

Oxygen Regeneration Test Unit for Zero Gravity Operation

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Theoretical and experimental studies have resulted in the development of a carbon dioxide reduction reactor capable of continuous operation at a high rate of reaction. The capability for continuous removal of product carbon has been developed. Satisfactory long duration operation (25 days) of the carbon dioxide reduction unit has been demonstrated. Development of an oxygen regeneration unit which is adaptable to zero gravity operation also required the development of other critical components such as the water condenser-separator and electrolysis unit. Additional catalyst studies should be conducted to reduce the rate of catalyst consumption now obtained through the use of iron catalysts. Unit development and testing should continue until an oxygen regeneration test unit is actually tested in orbit.

IN ENVIRONMENTAL CONTROL systems designed for use in closed cabins over extended periods the oxygen regeneration unit is one of the most critical components yet to be developed. It is not the purpose of this paper to discuss the merits of the various methods used for the accomplishment of the oxygen regeneration process. This paper will discuss, however, the work already accomplished leading to the selection of the type of oxygen regeneration unit now under development. For the purpose of this presentation the concentration or separation of carbon dioxide is not considered to be a part of the oxygen regeneration unit. This separation of functions will have to be abandoned as development proceeds, since carbon dioxide concentration and oxygen regeneration should be considered as a single integrated subsystem.

The task of developing reliable Life Support Systems on schedule for use in first generation manned orbiting space stations requires the selection of subsystems and components which have already shown proof of principle and have exhibited hardware feasibility. Until very recently long duration operation of an oxygen regeneration unit suitable for use in a *closed* system had not been demonstrated. The first step in developing this regeneration unit is the demonstration of such operation. Additionally, the unit would be designed such that the principles of operation are compatible with zero gravity operation. Before proceeding with the development of a full scale operational unit small orbital test units should be developed. It is this type of small test unit which is now under development.

Experimental and theoretical studies over the past four years have covered a variety of methods for achieving oxygen regeneration. Table I presents a summary of the oxygen regeneration studies carried out by TRW.

TABLE I. OXYGEN REGENERATION PROGRAM SUMMARY

EXPERIMENTAL PROGRAMS	THEORETICAL PROGRAMS
1. Photosynthetic Regeneration a. Low intensity illumination	1. Photosynthetic Regeneration a. Low intensity illumination b. High intensity illumination c. Solar illumination
2. CO ₂ Reduction over Catalyst a. Sabatier Reaction b. Bosch Reaction 1. Steel wool beds 2. Fluidized beds 3. Fixed plate beds 4. Rotating disk beds	2. CO ₂ Reduction over Catalyst a. Sabatier Reaction b. Bosch Reaction 1. Catalyst configuration studies
3. Reduction by Activated Hydrogen a. Electrolysis cell b. Catalyst activation	3. Reduction by Activated Hydrogen 4. Glow Discharge Reduction of CO ₂ 5. Electrolytic Reduction a. Molten salts 6. Long Chain Hydrocarbon Production

On the basis of these studies the direct reduction of carbon dioxide over a catalyst was selected for continued development. The methods using Sabatier and Bosch reactions each have attractive characteristics but for long duration closed cycle operation the Bosch method is more desirable. An oxygen regeneration system using the Bosch reaction has the following desirable characteristics:

- Feasibility has been demonstrated.
- Engineering hardware has been tested.
- Weight and volume requirements are low.
- One hundred per cent separation of products (H₂O and carbon) from circulating gases can be achieved.
- A use exists for the carbon by-product.
- The catalyst material is not easily poisoned.

Referring to Figure 1, CO₂ Reduction Unit Schematic, a brief description of the selected oxygen regeneration unit operation is given. Carbon dioxide is reduced by hydrogen over an iron catalyst in the reduction reactor, producing water and solid carbon. The carbon is continuously removed from the reaction loop by a carbon filtering system. Reaction water is continuously removed by a stationary condenser-separator device, which feeds the collected water to the electrolysis unit where hydrogen and oxygen are evolved as gases. The oxygen is available for metabolic needs, while the hydrogen is fed to the reactor. Necessary instrumentation and controls required for proper operation are not shown on the schematic. Although the reduction reaction is

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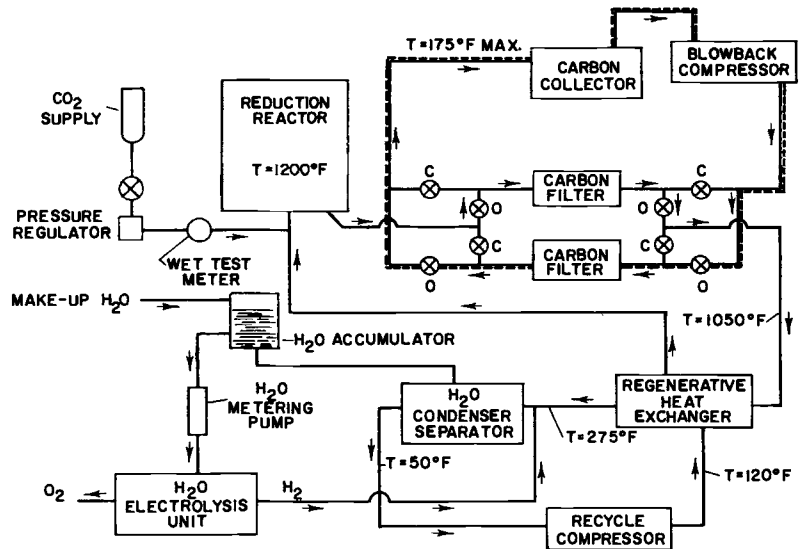


Fig. 1. Closed loop CO₂ reduction unit schematic.

exothermic heat must be supplied to the reactor to compensate for heat losses in the condenser-separator and to raise the reaction gases to reaction temperature. The lower the recirculating reaction gas flow rate the less heat input to the reactor is required. However, the higher flow rates produce higher reaction rates. Thus in emergencies a high flow rate through the reactor will increase its capacity at the expense of the energy input. The reaction rate or unit capacity can be varied over a considerable range by this technique. Side reactions produce some CH₄ and CO but the concentrations of these gases rises only to some equilibrium value since they are not removed from the recirculating gas stream.

Problems requiring prime consideration in the development of an oxygen regeneration unit as just described were:

1. Determination of a suitable catalyst and catalyst configuration.
2. Development of a method for continuously removing carbon from the reactor.
3. Development of a compact and efficient electrolysis unit.

Before deciding on a geometrical arrangement for the catalyst bed, studies were carried out in a cylindrical reactor using various catalyst materials, in both fluidized and fixed beds. A summary of materials tested and an indication of catalyst activity obtained is given in Table II.

Using powdered catalysts, or steel wool, very high reaction rates per unit volume of catalyst bed were obtained. For operation in a normal gravity environment the steel wool or steel screen is attractive for discontinuous operation or the fluidized bed for continuous operation. The fluidized bed is suitable for lunar base use or through further research the fluidized bed reactor can be adapted to zero gravity operation. Flat catalyst plates offer the compromise between high reaction rates and a suitable geometry for continuous carbon removal in zero gravity operation.

To determine what configuration the iron plate catalysts were to take for most efficient area utilization

TABLE II. CATALYST EFFECTIVENESS SUMMARY

Material Tested	Type of Bed	Level of Reaction
Steel Wool	Fixed	High
Iron Shot	Fixed	Moderate
Iron Plates	Fixed	High to Very High
Nickel Screen	Fixed	Very Low
G-52 ²	Fluidized	Moderate
Iron Powder ³	Fluidized	Low
Nickel Powder ³	Fluidized	Negligible
Stainless Steel ³	Fluidized	Very Low
Sponge Iron ³	Fluidized	Low
Carbonyl Iron & G-52 ²	Fluidized	High to Very High
Commercial Iron ³ & G-52	Fluidized	Low
No Catalyst (Higher Temperature)	—	Low

a theoretical analysis was performed.² Geometries compared were the parallel iron plates and parallel iron disks. With the disks gas flow was outward from the center.

For design purposes it was desirable to know the order of magnitude of the dimension of plate separation, *h*, such that the desired reaction rates could be obtained with a minimum area and weight of catalyst. The reaction was assumed to occur between hydrogen and carbon dioxide on the surface of the catalyst plates. Collision theory was assumed with the Maxwellian velocity distributions being assumed for all molecules of all classes. The number of molecules of a given class, in this case either H₂ or CO₂, which collide with the plane surface at *z*=0, per unit time per unit area, is given by:

$$N_{H_2} = \left[\frac{hm}{\pi} \right]^{3/2} \int \int \int \eta_{H_2} e^{-hm([u-U]^2 + v^2 + w^2)} dw dv du \quad (1)$$

where η_{H_2} is the volume density of H_2 molecules per unit volume, w , v and u are the molecular velocity components in the z , y and x directions. U is the bulk velocity of the gas containing the H_2 molecules. The number of H_2 and CO_2 molecules colliding with the plane $z=0$ at the same time at a given point $(X_0, Y_0, 0)$ can be expressed as

$$N_{Coll} = \left[\frac{hm}{\pi} \right]^{3/2} \iiint \eta_{H_2}(r) \eta_{CO_2}(r) \phi(r) e^{-hm([u-U]^2 + v^2 + w^2)} dw dv du \quad (2)$$

where $\phi(r)$ is the probability of an H_2 and a CO_2 molecular collision with the catalyst plane at a given point and time. Thus with reaction flow in a radial outward direction on a circular plate the bulk velocity is a function of r and is given by

$$U = \frac{V_0 r_0}{r} \quad (3)$$

where V_0 is the velocity at the point where the flow enters the catalyst region and r_0 is the plate radius at this point. Since the number density of the particles is not constant their functional relation on r must also be considered. Thus

$$-\text{Div} \eta_{H_2} \nabla = \frac{\delta \eta_{H_2}}{\delta t} \quad (4)$$

where the right hand side of the above equation is proportional to the collision frequency. An identical relation holds for CO_2 . The flow through the catalyst channels is assumed to be completely incompressible. Thus, we also have

$$\eta_{H_2} = \eta_{CO_2} \approx Q \approx V_0 h \approx h = Kh \quad (5)$$

Since it is desired that at a given flow rate (including the recycle gas) the number of collisions occurring per unit time be equal to the rate of supply of reactant particles, the following relation must hold.

$$K'h = \int_{r_0}^{R_p} N_{Coll}(r) 2\pi r dr \quad (6)$$

Therefore we may write

$$K''h = \int_{r_0}^{R_p} \iiint \eta_{H_2}(r) \eta_{CO_2}(r) \phi(r) e^{-hm\left(\left[u - \frac{V_0 r_0}{r}\right]^2 + v^2 + w^2\right)} rwdw dv du \quad (7)$$

In the present analysis ϕ will be assumed to be independent of the type and geometric configuration of the catalyst bed. The evaluation of ϕ was carried out in the following manner. The fluidized bed data was analyzed and used as follows. It was assumed that in the fluidized bed, the reaction occurs through the mechanism of the collision between the reactant molecules and the fluidized bed particles. It has been assumed that the random velocity distribution of the fluidized bed particles is also Maxwellian with magnitudes three orders of magnitude below that of the molecular velocities. Under these assumptions one obtains

$$\phi = \frac{C'e^{-E/RT}}{\iiint \eta_{H_2} \eta_{CO_2} \eta_e^{-hm([u-U]^2 + v^2 + w^2)} dw dv du}$$

where E is the activation energy and U is the bulk velocity through the fluidized bed. Thus, the system of equations to be solved is

$$K'h = \frac{C_0 e^{-E/RT} \iiint \eta_{H_2} \eta_{CO_2} \eta_e^{-hm\left(\left[u - \frac{V_0 r_0}{r}\right]^2 + v^2 + w^2\right)} rwdw dv du}{\iiint \eta_{H_2} \eta_{CO_2} \eta_e^{-hm([u'-U]^2 + v'^2 + u'^2)} dw' dv' du'}$$

$$-\text{Div} \nabla \eta_{H_2} = \frac{\delta \eta_{H_2}}{\delta t}$$

$$\eta_{H_2} \approx \eta_{CO_2} \quad (8)$$

This system will yield a relationship between h and R_p , the plate separation distance and the plate radius, respectively, which will, within the framework of collision theory, be most economical of a catalyst surface area. Since, however, the assumptions made can be very critical in effecting the solution and it is not apparent that these assumptions have a quantitatively rigorous basis, and in view of the difficulty in carrying out an exact solution of Equation 8, only an order of magnitude analysis is considered. An order of magnitude analysis results in

$$h/R_p \leq O(1/10) R_p \quad (9)$$

Thus Equation 9 represents a condition which must be fulfilled in order to obtain a reactor which will reproduce at least the level of available results and it can be shown to minimize the reactor catalyst weight. Thus the analysis presented here gives a relationship between reaction rate and catalyst weight.

The system of Equation 8 may be examined to determine that inter-relationship which exists between the geometric and phenomenological terms. The most significant effect on the gross reaction rate is felt through the divergence expression of the system of Equation 8. This expression can be written:

$$\text{Div } \eta_{H_2} \nabla = \frac{\delta \eta_{H_2} V}{\delta r} + \frac{\alpha \eta_{H_2} V}{r} = \frac{\delta \eta_{H_2}}{\delta t} \quad (10)$$

where $\alpha = 0$ for the plane case, 1 for a cylindrical geometry and 2 for a spherical geometry. It becomes apparent that the magnitude of α is the significant parametric factor contributing to the efficient use of catalyst area, the greater the α -value the better the process. Thus we are led away from plane flows over catalyst surfaces and it would be desirable to have a spherical flow geometry. However, practical considerations rule out a spherical reactor and this serves as justification for the cylindrical geometry. Additionally the cylindrical geometry lends itself to a practical method of carbon removal.

Based on the considerations presented here a reactor using the cylindrical catalyst configuration has been

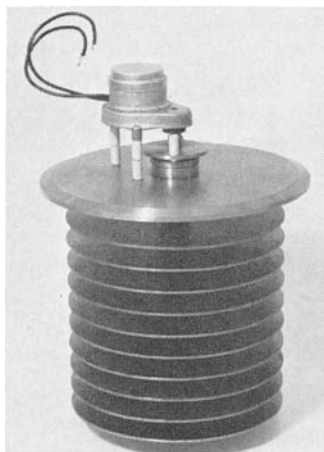


Fig. 2. Catalyst assembly and drive motor.

developed and successfully operated. The cylindrical catalyst stack is shown in Figure 2.

During the reduction reaction carbon is continuously deposited on the catalyst surfaces. The catalyst surface need not be free of carbon to maintain a satisfactory reaction rate. Thus during the carbon removal process a layer of carbon is allowed to remain on the surfaces of the parallel disks. Merely a flow path between the disks must be maintained by carbon removal. The removal is accomplished by rotation of the entire catalyst stack past a bank of stationary scraper blades. Carbon dislodged from the catalyst is carried from the reactor into porous stainless steel filters by the recirculating reaction gases. Two such porous filters are required, such that one filter is removing carbon from the recycle gas stream while the second filter is idle or is being cleaned by back flow into a low temperature carbon collector. The gas flow path during back flow is indicated by the dashed lines on the Flow Schematic, Figure 1. The carbon thus collected is a fine powdery material having a bulk density of 0.3-0.4 grams per cubic centimeter. By compressing this carbon powder with slight pressure (~ 10 psi) the density is increased to approximately 0.7 grams per cubic centimeter. Due to the small iron content the carbon is slightly magnetic. Specific area measurements indicate a moderately large adsorption capability for the carbon (180 square meters per gram). This specific area is sufficiently high to speculate on the use of this carbon as an odor control agent and for liquid purification in closed life support systems.

During the reduction reaction some iron is consumed forming iron carbide (largely Fe_3C) compounds along with the free carbon. The amount of iron consumed is a function of a number of variables. These are type of iron catalyst used, reaction temperature, reaction rate per unit catalyst area and gas composition in reactor. Future experimental programs should be carried out to determine that combination of catalyst and reaction conditions which yield a high reaction rate and a low catalyst consumption rate. Table III presents data on iron content of carbon samples obtained from various experimental runs.

TABLE III. IRON CONTENT OF CARBON SAMPLES

Percent Weight Iron in Carbon	Duration of Experimental Run	Reaction Temp. °F	Cond. Temp. °F
10.90	6 hours	1200	63
15.44	15 hours	1220	62
20.51	27 hours	1100	
11.90	73 hours	1270	55
16.85	600 hours	1200	60
		1200	75

It is seen from the above table that iron consumption varies widely from run to run. This occurs since the reaction conditions were varied widely during the experimental program. The immediate goal is to achieve a carbon to iron weight ratio of 20.

An oxygen regeneration unit designed for zero gravity operation must have a simple yet effective means for separation of water from the process gases. This is accomplished most efficiently by passing the recirculating gas stream between two cold porous metal plates.

Reaction water condenses on the plates and is drawn into the pores by capillary forces. On the opposite side of the porous plates is a water cavity maintained at a pressure lower than the pressure in the gas cavity. This pressure differential continuously forces the water through to the water cavity. The porous plates used in this application are able to withstand in excess of six psi pressure differential from gas to liquid side without allowing any gas bubbles to penetrate the plate and be evolved on the liquid side. Thus, aside from dissolved gases, we effectively have one hundred percent separation from gas using a device which has no moving parts. Devices of this type have been successfully operated in excess of one thousand hours. Water output from this condenser separator is delivered directly to a water accumulator for subsequent use in a water electrolysis unit.

Electrolysis unit design must also be based on principles compatible with zero gravity operation. Water is metered from the accumulator by a small positive displacement pump. A reservoir of water is contained in the lower end of the electrolysis unit. Transport of water to the electrodes is accomplished by wicking material capable of supplying water at the use rate. Electrodes are platinum black coated nickel screens. An asbestos membrane serves as matrix for the potassium hydroxide electrolyte and provides a barrier between the hydrogen and oxygen gas compartments. With this type of cell structure it is possible to maintain a pressure differential between the oxygen and hydrogen gas cavities approaching the bubble point of the asbestos diaphragm used. By properly controlling water feed to the unit no bulk carry-over of water or electrolyte in the product gases is observed. Cell cooling is obtained by the evaporation of water from the wet asbestos diaphragms. Equilibrium operating temperature is approximately 130°F when the unit is operating at 100 amperes per square foot and a voltage per cell of 1.64 volts. The electrolysis unit capable of providing one half the daily oxygen requirements of one man re-

quires a power input of 107 watts, weighs two pounds and occupies a volume of 40 cubic inches.

Using components whose designs were based on the previously discussed principles a test unit capable of reducing 1.2 pounds of CO₂ per day was fabricated and tested. The work was carried out under Contract No.

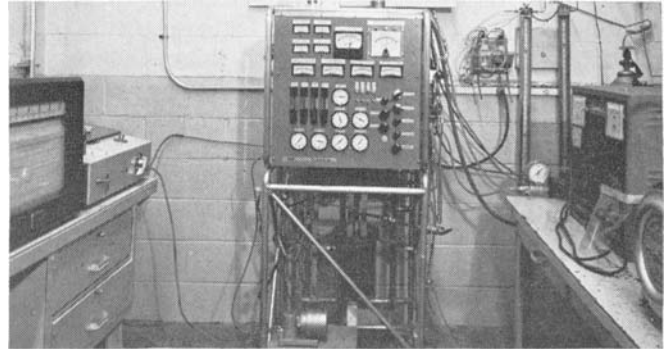
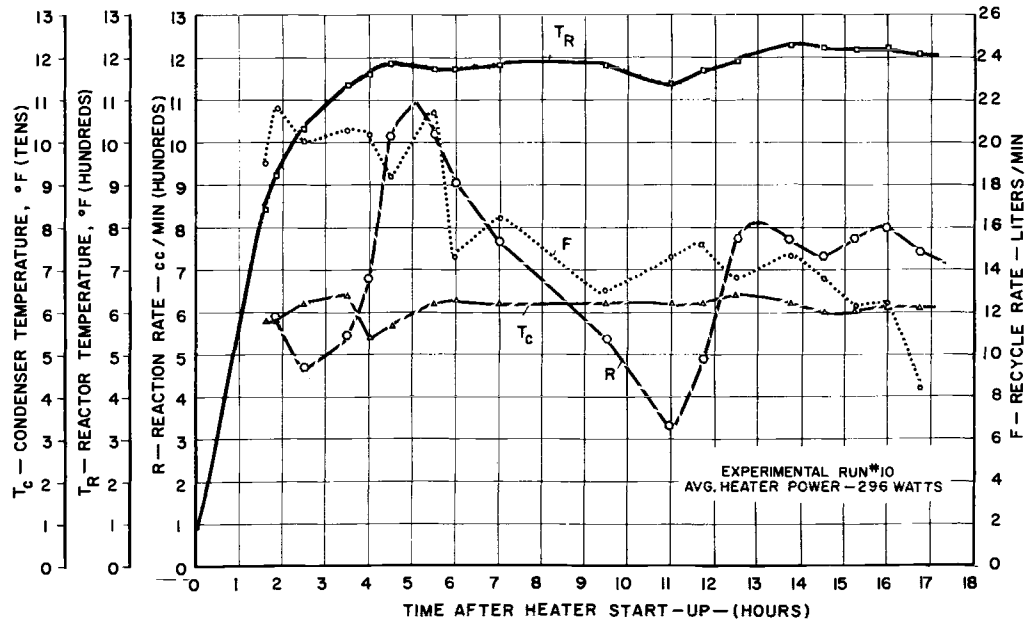


Fig. 3. CO₂ reduction unit on test stand.



Fig. 4. Low temperature carbon collector after first filter blowback cycle.

Fig. 5. The relationship of reaction rate, reactor temperature and condenser temperature and recycle flow rate as a function of running time after heater start-up for a portion of one of the shorter runs.



NASw-650. The completed unit is shown on the test stand in Figure 3. This unit successfully demonstrated long duration operation, continuous carbon removal, integrated operation of CO₂ reduction and water electrolysis and stable catalyst performance. Design information obtained from operation of this unit is already being used for design of more advanced oxygen regeneration units.

Total testing time obtained with the reduction unit was approximately 40 days, the two longest continuous runs covering nine and 25 days respectively. At times reaction rates in excess of 1200 cc/min. of reaction gases were obtained. The nominal design rate is for 600 cc/min. of reaction gases. Figure 4 is a close-up view of the low temperature carbon collector after the first transfer of free carbon from the filters to the collector by the blowback cycle. Figure 5 presents a plot of reaction rate, reactor temperature, condenser temperature and recycle flow rate as a function of running time after heater start-up for a portion of one of the shorter runs. Fluctuations in the recycle gas flow rate are due to build-up and blowback of carbon in the filtering system.

Variations in reaction rate are caused by varying recycle flow rate, varying gas composition and small changes in reactor temperature.

During the 25-day run carbon was successfully removed from the reactor over the entire operating period. Reaction conditions varied widely³ but the reaction rate average was maintained close to the nominal design rate. The variation in reaction rate was caused by large excursions in the recycle gas composition. Automatic control of gas composition was not provided on this unit. By properly adjusting the recycle gas composition the reaction rate could always be increased to a level above the nominal design rate.

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