OXYGEN SUPPLY SYSTEM FOR MANNED SPACE ENCLOSURES

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BRUCE BAILEY

FOREWORD

This research was conducted by Air Products and Chemicals, Inc., P. O. Box 538, Allentown, Pennsylvania 18105 under Air Force Contract No. AF 33(615)-3335, and in support of Project 6373, "Equipment for Life Support in Aerospace," and Task 637302, "Respiratory Support Equipment." The work was performed under the direction of the Life Support Division, Biomedical Laboratory, Aerospace Medical Research Laboratories, Wright-Patterson Air Force Base, Ohio, with Mr. C. M. Meyer of the Biotechnology Branch as contract monitor. The work covered by this report was performed during the period 1 December 1965 and 30 September 1966.

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The authors acknowledge the contributions of Lowell G. Frederick, senior laboratory technician, who conducted much of the experimental program and fabricated the laboratory model.

This technical report has been reviewed and is approved.

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ABSTRACT

This study was conducted to design, construct, and test an Oxygen Supply System for Manned Space Enclosures. The system was designed to provide oxygen at a rate of 0-91 grams/hr (0-0.2 lbs/hr) for a period of 24 hours, under weightless conditions. The design utilized the catalytic decomposition of hydrogen peroxide to breathing oxygen and potable water on demand. It consists of a positive expulsion peroxide storage tank, a catalytic reactor, a heat exchanger, a gravity independent phase separator, and a product storage tank. A laboratory model was constructed and tested to demonstrate the feasibility of the design. This unit produces breathing oxygen and potable water at the design capacity in any gravitational orientation.

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INTRODUCTION

Air Products and Chemicals, Inc., has conducted a program to investigate the feasibility of a hydrogen peroxide oxygen supply concept for manned space vehicles. The system stores the oxygen as hydrogen peroxide and provides for the catalytic decomposition of the hydrogen peroxide to breathing oxygen and potable water on demand. The study included a preliminary investigation to establish the design criteria, the design, and fabrication of a laboratory model based on the established criteria, and the performance testing of the laboratory model to ascertain its operational characteristics and capabilities.

The laboratory model consists of a positive expulsion type hydrogen peroxide storage tank, a catalytic decomposition chamber, a heat exchanger, a gravity independent phase separator, and a product storage tank. This unit was tested to demonstrate the feasibility of the design and satisfactorily provided breathing oxygen and potable water at the design rate and capacity in any gravitational orientation. The design rate is 91 g/hr (0.2 lbs/hr) for a period of 24 hours. Thus, the design capacity is 2184 g/day (4.8 lbs/day).

SECTION II

SYSTEM REQUIREMENTS

The following system requirements were established as design guidelines.

A. The atmospheric conditions of the space enclosure are:

1. Total Pressure - 258-260 mm Hg (5 psia)
2. Temperature - 23.9 ±2.8 C
3. Relative Humidity - 50%
4. Gas Composition - 100% oxygen

B. The controlled flow of oxygen should be in a range between 0-91 g/hr (0 - 0.2 lbs/hr) for a period of 24 hours. This is equivalent to the metabolic requirements of one man for a 24-hour mission and satisfaction of space enclosure leakage.

C. The system should be storable for a period of at least one year at temperatures varying between 4.4 - 49 C.

D. The expulsion of hydrogen peroxide from the storage tank must be capable of taking place under weightless conditions.

E. The temperature of the oxygen produced must be less than 32.2 C, preferably 23.9 C; have a hydrogen peroxide concentration of less than 4 ppm; and have a relative humidity of less than 100%, preferably between 40 - 60% when tested under the atmospheric conditions mentioned above.

F. A large fraction of the water produced from the peroxide decomposition should be collected for life support purposes and therefore should be free of contamination.

G. The gas-liquid phase separator should be capable of operation in a weightless condition.

H. The system should be mechanically simple, require no power, be nonhazardous in both the standby and operating mode and be capable of being developed into a high efficiency, lightweight piece of hardware.

SECTION III

THE DESIGN CONCEPT

The system as originally conceived consisted of a positive expulsion, hydrogen peroxide storage tank, a catalytic reactor, a heat exchanger to dissipate the heat of reaction, a phase separator capable of operating under weightless conditions, and a positive expulsion water storage vessel. A schematic of these components is shown in figure 1.

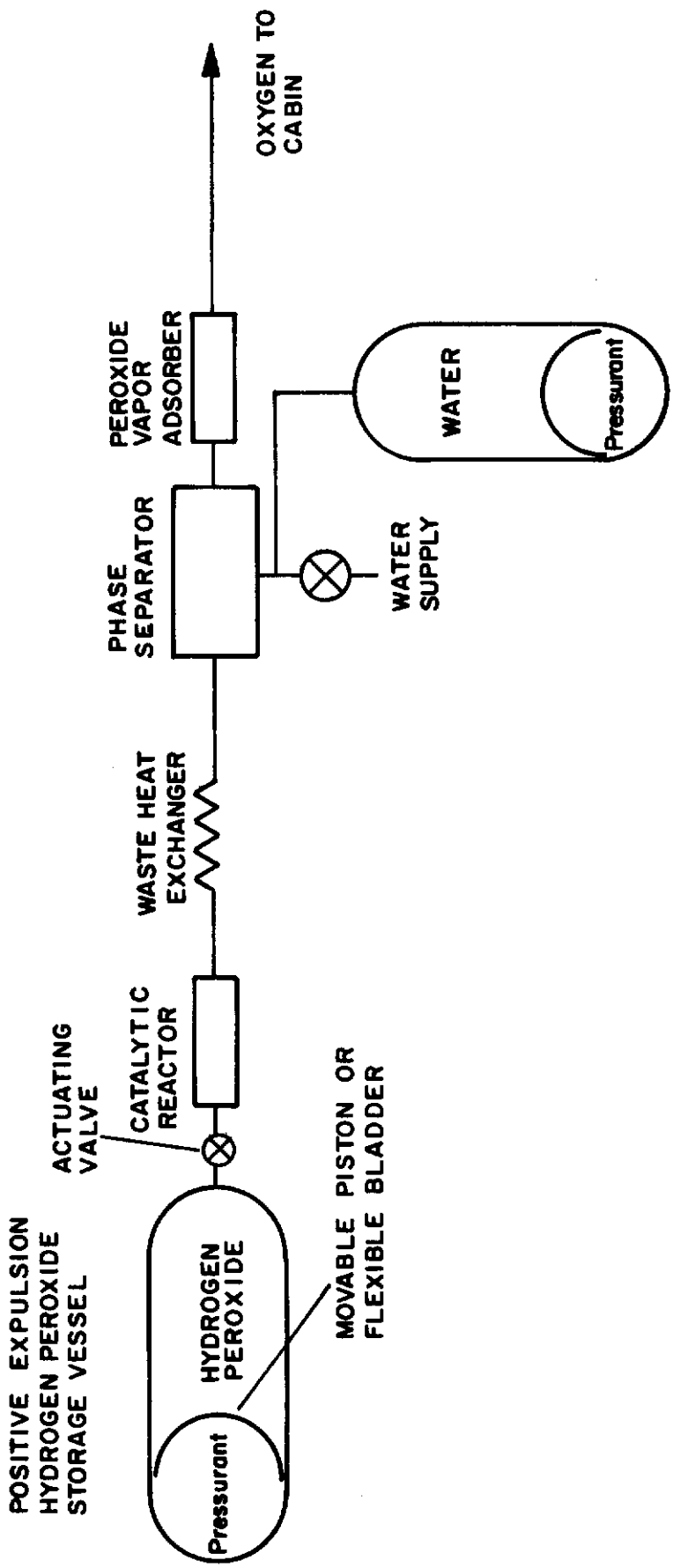


Figure 1. Hydrogen Peroxide – Oxygen Supply Schematic

SECTION IV

PRELIMINARY INVESTIGATION

The preliminary investigations were divided into various discrete areas involving the following system components.

- Positive expulsion peroxide storage tank
- Catalytic Reactor
- Heat Exchanger
- Phase Separator

Each component was designed and studied on a preliminary basis to insure the feasibility of component design and performance prior to incorporation into the complete system design. The preliminary design and experimental work performed in each of these areas is discussed below.

Positive Expulsion Peroxide Storage Tank

Six facets of the positive expulsion peroxide storage tank are presented.

Expulsion Method

One of the more prominent problems of space hardware design is that of getting a liquid out of a tank during weightlessness. Several schemes which are under study involve orienting the liquid with respect to the tank outlet by utilizing surface forces, by establishing an electrostatic field, by accelerating the container, by rotating it, or by containing the liquid in a variable volume vessel such as a cylinder with piston, a flexible bag, or a bellows. The stated requirement of the use of no external power led to discarding acceleration, rotation, and the electrostatic field. Considerable work has been done in the use of surface forces for liquid orientation in space (Petrash, 1962; Petrash, 1963a; Petrash, 1963b; Masica, 1964; Nussel, 1965; Siegert, 1965; Olsen, 1966) but it proves difficult to demonstrate in a laboratory model designed for use in the earth's gravity. In addition, the long term storability of hydrogen peroxide is adversely affected by a large surface area to volume ratio as reported by Schumb (1949). The most favorable geometry would be spherical particularly during the storage mode of the mission. The cylinder and piston, in addition to being difficult to adapt to a near spherical shape, introduces the problem of moving seals and their potential leakage. The bellows by its nature has a poor S/V ratio. A spherical tank with a hemispherical diaphragm or bladder attached around its equator approaches the ideal configuration and was considered until the problem of achieving a leak tight seal of the bladder to the tank without a heavy flanged joint around the large diameter eliminated it. The remaining

choice is a spherical tank with a balloon shaped bladder attached to the tank at its neck. The peroxide could be introduced outside of the deflated bladder and expelled by inflating the bladder or stored inside the bladder and expelled by a pressurant between the bladder and the tank. The latter configuration reduces the problem of peroxide compatibility with the tank material since it is contained, except at the outlet fitting, by the bladder material. This was the configuration chosen except for a modification in the shape. A cylindrical shape is much easier to work into a compact package design so a slight trade-off was incorporated. Figure 2 shows the comparison of length to diameter ratios (L/D) to surface area to volume ratios (S/V) for tankage of the volume required. A change from L/D = 1 (spherical) to L/D = 3 only increased the S/V ratio by 20% but greatly improved the shape of the resulting package from the point of view of ease in handling.

Bladder Materials

Several elastomers were screened as possible bladder materials. Those which proved least catalytic to high strength hydrogen peroxide were:

A. "Fluorel", a 70/30 copolymer of vinylidene fluoride and perfluoropropene.

B. "Aclar", a thermoplastic film made from fluorinated chlorinated resins.

C. "Teflon", a brand of tetrafluoroethylene.

D. "Silastic", a silicone rubber.

Fluorel was rated by the literature as one of the best materials to use in contact with high strength hydrogen peroxide to avoid catalytic decomposition. It is, however, quite difficult to fabricate. The price quotations received for bladders made from this material rendered it noncompetitive for the purposes of this study. It should be kept in mind, however, as a candidate where the ultimate in long term storage of peroxide is required regardless of economics.

Aclar, while highly rated as being nonreactive with hydrogen peroxide, developed fatigue cracks upon cycling in expulsion tests. It still remains a candidate for a one shot disposable bladder where cycling is not required, but not for a laboratory model.

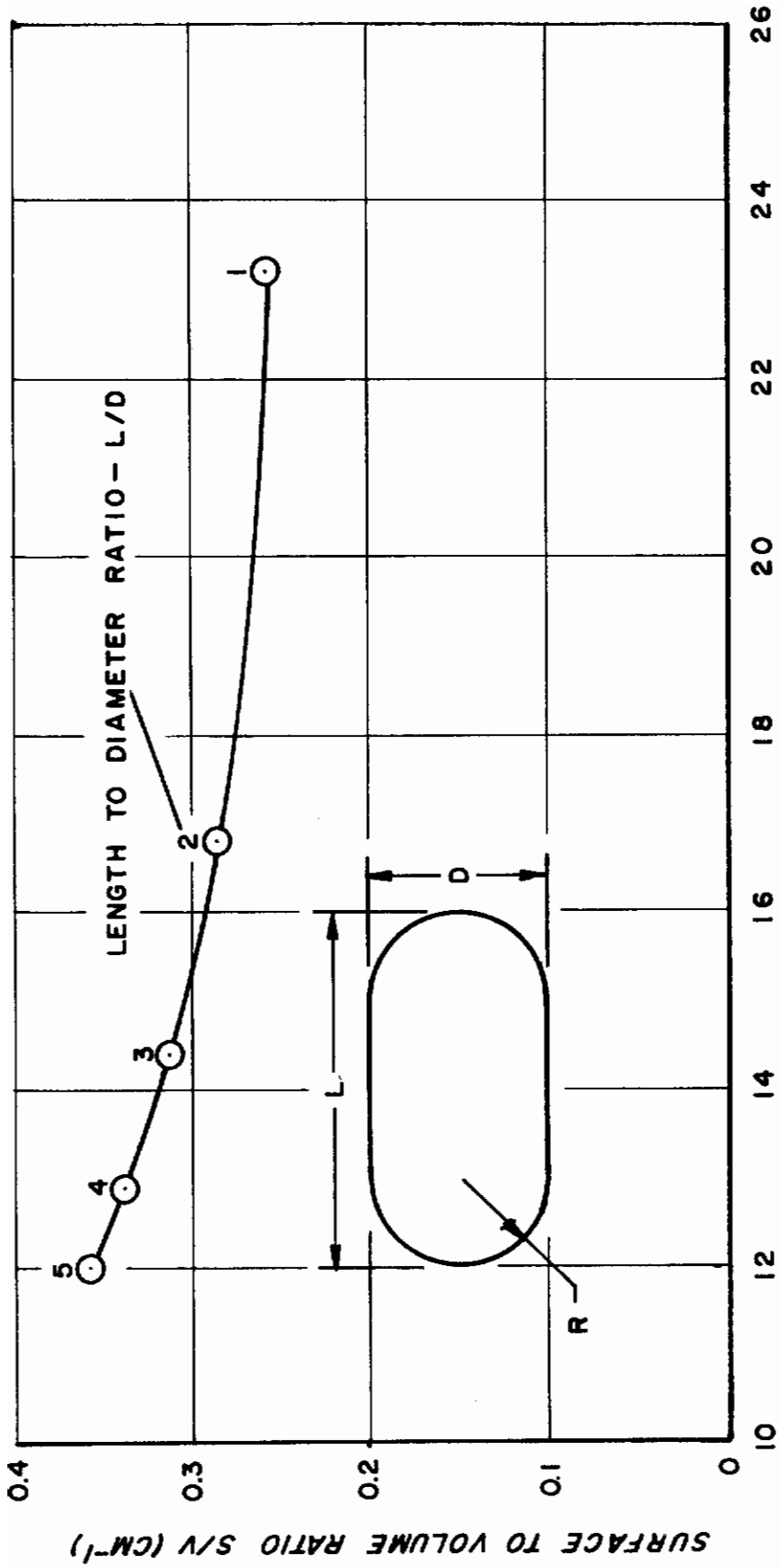


Figure 2. Surface Area to Volume Ratios For Tanks with a Volume of 6.26 Liters

Teflon's compatibility with hydrogen peroxide rates on the same order as the elastomers above but it also suffers from fatigue when expulsion causes it to crease sharply. It has been used for expulsion bladders where the cycling is limited and has been qualified in some cases for 200 cycles of expulsion.

Silastic, while being rated well below the elastomers above in its catalytic effect on hydrogen peroxide, does not suffer from fatigue upon creasing during cycling. Hydrogen peroxide stored in Silastic decomposes about twice as fast as in the previously mentioned materials. It is quite easily fabricated and will withstand hundreds of cycles of expulsion without apparent deterioration.

Teflon and Silastic were selected for fabrication of expulsion bladders for use in the laboratory model.

Pressurant Selection

The original concept envisioned a two phase pressurant stored in the space between the peroxide containing bladder and the tank wall. This would provide automatic pressurization by vaporizing the liquid phase to keep the pressure level at the vapor pressure of the pressurant fluid. The propelling force then would be dependent only on temperature and require no other regulation.

The selection of a propellant fluid requires the setting of temperature and pressure limits to be encountered. The storage temperatures of 4.4 - 49 C and the operating temperature of 23.9 ±2.8 C have been previously mentioned. A tentative maximum pressure of 7.03 kg/cm^2 (100 psia) was selected to achieve lightweight tankage. An operating pressure range of 2.81 - 5.62 kg/cm^2 (40 - 80 psia) was selected to take into account pressure drop through the system and a final throttling to regulate humidity. Figure 3 shows the vapor pressure curves for some of the propellants considered. The 50 mole % mix of dichlorodifluoromethane and dichlorotetrafluoroethane provided the best temperature-pressure properties for this use with vapor pressures of 1.69 kg/cm^2 (24 psia) at 4.4 C, 3.30 kg/cm^2 (47 psia) at 23.9 C, and 7.60 kg/cm^2 (108 psia) at 49 C.

At this point the disadvantages of an expulsion vessel which is constantly pressurized with a propellant were considered.

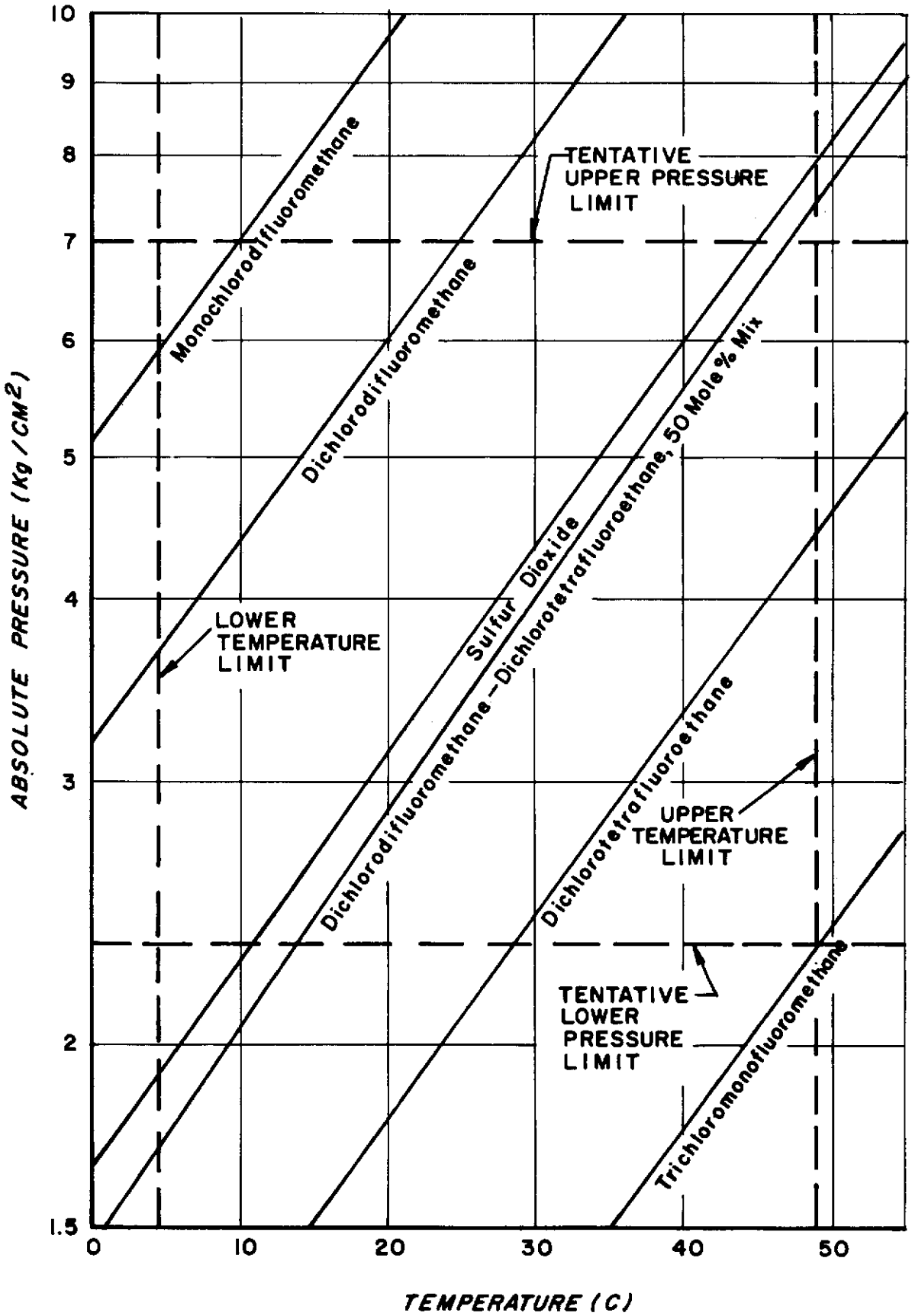


Figure 3. Vapor Pressures of Some Available Pressurants

First, a substantial ullage space must be provided to accommodate the oxygen evolved by decomposition during prolonged storage, therefore, if the bladder is constantly pressurized, it will be wrinkled and folded providing a very poor S/V ratio. This as discussed earlier will promote a faster decomposition.

Second, the bladder materials which are compatible with hydrogen peroxide are all somewhat permeable. Prolonged storage will allow H_2O_2 to diffuse through the bladder into the pressurant and pressurant will diffuse into the stored H_2O_2. This introduces not only the possibility of toxic concentrations of pressurant in the products of the system but also the increase in decomposition rate of the H_2O_2 due to the presence of the catalytic organic pressurant in solution.

These two major disadvantages eliminated from further consideration the storage of the pressurant as a two phase fluid within the expulsion vessel.

The conventional approach to pressurized expulsion is an external high pressure tank, a regulator, and a pressurizing valve. This was the method finally adopted for the laboratory model. A pressurant for this configuration should be single phase for accurate regulation and compatible with the H_2O_2 tank and bladder materials. The gases, hydrogen, helium, nitrogen, oxygen, neon, and argon fit these requirements. Nitrogen and oxygen are the economical choices and have both been used in the laboratory model with equal facility.

Tank Material Selection

Initial calculations of tentative pressures and tank wall thickness indicated that with most of the materials under consideration the thickness of the fabricated tank would be determined by the minimum thickness in which a reliable weld could be achieved rather than by the stress level. Titanium, for instance, in the size tank required might only require a wall thickness of 0.254 mm (0.010 in.) at a pressure of 7.03 kg/cm^2 (100 psi) but the ordinary welder cannot weld this thickness material into a pressure vessel. The minimum wall thickness for easy welding came out to be about 1.27 mm (0.050 in.) and this, in a 152 mm (6.0 in.) cylindrical tank at a pressure of 7.03 kg/cm^2 (100 psi), calls for a stress level of only 422 kg/cm^2 (6000 psi). A 6061-T6 aluminum alloy is rated at this stress level by the ASME boiler and pressure vessel code. This alloy is readily available, easily welded, and can be spun into rounded tank heads. These reasons led to the selection of this alloy for the hydrogen peroxide storage tank.

Selection of Peroxide Concentration

Preliminary experiments indicated that the level of unreacted H_2O_2 in the products was directly related to the reaction temperature. This would indicate that 100% H_2O_2 would be the best concentration to use. A difficulty arises, however, with high concentrations in that the decomposition temperature rises with concentration as shown in figure 4. This requires that the maximum concentration used must produce a reaction temperature below the breakdown temperature of the catalyst. The catalyst choice, discussed below, was silver. The melting point of silver in high pressure oxygen dictated that the H_2O_2 concentration be kept at 90% or less. High strength H_2O_2 is commercially available in concentrations of 50, 70, 90, and 98%. The 90% concentration was selected for use in the laboratory model although a lesser concentration could be used with a slight increase of unreacted H_2O_2 in the products and a corresponding increase in weight of peroxide required for a fixed oxygen output.

Tank Size and Volume of H_2O_2

The work of McCormick (1961) showed a H_2O_2 decomposition rate of 0.6% by weight/yr for 90% commercial H_2O_2 stored in Teflon bladders at 20 C. A design decomposition rate of 2%/yr was selected for the laboratory model.

The quantity of oxygen to be available is:

$$\frac{91 \text{ g } O_2}{\text{hr}} \quad \text{x} \quad 24 \text{ hr} \quad = \quad 2184 \text{ g } O_2$$

This must be increased by the expected loss in one years storage:

$$\frac{2184 \text{ g } O_2}{0.98} \quad = \quad 2228 \text{ g } O_2$$

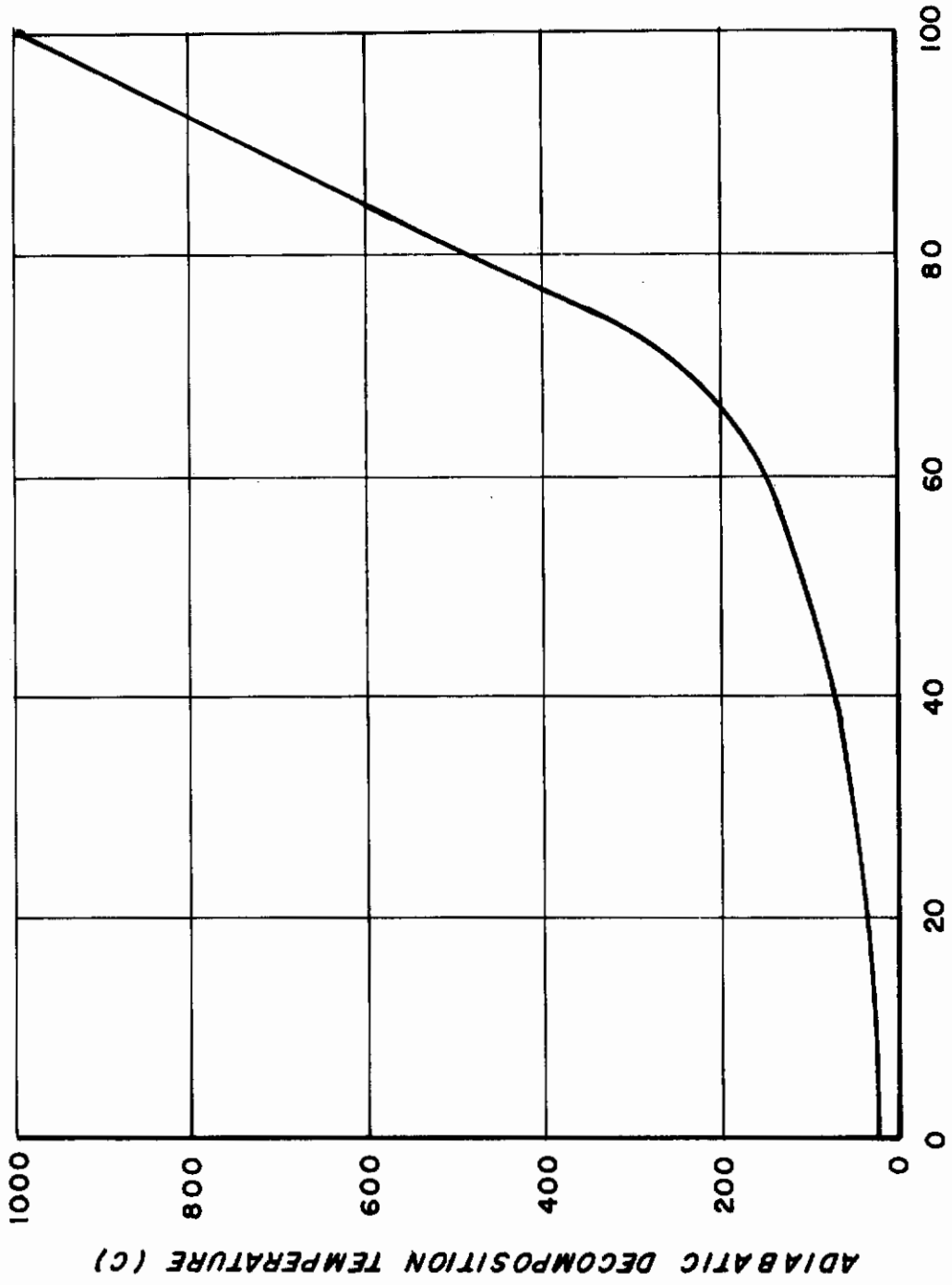


Figure 4. Adiabatic Decomposition Temperature of Hydrogen Peroxide

The 90% H_2O_2 contains 42.3% available oxygen content by weight. The weight of the H_2O_2 is then:

$$2228 \text{ g } O_2 \times \frac{100 \text{ g } H_2O_2}{42.3 \text{ g } O_2} = 5273 \text{ g } H_2O_2$$

The density of 90% H_2O_2 at 20 C is 1.392 g/cm^3 therefore the volume of H_2O_2 is:

$$5273 \text{ g } H_2O_2 \times \frac{\text{cm}^3 H_2O_2}{1.392 \text{ g } H_2O_2} = 3785 \text{ cm}^3 H_2O_2$$

The oxygen evolved by the 2% decomposition would be 44 g or 33.1 std liters. It was planned to eliminate some if not all of this oxygen by venting the space outside of the bladder and allowing the oxygen to diffuse through the bladder material. Data are available for the diffusion of oxygen through the bladder materials but only for a gas phase in contact with the membrane. In the area in contact with the peroxide, a nonequilibrium situation exists along with an associated concentration gradient in the fluid. This prevents an accurate determination of the effective partial pressure differential across the membrane and the expected diffusion of oxygen through it.

An ullage of 40% of the total volume was selected to compensate for uncertainty in the diffusion calculation and to accommodate fluctuations in oxygen evolution due to brief excursions in the storage temperature. The contained volume then should be:

$$\frac{3785 \text{ cm}^3 H_2O_2}{0.60 H_2O_2} = 6310 \text{ cm}^3 = 6.31 \text{ liters}$$

Catalytic Reactor

Some of the catalysts for the decomposition of hydrogen peroxide which have been considered are silver, copper, carbon, nickel, palladium, platinum, manganese, cobalt, iron, mercury, osmium, and the oxides of these elements. Others are listed in Schumb (1955) p. 468. The field was narrowed to silver and a manganese silicate by temperature and toxicity considerations. Laboratory tests indicated that the manganese silicate was slightly more effective as a catalyst than the silver screen due to its much greater surface area to volume ratio. There was, however, some fracturing of the ceramic-like manganese silicate and particles of catalyst were identified in the decomposition products. These tests led to the selection of the silver screen as the catalyst for the laboratory model.

Some improvement has been observed by Fisher and Zeilberger (1961) in the performance of silver screen as a catalyst by treating it with a samarium nitrate solution and then baking the deposit to reduce the samarium to the oxide. This method was tested and the improvement while small was confirmed. The method was therefore adopted for the catalytic reactor for the laboratory model.

Several reactors were built and tested to establish levels of product purity and pressure drop before a final geometry was selected.

The catalyst dimensions used for fabrication of the reactor for the laboratory model were 203 mm lg x 5.7 mm dia (8 in. long x 0.226 in. dia) of packed silver wire. The silver used was in the form of screen in a 40 x 40 mesh using 0.254 mm (0.010 in.) wire. The packed density was 40% silver, 60% void. The weight of silver wire used was 21.75 g (0.767 oz). The resulting pressure drop was 68.5 g/cm^2 (0.975 psi) at a flow of oxygen of 1.18 liters/min (2.5 std ft^3/hr).

Heat Exchanger

The decomposition of hydrogen peroxide proceeds according to the reaction:

$$H_2O_2\ (l) \longrightarrow H_2O\ (l) + 1/2\ O_2\ (g)$$

This produces a heat of decomposition of 23.28 kg-cal/g mole H_2O_2 (for a 90 wt % concentration H_2O_2) according to the recommended value of Schumb (1955) p. 247-8. At the design maximum flow rate of 91 g O_2/hr (0.2 lb O_2/hr) this produces 132.3 kg-cal/hr or 154 watts (526 BTU/hr).

This heat load in a manned space enclosure would probably be connected to the enclosure's atmosphere control system or connected to the airframe itself as a heat sink. The laboratory model was designed to operate independently of any such connections and therefore is designed to dissipate this heat into the atmosphere of the laboratory by means of a heat exchanger.

The adiabatic decomposition temperature of 90 wt % H_2O_2 as shown previously in figure 4 is 744 C so the primary mode of heat transfer will be by radiation. With this in mind the first heat exchanger tested was a laminated aluminum panel with the flow passages embossed into both sheets before lamination. These tests indicated that the radiation expected takes place from the catalytic reactor itself and from the connecting tubing to the heat exchanger. The products enter the heat exchanger at saturation temperature and thus the primary mode of heat transfer from the heat exchanger is by convection rather than by radiation. One of the desirable traits of a heat exchanger for this application is a steep temperature gradient, continuous from inlet to outlet. This could not be attained by the panel type tested because of the relatively short conductive path from the inlet to the outlet.

Several configurations of tubular heat exchangers were then tested. They are described below.

- Plain surface aluminum tubing 3.8 mm OD x 11 m long (1/8" OD x 36' long).

- Plain surface copper tubing 4.8 mm OD x 6.1 m long (3/16" OD x 20' long).

- Finned stainless steel tubing 4.8 mm OD x 3.05 m long (3/16" OD x 10' long) with circumferential copper finning brazed on, 3.8 mm high x 0.38 mm thick spaced 6.3 to the cm (1/8" high x 0.015" thick spaced 16 to the inch).

- Finned aluminum tubing 4.8 mm OD x 1.6 m long (3/16" OD x 5.3' long) with aluminum pin fins attached with an epoxy cement. The pins were 0.81 mm dia x 12.7 mm high, spaced 20 to the cm^2 (0.032" dia x 0.50" high, spaced 130 to the $in.^2$).

The results of these tests are listed in table I.

TABLE I

COMPARISON OF HEAT EXCHANGERS

Heat Exchanger	Length (m)	Weight (g)	ΔP (g/cm^2)	$T_{(outlet)} - T_{(ambient)}$* (C)	Wt x ΔT (g C)
2790 cm^2 Aluminum Panel Type (30 cm x 46 cm, Two Sides)	2 (passage length)	437	10.4	37	16200
Aluminum Tubing 3.8 mm OD	11	217	317	8	1730
Copper Tubing 4.8 mm OD	6.1	587	31.2	7	4100
Finned Stainless Steel 4.8 mm OD Circumferential Copper Finning	3.05	549	14.0	1.6	870
Finned Aluminum 4.8 mm OD Aluminum Pin Fins	1.6	381	8.2	0.2	76

*At design maximum product flow rate producing 91 g/hr of O_2 from 90 wt% H_2O_2

The main attributes sought in a heat exchanger for this application are low weight and low resulting temperature difference so the product of these two figures are tabulated in the last column of table I as a measure of effectiveness for this particular application. The aluminum pin fin heat exchanger was selected for use in the laboratory model.

Phase Separator

Several preliminary tests were run using the resistance of a wetted screen to the passage of the gas phase in the manner of Chipchak (1963). This method while fairly efficient in expelling a bulk liquid in reduced gravity from a container with some entrained gas phase is not readily adapted to separating an entrained liquid from a primarily gaseous flow process.

A method of providing a venting device for the gas phase in a liquid tank utilizing a nonwetting porous material was suggested by Boraas (1965) pp. 48-49. The devices described in this reference however did not provide a positive expulsion of the liquid phase which would work in a gravitational field, independently of the direction of the gravity vector. The positive expulsion problem probably could be solved if a permanently nonwetting porous material could be found which would sustain a substantial differental pressure without the liquid phase being driven through it. With this goal in mind samples were obtained of porous polyethylene, porous Teflon, porous "Kel-F" (a polymer of trifluorochloroethylene), and porous stainless steel which had been treated with a silicone compound to make it nonwetting.

An apparatus was set up to measure the limiting liquid pressure which could be sustained by these samples before the liquid was forced through. The results of these tests are listed in table II.

Data on the pressure drop vs flow rate were taken on the three polymers to establish criteria for area requirements and the results are plotted in figure 5. The analysis of these data led to the selection of porous Teflon in a thickness of 3.18 mm (1/8") or more for the phase separator of the laboratory model.

One method of achieving the positive expulsion mentioned above is to provide a variable volume container for the liquid phase. Typical variable volume containers are fabricated with a piston and cylinder, a bellows, or an elastic bladder. The elastic bladder was selected as the simplest and most economical.

TABLE II

BREAKTHROUGH PRESSURES OF POROUS MATERIALS

Material	Thickness (mm)	Nominal Porosity (microns)	Breakthrough Pressure (g/cm^2)
Teflon	3.18	9	205
Teflon	1.59	9	157
Kel-F	3.18	15	2
Stainless Steel	3.18	5	10
Stainless Steel	1.59	5	10

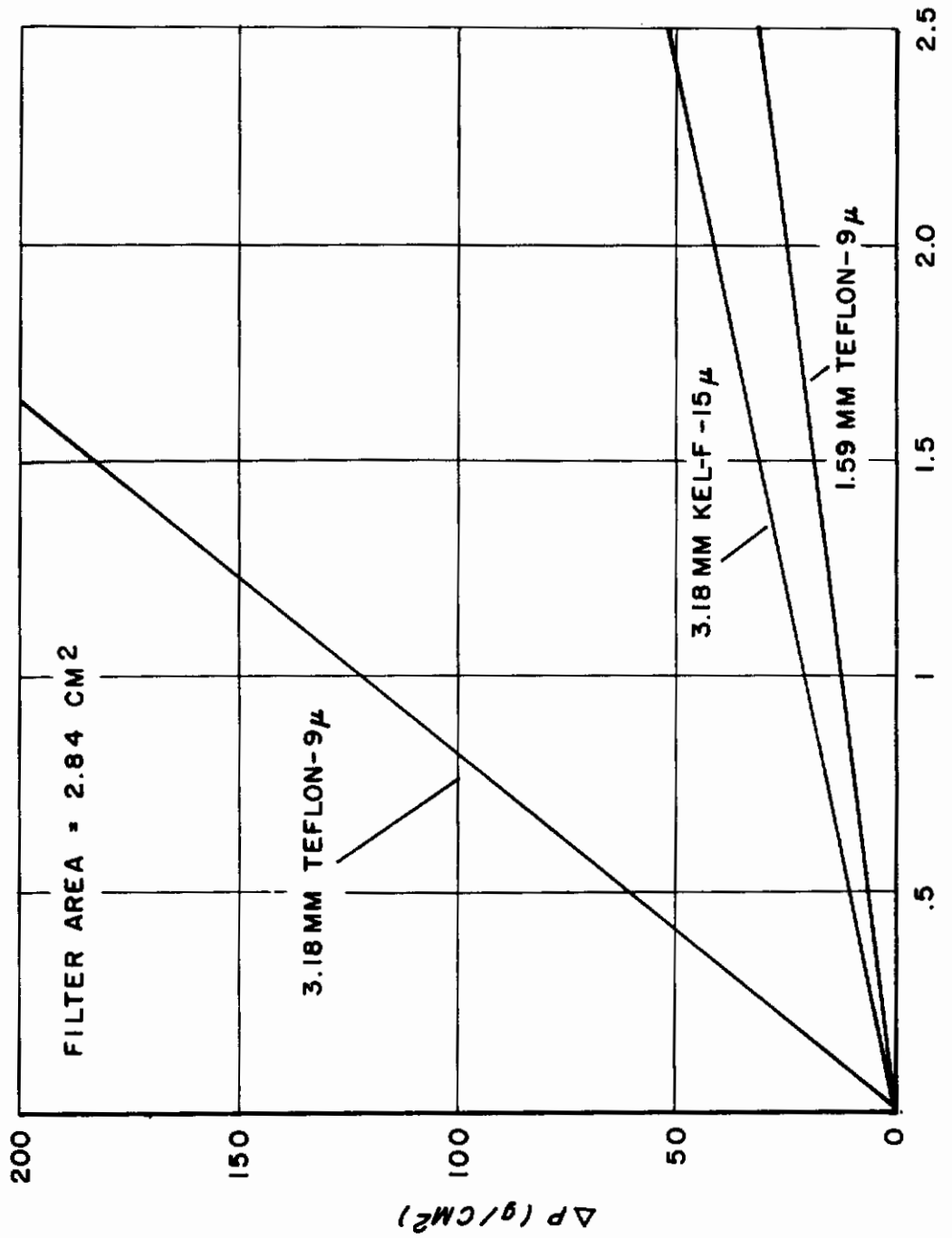


Figure 5. Pressure Drop in Porous Filters

Three materials were identified as being compatible with water and oxygen and having the elastic properties required for bladder fabrication. They are butyl, neoprene, and silicone rubber.

The oxygen reservoir tank which houses the phase separator has the same pressure requirements as the peroxide storage tank and the reservoir volume is rather arbitrary. The tank material and dimensions were selected identical to those of the peroxide storage tank for fabrication economy and mounting ease.

SECTION V

DESCRIPTION OF EQUIPMENT

The laboratory model is designed to produce 91 g/hr (0.2 lb/hr) of oxygen and to be suitable for operation under weightless conditions or at 1-G in any orientation. Overall views of the completed laboratory model are shown in figures 6 and 7. The weight of the completed unit charged and ready to operate is 12.868 kg (28.33 lb). The protecting handles on the front and the rubber bumpers on the corners allow it to be tipped to any orientation while resting on the laboratory table to demonstrate its independence of orientation.

Figure 8 is the flow diagram of the completed system showing the relationship of its components. In operation the pressurant shut-off valve is opened allowing the pressurant gas to flow through the pressure regulator into the space outside the bladder in the peroxide storage tank. The peroxide valve can then be opened to allow the pressurized peroxide to flow into the catalytic reactor where it decomposes to water and oxygen at a high temperature. The hot products flow through the heat exchanger and then into the phase separator as oxygen and liquid water. These products are then available to be drawn off as required.

Pressurant Tank

The pressurant tank is a welded 304 stainless steel cylinder 31.8 mm (1.25 in.) in diameter by 305 mm (12 in.) long. The tank has a volume of 180 cm^3 (11 $in.^3$) and weighs 449 gm (0.99 lb). It has been pressure tested to 169 kg/cm^2 (2400 psi). A picture of the completed pressurant tank is shown in figure 9.

Pressure Regulator

The pressure regulator was designed and fabricated by Air Products and Chemicals, Inc., Welding Products Department. It is rated for an input pressure of 211 kg/cm^2 (3000 psi) and an output of 0 - 7 kg/cm^2 (0 - 100 psi). It is a single stage, rubber diaphragm-type regulator and weighs 225 gm (0.32 lb). The regulator can be seen in the right center of figure 6.

A relief valve has been installed immediately downstream of the regulator and set to relieve at 6.47 kg/cm^2 (92 psi).

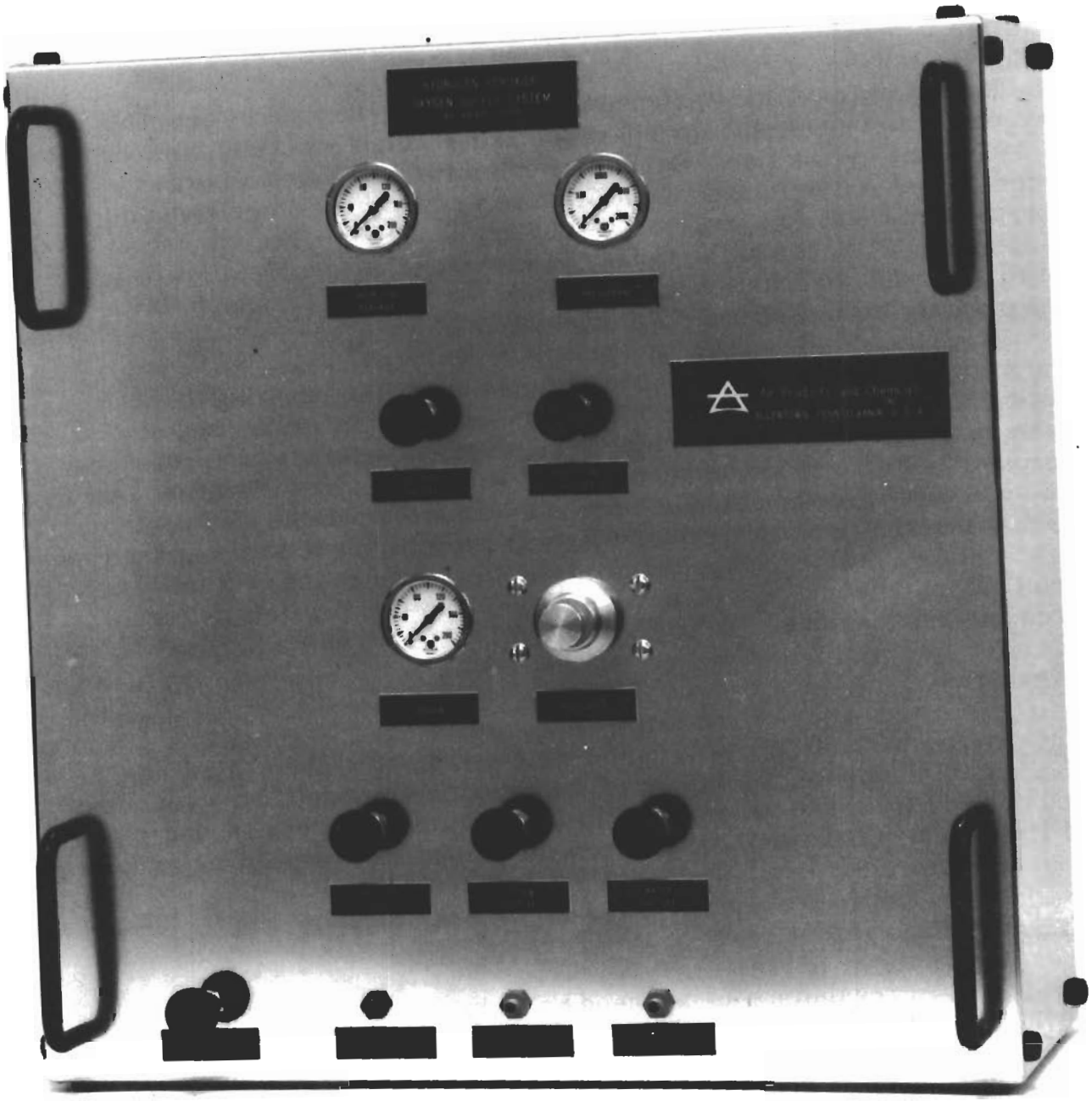
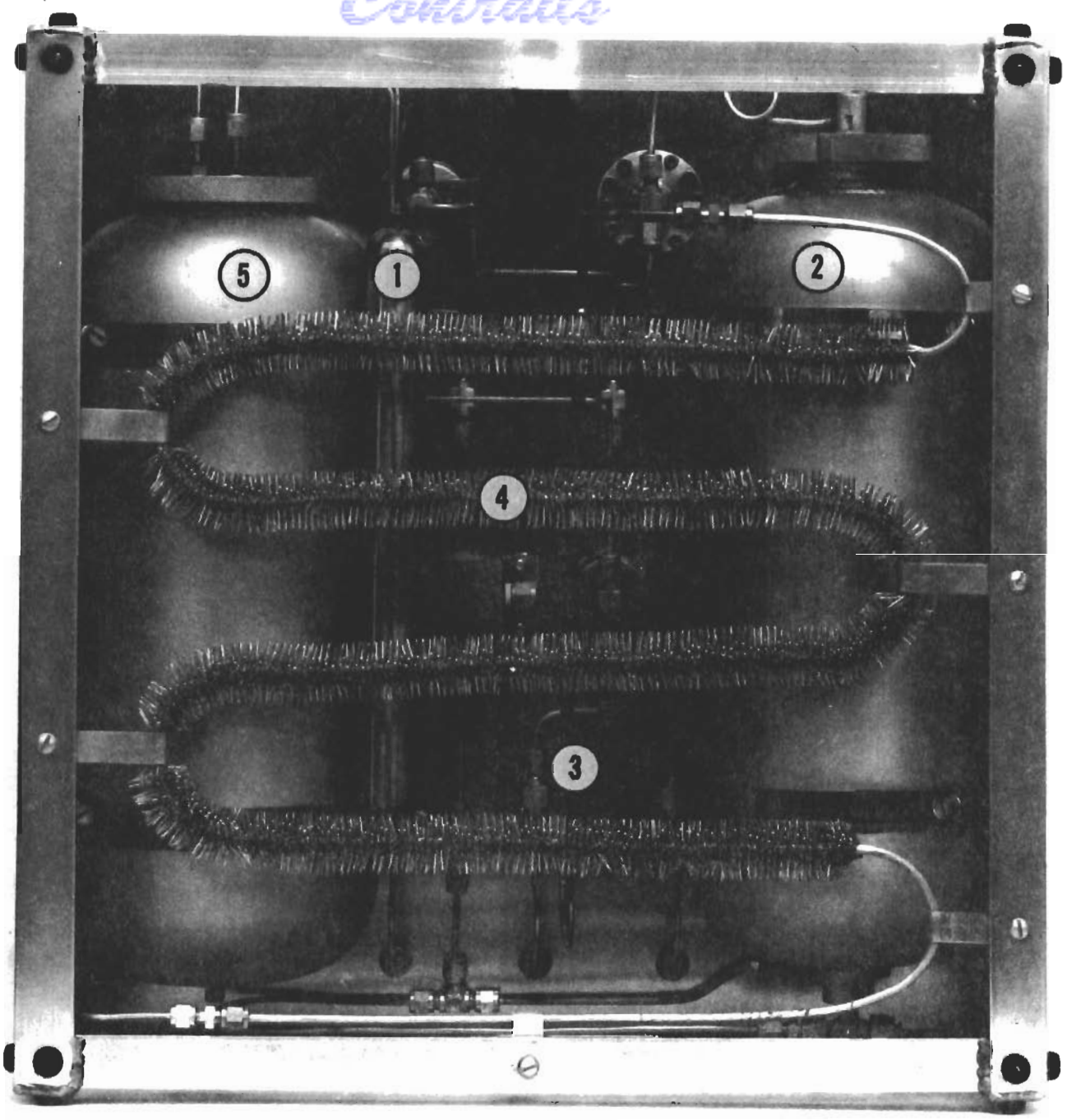


Figure 6. Front View of Laboratory Model



1. PRESSURANT TANK
2. PEROXIDE STORAGE TANK
3. CATALYTIC REACTOR
4. HEAT EXCHANGER
5. PHASE SEPARATOR and PRODUCT STORAGE

Figure 7. Rear View of Laboratory Model

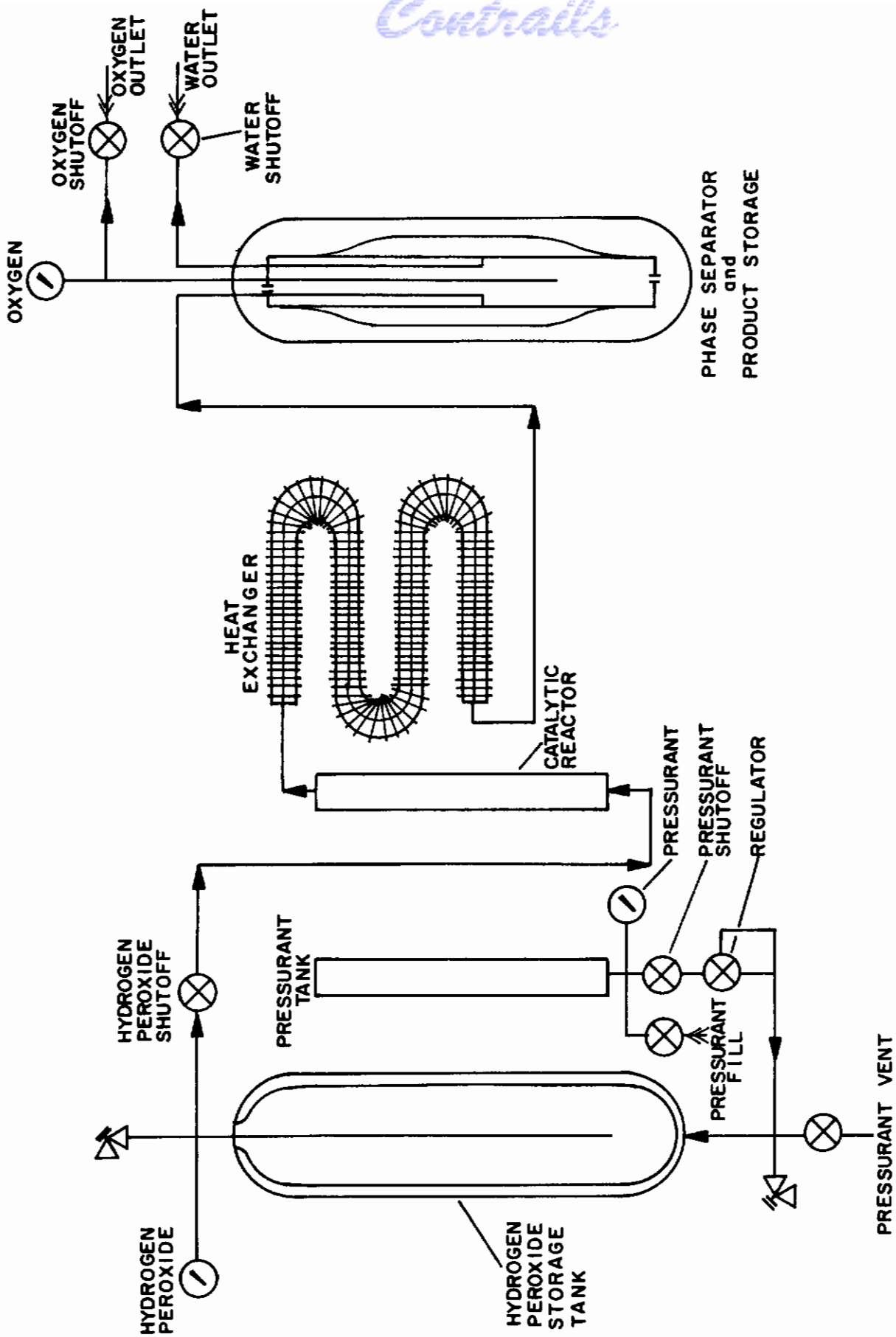


Figure 8. Oxygen Supply Flow Diagram

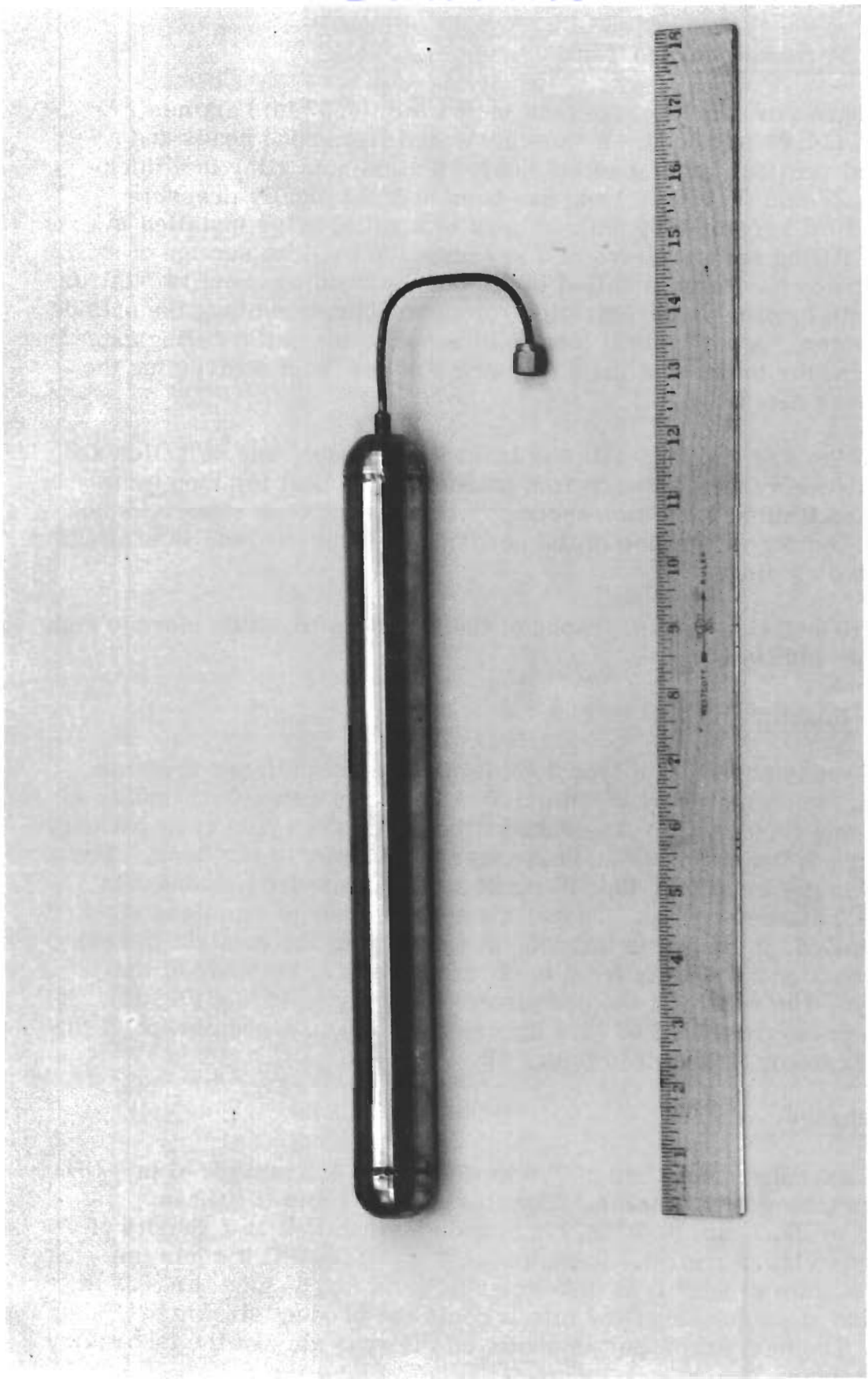


Figure 9. Pressurant Tank

Hydrogen Peroxide Storage Tank

The hydrogen peroxide storage tank is 161 mm (6.32 in.) diameter x 381 mm (14.98 in.) long. It was fabricated from spun heads and a cylindrical section. It is made of 6061-T6 aluminum alloy in a thickness of 1.27 mm (0.050 in.) and has been hydrostatically pressure tested to 10.5 kg/cm^2 (150 psi). There is a relief valve installed in the outlet fitting set to relieve at 7 kg/cm^2 (100 psi). A section of plastic screen has been installed in the tank, extending about two-thirds of its length to provide unrestricted gas communication along the outside of the bladder. A withdrawal tube is attached to the outlet fitting extending into the bladder to prevent the collapsing bladder from obstructing the outlet during discharge.

Two bladders are supplied with the laboratory model, one of Teflon and one of silicone rubber. The Teflon bladder is the best for long term storage and limited expulsion cycling, while the silicone rubber, which catalyzes the decomposition of the peroxide to some degree, is unaffected by repeated cycling.

Figures 10 and 11 are photographs of the hydrogen peroxide storage tank and the two bladders.

Catalytic Reactor

The catalyst is housed in a type 304 stainless steel cylinder 6.35 mm (0.250 in.) in diameter by 267 mm (10.5 in.) long with a wall thickness of 0.305 mm (0.012 in.). The catalyst consists of a cylinder of packed silver wire 5.7 mm (0.226 in.) diameter by 203 mm (8 in.) long. The silver is in the form of a 40 x 40 mesh screen made from 0.254 mm (0.010 in.) diameter wire. There is a spacer made of stainless steel wire installed, in the same fashion, at each end of the catalyst to keep the hot reaction area away from the brazed joints at the ends of the assembly. The weight of the completed assembly is 46.0 g (0.1 lb). It has been pressure tested to 14.1 kg/cm^2 (200 psi). A photograph of the catalytic reactor is shown in figure 12.

Heat Exchanger

The heat exchanger consists of 1.6 m (64 in.) of 4.8 mm (3/16 in.) OD aluminum tubing with pin fins. The fins are 0.81 mm (0.032 in.) diameter by 12.7 mm (0.50 in.) high and are installed at a density of 20 per cm^2 (130 per in.^{2}). In an ambient air of 23.9 C it cools the product stream to 24.1 C at the design flow rate of 91 g O_2/hr (0.2 lb O_2/hr) and at double this flow rate it cools the product stream to 32.2 C. The heat exchanger is shown on the rear view of the laboratory model in figure 7.

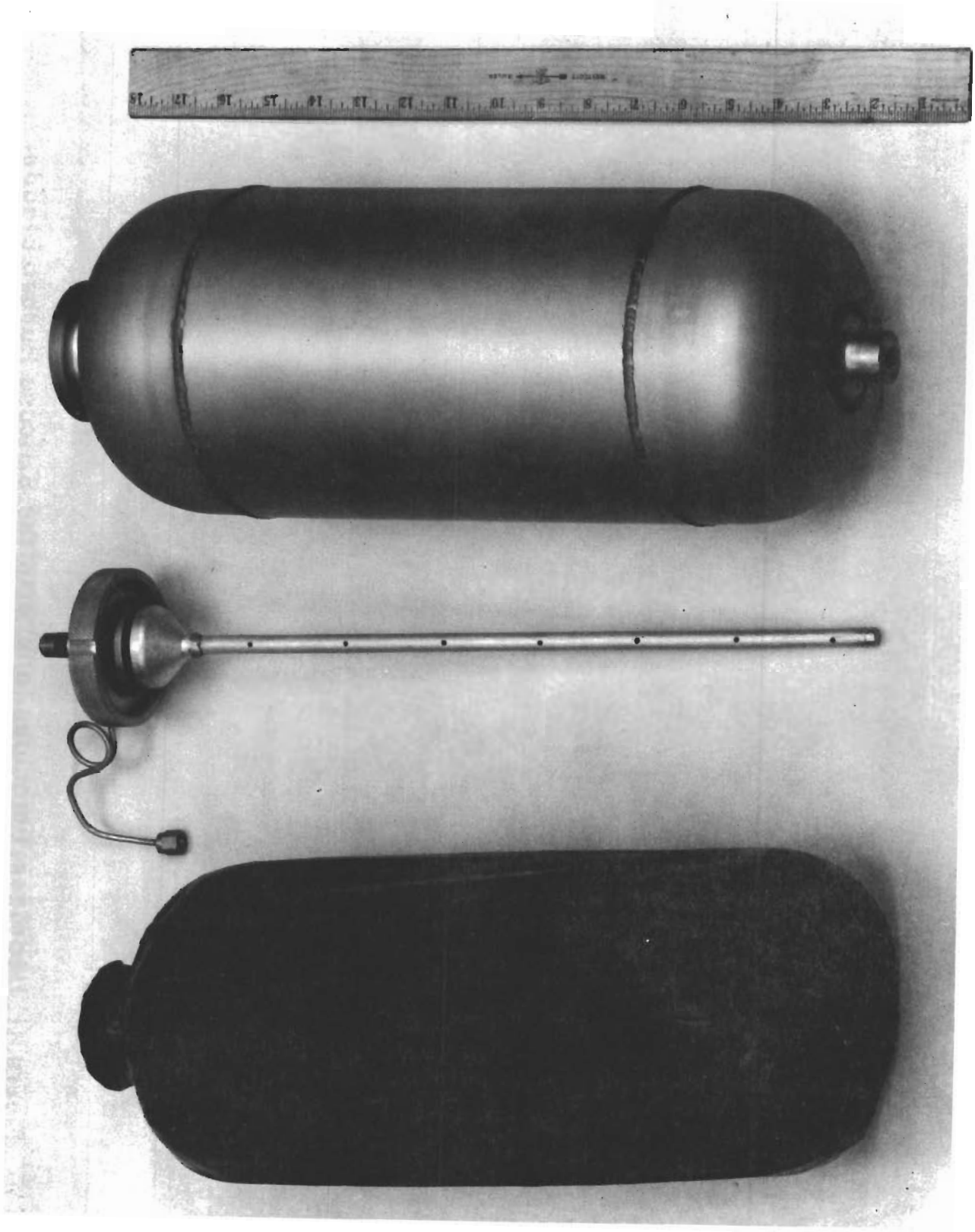


Figure 10. Hydrogen Peroxide Tank with the Teflon Bladder

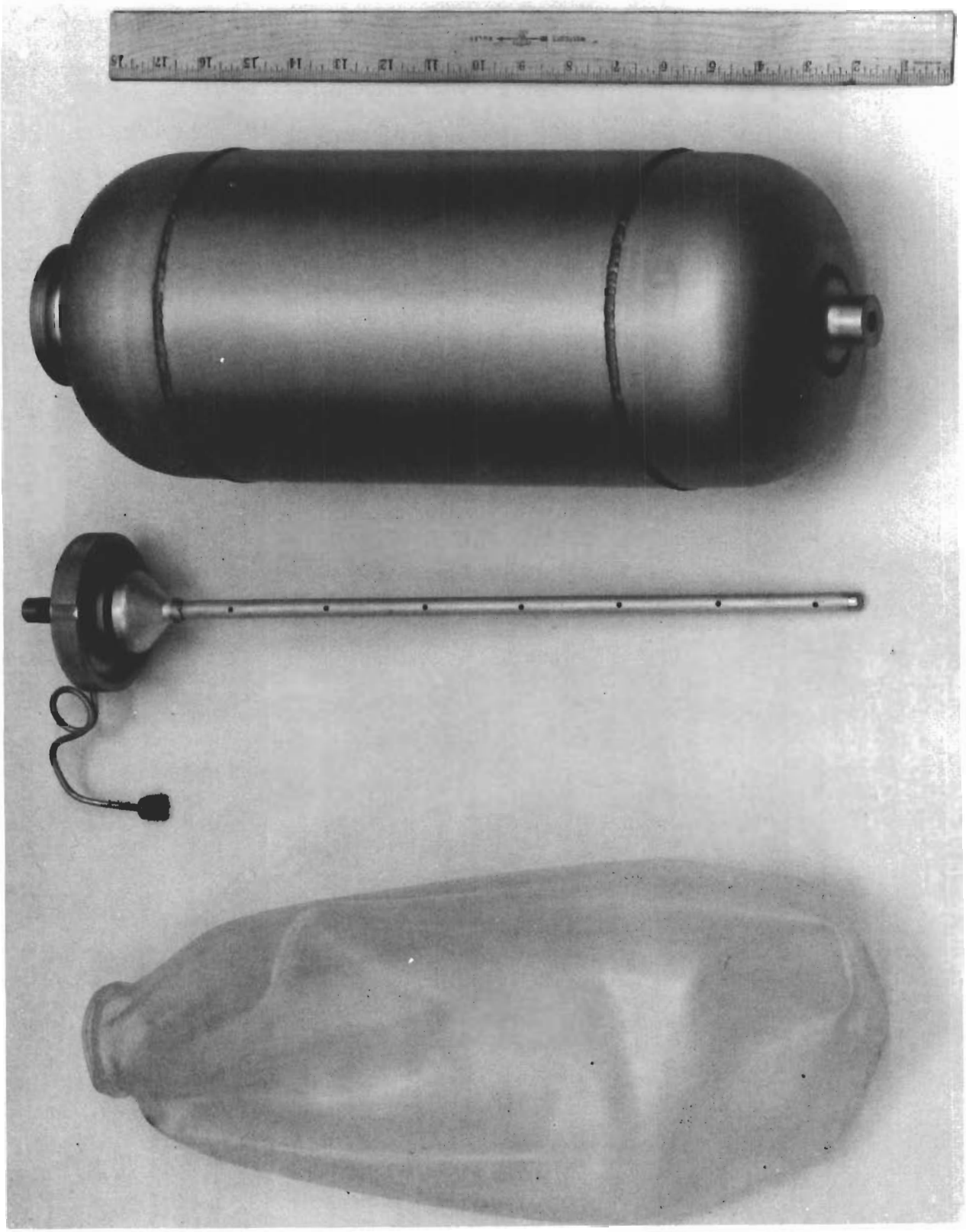


Figure 11. Hydrogen Peroxide Tank with the Silicone Rubber Bladder

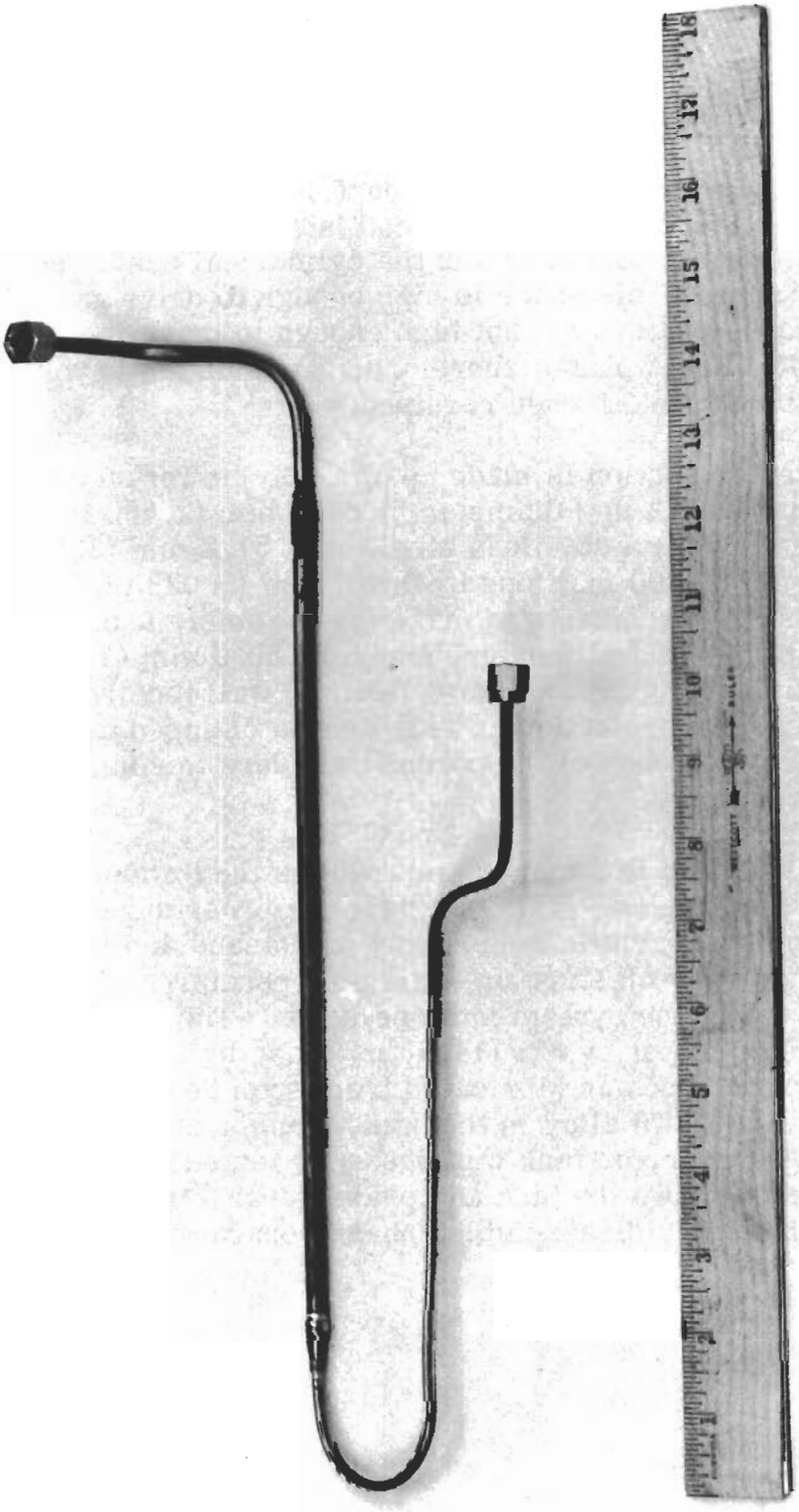


Figure 12. Catalytic Reactor

Phase Separator and Product Storage

A diagram of the phase separator and product storage tank is shown in figure 13. The two phase flow is introduced into the annular space between the elastic liquid container and the cylindrical center section. The inflation pressure of this space is high enough to drive gas through the non-wetting porous filters but not high enough to drive the liquid phase through. The liquid phase, therefore, accumulates in this annular space to be drawn off when required.

The cylindrical center section is made up of a porous Teflon cylinder at each end, 55.1 mm (2.172 in.) diameter by 63.5 mm (2.500 in.) long by 6.35 mm (0.250 in.) wall; a stainless steel tube, 57.2 mm (2.250 in.) diameter by 208 mm (9.200 in.) long by 0.687 mm (0.028 in.) wall; and the necessary O-ring attachments to make the assembly leak-proof. The elastic liquid container is a silicone rubber tube 50.9 mm (2 in.) diameter by 356 mm (14 in.) long by 1.118 mm (0.044 in.) wall (before stretching over the cylindrical center section). This tube is clamped to the O-ring attachments at the outer ends of the porous cylinders to complete the phase separator assembly.

The assembly is installed in a tank which collects the oxygen that passes through the porous cylinders. This tank forms a pressurized reservoir of oxygen to smooth out variations in supply or demand and in addition it gives a temporary supply on start-up while the operator is actuating the necessary valves to put the system into operation. The reservoir tank is 161 mm (6.32 in.) diameter by 381 (14.98 in.) long by 1.27 mm (0.050 in.) wall. This reservoir tank was fabricated from spun heads and a cylindrical center section of a 6061-T6 alloy in the same manner as the peroxide storage tank. This reservoir tank was pressure tested to 10.5 kg/cm^2 (150 psi). Figure 14 shows the tank and phase separator assembly and figure 15 shows the partly disassembled phase separator.

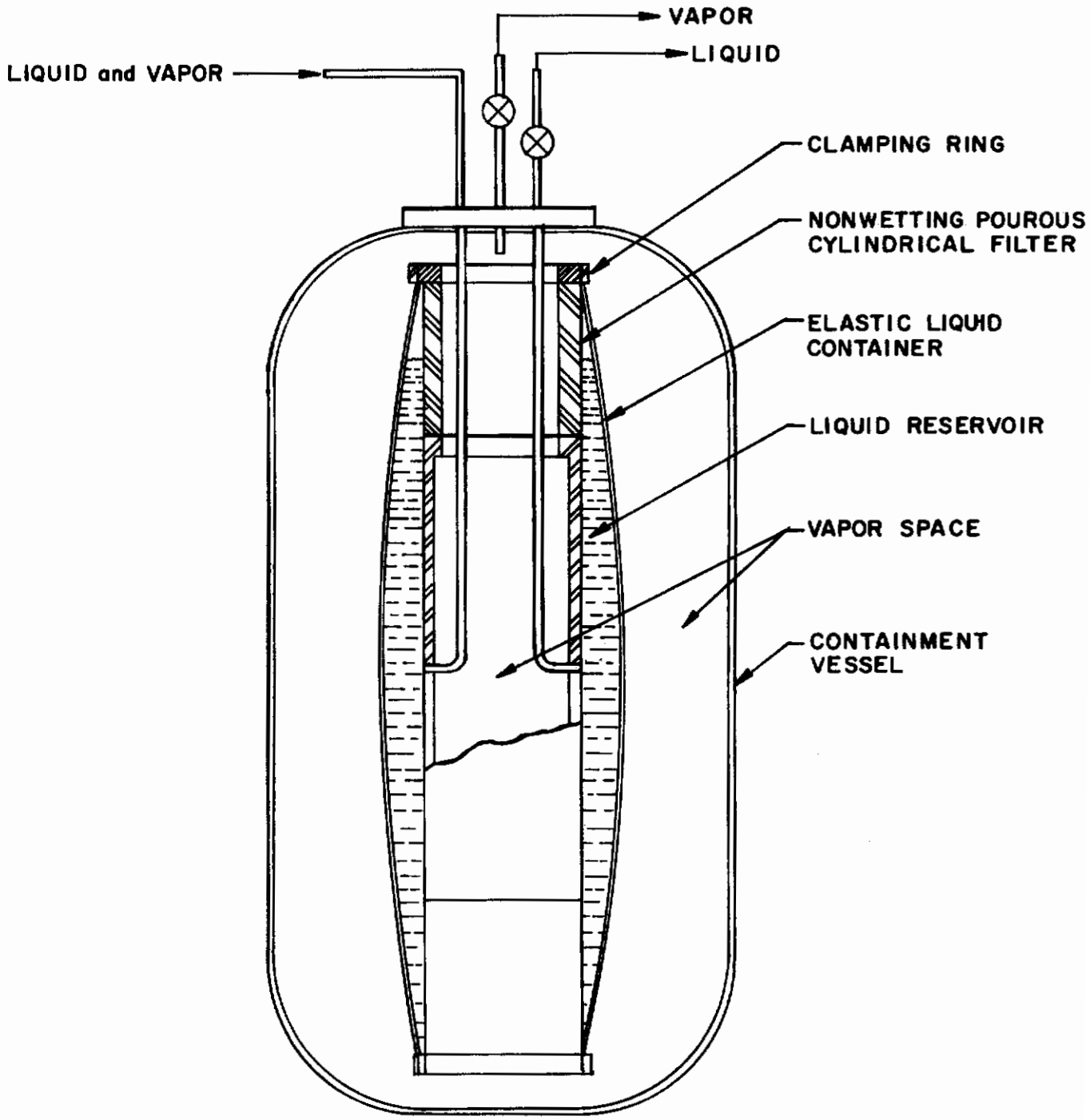


Figure 13. Diagram of Phase Separator and Product Storage Tank

Figure 14. Phase Separator Assembly and Product Storage Tank

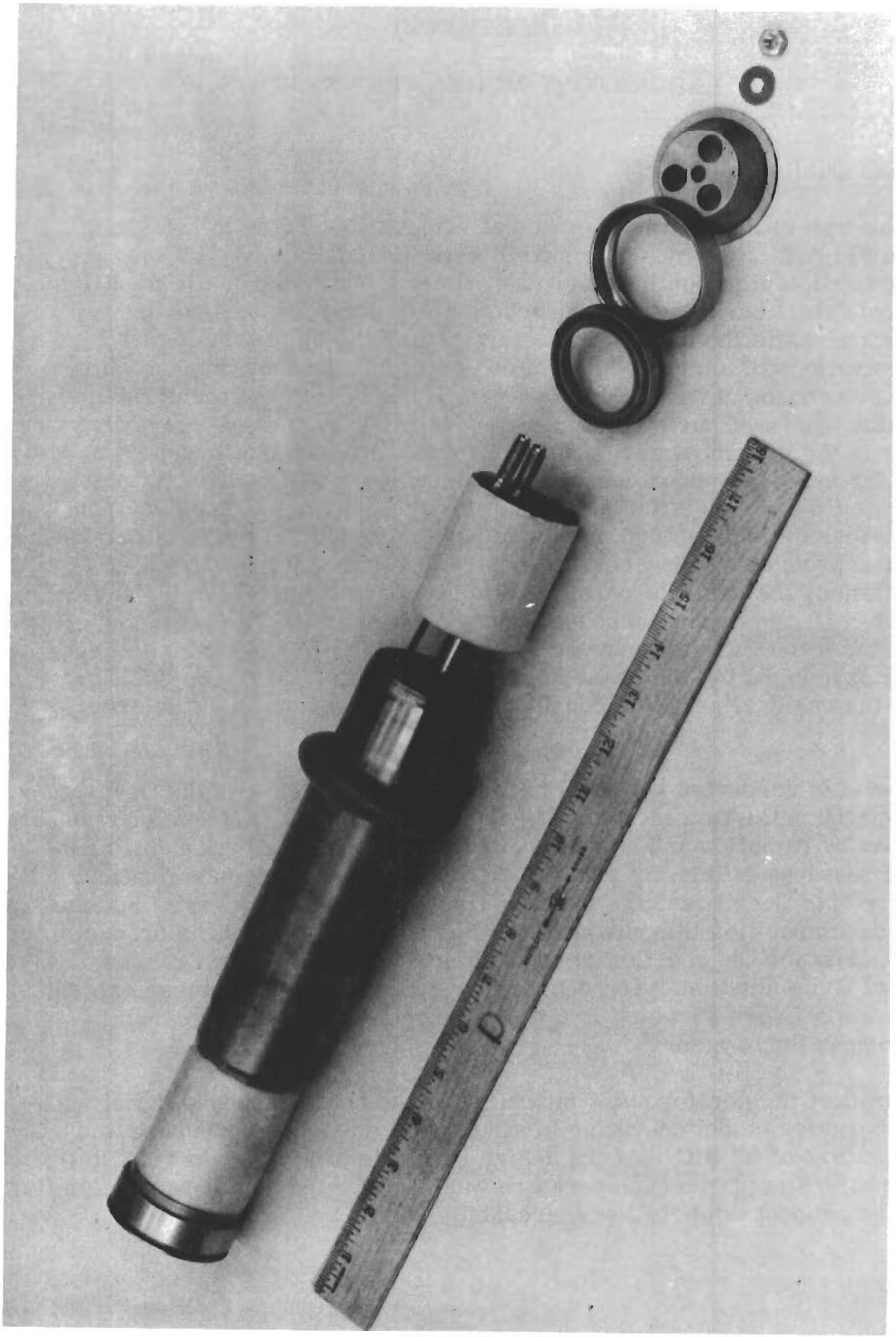


Figure 15. Partly Disassembled Phase Separator

SECTION VI

LABORATORY MODEL TEST RESULTS

Product Quality

The laboratory model was operated at various flow rates to establish levels of product purity. The initial tests indicated quite a bit of peroxide contamination in the product water. This was finally identified as a cold start problem. The products of the first few seconds of operation, while the catalytic reactor is warming up, carry higher concentrations of unreacted hydrogen peroxide. This warm up requires about 10 seconds at the design flow rate. The quantity of the unreacted peroxide produced during this transient is not enough to be injurious either in the product water or in the oxygen. The human threshold of taste for hydrogen peroxide was very much below that concentration which could be considered hazardous through ingestion. Peroxide concentrations as high at 1000 ppm have been measured in the first portion of water produced. However, after steady-state operation has been established, the residual peroxide concentration in the water is usually less than 10 ppm. The increased contamination in the first few cm^3 of oxygen was too little to measure since the water has a scrubbing effect on the oxygen during the phase separation process. At the design flow rate, the residual peroxide concentration in the oxygen is of the order of 0.1 ppm.

The level of unreacted peroxide in the products varied with the flow rate through the catalytic reactor. At very low flow rates, the heat of reaction escapes by radiation and convection from the reactor allowing it to run cooler and less efficiently producing increased product contamination. At very high flow rates, the reaction temperature is very near the adiabatic decomposition temperature but the residence time of the products is too short for the reaction to go to completion. This again causes product contamination. The design flow rate falls between these extremes as shown in figure 16 which is a plot of oxygen flow rate vs residual peroxide in the oxygen.

The product temperature was measured at the heat exchanger outlet with the laboratory model operating in air at one atmosphere pressure and a temperature of 23.9 C. At the design flow rate of 91 g O_2/hr (0.2 lb O_2/hr) the equilibrium product temperature was 24.1 C. At double the design flow rate the product temperature increased to 32.8 C.

efficiency). They were filled to the design capacity and then pressurized to expel the contents. The volume of liquid expelled was measured and the efficiency determined. These efficiencies were:

Teflon bladder	98.33%
Silicone rubber bladder	99.30%

Other Observations

A plugging problem occurs in the phase separator when it is allowed to stand for a period of several days with the porous filters exposed to water. Something seems to go into solution in the water and deposit a molecular layer on the surface of the filters. At this point they lose their nonwetting property which is the basis of the operation of the phase separator. The Teflon surface becomes wetted and the pressure drop across the filter increases to the point where both water and oxygen pass through. However, when the phase separator is kept dry (as it would be prior to the initial startup), it will function at or above the design capacity even after prolonged storage or stand-by periods.

An infrared analysis of residue from solvent washing the filters showed traces of the bladder compound. A test was set up with water sealed inside of the porous filters. A sample of the bladder material was placed in one of these containers. After one day the cylinder with the bladder material in the water was wetted by the water. Figure 18 is a photograph of these two cylinders after one day. The bladder material is in the cylinder on the left.

Tests to determine if other materials would cause this effect, were performed using samples of porous Teflon in beakers of distilled water together with samples of the various materials from which contamination could come. The results of these tests are tabulated below.

Beaker with Distilled Water, Porous Teflon and:	Time before Teflon becomes Wetted
Stainless Steel	1 month
Plain Aluminum	1 month
Anodized Aluminum	1 month
Silicone Rubber	1 day
Neoprene	2 hours
Butyl	4 hours
Blank (Porous Teflon in distilled water)	6 weeks

Decomposition in Storage

The hydrogen peroxide storage tank with the silicone rubber bladder installed was filled to the design capacity with 90% H_2O_2 and sealed. The pressure buildup was monitored for 6 days to determine the decomposition rate. The rate observed corresponded to 49%/yr.

The silicone rubber bladder was removed and the Teflon bladder installed. The test above was repeated. The observed decomposition rate in this test was equivalent to 26%/yr. This rate is very much higher than the predicted rate cited by McCormick (1961) of 0.6%/yr.

This discrepancy led to a second test with the Teflon bladder. The passivation method was changed from 1 hr in 20% HNO_3 at room temperature to 2 hrs at 60 C. The observed decomposition rate in this second test was equivalent to 5.75%/yr.

A similar reduction is expected in the decomposition rate in the silicone rubber bladder if it is carefully passivated. Further refinement of the cleaning and passivation technique may reduce the decomposition to the rates cited in the above reference.

Some bleaching was observed in both bladder materials during the above storage tests. The silicone rubber bladder when removed after being filled with peroxide for three weeks had turned from a clear slightly amber color to a milky white. Tests showed that the material was saturated with peroxide and could not be handled without rubber gloves even after many hours of washing in water. After drying in air for 10 days it returned to its original color and there was no apparent change in the mechanical properties of the material.

The diffusion of the evolved oxygen through the silicone rubber bladder was as rapid as expected. With the pressurant side vented the equilibrium pressure inside the sealed bladder was only 21 g/cm^2 (0.3 psi) even at the 49%/yr decomposition rate.

Time did not allow the achieving of an equilibrium pressure in the Teflon bladder with the outside vented, but the expected equilibrium pressure as a function of decomposition rate was calculated and the results are shown in figure 17.

Expulsion Efficiency

Both bladders were tested while installed in the tank to determine the quantity of fluid remaining after no more could be expelled (expulsion

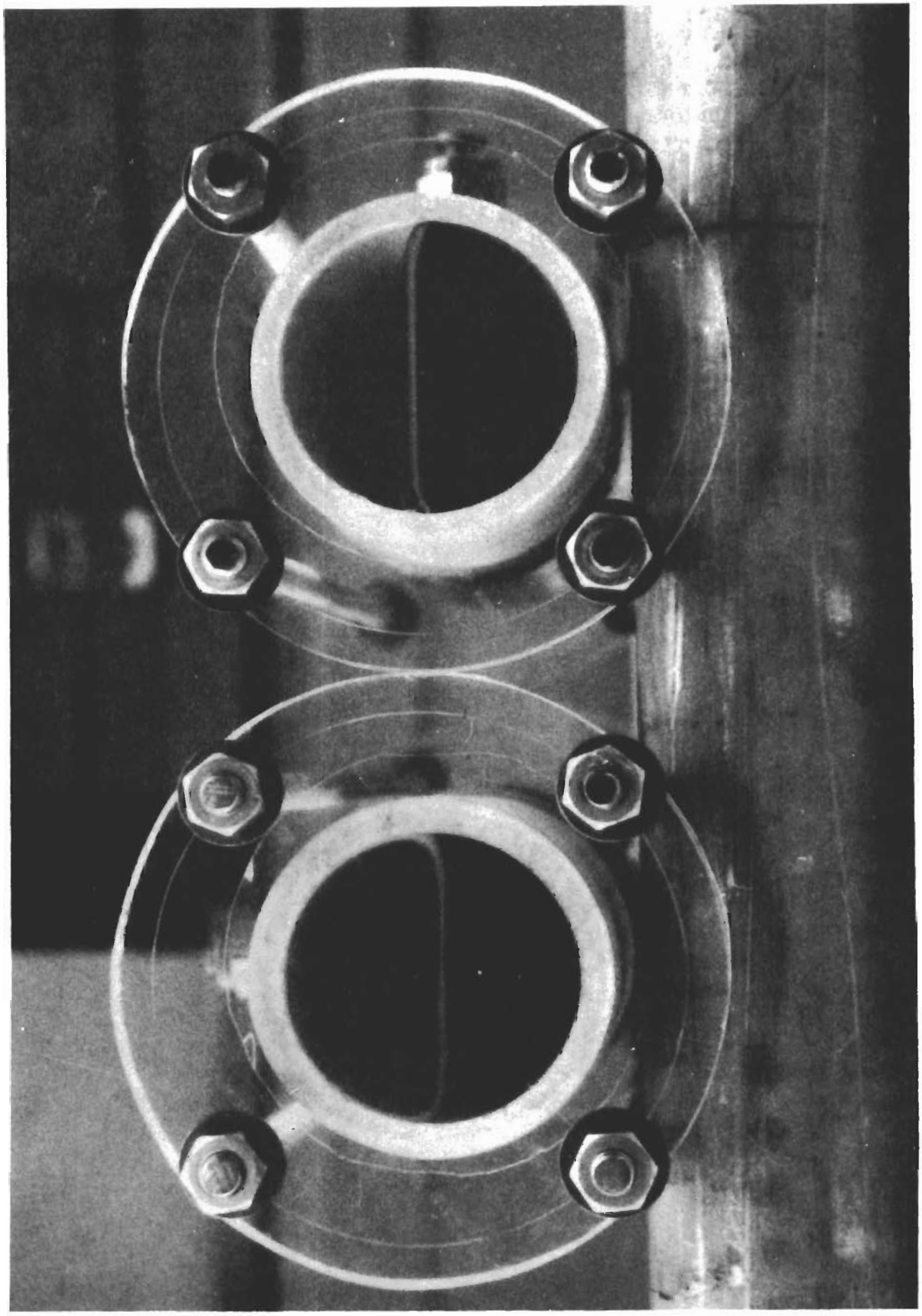


Figure 18. Wetted and Nonwetted Filters

No satisfactory method was found to clean or restore the nonwetting property to the surface in situ once it was contaminated. Solvent washing partially restored the nonwetting property to the porous Teflon but not sufficiently to achieve the designed flow capacity. The best way to effectively restore the nonwetting property to the filters was to mechanically remove a small amount of material from the surface by sanding. This apparently removed the contamination along with the thin layer of surface material.

SECTION VII

OPTIMIZATION AND EXTENSION TO OTHER MISSIONS

The final performance testing of the laboratory model suggests several areas where optimization might be effected. The discussion of these areas will follow the component pattern of the preceding sections. The optimum weight and volume for a flight system of the capacity of the laboratory model was predicted and, with this as a basis, weight and volume predictions were made for other system capacities.

Pressurant Tank

A measurement of the pressure drop through the entire laboratory model system indicated a total of 622 g/cm^2 (8.85 psi) at the design flow rate. The delivery pressure to the space enclosure must be maintained at twice the atmospheric pressure of 258-260 mm Hg (5 psia) for humidity control. The minimum pressurization required to deliver the design rate at this pressure would be 1324 g/cm^2 (18.85 psia). The volume required would be the 6.311 (385 in.^{3}) plus the volume of the pressurant container or approximately 8.2 std liters (500 std in.^{3}) of pressurant gas. The pressurant tank of the laboratory model contains 18.0 std liters (1100 std in.^{3}) when pressurized to the design pressure of 105.3 kg/cm^2 (1500 psi).

A lighter weight pressure tank can be achieved by using a titanium alloy Ti-6Al-4V, such as that used in the Apollo reaction control system (Bell Aerosystems, 1965, p VI-12). This reference describes a space qualified pressure vessel of welded construction using a design stress of 4955 kg/cm^2 (70,500 psi) and a wall thickness of 1.548 mm (0.022 in.). Using this stress level and wall thickness and assuming the same tank diameter is maintained, the pressure is calaculated:

$$p = \frac{2\,St}{d} = \frac{2\,(4955)\,(0.1548)}{3.18} = 174 \text{ kg/cm}^2 \text{ (2480 psi)}$$

The minimum tank volume is then only 48.8 cm^3 (2.97 in.^{3}). This is contained in a tank with a total length including end caps of 102 mm (4 in.). The weight of a tank this size would be 294 g (0.65 lb) or a weight reduction of 154 g (0.34 lb).

Regulator

Further significant weight reductions cannot be made in the regulator.

Hydrogen Peroxide Storage Tank

The 40% ullage space was not required to achieve adequate diffusion area in the bladder. A 5% ullage to take care of thermal expansion would be adequate. This would reduce the volume requirement inside the bladder to 3985 cm^3 (243 $in.^3$) from 6310 cm^3 (385 $in.^3$). Using approximately the same L/D ratio the new tank dimensions are 127 mm (5 in.) diameter by 368 (14.5 in.) long.

The lower pressure requirement of 1324 g/cm^2 (18.85 psi) calculated above would allow a much thinner wall thickness than was used in the laboratory model. The stress levels used in other space qualified tankage are much higher than the ASME pressure vessel code which was used in the laboratory model.

Bell Aerosystems Company (1965) used a design stress of 1490 kg/cm^2 (21,200 psi) for 6061-T6 aluminum alloy in the Agena and Dyna Soar programs. If this criteria were used for the volume and pressure mentioned above the wall thickness would only be 0.06 mm (0.00236 in.) or only a foil. This thickness would present mounting and fabrication problems serious enough to render it impractical. The minimum thickness for practical fabrication seems to be about 28 gauge or 0.305 mm (0.0126 in.). The weight of a tank of this thickness complete with a head fitting is estimated to be 282 g (0.6 lb), a reduction of 725 g (1.6 lb).

The bladder would be reduced in size by the change in ullage requirement. The weight of a silicone rubber bladder to fit the tank described above would be about 161 g (0.354 lb) and that of a Teflon bladder the same size would be 138 g (0.302 lb). The Teflon bladder will be used for weight projections and this weight reduction is 53.5 g (0.118 lb).

The total projected weight reduction of the hydrogen peroxide storage tank is 770 g (1.7 lb). Its volume at this size would be 4250 cm^3 (259 $in.^3$).

Catalytic Reactor

The weight of the catalytic reactor in the laboratory model is 46 g (0.1 lb) and its volume 8.9 cm^3 (0.54 $in.^3$). Any reduction in the size of this component would be at the expense of product purity and produce no substantial gains.

Heat Exchanger

The heat exchanger cools the products to nearer atmospheric temperature than the specifications require when the unit is operated in air at 1 atmosphere pressure. For operation at the specified pressure of a space enclosure of 258-260 mm Hg (5 psia) it is anticipated that the product temperature will be near the maximum allowable. No reductions are expected from the weight of 381 g (0.84 lb) and volume of 1160 cm^3 (71 $in.^3$) of the heat exchanger in the laboratory model.

Phase Separator and Product Storage

There was no specification as to how often water would be drawn off in the normal operation of the laboratory model, therefore it was built with a storage capacity for all the water produced in a 24 hour period. If the water were drawn off at least every 12 hours a size and weight reduction similar to that of the hydrogen peroxide storage tank can be achieved. This would make the product storage tank weight 282 g (0.6 lb) a reduction of 725 g (1.6 lb), and volume 4250 cm^3 (259 $in.^3$).

The stainless steel center section could be eliminated by using one long porous Teflon filter and save an additional 340 g (0.75 lb).

Control Panel and Mounting Hardware

The system as it would be adapted into a space vehicle would be integrated into the airframe and would not require the mounting panel necessary for use on the laboratory bench. The weight of this panel is 2580 g (5.7 lb). The hardware necessary to clamp the flight system in place is estimated to weigh 730 g (1.61 lb) and have a volume of 264 cm^3 (16.1 $in.^3$).

Weight and Volume Projections

A comparison of the weight and volume of the laboratory model and the projected weight and volume of an optimized system of the same flow rate and capacity is presented in table III.

TABLE III

WEIGHT AND VOLUME PROJECTIONS

	Laboratory Model		Projected	
	Weight (g)	Volume (cm^3)	Weight (g)	Volume (cm^3)
H_2O_2 Tank and Bladder Assy.	1190	6390	408	4250
6 Valves	204	98	204	98
3 Gauges	312	147	312	147
Regulator	145	65	145	65
Pressurant Tank	448	241	294	49
Catalytic Reactor	46	9	46	9
Heat Exchanger	381	1160	381	1160
Phase Separator and Product Storage Tank	1840	6390	775	4250
Plumbing	416	210	416	210
Total working components	4982	14710	2981	10238
Panel and Mounting Hardware	2580	666	730	264
H_2O_2	5270		5270	
Pressurant	36	____	17	____
Total for charged units	12868	15376	8998	10502

This summary indicates that the weight of an oxygen supply system of the capacity of the laboratory model but incorporating the weight and size reductions mentioned above, would be about 9.0 kg (19.86 lb) fully loaded and its volume would be 10.5 l. (640 $in.^3$) while the laboratory model weighs 12.8 kg (28.2 lbs) and occupies a volume of 15.4 l. (938 $in.^3$).

The projected sizes and weights of hydrogen peroxide fueled oxygen supply units for supply rates other than 91 g O_2/hr (0.2 lb O_2/hr) and for mission times other than one day have been calculated and the results plotted in figures 19 and 20. The design flow rate of the laboratory model of 91 g O_2/hr was based on the assumed metabolic requirement of 45.5 g/hr for one man plus an equal amount for leakage. The weight and size projections above are based on this 2 man rate as the design point and are extrapolated to longer periods than 24 hours and to flows equivalent to 2, 3, 4, and 5 man rates. An increase in time for any one flow rate only requires more peroxide and storage tank. An increase in demand rate up to that of 5 men only requires more heat exchanger. These projections assume, (1) the weight of the heat exchanger varies approximately linearly with the heat to be dissipated, and (2) the shape of the peroxide storage tank retains the L/D ratio of 3 at the increased volumes.

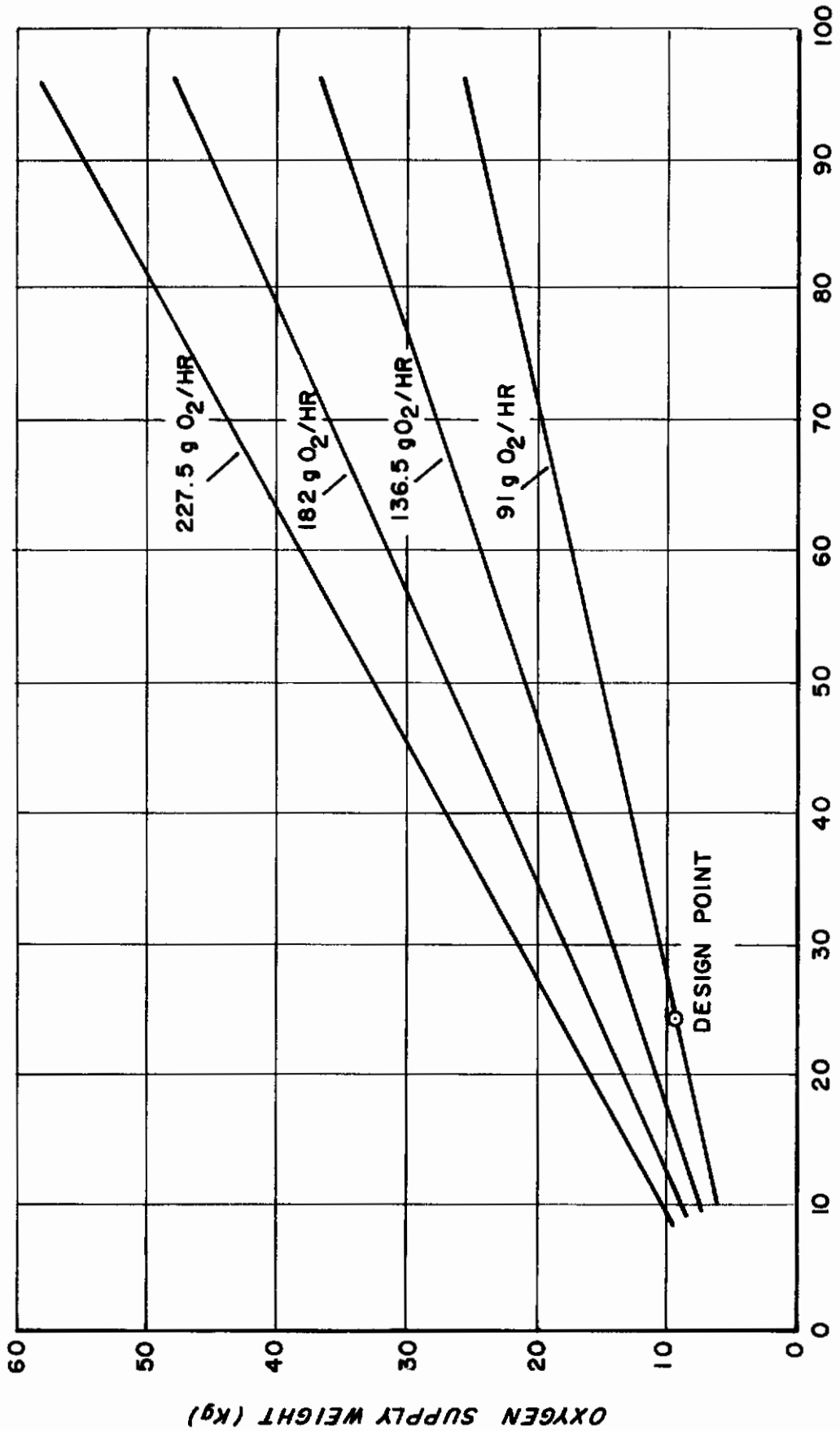


Figure 19. Mission Time vs Oxygen Supply Weight For 2, 3, 4, & 5 Man Rates

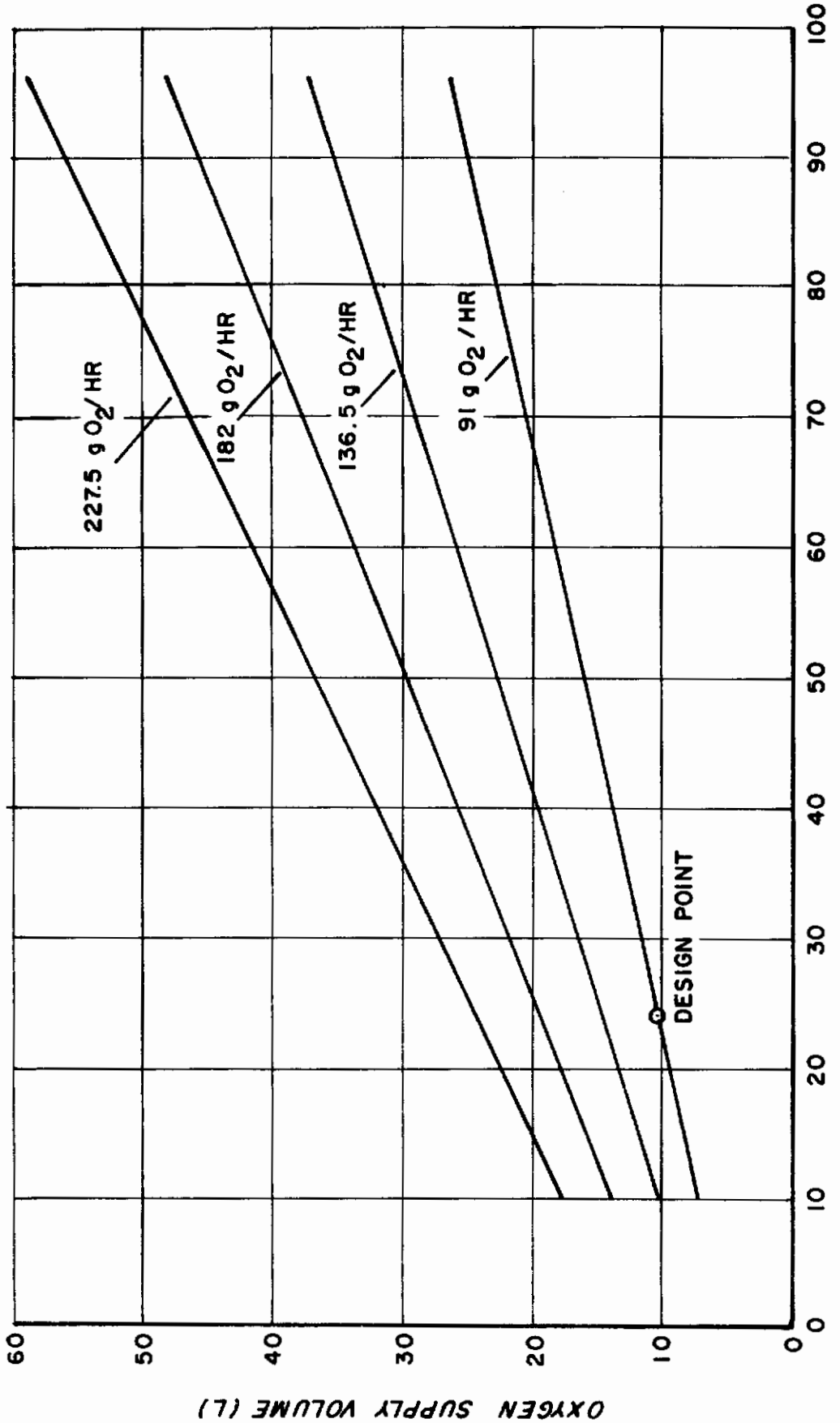


Figure 20. Mission Time vs Oxygen Supply Volume For 2, 3, 4, & 5 Man Rates

SECTION VIII

SUMMARY AND CONCLUSIONS

Preliminary investigations were conducted to determine the design criteria for a hydrogen peroxide based oxygen supply for manned space enclosures. Using these criteria, a laboratory model of such an oxygen supply system was designed and fabricated. The laboratory model produces, on demand, 91 g/hr (0.2 lb/hr) of oxygen for a period of 24 hours. It is storable, fully charged, for periods in excess of one year either in a gravitational field or in a weightless environment. Its operation is independent of either the presence of gravity or of its gravitational orientation. The oxygen produced by the laboratory model has a residual hydrogen peroxide content of less than 1 ppm. Potable water is also produced in a mass ratio of 1.36 H_2O : 1 O_2. The residual hydrogen peroxide in the water is less than 10 ppm.

The final performance tests of the laboratory model produced further design criteria which were used to predict the weights and volumes of hydrogen peroxide oxygen supply systems of other capacities.

The decomposition of hydrogen peroxide to breathing oxygen and potable water for manned space enclosures proved to be a feasible concept. It could be used either for a primary supply in a nonregenerative system or to make up losses in a system with recovery facilities.

SECTION IX

RECOMMENDATIONS

The operation and testing of the laboratory model of the hydrogen peroxide oxygen supply system has demonstrated the feasibility of the concept. However, just as with most studies of this type, new problem areas are uncovered during the program. In this study, the major difficulty arose in conjunction with the new and novel concept for phase separation and product expulsion, which is operative in both gravitational and non-gravitational field without dependence on orientation. This separator concept which utilizes the nonwettable surface of a porous material for separation was satisfactorily demonstrated in the laboratory.

However, on prolonged exposure to the aqueous phase, the porous surface loses the nonwettable property and the separator fails to perform. This problem is attributed to the accumulation of contaminants on the porous surface which allow wetting. The elastic sleeve that provides the differential pressure across the porous barrier has been shown to be responsible for this contamination. However, other components can also yield contaminants that produce the same result. With the exception of this unexpected wetting problem, the phase separator concept was demonstrated as an entirely feasible approach to phase separation under zero-gravity conditions. This phase separator concept is not applicable only to this oxygen supply system for space use but can be applied to any situation where liquid and vapor phases must be separated. It may provide new approaches to urine and wash water reprocessing in space or water electrolysis in zero gravity as well as other situations where separation is needed. Air Products and Chemicals, Inc. recommends a continuation of this novel phase separator study to reduce this concept of demonstrated feasibility to a more practical state of technology.

As shown in the preceding report, the feasibility of the hydrogen peroxide oxygen supply system concept has been demonstrated. A laboratory model was successfully designed, fabricated, and operated. The report shows the projected weights and volumes of flight-type units of similar and larger capacities. Air Products and Chemicals, Inc. recommends that the development of a flight-type system for ultimate space test be conducted in an effort to make this system a proven approach to emergency or supplemental oxygen and water supply in space. In addition to space vehicles and enclosures, this concept must be considered as a means to getting water and oxygen to space stations or moon bases. Hydrogen peroxide is a convenient, storable, transportable, and readily available form of water and oxygen for a variety of space application where primary sources or make-up fluids are required.

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13. ABSTRACT

This study was conducted to design, construct, and test an Oxygen Supply System for Manned Space Enclosures. The system was designed to provide oxygen at a rate of 0-91 grams/hr (0-0.2 lbs/hr) for a period of 24 hours, under weightless conditions. The design utilized the catalytic decomposition of hydrogen peroxide to breathing oxygen and potable water on demand. It consists of a positive expulsion peroxide storage tank, a catalytic reactor, a heat exchanger, a gravity independent phase separator, and a product storage tank. A laboratory model was constructed and tested to demonstrate the feasibility of the design. This unit produces breathing oxygen and potable water at the design capacity in any gravitational orientation.

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Space oxygen supply Hydrogen peroxide Breathing oxygen Chemical oxygen source						

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