	10.5
	Cl^-	Foil (19.4 cm^2)	1100	0.19	11.0	10.4
			3003	0.19		
	Cu^{+2}		1100	0.12	11.0	10.0
			3003	0.08		
	$Cl^- + Cu^{+2} + Fe^{+3}$		1100	0.18	11.0	9.5
			3003	0.18		

---

*200 ppm each.

+Obtained from weight loss.

IV. CONCLUSIONS

Based on the results obtained in Phase II, we reached the following conclusions:

- Corrosion inhibitors commonly found in automobile antifreeze can effectively reduce aluminum corrosion in glycol solutions at temperatures below $100^{\circ}C$ or in some instances $130^{\circ}C$.

- An inhibitor composition (in g/liter) with (4.5) $Na_3PO_4 \cdot 12H_2O$, (2.0) $NaNO_3$, (10.0) $Na_2B_4O_7 \cdot 5H_2O$, (1.5) $Na_2SiO_3 \cdot 9H_2O$, (5.5) $C_7H_4NS_2Na$, and (2.0) NaOH was found to provide satisfactory protection to aluminum alloys at temperatures up to $130^{\circ}C$.

- Zinc is an effective scavenger for heavy metal ions in glycol solution.

- Zinc powder in glycol solution acts not only as a heavy metal ion scavenger but also as a sacrificial anode which protects aluminum cathodically.

- The combined use of zinc powder and corrosion inhibitors is most attractive. Aluminum corrosion can be effectively suppressed, even in the most corrosive situation.

- Propylene glycol is less corrosive to aluminum than ethylene glycol. However, the use of uninhibited propylene glycol solution in aluminum solar collectors is still *not* recommended.

- Glycol solution becomes less corrosive to aluminum as its glycol concentration increases.

- The propagation of pits indeed obeys the cube root law which has been adopted in the program.

V. REFERENCES

1. M. Stern and A. L. Geary, J. Electrochem. Soc., 104, 56 (1957).
2. S. Evans and E. L. Koehler, J. Electrochem. Soc., 108, 509 (1961).
3. M. S. Walker and W. D. Frances, Jr., Materials Protection, 8, 47 (1969).
4. M. S. Walker, Materials Performance, July, 37 (1974).
5. C. Wagner and W. Traud, Z. Electrochem., 44, 391 (1938).
6. F. Mansfeld and K. B. Oldham, Corrosion Science, 11, 787 (1971).
7. H. P. Godard, W. D. Jepson, M. R. Bothwell and R. L. Kane, Corrosion of Light Metals, p. 60, John Wiley and Sons, Inc. (1967).
8. ASTM Standars G1-72
9. H. H. Uhlig, Corrosion Handbook, P. 1052, Wiley, New York (1948).
10. S. C. Byrne, Solar Age, 19, May (1977).
11. M. S. Walker, Materials Performance, 12, 29 July (1973).
12. General Motors Engineering Standards, GM 6038-M.
13. J. Duvrier-Ruffet and J. Pagetti, Metaux Corros. 50, (597), 180 (1975).
14. G. Daufin, J. P. Labbe, and J. Pagetti, Corrosion Science, 17, 901 (1977).
15. H. Bohni and H. H. Uhlig, J. Electrochem. Soc., 116, 907 (1969).

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