HYDRAZINE ELECTROLYSIS CELL
SAFETY LIMITS TESTS

PREPARED BY
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SUMMARY REPORT

TASKS VII AND VIII

JPL CONTRACT No. 951720

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HYDRAZINE ELECTROLYSIS CELL SAFETY LIMITS TESTS

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ABSTRACT

The work reported herein is a continuation of a previous program of testing an experimental hydrazine electrolysis cell. The purpose of this program was to investigate the performance of the electrolysis cell at extreme conditions of voltage, current, and temperature to determine if any controllability problems existed. Early in the planned test program a failure which destroyed the electrolysis cell was experienced. The subsequent failure investigation indicated that the probable cause was thermal decomposition due to local hot spot on the cathode screen.

INTRODUCTION

This report summarizes the work performed under Tasks VII and VIII of JPL Contract 951720 during the period of 1 April to 29 May 1969. This effort was a continuation of the hydrazine electrolysis experimental work conducted under Task V of the same contract during 1968, and had as its objectives:

- Determine if a controllability problem exists.
- Determine the effects of a short circuit in the electrolysis cell.

The previous work under Task V consisted of design, fabrication, and test of a full scale experimental hydrazine electrolysis cell. That test program was devoted primarily to characterizing the cell performance and identifying problem areas. At the end of Task V, questions of electrolysis cell operating safety limits and controllability remained unanswered. Hence, the contract was ammended to include Tasks VII and VIII which involved exploration of cell performance at extreme off-design conditions. This work was performed using the same electrolysis cell which had been built and successfully tested for over 950 hours in Task V.

SUMMARY

The experimental hydrazine electrolysis cell, previously built and tested under Task V, was thoroughly cleaned and re-assembled for the test program described in this report. Aside from a new wick, new electrical insulation material, and new o-ring seals, the cell consisted of the same parts as previously tested.

To demonstrate adequate structural integrity, the tank shell was proof tested at 300°F and 750 psig. After assembly of the electrolysis cell and leak testing it and the test set-up, the first series of electrolysis tests was started. In accordance with the test plan, these tests were to consist of electrolysis of neat hydrazine (no electrolyte) up to 60 volts, with the liquid at three different levels in the tank.

The first test was a voltage-current survey with the tank 90 percent full of neat hydrazine (10 percent ullage) for the purpose of determining the cell current characteristics at several voltages up to 60 volts. The results of this test indicated a linear voltage-current trace. It also indicated a low resistance value for the cell that went unnoticed at the time.

The second test consisted of over 5 hours of electrolysis with the tank still 90 percent full of neat hydrazine. Of this operating time, 100 minutes was at 60 volts, with most of the remaining time at 40 and 50 volts. During this test, two current surges were detected. One was noticed in time to reduce power, but the other tripped a 15 ampere circuit breaker. The cell resistance dropped to 2 ohms before apparently shorting out. Subsequent analysis of the test data showed a greater increase in pressure than could be accounted for by electrolytic gas generation and cell temperature rise. It is believed that this excessive pressure rise was caused by thermal decomposition resulting from a local hot-spot on the cathode screen. The hot-spot resulted from high power dissipation across a near short area.

Prior to the third test, half of the propellant was removed from the tank, leaving it 45 percent full of neat hydrazine (55 percent ullage). The test consisted of a voltage-current survey up to 60 volts similar to the first test. Cell operation appeared normal as voltage was increased stepwise to 60V, then down to 20V. At 20V rapidly rising temperatures were observed, immediately followed by rupture of the tank and destruction of the electrolysis cell.

A thorough failure investigation was conducted for various failure modes which are discussed in the following sections of this report. The most probable failure mode was concluded to be thermal decomposition, resulting from a local hot spot on the cathode screen above the liquid level of the 45 percent load. Without the propellant acting as a partial heat sink, the hot spot on the screen was able to get out of control.

The failure investigation also included a review of special elevated temperature and current tests conducted on the NASA Goddard hydrazine electrolysis flight experiment. The flight experiment passed the 140°F ambient test due to its improved thermal design. A current limiter in the circuitry prevents the unit from ever seeing above 1 ampere thus the flight experiment was found non-susceptible to the type of failure experienced in this program. Test details are present later.

CONCLUSIONS

Controllability

To maintain control of gas generation at high power levels, proper thermal management and cathode design for that power level must be designed into the electrolysis cell.

Cause of Failure

The results of the failure investigation points to thermal decomposition resulting from local heating on the cathode screen as the most likely failure mode.

The source of the failure is probable loose wires on the edge or bottom of the screen penetrating the fiberglass.

TEST DESCRIPTION

TEST PLAN

The design and test of a full scale experimental hydrazine electrolysis cell conducted under Task V of this contract is described in Reference 1. At the end of that program, questions regarding the operating safety limits remained unanswered because the primary effort had been directed at establishing operating characteristics of the cell and identifying problem areas. The present test program was negotiated as an extension of the previous contract and consisted of Tasks VII and VIII. The objectives of these additional tasks were:

Task VII - To determine if a controllability problem exists in the hydrazine electrolysis process at conditions greatly in excess of the normal limits of electrolysis cell operation.

Task VIII - To determine the effects of a short circuit in the electrolysis cell.

To accomplish these objectives a test plan was formulated which involved electrolysis cell operations well beyond the normal limits of operation. Appendix A contains the complete Test Plan for Tasks VII and VIII. It was recognized from the start that some of these tests would be hazardous, and that a high probability existed that some type of failure would occur before completion of the program. Hence, all reasonable precautions were taken to insure the safety of personnel and facility equipment should hazardous conditions arise during the course of the program. The test plan included a matrix of all the tests which were planned. The maximum planned values of test parameters were:

Current - 30 amperes
Voltage - 60 Volts D.C.
Propellant Temperature - 300^{o}F
Pressure - 400 psig

To summarize; the Test Plan included these general types of tests:

a. High voltage, low current, ambient temperature with neat hydrazine at three liquid levels in the tank.

b. Low Voltage, high current, ambient and 300^{o}F temperature, pressure up to 400 psig with electrolyte at required concentration and with three liquid levels.

c. Short circuit tests.

ELECTROLYSIS CELL CONFIGURATION

The cell configuration was the same as that used previously in Task V, and is described completely in Reference 1. It consists of an electrode module which is installed inside a Surveyor propellant tank.

ELECTROLYSIS CELL ASSEMBLY

Before assemblying the cell for the tests of Task VII, all component parts were cleaned in accordance with the HAC Specification for processing parts for hydrazine service, and then were sealed in clean polyethylene bags until ready to be installed in the unit. During assembly parts were handled only with clean lint-free white gloves.

All parts were those used previously in Task V except for the wick, O-rings, insulating material and thermocouple. It has been common practice to replace the wick on each assembly of the cell, because the wick material is easily frayed by excessive handling. The new wick was cut from the same piece of material as all previous wicks. New O-rings of the same compound (Ethylene-Propylene Rubber) as used previously were installed. Insulating material previously used on the anode conductor and the inner cell enclosure had been destroyed when removed for cleaning these parts. New material of the same type was re-installed, (polyolefin shrinkable sleeving for the anode conductor insulation and polyethylene film on the inner cell enclosure). The thermocouple previously used was found to be faulty and was replaced with a new one of the same type, i.e., enclosed junction iron-contrantan probe, adjusted in length to sense liquid temperature 0.25 inch below the electrolysis module.

After completing the assembly of the electrode module it was installed in the tank, and the complete unit was leak tested at 250 psig with nitrogen gas. A small leak was found at the tank flange joint. Upon investigation it was found that the tank flange O-ring had a small cut. It was replaced with a new O-ring. The wick was also replaced, because the first wick had been damaged when the unit was dis-assembled. After re-assembly the tank was leak-tested again and found to be free of any detectable leakage.

The anode/cathode resistance was checked to verify absence of short circuit and was found to be very high (approximately 20 megohms). The cathode/tank resistance was verified to be zero, indicating proper grounding of the cathode. The assembled electrolysis cell was then installed in the test chamber for system leak test and electrolysis testing.

PROOF TEST

Prior to final assembly of the electrolysis cell, the tank shell and flange closure were proof tested to insure structural integrity at conditions above the expected test conditions. The proof test consisted of heating the tank, filled with de-ionized water, to 300 $\pm$ 20^{o}F and applying three pressurization cycles to 750 psig. This test was performed satisfactorily, and no adverse effects were noted.

TEST STAND DESCRIPTION

The test chamber was located in an isolated hazardous test area as shown in Figure 1. The electrolysis cell/tank assembly was placed in the chamber as shown in Figures 2 and 3 and was connected in accordance with the schematic diagram of Figure 4. The power supply, along with a voltmeter and a clip-on ammeter shown in Figure 5, were located in a protected area approximately 50 feet from the test chamber. The voltmeter and ammeter at this location were used to monitor voltage and current at the power supply location. The data acquisition center was located approximately 50 feet farther away where all parameters were read periodically on a digital voltmeter and recorded by hand on the data sheet. Communication, by means of two-way intercom, existed between the power supply room and the data acquisition room.

ELECTROLYSIS TESTS

For the first series of tests, the tank was loaded with 23.50 pounds of neat hydrazine, which is 90% of the total tank capacity. Loading was accomplished by evacuating the tank, then transferring propellant into the tank from a closed container located on a weighing scale. Propellant transfer is accomplished by pressurizing the supply container with nitrogen to 50 psi.

Voltage Current Survey (Test 713-1)

In accordance with the test plan, the first test was a survey of voltage-current characteristics with the tank 90% full of neat hydrazine. At this loading the liquid level was approximately one inch below the top of the anode. The data from this test are plotted in the upper curve of Figure 6. The inflection and hysteresis in the curve is not unusual and is caused by polarization characteristics of the electrolysis cell and by variation in effective electrode area due to formation and expulsion of gas bubbles in the wick/electrode interface.

The low resistance value is attributed to a local area of the cathode screen being in a near short condition with the anode. This is based on the fact that the distance between cathode and anode is the largest resistance in the unit and is the only variable large enough to explain such a low reading.

Electrolysis at 60V (Test 713-2)

On the day following the voltage-current survey, the first electrolysis test at high voltage was conducted in accordance with thetest plan. With the tank still 90% full of neat hydrazine, the voltage was increased in steps up to 60V. The voltage, current, temperature and pressure history of this test is shown in Figure 7 & 8. The data acquired during this test is included in Appendix B.

During this test an unexpected current increase occurred on two occasions. After 118 minutes of operation it was noted that the current was increasing and exceeded 10 amperes. This necessitated a reduction of voltage to keep the current below that value. Later in the test, the current suddenly increased and tripped the 15 ampere circuit breaker on the power supply. This current surge was coincident with the first vent cycle of the system relief valve.

These current surges were probable due to the near-short area of the cathode contacting the anode. It could have been caused by higher pressure, deformation of the screen at much higher temperatures, or the action of gas bubbles when the relief valve opened.

FIGURE 1

HAZARDOUS TEST AREA

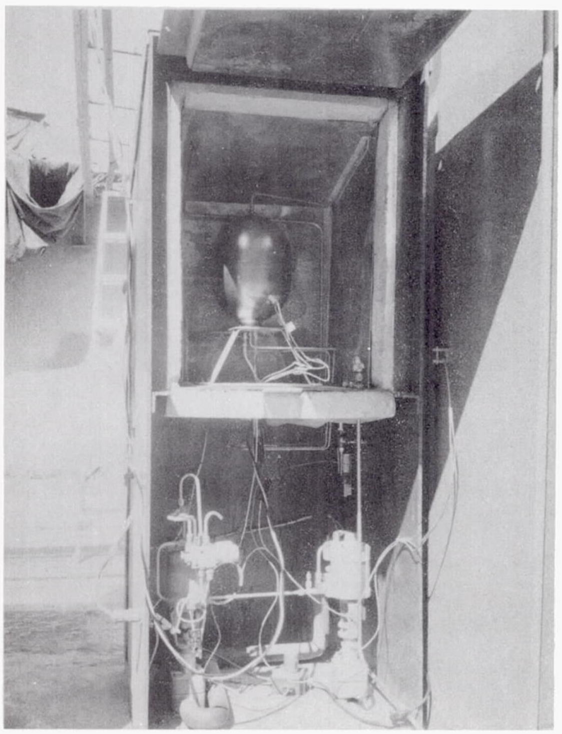
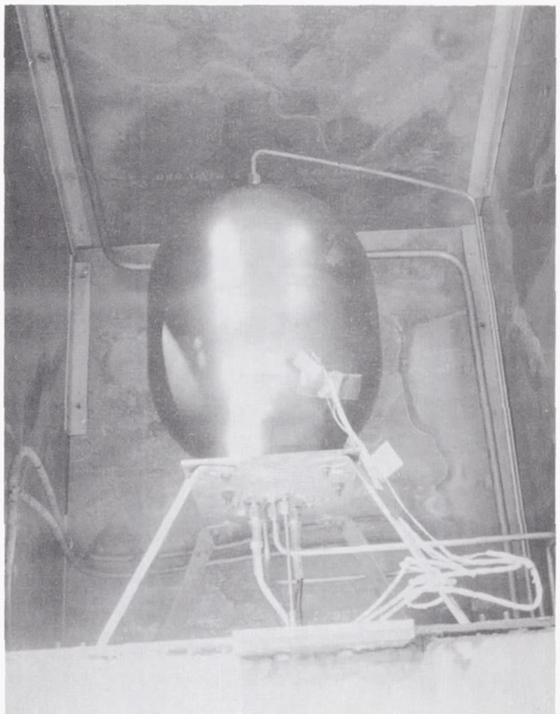


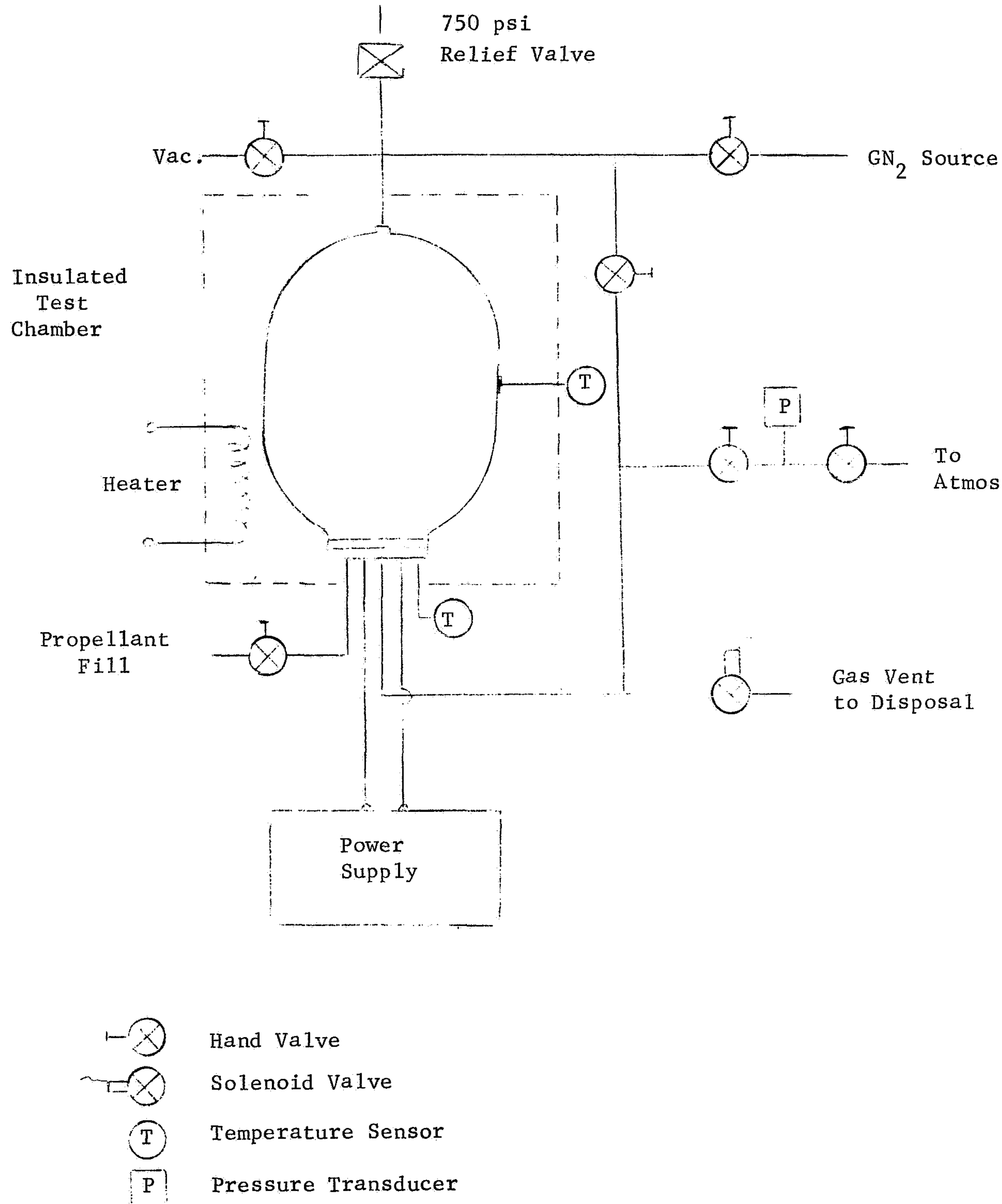
FIGURE 2

HYDRAZINE ELECTROLYSIS TEST CHAMBER



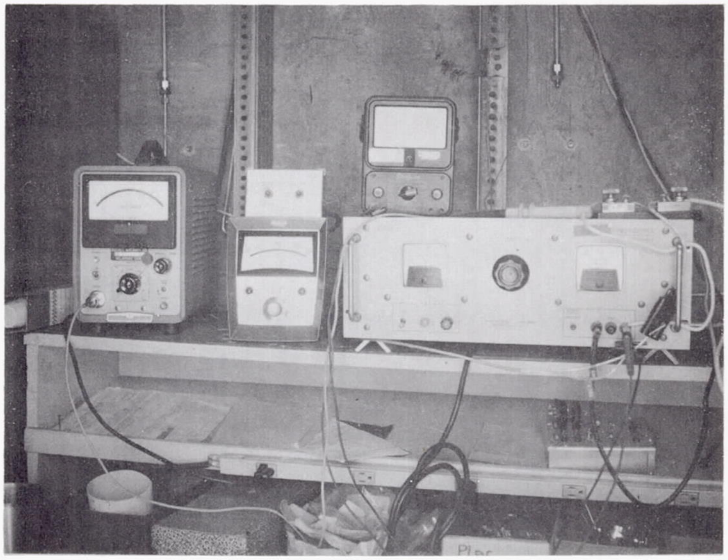
HYDRAZINE ELECTROLYSIS CELL/TANK ASSEMBLY
IN TEST CHAMBER

FIGURE 3



Test System Schematic

Figure 4



POWER SUPPLY AND METERS

FIGURE 5

VOLTAGE-CURRENT CHARACTERISTICS

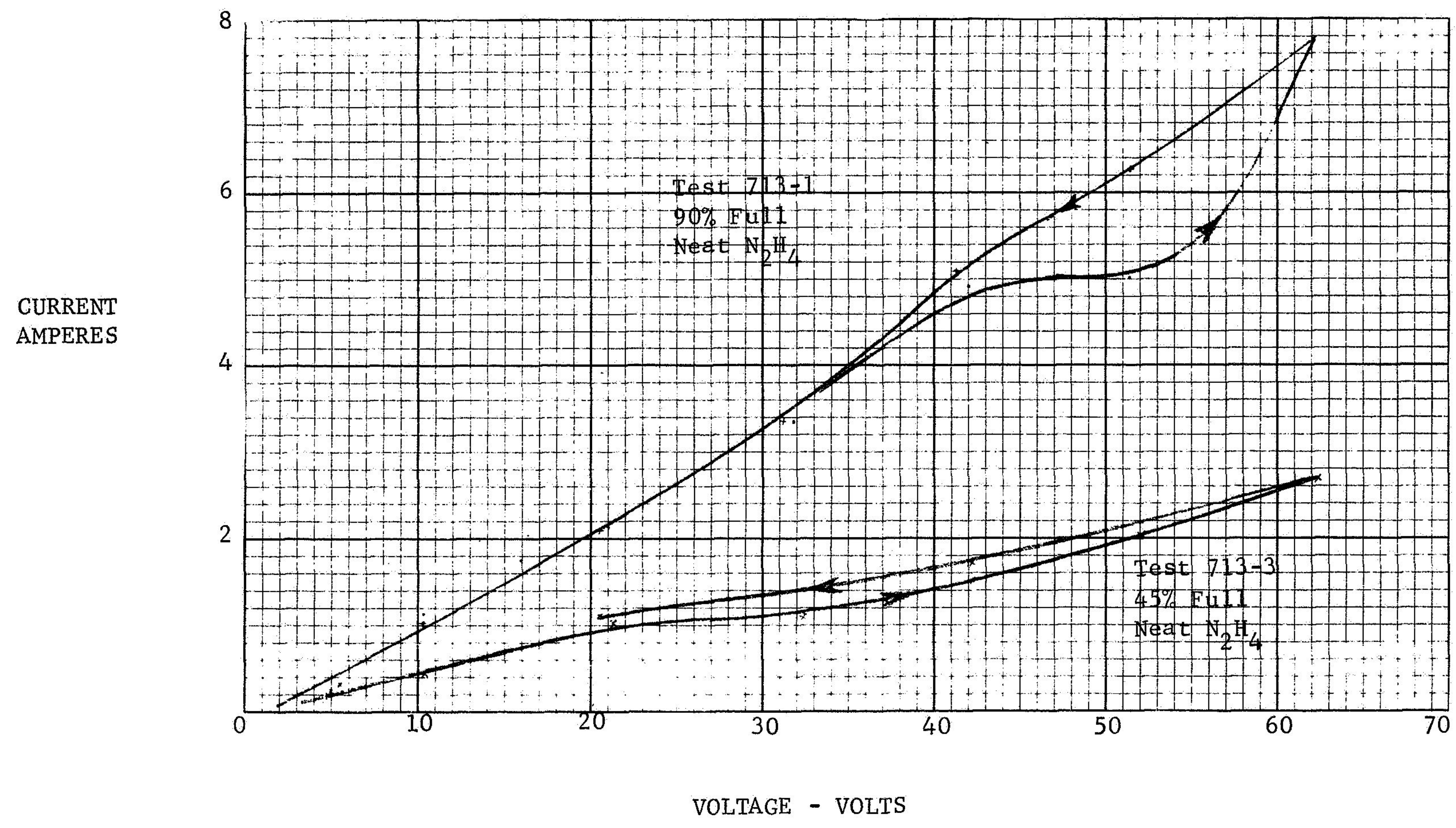


FIGURE 6

VOLTAGE-CURRENT HISTORY - TEST NO. 713-2

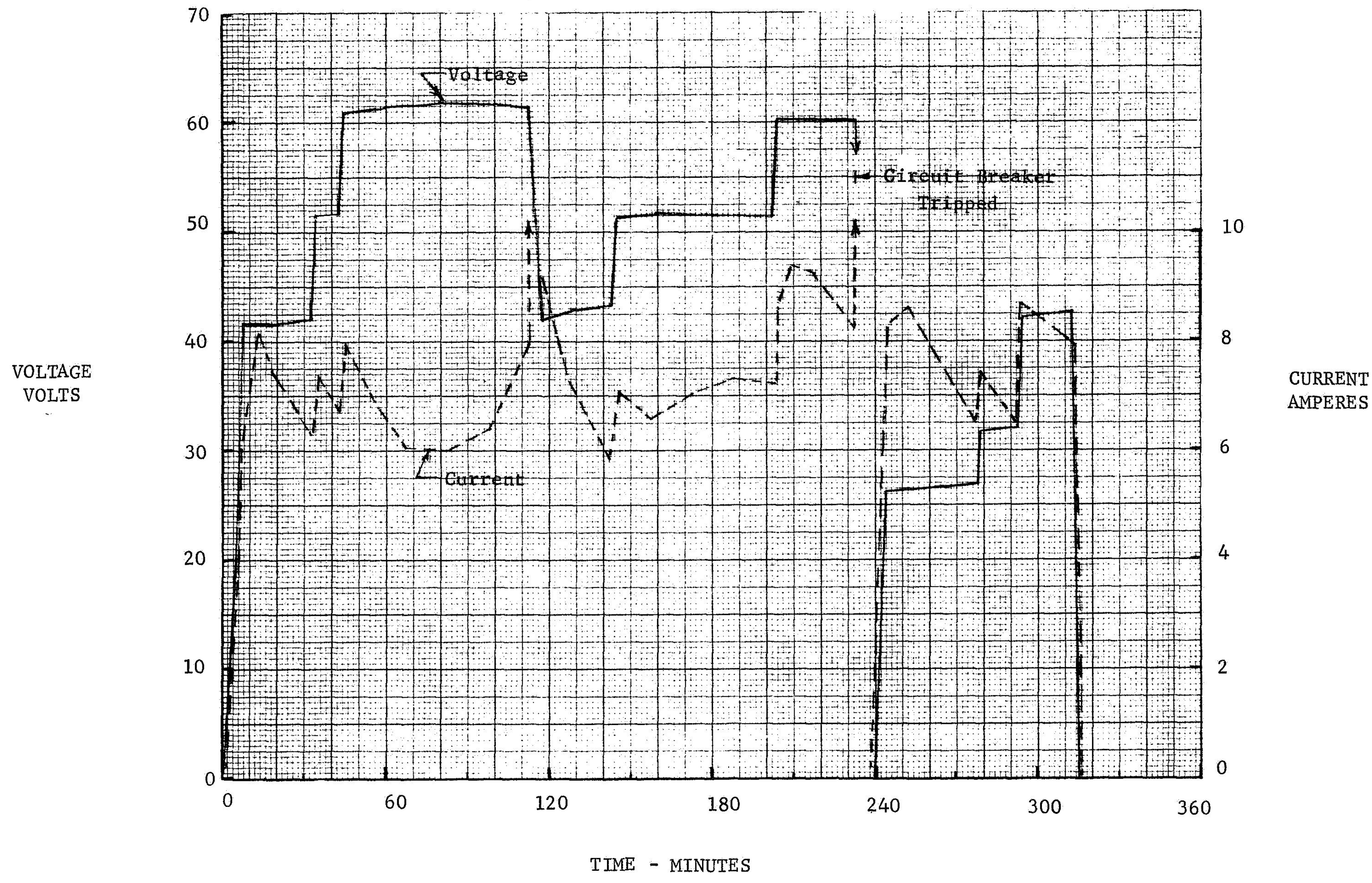


FIGURE 7

PRESSURE TEMPERATURE HISTORY - TEST NO. 713-2

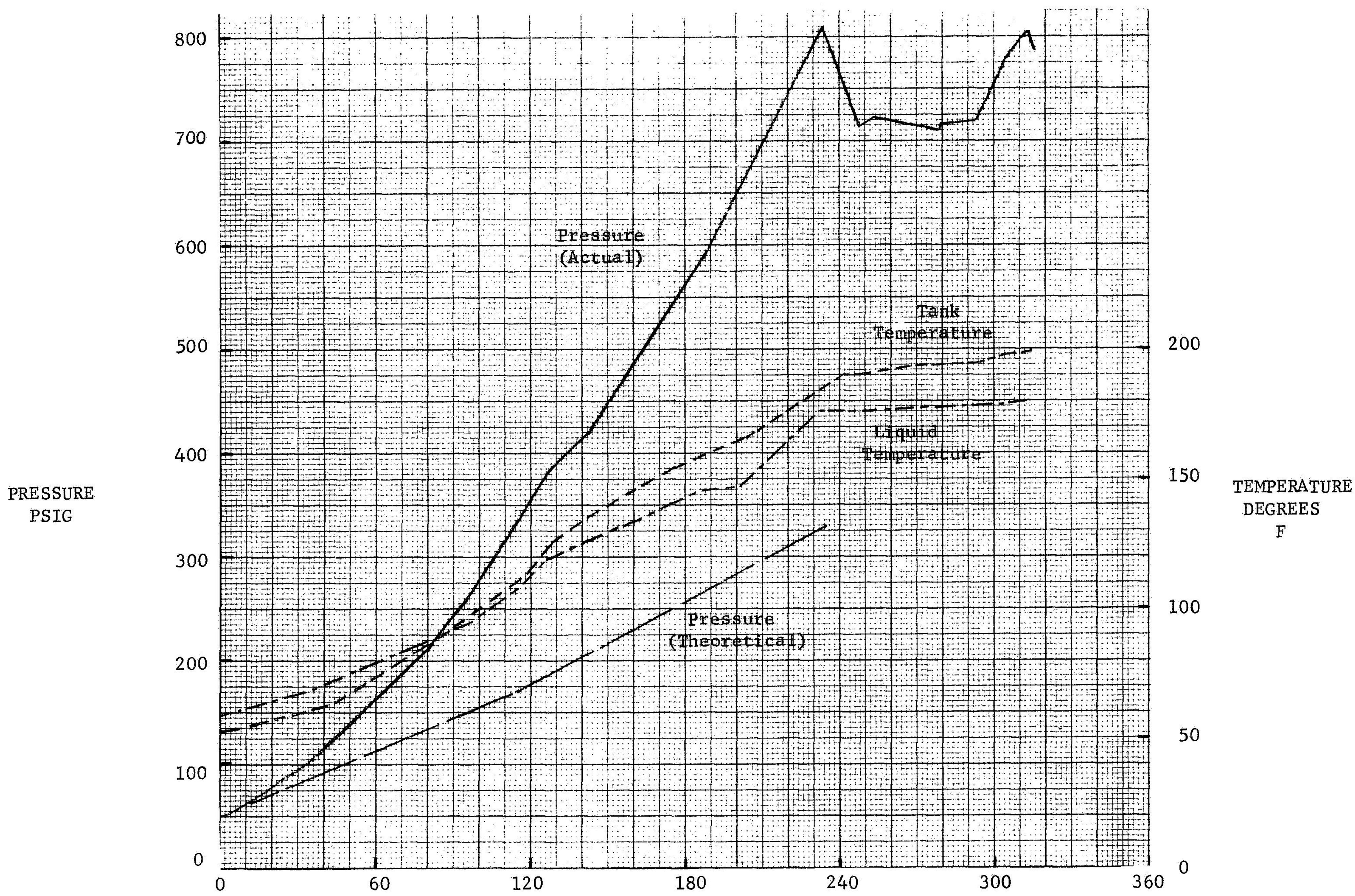


FIGURE 8

Aside from these events the operations of the cell appeared to be normal throughout this test. However, later analysis of the data showed that the actual pressure rise during the first 238 minutes of this test (i.e., up to the time the relief valve first vented) was much greater than could be accounted for by temperature rise and electrolytic gas generation. For reference purposes the pressure increase due to these two factors is plotted in Figure 8. For further discussion of this abnormal pressure rise and current surges see paragraph on "Failure Investigation".

Voltage-Current Survey (Test 713-3)

The next test scheduled was the voltage-current survey up to 60V with the tank 45% full of neat hydrazine. Pressure remaining in the tank from the previous day's test was used to expell half (11.75 lb) of the hydrazine which was weighed in a receiver vessel as it was off-loaded.

After completion of propellant off-loading and leak testing, the voltage-current survey was started. Voltage was increased in steps up to 60V. Cell operation appeared normal and satisfactory. Data from this test are included in Appendix B, and the current-voltage data are plotted in the lower curve of Figure 6.

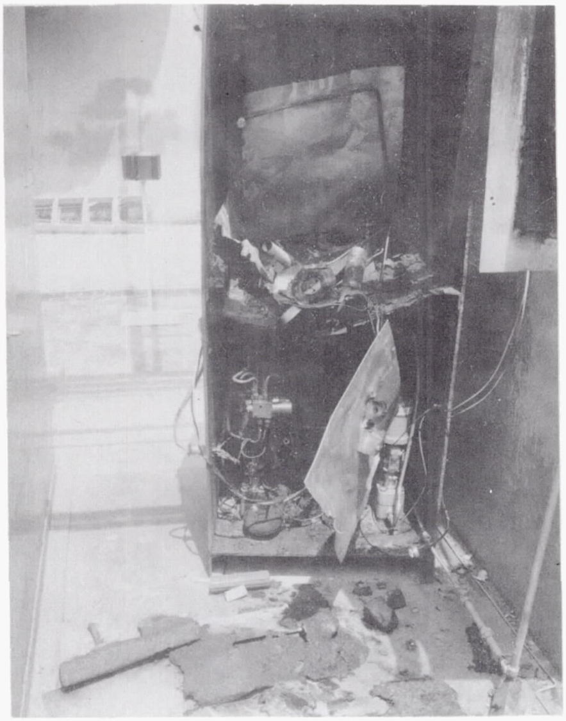
After recording the data on 60V, the voltage was lowered to 40V, data was recorded there then lowered to 20V. While recording data at 20V, it was observed that the temperatures were rising very rapidly (see notes on data sheet in Appendix B). Before the pressure data channel could be selected to obtain a reading of pressure, the tank ruptured. The electrolysis cell and test chamber were severelydamaged by the force of the explosion and the subsequent fire, which was fed largely by the thermal insulation of the test chamber.

FAILURE INVESTIGATION

The failure investigation started by noting the location and condition of all parts of the electrolysis cell which could be found. The notes made at that time are reproduced in Appendix C. The photographs of Figures 9 through 12 show the test chamber and some of the electrolysis cell parts following the failure. Figure 13 shows all of the cell parts which could be found arranged on a display table.

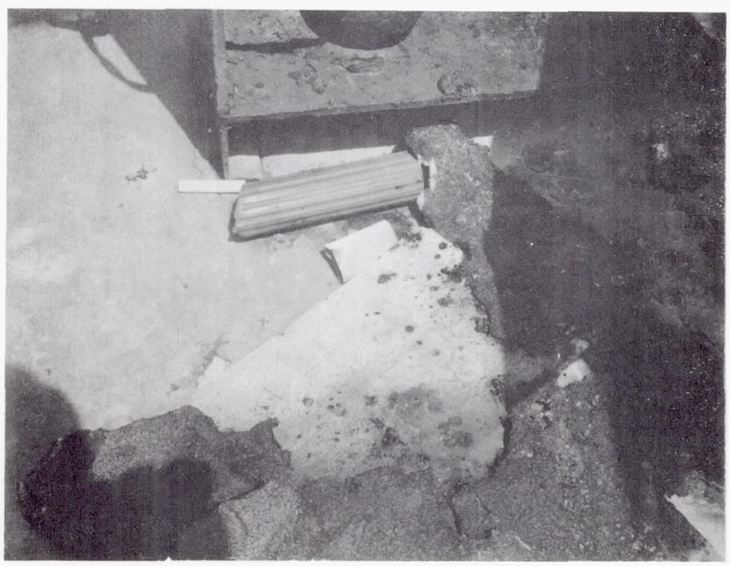
Four possible failure modes were considered in the investigation. These were:

1. Short circuit
2. Electrical arcing
3. Thermal decomposition



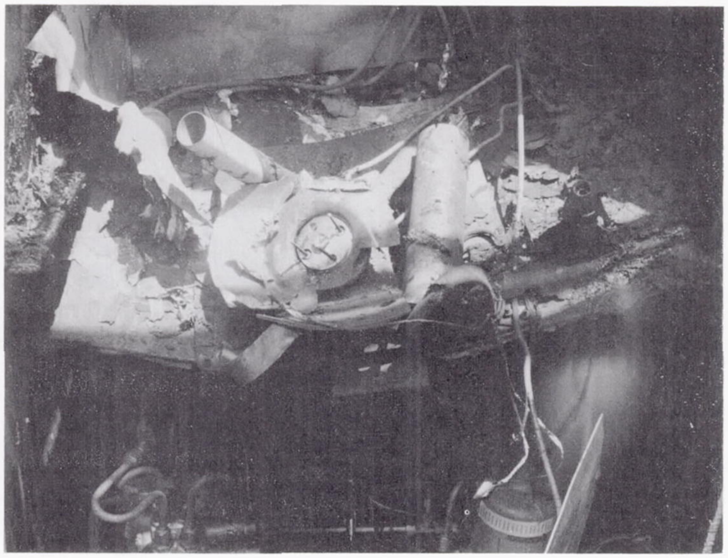
TEST CHAMBER
AFTER FAILURE

FIGURE 9



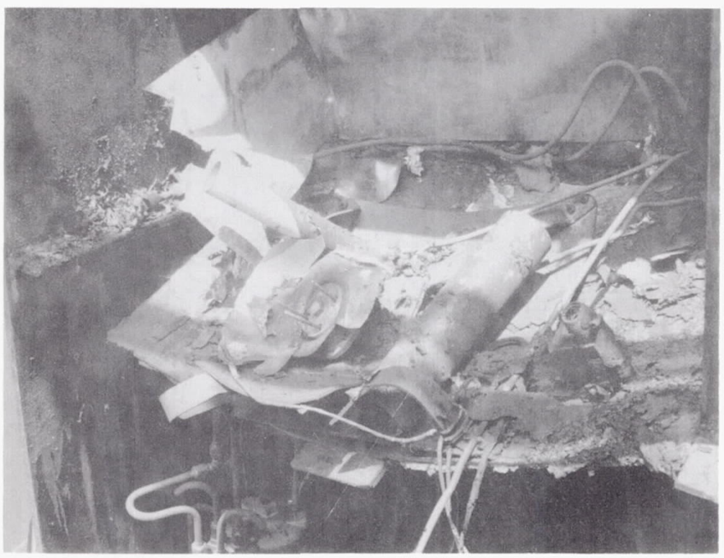
ANODE AND OTHER PARTS
AT BASE OF TEST
CHAMBER

FIGURE 10



TANK FLANGE,
INNER AND OUTER
ELECTRODE ENCLOSURES

FIGURE 11



PARTS OF ELECTROLYSIS
CELL REMAINING
IN TEST CHAMBER

FIGURE 12

FIGURE 13

ELECTROLYSIS CELL PARTS
AND FRAGMENTS

4. Chemical reaction (possibly involving changes in compatibility of some materials resulting from temperatures reached in previous days testing).

The failure investigation included the following specific tasks:

1. Examine identifiable parts and debris from electrolysis cell, tank, and test chamber.
2. Analyze tank fragments for evidence of stress corrosion.
3. Examine power supply and clip-on ammeter for evidence of malfunction or damage.
4. Investigate reason for erroneous pressure data in previous day test.
5. Analyze data from Tests 713-2 and 713-3 for clues to cause of failure.
6. Analyze sample of propellant for same barrel as that used for test.
7. Verify that pressurization gas was nitrogen.
8. Investigation possibility of electrical arcing at 20 and 60 volts.
9. Investigate compatibility of questionable materials at temperatures up to 240°F.
10. Determine activity of other test station personnel at time of failure and determine what other electrical equipment was operating at that time.
11. Review special test results of NASA Goddard flight experiment electrolysis cell.

Examination of Cell Debris

The following observations were made in the coarse of collecting and examining the parts and debris from the electrolysis cell:

a. The outer enclosure of the electrode module was bulged out locally at its lower edge from a high internal pressure. This was a very local condition. The remainder of the part was still round and relatively undamaged except for the top edge being torn out at the attachment screw hole.

b. The inner enclosure of the electrode module was collapsed inwardly at its lower end from an external force. Some metal was mission from along one side of the lower edge.

c. The lower 1 to 2 inches of the anode were shattered into many small fragments,but the remainder of the part was still intact.

d. Many pieces of the cell were found scattered on the hillside up to 20 feet away. Some of these showed damage from heat, while others did not.

The available evidence indicates that a reaction sufficiently violent to damage the aluminum inner and outer enclosures and shatter the lower end of the anode occurred between the inner and outer enclosures. Based on the orientation of the parts, the location of the reaction was established near to the bottom of the cell and also near the surface of the main body of liquid in line with the cathode connector.

Upon examination in the Power Systems Laboratory the ammeter probe connector was found to be loose. After tightening this connector, and de-gaussing the probe, the ammeter could be "zeroed" and appeared to operate normally although it was reported to be somewhat more sensitive than the typical ammeter of this type.

The power supply, leads, system grounding, etc. were also examined. There was no evidence of any damage, malfunction or other discrepancies which could possibly be related to the cell failure.

Erroneous Pressure Data

During the test of the day preceding the cell failure, erroneous pressure data had been acquired because of a decimal error in reading pressure on the digital voltmeter used for displaying all the parameters from this test. This error occurred because a single digital voltmeter was used to display each of the five parameters (voltage, current, tank temperature, liquid temperature, and pressure) by selecting the desired parameter with a selector switch. When switching from one parameter to another it was necessary to mentally relocate the decimal point because of differing sensitivity of signal conditioning equipment in the various channels. This led to confusion and resulted in an error when initially pressurizing the tank prior to Test 713-2. This error was carried through the rest of that test and was not detected until the following day when pressurizing the tank to perform a leak test. These erroneous pressure data were identified and corrected prior to test 713-3 and hence have no direct bearing on the failure other than the tank's being exposed to higher pressures than had been planned on the day before failure occurred. However, these overpressure conditions still did not exceed the stress-temperature conditions of the proof test.

The cathode electrical connector tab and clamp ring, which hold it to the electrical feed-through conductor, were found on the hillside several feet from the test chamber. These parts showed no damage from heat or electrical arcing. It must be concluded that they were blown clear by the force of the explosion and were not involved in initiating the reaction. The stud which was screwed into the anode to form an electrical connector attachment was not found. However, half of the aluminum sleeve which connected this stud to the positive electrical feed-through was found. The sleeve apparently was broken in the middle by the force of the explosion with the missing part perhaps still attached to the anode stud. There was no evidence of electrical damage (arcing or burning) on the part of the sleeve which was found.

Stress Corrosion Investigation

Sections of the 6Al-4V titanium tank shell were subjected to metallographic examination by personnel of the Hughes Aircraft Company Materials Technology Department. There was no evidence of stress corrosion or any other tank shell defect. The report on this examination is included in Appendix C.

Power Supply and Ammeter

The power supply and clip-on ammeter used in the test were examined for damage and/or evidence of malfunction. These examinations were performed by personnel of the Hughes Aircraft Company Power Systems Laboratory. Following the electrolysis cell failure, it was found that the ammeter could not be 'zeroed' and that its needle was very slightly bent.

Analysis of Test Data

The raw test data from Tests 713-1, and -2 and -3 are plotted in Figure 6, 7 and 8. These raw data do not show any unusual characteristics or departure from anticipated performance of the electrolysis cell at high voltages. However, as previously reported, the actual pressure increase measured during Test No. 713-2 was significantly greater than could be accounted for. Based on the current-time- temperature history recorded for that test, the pressure rise due to gas generation by electrolysis and to temperature rise was calculated as 274 psi. up to the point at which the relief valve first vented. The actual measured pressure rise during the same time period was 757 psi. Applying the same analysis to the meager amount of data obtained during Test 713-3 before failure gave a possible pressure rise of 0.4 psi,whereas the test data showed 7 psi. The gas generation rate,when compared to the predicted rate increased with power level from 150 to 400% during Test 713-2 and to almost 900% immediately prior to failure in Test 713-3. Possible explanations for these discrepancies include:

a. Error in tank ullage volume.
b. Pressure measurement errors.
c. Thermal decomposition.

To account for the pressure discrepancy observed for Test 713-2, the ullage volume would have to be 3.6% instead of 10% of the total tank volume. This would require an error of 1.7 lbs in the amount of propellant loaded into the tank. Such an error is highly unlikely since the loaded propellant weight could be controlled to 0.01 lb,and the loading weight calculations were verified to be correct. Furthermore,such an ullage error with the tank 90% full would have completely inadequate to explain the excessive pressure rise noted in Test 713-3 when the nominal ullage volume was 55%. Previous tests at low voltages show very good correlation between actual pressure rise and the current-time-temperature history of the test.

After correcting the pressure data from Test 713-2 for a decimal error, it appears very unlikely that these data could have been in error by more than about 2%. When the pressure signal conditioning equipment was re-checked by resistance substitution prior to Test 713-3, it was found to have drifted less than 10 psi in 600 since the previous calibration 24 hours earlier. The transducer had been calibrated against a precision pressure gage just prior to Test 713-1, two days before the cell failure. The relief valve venting pressure was independently verified by two technicians prior to the start of testing as being 750 psig. Following cell failure the relief valve was checked again, and the venting pressure was found to be 740 to 750 psi. The relief valve was located in the lower compartment of the test chamber (separated from the cell by a shelf of 1/2" steel plate) and hence was undamaged by the explosion and fire. During the Test 713-2 the relief valve appeared to vent a 812 psia the first time and subsequently vented and reseated to maintain pressure between 712 and 805 psig. The relief valve operation during the tests tend to confirm that the pressure data on Test 713-2 could not have been in error by more than abou5 50 psi, whereas an error of almost 500 psi would have been required to explain the high observed pressure. These factors would seem to eliminate pressure measurement error as a probable explanation for the excessive pressure rise.

Since the actual gas generation rates disparity increases with predicted rates significantly with power level, it was concluded that thermal decomposition resulting from high power dissipation is the most probable source of the pressure discrepancy.

Propellant Analysis

The hydrazine used for this program was supplied by the JPL Edwards AFB Test Station. A sample from this drum of hydrazine was assayed by the Hughes Materials Technology Laboratory. A titration technique was used, and two samples proved to be 99.92% and 99.99% hydrazine. The trace impurities were not identified.

Pressurization Gas

A sample of gas used for pressurization during these tests was checked to verify that it was not oxygen. The gas was taken from a compressed gas cylinder clearly marked "Nitrogen Gas". A sample from this cylinder failed to support combustion, thus verifying that it was not oxygen but rather an inert gas.

Electrical Arcing Tests

In order to evaluate the possibility of an electrical arc being responsible for initiating a reaction which led to failure of the electrolysis cell, a series of arcing tests were conducted. Tests were conducted with stainless steel and tungsten electrodes in open and closed containers with the spark gap above, at, and below the liquid hydrazine surface at voltages of 20, 40 and 60 volts and at both room temperature and 160^{o}F. At no time was any sustained hydrazine decomposition reaction achieved. Only one combination of test conditions appeared to give even a mild reaction. With tungsten electrodes touching the hydrazine surface in a closed test tube with the hydrazine temperature at 155^{o}F and 60 volts applied, a large bright blue-green spark was observed, and the cap was blown off the test tube. However, the reaction appeared localized around the spark gap which would indicate that neither the bulk of the liquid nor the bulk of the vapor were involved in the reaction outside the immediate locality of the spark. From the results of these tests it is not conclusive that electrical arcing could have been the initiator of the reaction which destroyed the electrolysis cell on Test 713-3.

Compatibility Tests

Because data on the compatibility with hydrazine of several of the electrolysis cell materials at elevated temperatures was non-existant, or at least very meager, a series of compatibility tests were initiated. Materials subjected to these tests were:

a. Irradiated, cross-linked polyolefin heat shrinkable sleeving used for electrical insulation on the anode connector.

b. Graphite - Grade ATJ - a fragment from the shattered area of the electrolysis cell anode.

c. Polypropylene - from same raw stock as used for the upper and lower anode insulators.

d. Polyethylene film - used as electrical insulation on outside of inner electrode enclosure to prevent it from acting as an auxiliary cathode.

e. Strip of 2024 aluminum alloy representative of material used of inner and outer electrode enclosures and other parts of the electrolysis cell.

Specimens of the above materials were cleaned in accordance with the appropriate Hughes cleaning specification for hydrazine service. The specimens were then weighed, placed in glass combustion tubes partially submerged in hydrazine, and pressurized initially to 5 psig. The tubes were then placed in a thermal test chamber and subjected to environmental temperatures of 160, 200 and 240°F for eight hours each. After each 8 hour exposure, the specimens were examined for changes in appearance and after 200 and 240°F exposures the specimens were weighed. Pressure in each tube was monitored and recorded hourly. None of the specimens exhibited any pressure rise beyond that which could be attributed to the environmental temperature.

The test results are summarized below:

a. Polyolefin - After 200°F test, specimen was slightly whiter and more opaque than the original sample, and showed a weight gain of 6.4%. After 240°F it was very white and opaque, had reduced in diameter from 1/4" to 3/16" and showed a total weight gain of 35.8%.

b. Graphite - no change in appearance, weight gain of 0.08%.

c. Polypropylene - No change in appearance, weight gain of 0.29% after 200°F and 0.57% after 240°F.

d. Polyethylene - After 200°F test, no change in appearance, no weight change. After 240°F, specimen had melted, could not be removed completely from tube so no weight measurement possible.

e. 2024 Aluminum - no change in appearance, weight gain of 0.08% after 240°F test.

Although these tests showed the inadviseability of using polyolefin and polyethylene in hydrazine at 200°F or above, they did not yield any conclusive evidence that these materials could have contributed in any way to the electrolysis cell failure.

These compatibility tests did not include all materials used in the electrolysis cell. They might well be expanded to investigate 5056 aluminum screen (cathode), glass cloth wick material, the EPR O-ring compound, and other materials of construction and be extended to higher temperatures which may have existed locally in the electrode area.

Concurrent Activities

It was determined that there was no other test site activity immediately prior to electrolysis cell failure which conceivably could have contributed to that failure. Personnel not directly involved in the electrolysis cell test were inspecting and cleaning a propellant servicing cart. The only major electrical equipment in operation at the time was the motor driving a vacuum pump used on the facility altitude chamber. This motor had been operating continuously and normally for approximately two hours before cell failure, and it continued normal operation following the failure. No other equipment was in operation which conceivably could have caused a current surge which might have affected cell operation.

NASA Goddard Flight Experiment Testing

As a result of the failure in Test 713-3, special elevated temperature and current tests were conducted with the NASA Goddard flight experiment electrolysis cell. The test data was reviewed as a part of the failure investigation since it might reveal something significant for the JPL unit. Two over tests were conducted. The first test called for operating the unit at 140^{o}F ambient temperature and; the second test called for operating the unit at 4 amperes. (Normal operation is 60 to 100^{o}F and 1 amp). The flight experiment unit had no difficulty operating at 140^{o}F since it is a high mass design especially around the cathode and in outer tank. The bottom of the tank is a flat plat used for attachment, and it provides good thermal conductance.

The entire unit has not been subjected to 4 amperes. A stainless steel spring used as the anode electrical connection was identified as the weakest component in the unit and it was subjected to 4 amperes. The spring reached an estimated 200 to 300^{o}F. Thus testing the entire unit would be unwise. We are currently planning to test the entire unit at 2 amperes. In flight the unit will experience 1/2 to 1 ampere maximum and as further protection a one ampere current limiting device is contained in the power conditioning circuitry.

Based on this special testing and design differences it was concluded that the flight experiment is not susceptible to the type of failure we experienced. The heavy metal cylinder backing up the cathode screen offers a good heat sink for hot spots. The wick and screen are rolled away from the anode and back around the same metal cylinder. This precludes the suspect failure mechanism discussed later.

Summary of Failure Investigation

The facts derived in the failure investigation tend to eliminate the following factors as possible contributors to the electrolysis cell failure:

- Stress corrosion of the tank shell
- Power supply or instrumentation malfunction
- Propellant contamination
- Pressurant gas contamination
- Other concurrent activities at the test site.

The tests which have been conducted to evaluate electrical arcing as a possible initiator seem to have indicated only a remote possibility that this could have contributed to the failure.

A cathode screen hot-spot is the only mechanism that fits all the evidence. It accounts for low resistance in a near-short condition; it explains the additional gas generation above prediction and why it increases with higher power; it explains the two current surges as shorts; and it explains the failure occurring during the second day rather than the first day, since the area in question is above the assumed propellant level in the electrolysis cell as evidenced by the failed hardware description.

The most probable cause of the near-short condition is the loose edge wires on the screen digging into or between the loose weave of the wick. This condition has occurred at least once before when a low resistance (5 ohms) was recorded. At normal cell power levels it would not be a serious problem. Most of the power dissipation would occur at this point. When the liquid level was above this point, as in Test 713-2, it apparently kept the temperature under control, but the temperature was still high enough to decompose hydrazine. When the liquid level was dropped for Test 713-3 this area quickly heated out of control. (5 minutes above 40 volts) The wick retained liquid to allow current flow.

REFERENCES

1. W. W. Butcher, W. H. Jones, R. M. Lodwig, N. E. Morgan - Hydrazine Electrolysis for Spacecraft Propulsion, Final Report JPL Contract No. 951720, August 1968.

APPENDIX A

TEST PLAN

TEST PLAN

FOR

JPL CONTRACT 951720

Tasks VII and VIII

MARGIN LIMIT TESTS ON

HS-209 HYDRAZINE ELECTROLYSIS CELL

Prepared by: N. E. Morgan

Reviewed by: W. W. Butcher

Approved by: D. A. Mahaffy

1.0 INTRODUCTION

This document describes the test program to be conducted under Tasks VII and VIII of JPL Contract 951720 on the HS-209 Hydrazine Electrolysis Cell. The tests described herein are of a margin limits nature to determine if a controllability problem exists in the electrolysis of hydrazine at conditions well beyond the normal limits of electrolysis cell operation.

The purpose of this document is to provide information, outline requirements for the test program, and describe the general test plan. Detailed test procedures and specific requirements for individual tests will be prepared as required. All procedures, inspections and tests shall be approved by the cognizant project engineer.

2.0 REFERENCE DOCUMENTS

The following documents are applicable to the extent indicated herein:

2.1 Government Documents

MIL-P-26536B	Hydrazine

2.2 HAC Documents

X3106813	Hydrazine Electrolysis Cell, HS-209.
CS 31023-400	Processing Parts for Hydrazine Service.
DP 30929-004	Specification for Safety of Personnel and Property in the Presence of Hydrazine and Various Passivation Agents.
SSD 80316R	Final Report JPL Contract 951720 August 1968. Hydrazine Electrolysis for Spacecraft Propulsion.
Contract Brief No. 005 Dated 23 January 1969 Reference No. B1183	HS-209 Spacecraft Attitude Control-Statement of Work for Tasks VII and VIII of JPL Contract 951720

3.0 GENERAL OBJECTIVES

The general objectives of this test program are to:

3.1 Determine if a controllability problem exists in the hydrazine electrolysis process at conditions in excess of the normal limits of electrolysis cell operation.

3.2 Determine the effects of a short circuit in the electrolysis cell.

3.3 Maintain a record log book of all Task VII and VIII activities.

3.4 Prepare and submit a Task Report describing the test program, including a discussion of the results and conclusions.

4.0 SYSTEM CONFIGURATION

The system to be tested consists of a hydrazine electrolysis cell installed in a propellant tank. The basic arrangement is shown in HAC Drawing X3106813, defined in detail by HAC Drawings X3106834 through X3106854 inclusive, and modified as described in HAC Report SSD 80316R.

5.0 TEST PROGRAM

NOTE: See Figure 1 for Test System Schematic

5.1 Tank Safety Tests

5.1.1 Proof Test - Conduct a hydrostatic proof test of tank shell and flange closure by pressurizing to 750 psig with GN_2 while the tank shell is heated to 300^{o}F. Apply three proof pressure cycles of 5 minutes duration each.

5.1.2 Leak Test - Conduct leak test of tank and flange closure using GN_2 at 200 psig and ambient temperature.

5.2 Assembly and Check-Out

5.2.1 Clean tank shell and all electrolysis cell parts per CS 31023-400.

5.2.2 Assemble electrolysis cell module as noted in Paragraph 4.0.

5.2.3 Measure electrical resistance across electrodes to verify absence of a short circuit.

5.3 Controllability Tests (See Test Matrix in Table I)

Safety Note:

Maximum values of test parameters are as follows:

a. Current: 30 amperes
b. Voltage: 60 volts D.C.
c. Temperature (Propellant): 300^{o}F
d. Pressure: 400 psig

Simultaneous operation at the above limits is not planned. Tank pressure may be increased to a maximum of 600 psig if test data indicate a strong influence of pressure on the electrolysis rate.

Testing shall proceed with caution and tests will be terminated before the above limits are reached if there is evidence of instability or other hazard to personnel or equipment.

5.3.1 High Voltage Tests

5.3.1.1 Install electrolysis cell/tank assembly in test chamber and load 90% full with neat hydrazine.

5.3.1.2 Survey - Conduct a voltage-current survey up to 60V.

5.3.1.3 Functional Test - Operate cell at 60V until operating parameters stabilize. Continue electrolysis for one additional hour.

5.3.1.4 Repeat Paragraph 5.3.1.1, 5.3.1.2 and 5.3.1.3 with tank 45% full of neat N_2H_4.

5.3.1.5 Repeat Paragraph 5.3.1.4 with tank 10% full of neat N_2H_4.

5.3.2 High Current, High Temperature Tests

5.3.2.1 Load tank 90% full with hydrazine plus 0.5% oxalic acid.

5.3.2.2 Conduct voltage-current survey up to 30 amperes or maximum attainable with available power supplies if less than 30 amperes.

5.3.2.3 If unable to reach 30 amperes in Paragraph 5.3.2.2, change electrolyte level as necessary to attain a current of 30 amperes with available power supplies.

5.3.2.4 Operate cell at following current levels:

a. 10 amperes
b. 20 amperes
c. 30 amperes

Allow propellant temperature to stabilize at each current level and allow pressure to increase over a great enough range to determine if pressure level has a significant affect on electrolysis rate.

5.3.2.5 If equilibrium temperature in Paragraph 5.3.2.4 at 30 amperes was less than $300^{\circ}F$, thermally condition test chamber until propellant temperature reaches $300 \pm {}^{0}_{20}\ {}^{\circ}F$. Continue electrolysis for a minimum of one hour or until tank pressure reaches 400 psig.

5.3.2.6 Repeat tests of Paragraph 5.3.2.2, 5.3.2.4 and 5.3.2.5 with tank 45% full and the electrolyte concentration twice that used in above tests.

5.3.2.7 Repeat tests of Paragraph 5.3.2.6 with tank 10% full and electrolyte concentration 9 times that used in tests of Paragraph 5.3.2.2, 5.3.2.4 and 5.3.2.5.

5.4 Short Circuit Tests

5.4.1 Short Circuit Below Liquid Level

5.4.1.1 Re-build electrolysis cell with the electrodes electrically short circuited by means of a wire between the cathode and anode. The short circuit is to be located below the liquid level when the tank is 90% full.

5.4.1.2 Load tank 90% full of hydrazine with 0.5% oxalic acid.

5.4.1.3 With tank at ambient temperature and pressure of approximately 50 psig, slowly increase voltage applied to cell until short circuit burns out. Do not exceed limits noted in Paragraph 5.3. Pressure is not to exceed 100 psig during this test.

5.4.2 Short Circuit Above Liquid Level

5.4.2.1 Repeat Paragraph 5.4.1 except:

a. Short circuit is to be located above the 10% full liquid level.

b. Tank is to be filled 10% full of hydrazine with 4.5% oxalic acid.

6.0 FACILITIES REQUIREMENTS

6.1 Safety

6.1.1 Hydrazine - Hydrazine in a very toxic and combustible material and must be handled with extreme catuion and strictly in accordance of to accepted procedures. HAC Document DP 30929-004 "Specification for Safety of Personnel and Property in the Presence of Hydrazine and Various Passivation Agents" shall apply to this program.

6.1.2 Gases - One of the products of hydrazine electrolysis is hydrogen gas which is highly combustible when mixed with air or is in the presence of other oxidizers. The requirements for test cell ventilation and absence of sources of combustion included in the above document (DP 30929-004) relative to hydrazine shall be equally applicable to hydrogen gas. These requirements shall apply whenever there is the possibility of hydrogen leakage from the system and whenever hydrogen is being vented.

6.1.3 Pressure Vessels - The Surveyor propellant tanks shell (HAC P/N 254094 or P/N 254175) to be used in this program has design burst pressure of 1050 psi. With a safety factor of 4:1, the maximum man-rated operating pressure is 262.5 psi. The individual tank to be used for the hydrazine electrolysis cell shall be proof-tested at 750 psi and 300°F, and subsequently inspected for damage before use. Whenever a tank is being pressurized it shall be located behind a suitable barracade. Under no circumstances shall any personnel be on the tank side of the barracade if the tank pressure should exceed 262.5 psi.

Should the tank be subjected to any shock, blow, be dropped or otherwise mis-handled, it shall be again proof-tested at 750 psi before it is used again for test purposes.

6.2 Instrumentation and Test Equipment - The following equipment is required for performance of the tests described herein:

Power Supplies - Regulated D.C. NJE Model EQR-10-10

- Sorensen - 6V, 30 amperes

- Kepco - 80V, 8 amperes

Pressure Transducer 0-500 psi

Thermocouples - 0-300^{o}F, Chromel-Alumel, Immersion Type

Thermistor - 0 -300^{o}F (Tank shell temperature)

Recorder - Periodically sample data on voltage, current, pressure and temperature.

Solenoid Valves (1)

Hand Valves (6)

Lines, Fittings, Etc.

Test Chamber - Enclosed, insulated, heated to 300^{o}F.

6.3 General Facility Requirements - General Facility requirements include the following:

Hydrazine - To be supplied by JPL

Solvents - IPA, Freon, Etc.

Nitrogen

Helium

Distilled, de-ionized water

Propellant loading and disposal facilities

Safety Equipment

Recorder Paper

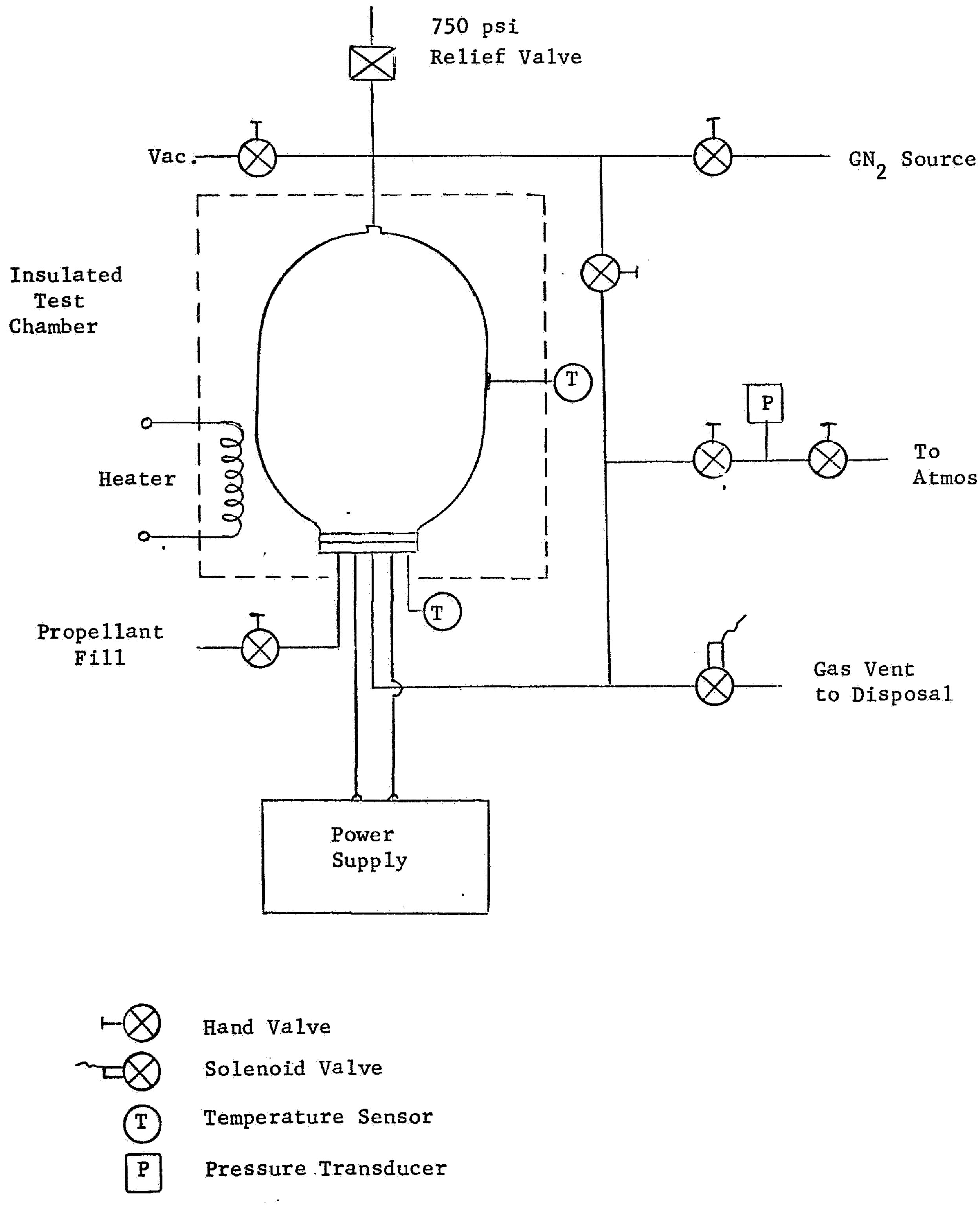
Other equipment, facilities, supplies normally required for hydrazine propulsion system testing.

TABLE I

HS-209 HYDRAZINE ELECTROLYSIS

TEST MATRIX

Test No.	Propellant Quantity %Full	Electrolyte Conc. %	Voltage Volts	Current Amps	Propellant Temperature °F	Pressure PSIG	Remarks
1	100%	Water	-	-	300	750	Tank shell proof test
2	90%	0	0-60	5	Amb	100	Survey - Neat N_2H_4
3	90%	0	60	5	Amb	50-200	Cell operation at 60V
4	45	0	0-60	5	Amb	100	Survey
5	45	0	60	5	Amb	50-200	Cell operation at 60V
6	10	0	0-60	5	Amb	100	Survey
7	10	0	60	5	Amp	50-200	Cell Operation at 60V
8	90	0.5	0-10	0-30	Amb	100	Survey with 5% Electro
9	90	0.5	A/R A/R A/R	10 20 30	Amb Amb Amb	50-200 50-200 50-200	High Current Tests at ambient temp.
10	90	0.5	A/R	30	300	50-400	Heat test chamber
11	45	1.0	0-10	0-30	Amb	100	Survey
12	45	1.0	A/R	10 20 30	Amb Amb Amb	50-200 50-200 50-200	
13	45	1.0	A/R	30	300	50-400	
14	10	4.5	0-10	0-30	Amb	100	Survey
15	10	4.5	A/R	10 20 30	Amb Amb Amb	50-200 50-200 50-200	
16	10	4.5	A/R	30	300°F	50-400	
17	90	0.5	A/R	A/R	Amb	50 max	Short circuit test
18	10	4.5	A/R	A/R	Amb	50 max	Short circuit test



Test System Schematic

Figure 1

APPENDIX B

TEST DATA

Test No. 713-2   4/30/69

Tank 90% Full of Neat Hydrazine

Time	Volts: Simpson Multi-meter	Volts: Digital Volt-meter	Current - Amps: Clip-on Ammeter	Current - Amps: Digital Volt-meter	Tank Temperature °F	Liquid Temperature °F	* Pressure psig
1018	10.0	10.27	1.15				
	Cell Off						
1038	10.0	-	1.18	-	55.1	60	5.5
1042	20.0	21.24	2.80	-	55.3	60	5.6
1045	40.0	41.79	6.4	-	55.6	62	6.0
1050	40.0	41.75	8.2	-	55.9	64	7.0
1055	40.2	42.06	7.5	-	56.5	66	8.0
1110	40.4	42.48	6.35	-	60.0	69	10.3
1112	50.0	51.70	7.45	-	61.4	70	11.1
1120	50.1	51.95	6.70	-	64.3	73	12.4
1122	59	61.20	8.0	-	65.3	73	12.9
1125	59	61.37	7.6	-	67.0	75	14.0
1130	59	61.51	7.1	-	70.0	77	15.0
1145	59	61.84	6.1	-	79.7	82	18.8
1200	60	62.12	6.0	6.27	88.6	88	22.4
1215	60	61.97	6.4	6.62	99.4	97	27.2
1230	59	61.47	8.0	8.16	110.2	107	33.6
**1235	40.1	42.37	9.2	9.20	113.6	111	35.0
1245	41	42.95	6.95	7.30	125.8	122	38.8
1300	41.5	43.44	5.65	5.85	137.2	125	42.4
1302	50	51.53	6.75	7.10	138.5	128	43.1
1315	50	51.76	6.40	6.65	145.2	130	48.0
1330	50	51.60	6.85	7.08	153.1	138	53.8
1345	50	51.52	7.10	7.36	160.3	143	59.9
1400	50	51.58	6.9	7.22	166.2	148	67.3
1402	58	60.23	8.4	8.65	167.4	150	68.9
1407	58	59.97	9.3	9.40	170.1	155	74.4
1415	58	59.98	9.0	9.27	176.3	166	79.8
1430	58	60.19	7.8	8.21	185.7	178	81.2
1435	P/S	Circuit breaker tripped (15 amp)					
1438	0	0	0	0	191.4	167	75.6
1445	25	26.42	8.6	8.40	191.3	176	71.8
1450	25	26.37	8.3	8.58	192.0	178	72.5
1515	25.5	27.08	6.2	6.53	193.3	178	71.2
1516	30.0	31.96	7.3	7.50	195.1	177	71.8
1530	30.5	32.25	6.3	6.46	195.5	178	72.3
1532	40	42.36	8.5	8.72	196.3	178	73.2
1540	-	42.55	-	8.33	198.0	179	78.0
1550	40.8	42.65	7.65	7.98	199.6	181	80.5
1552	0	0	0	0	199.8	180	78.8

* Note:

Multiply pressurereadings by 10 to get true pressure (i.e. final pressure was 788 psi not 78.8 psi). This was due to mislocated decimal on digital volt meter readout of pressure.

** Between 1230 and 1235 current exceeded 10 amps. Voltage was lowered to 40V to reduce current below 10 amps.

Test No. 713-3 5/1/69

Voltage-Current Survey - Tank 45% Full of Neat Hydrazine

Time	Volts		Current-Amps		Tank Temperature °F	Liquid Temperature °F	Pressure psig
	Simpson Multi-meter	Digital Volt-meter	Clip-on Ammeter	Digital Volt-meter			
0958	0	0	0	0	54.4	59	52
0959	1.1	-	.050	-	-	-	-
1000	2.1	-	.150	-	-	-	-
1001	5.2	5.50	.40	.32	54.3	59	53
1009	5.4	5.65	.29	.26	54.5	59	52
1010	10.0	10.23	.42	.42	54.6	59	54
1013	20.0	21.28	1.00	1.00	54.6	59	53
1015	30.0	32.40	1.1	1.15	54.7	59	54
1016	40.0	42.30	1.53	1.59	54.7	59	54
1017	50.0	51.97	2.0	2.05	54.7	59	54
1018	60.0	62.42	2.7	2.67	54.8	60	57
1019	40	42.18	1.7	1.74	54.8	61	59
1020	20	20.56	*	1.12	**	***	****

* Clip-on ammeter was still reading 1.1 amp <u>after</u> temperature rise was first observed.

** 130 to 150°F and rising rapidly

*** Read as 810°F and rising rapidly

**** Tank ruptured before pressure data could be read.

APPENDIX C

FAILURE INVESTIGATION

FAILURE INVESTIGATION

Notes on Location and Condition of Electrolysis

Cell Parts

1. "Dome" - Found about 10 feet from test chamber. Had been dented on top from impact with solid object, probably top of chamber. Set screw was still in dome had been stripped out of top of outer shell. Dome still contained gas transfer tube and part of control support tube which fractured through radial gas outlet parts.

2. Anode - Found on ground just below chamber with lower 1 to 2 inches missing. Fragments of anode were found scattered on hillside up to approximately 20 feet from chamber.

3. Cathode Screen - A piece approximately 7" x 7" was still inside outer shell. A few fragments of cathode screen were found on hillside including piece with electrical connector tab. Fragments found on hillside showed only slight effects of heat while the lower part of the large piece remaining inside the outer shell was damaged by heat (probably in resulting fire).

4. Wick - Part of wick approximately 7" x 7" was found inside the outer shell along with the cathode. The lower edge was badly blackened by the fire. A small '" x 1" piece of wick was found about 10 feet away on the hillside, it showed no evidence of heat, was only very slightly dirty from exposure.

5. Outer shell (2 1/2" dia. tube) - Remained in test chamber, was blackened by fire. Set screw attaching outer shell to dome had stripped out longitudinally. At lower edge, a section about 1" wide was bulged out tearing away some of the metal from off the edge of the part.

6. Inner Shell - Lower end (about 3" length) was collapsed inward from an external force. At bottom edge, 3/4" was missing over 180^{o}F of circumference. Inside surface was very clean in lower end of part; upper part slightly discolored inside. Outside surface was badly blacked from fire except top 2" to 4".

7. Screen Compartments - Fragments, probably from top compartment found on hillside, no heat damage. One of the three lower compartment, with cup part missing, was found on ground at base of test chamber near anode. This was probably the top section of the large screen compartment and showed no heat damage. Another section of screen from the large screen compartments was found inside, protruding slightly, the inner shell. This was probably the center compartment. A third section of screen was found wedged in a crack in the tank shell which remained attached to the tank flange. This was probably the lower compartment. Both of these latter were badly discolored from heat. Fragments of screen found on hillside were mostly free of heat discoloration, but a few small pieces showing heat damage were also found.

8. Central support tube - Main part of tube was found still inside inner shell. Tube fractured at top face of jam nut locking it to flange closure. Tube also fractured at 4 radial gas outlet ports inside top screen compartment. Section of tube above these holes was still attached to dome. Part above dome was sheared off, flattened.

9. Teflon Spacers - lower spacer was still on tube, badly damaged by heat. Middle spacer still on tube blackened by fire - but displaced upward 2". Top long spacer was found on ground near anode. Short flanged spacer was found on hillside. Both top spacers were undamaged by heat.

10. Insulators - Top - Two pieces each about 90^{o} qudrant found on hillside.

    Bottom - Several small pieces badly damaged by heat, unidentified.

11. Tank Flange Closure - Discolored by heat but no evidence of electrical damage, arcing. etc. Three screws holding flange closure to tank had heads popped off.

12. Electrical Connectors - Anode - Found part of aluminum sleeve to connect feed through connector to stud screwed into anode. It showed no heat damage but was broken in middle, only one half found.

    Cathode - Found connector attaching feedthrough conductor to tab on cathode screen. Neither it nor tab nor feedthrough were damaged by heat except for feedthrough damaged by resulting fire.

13. Missing Parts:

    a. Anode electrical connector stud.

    b. Identifiable parts of lower insulator.

    c. One-half of upper insulator

    d. O-ring from bottom of outer shell.

    e. Identifiable parts of upper screen compartment.

HUGHES AIRCRAFT COMPANY

INTERDEPARTMENTAL CORRESPONDENCE

TO: F. W. Anderson
ORG. 22-27

CC: Distribution

DATE: 15 May 1969
REF. 2748.20/1800

SUBJECT: Burst of Ti 6Al-4V Tank
S/N 41-Hydrazine Electrolysis Study

FROM: G. A. Dreyer
ORG. 27-48-20

BLDG. 6 MAIL STA. D-133
EXT. 4907

Reference: Final Report on JPL Contract No. 951720 August 1968 SSD 80316R, Propulsion and Power Systems Laboratory

Tank S/N 41, which had been manufactured during the Surveyor program for propellant storage, failed during a hydrazine electrolysis study. Prior to failure the tank had been subjected to over 950 hours of testing. This testing is detailed in the reference.

Metallographic examination of tank sections from both hemispheres and across the girth weld revealed the titanium structure to be satisfactory. There was no evidence of corrosion.

From conversations with test personnel at Placerita Canyon it was learned that the tank had been experiencing an increase in pressure and temperature at the time of failure. Since the hydrazine electrolysis reaction involves the formation of gas and the tank had been heavily fragmented it appears failure was due to pneumatic overloading and not to any attack on the tank material.

APPROVED: G. L. Robinson
G. L. ROBINSON, Head
Advanced Techniques Section
Materials Technology Department

GAD:slo

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