CORROSION OF ALUMINUM IN WATER

By D. N. Fultonberg

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

FOREWORD

The research described herein, which was conducted by the Westinghouse Atomic Power Divisions, was performed under NASA Contract NAS-3-5215 with Mr. M. H. Krasner, Nuclear Systems Division, NASA-Lewis Research Center, as Technical Manager. The report was originally issued as Westinghouse document WCAP-7029, May 1967.

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I. ABSTRACT

Tests were performed in autoclave systems and in pumped loops in order to determine the corrosion and hydrogen generation of aluminum when subjected to conditions typical of those anticipated in a Tungsten Water-Moderated Reactor (TWMR). These tests, the equipment used, and the results obtained are discussed. It was concluded that the hydrogen generation could be excessive under certain conditions and that a broader program would be necessary in order to predict it with some confidence.

II. SUMMARY

A test program was conducted which was directed toward obtaining relationships establishing the generation of hydrogen as a result of aluminum corrosion in water. This information could then be utilized in the design of a Tungsten Water-Moderated Reactor (TWMR) whose moderator fluid (water) would be contained in an aluminum pressure vessel.

Two general types of tests were performed; autoclave and loop tests, each at several conditions. Test variables included temperature, test duration, surface treatment, and heat flux.

Interpretation of the test results was attempted by several methods; some of which yielded apparently useful relationships, others being discarded. The scatter of data from these few tests indicate that many more tests, with fewer variables, and more closely controlled conditions will be required if meaningful relationships are to be evolved.

The steam treatment of aluminum at the conditions used in this program reduced the subsequent corrosion of the aluminum significantly as compared to the "Hardcoat" treatment, and as evidenced by the autoclave test results. This aspect can also be improved upon by further experimentation with steaming conditions.

III. INTRODUCTION

The moderator fluid in the Tungsten Water-Moderated Reactor (TWMR) is contained in a pressure vessel constructed of aluminum. The aluminum pressure tubes and flow baffles are immersed in, and therefore in contact with, this moderator fluid.

The moderator system is maintained at a pressure of 600 psig during reactor operation. This pressure is reduced to 100 psig when the reactor is shutdown so that large differential pressures will not exist between the moderator system and other systems. If the moderator water contains dissolved gases in sufficient quantities to exceed their solubilities at the reduced pressure of 100 psi, these gases will evolve from solution. The presence of excessive amounts of gas would cause an increase in system pressure, possibly above tolerable limits. This situation would necessitate correction; namely, removal of this excess gas. An additional system would therefore be required, to perform the function of collection and venting of the gas under conditions of zero gravity. It becomes necessary therefore to study the situation, examine the generation of gas, and determine the conditions effecting this gas generation.

It was the express purpose of this program to study the factors influencing the generation of gas in a system containing aluminum in contact with water. The gas in question is hydrogen, a product of the reaction of aluminum and water, the corrosion process. This reaction can be expressed by:

$$2Al + XH_2O \longrightarrow Al_2O_3 \cdot (X-3)H_2 + 3H_2$$
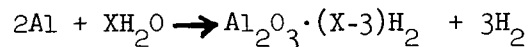
The water hydrating with the alumina has been known to vary from 7 moles per mole of alumina down to none. The specific reaction as well as the rate of reaction is dependent upon the environmental conditions. Some of these conditions which could influence the hydrogen generation include: temperature, pressure, aluminum surface condition, water purity and pH, water velocity, heat flux and duration of contact.

A literature survey revealed the large effect of solution pH on the corrosion of aluminum. Griess, et al[1,2], at ORNL found that other conditions being equal, oxide formed 2.7 times faster when the coolant pH was 5.17 to 7.10 than when the pH was 5.0. Lobsinger[3] and Draley[4,5] both found similar effects although the magnitude differed somewhat.

Lobsinger[3] reports that at velocities below about 60 ft/sec the erosive effect of the fluid should be negligible. English, et al[6] on the other hand, found that the corrosion of 6061-T6 alloy increased as the water velocity was increased from 20 to 107 ft/sec during 10 day tests.

It has been reported that heat flux itself is not a significant variable in determining aluminum corrosion.[1] With constant surface temperature, oxide buildup was independent of heat fluxes in the range 1 to 2×10^6 Btu/hr ft^2. The oxide formation in a solution of pH 5.10 was related to time and surface temperature by the relationship:

$$x = 443 \; \Theta^{0.778} \; \exp\left(\frac{-4600}{k}\right)$$

Where x is the oxide thickness in mils, Θ is the time in hours, and k the surface temperature in degrees kelvin. In the pH range 5.7 to 7.0 the coefficient changes from 443 to 1200, all other constants remaining the same. At heat fluxes below 1×10^6, the correlation predicts oxide thickness considerably higher than were observed, i.e. at 0.5×10^6 Btu/hr ft^2, the correlation predicted thickness twice those actually found. Earlier work by Griess[2] also showed that the rate of oxide formation was a function of the temperature at the specimen-water interface and that heat flux as well as flow rate and coolant temperature in the ranges investigated were important only in that they affected this temperature. Griess also found that at pressures high enough to prevent surface boiling, pressure is not a factor in determining corrosion rate.

The effect of surface pretreatment was touched upon by Griess[6] who found that at velocities up to 47 ft/sec at 260°C, specimens pretreated to obtain 0.04 to 0.09 mil of corrosion, corroded only 1/3 to 1/2 the amount of the "as-machined" specimens. Some comparative tests between "as-machined" 6061-T6 aluminum and 6061-T6 aluminum with a 0.002 inch "Hard Coat" surface run in cadmium sulfate solution at atmospheric boiling indicate a drastic reduction in the surface corrosion due to the hard coat treatment.[7] This treatment is a preprietary process of Alcoa Company. Additional tests run at ORNL[8] indicated that the hard coat treatment reduced corrosion considerably.

Certain impurities in the water could cause a considerable effect on the corrosion of the aluminum. Draley[4] found that chloride ion present to only 1 ppm induces pitting on 1100 aluminum. The presence of 34 ppm of hydrogen peroxide caused less corrosion during the initial period but about the same rate thereafter as for the distilled water case.

IV. PROGRAM REQUIREMENTS

A review of the conditions in the TWMR along with the information found
in some of the references just cited, lead to the establishment of a test
program designed to determine the generation of hydrogen expected during the
TWMR lifetime.

This program was divided into two phases. One phase would simulate
conditions to be experienced during reactor operation and the initial shut-
down periods. The second test phase would be representative of reactor
shutdown periods following the initial period included in phase one testing.

A. Phase I - Reactor Operation & Initial Shutdown

These tests were conducted in a loop in which the test fluid is pumped
at desired velocities and is maintained at the required chemistry
conditions. The aluminum specimens were actually immersion heaters,
clad in 6061-T6 aluminum generating the desired heat in order to
study the effect of heat flux on corrosion.

During each test the following was monitored: solution temperature
system pressure, water flow rate, and test heater power. Liquid
samples were periodically removed for hydrogen analysis. These
samples along with the water in the loop at the test conclusion,
were analyzed for aluminum content as well as other impurities.

Following a test, the heater specimens were weighed to measure the
weight change during test. The outer surface of some heaters were
chemically treated to remove oxide in order to determine reaction
rates.

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B. Phase II - Reactor Shutdown

These tests represented long periods of reactor shutdown. They were
conducted in stagnant autoclave systems at different temperatures.

Preweighed coupons of 6061-T6 aluminum were immersed in solution for
varying periods of time. After test they were all reweighed to deter-
mine test weight change. Some of these were chemically treated in a
manner similar to the heater in phase I.

The autoclave solution was periodically sampled for hydrogen as well
as impurity content.

V. EXPERIMENTAL PROGRAM

A. Phase I

1. Loop Design - The "Modified Materials Compatibility Test Loop", used for this part of the program is shown in Figure 1. The test facility consists of a primary loop with a centrifugal pump, a test section, a test section bypass, a loop cooler, a loop heater section, and a coupon holder section. Auxiliary loop systems consist of a purification and decontamination system with provisions for the addition of chemicals and hydrogen gas, and a pressurizer-volume control system.

The primary system piping is 1" Sch. 40, 316 SST with a design pressure of 2500 psi and $650^{\circ}F$. Primary system valves are Hancock, socket weld globe valves Type 347 SST rated for 1500 psi at $1050^{\circ}F$ and 3105 psi at $650^{\circ}F$. All Grayloc pipe connections are 316 SST rated for operation at 2500 psi and $650^{\circ}F$.

The primary system circulating pump is a Chempump Model CGH 1-1/2-3/4 S. The pump has an available head of 100 ft at 10 gpm flowrate and 85 ft of head at 30 gpm. The pump is rated for operation at 2000 psi and $500^{\circ}F$. This component, therefore, when in this system, is the limiting factor when setting the maximum operating temperature and pressure.

The test section bypass is fabricated of 1" Sch. 40, 316 SST pipe and has an orifice to measure bypass flow. A flow control valve is located downstream of the orifice. The valve is a Fischer Governor Type 657 D with a 316 SST body rated for 3600 psi at $100^{\circ}F$ and can operate at 2500 psi and $650^{\circ}F$.

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RECIRCULATING COOLING WATER SUPPLY

ION-EXCHANGE COLUMN

EVAPORATIVE COOLER

VENT

SAMPLING CYLINDERS

HEATER

THERMAL SLEEVE

TEST SPECIMENS DOUBLE ENDED WATLOW HEATER

CONTROL HEATER & ALARM AA

AA·ALARM

TRIP HEATER & ALARM AA

ION·EXCHANGE COLUMNS

HIGH ALARM·AA LOW

AA TRIP PUMP/ALARM AA·ALARM

MAIN CIRCULATING PUMP

AA·ALARM

THERMAL SLEEVE

SPECIMEN HOLDER

MITTY·MITE REGULATOR

ACCUMULATOR

DRAIN

ALL VALVES INDICATED AS ⋈ SHOWN HAVE HANDLES REMOVED

FROM DRAIN WATER

MAKE·UP TANK

MAKE·UP PUMP

DRAIN

HOUSE AIR SUPPLY

DRAIN

DECONTAMINATION TANK 55 GAL

Figure 1

Modified Materials Compatability Test Loop

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An 88 kw evaporative cooler serves as the loop cooler and operates at manually programmed primary flow exit temperature settings. The cooler downstream of the test section is fabricated from 2" Sch. 80 Inconel primary pipe in a 304 SST, 3 inch Sch. 10 shell. The shellside water level is regulated by a normally open solenoid valve located in the cooling water inlet line. The solenoid valve is wired to a Minneapolis-Honeywell Pyrovane, a temperature indicator of the cooler. The cooler is capable of operation either as the evaporative type or, partially or completely flooded.

The system pressure and volume is controlled by means of Hydrodyne Piston Type accumulator, model 62 A-300-4. The 1/2 gallon accumulator has been provided to prevent losing system fluid during operation from normal makeup and letdown and from temperature fluctuations.

The purification and sample system shown in the attached figure is valved out during test periods. It is only to be used to clean the system up prior to testing, for the addition of hydrogen for those tests requiring it, and for periodic sampling during test operation.

The loop testing required either 2, 3 or 4 specimens to be tested simultaneously, depending on the particular test. Therefore, a test section manifold was built to accommodate up to four specimens. The manifold consists of an upper and lower header, connected by 1" O.D. x 0.065" wall 304 SST tubing. The test pieces were inserted in this tubing and exit from the loop through Conax packing glands in the manner shown in Figure 2. A photograph of this manifold installed with driving heaters is shown in Figure 3.

Gate valves are provided on the inlet and outlet of each test unit to permit isolation and removal of any particular unit during operation. In order to prevent against hazards resulting from turning on power to a particular unit while the isolating gate valves are closed, Inconel rupture disks were added to each unit.

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WATLOW HEATER

CONAX PG PACKING GLAND
TYPE PG5-750-A-T
1000 PSI - @ 400°F RATING

SWAGELOK TFT TEE
1610-3 - 12 TfT

1" X 0.065 - 304 S/S TUBING

0.745" DIA.

NOTE: SIMILAR FITTING ARRANGEMENT AT BOTTOM

2-7/8"

3"

~ 5-1/2"

TEFLON
SEAL

SILVER
BRAZE
SEAL
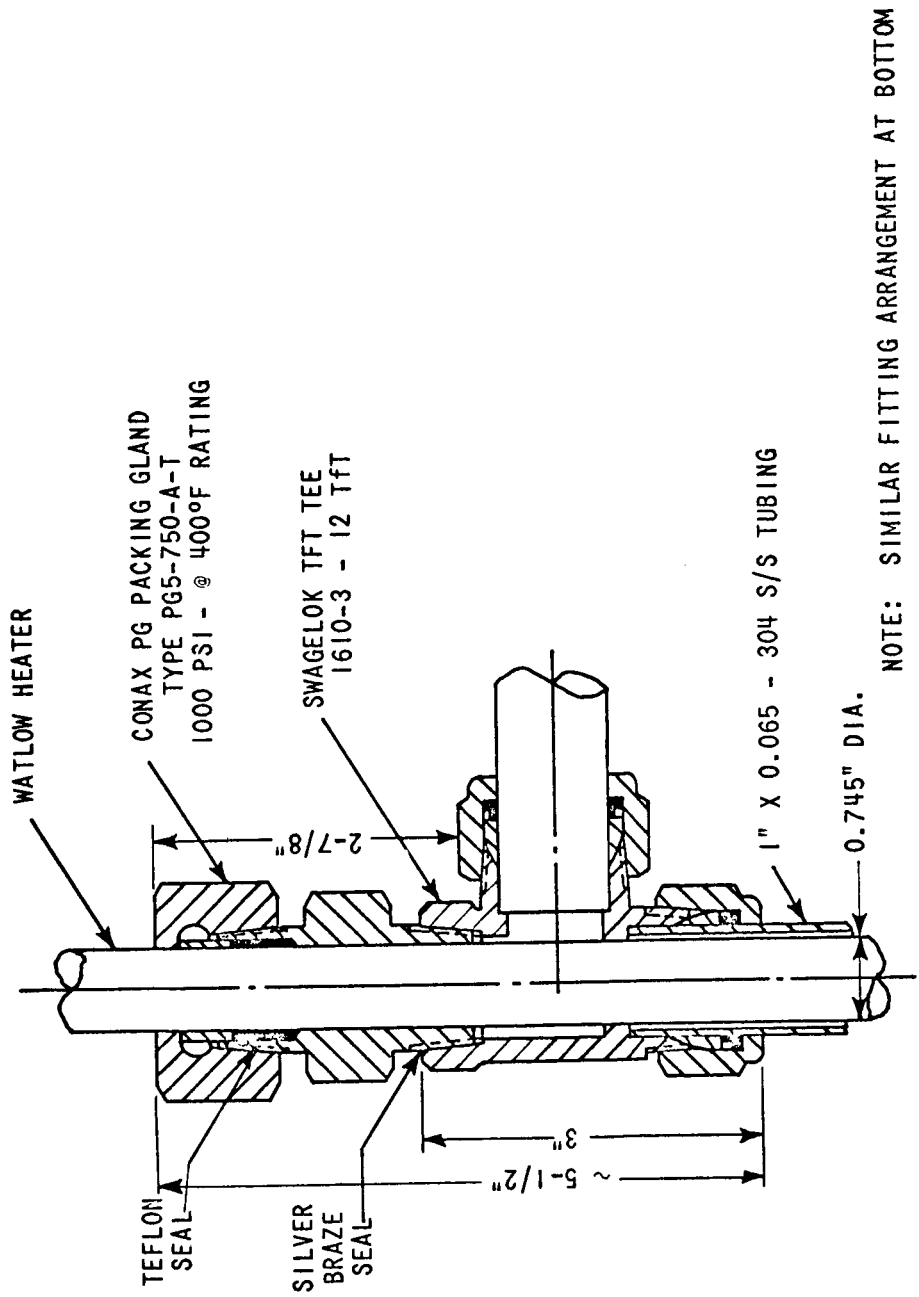
TEST SPECIMEN HEATER CONNECTION

Figure 2

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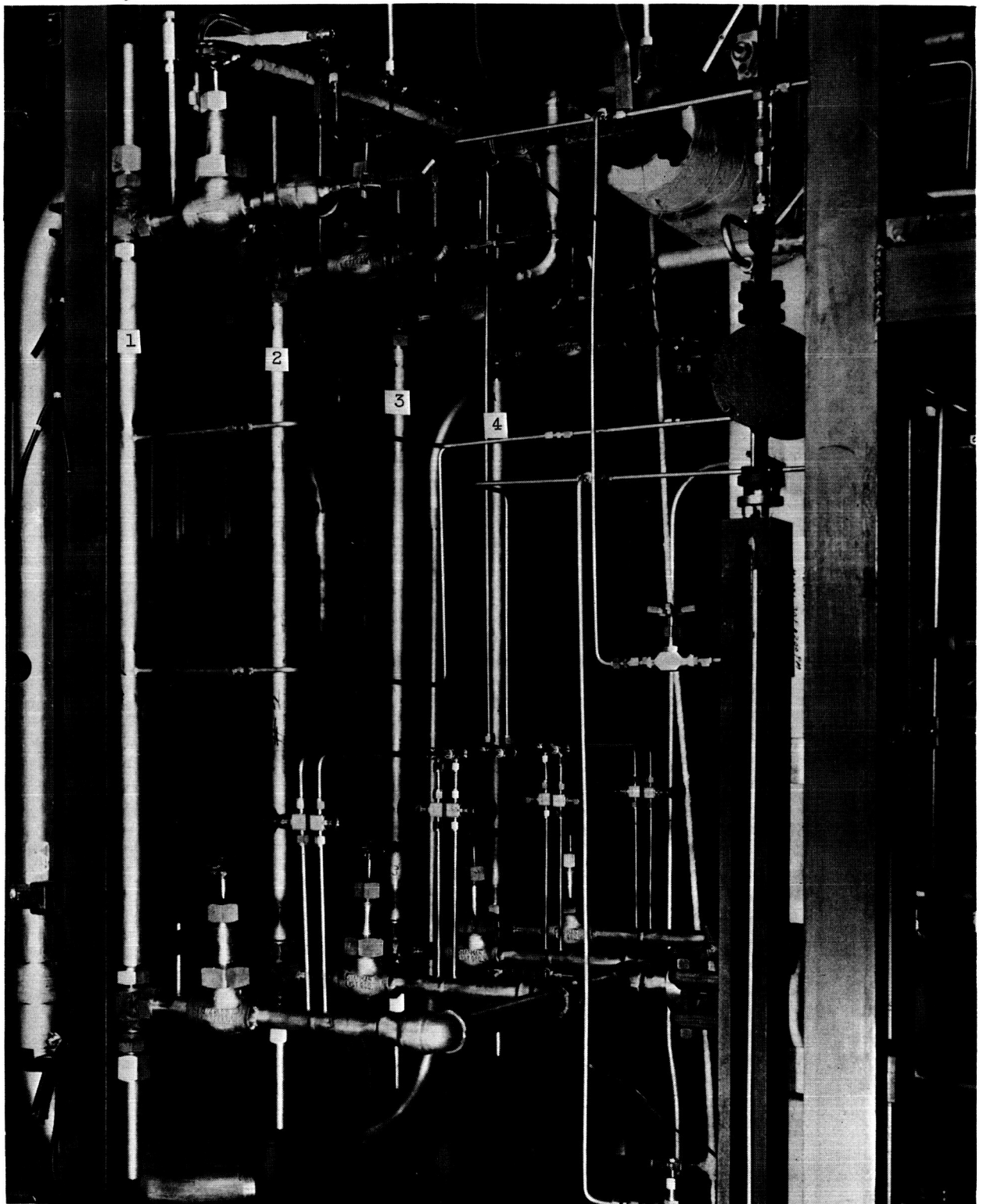
Figure 3

Test Section Manifold

A "floating piston" type accumulator, Hydrodyne Industries model number 62 A-3004, of 1/2 gallon capacity, was provided to prevent losing fluid during operation, which might be caused by normal temperature fluctuations. Fluid makeup to the system only provided to replace fluid removed during the hydrogen sampling period.

Additional electrical controls, flow monitoring devices, and thermocouples, were provided to permit the testing of up to four units together. The electrical schematic of the test heaters is shown in Figure 4. A control schematic of the loop is shown in Figure 5.

2. Test Specimen Design - The aluminum specimens were manufactured by Watlow Electric Company, St. Louis, Missouri in the form of right circular cylindrical heaters called "Firerods". The heater was clad with 6061-T6 aluminum and had an overall length of 51 inches. The heated section was 11 inches long with 18 and 22 inches of unheated length on each end respectively. The heater was of the double ended type with electrical leads exiting from both ends. The outside diameter of the cladding was 0.745 inch and was rated at 19 kw at 230 volts for the 11 inch heated length. There was no liquid seal at the penetration of the leads into the heater, therefore, both ends of the heater were kept out of the loop fluid.

V-A-3 Loop Preconditioning

Three methods were considered for determining the corrosion of the aluminum specimens and therefore the hydrogen generation during the loop tests. One of these was to periodically measure the hydrogen concentration in the loop solution and by difference, determine the rate of hydrogen buildup. However, this hydrogen buildup was a result not only of the specimen corrosion, but also the corrosion of the loop components.
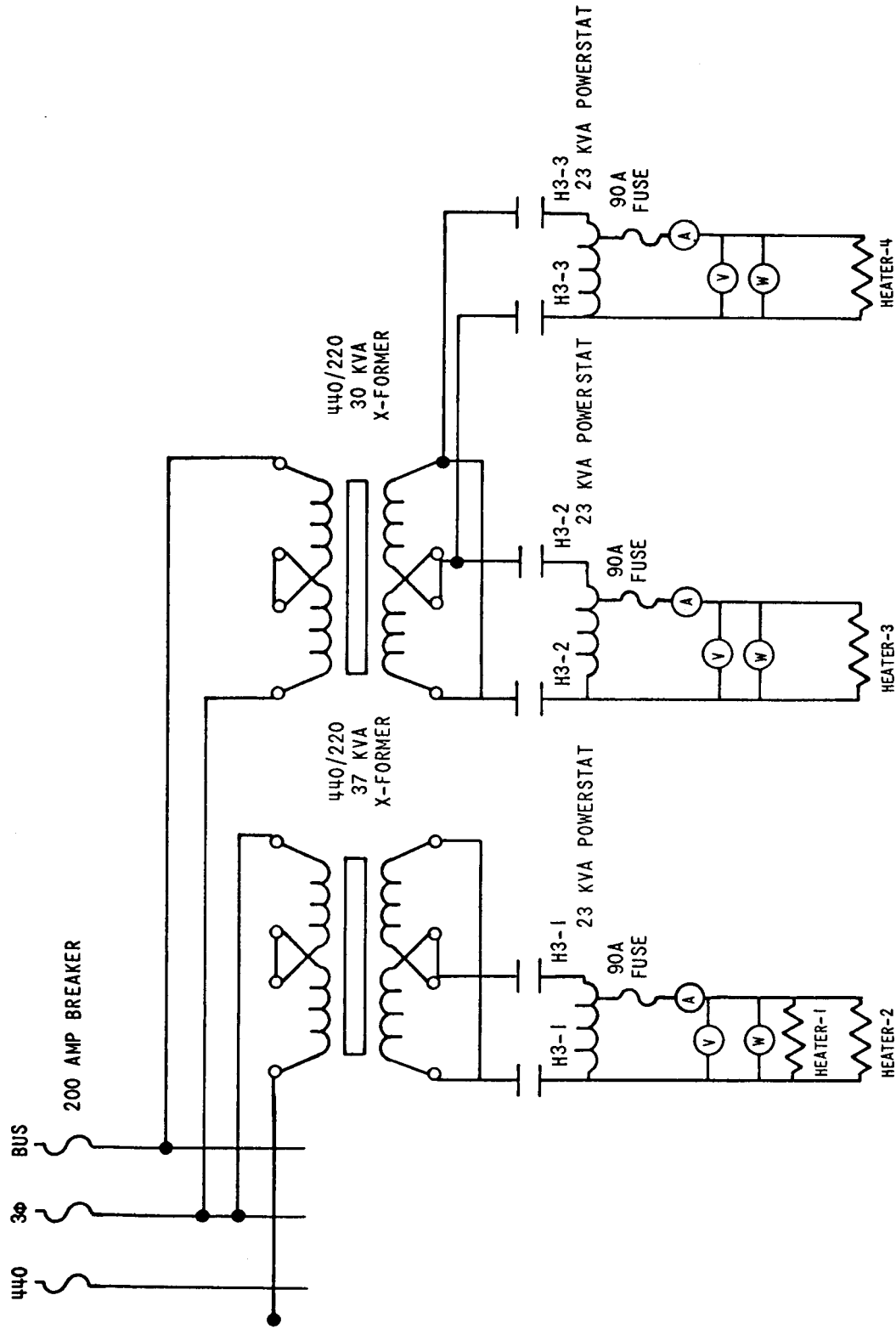
MODIFIED MATERIALS COMPATIBILITY TEST LOOP TEST SECTION HEATERS ELECTRICAL SCHEMATIC

Figure 4

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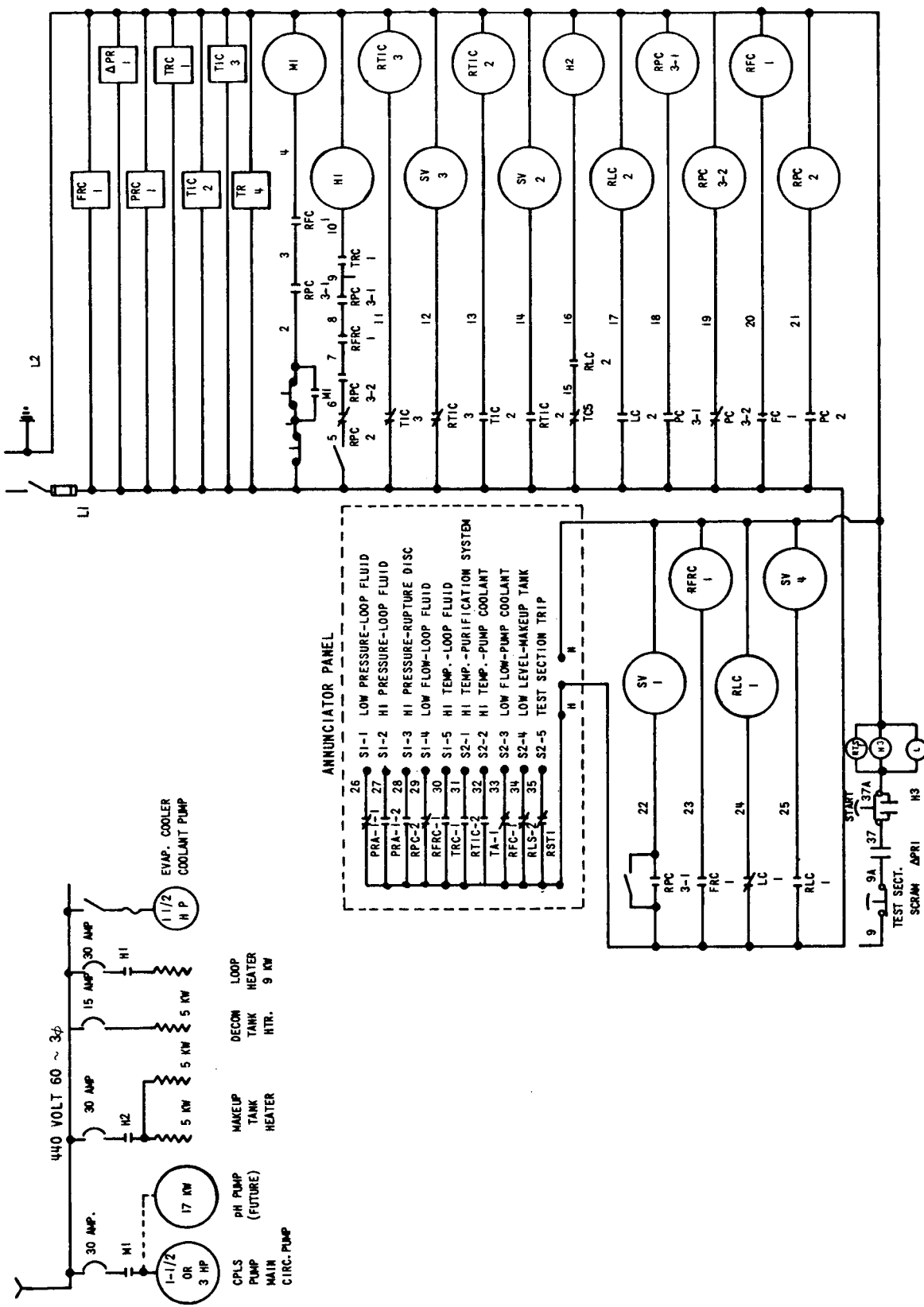
MODIFIED MATERIALS COMPATABILITY TEST LOOP CONTROL SCHEMATIC

Figure 5

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During the most severe loop test, the loop components would be subjected to a maximum temperature of $300^{\circ}F$. Therefore, in order to reduce the corrosion of loop components during tests, so that most or all hydrogen generation would be a result of aluminum corrosion, the loop was operated at $400^{\circ}F$ for about 10 days to precorrode or passivate its surfaces. The solution in the loop was adjusted to pH 10 by the addition of concentrated potassium hydroxide solution. This would accelerate the passivation process.

Samples of loop fluid were periodically taken in the high pressure sample cylinder and analyzed for hydrogen content by the method described in the Appendix. The results are shown in Figure 6. This information is replotted in Figure 7 by taking the difference between hydrogen analyses, dividing by the time between analyses, resulting in a generation rate. It appears that the passivated hydrogen generation rate has reached an equilibrium value of about 0.2 cc/kg/hr.

It should be noted here, that these hydrogen generation numbers as well as all those to be reported and discussed in subsequent sections, have been corrected to standard conditions of temperature and pressure.

V-A-4 Base-Line Loop Operation

Once the loop has been passivated, it becomes necessary to establish the loop corrosion and hydrogen generation rate at conditions to be experienced during testing. Therefore, the loop was operated at $300^{\circ}F$ with its solution adjusted to a pH of 5 by the addition of sulfuric acid through the sample cylinder.

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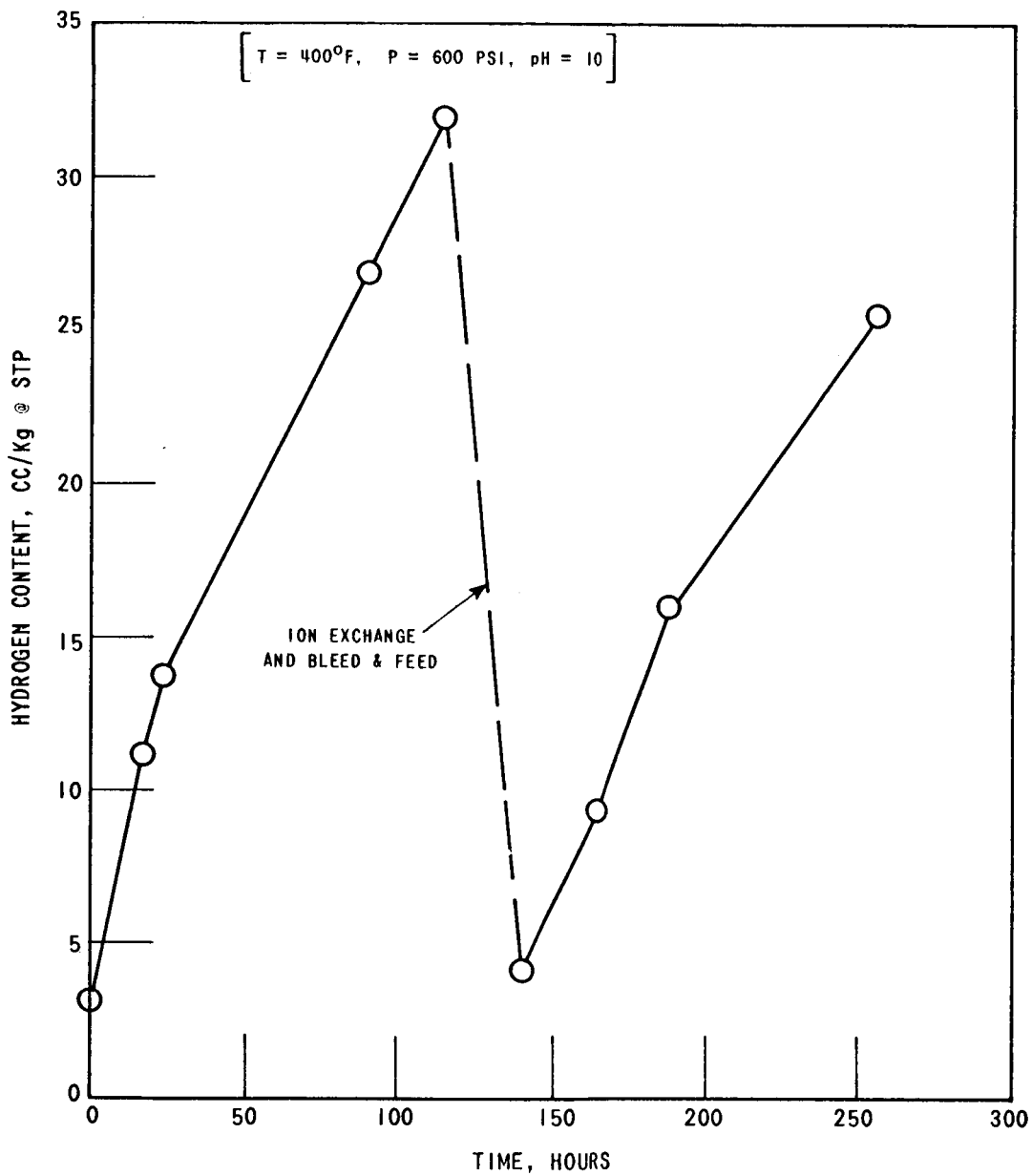
HYDROGEN GENERATION DURING PASSIVATION RUN IN TEST LOOP

Figure 6
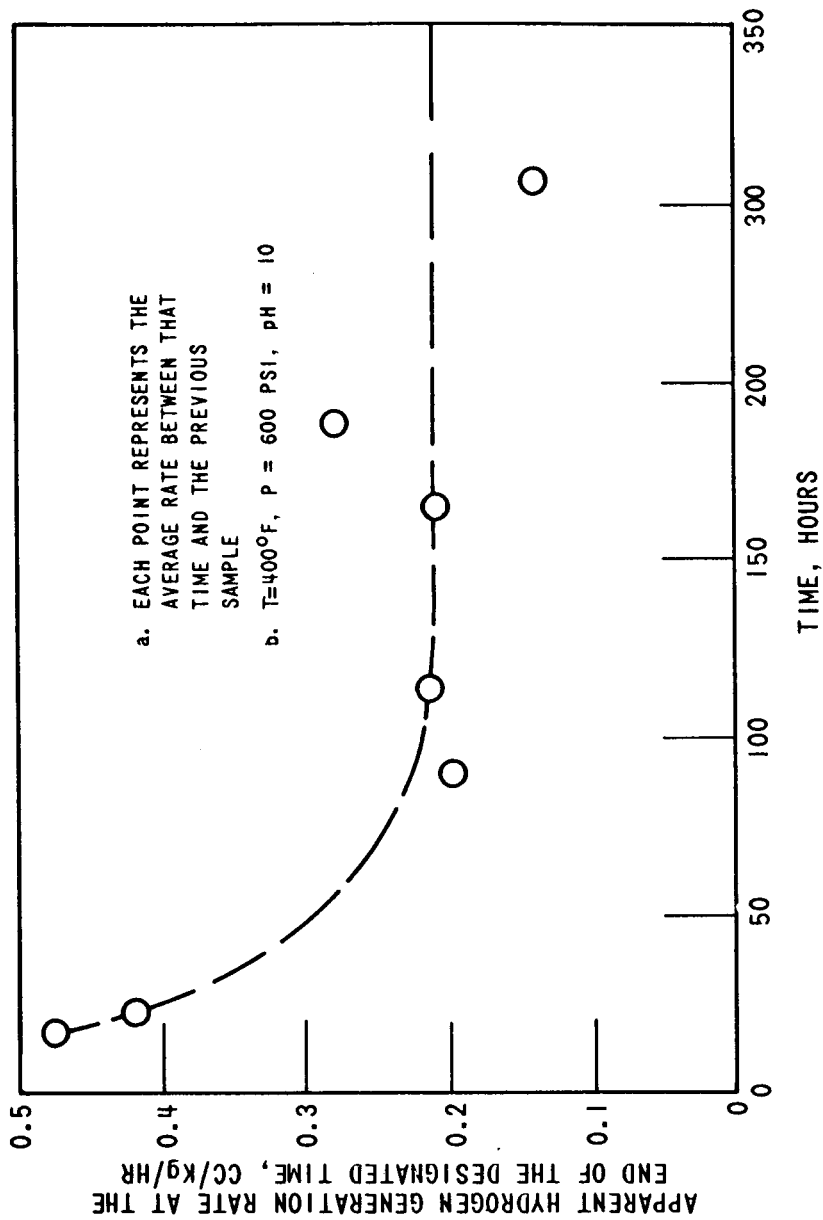
HYDROGEN GENERATION RATE DURING PASSIVATION RUN IN TEST LOOP

Figure 7

a. EACH POINT REPRESENTS THE AVERAGE RATE BETWEEN THAT TIME AND THE PREVIOUS SAMPLE

b. T=400°F, P = 600 PSI, pH = 10

TIME, HOURS

APPARENT HYDROGEN GENERATION RATE AT THE END OF THE DESIGNATED TIME, CC/kg/HR

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Hydrogen analyses were performed periodically and after about 6 days it appeared that equilibrium had been attained. The results are plotted in Figure 8. The rates, plotted in the bottom portion of the figure have reached equilibrium between 0.1 and 0.15 cc/kg/hr.

Loop solution was collected and filtered to determine crud content, which was 17.3 ppm.

V-A-5 Low Power Test

A. Pretreatment of Loop Specimens

The corrosion of aluminum, like most metals, is relatively rapid during initial periods; the rate becoming drastically reduced as corrosion products build up on the surface. It was deemed desirable to avoid this initial period of rapid corrosion by pretreating specimens in order to establish an oxide film on surfaces so that during subsequent tests, the corrosion rate, and therefore the hydrogen generation rate, would be greatly reduced. Consultation with others in the field,[10,11] and autoclave tests which will be described later, helped establish the pretreatment conditions.

The loop was modified slightly by the addition of clamp-shell heaters to the specimen holders in order to get additional heat required for the pretreatment. The conditions selected were $350^{\circ}F$ steam, near or at saturation. Small amounts of this steam would flow by the specimens for about 100 hours, as determined in the autoclave tests, to insure the formation of the oxide coating.

The operation of the loop was to flow all the fluid through the test section bypass at $400^{\circ}F$. Approximately 100-200 cc/min were expanded to steam across a valve and reheated to $350^{\circ}F$, and directed across the specimens. This fluid was then removed from
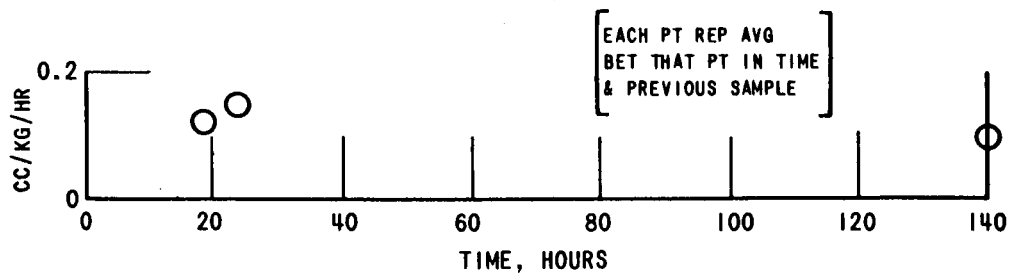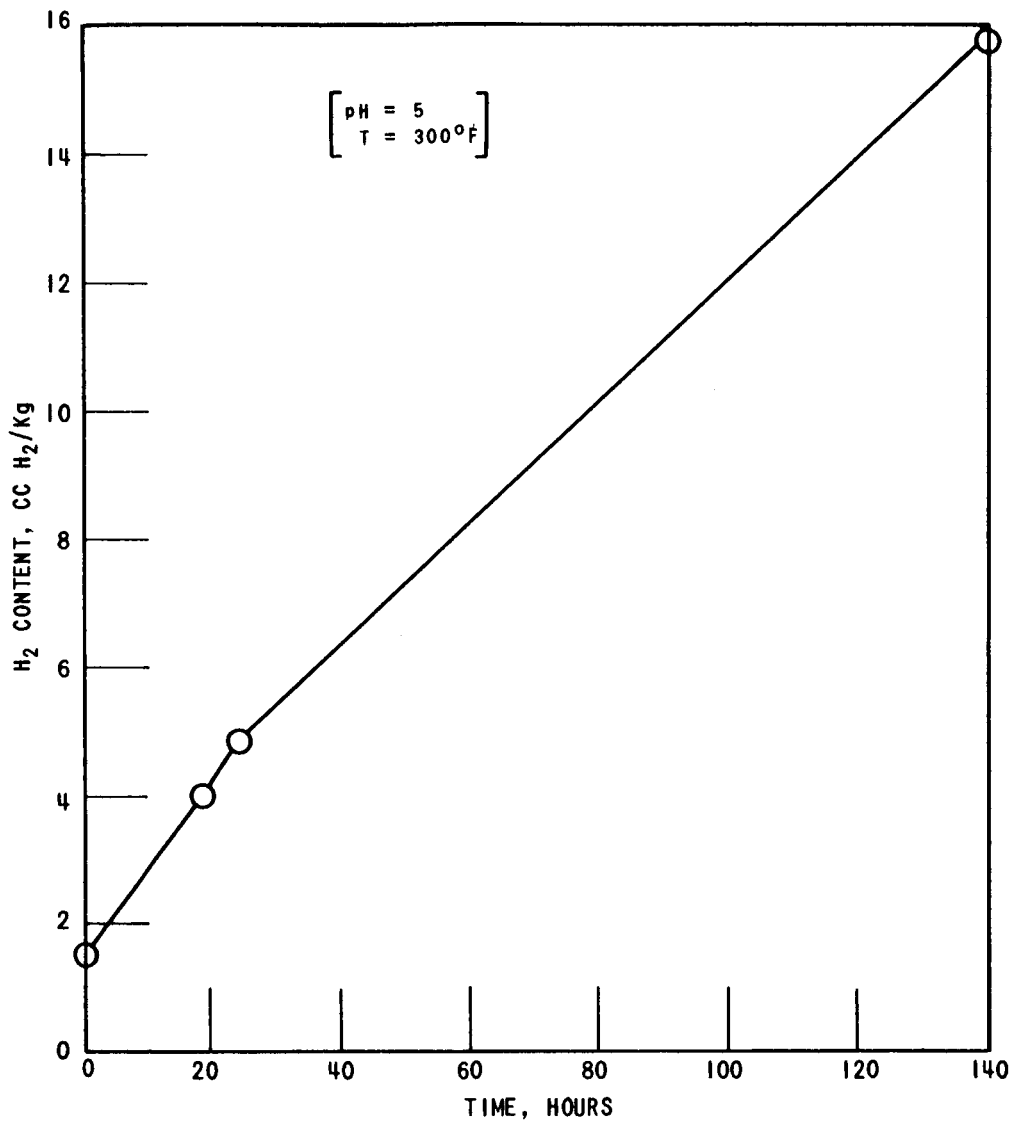
HYDROGEN GENERATION IN LOOP, NO SPECIMENS

Figure 8

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the loop via the letdown regulator installed at the exit of the test specimens. Control of the steam flowrate, the letdown pressure and the clamp-shell heater power regulated the pretreatment conditions.

Weighing the test specimen heaters is inaccurate at best for several reasons. Mainly, the ends of the heater are open to the atmosphere, exposing the magnesia insulation between the heater element and the sheath. The magnesia, which readily absorbs water, will release the water if heated above boiling or if the heater is held in a vacuum. This absorption and release are unknown and not repeatible or controllable for specimens of this nature. Therefore, any weight measurements made of the heaters, especially since the difference in weights is small compared to absolute weights, are inaccurate.

To minimize this effect, the specimens were held in a vacuum for 24 hours at room temperature to remove the moisture prior to making the weighings required. This same procedure was repeated after the pretreatment. The four heaters so treated, had indicated weight increase during the pretreatment of 15., 11.5, 16. and 21.4 mg/dm^2. These values look reasonable compared to autoclave specimens which underwent similar treatment.

B. Test Operation

The four test specimen heaters were then repositioned in the loop, the loop filled with fresh, degassed demineralized water whose pH had been adjusted to 5.0 and the low power test run under the following conditions:

TABLE 1

Low Power Loop Test Conditions

Number of Specimens	4
Heat Flux Across Specimen	13.3 Btu/sec, ft^2
Loop Fluid Flowrate	1.0 gpm per specimen
Test Duration	2 specimens - 167 hours
	2 specimens - 330 hours
Fluid Temperature @ Test Specimen	inlet - 245°F
	outlet - 264°F
Specimen Surface Temperature	inlet - 281°F
	outlet - 300°F
System Pressure	600 psig

The loop fluid was periodically sampled and analyzed for
hydrogen content using the gas partitioner. The results of
these analyses are shown in Figure 9. After 167 hours, the
test was halted and two of the four specimens removed. Their
sample bolders were valved out of the system and the test then
continued with the two remaining specimens for an additional
163 hours. Therefore, the break in Figure 9, represents the
time required to remove the two specimens and restart the test.
It should also be noted that the hydrogen content was not reduced
all the way to zero between tests.

The rate of hydrogen generation for the first part of the test,
as determined by the average lines drawn through each section
of Figure 9, is about twice that for the second part of the test.
This is expected since there was twice the area of aluminum in
the first portion (4 specimens vs 2 specimens). These rates,
however, are considerably lower than that experienced during
the base-line operation tests where rates of 0.1 to 0.15 cc/kg/hr

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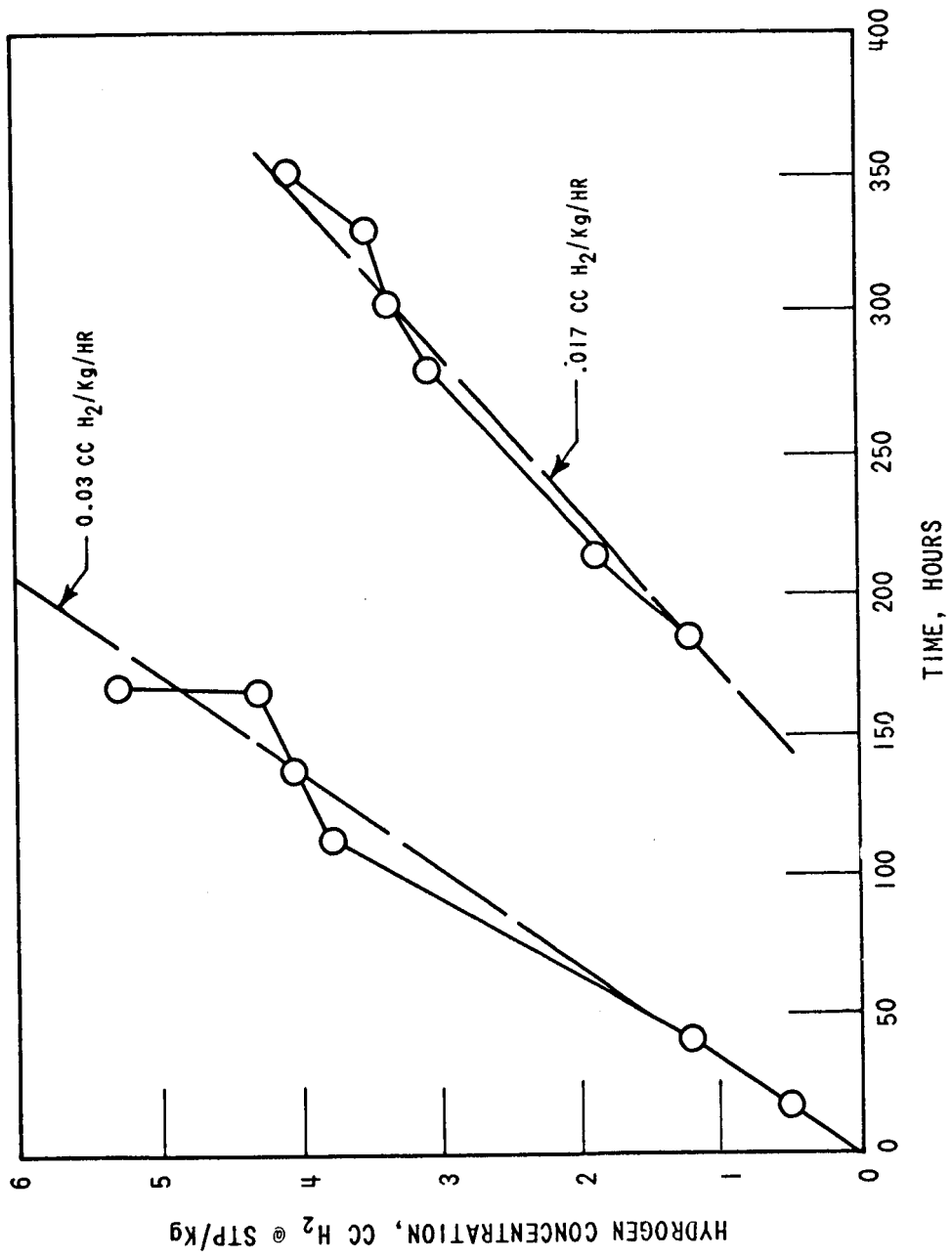
HYDROGEN GENERATION IN LOOP DURING LOW POWER TEST

Figure 9

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were experienced at the same loop conditions, without aluminum.
This discrepancy is probably due to the increasing loop passivation
as the tests continue to operate. Since twice the number of specimens
caused about twice the hydrogen generation, the contribution of hydrogen
due to the loop corrosion will be neglected since it obviously is
too small to perturb this relationship. This will result in some
conservatism if all hydrogen generation is associated with the
specimens.

The solution pH was adjusted to 5 at the beginning of the test
by the addition of sulfuric acid to the loop. The pH gradually
rose so that by the end of the test, the pH was about 6. The
loop fluid resistivity during the testing also varied; between
a low of about 61,000 ohm-cm at the beginning of the test to a
high of about 75,000 ohm-cm.

Examination of a heater so tested, after removal from the loop,
indicated that surface corrosion had continued as evidenced by
the change of appearance. In addition, the region of the specimen
containing the eleven (11) inch long heater, had experienced
deposition of a brownish-yellow colored substance on its surface.
This deposit was not uniform; it was rather spotty.

The specimens were again vacuum dried and weighed with the
following results.

TABLE 2

Low Power Test-Specimen Weight Change

Specimen	Test Duration, hrs.	Preoxidation Weight Change, mg/dm^2	ΔWt Test, mg
11	167	15.0	+21
12	167	11.5	-549
16	330	16.0	-33
18	330	21.4	-1393

Two of the four specimens apparently lost large amounts of weight while one other lost a small amount and the fourth gained a small amount. The loop solution was subsequently analyzed for aluminum to confirm these weight losses. The analysis of samples taken at the beginning of the test, after the 167 hour break, and at the end of the test are shown in Table 3. The analyses of residues collected by filtration of the second two liquid samples are also shown. It is very obvious from these results that practically no aluminum had actually left the specimens. Therefore, the weight losses experienced were probably a result of water being driven out of the specimen heater insulation.

TABLE 3

Chemistry Analyses from Low Power Loop Test

(Spectrographic Analyses)

Element	Solution Analyses			Analyses of Filtered Residues	
	5 hrs. into test*	167 hrs. into test*	330 hrs. into test*	167 hrs. into test**	330 hrs. into test**
Ag	<0.02	<0.02	<0.02	4.3	0.03
Al	<0.04	0.05	<0.04	0.55	0.60
As	-	-	-	-	-
Au	<0.2	<0.2	<0.2	-	-
B	0.17	0.10	0.40	0.0016	0.0015
Ba	<0.02	<0.02	<0.02	-	-
Be	<0.0006	<0.0006	<0.0006	-	-
Bi	<0.02	<0.02	<0.02	<0.003	0.004
Ca	0.01	0.40	0.09	0.45	0.25
Cd	0.14	0.16	0.50	1.5	0.22
Co	<0.06	<0.06	<0.06	0.010	0.010
Cr	<0.06	<0.06	<0.06	0.64	0.61
Cs	-	-	-	-	-
Cu	<0.002	0.004	0.002	0.17	0.08
Fe	0.09	0.06	0.17	38.8	21.2
In	<0.06	<0.06	<0.06	-	-
K	-	-	-	-	-
Li	-	-	-	-	-
Mg	0.031	0.13	0.11	0.26	0.30
Mn	0.04	0.16	0.16	0.31	0.020
Mo	<0.02	<0.02	<0.02	0.16	0.35
Na	-	-	-	-	-
Nb	<0.02	<0.02	<0.02	-	-
Ni	0.11	0.07	0.10	0.12	0.36
P	<0.2	<0.2	<0.2	-	-
Pb	<0.06	<0.06	<0.06	0.52	0.31
Rb	-	-	-	-	-
Sb	<0.2	<0.2	<0.2	-	-
Si	0.7	0.47	0.23	3.1	2.1
Sn	<0.06	<0.06	<0.06	0.003	0.03
Sr	<0.006	<0.006	<0.006	-	-
Th	<0.06	<0.06	<0.06	<0.03	0.04
Ti	<0.006	<0.006	<0.006	0.033	0.090
Tl	-	-	-	-	-
U	-	-	-	-	-
V	<0.06	<0.06	<0.06	<0.003	<0.003
W	<0.06	<0.06	<0.06	-	-
Zn	<0.2	<0.2	<0.2	0.06	0.04
Zr	<0.006	<0.006	<0.006	<0.003	<0.003
Total Wt. of Residue MG				5.4	11.5

* Results in µg/ml ± 30% relative
** Results in wt% ± 50% relative

V-A-6 High Power Test

The "high power test" had as its function, the determination of hydrogen generation as a result of the corrosion of aluminum under conditions of high heat flux and high fluid velocity.

The specimens were pretreated prior to testing in the same manner as described for the low power test.

The test conditions for this test are listed below in Table 4.

TABLE 4

High Power Loop Test Conditions

Number of Specimens	3
Heat Flux across specimens- fluid interface	92.5-93.8 Btu/sec ft^2
Loop Fluid Flowrate	7.5 gpm per specimen
Test Duration	10 hours
Fluid Temperature @ Test Sec.	Inlet - 225°F Outlet - 245°F
Specimen Surface Temp.	Inlet - 280°F Outlet - 300°F
System pressure	600 psig

This test was of very short duration compared to the previous test. This necessitated careful control during the period preceding the test so as not to drastically effect test results. Basically, this meant keeping the loop fluid away from the test specimen by flowing only through the bypass leg until the test was to begin. Proper test conditions of temperature and chemistry were attained during this bypass flow period. Samples were taken for hydrogen analyses at 0, 3-1/2, 7, and 10 hours. The results are shown in Figure 10.

The specimens were weighed after removal from the loop and vacuum drying. The weight change results were similar to those experienced for the low power test; that is, the specimens lost weight, but the solution analysis showed essentially none of the aluminum was present. Therefore, it again was assumed that the weight change information was affected by the heating and drying process and their effects on the insulation moisture. These weight change data are shown in the following table.

TABLE 5

High Power Loop Test - Specimen Wt Change

Specimen	Preoxidation wt Change, $\frac{mg}{dm^2}$	ΔWt Test, mgs
10	28.6	-201
17	0.2	-102
21	2.0	-175

It should be noted that the preoxidation weight changes for these specimens varied more than for the low power test specimens. Since they were both pretreated under identical conditions, and had a similar visual appearance, it is assumed that variations were caused by differences in vacuum drying of the specimens.
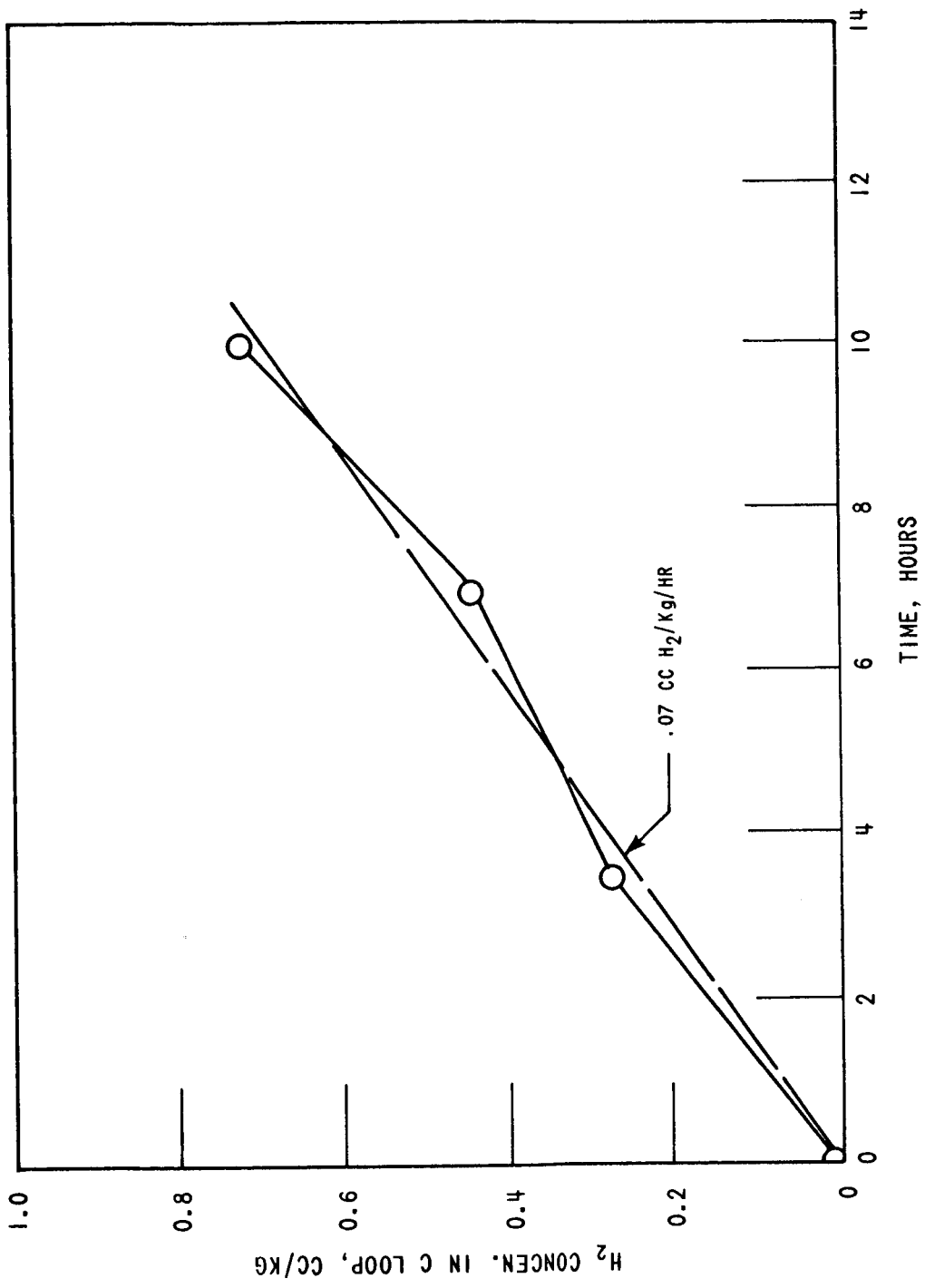
HYDROGEN GENERATION IN HIGH POWER LOOP TEST

Figure 10

The solution pH varied between 5.2 and 5.7 during the ten hour test duration while the solution varied from 66,000 to 96,000 ohm-cm respectively.

The solution analysis after test indicated that the aluminum content was <0.04 mg/ml. This confirms, as with the low power test specimens, that the apparent loss of weight of the specimens due to testing was not due to a loss of aluminum.

V-B Phase II Tests

1. Autoclave Systems

Two independent autoclave systems were set up for this phase of the program. Figure 11 is a schematic diagram of one of these facilities. A description of the operation of the system would best describe the function of the equipment shown.

The system was first evacuated to insure removal of atmospheric gases. The fill tank was violently boiled to remove atmospheric gases and then pumped into the autoclave. All lines were bled to insure complete filling. The system was then heated to boiling while a vacuum was pulled for a short time to insure complete degassing. The system was then heated to the desired temperature. The Sprague or the Mighty-Mite 1, let-down regulator was then used to adjust the system pressure to 600 psi.

During test operation, samples were periodically taken for hydrogen analysis. Prior to sample taking, the fill tank was heated and boiled. Might-Mite 1 was valved out while the valve in the sample train was opened. The Sprague pump was started and set just above 600 psi. This continued until fluid was let-down from Might-Mite 2 which was set just above 600 psi. The sample for analysis was contained in sample cylinder-1. Sample cylinder-2 was put in the line just to insure that the sample taken was truly representative of the autoclave solution at the sample time.

AUTOCLAVE TEST SETUP
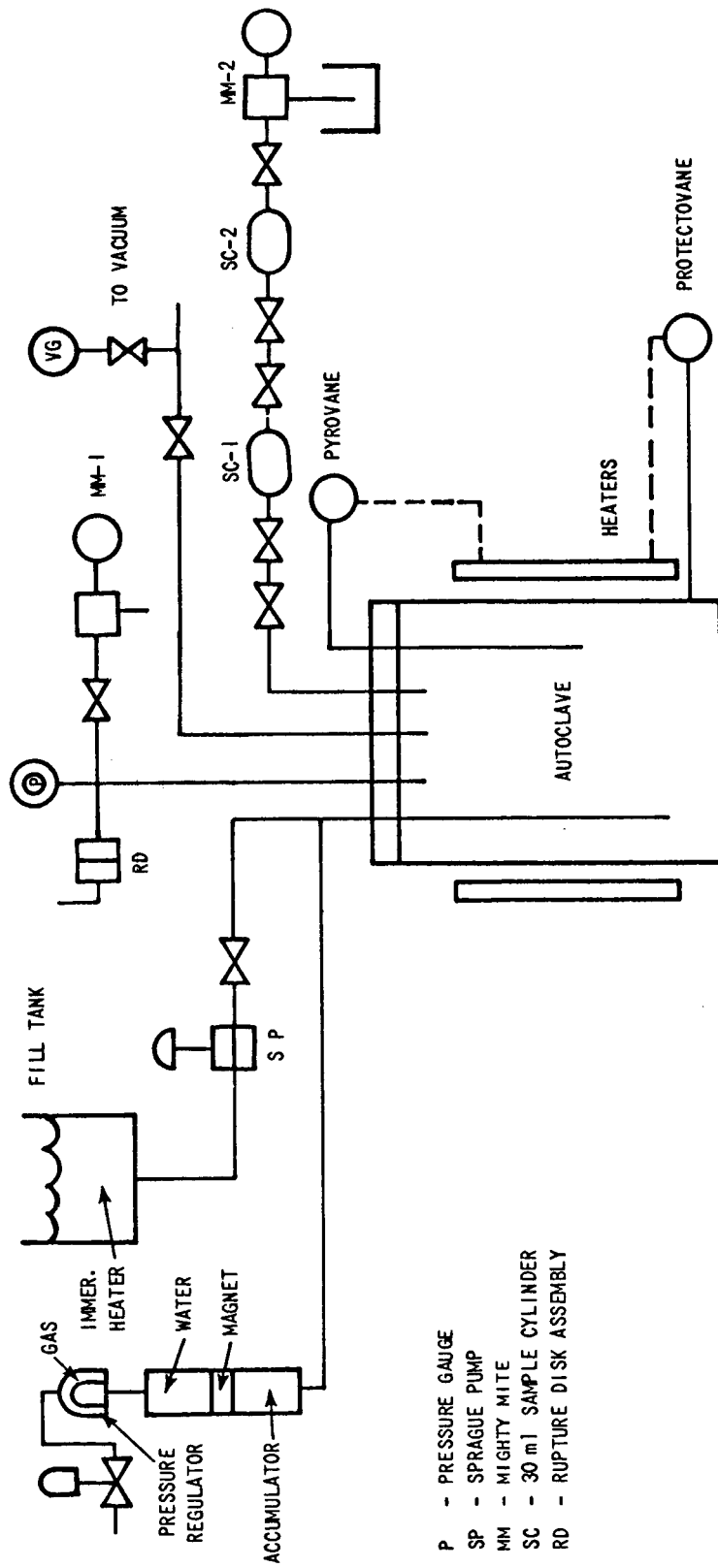
Figure 11

P - PRESSURE GAUGE
SP - SPRAGUE PUMP
MM - MIGHTY MITE
SC - 30 ml SAMPLE CYLINDER
RD - RUPTURE DISK ASSEMBLY

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2. Specimen Preparation

The test specimens were 1" x 1-1/2" x 1/8" thick. Each had an 1/8" diameter hole drilled through the 1/8" thickness near the top for hanging on a tree.

Nine specimens were cleaned, and weighed and run in the autoclave in $350^{\circ}F$ saturated steam for up to 96 hours to determine the optimum pretreatment conditions. The results are shown in Figure 12.

Some specimens were taken out at intervals of 24 and 48 hours respectively. One specimen was scratched and is not shown here. The curve indicates that the initial period of rapid corrosion occurs within the first 24 hours but that a period of about 96 hours probably would be desirably for pretreatment. The specimens all had turned a uniform dull color, and when checked with a micrometer had increased in thickness 0.1 - 0.3 mils for the 24 hour specimen, to 0.3 - 1.7 mils for the 96 hour specimens.

3. Autoclave Base-Line Operation

The two autoclave systems were operated at the test conditions with solution of proper chemistry but without aluminum specimens, in order to establish the hydrogen generation rate caused by corrosion of the autoclave internals.

One system was maintained at $200^{\circ}F$ and the other at $300^{\circ}F$ for 12 days or 288 hours. The pressure was maintained at 600 psi in both systems. The pH of each autoclave fluid was initially adjusted to 5.0 by the addition of sulphuric acid.

Samples for hydrogen analysis were periodically taken. No measurable amounts of hydrogen were found in either system anytime during the test duration. The sample and detection system were checked with standards to insure the taking of representative samples. The minimum detectable
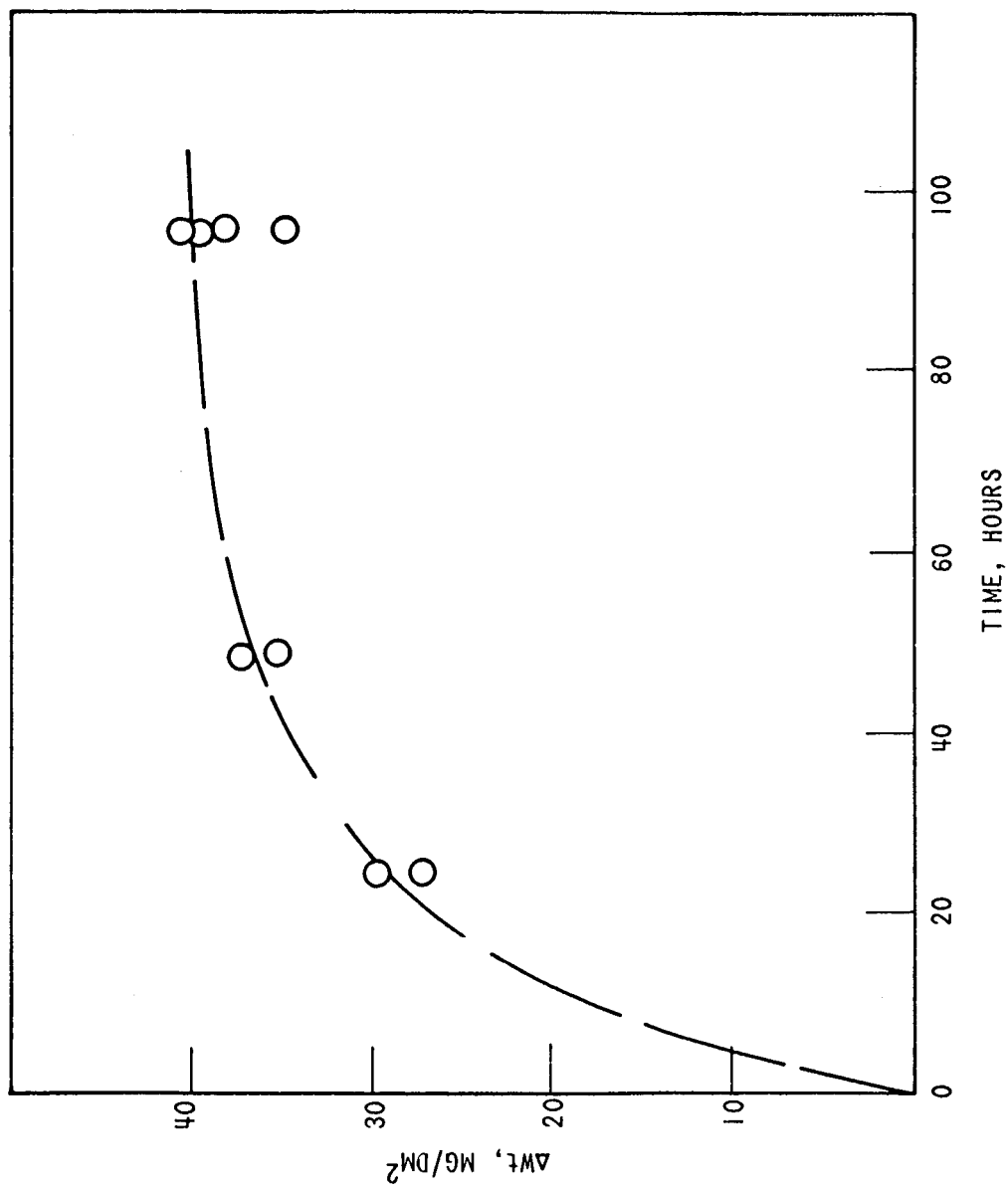
RESULTS OF PRETREATING AUTOCLAVE SPECIMENS
IN 350°F SATURATED STEAM

Figure 12

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limit of hydrogen with the sample size available 9.5×10^{-2} cc H_2 per Kg solution.

The pH of the sample solution was also checked at each hydrogen sampling. The $200^{\circ}F$ test pH varied between 5.0 and 6.5 while the $300^{\circ}F$ test pH varied between 5.0 and 6.4. Analyses of the solutions and filtered residues after test, indicate sufficient quantities of corrosion product iron to cause the pH to rise to these levels. These chemical analyses are shown in Table 6.

V-B-4 Autoclave Test Operation

Two autoclave tests were run simultaneously; one at $200^{\circ}F$ and one at $300^{\circ}F$. Each autoclave was loaded with twenty-one (21) specimens; sixteen (16) which had been pretreated for 96 hours in $350^{\circ}F$ steam, and five (5) which had been treated by the "Hardcoat" process resulting in a 2 mil coating.

The two systems were sampled periodically and determinations made of solution pH, resistivity and hydrogen content. These results are shown in Tables 7 and 8. The hydrogen analyses are also plotted in Figure 13 and 14. All analyses are connected by straight lines.

The tests were interrupted at each of the periods shown in these two figures. At each interruption coupons of both the steam treated variety and hard coat treated were removed for further examination.

These specimens were weighed to determine the test weight change. The results are shown in Tables 9 and 10 for the $200^{\circ}F$ and $300^{\circ}F$ autoclave tests respectively. The weight change data for the steam treated specimens are shown in Figures 15 and 16.

Autoclave sample solutions were periodically analyzed spectrographically to determine impurity content, specifically aluminum.

These analyses for both autoclave systems are shown in Tables 11 and 12. Also shown are the analyses for the residues obtained by filtration of all solutions (mostly the final solution) collected for a given system and combined into one.

TABLE 6

Chemical Analyses - Autoclave Base-Line Operation

Element	Solutions[1] ug/ml		Residues[1] wt%	
	200°F Test	300°F Test	200°F Test	300°F Test
Ag	<1	<1	0.03	<0.01
Al	11	10	0.4	1.0
As	-	-	-	-
Au	<30	<30	<0.3	<0.3
B	100	16	0.02	0.03
Ba	5.0	3.0	<0.03	<0.03
Be	<0.3	<0.3	<0.003	<0.003
Bi	<10	<10	<0.1	<0.1
Ce	110	60	0.70	0.25
Cd	830	500	2.8	0.95
Co	<30	<30	<0.3	<0.3
Cr	<10	<10	2.5	2.7
Cs	<30	<30	<0.3	<0.3
Cu	3.0	4.5	6.0	4.0
Fe	130	140	16	25
In	<100	<100	<1	<1
K	100	75	0.15	0.05
Li	50	1.0	0.03	0.01
Mg	29	24	0.40	0.30
Mn	50	67	0.50	0.32
Mo	30	<10	0.22	0.95
Na	500	175	0.2	0.05
Nb	<10	<10	<0.1	<0.1
Ni	<10	33	1.2	1.2
P	<100	<100	<1	<1
Pb	<30	<30	0.3	<0.3
Rb	<30	<30	<0.3	<0.3
Sb	<30	<30	<0.3	<0.3
Si	100	150	4.0	2.6
Sn	<30	<30	<0.3	<0.3
Sr	20	<10	<0.1	<0.1
Th	<30	<30	<0.3	<0.3
Ti	4.0	<3	0.80	0.25
Tl	<100	<100	<1	<1
Ta	<30	<30	<0.3	<0.3
V	<10	<10	<0.1	<0.1
W	<30	<30	<0.3	<0.3
Zn	<30	<30	<0.3	<0.3
Zr	<3	<3	0.05	<0.03

Wt Residue mgs   4.888   8.631

(1) Results obtained spectrochemically.

TABLE 7

Chemistry Summary, 200°F Autoclave Test

Date	Time	pH	Resistivity ohm-cm	Hydrogen cc/kg	Volume Removed, mls	Volume Added, mls
12-4-65	Initial	5.08	-	-	126	5300
12-4-65	1610	-	-	-	-	-
12-6-65	0845	5.85	73,000	0.32	68 mls	-
12-7-65	1535	5.55	57,000	0.66	68	-
12-10-65	1420	6.00	58,000	0.92	68	-
12-10-65	1425	-	-	-	-	200
12-13-65	1030	5.85	47,000	0.93	68	-
12-16-65	1400	6.52	47,000	1.17	68	-
12-20-65	0845	5.72	46,000	2.45	68	-
				-	50**	250
12-23-65	1330	6.80*	29,000*	1.90	68	-
12-27-65	1430	6.03	39,500	2.80	68	200
12-30-65	1345	5.73	49,000	6.60	68	-
1-4-66	1120	6.08	42,500	4.03	68	-
1-4-66	1645	5.76	45,000	2.73	68	-
				-	75**	500
1-11-66	1515	5.98	45,000	3.68	68	-
1-18-66	0935	5.98	47,000	3.26	68	-
				-	85**	550
2-2-66	1000	6.18	43,000	2.11	68	-

* Sat over 3 day weekend

** Result of vacuum degassing

TABLE 8

Chemistry Summary - 300°F Autoclave Test

Date	Time	pH	Resistivity ohm-cm	Hydrogen cc/kg	Volume Removed, mls	Volume Added, mls
12-4-65	Initial	5.08	-	-	405	7300
12-4-65	1600	-	-	-	-	-
12-6-65	1030	5.58	67,000	0.61	68	-
12-7-65	1415	5.85	89,000	0.79	68	-
12-10-65	1330	5.53	71,000	1.87	68	-
12-10-65	-	-	-	-	-	200
12-13-65	0915	5.47	56,000	0.73	68	-
12-16-65	1525	5.90	54,000	0.73	68	-
12-20-65	0945	5.72	46,000	1.78	68	-
				-	60**	250
12-23-65	1430	6.40*	58,000*	0.26	68	-
12-27-65	1330	6.23	48,000	0.63	68	-
12-30-65	1545	5.90	50,000	0.81	68	-
1-4-66	0940	5.68	49,000	1.23	68	-
1-4-66	1740	5.15	44,500	-	68	-
				-	170**	650
1-11-66	1415	5.32	48,000	0.28	68	-
1-18-66	0820	5.54	51,500	0.32	68	-
				-	22**	300
2-2-66	0840	6.04	48,000	0.43	68	-

* Sat over 3 day weekend.

** Result of vacuum degassing.
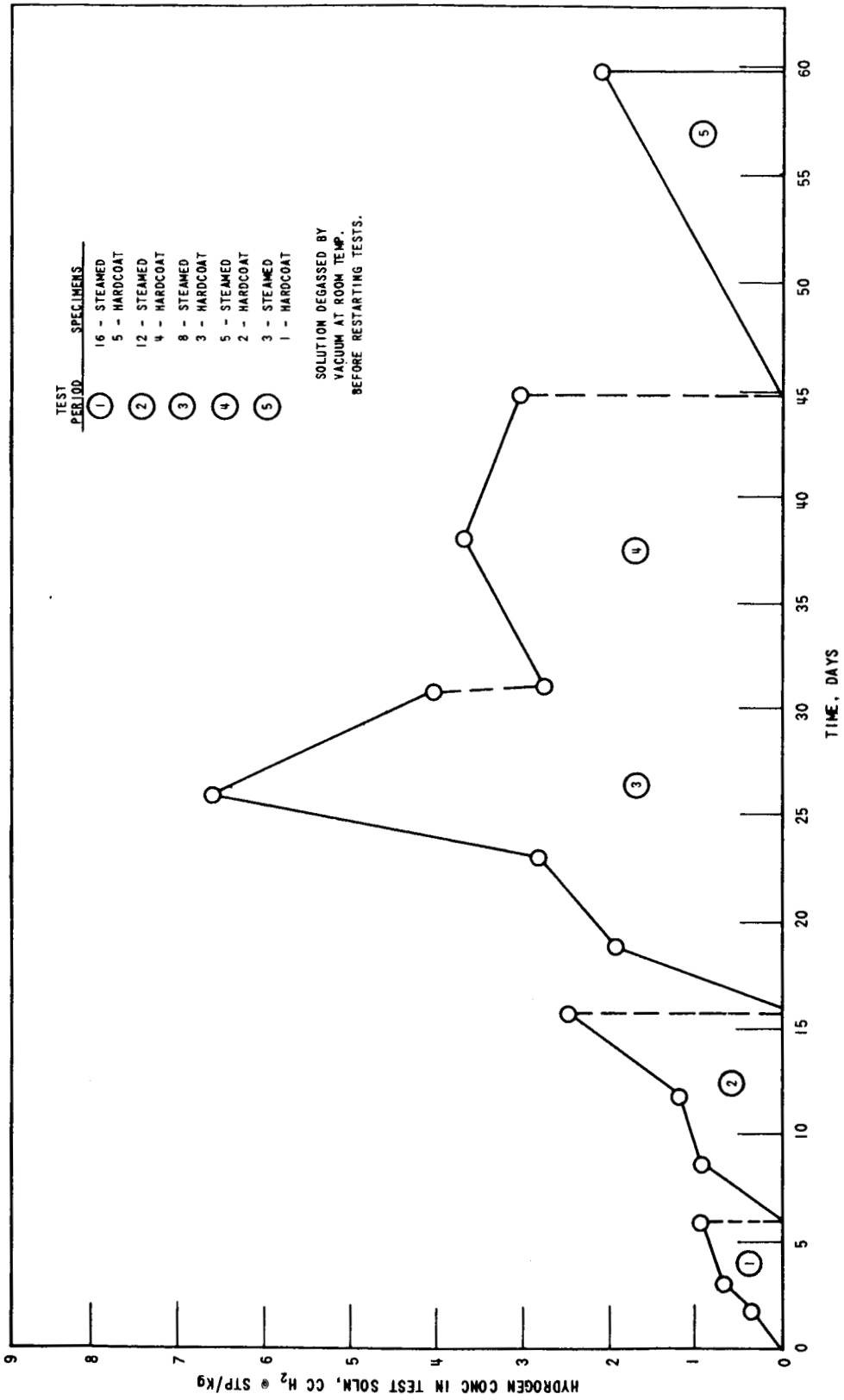
HYDROGEN ANALYSIS OF 200°F AUTOCLAVE TEST

Figure 13

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HYDROGEN ANALYSIS OF 300°F AUTOCLAVE TEST

Figure 14

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TABLE 9

Weight Change Results from 200°F Autoclave Test

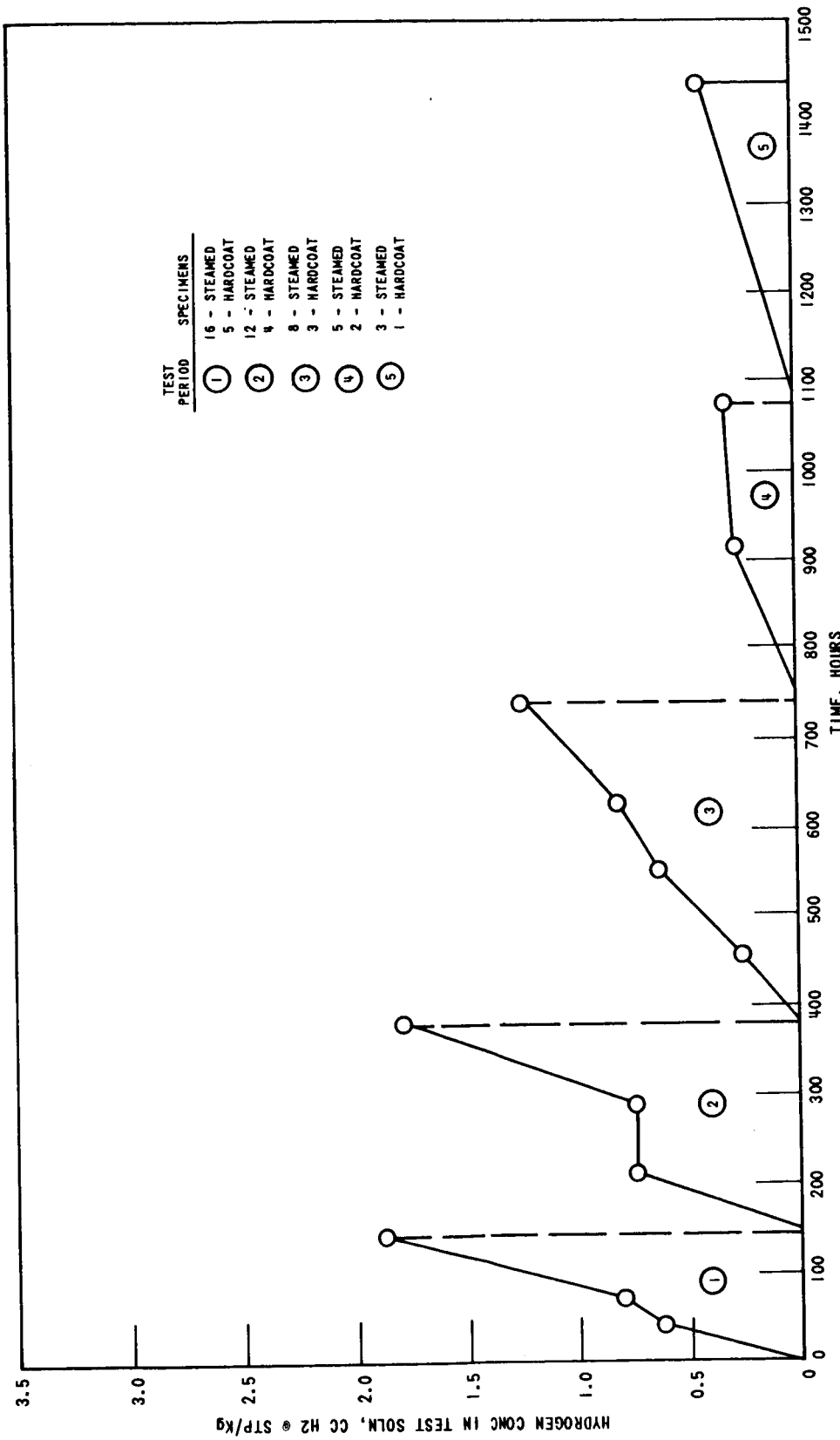| Spec. No.	Preoxid. Weight gms	Weight After 1 Oxid. gms	Weight After 2 Oxid. gms	Weight After Test gms	Δ Weight(1) 1 Oxid. mg/dm²	Δ Weight 2 Oxid. mg/dm²	Tot. Δ Weight Oxidation mg/dm²	Δ Weight Test mg/dm²	Corrosion Rate mg/dm²/hr.	Time hrs.
4-36-T	8.130332	8.132545	8.132672	8.132758	9.478	0.544	10.022	0.368	2.59×10^{-3}	142
50-B	8.017398	8.017988	8.018651	8.018785	2.527	2.839	5.366	0.574	4.04×10^{-3}	142
55-B	8.081914	8.083167	8.084762	8.084911	5.366	6.831	12.197	0.638	4.49×10^{-3}	142
61-T	8.113574	8.115445	8.116588	8.116704	8.013	4.895	12.908	0.497	3.50×10^{-2}	142
69-T-H	8.098099	8.126633		8.128983	122.201	-	122.201	10.064	7.09×10^{-2}	142
4-38-T	8.133992	8.136935	8.137071	8.137289	12.604	0.582	13.186	0.934	2.52×10^{-3}	370.75
41-B	8.075923	8.079506	8.079662	8.079898	15.345	0.668	16.013	1.011	2.73×10^{-3}	370.75
43-T	8.079226	8.081379	8.081478	8.081772	9.221	0.424	9.645	1.259	3.39×10^{-3}	370.75
46-B	8.087898	8.088382	8.088556	8.089400	2.073	0.745	2.818	3.615	9.74×10^{-3}	370.75
70-B-H	8.124652	8.153024		8.155512	121.507	-	121.507	10.655	2.88×10^{-2}	370.75
4-27-T	8.044692	8.046732	8.046760	8.047362	8.737	0.120	8.857	2.578	3.55×10^{-3}	725.75
48-B	8.147827	8.148320	8.148517	8.150361	2.111	0.844	2.955	7.897	1.089×10^{-2}	725.75
57-B	8.064357	8.069407	3.070420	8.070848	21.627	4.338	25.965	1.833	2.53×10^{-3}	725.75
71-T-H	8.125940	8.155860		8.159349	128.137	-	128.137	14.942	2.06×10^{-2}	725.75
4-29-T	8.115362	8.118713	8.118807	8.119264	14.351	0.403	14.754	1.957	1.854×10^{-3}	1054.5
59-B	8.065748	8.066487	8.069266	8.069756	3.165	11.901	15.066	2.099	1.99×10^{-3}	1054.5
73-B-H	8.154600	8.182761		8.186754	120.604	-	120.604	17.101	1.621×10^{-2}	1054.5
4-37-T	8.123825	8.126418	8.126578	8.127111	11.105	0.685	11.790	2.283	-	1335.5
39-T	8.039966	8.043023	8.043296	8.043843	13.092	1.169	14.261	2.343	-	1335.5
49-B	8.106256	8.106842	8.107163	8.108230	2.510	1.375	3.885	4.570	-	1335.5
74-T-H	8.130378	8.159136		8.162714	123.161	-	123.161	15.323	-	1335.5

(1) Area of each specimen is 0.2335 dm²

Notes: a) "T" designation after Spec. No. means Top row of specimens in autoclave, "B" means Bottom row.
b) "H" designation is for the Hardcoat specimens.

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TABLE 10

Weight Change Results from 300°F Autoclave Test

| Spec. No.	Preoxid. Weight gms	Weight After 1 Oxid, gms	Weight After 2 Oxid. gms	Weight After Test gms	Δ Weight(1) 1 Oxid. mg/dm2	Δ Weight 2 Oxid. mg/dm2	Tot. Δ Weight Oxidation mg/dm2	ΔWeight Test mg/dm2	Δ Weight mg/dm2 / hr.	Time hrs.
4-30-B	7.983355	7.987110	7.987194	7.987600	16.081	0.360	16.441	1.739	1.23×10^{-2}	141.5
33-B	8.070792	8.072728	8.072273	8.075028	8.291	-1.949	6.342	11.799	8.33×10^{-2}	141.5
34-T	8.103895	8.106283	8.106381	8.108247	10.227	0.420	10.647	7.991	5.65×10^{-2}	141.5
35-T	8.044488	8.046623	8.047389	8.048020	9.143	3.281	12.424	2.702	1.91×10^{-2}	141.5
63-T-H	8.064922	8.095503	-	8.099652	130.968	-	130.968	17.769	1.26×10^{-2}	141.5
4-28-B	8.061587	8.066005	8.066086	8.066959	18.921	0.347	19.268	3.739	1.01×10^{-2}	370.75
31-T	8.102659	8.105857	8.105952	8.106959	13.696	0.407	14.103	4.313	1.16×10^{-2}	370.75
32-B	8.051547	8.052347	8.052378	8.055151	3.426	0.133	3.559	11.876	3.20×10^{-2}	370.75
56-T	8.187509	8.188538	8.189637	8.191556	4.407	4.707	9.114	8.218	2.22×10^{-2}	370.75
64-B-H	8.123472	8.153622	-	8.158219	129.122	-	129.122	19.687	5.31×10^{-2}	370.75
4-40-B	8.052128	8.055706	8.055848	8.057324	15.323	0.608	15.931	6.321	8.72×10^{-3}	724.75
44-B	8.127182	8.127685	8.127875	8.130917	2.154	0.814	2.968	13.028	1.80×10^{-2}	724.75
53-T	8.079268	8.080778	8.081118	8.084163	6.467	1.456	7.923	13.041	1.80×10^{-2}	724.75
65-T-H	8.120036	8.149085	-	8.154016	124.407	-	124.407	21.118	2.92×10^{-2}	724.75
4-58	8.066558	8.067493	8.070211	8.072073	4.004	11.640	15.644	7.974	7.54×10^{-3}	1051
60	8.113714	8.115766	8.117094	8.119937	8.788	5.687	14.475	9.178	8.73×10^{-3}	1051
66-H	8.054253	8.083132	-	8.088828	123.679	-	123.679	24.394	2.32×10^{-2}	1051
4-42-T	8.063882	8.067093	8.067237	8.069529	13.752	0.617	14.369	9.816	7.00×10^{-3}	1403
51-T	8.099152	8.099636	8.100404	8.103490	2.073	3.289	5.362	13.216	9.41×10^{-3}	1403
52-B	8.033808	8.034192	8.035492	8.037916	1.645	5.567	7.212	10.381	7.39×10^{-3}	1403
67-T-H	8.157616	8.187274	-	8.192575	127.015	-	127.015	22.702	1.62×10^{-2}	1403

Notes: a) "T" designation after Spec. No. means Top row of specimens in Autoclave, "B" means Bottom row.

b) "H" designation is for the Hardcoat Specimens.

(1) Area of each specimen is 0.2335 dm^2

41
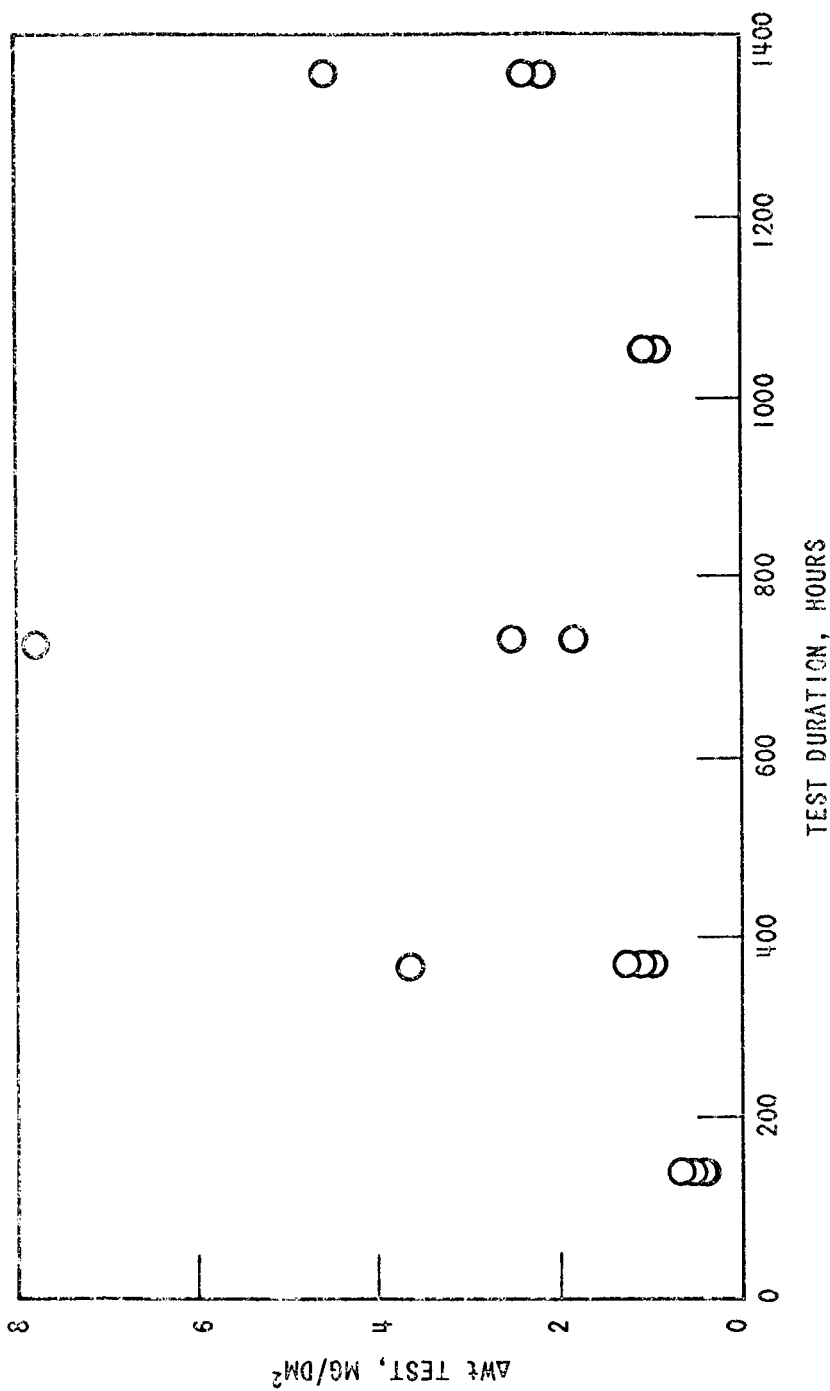
TEST WEIGHT CHANGE FOR 200°F AUTOCLAVE TEST

Figure 15

42
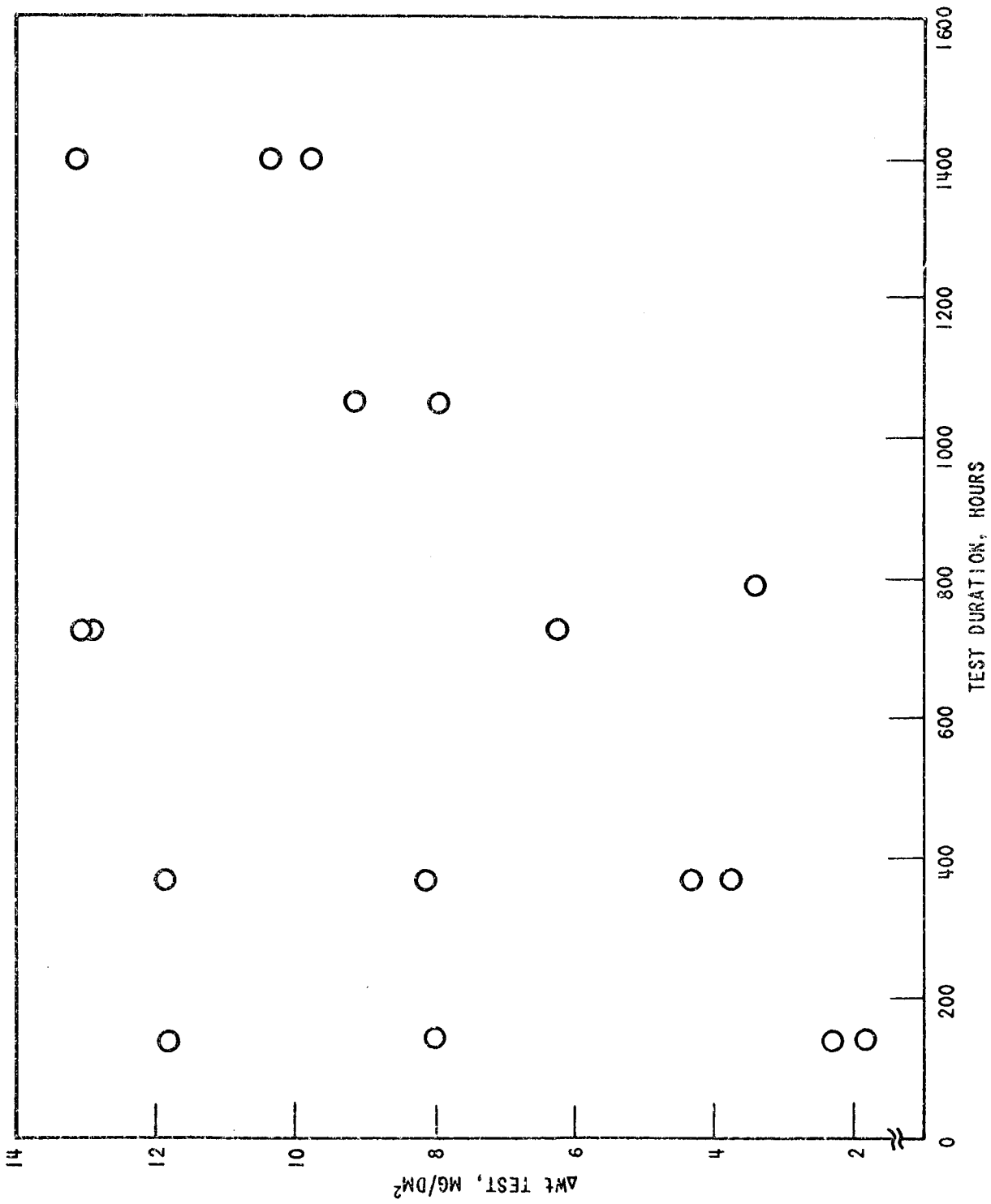
TEST WEIGHT CHANGE FOR 300°F AUTOCLAVE TEST

Figure 16

TABLE 11

200°F Autoclave Test - Analyses of Solutions and Composite Residue

Element	Initial[1][2] Soln.	140 hrs. into test	370 hrs. into test	730 hrs. into test	1070 hrs. into test	Final Soln.
Ag	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Al	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
As	-	-	-	-	-	-
Au	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
B	0.03	0.05	0.07	0.09	0.35	0.25
Ba	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Be	<0.0006	<0.0006	<0.0006	<0.0006	<0.0006	<0.0006
Bi	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Ca	0.10	0.04	0.10	0.10	0.10	0.10
Cd	0.12	0.87	1.2	0.86	1.1	0.60
Co	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
Cr	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
Cs	-	-	-	-	-	-
Cu	0.02	0.01	0.02	0.02	0.02	<0.002
Fe	<0.04	0.13	0.52	0.43	0.48	<0.04
In	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
K	-	-	-	-	-	-
Li	-	-	-	-	-	-
Mg	0.05	0.08	0.14	0.18	0.43	0.11
Mn	0.03	0.06	0.14	0.14	0.30	0.15
Mo	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Na	-	-	-	-	-	-
Nb	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Ni	0.07	0.07	0.07	0.05	0.08	0.04
P	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Pb	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
Rb	-	-	-	-	-	-
Sb	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Si	0.07	0.12	0.12	0.12	0.14	0.09
Sn	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
Sr	0.006	0.006	0.006	0.006	0.007	<0.006
Th	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
Ti	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
Tl	-	-	-	-	-	-
U	-	-	-	-	-	-
V	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
W	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
Zn	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Zr	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006

Composite Residue[2]

Al	5.1*	Cu	4.9
Cd	1.4	Fe	17.5
Cr	<0.02	Ni	0.15
	Total Weight	42.4 mg	

(1) All solution analyses are μg/ml.

(2) Results obtained spectrochemically.

* Weight %

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TABLE 12

300°F Autoclave Test - Analyses of Solutions and Composite Residue

Element	Initial[1][2] Soln.	140 hrs. into test	370 hrs. into test	1070 hrs. into test	Final Soln.
Ag	<0.02	<0.02	<0.02	<0.02	<0.02
Al	<0.04	<0.04	<0.04	0.06	<0.04
As	-	-	-	-	-
Au	<0.2	<0.2	<0.2	<0.2	<0.2
B	0.031	0.07	0.035	2.0	0.08
Ba	<0.02	<0.02	<0.02	<0.02	<0.02
Be	<0.0006	<0.0006	<0.0006	<0.0006	<0.0006
Bi	<0.02	<0.02	<0.02	<0.02	<0.02
Ca	0.07	0.15	0.11	0.19	0.11
Cd	0.07	0.39	0.35	0.60	0.70
Co	<0.06	<0.06	<0.06	<0.06	<0.06
Cr	<0.06	<0.06	<0.06	<0.06	<0.06
Cs	-	-	-	-	-
Cu	0.008	0.024	0.015	0.033	0.15
Fe	<0.04	0.13	0.25	0.23	0.11
In	<0.06	<0.06	<0.06	<0.06	<0.06
K	-	-	-	-	-
Li	-	-	-	-	-
Mg	0.037	0.12	0.09	0.12	0.13
Mn	0.03	0.09	0.09	0.18	0.16
Mo	<0.02	<0.02	<0.02	<0.02	<0.02
Na	-	-	-	-	-
Nb	<0.02	<0.02	<0.02	<0.02	<0.02
Ni	<0.04	<0.04	<0.04	0.08	<0.04
P	<0.2	<0.2	<0.2	<0.2	<0.2
Pb	<0.06	<0.06	<0.06	<0.06	<0.06
Rb	-	-	-	-	-
Sb	<0.2	<0.2	<0.2	<0.2	<0.2
Si	0.07	0.17	0.10	0.20	0.15
Sn	<0.06	<0.06	<0.06	<0.06	<0.06
Sr	<0.006	<0.006	<0.006	0.006	<0.006
Th	<0.06	<0.06	<0.06	<0.06	<0.06
Ti	<0.006	<0.006	<0.006	0.06	<0.006
Tl	-	-	-	-	-
U	-	-	-	-	-
V	<0.06	<0.06	<0.06	<0.06	<0.06
W	<0.06	<0.06	<0.06	<0.06	<0.06
Zn	<0.2	<0.2	<0.2	<0.2	<0.2
Zr	<0.006	<0.006	<0.006	<0.006	<0.006

Composite Residue[2]

Al	5.1*	Cu	4.9
Cd	1.4	Fe	17.5
Cr	< 0.02	Ni	0.15

Total Weight 42.4 mg

(1) All solution analyses are μg/ml.

(2) Results obtained spectrochemically.

* Weight %.

VI. STRIPPING OF SPECIMENS

The tests just described were designed to yield information that could be used in predicting the generation of hydrogen as a result of aluminum corrosion. One obvious method of doing this was to measure the hydrogen directly by chemical means. The measurement of hydrogen in a solution is very precise and reproducible. However, there were many complicating factors. In the autoclave tests, two specimen surface treatments were being tested simultaneously, and although the hydrogen sampling and analysis was precise, the different corrosion rates of the two specimen types defied one to determine where the hydrogen was coming from. In the loop tests, the hydrogen generation appeared to be smaller with the specimens installed than had been the generation rate during the base-line operation. This was probably caused by the change of corrosion rate of the stainless steel loop surfaces complicated by the testing and volume control methods.

The weight change of specimens during test could be used as a measure of the corrosion and therefore the hydrogen generation providing a number of factors were known. First, the reaction equation has to be defined; that is, the number of waters hydrating with the alumina must be determined. Secondly, it must be determined whether corrosion product is remaining on the surface where it is formed, or whether it is leaving the surface and can be found in solution or in residues.

Since neither of these methods appeared to be completely satisfactory for all cases, another approach was also pursued. If the total aluminum attack and the pretreatment weight change could be ascertained, and if the pretreatment reaction equation could be defined, then by difference, the aluminum reacted during test could be found. This would be used in determining hydrogen generation.

Draley[10] at Argonne National Laboratory had developed a procedure for preferentially stripping aluminum oxide off aluminum specimens without significant base metal attached. The method was modified slightly to suit the needs of this program and appears as used in the appendix. A pretreatment in a

basic acid solution is used to loosen the adhering oxide, the actual stripping is performed in the chromic-phosphoric acid solution. The weight change of the specimen during stripping and the analysis of strip solution for aluminum content can both be used to determine aluminum attack.

Specimens that had been steam treated in the autoclave were stripped to determine the ability of the method to remove oxide. These results are shown in Table 13. Using the equation for the reaction involving one and two waters of hydration, the ratios of the various weight changes are shown to agree reasonably well with those predicted for one water of hydration. This confirmed the usability of the method.

Additionally, stripping was performed on an untreated blank and on a steam treated sample taken from the batch to be tested. These results are shown in Table 14. The ratio comparisons as described above, made with specimen 54, also agree with what is expected for this treatment. The weight loss of strip step number 1 for specimen 68 is attributed to a probable surface covering of thin oxide.

The results of Table 14 that proved surprising were the aluminum analyses of the strip solutions for specimen 54 and 68 respectively, there was apparently better than 2 and 3 times the aluminum in strip solution as had been evidenced by specimen weight change (total metal attack).

Prior to these analyses, standard soltuions were prepared and analyzed in order to determine the lower limits of detection of various elements in the solution, and the amounts of these elements present in freshly prepared chromic-phosphoric strip solution. These results along with those for specimens 54 and 68 are shown in Table 15.

TABLE 13

Results of Stripping Steam Treated Specimens

Specimen	14	18	12	19
Steam Duration, hrs.	24	48	96	96
Weight Gain During Steaming, mgs	5.317	7.095	7.757	7.900
Weight Loss During Stripping, mgs	8.987	13.290	13.513	13.827
Total Metal Attack, mgs	3.670	6.195	5.756	5.927
ΔWt Strip/ΔWt Steaming	1.69	1.87	1.74	1.75
Total Met Att/ΔWt Steaming	0.69	0.87	0.74	0.75
Total Met Att/ΔWt Stripping	0.41	0.47	0.43	0.43

<u>Theoretical:</u> $2Al + (3+n)H_2O \longrightarrow Al_2O_3 \cdot nH_2O + 3H_2$
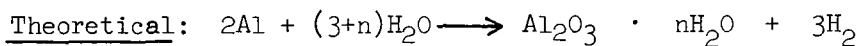
		$n=1$	$n=2$
(a) Δ wt.strip/Δ wt.steaming $= [Al_2O_3 \cdot nH_2O]/[O_3 \cdot nH_2O]$	$=$	1.82	1.64
(b) $\dfrac{\text{Total metal attack}}{\Delta \text{ wt.steaming}} = [2Al]/[O_3 \cdot nH_2O]$	$=$	0.82	0.65
(c) $\dfrac{\text{Total metal attack}}{\Delta \text{ wt.stripping}} = [2Al]/[Al_2O_3 \cdot nH_2O]$	$=$	0.45	0.39

TABLE 14

Results of Stripping Untested Samples

Specimen		54	68
Condition		96 hr Steaming	Clean
Wt Gain During Steaming, mgs		4.271	
Wt Loss During Stripping, mgs			
Strip	1	3.629	0.569
	2	1.879	0.008
	3	1.006	0.000
	4	0.547	0.003
	5	0.337	+0.011
	6	0.110	0.005
	7	0.007	0.017
Total, mgs		7.517	0.591
Total Metal Attack, mgs		3.244	0.591
ΔWt Strip/Δ Wt Steaming		1.76	-
Tot Met Att/ΛWt Steaming		0.76	-
Tot Met Att/ΛWt Stripping		0.43	-
Alum in Strip Solution, mgs		6.99	1.84

TABLE 15

Analyses of Strip Solutions

Elemental Analysis	Spec 54 ug/ml	Spec 68 ug/ml	Fresh Strip Soln, ug/ml	Limits of Detection, µg/ml
Al	$36^{(1)}$	$10^{(2)}$	1.0	1.0
Cu	0.56	0.22	<0.1	0.1
Fe	1.7	1.1	1.1	1.0
Cd	<4.0	<4.0	<4.0	4.0
Ni	0.11	0.44	0.1	<0.1

(1) Should be 16.7 based upon total aluminum attack, solution wt. was 209.4 gms

(2) Should be 3.2 based upon total aluminum attack, solution wt. was 198.4 gms

The specimens were subsequently examined using x-ray techniques to determine if any chrome from the solution or platinum from the electrode had plated out on the aluminum specimen during the oxide stripping operation. Nothing above minimum detectable amounts was encountered. The discrepancy between weight change data and analyses for aluminum in solution remains unsolved.

In spite of these apparent discrepancies, stripping of both autoclave coupons and loop heater specimens was carried out in order to establish additional methods of comparison of results to determine hydrogen generation. The results of stripping autoclave coupons, both specimen weight changes and solution analyses are shown in Table 16. The loop heater specimen results are shown in Table 17.

TABLE 16

Results of Stripping Autoclave Specimens

Specimens	Test Time	Temperature	Wt After Strip	Δ Wt Strip	Total Metal Attack*	Total Met.Attack/ Δ Wt Strip
4-36	142 hrs.	200°F	8.128457 gms	4.352 mgs	1.875 mgs	0.431
4-55	142 hrs.	200°F	8.079772 gms	5.188 mgs	2.142 mgs	0.413
4-61	142 hrs.	200°F	8.111021 gms	5.683 mgs	2.553 mgs	0.449
4-37	1336 hrs.	200°F	8.121527 gms	5.584 mgs	2.298 mgs	0.412
4-35	142 hrs.	300°F	8.041287 gms	6.88 mgs	3.36 mgs	0.489
4-42	1403 hrs.	300°F	8.059493 gms	10.02 mgs	4.39 mgs	0.438
4-51	1403 hrs.	300°F	8.096511 gms	6.957 mgs	2.641 mgs	0.380
4-52	1403 hrs.	300°F	8.031170 gms	6.705 mgs	2.638 mgs	0.393
4-68	-	Blank	8.018546 gms	0.591 mgs	0.591 mgs	
4-54	-	Just Pre-oxidized	8.123129 gms	7.515 mgs	3.24 mgs	0.431

Chemistry Analysis of Strip Solution

Specimens	Solution Wt	µg/ml				Al mgs**	Aluminum Solution/ Total Metal Attack
		Cu	Fe	Ni	Cd		
35	221.8 gms	.34	1.2	.23	<4.0	7.19	2.14
37	217.3 gms	.46	1.4	.12	-	7.45	3.24
42	212.5 gms	.72	1.5	.60	-	7.88	1.80
54	209.4 gms	.56	1.7	.11	-	6.99	2.16
61	208.0 gms	.34	1.2	<.1	-	6.36	2.50
68	198.4 gms	.22	1.1	.44	-	1.84	3.11
36	195.0 gms	-	-	-	-	6.51	3.48
51	191.0 gms	-	-	-	-	6.73	2.55
52	204.0 gms	-	-	-	-	7.38	2.80
55	200.0 gms	-	-	-	-	5.19	2.42

* Total Metal Attack = (weight before test)-(weight after strip)
** Used density of 1.079 gm/cc.

TABLE 17

Results of Stripping Loop Test Specimens

	Low Power Test	High Power Test
Spec. No.	18.0	10.0
ΔWt Strip, mgs	248.0	235.0
Strip Area, dm^2	1.66	1.66
Wt Strip Solution, gms	1011.0	1008.0
Chemistry Analysis of Solution		
Aluminum, µg/ml	59.0	57.0
Cadmium	<3.0	<3.0
Copper	3.2	6.8
Iron	10.0	6.3
Nickel	16.0	21.0
Wt Aluminum in Strip Solution, mgs	55.4	53.2

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VII. EXPERIMENTAL RESULTS

The objective of the test program was to determine hydrogen generation as a result of the corrosion of aluminum under various conditions. Each phase of the program presented a few independent means of determining this generation at a given set of conditions. It was originally planned to use these separate means as checks, one upon the other; thereby resulting in meaningful generation information. However, too many of the techniques proved not to be applicable and others just didn't work for one reason or another. All of them will be discussed in this section with only the applicable results being used to establish the hydrogen generation.

A. Autoclave Tests

Hydrogen generation could be determined by direct measurement as a result of sample analysis periodically drawn from each autoclave system. The weight change of the specimens during test, coupled with an aluminum analysis of the test solution could also be used to determine hydrogen generation. If specimens were stripped, hydrogen generation during test could be determined by an analysis of the strip solution coupled with information about weight change during pretreatment. Specimen weight change during stripping could be used as a check of the strip solution analysis.

1. Direct Hydrogen Measurement

The direct measurement of hydrogen was made for both the $200^{\circ}F$ and $300^{\circ}F$ autoclave tests. The results were shown in Figures 13 and 14. It would be very difficult to determine hydrogen generation rates for the aluminum specimens from this information, because there were two types of specimens included in each test. Each test started with 16 specimens that had been steam treated prior to test and 5 specimens that had a hard-coat applied prior to test. When the specimen weight change information was made available at the end of each period of testing, attempts were made to correlate

this with hydrogen generation measurements. This was unsuccessful.
All specimens were not removed and weighed at each period, therefore
one had to assume that those specimens removed represented an
average. This was later found not to be necessarily true. Therefore,
after many attempts to establish correlations, the direct measure-
ment information was temporarily discarded. It was realized that
much simpler tests each with fewer specimens, all of the same type,
would be required to make this measurement more meaningful.

2. Measurement of Test Weight Change

The specimens were rinsed and dried then weighed on the micro-
balance after removal from the autoclave test. These results were
shown in Figures 15 and 16. It became very obvious with the apparent
scatter on these two figures that the test weight change was dependent
on something more than just test duration. After study of the
results, it became apparent that there was some correlation between
test weight change and the pretreatment weight change for the steam
treated specimens. This is plotted in Figures 17 and 18. The trend
is that, the greater the pretreatment weight change, the smaller is
the subsequent test weight change. This makes more sense when it
is realized that initial corrosion rates are high until a film is
established. These rates probably decrease with time. However,
surface condition has a big effect on corrosion rates as evidenced
by the variation of preoxidation weight changes, all specimens being
treated simultaneously.

Examination of Figures 17 and 18 reveals that below a preoxida-
tion weight change of about 12 mg/dm^2 the weight change during test
is not a function of test duration. Since the test weight change
is inversely proportional to the preoxidation weight change, only
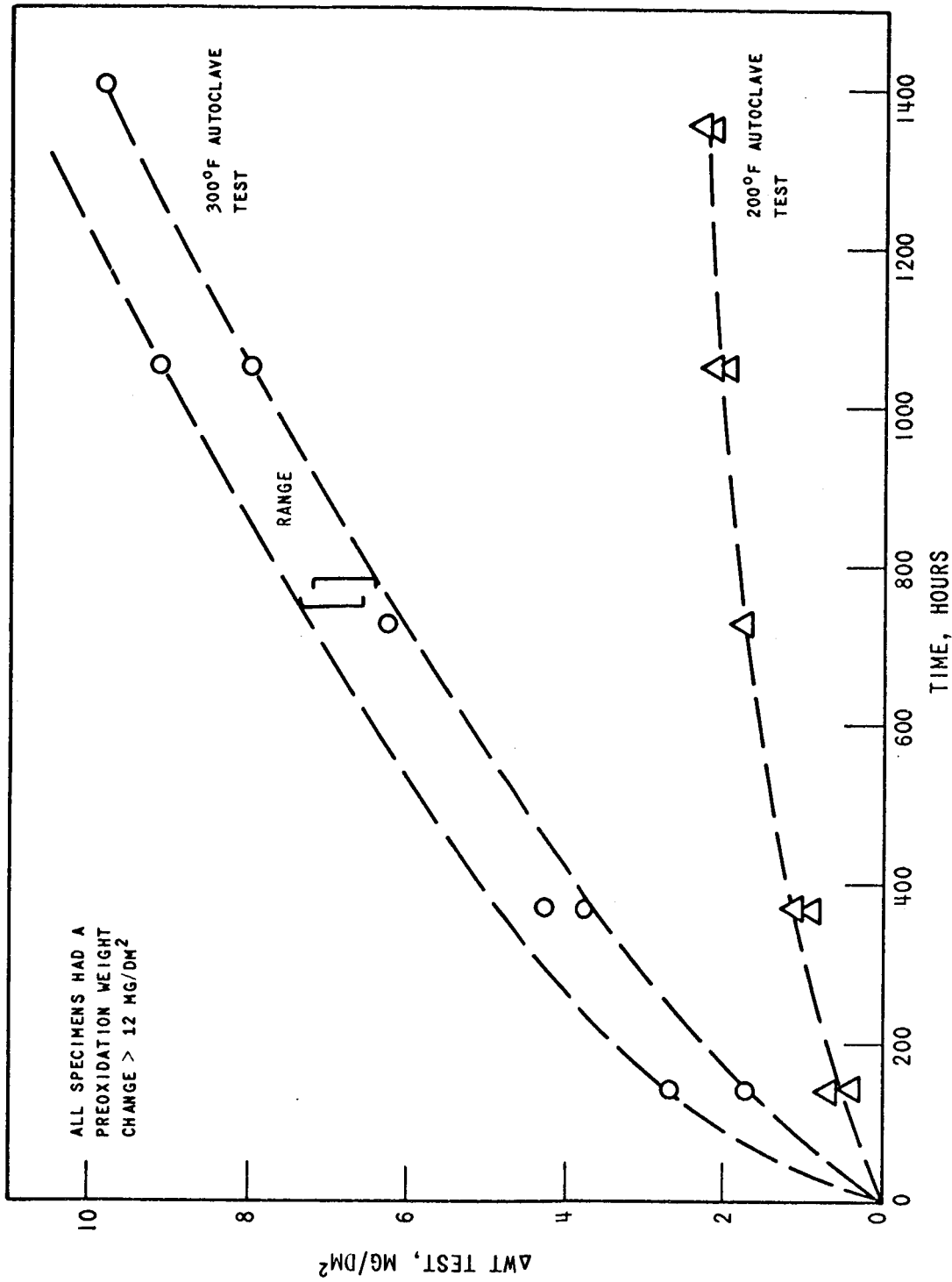the data points above 12 mg/dm^2 perox Δ weight were replotted in
Figure 19.
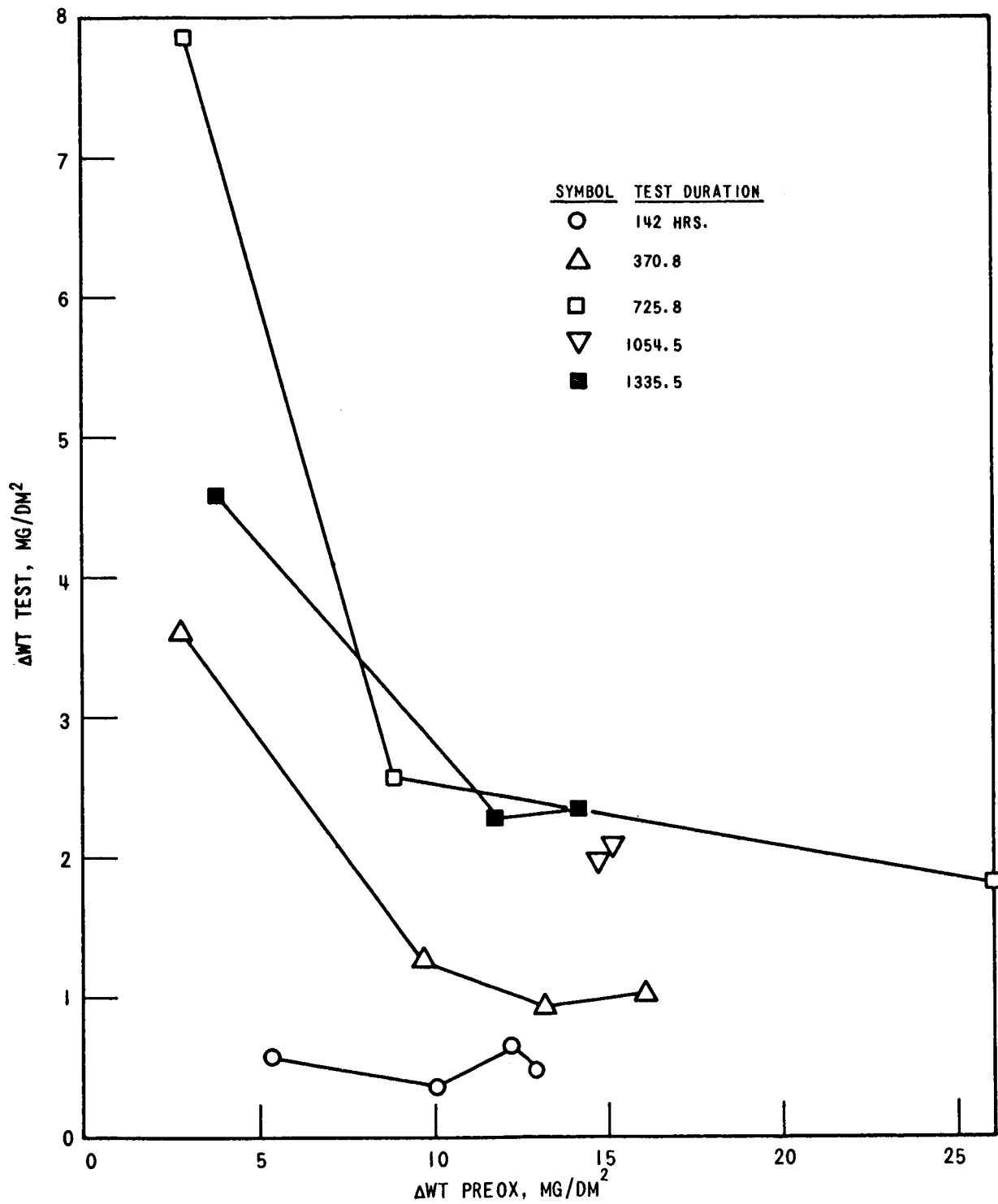
TEST WEIGHT CHANGE AS A FUNCTION OF PREOXIDATION WEIGHT CHANGE
FOR THE 200°F AUTOCLAVE TEST

Figure 17
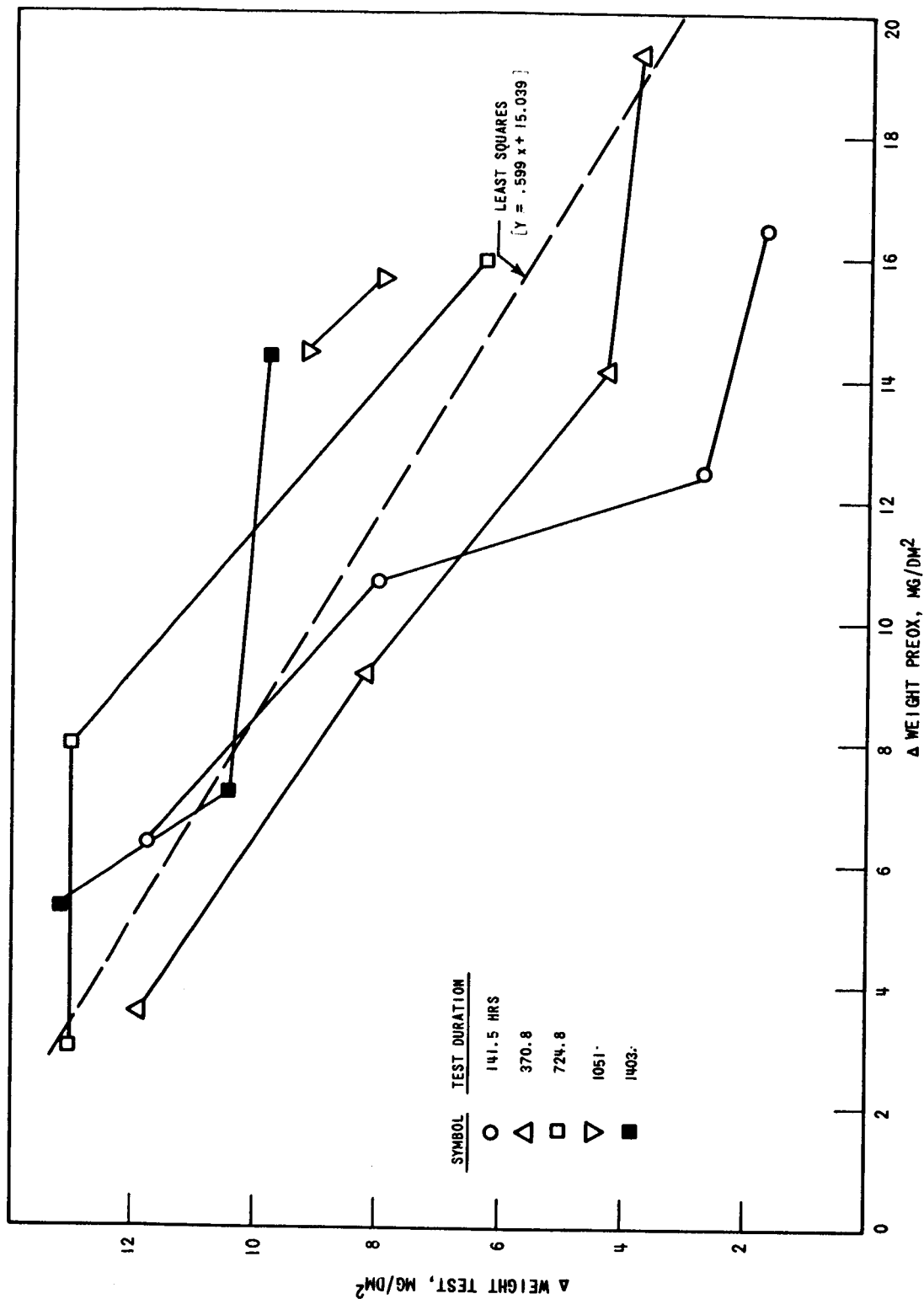
Figure 18

TEST WEIGHT CHANGE AS A FUNCTION OF PREOXIDATION WEIGHT CHANGE FOR 300°F AUTOCLAVE TEST

AUTOCLAVE TEST SPECIMEN WEIGHT CHANGE DURING TEST vs. TEST DURATION

Figure 19

The solutions collected from the autoclave tests and their filtered residues were analyzed for aluminum content. Only minimum detectable amounts were found. Therefore, it was assumed that the specimens in these solutions exhibited little or no spalling or flaking of the oxide film. This assumption then allows for the direct conversion of test weight change to hydrogen generation. This was done using the formula.

$$2 \ Al + 4 \ H_2O \longrightarrow Al_2O_3 \cdot H_2O + 3 \ H_2$$

For every 2 moles of aluminum reacted, the weight increase would be 66 grams, and there would be 3 moles of hydrogen generated. The calculated hydrogen generation from the test weight change for the specimens undergoing $> 12 \ mg/dm^2$ proxidation weight change (shown in Figure 19) is plotted in Figure 20. This figure also contains other information obtained from other tests and will be referred to in subsequent sections.

3. Coupon Stripping

Some of the coupons tested at both $200^\circ F$ and $300^\circ F$ were stripped of their oxide films in the manner previously described. The weight change data and solution analyses were shown in Table 16. The information obtained from the stripping could be interpreted by two means: using the strip weight change data or using the solution analyses data.

The total metal attack is calculated from the difference in preoxidation (before autoclave treatment) specimen weight and the post-strip weight. Of this amount, some aluminum was reacted during preoxidation, the remainder is the weight of aluminum reacted during the test. This test metal attack can then be used to compute the test hydrogen generation. The results are shown in Table 18 and are plotted in Figure 20. There appears to be
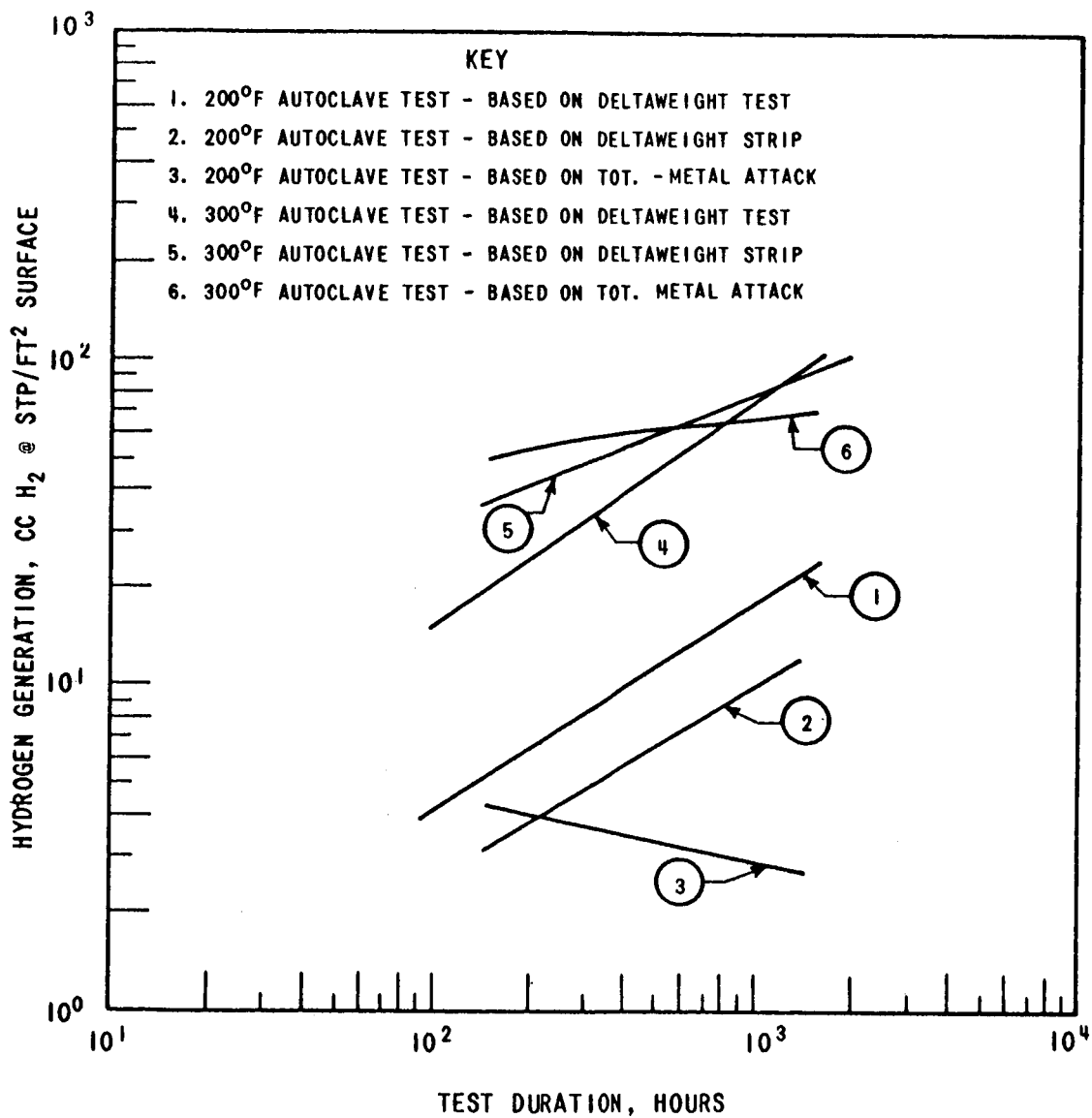
HYDROGEN GENERATION RESULTS

Figure 20

TABLE 18

Hydrogen Generation from Autoclave Specimens - Calculated Using Strip Weight Change Information

Spec.	Total Met Attack, mgs	Met Attack During Preox, mgs	Met Attack During Test, mgs	H₂ Generation During Test		
				cc	cc/dm²	cc/ft²
36	1.875	1.92	Neg.	-	-	-
55	2.142	2.33	Neg.	-	-	-
61	2.553	2.45	0.10	0.12	0.51	4.7
37	2.298	2.24	0.06	0.07	0.30	2.8
35	3.36	2.36	1.00	1.25	5.35	49.6
42	4.39	2.76	1.63	2.03	8.70	80.8
51	2.641	1.03	1.61	2.01	8.60	79.9
52	2.638	1.38	1.26	1.57	6.73	62.5

Spec.	Δ Wt (1) Strip, mgs	Δ Wt Preox, mgs	Oxide Assoc. (2) with Preox, mgs	(1-2) Oxide Formed in Test mgs	H₂ Generation During Test*		
					cc	cc/dm²	cc/ft²
36	4.352	2.33	4.24	0.11	0.062	0.26	2.41
55	5.188	2.85	5.19	-	-	-	-
61	5.683	3.02	5.50	0.18	0.10	0.43	4.00
37	5.584	2.76	5.02	0.56	0.31	1.33	12.3
35	6.88	2.90	5.27	1.61	0.90	3.86	35.8
42	10.02	3.36	6.11	3.91	2.19	9.38	87.0
51	6.957	1.26	2.29	4.67	2.62	11.22	104.0
52	6.705	1.68	3.06	3.65	2.04	8.73	81.0

* Calc. assuming one water of hydration

good agreement between these results and those obtained from the test weight change information for the $300^\circ F$ autoclave test.

Another calculation involving the strip weight change is also shown in Table 18 with the results plotted in Figure 20. In this one, the steam treatment oxide formation is subtracted from the strip weight change, the result being the amount of oxide formed during test. This is then converted to hydrogen generation assuming one water of hydration. The ratio of total metal attack to the strip weight change for these specimens was shown in Table 16. The average of all specimens was 0.426 as compared to a theoretical of 0.45 for the one water of hydration relationship. This then allows one to use this equation without much error. When plotted in Figure 20, they also agree with the weight change results.

The remaining method of analysis involving the stripping procedure, is the use of the chemical analyses of the strip solutions. It was shown in Table 16 that the aluminum in strip solutions was from 1.8 to 3.5 times as high as the total aluminum attack, the average being 2.6 times as great. Therefore the hydrogen generation calculated in this manner will be high by the same amount and will not be plotted in Figure 20.

4. Empirical Relationships Derived from Autoclave Results

The autoclave test data shown in Figure 20 represent the results of three analyses of test information:

a. measured weight change of specimens during test (curves 1 and 4)

b. measured weight change of specimens as a result (curves 2 and 5) of stripping the aluminum oxide

c. total metal attack calculated from the difference between pre-oxidation specimen weight and post-strip specimen weight (curves 3 and 6)

The empirical hydrogen generation correlations are based on a, the measured weight change during test. The stripping data were not directly used to determine empirical hydrogen generation re-

lationship because of the disagreement between the strip weight change and the strip solution analyses. Data obtained by direct hydrogen measurement were disregarded because of large differences in corrosion between the two types of specimen present ("hard coat" and steam treated, see paragraph A.1, p. 53). Curves 1 and 4 of figure 20 have similar slopes and for simplifications it was assumed they had the same slope with the following result:

for 300°F test, H_2 gener $(cc/ft^2) = 0.567 (t)^{0.711}$

for 200°F test, H_2 gener $(cc/ft^2) = 0.142 (t)^{0.711}$

where t is the test duration in hours.

In order to combine these two equations into one, the following was done. The above equation is the form:

$$\log H_2 = \log a + b \log t$$

where a and b are the constants in the previous equations.

$$\text{let } \log a = \log P + Q \log T$$

where P and Q are constants and T is the temperature in degrees Fahrenheit.

The result is an equation where hydrogen generation is a function of test duration and specimen temperature with no heat flux across the specimen-liuqid interface. The relationship is:

$$H_2 \text{ gener} = 1.32 \times 10^{-2} \left(\frac{T}{100}\right)^{3.44} (t)^{0.711}$$

This empirical correlation is again plotted in Figure 21 along with the hydrogen generation values determined from the weight change data. Also shown is the correlation developed by Griess (Reference 1) for heat fluxes between one and two million Btu/hr-ft^2. It should be noted that the hydrogen generation in a system experiencing heat flux is proportional to the hydrogen generated in a system without heat flux, e.g. the curves are approximately parallel.

B. Loop Tests

    1. Low Power Test

        The generation of hydrogen from this test can theoretically be determined from the same type of analysis as was just described for the autoclave tests; namely, by direct measurement, by utilizing specimen stripping data such as weight change and solution analyses, and by knowledge or test weight change.
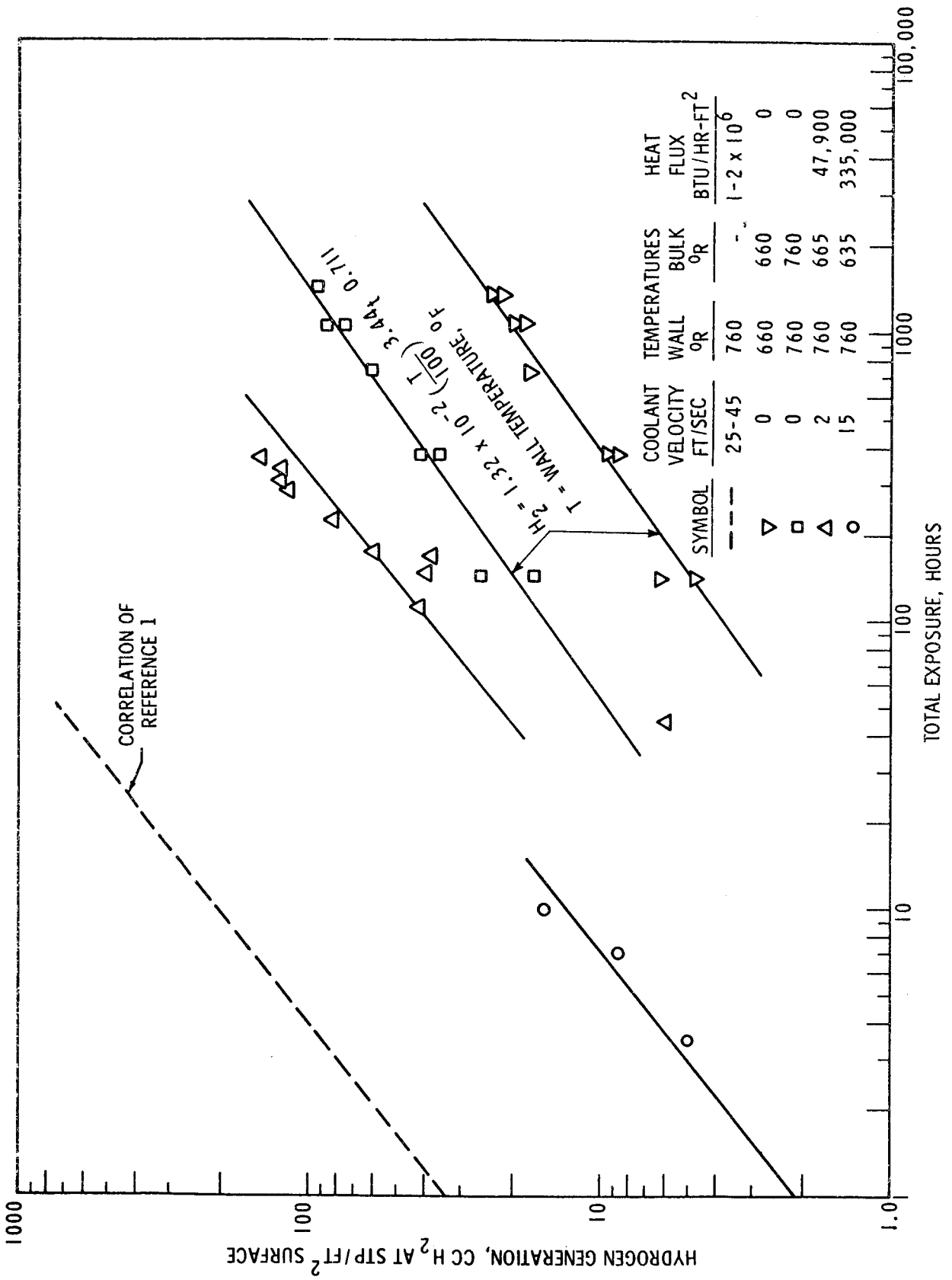
TOTAL HYDROGEN GENERATION CAUSED BY ALUMINUM CORROSION

Figure 21

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a. Direct Hydrogen Measurement

The results of analyzing liquid samples from the loop
fluid for hydrogen content were shown in Figure 9. The amount
of hydrogen present in solution at any time is a result of
corrosion in the heat flux region of the specimen, corrosion
in the non-heat flux region of the specimen and corrosion of
the loop metal surfaces. These amounts could be diminished
by losses of hydrogen from the system.

The purpose of the loop preconditioning described in
section V-A-3, was to passivate the loop metal surfaces or
preoxidize them, so that the contribution of hydrogen from
this source during testing would be small. The subsequent
loop "base-line" operation, described in section V-54,
served the function of determining this generation rate
which was to have been subtracted from the generation rate
during test, resulting in a value which could be associated
with specimen corrosion. The rate obtained during this
"base line" operation varied between 0.10 and 0.15 cc of
hydrogen per kilogram of solution per hour. During the low
power test the hydrogen generation was 0.03 cc H_2/kg/hr with
four specimens in the loop and 0.017 cc H_2/kg/hr with two
specimens. Each of these are significantly less than the
result of the "base line" operation. In addition, the two
test results are in a ratio of about 2 to 1, the same ratio
as the area of aluminum in the respective tests. The low
level of this generation and the relationship between the two
rates indicates that loop corrosion and therefore its hydrogen
generation have been reduced significantly enough to be ignored.

The loss of hydrogen from these tests has been ignored in all of these calculations. In all cases the amount of hydrogen present has been well within the solubility limits of the loop solution. This coupled with the low loop operating temperature, and the fact that there was no liquid-gas interface present in the loop, precludes the preferential loss of hydrogen from solution without losing significant amounts of loop fluid, which were at a minimum.

The remaining sources of hydrogen were from corrosion of both the heat flux regions and non-heat flux regions of the aluminum specimens.

The specimens had 51 inches of length exposed to loop solution at a temperature between $245^{O}F$ and $264^{O}F$. Only 11 inches of this surface is subject to a heat flux across the interface with the loop fluid. The hydrogen generated in the 40 inches of unheated surface was determined using the empirical correlation specified above, assuming an unheated surface temperature of $264^{O}F$.

The hydrogen generated in the heat flux region was calculated as follows:

1. The total hydrogen generated in the loop at various times is obtained by multiplying the measured hydrogen concentration (data points shown in Figure 9) by the mass of water in the loop (15 kg).

2. The total hydrogen from the unheated surface of the specimens is obtained by multiplying the total unheated specimen area (0.65 ft^2/specimen) by the hydrogen generation at $264^{O}F$ as determined by the empirical correlation.

3. The total hydrogen from the heated surface is the difference between 1. and 2. The hydrogen generation per square foot of heated surface is obtained by dividing by the heated surface area (0.18 ft^2 per specimen).

After 167 hours' exposure, two of the four heaters were permanently removed for examination and the experiments continued with only half the surface exposed. This change of surface area was accounted for in the above mentioned calculations. The values of hydrogen generation calculated from the data of Figure 9 are shown as data points in Figure 21. A correlating line was drawn through these data parallel to the lines describing the autoclave test results. This was done because a comparison of the correlation for heat fluxes between one and two million Btu/hr-ft^2 presented by Griess (ref. 1) and the "zero-heat flux" correlation presented herein indicates heat flux has little or no effect on the slope of the "log-log" plots, e.g. the hydrogen generation with heat flux is proportional to the hydrogen generation without heat flux.

b. Stripping of a Loop Test Specimen

One of the test specimens (Number 18) was stripped of the surface oxide in the 11 inch region associated with the heat flux. The specimen was weighed before and after stripping and the strip solution was analyzed for aluminum content.

The strip solution contained 59 µg aluminum per milliliter of solution, which converts to 33 mg aluminum per square decimeter of surface area. It had been shown that of the aluminum stripped, 21 mgAl/dm^2 had been attacked during pretreatment. Therefore, the aluminum attacked during test is 33 - 21 or 12 mgAl/dm^2.

Using the equation previously discussed, 2 m-moles or 54 mg of aluminum attacked produce 3 m-moles or 67.2 cc of hydrogen, the result is 150 cc H_2 per ft^2 of heated surfaces. This agrees very well with the value based on hydrogen measurements shown in Figure 21 (150 cc/ft^2). This analysis assumed no base metal attack during strip, which would tend to lower this point.

The weight change of the specimen during the stripping operation was a loss of 248 mg. An analysis of the strip solution for five elements yielded the following results:

Element	μg/ml
Al	59
Cd	< 3
Cu	< 3.2
Fe	10
Ni	16
Total	91 μg/ml

The solution volume was 1011 ml, resulting in 92 mg of these metals. If it is assumed that they exist as their respective oxides of which about 45% is metal, then the oxide weight was 92/.45 or 205 mg. Therefore, there is some agreement between this 205 mg loss of oxide during strip and the weight change of the specimen of 248 mg during the same operation.

c. Specimen Test Weight Change

The hydrogen generation can also be calculated if one knows the specimen weight change during test and has an analysis of solutions and residue to determine aluminum lost from the specimen. The test weight change information is shown on the following page.

Spec. No.	Preox. Δ wt* mg/dm^2	Test Δ wt mg	Test Duration Hrs.
11	+15.0	+21	167
12	+11.5	-549	167
16	+16.0	-33	330

*Based upon entire surface exposed to fluid.

These weight losses were not expected based upon visual examination of the specimen. Analysis of the loop solution yielded the minimum detectable amount of aluminum, < 0.04 μg/ml which for a loop, volume of 15 liters, is < 0.6 mg. Two residues were collected and analyzed for aluminum with the following results:

Residue	Wt % Al	Wt Residue	Wt Al
1	0.55	5.4 mg	3 mg
2	0.60	11.5 mg	7 mg
		Total	10 mg

This total amount of aluminum found is so small compared to that apparently lost, that the test weight change data will not be used for determining hydrogen generation. It is assumed that the drying process used both before and after test, was sufficiently different to cause the discrepancy just described.

2. High Power Loop Test

The results obtained from the high power loop test were analyzed in the same fashion as was just described for the low power test specimens.

a. Direct Hydrogen Measurement

The direct measurement of hydrogen generation in the loop was shown in Figure 10. These values were converted to cc per ft^2 using the same procedure described for the low power tests

and the data shown in Figure 10. The loop fluid mass was 15 kg but only three specimens were used in the high power tests. The hydrogen generation per square foot of heated surface is shown in Figure 21. This curve has about the same slope as the autoclave tests.

b. Stripping of a Loop Test Specimen

The heat transfer region of one of the specimens was stripped; the solution then analyzed for aluminum. The aluminum concentration was 57 ug/ml in the strip solution. Performing the same calculations and allowing for a pretreatment aluminum attack of 28.6 mg/dm^2, the resulting hydrogen generation for a 10 hour test was 42 cc H_2 per ft^2. This is about a factor of three higher than the hydrogen measurement results shown in Figure 21.

The solution analysis for the five metallic elements is confirmed by the weight change of the specimen during the strip operations. The analysis was:

Element	$\mu g/ml$
Al	57
Cd	< 3
Cu	6.8
Fe	6.3
Ni	21
Total	95 $\mu g/ml$

This converts to 213 mg of the metal oxides, which compares favorably with the strip weight change of 235 mg.

c. Specimen Test Weight Change

The specimen weight change during this test appears to suffer the same fate as the low power test results. The weight changes shown below indicate substantial weight losses presumably aluminum, when in fact practically no aluminum was found in either the post-test loop solution or its residue

Spec. No.	Preox, wt mg/dm^2	Test Wt mg
10	28.6	-201
17	0.2	-102
21	2.0	-175

VIII. <u>CONCLUSIONS</u>

The objectives of the program were to determine the generation of hydrogen caused by corroding aluminum under certain conditions. These objectives have been fulfilled and have been described in the previous sections, specifically on Figure 20.

One set of conditions that were analyzed represent power operation of the TWMR and initial shutdown. These conditions were simulated in the loop tests with the results typically illustrated in Figure 21. These results indicate that heat flux causes the hydrogen generation rate to increase. The greater the heat flux, the higher the hydrogen generation rate. These results were determined from a limited number of tests and conditions but the slopes of the curves appear to agree with work done by other investigators.

A second set of conditions investigated represented shutdown of the TWMR for periods of time following periods of reactor operation. The autoclave tests were used for this phase, and their results were summarized by the equation:

$$H_2 \text{ generation, cc/ft}^2 = 1.32 \times 10^{-2} \left(\frac{T}{100}\right)^{3.44} (t)^{0.711}$$

Again it must be emphasized that a limited number of tests were performed and these results are by no means conclusive.

Treatment of aluminum to establish an oxide film on the surface prior to subjecting to the tests conditions, proved successful and quite valuable. It was determined that a treatment in 350°F wet steam produced specimen weight change of about 15 mg/dm^2 of surface which corresponds to about 150 cc hydrogen generation per square foot of surface. This film is adherent, since none appeared to break away during subsequent testing. The use of a pretreatment, for a system where total hydrogen generation could be critical, would mean that the initial rapid corrosion rates which generate large amounts of hydrogen would be experienced prior to system operation. This would minimize hydrogen generation during periods when it could not be tolerated.

The preoxidation weight change data indicates that some factor such as surface condition may effect corrosion rate. This was indicated by the large variation in sample weight changes in samples preoxidized simultaneously for the same length of time.

Whether the hydrogen generation in the TWMR would be excessive as determined by the results of this program, would not absolutely be answered at this time. The maximum allowable hydrogen generation for the TWMR based upon conditions established by the NASA is 164 cc H_2 per ft^2 surface. Beyond this value, hydrogen will leave the solution when system pressure is reduced. This is not tolerable unless provision is made for the removal of this gaseous hydrogen. Depending upon the actual combination of power operation of the periods, this condition could be reached if the results of this program are used as a guideline. Since it is necessary to know whether or not this condition will be reached and if so, how much gas will be evolved, so that equipment can be properly sized, it is recommended that proof tests at actual TWMR conditions be performed.

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APPENDIX A

Analysis of Hydrogen in Solution

The hydrogen generation rate can be directly measured during the loop and autoclave tests by analyzing for the hydrogen content of the test fluid periodically. In the loop tests, small liquid samples, 25 to 100 cc, were extracted from the system for analysis of hydrogen content and pH. The sample container was a high pressure sample cylinder that was valved into the test system. The sample was swept with the appropriate gas (Nitrogen or Argon) depending upon the anticipated concentration of hydrogen.

A known quantity of the mixture of swept gas and hydrogen was injected into a Fisher Gas Partitioner, Model 25 where the thermal conductivity of the mixture is compared to that of the pure sweep gas. The signal generated by the conductivity difference is recorded on a Minneapolis Honeywell Brown Electronik Recorder 0-1 mv full scale deflection. The partitioner is kept at a constant temperature and is regulated by a Fisher Constant Current Supply, Model 28. The signal sent to the recorder can be controlled by the 5 ranges available on the Partitioner capable of sending 100, 50, 25, 10 or 2% of the signal depending upon the anticipated gas concentration and its conductivity.

The system was calibrated with the following results using Argon sweep gas for hydrogen detection:

Partitioner Scale, %	Max. H_2 Content, cc/kg	Min. Detectable Limit, cc/kg	Repeatability cc/kg
100	40	0.2	0.2
50	80	0.4	0.4
25	160	0.8	0.8
10	400	2.0	2.0
2	2000	10.0	10.0

With knowledge of the sample size, the injected sample size, and the system calibration, the hydrogen content of the loop fluid was calculated.

APPENDIX B

Aluminum Stripping Procedure (6061-T6)

A. Solutions:

No. 1 - Saturated aqueous solution of boric acid.

No. 2 - Aqueous solution of 4 w/o chromic acid (CrO_3) and 10 w/o phosphoric acid (H_3PO_4).

B. Procedure:

1. Pretreat piece to be stripped by immersing in solution No. 1 (saturated boric acid). Apply an alternating current of 11 ma/cm^2 against a platinum cathode for a period of 4 minutes solution temperature of $25^{\circ}C$.

2. Rinse and immerse immediately in solution No. 2 (CrO_3 + H_3PO_4). Apply a direct current of 4.5 - 5.0 ma/cm^2 against a platinum anode for 60 minutes at a solution temperature of $80^{\circ}C$.

3. Rinse with demineralized water and alcohol, oven dry at $110^{\circ}C$ for one hour; cool and weigh.

4. Repeat steps 2 and 3 until the weight change due to each stripping is nearly constant. 1 (usually 5 strippings (step 2) were found to be sufficient for oxides formed in $165^{\circ}C$ water.)

5. Specimens must be stripped completely without interruption to prevent excessive formation of oxide at ambient temperature.

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1 A new clean 6061-T6 aluminum specimen was found to lose on the order of 2.5 mg/dm^2 total with this method.