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UNIVERSITY ROLE IN ASTRONAUT LIFE SUPPORT SYSTEMS: ATMOSPHERES

by Robert C. Reid

Prepared by
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge, Mass.
for

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INTRODUCTION

The Biotechnology and Human Research Division of the National Aeronautics and Space Administration's Office of Advanced Research and Technology is vitally interested in fostering and developing new ideas which will advance the technology of life support and astronaut protective systems. Many excellent ideas and operating systems have been brought to fruition in NASA laboratories and by associated contractors. However, involvement of academic laboratories and personnel has not been as great as was originally hoped. Perhaps this has been due to the fact that academic personnel were not aware of the critical problem areas in life support and protective systems, nor were they cognizant of the fact that NASA is interested in joining with colleges and universities to develop new ideas to solve future space flight problems.

This brochure on Atmospheres in Life Support Systems is intended to introduce you to some of the existing technology involved in keeping crews alive in spacecraft and in the extravehicular environment and to pinpoint areas where problems exist. We encourage you to study this brochure. If in your research, you have already developed new ideas, theories, chemicals, etc., which would be applicable to NASA's effort, we hope you will feel inclined to contact us to see whether a joint research effort can be initiated.

Walton L. Jones
Director, Biotechnology and
Human Research Division

I. STORAGE OF ATMOSPHERIC GASES

The atmosphere in future manned space vehicles will consist of oxygen diluted with nitrogen or other inert gases such as helium. The oxygen partial pressure will be maintained close to that on earth, i.e., at least 0.2 atm. The diluent partial pressure has not been fixed though it will usually be less than 0.8 atm.

In the present section, we will explore possible techniques to store and deliver atmospheric gases at the correct flow rate, temperature, and pressure. The inert diluent gas will be assumed to be nitrogen.

One might first expect that there would be little need to store a diluent in that it is not consumed in any metabolic process. Likewise, one could question the necessity of oxygen storage since advanced, long-duration space vehicles will recover oxygen from metabolic carbon dioxide and water. The storage we are interested in is that necessary to:

- replenish cabin leakage
- replenish any air-lock losses
- repressurize the vehicle in case of total or near-total atmospheric loss
- replace gases vented from any processing equipment or lost in equipment malfunctions, minor fires, etc.

Also, in the general area of atmosphere gas-storage and supply, we will discuss ways to supply oxygen for short-term extra-vehicular activities.

Before suggesting some interesting problem areas which require new ideas for an optimum solution, a number of different storage techniques which have been proposed previously are discussed and evaluated.

High Pressure, Ambient Temperature Gas Storage

For laboratory or industrial use, gas is usually supplied in high pressure storage vessels. Even in the Project Mercury program, oxygen stored at 7500 psia was used to supply the astronaut. However, in subsequent NASA and Air Force programs, high-pressure, ambient temperature storage has proven to be heavier than other techniques and, except to meet emergency storage requirements, it has not been extensively used.

High-pressure gas storage vessels can certainly be designed with a very high degree of reliability; they can also be used to supply gas at the low rate compatible with cabin leakage requirements as well as at the high rates necessary to repressurize a large compartment. From all considerations except mass penalties, high-pressure gas storage is an attractive concept.

The development of very light-weight storage vessels has been disappointing, and major technological breakthroughs are necessary. Presently, oxygen storage tanks are usually made from stainless steel and, depending upon size and pressure level, one can store in the range of 0.9-1.0 lb of oxygen per pound of vessel, i.e., imagining the tank and oxygen to be a unit, we might speak of this unit having about 50% oxygen by weight. Titanium tanks are somewhat lighter but high-pressure oxygen should not be stored in titanium vessels.

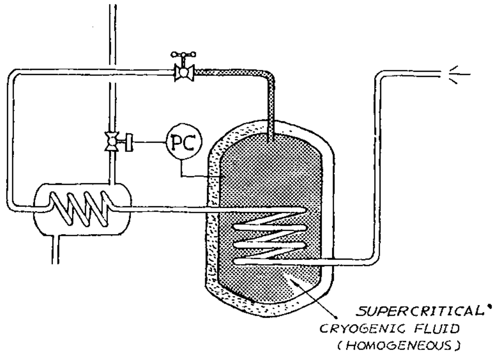
In the development stage are boron-wound filament tanks with an inner metal liner. Though not optimized, even for this new tank, only about 1.3 lbs of oxygen may be stored per pound of tank. Values of 2 to 3 lbs of oxygen per pound of tank would be necessary to allow high-pressure gas storage to compete with some of the cryogenic storage techniques discussed later.

Nitrogen or other diluent gas storage problems are similar to those for oxygen.

Cryogenic Storage

Oxygen and nitrogen may both be stored as liquids in equilibrium with their vapors or, at higher pressure and temperatures, they may be stored as supercritical, homogeneous fluids. The first method noted above is often referred to as sub-critical storage.

In supercritical storage, the gas pressure is held constant and greater than the critical pressure. The temperature increases during draw-off since, for isobaric operation, energy must be added. Careful design of the tank insulation may allow one to match closely the cabin leakage requirements with the designed venting rate. For more rapid venting, additional energy must be added. Electrical heating is inefficient and internal fluid heaters are usually preferable. For example, vented gas may be heated and passed back through an internal coil to maintain the tank pressure constant.

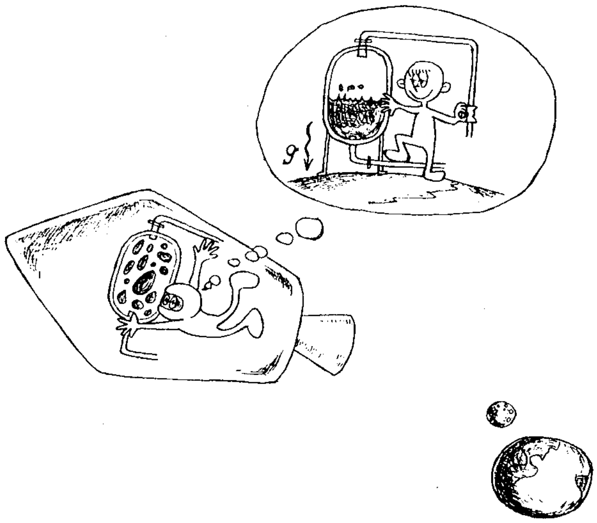


Few problems have plagued existing supercritical storage devices and these have been used successfully for the Gemini and Apollo programs. Super-insulation has been favored to minimize heat leak and sometimes the radiation shields are cooled by the venting vapor. An optimum supercritical storage container is more of a design-weight minimization problem rather than one that demands any major inovation or development.

In sub-critical storage, liquid oxygen and nitrogen (or other diluent) are stored in insulated tanks at pressures below the critical where two phases exist. The use of low pressures and temperatures leads to a low weight and small volume system.

During venting, to keep the pressure from decreasing, energy must be added. As noted in the discussion of supercritical storage, this may be done using electrical power or internal fluid heat exchangers. One real problem which faces the designer and user of a zero-gravity sub-critical storage tank is how to make a phase separation without a gravity body force field. For operation where only cabin leakage must be satisfied, vapor venting may be preferable. For those times of high demand flow, perhaps a liquid vent, with subsequent vaporization, might be more desirable.

In either case, one must have some idea where the liquid and vapor is at any time. In a simple tank, the vapor-liquid mixture will, most likely, not be homogeneous and a number of techniques have been suggested to aid in providing a definite separation of the vapor and liquid. For example, capillary forces at solid-liquid interfaces can be utilized to hold large masses of liquid as one entity. Fiber mats are positioned in the tank to cover liquid vents. Another technique would employ dielectrophoretic fluid control, i.e., electric polarization forces can be used to orient liquids. Stability results when the liquid interface is tangential to the electric field and perpendicular to the gradient of the field. Ozone formation may, however, be a problem with high field strengths.



In addition to the surface and electric forces suggested above, a simple bladder, bellows or membrane separating liquid and gas has appealing simplicity. Increasing the pressure on the gas side of the membrane would expel only liquid out of a convenient exit duct. The principal drawback to such a simple device is that there are no reliable, flexible membranes suitable at the temperatures of liquid oxygen or nitrogen, though metallic bellows are under development.

Another serious problem is to determine, at any time, the amount of material stored in a sub-critical, zero-g environment. If definite interfaces could be attained, then interface sensors could be used. With, however, the possibility of arbitrary configurations of liquid and vapor, other measurement techniques have to be employed. One of the simplest is an integrating flowmeter to measure the total quantity removed from the tank. By difference from that present originally, the amount of liquid and gas present at a given time may be determined. While such techniques often are acceptable, direct means to determine liquid and gas contents would still be preferable.

To summarize, sub-critical cryogenic is a very light weight technique to store cryogens. The insulation must be of very high quality to minimize boil-off, i.e., the nominal boil-off should probably be designed to be slightly less than that required for supplying cabin leakage. Energy must be supplied from external means to maintain isobaric operation in periods of high use but thermal stratification should be avoided. The main problems encountered are phase discrimination in venting and measurement of the mass present in the two-phase system.

Solid Oxygen Storage

Oxygen freezes at 54.4°K. It is possible to store oxygen as a solid below this temperature; it has even been suggested to transfer solid oxygen by magnetic fields since the solid is paramagnetic. The heat of fusion of solid oxygen is 5.98 Btu/lb. There is a remote possibility that the low energy storage state may be utilized to condense and remove carbon dioxide, the oxygen vaporizing in the process. Preliminary calculations indicate that this hope is marginal unless the system is designed to minimize any utilization of the oxygen enthalpy change to cool the circulating cabin air, i.e., close approach temperatures are required in any heat exchange equipment.

As with any solid storage system, there would be problems in charging, insulating, phase discrimination, total mass inventory determination, and vaporization. Possible advantages might be:

- for long term storage with little or no use, venting losses are low;

- in a weightless environment, a subliming solid should remain at the "thermal" center of a container;
- no pressure shell is required.

Chemical Storage

Many proposals have been made to supply oxygen and diluent nitrogen from chemicals. For example, suppose a chemical decomposes to give a nonvolatile salt and oxygen gas. Such a technique might be a very convenient method to store oxygen at high density. Consider, for example, lithium perchlorate, $LiClO_4$. If this could be decomposed to LiCl and O_2, it would be possible to recover about 0.6 lbs of oxygen per pound of original salt. Unfortunately, the reaction is quite endothermic and requires a net energy input at a rather high temperature (circa 700-800°F). Ordinarily other fuels such as Al, B, Fe, or Mn are added to provide this energy. Also side reactions can produce chlorine gas so materials such as Li_2O_2 are added as scavengers. Perhaps if the reaction mechanism were better understood, some of these difficulties might be circumvented.

The example given above is illustrative of the many oxygen containing chemicals that have been studied. One can note the following as but a partial list: KO_2, Li_2O_2, NaO_2, H_2O_2, $NaClO_3$, $KClO_3$ and organic hydroperoxides. Compared to cryogenic storage, all have rather poor oxygen yields per unit mass of oxide. The superoxides KO_2 and NaO_2 as well as lithium peroxide have also been studied as a technique to remove both carbon dioxide and water as well as some trace contaminants. Ideally such reactions as illustrated below would occur:

$$2KO_2 + 2CO_2 + H_2O \rightarrow 2KHCO_3 + \frac{3}{2} O_2$$

Unfortunately the CO_2 is now held strongly in the bicarbonate salt and, as such, it is difficult to break down to regenerate oxygen for further metabolic use. Also KO_2 is quite toxic if dusting occurs, and is reported to cause fires when in contact with certain organic materials.

Little work is now being carried out to improve chemical techniques for oxygen production. Essentially the same can be said for chemical techniques to produce nitrogen. Several nitrogen producing chemicals have been suggested, e.g., ammonia, hydrazine, ammonium and lithium azides, nitric oxide, nitrous oxide, and ammonium nitrate. None have yet proved to be reliable and most produce by-products which must be removed before the nitrogen can be considered for use in a manned atmosphere. One interesting method to produce both oxygen and nitrogen in any ratio, involves the reaction between hydrazine and nitrogen tetroxide. Oxygen, nitrogen and water are produced. The reaction is hypergolic and under some conditions it goes to completion, but the reactants are extremely harmful to man and must not carry over into the product atmosphere.

Hydrogen peroxide liquid may be decomposed to yield water and oxygen. The water could be used as make-up or electrolyzed to produce additional oxygen and the hydrogen fed to a carbon dioxide reduction process. Prototype units which have been constructed have employed 90% H_2O_2 with a positive expulsion bladder to eject the liquid. Decomposition occurred over a silver screen coated with samarium oxide. The adiabatic decomposition temperature was about 750°C so expansion in a turbine or aftercooling was necessary to condense the water. As with many processes, there was difficulty in obtaining a suitable zero-gravity phase separator. Also, on occasion, some traces of H_2O_2 were found in the product.

Chemical techniques to store oxygen and nitrogen are certainly novel and interesting, but, from practical considerations, the weights of such systems are not competitive with simple cryogenic storage. True, because of heat leak, cryogenic storage has a definite time limit of operation whereas most chemicals are stable for long periods under conditions encountered in space. When very long term storage is necessary, a careful study is required to choose between high-pressure gas storage, solid chemical storage, or even solid oxygen.

What are needed are new, radical ideas on how to store oxygen and nitrogen in chemically bound states. Suggestions have been made concerning the possibility of isolating CaO_4. Is this material stable? Are other alkaline earth or alkaline earth ozonides stable? Can one find adsorbents for oxygen where the oxygen approaches a density near that obtained cryogenically? A new patent describes results wherein oxygen is "complexed" with inert materials such as water, nitrogen dioxide, and olefins so that the resulting mixture is stable at temperatures above the normal boiling point of oxygen. The technique suggested is simple. The oxygen and inert are rapidly frozen out at liquid helium temperatures, warmed and pumped to remove some oxygen. The residual solid may then be caused to evolve oxygen by heating. As stated in the patent, "the solid complexed material is much more stable than pure solidified oxygen and consequently may be stored indefinitely at much higher temperatures, up to 200°K." This technique needs further study; at present, the ratio of inert-to-oxygen is large and must be reduced before the method becomes a practical one to store oxygen. Also, many possible variations of the decomposition techniques can be suggested to vary the capacity of the inert to store oxygen.

Electrolysis of Water

Electrolysis of water may be carried out either in the liquid or vapor phase. The techniques which are discussed fully in a later section may be employed as a means to prepare oxygen from the water formed in various carbon dioxide reduction processes. However, the same equipment could presumably be used to generate oxygen for supplying cabin leakage and repressurization. There are, however, two disadvantages.

First, to provide the low rate of flow necessary for replenishing cabin leakage, the present electrolysis equipment with the associated power penalty may be too heavy to be competitive with other techniques. Second, electrolysis is not suited for supplying the large flow rates necessary for repressurization, unless one would electrolyze at high pressure and store the oxygen for later use.

For very long missions, the use of electrolysis becomes more attractive since the power penalty is correspondingly less.

Extra-Vehicular-Activity Storage of Oxygen

Until recently, all EVA plans included high-pressure gaseous oxygen storage tanks to supply an astronaut with the necessary oxygen. Weight in this case is sacrificed for convenience as cryogenic storage is somewhat less reliable. The actual total mass difference between most systems is, however, not large.

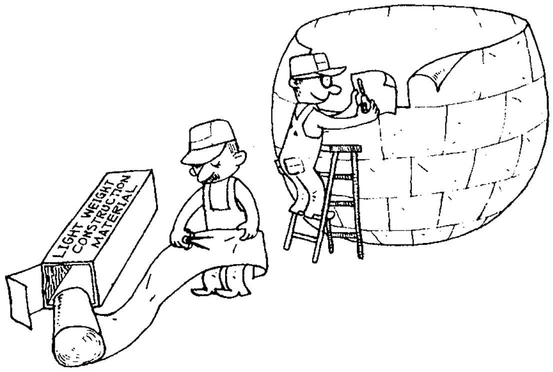
Recently, there has been interest shown in the use of sodium chlorate candles to provide oxygen by the decomposition reaction:

$$NaClO_3 \rightarrow NaCl + 3/2\ O_2$$

Similar candles ($KClO_3$) were proposed by Jules Verne in his novel "From the Earth to the Moon." Also Japanese fighter pilots utilized chlorate candles during World War II and the U.S. Navy still employs them for the major oxygen source on conventional and nuclear submarines. Considerable effort has been expended to blend the sodium chlorate with other ingredients such as powdered iron to prevent chlorine production and to make the reaction self-sustaining. At the present time, the major drawback to this system is the fact that unless the candles are contoured, they produce oxygen at a constant rate. The metabolic activity of an astronaut may vary greatly and therefore, oxygen flow requirements will also vary. Thus, the burning rate of the candles must match the maximum metabolic rate. Unless one can program an astronaut's work load to lead to a more constant metabolic rate, or unless one can vary the burning rate of a candle, this chemical method to store oxygen is not of much interest.

Recommendations for University Research

- Develop more satisfactory membranes or bladders to expel cryogenic liquids from storage.
- Suggest new ideas to provide phase separation of liquids and vapors in a zero-g environment.
- Develop accurate techniques to monitor the mass of cryogen present in a zero-g sub-critical storage tank.
- Develop new high-strength, light-weight pressure vessels to store atmospheric gases.



- Propose new, novel chemicals which may be exploited to produce oxygen, nitrogen (or other diluents). Or, suggest new ideas wherein more common oxygen or nitrogen chemicals may be utilized to provide O_2 and N_2 and other chemicals useful in the overall life support system.

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II. REGENERATIVE CARBON DIOXIDE REMOVAL SYSTEMS

Each astronaut, assuming normal metabolism, produces about 2.25 lbs of CO_2 per day. For long duration missions, it is usually advisable to recover most if not all of the oxygen bound in the CO_2.

Various processes to treat CO_2 and recover oxygen are described in a later section. Most require that the CO_2 feed be separated rather completely from oxygen, nitrogen, trace contaminants, and water, i.e., the purity of the recovered CO_2 should exceed 99%.

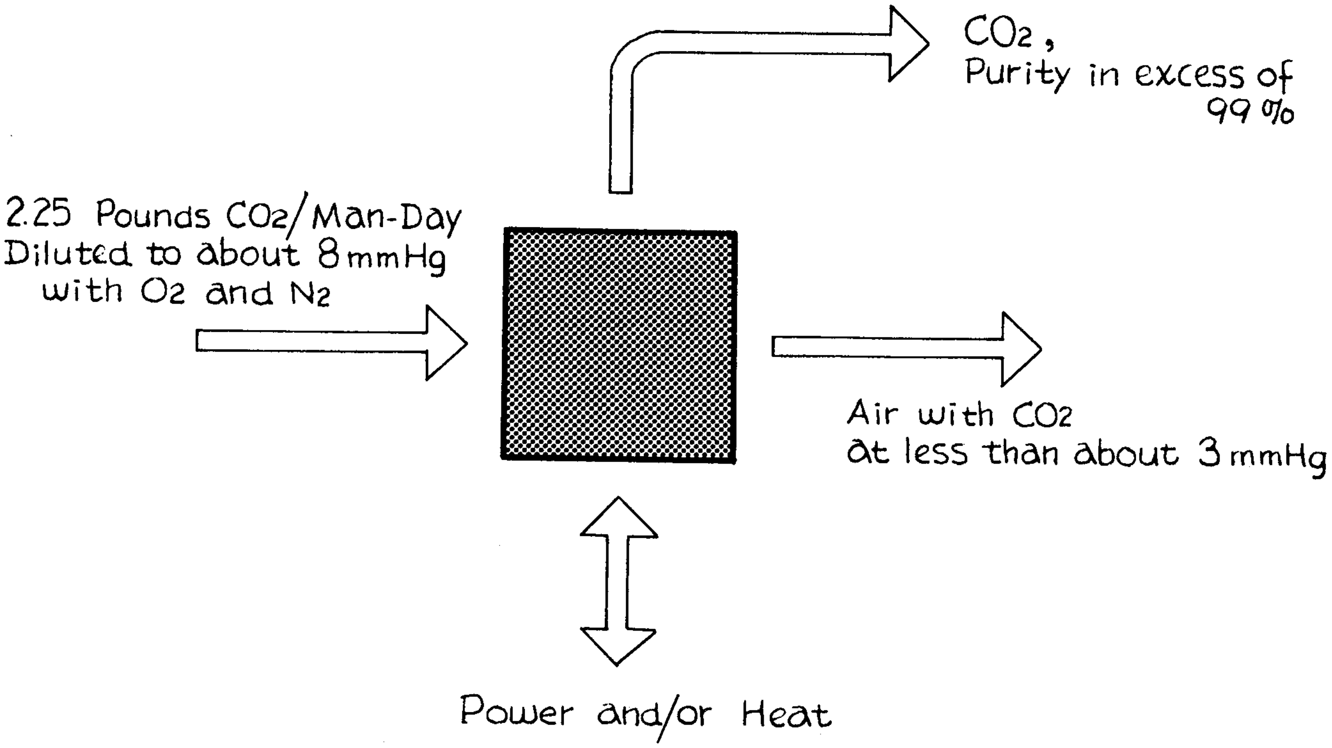
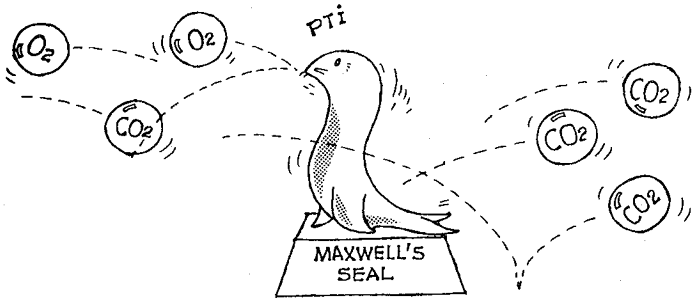


Figure 1.

In the present section, some techniques are described to remove CO_2 from cabin air so as to maintain the partial pressure within the 3 to 5 mm Hg range. Also, to function for long periods of time, the removal system must be of a regenerative type, i.e., it should operate in a steady state or cyclic manner.

A very large number of methods have been proposed. All seem technically feasible though many have not been adequately tested to allow a fair appraisal for space applications. At the end of this section, a brief summary is presented and a number of possible problem areas outlined. New process schemes are still desired if they could lead to significant reductions in weight and volume.



Molecular Sieve - Silica Gel Four-Bed System

Certainly one of the most thoroughly tested systems, the 4-bed Sieve-Gel system has already been demonstrated successfully in long-time laboratory tests both in the U.S. and in the U.S.S.R. The cabin air is first dehumidified in a cold silica-gel bed to a dew point near -50°F. It then passes through a cold molecular sieve or artificial zeolite bed and the carbon dioxide adsorbed. Purified air from this latter bed is then cycled back to the cabin through the alternate silica-gel bed to remove the water adsorbed therein in a previous cycle. The humidified, CO_2-free-air reenters the cabin atmospheric system.

The zeolite bed that is not in contact with the cabin air is evacuated and the desorbed carbon dioxide stored in an accumulator for later use. To optimize the quantities adsorbed and to obtain the desired rates, the beds are usually cooled during adsorption and heated during desorption.

A typical system is shown in Figure 2. This or a similar system will probably be used on the first flights wherein CO_2 must be removed from the cabin air. The drawbacks or disadvantages to such a system may be summarized as follows:

- unless the zeolite bed is pre-evacuated (with gases recycled to the cabin air inlet), when CO_2 desorption occurs, some O_2 and N_2 is carried with the CO_2 to the accumulator. The oxygen impurity will degrade the CO_2 reduction system and the N_2 will eventually have to be purged or recycled.
- care must be taken to prevent carry-over of moisture from the silica-gel to the zeolite beds. The capacity of zeolite beds for CO_2 decreases sharply if the beds have adsorbed much water. Also water is difficult to remove from zeolite beds and a prolonged, high-temperature bake-out is necessary.
- the valves and timing mechanism must operate in a

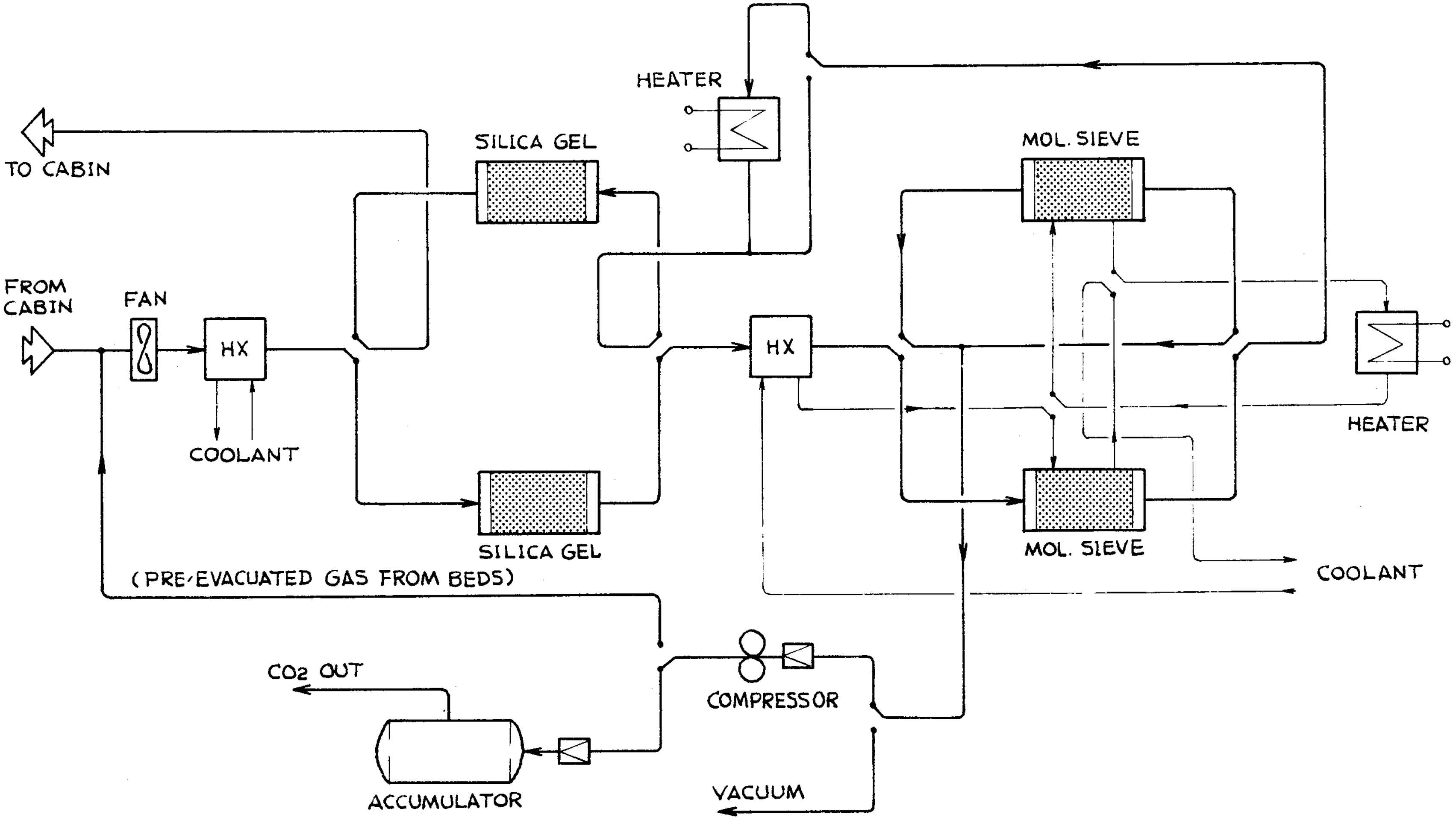


Figure 2. CO_2 Concentrator ~ Four-Beds Silica Gel/Molecular Sieve

cyclic manner for long periods. The reliability of such a system is obviously in doubt without providing redundunt piping and carrying necessary spare parts.

- a number of prototype and laboratory experiments have been carried out to delineate the limiting heat and mass transfer steps; these studies have not yet lead to a unified design technique for new systems.

- there is still no proved "best technique to desorb CO_2 from the zeolite bed. If the bed desorption temperature is low, a high vacuum must be applied. If adiabatically desorbed, a vacuum of at least 0.01 psia would be necessary. If the temperatures were 180°F or 350°F, vacuums of 0.1 and 1.0 psia might be suitable. The evacuation compressor must provide sufficient compression to store the desorbed CO_2 at about 40 - 50 psia. Thus the characteristics of desorption are closely linked to the capacity and type of CO_2 compressor.

- it is still difficult to heat and cool the beds during desorption and adsorption.

- in many cases, severe dusting occurred and filters employed downstream became plugged.

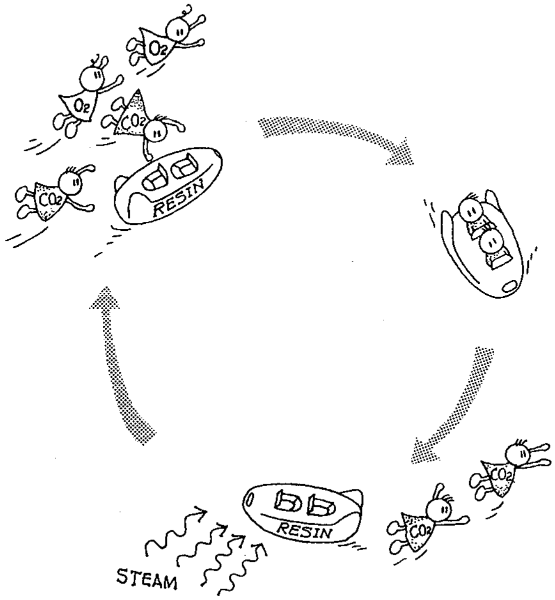
Other Adsorption Systems

A number of other types of carbon dioxide adsorption systems have been proposed. These include various metal oxide catalysts, porous metals and glass, gels and spinel catalysts.

Immobilized, solid amines have also been suggested and there is no reason to suppose that other solid organic bases might not be used either as adsorbents or as ion exchangers. For example, desirable characteristics would include:

- little or no cosorption of water since this water would have to be removed prior to CO_2 reduction. Most solid amines cosorb water. In desorption, this water is condensed and separated from the rich CO_2 stream.

- ease of regeneration. Some proposed systems use steam regeneration with the CO_2 being separated from the steam by condensation. Other designs use internal liquid heating coils with evacuation to remove the adsorbed carbon dioxide and water.



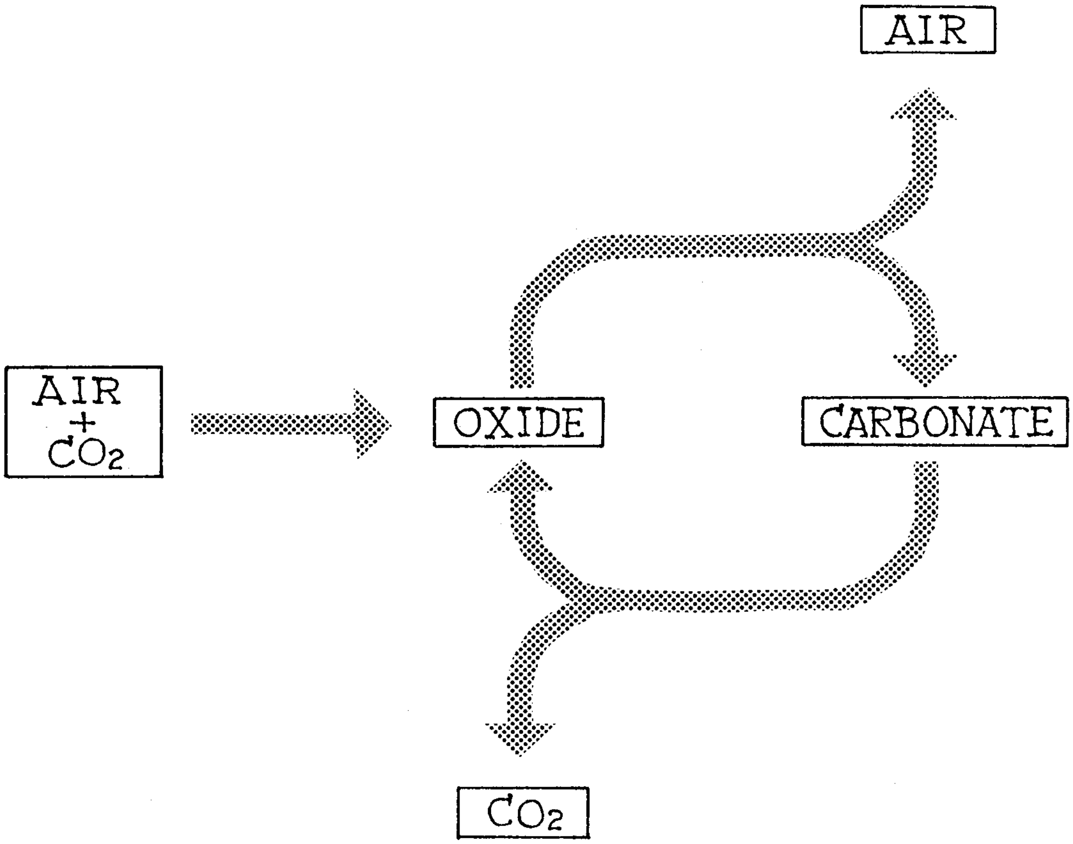
There does not seem to have been extensive research and development to optimize the operation of one or two bed systems. (One bed systems appear feasible only if desorption is sufficiently rapid to allow sorption for a large fraction of the cycle time). New adsorbents may be superior to those now available; these materials must, in addition to possessing the desirable characteristics noted above, also be long-lived, have high CO_2 but low oxygen and nitrogen capacities, produce no carry-over of chemicals to contaminate the cabin air and show little dusting. One candidate studied was charcoal. Water apparently does not affect the CO_2 adsorption, but charcoal has too low a CO_2 capacity to be considered seriously. Also, the amount of cosorbed oxygen is reputed to be rather large - in a desorption step, some efficient means would have to be devised to recover this oxygen separately from the CO_2.

Solid Chemical/Reaction-Absorption Systems

Many oxides have been suggested as CO_2 absorbers. The desirable characteristics of such oxide-carbonate systems are:

- high capacity, expressed as pounds of CO_2 removed per pound of oxide
- rapid rate of reaction between the oxide and CO_2
- low decomposition temperature of the carbonate to yield CO_2 and fresh oxide
- non-dusting characteristic of beds cycled a large number of times
- light weight, non-corrosive, non-toxic, etc.

One oxide studied in detail was Ag_2O. Low desorption temperatures are quoted. However, the rate of CO_2 removal is not very high for gases with a low CO_2 content even with a Y^{+++} catalyst.



Requirements -

- High Capacity Oxide
- Fast Rates
- Little Dusting or Solid Degradation on Cycling
- Low Decomposition Temperature
- Non-Toxic

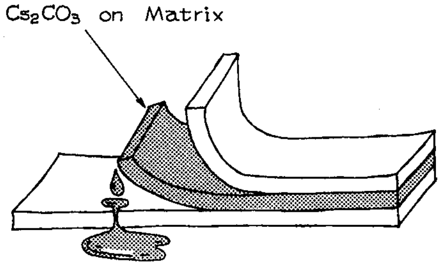
Figure 3. Oxide CO_2 Removal

The relative humidity also seems to be important. In long term desorption tests some decomposition of the carbonate occurred and metallic silver was formed.

Other oxides such as MgO, CaO, CdO, ZnO, PbO, etc. have been considered but none seem to show a weight saving or be proved reliable for many absorption and regeneration cycles. Some of the reasons why these basic oxides have not proved effective can be traced to the difficulty of cycling a solid chemical between two molecular states without destroying the crystalline structure. Also gas diffusivities within solids are low and usually only the outer skin of a solid particle is effective in a short absorption cycle.

Membrane Diffusion

A very simple and appealing technique to remove CO_2 from cabin air would involve the use of a semipermeable membrane that would pass only CO_2. Such a specific membrane does not exist. Silicone rubber will pass CO_2 preferentially, but new membranes now developed show a preference factor of some 4000 for CO_2 relative to O_2. These highly selective membranes are termed "liquid" membranes and the process



"facilitated membrane transport." The transport cells involve a thin sandwich, the center portion of which contains a matrix impregnated with a basic, aqueous solution such as cesium carbonate.

CO_2, on the cabin air side, dissolves in the basic solution and forms bicarbonate ions.

$$CO_2 + H_2O + CO_3 \rightarrow 2HCO_3^-$$

The bicarbonate ions diffuse across the membrane to the low pressure side. The reaction shown above is then reversed reforming CO_2 (gas) and carbonate ions. The latter diffuse back to the high pressure side.

As one might expect, there are several problems with bringing this concept into fruition. The operation is sensitive to the humidity on the upstream and downstream sides. Catalysts must be found that accelerate the chemical reactions. Arsenites have been used but potential toxicity problems exist. The permeability of such cells to CO_2 are only about 2×10^{-7} cm^3 (STP) - cm/sec-cm^2-cm Hg and it must be increased to avoid the necessity of using very large surface areas.

The actual construction of any large area membrane unit necessarily introduces the problem of leaks and ruptures. Instrumentation must be available to indicate where and when isolation is necessary.

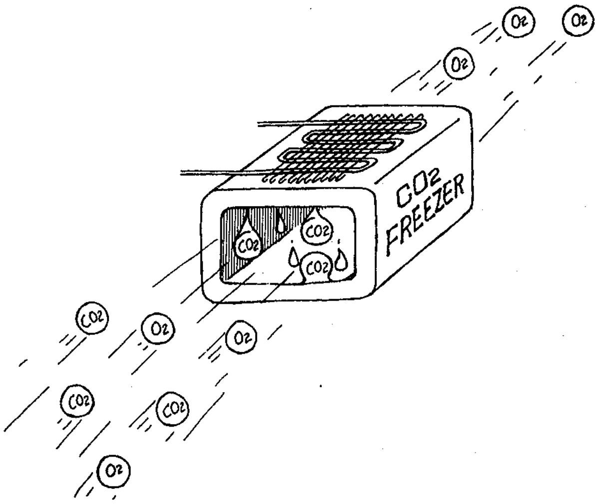
By cascading membrane systems, extremely pure CO_2 can be produced. To prepare 99^+% CO_2, two stages probably would be required with an interstage compression.

Liquid Absorption

CO_2 scrubbers in the chemical industry and for submarines use liquid absorption columns. Organic amines are often employed as the absorbent. By absorbing at a low temperature and desorbing at a higher temperature, a convenient cycle can be operated. However, such processes do not appear to have been very appealing for spacecraft use. The foremost objection usually stated is that maintenance would be difficult. This is certainly true; the repair of any system containing liquids could involve real problems in the weightless environment. Also, with present absorbents, very efficient liquid-vapor separators would be necessary to prevent any of the toxic absorbent from entering the cabin air. Finally, there is some doubt whether one could achieve the desired cabin air purity.

Freeze-Out Methods

Carbon dioxide is less volatile than oxygen or nitrogen and may be frozen out of a cabin air stream if the temperature is sufficiently reduced. To reduce the partial pressure of CO_2 to 6,4,



and 2 mm Hg, temperatures of -123°C, -127°C, and -131°C must be reached.

Water will also be frozen out during the cooling step unless some means are taken to remove it prior to the CO_2 freeze out. Dual silica-gel desiccant beds have been suggested, that is, dry cabin air from one silica-gel bed would be cooled, CO_2 frozen out, the air reheated and humidified by passing it through the alternate gel bed.

The real problems lie in developing better refrigeration systems and in achieving low power/weight/volume techniques to cool large gas flows and remove small amounts of solid CO_2. The refrigeration loads necessary to overcome inefficiencies and to condense CO_2 are not small. Radiation to space has been suggested, but rejected as impractical. Compression followed by cooling and expansion will produce a CO_2 fog which must be separated and later sublimed to storage.

Little is known about the physical or thermodynamic properties of CO_2 frosts at low temperatures. Design is hampered by the lack of data. However, there exists evidence that freeze-out methods are not competitive in a weight and power basis with most of the other techniques described earlier. Perhaps new cycles can be developed which will change this picture.

Hydrogen Depolarized Concentration Cell

A novel technique to remove CO_2 from cabin air utilizes a modified hydrogen - oxygen fuel cell. One cell of this type is shown in Figure 4. CO_2 and oxygen flow by the cathode where the following reactions occur:

$$1/2\ O_2 + H_2O + 2e \rightarrow 2OH^-$$

$$CO_2 + 2OH^- \rightarrow H_2O + CO_3^=$$

At the anode, hydrogen is oxidized and CO_2 liberated:

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e$$

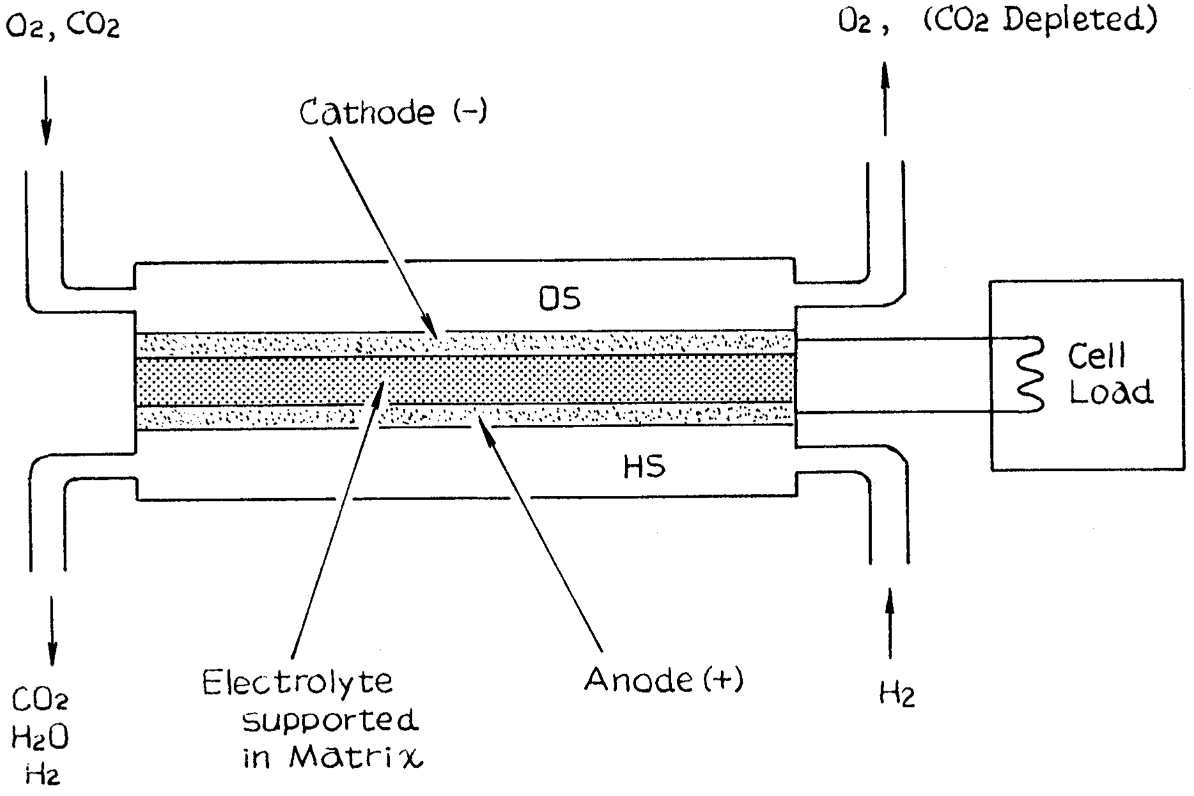
$$H_2O + CO_3^= \rightarrow CO_2 + 2OH^-$$

The overall reaction is simply written as:

$$1/2\ O_2 + H_2 + CO_2\ \text{(cathode)} \rightarrow H_2O + CO_2\ \text{(anode)}$$

The $CO_3^=$ ions are transferred across the cell under a potential and concentration gradient. Platinum fuel-cell electrodes are used and the electrolyte is potassium or cesium carbonate absorbed in an asbestos matrix. The cathode gas consists of CO_2, water, and excess hydrogen. If the water were condensed out or electrolyzed in a vapor electrolysis cell, the CO_2-H_2 stream could be adjusted in composition to provide feed to a Sabatier or Bosch reactor; alternately, the stream could be vented overboard if oxygen were not to be recovered.

This CO_2 removal technique is continuous in operation, provides power and has no moving parts. A typical unit as developed to date to remove the CO_2 produced from one man would have some 10 cells (similar to that shown in Figure 4)



$$2\,e^- + \tfrac{1}{2}O_2 + H_2O \longrightarrow 2\,OH^-$$

$$CO_2\big|_{OS} + 2\,OH^- \longrightarrow H_2O + CO_3^=$$

$$H_2 + 2\,OH^- \longrightarrow 2H_2O + 2\,e^-$$

$$H_2O + CO_3^= \longrightarrow CO_2\big|_{HS} + 2\,OH^-$$

Overall Reaction:

$$CO_2\big|_{OS} + H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O + CO_2\big|_{HS}$$

Figure 4. CO_2 Concentrator Cell

in series. Each cell has an electrode area of about 0.25 ft^2 and produces 7 amps at 0.5 v. About 0.5 moles O_2/CO_2 and 1.75 moles H_2/CO_2 are required.

Considerably more testing is necessary to determine the suitability of this technique. Care must be taken to prevent the cells from becoming too dry or overheating. Optimization of the matrix material has not been made; also the use of reaction catalysts such as arsenite ions to increase the CO_2+OH^- reactions might prove interesting. In many ways, this removal scheme resembles the membrane facilitated transport method except that here CO_2 may be moved from a low to a higher partial pressure, whereas, in the simple membrane scheme, the partial pressure of CO_2 on the downstream side must always be lower.

Carbonation Cells

Electrochemical concentration cells may also be used to separate CO_2 from oxygen. One arrangement is shown in Figure 5. Cabin air containing CO_2 is blown by the cathode in Stage I. The electrolyte is basic, i.e., a carbonate salt such as cesium carbonate, and the following reactions occur:

$$1/2\ O_2 + H_2O + 2e \rightarrow 2OH^- \quad \text{cathode}$$

$$CO_2 + 2OH^- \rightarrow H_2O + CO_3^= \quad \text{catholyte}$$

The carbonate (and some OH^- and HCO_3^-) are transferred to the anode by an electrical and concentration gradient where oxygen

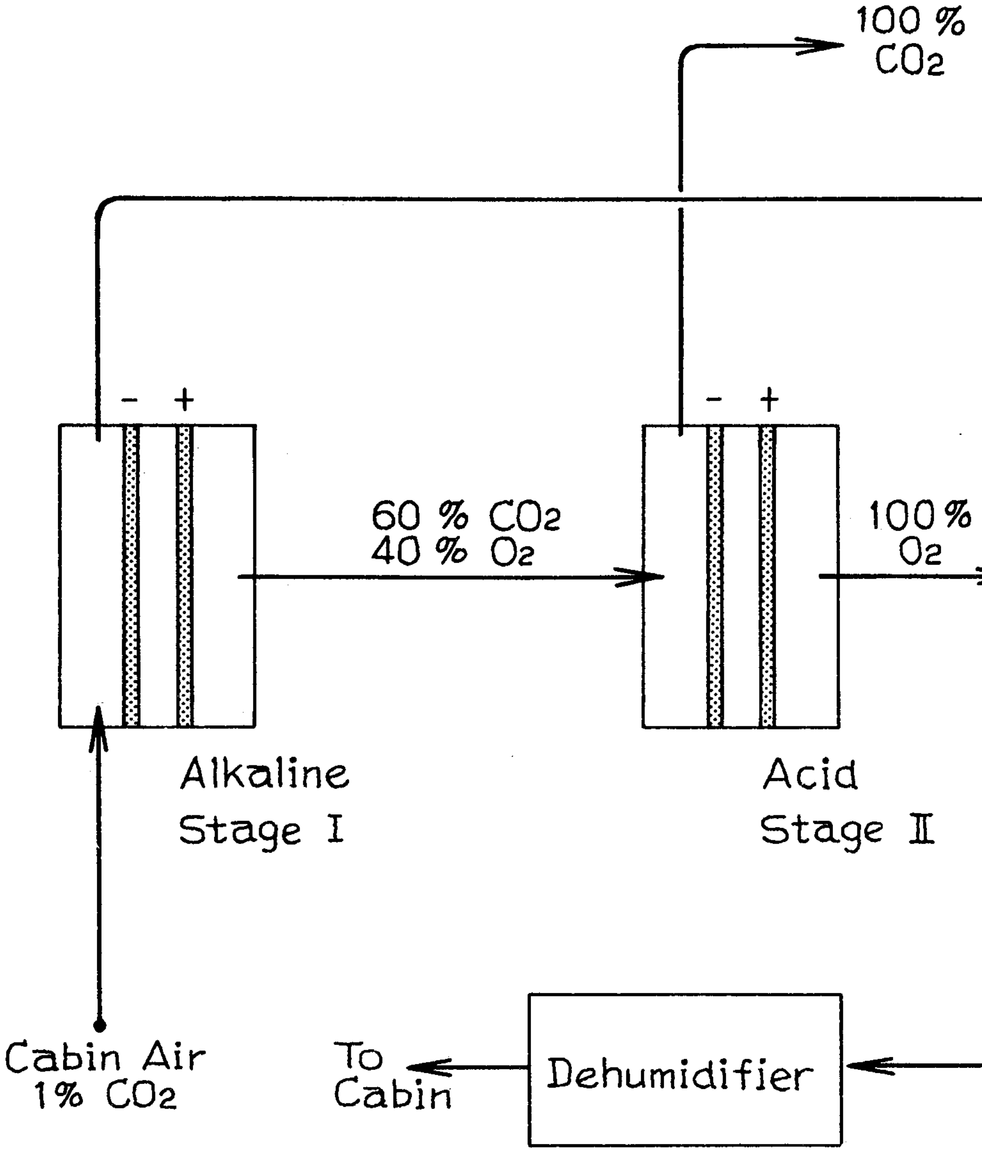


Figure 5

Two-Stage Carbonation Cell

and CO_2 are evolved.

$$2OH^- \rightarrow 1/2\ O_2 + H_2O + 2e \qquad \text{anode}$$

$$H_2O + CO_3^= \rightarrow CO_2 + 2OH^- \qquad \text{anolyte}$$

The overall reaction is simply:

$$1/2\ O_2\ (U) + CO_2\ (U) \rightarrow 1/2\ O_2\ (D) + CO_2\ (D)$$

where U and D represent conditions upstream and downstream in Stage I. The ratio of the various species transported depends upon the partial pressures of both gases at the cathode, the temperatures, the current density, and the cathode gas flow rate. Considerable enrichment of CO_2 results. Results indicate that with 0.1% CO_2 in the cabin air, the CO_2 concentration downstream of Stage I is in the range of 40-50% CO_2; CO_2 concentration in the anode gas increases with an increase in CO_2 in the cabin air. For a 1% CO_2 in the cathode gas, there is about 60% CO_2 in the anode gas.

The matrix for Stage I is asbestos impregnated with the $CO_3^=$ salt, and operating temperatures are near 175°F. The pressure of the anode gas may actually exceed the cathode gas since the device may act as a pump.

The Nernst voltage required for such a cell (Stage I) is given by:

$$E = -(RT/2F)\ \ln \left[(P_{O_2})_D^{1/2}\ (P_{CO_2})_D \ /\ (P_{O_2}{}^{1/2})_U\ (P_{CO_2})_U \right]$$

To this value must be added any polarization potential; also

E must be maintained below about 1.5 V to prevent electrolysis of the water.

The current flow is more difficult to delineate. The simple anode reactions shown above might better be expressed as follows:

$$2OH^- \rightarrow 1/2\ O_2 + H_2O + 2e$$

$$CO_3^= \rightarrow CO_2 + 1/2\ O_2 + 2e$$

$$2HCO_3^- \rightarrow 2CO_2 + 1/2\ O_2 + H_2O + 2e$$

These are the possible discharge mechanisms. If only the first were applicable, two Faradays would produce 1/2 mole of oxygen or (22,400/2)/(96,500x2) = 0.058 ml O_2 (STP) per amp-sec. In the second, 1 mole of CO_2 and 1/2 mole of O_2 are formed for each two Faradays, thus the total anode gas flow would be (3)(0.058) = 0.174 ml gas (STP) per amp-sec. Similarily for the third reaction, the rate is (5)(0.058) = 0.29 ml gas (STP)/amp-sec. Actual measured values for the gas rate vary between these extremes as shown in Figure 6. Thus the ion transfer mechanism depends strongly upon the cathode gas composition.

The rich CO_2 stream from Stage I is passed over the cathode in Stage II. This stage employs an electrolyte of aqueous sulfuric or phosphoric acid on asbestos. CO_2 does not dissolve in the acid. The cathode reaction is:

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O$$

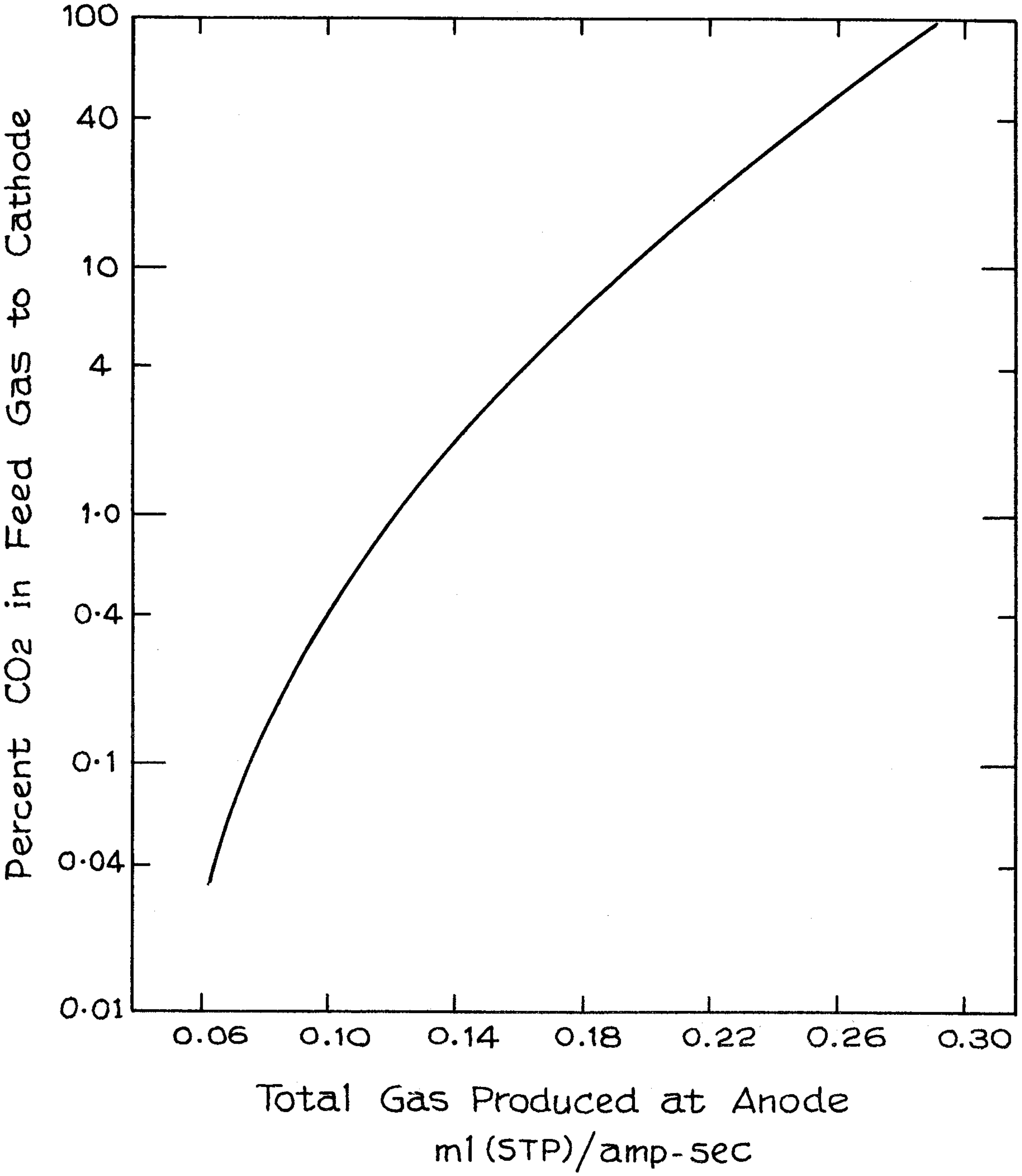


Figure 6

Effect of CO_2 Concentration in Feed Gas on Anode Gas Production in Carbonation Cell and at the anode:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e$$

This stage operates up to 200°F. The cathode gas exiting from Stage II has had most of the O_2 removed and may be stored for later use in a reduction process.

The concept is attractive and simple. Insufficient data are available to indicate the reliability for long times; also, if there is a high power penalty, the adjusted weight of this device may easily exceed that of other systems which do not require large amounts of electrical power.

Other Electrochemical CO_2 Concentrators

A number of other different techniques have been proposed to separate CO_2 from cabin air in electrochemical devices other than the hydrogen depolarized concentration cell and carbonation cell described above. Only one other technique is covered here to indicate a somewhat different scheme. Figure 7 shows schematically a combined electrolysis and CO_2 removal cell. This cell has four compartments; each contains macroporous ion-exchange packing to provide an electrically conductive path while still permitting gas and liquid flow. Separation between compartments is by ion-exchange membranes. Each compartment is on the order of 0.1-in. thick.

In the cathode compartment water is fed and electrolyzed to H_2 and OH^- ions. These ions migrate under a concentration

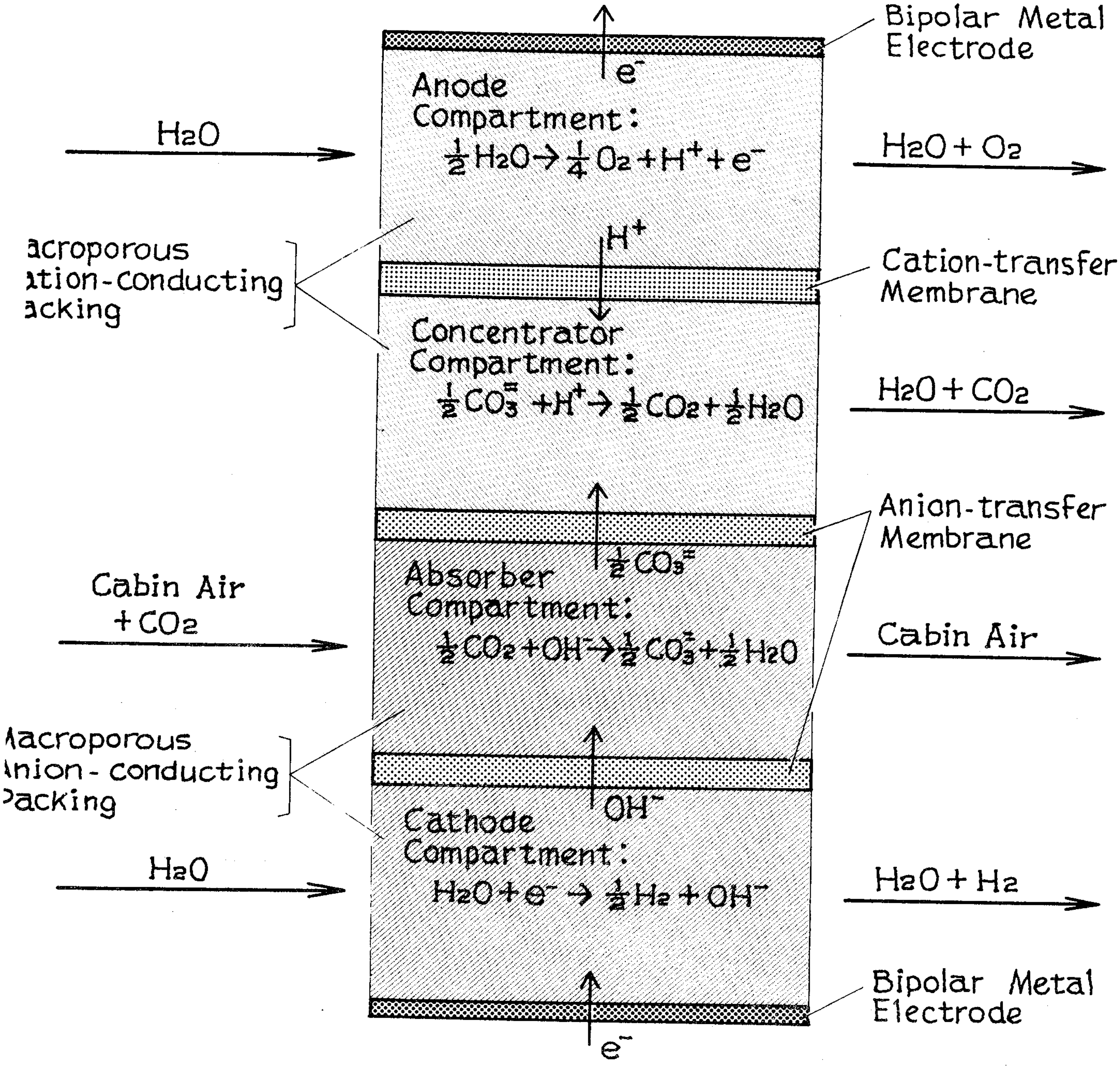


Figure 7

Electrolysis and Carbon Dioxide Removal Unit and electrical gradient across an anion-exchange membrane to the absorber where some react with CO_2 in cabin air to form $CO_3^=$ and HCO_3^-. Ion migration toward the anode is then by carbonate, bicarbonate, and hydroxyl ions; these ions are neutralized in the concentration compartment by H^+ ions migrating from the anode. It is here that CO_2 and H_2O are liberated.

Multiple repeating units as shown in Figure 7 are employed. Each Faraday of current may transfer 0.5 moles CO_2 if all ion transfer is $CO_3^=$, zero moles if by OH^-, and 1 mole if by HCO_3^-. Experiments indicate that about 0.55 moles of CO_2 are transported per Faraday. Also this Faraday produces 0.25 moles O_2 and 0.5 moles H_2 at the anode and cathode.

As in other electrochemical devices of this and similar types, the concept is sound and the principle uncertainty lies in developing a cell with high reliability, low weight and volume, and with high efficiency. The power penalty may also be severe and the adjusted weight may well be large.

Carbon Dioxide Removal in Extravehicular Missions

For astronauts involved in extravehicular activities (EVA) there must be positive ways to prevent the concentration of carbon dioxide from increasing beyond a few mm Hg partial pressure. The metabolic rate of an astronaut engaged in EVA may vary widely. Whereas for the average space cabin requirements run about 2.25 lb CO_2/day-man (0.094 lb CO_2/hr-man), for EVA activities, CO_2 generation rates may average as high as 0.5 lb CO_2/hr-man with peaks to 1.0.

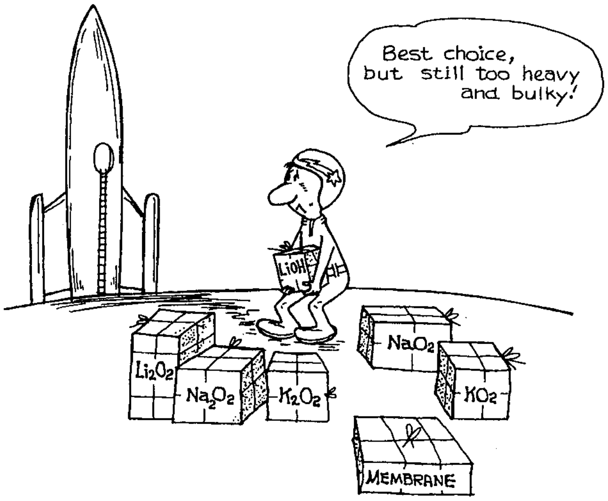
The small oxygen mass present in the circulation loop of an astronaut's suit, permits the partial pressure of CO_2 to increase rapidly, therefore any removal system must be responsive to this rapid rise.

In reality, what this means is that one usually overdesigns the carbon dioxide removal device to take care of the highest expected metabolic rate; it then should work quite satisfactorily for lower rates. This design philosophy produces a safe design but often one with a large mass and volume.

There does not appear to be a severe problem for short EVA. LiOH - charcoal beds work well, if not overloaded with water, and respond rapidly to changes in the partial pressure of CO_2. Operating units have a CO_2 capacity of about 0.8 g CO_2/ g LiOH (theoretical value is 0.92). The package is, however, bulky and constitutes a sizeable fraction of the EVA life support systems.

Attempts have been made to use Li_2O rather than LiOH but it appears that the oxide must first be hydrated to the hydroxide before it becomes a good CO_2 absorbent. Thus the reactivity becomes sensitive to the humidity and required H_2O/CO_2 ratios of 1.5 to 2 have been mentioned. Also crusts of Li_2CO_3 are said to block access to the particle interior.

No other oxides seem practical. Membranes thus far are too large and bulky for CO_2 removal. The superoxides and peroxides may be useful in certain situations but as yet none appear to have any real advantages over stored oxygen-lithium hydroxide. Work is still continuing on the Li_2O_2 system but problems have been encountered in liberating oxygen even though CO_2 and water are absorbed.



What will be needed in the future will be better CO_2 removal system for long EVA. For mission times greater than a few hours, the LiOH required becomes too large and more efficient, smaller volume light weight portable CO_2 removal systems will become necessary. Perhaps, as has been recently suggested, a continuous purge stream may even be preferable!

Recommendations for University Research

- Delineate new techniques to design and operate molecular sieve CO_2 adsorption beds to enhance heating and cooling during desorption and adsorption. Can thin layers be employed effectively on heat exchanger walls; can thermoelectric devices be employed?

- Define the advantages for operating sieve beds in an optimum cyclic mode as determined from a parametric pumping analysis and suggest techniques for implementation.

- Develop new long-life CO_2 absorbents and adsorbents which are insensitive to water, O_2 and N_2 and which can be easily regenerated.

- Define the adsorptive capacity of commercial molecular sieves to typical trace contaminants found in space cabin atmospheres; also define the ease of removing such impurities in typical heating/evacuation regeneration steps.

- Suggest new, novel and effective ways to make and use membranes which would separate CO_2 from an O_2 - N_2 stream.

- Suggest better techniques to remove and vent CO_2 in portable life support systems.

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III. RECOVERY OF OXYGEN FROM CARBON DIOXIDE

As noted earlier, each astronaut, with normal metabolic activity, exhales about 2.25 lbs CO_2/day. Of this amount, slightly over 1.63 lbs are oxygen. For long-duration flights, it is necessary to recover and recirculate this oxygen. In most oxygen recovery systems that have been proposed, solid carbon is a residue. In one process, however, the carbon is rejected in methane, CH_4. Stored hydrogen is then necessary to replace that lost in the rejected methane.

Before describing the more promising processes in any detail, some general observations may be useful.

We start by considering the direct reaction:

$$CO_2 \rightarrow C(s) + O_2$$

Equilibrium thermodynamics indicates that this reaction is not favored except at very high temperatures - temperatures in the range of 10,000°F will produce only some 0.04% decomposition at one atmosphere.

Several techniques have utilized hydrogen as an additional reactant to provide a set of sequential reactions each with a more favorable equilibrium. For example, suppose in the reaction as shown above, hydrogen were added. Most certainly, free oxygen would not appear but the oxygen-containing product would instead be water. Likewise, depending upon conditions, the carbon may or may not be combined with hydrogen. In the Sabatier reaction, methane is produced. In the Bosch, elemental carbon. Different catalysts and temperatures are employed in these two reactions as described later. At present, it is sufficient to note that a general method to decompose CO_2 is to use elemental hydrogen to extract the oxygen. Presumably in such a method, one would expect to obtain water, carbon and/or hydrocarbons, and perhaps CO in addition to unreacted CO_2 and H_2. Thermodynamics can specify the maximum yield for any assumed product -- but the actual product distribution will be a very strong function of the temperature, pressure and catalyst employed.

Besides the hydrogen induced CO_2 decomposition, one might note that at high, but not unreasonable temperatures, and if the oxygen could be removed from the reaction zone, the following reaction may be significant:

$$CO_2 \rightarrow 1/2\ O_2 + CO$$

The carbon oxides could then be sent to a different reactor, at lower temperatures, where the reaction

$$2CO \rightarrow CO_2 + C$$

is favored. Separation of carbon occurs in this reactor and recirculation of the residual gases to the oxygen removal zone would follow. This process is under development in the solid electrolyte process.

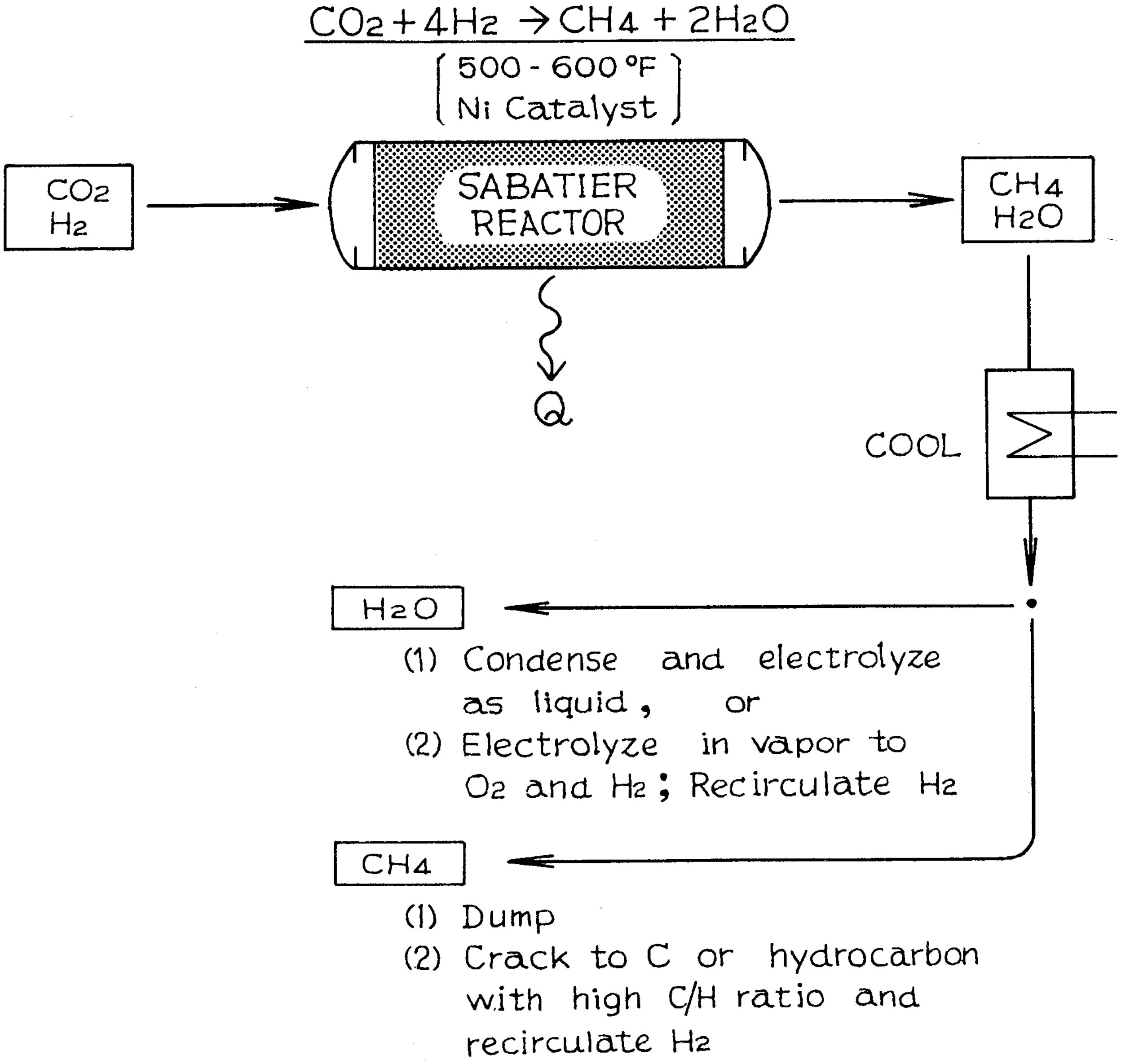
Better oxygen recovery processes still need to be developed. All those suggested and under development require one or more high temperature reactions. All components are, therefore, subjected to operating conditions which increase the likelihood of failure; maintenance is also quite difficult and access is limited. All but one process requires periodic shutdown of one or more parts of the process for removal of accumulated solid carbon. These problems and others will become obvious when individual techniques are described. Following these descriptions, the processes are summarized and recommendations made. No photosynthetic or other biologically based methods are covered here as these do not appear to be attractive for spacecraft oxygen recovery systems in the immediate or near future.

Sabatier Process

The reaction scheme:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

is referred to as the Sabatier process. It is exothermic to the extent of about 1640 Btu/lb CO_2, thus methane formation is favored at low temperatures. The process scheme is shown in Figure 1 and an equilibrium conversion curve is shown in Figure 2. Reaction temperatures range between 200-to-850°F. The lowest values have been reported on powdered ruthenium



H_2O

(1) Condense and electrolyze as liquid, or

(2) Electrolyze in vapor to O_2 and H_2; Recirculate H_2

CH_4

(1) Dump

(2) Crack to C or hydrocarbon with high C/H ratio and recirculate H_2

Figure 1

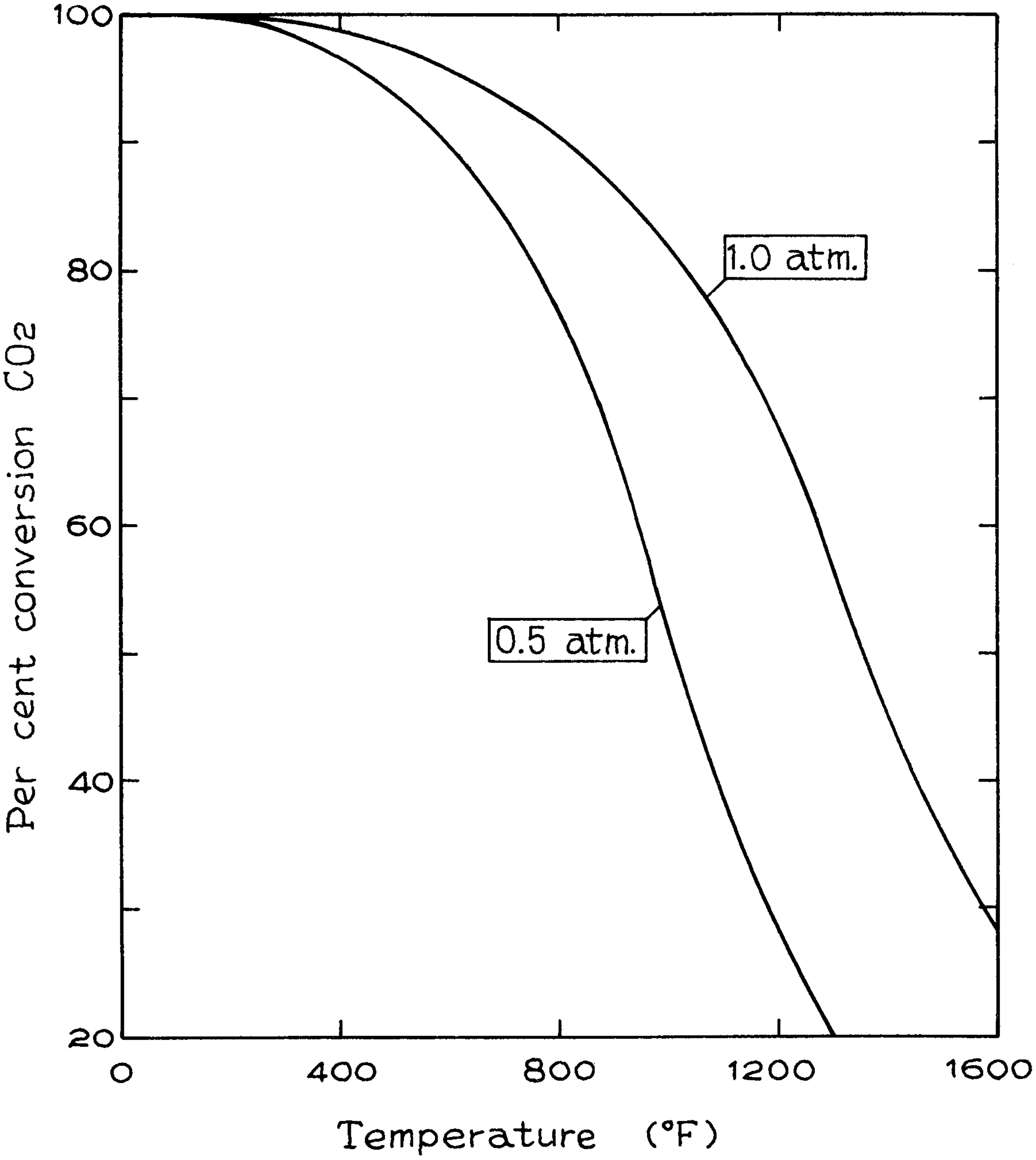


Figure 2

Per cent theoretical conversion of Sabatier reaction catalysts. Most studies have, however, employed supported nickel catalysts and have operated between 500-600°F. There may be large temperature gradients in the reactor if not insulated carefully so as to minimize them.

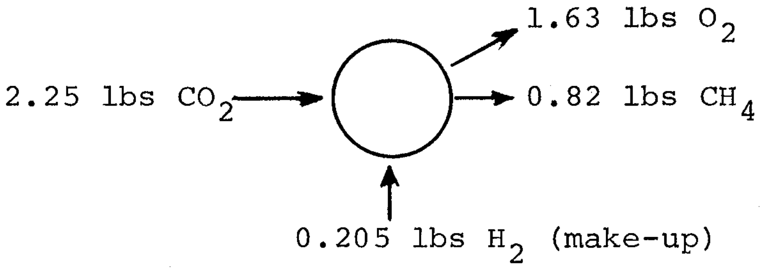
Yields of methane exceed 90% in a well designed bed. By-products such as carbon or CO are minimized when the H_2/CO_2 feed ratios slightly exceed stoichiometric values. However, one often operates with a feed somewhat lower than the stoichiometric H_2/CO_2 ratio to increase the efficiency of hydrogen utilization.

The limiting step in the process appears to be the surface reaction; in fact, rather large rate increases have been reported for promoted nickel catalysts. Suggested promoters are ThO_2 and BeO. Such promotors have not been used in recent studies and perhaps deserve some consideration. Materials such as ZnO have, however, been employed prior to the reactor to remove trace sulfur impurities and thus have prolonged the catalyst life.

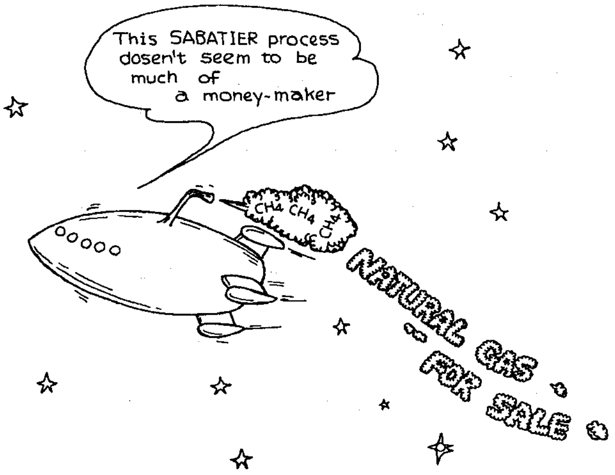
Prototype systems have been operated successfully for long times with few problems of catalyst deactivation. Except for some additional work using promotors, there is little further research needed for this process.

The water that is formed in the reaction must be electrolyzed as a vapor, condensed out as a liquid, or absorbed on a desiccant. Eventually, all or most of the water is electrolyzed to form oxygen and hydrogen. The former is fed back into the cabin air supply while the latter is recycled to the inlet of the Sabatier reactor, where fresh hydrogen may be added.

The foremost problem in this process is the disposition of the methane. The simplest solution is, of course, to vent it overboard. This conveniently solves the carbon disposal problem that plagues other processes. However, in so doing, there is a loss of hydrogen. In terms of a man-day,



This simplified point of view assumes 100% efficiency in the water electrolysis step. The key item to note is that 0.205 lbs of hydrogen are lost each man-day. This hydrogen would have to be carried from earth as elemental hydrogen, water, ammonia or in another chemical form, or resupplied during the mission. Because of the hydrogen requirement, it has been proposed that the methane be broken-down to release the bound hydrogen. This methane cracking reaction is well known, but, reasonable yields are only obtained at high temperatures (circa 2000°F). A soft, hard-to-collect carbon is believed formed which degrades the catalyst emploed. Also, at these high temperatures, the power consumption is large.



Other suggestions entail partial cracking processes to produce acetylene or ethylene. These gases have a lower H/C ratio and less hydrogen would be lost if they, rather than methane, were vented overboard. However, partial cracking schemes are very difficult to carry out. For acetylene production, for example, very high temperatures and short residence times are required, and an arc or plasma flame is necessary. Yields are low and an extremely rapid quench of the acetylene-methane-hydrogen gas mixture is necessary to prevent further reactions.

New ideas would be welcome in how to recover all or some of the hydrogen or the methane product. Could cryogenic glow discharges be used to form acetylene or ethylene? Could ozone induced methane cracking be used? Can CH_4 be reacted with fresh CO_2 to produce carbon and water without forming CO and H_2 in any appreciable amounts? These and other suggestions have received only limited study.

Bosch Process

Another process scheme using a hydrogen reaction with carbon dioxide involves the Bosch process as shown in Figure 3.

$$CO_2 + 2H_2 \rightarrow C + 2H_2O$$

The reactants are the same as those in the Sabatier process; however, by using temperatures near 1200°F with an iron catalyst,

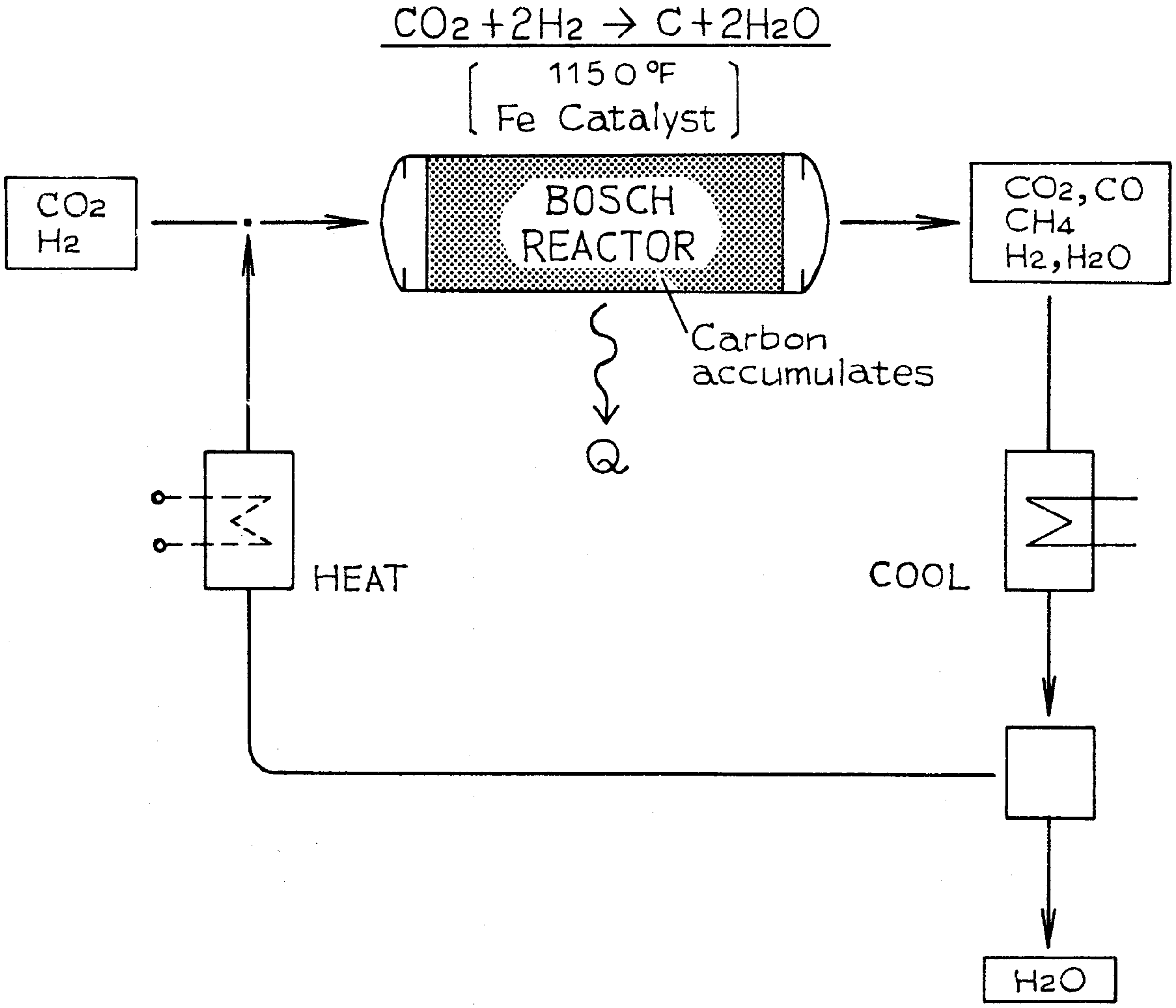

CO2 + 2H2 → C + 2H2O
1150 °F
Fe Catalyst
CO2
H2
BOSCH
REACTOR
Carbon
accumulates
Q
CO2, CO
CH4
H2, H2O
HEAT
COOL
H2O

Figure 3

methane formation is inhibited and solid carbon is deposited directly on the catalyst. The yield per pass is only a few per cent thus recycle ratios of 10 to 20 are necessary. In the recycled stream, water is removed and fresh CO_2 and H_2 added. Water may be electrolyzed in the vapor phase or cooled and condensed with the concomitant problems associated with a zero-gravity-vapor-liquid separator - or it may be removed by desicant beds which are later desorbed with a purge stream (usually of cabin air). In any case, the recycle stream must be cooled well below 1200°F and then later reheated to this temperature before flowing into the reactor. A compressor in the recycle loop is also necessary.

The Bosch scheme is simple. Nothing is vented (except an occasional purge of accumulated inert gases); everything continues to recycle until it is removed as solid carbon (in the reactor) or water (in the recycle circuit). CO and CH_4 concentrations reach a steady state value in the recycle stream. Leakage could, however, be hazardous since there is a reasonable concentration of CO in the cycle.

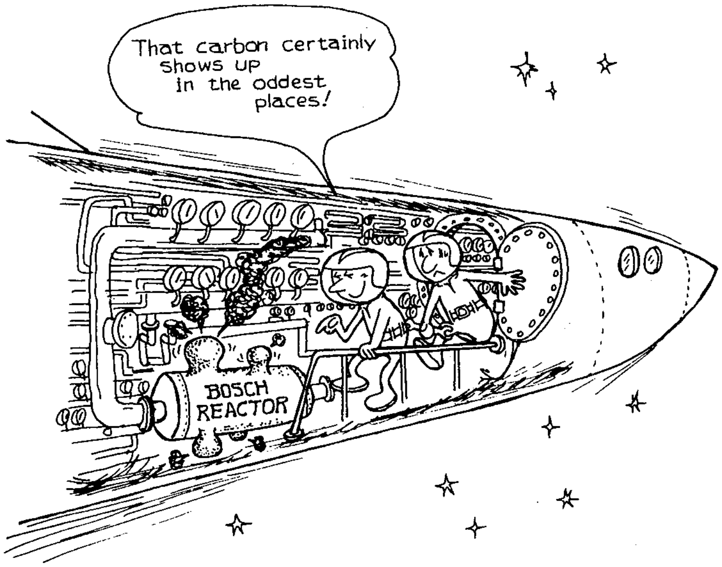
In the reaction system between CO_2 and H_2, at temperatures near 1000-1200°F, the only significant species that exist are CO_2, H_2, CH_4, CO, H_2O and C. These components are related by the reactions:

$$CO_2 + 2H_2 \rightleftarrows 2H_2O + C$$

$$CO_2 + C \rightleftarrows 2CO$$

$$2H_2 + C \rightleftarrows CH_4$$

As written, all reactions are exothermic; the first, for example, yields about 920 Btu/lb of CO_2. Equilibrium yields are a function of temperature, pressure, and CO_2/H_2 feed ratios. A typical computer generated curve is presented in Figure 4 where equilibrium product compositions are shown as a function of the O/H ratio of mixture. The water yield is seen to maximize at an O/H ratio of about 0.5, i.e., at the stoichiometric ratio for the first (Bosch) reaction in the sequence shown above.



The main problem with the Bosch process is the carbon containment. The initial catalyst used is usually iron in the form of steel wool. Carbon soon deposits on this wool and it is believed, but not substantiated, that the deposited carbon then acts to some degree as a catalyst. The carbon has been reported to be of a hard, granular type which exhibits magnetic properties. Thus, there may well be some iron present in the deposit either free or as a carbide. The magnetic properties have lead to suggestions for removal or containment by a magnetic field; this, as yet, has not proved practicable.

One must be very careful to eliminate any iron (or other catalyst) from the portions of the reactor where one wishes to avoid solid carbon or in auxiliary heat exchangers, pipes, etc.

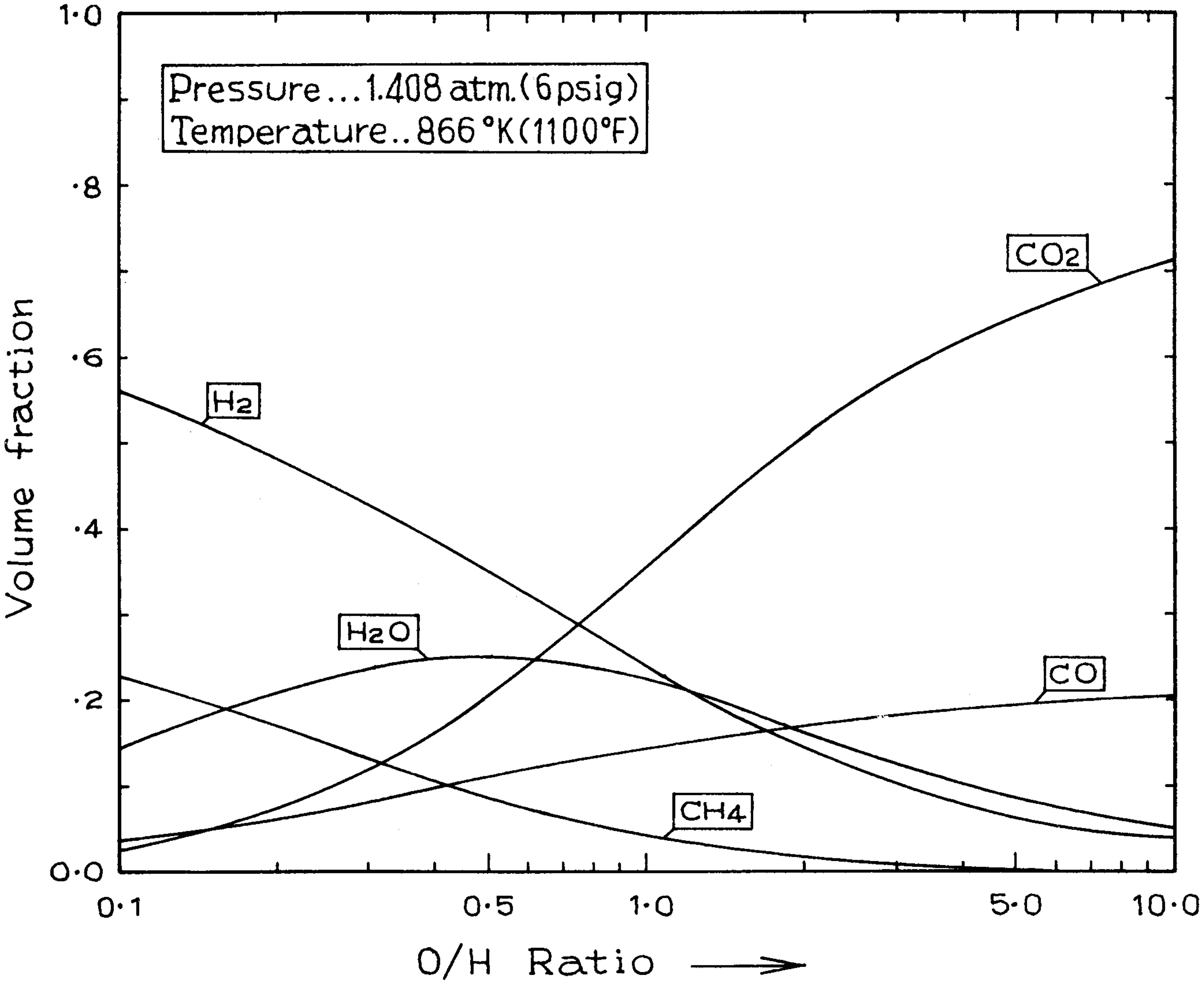


Figure 4

Equilibrium volume fraction as a function of O/H Ratio that are at high temperatures. Copper and nickel are apparently suitable, but stainless steel is not. Also, one must contain the carbon if it should prove to be a catalyst. That is, if carbon were to be allowed to deposit in the high temperature zone, then it may act as an auto-catalytic site for further reactions and eventually lead to plugging at that point.

Solid Electrolyte Process

In the solid electrolyte process, advantage is taken of the fact that oxygen anions will diffuse through certain ceramic oxides at high temperatures. Diffusion cells consist of thin ceramic tubes or discs made from materials such as ZrO_2-Y_2O_3 in a 9-1 mole ratio, or ZrO_2 and CaO in an 8.5-to-1.5 ratio. The feed gases, CO_2 and recycle CO, are heated to about 1600 to 1800°F and fed to one side of the solid electrolyte. Both sides of the electrolyte are coated with a metal such as platinum and connected electrically so that cathode reactions such as the following occur:

$$CO_2 \rightarrow CO + 1/2\ O_2$$

$$1/2\ O_2 + 2e \rightarrow O^{=}$$

Oxygen diffuses across the electrolyte by ion conduction; at the anode the oxidation step occurs.

$$O^{=} \rightarrow 1/2\ O_2 + 2e$$

The oxygen product gas is then recirculated to the cabin. This high temperature electrolysis scheme is shown in Figure 5.

Unreacted CO_2 and the CO leave the cell, are cooled to 1000°F, and enter another reactor where some of the CO reacts as follows:

$$2CO \rightarrow C + CO_2$$

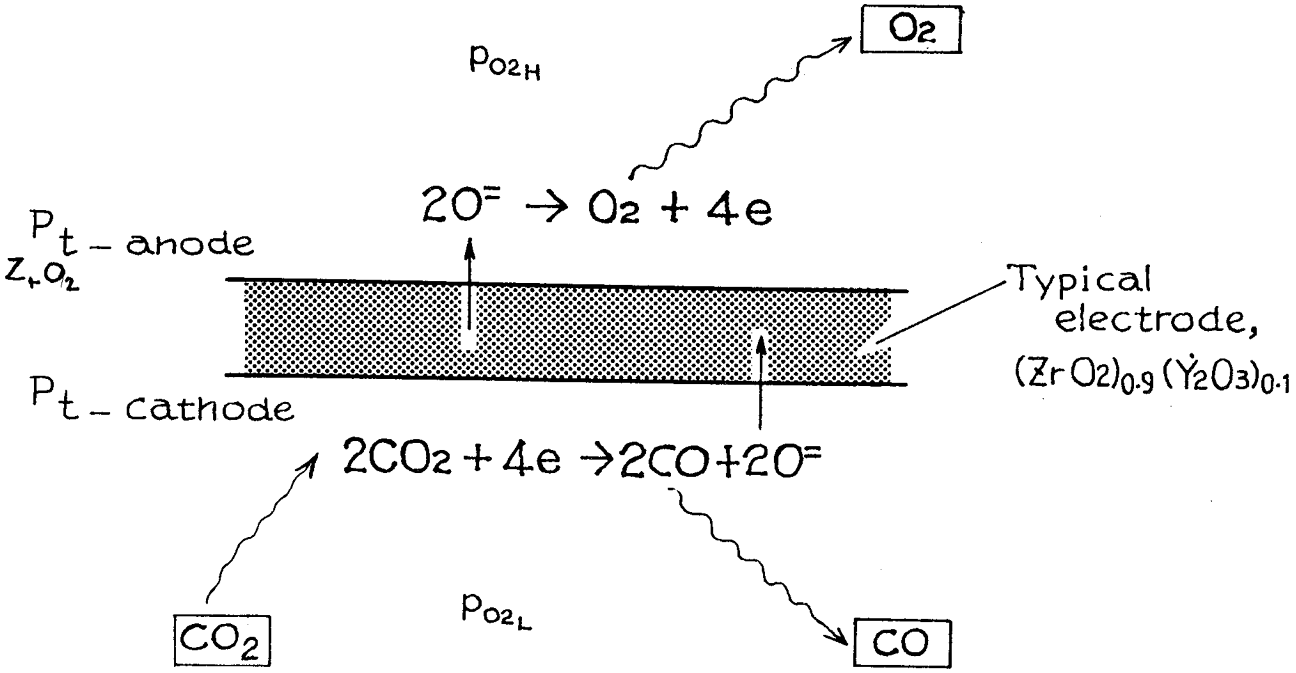
Solid carbon deposits and the gases are removed, reheated, and recycled to the cell inlet. In the CO reactor, nickel, iron or cobalt catalysts are ordinarily used to accelerate the reaction.

The process is still in a relatively early stage of development. Some of the more important problem areas are:

- high power requirements. The electrolysis current is a function of the oxygen partial pressure on both sides of the electrolyte. As the partial pressure of oxygen at the cathode is low, to reduce the required voltage, the oxygen partial pressure on the inside (anode) must also be kept low. This requires a sweep gas or a high vacuum on the anode side. Even more important, however, are power losses resulting from electronic conduction and from polarization.

- integrity of cells. To reduce power losses, the cell walls are usually thin. The ceramic is brittle and difficult to fabricate into large area cells. Yet leakage must be avoided to prevent CO from entering the cabin air. Seals must be proved leak-tight and reliable.

- new ceramic formulae would be very desirable to increase



Theoretical voltage

$$\xi = \frac{RT}{4\mathcal{F}} \ln \frac{p_{O_{2H}}}{p_{O_{2L}}}$$

Figure 5

Solid Electrolyte process

ion conduction rates with low power losses. High current densities are also desirable, but there is some evidence that if the rates become too large, the current efficiency decreases and some of the solid oxide may electrolyze. The ceramic must also be stable with respect to reduction by CO at the high temperatures.

- carbon deposition in the diffusion cell or connecting piping must be avoided, i.e., the thermodynamics and reaction rates of the $CO \rightarrow CO_2 + C$ reaction must be known throughout the system under different operating modes, start-up, shut-down, or during malfunctions.
- the carbon deposition reactor must be designed in such a way so as to contain the carbon and to show a reasonably high yield per pass.

The method also has a real potential advantage. Water may also be electrolyzed to H_2 and O_2 simultaneously with the CO_2*. With hydrogen in the gas, the low temperature reactor then functions to some degree as a Bosch reactor, i.e., reactions of the type shown below would undoubtedly occur.

$$CO_2 + 2H_2 \rightarrow 2H_2O + C$$

$$CO + H_2 \rightarrow 2H_2O + C$$

This reaction scheme then suggests that the overall method resembles a Bosch process with vapor phase electrolysis. In the

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*Recent tests with a $(ZrO_2)_{0.85}$ $(CaO)_{0.15}$ cell has shown that small quantities of water are <u>necessary</u> to obtain high current efficiencies.

solid electrolyte scheme, electrolysis is carried out at very high temperatures, whereas in normal vapor phase electrolysis (to be discussed later), the operation is at room temperature or slightly above. Considerably less water would, however, have to be electrolyzed in the solid electrolyte process, but still the hydrogen must be removed. It has been proved that hydrogen can be removed continuously by diffusing it through a hot palladium alloy tube at about the same temperature as the electrolysis reaction, i.e., 1600-1800°F. This high temperature is necessary to prevent carbon deposition on the palladium metal.

This oxygen recovery process is still in the early developmental phase. Certainly it shows great potential if long time leak-free operation can be demonstrated, if the power requirements can be held low, and if the carbon and hydrogen can be removed without any system degradation.

Electrolysis of Carbon Dioxide in a Fused Salt Bath

A process which does not require a separate carbon dioxide concentration step involves the dissolution of carbon dioxide from a dry air stream in a molten salt and subsequent electrolysis to elemental carbon and oxygen. The process is shown schematically in Figure 6. The chemistry and electrochemistry of the process are quite complex. The fused salt usually comprises lithium carbonate with lithium chloride, or other halides added to reduce the melting point. The lithium carbonate ionizes and the lithium

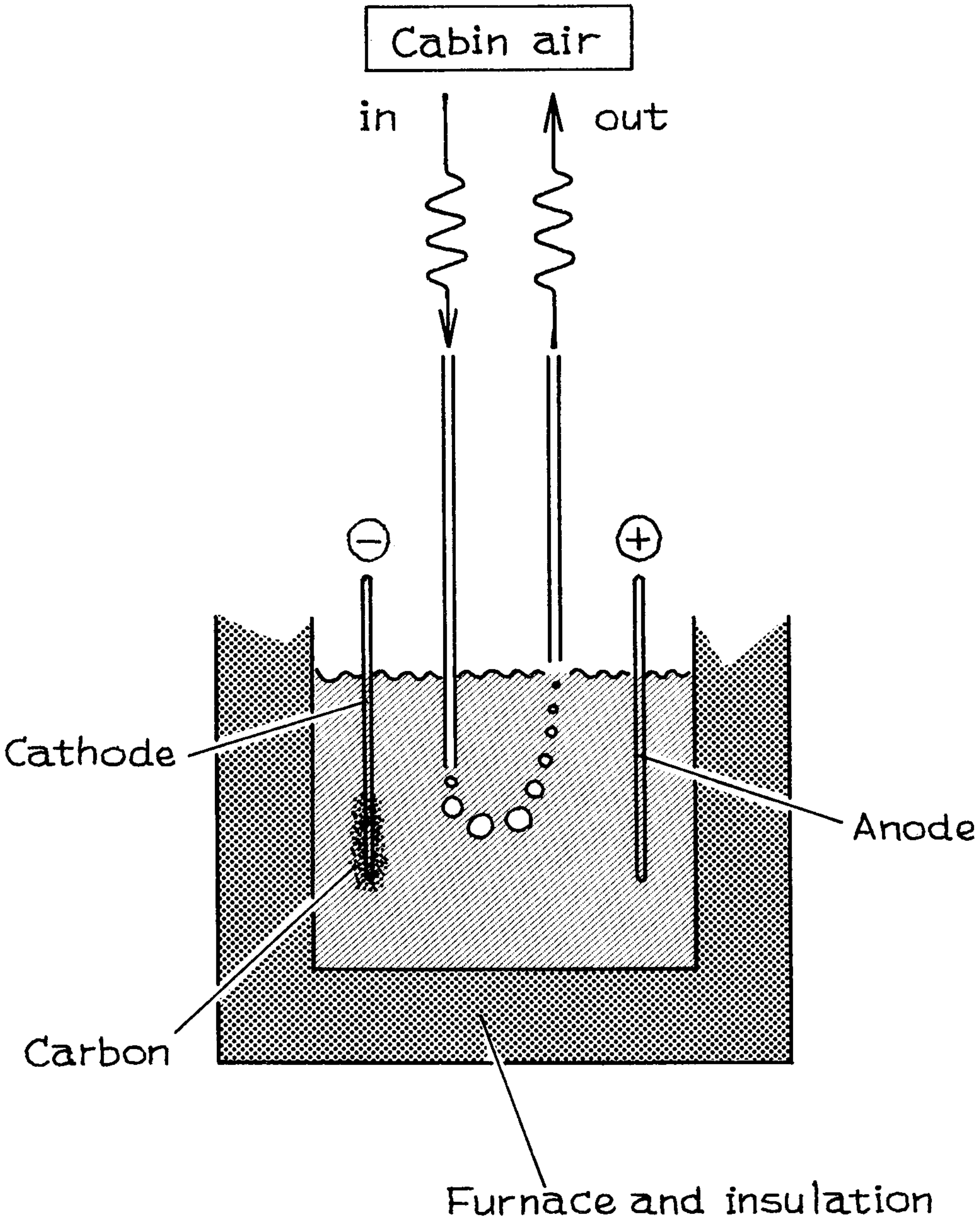


Figure 6

Fused salt/ Carbon dioxide Electrolysis

ion is reduced at the cathode to form lithium metal.

$$Li^+ \rightarrow Li - e^-$$

Elemental lithium then reacts with CO_2 in the immediate vicinity of the cathode to form carbon and probably Li_2O or Li^+ and $O^=$.

$$4Li + CO_2 \rightarrow 4Li + C + O^=$$

$$\text{or } 2Li_2O + C$$

The carbon appears to collect as a hard deposit on the cathode.

The anode reactions are not known with much certainty. It has been postulated that either $O^=$ is oxidized to O_2 or $CO_3^=$ to CO_2 and O_2. Alternatively, chloride ions (from added LiCl) could be oxidized to form chlorine. This chlorine gas would then chemically oxidize $O^=$ or $CO_3^=$ near the electrode surface to release oxygen. The free oxygen is returned to the cabin.

The temperature of the bath is maintained near 640°C. At this high temperature and with the corrosive nature of the bath, the service life of the anode and other cell construction materials is often short. Noble metal anodes have proved best, but even here some anode sludge is formed. Anode dissolution is apparently lessened when the oxide ion activity is high but dissolution rates are increased by higher halide concentrations.

Potential problems with this cell are:

- reaction of CO_2 with cathodic carbon may form CO. This reaction would lead to contamination of the cabin air.

- short or long term transients may result from low mass transfer rates in transferring CO_2 to the cathode and $CO_3^=$ or $O^=$ to the anode. Stirring or agitation may prove necessary to reduce outlet CO_2 levels sufficiently.

- there may be contamination of the cathode carbon deposit with fused salt. This leads to a less dense, more difficult to handle residue.

- water levels in the entering gas must be held to below a -15°F (probably nearer to -40 or -50°F) dew point to prevent hydroxide levels from becoming large. Water contamination will lead to the formation of CH_4. Elimination of water requires a dehydration step before cabin air is heated and contacted with the bath. In fact, the concentrations of both water and CO_2 in the inlet gas appears to be critical. A general formulation of the problem might indicate that:

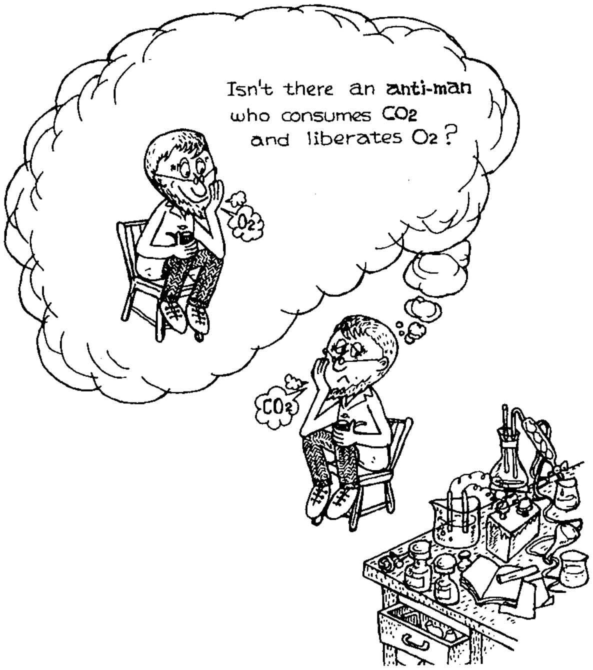
p_{H_2O}	p_{CO_2}	Result
too high	too low	H_2 formed
too high	too high	CH_4 formed
too low	too low	Li formed
too low	too high	CO formed

- volatile and particulate carry-over is possible and must be prevented to avoid cabin contamination or line plugging in the colder sections.

- it is difficult to operate in a weightless environment; this limitation may be removed with clever mechanical designs, e.g., with rotating equipment, but not without some increase in complexity.

These problem areas are all amenable to solution with sufficient additional research and development. The long-term, high reliability requirements that are imposed on any oxygen production process have, however, not been demonstrated. At present, fused salt electrolysis in a LiCO$_3$-LiCl bath does not appear to rank as promising as some other carbon dioxide processes; however, ideas to improve the reliability of the process may change completely the present concept.

Recommendations for University Research



Four separate techniques have been presented to separate oxygen from carbon dioxide. Biological or photosynthetic methods were not considered.

All techniques are characterized by high temperatures with maintenance and access problems. All show both advantages and disadvantages. None are clearly the best. Separate analyses have indicated that if the Sabatier (with methane decomposition) were compared with the Bosch and solid electrolyte, all would rank within a few per cent on weight, volume, and required power. Many prefer the solid electrolyte since separate water electrolysis is not needed.

New, fresh ideas are needed in the area of oxygen recovery. Perhaps some of the proposed techniques may be improved - or perhaps new ways to break the carbon dioxide molecule may be forthcoming. None of the present techniques are well understood and all could benefit from more fundamental research.

Some definitive suggestions for additional work are outlined below; the list is not intended to be exhaustive but rather provocative to encourage new ideas.

- Propose new ideas to convert metabolic carbon dioxide and water to oxygen and, possibly, activated charcoal.
- Propose basic studies to delineate carefully the effect of promotors on the activity of Sabatier catalysts and also define more carefully the effect of poisons, especially if the CO_2 feed has been desorbed from molecular sieves which have also adsorbed trace contaminants from the cabin atmosphere.
- Suggest new ideas to decompose the methane product from the Sabatier reaction and form a gas with a low H/C ratio or solid carbon.
- Propose a well planned experimental and theoretical program to measure rates of carbon deposition in an iron-catalyzed Bosch process reactor and, in particular, clarify the auto-catalytic role of carbon, the activity of non-ferrous materials of construction, and the effect of contaminants adsorbed and subsequently desorbed from a CO_2 molecular sieve unit.

- Propose new techniques to convert CO to CO_2 and C in a manner to require a small amount of catalyst and to remove accumulated carbon easily. Preferably the carbon should also be of the type suitable for adsorption processes in other portions of the Life Support System.

- Propose new high temperature ceramic oxides through which oxygen ions readily diffuse but which have low electrical power losses.

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IV. ELECTROLYSIS OF WATER

A recent review article (Ingelfinger and Secord, 1968) indicates "The design of a flight-type electrolysis unit for long-duration usage has been one of the most difficult technological problems to solve. Yet the development of the operational electrolysis unit is a "key" to the first-generation oxygen recovery system, as well as an atmospheric supply system that provides oxygen from electrolyzed resupplied water."

Many different design configurations have been suggested to carry out this electrolysis but none has been shown to be superior in all applications. Several typical designs are considered below with a discussion of their advantages and disadvantages, and areas requiring more research and development are delineated. First, however, it is instructive to review very briefly the basic concepts of water electrolysis.

Thermodynamic Considerations

Decomposition of water by electrolysis proceeds according to the following reaction:

$$H_2O\ (l) \rightarrow H_2\ (g) + 1/2\ O_2\ (g)$$

Under the thermodynamic equilibrium at 25°C and one atmosphere, the change in free energy, ΔG, of the reaction is -56,690 cal/g mole of water; this corresponds to a theoretical minimum electromotive force of 1.23 volts. The accompanying change of enthalpy, ΔH, of the system is 68,317 cal/g mole of water. The overall reversible reaction is then endothermic by 11,627 cal/g mole (or 1163 Btu/lb) of water electrolyzed. Under practical conditions, however, electrolysis cells require cooling since the actual cell voltages are considerably higher than values predicted from thermodynamic equilibrium considerations. Irreversibilities result from:

- The voltage drop through the electrolyte due to its ohmic resistance
- The electrochemical discharge of hydrogen and oxygen on the inert metal electrodes.
- The concentration polarization in the electrolyte-gas electrode interface due to concentration gradients.

Of the above factors, the irreversibilities at the hydrogen and oxygen electrodes, especially that of the oxygen electrode, contribute 80 to 90% of the electrical energy that is dissipated into an irreversible production of heat, over and above the quantity of electric work that is usefully converted into dissociating the water molecule.

The above suggests that at a certain cell voltage level the reaction of decomposing water proceeds adiabatically. The quantitative value of this "adiabatic" cell voltage, Va, can readily be defined using the first and second laws of thermodynamics.

The final relationship is:

$$Va = V^{o} + \frac{T \Delta S}{nF}$$

where

V^{o} = the reversible cell voltage based on the change of free energy at the operating conditions of the system

T = system temperature

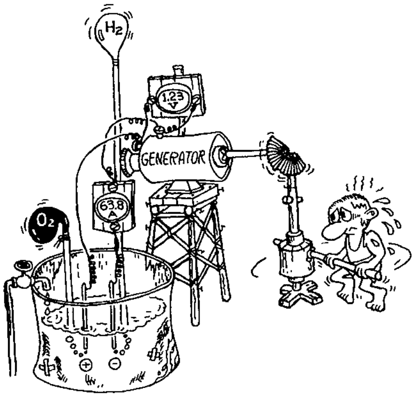
ΔS = change in entropy of the system

n = equivalents per mole of water

F = Faraday's Constant

At 25°C and one atmosphere, the second term in the foregoing equation equals 0.25 volts. Va, therefore, is equal to 1.48 volts. This defines the practical lower voltage limit for steady-state (no external heat input) operation of an electrolysis cell at the conditions stated.

The waste heat generation rate can be calculated using the actual and adiabatic cell voltage values. Based on Faraday's law, 1520 amp-hr liberate one pound of oxygen and 0.125 pounds of hydrogen (or 63.3 amps per O_2 per day). The power requirements of an electrolysis system can, therefore, simply be expressed as (1520) (V_C) watts per pound of oxygen per hour; (V_C = cell voltage). Every pound of oxygen produced by electrolysis requires 1.125 pounds of water. To this must be added any water lost



IDEAL Electrolysis Cell
for 1Lb of oxygen/day

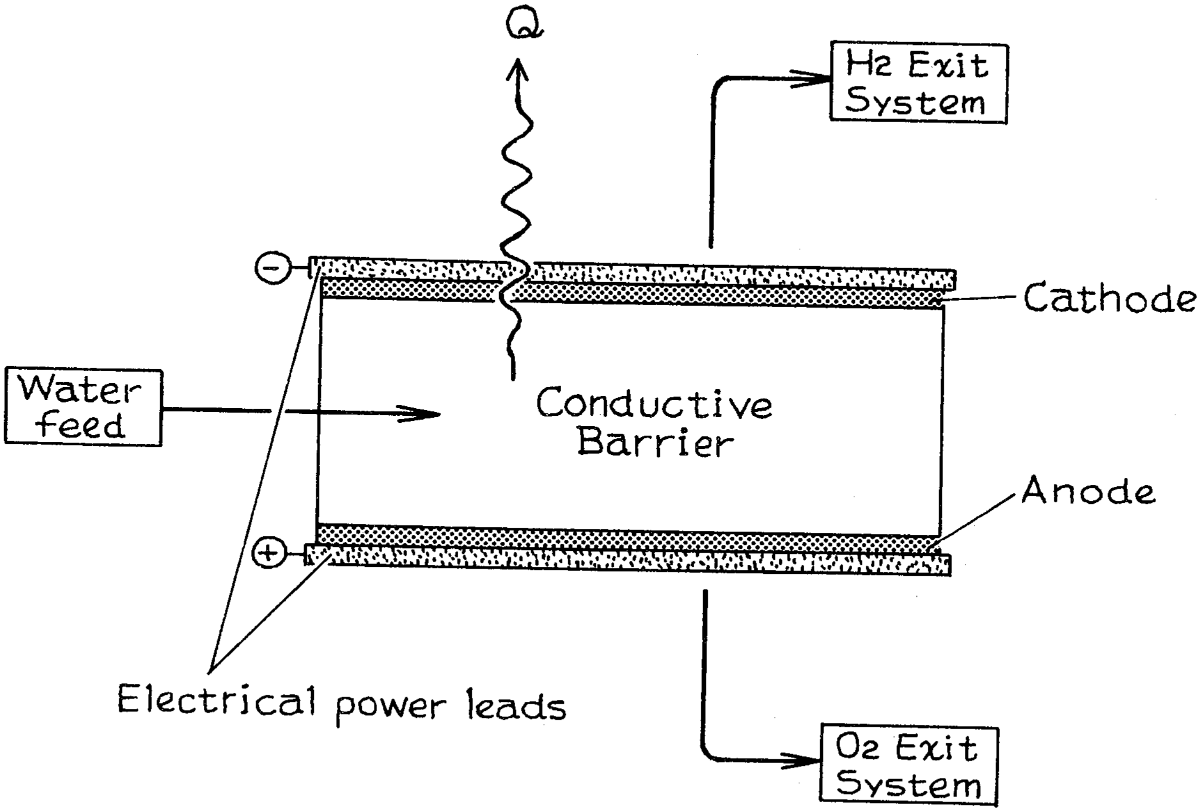


Figure 1

Simple Electrolysis Cell

or vented with the product gases. In a low-pressure (5 psia) cell operating at a high temperature (175°F), this loss can increase the water that must be fed into the cell by 500%!

General Design Concepts

As shown in Figure 1, the principal items in any electrolysis system are:

- Feed water supply
- Cathode where hydrogen gas is formed
- Anode where oxygen gas is formed
- Conductive barrier between anode and cathode (electrolyte)
- Exhaust system for product gases
- Electrical power leads
- Energy-removal capability
- Current regulator and other electrical devices

Electrolysis cells differ in the type and arrangement of these various components. To fix the type of material and cell configuration requires generally only the definition of four basic concepts:

- The nature of the cell electrolyte.
- How the electrolyte is incorporated into the cell.
- The cooling technique used to remove waste heat.
- The method used in supplying water to the electrolysis site.

Selection of Electrolyte:

Electrolytes may either be alkaline, neutral or acidic in nature. Although the half-cell electrolysis reactions are dependent upon the pH of the electrolyte, the theoretical net potentials are identical in value. These reactions are depicted in Figure 2. The low conductivity of pure water (low ionization levels) makes its use impractical. For a given current level and any given configuration, actual water electrolysis cells using alkaline electrolytes require less power (lower cell voltages) than cells using acid electrolytes.

Acid electrolytes also present more severe material compatability problems; however, they have the advantage of being insensitive to the presence of carbon dioxide in either the feed water or circulating gas streams. This eliminates the need for an ion-exchange resin cartridge in the feed water to remove carbon dioxide. These cartridges could, however, serve a multiple function since they would also remove other electrolyte contaminants, such as chloride or sulfate ions, which would otherwise degrade cell performance. It should be remembered, however, that using an acid electrolyte does not necessarily preclude the requirement of a water treatment cartridge as one would be required if ammonium ions are present, a possibility in a reclaimed spacecraft water supply.

Electrolyte Incorporation:

Electrolytes can be incorporated into the electrolysis module by three methods:

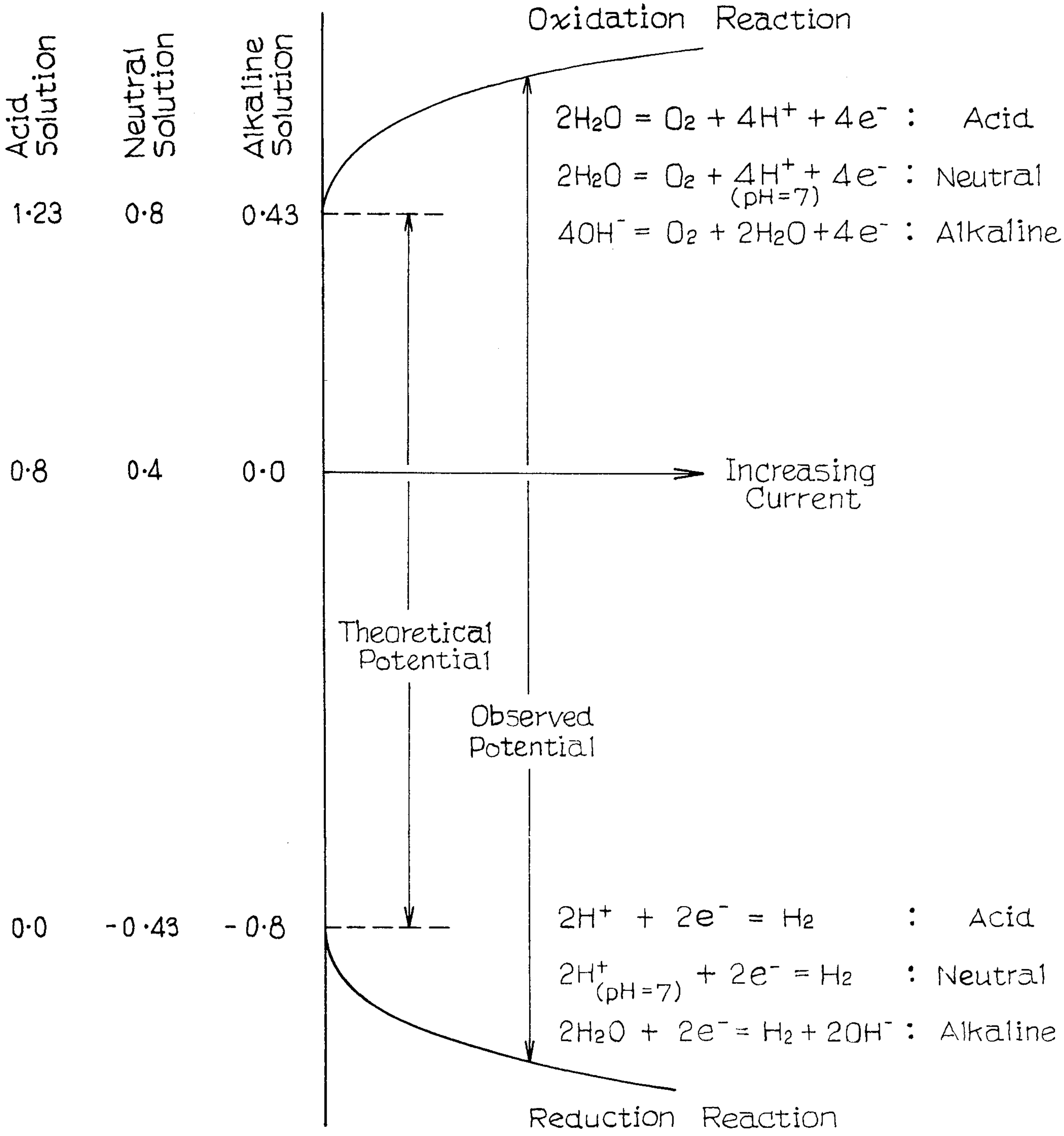


Figure 2

Effect of Electrolyte Nature on Electrolysis Electrode Reactions

- being held in a porous matrix sandwiched between the cell electrodes
- as bulk liquid circulating between the cell electrodes or through the "gas" compartment(s)
- as an ion-exchange membrane

Systems that use bulk electrolyte have inherently large electrolysis module weights and problems of aerosol elimination and gas/liquid separation in zero gravity. In these systems, intercell electrolysis may occur resulting in a decrease in gas generating (current) efficiency and accumulation of a gaseous mixture of hydrogen and oxygen within the circulating electrolyte loop.

Systems employing ion-exchange membranes are limited in current densities and, therefore, may not have the necessary overcapacity capabilites for emergencies. They are also limited to lower operating temperatures; this results in higher power requirements since the power required to decompose water decreases as the operating temperature increases.

Systems utilizing matrix-held electrolytes are quite common. The matrix material must be chemically stable in the presence of electrolyte at the operating conditions. In addition, it should have a porosity between 50 and 90% to retain sufficient electrolyte to prevent low conductivities but still it must restrict gas flow with the cell. It should also have sufficiently small pore sizes to prevent liquid loss during rapid vehicle acceleration. In addition, it must withstand normal wet - and dry periods of operation, by readily wetted by the electrolyte, expand (rather than shrink) when wetted, and be usable in thin sections to reduce ohmic conduction but still prevent any internal discharges.

Some matrices now used are sufficiently thin that the cell electrodes are spaced only 0.03 inches apart! Such packaging greatly reduces the weight and size of a multi-cell electrolysis unit.

Cooling:

Practical water electrolysis modules require cooling. This can be accomplished by

- use of air-cooled fins,
- circulating electrolyte through an external heat exchanger
- circulating a coolant within the module,
- evaporation of water from the water feed compartments,
- circulation of the water feed compartment "fluid",
- circulation of product gases through the module,
- conduction to a cold plate.

Since the module cooling depends upon cell voltage, it is less (by about 70%) when an alkaline electrolysis is selected instead of an acid.

In selecting the optimum cooling technique, one must make allowances for the system application, the increase in cooling load with operating life, the increase in cooling load during emergency operations, and the reduction of cooling load weight penalty as the operating temperature is increased. The maximum operating temperature is generally dictated by the availability of materials able to withstand the corrosive environment at elevated temperatures and/or the operating pressure. The latter affects the moisture content of the vented hydrogen and oxygen gases. The lower the pressure, the more the gas is humidified and the greater the evaporative cooling which occurs within the module.

Water Feed:

Various methods are available for feeding water to the module. These include

- a wick feed system that transports water by capillary action directly from a reservoir to the cell electrolyte matrix,
- a vapor feed system whereby water is transferred to the cell through a recirculating gas stream using an external humidifier,
- a static feed system where water is drawn into a feed compartment adjacent to each cell as a result of the vacuum created by distillation of make-up water to the cells,
- those methods whereby make-up water is added to the electrolyte being circulated through the flooded compartments or between the cell electrodes.

Concept Summary:

Most combinations of the techniques cited under the four concepts above are possible. For example, an acid or an alkaline electrolyte can be used with any electrolyte incorporation, cooling or water feed technique. Obviously, some combinations such as bulk electrolyte in both gas compartments and water vapor feed are incompatible. Table 1 lists some practical combinations used in present-day systems.

Cell Configurations

The desirable characteristics of an electrolysis system for spacecraft application are almost self-evident:

- High reliability over long periods
- Excellent maintainability
- Low overvoltage, i.e., low power and heat rejection
- Small volume
- Small number of auxiliary components
- Operability in zero-gravity environment
- Safe, no mixing of H_2 and O_2

The relative rating of these factors is not always consistent but depends on the specific mission requirements.

Standard industrial electrolysis cells are not suitable for spacecraft life support systems since they generally have a high mass and volume per pound of product gases and are not designed for zero-gravity operation.

TABLE 1 COMPARISON OF ELECTROLYSIS CONCEPTS

CONCEPT	ELECTROLYTE NATURE	ELECTROLYTE INCORPORTN.	HEAT REMOVAL MECHANISM		WATER FEED MECHANISM	
			FROM MODULES	FROM SUBSYSTEM	STATE	TRANSFER AGENT
Circulating Humidified Cabin Air	Acid	Matrix	Circulating Cabin Air	In Cabin Air	Vapor	Cabin Air
Circulating Humidified Gas (O_2)	Alkaline	Matrix	Circulating Coolant	In Coolant	Vapor	Circulating O_2 Gas
Static Feed (Degassing Required)	Alkaline	Matrix	Water Evaporation	Transfer to Coolant	Liquid	None
Circulating Water in Gas Compartments	Acid	IEM*	Circulating Feed Water	Transfer to Coolant	Liquid	None
Circulating Electrolyte in Gas Compartments	Acid	Bulk	Circulating Coolant	In Coolant	Liquid	Circulating Electrolyte
Circulating Electrolyte Between Electrodes	Acid	Bulk	Circulating Electrolyte	Transfer to Coolant	Liquid	Circulating Electrolyte
Rotating Module/Cabin Humidity Feed	Acid	Matrix	Circulating Cabin Air	In Cabin Air	Vapor	Cabin Air
Static Water Feed	Alkaline	Matrix	Cabin Air Cooled Fins	In Cabin Air	Liquid	None

*IEM - Ion Exchange Membrane

Those prominent cell configurations that have emerged and are employed in state-of-the-art electrolysis systems are ones that use

- the static water feed with the electrolyte supported in a porous matrix,
- ion-exchange membranes, and
- circulate humidified gas streams for moisture addition.

Static Water Feed Method:

Figure 3 shows the cell configuration used with the static water feed technique. The cell operates as follows. When power is applied to the electrodes, water from the cell electrolyte is decomposed. As a result, the concentration of the cell electrolyte increases and, therefore, the vapor pressure of water decreases to a level below that in the feed compartment. This vapor pressure differential causes water vapor to diffuse from the water feed matrix through both the hydrogen cavity and cathode into the cell electrolyte. This process continues as long as the water vapor pressure of the cell electrolyte is lower than that of the water in the feed matrix. The transfer of water causes a decrease in volume or pressure level in the feed compartment which in turn draws make-up water into the feed cavity from an external resorvoir.

The advantages of a cell using this type of configurations are:

- Simplicity, i.e., no moving parts
- Does not require zero-gravity electrolyte-gas separators

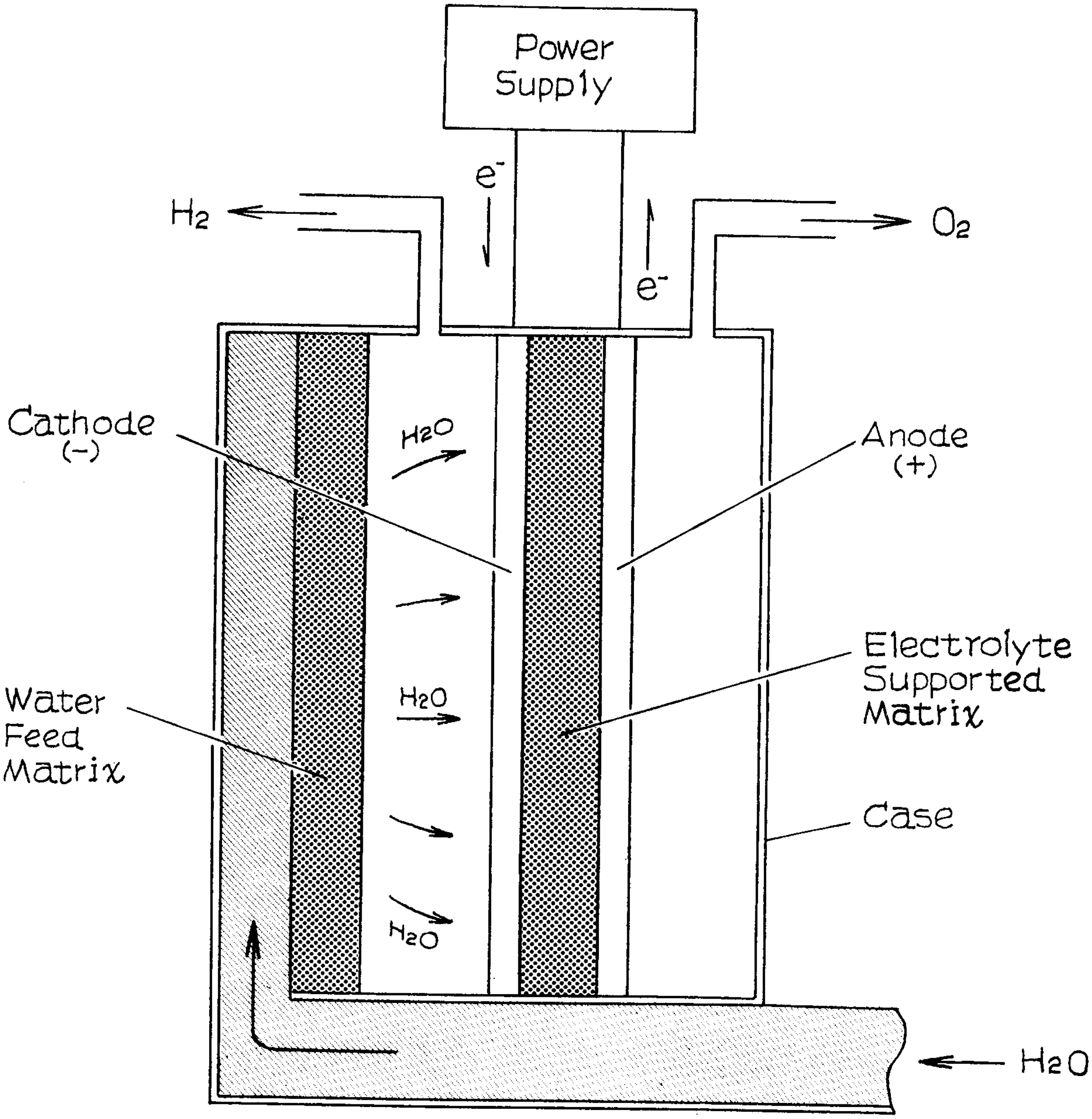


Figure 3

Static Feed Configuration

- Allows cell electrodes to be spaced closely together resulting in low internal resistance
- Prevents contamination of cell electrolyte
- Reduces aerosol formation
- Relatively insensitive to pressure differentials

One problem with the static feed method is that there is an accumulation of dissolved gases in the feed compartments. Excessive amounts of gas accumulation may eventually lead to failure in the water feed transfer mechanism.

Ion-Exchange Membrane:

An ion-exchange membrane can serve as the conductive barrier between the anode and cathode. Present-day practical ion-exchange membranes are acidic in nature (cation membranes). These membranes depend upon ion-dipole forces in addition to the usual van der Waals forces to aid in gas-liquid separation.

Ion-exchange membranes are similar to porous matrices when used as shown in Figure 4, since thay eliminate free electrolyte within the cell. These membranes also have the desirable feature of being capable of withstanding relatively high pressure differentials. Their main disadvantage is the high overvoltage (due to the acidic nature) and the high internal resistance experienced in actual use. They are structurally limited to lower temperature operation than, for example, asbestos matrices. This again results in high power requirements.

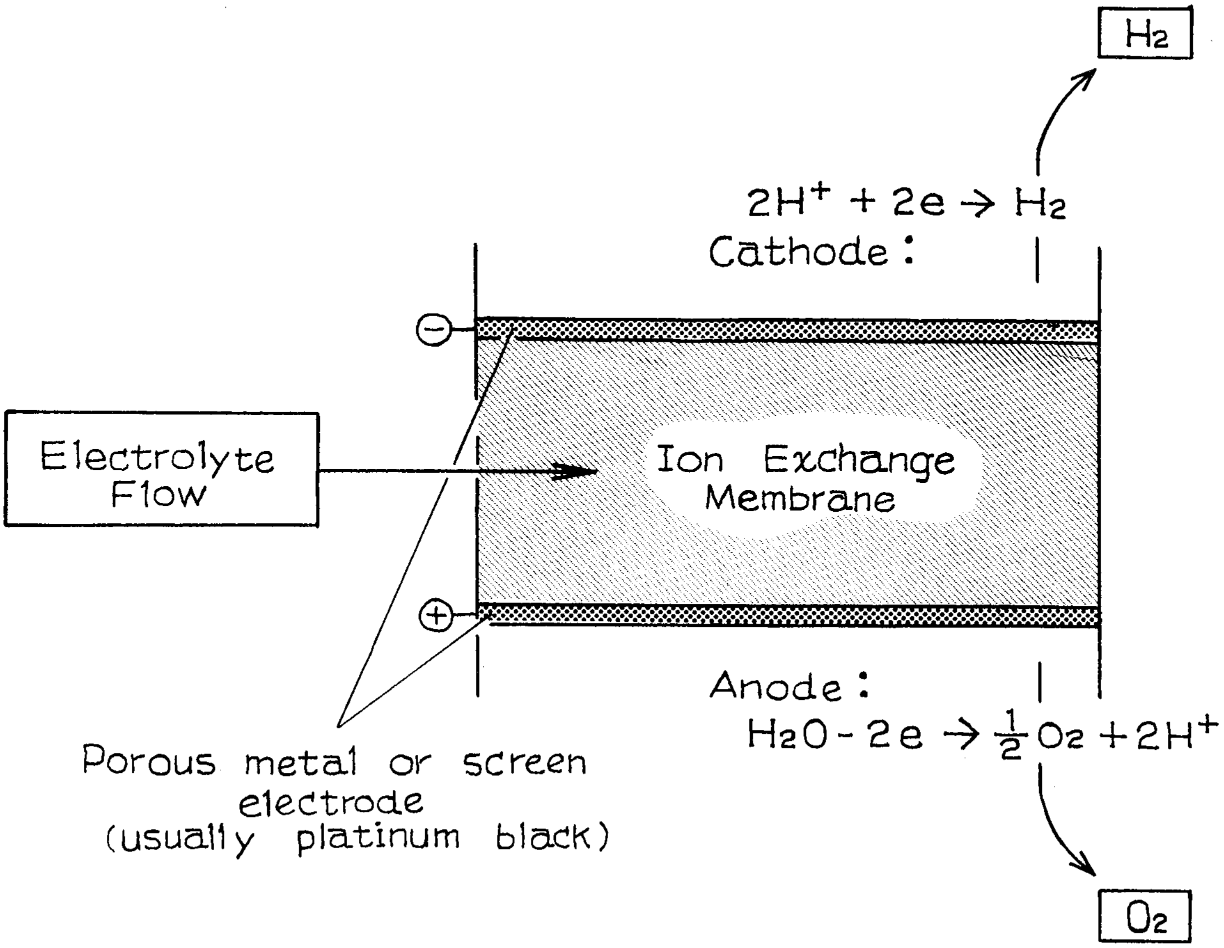


Figure 4

Typical Membrane Electrolysis Cell

Ion-exchange membranes should not be confused with electrolyte equilibrium membranes which appear similar in nature but actually constitute an example of an electrolyte supported in a porous matrix. The latter type membrane can, therefore, be either alkaline or acidic in nature.

An example of a membrane cell configuration is shown in Figure 4. Any water feed and electrolyte incorporation techniques are applicable to a membrane system. They are often used, however, in bulk electrolyte systems, e.g., in those using electrolyte circulation between electrodes, as shown in Figure 4.

Vapor Phase Cells:

The vapor phase electrolysis cell is shown in its simplest form in Figure 5. In this cell, water is supplied to the cell as a vapor since humidified cabin air is circulated. Water is absorbed in the matrix on materials such as P_2O_5 on microporous rubber or H_2SO_4 on asbestos or silica gel. Asbestos/microporous rubber combinations have been found satisfactory to hinder mixing of the product gases. In the P_2O_5 cell, the absorption reaction is believed to be

$$P_2O_5 + H_2O \rightarrow 2HPO_3$$

The HPO_3 is electrolyzed to form O_2 and H_2 and the P_2O_5 regenerated.

Cabin air is introduced on the anode side. Water vapor is condensed, adsorbed and electrolyzed raising the pressure of the

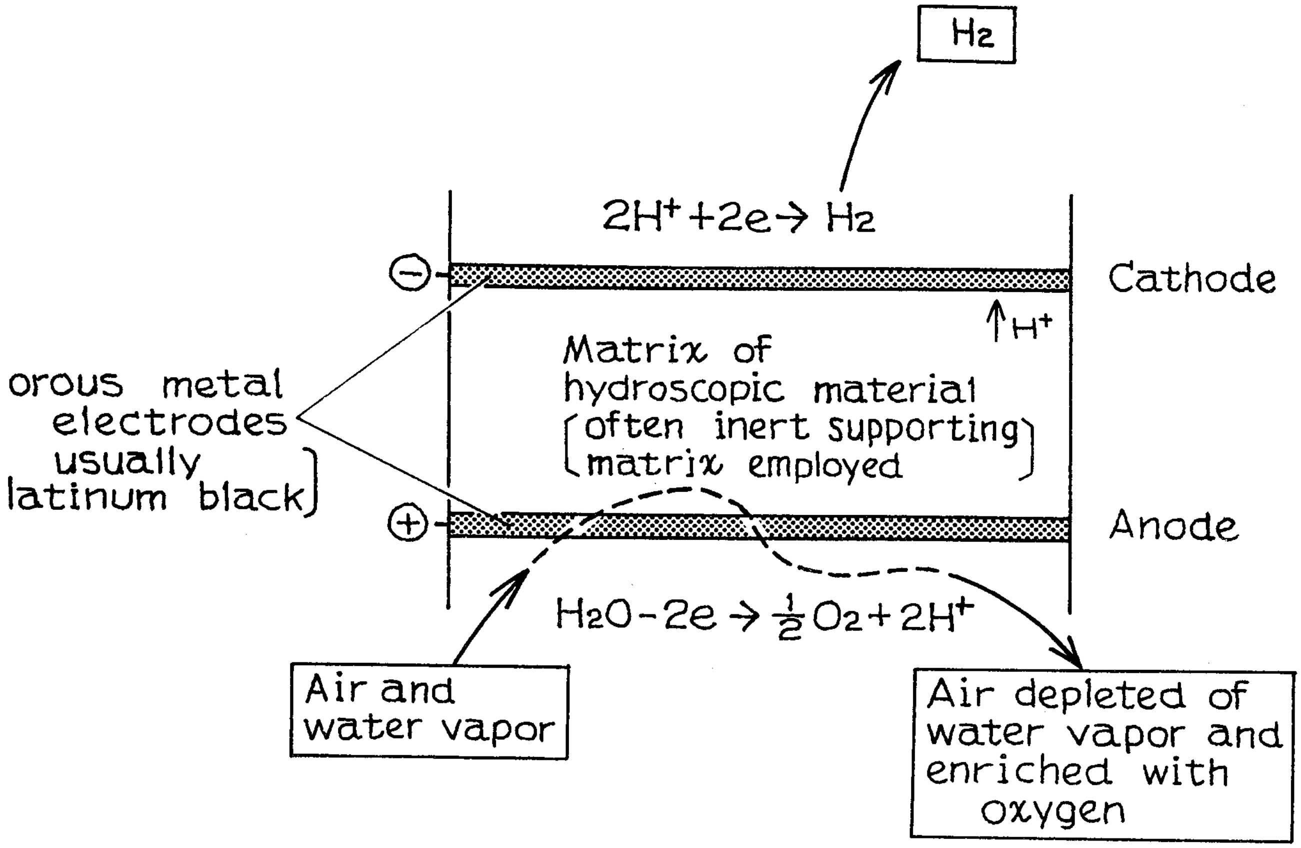


Figure 5

Typical Vapor Phase Electrolysis Cell

oxygen in the air stream. Hydrogen is vented from the cathode side. Acid electrolytes are employed in this type of system to prevent simultaneous absorption of carbon dioxide. Alkaline electrolytes could be used provided the CO_2, typically present in spacecraft atmospheres, is removed prior to the cell. During operation the hydroscopic matrix reaches a steady-state water content when absorption and electrolysis occur simultaneously. Heat removal is accomplished by the circulating air stream.

High power requirements have been quoted for such vapor cells due to the low temperature operation and the inherently high overvoltages experienced with acid systems especially when operating with the high acid concentrations required to remove water from low-humidity air streams. To route the low pressure air streams through manifolding and cell gas compartments at reasonable pressure drops results in high system volumes for a given oxygen generation rate.

The attractiveness of this system is its inherent simplicity.

State-of-the-Art

Several recent papers summarize the current state-of-the-art, e.g., Wydeven and Johnson (1968) and Schubert, Huebscher and Wynveen (1969). Table 2 presents a summary of the 1969 state-of-the-art and, in Figure 6, some typical performance data are shown.

Table 2 STATE-OF-THE-ART IN WATER ELECTROLYSIS

Categories	System Descriptions								
Design Concept									
Water Feed Method	Static	Static	Static	Static	Circulate(a)	Circulate(a)	Circulate(a)	Vapor in O_2	Vapor in O_2
Electrolyte/Concentration WT. %	KOH/25	KOH/25	KOH/32	KOH/35	KOH/35	KOH/--	H_2SO_4/25	H_3PO_4/80	H_2SO_4/60
Electrolyte Incorporation	Matrix	Matrix	Matrix	Matrix	Matrix	Bulk	Bulk	Matrix	Gel
Cooling Method/Fluid	Fin/Air	Fin/Air	Conduction	Evaporation	Fin/Air	Circulate Electrolyte	Liquid Coolant	Forced Convection/O_2	Forced Convection/ O_2
Operating Conditions									
Temperature, °F	175	150	90	160	125	80	90	83	95
O_2 Pressure, PSIA	30	80	14	14	15	15	10	15	15
Performance									
Current, Amps./Stack	23	23	6	11	11	15	10	35	4.3
Current Density, Amps/Ft^2	100	100	100	100	50	150	27	20	31
Voltage, Volts/Cell (Initial)	1.6	1.6	1.6	1.6	1.7	--	1.9	2.3	2.1
Power, Watts Per Man(b)/Time(c)	250/5000 Hr	200/30 Hr	210/24 Hr	200/280 Hr	215/300 Hr	240/720 Hr	260/100 Hr	300/1500 Hr	265/-- Hr
Reported Operating Time, Hrs.	6500	50	24	286	370	720	1727	1700	900
Development									
Laboratory System, LB O_2/Day	3.6	--	--	--	--	--	--	--	0.07
Prototype System, LB O_2/Day	--	3.6	0.3	8.0	1.4	8.0	8.0	0.5	--
Design Completed	1967	1967	1966	1967	1965	1965	1964	1966	1967
References	(1)	(2)	(3)	(4)	(5)	(6),(7)	(8),(7)	(9),(7)	(10),(7)

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(8) Glanfield, Miller and Rudek, 1966
(9) Clifford, et al., 1967
(10) Wydeven and Smith, 1967

(a) Water Added Externally to Electrolyte

(b) Based on 2 Lbs of O_2 Per man Day

(c) The Operating Time (In Hours) at Which the Power Levels Specified Were Determined (Using Cell Voltage Observed at That Time).

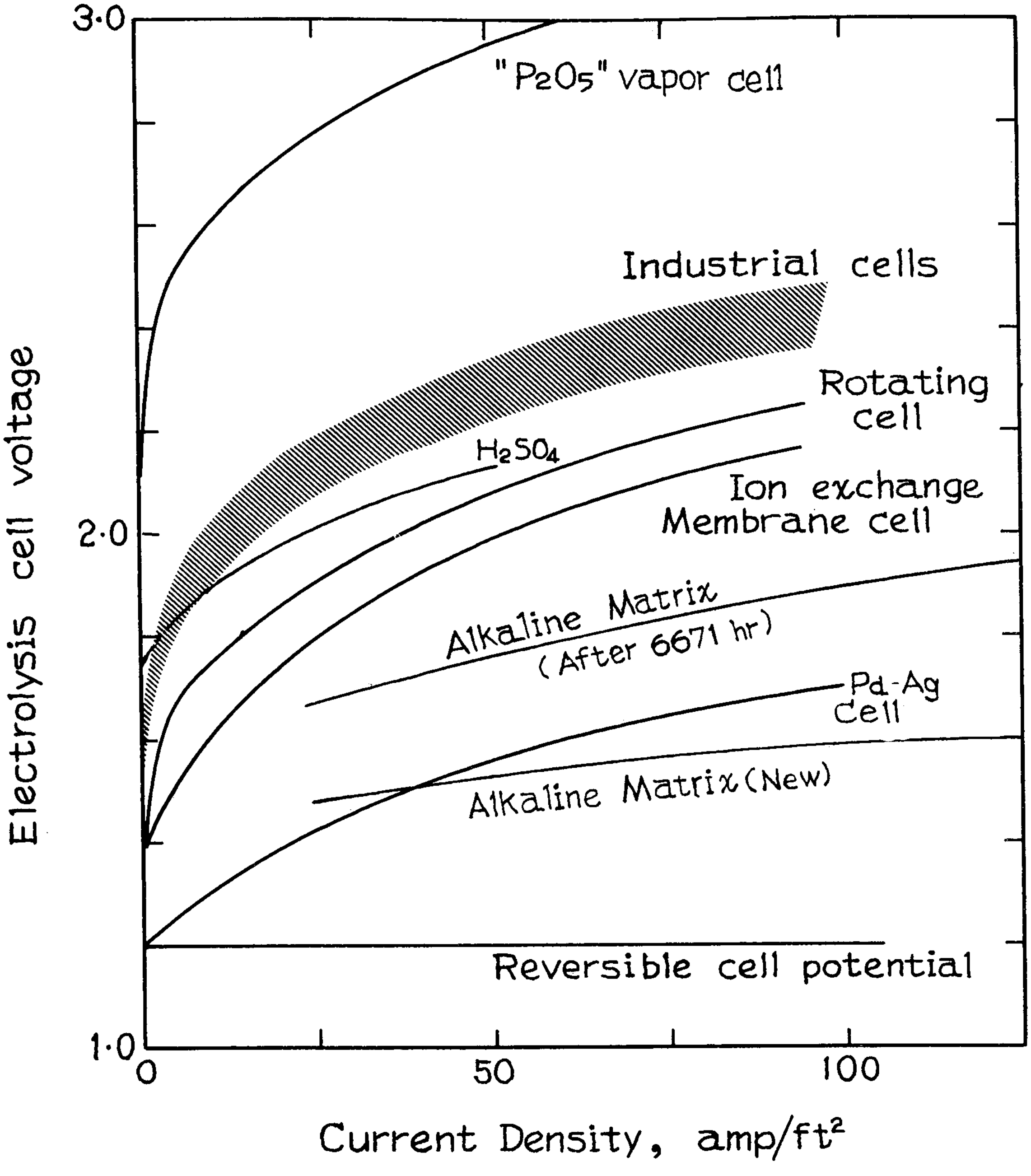
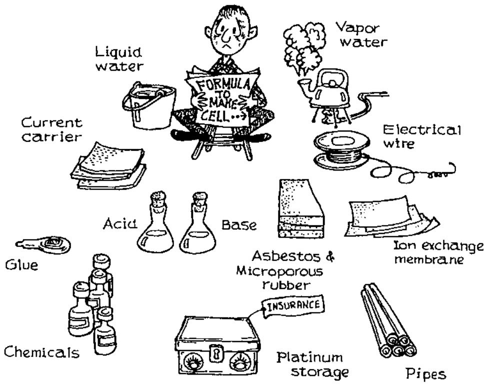


Figure 6
Cell voltages

Recommendations for University Research

In their survey paper, Wydeven and Johnson (op. cit.) reviewed some of NASA's efforts in developing techniques to electrolyze water aboard spacecraft. The remaining NASA activities have been described by Kiraly, Babinsky and Quattrone (1968). From an evaluation of these activities and through discussions with electrolysis specialists at the foreground of the technology, it has been possible to identify several areas where insufficient technology exists to meet the demands of the projected future space missions. These are listed below to aid in focusing on the challenges that exist for man to use his imagination and his creativity to arrive at solutions that can yield significant technological advances.

- Higher operating temperatures lower the power required to generate oxygen from water. Because the weight penalty for space power is large (150 to 1000 pounds per kilowatt), any savings in power offers a significant launch weight saving. This requires, however, better construction materials for operation at temperatures above 200°F. Since all cells operate in strong electrolytes, the problem becomes one familiar to the chemical processing industry. The difference, however, is that the time-honored solution of repairing worn equipment is difficult to make in space. A specific problem is to identify an electrolyte holding matrix that will permit operation at the more efficient (high temperature) operation, say above 250°F. Current materials tend to break down in a manner that reduces their ability to perform the functions required of the electrolyte holding matrix. For example, asbestos reacts with an alkali at high temperatures to form silicates. In addition to matrix materials, the elastomers used for gaskets and the polymers used for structural materials are not expected to maintain their integrity for long missions at the higher temperatures.

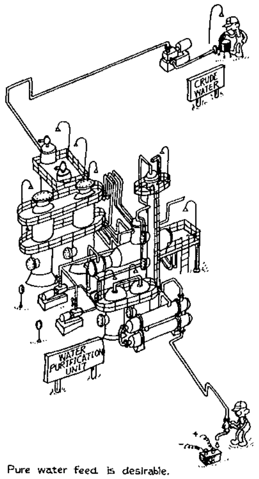


- More consideration must be given to the prevention of electrolyte carryover into the product gas streams. Electrolyte carryover is increased as the operating pressure decreases, and the collection of fine aerosols in zero-gravity is still a challenge.

- An explanation for and solution to the rather rapid increase in cell operating voltage during the first 0-250 hours is needed. Typically, the performance degradation occurring during this time period amounts to a 10-20% increase in the power required to electrolyze a given quantity of water. This is particularly true of the high-performance systems being considered for space. Low-performance systems do not exhibit this effect because their efficiencies are less initially. Such systems have an overall performance that matches that of the high-performance systems only after thousands of hours of operation.

- From an electrochemical viewpoint, the major power consuming process in the electrolysis system is associated with the anodic evolution of oxygen. Much effort has been spent in trying to identify ways to lower the activation polarization at this electrode. Some techniques tried have included raising the operating temperature (where material problems appear) or using more active catalysts (when sensitivity to poisons and cost become problems). What is needed is a catalyst-temperature combination that allows long life with currently available materials without using excessive quantities of costly noble metals or materials that are sensitive to impurities formed from the interaction of hot alkaline or acid electrolyte with cell materials.

- Feed water purification is important. Carbon dioxide dissolved in the water will neutralize an alkaline electrolyte. Ammonia or other basic gases will neutralize acid electrolytes. Regardless of the acidic or alkaline nature of the water, however, impurities must be removed to prevent build-up of "scale" similar to that in conventional heat exchangers. The need for removal of impurities is compounded in the case of long (5 to 10 year) operating times since the products of the accumulation may build to a level where they can poison the electrode catalysts that are used to lower the activation polarization.



Pure water feed is desirable.

- From the electrical engineering viewpoint much remains to be done: (a) to develop better current regulators to interface with power producing units such as solar or fuel cells, (b) to arrive at simple fault isolation mechanisms, (c) to establish methods for sensing the status of the individual cells and, thereby, identify module performance trends, and (d) to sense malfunctions rapidly enough to take corrective action and prevent system damage. Much development time and experimental testing could be saved if a way was found to predict say, after 200 hours of operation, what the performance of an electrolysis system or module would be after 5000 hours of operation.

- Multiple analytical studies remain to be completed that will aid in explaining system performance limitations from an engineering point of view. Such analyses include mass and heat transport and structural studies which will allow "tuning" existing systems in a way to decrease further the weight, power, volume, and to increase the reliability and maintainability.

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