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J. Weissbart and W. H. Smart

SECOND ANNUAL REPORT
May 1970

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
AMES RESEARCH CENTER
Moffett Field, California 94035

Prepared Under Contract NAS2-4843

APPLIED ELECTROCHEMISTRY INC.
2425 Leghorn Street
Mountain View, California 94040

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FOREWORD

The research and development work reported here was performed at Applied Electrochemistry Incorporated, Mountain View, California, from April 1, 1969 to March 31, 1970, under Contract NAS2-4843. The work was carried out by Dr. J. Weissbart, Dr. W. H. Smart, who were the principal investigators, Mr. C. M. McCullough, Mr. S. A. Ring, and Mrs. Maria Roja. The project was under the overall direction of Dr. Weissbart. The technical monitor was Dr. T. Wydeven, Environmental Control Research Branch, NASA Ames Research Center, Moffett Field, California.

Distribution of this report is provided in the interest of information exchange. Responsibility for the contents resides in the authors and organization that prepared it.

ABSTRACT

Development of an aerospace life-support system for oxygen production from CO_2 proceeded successfully from the 12-ampere to the 127-ampere (one-man) level during this program period. The system consisting of a 127-ampere three-module CO_2-H_2O solid oxide electrolyte electrolyzer at 880°C and CO-disproportionation reactor at 556°C was tested and operated continuously beyond 250 hours. The unit generated oxygen at a rate of 481 ml/min with a faradaic current efficiency near 100% and an average CO_2 content of only 2.4%. The CO_2 was converted in the electrolyzer to 53% CO, and one-third of this CO was disproportionated in the reactor to carbon and CO_2. Each module, rated at 48 amperes and operated at 42 amperes at a current density of 175 mA/cm^2, contained twelve cells arranged as six two-cell drums.

Each drum consisted of two electrolyte disks, each having 20 cm^2 electrodes, sealed to a 6.3 cm diameter zirconia-calcia ring body. Disks were made from hot-pressed compacts of scandia-stabilized zirconia and the disk thickness was in the range 0.08 to 0.22 cm. Forty-eight compacts, 255 disks, and 48 drums of this type were made. Electrolyzer modules were assembled by connecting drums to alumina manifold tubes by means of metal gas-feed tubulations. Modules incorporated parallel gas flow through the drums and series electrical connection between the cells. Application of an improved disk-to-body sealing method, the edge seal, combined with previously perfected current-lead and metal tube seals through the drum body, yielded 25 gas-tight drums out of the 26 attempted of this type. Room-temperature tests for gas-tightness of seals were developed which gave a useful correlation with high-temperature behavior for both single drums and multi-drum modules. A test electrolyzer having one edge-sealed drum was operated at eight amperes (four amperes per cell, 200 mA/cm^2) and 100% faradaic current efficiency to electrolyze CO_2 with the production of CO_2-free oxygen (<0.01% CO_2) for more than 30 days. These results show that the high-temperature sealing process has been developed to a level equal to, or higher than, that of the other technologies required for construction and operation of CO_2 electrolyzers for life-support systems.

Fabrication of interchangeable components of this design, room-temperature testing, and maintaining an inventory in preparation for assembly has raised the present state of solid oxide device technology from the laboratory to the prototype stage for production of one-man electrolyzer-reactor systems.

CONTENTS

ILLUSTRATIONS

TABLES

Section 1

INTRODUCTION

The main purpose of the work during the past contract year was to scale the size of CO_2-H_2O electrolyzers based on solid oxide electrolytes for oxygen generation for aerospace life support to the the one-man capacity level (127 A) from the one-tenth man level (12 A) of the preceding year. A 250-hr operational test of the one-man electrolyzer coupled to a catalytic reactor of equivalent capacity for disproportionation of the CO produced by electrolyzing CO_2, saturated with H_2O at room temperature, was required. A supporting research effort was called for, in addition to the electrolyzer and reactor fabrication program, to improve the quality of components of the electrolyzer and reactor system and to develop further solid oxide device technology and operational reliability.

Experience with 12-A electrolyzers during the year preceding this one and improvement of fabrication methods for making components and assembling multi-cell high-temperature electrolyzers led to a modification of design. The modules of the one-man unit retained the basic design features of the 12-A units as regards the electrolyte configuration, electrical series connections, parallel gas flow, and other significant parameters, but differed in body shape, sealing configuration, manifold design, and materials of construction. The superiority which was expected for the new design with respect to the old was borne out in the course of CO_2-H_2O electrolysis at ~850°C with electrolyzers of both types and of comparable capacities.

The fabrication procedure for the 127-A electrolyzer involves a number of technologies, among which are hot pressing of ceramics, diamond machining, electroplating, and making ceramic-to-ceramic and ceramic-to-metal seals which remain gas-tight on prolonged exposure to both oxidizing and reducing atmospheres at ~850°C. Although modifications and improvements were made in each of these areas in the past contract year, the most significant advances occurred in the high-temperature sealing area. The work described in this report has brought these seals to a level of performance equal to, or higher than, that of the electrodes, electrolyte, and other electrolyzer components.

A steel pipe catalytic reactor similar to the type used the preceding year with the 12-A units was used to deposit carbon from the CO effluent of the one-man, 127-A CO_2-H_2O electrolyzer. Inasmuch as the technology of catalytic reactors is well developed by comparison with high-temperature solid oxide electrolysis technology, relatively little technical effort was devoted to reactor improvement and scale-up. Operational data for the reactor were obtained as part of the testing of the one-man integrated CO_2-H_2O electrolyzer-reactor system.

A meaningful correlation between room-temperature test results of the gas-tightness of the various required seals and the operational results on working units at the operating temperature of ~850°C has been achieved during this year. This has required further development of the room-temperature testing procedures. The room-temperature test of components for gas-tightness has become an invaluable aid in the preparation and inventory of components for final assembly. The seals of a two-cell electrolyzer were found to be gas-tight at room temperature and tested out gas-tight by gas chromatographic analysis of the CO_2 content in the oxygen stream produced by CO_2 electrolysis at 870°C. The room-temperature tests of the three 42-A modules of the one-man CO_2 electrolyzer also correlated well with the high-temperature operational results.

The attainment of the primary goal of this year's effort on the project—the development of operational hardware at the one-man level—has been amply demonstrated by the design, construction, testing, and operation of a 127-A capacity CO_2-H_2O electrolyzer/CO disproportionation reactor system. The problem of assembling solid oxide electrolyte cells (ceramic disks) into gas-tight multi-cell electrolyzer modules of at least 48-A capacity has been solved.

Section 2

TWELVE AMPERE UNIT OF SQUARE DESIGN (NUMBER Z-4)

2.1 INTRODUCTION

Details of the design, construction, and preliminary testing of the 12-A electrolysis unit have been presented in the First Annual Report (Ref. 1). Subsequent life testing of the CO_2-H_2O electrolysis unit carried out separately and in conjunction with an integrated carbon deposition reactor are described below.

The 12-A unit consisted of three cells connected electrically in series and incorporated a parallel gas flow arrangement to the electrode chambers. Each cell was made up of an electrolyte disk of zirconia-scandia and a square cell body of zirconia-calcia having internal manifolds. The disk-to-body and body-to-body seals were made with gold and gold-palladium alloys. The individual cells each had a platinum electrode area of 20 cm^2.

Electrolytic oxygen transfer experiments were first undertaken for several days with a variation of current from 1 to 4 A. Electrolysis of carbon dioxide to generate oxygen was carried out with tank carbon dioxide flowing at 165 ml/min. The carbon dioxide was passed through a water saturator at ambient temperature before entering the cathode chambers of the electrolyzer. The initial CO_2-H_2O electrolysis experiments were made at 820°C and with a variation of current from 1 to 4 A. Electrical operating parameters obtained from the CO_2-H_2O electrolysis and the electrolytic oxygen transfer experiments could then be compared under similar operating conditions (Ref. 1).

2.2 LIFE TEST

Life testing under conditions of CO_2-H_2O electrolysis was carried out in the 12-A unit at 820°C and 4 A (200 mA/cm^2) for a period of eleven days. The temperature of the electrolyzer was then raised to 870°C and the electrolysis of CO_2 was carried out with the carbon deposition reactor connected into the system as shown schematically in Fig. 2-1. The reactor vessel, a steel pipe whose walls acted as the catalyst for the disproportionation of CO to C and CO_2, was operated at 565°C. During the next sixteen days, the CO-CO_2 mixture from the cathode chambers of the electrolyzer flowed through the carbon deposition reactor and the resultant CO-CO_2 stream was vented to the atmosphere. CO_2 electrolysis proceeded for approximately 28 days (~670 hr) before it was interrupted by a furnace failure on the 29th day of operation. The electrical performance data for the 28-day life test is presented in Tables 2-1 and 2-2. Very little electrical degradation (i.e., rise in total applied voltage) occurred over the period of the life test. After correction for the IR drop in the lead wires, the variation in degradation from cell to cell for each of the three 20 cm^2 cells is approximately equal.

Analyses of the CO-CO_2 gas stream leaving the electrolyzer, the CO-CO_2 gas stream leaving the reactor, and the oxygen gas stream from the electrolyzer anode chambers were made by means of gas chromatography. Aliquots of the gas samples obtained from the gas stream by means of a gas-tight syringe were injected into the gas chromatographic apparatus.

The analysis of the carbon dioxide gas stream from the electrolyzer during the initial period of the life test contained about 40 to 43 volume% carbon monoxide. A theoretical yield would have resulted in carbon monoxide concentration of about 55 volume%. The gas content of the oxygen compartment of the electrolyzer was found to contain 10 to 15% carbon dioxide. These results correspond to a leak rate of carbon monoxide and carbon dioxide of about 5 ml/min. Under these experimental conditions, an analysis of the CO-CO_2 gas stream leaving the carbon deposition reactor indicated a carbon monoxide conversion rate to carbon dioxide of about 25%. A higher catalytic efficiency may be obtained by increasing the carbon monoxide content of the feed stream to the reactor. Before termination of the life test, the CO-CO_2 gas stream leaving the electrolyzer contained about 37% CO. The CO_2 content of the oxygen was about 20%. Examination of the reactor indicated packed carbon near the wall and fluffy carbon near the center of the tube. Variation in carbon appearance may be due to variation in crystallinity depending on its iron content and the H_2 content in the gas stream as discussed by Walker et al. (Ref. 3).

Examination of the 12-A electrolyzer showed leaks in the body-to-body seal region. Leaks were also found emanating from several hairline cracks in the cell body walls. No quantitative analysis was made of the carbon collected in the reactor during the life test.

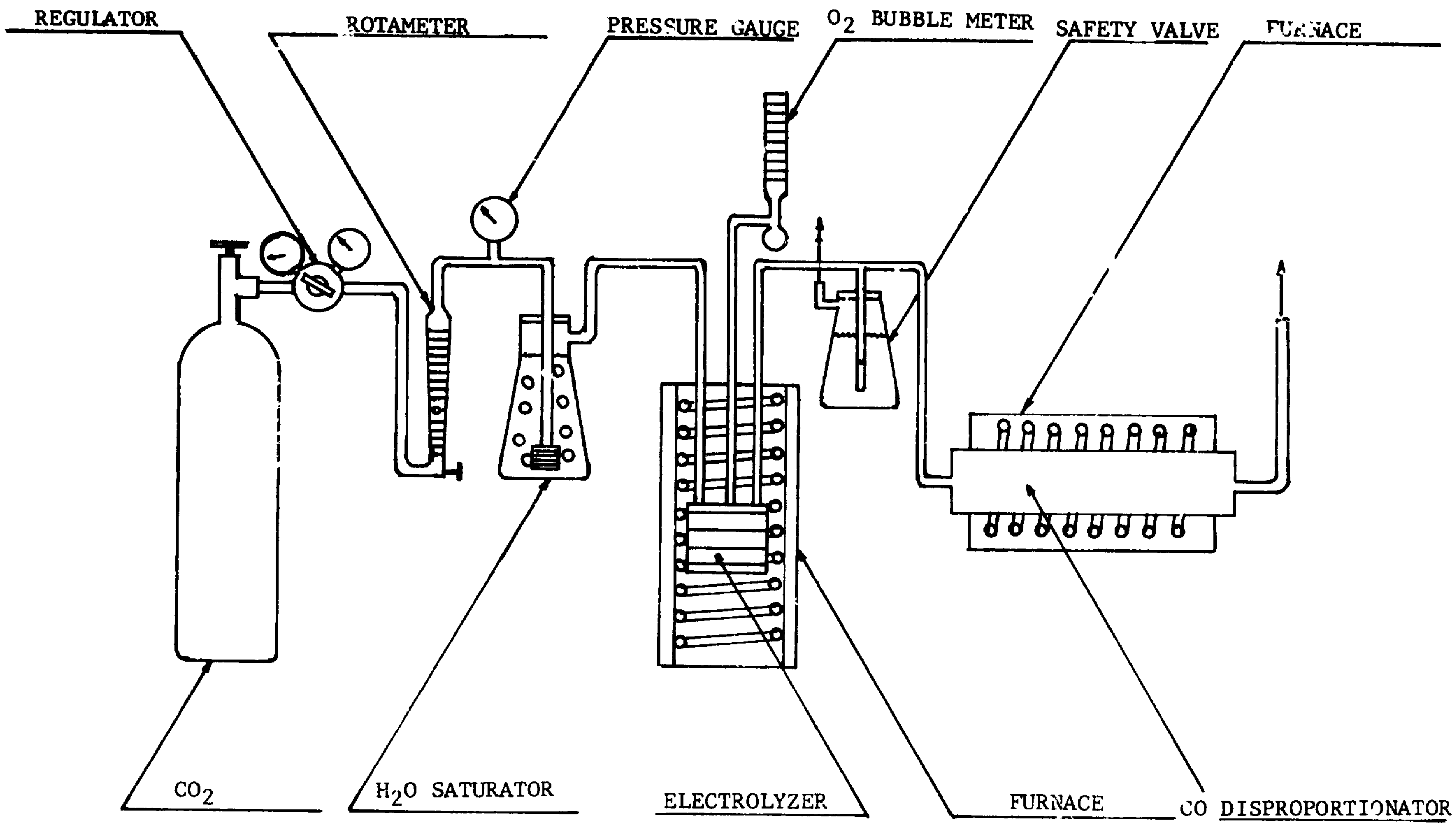

Fig. 2-1 Schematic Diagram of Electrolyzer and Reactor

Table 2-1

ELECTROLYZER PERFORMANCE DATA[a]

Test Days	Current (I)	APPLIED VOLTAGE[b] (V)			
		Total	Cell 4	Cell 5	Cell 6
1	3.00	6.73			
2	4.00	7.23[c]			
3	4.00	6.68			
4	4.00	6.78			
5	4.00	6.78			
5	0-10 min[d]				
5	4.00	5.64			
6	4.00	5.78	2.06	1.83	2.01
7	4.00	5.85			
8	4.00	6.01			
8-9	0-24 hr[d]				
9	4.00	7.41[c]	2.66	2.35	2.47
10-11	4.00				
12	4.00	6.03	2.09	1.90	2.12

[a] Electrolyzer at 820°C

[b] Not corrected for IR drop in the lead wire resistance

[c] Voltage on start-up

[d] Current interruption

Table 2-2

PERFORMANCE DATA ON 12-A ELECTROLYZER INTEGRATED WITH CARBON DEPOSITION REACTOR[a]

Test Days	Current (I)	APPLIED VOLTAGE[b] (V)			
		Total	Cell 4	Cell 5	Cell 6
12	4.00	5.49	1.93	1.70	1.93
12	0-1 hr[c]				
13	4.00	6.94	2.14	2.26	2.61
14	4.00				
15	4.00	6.39	1.98	2.08	2.39
16	4.00	6.25			
17	4.00	6.40			
18	4.00				
19	4.00	6.60	2.08	2.06	2.54
20	4.00	6.78			
21	4.00	6.88			
22-27	4.00				
28	4.00	6.99	2.07	2.39	2.68

[a] Electrolyzer at 875°C, carbon deposition reactor at 565°C

[b] Not corrected for IR drop in the lead wire resistance

[c] Current interruption

Section 3

DESIGN

3.1 ELECTROLYZER OF ONE-MAN CAPACITY (127 A)

Based on the experience of fabricating and testing the 12-A electrolyzers described in the First Annual Report (Ref. 1) and in Section 2 above, the design was modified to improve ease of fabrication and operating performance of modules for the one-man unit. The basic design principles that have guided this work remain unaltered and can be summarized as follows:

(1) The ceramic electrolyte is in the form of a disk or plate for ease of fabrication and electrode processing.

(2) The electrolyte is a separate component from the cell body segment and does not provide structural support other than for electrodes.

(3) There is accessibility and interchangeability of anode and cathode surfaces for the fabrication of flat, porous electrodes.

(4) The seals are high-temperature, gas-tight, ceramic-to-ceramic or metal-to-ceramic.

(5) The cells are connected in series electrically obviating high-current conductors and minimizing heat losses due to conduction.

(6) Shunt currents are avoided by proper separation of cell elements in multi-cell modules.

(7) The gas flow to the cells is in parallel to maintain uniform gas composition in each cell preventing preferential chemical reduction and electronic conduction paths in the electrolyte.

(8) Structural components have compositions which are essentially unrelated to the composition of the electrolyte disks, but which are thermally and mechanically compatible.

(9) Individual cells or multi-cell sub-assemblies can be tested before final assembly.

(10) The number of cells can be increased without major design changes.

(11) The size of cells can be increased without major design changes.

(12) External area-to-volume ratio is controlled to reduce heat losses via radiation.

(13) Electrolyte disks can be modified by composition, thickness, or be replaced by thin supported films without requiring major design modifications.

The one-man capacity (127-A) electrolyzer consists of three modules of the design shown in Fig. 3-1. Each module contains twelve cells of 20 cm^2 active electrode area arranged as six sub-modules of two cells each. This sub-module, called a "drum", constitutes the basic building block of the electrolyzer. A drum in which the electrolyte disk is sealed to the body in a configuration termed a "butt" seal is shown in Fig. 3-2.

Carbon dioxide is fed to the solid oxide cells through the ceramic inlet manifold and metal inlet tubulations on each drum and the outlet CO-CO_2 mixture flows through the outlet metal tubes and ceramic manifold. Oxygen is produced at the external electrodes of each drum and is contained within the ceramic envelope in which the drums are enclosed. The twelve cells of each one-third man module are connected in series electrically and operated at 3.5 A per cell or 42 A per module.

Design parameters for the one-man electrolyzer are as follows:

O_2 mass output	two pounds per day or 907 g/day
Total current	127 A
O_2 volume flow	693 l/day (25°C, 1 atm) or 481 ml/min (25°C, 1 atm)
CO_2 consumed	962 ml/min (25°C,1 atm)

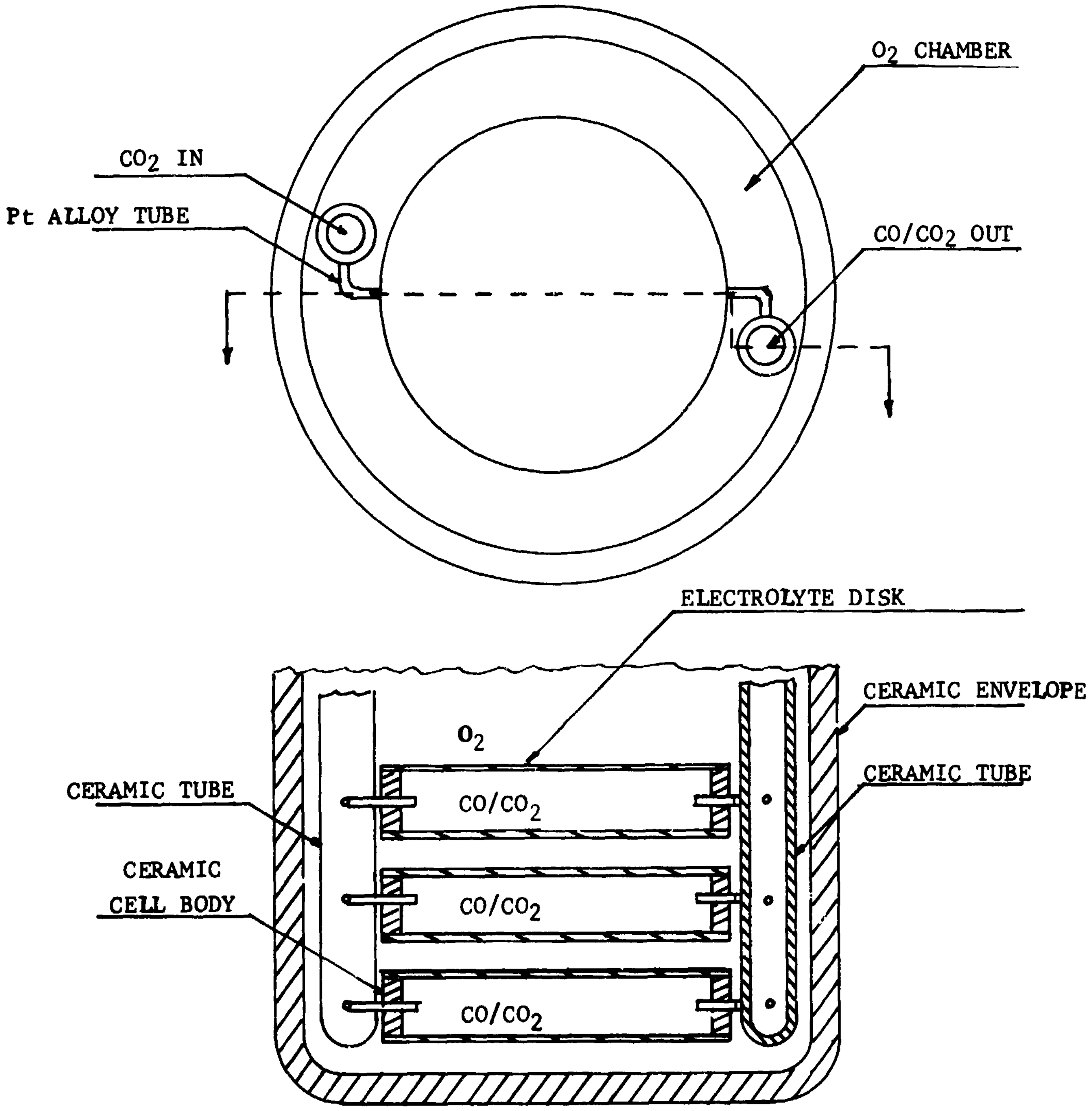

Fig. 3-1 Electrolyzer with External Manifolds and Envelope

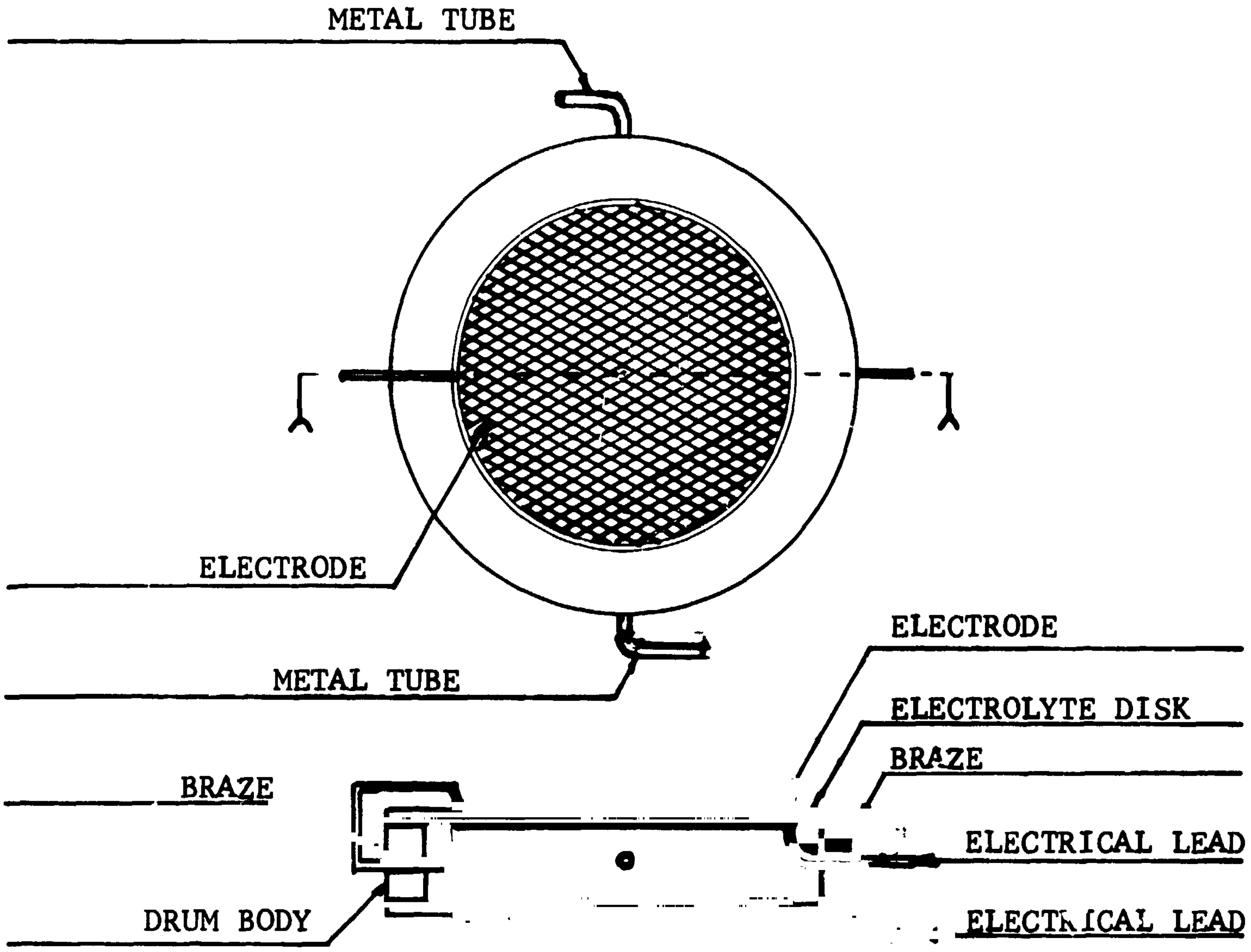

Fig. 3-2 Drum with Butt Seals

Design conversion of CO_2	0.5 to 0.9 (i.e., 50 to 90% CO in cathode exit gas)
Gas flow rates at 25°C, 1 atm are	
CO_2 inflow	1,924 to 1,070 ml/min
CO outflow	962 ml/min
CO_2 outflow	962 to 107 ml/min
O_2 outflow	481 ml/min
Design operating temperature	850°C
Gas flow rates at 850°C, 1 atm are	
CO_2 inflow	7,250 to 4,040 ml/min
CO outflow	3,630 ml/min
CO_2 outflow	3,630 to 404 ml/min
O_2 outflow	1,820 ml/min
Electrolyte disk	6.3 cm diameter
Electrode area per disk	20 cm^2
Current density	175 mA/cm^2
Amperes per disk	3.5 A
Number of disks	36
Theoretical power	~127 watts
Design electrolysis power efficiency	>0.5
Design electrolysis power	190 to 250 watts
Design current efficiency	~1
Estimated mass of electrolyzer and gas manifold tubes	2.3 to 5.5 kg
Disk composition	scandia-stabilized zirconia

Composition of other ceramic parts	alumina and zirconia
Electrode material	platinum
Electrolyte thickness	0.15 ± 0.07 cm
Radius of gas tube bends	0.45 cm
Gas tube o.d.	0.18 cm
Gas tube i.d.	0.10 cm
Gas tube length	2.54 cm
Manifold i.d. x wall	0.63 cm x 0.15 cm

3.2 APPLICATION TO LARGER UNITS

Solid oxide electrolyte units employing two-cell drums need not follow the exact design discussed above for the one-man unit. A number of variations are possible which might be advantageous for future work with units larger than one-man capacity. Several such modifications are presented here as examples of the flexibility of design which the drum permits.

Fig. 3-3 shows an electrolyzer consisting of a stack of drums with four gas manifolds. This design does not require an envelope and it is symmetrical with respect to the cathode and anode gas chambers. These properties might have advantages in some applications.

If the drums were operated with the inside as the oxygen chamber, only one gas tube per drum, rather than two, would be required. A design such as that shown in Fig. 3-4 would then be possible. It would be desirable to introduce the entering CO_2 under sufficiently turbulent flow conditions to prevent starving the cathodes. A gas sparging system (not shown in the figure) and high packing density of drums in the envelope would help in creating this flow condition.

Fig. 3-5 shows a further design modification in which some of the drums with the oxygen chambers on the inside are connected together simplifying the oxygen outlet manifold. Introduction of the CO_2 to the cathodes and removal of the CO would present the same problem as mentioned above.

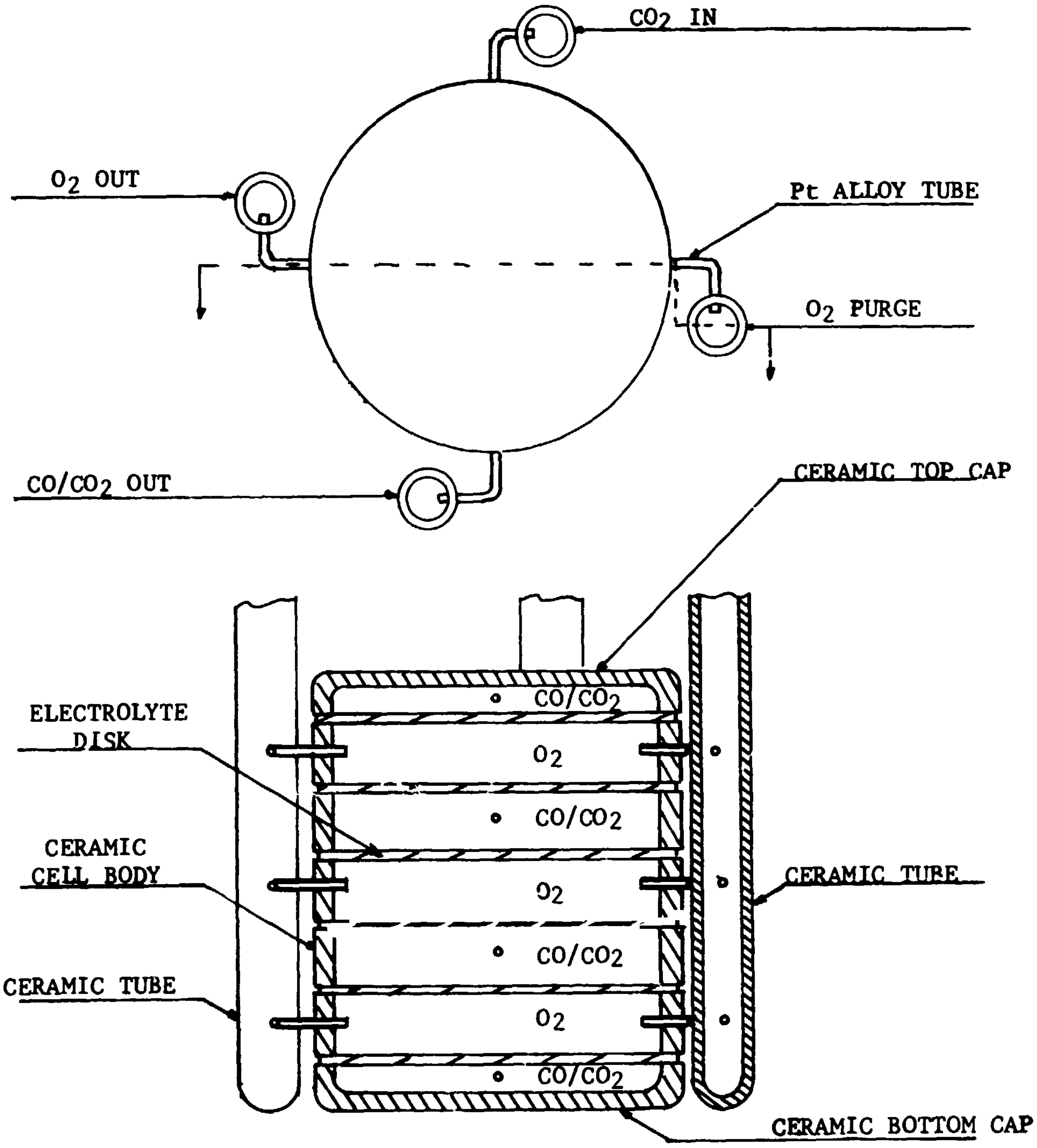

Fig. 3-3 Electrolyzer with Four Gas Manifolds

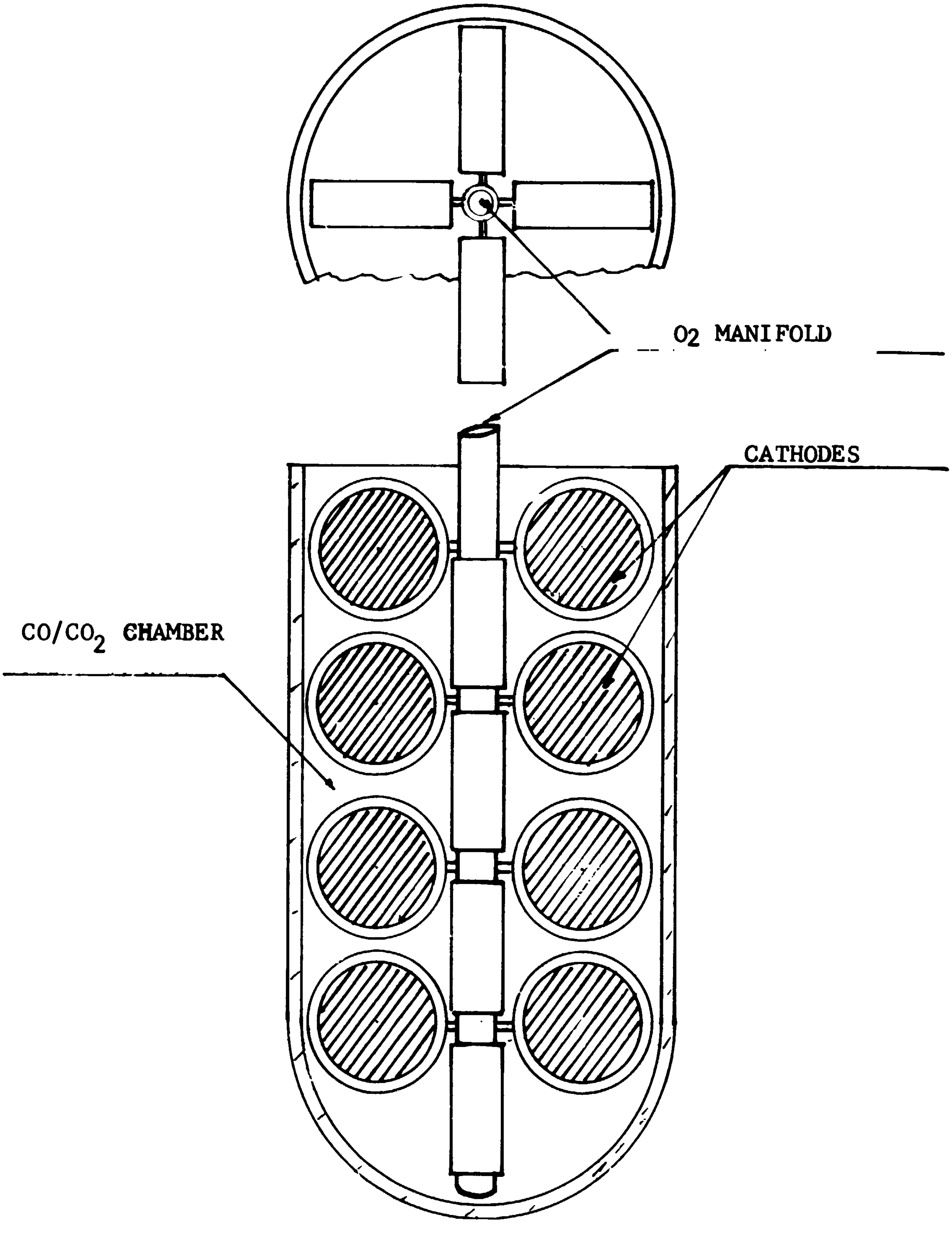

Fig. 3-4 Electrolyzer Using Drums with Internal Oxygen Chambers

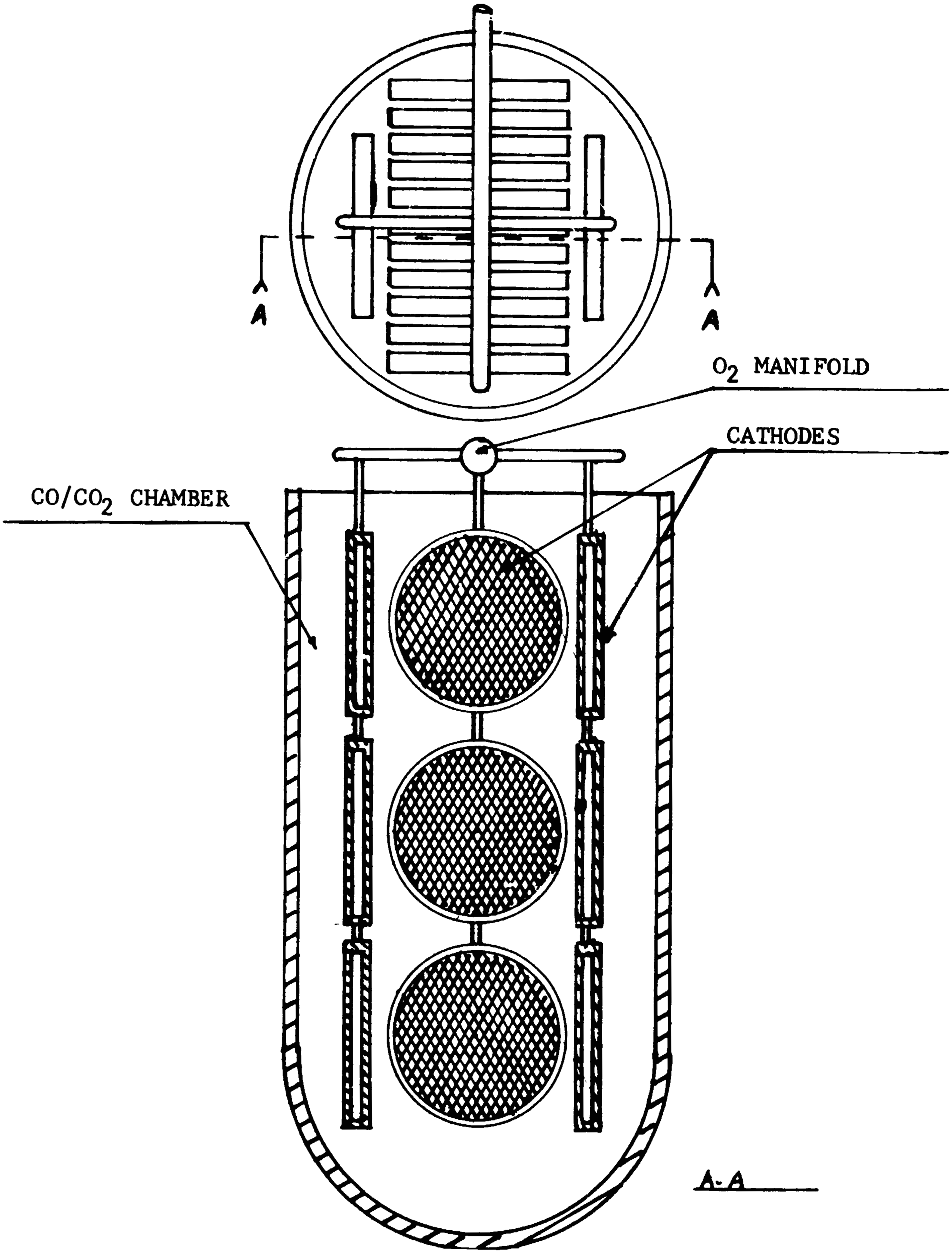

Fig. 3-5 Electrolyzer with Interconnected Drums

In the six-drum, twelve-cell modules for the one-man unit, equality of gas flow through the cathode chambers depends upon the small metal tubes all having the same inside diameters, lengths, and being free of burrs or other obstructions. Great care is exercised during the fabrication steps to insure that these conditions are met. In larger modules in the future, however, it would be more convenient to be able to add or remove drums and to set the gas flow through each drum individually by means other than reliance on the gas channels being identical to high precision. These aims could be achieved by substituting torch brazing at room temperature for the furnace brazing step now used for final assembly of an electrolysis module. Any of the electrolyzer designs based on drums discussed here or in earlier reports could be assembled by torch brazing using small metal fittings of the types shown in Fig. 3-6. These parts are essentially small versions of conventional plumbing fittings. Adjustment of gas flow could be done by crimping the tube slightly while measuring the flow rate or by using specially-designed fittings torch brazed between the drum tubulations and the manifolds.

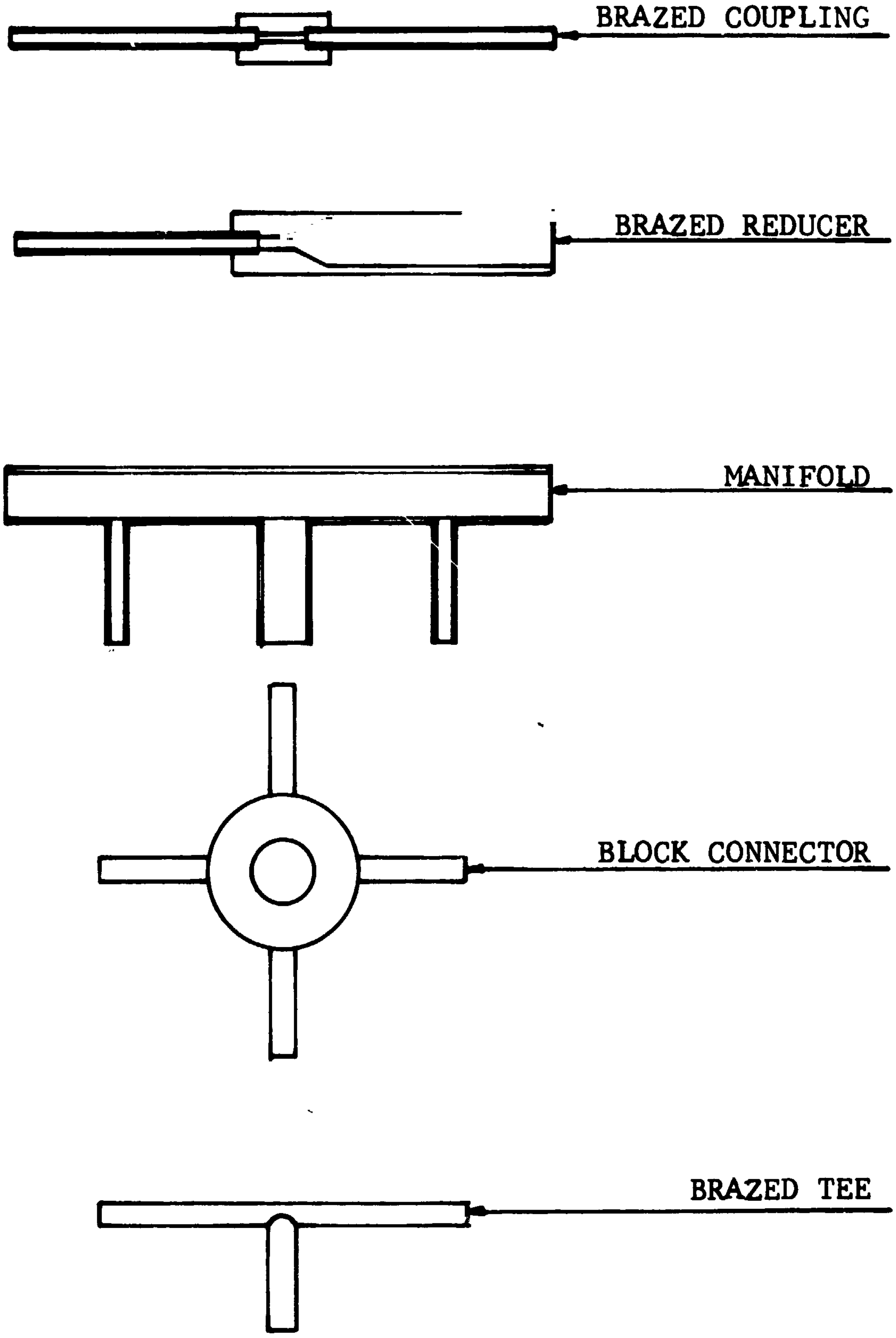

Fig. 3-6 Brazed Tube Fittings

Section 4

HIGH-TEMPERATURE CERAMIC SEALS

4.1 PROCEDURE

Fabrication of drums, their assembly to make electrolysis modules of the design presented in the preceding section, and their operation requires the use of ceramic-to-ceramic and ceramic-to-metal sealing methods capable of producing seals that remain gas-tight at 850°C under both oxidizing and reducing conditions for prolonged periods. The sealing procedure used during the first year of this contract (Ref. 1) was developed further to meet these requirements. The only sealing geometry that presented a serious problem was the seal at the periphery of the 6.3 cm diameter electrolyte disk and a series of sealing experiments involving variations in the basic sealing procedure was necessary to solve this problem.

The basic sealing procedure can be described as follows:

> Fabrication of Components - Although not strictly a part of the sealing procedure, the processes used in making the parts to be sealed significantly affect the seals subsequently made with them. For example, processes involving high temperature and pressure during fabrication of the ceramics themselves determine the density, grain size, degree of homogeneity, and chemical composition. These factors will influence the surface finish obtained during later machining and polishing steps and will affect the adhesion of the metallization applied as part of the seal. Machining and abrasive grinding affects the seal, additionally, by determining the precision to which the parts fit together and the evenness of the mating surfaces. For these reasons, an experimental approach to improving the seals cannot ignore the ceramic processing and machining operations used to make the components.
>
> Abrasive Polishing - The surfaces to be sealed together are ground and polished to improve mechanical fit and to prepare them for metallizing. Bonded diamond tools, diamond pastes, and silicon carbide papers are used. Washing or solvent cleaning, depending on the abrasive system, is used to remove dirt resulting from the polishing steps.

Masking - Areas that are not intended to be metallized are masked with plater's tape or stop-off lacquer.

Cleaning - The parts are cleaned in non-abrasive alkaline cleaning solutions.

Sensitizing - The unmasked surfaces are prepared for electroplating by depositing a very thin precious metal film by chemical reduction. Both platinum and palladium have been used. Sodium borohydride and hydrazine have been used as the reducing agents.

Electroplating - The sensitized areas are electroplated with platinum to prepare them for the brazing operation. Deposit thicknesses in the range 2 to 30 microns (0.08 to 1.2 mils) have been used.

Brazing - The metallized surfaces are joined by furnace brazing with precious metals or precious metal alloys melting above the operating temperature of the electrolyzer. Several furnace brazing operations are necessary during assembly of an electrolysis module, the number depending upon the design of the module.

4.2 SEALING EXPERIMENTS

4.2.1 Disk-to-Body Seals

Seventy-eight drums using 6.3 cm diameter electrolyte disks were made by the general sealing procedure outlined in subsection 4.1 above using either gold or 1150°C gold-palladium alloy braze. The first thirty drums can be considered as preliminary experiments since most of them had neither electrodes, electrical leads, nor one of the two gas tubulations and were made solely to develop the disk-to-body sealing technique. The other forty-eight drums were made after significant improvement in performance of the seals had been obtained during the preliminary experiments. These drums had electrodes, electrical leads, and gas tubulations and they were considered as potential components of the one-man unit. The drums actually used in the one-man unit were selected from this set. It is convenient to discuss separately the preliminary series of forty-eight drums which, although experimental, were made to be potential electrolyzer components.

Preliminary Experiments Although the basic sealing procedure described in the preceding sub-section was used to fabricate these drums, there were many variations between individual runs as a result of the following factors:

(1) Intentional variations were made in an effort to improve the seals.

(2) Unintentional variations undoubtedly occurred as a result of a lack of understanding, at that stage of the program, of the relative importance of all of the many parameters involved.

(3) There were unavoidable variations in the raw materials, such as chemicals, ceramic parts, metals, and tooling. Every effort was made to control factors thought to be of primary importance to seal quality, but unknown important factors might have been neglected.

(4) Variations occurred over time as a result of experience with the process, wear of tooling, and cumulative changes in the chemical composition of plating baths and other solutions.

These thirty drum experiments can be grouped into three categories according to the extent of intentional modifications in the sealing procedure. The selection of the three groups depends on increased sealing experience with time and for this reason the groups are essentially chronological. The three groups can be described as follows:

Group 1 - This group contains all gold and gold-palladium alloy 6.3 cm diameter disk seals through drum number F-84. All of these drums contained butt seals (see Fig. 3-2 above). No particular attention was given to the grinding and polishing steps, all were heavily palladium sensitized, and the furnace brazing procedure was relatively unstandardized at that time. Most of these drums were made before the testing method now in use had been adopted but they were leaky in the soap solution test and would therefore definitely fail to meet the criteria of the present test. The present "$\Delta t/\Delta p$ test" is discussed in Section 7 below.

Group 2 - This group contains all gold seals to 6.3 cm diameter disks after F-84 through F-111. No alloy seals were made during this period. Some attention was given to modifying and controlling the grinding and polishing steps. All were lightly palladium sensitized. The present $\Delta t/\Delta p$ test procedure was used to leak test all of these drums. One drum was of a different sealing configuration, termed a "valve" seal, shown in Fig. 4-1.

Group 3 - This group contains all gold seals to 6.3 cm diameter disks after F-111 through F-122. No alloy seals were made during the period. Variations were made in the grinding and polishing steps. All were lightly platinum sensitized. The present $\Delta t/\Delta p$ test procedure was used to leak test all of these drums. Two drums were made with valve seals.

The results of the sealing runs are summarized in Table 4-1. The data in the table illustrate that the modifications that were made during these sealing experiments improved the quality of the seals as determined by meeting the two-minute $\Delta t/\Delta p$ test criterion after one thermocycle. The test and thermocycle procedures are described in Section 7 below.

Since the disk-to-body seals have to undergo more than one thermocycle in the course of assembling and operating electrolysis modules, several drums were thermocycled more than once and re-tested. These data are shown in Table 4-2. The first two thermocycles of F-88 were not programmed as described below in Section 7 and this fact makes comparison with the other runs difficult. The other four multiple thermocycle runs indicate the degradation on the second and third thermocycles is less severe than on the first thermocycle. The 850°C runs were made before the present thermocycle temperature of 1000°C was adopted, but there seems to be no obvious difference between the effects of these two temperatures.

The improvements in both the quality of seals and percentage of seals meeting the two-minute criterion that resulted from the sealing experiments discussed above were judged to be sufficient to proceed to multi-drum test electrolyzers. These units were not intended to be modules of the one-man electrolyzer but were built primarily to determine the significance of the two-minute test criterion in terms of performance under actual high-temperature operating conditions and to provide other operating data necessary to the design of the one-man unit. The two drums of unit Z-7, drums F-118 and F-119, just met the two-minute criterion and the CO_2 concentration of the operating unit was ~5%, as discussed in Section 8 below. Since the other drums of Table 4-2 were better than these, less CO_2

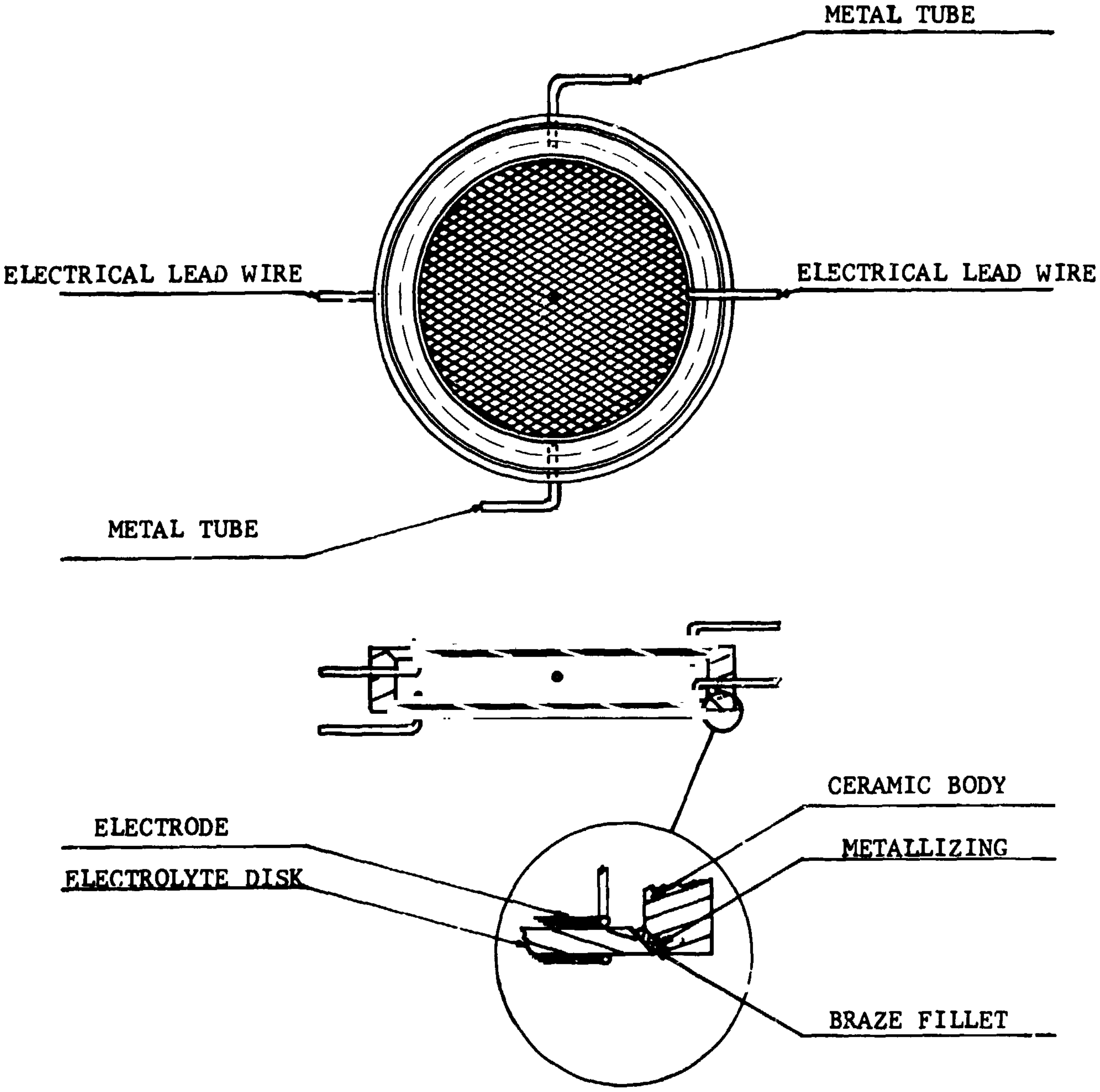

Fig. 4-1 Drum with Valve Seal

Table 4-1

DRUMS PASSING THE TWO-MINUTE TEST ON FIRST THERMOCYCLE

Category	Drum Numbers	Total	Number Passing Test	%
GROUP 1 - Heavy Pd, Au, and Au-Pd Braze	Au: F-50, 78, 87, 88, 96 Au-Pd: F-63, 64, 67, 68, 69, 72, 74, 81, 82, 83, 84	16	3	19
GROUP 2 - Multi-Step Polishing, Light Pd, Au Braze	F-97, 98, 100, 102, 103, 109, 111^{v}	7	4	57
GROUP 3 - Multi-Step Polishing, Light Pt, Au Braze	F-114, 115, 117^{v}, 118, 119, 120, (122^{v})	6	5	83

Notes

(a) Drum F-64 was made before the present test was devised, but its behavior on other similar testing leads to the conclusion that it probably would have met the two-minute criterion.

(b) Drums passing the test are indicated by underlining.

(c) Superscript v denotes valve seal.

(d) Drum F-122^{v} was not thermocycled by the regular procedure but was heated and cooled rapidly causing it to become leaky and it has been excluded from the calculations.

Table 4-2

DEGRADATION ON MULTIPLE THERMOCYCLE

Drum	Initial Test (Minutes)	THERMOCYCLES					
		FIRST		SECOND		THIRD	
		Temp. (°C)	Test (Minutes)	Temp. (°C)	Test (Minutes)	Temp. (°C)	Test (Minutes)
F-88	-	900[a]	-	1000[a]	17.0	1000	2.0
F-96	-	1000	24.5				
F-97	12.0	850	6.5	850	6.7	1000	6.1
F-100	17.6	1000	5.7				
F-103	3.8	1000	2.8				
F-111	15.0	1000	7.1	1000	7.8	850	8.7
F-114	19.0	1000	3.5	1000	2.6		
F-115	24.5	1000	17.7	850	12.5	1000	10.0
F-117	10.0	1000	8.2				
F-118	8.3	Z-7[b]	2.1				
F-119	9.5	Z-7[b]	2.1				

[a] Temperature was not controlled on the first and second thermocycles of F-88.

[b] The tube sealing (985°C) during assembly of unit Z-7 was the first thermocycle for drums F-118 and 119.

would be expected in the oxygen produced by high-temperature electrolytic operation of these drums. Accordingly, in the next series of drums, the electrodes, electrical leads, and gas tubulations were sealed in to permit successful drums to be operated as components of electrolyzers.

Potential Components of Electrolysis Units Forty-eight two-cell drums complete with electrodes, electrical leads, and gas tubes were fabricated and tested. Each of the drums was carefully made using jigs to insure that they would be mutually interchangeable in electrical or gas manifold connections. During the course of fabricating these drums, many procedural modifications were made in order to further develop the techniques involved.

Three sealing configurations were used in the drums intended as potential components of the one-man unit. These included the butt and valve seals described previously and a configuration termed an "edge" seal shown in Fig. 4-2. In an edge seal, only the edge of the disk and the contiguous vertical area of the body are metallized and brazed. This geometry is essentially a variant of the valve seal with a ninety-degree angle. Drums made with all three sealing configurations employed scandia-stabilized zirconia electrolyte disks, having electrodes 20 cm^2 in area, sealed to the zirconia bodies with pure gold. Drums were leak-checked at room temperature by the "$\Delta t/\Delta p$ test." Δt is the time for the gauge pressure, Δp, to drop from 6 to 5 inches of water inside the drum (see Section 7).

The results of the $\Delta t/\Delta p$ test for the drums with butt seals are summarized in Table 4-3. Thirteen of the eighteen butt-sealed drums met the two-minute test criterion.

Table 4-4 shows the results of the four valve seal runs that were made. The yield of acceptable drums and the fabrication difficulties were such that this geometry was not pursued further.

The edge seal runs are summarized in Table 4-5. The middle column of the table gives the difference in radii for each electrolyte disk between the edge of the disk and the contiguous vertical wall of the body after machining but prior to the sealing operations. Placing the gold brazing wire into or adjacent to this gap was originally a problem and probably contributed to the initial failure of the first two sealing attempts (runs F-150 and F-154) having the edge seal configurations. Further experience with this geometry has led to the successful edge seals given in Table 4-5. In general, thicker

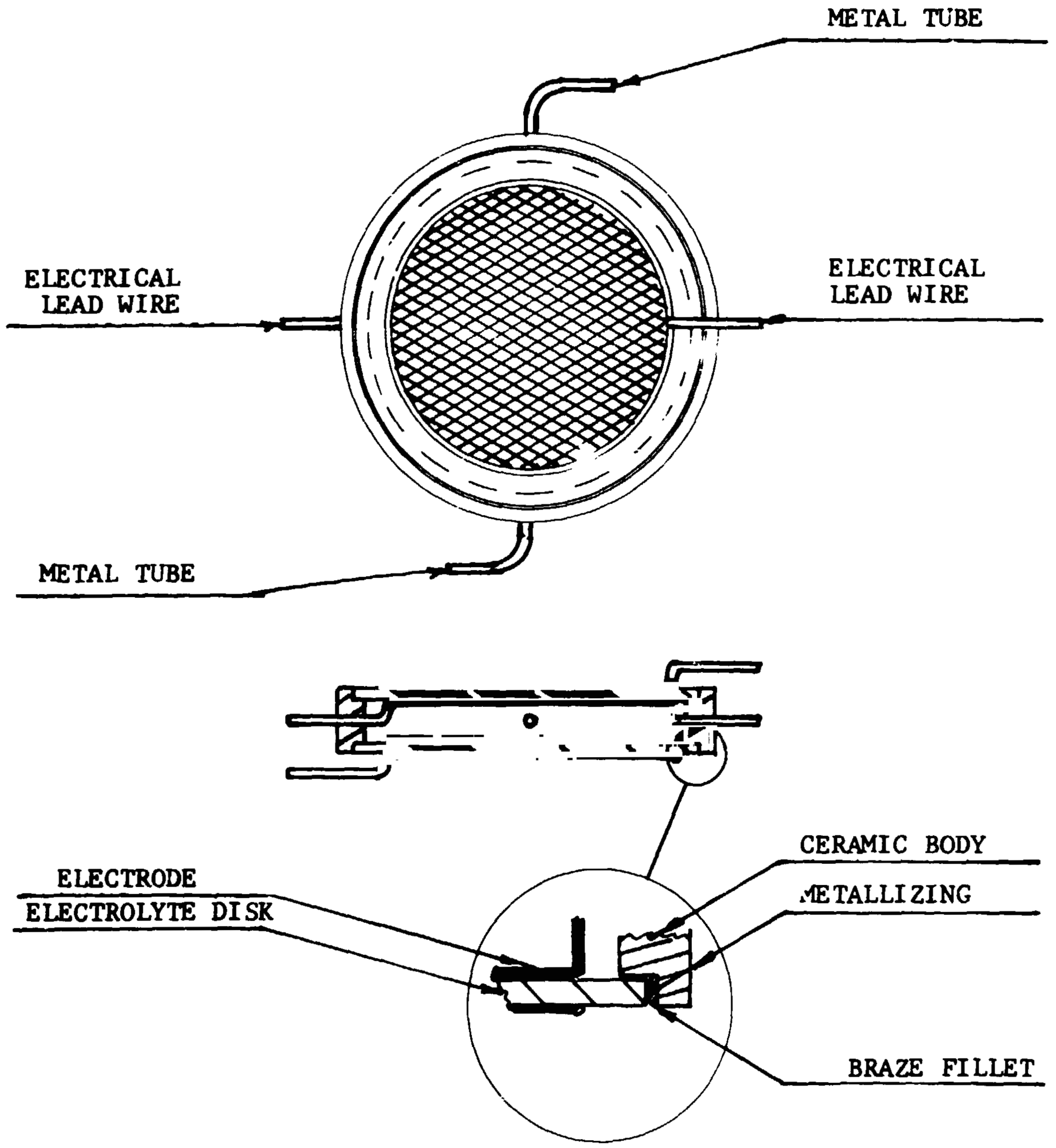

Fig. 4-2 Drum with Edge Seals

Table 4-3

DRUMS WITH BUTT SEALS

Drum	Disk Thicknesses (inch)		Δt/Δp TEST (MINUTES)	
			Seal-up	Thermocycle
F-134	0.050	0.053	9.8	large leak
F-135	0.050	0.053	15	1.2
F-136	0.051	0.050	336[a]	11.4
F-137	0.055	0.050	large leak	-
F-138	0.055	0.047	17	3.3
F-139	0.045	0.055	35	30
F-144	0.055	0.059	66[b]	3.7
F-145	0.060	0.055	18	4.4
F-146	0.055	0.055	40	4.7
F-147	0.059	0.056	21	large leak
F-148	0.055	0.059	20[c]	4.9[c]
F-149	0.060	0.055	28.5[d]	2.1
F-159	0.055	0.055	15.4	10.7
F-160	0.055	0.055	6.9	4.3
F-161	0.055	0.055	27	7.3
F-164	0.055	0.055	29	10.3
F-165	0.055	0.054	2.6	1.9
F-166	0.054	0.055	32	13.4

[a] 42 min for 1/8 inch.

[b] 33 min for 1/2 inch.

[c] Both electrical lead seals leaked and these leaks were closed with lacquer for the Δt/Δp test of the disk-to-body seals.

[d] 19 min for 2/3 inch.

Table 4-4

DRUMS WITH VALVE SEALS

Drum	Disk Thicknesses (inch)		$\Delta t/\Delta p$ TEST (MINUTES)	
			Seal-up	Thermocycle
F-141	0.075	0.085	10	large leak
F-142	0.077	0.075	[a]	-
F-143	0.075	0.075	6.1[b]	0.2[c]
F-153	0.080	0.075	6.8	2.5

[a] Drum tipped in sealing furnace and failed.

[b] One tube seal leaked and this leak was closed with lacquer for the $\Delta t/\Delta p$ test.

[c] The leaky tube seal was resealed with 1000°C Au-Ag alloy.

Table 4-5

DRUMS WITH EDGE SEALS

Drum	Disk Thicknesses (inch)		Gaps (inch)		$\Delta t/\Delta p$ TEST (MINUTES)	
					Seal-up	Thermocycle
F-150	0.061	0.079	0.001	0.003	large leak	39[a]
F-154	0.100	0.100	0.001	0.001	large leak	[b]
F-156	0.075	0.075	0.001	0.001	11.4	7.9
F-162	0.080	0.080	0.002	0.005	32	2.5
F-163	0.090	0.089	0.001	0.0015	96[c]	160[d]
F-167	0.080	0.078	0.0015	0.0035	22.5	20.4
F-168	0.069	0.067	0.001	0.001	2.5	2.5
F-171	0.075	0.073	0.001	0.002	[e]	13.6[f]
F-172	0.080[g]	0.080[g]	0.002	0.002	6.7	6.0
F-173	0.080[g]	0.080[g]	0.002	0.002	23.7	16.4
F-174	0.080[g]	0.080[g]	0.002	0.002	4.5	4.6
F-175	0.060	0.060	0.002	0.002	11.3	9.9
F-176	0.061	0.061	0.003	0.003	16	21.6
F-177	0.059	0.059	0.004	0.005	large leak	7.0[h]
F-178	0.091[i]	0.087[i]	0.0025	0.002	10.7	11.7
F-179	0.078[j]	0.082[j]	0.002	0.002	11.9	13.1
F-181	0.071[k]	0.074[k]	0.002	0.002	31	31
F-182	0.066	0.066	0.002	0.0015	52	>100
F-183	0.060	0.060	0.001	0.0005	95	100
F-184	0.066	0.066	0.002	0.002	31	26
F-185	0.058	0.065	0.0015	0.0015	12	11.3
F-186	0.060	0.057	0.0005	0.001	11	9.1
F-188	0.085	0.085	0.0025	0.002	88	57
F-189	0.076	0.078	0.002	0.002	23	64
F-190	0.084	0.084	0.0025	0.004	60	98
F-191	0.084	0.084	0.004	0.004	44	114

[a] Resealed with 1000°C Au-Ag alloy.

[b] Attempted re-seal with 1000°C Au-Ag alloy failed, drum cut apart for examination.

[c] 48 min for 1/2 inch.

[d] 30 min for 3/16 inch.

[e] One electrical lead seal had a large leak.

[f] Leaky electrical lead resealed with Au.

[g] Sealing edge thickness was 0.080 inch, thickness of electroded area was milled to 0.045 inch.

[h] Resealed with Au.

[i] Thickness of electroded area was milled to 0.047 inch.

[j] Thickness of electroded area was milled to 0.045 inch.

[k] Thickness of electroded area was milled to 0.046 inch.

disks were used for edge seals than for butt seals to maximize the sealing area. Drums F-172, F-173, F-174, F-178, F-179, and F-181 were made using disks having relatively thick edges but thinner milled-out electroded areas. The data of Table 4-5 indicate, however, that electrolyte thicknesses of the same order as were used for butt seals can be used successfully in the edge seal configuration. A total of twenty-six edge-sealed drums were made, of which all except one met the two-minute criterion of the Δt/Δp test.

In addition to the Δt/Δp test, an electrical resistance test was made on each of the drums listed in Tables 4-3, 4-4, and 4-5. These tests indicated that the metal parts, i.e., electrodes, seals, and tubes, were electrically isolated for all drums except F-156, F-162, and F-163, in each of which the inner electrodes of the two cells were electrically connected. The explanation for this is believed to lie in the use of electroplated metal tabs on both the disks and bodies during the fabrication steps of edge-sealed drums to allow electroplating of the edges of the disks and the holes for the gas tubes and electrical leads in the bodies. These tabs were intended to be abrasively buffed off after plating. In drums F-150 through F-168 the tabs on the disks were on the sides of the disks exposed to the insides of the drums. The unintentional electrical connections found in drums F-156, F-162, and F-163 are ascribed to the close proximity of the improperly removed tabs and either the electrode lead wires or vestiges of tabs on the drum bodies. Conducting metal tabs not sufficiently buffed away could act as paths for brazing metal to cause unintentional electrical connections. In drum F-171 and subsequent drums, care was taken to have the tabs on the outside, rather than the inside, and to insure that electrically conducting paths of this kind were absent.

The drum runs using butt, valve, and edge seals are summarized in Table 4-6. In view of the trend of the data and the improvement of our ability to machine the disks and bodies to high precision, concentration was placed on drums having the edge sealing configuration as the most promising potential components for the one-man unit, although the acceptable butt-sealed drums on hand were used in the assembly of multi-cell test units and one twelve-cell module.

Variations in Size Inasmuch as seals in the drums discussed above range in size from 0.1 cm diameter (for the electrical leads) to 6.3 cm diameter (for the disk-to-body seals), the question of the effect of size on seal quality and reliability

Table 4-6

SUMMARY OF DRUM RUNS

Type	Total	Number Passing Test	%
Butt	18	13	72
Valve	4	1	25
Edge	26	25	96
TOTAL	48	39	

arose. The seals contained in the 6.3 cm diameter drums do not, of themselves, answer this question because they are of different types, namely, electrical leads, tube, and disk-to-body. Accordingly, nine experiments employing disk-to-body seals of two sizes smaller than 6.3 cm were conducted. Six experiments used 4.4 cm diameter disks and drums; three experiments were done with 1.9 cm diameter disks and drums. The runs are summarized in Tables 4-7 and 4-8.

The conclusions drawn from these nine experiments as compared to the 6.3 cm diameter results are that there is no significant difference between the 6.3 and 4.4 cm diameter seals but that there is a significant improvement in seal quality at 1.9 cm diameter. It should be noted, however, that the $\Delta t/\Delta p$ test results for the best 6.3 cm drums exceeded those for any of the three 1.9 cm drums. There, therefore, appeared to be no incentive to reduce the size of the disks in the one-man unit to ~4.4 cm diameter. It was further concluded that ~1.9 cm diameter cells (electrode area of approximately 2 cm^2) would create an iteration problem (in making the very large number of cells and of electrical and gas interconnections that would be required) that would greatly exceed the problems involved in using 6.3 cm diameter drums. For example, instead of the eighteen two-cell drums of 6.3 cm disks discussed in sub-section 3.1 above, a one-man unit using 2 cm^2 cells containing the same total of 720 cm^2 of active electrode area would require 360 cells or 180 two-cell drums. On the basis of these data, there is an incentive to explore the effects of using electrolyte disks larger than 6.3 cm diameter.

4.2.2 Ceramic Tube Seals

Sealing experiments were made involving alumina and zirconia tubes having nominal o.d.'s of 1/4 and 3/8 inch in the configurations shown in Fig. 4-3. The top two drawings in Fig. 4-3 represent a zirconia drum to which the ceramic tube is sealed in a conical joint. Alumina and zirconia tubes were sealed successfully to zirconia drums. The next drawing shows an alumina end cap sealed to an alumina tube. This sealing configuration was done successfully. The bottom drawing depicts two tubes sealed together at a conical joint. These seals were gas-tight for zirconia-to-zirconia, alumina-to-alumina, and alumina-to-zirconia. The ability to make these seals permits a wide range of gas manifolding designs to be considered.

Table 4-7

DRUMS WITH BUTT SEALS 4.4 CM DIAMETER

Drum	$\Delta t/\Delta p$ TEST (MINUTES)	
	Seal-Up	Thermocycle
F-99	[a]	-
F-101	31.5	44.5
F-126	39.8[b]	2.2[b]
F-127	25.9	6.8
F-128	9.5	3.8
F-129	52	0.7

[a] Drum leaked badly at one disk; removal of this disk and test of the other disk gave 12 minutes.

[b] One electrical lead seal leaked and it was sealed with lacquer for test of the other seals.

Table 4-8

DRUMS WITH BUTT SEALS 1.9 CM DIAMETER

Drum	$\Delta t/\Delta p$ TEST (MINUTES)	
	Seal-Up	Thermocycle
F-155	52.9	27.9
F-157	46	61.4
F-158	60.1	29.3

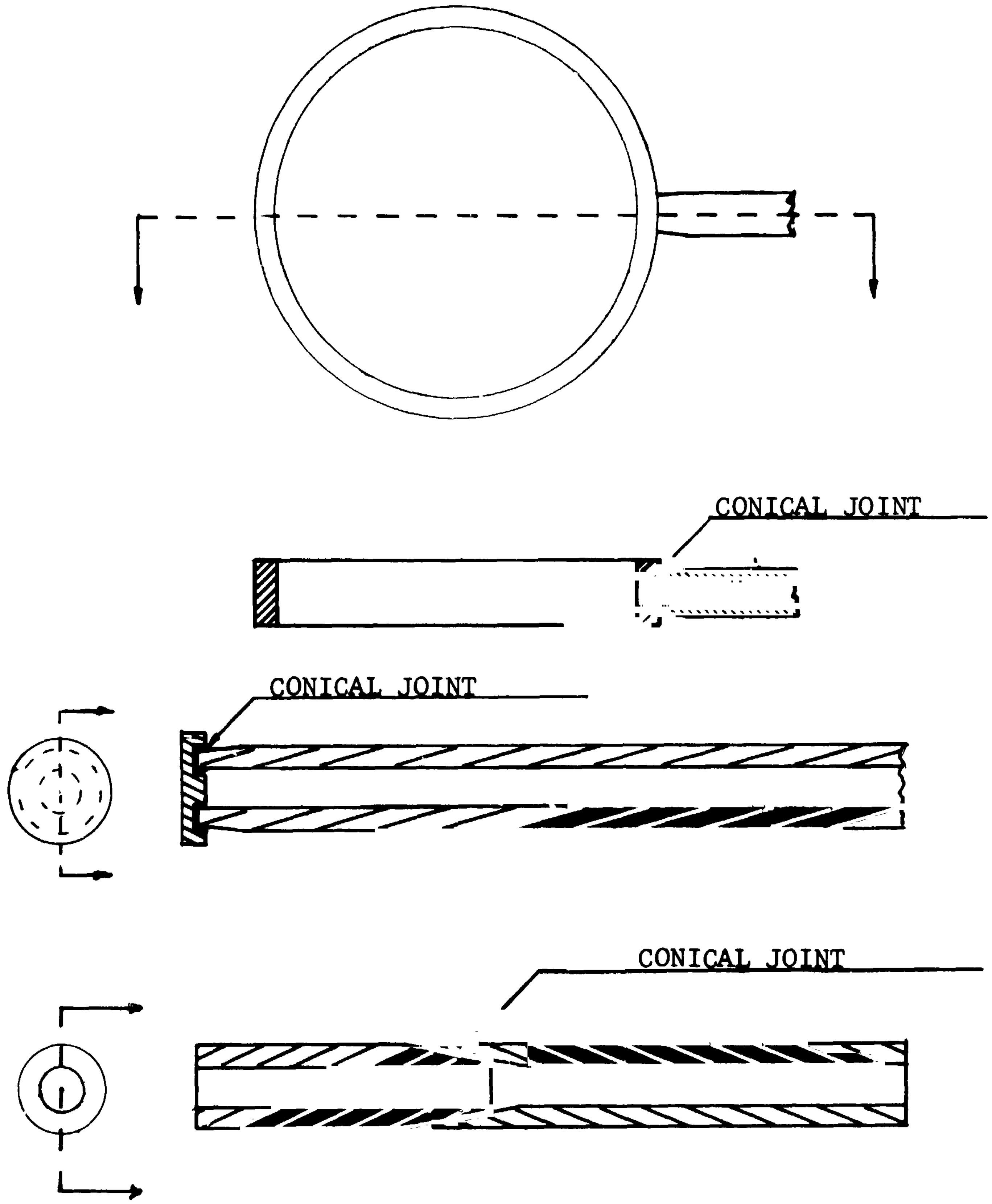

Fig. 4-3 Ceramic Tube Seals

4.2.3 Wire and Metal Tube Seals

Hundreds of noble metal wire and tube seals of the types illustrated in Fig. 4-4 have been made both as separate experiments and during assembly of electrolyzers. Only a few have failed and in every case of failure there was an obvious explanation (poor plating, slippage of the braze wire, insufficient braze metal).

4.3 CONCLUSIONS

The seals developed in the course of these experiments were adequate in both performance and yield to assemble electrolysis modules of the design presented in sub-section 3.1 above. The apparent ease of making gas-tight ceramic tube, metal tube, and wire seals that was observed initially was borne out by further experience with many seals of these configurations. The serious initial difficulties of making seals (between 6.3 cm diameter electrolyte disks and drum bodies) which remained gas-tight on cycling over a wide temperature range were overcome. The extent to which this sealing problem was solved by these experimental drums is illustrated by the operation of Unit Z-8 at <0.01% CO_2, described below in subsection 8.2.

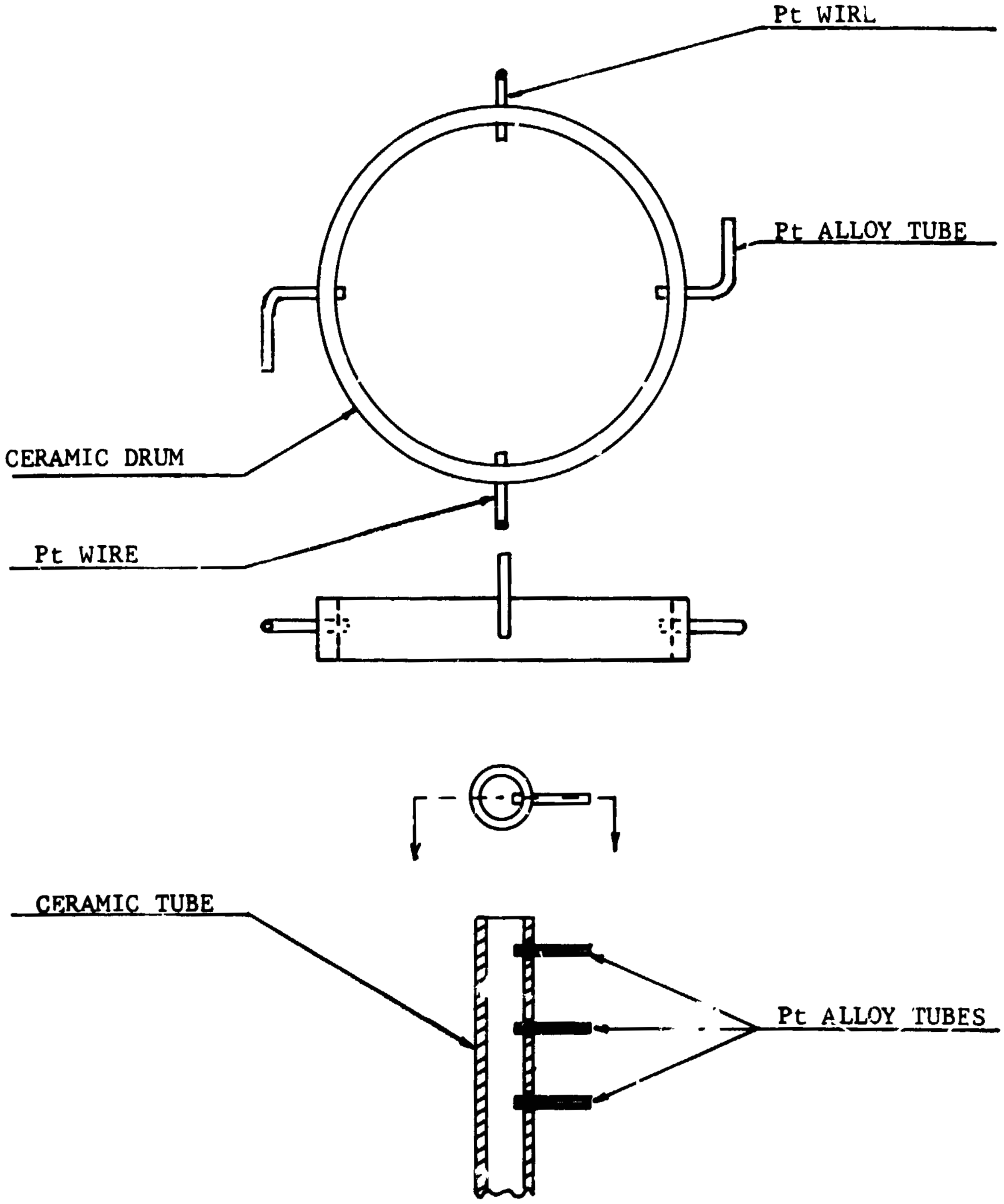

Fig. 4-4 Wire and Metal Tube Seals

Section 5

HOT PRESSING

5.1 TECHNIQUE

All of the stages in the manufacture of the electrolyte disks used in the one-man electrolyzer and in the several test units were carried out in-house. The manufacturing steps--including powder preparation, densification by hot pressing, slicing, and polishing--were developed during the effort of the previous year and have been described before (Ref. 1). Currently, approximately 400 g of prepared powder is loaded into a die and cold pressed at about 9 tons total load. The loaded die is then set up in the furnace. Following evacuation and pressure loading, the temperature of the furnace is raised to the desired value and held for 10 to 14 minutes. The ram pressure is then removed and the operating temperature maintained for an additional 10 minutes before cooling the furnace at a rate up to 14°C per minute. When cold, the die is removed from the hot press furnace, then the ceramic compact is removed from the die. source materials and compositions of the prepared powders as well as the hot-pressing parameters for the compacts made this year are given in Tables 5-1, 5-2, and 5-3.

The graphite dies are machined in-house to a nominal 63.5 mm i.d., from National Carbon ATJ graphite stock. Our two-year operating experience has shown that an individual die is good for approximately twenty runs, at which time the inside surfaces have become so irregular that it is difficult to remove the hot-pressed compact from the die.

Following hot pressing, the compact is dark gray to black due to reduction of the ceramic in the carbonaceous environment. The pressing is sliced into thin disks using a diamond cut-off wheel and the disks are fired in air at a nominal 1300°C. The air firing oxidizes the sawed disks to a light yellow or white color and also serves as a test for thermal shock resistance. After air firing, the disks are tested for relative porosity by placing each one over a port in a vacuum chamber and noting the final pressure obtainable in the system between the disk and the vacuum pump.

Table 5-1

HOT PRESSINGS - $(ZrO_2)_{0.92}(Sc_2O_3)_{0.08}$ POWDER

Pressing	Powder	Sc_2O_3 Source	ZrO_2 Source	Pressure (psi)	Temp. (°C)	DENSITY Sp. Gr.	DENSITY % Theoretical
G-63	B-43	ROC/RIC	TAM Lot 11	3880	1535	5.55	95
G-64	B-44	ROC/RIC	TAM Lot 11	3910	1515	5.59	96
G-65	B-43 & 44	ROC/RIC	TAM Lot 11	3880	1505	5.56	96
G-66	B-45	ROC/RIC	TAM Lot 11	3860	1505	5.57	96
G-67[a]	B-46	ROC/RIC	TAM Lot 11	3820	1505	5.53	95
G-70	B-47	ROC/RIC	TAM Lot 11	3440	1555	5.54	95
G-71	B-45 & 47	ROC/RIC	TAM Lot 11	3060	1560	5.53	95
G-72	B-48	ROC/RIC	TAM Lot 11	3000	1555	-	~95
G-73	B-49	ROC/RIC	TAM Lot 15 #1	3360	1560	5.46	94
G-74	B-50	ROC/RIC	TAM Lot 15 #1	3520	1560	5.50	95
G-75	B-49 & 50	ROC/RIC	TAM Lot 15 #1	3760	1560	5.58	96
G-76	B-51	ROC/RIC	TAM Lot 15 #1	3820	1560	5.57	96
G-77	B-46, 48 & 51	ROC/RIC	TAM Lot 11/15 #1	3320	1565	5.57	96
G-78	B-53	RC#1	TAM Lot 15 #1	3770	1550	5.49	94
G-79	B-54	RC#1	TAM Lot 15 #1	3670	1550	5.55	95
G-80	B-53 & 54	RC#1	TAM Lot 15 #1	3860	1550	5.55	95
G-81	B-55	RC#1	TAM Lot 15 #1	3910	1560	~5.55	~95
G-82	B-56	RC#1	TAM Lot 15 #1	3840	1560	5.53	95
G-84	B-55 & 56	RC#1	TAM Lot 15 #1	3860	1560	5.55	95
G-85	B-58	RC#1	TAM Lot 15 #1	3910	1560	5.54	95
G-87	B-59	RC#1	TAM Lot 15 #1	3880	1560	5.52	95
G-88	B-58 & 59	RC#1	TAM Lot 15 #1	3930	1560	5.58	96
G-89	B-61	RC#1	TAM Lot 15 #1	3990	1565	5.51	94.5
G-91	B-64	RC#1	TAM Lot 15 #1	3940	1545	5.48	94
G-93	B-61 & 64	RC#1	TAM Lot 15 #1	3920	1560	5.47	94
G-95	B-66	RC#2	TAM Lot 15 #1	3940	1565	5.26	90.5
G-96	B-68	RC#2	TAM Lot 15 #1	3890	1565	5.49	94
G-97	B-66 & 68	RC#2	TAM Lot 15 #1	3950	1565	5.40	93
G-101	B-72	RC#2	TAM Lot 15 #1	3940	1550	5.47	94
G-102	B-73	RC#2	TAM Lot 15 #1	3980	1560	5.48	94
G-103	B-72 & 73	RC#2	TAM Lot 15 #1	3940	1560	5.48	94
G-104	B-74	RC#2	TAM Lot 15 #1	3940	1555	5.30	91
G-105	B-75	RC#2	TAM Lot 15 #2	3940	1555	5.48	94
G-106	B-74 & 75	RC#2	TAM Lot 15 #1/#2	3920	1560	5.41	93
G-107	B-76	RC#3	TAM Lot 15 #2	3940	1555	5.56	95.5
G-108	B-77	RC#3	TAM Lot 15 #2	3940	1560	5.39	92.5
G-109	B-76 & 77	RC#3	TAM Lot 15 #2	3960	1565	5.58	96
G-98	B-69	RC#2	VAR 1146 #4	4010	1555	5.73	98
G-99	B-70	RC#2	VAR 1346 #2	3940	1555	5.71	98

[a] 500 g die charge. All others close to 400 g.

Table 5-2

HOT PRESSINGS - $(ZrO_2)_{0.93}(Sc_2O_3)_{0.07}$ POWDER

Pressing	Powder	Sc_2O_3 Source	ZrO_2 Source	Pressure (psi)	Temp. (°C)	DENSITY	
						Sp. Gr.	% Theoretical
G-110	B-78	RC#3	TAM Lot 15 #2	3940	1555	5.77	98.5
G-111	B-79	RC#3	TAM Lot 15 #2	3840	1560	5.76	98.5
G-112	B-78 & 79	RC#3	TAM Lot 15 #2	3720	1565	5.73	98
G-113	B-80	RC#3	TAM Lot 15 #2	3600	1565	5.74	98
G-114	B-81	RC#3	TAM Lot 15 #2	3520	1565	5.69	97
G-115	B-80 & 81	RC#3	TAM Lot 15 #2	3500	1565	5.71	97.5
G-116	B-82	RC#3	TAM Lot 15 #2	3600	1560	5.62	96
G-117	B-83	RC#3	TAM Lot 15 #2	3580	1560	5.66	96.5
G-118	B-82 & 83	RC#3	TAM Lot 15 #2	3640	1560	5.65	96.5

Table 5-3

HOT PRESSINGS - ZrO_2-Yb_2O_3 AND/OR Y_2O_3 POWDER[a]

Pressing	Powder	Composition	Pressure (psi)	Temp. (°C)	DENSITY[b]	
					Sp. Gr.	% Theoretical
G-100	B-71	4.0 mole% Y_2O_3	3940	1555	5.82	97
G-90	B-63	4.0 mole% Y_2O_3 plus 4.0 mole% Yb_2O_3	3950	1565	5.90	94
G-86	B-60	10.0 mole% Yb_2O_3	3960	1585	6.17	92
G-83	B-57	6.0 mole% Yb_2O_3	3880	1560	6.38	98.5
G-92	B-55	4.0 mole% Yb_2O_3	3960	1565	6.40	101

[a] All ZrO_2 in this table from TAM Lot 15 #1.

[b] Theoretical values estimated.

5.2 PREPARATION OF ZrO_2-Sc_2O_3 ELECTROLYTE

5.2.1 $(ZrO_2)_{0.92}(Sc_2O_3)_{0.08}$

Thirty-seven hot-pressed compacts of this composition were made this contract year using two lots of Zr source material from TAM Division, National Lead Company (designated TAM lot #11, etc.). The Sc_2O_3 was obtained from Research Organic/Inorganic Chemical Corporation (designated ROC/RIC) and from Research Chemicals Division of Nuclear Corporation of America (designated RC #1, etc.). Data on these pressings are summarized in Table 5-1. With reference to the tables of hot-pressing data, the numbers following the source and/or log designation refer to separate containers carrying the manufacturer's same lot number.

The hot-pressed compacts prepared from powder made with TAM Lot No. 11 material exhibited very little change in overall density with variations in die pressure. 400 g pressings prepared at 3440 psi and higher did not have porous centers near the top of the compacts, as did pressings made last year. Slices cut from the non-porous pressings appeared to be more brittle and would not sustain as severe machining operations as those prepared formerly from the previous lots of raw material. The porosity reappeared when the die pressure was reduced to near 3000 psi or when the die charge was increased to 500 g.

All of the $(ZrO_2)_{0.92}(Sc_2O_3)_{0.08}$ composition pressings derived from TAM Lot 15 source material exhibited the usual variation in porosity from top to bottom of the compact; and variation in die pressure did appear to affect the overall density value. These observations may be interpreted to indicate the presence of an impurity in TAM Lot 11 which was acting as a "fluxing agent." All of these observations on variations in properties of the pressings are actually small and subtle. No detrimental effect has been noted on the usefulness of slices cut from these compacts for electrolyte disks, regardless of these variations.

Starting with hot-pressed compact G-89, the density achieved began to vary, usually averaging slightly lower than the 95 to 96% obtained earlier in the series. This decrease in density led to the production of generally more porous disks, some of which were leaky enough to influence the $\Delta t/\Delta p$ test (see Section 7) following seal-up of the electrolyte disks into drums. The decrease in density cannot be correlated with a change in source material and the cause remains unknown at this time.

Two hundred and nineteen disks from the $(ZrO_2)_{0.92}(Sc_2O_3)_{0.08}$ TAM pressings were processed through slicing, firing, and polishing. None failed the air firing-thermal shock test.

5.2.2 $(ZrO_2)_{0.93}(Sc_2O_3)_{0.07}$

Nine hot pressings were made using this lower scandia-content powder in an effort to increase the density of the compacts and thereby reduce the porosity of the disks. The conditions and results are given in Table 5-2. All the pressings had densities higher than those achieved with the $(ZrO_2)_{0.92}(Sc_2O_3)_{0.08}$ composition, even after some reduction of ram pressure. Six of the lower scandia-content pressings have been processed to give thirty-six finished disks. All of the disks survived the thermal shock test and all have little or no porosity as measured on the vacuum test.

5.3 EXPERIMENTS

Last year three hot-pressed compacts were made using Zr source material from Varlacoid Company (designated VAR). The pressings had high densities and the air-fired disks cut therefrom were white (whereas the TAM-source disks are yellow). However, only one of the compacts yielded useable disks (see Ref. 1). This year two additional pressings were made from powders using two lots of Varlacoid material (see Table 5-1). The densities of the compacts were again high and the disks were white after air firing. However, most of the disks cracked and blistered during air firing and were, therefore, unuseable as electrolyte cell components. We must conclude that the Varlacoid source material is not suitable for use in the present disk-making procedure (possibly because of a variable impurity content).

Five other hot pressings were made this year using TAM zirconium source material but stabilized with Y_2O_3 and/or Yb_2O_3 (see Table 5-3). The Y_2O_3 was taken from a single lot obtained from American Potash and Chemical Corporation and the Yb_2O_3, likewise, from Research Chemicals. For both Yb_2O_3 and/or Y_2O_3 stabilizers, decreasing the amount of stabilizer leads to higher pressed densities for equivalent pressing conditions.

The degree of resistance to thermal shock also runs inversely to the quantity of stabilizing oxide employed. In the case of Yb_2O_3 stabilization at 10 mole%, the pressing fractured in the hot press; at 6 mole% some of the sliced disks survived a single air firing at 1300°C, but fractured on refiring; while at 4 mole% most of the disks have survived multiple air firings. The 4 mole% Y_2O_3 plus 4 mole% Yb_2O_3 pressing split on heating to ~150°C. Half of the sliced disks from the 4 mole% Y_2O_3 have survived two air firings at 1300°C. (This represents an improvement over 9 to 10 mole% Y_2O_3-stabilized disks which in the past have all failed to survive firings at 1300°C.)

These experimental tests have shown that the thermal shock resistance of Y_2O_3 or Yb_2O_3-stabilized hot-pressed zirconia can be significantly improved by reduction of the amount of stabilizer employed. Samples of the 4 mole% ZrO_2-Y_2O_3 and ZrO_2-Yb_2O_3 pressings were submitted for x-ray powder diffraction runs. The diffraction spectra from both materials were substantially the same and indicated the presence of some monoclinic baddeleyite phase in each. The major component was cubic or tetragonal stabilized zirconia with unit cell dimensions the order of 5.10 to 5.13 Å.

Section 6

FABRICATION

6.1 COMPONENTS

Electrolysis test units and the modules of the one-man, 127-A electrolyzer were assembled using drums selected from those produced during the sealing runs described in Section 4 above. Prior to selection as an electrolyzer component, each drum had been tested, heated to 1000°C, cooled, and re-tested. A butt-sealed and an edge-sealed drum are shown in Figs. 6-1 and 6-2, respectively.

Alumina manifold tubes were used in each electrolyzer. They were prepared for seal-up by drilling and plating holes to receive the metal tubulations of the drums.

6.2 ELECTROLYZER MODULES

Eight electrolysis units of the design described in sub-section 3.1 above were assembled. Four modules (Z-9, Z-10, Z-11, and Z-12) contained six drums or twelve cells each and three of these modules constituted the one-man unit. The other electrolyzers (Z-5, Z-6, Z-7, and Z-8) were experimental units which were made to aid in the development of the fabrication and operating procedures. The main assembly step consisted of furnace brazing the drum tubulations to the alumina manifold tubes using silver-gold alloy braze. The drums and manifolds were held in position in a ceramic jig during this operation. Fig. 6-3 shows an electrolyzer still in the jig after completion of the brazing step. The split rings between the drums support them during the set-up and brazing procedure and they are removed afterward. The material on the metal gas tubulations near the manifold tubes is a ceramic cement used to retard flow of the brazing alloy away from the braze area and it is also removed later. The jig is removed after the brazing operation and the unit is handled without additional support. The unit without the jig is shown in Fig. 6-4. This figure also shows the series electrical interconnections, the lead wires which will carry the current, and the connecting leads for the voltage probes to each cell.

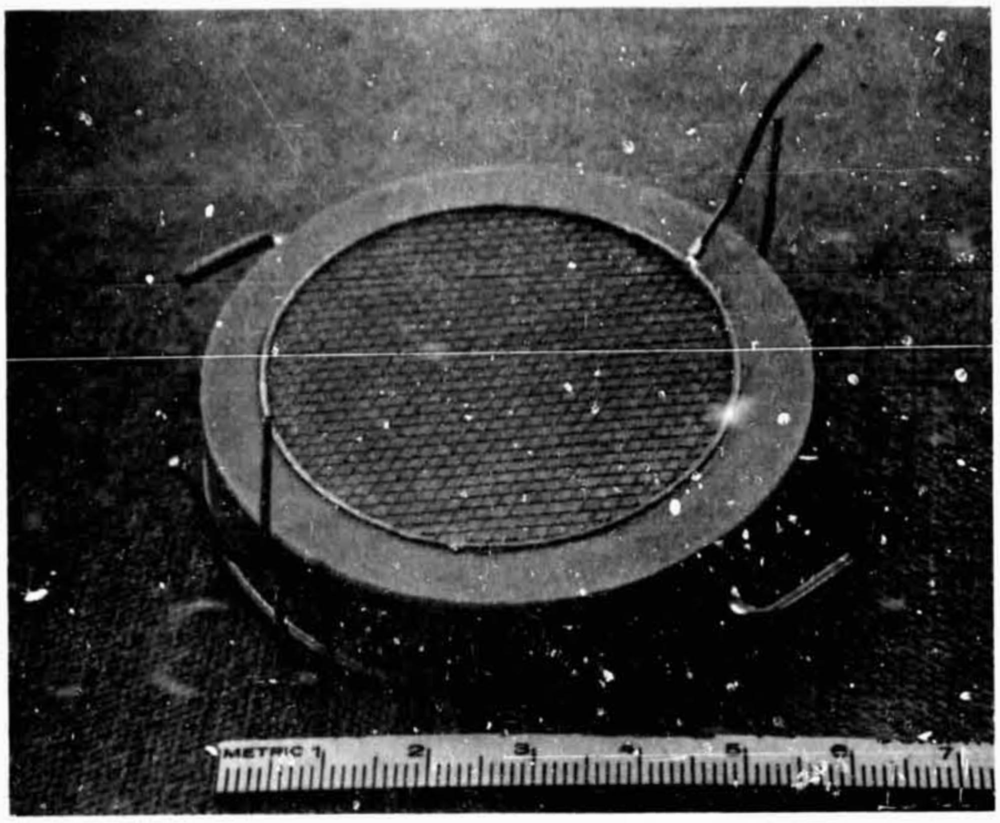

Fig. 6-1 Butt-Sealed Drum

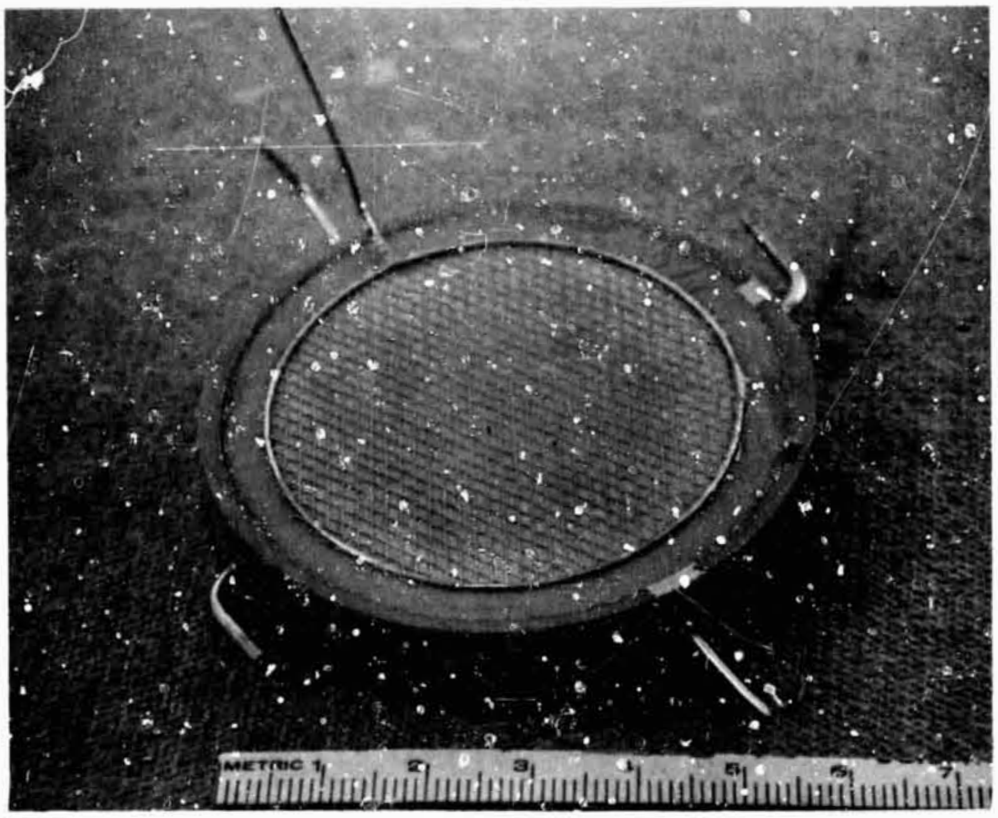

Fig. 6-2 Edge-Sealed Drum

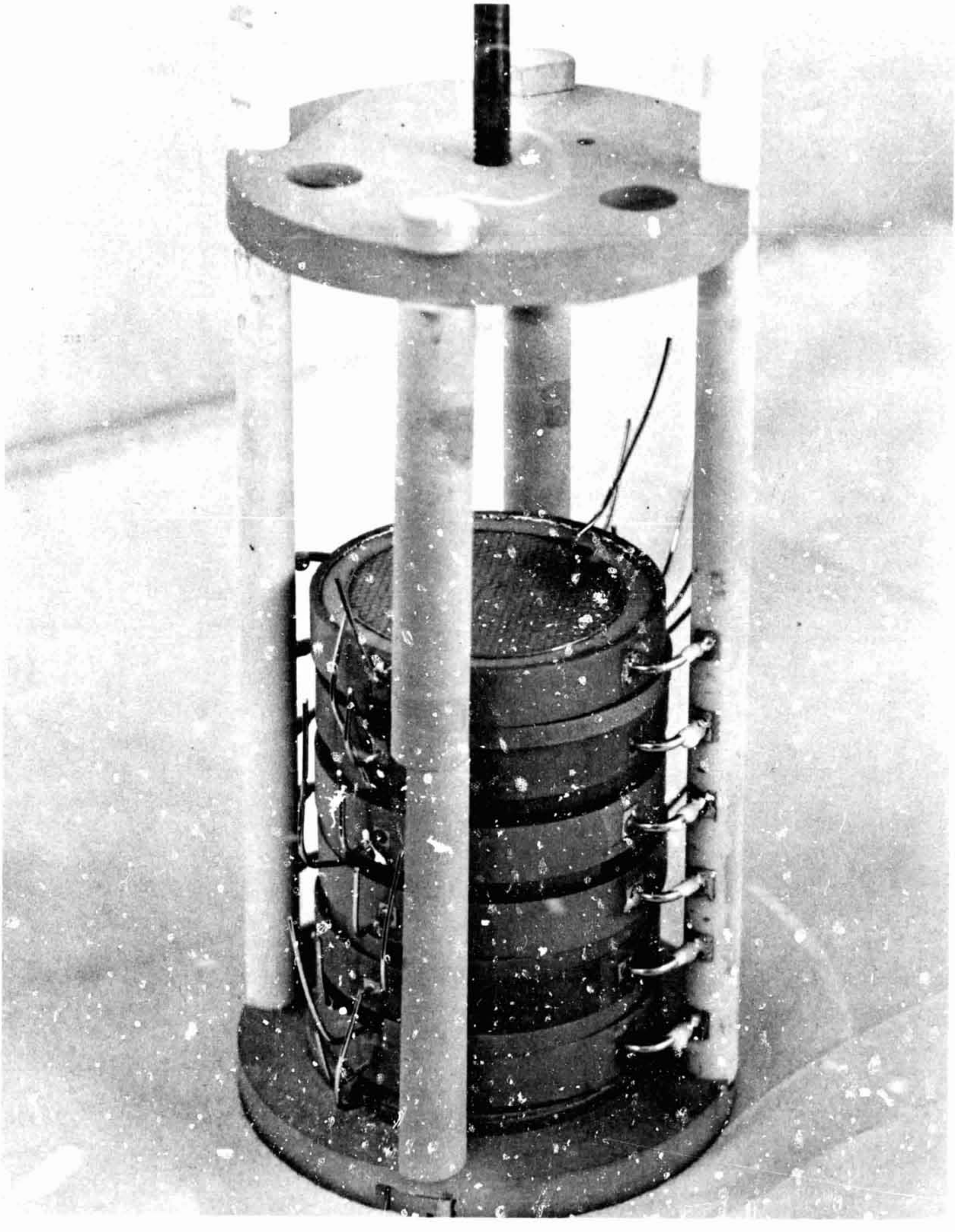

Fig. 6-3 Electrolyzer in Brazing Jig

Fig. 6-4 Electrolyzer after Removal from Brazing Jig

For laboratory testing, the unit is held by a metal plate which also contains the required electrical and gas lead-throughs as shown in Fig. 6-5. The fluffy packing is high-temperature thermal insulation. The unit is then placed into its ceramic envelope, shown in Fig. 6-6, which functions as the oxygen chamber. After being placed into a furnace and making the electrical and gas connections, the electrolyzer shown in these figures is capable of operation at 48 A at a current density of 200 mA/cm^2.

The CO_2 electrolyzers that were made during the past year are summarized in Table 6-1. Unit Z-5 was assembled to aid in developing the design and fabricating procedures and it was destructively examined without having operated as an electrolyzer. Details of the operating performance of the other units are given in Section 8.

Table 6-1

SUMMARY OF MULTI-CELL ELECTROLYZERS

Unit Numbers	Drum Type	No. of Drums	Comments
Z-5	Butt	3	First unit using the drum design; destroyed during examination; not operated.
Z-6 and Z-7	Butt	3	One faulty drum removed from each unit; Z-6 failed shortly after start-up; Z-7 operated as CO_2 electrolyzer at 16 A.
Z-8	Edge	1	Operated for >800 hr at <0.01% CO_2 in the O_2 produced electrolytically at 8 A.
Z-9	Butt	6	Standby module of the 127-A, one-man electrolyzer.
Z-10 Z-11 and Z-12	Edge	6	These three modules were operated together at 42 A each for >250 hr and produced two pounds of O_2 per day from CO_2.

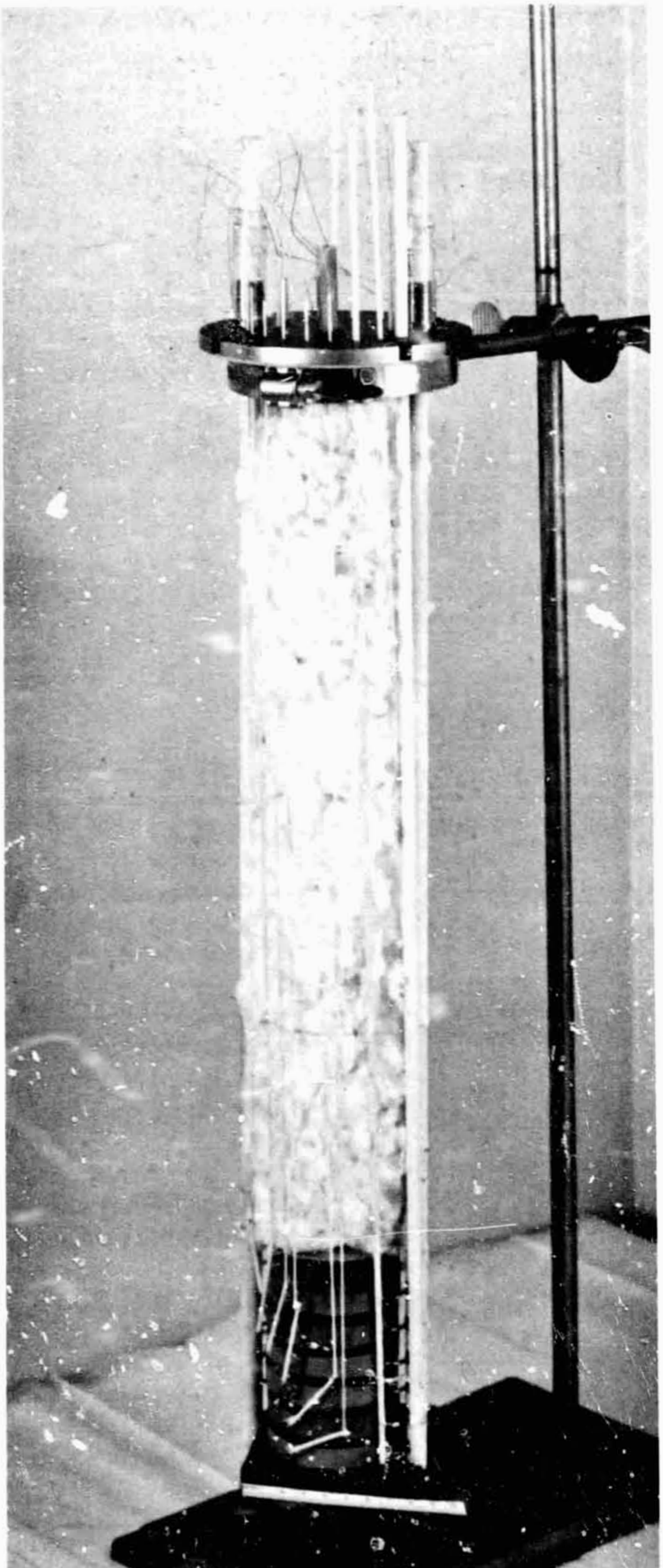

Fig. 6-5 Electrolyzer with Top Plate, Insulation, and Electrical Connections

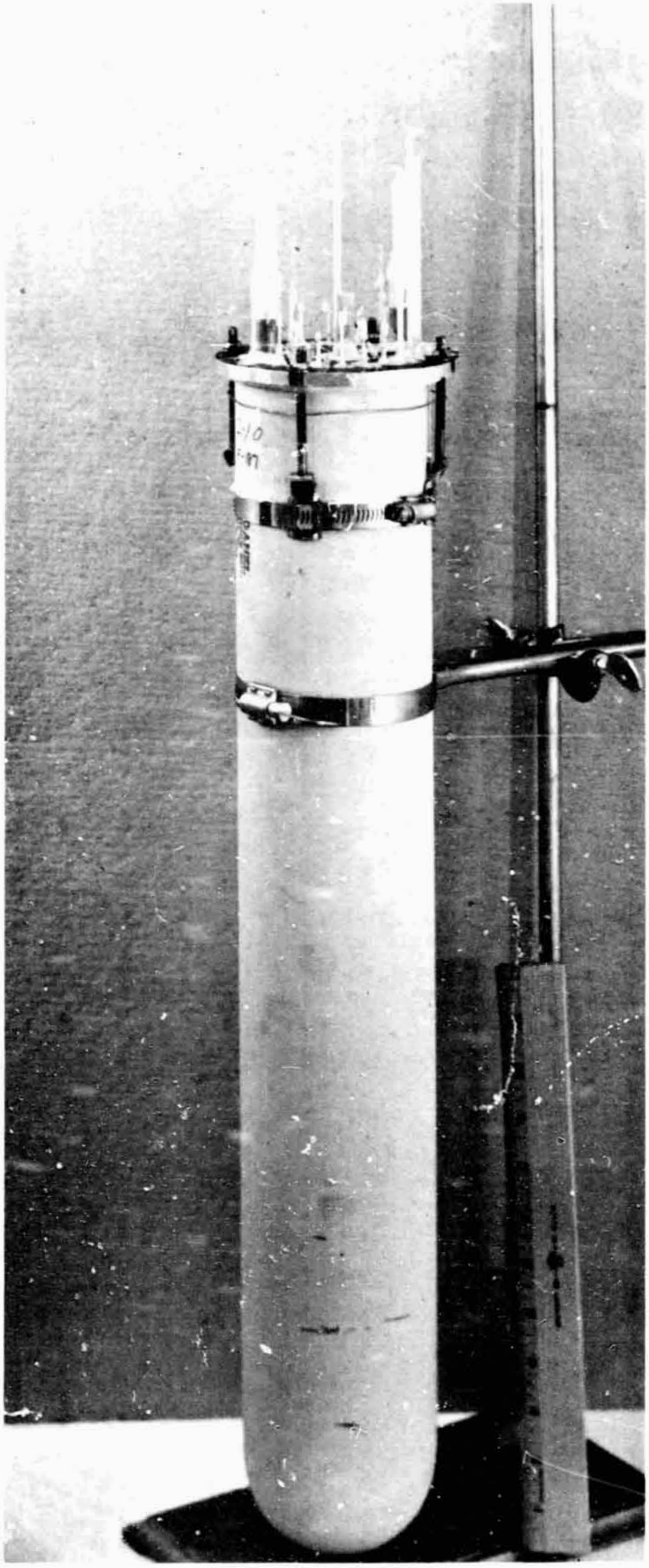

Fig. 6-6 Complete Electrolyzer of 48-A, One-Third Man Capacity

Section 7

TESTING AT ROOM TEMPERATURE

A method of testing drums and electrolysis modules at room temperature for gas leaks is necessary to permit selection of those units which will be assembled into high-temperature operating electrolyzers. The initial testing procedure was to pressurize the sealed drum or module with air at pressures of 0.5 to 1 psi (34.5 to 69 millibars) and check for leaks with soap solution or by immersion in water. Higher pressures were not adopted for routine use because of the large forces they impose on the electrolyte disks, a pressure of 1 psi corresponding to a force of five pounds on the disk. Concern about forces of this magnitude might have been unnecessary since a pressure of 5 psi was applied in one drum test without damage and another drum was evacuated to less than one torr without damage. However, as the quality of the seals improved during the course of the program, it was found that tests involving water or soap solution gave misleading results and a new procedure was adopted.

This procedure, the $\Delta t/\Delta p$ test, consists of observing the time required for the pressure inside the dry sealed unit and a constant volume test apparatus to decrease from six inches of water to five inches of water (15.0 to 12.5 millibars). Drums having small leaks as determined by this test show no apparent leak with the previous soap solution or water immersion tests, and after being wet with either soap solution or water give no apparent leak on the current test, very small leaks being completely plugged by water or soap solution. In one case, a drum with a slight leak was wet with soap solution and pressurized to 2.5 psi (170 millibars) without showing bubbles or foam. Additionally, there is evidence that atmospheric water vapor can condense in the leak channels and plug them. If a drum has been allowed to sit in the laboratory exposed to air for more than a day, it has been found necessary to dry it at 150°C in order to obtain reproducible $\Delta t/\Delta p$ test results.

Drums testing greater than two minutes are re-heated to ~1000°C, cooled back to near room temperature with rates of temperature rise and fall held to less than five degrees per minute, and tested again. This procedure is termed a "thermocycle". The pass-fail point has been taken arbitrarily as a test result of two minutes after one thermocycle. The significance of this arbitrary point in terms of oxygen purity, oxygen production rate, and degradation on long-term operation of electrolysis units can be seen by comparing the data in Section 8 below for actual high-temperature CO_2 electrolysis runs with the $\Delta t/\Delta p$ test values of the drums in those electrolytic units.

The $\Delta t/\Delta p$ test was originally introduced as a convenient ad hoc method of obtaining a more meaningful qualitative idea of the leak rate of drums in conjunction with the sealing experiments. Its primary function was to provide a rapid means of determining whether changes in sealing technique were producing tighter seals. It is useful, however, to know the relationship between a test result (in minutes) and the actual amount of gas (oxygen) that had to leak from the drum during the test. The test apparatus that was used in obtaining all $\Delta t/\Delta p$ test data reported here consists of a water manometer connected by flexible tubing to the drum on test with provision for admitting oxygen at a pressure slightly above six inches of water. The volume of gas that leaks from the system itself with no drum attached in going from a pressure of six to five inches of water was 0.85 cm^3 (measured with a syringe). Most of this gas comes from the reduction of gas volume in the water manometer as the system pressure decreases and water rises in the tube. The volume of gas (i.e., the volume of a constant volume test system) that would leak this same amount (number of moles) of gas for the same pressure change can be calculated from Boyle's law as follows:

$$P_A V = P_B (V + \Delta V)$$

where A = system at six inches of water + atm
B = system at five inches of water + atm

and since 1 atm = 407 inches of water
and $\Delta V = 0.85$ cm^3

therefore $413 V = 412 V + 412 \Delta V$
$V = 412 \Delta V = 348$ cm^3

The effective system volume is 348 cm^3 and this is the volume of a system containing a manometer of invarient volume that would give the same $\Delta t/\Delta p$ test results as the actual system using the water manometer (in which the volume is a function of pressure).

Comparison of $\Delta t/\Delta p$ test results for units of different types must consider whether the total volume (348 cm^3 + volume of unit being tested) is equal in each case. Approximate volumes of several electrolyzer components are:

Edge-sealed drum	12 cm^3
Butt-sealed drum	24 cm^3
Manifold tube	19 cm^3

Since $348+12 = 360$ cm^3 is only 3% different from $348+24 = 372$ cm^3, $\Delta t/\Delta p$ test results for edge- and butt-sealed drums can be directly compared. Approximate factors for comparing $\Delta t/\Delta p$ test values for multi-drum units can be calculated by comparing total volume (of test unit + system) per drum in test unit. Some results of this type of comparison are shown in Table 7-1. Calculation of these factors assumes that the seals made to the manifolds during assembly of an electrolysis unit are leak-free. For example, if six edge-sealed drums testing at ten minutes each were sealed to two manifolds to make a unit such as Z-10 (described in Section 8), the unit would test at 2.1 minutes in the absence of any seal degradation occurring during the final assembly procedure.

Table 7-1

COMPARISON FACTORS FOR $\Delta t/\Delta p$ TEST VALUES
(SYSTEM WITH WATER MANOMETER)

Type of Unit	Volume of Unit cm^3	Total Test Volume cm^3	Volume per Drum cm^3	Factor
Edge-sealed drum	12	360	360	1
Butt-sealed drum	24	372	372	1
1 Edge-sealed drum (Z-8)	50	398	398	1.1
2 Butt-sealed drums (Z-7)	86	434	217	0.60
6 Butt-sealed drums (Z-9)	182	530	88	0.24
6 Edge-sealed drums (Z-10)	110	458	76	0.21

As the seals were improved during the sealing experiments discussed in Section 4 above, Δt/Δp test times became inconveniently long and, in addition, the presence of water vapor from the manometer in the system was cause for greater concern because of possible water adsorption effects. Both of these problems were overcome by performing an alternate version of the Δt/Δp test on a new apparatus having a smaller dead volume and a mechanical pressure gauge (Wallace and Tiernan Model 62C-2C-0010, 0 to 10 inches of water, 6 inch diameter). This system leaks 0.10 cm^3 of oxygen for a pressure change from six to five inches of water which gives it an effective volume of 41 cm^3. Table 7-2 contains comparison factors for testing units of different types.

Table 7-2

COMPARISON FACTORS FOR Δt/Δp TEST VALUES
(DRY SYSTEM WITH PRESSURE GAUGE)

Type of Unit	Volume of Unit cm^3	Total Test Volume cm^3	Volume per Drum cm^3	Factor
Edge-sealed drum	12	53	53	1
Butt-sealed drum	24	65	65	1.2
1 Edge-sealed drum (Z-8)	50	91	91	1.7
2 Butt-sealed drums (Z-7)	86	127	64	1.2
6 Butt-sealed drums (Z-9)	182	223	37	.70
6 Edge-sealed drums (Z-10)	110	151	25	.47

The Δt/Δp test times with the gauge system are shorter than those obtained with the water manometer system because of the smaller effective volume. The ratio between results from the two systems is the ratio of the effective volumes of each system with a test unit connected. These ratios are tabulated in Table 7-3.

Table 7-3

RATIOS OF $\Delta t/\Delta p$ TEST VALUES
(WATER MANOMETER VERSUS GAUGE SYSTEM)

Type of Unit	Volume of Unit cm^3	Total Test Volumes cm^3	Ratio
		Water Manometer/Gauge	
Edge-sealed drum	12	360/53	6.8
Butt-sealed drum	24	372/65	5.7
1 Edge-sealed drum (Z-8)	50	398/91	4.4
2 Butt-sealed drums (Z-7)	86	434/127	3.4
6 Butt-sealed drums (Z-9)	182	530/223	2.4
6 Edge-sealed drums (Z-10)	110	458/151	3.0

For example, an edge-sealed drum testing at 68 minutes on the water manometer system will have a test value of 10 minutes on the gauge system.

The $\Delta t/\Delta p$ test provides an indication of the total leak rate of a drum or multi-drum unit but it does not indicate the location of a leak. The leaks are too small to use soap solution to give bubbles or foam but soap solution can be used in conjunction with the $\Delta t/\Delta p$ test. If the leak rate is sufficiently high that the gauge needle or manometer meniscus is visibly moving, application of soap solution or water to areas of suspected leaks will result in slowing or stopping of the needle or meniscus when the leak is wet.

A more generally applicable method that is useful for locating leaks in seals and which is also of sufficient sensitivity to detect porous ceramic areas is the halogen leak detector. The drum or multi-drum unit is purged with Freon-12, pressurized to $\sim$6 inches of water with Freon-12, and then probed with the leak detector probe (General Electric Halogen Leak Detector Type H-10). Contact of the probe with Freon-12 results in flashing of an indicator lamp. After 40 days of operation, unit Z-8 was tested at room temperature using the halogen leak detector and found to have retained leak-tight seals (see Section 8).

Section 8

HIGH-TEMPERATURE TESTING AND OPERATION

8.1 MULTI-DRUM TEST UNITS (NUMBERS Z-6 AND Z-7)

8.1.1 Introduction

The construction, assembly, and room-temperature leak testing of two-cell drums and multi-drum units has been described in Sections 6 and 7. The construction of the first multi-cell unit using drums (Z-5) was undertaken to aid in developing the assembly procedures described in sub-section 6.2. During removal of a leaky drum, several previously leak-tight Pt alloy tube-to-body seals in the other drums sprung open. Modifications in the design and assembly procedure were made after unit Z-5 and again after Z-6 allowing removal of a drum with the retention of all other leak-tight seals in unit Z-7 as described below.

The general arrangement of a three-drum electrolyzer with external plumbing and a ceramic envelope is shown schematically in Fig. 3-1 above. Pt alloy tubes of one inch (2.54 cm) length and 70 mil o.d. x 40 mil i.d. (0.178 x 0.102 cm) bent at an approximate ninety-degree angle in the middle are used to carry gas in a parallel flow pattern between the 3/8 inch o.d. (0.95 cm) alumina manifold tubes and the drums. The Pt alloy tubes are connected to the drums and manifold tubes by brazing operations using silver and gold. For these operations a careful jigging procedure using a Lava A assembly is required. In all sealing operations in the assembly of multi-cell units the rate of heat-up and cool-down of the furnaces is held to approximately five degrees per minute or less. After the final sealing operation the unit is tested for leaks using the $\Delta t/\Delta p$ leak check procedure described in Section 7. Electrical lead connections between drums are made and voltage probes between cells are attached. The unit is placed in a ceramic envelope which is sealed up by means of a removable aluminum closure plate. Cell electrical leads, thermocouple leads, CO_2 manifold, oxygen outlet, and purge tubes are brought out through the plate and sealed into the plate with Torr Seal (Varian Associates, Vacuum Division).

8.1.2 Unit Z-6

Unit Z-6 consists of three drums or six cells. The drums are designated F-81, F-82, and F-83. Further details concerning drums are to be found in Section 4. The individual drums were sealed with 1150°C Au-Pd alloy and did not have one end of the Pt alloy tubes sealed to them during this step.

Before assembly into the sealing jig to make the Pt alloy tube seals, 20 mil (0.051 cm) Au wire was wrapped around each disk seal of each drum. After insertion of Pt alloy tubes into the alumina tubes and zirconia drum holes, 20 mil (0.051 cm) Au wire was wrapped around each end of the Pt alloy tube and pushed against the drum body and alumina tube, respectively. After seal-up and cool-down, it was noted that all the gold had melted but did not flow into several of the alumina and drum holes and instead flowed in the opposite direction. A reseal was attempted using silver strip wrapped around each Pt tube joint that did not seal on the first attempt with gold. A dab of high-temperature cement was placed around each tube just behind the wrapped silver to restrict flow of the molten metal in the wrong direction. The silver reseal was successful. A leak was found in unit Z-6 by the $\Delta t/\Delta p$ test. The leak was stopped by squirting leak-check fluid over the unit. A sufficiently small leak was assumed to be present warranting proceeding to testing the unit under current at high temperature. During preliminary oxygen transfer experiments a large leak developed between cathode and anode chambers and the unit was shut down. Leak tests indicated a severe leak in a disk-to-body seal. As a consequence of these results, the more rigorous leak testing and thermocycling procedures described in Section 7 were instituted.

8.1.3 Unit Z-7

Assembly

Unit Z-7 initially incorporated drums F-118, F-119, and F-120. Pt alloy tubes were sealed into these drums during the disk-to-body gold brazing operation. The initial leak check of these drums using the $\Delta t/\Delta p$ test gave values of 8.3, 9.5, and 8.6 minutes for F-118, F-119, and F-120, respectively. Silver was used to seal the Pt tubes to the alumina manifold tubes as described above for the successful Z-6 silver reseal. After assembly the unit was leak checked and the top disk seal of the F-120 drum was found to leak. The Pt alloy tubes were cut and the F-120 drum was removed from the unit. The severed tubes were torch sealed with gold. A retest found a leak still present due to a F-120 tube split at the ninety-degree bend. This leak was also closed up by torch sealing with gold. The unit was then dried in a furnace at ~200°C for several hours and then retested. A leak rate of 2.1 minutes was obtained just meeting the minimum established test criterion of two minutes.

Electrolysis

The two-drum, four-cell Z-7 electrolyzer was electrically hooked up and placed into operation at ~852°C in a manner analagous to unit Z-6. The electrical testing procedure was similar to that previously described (Ref. 1). The electrolyte disks were all of ~0.050 inch (0.127 cm) thickness.

Oxygen was flowed through the outer envelope (see Figs. 3-1 and 6-6) at ~150 ml/min. Electrolytic oxygen transfer was carried out from the cathode chamber to the inside (anode) chambers of the drums by means of passage of a constant current in series through the four cells of the unit. The current was varied from 0.5 to 4 A over a period of several days to obtain relatively stable applied voltage values. These results are plotted in Fig. 8-1 in terms of total applied voltage for the four cells uncorrected for lead resistance losses. Values of individual cell voltages corrected for lead resistance losses for cell no. 2 (bottom cell of F-118) and cell no. 3 (top cell of F-119) are plotted in Fig. 8-2.

After these initial oxygen transfer runs, CO_2 taken through a water bubbler at room temperature was introduced into the drums at a flow rate of ~150 ml/min. The CO_2 flow rate was increased to ~160 ml/min at the 4 A value. A series of applied voltage versus current values was obtained under operating conditions (of temperature, lead resistance losses, I^2R heating) otherwise similar to the oxygen transfer experiments. These curves are also shown in Figs. 8-1 and 8-2 where they can be compared with the oxygen transfer results to obtain approximate polarization values directly by difference without the necessity of making any corrections for IR losses. Polarization losses for O_2 transfer at 200 mA/cm^2 are negligible.

Table 8-1 gives the individual cell values corrected for IR drop due to lead losses of these initial runs with O_2 and carbon dioxide. These corrections are 0.20 to 0.24

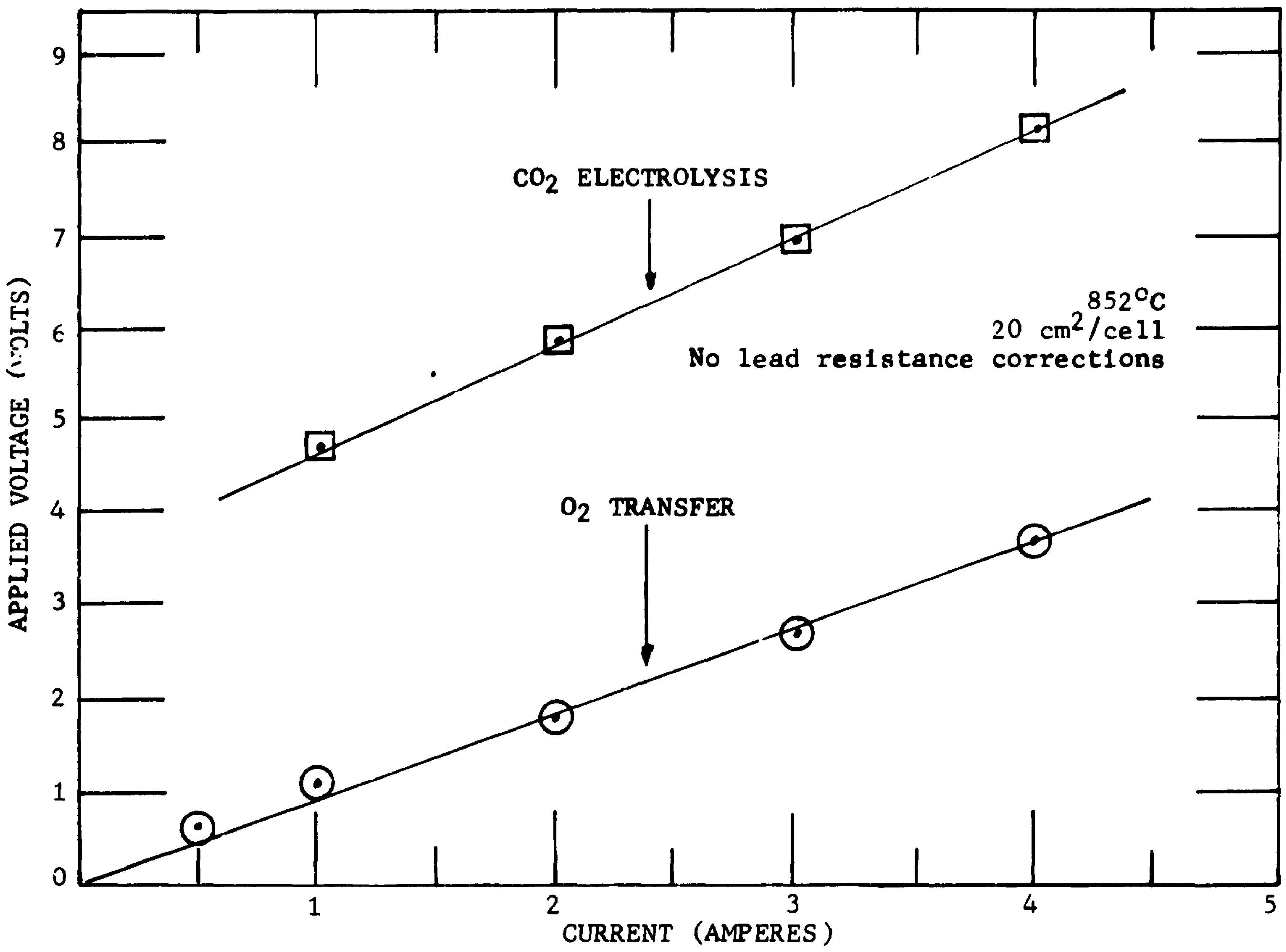

Fig. 8-1 Current-Voltage Curves for Four-Cell Electrolyzer Z-7

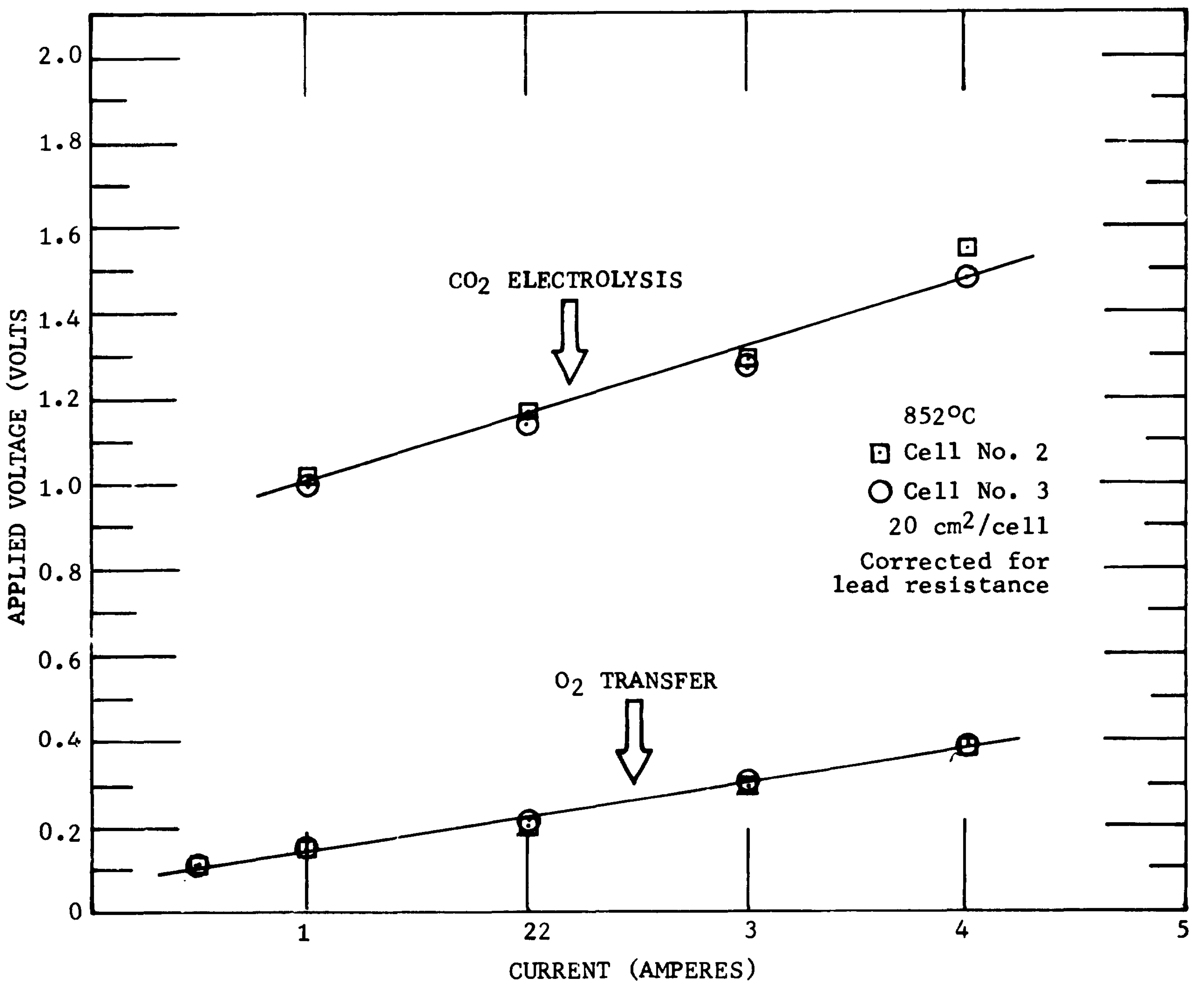

Fig. 8-2 Current-Voltage Curves for
Cells No. 2 and 3 in Four-Cell Electrolyzer Z-7

volts (at 4 A) for the inner cells no. 2 and 3 and are approximately 3 to 4 times these values for the two outer cells no. 1 and 4 because of the current lead resistances.

Table 8-1

INDIVIDUAL CELL CURRENT-VOLTAGE VALUES FOR UNIT Z-7

Current (A)	Process	APPLIED VOLTAGE (V)			
		Cell No. 1	Cell No. 2	Cell No. 3	Cell No. 4
4	oxygen transfer	0.42	0.38	0.40	0.44
3	carbon dioxide electrolysis	1.38	1.33	1.34	1.35
4	carbon dioxide electrolysis	1.55	1.57	1.49	1.51

After the oxygen transfer experiments, carbon dioxide electrolysis in unit Z-7 was continued at 3 to 4 A (150 to 200 mA/cm^2) or at a 12 to 16 A capacity level. The oxygen stream obtained by the electrolysis of CO_2 was monitored for CO_2 content by gas chromatographic analysis. The CO_2 content during a period of 21 days (~500 hr) remained constant at ~5 volume% indicating the presence of a small leak but no degradation of the seals with time. Applied voltage values for the four cells are presented in Table 8-2. The two inner cells, no. 2 and 3, have voltage probes attached at the inter-cell electrical connections. No IR corrections for lead losses of cells no. 1 and 4 have been made in Table 8-2.

Table 8-2

CO_2 ELECTROLYSIS - LIFE TEST PERFORMANCE OF UNIT Z-7

Days of Operation	Current (A) per Cell	APPLIED VOLTAGE (V)			
		Cell No. 1	Cell No. 2	Cell No. 3	Cell No. 4
8	4		1.77	1.73	
8	3		1.48	1.52	
10	4	2.35	1.80	1.70	2.19
10	3		1.51	1.49	
13	4[a]	2.82	2.08	1.63	2.22
15	4	2.68	1.70	1.81	2.31
19	4		1.70	1.73	
20	4	2.88	1.70	1.70	2.94
21	3		1.53	1.54	

[a] Operation interrupted for cell resistance measurements.

The approximate similarity of applied voltages to cells no. 2 and 3, which are of equal electrolyte thickness but belong to different drums, indicates that the distribution of the CO_2 gas stream from the inlet manifold tube is occurring approximately equally.

During the period of operation, conversion per pass of CO_2 to CO (i.e., CO concentration in the cathode outlet gas) as high as 80% was obtained again showing that equality of gas distribution among the four cells is being achieved.

The onset of a catastrophic leak on the twenty-first day of operation was noted by a sudden jump in CO_2 content from ~5% (4.4 to 6.1%) to ~40%. Pressure exerted by the alumina thermocouple tube resting on the top disk may have caused the crack found in it. Examination of the bottom seal of this drum indicated that it also had opened up.

In order to check the strength of the drum-to-manifold connecting tubes, the unit was removed from the Lava A assembly jig. The mechanical strength of the seals and tubes were tested by handling the unit alternately by the two manifold tubes and by one of them. The metal interconnecting tubes appeared to have sufficient strength to be able to eliminate the Lava A jig and to hang the subsequently assembled units directly from the aluminum cover plate by the manifold tubes.

The results of two-drum unit Z-7 demonstrated that the general approach being pursued in the construction, sealing, assembly, and testing of drums and multi-drum units was sufficiently promising to be adopted with modifications and improvements for the construction and assembly of multi-drum modules required for the one-man electrolysis unit.

8.2 GAS-TIGHT, EIGHT-AMPERE TEST UNIT (NUMBER Z-8)

8.2.1 Introduction

Assembly and testing of a one-drum CO_2 electrolysis unit was undertaken to obtain information on (a) correlation between room-temperature and high-temperature leak tests and (b) to serve as a basis for comparison of the pressure drop across the manifold-to-drum interconnecting tubes and the current-voltage characteristics of a one-drum unit versus the multi-drum units required for the one-man unit.

Unit Z-7, which just met the two-minute minimum $\Delta t/\Delta p$ test criterion, produced oxygen at high temperature at a rate of 4 A per cell for four cells at ~100% faradaic current efficiency and with a CO_2 content from leakage of ~5% volume. Further correlation was required to lend general validity to the room-temperature tests for drums and Z units (electrolyzers using drums) exceeding the minimum time of two minutes by a factor of ten or better.

Uniform parallel CO_2 flow between drums (equal flow rates in multi-drum electrolysis units is required. To achieve these conditions, the pressure drop across the inlet metal gas ports (between drums and inlet alumina manifold tube) should be at least a factor of ten greater than the pressure drop down the alumina manifold tube and uniform from drum to drum. In the previous ceramic bodies of unit Z-4, inlet and outlet port holes drilled in the bodies between the cell and the inlet and outlet manifold were of ~0.10 cm i.d. For a flow of ~160 ml/min of CO_2, the pressure drop across the port holes of each set of manifold chambers was ≤0.5 inch of water (~0.02 psi). The present drum-to-manifold interconnecting metal tubes are of the same 0.10 cm i.d. but are 2.54 cm long, a factor of 3 to 4 longer than the Z-4 ports, in order to increase the pressure drop by an equivalent factor. The pressure drop across a one-drum Z unit can then be correlated with the pressure drop across a multi-drum Z unit at the same gas flow per drum, taking into consideration the increase of total gas flow inside the alumina manifold tubes with increasing number of drums.

High conversion of CO_2 to CO per pass through the drums is required for optimal operation of the CO disproportionation reactor. Local non-uniform buildup of CO or concentration gradients from the cathode surface to the bulk gas phase can occur due to inadequate mixing. Higher than average values of CO at the electrode can lead to deposition of carbon, blocking of the electrode, and eventual reduction of the electrolyte surface. Adequate mixing of the gas must be obtained inside the drum for the operating conditions chosen. Operational data on the allowable upper limits for conversion per pass as a function of flow rate, current density, and temperature is, therefore, required for a one-drum Z unit to serve as a basis of comparison with results from multi-drum Z units.

8.2.2 Assembly

The details of the fabrication and leak testing of this one-drum unit, Z-8, will follow in general the description previously presented for unit Z-7 above and in Section 6. The designation of the drum is F-163. The top and bottom electrolyte disks of the drum are 0.089 and 0.090 inch (0.23 cm) in thickness, respectively. The disk-to-body seals are of the edge type made with Au and described in sub-section 4.2.1. The general arrangement of drum and manifold tubes connected by Pt alloy tubes is similar to Unit Z-7. The Pt alloy tubes were brazed to the alumina manifold tubes by means of Au-Ag alloy melting at 1000°C. After seal-up the $\Delta t/\Delta p$ test (see description in Section 7) was carried out with unit Z-8 remaining in the Lava A sealing jig. The test result was 20 minutes. In contrast to unit Z-7, unit Z-8 was removed from the Lava A sealing jig and hung from the aluminum closure plate of the mullite envelope by means of the alumina manifold tubes. The Pt alloy tubes and seals were sufficiently strong mechanically to hold the drum in place without additional support. The tube bends allow relief of stress transmitted from the alumina tubes. The two cells were electrically connected in series and current and voltage leads were attached and taken to the outside through the aluminum closure plate. After placing into the external mullite envelope and making a gas-tight connection between the envelope and the closure plate, a $\Delta t/\Delta p$ test result of 20 minutes was obtained. The unit was then placed in operation at ~850°C.

8.2.3 Testing

Preliminary Experiments

Experiments involving electrochemical oxygen transfer between the outside chamber of the mullite envelope and the inside chamber of the drum, electrolytic decomposition of CO_2, and measurement of cell voltages and faradaic oxygen efficiencies indicated that the top cell of this drum was short-circuited. CO_2 electrolysis in unit Z-8 with the top cell short-circuited was continued for nearly two days at an oxygen output of ~5 ml/min. Gas chromatographic analysis indicated the presence of only 0.05 to 0.06 volume% CO_2 in this oxygen stream. Details of the gas chromatographic analyses are presented below. The unit was then shut off and cooled down to room temperature for examination of the wiring. The discovery of an electrical connection inside the drum between the two inner electrodes and the top seal required that the two leads from the internal electrodes be interconnected externally to a common 0.040-inch Au current lead and that the two cells be operated independently. A probable explanation for the internal short in drum F-163 is to be found in sub-section 4.2.1. After rewiring and re-assembly in the mullite envelope, the $\Delta t/\Delta p$ test gave a reading again of 20 minutes. Unit Z-8 was then put back into operation at ~870°C. The value of the room-temperature $\Delta t/\Delta p$ test as a diagnostic test for drums and assembled units is clearly established by these results.

Before proceeding with the electrolysis experiments, a pressure gauge capable of measuring 0 to 15 inches water pressure was installed in the CO_2 line between the water bubbler and the inlet alumina manifold tube of Unit Z-8. The pressure drop at various flow rates of CO_2 was measured with unit Z-8 at ~870°C. The results are shown in Fig. 8-3.

Electrolysis

Electrolytic oxygen transfer experiments from the outer chamber to the drum chamber were made to pre-treat the electrodes and to use as reference for comparison purposes with CO_2 electrolysis experiments made under similar conditions. A constant current of 1 to 4 A was passed through each cell (50 to 200 mA/cm^2) over a period of several days to obtain relatively stable voltage values. Current-voltage data for the top and bottom cells are plotted in Fig. 8-4. The applied voltage values are obtained by means of voltage probes and can be assumed essentially free of lead IR losses. The currents are always measured using shunts having an accuracy of ± 0.2% at 2 and 4 A. Except during experiments, CO_2 electrolysis was continued at 4 A per cell. The CO_2 flow rate to the unit was maintained at 140 ml/min.

The faradaic current efficiency was monitored at frequent intervals using soap bubble flow meters to measure the oxygen production rate. The faradaic current efficiency for oxygen transfer and CO_2 electrolysis under the conditions described was essentially 100%. At 25°C, one atmosphere, and for a total current of 8 A, the oxygen production rate should be 30.4 ml/min. Uncorrected data from the bubble meter gave the following typical values:

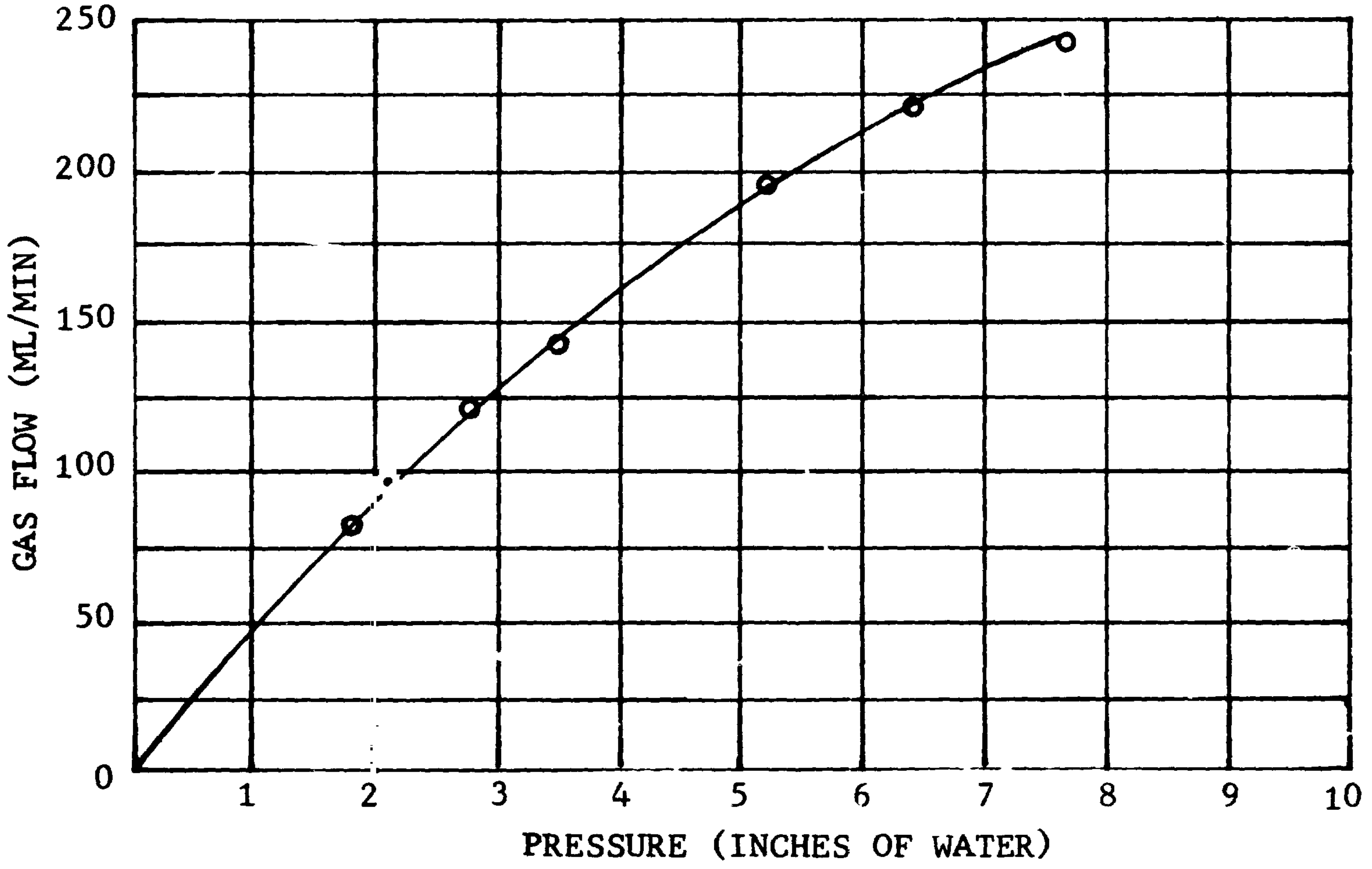

Fig. 8-3 Pressure Drop Across Manifold Tubes of Unit Z-8 Containing One Drum

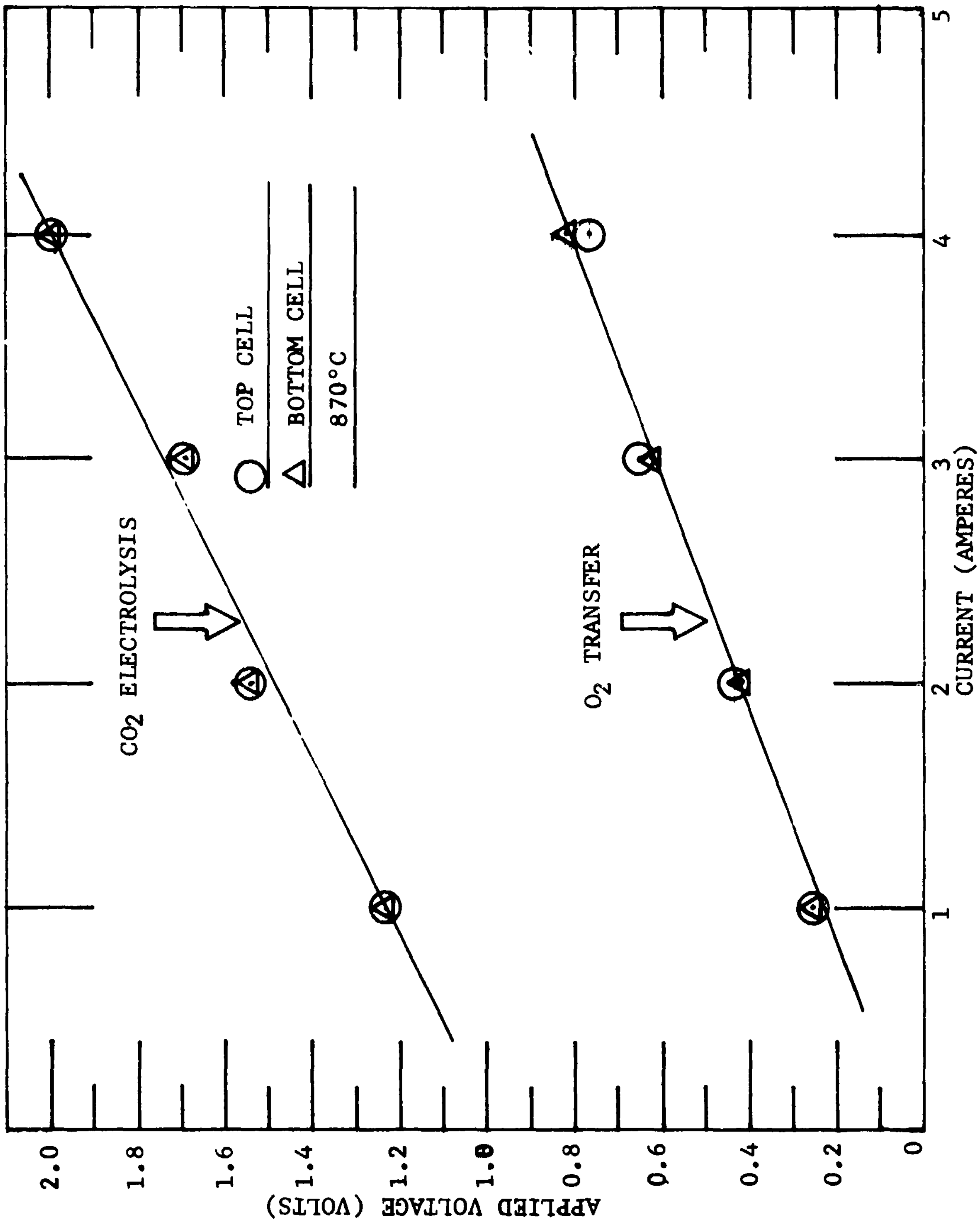

Fig. 8-4 Current-Voltage Curves for Electrolyzer Z-8

Oxygen transfer - 30.5, 30.8 ml/min at 22.0°C

CO_2 electrolysis - 30.3, 30.3 ml/min at 23.3°C
31.1, 31.3 ml/min at 27.2°C

The voltage values for the individual cells of unit Z-8 (Fig. 8-4) are higher than those of unit Z-7 (Fig. 8-2) for electrolytic O_2 transfer and CO_2 electrolysis. The higher values are directly ascribable to the higher IR drop across the cells because of the thickness of the electrolyte disks, 0.090 versus 0.050 inch. The voltage difference for CO_2 electrolysis minus O_2 transfer for the cells in each Z unit correspond relatively closely although some differences in CO_2 flow rate and temperature exist.

The electrolytically produced oxygen was monitored for CO_2 at frequent intervals by the gas chromatographic technique discussed below. The CO_2 content in the oxygen stream was <0.01% corroborating the existence of gas-tight seals found by the room-temperature $\Delta t/\Delta p$ test. For unit Z-8 the oxygen production current efficiencies and the faradaic oxygen current efficiencies are equivalent because of the absence of a leak between the cathode and anode gas chambers.

Gas Analysis

Analysis for CO_2 contained in the oxygen stream produced by electrolysis of CO_2 is monitored by gas chromatography. A Varian Aerograph model 1720-1 gas chromatograph with a four-filament thermal conductivity detector using type WX filaments was used here as well as for earlier multi-cell test electrolyzers. For the separation of the CO_2 from oxygen, Poropak Q and molecular sieve columns are connected in series with provision to bypass the molecular sieve column by means of an externally operated valve. Samples of 0.5 ml taken with a Hamilton gas syringe from the oxygen stream are injected into the column port. Chromatograms and their integration are obtained on a Hewlett-Packard model 7101B ten-inch strip chart recorder with 17501A input module, 17107A input filter and disk integrator. The responsivity of the detector to CO_2 and O_2 is calibrated by using the pure gases. After the preliminary indications of gas-tight seals noted above, further testing was carried out with the rewired Z-8 unit. At an output rate of oxygen ~30 ml/min with electrolysis at 4 A per cell, no CO_2 was detectable in the O_2 stream, as can be seen in Fig. 8-5 from the flat base line. An attenuation factor of

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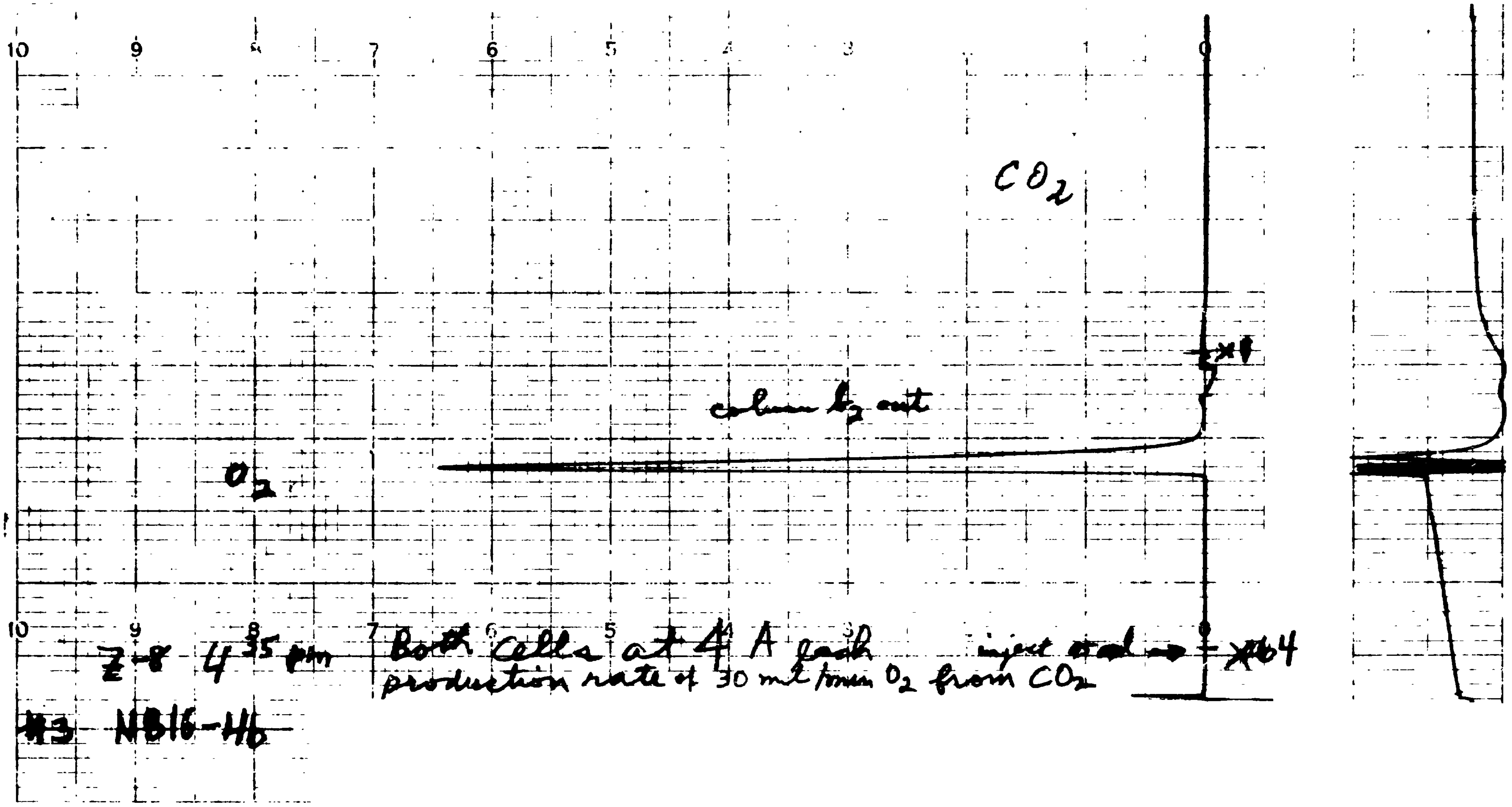

Fig. 8-5 Chromatogram Showing Absence of CO_2 in O_2 Stream from Electrolyzer

unity for CO_2 and times 64 for the oxygen peak is used. For comparison, a 0.5 ml air sample containing 0.06% CO_2 is shown in Fig. 8-6. With CO_2 electrolysis reduced to an oxygen output rate of ~6 ml/min or ~1/5 of the 4 A per cell rate, the CO_2 content in the oxygen stream is calculated to be 0.03% as shown in Fig. 8-7. The lower limit of detectability by the present analytical technique is 0.01% CO_2 in O_2.

Life Testing

The electrical performance of unit Z-8 during testing is shown in Table 8-3 as a function of number of days of operation.

Table 8-3

PERFORMANCE OF UNIT Z-8 DURING
CO_2 ELECTROLYSIS AT 4 A PER CELL[a]

Days of Operation	APPLIED VOLTAGE (V) Top Cell	APPLIED VOLTAGE (V) Bottom Cell
1	electrolytic O_2 transfer	
1	2.27[b]	2.21[b]
2	1.93	1.95
9	2.04	1.95
10	2.00	2.01
11	1.98	1.92
12	1.95	1.93
13	1.98	1.98
16	1.95	2.06
17	2.01	2.13
19	1.96	2.23
20	1.96	2.22
23	1.96	2.48
26	2.00	2.59
31	1.95	2.63
31	current off for TC repair	

[a] Faradaic current efficiency was ~100% and CO_2 in O_2 was <0.01% throughout this period.

[b] Initial voltage on start-up.

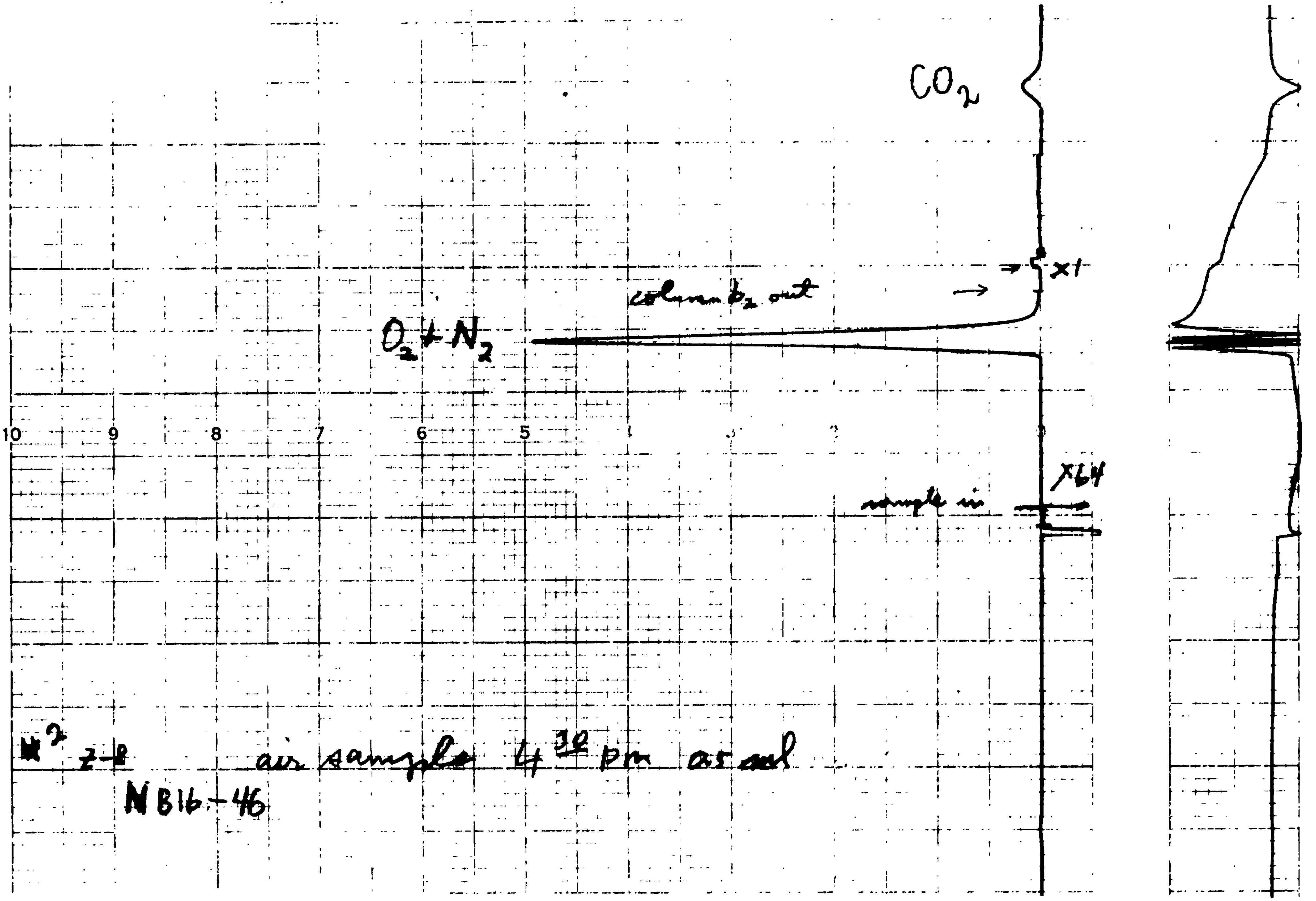

Fig. 8-6 Chromatogram of CO_2 in Air

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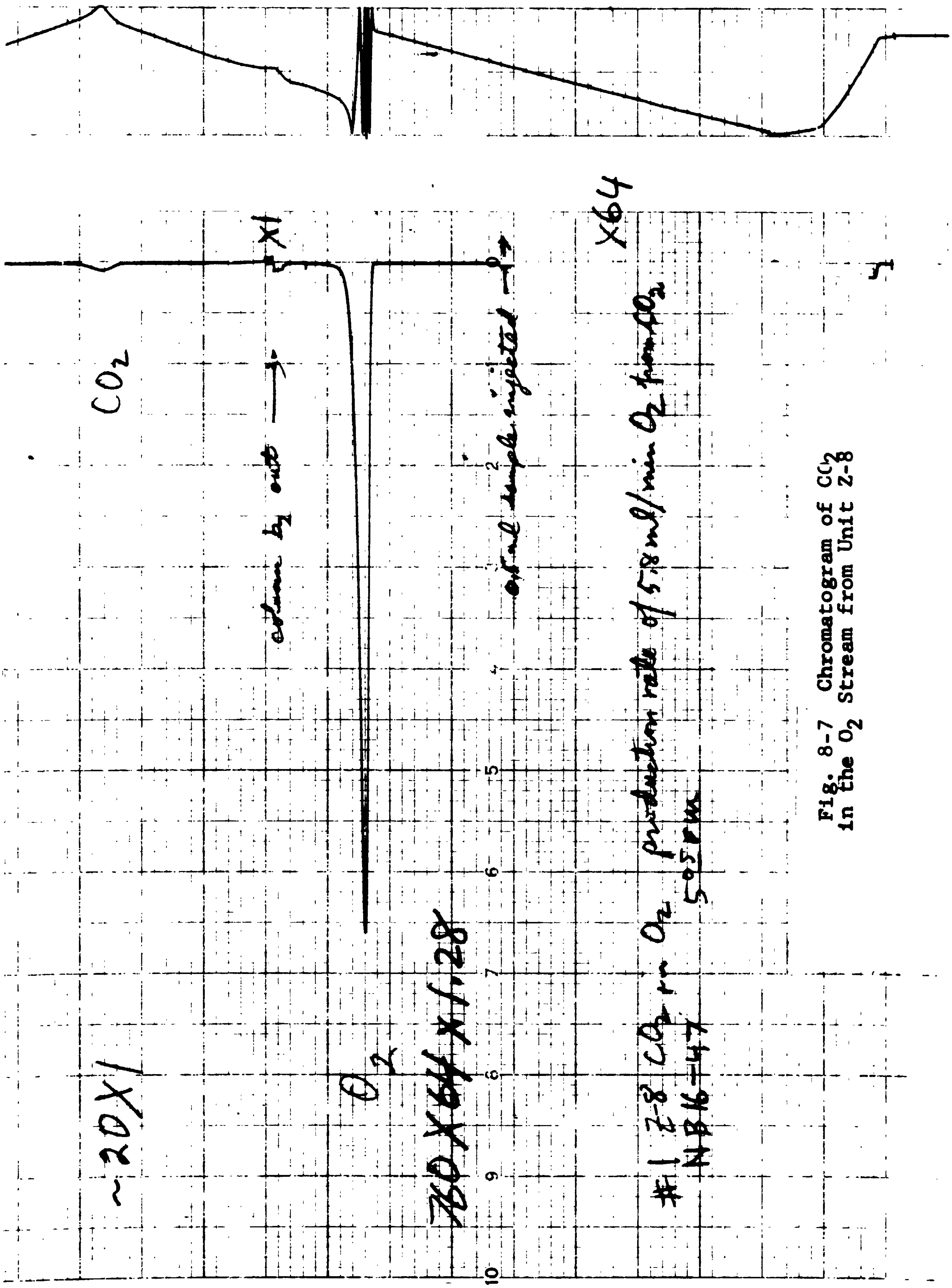


Fig. 8-7 Chromatogram of CO_2 in the O_2 Stream from Unit Z-8

At the end of 30 days of operation the current to both cells was shut off to purge the line from CO before proceeding to repair a thermocouple break on top of the mullite tube closure plate. Except for some rise in voltage of the bottom cell, unit Z-8 operated flawlessly during this period. Before continuing with CO_2 electrolysis, several hours of electrolytic O_2 transfer from 1 to 4 A was carried out. CO_2 electrolysis was then continued with 100% faradaic current efficiency and absence of CO_2 in the O_2 being produced.

The first sign of deviation from near perfect operation of unit Z-8 was noted in a drop in the current efficiency value and a large rise in the voltage of the top cell on day 37 after the usual unattended continuous operation over the weekend. When the current to the top cell was turned off, the current efficiency (for operation of the bottom cell by itself) recovered, but for the first time in the operation of unit Z-8 the presence of significant CO_2 was detected in the oxygen stream. The current to the bottom cell was then also turned off because it was noted that corrosion of the pressure gauge had occurred by the action of the water vapor from the bubbler, and reddish-brown water had condensed out and collected in the CO_2 line downstream from the pressure gauge. No obvious connection between the performance of the top cell and possible contamination with solid corrosion products could be established. The gauge was removed from the line. Further testing of the unit by means of electrolytic O_2 transfer experiments again indicated a severe rise in the voltage of the top cell. Continuation of CO_2 electrolysis experiments in absence and presence of current to the top cell clearly established the top cell as the source of the drop in current efficiency and the CO_2 leak. A listing of these experiments is given in Table 8-4.

The operation of unit Z-8 was discontinued in favor of disassembly for further room-temperature examination. After removal from the furnace and removal of the unit from the envelope, leak checks were made. Pressurizing to twelve inches of water gave no leaks at the seals using leak check fluid. Pressurizing to six inches of water with Freon-12 and using the halogen leak detector showed that the major leak appeared to be through the top disk. Repressurizing to six inches of water and painting the top disk over the grid with water indicated that the leak rate fell drastically as the surface of the disk was covered with water. Therefore, it was confirmed that there were no leaks at the seals but there was a

Table 8-4

PERFORMANCE OF UNIT Z-8 AFTER 31 DAYS OF CO_2 ELECTROLYSIS AT 4 A PER CELL[a]

Days of Operation	APPLIED VOLTAGE (V)		Faradaic C.E. (%)[b]	CO_2 in O_2 (%)
	Top Cell	Bottom Cell		
32	electrolytic O_2 transfer		98	
32	2.51[c]	2.74[c]	101	
33	2.48	2.64	95	
33	1.98	2.14	102	<0.01
37	~2.9	~2.4	84	
38	0.89[d]	2.42	99	7.3
38	current off - removed pressure gauge			
39	3.64[e]	1.65[e]	101	
40	0.85[d]	2.47	100	3.4
40	3.13[f]	2.31[f]	90	7.4

[a] Operation interrupted on day 31 to repair thermocouple break.

[b] Uncorrected for room temperature fluctations.

[c] Initial voltage on start-up.

[d] Open-circuit cell voltage.

[e] Electrolytic oxygen transfer at 4 A.

[f] Current through cells at 2 A.

leak through the top disk. The drum was then sliced through the middle of the drum body parallel to the disks to examine the top and bottom disks from the inside. The inside grid of the bottom disk remained adherent to the disk surface. Except for a purplish tinge on the surface of the disk on peeling back the grid, no changes from its original appearance were noted. The grid of the top disk appeared to have been removed during the sawing. Pieces of the ceramic electrolyte were pulled out of the inside surface along with the grid. Major damage to the top disk appeared to have taken place in a 1/4 to 3/8 inch band around the perimeter of the grid circle. From the physical appearance of the inner surface of the top electrolyte disk and its current-voltage behavior in contrast to the bottom disk, it may be concluded that the loss of a large fraction of electrode contact area occurred between day 33 and 37 of operation (see Table 8-4). As a consequence, high current density areas near the perimeter produced local heating leading to a runaway condition and electrode-electrolyte breakdown. Previous measurements of the surface conductivity from the center to the perimeter and the present results indicate that the electrode grid structure should be modified by the addition of current-carrying elements on the electrode surface to maintain uniform current density over the whole 20 cm^2 electrode area. It should be noted that 5 cm^2 area electrodes of similar construction on smaller disks at 100 ma/cm^2 CO_2 electrolysis showed no deterioration of electrical or mechanical properties of the electrodes or electrolyte after 3 months of continuous operation (Ref. 2).

8.3 ELECTROLYZER-REACTOR SYSTEM OF ONE-MAN CAPACITY (127 A)

8.3.1 Electrolyzer Test Stand

A multi-station test stand has been constructed to accommodate the test operation of several electrolyzers concurrently. The stand incorporates common carbon dioxide and oxygen supplies from cylinders which can be metered individually to each station. The oxygen output from each station can be manifolded to a common vent or sent, individually or in combination, through a soap bubble flowmeter to monitor the rate. The CO/CO_2 output from each station can be routed individually or in combination directly to an exhaust vent or through a heated reactor for the disproportionation of carbon monoxide to carbon dioxide and carbon.

A schematic representation of the gas flow system available at each test station is given in Fig. 8-8. The incoming, metered CO_2 is humidified at ambient by sparging through water. The pressure drop across the CO_2 inlet to CO/CO_2 exit side of the electrolyzer is measured with a dip-tube manometer using water as the working fluid. This manometer also serves as an overpressure safety release, preventing full CO_2 line pressure from being impressed on the electrolyzer should a line become plugged. All tubes, fittings, and valves in the oxygen and CO/CO_2 exit lines have a minimum diameter of 6.3 mm to minimize back pressure on the electrolyzer.

A schematic representation of the electrical system available at each test station is given in Fig. 8-9. The DC power supply may be operated in either a constant voltage or constant current mode with current limiter. The output current can be measured and regulated accurately by use of the shunt. Thirteen test taps are available for measurements of EMF values from within the electrolyzer. Three thermocouple pairs are also provided. Each station contains an electric furnace with accompanying AC power supply and temperature controller.

8.3.2 Reactor

A reactor for the disproportionation of CO to carbon and CO_2 consists of a carbon steel tube, 76 mm i.d. by 1.68 m long. The ends are closed with welded steel plates accommodating small diameter inlet and exit tubes. A furnace with cylindrical heating elements 460 mm long surrounds the reactor tube concentrically. The furnace can be moved along the length of the tube to provide new heated volume as the previously heated section fills with carbon deposit. A schematic representation of the reactor flow system is presented in Fig. 8-10. Analytical sample ports have been provided so that the composition of the gas stream before and after the reactor may be determined. Samples are taken by hypodermic syringe through a septum in the port. A provision has been made to flush the reactors with nitrogen prior to introduction of CO, if required. The reactor and bypass-vent lines are connected through a dip-tube manometer (identical to those used in the electrolyzer station flow system). This manometer measures the pressure drop through the reactor and also serves as an overpressure release should the reactor become plugged.

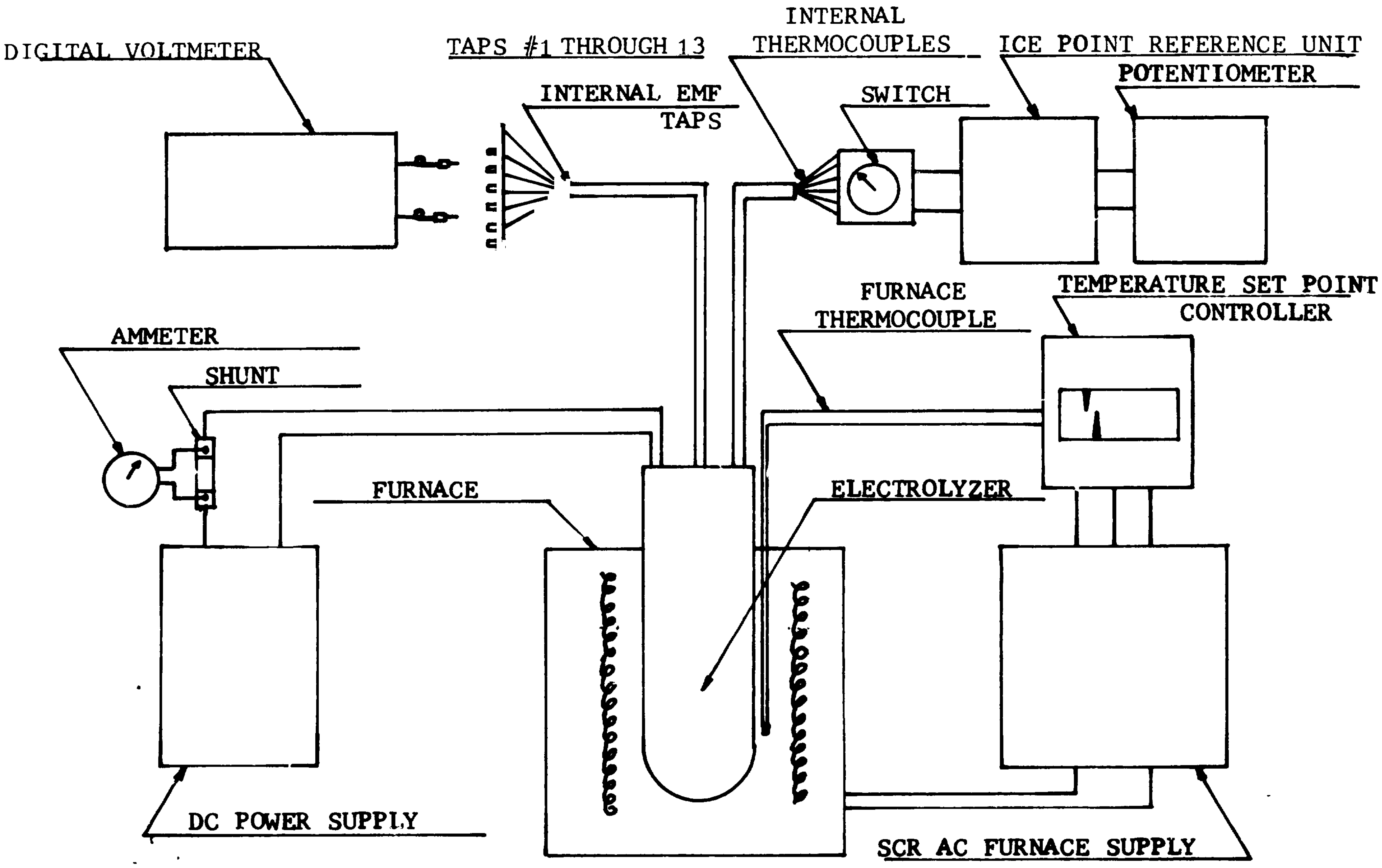


Fig. 8-8 Electrolyzer Test Stand Schematic of Electrical System for One Station

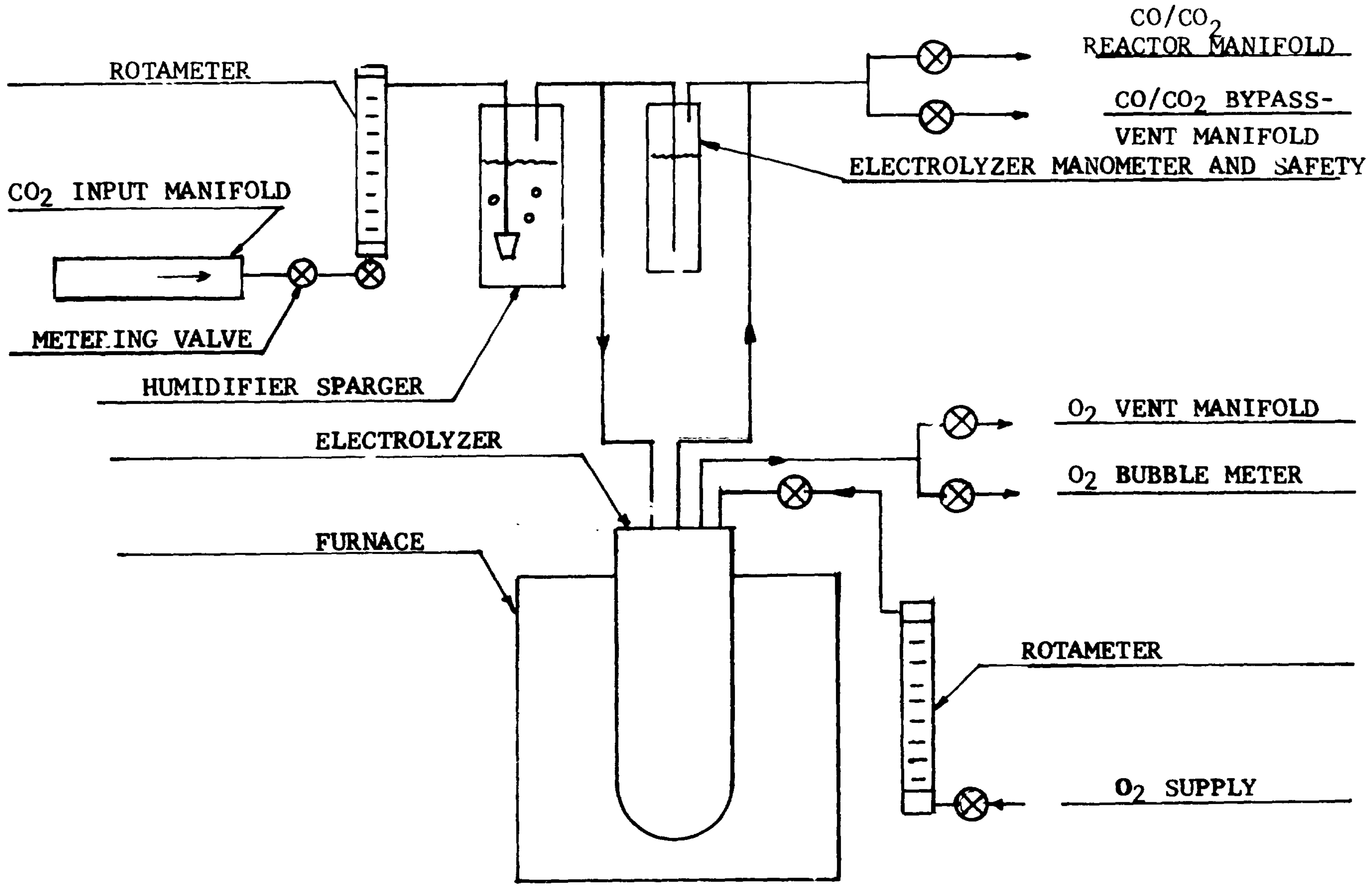


Fig. 8-9 Electrolyzer Test Stand Schematic of Gas Flow System for One Station

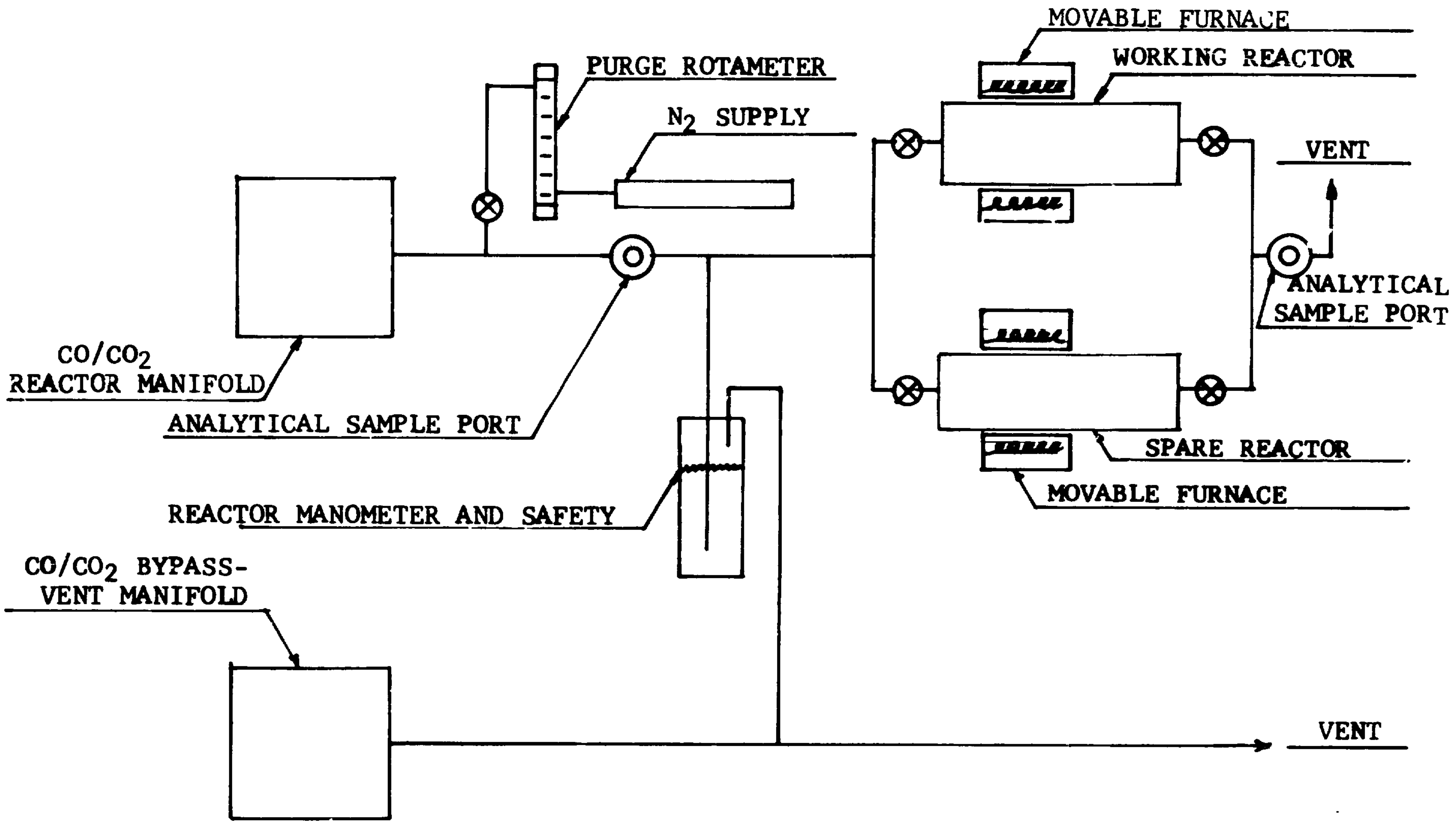


Fig. 8-10 Schematic of Reactor Flow System

8.3.3 250-Hr CO_2 Electrolysis Life Test

The construction of units Z-9, Z-10, Z-11, and Z-12 has been described in detail in Section 6. Each of the units consists of six drums or twelve cells connected in series electrically and having parallel gas flow manifolding. The zirconia disks were sealed to zirconia drum bodies by means of butt seals in unit Z-9 and edge seals in units Z-10, Z-11, and Z-12 as discussed in Section 4. The capacity of each unit for electrolytic O_2 production is rated at 48 A for operation at a current density of 200 mA/cm^2.

Unit Z-10, after assembly and room-temperature testing for gas leaks and electrical shorts, was connected to the multi-station test stand for preliminary testing and evaluation of a six-drum, twelve-cell CO_2 electrolyzer module. A photograph of a six-drum Z unit is shown in Fig. 8-11. This was before assembly into the outer envelope. Other stages of the assembly of Z units are shown in Figs. 6-1 to 6-5 above. The schematic diagram for unit Z-10, which is similar for the other six-drum Z units, is presented in Fig. 8-12. The diagram shows the current leads to the power supply, the location and numbering of the voltage test probes for all of the twelve cells, and the location of the three Pt/Pt 10% Rh thermocouples. The polarity is shown for CO_2 electrolysis as carried out in the Z units with the cathode chambers located on the inside of the drums and the electrons and oxide ions flowing in the direction of increasing numbers. The polarity is reversed for electrolytic O_2 transfer from the outer chamber to the inside of the drums. The electrodes were pretreated by electrolytic oxygen transfer in both directions as previously described for units Z-7 and Z-8. CO_2 electrolysis was carried out at 860 to 870°C at 3.5 A per cell or at a total capacity of 42 A for a period of two days. At 3.5 A per cell (42-A total) the oxygen flow rate obtained from the decomposition of the CO_2 was 158 to 160 ml/min (the theoretical rate is 159 ml/min at 25°C, 1 atm) using a soap bubble flow meter. The faradaic current efficiency was ~100% uncorrected for the CO_2 content in the O_2 stream. Analysis of the oxygen stream by gas chromatography (see sub-section 8.2.3 for details) gave a value of 1.6% for the CO_2 content. Unit Z-10 was shut off and cooled down to room temperature. The electrolyte thickness of the cells in unit Z-10 and those in units Z-11 and Z-12 are given in Table 8-5.

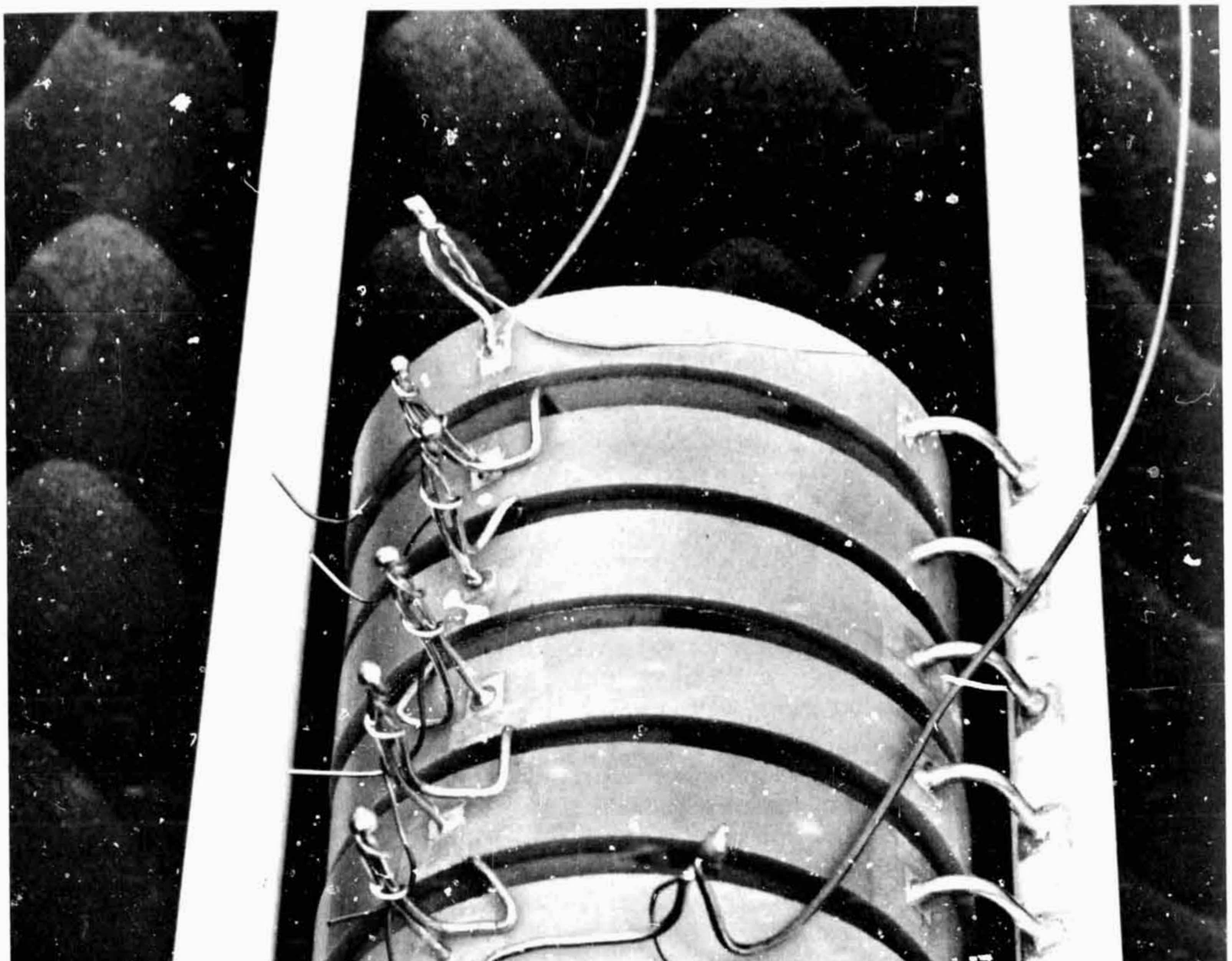
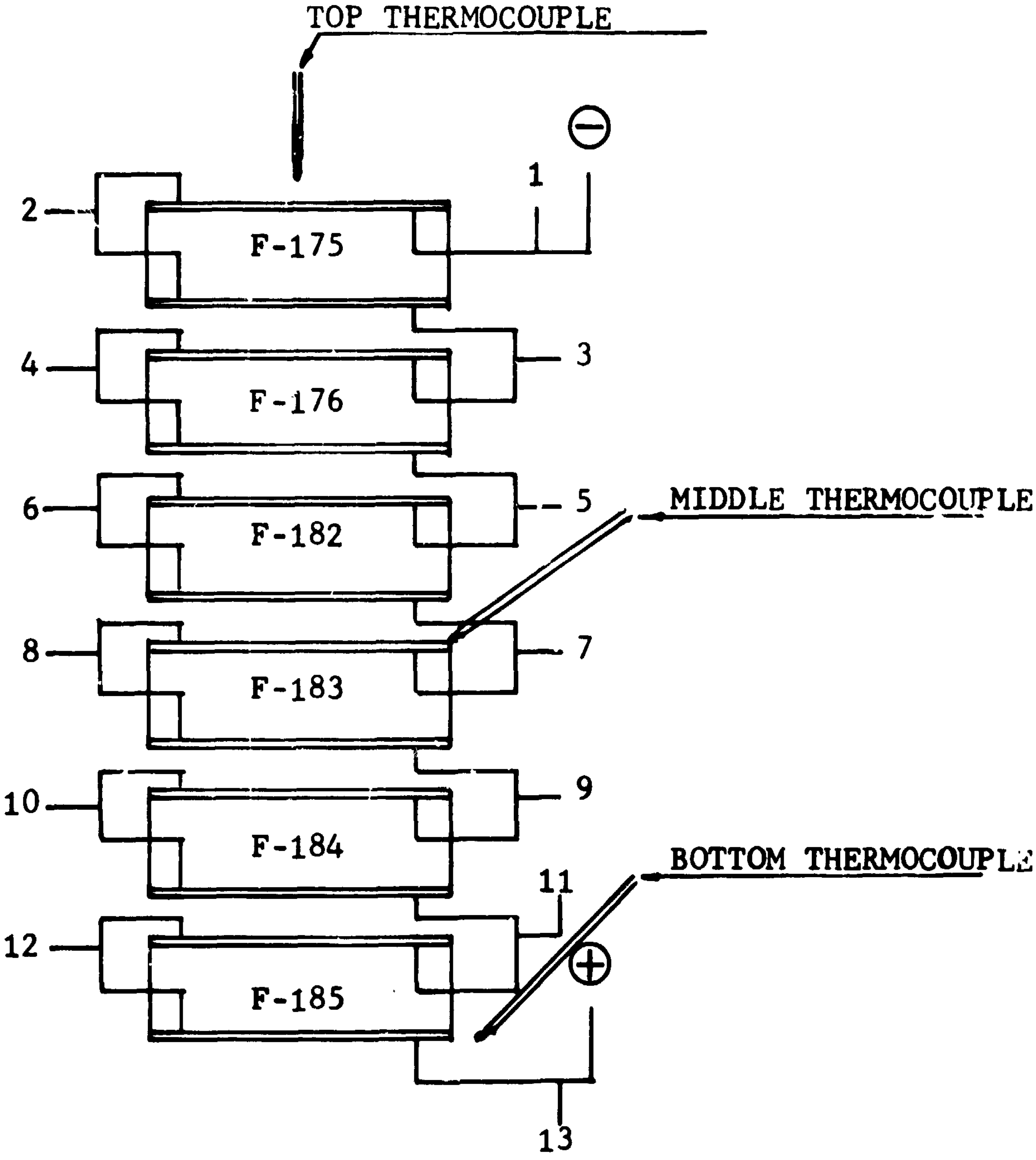


Fig. 8-11 Close-Up View of Six-Drum Electrolyzer



Numbers 1 to 13 - voltage probes
⊖,⊕ - leads to power supply

Fig. 8-12 Schematic of Unit Z-10

Table 8-5

127-A ELECTROLYZER ELECTROLYTE THICKNESS

Unit	Drum	ELECTROLYTE THICKNESS (INCHES)		
		Top	Bottom	Average
Z-10	F-175	0.060	0.060	0.062
	F-176	0.061	0.061	(0.159 cm)
	F-182	0.066	0.066	
	F-183	0.060	0.060	
	F-184	0.066	0.066	
	F-185	0.058	0.065	
Z-11[a]	F-172	0.045	0.045	0.045
	F-173	0.045	0.045	(0.114 cm)
	F-174	0.045	0.045	
	F-178	0.047	0.047	
	F-179	0.045	0.045	
	F-181	0.046	0.046	
Z-12	F-167	0.080	0.078	0.081
	F-171	0.075	0.073	(0.204 cm)
	F-188	0.085	0.085	
	F-189	0.076	0.078	
	F-190	0.084	0.084	
	F-191	0.084	0.084	

[a] The electroded areas of these disks were machined down to the thickness shown. For sealing edge thickness values see Table 4-5.

Units Z-11 and Z-12, after completion of assembly and room-temperature testing, were connected in the test stand along with unit Z-10 for operation at the one-man or 127-A capacity level. Oxygen was passed electrolytically at a rate equivalent to 1 to 3 A per cell from drums to envelope and from envelope to drums in each unit to pre-treat the electrodes before initiation of CO_2 electrolysis. CO_2 electrolysis was started at 0.5 A per cell and gradually raised to 3.5 A per cell over a period of 4 hr. The CO_2 flow rate was adjusted to give a 50% conversion rate. After attaining the 3.5 A per cell rate, the CO/CO_2 flow from the 127-A unit was routed through the carbon disproportionator reactor to begin the 250-hr life test. The temperature of the three Z units was in a range of 880 to 895°C as measured by the middle thermocouple. The other thermocouples were not significantly lower. The reactor temperature was ~556°C. At an operating flow rate of ~640 ml/min of CO_2 through each six-drum Z unit, the pressure differential across each Z unit (CO_2 inlet to CO_2 outlet manifold) was 2.5 $\pm$ 1/16 inches of water in close agreement with the value found for the one-drum unit Z-8 for a flow rate of ~107 ml/min or 1/6 of 640 ml/min (see Fig. 8-3). The performance of the 127-A electrolyzer as a function of the number of hours on the 250-hr life test is presented in Figs. 8-13, 8-14, and 8-15 for units Z-10, Z-11, and Z-12, respectively. Shown are values per Z unit for applied voltage, faradaic current efficiency (uncorrected for the CO_2 content and room temperature fluctuations), and the CO_2 content in the O_2 stream. Only a gradual rise in CO_2 content occurred in units Z-10 and Z-11 during the 250-hr life test. In contrast, unit Z-12, with CO_2 content of 0.5% for the first 100 hr, developed a leak after 110 hr of operation. The degree of conversion of CO to CO_2 and carbon in the reactor was also determined periodically during the 250-hr run by gas chromatographic analysis of the CO/CO_2 stream before and after passing through the reactor. For a CO/CO_2 stream leaving the electrolyzer with only a 53% CO content, the CO removed during passage through the reactor was found to be 32%. Most of the carbon filling up the steel tube was formed at this rate. Higher rates of CO removal are easily attainable with more complete electrolytic conversion of CO_2 to CO. The catalytic activity of the steel wall is enhanced by the H_2 and H_2O content of the CO-CO_2 stream from the electrolyzer, and the concentration of H_2 and H_2O can be varied by adjusting the rate of addition of H_2O to the CO_2 feed stream to the electrolyzer. Indication that the working reactor has become plugged with carbon and that the spare reactor should be turned on is provided by the manometer.

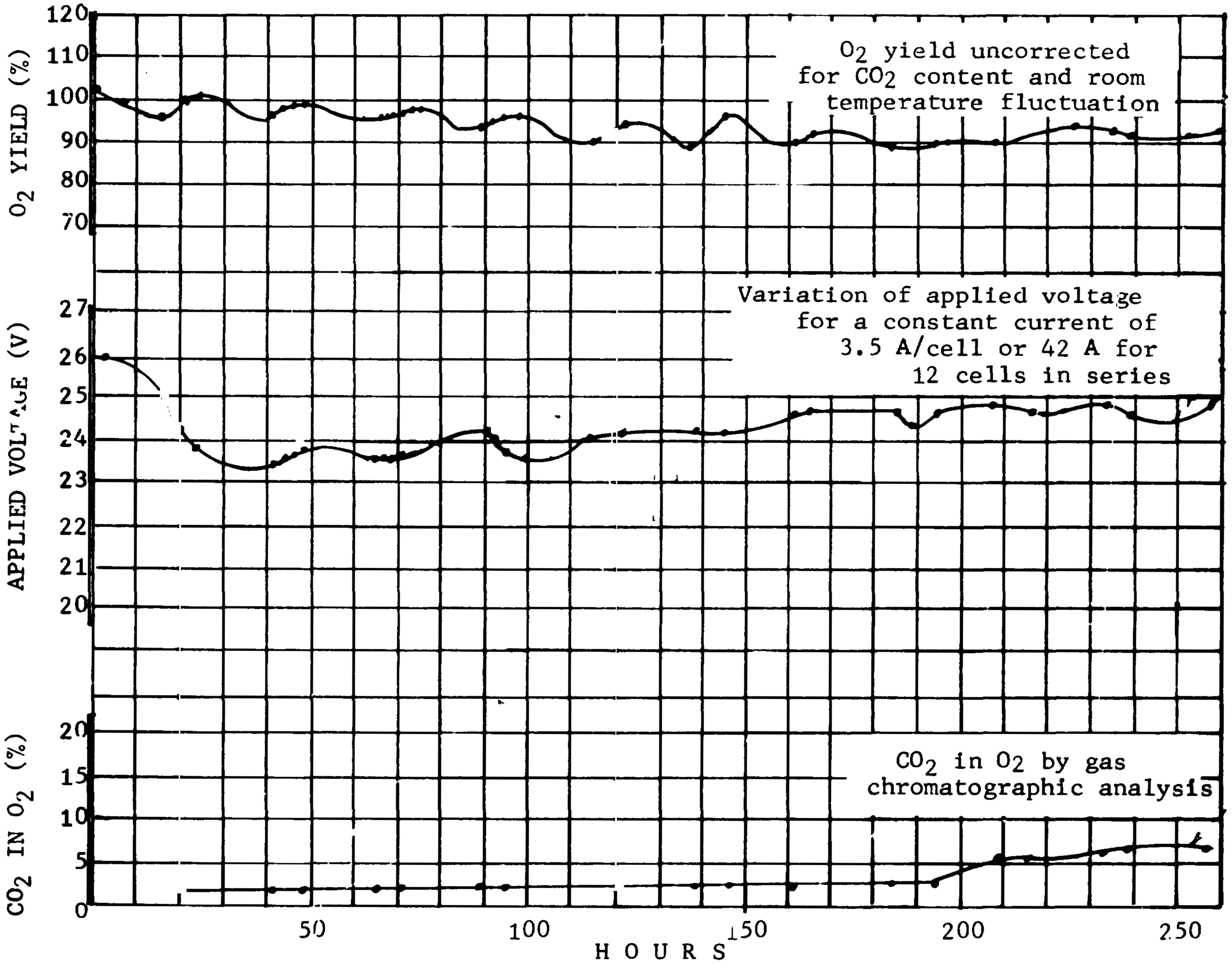


Fig. 8-13 Performance of 42-A Module Unit Z-10 of 127-A CO_2-H_2O Electrolyzer

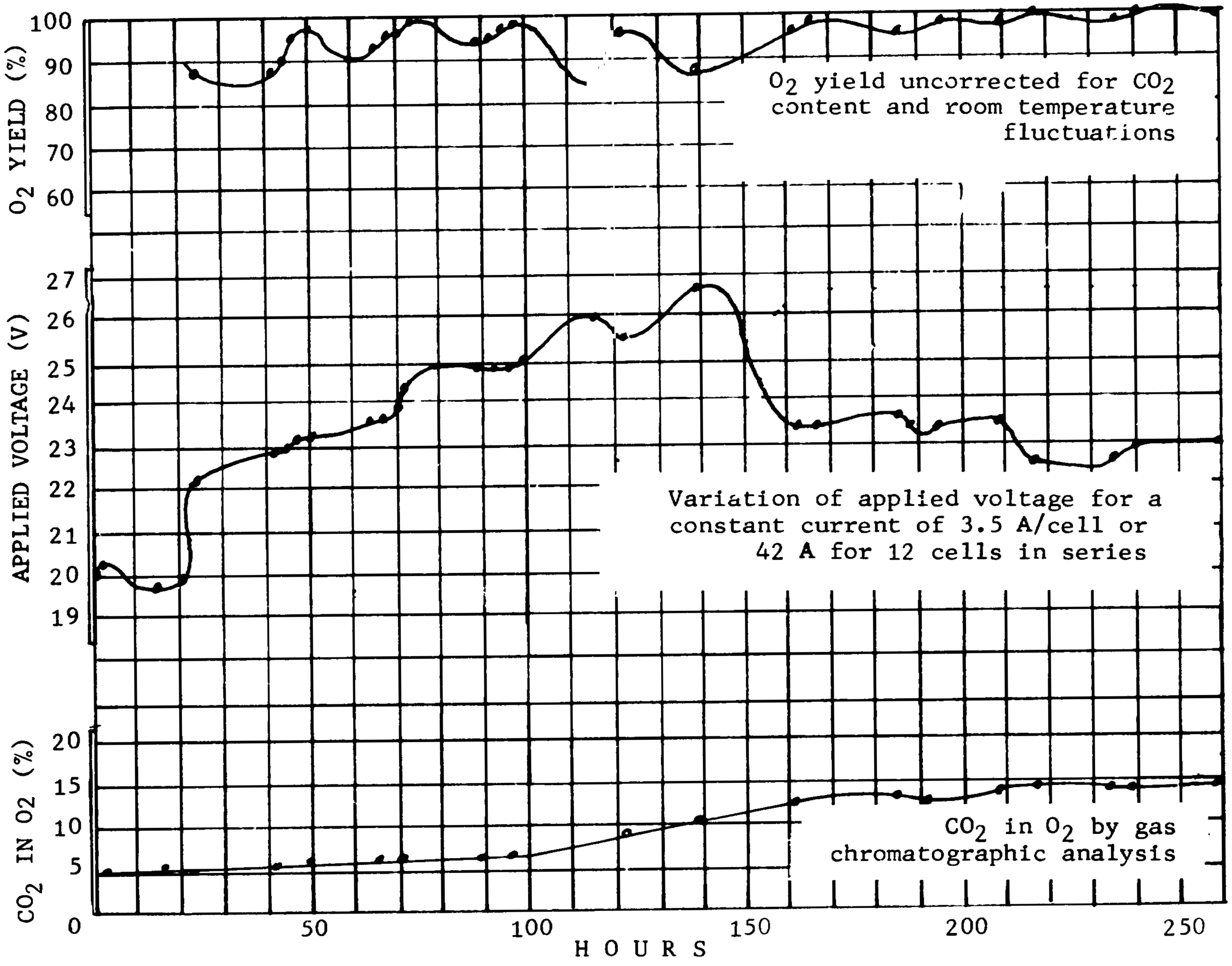


Fig. 8-14 Performance of 42-A Module Unit Z-11 Of 127-A CO_2-H_2O Electrolyzer

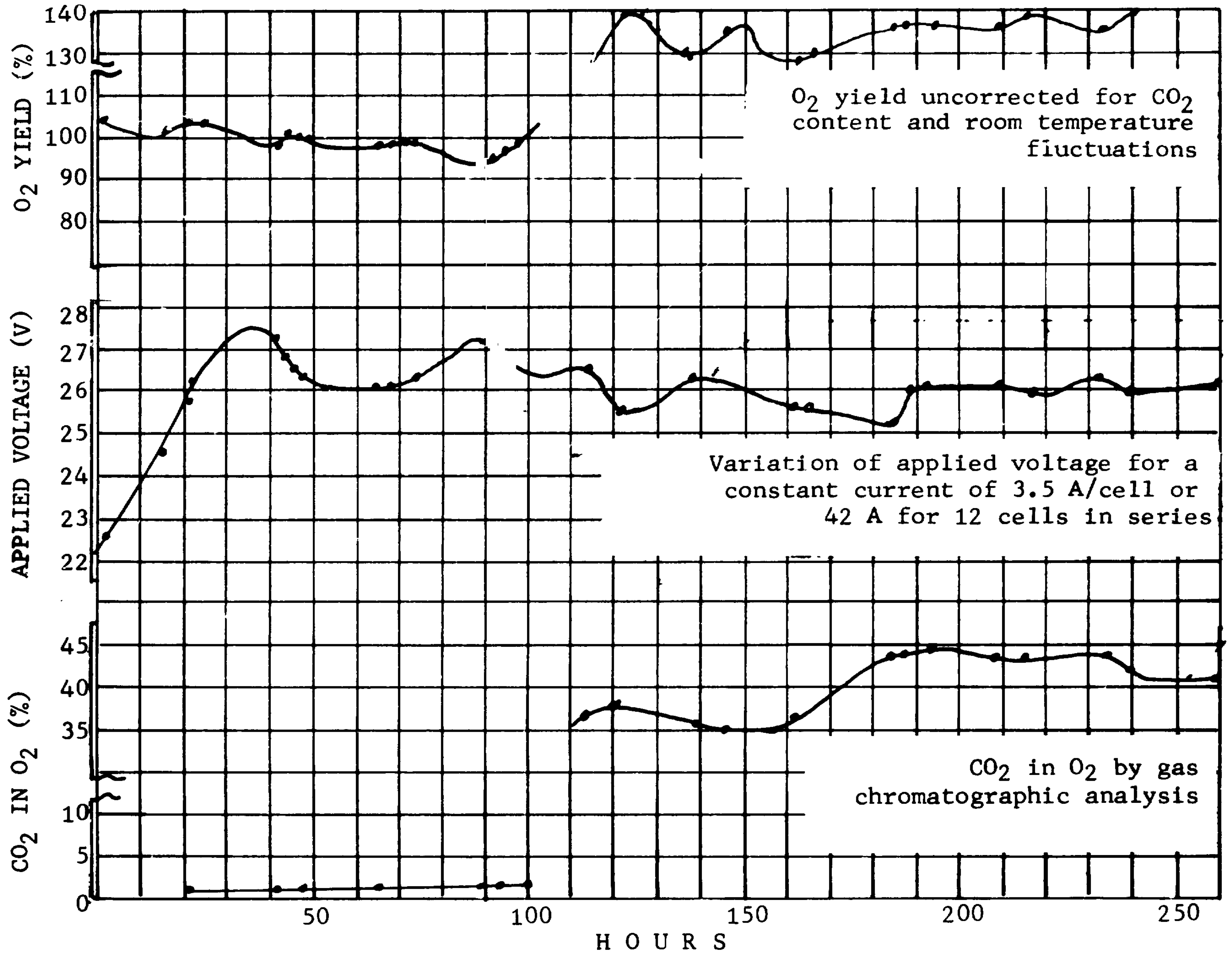


Fig. 8-15 Performance of 42-A Module Unit Z-12 of 127-A CO_2-H_2O Electrolyzer

Section 9

DISCUSSION

9.1 PRESENT STATE OF DEVELOPMENT

The technology required for the construction and operation of CO_2-H_2O electrolyzer-reactor systems based on stabilized zirconia electrolyte disks and capable of delivering breathable O_2 from CO_2 at a constant rate with near 100% faradaic efficiency and 50% power efficiency has been brought to a sufficiently high level to allow production of units at the one-man level (127 A) beyond the laboratory scale approaching the prototype stage.

Development of an operating unit of this size was brought about by a program in which a scale factor of 10 to 12 was applied each year starting from laboratory disk cells of area ~ 1 cm^2 and electrolytic current of ~ 100 mA (Refs. 1 and 2). The ability to proceed from such small individual cells to an electrolytic unit containing 36 electrolyte disks, each having a 20 cm^2 electrode area, sealed into ceramic bodies with high-temperature, gas-tight seals and containing gas manifolding, electrical leads, and other components capable of operation at $\sim 850^{\circ}$C has involved solving many problems. As the size of the units was increased, the principal problem areas changed, and at various developmental stages the key problems were ceramic fabrication, sealing, electrodes, gas manifolding, and electrical connections. Effort was directed, at each point during the scale-up process, to the solution of the most important problems in order that the development of larger operating units would not be impeded. The 127-A scale is a convenient size for application of engineering methods utilizing the present technology to develop CO_2-H_2O electrolyzer modules producing oxygen as components in actual life-support systems.

The design concepts previously found to be useful were retained in the development of this technology. The concept of using components or sub-units was retained throughout as exemplified in the construction and assembly of large-size multi-cell electrolyzer modules of up to 48-A capacity as used in the one-man device. In practical terms, components and sub-units are produced, tested at room temperature, and inventoried to be available for assembly into electrolyzer modules. The development of reliable sub-units or drums of 8-A capacity with gas-tight edge seals has made construction of reliable multi-cell or multi-drum units practical by avoiding the attaching together of a large number of ceramic disks and bodies in an unfavorable monolithic fashion. This has been accomplished by attaching drums separated from one another on manifold tubes by means of metal gas-feed tubulations.

The performance of unit Z-8 in producing oxygen containing <0.01% CO_2 shows that the sealing problem, which was the most serious problem of this contract year, has been solved. Seals of similar quality are now being made with >90% yield on drums, each of which is an 8-A electrolyzer sub-unit.

The canister reactor used for CO disproportionation during the integrated test of the one-man electrolyzer and reactor operated at a sufficiently high CO conversion efficiency, for inlet CO concentration range, to show the applicability of this type of reactor for the one-man level. The canister reactor system has the significant advantage of avoiding handling loose carbon with its problems of dirtiness, static electricity, and carcinogenic properties. Although the one-man test employed two steel pipe reactors, one of which was in use at any time and the other a standby, a larger system would use much lighter reactors of a size and number to be determined by later optimization studies based on performance data for large-scale operating units.

9.2 FUTURE DEVELOPMENT

The next stage in the development of CO_2-H_2O electrolysis modules capable of supplying oxygen for aerospace life support should consist of improving the design, components, and fabrication procedures of units of approximately the present one-man (127-A) size and of obtaining operational and long-term reliability data for such units. Further increase in electrolyzer size by a factor of 10 to 12, as was done under this program in the past, does not appear to be warranted inasmuch as the attained unit size is close to that desirable for modules of the 4 to 10 man missions for which this system is contemplated. Areas in which additional work should be done are as follows:

(1) The electrodes should be modified to permit higher current density operation, improve adhesion to the electrolyte, prevent non-uniform current distribution, and reduce the resistance of the electrode-electrolyte interface. These goals can be approached by better control of the deposition of the porous electrode film, better grid design, and the use of materials having higher electrical conductivities.

(2) Electrical leads of higher conductivity should be used.

(3) The gas flow pattern can probably be improved by modifying the metal tubulations to create additional mixing inside each drum and also to allow more precise control over the gas distribution among the drums.

(4) Electrolyte disks of lower porosity can be made by adjusting the parameters of the hot-pressing process Very low gas leakage through the improved seals has led to detection of a contribution to leakage from relatively thin disks.

(5) Although the present scandia-stabilized zirconia electrolyte is satisfactory, other compositions should be investigated for improved ionic conductivity, better machinability, and lower porosity.

(6) The size of each cell could be increased by increasing the disk diameter or by applying electrodes to a larger part of the disk of the present size. The disks now being used have an area of 30 cm^2 and the present electrode area is 20 cm^2. Sealing in the edge-sealed configuration allows almost the entire disk surface to be used for electrodes in contrast to the butt seals where a significant area was required as part of the seal and was unavailable for electrode application.

(7) The zirconia drum bodies now in use have the disadvantages of high density, low thermal conductivity, and relatively poor resistance to thermal shock but the important advantage of acceptably matching the coefficient of thermal expansion of the zirconia electrolyte. A body material of ceramic or metal with improved properties would be desirable.

(8) Torch brazing the drums to the gas manifolds would give greater flexibility to this assembly step and would avoid the thermal cycling involved in the present furnace brazing procedure.

(9) The drums and manifolds should be packaged in a lighter and smaller envelope than the mullite tube that is now used in laboratory testing.

(10) A considerable amount of operational data should be obtained by running units of approximately one-man capacity to enable calculation of reliability and redundancy factors for design of life-support systems.

(11) The canister-type catalytic reactor for CO disproportionation should be further improved to reduce its weight, optimize the gas flow pattern, and maintain, for larger units, the degree of conversion per pass of CO to C and CO_2 (depending on the CO inlet content) at the high level previously achieved.

Section 10

REFERENCES

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