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A CARBON DIOXIDE REDUCTION UNIT USING BOSCH REACTION AND EXPENDABLE CATALYST CARTRIDGES

by R. F. Holmes, E. E. Keller, and C. D. King

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16. Abstract

The feasibility of producing an efficient and reliable flight-qualified carbon dioxide reduction unit for use in life support systems for long-duration space missions has been demonstrated.

A prototype reduction unit utilizing the Bosch catalytic reaction and expendable catalyst cartridges was developed for the National Aeronautics and Space Administration, Langley Research Center.

The unit has two reactors with replaceable catalyst cartridges, each reactor having process capacity for continuous reduction of the carbon dioxide which would be produced metabolically by a four-man crew. Reaction was easily alternated between the two reactors allowing cartridge replacement without process interruption.

Reaction within the catalyst cartridge was readily initiated and maintained. No carbon migrated from the cartridge or was formed by reactions outside of the cartridge. Cartridge life was approximately three days and replacement was a simple and clean operation.

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Foreword

The Bosch process recovers oxygen from metabolically produced CO_2 and precipitates out the carbon. Previous programs for development of this process attempted to produce a continuously operating reactor with the carbon being removed while the unit was in operation. Problems were experienced in clogging of the carbon and precipitation of carbon on surfaces where it was not desired. The present program was therefore oriented toward elimination of the carbon removal problem by using a removable cartridge in which the carbon was precipitated. The cartridge is replaced when it is full by providing two cartridges in the system. Replacement can be accomplished without interruption of the process.

Optimization of weight volume or power were not objectives of this program. Additional effort is therefore required to determine an optimum design and a trade off with a continuous carbon removal system to determine the optimum system should be made.

The technical monitor of this program for the Langley Research Center was Lenwood G. Clark. Funding for this effort was provided by the Biotechnology and Human Research Division, NASA Office of Advanced Research and Technology, Washington, D.C.

Lenwood G. Clark
Aerospace
Technologist
Life Support Branch

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A CARBON DIOXIDE REDUCTION UNIT USING

BOSCH REACTION AND EXPENDABLE CATALYST CARTRIDGES

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Convair division of General Dynamics

SUMMARY

A prototype carbon dioxide reduction unit utilizing the Bosch catalytic reaction and expendable catalyst cartridges was developed and delivered to the National Aeronautics and Space Administration, Langley Research Center, under Contract NAS1-8217.

The unit had two reactors, each having process capacity for continuous reduction of the carbon dioxide which would be produced metabolically by a four-man crew. Alternating the reaction between the two reactors without loss of reduction rate was easily accomplished, allowing catalyst cartridge exchange without process interruption. Cartridge life was approximately three days and cartridge replacement was a simple and clean operation.

Material combinations and engineering techniques developed during the experimental phase were effectively used to retain all carbon formed within the catalyst cartridge and to avoid carbon-forming reactions outside of the cartridge.

A catalyst preactivation process was developed which assured prompt reaction initiation and the process rate was adequate and controllable.

The feasibility of producing an efficient and reliable flight-qualified reduction unit for use in life support systems for long-duration space missions was demonstrated.

1.0 INTRODUCTION

For long-duration manned space missions, supply problems can be materially reduced by reclaiming oxygen from the carbon dioxide produced by the crew. One attractive method for accomplishing this involves the Bosch process which catalytically reacts hydrogen with carbon dioxide to produce water and solid carbon. The water is subsequently electrolyzed to yield hydrogen for reuse in the Bosch reactor and oxygen for the crew.

A carbon dioxide reduction unit using the Bosch reaction was included in the integrated life support system (ILSS) at the NASA-Langley Research Center (ref. 1). This unit showed good processing characteristics but required excessive mechanical maintenance and frequent repairs during an extensive development program (ref. 2, 3). The mechanical problems stemmed primarily from difficulty in (1) separating carbon from the catalyst, (2) removing carbon from the system, and (3) preventing carbon-forming reactions in regions where carbon deposits could not be tolerated. This experience suggested that a reliable system based on total carbon containment within a replaceable catalyst cartridge could be more readily developed.

The results of a contract with the NASA-Langley Research Center to pursue this approach are reported herein.

2.0 OBJECTIVES

The broad objective was to prove that a Bosch CO_2 reduction unit using replaceable catalyst cartridges was operationally practical and thereby to enhance the position of this process in considerations of oxygen recovery systems for long-term manned space missions. The several sub-objectives leading to the broad objective were to: (1) demonstrate controlled reaction in the catalyst cartridge, forming carbon and water at specific rates; (2) achieve complete carbon containment within the catalyst cartridge; (3) prevent reaction outside the cartridge; and (4) develop a workable design and procedure for replacing spent (carbon-loaded) cartridges with new ones.

Optimizing weight, volume, or power requirements was not included in this program and no effort was made to do so because of the adverse effect on contract cost which would have resulted.

3.0 APPROACH

The program was divided into development and demonstration efforts. The development effort used the experimental approach, supported by literature search and engineering analysis, to acquire the technology necessary to design and build a prototype reduction unit capable of demonstrating that the program objectives had been met.

3.1 Development

A reduction unit sized for processing the CO_2 output from four men was assembled to provide a realistic test environment and configuration for screening materials, evaluating design concepts, and checking fabrication techniques. Several experimental reactor and heat exchanger assemblies were installed in the unit and tested during the development period. The use of various configurations and material and coating combinations provided opportunities for design and fabrication evaluation and a screening of materials for properties compatible with the reactor environment. To broaden the scope and accelerate the screening process, additional material specimens were tested by exposure within the operating reactor.

3.2 Demonstration

Proof of the validity of the information gained during the development period consisted of designing and building a prototype unit meeting contract specifications and performance requirements.

3.2.1 Prototype Unit Specifications. - The specifications called for a prototype CO_2 reduction unit utilizing a static catalyst reactor configuration to support the Bosch reaction and having the following characteristics:

a. A reaction rate adequate to process CO_2 produced by a four-man crew based on a metabolic production rate of 2.32 pounds of CO_2 per man-day.

b. Dual reactors allowing cartridge replacement without unit shutdown.

c. Component and assembly quality consistent with a 90-day run period.

d. Instrumentation necessary to determine operating characteristics.

e.   Self-containment allowing bench testing or ILSS test chamber installation and requiring nothing other than interfacing with support structure, coolant and gas lines, instrumentation, and electrical supply.

f.   Capable of being installed in the ILSS through a 30-inch-diameter hatch.

g.   Ability to operate with H_2 and CO_2 gases at 5 to 10 psig supply pressures, with feed gas impurities of up to one percent (volume), and with internal pressure maintained greater than 14.7 psia.

3.2.2   Prototype Unit Performance Requirement. - A performance test at the contractor's plant was required to demonstrate:

a.   Continuous operation at rated capacity (9.28 ± 5% pounds of CO_2 per day) for 120 hours without repair.

b.   A complete cartridge change cycle.

c.   A proof pressure test of 1.5 times working pressure at operating conditions.

d.   Reduction unit leakage less than the equivalent of 10 cc/min (nitrogen or carbon dioxide) at operating conditions.

e.   Automatic heater shut-off for low recycle gas flow.

4.0 TECHNICAL DISCUSSION

Figure 4.1 is a simplified diagram of the Bosch reaction for CO_2 reduction. The Bosch catalytic reactions occur at temperatures in the range of 1000 to 1400°F and have the net effect:

$$2 H_2 + CO_2 \rightleftarrows 2 H_2O + C$$
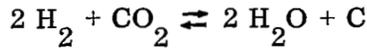
Intermediate reactions include:

$$CO_2 + C \rightleftarrows 2CO \text{ and}$$

$$2H_2 + C \rightleftarrows CH_4$$
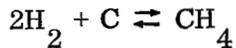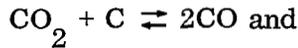
Combining the above equations provides a more complete representation,

$$xH_2 + yCO_2 \rightleftarrows aH_2O + bC + cCO + dCH_4,$$
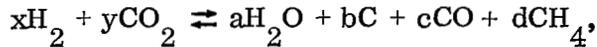
where $x = 2y$ and the coefficients a, b, c, and d are variable with time, temperature, pressure, and initial concentrations of the reactants.
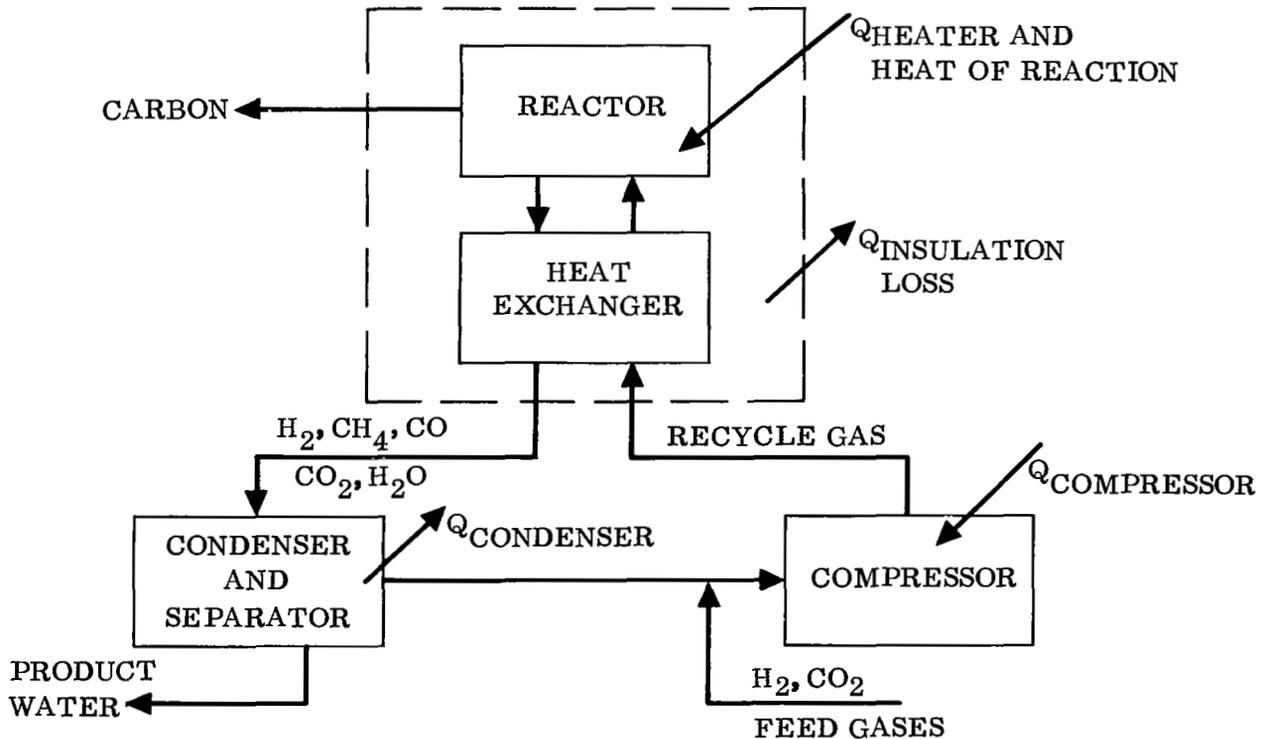
Figure 4.1 – Bosch Process Flow Diagram

4.1 Process Factors

The reactor gas mixture is composed of product water vapor, unreacted H_2 and CO_2, and the intermediate products CH_4 and CO. This mixture approaches an equilibrium composition for the existing temperature, pressure, and feed gas ratio to the degree allowed by reaction rate and space velocity. Carbon is formed and retained in the catalyst bed. The gas mixture passes from the reactor through a recuperative heat exchanger to the condenser and water separator, where the product water is removed as liquid. The relatively dry gases remaining are recycled, with CO_2 and H_2 feed gases added to replace the volume reductions due to the reaction and to water condensation and separation. A compressor returns the gases through the heat exchanger to the reactor, which continually tries to restore the reaction equilibrium which was upset by water removal. An electrical heater in the reactor supplies the heat to the gas necessary to reach and maintain reaction temperatures. During stabilized operation, the heater makes up the deficiency by which heat losses exceed heat gains. The losses are: (1) to the condenser, (2) through the insulation surrounding the reactor and heat exchanger, and (3) from exposed plumbing above ambient temperature. The gains are: (1) from the compressor, (2) the exothermic heat of reaction, and (3) to exposed plumbing below ambient temperature.

4.2 Materials

Since satisfactory process characteristics had been demonstrated in prior research, a major challenge of this program was to select satisfactory materials and use them in combinations that would: (1) guarantee CO_2 reduction in the reaction zone, (2) retain the product carbon in this zone without unduly restricting recycle gas flow, (3) cause no carbon-forming reaction outside of the desired zone, (4) posses the required structural characteristics, and (5) resist deterioration during extended exposure to the operating environments.

4.2.1 <u>Catalyst.</u> - Iron is the accepted catalyst for the Bosch reaction and the forms normally used are iron powder, steel wool, or mild steel in plate, tube, or screen geometries. Evaluation of previous work suggested steel wool as the initial choice. During the reaction process, iron diffuses into the product carbon but does not lose its catalytic property. Migration of the catalyst-bearing carbon from the reaction zone must be prevented not only for a clean cartridge exchange procedure but also to avoid accumulation and continued reaction outside of the cartridge.

4.2.2 <u>Carbon Containment Material.</u> - A filter or porous liner around the reaction zone must retain the carbon, be catalytically inactive, and resist deterioration at temperatures up to 1400° F in the reducing atmosphere. Porous ceramics, metallic filter screens, and ceramic fiber mats were considered, with mats being chosen for the first trial.

4.2.3 <u>Cartridge Shell.</u> - Materials for the cartridge shell must be non-catalytic and able to resist the rupturing forces generated by growth of dense carbon in the reaction zone and by differential thermal contraction between the shell and the carbon block during reactor cooldown.

4.2.4 <u>Reactor Shell and Heat Exchanger.</u> - Materials of the reactor shell and heat exchanger must be structurally acceptable for non-fired pressure vessels at 1200° F. They must be non-deteriorating with exposure to the reducing internal environment or the oxidizing external atmosphere. The inner surfaces must also be non-catalytic. Differences in thermal expansion characteristics further limited the choice of material combinations. Initially, no catalytic activity was expected from quartz and other ceramic materials or from copper, bronze, brass, nickel, or Monel. There was conflicting information on the catalytic activity of high-temperature structural materials such as Inconel and the stainless steels. It was suspected that alloys bearing appreciable amounts of iron should be avoided if possible or be protectively coated, and that non-ferrous materials were preferable if they had the required forming and structural characteristics.

5.0 DEVELOPMENT PROGRAM

The development program consisted of constructing, operating, and modifying a single-reactor, static-catalyst CO_2 reduction unit to gain the information necessary to assure that the specifications of the deliverable prototype unit could be met. Three reactor shells, two heat exchangers, and 13 catalyst cartridges were tested during this period. Although each change affected performance in some manner, discussion will be limited to factors contributing to a successful design.

5.1 Development Reactor and Heat Exchanger

The final configuration of the development reactor and heat exchanger assembly is shown in Figure 5.1. Recycle gas flow from the compressor entered this assembly through the heat exchanger cold-side inlet, passed between the electric heater and heater shroud to the cartridge core area, flowed radially outward through the cartridge and returned behind the reactor baffle plate to the heat exchanger hot-side inlet.

5.1.1 Reactor Shell Configuration. – The reactor shell was nominally 8 inches in diameter and 10 inches long with flanges at each end. A removable cover plate, to which the cartridge was attached, was bolted to the front flange, and the base plate was bolted to the other. Studs in the base held the reactor adapter, electric heater, and heater shroud in the proper relationship. The heat exchanger cold-side outlet and hot-side inlet tubes were welded to the adapter and supported the heat exchanger. This method of assembly provided optimum conditions for applying protective plating.

The 0.5-inch annulus between the reactor and cartridge shell was more than adequate for the recycle flows involved and allowed material specimens to be placed on the reactor shell. Specimens were also placed inside the cartridge core. A 0.25-inch-thick gasket of compressible ceramic fiber batt between the cartridge cover and baffle plate provided differential thermal expansion compensation and acted as a gas seal to restrict cartridge bypass flow.

5.1.2 Catalyst Cartridge Configuration. – Figure 5.2 shows the development unit catalyst cartridge design which had the most promising characteristics. Recycle gas entered the core area and passed radially outward through the perforated core, core liner, catalyst bed, shell liner, and perforated shell. The functions of the core and shell liners were to provide carbon growth boundaries and prevent carbon migration. The core and shell provided the structural envelope to resist the rupturing forces generated by the carbon block. The ceramic fiber liners at each end of the cartridge, together with careful packing techniques, were required to prevent flow channeling. The cartridge shell was attached to the reactor coverplate before the catalyst was packed, and the coverplate served as the cartridge base.

COLD-SIDE
INLET

HOT-SIDE
OUTLET

SEAL

BAFFLE PLATE

CARTRIDGE GASKET

REACTOR SHELL

CARTRIDGE

SEAL

COLD-SIDE
OUTLET

COVERPLATE

HEATER
SEAL

HEATER JACKET

HEATER SHROUD

ADAPTER

HEAT EXCHANGER
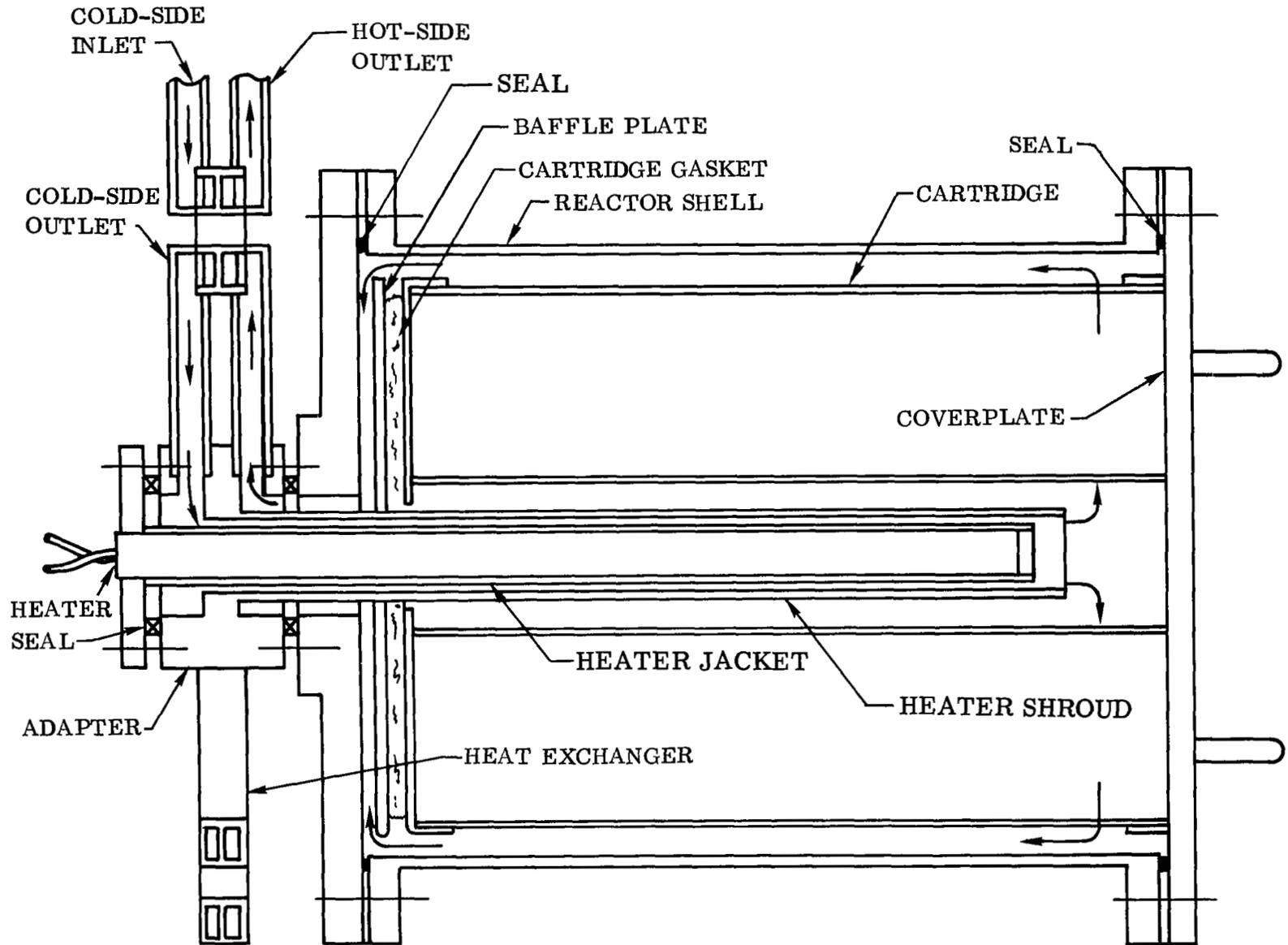
Figure 5.1 – Development Reactor Sketch

QUARTZ WOOL LINERS

COVER

PERFORATED CORE

PERFORATED SHELL

CATALYST

ATTACHMENT BAND

QUARTZ FIBER SHEET

REACTOR COVERPLATE

7.0 DIA

9.8
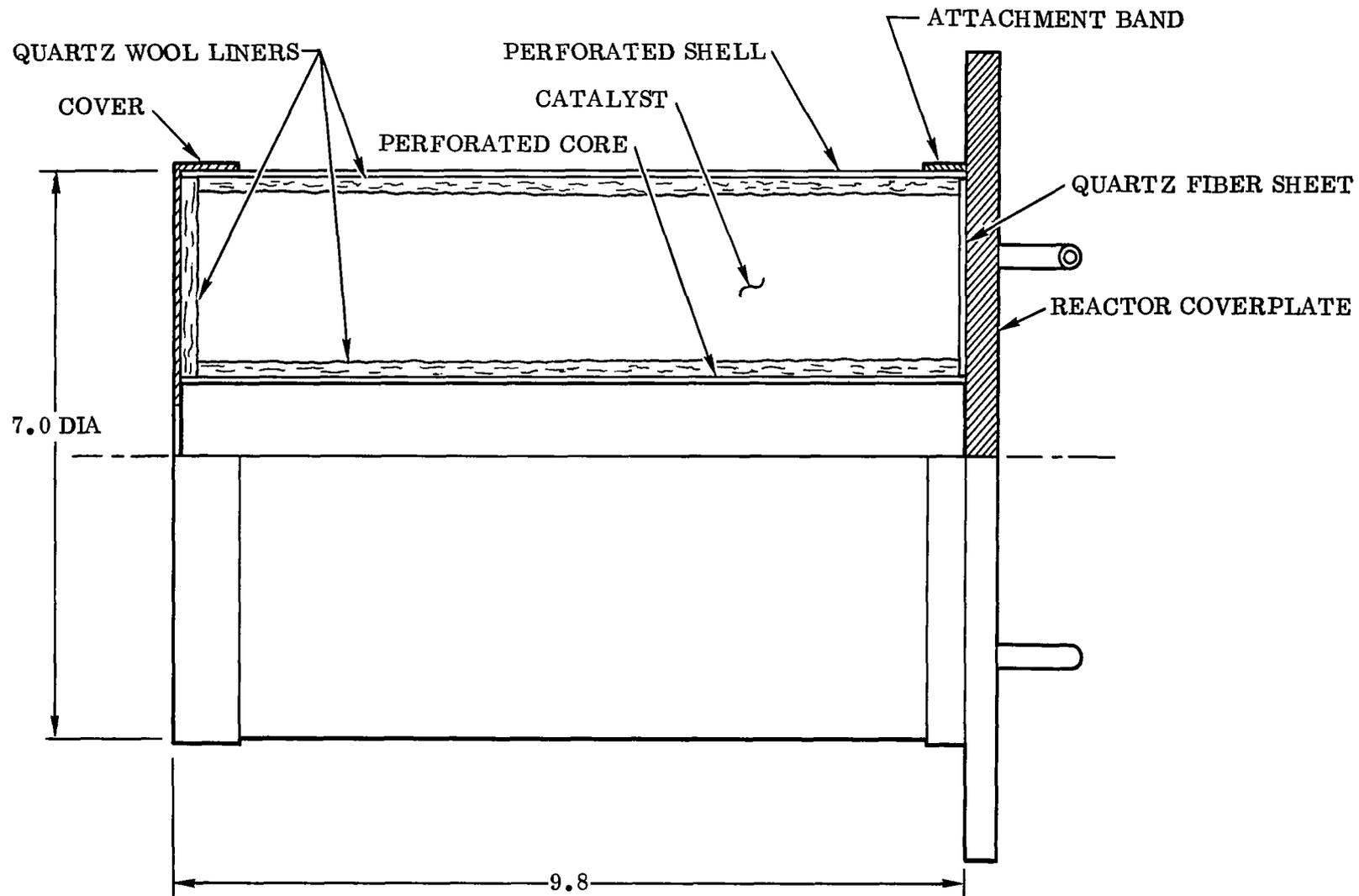
Figure 5.2 – Final Development Unit Cartridge Configuration

The annular configuration provided good relationships between flow area, path length, and carbon containment volume. These factors directly affect cartridge life, which is dependent upon ability to maintain the required recycle flow rate through the catalyst bed as carbon forms an increasing flow restriction. The cartridge was approximately 9.8 inches long with an outer shell diameter of 7.0 inches and a core diameter of 2.0 inches. Correcting for shell and liner volumes, and assuming a final carbon packing density of 0.5 gm/cc could be obtained without excessive flow restriction, a cartridge life of 2.0 to 2.3 days was anticipated.

5.1.3 Reactor Seals. - High-temperature seals were required at both faces of the reactor adapter and between the reactor flanges and end plates to prevent the escape of toxic and combustible gases. Seals tested included copper wire rings, Inconel "O"-rings, and rectangular-sectioned rings of brass and aluminum bronze. The aluminum bronze rings, coated with a high-temperature dry-film lubricant to prevent bonding of the bearing surfaces, gave the most satisfactory service.

5.1.4 Heat Exchanger. - Two types of heat exchangers, with several attachment variations, were used consecutively in support of the development program. A coiled concentric tube configuration, shown attached to the original development reactor in Figure 5.3, was thermodynamically superior but required extra space and was difficult to protectively plate internally or externally. The configuration shown in Figure 5.1 was designed primarily for convenience in fitting it into the reduction unit assembly, with ease of applying external plating and enclosing it in thermal insulation also given high priority. Exchange effectiveness and pressure differential characteristics were compromised as a result.

5.1.5 Thermal Insulation. - The reactor and heat exchanger assembly was insulated to conserve heat and protect personnel. Sheets of one-inch-thick, 8 lb/ft^3 ceramic fiber were held in place with aluminum foil, which also acted as a radiation barrier. Most areas were covered with three inches of the ceramic fiber insulation. A removable insulation cap allowed access to the reactor cover plate for cartridge exchanges.

5.2 Development Unit Controls

Controls were required to: (1) prevent system overpressures, (2) allow product water removal, (3) maintain a reactive temperature, (4) prevent heater overtemperatures, (5) maintain a reactive mixture, and (6) regulate the CO_2 conversion rate. The unit had a compressor bypass relief valve to prevent compressor overload and a system pressure relief valve for system safety. A manually operated water discharge valve provided for periodic removal of product water from the separator. Automatic controls were used for the other functions listed except for manual control of the conversion rate and of heater power.
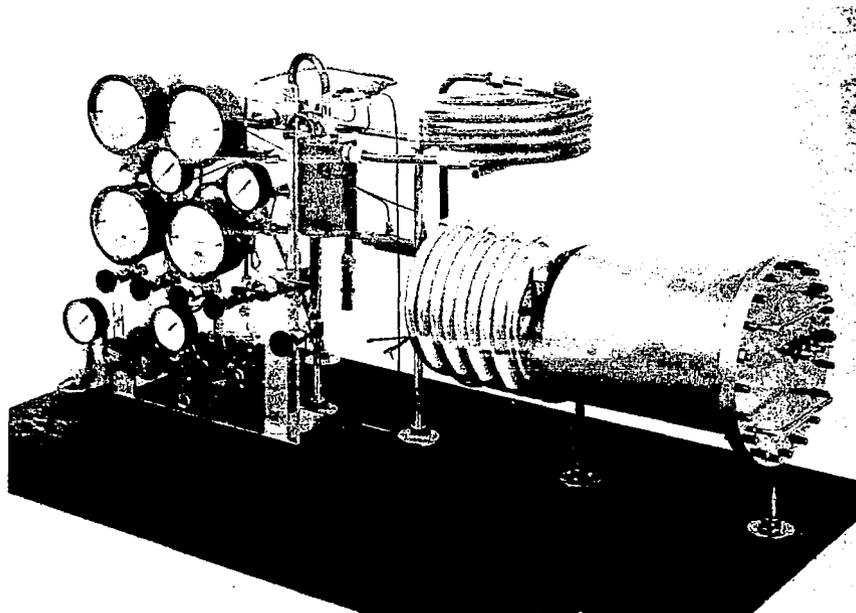
Figure 5.3 - Initial Development Unit Configuration

5.2.1 Temperature Controls. - Thermocouples embedded within the catalyst cartridge and in the electric heater were connected through a selector switch to a pyrometer with a temperature scale and set-point limit relay. Power to the heater was manually controllable by means of a Variac, which required little attention after conditions were stabilized. With the selector switch turned to the heater sheath thermocouple, heater power was automatically interrupted if the set-point temperature was exceeded, thereby protecting the heater. When the sheath temperature dropped below the set point, heater power was returned.

5.2.2 Mixture Controls. - The flow diagram in Figure 5.4 shows the relationship of the feed gas section to the recycle loop. Three feed gas regulators, a solenoid valve, two manually adjustable valves, and a CO_2 analyzer with set-point and relay actuation capability provided for maintaining a reactive mixture in the recycle loop. The H_2 pressure regulator was set to maintain a recycle loop feed-point pressure of 2 to 5 psig. One CO_2 regulator was set at a slightly lower pressure than the H_2 regulator so that a positive pressure would be maintained at the feed point if the H_2 supply failed. The second CO_2 regulator, in line with the control solenoid valve, was set to deliver a slightly higher pressure than the H_2 regulator so that if the CO_2 supply was interrupted and the feed point reached the H_2 pressure setting, CO_2 would be admitted when it was again

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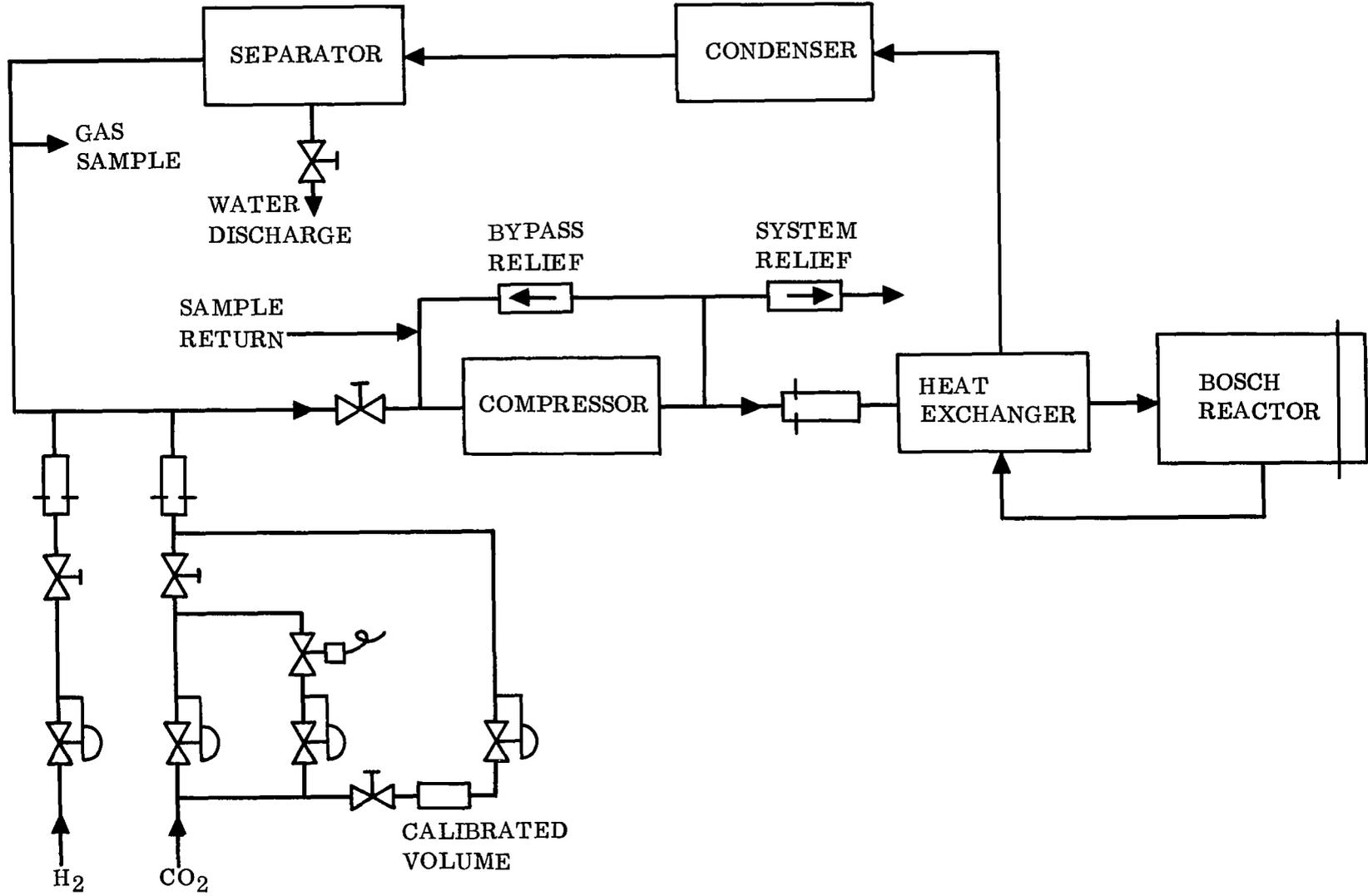
Figure 5.4 - Development Reduction Unit Flow Diagram

available. For this condition, the system would be low in CO_2 concentration causing the solenoid valve to be open as explained below. The manual valves in the feed lines were adjusted so that during normal operation the concentration of CO_2 in the recycle loop slowly declined when the solenoid valve was closed and increased with the solenoid valve open. A continuous sample of recycle gas was passed through the analyzer and returned to the system. The analyzer monitored the CO_2 concentration and actuated a relay whenever the concentration exceeded a set-point value. This action closed the CO_2 control solenoid valve and caused the concentration to decline until the solenoid valve was again opened. The set-point for best conversion rate varied with reactor temperature but the setting was not critical.

5.2.3 Process Rate Control. - The conversion rate response to a change in recycle flow rate was prompt and proportional, and the flow rate was easily altered by adjusting the manual valve in the recycle loop at the compressor inlet. This adjustment allowed recycle flow control within the limits of compressor capability, thereby providing process rate control while other process-affecting parameters such as reactor temperature, mixture composition, catalyst bypass, and condenser temperatures were being stabilized or changed.

5.2.4 Leakage Rate Determination. - The third pressure regulator in the CO_2 supply line, in conjunction with a shut-off valve and calibrated supply volume, allowed the system leakage rate to be readily determined. For accuracy, the CO_2 supply pressure had to be sufficiently higher than the regulator delivery pressure to allow measurable decrease in supply pressure without affecting the delivery pressure. To check the leakage rate, the system pressure was allowed to stabilize at the regulator delivery pressure with the shut-off valve open. After stabilization was reached, the shut-off valve was closed, and the supply volume pressure decay rate was measured. The leakage rate was then calculated or obtained from a curve of leakage rate versus pressure decay rate for the known supply volume.

5.3 Development Unit Fabrication

Development program experience emphasized several points to be observed during unit fabrication.

5.3.1 Protective Plating. - If a catalytic structural material is used for reactor or heat exchanger fabrication, a good quality of protective plating is required. Flawless plating on stainless steel was difficult to obtain where there were inaccessible recesses, sharp corners, or cracks between two parts. In the final development reactor configuration, inaccessible recesses were avoided by sectional fabrication and bolt-together assembly. Sectional fabrication facilitated the use of non-reactive material for parts

that were not structurally critical. Internal machined corners were radiused and a continuous surface for plating was formed, for example, at the intersection between the reactor shell and flange, by complete weld penetration or by internal filler welding.

After these precautions were taken, good plating practices were strictly observed. A flash coat of electrolytic nickel followed by a minimum of 1 mil of electroless nickel provided a coating surface sufficiently durable for the disposable stainless steel cartridge shells where exposure times were relatively short. For interior reactor surfaces, one additional 3-mil coat each of electrolytic nickel and copper plate was applied. Iron in contact with nickel had been found to initiate a carbon-forming reaction which continued after the iron was removed. The copper plate was applied to prevent this reaction should a particle of catalyst escape from the cartridge. Seal surfaces were not copper plated because of the oxidation problem at the outer edge of the seal.

5.3.2 <u>Catalyst Packing.</u> - The process of packing the steel wool catalysts between the quartz wool core and shell liners required special attention to avoid flow channeling and contamination of the outer surface with reactive particles. Tooling used for this purpose consisted of metal shields placed against the liners, holding them in place and protecting them while strips of expanded steel wool were wound into the annular space. The steel wool was lightly tamped to remove large cavities, and care was taken to prevent it from hanging up on protrusions such as thermocouple probes or wells. The interfaces between the catalyst and the cartridge base and cover were especially vulnerable to flow channeling. A dense pack next to the base surface and a springy overfill at the cover end reduced the tendency to channel in these areas. The liner-protecting shields were removed before the cartridge cover was installed.

5.3.3 <u>Sectional Assembly.</u> - Three problems generated by sectional assembly and the requirement for coverplate removal were: (1) undesired bonding of mating surfaces under pressure in the high-temperature reducing environment, (2) tendency of threads to gall and seize in the high-temperature oxidizing atmosphere, and (3) excessive yield and set of seal and bolt materials in high-temperature cyclic operation if thermal expansions were not matched.

Two fairly successful methods of bond prevention were used. A silicone grease, thoroughly loaded with fine aluminum powder and applied to the mating surfaces, left a separating powder film when the grease was driven off during heating. A commercial high-temperature, dry-film lubricant, sprayed and baked on one of the mating surfaces, also provided the necessary separation. The first method required reapplication each time the surfaces were rejoined and the latter after three or four separations.

Thread seizure in the oxidizing atmosphere was prevented by generous application of commercial high-temperature antiseize compounds each time the part was reassembled.

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Considerable difficulty was experienced when bolts of 400-series stainless steel were unknowingly used for cover plate attachment. Thermal expansion of the 300-series stainless steel flange and cover plate was approximately 60 percent greater than that of the bolts. The resulting stresses caused the seals to yield in compression and the bolts to yield and set in tension, allowing excessive leakage after return to ambient temperature. When, after repeated cartridge change cycles, the reason for this leakage phenomenon was discovered, the used bolts were noticeably longer than new bolts. Substitution of 300-series bolts eliminated this difficulty.

5.4 Development Unit Performance

As previously noted, three reactor shells, two heat exchanger configurations, and 13 cartridges were used during the development period. Discussion of performance is based primarily on data and observations made during tests of the last five development cartridges, numbered D-9 to D-13. These cartridges were all similar in geometry to that previously described and shown in Figure 5.2. With this configuration, a four-man CO_2 conversion rate was maintainable for a two-day period.

5.4.1 Gas Mixture Composition. - Data obtained from the original Bosch CO_2 reduction unit in the ILSS at the NASA, Langley Research Center, showed a typical dry recycle gas composition (volume) to be 0.40 H_2, 0.30 CH_4, 0.20 CO, and 0.10 CO_2. Gas property calculations were simplified without introducing serious error by ignoring the water vapor component of the recycle gas. Viscosity, specific heat, and thermal conductivity characteristics of this mixture were calculated for different temperatures and are plotted with the individual component gas characteristics in Figures 5.5, 5.6, and 5.7. Mixture and component gas constants are given in Table 5.1.

These values were used in the design and selection of components for the development unit and the mixture composition assumption was reviewed prior to prototype unit design. Depending on the reactor temperature and CO_2 control settings, the development unit showed satisfactory performance at mixtures ranging from 0.58 H_2, 0.27 CH_4, 0.13 CO, and 0.02 CO_2 to 0.20 H_2, 0.20 CH_4, 0.40 CO, and 0.20 CO_2. Data for the originally selected composition was therefore considered to provide a reasonable base for prototype unit design calculations.

5.4.2 Recycle Flow Rate. - A review of the recycle flow rates required to maintain a four-man CO_2 conversion rate also showed a wide variation. Until the amount of carbon accrued in the cartridge was equivalent to approximately 20 hours at a four-man CO_2 reduction rate, flow requirements for the last five cartridges varied from 4.5 to 8.0 lb/hr. Fully loaded with carbon equivalent to 45 to 50 hours at the specified rate, the corresponding recycle flow requirements were 5.0 to 12.0 lb/hr. The increases
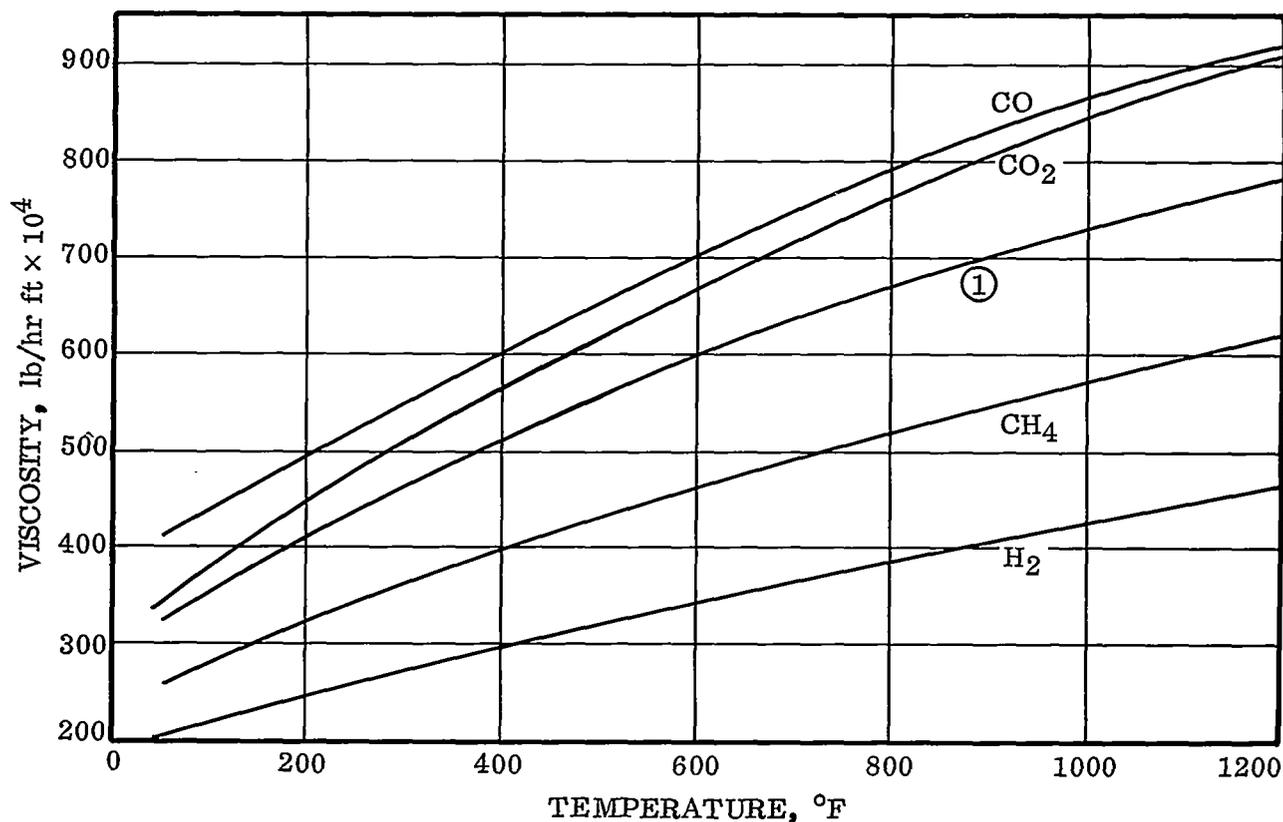
$$\textcircled{1} \text{ MIXTURE: } 0.40 \text{ H}_2, \quad 0.30 \text{ CH}_4, \quad 0.20 \text{ CO}, \quad 0.10 \text{ CO}_2$$

Figure 5.5 – Component Gas Viscosities

probably reflect changes in cartridge bypass flow as catalyst bed restrictions rose to 5 to 8 psid. Assuming that the conditions resulting in the lower flow requirements could be achieved, a value of 6.0 lb/hr was chosen for prototype design purposes.

5.4.3 Cartridge Pressure Drop. – Figure 5.8 is a plot of the approximate relationship of cartridge pressure differential to carbon density or specific gravity as obtained from data for the last five development cartridges. The carbon envelope dimensions shown were assumed to be the same for all cartridges. No attempt was made to normalize the data to a single gas temperature, composition, flow rate, or pressure level, but the points represent near-normal CO_2 conversion rates.

5.4.4 Process Temperatures. – Limited instrumentation showed a temperature spread of 50 to 130° F inside the cartridges tested. The higher values usually occurred toward the end of a run as flow restriction increased the tendency for bypass flow. Good performance was experienced at average reactor temperatures from 1150 to 1300° F with 1250° F appearing to be typical a major portion of the time. These observations suggest that the reaction is not highly sensitive to minor temperature changes, nor is an even temperature distribution critical.

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Figure 5.6 – Component Gas Specific Heats

Figure 5.7 – Component Gas Thermal Conductivities

① MIXTURE: 0.40 H_2, 0.30 CH_4, 0.20 CO, 0.10 CO_2

CARBON BLOCK

VOLUME, V_D = 312 in.^{3}
FLOW AREA, A_D = 139 in.^{2}(at mean dia.)
PATH LENGTH, d_D = 2.25 in.
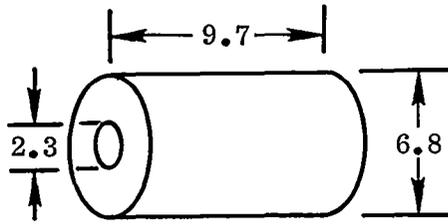
CARTRIDGE NO.

○ D-9
□ D-10
◇ D-11
△ D-12
◁ D-13
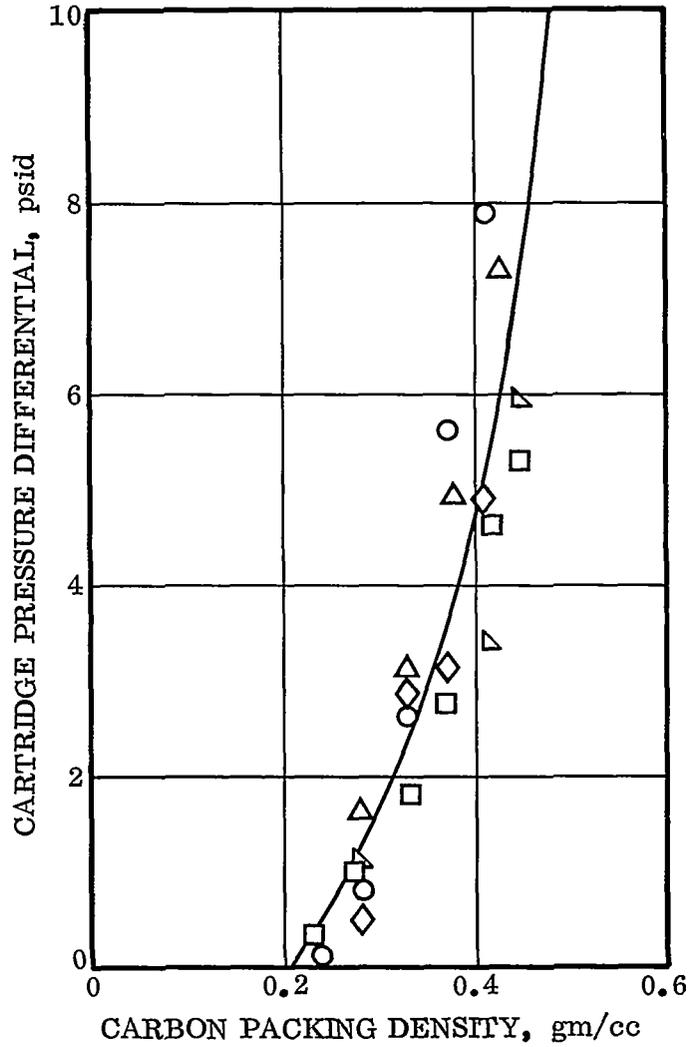
Figure 5.8 – Development Cartridge Pressure Differential Versus
Carbon Density

TABLE 5.1

GAS CONSTANTS

Gas	Molecular Weight (ω)	Ratio (1545/ω)
H_2	2.016	772.0
CH_4	16.043	96.5
CO	28.011	55.1
CO_2	44.011	35.1
H_2O (Vapor)	18.016	85.8
0.40 H_2, 0.30 CH_4, 0.20 CO, 0.10 CO_2	15.600	99.0

Saturation temperatures in the water-cooled condenser were between 50 and 60°F and condenser pressures were normally between 2 and 4 psig.

5.5 Materials Evaluation

During the development phase of the program, many metals, coatings, and non-metallic materials were evaluated for possible use in construction of the prototype unit.

5.5.1 Evaluation Techniques. - Some materials were tested by using them in construction of the development reactors. Others were exposed to reactive conditions by placing specimens inside the reactor between the outer wall and the cartridge shell or between the heater shroud and the inner surface of the cartridge core.

Preliminary evaluations were made by visual examination for carbon deposition or surface degradation. In some cases, microscopic and metallographic examinations were made and simple bend tests were performed to see if material properties had been affected.

5.5.2 Evaluation Results. - The materials evaluated as components of the development reactor assemblies are listed with exposure comments in Table 5.2, and the results of both the component and the specimen evaluation tests are presented in Table 5.3. From these tests, the following are general observations applicable to reduction unit design.

a. Copper and copper alloys are non-catalytic but have various deficiencies in physical and chemical characteristics. Oxygen-bearing copper is porous and weak after fairly short exposure to the reducing environment. Oxygen-free copper does not

TABLE 5.2

DEVELOPMENT REACTOR COMPONENT MATERIALS

Run No.	Hours	Reactor Shell	Reactor Cover	Reactor Seal	Heat Exch.	Adapter Body	Adapter Seals	Heater Jacket	Heater Shroud	Cartridge Shell	Cartridge Cover	Baffle Plate
D-1	56	321ss[a]	321ss	Copper	Copper[b]	321ss[a]	316ss[h]	None	321ss[a]	304ss	None	321ss
D-2	27	321ss[a]	321ss[c]	X-750[f]	Copper[b]	321ss[a]	316ss[h]	None	321ss[a]	304ss[c]	None	321ss[c]
D-3	40	321ss[a]	321ss[d]	Copper	Copper[b]	321ss[a]	316ss[h]	None	321ss[a]	Copper	None	Copper
D-4	46	321ss[d]	321ss[d]	X-750[f]	Copper[b]	321ss[d]	316ss[h]	None	321ss[d]	K-500	None	321ss[d]
D-5	21	K-500[c]	321ss[d]	X-750[f]	Copper[b]	(K-500	316ss[h]	None	Brass	K-500	None	321ss[d]
D-6	28	K-500[c]	321ss[d]	X-750[f]	Copper[b]	& brass)	316ss[h]	None	Quartz	K-500	None	321ss[d]
D-7	39	321ss[e]	321ss[d]	X-750[f]	Copper[b]	Ni 201	Brass	None	K-500[e]	K-500	None	K-500
D-8	51	321ss[e]	321ss[d]	Brass	Copper[b]	Ni 201	Brass	None	K-500[e]	K-500	K-500	K-500
D-9	42	321ss[e]	321ss[d]	Brass	Copper[b]	Ni 201	Brass	None	K-500[e]	X-750	X-750	K-500
D-10	49	321ss[e]	321ss[d]	Brass	Copper[b]	Ni 201	Brass	None	K-500[e]	304ss	X-750	K-500
D-11	44	321ss[e]	321ss[d]	A.B.	Copper[i]	321ss[d]	A.B.	None	Copper	304ss[d]	X-750	K-500
D-12	48	321ss[e]	321ss[d]	X-750[g]	Copper[i]	321ss[d]	A.B.	Copper	Copper	304ss[d]	X-750	K-500
D-13	53	321ss[e]	321ss[d]	X-750[g]	Copper[i]	321ss[d]	A.B.	Copper	Copper	304ss[d]	X-750	K-500

Notes:

a. Reaction-exposed surfaces electroplated with nickel.
b. Concentric tube coil, externally nickel-plated to protect from oxidation.
c. Electroplated with copper.
d. Electroless nickel plated.
e. Electroless nickel plus nickel electroplate plus copper plate.
f. Silver plated.
g. Coated with dry film lubricant.
h. Ferrules.
i. Double ring, externally nickel-plated.

Abbreviations

ss	Stainless steel
X-750	Inconel X-750
K-500	Monel K-500
A.B.	Aluminum Bronze
Ni	Nickel

TABLE 5.3

MATERIALS EVALUATED IN THE DEVELOPMENT REACTORS

Material	Surface Treatment	Catalytic Carbon Formed	Material Properties Affected	Suitable for Exterior Use	Structural Properties at 1200°F	Remarks
Stainless Steels, Austenitic	Bare & welded	Yes	Yes	Yes	Good	Especially catalytic in weld areas
	Electroless nickel plated	No	No	—	—	Satisfactory performance. Plating darkens with time
	Copper plate over nickel plate	No	No	No	—	Satisfactory performance
	Coated with silver braze	No	Yes	—	—	Coating did not protect substrate from embrittlement
	Aluminided with Vac-Hydes 1, 14, 19, or 28	No	No	Yes	—	Coatings were somewhat powdery and dark
Nickel 200, 201, & TD	Bare & welded	No	No	Yes	Fair	Satisfactory for some applications
Nickel 200	Plated with silver, copper, gold, or rhodium	No	No	—	—	Silver & gold plating blistered. Copper & rhodium satisfactory
	Bare in contact with iron	Yes	Yes	—	—	Nickel disintegrated in reactive areas near iron
Monel K-500	Bare & welded	Yes	Yes	Yes	Fair	Reactivity & structural properties are marginal
	Copper plated	No	No	No	—	May be satisfactory for low stress applications
Inconel X-750	Bare and welded	Yes	Yes	Yes	Good	Carbon formed in weld areas and Inconel embrittled
	Fel Pro C-300 coated or silver plated	No	Yes	Yes	—	Inconel became brittle
	Nickel or rhodium plated	No	No	Yes	—	May be satisfactory in some applications
	Copper plated	No.	No	No	—	Small blisters developed in plating
	Aluminided with Vac-Hydes 1, 14, 19, or 28	No	No	Yes	—	Coatings were powdery and dark
Incoloy 800	Bare & welded	Yes	Yes	Yes	Good	Catalytic activity was very slight
	Nickel plated	No	No	Yes	—	Nickel darkened (heater sheath exposure)
Alumel	Bare	No	No	Yes	—	May be satisfactory in some applications
Steel, 1020	Chromium plated	No	Yes	—	—	Plating cracked and darkened
Cobalt	Bare	Yes	Yes	Yes	—	Quite catalytic
Hastelloy X & R235	Bare	Yes	Yes	Yes	Good	Embrittled
Columbium	Bare	No	Yes	—	Good	Embrittled
Titanium 6Al4V, 8-1-1	Bare	No	Yes	No	—	Embrittled
Graphite	Bare	No	No	No	—	May be satisfactory for some applications
Silver	Bare	No	No	Yes	Poor	Not very useful
Copper, oxygen free	Bare & welded	No	No	No	Poor	Satisfactory for very low stress applications
	Gold plated	No	Yes	No	—	Gold diffused into copper
	Electroless nickel plated	No	No	Yes	—	Nickel darkened with time
Copper, oxygen bearing	Bare & welded	No	Yes	No	Poor	Became very porous and weak
Brass, yellow	Bare & welded	No	Yes	Yes	Fair	Zinc volatilized from surface at operating temperatures
Bronze, commercial	Bare	No	Yes	—	—	Satisfactory for low stress applications
Beryllium copper	Bare	No	No	—	—	May be satisfactory for some applications
Aluminum bronze, CA614	Bare & welded	No	No	Yes	Fair	Satisfactory performance
Asbestos, paper & yarn	As received	No	Yes	—	—	Quite fragile after reinforcing fibers are destroyed
Quartz, fiber & tubing	As received	No	No	Yes	—	Satisfactory performance
Fiberglass, E glass cloth	As received	No	Yes	—	—	Fibers soften at operating temperatures
Alumina silica ceramic fiber	As received	No	No	Yes	—	Satisfactory performance

deteriorate in the reducing atmosphere but has low mechanical strength and little oxidation resistance at operating temperatures. Yellow brass is non-catalytic, has marginal oxidation resistance, and poor mechanical properties at reactor temperatures. Zinc volatilizes from brass exposed to the internal environment leaving a copper-colored surface. Although the mechanical properties of aluminum bronze at 1200°F have apparently not been determined, they appeared to be better than for copper and brass. Aluminum bronze was non-catalytic and did not deteriorate with high-temperature exposure to air. These characteristics make it a good candidate for low-stressed components simultaneously exposed to oxidizing and reducing conditions. If the high-temperature strength of aluminum bronze were found to be adequate for reactor shell requirements the problems generated by the need for protective plating could be avoided.

b. Nickel and its alloys varied in catalytic activity. Nickel did not produce a carbon-forming reaction except in one case. In that case, iron in contact with a nickel surface initiated a carbon-producing reaction that continued to produce carbon and to penetrate the nickel even after the iron and loose carbon were removed. Nickel also tends to darken with prolonged exposure to the reactive environment. Nickel 201 is ASME-rated for construction of unfired pressure vessels, but compared to stainless steel or Inconel its mechanical properties at 1200°F are relatively poor.

Inconel X-750 and Incoloy 800 were slightly catalytic in some circumstances. Both are ASME-rated for unfired pressure vessels and have good oxidation resistance but would require an effective coating to eliminate catalytic activity or deterioration due to carburization.

Monel K-500 was evaluated as a reactor shell and cartridge material. It appeared to be oxidation resistant but was slightly catalytic in higher temperature regions. Copper plating effectively prevented carbon formation but the mechanical properties were marginal at operating temperatures.

c. Austenitic stainless steels, types 301, 304, 316, 321, and 347, act as catalysts under some conditions but have acceptable oxidation resistance and high-temperature strength for reactor applications. An effective way to prevent catalytic activity is to plate the surface with electroless nickel which is nonporous and can be uniformly deposited on complex shapes. Copper can be deposited over the nickel when a surface which will not darken with prolonged exposure to recycle gases or be adversely affected by contact with iron is required.

d. Development reactor seals included annealed copper wire rings, flat brass and aluminum bronze rings, and Inconel X-750 "O"-rings with silver and nickel plate. In the high-temperature reducing environment, mating surfaces tended to fuse together,

and breaking this bond was often difficult. Separation of sealed surfaces often caused failure of seal or flange platings causing the seal to be discarded and the flange surface to be refinished. Aluminum powder mixed with silicone grease was fairly effective in preventing bonding, but application was an untidy process and smoke was generated when the seal was heated. The aluminum bronze rings gave satisfactory service when coated with a commercial dry-film lubricant suitable for 1200° F service.

e. Non-metallic materials were evaluated within the reactor for such applications as heater shrouds, carbon containment liners, soft seals, and spacer gaskets. Quartz tubing, cloth, and batt and alumina silica ceramic fiber insulation were non-catalytic and chemically unaffected by prolonged exposure to the reaction environment. Repeated expansion and contraction cycles tended to cause the quartz batts to degrade by breaking the fibers into short lengths. Asbestos products were non-catalytic but their physical characteristics were impaired by exposure to operating temperatures and binder decomposition products contaminated the product water.

6.0 PROTOTYPE DESIGN CRITERIA

This section presents the performance objectives, criteria for design calculations, and abbreviated results of design analyses.

6.1 Process Parameters

Process parameters based on contract specifications and background technology gained from experience with the development unit are presented in Table 6.1 and Figure 6.1. Table 6.2 gives process rates for the reactants and products of the Bosch reaction based on a stoichiometric balance for the specified CO_2 conversion rate of 2.32 lb/man-day. The recycle flow rate of 6.0 lb/hr is based on development unit experience as discussed in Paragraph 5.5.2.

6.2 Thermal Analysis

6.2.1 Heat Exchanger Temperatures and Design Load. – Referring to Figure 6.1, the hot-side inlet gas temperature was assumed from development unit operations to be, $T_1 = 1100°F$ for reactor temperature, $T_6 = 1250°F$. The difference reflects heat lost through the reactor insulation. The approximate temperature of the recycle gas after passing through the compressor was $T_4 = 120°F$. The desired exchanger temperature effectiveness was e = 0.85 using the equation

$$e = \frac{T_1 - T_2}{T_1 - T_4}$$

from which

$$T_2 = 1100 - [0.85 (1100 - 120)] = 268°F$$

The heat exchanger design load should then be,

$$Q_{HX} = \dot{w} \, Cp \, (T_1 - T_2) = 6.0 \, (0.60) \, (1100 - 268) = 3000 \text{ Btu/hr}$$

Since the gas specific heat is nearly the same on hot and cold sides of the exchanger,

$$T_1 - T_2 = T_5 - T_4, \text{ from which } T_5 = (1100 - 268) + 120 = 952°F.$$

TABLE 6.1

PROTOTYPE REDUCTION UNIT DESIGN PARAMETERS

Capacity, number of men	4
CO_2 rate, lb/man-day	2.32
Feed gas impurities, maximum % by volume	1.0
Feed gas pressure range, psig	5 to 10
Catalyst cartridge replacement interval, days	3
Condenser coolant	Water
Coolant inlet temperature, °F	40
Coolant flow, lb/hr	60
Ambient temperature, °F	75
Ambient pressure, psia	14.7
Reduction unit pressures, psia	>14.7
Maximum reactor pressure, psig	15.0
Dry recycle gas composition, % by volume	
$\quad H_2$	40
$\quad CH_4$	30
$\quad CO$	20
$\quad CO_2$	10

TABLE 6.2

PROTOTYPE DESIGN PROCESS RATES

	lb/day	lb/hour	lb/minute
Reactants			
$\quad CO_2$	9.28	0.387	0.00645
$\quad H_2$	0.85	0.035	0.00059
Products			
$\quad H_2O$	7.60	0.317	0.00528
$\quad C$	2.53	0.1055	0.00176
Recycle flow rate	144	6.0	0.10

28
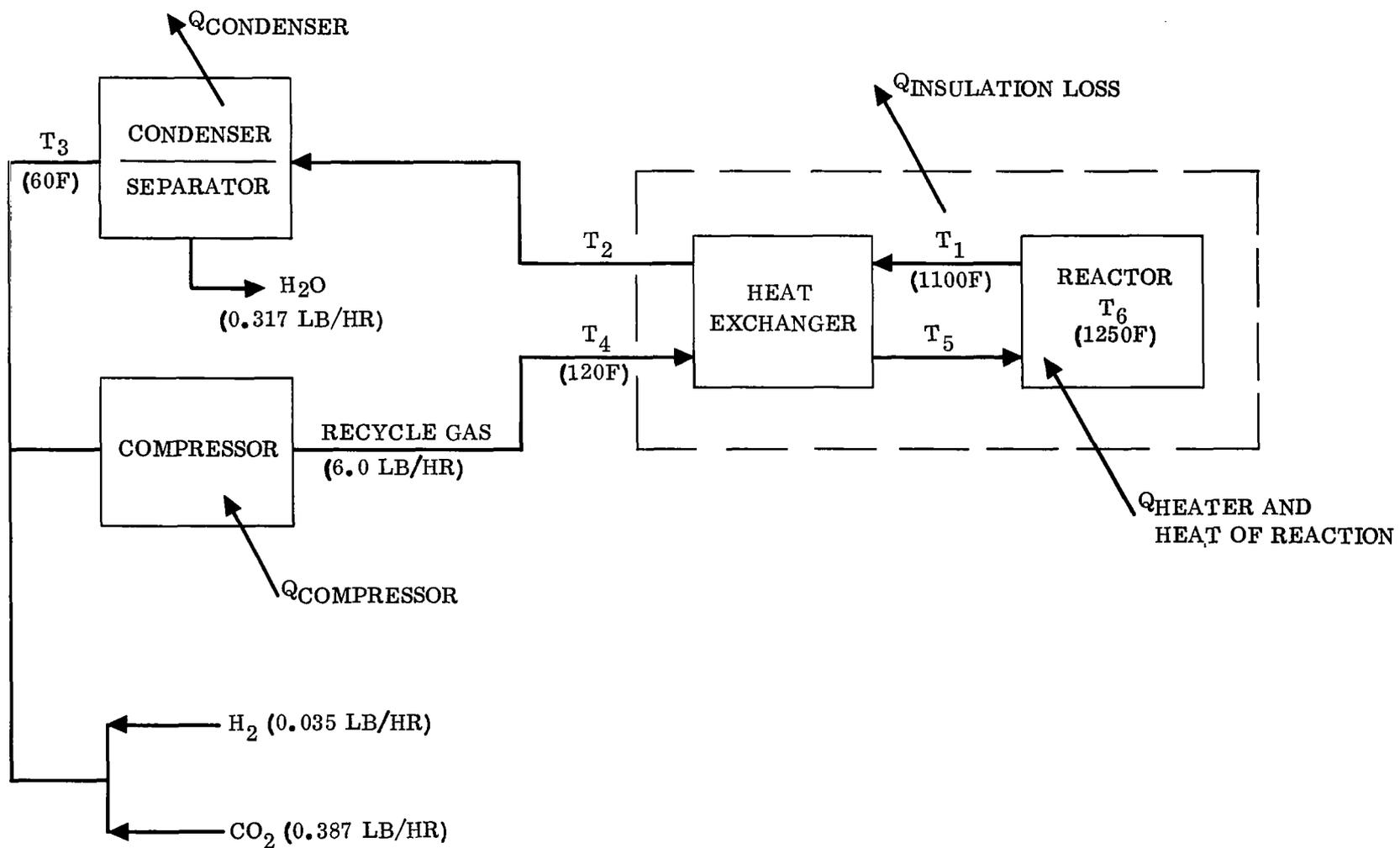
Figure 6.1 - Process Parameters for Prototype Design

6.2.2 <u>Condenser Temperatures and Heat Dissipation.</u> - A condenser heat dissipation rate of approximately 1000 Btu/hr was calculated using inlet and outlet gas temperatures of 268°F and 60°F respectively, a recycle flow rate of 6.0 lb/hr, and condensation rate of 0.317 lb/hr.

6.2.3 <u>Heat of Reaction.</u> - The heat of reaction is found from the relationships,

$$CO_2 + 2 H_2 \rightarrow 2 H_2O + C + 42,900 \text{ Btu/lb-mol of } CO_2, \text{ and}$$
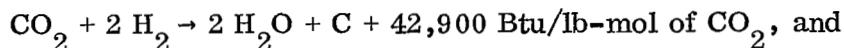
$$\dot{w}_{CO_2} = 0.387 \text{ lb/hr, from which}$$

$$Q_R = \frac{42,900}{44} (0.387) = 377 \text{ Btu/hr}$$

6.2.4 <u>Compressor Heat Input.</u> - Discharge temperatures of the diaphragm compressor used during the final development unit tests ranged from 110 to 140°F. The higher temperatures occurred as cartridge flow restrictions demanded more pressure to maintain the required recycle gas flow rate. A discharge temperature of 120°F was assumed for prototype unit design purposes. At 6.0 lb/hr and 60°F inlet temperature the calculated compressor heat input was 160 Btu/hr.

6.2.5 <u>Reactor Insulation Heat Loss.</u> - The calculated heat loss for a reactor and heat exchanger assembly 8 inches in diameter, 14.5 inches long, with 1150°F surface temperature and enclosed in 3 inches of 8 lb/ft^3 (0.50 Btu-in./ft^2-°F-hr) ceramic fiber insulation, was 840 Btu/hr. Four inches of this insulation would reduce the heat loss to 670 Btu/hr, but the resulting dual reactor assembly dimensions would complicate passage through the specified 30-inch hatch diameter.

6.2.6 <u>Reactor Heater.</u> - The 1000-watt heater used in the development unit had been more than adequate for cold reactor warmup, which was the controlling consideration in heater selection. The anticipated increase in prototype reactor size was minor and no change in recycle flow requirement was indicated. Thus 750 to 1000 watts was considered adequate for the prototype design.

6.3 Prototype Component Sizing

The following considerations determined the geometry and dimensions of the various components of the prototype unit.

6.3.1 <u>Reactor Shell.</u> - The reactor shells had to be large enough to contain cartridges with the desired conversion capabilities, carbon storage capacity, and pressure drop characteristics but not too large for the two insulated assemblies and common

mounting base to pass through a 30-inch circular hatch. With 3 inches of insulation surrounding each reactor and heat exchanger assembly, an 8-inch diameter by 12-inch-long reactor chamber could readily pass through the hatch and could enclose an adequate cartridge.

6.3.2 Cartridge. - A 3-day cartridge life was chosen somewhat arbitrarily but with the following rationale. At a carbon packing density of 0.4 to 0.5 gm/cc, its size and weight would not be difficult to manage. A dual reactor unit utilizing a 3-day cartridge could be designed to pass readily through a 30-inch-diameter hatch. A 5-day cartridge design could probably be made to the same constraints and might demonstrate a greater thermal efficiency, lower ratio of expendable-to-product weight, and less expenditure of crew time, but would be no more effective in demonstrating feasibility. It would be less effective in demonstrating reactor warmup and changeover characteristics because of the less frequent occurrence of these procedures.

The known characteristics and dimensions of the development cartridges were used to extrapolate to a 3-day cartridge design. The prototype reactors should operate at about the same recycle gas composition, temperature, and flow rate as the development reactor since the conversion requirements were identical. Flow through the carbon should be laminar; consequently, the pressure drop for a given carbon density should be directly proportional to path length and volume rate of flow per unit area. Assuming a reactor shell internal diameter of 8.0 inches and length of 12.0 inches, the maximum cartridge dimensions that would allow for attachment clearance and flow passages are 7.6 inches in diameter and 11.7 inches in length. Allowing for liners, carbon block dimensions of outside diameter, D_o = 7.4 inches, inside diameter, D_i = 2.7 inches, and length, L = 11.6 inches, were assumed. The final pressure drop for this design was estimated as follows:

Path length, $d_P = (D_o - D_i)/2 = (7.4 - 2.7)/2 = 2.35$ in.

Flow area at mean diameter, $A_P = (D_o + D_i) \pi L/2 = (7.4 + 2.7)(11.6) \pi/2 = 184$ in.^{2}

Carbon volume, $V_P = (D_o^2 - D_i^2) \pi L/4 = (7.4^2 - 2.7^2)(11.6) \pi/4 = 435$ in.^{3} = 7120 cc

Carbon weight, w = 2.53 lb/day × 3 days = 7.59 lb = 3450 gm

Carbon density, ρ_P = w/V = 3450/7120 = 0.484 gm/cc

From Figure 5.8, the pressure drop for the development cartridges at this density was 10.0 psid. The estimated pressure drop for the prototype design should be,

$$\Delta P_P = \Delta P_D \left(\frac{A_D d_P}{A_P d_D} \right) = 10.0 \frac{139 \times 2.35}{184 \times 2.25} = 7.9 \text{ psid which is an acceptable value.}$$

6.3.3 **Insulation.** - Development unit experience showed three inches of alumina silica ceramic fiber insulation around the heat exchanger and reactor assembly to be adquate for heat conservation and protection of personnel from contact with hot surfaces. Calculations showed an additional inch would reduce the heat loss by approximately 20 percent, but the increase in size of the assembly could not be tolerated. Each insulated assembly is 14 inches in diameter and 20 inches in length.

6.3.4 **Heater.** - The cartridge heater is the same model used during development tests. The Incoloy sheath is 12 inches long and 0.75 inch in diameter and is flanged for mounting. For long service life, a 4000-watt, 240-volt, 60-cycle heater with maximum recommended element temperature of 1600° F was selected which, when operated on 120-volt supply, is limited to 1000 watts for a sheath power density of 27 watts per square inch. Since the power demand is usually approximately 500 watts and the heating element temperature is normally below 1400° F, prolonged life should result.

6.3.5 **Heat Exchanger.** - For a compact exchanger and reactor assembly within a common insulation package, a flat ring heat exchanger with the same outer diameter as the reactor flange was designed. The hot and cold side geometries are identical, each having 14 concentric trapezoidal flow paths with inlet and outlet manifolds at a break in the ring. It has a calculated thermal effectivity of 0.85, heat transfer area of 1.4 ft^2, mean flow path length of 2.3 feet, and pressure drop of 0.40 psi at 6.0 lb/hr recycle flow rate.

6.3.6 **Condenser and Separator Assembly.** - The condenser is cooled with 60 lb/hr of water at 40° F inlet temperature. The gas outlet temperature is 60° F, which proved to be satisfactory during development tests, and the design condensate rate is 7.6 lb/day.

The condenser geometry consists of a tube which is longitudinally finned externally and circumferentially finned internally with an outer shell for gas containment and closed core to increase the velocity of coolant flow over the inner fins. The condenser is 1.5 inches in diameter and 10.5 inches long with gas-side transfer area of 1.34 ft^2, coolant side transfer area of 0.43 ft^2, and calculated gas-side pressure drop of 0.04 psi.

Space requirements were reduced and connective plumbing eliminated by making the condenser and separator a single assembly. This assembly is covered with asbestos insulation primarily to inhibit external condensation from forming and dripping on other components. The separator is a gravity-dependent water trap. A sight gage allows the water level to be monitored and measured. The separator storage capacity is sufficient for four hours of operation at normal conversion rate. The major diameter and overall height of the separator are 3.0 and 8.0 inches respectively.

6.3.7 <u>Compressor.</u> - Design parameters influencing compressor sizing for single-reactor operation are: (1) a flow of 6.0 lb/hr, (2) inlet pressure of 18 psia, (3) discharge pressure of 28 psia, and (4) a nominal gas composition of 0.4 H_2, 0.3 CH_4, 0.2 CO, and 0.1 CO_2. The calculated gas density at the compressor inlet is 0.047 lb/ft^3 and theoretical compressor displacement requirement is 2.12 ft^3/min. Assuming the dormant reactor will require 3.0 lb/hr during the warmup period, the total theoretical displacement becomes 3.18 ft^3/min. Other considerations are that the compressor be gas tight, compact, and reasonably quiet. A commercial single-stage compressor with four cam-driven diaphragms was selected. It has a rated displacement of 3.9 ft^3/min. at 10 psi pressure rise.

6.3.8 <u>Gages, Valves, Fittings, and Connective Plumbing.</u> - A compact arrangement of the control section was required because of space limitations but maximum accessibility of each component and fitting was also needed to facilitate tracing and eliminating leaks. Good accessibility was obtained by using the smallest line size consistent with the particular flow requirement and by using welded manifold sections where practical. Generally, 1/8-inch valves, fittings, and tubing were used for feed section and instrumentation lines; 1/4-inch for the selector valve bypass system; and 3/8-inch for the normal recycle loop.

6.4 Prototype Controls

A flow diagram of the engineering prototype reduction unit system is shown in Figure 6.2. The major components serve the same purposes as described for the development unit, but the need for uninterrupted operation during cartridge exchange procedures dictates the use of two reactor assemblies and a more complex recycle gas control system. The reactor selector, selector bypass, vent, and purge valves provide the necessary flexibility to operate either reactor individually during the normal mode or both simultaneously while starting the alternate reactor. They also provide for dormant reactor purging, venting, and leak checking procedures.

6.4.1 <u>Temperature Control.</u> - Temperature controls are required to prevent heater failure due to overtemperature operation and to establish the desired process temperatures. A thermocouple embedded in each reactor heater is connected to individual indicating controlling pyrometers with set-point limit relays which interrupt power to the heater if the set-point temperature is exceeded. Two solid-state power controls allow power to each heater to be manually adjusted for warmup and process heat requirements. A thermocouple well in each reactor base extends into a well in each cartridge, and the thermocouples are connected through a selector switch to an indicating pyrometer for process temperature monitoring.
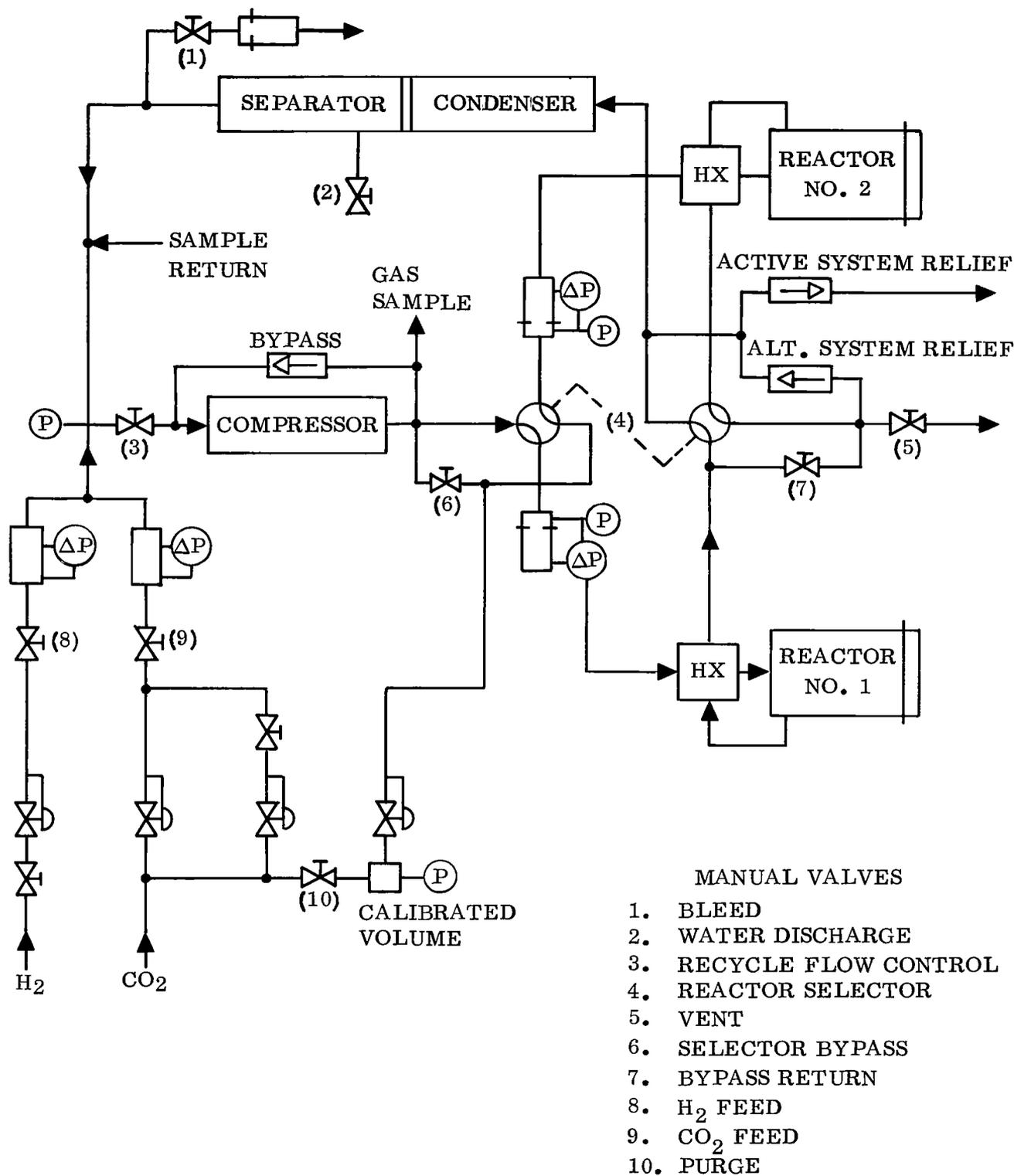
Figure 6.2 – Prototype Reduction Unit Flow Diagram

MANUAL VALVES
1. BLEED
2. WATER DISCHARGE
3. RECYCLE FLOW CONTROL
4. REACTOR SELECTOR
5. VENT
6. SELECTOR BYPASS
7. BYPASS RETURN
8. H_2 FEED
9. CO_2 FEED
10. PURGE

6.4.2　Pressure Control. - The recycle loop is a closed system with base pressure established by feed gas regulator settings. Pressure differentials within the loop are determined by flow rate, compressor rise, and restriction characteristics of the flow path. Pressure maximums must be limited for safe and reliable operation. This is ensured by three 10-psid check valves located as shown in Figure 6.2. Compressor pressure rise is limited to 10 psid by the bypass valve. This valve limits the system maximum to 10 psi above feed pressure during normal operation. During the initial reactor warmup period, the bleed valve (1) is normally opened slightly to avoid the system pressure rise that would result from heating the gas in the reactor from ambient to process temperature. However, if the valve is not opened, the active reactor relief valve will prevent overpressure. Similarly, if the selector bypass valves were closed during alternate reactor warmup, the alternate relief would prevent overpressure by discharging gas to the recycle loop.

6.4.3　Process Rate Control. - The specification that continuous operation of the prototype unit be demonstrated at a rated capacity of 9.28 ± 5% pounds of CO_2 per day establishes the need for process rate control. Based on accumulated operational experience, the flow meters, catalyst cartridge thermocouples, and CO_2 analyzer supply information needed to reach and maintain a good reaction environment, but the process rate is most responsive to recycle flow rate. The manually operated recycle flow control valve at the compressor inlet provides immediate process rate adjustment during single-reactor operation and allows the total flow to be increased to meet the simultaneous demands of both reactors during alternate reactor warmup periods.

6.4.4　Recycle Gas Mixture Control. - The recycle gas composition must be kept within a range giving good conversion rates. This range varies with reactor temperature but has fairly broad limits making precise control unnecessary. Satisfactory control is obtained by maintaining a selected concentration of CO_2 in the recycle loop using the method described for the development unit. The gas sample for the CO_2 analyzer is continuously removed from the recycle loop at the compressor discharge pressure and is returned at feed section pressure. A valve and flow meter in the sampling line allow rate control. Gas chromatograph samples are periodically removed from this line to obtain more detailed information on recycle gas composition.

6.4.5　Leakage Control. - For convenience in determining and controlling leakage rate, an integral checking system is used. It operates as described in Paragraph 5.3.4 but is incorporated in the purge gas supply line, as shown in Figure 6.2, so that the alternate reactor can be checked prior to warmup after each cartridge exchange procedure. If excessive leakage is indicated, immediate corrective action can be taken before the system is filled with process gases. A curve of leakage rate versus pressure decay rate in the calibrated volume is given in Figure 6.3.

6.4.6　Cartridge Exchange Procedure Controls. - The functions of the individual controls involved in the cartridge exchange procedures will be explained by describing a

LEAKAGE RATE CURVE FOR $V_C = 135$ cc & $T_C = T_S$

$$Q_S = \frac{V_C \, T_S}{P_S \, T_C} \times \frac{\Delta P}{t} = 9.18 \, \Delta P / t$$

Q_S — LEAKAGE RATE, STD. cc/min

V_C — CALIBRATED VOLUME, cc

P_S — STANDARD PRESSURE, psia

T_S — STANDARD TEMPERATURE, °R

T_C — CHECKING UNIT TEMPERATURE, °R

ΔP — PRESSURE DECAY, psid

t — TIME OF DECAY, min.
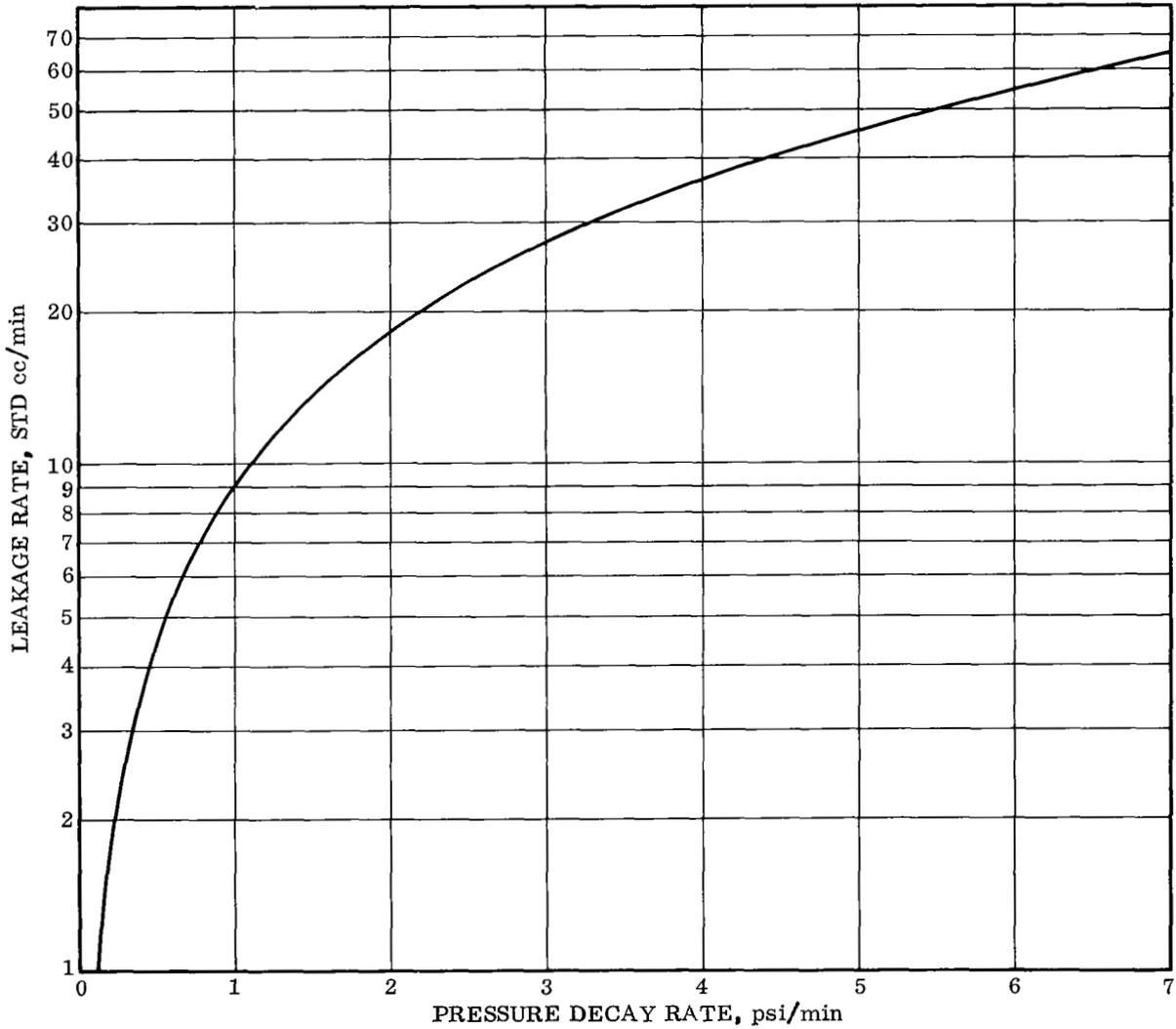
Figure 6.3 – Prototype Unit Leakage Rate Curve

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complete cartridge exchange process. Assume that reactor No. 1 is initially the active one as indicated by the position of the selector valve (4) in Figure 6.2, and that the alternate reactor (No. 2) is cooling. In cooling from 1250°F to ambient temperature, the pressure will drop considerably below ambient unless provisions are made to maintain pressure. This pressure differential would introduce a shell crushing load and also would encourage air leakage into the system. This situation is avoided by leaving the selector bypass valve (7) open to maintain the reactor at essentially the feed section pressure. After the alternate reactor has reached ambient temperature, it must be purged of toxic and combustible gases and vented to ambient pressure before being opened for cartridge replacement. The purge is accomplished by opening the purge gas valve (10) and allowing CO_2 to flow through the reactor and into the recycle loop through bypass valve (7). The purge rate must be sufficiently slow to avoid excessive disruption of the recycle gas equilibrium. After completion of the purge, the bypass and purge valves (7) and (10) are closed and the vent valve (5) is opened to reduce the reactor pressure to ambient. The reactor is then opened and the expended cartridge replaced. Air is purged from the re-sealed reactor by opening valves (10) and (5) after which the vent valve (5) is closed. A pressure check is made by letting the reactor pressure stabilize at the purge gas regulator pressure setting, then closing the purge valve (10) and noting the rate at which the pressure in the calibrated volume decays. Leakage rate can be determined from Figure 6.3.

The alternate reactor is now ready for service. As the cartridge in the active reactor approaches its maximum carbon packing density, the alternate reactor must be activated. Activation is accomplished by opening the selector bypass valves (6) and (7) and applying heater power to bring the alternate reactor up to temperature. When a reaction in the alternate reactor has been established, the selector valve (4) is shifted and bypass valve (6) is closed making reactor No. 2 the active one and No. 1 the alternate. Heater power to No. 1 is turned off, allowing it to cool for cartridge exchange.

6.5 Prototype Materials Criteria

Routine engineering and economic factors were considered in selecting materials for the low-temperature components. These factors included performance, durability, cost, and availability. The environmental conditions imposed on the high-temperature components restricted the types of materials which could be considered and forced occasional compromises. Criteria for reactor/exchanger materials selection are:

a. The catalyst material must readily support the Bosch reaction and remain uniformly distributed within the reaction zone of the catalyst cartridge.

b. All internal surfaces other than the catalyst must be non-catalytic to the Bosch reaction.

c. Materials exposed to the reactive gases must not be structurally deteriorated by carburization, oxide reduction, or hydrogen embrittlement.

d. Mating surfaces must not fuse together under pressure in the internal reducing atmosphere.

e. Seal surfaces must not fuse where exposed to the inner reducing environment or progressively oxidize where exposed to the outside atmosphere and other surfaces exposed to air must not be destructively oxidized.

f. Allowable stress and creep rate values at working temperatures must be compatible with the mechanical, pneumatic, and thermal loads imposed.

g. Thermal expansion characteristics of joined materials must be sufficiently compatible to avoid failures due to thermal stress.

h. High-temperature coatings and lubricants must be effective and non-toxic.

i. Material fabricating properties must be compatible with common techniques applicable to each component. These techniques might include combinations of shearing, bending, spinning, machining, welding, and plating.

7.0 PROTOTYPE DESIGN AND FABRICATION

Based on the design criteria discussed in Section 6, materials were selected, working drawings were prepared, and the prototype reduction unit was assembled.

7.1 Material Selections

Material selections were made according to the criteria summarized in Paragraph 6.5 and using the results of the materials screening activities of the development period as summarized in Paragraph 5.6.

7.1.1 <u>Low-Temperature Components.</u> - Stainless steel was chosen as the basic material for the low-temperature valves, tubing, and fittings because previous experience indicated that stainless steel connections were less likely to leak. Where stainless components were not readily available (for example, pressure gages, differential gages, and the selector valve), steel, aluminum, brass, or plastic were accepted. The support structure was made of aluminum alloy.

7.1.2 <u>Insulation.</u> - An inch-thick blanket of alumina silica ceramic fibers having a density of 8 lb/ft^3 was selected because of low cost, ready availability, ease of application, temperature range compatibility, and adequate thermal performance. Other insulations would have been used had weight, power, and volume considerations been dominant.

7.1.3 <u>Catalyst.</u> - The catalyst used is No. 2 steel wool which is one grade finer than the coarsest grade commercially available. Although a finer grade would provide more catalyst surface area and uniform distribution per given weight, the following logic determined the choice of a coarse grade. During the reaction process, iron diffuses into the product carbon but does not lose its catalytic property. This diffusion causes fairly rapid deterioration of the steel wool fiber. If disintegration occurs before sufficient carbon has been formed to support the iron and to maintain a fairly uniform distribution throughout the reaction zone, flow channels will develop and adversely affect the process rate. A coarse grade will disintegrate more slowly, allowing more time for supporting carbon growth.

No experimental effort was made to evaluate steel wool grades or to determine minimum quantities for desired reaction and carbon packing characteristics.

7.1.4 <u>Reactor and Heat Exchanger.</u> - The materials and coatings for the reactor/exchanger components are as follows:

a. Reactor Cartridge: The cartridge ends are spun from type 321 stainless steel and the shell and core are rolled and welded from type 304 stainless steel perforated with 3/32-inch holes on 5/32-inch centers. These parts are plated with an electrolytic nickel strike followed by one to two mils of electroless nickel. The thermocouple well is Alloy 122 phosphorous-deoxidized copper and the cover clips are Inconel X-750. Core, shell, and end liners are of quartz-fiber batt and sheet.

b. Reactor Body: The reactor shell, flange, and base are of type 321 stainless steel with an electrolytic nickel strike, 1 mil of electroless nickel, and 4 mils of nickel electroplate. The reactor thermocouple well is of type 304 stainless steel similarly plated. Three mils of copper electroplate is added to the surfaces exposed to recycle gases except in seal bearing areas. The reactor cover plate is of the same material and similarly plated without the final copper coat.

c. Other Parts: The heater sheath and flange are of Incoloy 800 and Inconel X-750. The heater jacket and shroud are phosphorous deoxidized copper with aluminum bronze flange and adapter body. The baffle plate and seal rings are also of aluminum bronze, and the cartridge gasket is of alumina silica ceramic fiber mat.

7.2 Configuration

The prototype unit consists of two interconnected reactor and heat exchanger assemblies served by common feed controls, recycle controls, and water removal components as diagrammed in Figure 6.2. The relationship of the various reactor assembly components is shown in Figure 7.1. Since the heater sheath is slightly reactive, it is isolated from the recycle gases by a copper heater jacket. The inner surface of the jacket is electroless nickel plated to prevent oxidation since there is no seal between the heater and jacket flanges. The heater shroud directs the recycle flow over the full length of the jacket and supports the baffle plate and cartridge gasket.

The cartridge components are shown in Figure 7.2, and a catalyst-packed cartridge is shown ready for cover attachment in Figure 7.3. Each cartridge weighs about 2.85 pounds when packed with 150 grams of catalyst. The shell, core, base, and cover weigh approximately 2.35 pounds and the liners 0.17 pound. Figure 7.4 shows the completely assembled cartridge locked to a reactor coverplate.

Figure 7.5 shows two views of a reactor and exchanger assembly without insulation, and Figure 7.6 is a sketch of the insulation arrangement. The reactor supports are removable from threaded support bosses to simplify insulation application. The wrap-around sheet metal shell has two adjustable fasteners to allow proper fit of the insulation cap. The caps and exposed surfaces of the insulation shells are covered with asbestos sheet to prevent personnel from contacting warm metal.

HOT-SIDE OUTLET

COLD-SIDE INLET

HEAT
EXCHANGER

HOT-SIDE
INLET

COLD-SIDE
OUTLET

ADAPTER

SEAL

REACTOR BASE

CARTRIDGE BASE

CARTRIDGE
T/C WELL

REACTOR
T/C WELL

CARTRIDGE
GASKET

BAFFLE PLATE

SEAL RETAINER

REACTOR FLANGE

REACTOR SHELL

CARTRIDGE SHELL

SEAL

ATTACHMENT
LUG

COVERPLATE
HANDLE

HEATER

HEATER JACKET

HEATER SHROUD

CARTRIDGE CORE

CARTRIDGE COVER

REACTOR
COVERPLATE

REAR SUPPORT BOSS

REAR SUPPORT POST

Figure 7.1 – Prototype Reactor Assembly

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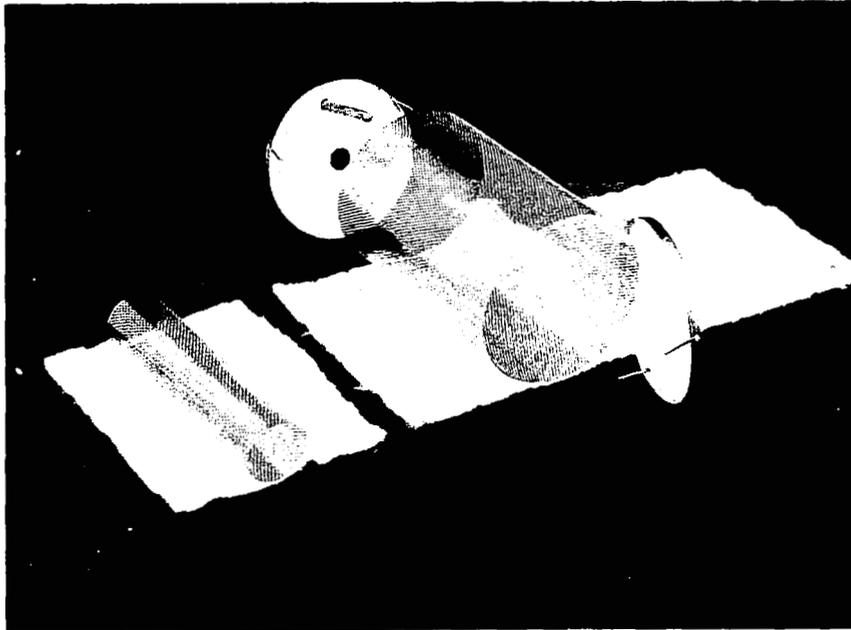
Figure 7.2 - Prototype Cartridge Components
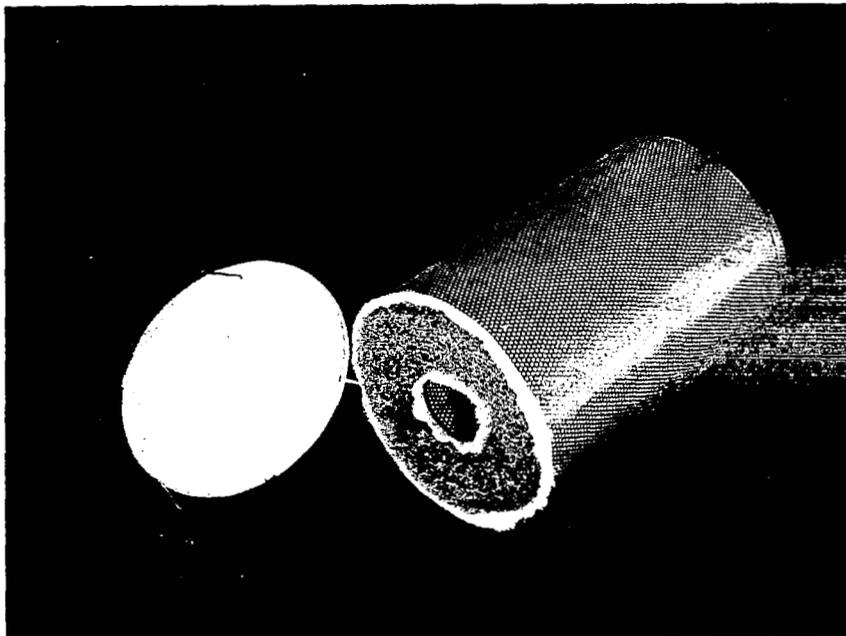
Figure 7.3 - Catalyst-Packed Cartridge
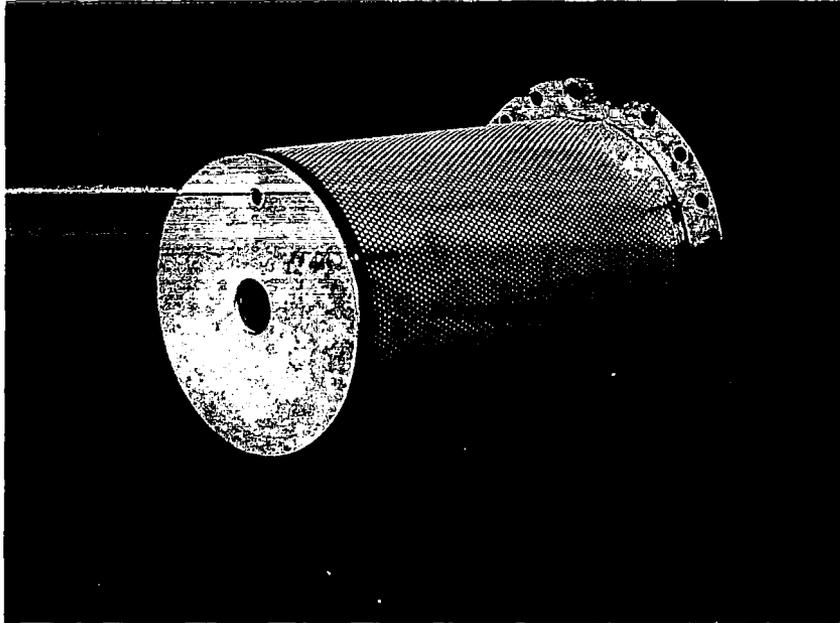
Figure 7.4 – Cartridge Ready for Installation

Front and rear views of the assembled prototype unit are shown in Figure 7.7. It is built in two severable sections to allow passage through a 30-inch circular hatch. The lower section contains the two reactor assemblies and supports the upper section which accommodates the low-temperature components and controls. The sections may be separated by removing four screws and uncoupling two power plugs, four recycle line fittings, and four thermocouple connectors. Total weight of the unit including two cartridges is 226 pounds.

7.3   Fabrication

The heliarc welding process was used to join the reactor base, shell, and flange. An internal bead was added to the intersection between the reactor base and the reactor shell to provide a continuous surface for plating. Internal beads were applied around the reactor thermocouple well and between the shell end and flange for the same reason.

The finned core of the heat exchanger ring was turned from aluminum bronze plate after which the shell plates were welded to the core. A section was removed from the ring as shown in Figure 7.5 and the inlet and outlet tubes were added. The cold-side outlet and hot-side inlet tubes were welded to the reactor adapter to which the heater shroud was also welded.
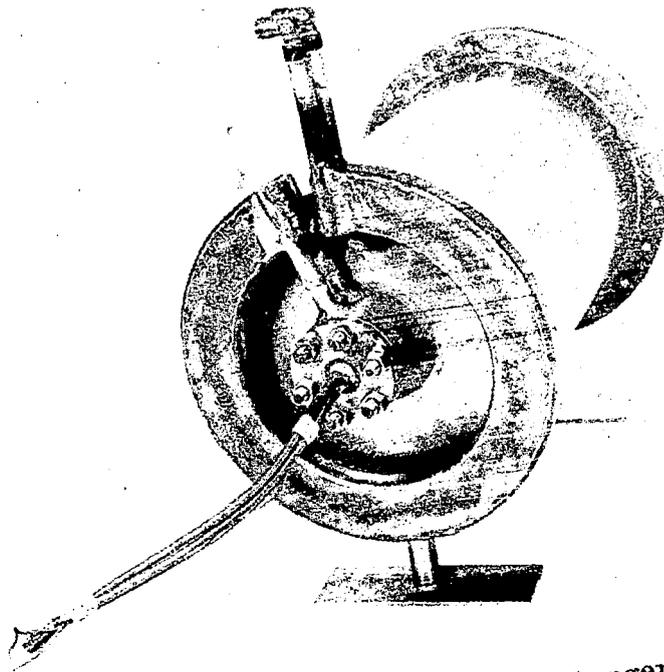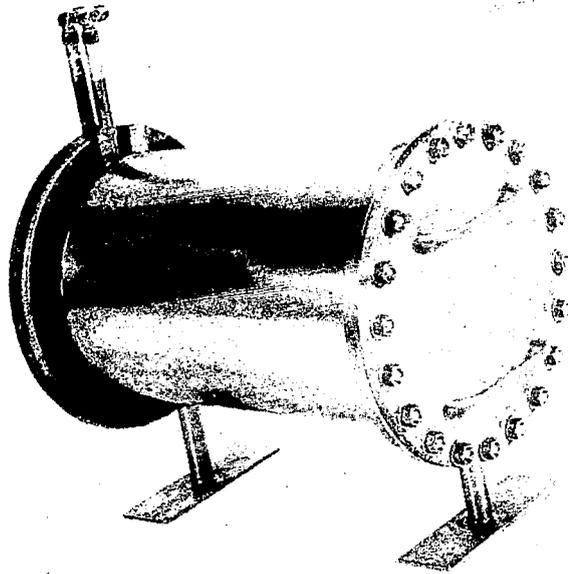
Figure 7.5 – Reactor and Heat Exchanger Assembly
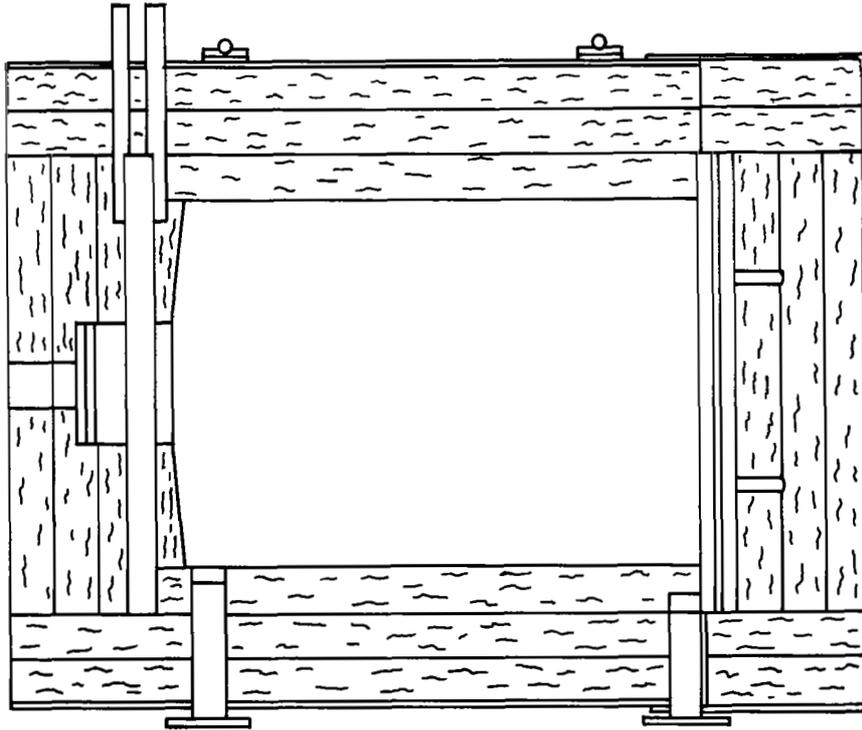
INSULATION SECTION
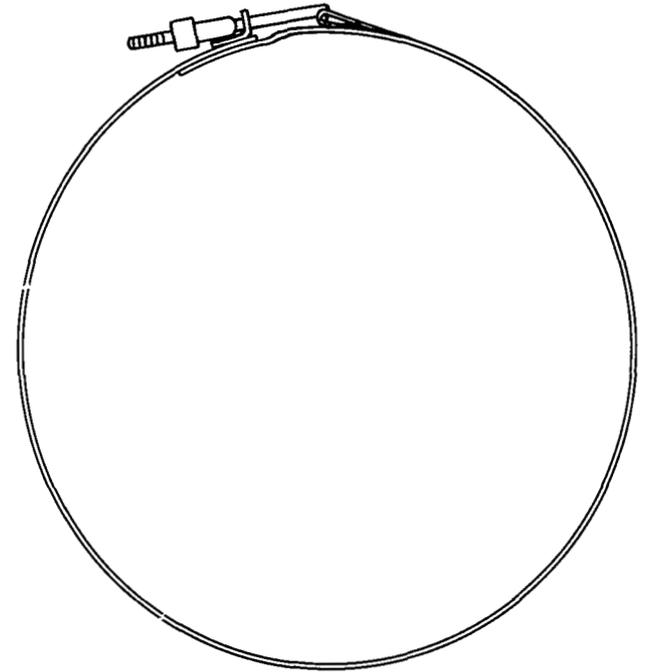
WRAP-AROUND SHELL

Figure 7.6 – Sketch of Insulation Arrangement
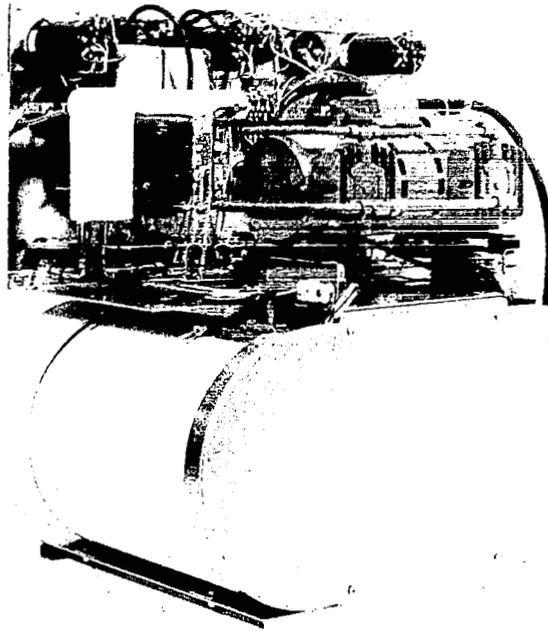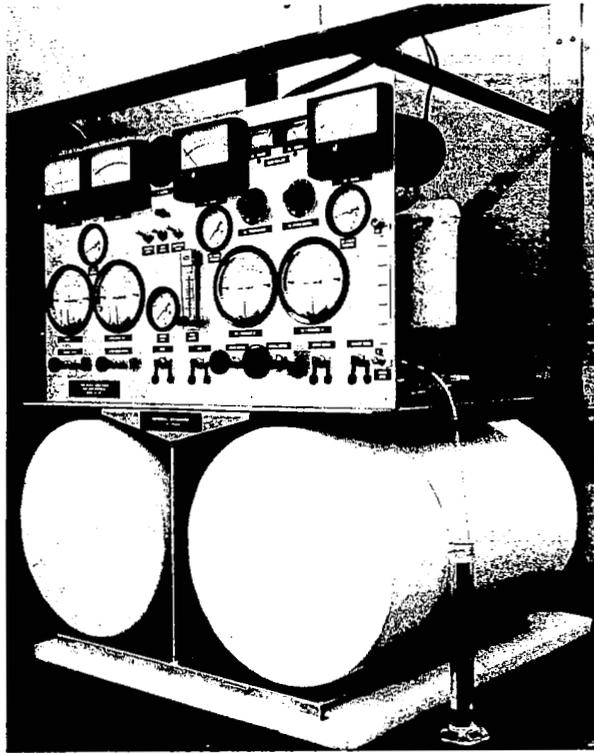
Figure 7.7 - Prototype Reduction Unit Assembly

The reactor and heat exchanger assembly was insulated with inch-thick ceramic fiber blankets as indicated in Figure 7.6. Each blanket around the reactor shell is held in place with a wrap of aluminum foil which aids in assembling the package and provides thermal radiation shielding. The outer wraparound shell is not rolled to give it a permanent set but returns to its flat state when unfastened for insulation removal.

The cartridge base and cover are spun, and the clip and thermocouple-well holes are punched before plating. After the core, shell, base, and cover have been formed, they are given a flash coat of electrolytic nickel followed by 1 to 2 mils of electroless nickel. The thermocouple well is inserted and locked to the base with a press-fit copper retaining washer, and the cover and base clips are inserted and crimped as shown in Figure 7.2. The base (with thermocouple well and base liner) is attached to the shell in preparation for catalyst packing. The quartz-wool shell liner is positioned inside the shell and temporarily held in place with a three-piece metal shield which allows the catalyst to be packed without damaging the liner. The core liner is wrapped around the core which is then placed over a locating jig to keep it centered during catalyst packing operations. A two-piece metal shield is used to protect the quartz-wool core liner. The packing technique is the same as described in Paragraph 5.4.2 except that additional precautions are taken to prevent contamination of the core and outer surfaces by catalyst particles. To prevent particles from falling into the core opening, a plastic cap is placed over the end of the metal shield holding the core liner in place. A sectional paper apron, surrounding the cartridge shell and folded inward over the shield holding the shell liner, protects the outer surface from catalyst debris. The cap, apron, and shields are removed just prior to attaching the cartridge cover. All prototype unit cartridges were packed with approximately 0.33 pound of grade No. 2 steel wool obtained in 1-pound bulk packages.

8.0 PROTOTYPE PERFORMANCE

All activity with the prototype unit was oriented toward demonstrating compliance with the program objectives and contract specifications. As previously stated, the broad objective was to prove that a CO_2 reduction unit using the Bosch reaction was operationally practical, which required: (1) demonstrating controlled reaction in the catalyst cartridge to reduce CO_2 at a specific rate, (2) achieving complete carbon containment within the catalyst cartridge, (3) preventing reaction outside of the cartridge, and (4) developing a practical procedure for replacing spent cartridges. The specifications are as stated in Paragraph 3.2.

The two-week period between completion of construction and start of the 120-hour performance demonstration was used to gain familiarity with the operational characteristics of the unit. During this period, the prototype unit was operated for 240 hours and included five fresh cartridge starts, one changeover procedure, and two restarts with partially expended cartridges. Two cartridges were completely expended, and a continuous run of 135 hours was made. After the 120-hour performance demonstration, a brief catalyst pretreatment study was made involving 17 hours of unit operation. The unit was then delivered to Langley Research Center where 70 hours were added during unit demonstrations. Total time on the prototype unit at the end of these demonstrations was 447 hours.

8.1 Process Rate Control

Figure 8.1 is a plot of the quantity of carbon dioxide processed versus time for the 120-hour performance demonstration test. The initial cartridge (P-5) had been run a total of 12 hours at a previous date. It was restarted cold at T-2 and was producing water at an average rate equivalent to 11.1 lb CO_2 conversion per day at time zero.

The rate was readily adjusted downward to the desired range by reducing the recycle flow rate. During stabilized temperature periods, the unit was occasionally left unattended for from three to eight hours without serious deviation in process rate. An auxiliary water storage tank was connected to the water separator during these periods since the separator was limited to a four-hour storage volume. The unit was monitored and adjusted quite frequently during reactor changeover procedures since catalyst conditioning and temperature change in the alternate reactor caused quite rapid changes in process rate.

8.1.1 __Reactor Temperature.__ - Adequate CO_2 conversion rates were obtained in the prototype unit at reactor temperatures from 1070 to 1270°F. However, the rates were more easily maintained at 1240 to 1270°F when conditions had to be optimized to compensate for recycle flow limitations imposed by carbon build-up in the cartridge.
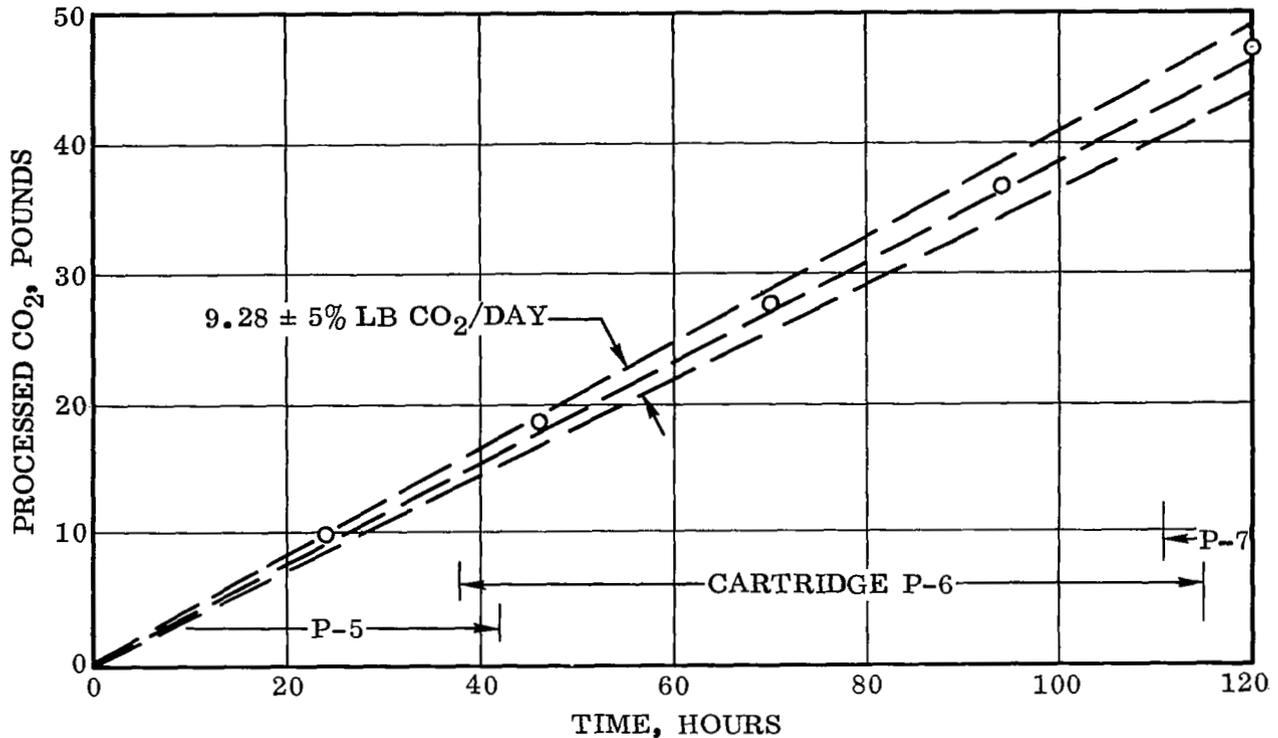
Figure 8.1 – CO_2 Processed Versus Time for the 120-hour Performance Demonstration Test

8.1.2 Recycle Flow Rate. – Process rates were responsive to recycle flow rate as previously noted. The recycle flow required for the design CO_2 conversion rate during the first 50 to 60 hours on each cartridge was 7 to 9 lb/hr. At 70 to 75 hours the required flow rate was 10.5 to 11.5 lb/hr.

Cartridge P-12 was operated intermittently at accelerated CO_2 conversion rates during the demonstration tests at Langley Research Center. When loaded with carbon equivalent to 50 hours of operation at a four-man CO_2 conversion rate, a seven-man CO_2 conversion rate could be obtained at a recycle flow of 11 to 12 lb/hr, or a four-man CO_2 rate at 8 lb/hr recycle flow. At the equivalent of 75 hours, a four-man CO_2 processing rate could be maintained with 8.5 lb/hr of recycle flow.

8.1.3 Recycle Gas Composition. – Although a wide range of recycle gas compositions was used during prototype unit tests, a dry gas mixture of approximately 0.33 H_2, 0.20 CH_4, 0.33 CO, and 0.14 CO_2 (volume) was typical much of the time when optimum process rates were being maintained at a given recycle flow rate. At the lower end of the operating temperature range, the optimum composition was generally higher in methane and lower in carbon monoxide concentrations.

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8.2 Carbon Containment and External Growth Prevention

The three cartridges used during the performance demonstration test are shown in Figure 8.2. Individual operating times, including the previous time on P-5, are 55 hours for P-5, 78 hours for P-6, and 9.5 hours for P-7. None of the cartridges showed any signs of carbon migration or external catalytic action. Figure 8.3 shows cartridge P-6 with the cover removed and liner lifted to expose the carbon block. The internal condition of the reactors at the conclusion of the performance demonstration is shown in Figure 8.4. No sign of carbon formation was observed at this time (360 total hours), nor at completion of the contract tests at 447 hours.

8.3 Feed Gas Impurities

No difficulty in maintaining normal conversion rate was experienced during 20 hours of operation with the hydrogen supply contaminated with 1.5% (volume) nitrogen. The contaminant bleed valve was opened sufficiently to stabilize the mixture at a maximum of 12% nitrogen in the recycle loop.


P-5

P-6

P-7
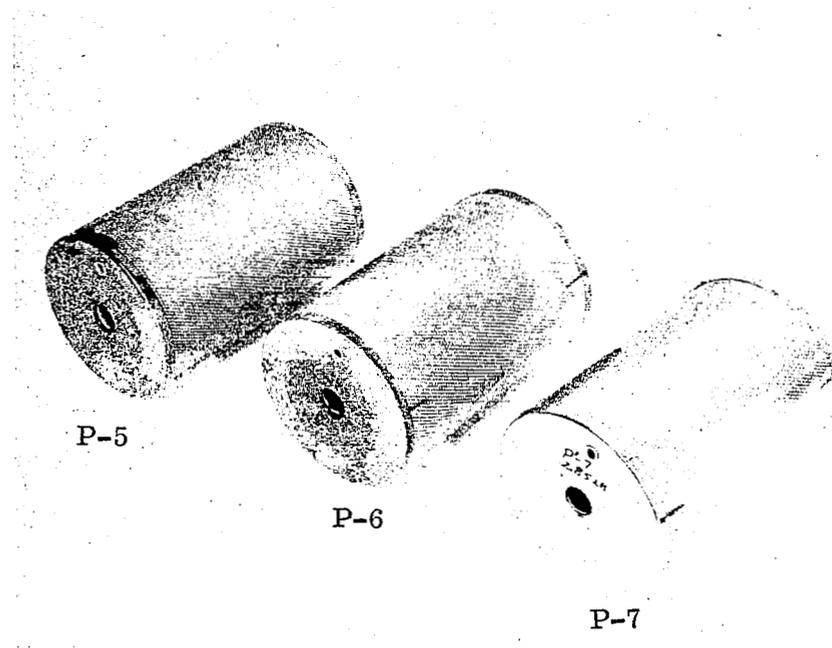
Figure 8.2 - Performance Demonstration Test Cartridges
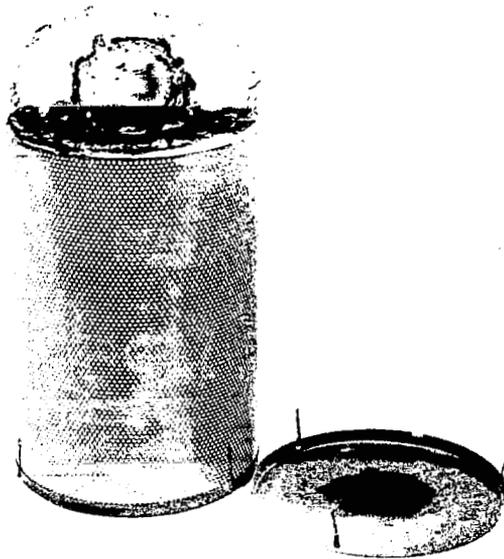
Figure 8.3 – Cartridge P-6 Showing Carbon Block
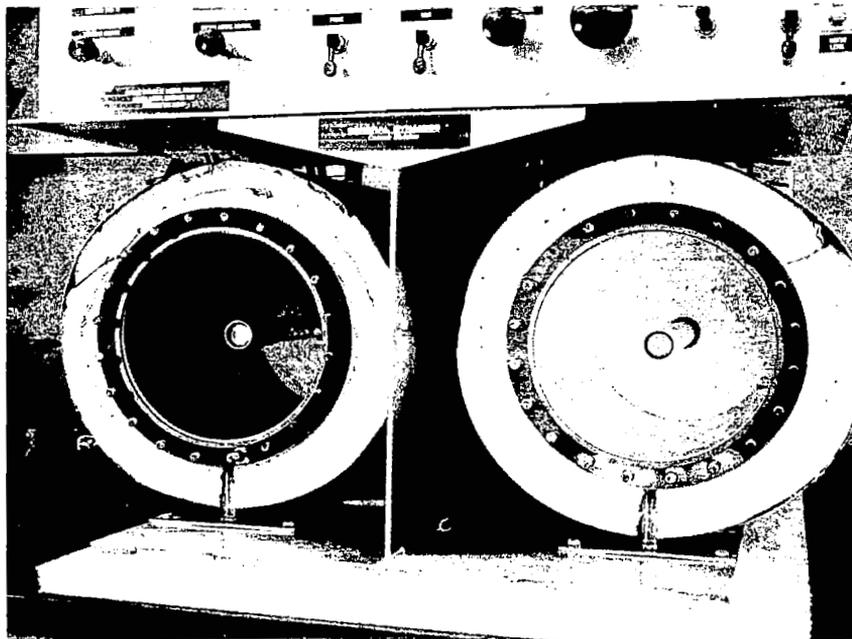
Figure 8.4 – Prototype Reactors After Performance Demonstration

8.4 Repairs

No repairs were required during the 120-hour performance demonstration. During a post-test inspection, however, the welds holding the end discs to the heater jackets were found to be porous, allowing recycle gas leakage. The tips were removed and new end discs were welded to the jackets using oxygen-free copper filler. The tips were then copper plated to isolate the weld material from the hydrogen in the recycle gas.

At conclusion of 68 hours of testing on cartridge P-12 at LRC, two Inconel X-750 cartridge base clips were found to be broken. This damage is probably the result of the manner in which the tests were conducted and of Inconel embrittlement in the reactive environment. The embrittlement could be avoided by plating the clips with electroless nickel, and clip stresses could be reduced by using more clips. The unusual bursting stresses generated during these tests were probably the result of intermittent operation. This effect was also observed during the development program. Cartridge P-12 went through four warmup and cooldown cycles. Shell shrinkage during cooldown tends to compress the carbon, and expansion during reheat leaves a space for further carbon growth which must again be compressed during the next cooldown. The effect noticeably extends the process life of a cartridge but also shows unmistakable signs of greater pressure such as warped cartridge covers and quartz-wool liner material forced through shell perforations.

8.5 Proof Pressure

Each reactor was subjected to a proof pressure test of 1.5 times working pressure at normal operating temperatures. This test was done during the performance demonstration at the completion of the changeover from reactor No. 2 to reactor No. 1 (cartridges P-5 and P-6) and the return to reactor No. 2 with cartridge P-7. Immediately after each changeover, while still at operating temperature, the dormant reactor was pressurized at 30 psia through the purge gas line. No adverse effects were observed.

8.6 Automatic Heater Shut-Off

Protection of the heater from overheat due to insufficient recycle gas flow was demonstrated during normal operation by turning the compressor off. The heater sheath temperature would slowly rise until the set-point temperature was reached at which time heater power was interrupted. If continued, a slow heating and cooling cycle was established.

8.7 Equivalent Leakage Rate

Leakage from the reduction unit must be limited because the rate of introduction of combustible or toxic contaminants into a closed, manned chamber cannot be allowed to exceed the contaminant removal capability. The important parameters to be monitored in the chamber are the volume component or parts per million of each contaminant in the enclosed atmosphere. Therefore, the equivalent leakage rates for the temperatures and pressures within the reduction unit during normal operation should be given in terms of volume rate at the nominal environmental temperature and pressure. The limit for the reduction unit is specified as less than the equivalent of 10 cc/min at operating conditions using nitrogen or carbon dioxide as the test gas, and the environmental conditions are specified to be 75°F and 14.7 psia.

Changes in leakage rates due to elastic deformations which might be induced by operational pressures or temperatures are not readily amenable to an analytical approach. Excluding elastic deformations, relative leakage rates can be estimated by assuming that the leakage follows capillary flow theory and that pressure and temperature conditions at the leakage sites are known. The basic equation is,

$$\Delta P = \frac{KQ\mu L}{D^4} \text{ where}$$

K = constant

Q = actual volume flow rate

μ = absolute viscosity

L = capillary length

D = capillary diameter

ΔP = pressure differential

From this relationship, the ratio of flow at one condition to that of an initial condition becomes

$$\frac{w_2}{w_1} = \left(\frac{\Delta P_2}{\Delta P_1}\right)\left(\frac{\mu_1}{\mu_2}\right)\left(\frac{\rho_2}{\rho_1}\right) \ [1 + c \ (T_2 - T_1)]^3$$

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where

w = mass flow rate

ρ = gas density

c = linear coefficient of thermal expansion of the capillary material

T = material temperature

Pressure checks of the inoperative unit at ambient temperature using CO_2 showed the leakage rate to be approximately 7 standard cc/min at 5 psig system pressure. If all of the leaks were in the ambient temperature portion of the system which operates at 3 psig, the equivalent leakage rate would be 4 standard cc/min as a result of the density and pressure differential being lower than during the leakage check. If, however, it is assumed that all of the leaks were at points which operate at 1175° F and 10 psig, the estimated equivalent would be less than 3 standard cc/min since the increased specific volume and viscosity more than offset the increased pressure differential and flow area.

8.8   Prototype Cartridge Pressure Differential

Recycle loop pressures were monitored at the recycle flow meters and at the feed section. The difference in pressure level between these two points was the pressure loss for a portion of the system which included the cartridge. The pressure loss in the fixed geometry portion of this section would naturally vary with changes in flow rate, recycle gas composition, and gas density, but, for conditions producing normal conversion rates, these deviations were assumed to be minor compared to the pressure differential change caused by carbon buildup in the cartridge. The increase in system pressure differential with operating time was, therefore, assumed to be primarily due to increased drop through the cartridge even though a flow rate increase may have been required to maintain the conversion rate.

The general relationship between cartridge pressure differential and average carbon packing density for the prototype cartridge is shown in Figure 8.5. Also shown is a curve obtained by extrapolation from the development cartridge curve of Figure 5.8 using the method described in Paragraph 6.3.2. Considering the quality of the data, agreement is quite fortuitous but should be indicative of the results to be expected if the cartridge is expended in one continuous run under normal reactor temperature and process rate conditions. If the reaction is interrupted by an occasional cooling and reheat period, the pressure differential for a given density is appreciably lower, presumably
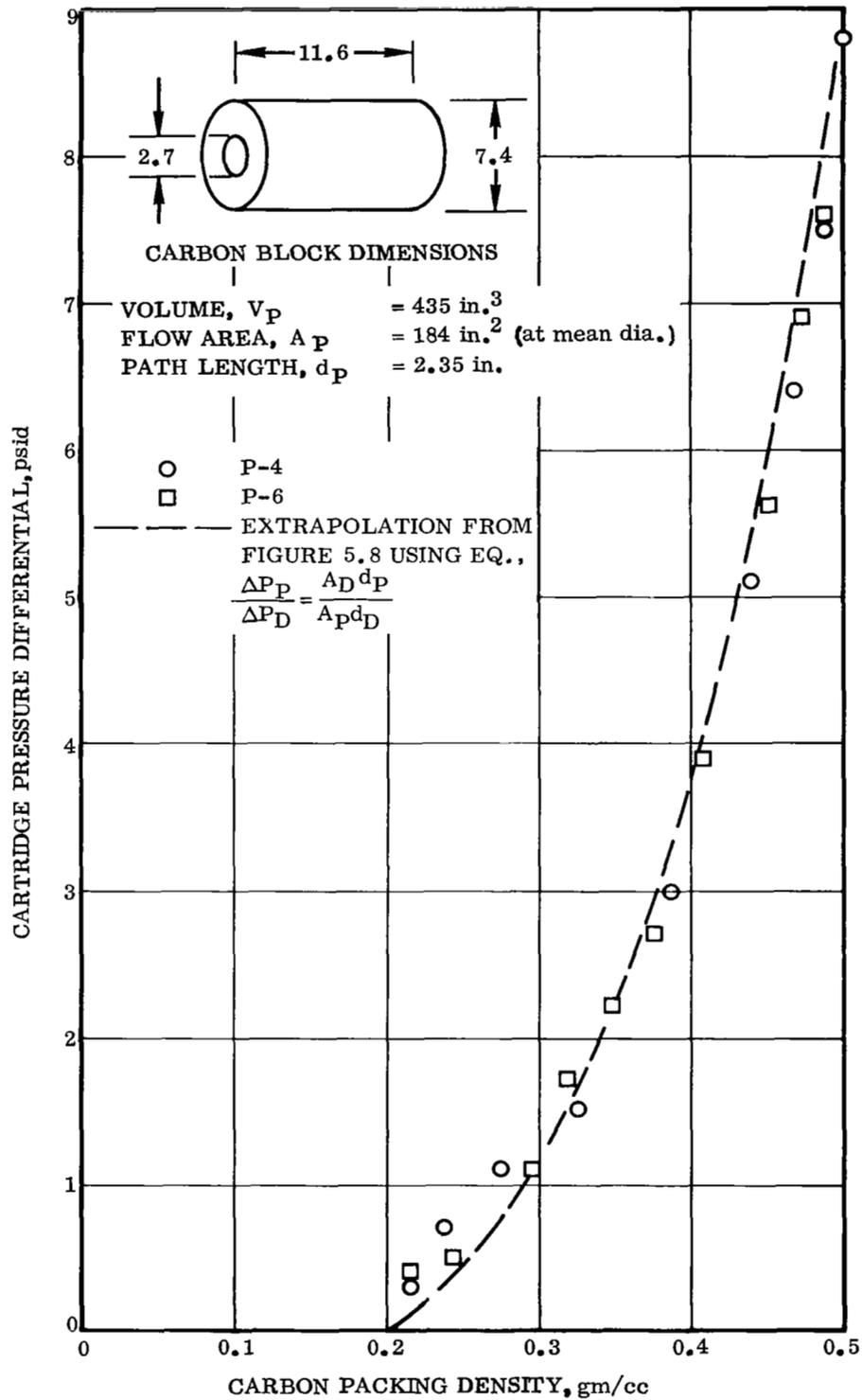
Figure 8.5 – Prototype Cartridge Pressure Differential Versus Carbon Density

due to disruption of the carbon structure by thermally imposed stresses. Extended operation with reactor temperatures at the 1070 to 1100° F end of the reactive range appeared to cause a more rapid flow restriction, perhaps because it favored carbon formation near the cartridge core where flow area is minimum.

8.9 Reactor Starting and Changeover Characteristics

Starting time limits are not specified but prompt starts and minimum deviation in starting characteristics allow definite procedures to be established and reduce monitoring requirements. If CO_2 reduction starts as soon as a reaction temperature is reached, the non-productive power expenditure is minimized.

8.9.1 Characteristics Without Catalyst Pretreatment. - A review of the starting characteristics of the 26 cartridges used during the experimental and prototype programs shows that the time required to reach a four-man CO_2 conversion rate ranged from 1.5 to 12.0 hours although a 1.5- to 2.0-hour period was normally sufficient to reach reactive temperatures. Breaking the starts into four categories as shown in Table 8.1, the following observations can be made. The first start of each of the three reactor shells used during the experimental program took 4.5 to 7.5 hours, and the corresponding starts for the prototype unit reactors were 10.5 and 12 hours.

Subsequent starts with fresh cartridges took appreciably less time for both units, and restarts were consistently made in the time required to reach a reactive temperature. These results suggest that both a reactor and a catalyst conditioning occurs. The reason for the difference in starting performance between the prototype and experimental reactors is not obvious. The prototype unit changeover starts were more rapid than starts from an inoperative condition, presumably because in the first case a reactive recycle gas composition was maintained by the active reactor. However, the unpredictability and the close monitoring required to keep conversion rates within bounds during the changeover period caused considerable frustration and suggested that a catalyst preactivation investigation was in order.

8.9.2 Characteristics With Catalyst Pretreatment. - After completion of the performance demonstration test, two approaches to catalyst preactivation were tried. The first hypothesized that an iron oxide in a high-temperature hydrogen-rich environment would be quickly reduced to catalytically active iron. The second approach was based on the observation that stainless steel which had been prepared for electroplating was much more active catalytically where poorly plated than were untreated stainless steel surfaces. It was surmised that the same treatment applied to steel wool might reduce its activation period. To test these possibilities, four cartridges were prepared and checked.

TABLE 8.1

REACTOR STARTING CHARACTERISTICS

Category	Starting Time, Hours		
	Development Test Period	Prototype Test Period	
		Before Catalyst Preactivation	After Catalyst Preactivation
First start of new reactor and cartridge	4.5 to 7.5	10.5 to 12.0	—
Subsequent start with new cartridge	2.5 to 4.5	7.0 to 8.0	1.5
Subsequent start with used cartridge	1.5 to 2.0	1.5 to 2.0	1.5
Reactor changeover with new cartridge	—	3.0 to 6.0	1.5

The steel wool for cartridge P-8 was dipped in deionized water and allowed to air dry. Where water drops coalesced at strand intersections, drying was slow and rust was formed. From a cold start, cartridge P-8 began producing water at 20% of normal rate in 1.5 hours. The rate increased slowly to 50% of normal at 6.5 hours, then increased rapidly to normal at 7.0 hours. The unit was shut down at 7.5 hours, and after cooldown the catalyst was removed for inspection. Examination showed large bands or regions of carbon formation, Figure 8.6(a), interspersed with areas of bright steel wool which showed no indication of reaction nor any sign of the original rust concentration points. This test was encouraging because at least some reaction had been obtained as soon as reactive temperatures were reached.

For cartridge P-9, the steel wool was surface-oxidized by heating to 530°F in an air furnace. Approximately 10% of the batch had a dark blue oxide and the rest was a dark golden brown. Four hours after reactor heater power was applied, only trace amounts of water were being obtained; consequently, the test was discontinued. As shown in Figure 8.6(b), the surface oxides had been reduced leaving the steel wool as bright as though untreated. No carbon formation was observable.

The batch of steel wool for cartridge P-10 was immersed in 5% hydrochloric acid for approximately five minutes, rinsed in distilled water, and dried in an oven at 230°F for two hours. Initial reaction was noted one hour after heater power was applied and a normal rate was being sustained at two hours. The reactor was shut down at 2.5 hours for cooling and catalyst examination. As shown in Figure 8.6(c), the reaction appeared to be fairly uniformly initiated at the outer surface of the package but showed no carbon at the core surface.
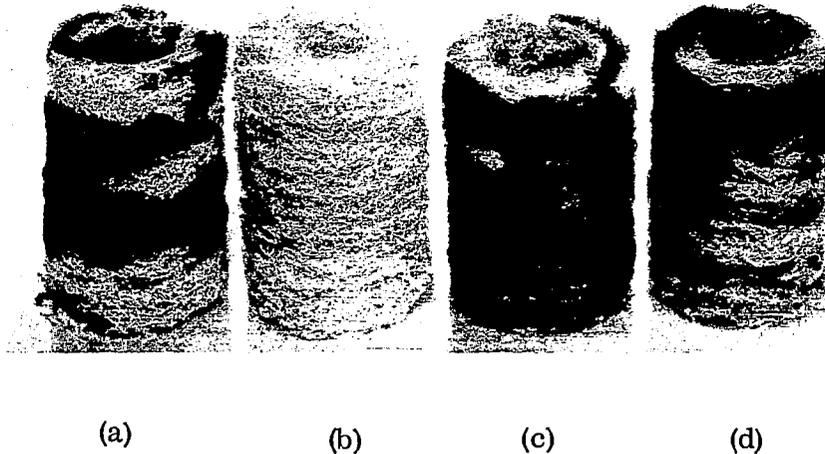
Figure 8.6 - Catalyst Conditions After Pretreatment Tests

Cartridge P-11 was packed with steel wool etched for four minutes in 3% hydrochloric acid and rinsed in distilled water. Excess water was shaken from the steel wool which was then oven-dried at 230° F for 30 minutes. A good reaction was initiated in 1.3 hours and normal conversion rate was maintained from 1.5 hours after start until 2.5 hours at which time the test was terminated. This cartridge, Figure 8.6(d), showed fairly uniform reaction from core to outer perimeter and from cover end to base.

Eight cartridges were delivered to the NASA-Langley Research Center. These cartridges were packed with steel wool treated in essentially the same manner as for P-11 except that the etching time was reduced to two minutes to minimize fiber deterioration. Excellent starting and changeover characteristics were demonstrated by the two cartridges used for 70 hours of unit demonstration tests at the Langley Research Center.

8.10   Power Consumption

Power requirements during stabilized operations were approximately 450 watts for the compressor and 500 watts for the heater and controls. During warmup periods the heater power was limited by the capacity of the solid-state controller to about 900 watts.

9.0 CONCLUDING REMARKS

The major difficulties affecting the development of a reliable Bosch CO_2 reduction unit have been resolved, thereby enhancing its consideration for use in oxygen recovery systems for long-term manned space missions.

The prototype Bosch CO_2 reduction unit developed under this contract demonstrated controlled reaction with complete carbon containment in catalyst cartridges with no external carbon-producing reactions during 447 hours of testing.

Quartz-wool-lined cartridges, initially weighing 2.85 pounds when charged with 150 grams of steel-wool catalyst, provided the desired reaction and carbon containment capability. Each cartridge could be operated at a four-man CO_2 conversion rate for 72 hours achieving a carbon packing density of 0.5 gm/cc.

Carbon-forming reactions were prevented from occuring external to the cartridge by careful use of materials and construction techniques. Aluminum bronze and oxygen-free copper were found to be non-reactive in the reducing environment. Nickel was also found to be apparently non-reactive unless contacted with iron. Combinations of these materials were used in prototype unit construction.

Unit operation was, for the most part, automatic with a feed gas control system which maintained proper H_2 and CO_2 flow to the unit, and a temperature control system which maintained reaction temperature at about 1250°F. Manual control was, however, required to periodically adjust the process rate which varied with cartridge loading. Dual reactors allowed continuous unit operation during cartridge exchange procedures. Cartridge replacement was a clean and relatively simple operation.

A catalyst preactivation process was developed which assured prompt reaction initiation in 1.5 hours. The process consisted of etching the steel-wool catalyst for 2 to 5 minutes in 3-percent hydrochloric acid, rinsing in distilled water, and oven-drying for 30 minutes before packing the cartridge.

Prototype unit weight and operating power requirements are 226 pounds and 950 watts, respectively. Reductions in weight and power should be possible, however, since these quantities apply to a non-optimized unit constructed for the purpose of demonstrating concept feasibility.

It is recommended that the development of a Bosch CO_2 reduction unit be continued. Suggested efforts include:

1. Reducing the expendable cartridge weight or developing a reusable cartridge.

2. Reducing unit weight and operating power requirements.

3. Conducting additional materials research to identify suitable high-temperature non-reactive materials which would simplify fabrication by eliminating the need for protective coatings. This work would also have direct application to other carbon-producing oxygen recovery processes currently being developed.

4. Developing an automatic process rate control system which would eliminate the requirement for manual control to compensate for cartridge loading.

5. Reducing the manual effort and eliminating the need for tools during cartridge exchange procedures by developing a quick-opening reactor with effective seal.

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