ANL-79-96

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**CORROSION BEHAVIOR OF SEVERAL METALS IN
ETHYLENE GLYCOL-BASE HEAT-TRANSFER FLUIDS
UNDER CONDITIONS ENCOUNTERED IN SOLAR ENERGY SYSTEMS**

by

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January 1980

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
I. INTRODUCTION	1
II. EXPERIMENTAL DETAILS	3
A. Materials	3
B. Fluid Corrosivity Sensor	4
C. Heat-flux-loop Facility	5
D. Static Autoclave	8
E. Rotating-disk Heat-flux Autoclave	8
F. Electrochemical Corrosion Measurement System	9
III. RESULTS	9
A. RDHFA Tests	10
B. Static Autoclave Tests	10
C. Heat-flux Loop Facility (HFLF)	17
D. Texas Instruments Corrosivity Sensor	30
E. Electrochemical Corrosion Measurements	34
IV. SUMMARY AND CONCLUSIONS	39
ACKNOWLEDGMENTS	42
REFERENCES	42

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Schematic of an Active Solar Energy System	2
2.	Fluid Corrosivity Sensor and Electronic Interface Developed by Texas Instruments Company	5
3.	Heat-flux Loop Facility Used to Evaluate the Corrosion Behavior of Materials in Ethylene Glycol-Water Solutions . .	6
4.	Schematic of the HFLF Flow System	6
5.	Schematic of the Ring Specimen Holder in the HFLF	7
6.	Schematic of the Static Autoclave Used to Expose Corrosion Specimens to Heat-transfer Fluids at Temperatures Simulating Flow Stagnation in Solar Collectors	8
7.	Schematic of the Rotating-disk Heat-flux Autoclave (RDHFA) .	9
8.	SEM Micrograph and EDAX Analysis of the Coating on a Copper Specimen after Exposure to a Solution of 50 Volume Percent GM-6038M Coolant in CW for 500 h at 450 K in a Static Autoclave	13
9.	Photograph of Ring Specimens of CA 122 Copper, Black Iron, 6061 Aluminum, and Galvanized Black Iron after Exposure to a 50 Volume Percent UEG-CW Solution for 48 h at 413 K in the Heat-rejection Loop of the HFLF	20
10.	Surface (a) and Cross Section (b) of the Aluminum Specimen Shown in Fig. 9, after Chemical Cleaning	21
11.	Aluminum (6061), Copper (CA122), and Black Iron Specimens after Exposure to a 50 Volume Percent IEG (GM-6038M)-CW Solution for 500 h in the Heat-rejection and Heat-absorption Loops of the HFLF at 413 and 378 K, Respectively, in Run 3	22
12.	Surfaces of Aluminum, Copper, and Iron Specimens Shown in Fig. 11	23
13.	Defilmed Metal Loss as a Function of Time for 6061 Aluminum, CA122 Copper, and Black Iron Specimens Exposed to a 50 Volume Percent IEG-CW Solution in the HRL of the HFLF at 413 K during Run 3	25
14.	Defilmed Metal Loss as a Function of Time for CA122 Copper and Black Iron Specimens Exposed to a 50 Volume Percent IEG-CW Solution in the HAL of the HFLF at 378 K during Run Run 3	26

LIST OF FIGURES (CONTD.)

<u>No.</u>	<u>Title</u>	<u>Page</u>
15.	Reserve Alkalinity and pH of the IEG-CW Solution as a Function of Time in the HFLF during Runs 2 and 3	27
16.	SFM Micrograph and EDAX Analysis of the Coating on a Copper Specimen Exposed to IEG-CW Solution for 1000 h at 393 K in the HRL of the HFLF during Run 2	29
17.	Potential Output of the TI Corrosivity Probe at 395, 423, and 453 K as a Function of the pH of 50 Volume Percent IEG-CW Solutions Degraded by the Addition of HCl	31
18.	Effect of Temperature on the Probe Potential in IEG-CW Solutions with Several pH Values, from the Results in Fig. 17	31
19.	Response of the Corrosivity Probe as a Function of Time and Temperature in a 50 Volume Percent IEG (GM-6038M)-Deionized Water Solution in the RDHFA	33
20.	Response of the Corrosivity Probe as a Function of Time and Temperature in a 50 Volume Percent UEG-Deionized Water Solution in the RDHFA	33
21.	Potentiodynamic Polarization Plots for (a) Black Iron, (b) ETP Copper, and (c) 6061 Aluminum at 348 K in a 50 Volume Percent IEG-CW Solution after 1000 h in the HFLF in Run 3	35
22.	Dependence of the Corrosion Potential and Instantaneous Corrosion Rate of Black Iron, ETP Copper, and 6061 Aluminum in a 50 Volume Percent IEG-CW Solution on the Specimen Equilibration Time before the Start of the Test	36
23.	Effect of Temperature on the Instantaneous Corrosion Rates of Black Iron, ETP Copper, and 6061 Aluminum in a 50 Volume Percent IEG-CW Solution in Which the Specimens Were (a) Not Equilibrated; (b) Equilibrated in the Fluid for 24 h before the Test	37
24.	Effect of Temperature on Corrosion Potential of Black Iron, ETP Copper, and 6061 Aluminum in a 50 Volume Percent IEG-CW Solution in Which the Specimens Were Equilibrated for 24 h before the Start of the Test	38

LIST OF FIGURES (CONTD.)

<u>No.</u>	<u>Title</u>	<u>Page</u>
25.	Effect of Temperature on the Corrosion Potential and Instantaneous Corrosion Rate of Black Iron in 50 Volume Percent IEG-CW Solutions in the As-formulated Condition and after 1000 h in the HFLF in Runs 2 and 3	41
26.	Effect of Temperature on the Corrosion Potential and Instantaneous Corrosion Rate of ETP Copper in 50 Volume Percent IEG-CW Solutions in the As-formulated Condition and after 1000 h in the HFLF in Runs 2 and 3	42
27.	Effect of Temperature on the Corrosion Potential and Instantaneous Corrosion Rate of 6061 Aluminum in 50 Volume Percent IEG-CW Solutions in the As-formulated Condition and after 1000 h in the HFLF in Runs 2 and 3	42

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
I.	Composition of Inhibited Ethylene Glycol Engine Coolant (GM-6038M)	4
II.	Corrosion Results for Aluminum, Copper, and Iron after Exposure to IEG Heat-transfer Fluids for 500 h at 450 K in a Static Autoclave	11
III.	Corrosion of Aluminum, Copper, and Iron after Exposure to 10 Volume Percent Ethylene Glycol Solutions with Different Inhibitors for 500 h at 450 K in a Static Autoclave	14
IV.	Decrease in Reserve Alkalinity and pH of Three Different Heat-transfer Fluids after 500 h at 450 K in Static-autoclave Tests	16
V.	Concentration of Corrosion Inhibitors and Products of Fluid Degradation in GM-6038M-CW Solutions after 500 h at 450 K in Autoclave Tests	17
VI.	Corrosion Results for Aluminum, Copper, Iron, and Galvanized Iron after Exposure to a 50 Volume Percent UEG Solution for 48 h in the HFLF (Run 1)	19
VII.	Corrosion Results for Aluminum, Copper, and Iron after Exposure to 50 Volume Percent IEG (GM-6038M)-CW Solution for 1000 h in the HFLF (Run 3)	24
VIII.	Concentration of Corrosion Inhibitors and Products of Fluid Degradation in 50 Volume Percent IEG (GM-6038M)-CW Solutions from HFLF Tests	28

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ABSTRACT

The corrosion behavior of aluminum, copper, and iron in inhibited ethylene glycol-ASTM corrosive water solutions was evaluated in a laboratory loop under isothermal and heat-flux conditions for 1000 h at temperatures between 378 and 413 K, in static autoclave tests at 450 K for 500 h, and by potentiodynamic polarization measurements at temperatures between 298 and 348 K. The effect of time, temperature, and ethylene glycol concentration of the heat-transfer fluid on the extent of inhibitor depletion was determined from analyses of the reserve alkalinity, pH, and inhibitor content of the solutions. The performance of an electrochemical sensor as a monitor of fluid quality was also evaluated. A heat flux of 0.4 to 1.0 kW/m² did not have a significant effect on the corrosion behavior of the various materials at temperatures between 378 and 413 K. The corrosion rates of aluminum, copper, and iron in the 50 volume percent inhibited ethylene glycol-corrosive water solution decreased as a function of time during the 1000-h test. At 413 K, the corrosion rate of copper was considerably higher than that of iron or aluminum at low flow velocity. Significant degradation of the fluid quality, as indicated by the measurement of the pH, reserve alkalinity, and inhibitor concentrations, occurred after several hundred hours at temperatures of ~ 450 K.

I. INTRODUCTION

Interest in solar energy systems has increased in recent years because of the rapidly escalating cost of fuel oil and natural gas. Although solar central power systems have received much attention, the major increase in effort has been in the area of commercial and residential systems. The use of solar energy as a heat source to supply or supplement the space- and/or water-heating systems of buildings can substantially reduce the demand on conventional heating sources.

An active fluid system for solar energy utilization typically has two heat-transfer loops (Fig. 1).^{1,2} The primary loop consists of a solar collector, a heat exchanger, and components used for containment of the heat-transfer fluid. The heat-transfer fluid in this loop must maintain suitable characteristics over a wide range of operating temperatures. The heat from the primary loop is transferred to the secondary loop, which supplies the heat to a thermal storage system and/or to the component that utilizes the heat, e.g., a water heater. In many cases, the primary heat-transfer loop requires freeze protection to prevent damage to the system during periods of low insolation, e.g., nighttime or periods of extensive cloud cover when the ambient temperature is low. The amount and type of freeze protection required depend on the climatic region in which the system is located. Although freeze protection is not needed for many heat-transfer fluids (e.g., silicone oils), these fluids are more expensive and have poorer heat-transfer properties than aqueous solutions.

Fig. 1. Schematic of an Active (Forced-flow) Solar Energy System.
ANL Neg. No. 306-79-918.

Heat-transfer fluids must exhibit adequate thermal stability over the expected service life of the fluid, and must have a minimal effect on the performance of containment materials used in the system. Although fluid temperatures in the solar collector are relatively low during normal operation (e.g., < 393 K), higher temperatures (> 448 K) can occur during periods of flow stagnation in the collector.³ The corrosion behavior of metals exposed to various heat-transfer fluids depends on temperature, heat flux at the metal-fluid interface, degree of aeration of the fluid, and the presence of dissimilar metals in the containment system.

In this investigation, the corrosion behavior of several metals (i.e., aluminum, copper, black iron, low-carbon steel, and galvanized black iron and low-carbon steel) was evaluated in ethylene glycol-water solutions under conditions of interest in solar systems. The corrosion experiments were conducted under isothermal and heat-flux conditions encountered in normal operation of solar collectors. Several experiments were performed at elevated temperatures, which simulate conditions during flow stagnation in the collector. The effect of time and temperature on the thermal stability and corrosivity of the fluids was evaluated. The feasibility of using an electrochemical sensor to monitor the corrosivity of the heat-transfer fluid was also investigated.

Several types of experimental apparatus were designed and constructed for use in this investigation. The corrosion behavior of materials was evaluated in an autoclave and in a heat-flux loop facility (HFLF). The HFLF was used to determine the corrosion behavior of materials under prototypic conditions, whereas fluid-stagnation temperatures were achieved in the static autoclave. The corrosion behavior of the metals was determined primarily from weight-loss measurements on defilmed specimens. The inhibitor content of the fluid was evaluated as a function of time and temperature during the experiments. The performance of an electrochemical sensor, purchased from the Texas Instruments Company (TI) to monitor the corrosivity of the fluid solutions, was evaluated under various conditions in this study.

Electrochemical corrosion-measurement techniques were also used to determine instantaneous corrosion rates for comparison with results from metal weight-loss determinations.

II. EXPERIMENTAL DETAILS

A. Materials

The heat-transfer fluids used in the corrosion study were aqueous solutions of ethylene glycol. Most of the experiments involved GM-6038M, an inhibited ethylene glycol (IEG) solution manufactured for use as an automotive coolant. The composition specification for GM-6038M is given in Table 1. The coolant was diluted with corrosive water (CW), prepared as specified in ASTM Standard D-2570 (i.e., deionized water with 100 ppm each of Cl^- , SO_4^{2-} , and HCO_3^- ions).⁵ For comparison, tests were also conducted with uninhibited ethylene glycol (UEG), i.e., antifreeze-grade (AFG) ethylene glycol, diluted with the above CW formulation. Other fluids will be described later in the text. Although considerable information on the corrosion behavior of materials in IEG-water solutions has been generated by the automotive industry,⁶ the conditions of interest for solar applications are different from those in automotive applications. Full stagnation in a solar collector could subject the heat-transfer fluid to temperatures more than 50 K higher than the maximum temperature experienced in an automobile engine.

TABLE I. Composition of Inhibited Ethylene Glycol Engine Coolant (GM-6038M)

	<u>Weight Percent</u>
Ethylene glycol	95.65
Sodium nitrate	0.20
Sodium tetraborate	1.00
Sodium metasilicate	0.15
Sodium orthophosphate	0.45
Sodium mercaptobenzothiazole (50% water solution)	0.55
Sodium hydroxide	0.20
Pluronic L-61 or equivalent	0.05
Green dye	0.005
Water	1.75

The pipe materials used in this study were 6061 aluminum, CA122 copper, black iron, and galvanized black iron. The sheet materials include 6061 aluminum, ETP copper, 1008 steel, and 1008 steel galvanized with a G90 zinc coating.

The metal weight loss of the various corrosion specimens was determined from the weight change of defilmed specimens after exposure to the fluids. Cleaning techniques specified in ASTM Standard G1 were used to defilm the specimens.

B. Fluid Corrosivity Sensor

The electrochemical sensor used in this study was adapted from a design used by the automotive industry to identify breakdown of corrosion inhibitors in engine coolants.⁷ Initially, corrosion inhibitors in coolant formulations form protective films on metallic surfaces of the coolant system. As the coolant degrades, the protective films become unstable. Thus, the acids formed during the degradation of ethylene glycol can increase the corrosion rate of the metals.⁸ The TI probe measures the corrosion potential with a steel-aluminum electrode pair and a silver reference electrode. The corrosion potential is a function of temperature, pH, concentration of ionic species in the fluid, and the nature of the protective film. Empirically, a corrosion potential < -0.4 V is indicative of corrosive conditions in a thermally degraded 50 volume percent IEG solution.⁷ The electrode assembly or probe for use in solar heat-transport systems was redesigned by TI to facilitate removal of the probe without draining the primary loop, and to increase the allowable operating pressure.

The sensor and the electronic interface used for solar-system applications are shown in Fig. 2. The electronic interface consists of an electrometer-type measuring circuit and a linear amplifier to convert the solution potential (0.0 to -1.0 V dc) to a 0 to 5 V dc output. The probe is contained in a 530-mm-long metal tube with epoxy seals at both ends. The hollow interior of the tube contains the lead wires for the electrodes. The electrodes at the fluid end of the probe protrude ~ 13 mm from the epoxy plug. The epoxy seal at the other end of the probe holds an electrical connector. The unit uses a 12-V (nominal) dc power supply and is designed to be compatible with the Site Data-acquisition System monitored by International Business Machines for the National Solar Heating and Cooling Demonstration Program.

Fig. 2. Fluid Corrosivity Sensor and Electronic Interface Developed by Texas Instruments Company. ANL Neg. No. 306-79-933.

A feedthrough assembly allows the insertion of the probe into the test facilities used in the present study. The response of the probe, as a function of pH of the coolant solutions and temperature, was determined in a glass apparatus. The output of the TI sensor was monitored on a strip-chart recorder and the potential was periodically checked with an electrometer to assure the accuracy of the amplifying circuit.

C. Heat-flux-loop Facility

The corrosion behavior of pipe materials in the ethylene glycol-water solutions was determined under typical conditions in solar collector systems. The HFLF is shown in Fig. 3, and a schematic of the flow system is illustrated in Fig. 4.

Fig. 3. Heat-flux Loop Facility (HFLF) Used to Evaluate the Corrosion Behavior of Materials in Ethylene Glycol-Water Solutions. ANL Neg. No. 306-79-932.

Fig. 4. Schematic of the HFLF Flow System. ANL Neg. No. 306-79-914.

The facility consists of two subsystems, i.e., a heat-rejection loop (HRL) and a heat-absorption loop (HAL). This nomenclature refers to the heat-flux condition at the surface of the corrosion specimens, which contained either an internal heater or an air-cooled tube, respectively. Each loop functions independently; i.e., different temperature and flow conditions are established in the two loops, and specimen insertion and removal are achieved without disruption of the rest of the system. During operation, the loops were maintained at different temperatures and a mixing flow

was maintained between the loops to simulate thermal cycling of the fluid in solar collector systems. Thus, the corrosion behavior of a metal at a low temperature could be evaluated in fluids subjected to high temperatures in the same flow system.

The HFLF was constructed of Type 304 stainless steel to minimize contamination of the fluid by the system materials; the system operated at elevated pressure and at temperatures above the normal boiling point of the aqueous solutions. Temperatures of ~ 450 K and flow velocities up to 0.6 m/s (2 ft/s) were achieved in the test sections.

The specimen holder for each subsystem incorporates a heat-flux (0.4 to 1.0 kW/m²) and an isothermal (~ 413 K) region. The specimens were 25.4-mm (1-in.)-long ring sections of 3/8-in. Schedule 40 pipe, the inner diameter of which was machined to 13.0 mm (0.510 in.) to fit the Teflon-coated specimen holder. The specimens were electrically isolated from each other and the specimen holder by Teflon. A schematic of the specimen holder is shown in Fig. 5. Only the outside surface of the specimens was in contact with the flowing coolant.

Fig. 5. Schematic of the Ring Specimen Holder in the HFLF.
ANL Neg. No. 306-79-931.

D. Static Autoclave

A stainless steel autoclave was used to determine the effects of high temperature and inhibitor breakdown on the corrosion behavior of metals under conditions that simulate fluid stagnation in a solar collector. A schematic of the static autoclave is shown in Fig. 6. The autoclave was equipped with a water-cooled coil to rapidly reduce the temperature of the fluid when the autoclave was periodically opened to the atmosphere to replenish oxygen in the system. The fluid temperature was monitored with a stainless steel-clad thermocouple, and the solution was stirred during the tests with a Teflon-coated bar magnet. The stainless steel specimen holder could accommodate four 25.4 x 76.2 x 0.8 mm (1 x 3 x 0.032 in.) flat samples, which were electrically isolated by Teflon grips. Two liters of solution were used for each test, and the ratio of fluid volume to specimen surface area was $\sim 13 \text{ ml/cm}^2$.

Fig. 6. Schematic of the Static Autoclave Used to Expose Corrosion Specimens to Heat-transfer Fluids at Temperatures Simulating Flow Stagnation in Solar Collectors. ANL Neg. No. 306-79-925.

E. Rotating-disk Heat-flux Autoclave

An autoclave was designed and constructed to perform rotating-disk corrosion tests. The unique feature of the design is the presence of a heater in the disk-shaped specimen holder to provide a heat flux across the specimen/fluid interface. A schematic of the rotating-disk heat-flux autoclave (RDHFA) is shown in Fig. 7. The autoclave was designed to operate at

a pressure of ~ 1 MPa (~ 150 psig), and a maximum rotational velocity at the outer edge of the sample of 0.9 m/s (~ 3 ft/s). The temperature, rotational speed, and heat flux could be controlled during the test.

Fig. 7. Schematic of the Rotating-disk Heat-flux Autoclave (RDHFA).
ANL Neg. No. 306-79-916.

F. Electrochemical Corrosion Measurement System

An electrochemical corrosion measurement system (Model 350) was purchased from Princeton Applied Research. This unit is a microprocessor-controlled system which performs several electrochemical corrosion measurements, e.g., potentiodynamic polarization plots, Tafel plots, and polarization-resistance plots. The glass corrosion cell consists of a flask, graphite counter electrodes, sample holder, and a saturated calomel reference cell. Instantaneous corrosion rates determined by electrochemical techniques were compared with results from other experiments.

III. RESULTS

Several tests were performed in the autoclaves under conditions which simulate fluid stagnation in a solar collector. The corrosion behavior of the various materials was also evaluated in two 1000-h corrosion

runs under isothermal and heat-flux conditions in the pumped-loop facility. The performance of the TI corrosivity probe was evaluated in the autoclave as well as in the loop experiments. Corrosion rates determined in these tests were also correlated with instantaneous corrosion rates determined from potentiodynamic polarization measurements on several of the materials. Relevant properties of the inhibited ethylene glycol-water solutions, namely, solution pH, reserve alkalinity, and inhibitor depletion, were evaluated during several of the corrosion experiments.

A. RDHFA Tests

Two tests were performed in the RDHFA to provide initial information relative to the operation of the TI probe and to evaluate the reliability of the apparatus. Inhibited and uninhibited ethylene glycol diluted with deionized water to a 50 volume percent solution was used in the two experiments. In an attempt to promote breakdown of the fluids, low-carbon steel was immersed in the solutions during both runs. The time-temperature conditions during these experiments were as follows: Slowly increase the solution temperature to ~ 373 K and hold at temperature for two days, increase the temperature to ~ 403 K and hold for two days, decrease the temperature to ~ 373 K and hold for one day, and cool the solution to room temperature. A more detailed description of these tests will be presented in a later section on the performance of the TI probe.

Problems were encountered with the rotational drive system in the RDHFA. After three hours, the rotating shaft froze, and attempts to re-establish disk rotation during this test were unsuccessful. Prior to the start of the second test, minor adjustments in the rotating assembly were made to free the rotating shaft. Shortly after the start of the second run, the shaft froze and could not be rotated. A posttest inspection of the assembly indicated that the thrust washers and bushings used in the rotating seal were damaged. Redesign of the rotating assembly and seal was necessary to rectify the problem; however, this effort was curtailed in favor of other work.

B. Static Autoclave Tests

The static autoclave was also used to evaluate the effects of high-temperature fluid stagnation on the corrosion behavior of the metals in IEC coolants. The solutions were held at ~ 450 K ($\sim 177^\circ\text{C}$) for 1.8 Ms (500 h). At weekly intervals, the solution was rapidly cooled to room temperature, the cover gas was purged with air, and the solution was heated to the test temperature. The solution was stirred during the tests to simulate the thermal siphoning in a collector during flow stagnation.

In these experiments, preweighed samples of aluminum, iron, and copper were exposed to solutions formulated with CW and GM-6038M coolant at concentrations of 10, 30, and 50% by volume. To determine the effect of surface condition on corrosion behavior, copper specimens were exposed to the solutions in both the as-received and polished (600 grit) conditions. All specimens were degreased and weighed prior to immersion in the fluid.

The total metal weight loss was corrected for metal removal during the cleaning procedure that was used to defilm the specimens. The corrected weight losses, i.e., those due to corrosion, are listed in Table II. Since surface condition had no discernible effect on the corrosion of copper, the average weight loss is reported. The uniform corrosion rates are also listed in Table II. The corrosion rate of aluminum in the 10% solution was much higher than in the other solutions. This may have been due either to the low inhibitor concentration in this solution or to degradation of the inhibitor at elevated temperature to the extent that a protective film did not form on aluminum. If the attack resulted from thermal degradation of the fluid, one may expect that the solutions with higher inhibitor concentrations will also become corrosive as the exposure time increases. With regard to the identity of the corrosive species, it has been reported that high concentrations of iron and copper (> 200 ppm) in UEG solutions can cause a hundredfold increase in the corrosion rate of aluminum.⁹ The increase in the corrosion rate is even greater when chlorides are also present in solution. A high iron-ion concentration in the 10% IEG solution probably accounts for the significant corrosion rate of aluminum in the present experiment.

TABLE II. Corrosion Results for Aluminum, Copper, and Iron after Exposure to IEG Heat-transfer Fluids^a for 500 h at 450 K in a Static Autoclave

Material	Concentration of GM-6038M Coolant, Vol. %					
	10		30		50	
	Defilmed Metal Loss, g	Corrosion Rate, ^b mm/y	Defilmed Metal Loss, g	Corrosion Rate, ^b mm/y	Defilmed Metal Loss, g	Corrosion Rate, ^b mm/y
Aluminum (6061)	1.37	2.21	nil ^c	nil	nil ^c	nil
Copper (ETP)	0.18	0.09	0.42	0.20	0.07	0.03
Iron (1008)	0.02	0.01	<0.01	<0.005	nil ^c	nil

^aHeat-transfer fluids were formulated from 10, 30, and 50 volume percent of GM-6038M engine coolant in CW.

^bSurface area of the specimens was 39 cm².

^cWeight loss of $\lesssim$ 2 mg.

The weight loss of the steel specimens decreased as the concentration of ethylene glycol increased. The dependence of the corrosion rate of steel on the ethylene glycol concentration may also be due to partial depletion of inhibitors in the solution.

Copper exhibited a large weight loss in the 30% ethylene glycol solution, and smaller losses in the 10 and 50% solutions. The reason for smaller copper loss in the 10% solution relative to the 30% solution is unclear. It is not known whether aluminum in the 10% solution contributed to the lower weight loss for the copper specimens. The black corrosion product formed on the copper readily spalled from most of the specimen surface during cleaning. Large flakes of similar material were found on the bottom of the autoclave after each run. Energy-dispersive x-ray analyses (EDAX) of the corrosion product (Fig. 8) indicate the presence of copper and sulfur only (oxygen cannot be determined by this technique). Spallation of this coating allows copper to react more readily, since a relatively clean surface is exposed to the fluid under the conditions of this test. In general, spalling occurs when coatings become relatively thick or during rapid temperature changes. Both conditions were present in the case of the copper specimens. Spallation of the coating may also contribute to the apparent discrepancy between the corrosion results for copper in the 10 and 30% solutions.

Corrosion tests on antifreeze solutions by the automotive industry are typically performed at lower temperatures than were used in the present investigation. The protective coating that forms on copper during simulated service tests on engine components is a loosely adherent film.¹⁰ The solid black layer observed in the present study apparently results from the higher temperature. The pungent odor and the sulfur content of the copper corrosion layer suggests that decomposition of the sodium mercaptobenzo-thiazole (NaMBT) occurred. The breakdown of NaMBT could be the source of sulfur in the solution. Sulfate in the CW is an unlikely source because of the relatively high stability of sulfate ions in solution.

The inclusion of NaMBT in ethylene glycol inhibitor packages is primarily for the protection of copper-base alloys and solders. Another inhibitor, e.g., sodium tolytriazole (NaTT), can be substituted in coolant formulations at lower concentrations than that of NaMBT and still provide the same corrosion protection for those metals.¹⁰ It has also been demonstrated that the stability of NaTT at 388 K (115°C) is superior to that of NaMBT.¹¹ Triazole inhibitors are stable at temperatures up to ~ 573 K (300°C)¹² and are superior to NaMBT in protecting copper from corrosion in the presence of chloride.¹³ Since the decomposition of NaMBT was suspected in the preceding high-temperature tests, two additional runs were conducted with ethylene glycol-base coolants to determine the relative merits of the two copper corrosion inhibitors. The inhibitor packages in the two coolants were identical, except that one contained NaMBT for copper protection and the other contained NaTT. The coolants were tested at 10 volume percent in CW, since GM-6038M was relatively aggressive at this concentration. The results of weight-loss measurements on specimens exposed in these solutions for 500 h at 450 K (177°C) are listed in Table III.

Fig. 8. SEM Micrograph and EDAX Analysis of the Coating on a Copper Specimen after Exposure to a Solution of 50 Volume Percent GM-6038M Coolant in CW for 500 h at 450 K in a Static Autoclave. ANL Neg. No. 306-79-910.

TABLE III. Corrosion of Aluminum, Copper, and Iron after Exposure to 10 Volume Percent Ethylene Glycol Solutions with Different Inhibitors^a for 500 h at 450 K in a Static Autoclave

Material	Coolant A (NaTT)		Coolant B (NaMBT)	
	Defilmed Metal Loss, g	Corrosion Rate, ^b mm/y	Defilmed Metal Loss, g	Corrosion Rate, ^b mm/y
Aluminum (6061)	0.67	1.10	0.43	0.71
Copper (ETP)	0.04	0.02	0.10	0.05
Iron (1008)	0.02	0.01	0.04	0.02

^aCoolants A and B consisted of 10 volume percent of IEG-base coolants in CW. The major inhibitors of copper corrosion in the two solutions were sodium tolyltriazole (NaTT) and sodium mercaptobenzothiazole (NaMBT), respectively; otherwise, the inhibitor packages for the two coolants were the same.

^bSurface area of the specimens was 39 cm².

The weight losses for the copper and iron specimens in the 10% solution of coolant A (NaTT) are somewhat lower than the weight losses for these materials after exposure to the 10% solution of GM-6038M. The weight-loss results for aluminum in coolants A and B are similar, and both are considerably higher than those for iron and copper under the conditions of these tests.

The effect of high temperature on the pH and reserve alkalinity (RA) of the fluids was also determined during the static-autoclave tests. The RA, which was evaluated by the procedure in ASTM Standard D-1121,¹⁴ is a measure of the capability of the solution to buffer acids formed during breakdown of the fluid. RA values are not a reliable indicator of protective film formation on all metals; they depend primarily upon the concentration of borates and phosphates in solution and are only slightly affected by NaMBT or NaTT. Silicate and nitrate inhibitors at concentrations present in automotive coolants also have little or no effect on RA. Despite these limitations, RA can under many circumstances give an indication of the corrosion protection afforded by a fluid, and is commonly used for this purpose.

The results of the evaluations of pH and RA of several heat-transfer fluids after 500 h at 450 K are listed in Table IV along with values for the as-formulated ethylene glycol solutions. The results for GM-6038M show that the RA decreases as the concentration of the coolant in the solution decreases. The extent of fluid breakdown is not a linear function of time, i.e., degradation of the fluid occurs more rapidly when the inhibitor concentration is relatively low. This effect is also evident in the pH values, i.e., the largest reduction in pH during the 500-h test period occurred for the most dilute solution.

Table IV also lists the pH and RA values of coolants A and B before and after the tests. The pH of a 10% solution of coolant A in corrosive water was higher than that of coolant B both before and after the tests; however, the pH of solution A showed a greater relative decrease during the experiments. In contrast, the RA of solution B was higher than that of solution A both before and after the tests, although the decrease in RA was somewhat greater for solution B.

The decreases in the pH of 10% solutions of GM-6038M and coolant A were comparable. Although the decrease in RA was greater for the coolant A solution than for the GM solution (Table IV), the corrosivity of coolant A for copper and aluminum was lower than that of the GM solution (Tables III and II, respectively). If RA were an accurate predictor of fluid corrosivity, a large decrease in RA would imply a high corrosion rate. The results contradict this premise and demonstrate that a more complete understanding of inhibitor chemistry during breakdown of the fluids is required. RA is only a measure of capability to buffer acids that form as the fluid degrades, and only the phosphate and borate inhibitors in these fluids have appreciable acid-buffering capability.

An investigation of inhibitor depletion and its relationship to corrosion behavior of the materials under stagnation conditions was initiated. Depletion of the various corrosion inhibitors was determined by analyzing the solutions before and after the tests. Because of the variety of compounds in corrosion-inhibitor packages, a complete analysis would require the use of an ion chromatograph, a liquid chromatograph, and an atomic absorption unit. Fluid samples of the 10, 30, and 50% GM-6038M solutions were analyzed* with an ion chromatograph after 500 h at 450 K. The concentrations of phosphates, nitrates, nitrites, NaMBT, and glycolic acids in the solution before and after the tests are listed in Table V. The values represent concentrations in the undiluted coolant, i.e., an equal volume of IEG was used for each evaluation so that a direct comparison could be made. The results show a degradation of the inhibitors due to the test conditions, and, as the corrosion results indicate, the degradation is greater for more dilute coolant solutions. Since nitrates and phosphates are used for corrosion protection of aluminum,^{15,16} the low inhibitor concentrations in the 10% coolant solution (e.g., 0.02% nitrates and no phosphates) could account for the large metal weight loss of the aluminum specimens in this solution. Although the concentrations of all of the iron-corrosion inhibitors (viz., phosphates, nitrates, silicates, and borates)

*Analyses performed by Northern Petrochemical Company, Morris, IL.

TABLE IV. Decrease in Reserve Alkalinity^a and pH of Three Different Heat-transfer Fluids^b after 500 h at 450 K in Static-autoclave Tests

Coolant Concentration, Vol. %	Reserve Alkalinity ^b	Percent Decrease	pH	Percent Decrease
<u>GM-6038M</u>				
50 (Initial)	17.6	-	10.0	-
50	15.0	15	8.5	15
30	12.2	31	8.2	18
10	11.6	34	8.0	20
<u>Coolant A^c</u>				
10 (Initial)	15.5	-	9.7	-
10	7.6	51	7.6	22
<u>Coolant B^c</u>				
10 (Initial)	18.0	-	8.8	-
10	8.1	55	7.1	19

^aReserve alkalinity (RA) is defined as the volume of 0.1 N HCl required to titrate 10 ml of IEG, diluted with distilled water to 100 ml, to a pH of 5.5.

^bHeat-transfer fluids were formulated from ethylene glycol-base engine coolants and CW.

^cSee Table III, footnote a.

TABLE V. Concentration^a of Corrosion Inhibitors and Products of Fluid Degradation in GM-6038M-CW Solutions after 500 h at 450 K in Autoclave Tests

Fluid Constituent	Concentration of GM-6038M Coolant, Vol. %			
	10	30	50	50 (As-formulated)
Sodium Phosphate	b	0.13	0.11	0.20
Sodium Nitrate	0.21	0.20	0.24	0.23
Sodium Nitrite ^d	<0.01	<0.01	0.02	b
NaMBT ^c	b	b	b	0.27
Glycolic Acid ^d	0.20	0.37	0.28	<0.01

^aConcentrations (in wt.%) are based upon equal volumes of coolant.

^bNone detected.

^cDetermined by spectrophotometry; other constituents were determined by ion chromatography. Analyses performed by the Northern Petrochemical Company, Morris, IL.

^dFluid degradation products.

were not evaluated, the decrease in the concentration of the phosphates and nitrates as the coolant concentration decreases is consistent with the slight enhancement of iron corrosion. The corrosion behavior of copper is primarily affected by the concentration of NaMBT in solution. High temperature led to the dissociation of NaMBT (Table V). The concentration of sulfate, chloride, and bicarbonate in the solution increases as the coolant concentration decreases, since CW is the primary source of these ions.

C. Heat-flux Loop Facility (HFLF)

The HFLF was used to evaluate the corrosion behavior of containment materials in heat-transfer fluids at temperatures similar to those in solar heat-transfer loop systems. In the first experiment (run 1), corrosion specimens of the various materials were exposed to a 50% solution of UEG in CW to provide baseline data for comparison with results from specimens exposed to IEG solutions. The specimens were exposed to flowing UEG solution for ~ 48 h at temperatures of 413 and 378 K in the HRL and HAL, respectively. The heat fluxes in the respective loops were ~ 1.0 and 0.4 kW/m².

The weight-loss results for the materials exposed to the UEG solution are given in Table VI along with the calculated uniform corrosion rates. The corrosion rates represent average values obtained from several specimens of each material. The results for the galvanized pipe are based on the assumption that all the weight loss was attributable to the removal of zinc. The 48-h exposure was sufficient to remove ~60% of the galvanized coating at 378 K (105°C) and ~70% of the coating at 413 K (140°C).

Figure 9 shows the appearance of the specimens after exposure to the UEG solution. The galvanized pipe had a black coating and the iron pipe exhibited a thin layer of rust. The 48-h exposure had little effect on the copper specimens; however, pitting attack occurred on the aluminum specimens. The maximum pit depth on specimens exposed at 413 K was 0.3 mm. Figure 10 shows the aluminum surface after cleaning, and a cross section of typical pits in the material. Although localized pitting of aluminum was severe in the 50% UEG solution, this mode of attack did not occur in IEG solutions under the conditions used in the present study, as discussed below.

Two 1000-h tests (runs 2 and 3) were performed in the HFLF with a 50% solution of GM-6038M coolant and CW. The specimens were removed near the midpoint of each run and several specimens of each material were defilmed and reweighed to determine the metal weight loss. Problems with the circulation pumps during run 2 necessitated a reduction in flow velocity past the specimens from ~0.2 m/s to a lower value, which was still sufficient to achieve good mixing of the fluid in all sections of the HFLF. All of run 3 was performed at this lower flow rate. The temperature of the fluid in the HRL was 393 K in run 2 and 413 K in run 3; the temperature in the HAL was 378 K in both runs. The appearance of the various materials after exposure to the fluid for 500 h in run 3 is shown in Fig. 11. Since all specimens of the same material had a similar appearance, only one set of samples is shown. The aluminum surfaces were coated with a black film that was easily removed by rinsing with water. Although an adherent black film coated the iron specimens exposed at 413 K, the film was not as apparent on the samples exposed at the lower temperature (e.g., compare the photographs of the polished iron specimens in Fig. 12). The copper specimens were coated with a layer of strongly adherent black material that resisted chemical cleaning solutions. Some of the corrosion product on the copper exhibited spallation; i.e., flakes of the layer began to lift away from the base metal, revealing another layer of black material beneath. This observation is consistent with results from the autoclave tests, in which large black flakes of copper- and sulfur-bearing material were found on the bottom of the autoclave.

The results of the weight-loss determinations for run 3 are shown in Table VII. The weight-loss data were corrected for the weight losses attributed to the removal of base metal during the defilming of the specimens. As the metal weight losses due to corrosion approach the losses due to chemical cleaning, an accurate evaluation of the weight loss due to the defilming process becomes critical. The corrections for the cleaning procedure in Table VII resulted in apparent weight gains for some of the materials. This is not unusual for specimens which exhibit very low corrosion rates.

TABLE VI. Corrosion Results for Aluminum, Copper, Iron, and Galvanized Iron after Exposure to a 50 Volume Percent UEG Solution^a for 48 h in the HFLF (Run 1)

Material	Specimen Location							
	HRL (413 K)				HAL (378 K)			
	Isothermal		Heat Flux (1.0 kW/m ²)		Isothermal		Heat Flux (0.4 kW/m ²)	
	Defilmed Metal Loss, mg	Corrosion Rate, ^b mm/y	Defilmed Metal Loss, mg	Corrosion Rate, ^b mm/y	Defilmed Metal Loss, mg	Corrosion Rate, ^b mm/y	Defilmed Metal Loss, mg	Corrosion Rate, ^b mm/y
Aluminum (6061)	14	0.69	13	0.64	6	0.30	5	0.25
Copper (CAl22)	9	0.13	9	0.13	2	0.03	2	0.03
Iron (Black)	228	3.84	218	3.68	44	0.74	60	1.01
Galvanized (Black Iron)	573 ^c	10.7	612 ^c	11.4	500 ^c	9.3	557 ^c	10.4

^aThe solution was formulated from 50 volume percent AFG ethylene glycol in CW.

^bSurface area of the 3/8-in. Schedule 40 pipe specimens was 13.8 cm².

^cWeight loss was attributed to the removal of the zinc coating.

Fig. 9. Photograph of Ring Specimens of CA 122 Copper, Black Iron, 6061 Aluminum, and Galvanized Black Iron after Exposure to a 50 Volume Percent UEG-CW Solution for 48 h at 413 K in the Heat-rejection Loop of the HFLF (Table VI). ANL Neg. No. 306-79-908.

RING SPECIMEN

(a)

MOUNT

Al

(b)

Fig. 10. Surface (a) and Cross Section (b) of the Aluminum Specimen Shown in Fig. 9, after Chemical Cleaning. Pitting attack has occurred (arrow). ANL Neg. No. 306-79-909.

Fig. 11. Aluminum (6061), Copper (CA122), and Black Iron Specimens after Exposure to a 50 Volume Percent IEG (GM-6038M)-CW Solution for 500 h in the Heat-rejection and Heat-absorption Loops of the HFLF at 413 and 378 K, Respectively, in Run 3. ANL Neg. No. 306-79-911.

HEAT REJECTION SURFACES

Al

Cu

Fe

HEAT ABSORPTION SURFACES

Al

Cu

Fe

Fig. 12. Surfaces of Aluminum, Copper, and Iron Specimens Shown in Fig. 11.
ANL Neg. No. 306-79-907.

TABLE VII. Corrosion Results for Aluminum, Copper, and Iron after Exposure to 50 Volume Percent IEG (GM-6038M)-CW Solution for 1000 h in the HFLF (Run 3)

Material	Time, h	Specimen Location							
		HRL (413 K)				HAL (378 K)			
		Isothermal		Heat Flux (1.0 kW/m ²)		Isothermal		Heat Flux (0.4 kW/m ²)	
		Defilmed Metal Loss, mg	Corrosion Rate, ^a mm/y	Defilmed Metal Loss, mg	Corrosion Rate, ^a mm/y	Defilmed Metal Loss, mg	Corrosion Rate, ^a mm/y	Defilmed Metal Loss, mg	Corrosion Rate, ^a mm/y
Aluminum (6061)	500 ^b	2	0.010	2	0.010	c	c	c	c
	1000	3	0.007	3	0.007	c	c	c	c
Copper (CA 122)	500 ^b	184	0.26	194	0.28	15	0.02	11	0.02
	500 ^d	63	0.09	-	-	15	0.02	-	-
	1000	292	0.21	257	0.18	28	0.02	25	0.02
Black Iron (As- received)	500 ^b	11	-	17	-	12	-	21	-
	1000	24	-	22	-	29	-	40	-
(Polished)	500 ^b	6	0.010	5	0.008	7	0.011	12	0.020
	1000	6	0.005	8	0.007	11	0.009	14	0.011

^aSurface area of the 3/8-in. Schedule 40 pipe specimens was 13.8 cm². Value based upon linear rate law.

^bTime corresponds to the first 500 h of the 1000-h experiment.

^cSpecimens exhibited a slight net weight gain after defilming and the correction for metal loss due to the chemical cleaning operation.

^dTime corresponds to the last 500 h of the 1000-h experiment.

The corrosion results for as-received iron pipe show considerable variability. This is, in part, due to the presence of varying thicknesses of mill scale, which was removed during the defilming process. When the corrosion rate of iron is relatively large, the effect of mill scale on the total metal loss is not significant; however, in cases where the corrosion rate is small, the uncertainty in the results is magnified. Therefore, the results obtained on polished specimens are viewed with a higher level of confidence than those for the as-received material. The corrosion rate of polished iron specimens in the IEG solutions was quite low in the static autoclave tests as well as in the HFLF.

As shown in Figs. 13 and 14, the majority of the weight losses generally occurred during the initial phase of the test; i.e., the corrosion rates of the various materials decreased as a function of exposure time. This would be expected for the aluminum because of the protective nature of the corrosion-product film. The decrease of weight loss with time for the other materials may be partially attributed to the time period required for the inhibitors to deposit a relatively stable protective film on the metal surfaces.

Fig. 13. Defilmed Metal Loss as a Function of Time for 6061 Aluminum, CA122 Copper, and Black Iron Specimens Exposed to a 50 Volume Percent IEG-CW Solution in the HRL of the HFLF at 413 K during Run 3. ANL Neg. No. 306-79-926.

Fig. 14. Defilmed Metal Loss as a Function of Time for CA122 Copper and Black Iron Specimens Exposed to a 50 Volume Percent IEG-CW Solution in the HAL of the HFLF at 378 K during Run 3. ANL Neg. No. 306-79-919.

Within the variability of the data, the corrosion rates of the metals under the conditions in these tests indicate almost no dependence on heat flux in the range of 0.4 to 1.0 kW/m². Heat flux over the range of 0 to 4.7 kW/m² had no influence on the corrosion rates of 122 copper and 3003 aluminum in a flowing (0.6 m/s) 50:50 mixture of propylene glycol and distilled water at 373 K.¹⁷ However, the corrosion of aluminum alloy 319 and cast iron A-159 in IEG-CW solutions was reported to be more severe at the surface that rejects heat to the coolant than at the surface that accepts heat from the coolant.¹⁸ In the latter study, a cracked protective film formed on the heat-rejecting surface of the aluminum alloy, which in part accounted for the higher corrosion rate. With regard to the effects of heat flux on the corrosion behavior of metals in aqueous solutions at low temperatures, corrosion tests on Type 316 stainless steel in several acid solutions (e.g., H₂SO₄, HNO₃, acetic acid, and H₃PO₄) indicate that the temperature of the metal at the liquid/solid interface, i.e., the skin temperature, was the controlling factor rather than the heat flux.¹⁹ A similar situation may exist with regard to the corrosion of the aluminum alloy in a phosphate-inhibited ethylene glycol solution.¹⁸

Although the low heat flux in the present investigation is prototypic of those encountered in solar collectors under conditions in which the area for heat absorption is approximately the same as the contact area of the heat-transfer fluid, additional corrosion data may be required for higher heat-flux conditions applicable to fin-tube collectors.

The decrease in the RA and pH of the heat-transfer fluid during runs 2 and 3 is shown in Fig. 15. The higher temperature of the fluid in the expansion tank during run 2 (450 versus 413 K) caused a more rapid degradation of the fluid quality. The concentrations of inhibitors and products of fluid degradation in the 50:50 ethylene glycol-corrosive water solutions from the 1000-h tests in the HFLF are given in Table VIII.

Figure 16 shows the surface structure of the film that formed on a copper specimen at 393 K in the HRL of the HFLF after a 1000-h exposure in run 2. The results of the x-ray analysis show that the coating consists primarily of copper and sulfur. The presence of oxygen in the film cannot be determined by this technique. The only other peaks correspond to the silver paint used to attach the specimen to the SEM holder. Since the film was insoluble in water, it is unlikely that CuSO_4 is present in the film. The corrosion-product film on the copper specimen from run 3 had similar characteristics.

Fig. 15. Reserve Alkalinity and pH of the IEG-CW Solution as a Function of Time in the HFLF during Runs 2 and 3.
ANL Neg. No. 306-79-924.

TABLE VIII. Concentration^a of Corrosion Inhibitors and Products of Fluid Degradation in 50 Volume Percent IEG (GM-6038M)-CW Solutions from HFLF Tests

Heat-transfer Fluid	Time, h	Fluid Constituents				
		Sodium Phosphate ^b	Sodium Nitrate	Sodium Nitrite ^e	NaMBT ^c	Glycolic Acid ^e
As-formulated	0	0.20	0.23	d	0.27	<0.01
Run 2	1000	0.10	0.22	0.02	0.04	0.16
Run 3	500	0.12	0.21	0.02	0.09	0.07
	1000	0.11	0.20	0.01	0.09	0.09

^aConcentrations (in wt.%) are based upon coolant content in the fluid.

^bConcentration based on trisodium phosphate.

^cDetermined by spectrophotometry; other constituents were determined by ion chromatography. Analyses performed by the Northern Petrochemical Company, Morris, IL.

^dNone detected.

^eFluid degradation products.

Fig. 16. SEM Micrograph and EDAX Analysis of the Coating on a Copper Specimen Exposed to IEG-CW Solution for 1000 h at 393 K in the HRL of the HFLF during Run 2. ANL Neg. No. 306-79-906.

D. Texas Instruments Corrosivity Sensor

The corrosivity sensor developed by TI for use in automotive coolant systems was redesigned for possible application in solar energy systems. The sensor consists of working and reference electrodes and a junction box which contains circuitry for potential measurement and signal amplification. The sensor monitors the solution potential of the working electrode in the fluid and indicates when the fluid becomes corrosive.

The response of the probe in different heat-transfer fluids was determined in a bench-scale apparatus. The probe was suspended in solutions of IIG which were artificially degraded by the addition of HCl. The sensor output was monitored continuously during a 24-h period in which the probe was equilibrated in the fluid (50% solutions of GM-6038M coolant in CW) prior to the measurement of the solution potential. The effect of pH on the probe potential was determined at several temperatures, viz., 295, 323, and 353 K (22, 50, and 80°C). Prior to each evaluation, the probe electrodes were dipped in a 50% HCl-H₂O solution, rinsed, and wiped clean to remove residual films which formed during the previous determination. Since the electrodes were in the same condition prior to each evaluation, the actual time required for the sensor to equilibrate could also be determined from the output, which was recorded on a strip chart. The equilibration time was found to depend on temperature; i.e., the equilibration time decreased as the solution temperature increased. Although 10 to 12 h were required before the probe potential stabilized at room temperature, only 4 to 6 h were required at 353 K (80°C).

The dependence of probe potential on solution pH is shown in Fig. 17. At all temperatures, the sensor was able to discriminate between acidic and basic solutions. Probe potentials above and below -0.3 V were indicative of basic and acidic solutions, respectively. The dependence of the probe potential on pH increases as the temperature increases. At room temperature, the potential was relatively independent of pH for values <6 or >8; however, at higher temperatures, the probe potential decreases as the pH of the solution decreases. Also, the difference in potential measured in acidic and basic solutions increases as the temperature increases. The dependence of the probe potential on solution temperature is shown in Fig. 18. The potential measured in a solution with a pH of 7.0 shows little dependence on temperature. However, probe potentials in acidic solutions decrease and those in basic solutions increase as the temperature increases. This is consistent with information relative to the higher sensitivity of the probe to determine a transition from noncorrosive to corrosive fluid conditions as the temperature increases.²⁰

A decrease in the solution potential to a value < -0.4 V was indicative of the transition from noncorrosive to corrosive conditions in the fluid evaluated by TI. The discrepancy between this value and the value of -0.3 V determined in the present study can be attributed to the difference in the fluids used in the two investigations. TI used thermally degraded solutions, which would have a different chemical composition than the solutions to which acid was added; i.e., the former solutions probably contained

Fig. 17. Potential Output of the TI Corrosivity Probe at 395, 423, and 453 K as a Function of the pH of 50 Volume Percent IEG-CW Solutions Degraded by the Addition of HCl. ANL Neg. No. 306-79-912.

Fig. 18. Effect of Temperature on the Probe Potential in IEG-CW Solutions with Several pH Values, from the Results in Fig. 17. ANL Neg. No. 306-79-929.

formic and glycolic acids,²¹ in contrast to the hydrochloric acid used for pH reduction in the present investigation.

The TI probe was installed in the various facilities to determine the time-temperature conditions required for fluid breakdown and to correlate the sensor output with the corrosion behavior of the materials. Numerous probe failures were encountered in this investigation. The failures were caused by thermal degradation of the epoxy seals, leakage of fluid into the cavity between the seals which contained the lead wires, and pressure damage to the seals. Only one corrosion-related failure occurred in a probe that was exposed to a corrosive fluid for a long period of time, i.e., the aluminum electrode broke off at a point near the epoxy seal. This can be attributed to galvanic coupling of the aluminum and iron electrodes in a corrosive environment. This corrosion failure does not detract from the proposed use of the probe, since it was not designed to nor is it required to resist corrosive environments for extended periods of time in automotive coolant systems.

Failures of the lower seal resulted in contact of the fluid with the lead wires in the cavity between the probe seals. Fluid in the cavity distorted the emf measurement, although this was not always evident from the sensor output; i.e., a breach in the lower seal could not be easily identified from the sensor output. Physical evidence of a leak in the probe occurred only after the secondary (upper) seal leaked. Although the conditions during the laboratory evaluations of the sensor were more severe than those encountered in most field installations, similar conditions could occur during off-normal operation of some solar systems. If temperatures $> 383\text{ K}$ (110°C) and pressures $> 0.38\text{ MPa}$ (40 psig) can occur in the region where the probe is located, the probe should be redesigned to ensure more reliable operation during extended service.

The response of the probe in solutions containing either UEG or IEG (50 volume percent in deionized water) was evaluated in conjunction with the tests of the RDHFA. Corrosion specimens were not present in the autoclave during these tests. Figure 19 shows the variation of probe potential with temperature and time during the test in the IEG solution. An increase in temperature to $\sim 410\text{ K}$ (137°C) resulted in a sharp decrease in the probe potential, to values indicative of a corrosive fluid. A subsequent decrease in the temperature caused the potential to increase with time. Although this rise in potential indicated that protective films were reforming, the value of the potential remained less than that observed prior to the high-temperature excursion. Since the response of the probe to temperature changes alone was not known, this run was repeated with UEG solution. Figure 20 shows the variation of probe potential with temperature during the latter test. The potentials in the uninhibited solution were indicative of a corrosive fluid except at $\sim 400\text{ K}$ (127°C). The response of the probe in the UEG solution was not consistent with that observed in the IEG solution. The probe potential in the UEG solution responded sluggishly to changes in temperature, and a significant period of time was required for the potential to either stabilize or change after the temperature of the solution was altered. The integrity of the probe seals during the last test was uncertain, since the probe failed a short time after the start of a subsequent test. The failure involved a pressure leak through both seals.

Fig. 19. Response of the Corrosivity Probe as a Function of Time and Temperature in a 50 Volume Percent IEG (GM-6038M)-Deionized Water Solution in the RDHFA. ANL Neg. No. 306-79-920.

Fig. 20. Response of the Corrosivity Probe as a Function of Time and Temperature in a 50 Volume Percent UEG-Deionized Water Solution in the RDHFA. ANL Neg. No. 306-79-913.

Additional data with more reliable probes are required for an assessment of the utility of the TI sensor in solar energy systems. Probes with an improved design, less prone to the failures noted above, would be useful for monitoring the corrosive quality of the inhibited heat-transfer fluids used in many solar energy systems.

E. Electrochemical Corrosion Measurements

Electrochemical measurements have been used to obtain information on the corrosion characteristics of metals and alloys in aqueous environments^{22,23} including ethylene glycol solutions.^{17,24-28} In many instances, good correlations among polarization-resistance and electrode-potential measurements and corrosion weight-loss data have been obtained. Consequently, electrochemical measurements have been used to evaluate the performance of corrosion inhibitors. Information from these experiments supplements but cannot replace results from weight-loss measurements under more prototypic service conditions.

Potentiodynamic measurements were used to obtain the corrosion potential E_{corr} , corrosion current I_{corr} , and the instantaneous corrosion rate of iron, copper, and aluminum in ethylene glycol-CW solutions in the as-formulated condition and after exposure to high temperatures in the HFLF. Figure 21 shows typical polarization plots for the three materials at 348 K in a 50 volume percent solution of IEG (GM-6038M)-CW from run 3 in the HFLF.

The corrosion rate of the material was calculated from the relation

$$\text{CR (mpy)} = \frac{0.13 (I_{\text{corr}}) (\text{EW})}{\rho} \quad (1)$$

where I_{corr} = corrosion current density, $\mu\text{A}/\text{cm}^2$,

EW = equivalent weight of corroding species, i.e., the gram-molecular weight divided by the number of electrons involved in the electrochemical reaction, and

ρ = density of the metal, g/cm^3 .

The corrosion current was obtained from an extrapolation of the cathodic Tafel curve (dashed line in Fig. 21b) to the corrosion potential.

The effect of equilibration time in the test solution, before the start of the test, on the corrosion potential and corrosion rate is shown in Figs. 22a and b for temperatures of 298 and 348 K, respectively. With the exception of the aluminum specimen at 348 K, the corrosion potential and corrosion rate are relatively independent of equilibration time after ~ 6 to 8 h.

The influence of temperature on the corrosion rate of iron, copper, and aluminum in the as-formulated 50 volume percent IEG-CW solution is shown in Figs. 23a and b for specimens evaluated upon immersion in the fluid

(a)

(b)

(c)

Fig. 21. Potentiodynamic Polarization Plots for (a) Black Iron, (b) ETP Copper, and (c) 6061 Aluminum at 348 K in a 50 Volume Percent IEG-CW Solution after 1000 h in the HFLF in Run 3.

Fig. 22. Dependence of the Corrosion Potential and Instantaneous Corrosion Rate of Black Iron, ETP Copper, and 6061 Aluminum in a 50 Volume Percent IEG-CW Solution on the Specimen Equilibration Time before the Start of the Test. From electrochemical measurements at (a) 298 K, (b) 348 K. ANL Neg. No. 306-79-927 and -915, respectively.

Fig. 23. Effect of Temperature on the Instantaneous Corrosion Rates of Black Iron, ETP Copper, and 6061 Aluminum in a 50 Volume Percent IEG-CW Solution in Which the Specimens Were (a) Not Equilibrated; (b) Equilibrated in the Fluid for 24 h before the Test. ANL Neg. Nos. 306-79-921 and -930, respectively.

and after a 24-h equilibration period, respectively. In both experiments, the corrosion rates increase as the temperature increases; however, the corrosion rates after equilibration of the specimens in the solution for 24 h are consistently lower. This can be attributed to the formation of a protective film on the surface of the specimens during the equilibration period. The corrosion rate of copper increases rapidly at temperatures ~ 325 K (Fig. 23b) and is higher than the rates for aluminum and iron at ~ 350 K. This result is consistent with weight-loss data for the three materials in the HFLF tests.

The effect of temperature on the corrosion potential of iron, copper, and aluminum in the as-formulated solution, after an equilibration period of 24 h, is shown in Fig. 24 for comparison with results obtained in solutions from the HFLF. The corrosion potentials for copper and aluminum decrease as the temperature increases, whereas the corrosion potential for iron is relatively independent of temperature.

Fig. 24. Effect of Temperature on Corrosion Potential of Black Iron, ETP Copper, and 6061 Aluminum in a 50 Volume Percent IEG-CW Solution in Which the Specimens Were Equilibrated for 24 h before the Start of the Test. ANL Neg. No. 306-79-917.

The influence of temperature on the corrosion potential and corrosion rate of iron, copper, and aluminum in the heat-transfer fluids from the HFLF after 1000 h in runs 2 and 3 is shown in Figs. 25-27, respectively. The dashed line corresponds to results from the as-formulated solution in Figs. 23b and 24. At temperatures above ~ 325 K, the corrosion rates of iron in solutions from the HFLF are greater than in the as-formulated solution, whereas the condition of the fluid did not have a large effect on the corrosion rates of copper and aluminum. The higher corrosion rates for iron in the solutions from the HFLF are consistent with the decrease in the reserve alkalinity and pH relative to the as-formulated fluid (Fig. 15). The corrosion rates of aluminum in the 50 volume percent IEG-CW solutions are very low, as determined from the weight-loss data and electrochemical measurements in solutions from the 1000-h corrosion experiments. The instantaneous corrosion rates for copper determined by electrochemical measurements are considerably lower than the rates obtained from weight-loss data on specimens exposed to the heat-transfer fluid under conditions of low flow in the HFLF. The higher temperature (~ 400 versus 350 K), fluid flow, and spallation of the corrosion-product film in the HFLF contribute to the difference in the corrosion rates for copper determined by the two methods.

IV. SUMMARY AND CONCLUSIONS

The corrosion behavior of aluminum, copper, and iron in inhibited ethylene glycol-corrosive water solutions was evaluated in a laboratory loop under isothermal and heat-flux conditions, from static autoclave tests, and from potentiodynamic polarization measurements. The effect of time, temperature, and coolant concentration in the heat-transfer fluid on the extent of inhibitor depletion was determined from analyses of the reserve alkalinity, pH, and inhibitor content of the solutions. The performance of an electrochemical sensor to monitor the fluid quality was also evaluated.

The following conclusions are based on results of the experimental program:

1. A heat flux of 0.4 to 1.0 kW/m^2 did not have a significant effect on the corrosion behavior of iron, copper, and aluminum in a 50 volume percent inhibited ethylene glycol-corrosive water solution at temperatures between 378 and 413 K. The corrosion rate of copper was considerably higher than those of iron and aluminum in the 1000-h tests at low flow velocities.

2. In a short-term (48 h) corrosion test at 413 K with a 50 volume percent solution of uninhibited ethylene glycol in corrosive water, aluminum exhibited localized pitting and 70% of the zinc coating on galvanized iron was removed. Under these conditions, the corrosion rate of iron was also significant; however, copper experienced minimal attack in the fluid at a low flow rate.

Fig. 25. Effect of Temperature on the Corrosion Potential and Instantaneous Corrosion Rate of Black Iron in 50 Volume Percent IEG-CW Solutions in the As-formulated Condition and after 1000 h in the HFLF in Runs 2 and 3. ANL Neg. No. 306-79-923.

Fig. 26. Effect of Temperature on the Corrosion Potential and Instantaneous Corrosion Rate of ETP Copper in 50 Volume Percent IEG-CW Solutions in the As-formulated Condition and after 1000 h in the HFLF in Runs 2 and 3. ANL Neg. No. 306-79-922.

Fig. 27. Effect of Temperature on the Corrosion Potential and Instantaneous Corrosion Rate of 6061 Aluminum in 50 Volume Percent IEG-CW Solutions in the As-formulated Condition and after 1000 h in the HFLF in Runs 2 and 3. ANL Neg. No. 306-79-928.

3. In general, the defilmed metal loss for iron, copper, and aluminum at 450 K decreased as the concentration of inhibited ethylene glycol in the corrosive water solution increased from 10 to 50 volume percent in static autoclave tests.

4. Measurements of the reserve alkalinity, pH, and inhibitor concentrations in ethylene glycol-corrosive water solutions indicated significant degradation of the fluid quality after 500 h at 450 K. Complete decomposition of the NaMBT copper-corrosion inhibitor occurred under these conditions.

5. The electrochemical fluid-corrosivity sensor developed by TI could readily distinguish changes in the pH of inhibited ethylene glycol-corrosive water solutions that were artificially degraded by the addition of HCl. The epoxy seals for the electrode and the electrical connector should be redesigned to ensure more reliable operation of the sensor at temperatures and pressures which are likely to be encountered in solar energy systems.

6. Potentiodynamic polarization measurements in 50 volume percent inhibited ethylene glycol-corrosive water solutions in the as-formulated condition and after exposure to a temperature of ~ 400 K for 1000 h indicated that the corrosion rates of iron and aluminum were somewhat higher in the latter solution; however, degradation of the fluid quality was not evident from the corrosion rates of copper in the two solutions.

ACKNOWLEDGMENTS

The author wishes to thank S. S. Malhotra, C. F. Cheng, and T. F. Kassner for helpful discussions during this work. P. J. Moses and B. Oakes of Dow Chemical Company and C. J. Korpics of Sherwin Williams Company provided helpful information. L. J. Marek and R. R. Schlueter assisted in evaluations of the specimens and the construction of the corrosion facilities, respectively. Special thanks are due to T. P. Yates, M. Abel, and personnel at Northern Petrochemical Company for analyzing the inhibitor concentrations in the fluids from the various experiments and for supplying several of the coolants used in this investigation. J. Olivier assisted with the electrochemical corrosion measurements.

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