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Prepared for
NATIONAL AERONAUTICS & SPACE ADMINISTRATION
GEORGE C. MARSHALL SPACE FLIGHT CENTER
HUNTSVILLE, ALABAMA 35812

August 25, 1967

FUEL CELL RELIABILITY ASSESSMENT

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Contract NAS8-2696

Modification 20

Prepared for

George C. Marshall Space Flight Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Huntsville, Alabama

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SUMMARY

The Reliability Assessment Program is directed toward the determination of fuel cell stack performance under high stress conditions, and toward the establishment of reliable operating limitations.

The Mod 20 program is an expansion of the scope of work on reliability assessment testing that began under Mod 12 and continued under Mod 18. This program provides for the following main efforts:

- Additional testing on three Mod 12 fuel cell stacks (Stacks 136, 137, and 138).
- Fabrication and testing of three new Mod 18 fuel cell stacks (Stacks 196, 197, and 198).
- Fabrication of one fuel cell system to be delivered as GFE to the NAS9-6737 program.
- Fabrication of one fuel cell system to be delivered to MSFC, Huntsville, Alabama.

Each fuel cell stack being tested under this program is a 29 volt, 2 kw, hydrogen-oxygen unit.

Status of the fuel cell stacks being reliability tested at the end of this reporting period is as follows:

TEST	STACK NUMBER	SCHEDULED TEST HOURS	TOTAL HOURS ON TEST
Low Power (1 kw) Life Test	136	1300	735
Thermal Cycle Test	137	1500	1400
High Power (2 kw) Life Test	138	1500	800

Testing of Stacks 136, 137, and 138 is proceding on schedule and should be completed by September 1, 1967.

Fabrication of Stacks 196, 197, and 198 is on schedule. All three of these stacks are identical in design to those being fabricated under the Design Verification Test program (Contract NAS9-6737) being conducted concurrently with the NAS8-2696 Mod 20 program.

Stack 196 will be subjected to a low power (avg. 300 w) endurance test of 4000 hours duration. Stack 197 will be operated continuously at loads varying between 300 and 2000 w. This stack will also be used to determine the minimum purging requirements for reactant gases of ultra-high purity. Stack 198 will be subjected to several high stress operating conditions. In addition, tests will be performed to determine the effects of various purge durations, cycle times, and flow rates, and to determine the minimum purging characterisitics when using reactant gases with various impurity levels. Electrical transient characteristics of fuel cell operation will be studied after completion of the above tests on Stack 198.

An analysis was conducted during this period to determine the effectiveness of oxygen flow purge restrictors during normal non-purge operation. This study will be used to determine flow rate specifications for uniform section performance.

An analysis of computerized data on stack and section voltages was completed during this period. Results indicate that the vacuum electrolyte loading process has increased the stability and uniformity of individual section voltages, has lessened voltage degradation rates, and has completely eliminated crossleaks within cells.

A study was completed on the time limitations of high spike loads as determined by the cooling capabilities of the fuel cell. The Mod 12 design is capable of satisfying the cooling requirements of continuous operation at approximately 130 amperes.

A flammable-mixtures investigation was concluded during this period. Data show that the observed canister gas mixtures were not in the flammable range.

INTRODUCTION

This report covers the technical progress accomplished under Modifications 18 and 20 to Contract NAS8-2696, "Fuel Cell Reliability Assessment" for the period April 8, 1967 to July 8, 1967. This program is directed toward determining fuel cell stack operation under conditions of high stress, and establishing limitations of reliable operation. In addition, a number of analytical studies relating to fuel cell operation are being conducted and two complete fuel cell systems are being fabricated for use on other NASA programs.

PROGRAM PLAN

Six fuel cell stacks will be reliability tested under this program. Three of these stacks were fabricated under Modification 12 and will be used for additional tests in the performance of Modification 20. Three new stacks will be constructed and tested under this program.

This program will also include construction of one complete fuel cell system that will be provided as GFE for testing under Contract NAS9-6737.

Mod 12 Stacks

At the conclusion of Modification 12, Stacks 136, 137, and 138 had been operated for 715, 887, and 515 hours, respectively. The continued testing to be performed on these three stacks is described below.

STACK 136 - LOW POWER (1 KW) LIFE TEST

This stack has been operated as a baseline performance standard. The load profile has been a constant current of 40 amperes interrupted every 100 hours for a 10 hour varying load profile used for the generation of volt-ampere characteristics. The stack will continue to be operated under the above conditions until a total elapsed on-load time of 1100 hours has been reached. It will then be placed in a variety of hot standby conditions to determine the influence of standby upon the degree of performance deterioration.

STACK 137 - THERMAL CYCLE TEST

This stack was operated under a thermal cycle test and was then operated under a moderately low temperature (165°F) life test. The latter test was continued to an elapsed time on-load of 1400 hours. The stack is scheduled to be subjected to steady state operation at seven temperature levels between 160 and 220°F. This is a repeat of a temperature level test performed earlier and is intended to determine temperature characteristics as a function of age. The stack will then be operated at reactant pressures ranging from 1.5 to 3.5 atmospheres to determine performance characteristics as a function of pressure.

STACK 138 - HIGH POWER (2 KW) LIFE TEST

After elapsed time 200 hours, this stack was operated at an average load current of 80 amperes in fulfillment of a high power life test. This test will be continued to 1500 hours on-load.

Mod 18 Stacks

The tests planned for the stacks fabricated under this program are described below.

STACK 196 - ENDURANCE TEST

A special endurance and performance test with an anticipated goal of 4000 hours will be performed on this unit. Operation will be essentially continuous. Average power drawn from the test unit will be approximately 300 watts with short daily segments during which the output power will be increased. Operating reactant pressure and stack temperature for this test may be set at values differing considerably from previous centerline values.

STACK 197 - CENTERLINE PERFORMANCE TEST

The second new stack will be operated continuously at loads varying between 300 and 2000 watts. This stack will also be used to determine the minimum purging requirements for reactant gases of ultra-high purity.

STACK 198 - STRESS PERFORMANCE TEST

The third new stack will be subjected to several high stress operating conditions to evaluate performance and life under these conditions. Extensive tests will be performed to establish the effects of various purge durations, cycle times, and flow rates, and to determine the purging characteristics when using reactant gases containing various quantities of inert impurities. This segment of the test will require approximately 1000 hours of operation. This test will be followed by a determination of the electrical transient characteristics of fuel cell operation. The stack may then be used to demonstrate bootstrap startup capabilities from below ambient temperature.

DVT System

Fabrication of the fuel cell system to be delivered as GFE to Contract NAS9-6737 is on schedule.

TESTING

Stack 136 - Low Power Life Test

Stack 136 has accumulated 735 hours elapsed time on load. The voltage - power performance characteristics for the stack are shown in Figure 1. The stack voltage degradation rate for the first 700 hours was 76 microvolts per hour per section.

Toward the end of this period, near ET 723 hours, frequent non-scheduled manual purges were necessary to maintain all sections at acceptable voltage levels. To investigate the relationship between reactant gas flow and the individual section voltages, the functions of the reactant gas inlet and outlet manifolds were interchanged. The hydrogen inlet - outlet reversal showed no change in section performance. When the oxygen connections were reversed, section 5, which had previously been a stable section, immediately exhibited a decreasing voltage. Manual purges at 10 minute intervals were required to restore the section's voltage above 0.9 volts. The stack was shut down at ET 723 hours for inspection of the reactant manifolds, and to install flow restrictors in the inlet side of the oxygen plates.

Corrosion deposits were found in the oxygen outlets. As well as could be determined using a boroscope, the extent of the corrosion was no greater than that observed in previous stacks during disassembly. The EDM slots and manifolds were subsequently cleaned and the stack was placed back in operation. During the shutdown, teflon coated conical washers were installed in the stack compression devices. Between ET 723 and 735 hours, sections 20, 4, 32, and 33 exhibited substandard performance. The performance of section 20 indicated that one of its EDM slots was partially blocked. A mono-plate purge of the oxygen plate eliminated the restriction.

A large quantity of gas was circulated through the stack between ET 723 and 735 hours for pressure drop tests, leak testing, and purging. The data is inconclusive, but it appears that the excessive circulation of dry gas without the fuel cell operating and producing water may have affected the performance of sections 4, 32, and 33. The stack was again shut down at ET 735 hours. A special leak test and an eight-hour performance investigation test are being designed to determine if the stack is suitable for further operation.

Stack Temperature $190 \pm 2°F$

Reactant Pressure 37 ± 1 PSIA

KOH Concentration See Table

CURVE	E. T.	% KOH
1	5	41.0
2	195	41.0
3	395	40.0
4	595	39.5
5	710	37.0

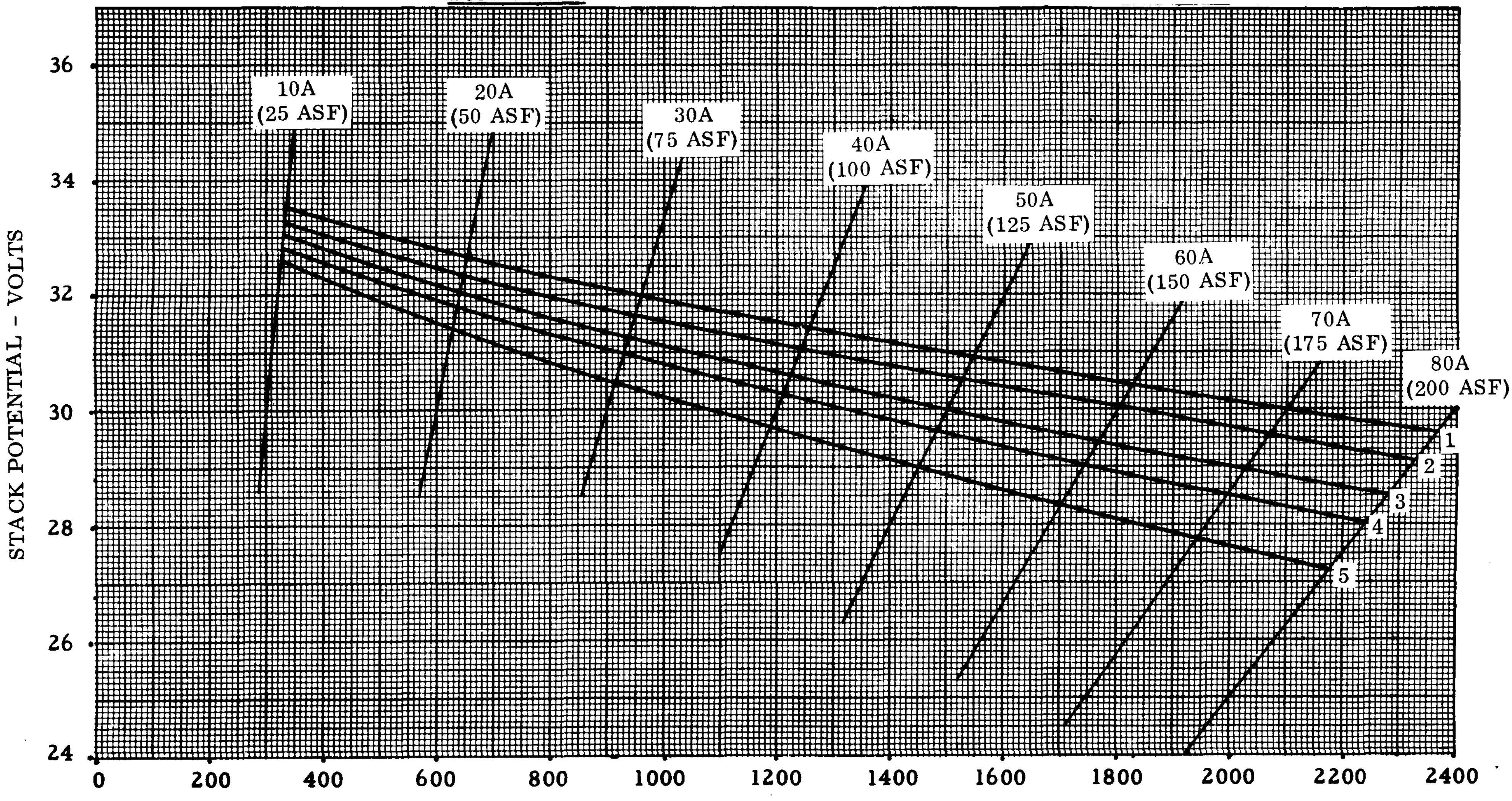

Figure 1. Voltage - Power Characteristics, Stack 136

Stack 137 - Thermal Cycle Test

Teflon coated conical washers were installed on Stack 137, individual plate flow restrictors were installed in the oxygen inlet manifold, and the internal purge tubing was removed.

Stack 137 has accumulated 1400 hours of elapsed time on load. The stack was operated at 165°F at an average and relatively constant load of 40 amperes between ET 705 and 1400 hours to determine stack performance at temperatures below the standard 190°F centerline operating temperature. The stack volt-power characteristics for this time interval are shown in Figure 2.

The average voltage degradation rate for the stack over this time interval was 42.0 microvolts per hour per section. The stack was shut down at ET 991 hours to install flow restrictors in the oxygen inlet ports. Prior to this shutdown (from ET 705 to 991 hours) the voltage degradation rate was 106.7 microvolts per hour per section. After the shutdown (from ET 991 to 1400 hours) the stack voltage degradation rate was 12.8 microvolts per hour per section.

Comparing the degradation rate of Stack 137 with that of Stack 136, which was operated at the identical load profile from ET 5 to 710 hours at 190°F, shows a significant improvement in the degradation rate. Stack 136 degraded at a rate of 75.5 microvolts per hour per section during that 700 hour period.

The electrolyte concentration of Stack 137 was optimized at ET 800 hours and was determined to be 40.0% KOH. The original program specifications required that the stack be operated at 1% below the optimum electrolyte concentration. In accordance with NASA's request that the Mod 12 stacks be operated at an unvarying electrolyte concentration from the time of the installation of the oxygen inlet flow restrictors to the end of the test, Stack 137 underwent its final determination of optimum electrolyte concentration at ET 1035 hours. The optimum concentration was again determined to be 40.0% KOH by weight. Continued operation at 39% KOH resulted in this stack being operated for 600 hours at an essentially constant electrolyte concentration.

Stack 137 was operated at various temperatures between ET 635 and 668 hours to determine the performance characteristics as a function of temperature. A similar test is scheduled to be performed on Stack 137 during the next reporting period to establish the effect of degradation on performance characteristics at various temperatures.

A reactant pressure test performed on Stack 132 resulted in failure of the stack due to the displacement of gaskets under a high pressure differential. Stack 137, which has been equipped with conical washers to maintain stack compression is scheduled to undergo a similar test.

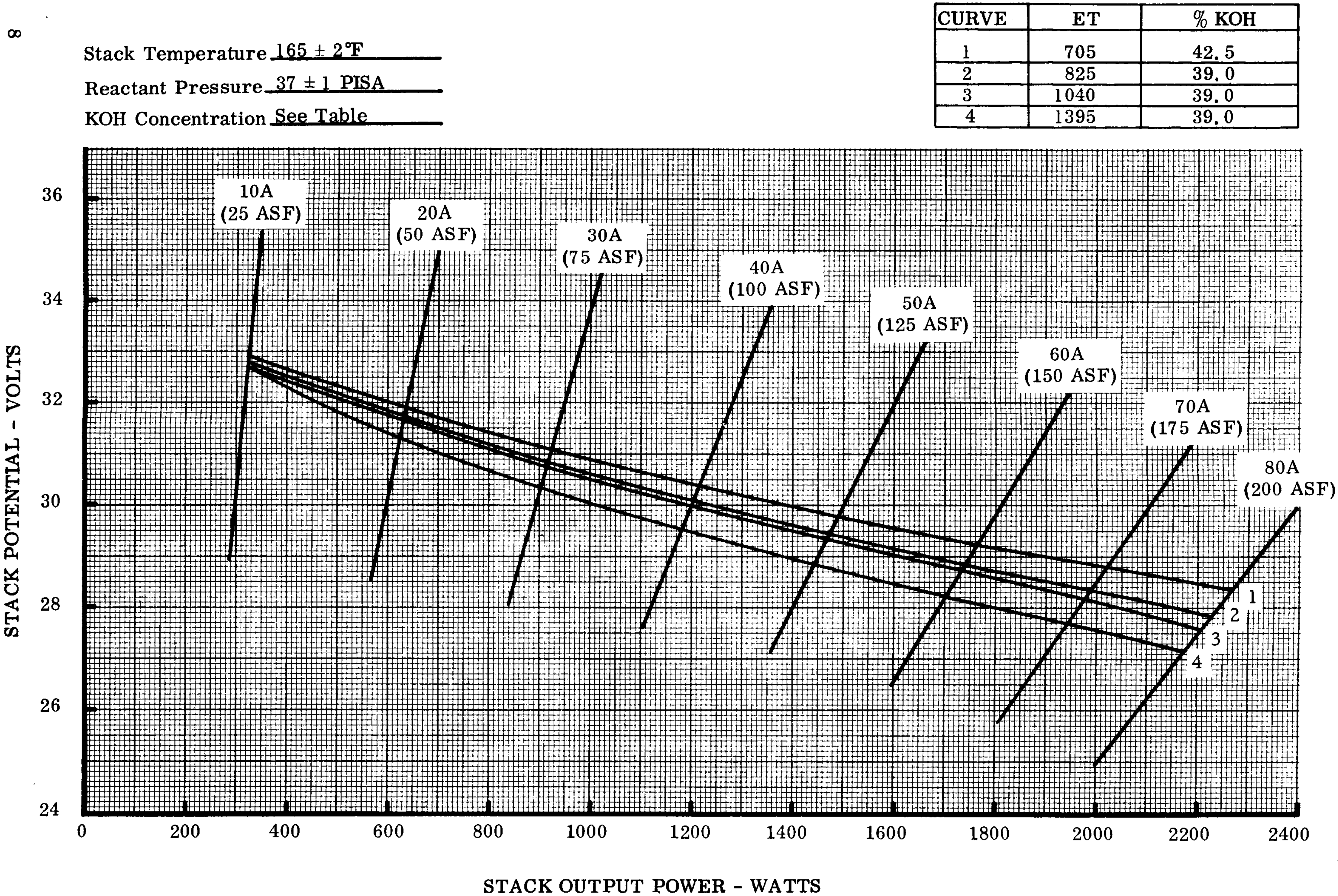

Figure 2. Performance Characteristics of Stack 137 at 165°F.

Stack 138 - High Power Life Test

Stack 138 was shut down at ET 800 hours to install conical compression washers and oxygen flow restrictors. Visual inspection and a pressure drop test showed that two EDM slots of two oxygen plates were blocked with corrosion. The ports were cleaned with a special tool attached to a boroscope.

Stack 138 has been operated according to the load profile shown in Figure 3 since ET 200 hours. Performance during this high load period showed a voltage degradation rate of 44 microvolts per hour per section, as compared with 74 microvolts per hour per section during the first 200 hours when an average load of 40 amperes was followed. Performance curves for the entire 800 hours of operation are shown in Figure 4.

Stacks 196, 197, and 198

Fabrication of Stacks 196, 197, and 198 is on schedule. Purchase orders have been written for most components. All three Stacks will be identical to the DVT system design. Stack 196 will be subjected to a low power endurance test. The centerline operating values for Stack 196 will be altered considerably to meet the endurance goal. Test bench components affected by the new operating conditions are being specified.

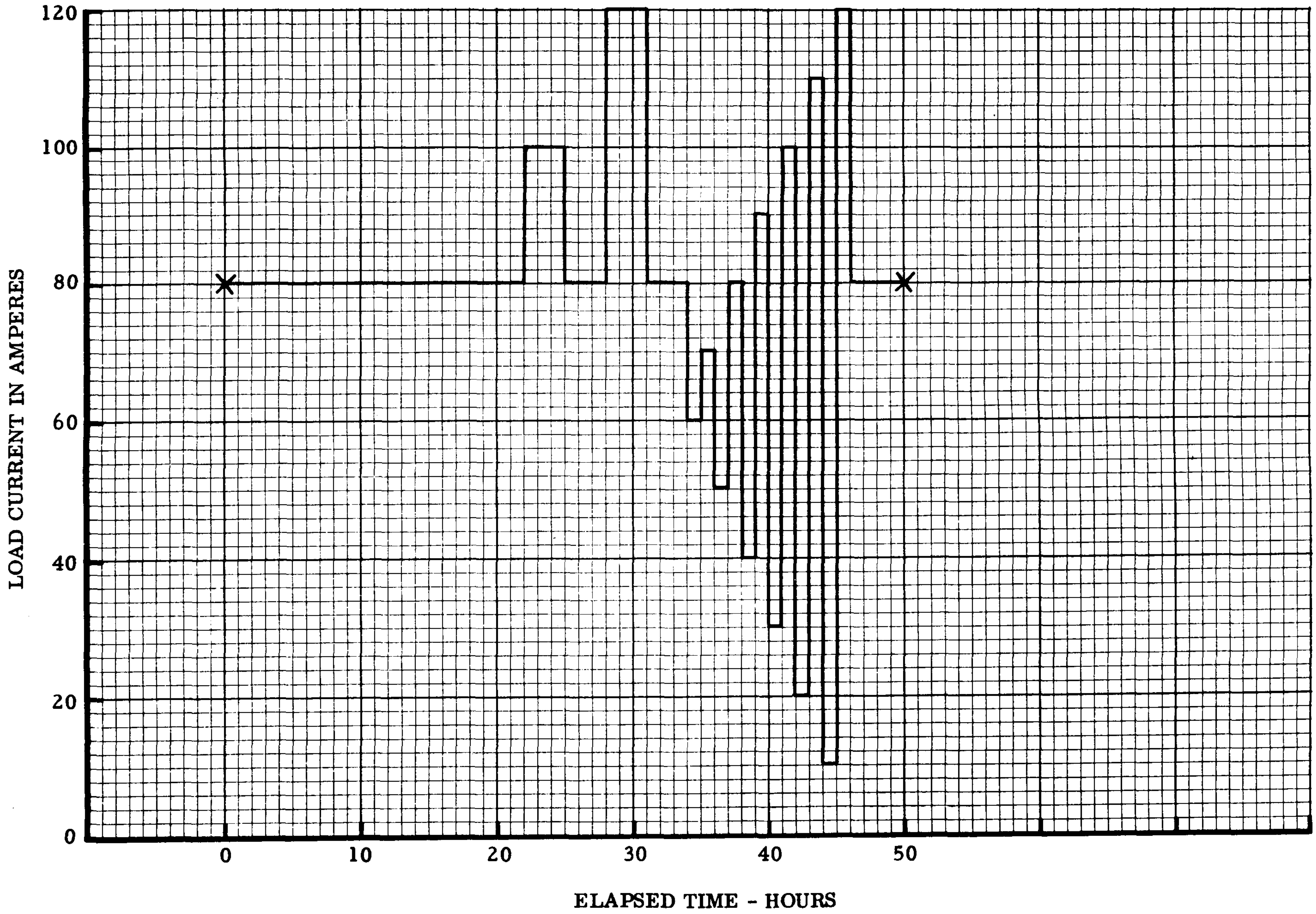

Figure 3. High Power Life Test Load Profile - Stack 138

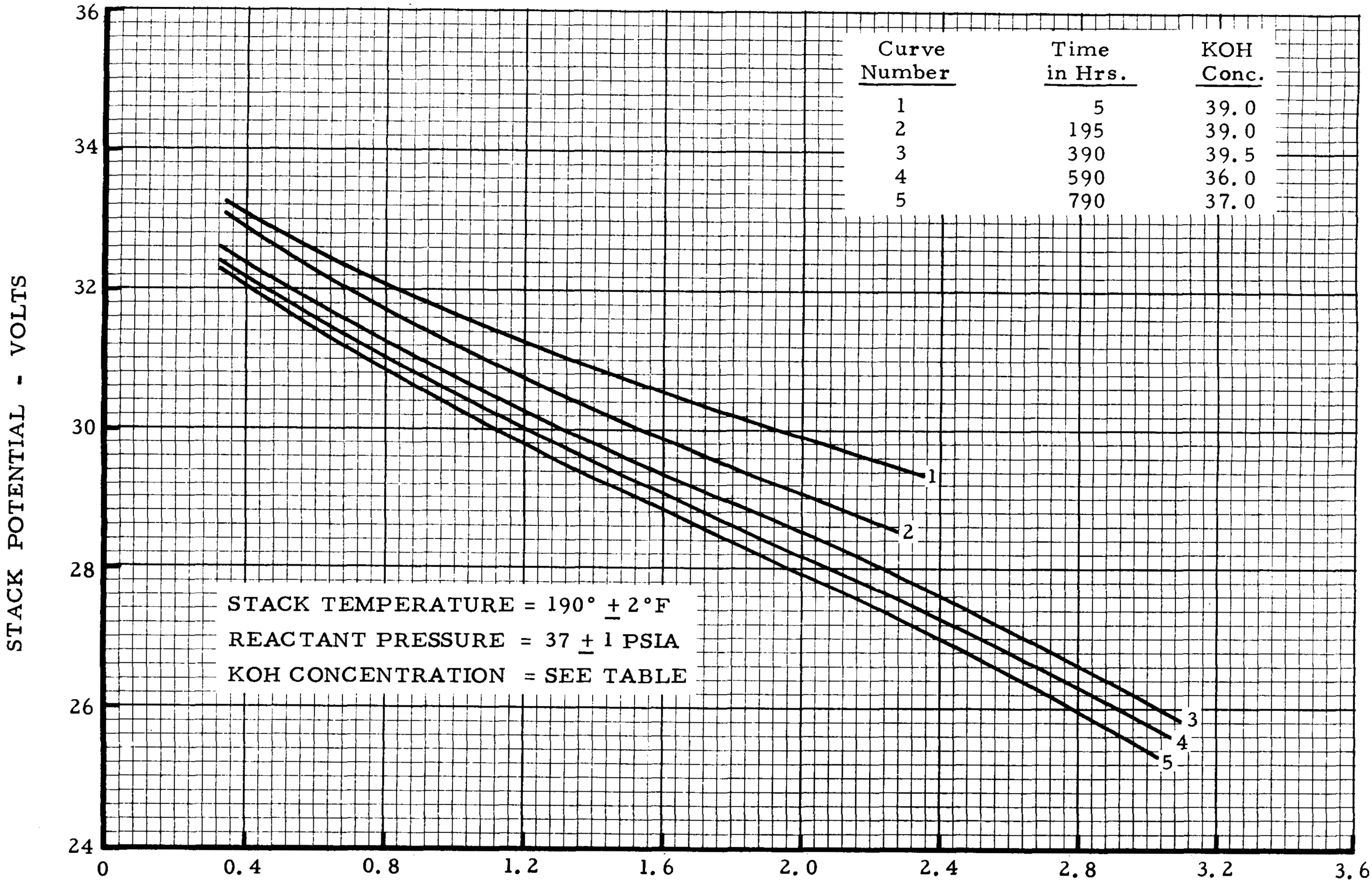

Figure 4. Voltage - Power Characteristics, Stack 138

ANALYSIS

Reactant Flow Distribution

An investigation was made to determine the effectiveness of the flow restrictors installed in the oxygen inlet ports of the fuel cell plates. These restrictors are used to control the flow of the oxygen reactant gas during purge. The analysis assumes that the pressure drop across the oxygen plate can be approximated by the following equation. The mode used for this analysis is shown in Figure 8.

$$\Delta P = R \times W \tag{1}$$

where

ΔP = Pressure drop

R = Flow resistance

W = Flowrate

During the pressure drop test, the pressure drop across the oxygen plate is measured using helium gas flowing at an equivalent stoichiometric consumption rate of 250 amps. Since the same flowrate is used for all the plates during the pressure drop test, the following relationship may be derived:

$$\sum_{i=1}^{33} \frac{1}{R_i} = W_t \sum_{t=1}^{33} \frac{1}{\Delta P_t} \tag{2}$$

where

R_i = Individual plate flow resistance

W_t = Flow rate during the pressure drop test

ΔP_t = Pressure drop for each plate during the pressure drop test

During purge, however, the pressure drop across each plate is the same and the flow rates are different, therefore:

$$\Delta P_p = R_i W_p \tag{3}$$

and

$$\overline{W}_p = \frac{1}{33} \sum_{p=1}^{33} W_p = \frac{1}{33} \Delta P_p \sum_{i=1}^{33} \frac{1}{R_i} \tag{4}$$

where

ΔP_p = Pressure drop during purge

W_p = Flow rate during purge

$\overline{W}_p$ = Average W_p

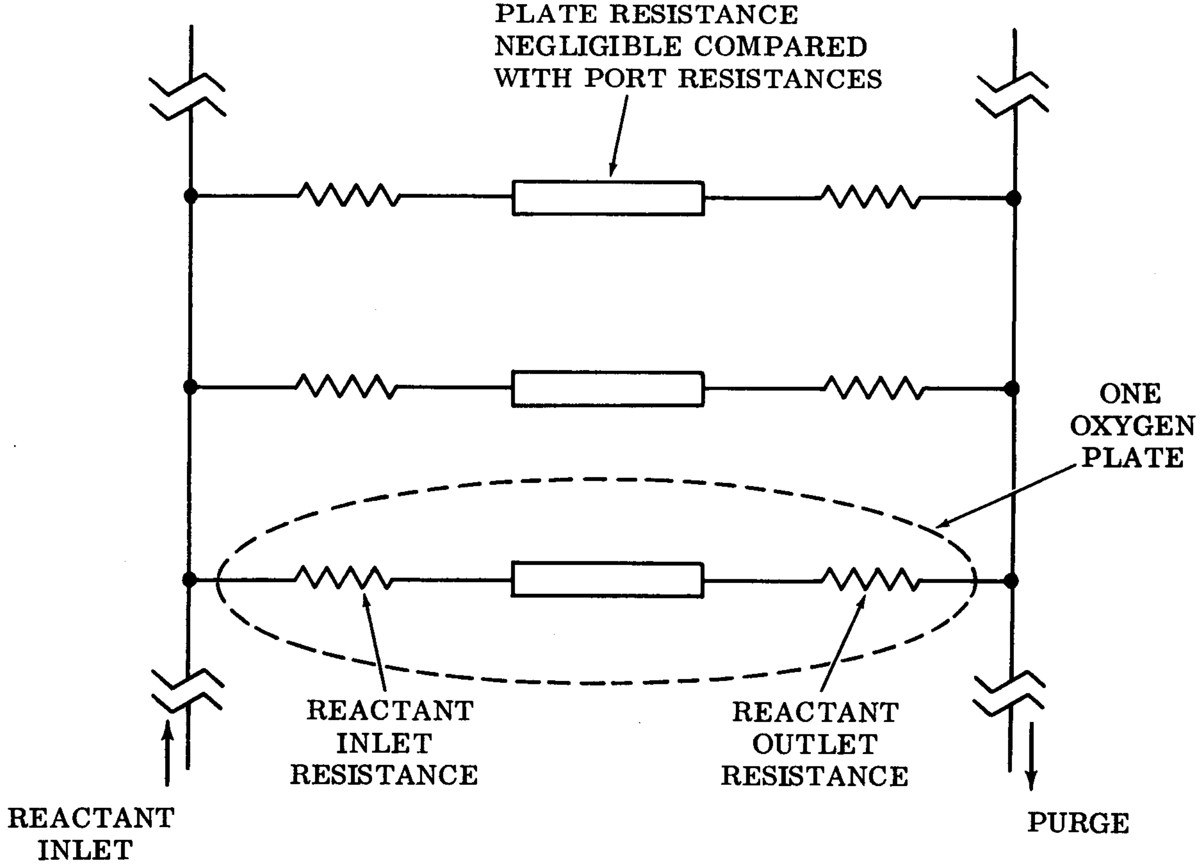

Figure 5. Schematic of Oxygen Flow Model

Equations 2 and 3 can then be substituted into equation 4 to yield:

$$\overline{W}_p = \frac{R_i \; W_t \; W_p \displaystyle\sum_{t=1}^{33} \frac{1}{\Delta P_t}}{33} \tag{5}$$

From the pressure drop test.

$$\Delta P_t = R_i \; W_t \tag{6}$$

Substituting equation 6 into equation 5 and rearranging terms yields:

$$\frac{W_p}{\overline{W}_p} = \frac{33}{\Delta P_t \displaystyle\sum_{t=1}^{33} \frac{1}{\Delta P_t}} \tag{7}$$

Equation 7 can then be used to calculate the flowrate during purge of any section relative to the average flowrate per section by calculating $\sum_{t=1}^{33} \frac{1}{\Delta P_t}$ from the pressure drops measured during the pressure drop test and substituting the pressure drop of the section in question for ΔP_t.

During normal operation, the stoichiometric consumption within each oxygen plate must be equal because all the sections operate at the same current. Also, the net pressure drop through the plates must be equal; that is, only a single value of pressure can exist in each manifold. Using typical values of flow resistances it was determined that a significant fraction of the reactant flow can be supplied from the purge manifold to the plate. Gas impurities would accumulate in plates fed from the purge manifold.

Equation 7 expresses the fact that the flowrate through the plate is inversely proportional to its pressure drop. Plates with pressure drops greater than the average value have less than average reactant flow entering through the inlet restrictor. Because of the stoichiometric flow requirement, the additional reactant must come from the purge manifold.

An example of this effect may have been section 20 in Stack 136 which exhibited a high pressure drop during pressure drop testing. Its fractional flowrate through the inlet port was 0.46 (relative to unity) as calculated from Equation 7. This section required unscheduled manual purges to maintain performance, which indicates that it had accumulated a high percentage of impurities in its reactant cavity. Stack 136 had to be purged at 10 minute intervals when sustaining a 40 ampere load during the time that section 20 had this characteristic.

This effect was also experienced in Stack 137 in which sections 12 and 25 exhibited high pressure drops during pressure drop testing. Their fractional flowrates were calculated to be 0.72 and 0.65 respectively using Equation 7.

The flow restrictors installed in Stacks 136 and 137 appear to be effective in maintaining a sufficient flowrate for all sections during purge as evidenced by the fact that the voltages of all sections were restored to a high performance level by purging.

Degradation Rates

It was reported in NAS8-2696-MPR-1212 that no significant difference existed between the voltage degradation rates for the Group I and Group II stacks based on the 200-hour performance evaluation tests. The performance evaluation tests were designed to be identical for each stack so that a valid comparison could be made between stacks. The voltage degradation rate for each stack was determined from a straight line fit through the stack voltage averages for 10-hour increments during the 200-hour tests.

Since the time of that report, computerized data became available for both stack and section voltages at 5-hour increments. The voltage degradation rates were then calculated based on section and stack data. A comparison of the section and stack voltage degradation rates for each stack showed a discrepancy between the rates obtained for Stack 137. Investigation showed that the difference between the total voltage obtained by summing the individual section voltages and the total stack voltage obtained at the stack output terminals were not constant with time. This caused the section and stack voltage degradation rates to differ. At ET 110 hours, this difference increased by approximately 0.12 volts, remained relatively constant until ET 600 hours, and then returned to its value prior to ET 110 hours. Further investigation indicated that improper mating of the power connector at the bottom of the stack probably caused a voltage drop across the connector between ET 110 and 600 hours. The individual section voltages are obtained through a separate connector; hence these were unaffected. The two degradation rates agreed favorably after the stack voltage data was corrected.

The voltage degradation rates for the eight stacks during the 200-hour performance evaluation tests (based on the stack voltage data) are tabulated below.

Stack	40 Ampere Voltage Degradation Rate (microvolts/hour/section)
131	51.65
132	88.09
133	55.28
134	52.65
135	64.99
	Group I Average 62.53 ± 15.23
136	35.85
137	48.23
138	31.46
	Group II Average 38.51 ± 8.70

A statistical t-test performed on the above data shows a significant improvement in the voltage degradation rate for the Group II stacks over the Group I stacks with 97.5% confidence. The result is identical to that based on the voltage degradation rates obtained from the section voltage-time data. Thus it appears that the vacuum loading technique used on the Group II stacks results in a 38% reduction in the 40 ampere voltage degradation rate and a 43% reduction in the variability of the voltage degradation rate during the performance evaluation tests.

High Spiked Loads

A study was made to determine the time limitations of high spike loads as determined by the cooling capabilities of the system. The Mod 12 design is capable of satisfying the cooling requirements of continuous operation at approximately 130 amperes.

Heat is generated by the stack according to the following equation:

$$Q = \left[\frac{(4.3)\,(N)}{V_T} - 3.413\right] P + PAR \tag{8}$$

where

Q = rate of heat generation in Btu/hour

N = number of sections in the stack

V_T = stack potential in volts

P = stack output power in watts

PAR = parasitic power input in Btu/hour

Figure 6 shows the time limitations of high power spikes based on Equation 8 and the 570-hour V-A characteristics of Stack 131. It is assumed that the stack is operating at 80 amperes with the coolant flowing at steady state conditions except during the spiked load periods. For this analysis it is assumed that the 80 amperes cooling rate is maintained after the load spike begins until the stack temperature reaches 192°F, at which time the maximum coolant flow rate required to maintain operation at 130 amperes is assumed. Figure 6 shows the operating times at a specific load spike for the stack temperature to rise 5 and 10°F. Experimental data for Stack 131 is also shown for load spikes at a base operation of 80 amperes to indicate the range of successful operation.

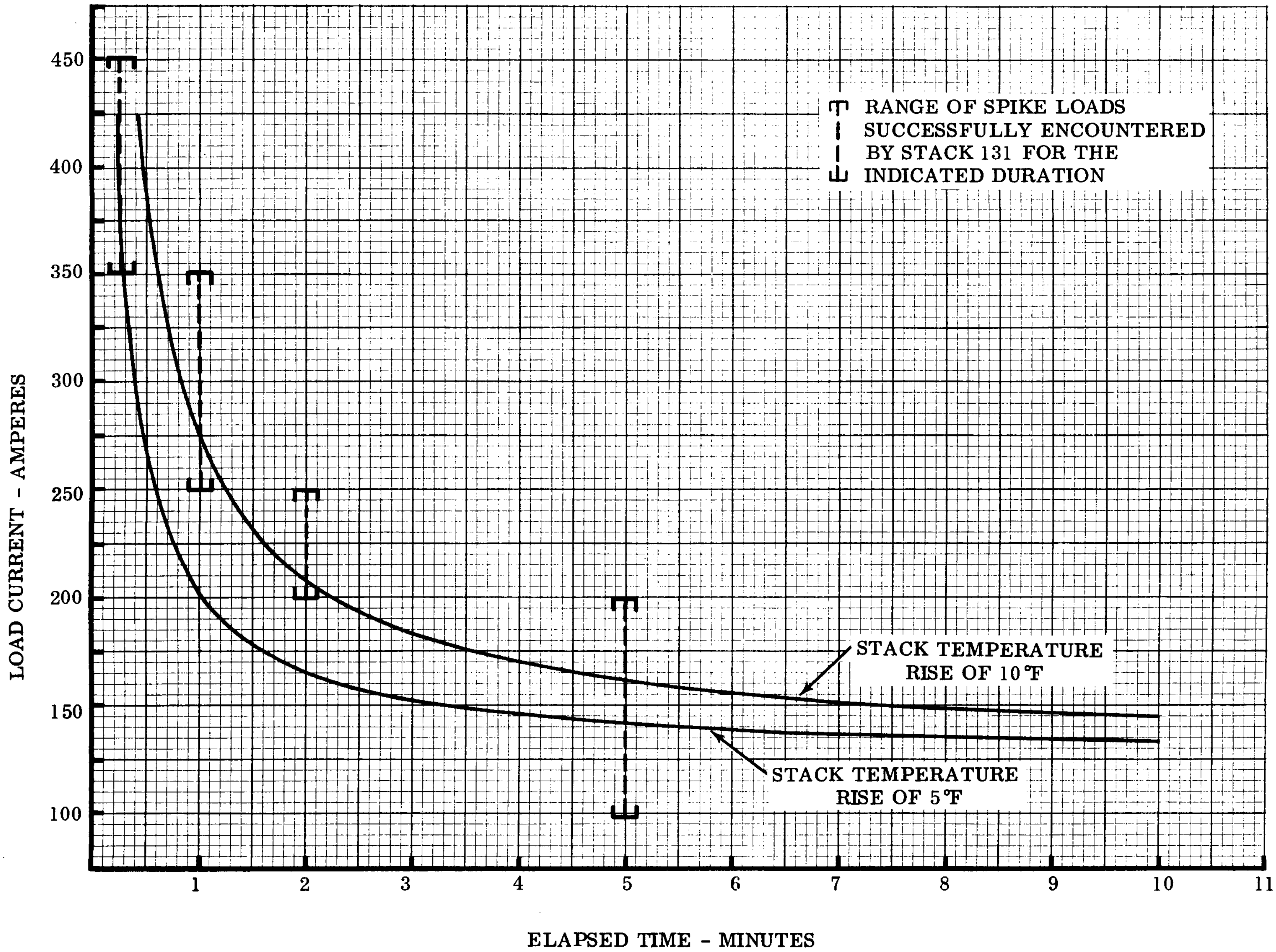

Figure 6. Time Limitations of High Power Spikes

Flammable Mixtures

During the testing of Stacks 136, 137, and 138, samples of the canister cooling gas were extracted and analyzed by means of a mass spectrometer to determine the composition of the gas. The canister is initially pressurized with pure helium.

Figures 7 and 8 depict the increasing concentrations of hydrogen and oxygen that were observed for the three stacks during the first 600 hours of operation. Trace quantities of CO_2, A, N_2, and H_2O were also detected.

After 600 hours on test, the gas in each of the three canisters was replaced with pure helium weekly until accurate information could be obtained concerning the flammability of this three-gas mixture.

The Explosive Research Center of the Bureau of Mines, Pittsburg, Pa. has recently performed flammability test on H_2 - O_2 - He mixtures. They provided a copy of a report entitled, "Flammability of Propellant Combinations" (ERC Report No. 3958). Data from this report is plotted in Figure 9 for the conditions of standard temperature and pressure. The Bureau of Mines has also investigated the effect of temperature and pressure upon the flammability mixture limits. At all temperatures and pressures encountered during normal fuel cell operation, the effect upon the flammability limits is insignificant so that Figure 9 may be used to accurately determine the condition of the canister gas.

The minimum auto-ignition temperature of the flammable mixture is 540°C. The fuel cell stacks are not operated much over 100°C.

It appears that the reactant gases are diffusing from the stack into the canister. The rate of hydrogen accumulation is about 16 to 20 times the oxygen accumulation rate. Equivalent diffusion processes would predict an 8 to 1 ratio (diffusion inversely proportional to the square root of the molecular mass, and twice as many hydrogen gaskets). Oxidation of the interior canister walls may account for the discrepency between experimental and theoretical calculations. Recent testing of fuel cell systems of other contracts has indicated diffusion of helium into the reactant cavities. This would account for the absence of an increasing canister gas pressure.

The gas composition of Stack 136 has also been plotted in Figure 9 for the 600 hour operating period. If the present accumulation rates of reactant gases were to continue it would require approximately 2000 hours for the canister gas mixture to enter the flammability region.

Further testing under this program will specify periodic sampling and determination of canister gas composition.

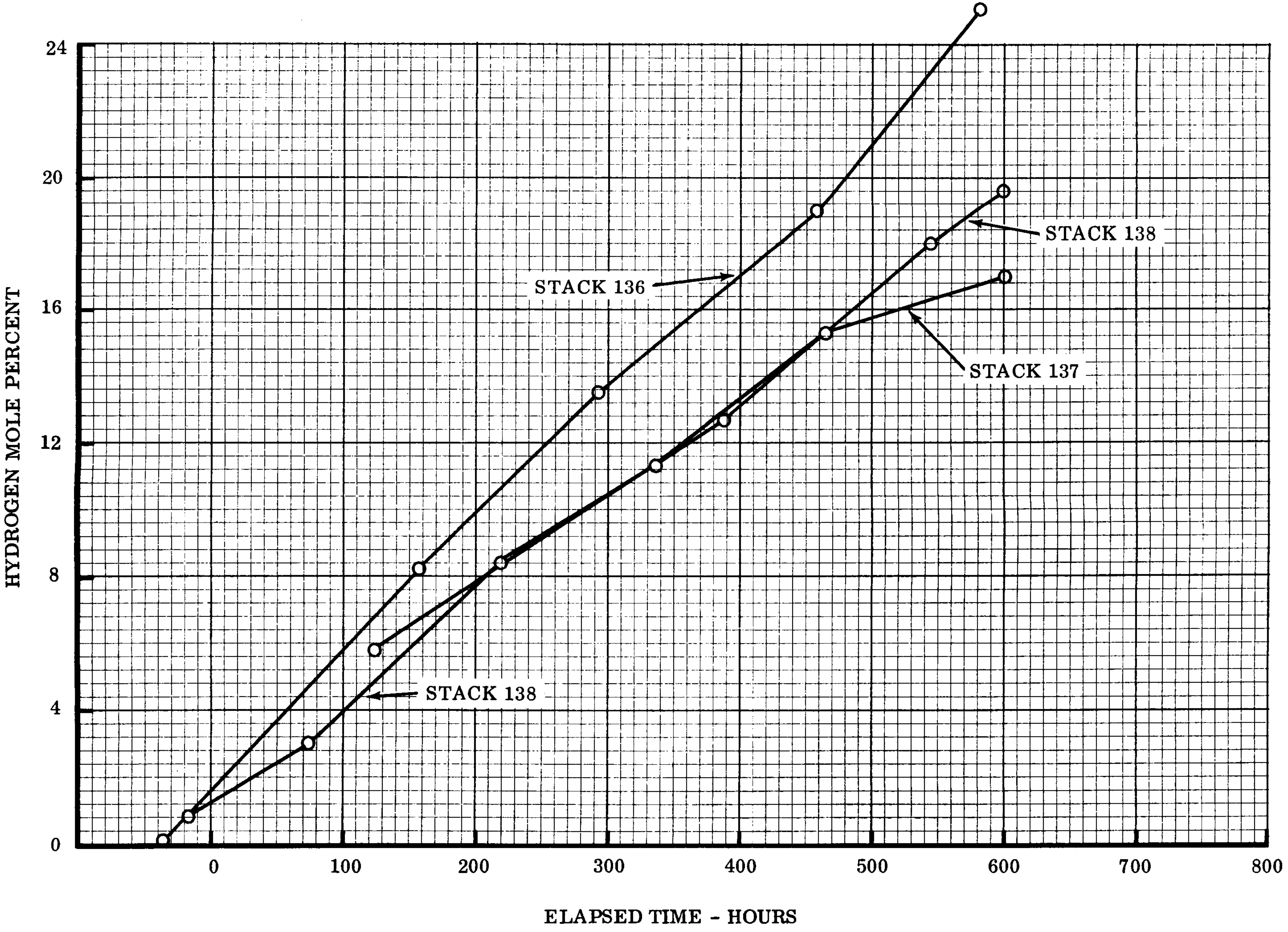

Figure 7. Hydrogen Content of Canister Gas Samples

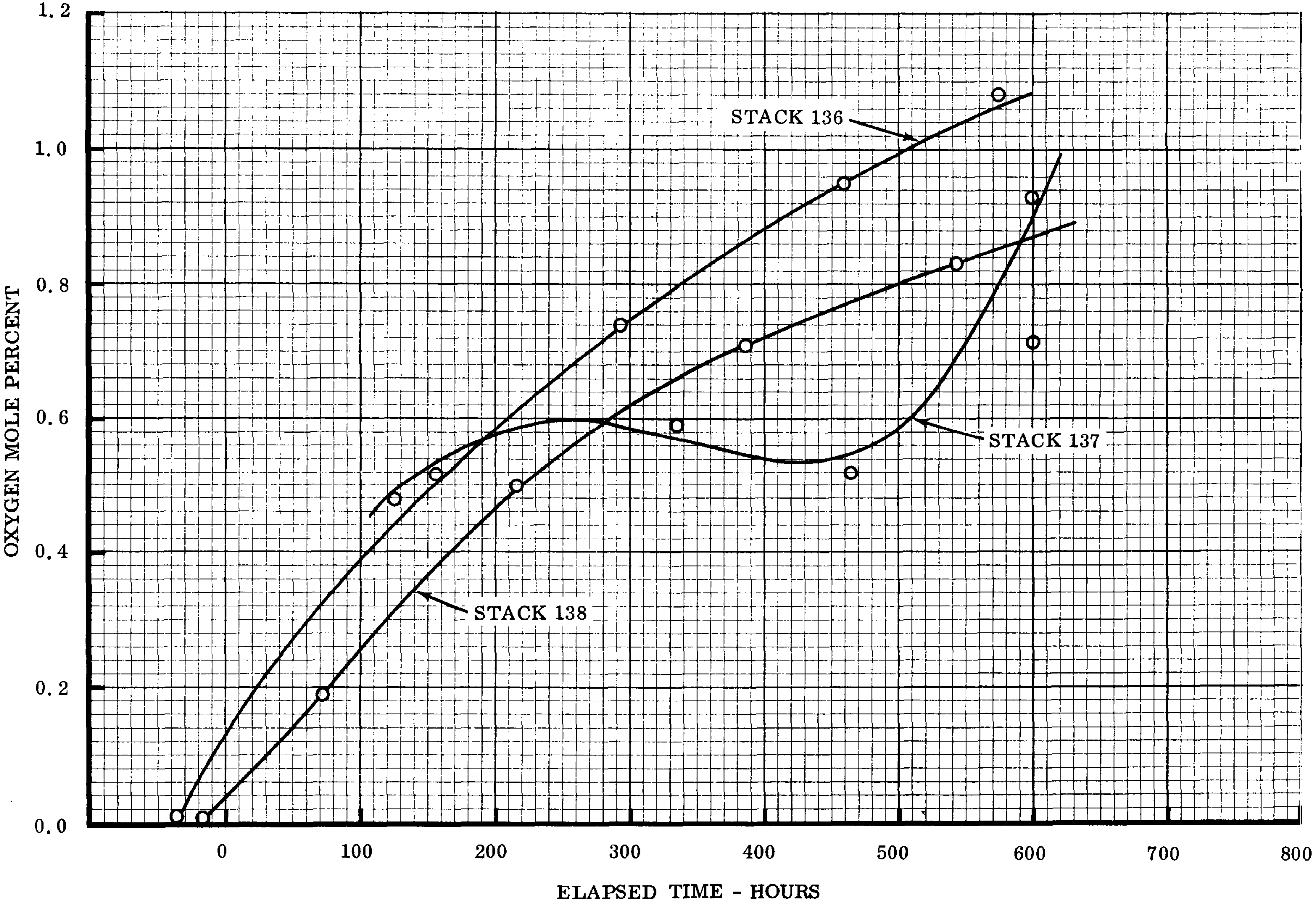

Figure 8. Oxygen Content of Canister Gas Samples

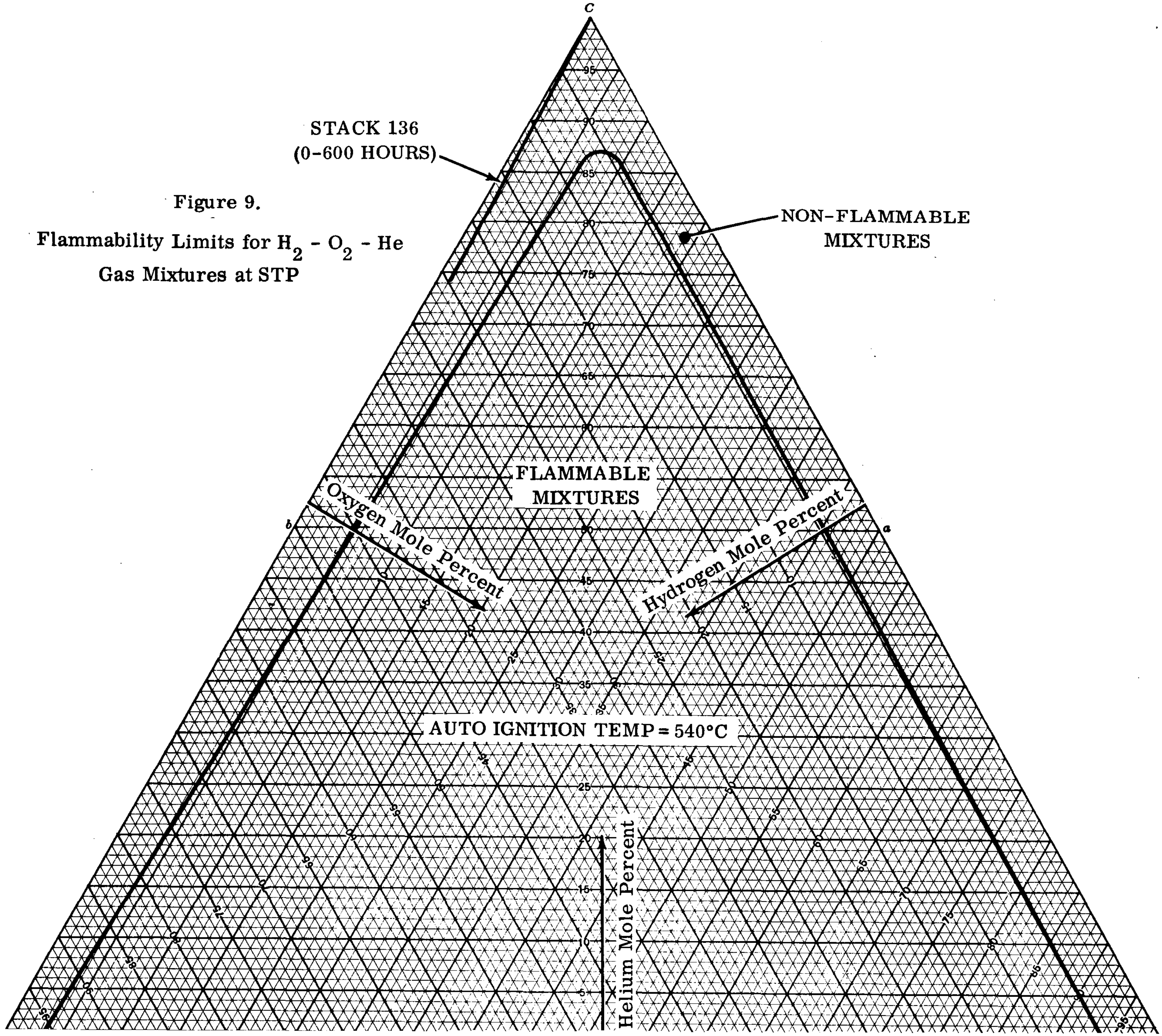

Figure 9.

Flammability Limits for H_2 - O_2 - He Gas Mixtures at STP

The existence of a flammable mixture would still require an initiating spark for ignition to occur. The fuel cell stack and all associated hardware has been designed to prevent such an occurrence. However, it is still desireable to extend the operating time during which only non-flammable mixtures are present. A number of approaches to this situation are being considered.

(a) Brute-force Methods

1. Periodically, or whenever the helium content drops below 90% flow pure helium gas through the canister.

2. Insert an oxygen-getting apparatus into the canister.

3. Use a catalyst to combine the reactant gases in the canister and collect the product water.

(b) Component Redesign Methods

1. Develop or locate another gasket material which is more impervious to gas diffusion.

2. Since it is possible that diffusion occurs primarily through the gaskets at the manifold, rather than around the cell where the electrolyte provides an additional liquid boundary, an insert or manifold redesign may inhibit the diffusion process.

3. A sealant material may be applied, or a process may be developed which would provide a tighter contact between gasket and plate.

(c) Stack Redesign Methods

1. Replace the helium in the canister with hydrogen. The hydrogen canister gas could then be fed into the hydrogen reactant cavity; hydrogen would then be supplied to the canister instead of directly to the reactant cavity. This method would provide continuous consumption of the trace quantities of oxygen gas diffusing into the canister. This would occur within the hydrogen reactant cavity where the platinum electrodes, acting as a catalyst, would combine the trace quantities of oxygen with the hydrogen. Other considerations associated with this type of redesign may negate its advantages.

2. Eliminate the gas coolant loop completely; e. g. employ a direct liquid coolant scheme.