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Quarterly Report No. 5

STUDY OF FUEL CELLS USING STORABLE ROCKET PROPELLANTS

19 February 1966 to 18 May 1966

by

R. F. Drake, L. F. Athearn, R. E. Chute
J. C. Orth, and J. O. Smith

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS3-6476

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SUMMARY

Purification of an impure H_2 product stream from the Aerozine-50 steam reformer by a Pd membrane diffuser has been demonstrated. The diffuser produces ultrapure H_2 at an efficiency of 80%. Scrubbing of unreacted N_2O_4 from the decomposer by water adsorption and subsequent phase separation was simulated and demonstrated.

Half cells of 1/3 ft size have been operated on H_2 and O_2. The H_2 half cell polarized less than 0.10 volt at 90 ASF and operated at a coulombic efficiency above 95% on the stream from the Pd membrane diffuser. The O_2 electrode appeared to operate at nearly the same coulombic efficiency. However, it polarized more under load. Operation of the unscrubbed N_2O_4 decomposer stream was attempted, but unstable electrode potentials were found.

A highly loaded Pt electrode capable of accepting the CO content of the reformer stream was demonstrated.

TABLE OF CONTENTS

		Page
I.	INTRODUCTION	1
	A. BACKGROUND	1
	B. PROGRAM ORGANIZATION	1
	C. SCOPE OF THIS REPORT	1
II.	COMPLETION OF PHASE I	4
III.	Pd MEMBRANE PURIFICATION OF AEROZINE STEAM REFORMER PRODUCT STREAM	5
	A. BACKGROUND	5
	B. RESULTS AND DISCUSSION	6
IV.	PURIFICATION OF N_2O_4 DECOMPOSER STREAM	17
V.	H_2/O_2 HALF CELL TESTING	21
	A. BACKGROUND	21
	B. INITIAL TESTING	21
	C. H_2 HALF CELL TESTING	24
	D. O_2 HALF CELL TESTING	27
	E. HALF CELL TESTING ON UNSCRUBBED N_2O_4 DECOMPOSER STREAM	27
	F. CO-TOLERANT ANODES	27

LIST OF TABLES

Page

1. Data From H_2 Purification of Steam Reforming Output Using Bishop Model A-1-DH Palladium Diffuser 13

2. 250-Hour Test of Diffuser. 15

3. **Initial and Final Gas Compositions for Diffuser Analysis by Vapor Phase Chromatography 16**

4. Initial H_2/O_2 1/3 Ft^2 Cell Testing 23

5. H_2 Half Cell Tests 26

6. O_2 Half Cell Tests 28

7. Half Cell Tests on Unscrubbed N_2O_4 Decomposer Stream . . 29

8. Electrode Tests with CO Containing H_2 Streams. 30

9. Anode Tests on CO Containing H_2 Streams. 32

LIST OF FIGURES

		Page
1.	Program Work Plan and Event Chart NAS3-6476	2
2.	NAS3-6476 Phase II Work Plan	3
3.	Analysis of Diffuser Operation	7
4.	A-1-DH Pd. Diffuser Efficiency vs Pressure	8
5.	A-1-DH Pd. Diffuser Efficiency vs % H_2 in Gas	9
6.	A-1-DH Pd. Diffuser Efficiency vs Total Input Rate	10
7.	Schematic Diagram of Palladium Diffusion Hydrogen Purification Unit	11
8.	Permeability of Gases Through MRD-C Electrode	18
9.	N_2O_4 Scrubbing Demonstration	19
10.	1/3 Ft^2 Test Cell	22
11.	O_2 Cathode Tests With Au Plated Components	25

I. INTRODUCTION

A. BACKGROUND

The objective of this research is to develop fuel cell systems operating on storable rocket propellants as primary or secondary reactants.

The present contract calls for the investigation and development of cells operating on gaseous N_2O_4 and Aerozine-50 as direct reactants, and for a reforming capability to use these reactants to produce O_2- and H_2-rich feedstreams for fuel cells. The construction and operation of working reformers and cells are the objectives of this work. Work on prior contracts in this investigation has been published.

B. PROGRAM ORGANIZATION

The project consists of three phases, to be performed roughly in series. The overall work plan shown in Figure 1 illustrates the major tasks to be performed. Detailed working plans for Phase I were illustrated in previous reports. Working plans for Phase II are shown in Figure 2.

C. SCOPE OF THIS REPORT

This report covers work done to complete one remaining task in Phase I. The following Phase II work is also reported:

(1) The purification of the product streams from the Aerozine-50 steam reformer and the N_2O_4 decomposer.

(2) The construction and operation of 1/3 ft^2 H_2/O_2 cells on the product streams from the reformer and decomposer.

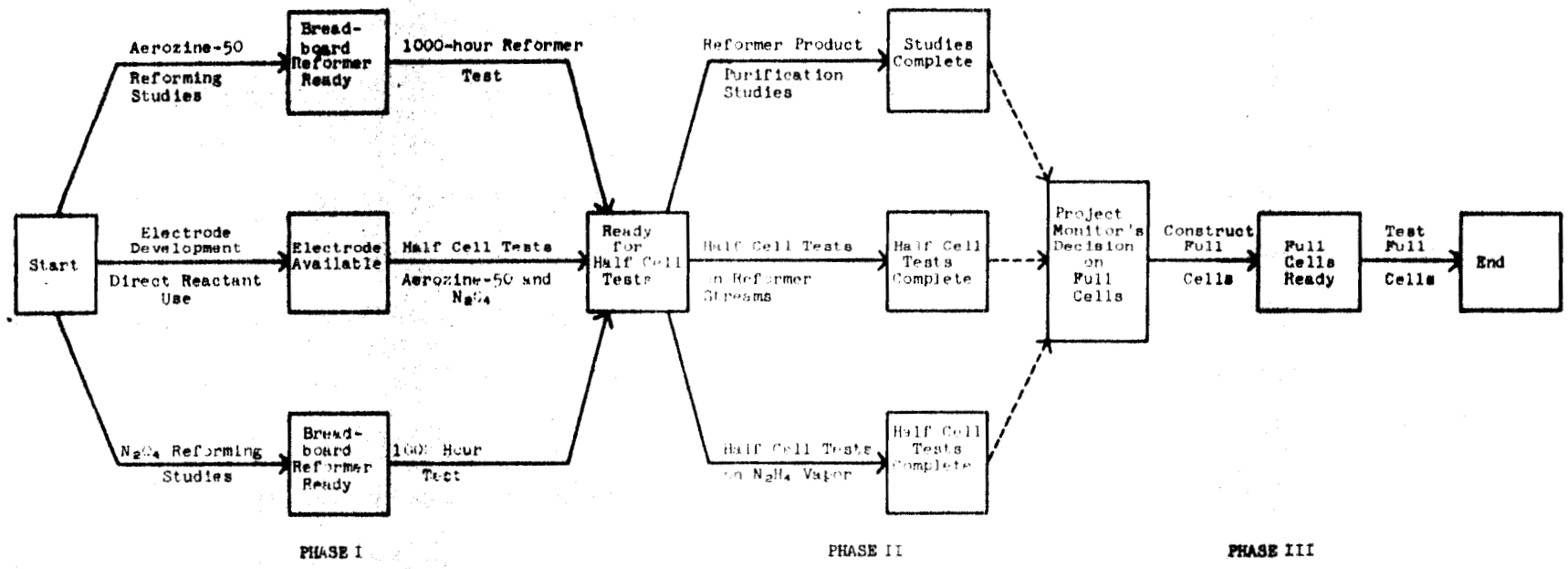


Figure 1. Program Work Plan and Event Chart NAS3-6476

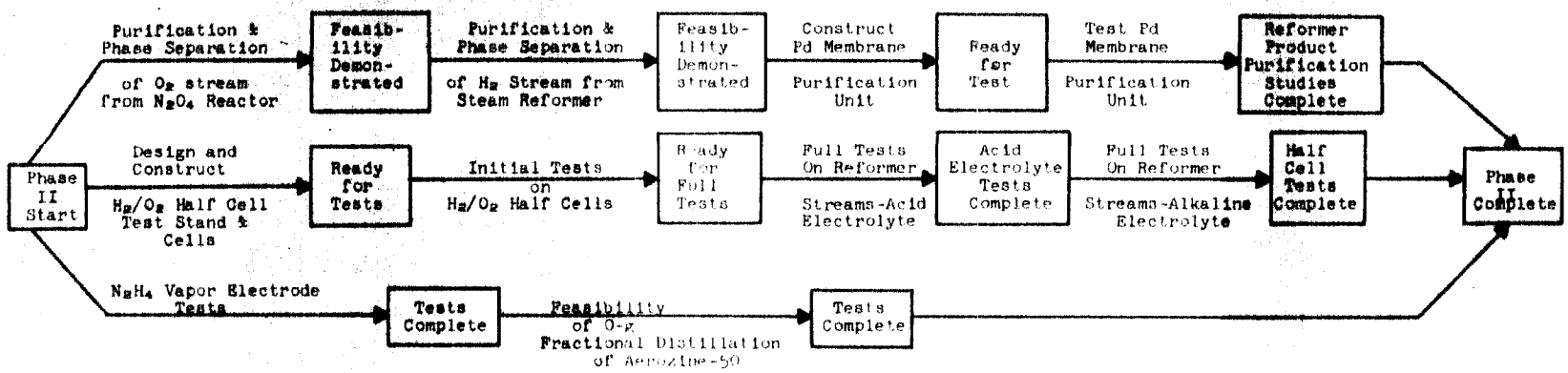


Figure 2. NAS3-6476 Phase II Work Plan

II. COMPLETION OF PHASE I

In the previous Quarterly Report (No. 4) the results of tests with 1/3 ft^2 MRD-carbon electrodes operating directly on N_2O_4 were reported. Briefly, many physical-mechanical problems were encountered in operating a half cell of this size. However, electrical performance was successfully demonstrated. A reactant flow plate design was described that optimized N_2O_4 contact with the electrode and allowed efficient utilization with a single pass through the electrode chamber. With this flow plate the electrode produced 22 watts at a coulombic efficiency of 27% at 30 amperes total current. This is an order of magnitude improvement over previous results.

During this period the N_2O_4 cathode investigation was completed by running a 1/3 $ft.^2$ half cell with (0.025 in.) reactant flow plate. The half cell set-up described in the last report (Quarterly Report No. 4) for tests with the 0.050 in. flow plate was used in these tests. The results were not satisfactory because severe electrode polarization was found at all reasonable current drains regardless of N_2O_4 flow rate. We had expected that the 0.025 in. thick plate might perform even better than the 0.050 in. plate because of higher local gas velocities and more turbulent flow (high Reynolds numbers). However, it appears that other factors have come into play. One possibility is that the flexible electrode "bulged" into the flow channels under the pressure applied in assembly of the cell. This could have caused uneven flow and perhaps even complete blockage of some of the channels.

In any case, it appears that the 0.050 in. thick flow plate will perform adequately, and no advantage can be gained by reducing the thickness. The work on this task is considered complete and ends the planned work on Phase I.

III. Pd MEMBRANE PURIFICATION OF AEROZINE STEAM REFORMER PRODUCT STREAM

A. BACKGROUND

The objective of this task is to modify the impure H_2 stream from the steam reformer to supply ultrapure H_2 to the fuel cell. The gas composition from the reformer is 70% H_2, 17% N_2, 12.5% CO_2, and trace CO and CH_4. If the impurities could be eliminated, the stream could be used in any type of H_2 fuel cell without purge, and the advantages might outweigh the disadvantages of increased complexity. We have investigated Pd-Ag alloy membranes for this application.

Palladium membranes purify hydrogen-containing streams by selectively transporting hydrogen, presumably in atomic form, under an H_2 partial pressure gradient. The steps involved in this transport are:

a. Diffusion to the membrane surface from the gas phase

b. Adsorption on the surface, and dissociation to atomic form

c. Activated diffusion of atomic hydrogen through the membrane

d. Recombination to molecular hydrogen at the surface

e. Desorption from the surface.

As long as the other gases are inert to the Pd membrane, the transfer rate depends on the temperature, the partial pressure of H_2 in the impure stream, and the pressure of the pure H_2 outlet.

Commercial Pd membrane units have been optimized and well characterized for the purification of H_2 streams. We have selected a Model A-1-DH (J. Bishop and Co.), which consists of a single Pd-Ag alloy tube, 1 ft. long and 0.063 in. O.D. with a wall thickness of 0.003 in., closed at one end. The tube is mounted in a jacket that serves as the impure stream purge manifold. Ultrapure H_2 exits through the open end of the Pd-Ag tube. The unit is rated at 1 SCFH of ultrapure H_2 at 370°C and 200 psig. The manufacturer supplied kinetic data for the unit in the form of transfer rate (ft ^{3}/hr) of H_2 vs pressure of H_2 at various pure H_2 output pressures.

For 1 atm H_2 output pressure, the rate data can be represented by:

$$R_H \ (ft^3/hr) = C_o \ P_{H_2}{}^{0.85} \text{ where } P_{H_2} \text{ is psig.}$$

With the appropriate C_o, this represents the kinetic data within 1% over the range 0 to 100 psig H_2.

The ideal representation of the kinetics of the system we are using is shown in Figure 3. Incremental elements along the length of the tube on the impure stream side will reach different steady state partial pressures of H_2. This means that the incremental removal rate will be a function of the distance (x) along the tube. For a given tube length, the steady state composition along the tube (and thus the overall H_2 removal efficiency) will depend on total pressure, initial H_2 content of the feed stream, total input rate, and temperature. To evaluate our experimental results, we have calculated the maximum removal efficiencies for various pressures, input rates and compositions, including the possibility of connecting two units in series. The details of the computer program used in these calculations are given in Appendix I, and the results of the calculations are shown in Figures 4, 5, and 6. In general, removal efficiencies of 60% to 80% with a single unit are possible in the range of conditions we will use, and the efficiency can be increased to over 90% by using two units in series. Our experimental results should approach these values. However, non-ideal conditions such as pulsed flows from the reformer, non-uniform gas mixing in the jacket, thermal gradients, inhomogenities in the diffuser tube, etc., all could tend to lower the actual efficiencies.

B. RESULTS AND DISCUSSION

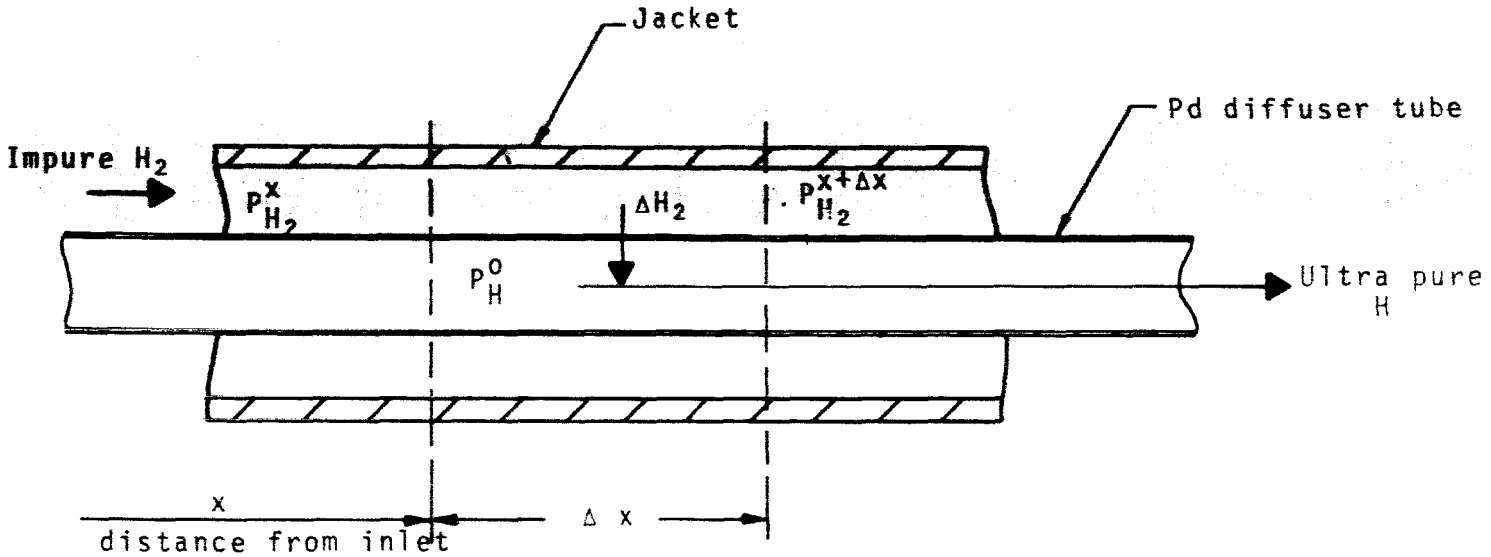
A schematic diagram of the equipment used in the experimental work is shown in Figure 7. A water trap condenses excess water from the stream reformer leaving the gas stream saturated with water vapor at 35-45°F. Provisions have been made for analysis (by VPC) of the input stream, the exit stream from the diffuser jacket and the ultrapure H_2 exit stream. Pressure in the jacket is maintained by a solenoid valve triggered by an adjustable pressure sensor. The volume output of each stream is measured with wet test meters. Input rates are changed through a bleed valve in the input line.

Initial testing with tank H_2 indicated the unit was operating satisfactorily; the H_2 diffusion rates were within experimental error of the manufacturers specifications. The unit was then operated on the reformer product stream in short-term testing.

The testing sequence was:

(1) Determine gas output rate (liters/hr) and composition from steam reformer over a 2-hr period.

(2) Switch stream to Pd diffuser and allow 30 min. for equilibrium.



$$P^o_H = \text{constant}$$

$$P^x_{H_2} = \frac{\text{moles } H_2 \text{ impure stream}}{\text{Total moles impure stream}} \times \text{Pressure of impure stream}$$

$$P^{x+\Delta x}_{H_2} = \frac{\text{moles } H_2 - \Delta H_2}{\text{Total moles} - \Delta H_2} \times \text{Pressure of impure stream}$$

$P^{x+\Delta x}_{H_2}$ at x = length of diffuser tube determines overall efficiency.

Figure 3. Analysis of Diffuser Operation

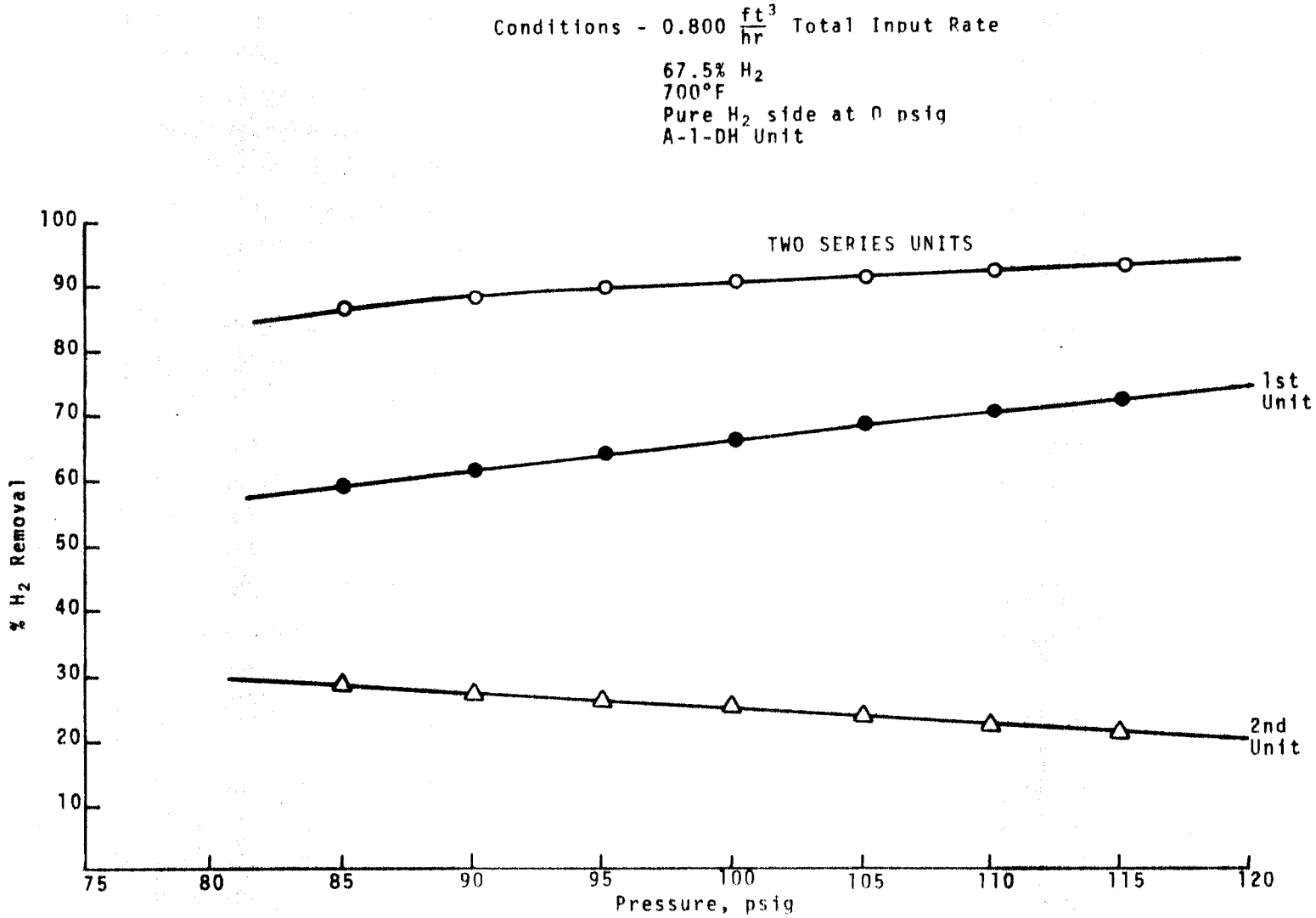


Figure 4. A-1-DH Pd. Diffuser Efficiency vs Pressure

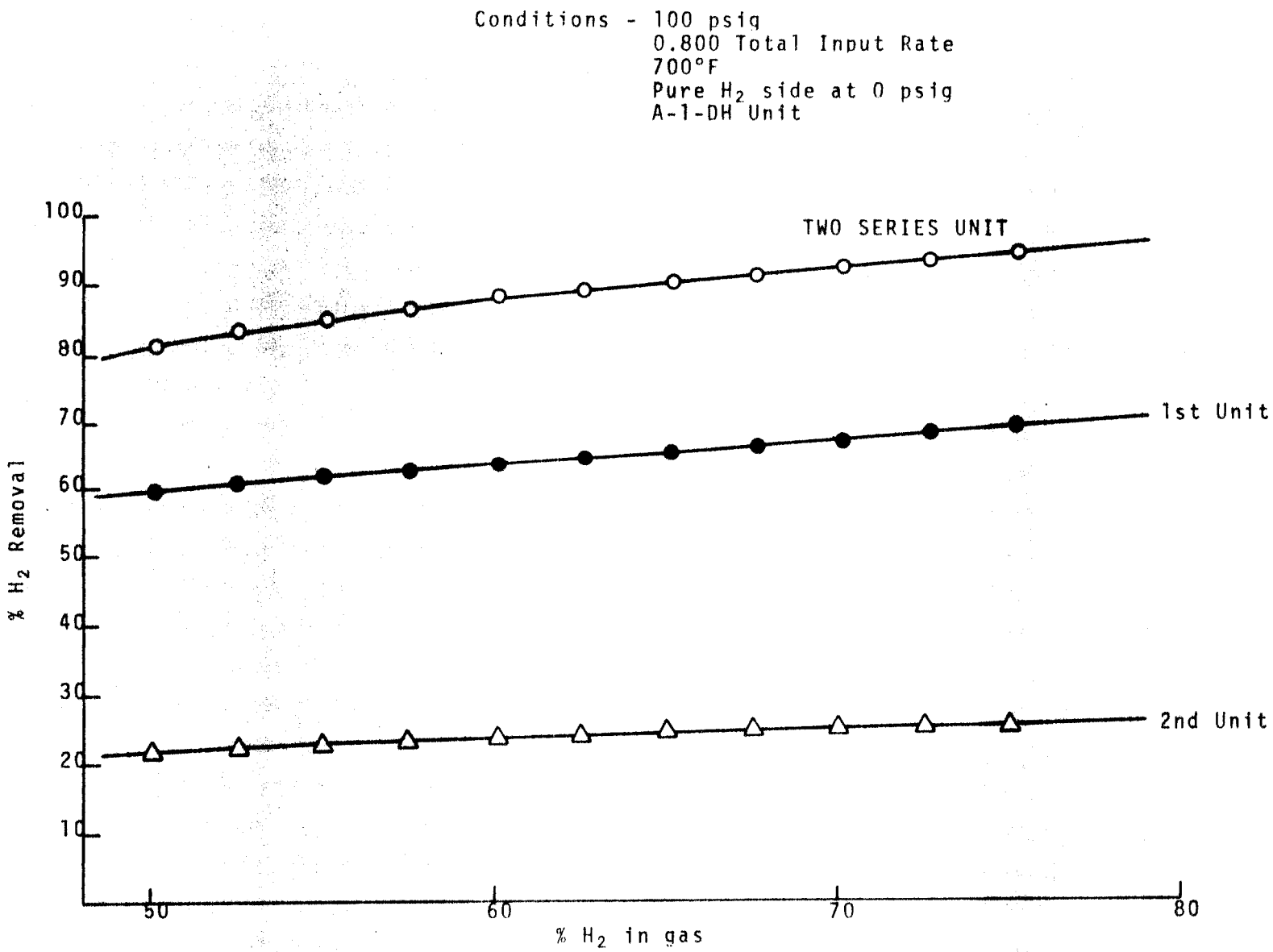


Figure 5. A-1-DH Pd. Diffuser Efficiency vs % H_2 in Gas

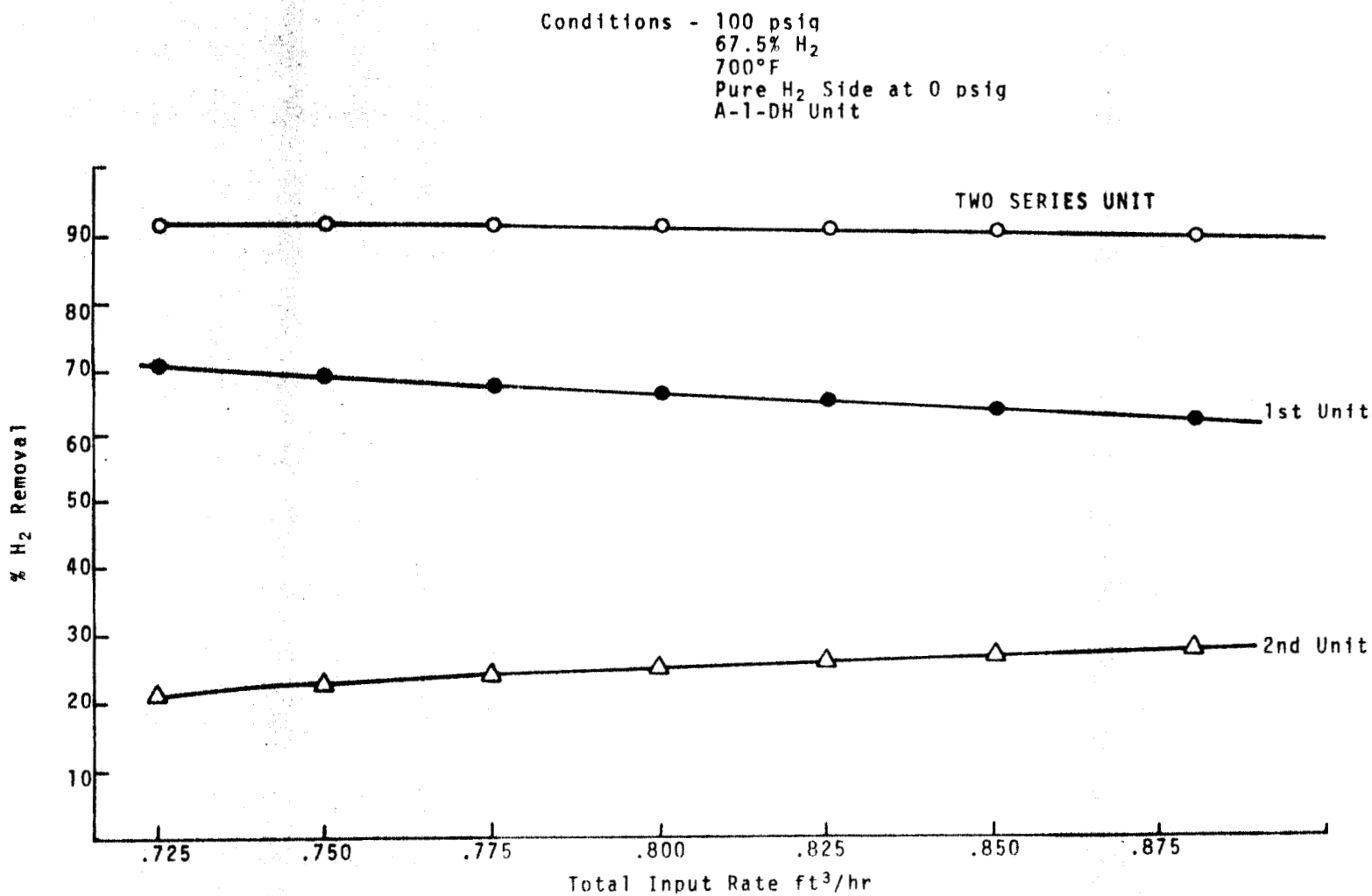


Figure 6. A-1-DH Pd. Diffuser Efficiency vs Total Input Rate

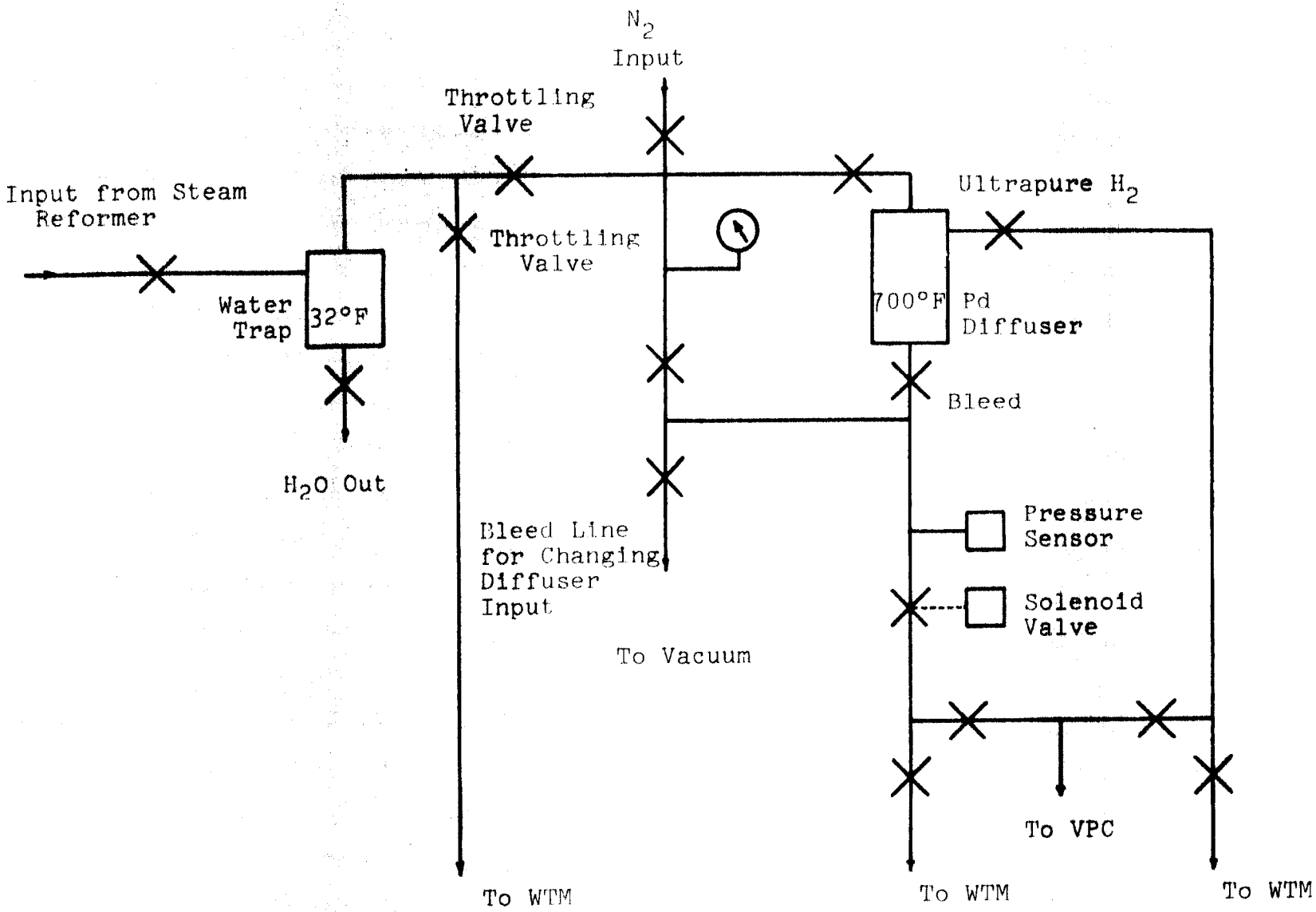


Figure 7. Schematic Diagram of Palladium Diffusion Hydrogen Purification Unit

(3) Measure gas output rate (liters/hr) from ultrapure H_2 line and from bleed stream for 1 hr.

(4) Determine gas output composition from bleed stream, and check pure H_2 output for possible leaks.

Total gas rates to the diffuser were decreased by splitting the reformer stream ahead of the diffuser. Since the bleed stream was not constant, but rather was pulsed because of the type of pressure control used, residence times in the diffuser varied and the data at the lower input rates are less accurate than at the high rates. Adding to this inaccuracy is the fact that VPC analysis of this stream is more difficult because of the non-uniform residence times. Thus, the most accurate calculation of purification efficiency is from the volumes recovered from each gas stream. Data from these tests are compiled in Table 1.

Eighty per cent H_2 recovery as ultrapure H_2 was obtained at the lowest input rate tested (7.22 liter/hr) at 100 psig input pressure. At 25 liters/hr input rate, 52% and 27% recovery was found at 100 psig and 50 psig, respectively. The following points are noteworthy:

(1) The diffuser system seemed to improve with time. Reasons for this might be removal of "poisons" caused by prior air contact, or changes in the membrane crystal structure in contact with the H_2 stream.

(2) The composition of the bleed stream was considerably higher in CO than can be accounted for by the change in volume due to loss of H_2 through the membrane. It seems probable that the reverse of the CO shift reactions was being catalyzed by the palladium surface through the reaction:

$$CO_2 + H_2 \rightarrow CO + H_2O$$

The excess water from the reformer was condensed out of the stream before it entered the diffuser and this would tend to favor the above reaction.

(3) The steam reforming equilibrium at 800°C yields 1.0% CH_4 at 100 psig compared to 0.3% CH_4 at 1 atm operating conditions used in the 1000-hr test. This higher pressure does not significantly decrease the reformer efficiency, but if still higher pressure were used to gain higher recovery of the H_2, its influence on the steam reforming efficiency would have to be taken into account for optimum conditions.

Following these tests, the reformer-diffuser combination was run continuously for over 250 hours. During this period the effect of varying input rates and of throttling the output stream

Table 1

DATA FROM H_2 PURIFICATION OF STEAM REFORMING OUTPUT USING BISHOP MODEL A-1-DH PALLADIUM DIFFUSER

Diffuser Temp. 700°F ± 5°F; Ultrapure H_2 output pressure **1 atm.**

Note: **Tests are in chronological** order, since improvement of the diffuser **with** time **is** suspected.

Input Pressure psig	Composition from Steam Reformer Mole % H_2	N_2	CH_4	CO	CO_2	Diffuser Input Rate L/Hr*	Bleed Output L/Hr*	UPH Output L/Hr	Hydrogen Efficiency %	Bleed Output Comp. Mole % H_2	N_2	CH_4	CO	CO_2
50	69.8	17.2	0.3	0.1	12.6	25.9	21.0	4.9	27.1	62.4	20.8	0.4	0.6	15.9
100	68.3	17.6	0.9	0.1	13.1	25.5	16.4	9.1	52.4	53.7	25.7	1.6	0.5	18.6
100	"	"	"	"	"	8.94	4.72	4.22	68.2	-	-	-	-	-
100	69.2	18.0	1.0	0.2	11.6	12.37	6.79	5.58	65.2	-	-	-	-	-
100						11.66	5.78	5.88	72.9	39.1	34.1	1.9	2.2	22.5
100	"	"	"	"	"	7.22	3.22	4.00	80.0	-	-	-	-	-
100	"	"	"	"	"	"	"	"	"	-	-	-	-	-
100	"	"	"	"	"	10.58	4.58	6.00	81.9	-	-	-	-	-

* All rates corrected to 25°C, 1 atm.

was also investigated. The results of these tests (Table 2) are in chronological order over the 250-hour period. Input and output analysis made on some of these tests are presented in Table 3. Examination of these data indicate the following:

(1) There was no degradation in performance of the unit over the 250-hour period, (compare tests 3 and 15) and the experimentally observed efficiencies are within experimental error of the calculated values.

(2) Throttling the output stream has a decided effect on efficiency: higher throttling produces higher efficiencies (compare tests 1, 2, 3). Throttling tends to reduce the gas surge through the diffuser jacket when the solenoid valve opens and thus increases the average residence time in the diffuser.

(3) The effect of input rate on performance is within experimental error of calculated values. These results confirm the calculations and show the validity of the calculation method for extrapolating the performance to larger units.

In general, the testing results have been quite promising. We have demonstrated that very reasonably sized purification units can be assembled that will operate at high efficiency and reliability for a minimum of 250 hours.

Table 2

250 - HOUR TEST OF DIFFUSER

Conditions: 700°F
Pure H_2 Outlet at 0 Psig.

Test No.	Total Input Rate ft^3/hr	Total H_2 in Input Stream mole %	Total H_2 in Input Stream ft^3/hr	Pressure Psig	Experimental Eff. %	Experimental Pure H_2 ft^3/hr	Calculated** Eff. %	Calculated** Pure H_2 ft^3/hr	Throttling*
1	0.819	67.5	0.553	100	38.9	0.215	65.5	0.362	O
2	0.814	67.5	0.549	100	49.6	0.273	65.7	0.361	M
3	0.789	67.5	0.533	106	68.3	0.364	69.8	0.369	H
4	0.799	67.5	0.539	105	65.2	0.352	68.3	0.368	H
5	0.792	67.5	0.535	108	67.5	0.361	70.0	0.375	H
6	0.805	67.5	0.543	103	64.5	0.351	66.7	0.362	H
7	0.811	67.5	0.547	107	66.9	0.366	67.9	0.371	H
8	0.800	67.5	0.540	98	38.0	0.205	65.0	0.351	O
9	0.703	67.5	0.475	109	73.4	0.349	76.5	0.363	H
10	0.720	67.5	0.486	109	73.7	0.358	75.5	0.367	H
11	1.181	66.3	0.783	108	51.7	0.405	51.4	0.402	H
12	1.205	66.3	0.799	100	49.2	0.393	47.5	0.380	O
13	1.190	66.3	0.789	103	51.0	0.402	49.2	0.388	M
14	1.173	66.3	0.778	104	53.5	0.416	50.2	0.390	H
15	0.779	67.5	0.526	100	66.2	0.348	67.1	0.353	H
16	0.523	67.5	0.353	108	86.1	0.304	86.9	0.307	H

*Throttling the output from the diffuser gave more uniform flow raising the efficiency to near calculated values. O-no throttling, M-medium throttling, H-high throttling.
**Calculated by computer from kinetic data: assumes steady state flow.

Table 3

INITIAL AND FINAL GAS COMPOSITIONS FOR DIFFUSER ANALYSIS BY VAPOR PHASE CHROMATOGRAPHY

Test No.	Input Rate ml/hr	Input Composition, Mole %					Reformer Eff. %	Output Composition, Mole %					Diffuser Eff.** %
		H_2	N_2	CH_4	CO	CO_2		H_2	N_2	CH_4	CO	CO_2	
1 to 3	20	66.1	17.5	1.0	0.4	15.0	90.0	not measured					39 to 68
4	20	67.5	17.8	0.9	0.3	13.4	93.8	34.8	33.9	2.1	2.0	27.3	65.2
6	20	not measured					----	40.2	33.5	2.0	1.8	22.5	64.5
8	20	not measured					----	57.3	25.0	1.3	1.2	15.2	38.0
13	30	66.3	18.5	0.9	1.1	13.2	87.8	not measured					51.0
10	18	not measured					----	37.1	35.9	2.6	1.7	22.7	73.7
16	20*	68.9	17.4	0.4	0.6	12.7	94.6	not measured					86.1

*This test input composition to reformer was 26.6% A-50 by weight. All other tests input composition was 35.7% A-50 by weight.
**Diffuser eff. calculated from volume of pure H_2 output, and known input rate and composition.

IV. PURIFICATION OF N_2O_4 DECOMPOSER STREAM

The test results with the N_2O_4 decomposer indicate that obtaining conversion efficiencies above 80-85% will require a prohibitively large catalyst volume and weight (see Quarterly Report No. 4).

Since it appears likely that the reactor product stream will contain substantial amounts of N_2O_4, which would limit its usefulness to acid electrolyte cells, a feasibility study of purifying this stream has been undertaken. One method would involve using the excess water from the steam reformer (which would normally be dumped) to extract the undecomposed N_2O_4 from the gas stream. In order to do this, the water must be separated from the reformer gas stream under zero-g conditions in which phase separation is a real problem. We have investigated the MRD electrode as a phase separation membrane. A 3 in. x 3 in. membrane was fixed horizontally in an apparatus that allowed a measured pressure differential to be developed across it. Water to a depth of 1/2 in. was poured on the membrane and pressure was applied from a nitrogen cylinder. No leakage of water through the membrane was observed at a ΔP of 540 mm Hg for times up to 10 minutes even though the membrane was noticeably distorted. This test verifies the "wet-proofness" of the electrode.

The diffusion of the gases of interest through the membrane were then determined. The results, (Figure 8) show that high gas permeabilities are possible through the electrode even when wetted with H_2O. We believe that these tests establish the feasibility of this electrode structure as a phase separation device.

Another test was made to demonstrate scrubbing of N_2O_4 from the reactor stream. This test used an air-N_2O_4 stream, in which the N_2O_4 content represented the amount remaining after 80% conversion at a feed rate of 180g of N_2O_4/hour (6 times normal). This stream was fed to a 300-ml flask in which a flowing tap water stream was mixed with the gas. The gas was then led through a series of bubblers containing distilled water and the pH of the water in each trap was determined as a function of time. The data, shown in Figure 9, can only be considered a rough indication of the results that could be obtained with more sophisticated equipment. However, a great reduction in N_2O_4 contamination has been demonstrated even with this simple apparatus. A pH of 3.1 in the third trap after 20 minutes of exposure does not represent very much N_2O_4 and would appear to be well within the limits required for final scrubbing with molecular sieve or KOH pellets. In addition, the pH difference between the three traps indicates the stream could be even further purified with more contact time with H_2O. This parameter could be optimized in the design of an operating scrubber.

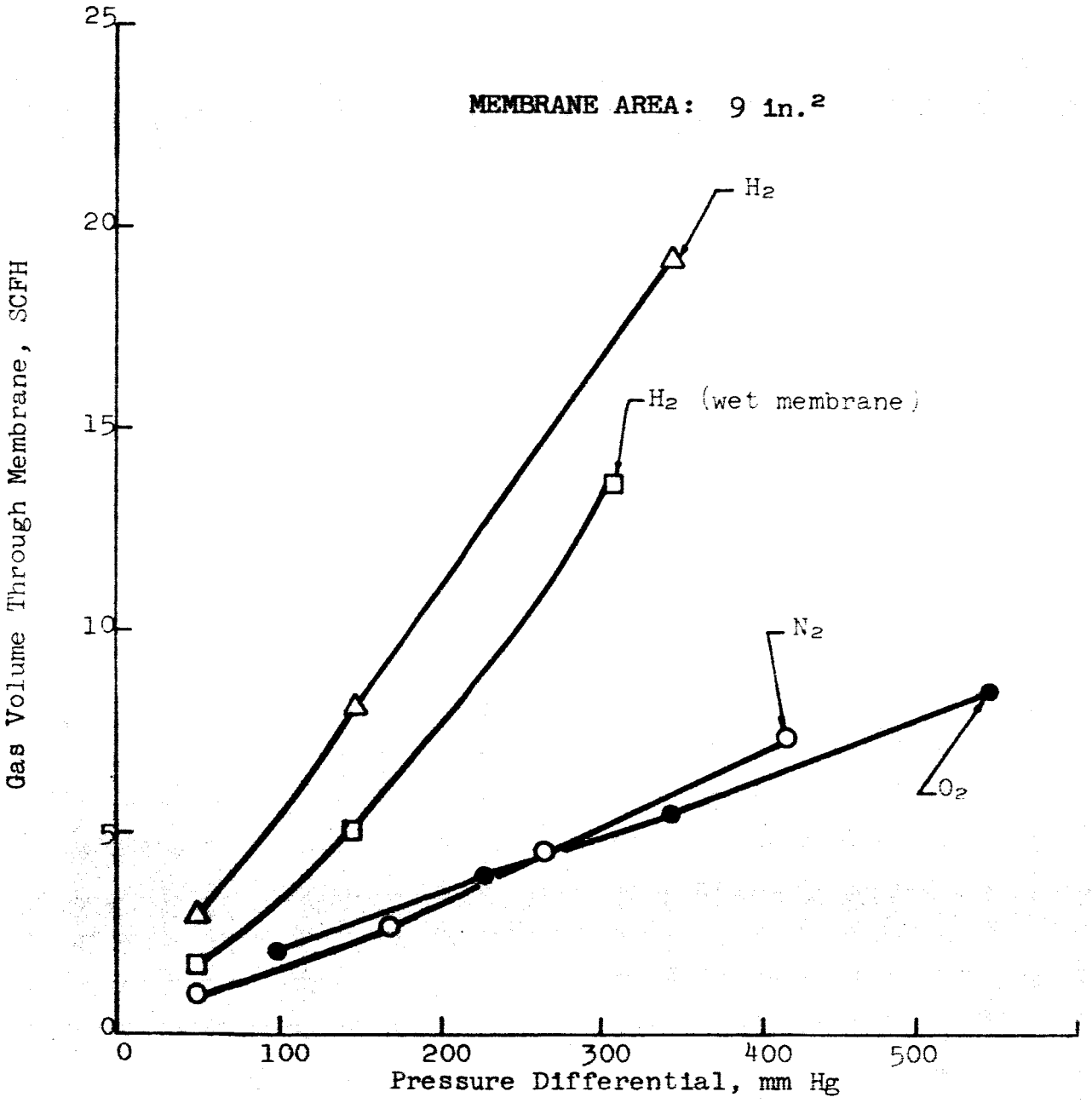


Figure 8. Permeability of Gases Through MRD-C Electrode

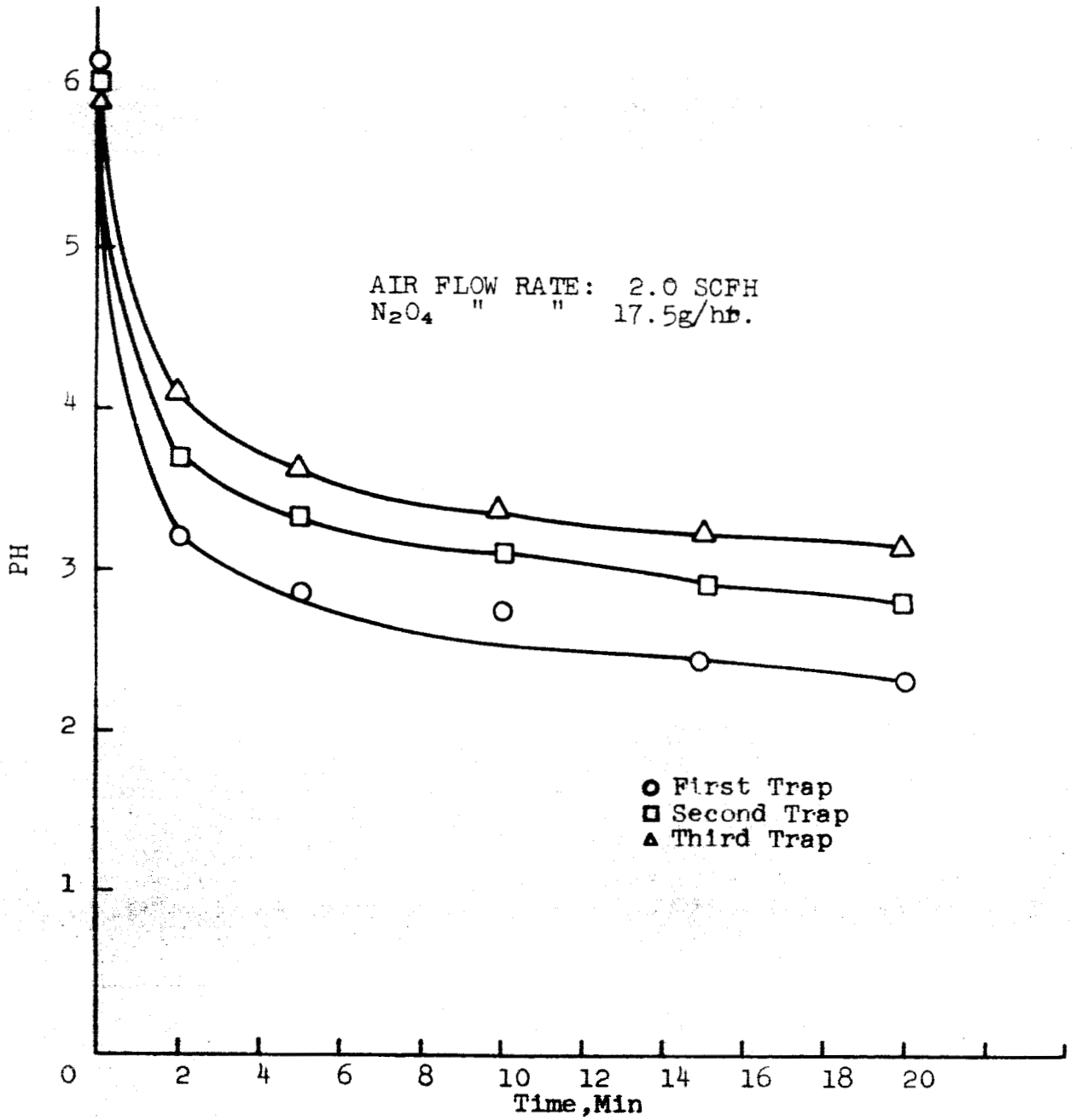


Figure 9. N_2O_4 Scrubbing Demonstration

We believe these simple tests have demonstrated the initial feasibility of purification-phase separation of the N_2O_4 reformer stream. Additional, more sophisticated studies would be necessary to finally determine the feasibility of developing operating units.

V. H_2/O_2 HALF CELL TESTING

A. BACKGROUND

The objective of this work is to determine electrode performance on the decomposed propellant streams in a 1/3ft^2 half cell. Both the power densities and coulombic efficiencies of the possible combinations of electrode, electrolyte, and reactant stream compositions are of interest.

A test cell construction was developed that combined both the H_2 anode and the O_2 cathode into a single free electrolyte cell. A schematic diagram of this equipment is shown in Figure 10. Electrolyte is pumped into both cell halves under a hydrostatic head of about 18 in. The two cell halves are separated by an ion exchange membrane, which allows characterization of each half cell independently of the other. The electrodes are either clamped into the stainless steel cell frame by the force of the cell insert and reactant flow plate or are held in place across the face of the cell frame by the Lucite frame. In either case extra support must be given to the electrode to insure that it is mated to the reactant flow plate. This is accomplished by the use of stainless steel rods, as shown in the diagram, or by heavy mesh stainless steel screen. A polypropylene felt paper insulates the support members from the electrode. Reactant gases are metered into the appropriate manifolds through calibrated flow meters. Current is withdrawn from the cell with a high capacity d-c power supply. Electrode potentials are measured with a Keithley electrometer. The reference electrodes are standard saturated calomel electrodes connected to the cell via a salt bridge consisting of an electrolyte-saturated, woven glass wool thread in a thin Teflon spaghetti tube. The end of the Teflon tube is pressed to the face of the electrode resulting in a "Luggin Capillary" type of salt bridge. The IR losses between this tube and the electrode due to electrolyte resistivity should be minumized with this configuration.

B. INITIAL TESTING

Electrodes used in these tests were standard MRD carbon/Pt laminar electrodes, with 50 mg of Pt/in.^{2} on a 0.025 in. thick carbon/Teflon matrix supported by a stainless steel screen.

The unit was assembled and run on tank O_2 and H_2 to characterize the electrode performance before reformer streams were used. The results of these tests are shown in Table 4.

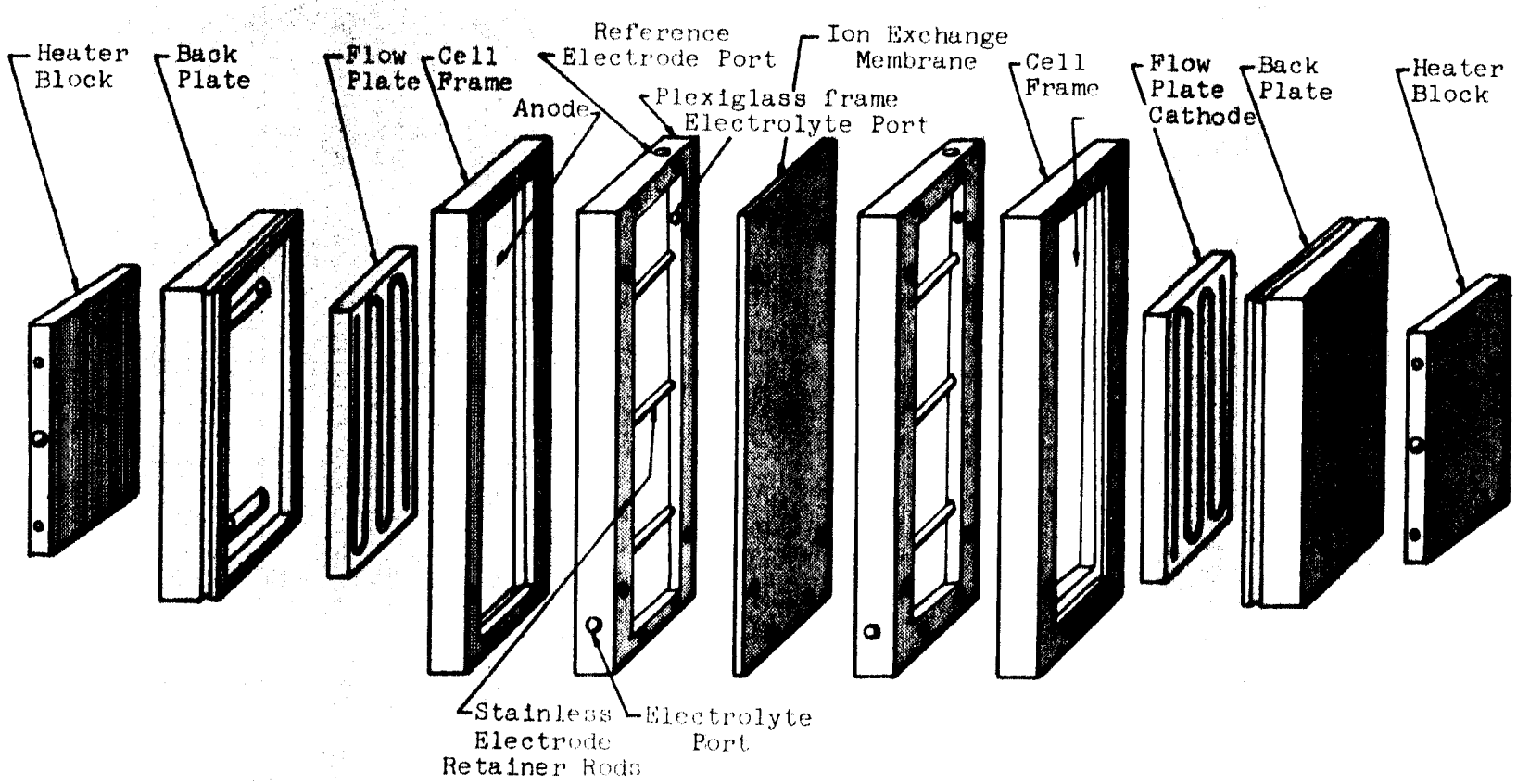


Figure 10. 1/3 Ft^2 Test Cell.

Table 4

INITIAL H_2/O_2 1/3 FT^2 CELL TESTING

Electrodes: MRD-C Carbon/Pt laminar electrodes on stainless steel screen, 40-50 mg Pt/in^2.

Electrolyte: 5M H_3PO_4 or 5M KOH (as noted), pumped through cell (IEM Separation)

Reactants: Tank O_2 and tank H_2 supplied at near atmospheric pressure.

Temperature	Electrolyte	Feed Rate	Current	Electrode Potential, volts vs SHE	
			ASF	Anode	Cathode
60°C	5M H_3PO_4	1 SCFH $H_2 + O_2$	0	0.01	0.99
			30	0.10	0.71
			60	0.18	0.57
			90	0.27	0.46
80°C	5M H_3PO_4	1 SCFH $H_2 + O_2$	0	0.03	0.99
			30	0.10	0.75
			60	0.19	0.16
			90	0.27	0.49
80°C	5M KOH	1 SCFH - H_2 1 SCFH - O_2	0	-0.86	+0.11
			30	-0.84	+0.09
			60	-0.80	-0.24
			90	-0.79	-0.37

Anode performance was reasonably satisfactory at both 60°C and 80°C in both acid and alkaline electrolytes. However, cathode polarization was severe at both temperatures and in both electrolytes. The performance appeared to be independent of O_2 feed rate, and there were indications that IR losses were the major source of polarization. Since the reference electrode was a "Luggin Capillary" the IR losses due to electrolyte resistivity should be quite small. The main resistance must then be in the electrode itself and the current collector on the reverse side of the electrode. This consisted of the electrode support screen and the reactant flow plate, both of which were stainless steel. Several other tests were run that tended to confirm these results. The electrode was removed from the cell and several small (ca. 3 cm^2) sections were tested in a glass half cell using a Kordesch-Marko bridge to obtain IR-free potentials. At 80°C using 5 M H_3PO_4 electrolyte, IR-free potentials of 0.81-0.83 volt vs SHE electrode were obtained at a current equivalent to 90 ASF.

The cell was subsequently rebuilt with the stainless steel electrode screen, the reactant flow plate, and the cell backing plate all gold plated over a nickel plate strike. The test results on this rebuilt cell are shown in Figure 11. The cathode polarization characteristics are much better and confirm the importance of low resistance current collection in a cell of this size. We estimate that the total resistivity of the electrode and current collector combination in the original tests was 14 milliohms. However, at 30 amperes, this resistance will produce 0.4 volt of IR polarization.

C. H_2 HALF CELL TESTING

Using the Au-plated components, the operation of the electrode on H_2 was more fully characterized. The results are summarized in Table 5. In Table 5A the results of testing on tank H_2 at various flow rates are shown. The limiting stoichiometric currents were calculated based on the reaction:

$$H_2 = 2H^+ + 2e^-$$

For this reaction, one standard cubic foot (SCF) of H_2 is equivalent to 62.5 ampere-hours. This 1 SCF per hour (SCFH) will support 62.5 amperes. The results show that the H_2 utilization is near stoichiometric with these electrodes and that polarization will be less than 0.10 volt up to the stoichiometric current.

In Table 5B the results of coupling the Aerozine stream reformer-Pd diffuser combination to the cell are shown. More exact measurements of flow rates and limiting currents were made. These results indicate that the H_2 utilization efficiency was greater than 95% in these tests.

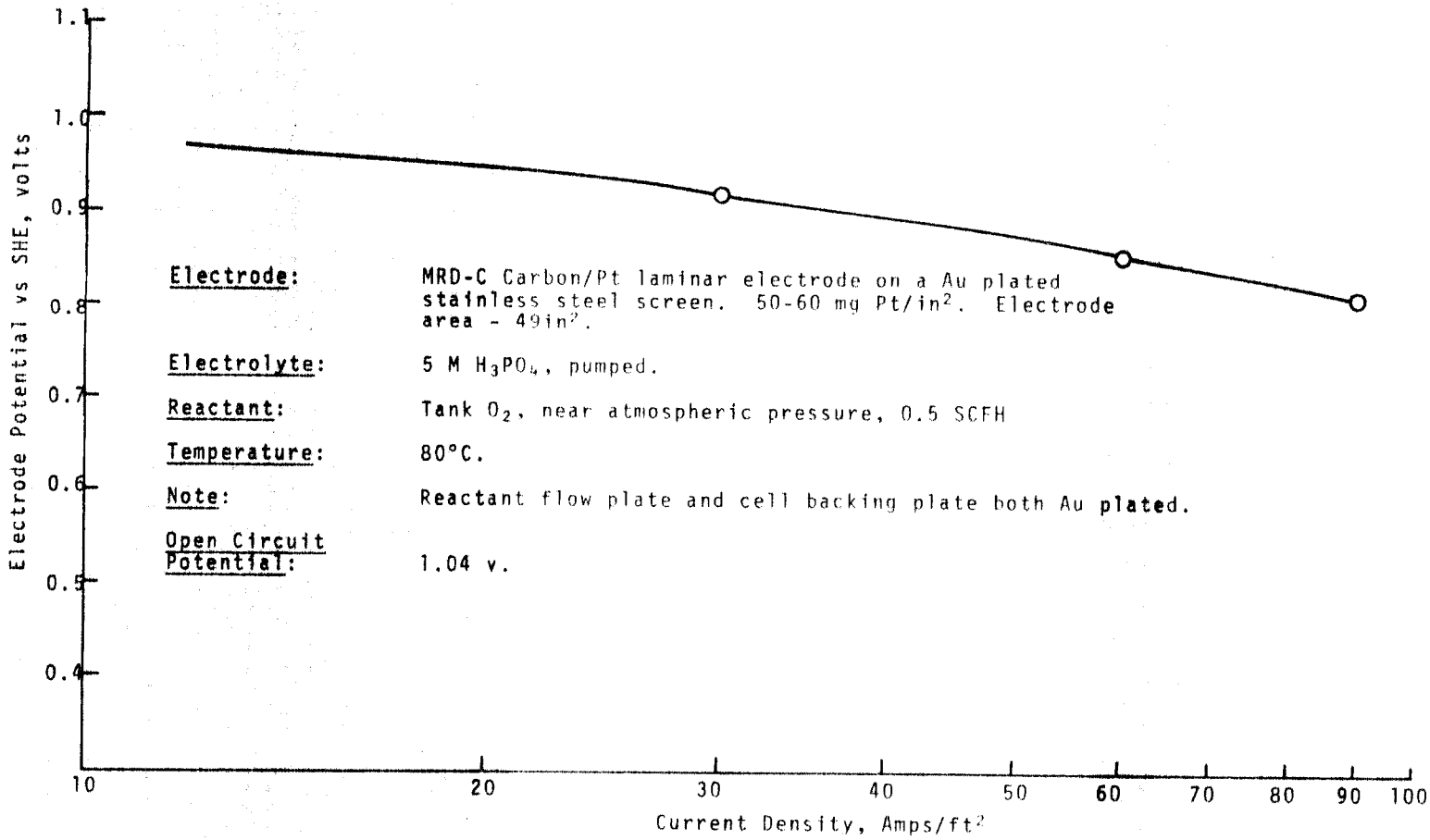


Figure 11. O_2 Cathode Tests With Au Plated Components

Table 5

H_2 HALF CELL TESTS

Electrode: MRD Carbon/Pt laminar, 50 mgPt/in^2 60 mesh s.s. screen Au plated over Ni strike. Electrode Area = 49in^2

Electrolyte: 5 M H_3PO_4, pumped

Temperature: 80°C

A. OPERATION ON TANK H_2

Measured H_2 Flow Rate SCFH	Limiting Stoichiometric Current for This Flow Rate (100% efficiency) Amperes	Electrode Potential, volts vs SHE, at indicated current, Amperes, from 1/3ft^2 Electrode				
		0	10	20	30	40
0.30	19	0.06	0.09	heavy polarization		
0.40	25	0.07	0.10	0.12	heavy polarization	
0.50	31	0.06	0.08	0.10	0.15	----
0.60	38	0.05	0.08	0.10	0.14	----

B. OPERATION ON H_2 FROM REFORMER-PD DIFFUSER COMBINATION

Ultrapure H_2 measured rate: 0.312 SCFH

Amperage Equivalent: 19.4 Amp

Current From* Cell, amperes	Electrode Potential,**Volts to SHE
0	0.05
19	0.10
20	0.10
21	Heavy polarization
20	0.25
19	0.10

* Values in chronological order
** Steady state values after 10 minutes at indicated current.

D. O_2 HALF CELL TESTING

The results of similar testing on tank O_2 are given in Table 6. Although near stoichiometric utilization was realized before heavy polarization occurred, the magnitude of polarization up to this point was generally much higher than was found with H_2. In addition, the values were sometimes difficult to reproduce exactly and it was found that the electrode potential depended to some extent on pretreatment. A period of slow cathodization without O_2 flowing seemed to have a beneficial effect. These results are completely in agreement with the well-documented fact (both in our work and that of others in the field) that a Pt-catalyzed O_2 electrode is not reversible in acid electrolytes. Larger polarizations and difficulty in exact reproduction of data are to be expected.

E. HALF CELL TESTING ON UNSCRUBBED N_2O_4 DECOMPOSER STREAM

The objective of this test was to determine if higher electrochemical utilization of N_2O_4 could be realized by partially decomposing the reactant first. In the previous Quarterly Report the results of testing $1/3 ft^2$ cells on pure N_2O_4 were reported. Coulombic efficiencies of 27% were measured in those tests.

The product stream from the N_2O_4 decomposer was fed directly to the cell through a heated line (to prevent condensation of the unreacted N_2O_4). The results of the subsequent tests are summarized in Table 7. Very unstable electrode potentials were found, there seemed to be a slow cycling of the potential that was independent of current density and reactant feed rate.

This type of behavior had not been found in prior testing with pure N_2O_4. The data are very difficult to interpret and no reliable conclusions can be made about utilization efficiency of this stream.

F. CO-TOLERANT ANODES

If the Aerozine-50 reformer product stream is fed to a fuel cell directly (no Pd membrane diffuser), two gas impurity components must be accommodated: CO_2 and CO. The first requires a CO_2-rejecting electrolyte, either acid or K_2CO_3. Accommodation of CO is much more difficult since it tends to poison the anode catalyst in both acid and alkaline fuel cells. The level of CO in the reformer output is small -- only 0.2-0.3 volume %. However, even this concentration is harmful to the standard carbon/Pt electrode as can be seen from the data in Table 8.

Table 6

O_2 HALF CELL TESTS

Electrode: MRD Carbon/Pt laminar, 50mgPt/in^2 60 mesh s.s. screen Au plated over Ni strike. Electrode Area = 49in^2

Electrolyte: 5 M H_3PO_4, pumped

Temperature: 80°C

Reactant: Tank O_2

Measured O_2 Flow Rate SCFH	Limiting Stoichiometric Current for this Flow Rate (100% efficiency) amperes	Electrode Potential, volts vs SHE, at indicated current, amperes, from 1/3ft^2 Electrode				
		0	10	20	30	40
0.08	10	0.98	0.78	heavy polarization		
0.16	20	0.99	0.79	0.72	heavy polarization	
0.25	31	0.99	0.80	0.74	0.69	heavy polarization

Table 7

HALF CELL TESTS ON UNSCRUBBED
N_2O_4 DECOMPOSER STREAM

Electrode: MRD Carbon/Pt laminar, 50mgPt/in^2 60 mesh s.s. screen Au plated over Ni strike. Electrode Area = 49in^2

Electrolyte: 5 M H_3PO_4, pumped

Temperature: 80°C

Reactant: Product stream from N_2O_4 Decomposer Measured Rates: 0.268 SCFH of gas of composition 67.6% O_2 and 32.4% N_2 (by VPC) plus 4g/hour of unreacted N_2O_4.

Stoichiometric Limiting Currents: For O_2 alone: 23 amps
For total stream: 32 amps

Current From Cell amperes*	Electrode Potential vs SHE** volts
10	0.77 - 0.94
15	0.51 - 0.78
10	0.60 - 0.94
11	0.63 - 0.93
12	0.59 - 0.90
13	0.53 - 0.90
14	0.59 - 0.86
15	0.48 - 0.74
16	0.45 - 0.50

* Chronological order
** Values are lowest and highest potentials recorded during 20-30 minutes at each current.

Table 8

ELECTRODE TESTS WITH CO CONTAINING H_2 STREAMS

Equipment: Glass Half Cell with Luggin Capillary Salt Bridge to Reference Electrode
Cell area: 3.5 cm^2
IR. - Free readings by Kordesch-Marko Bridge.

Electrode: Standard MRD carbon/Pt. on stainless steel screen. 40-50mg Pt/cm^2.

Temperature: 60°C.

Electrolyte: 5M H_3PO_4

Gas Stream	Current Density (ma/cm^2)	IR Free Electrode Potential vs SHE
100% H_2	0	0.00
	50	+0.02
	100	+0.01
	120	+0.02
H_2 containing 0.25% CO (initial readings)	0	+0.04
	50	+0.10
	100	+0.16
	120	+0.18
H_2 containing 0.25% CO (after 15 minutes of exposure)	0	+0.04
	50	+0.23
	100	+0.25
	120	+0.32
H_2 containing 0.5% CO	Open circuit and all readings cathodic.	
100% H_2 after standing in N_2 atmosphere overnight and 20 min flush with H_2	0	0.00
	50	+0.03
	100	+0.03
	120	+0.04

We have tested a highly loaded, all-Pt electrode for this service. The results of these tests are given in Table 9 along with similar test results for other commercially available electrodes. The Chemcell electrode is the best of the commercially available types, but its performance will be marginal at the CO concentrations we expect in the reformer output. In addition, these results could not be duplicated in a retest of a similar electrode with higher Pt loading.

Table 9

ANODE TESTS ON CO CONTAINING H_2 STREAMS

Equipment: 3.5 cm^2 glass half cell with Luggin capillary reference electrode and K-M Bridge Power Supply.

Electrolyte: 5M H_3PO_4

Temperature: 80°C

Current Density: 100ma/cm^2 for all tests

Reactant Supply: H_2 (5% CO) and pure H_2 tank supplies metered through calibrated flow meters and mixed in proper proportions before entering cell. Total flow rate constant for all tests.

Electrode	CO Content of Feed Stream	IR-Free Anode Potential volts to SHE at 100ma/cm^2			
		Initial	15 min	3.0 min	1 hr
MRD Carbon-Pt 40-50 mg Pt/cm^2	0.175%	0.10	0.14	0.39	----
	0.25 %	0.03	0.06	0.28	0.38
Engelhard	0.175%	0.0	0.20	0.30	----
	0.25 %	0.24	0.26	0.27	----
American Cyanamid "LAA" Ta mesh ~60 mg Pt/in^2	0.25 %	0.08	0.10	0.44	----
Chemcel 9 mg Pt/cm^2 on Ta mesh screen	0.175%	0.03	0.04	0.05	0.06
	0.25 %	0.07	----	0.08	0.09
	0.5 %	0.44	0.45	----	----
MRD - high loaded Pt on Stainless Steel Screen 0.84g Pt/in^2	0.175%	0.04	0.05	0.05	----
	0.250%	0.04	0.05	0.06	----
	0.50 %	0.08	0.09	0.09	----

VI. APPENDIX

COMPUTER CALCULATION OF DIFFUSER EFFICIENCIES

The rate of hydrogen removal at any point in the palladium diffuser depends on the hydrogen partial pressure:

$$\text{Rate } (ft^3/hr) = R_H = C_o \, P_{H_2}^{0.85} \quad \text{P is in psig.}$$

By dividing the diffuser length into a large number of short sections, we can approximately calculate the partial pressure in each section, knowing the amount of hydrogen removed in the previous section, the volume passing through the section in ft^3/hr, and the total pressure of the reactor in psia.

Thus at any section:

$$\text{Hydrogen removed} = \frac{\text{Rate of removal per foot of palladium}}{\text{No. of sections}}$$

$$\text{and rate of removal per foot} = R_H = C_o \, P_{H_2}^{0.85}$$

$$= C_o \left(\frac{H_2 \text{ Remaining x Total Pressure in Psia}}{\text{Total Gas}} - 14.7 \text{ psia} \right)^{.85}$$

Then H_2 remaining = H_2 entering previous section - H_2 removed by previous section

and total gas = total gas entering previous section - H_2 removed in previous section

Thus we add the H_2 removed in each section for the total removal rate per unit. As the number of sections used increases, the accuracy of the calculation increases. It was found by testing on the computer, that the difference between 100 and 200 sections was less than 0.1%.

The following program allows calculated results for 2 units in series, by changing the output of the first unit to the input of the second unit.

The input variables are:

XPTOT = Total pressure, psia
GTOT = Total gas rate input, ft^3/hr
XH2I = Initial H_2 rate, ft^3/hr, to diffuser
XINCR = No. of sections

The output variables (lines 118 and 129)

XHR = H_2 remaining in output stream, ft /hr
GFIN = Final output rate, ft^3/hr
XH2P = Pure H_2 output rate, ft^3/hr
EFF = Efficiency for that unit
XH2PT = Total output H_2 rate for both units
EFFT = Total efficiency

RH **is the hydrogen removal rate.**

```
101. =      CF    PROGRAM H2PURE
102. =      CF    READ 0,XPTOT,GTOT,XH21,XINCR
103. =            J=0
104. =          5 K=0
105. =            XH2P=0
106. =            DO 10 I=1,200
107. =            K=K+1
108. =            XHR=XH21-XH2P
109. =            RH=.01296*(XHR*XPTOT/(GTOT-XH2P)-14.7)**.85
110. =            RH=RH/XINCR
111. =            XH2P=XH2P+RH
112. =            XK=K
113. =            IF(XINCR-XK)10,20,10
114. =         10 CONTINUE
115. =         20 XHR=XH21-XH2P
116. =            GFIN=GTOT-XH2P
117. =            EFF=XH2P/XH21
118. =      CF    PRINT 0,XHR,GFIN,XH2P,EFF
119. =            J=J+1
120. =            IF(J-2)25,30,25
121. =         25 XH211=XH21
122. =            XH2P1=XH2P
123. =            GTOT=GFIN
124. =            XH21=XHR
125. =            GO TO 5
126. =         30 CONTINUE
127. =            XH2PT=XH2P+XH2P1
128. =            EFFT=XH2PT/XH211
129. =      CF    PRINT 0,XH2PT,EFFT
130. =            END
```

Experimentally, it would be simpler to put the reformer output stream, containing all components, including water, directly into the diffuser. This would also eliminate CO production at the expense of H_2 and deter carbon formation.

Therefore, the diffuser efficiency was calculated,leaving the excess water from the steam reformer in the composition of the input gas. This causes the percentage of H_2 in this gas to be lowered to 50% from the value of 67.5% which would correspond to a "dry" input. The total gas input rate is increased by 50%. Both changes combine to reduce the efficiency of the diffuser from 66% to 48% for a single stage, and from 91% to 79% for two units in series. Under the same input conditions, if the

diffuser pressure were increased to 150 psig, a single unit would be 60% efficient, and two units, in series or parallel, would be 85% efficient.

The experimental data approximate the computer calculated data reasonably well. Thus, later scale-up optimization can be readily determined.