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Abstract

Atmosphere controls for advanced manned space vehicles will in some cases require techniques different from those selected as optimum for the Mercury environmental control system (ECS). Water conservation will be rigorous for vehicles which use a solar or nuclear auxiliary power unit (APU). For missions longer than a few hundred hours, CO_2 will be removed in a regenerable process. Several promising regenerable CO_2 removal systems are presented, including freeze-out.

Regeneration of oxygen from CO_2 is discussed as the next step in atmosphere control advancement. Test work on CO_2 hydrogenation by the Sabatier process is cited. The recommended makeup of ECS elements is presented as a function of mission duration.

Introduction

Environmental control systems (ECS) include at least the following functional elements:

1. Thermal management

2. Water management

3. Atmosphere composition management

4. Food management

5. Waste management

6. Power management

In terms of the equipment selected to perform these functions, considerable overlap exists because of multi-function elements. For example, a cooler-condenser-water separator performs in one component essential functions of thermal management, water management, and atmosphere composition management. Functional tie-ins exist between the ECS and other subsystems. For example, thermal management should extend to the thermal design of power-consuming equipment, to provide a suitable path for heat flow from source to sink, compatible with low-penalty liquid cooling media[1,2].

This paper considers in detail the subjects of water management and the part of atmosphere composition management related to CO_2 removal. Other ECS elements are considered only in a summary chart which makes recommendations as a function of mission duration.

Water Management

Water management is a key problem in space vehicle environmental control, for three reasons:

1. Water is essential to human life over time spans short compared to durations of presently planned space missions.

2. The quantities of water required for life support are larger than required quantities of any other constituent.

3. Water management is functionally interrelated to several other elements of environmental control, such as energy-balance comfort in terms of atmosphere humidity control, and CO_2 removal.

Table I shows a typical human material balance, as estimated for a space mission of several days or longer. As shown by the footnotes to the table, the numbers contain varying degrees of arbitrariness; however, they should be quite adequate for purposes of system parametric analysis and evaluation.

Table II is made up of the water entries from Table I. The listing shows a total of water produced of 12.25 lb/man day, compared with a total consumption of 11.0 lb/man day. The excess of 1.25 lb represents approximately 1.0 lb metabolic water (formed by oxidation of hydrogen in food) and 0.25 lb of water present as H_2O in the food supply. (The 0.25 lb of water in the food supply represents a free source of water as long as stored food is carried. Missions for which food is reprocessed are beyond the scope of this paper.)

Given the objective of closing the water loop to the extent of providing all the drinking, cooking and wash water needed, the favorable margin of 1.25 lb/man day is narrow enough to pose a challenging problem to the vehicle and ECS designers. They must not only design efficient water recovery equipment, but also minimize casual losses of water from the system, as by leakage overboard or migration into unrecoverable areas on the vehicle.

A more ambitious water loop closure would include oxygen recovery from the metabolic water as well as purification of the waste water. This is not recommended, even for a 3000 hour mission, although on a mission of this length oxygen would be recovered from CO_2. Some material losses are inevitable in a nominally closed system. Water storage can be provided to make up these losses. Oxygen recovery will be discussed further under CO_2 management.

The allocation of 5.7 lb/man day for production of exhaled and perspired water vapor merits some discussion. This water production is consistent with a metabolic rate approximately 150% of the basal metabolic rate (BMR) for a 90 percentile man, and with a 50-50 split of the metabolic heat output between latent and sensible cooling. The assumed metabolic level appears reasonable for space missions of a few days or longer, where physical activity will be inherently somewhat limited. The 50-50 latent-sensible split of the metabolic heat load is based on the assumption that the astronaut spends about half his time in a pressure suit (where the cooling load is

about 65% latent), and the other half of his time in a shirt-sleeve environment (where the cooling load is about 65% sensible). The cooling load for suit occupation is largely latent because of the restricted suit ventilation rates compatible with reasonable power consumption.

The 5.7 lb/man day figure is representative of the average quantity of exhaled and perspired water vapor available for recovery; the actual design of recovery equipment could well be predicated on even higher peak rates.

As far as the human water balance is concerned, any recovery system which comes within (approximately) 1.25 lb/man day of recovering all the produced water will be satisfactory. A high latent load will increase water vapor produced and drinking water consumed by equal amounts.

The water sources listed in Table II are designated primary sources. They are: water vapor (exhaled and perspired), waste water (urine and wash water), and fecal water. It has been pointed out that operating at a break-even or favorable water balance is a feasible but challenging problem, requiring highly efficient recovery equipment. Fortunately, this problem will be relaxed in space missions where by-product water sources are available. Table III repeats the primary water balance of Table II, with supplemental entries for two by-product water sources expected to be available in space missions in the two-week class. The two enumerated by-product sources are LiOH (used for CO_2 removal) and a hydrogen-oxygen APU, which could be either a fuel cell or a combustion heat engine.

When absorbing CO_2, LiOH produces water vapor according to the reaction

$$2LiOH + CO_2 = Li_2CO_3 + H_2O$$
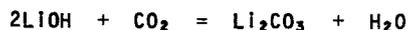
Practically all the water produced by this reaction shows up as vapor in the gas flow out of the bed, and is therefore recoverable to the same extent as is the exhaled and perspired water vapor. The quantity of water produced by LiOH (0.9 lb/man day) could be a significant entry on the plus side of the water balance, were it not overshadowed by the much larger quantity of water available from the APU.

The water available from the APU has been estimated to be 8.0 lb/man day, consistent with an average electrical load of 1/3 KW/man, and a specific fuel consumption of 1 lb/KW hr. Lower rates of APU water availability per man are believed unlikely.

Table IV shows the effect on water balance of various combinations of water recovery sources, primary and by-product. Combinations of the primary sources are listed as column headings. The first column depicts an all-out recovery effort utilizing all three primary sources (fecal, waste, vapor). The other columns depict successively less rigorous recovery schemes. The rows show the effect on water balance of the two by-product recovery sources, alone or in combination. Unfortunately, neither the hydrogen-oxygen APU nor LiOH for CO_2 removal is compatible with long space missions (of the order of months in duration); so that in the absence of by-product water, these missions will require the most rigorous water management.

A brief discussion of water recovery techniques is now in order. Exhaled and perspired vapor, together with any LiOH-generated water vapor, is recovered by condensation and separation from the space vehicle atmosphere. Figure 1 shows typical atmosphere, water and water-glycol coolant flow rates for handling cooling and dehumidifying requirements of one man. The water-glycol would of course be cooled in a space radiator.

For comparison, a comparable process without water recovery is shown in Figure 2. Here, the load on the water-glycol coolant is reduced by reevaporation (to space vacuum) of the condensed water, providing full thermodynamic recovery of the heat of water condensation.

Equipment capable of functioning as indicated by Figure 1, Figure 2, or an intermediate case where the water condensate is partially recovered and partially reevaporated has been built and tested. Figure 3 is a photograph of a development cooler-condenser-water separator. The unit is a conventional plate-fin liquid-cooled heat exchanger, with the addition of bats of wicking material between adjacent fin rows on the atmosphere side. The cooling liquid keeps the metal surfaces of the heat exchanger below the dew point. Water from the moist atmosphere throughflow is condensed on these surfaces, forming a thin condensate film from which it is drawn into the wicking material by capillarity. The wicking bats pass through a side wall of the heat exchanger into a water-collecting manifold. This manifold is packed with material which, when wet, effectively blocks the flow of air, thereby preventing air entrainment in the recovered water.

Tests of this device have been encouraging, having demonstrated negligible air loss and 100% water separation efficiency with the atmosphere flow downward. Performance with flow downward, the least favorable direction for full water recovery, indicates a probable performance margin under zero-g conditions.

Development of this water recovery unit is believed to represent a significant advancement in the technology of zero-g water separation, for the following reasons:

1. The device is passive.

2. Negligible power is required.

3. Weight penalty chargeable to separation is small.

4. Water is removed at ths point of condensation, eliminating the need for back-pressure producing blowoff of the water from the cooler-condenser.

5. Ultimate performance in terms of separation efficiency and air loss is achieved.

Order-of-magnitude estimates of the penalty involved in condensing and recovering water have resulted in a penalty of 10 lb of fixed weight per lb/hr of water recovered. This figure includes the portion of radiator, liquid coolant system and coolant pumping power chargeable to water condensation. It does not include tankage for stored water. This figure indicates the desirability of recovering exhaled and perspired water vapor from the space vehicle atmosphere in missions of duration

beyond a few hours.

Urine-waste water recovery poses a number of problems, the most important of which is purity of the product. Pretreatment of the feed with acid to a pH of 4 or 5, processing at a low temperature, and charcoal filtration (and possibly ultraviolet radiation) of the product are recommended.

Although many schemes of waste water treatment are possible, batch distillation under vacuum conditions appears to be the best. In the absence of forced flow, both the evaporation and condensation portions of the process have to be designed carefully to work in a zero-g environment. The distillation process is thermodynamically straightforward. For a nominally constant-pressure process, a temperature difference of about $5^\circ F$ (at $150^\circ F$) is required; for a nominally isothermal process, a pressure lift of about .5 psi is necessary. These lifts are those required to overcome the vapor pressure depression associated with the solids dissolved in urine at the end of a batch recovery process. An additional temperature difference is required for heat transfer. Figure 4-a, b, and c shows three ways of providing the required temperature or pressure lift: use of an available heat source and sink, vapor compression, and a thermoelectric heat pump. Because of the low flow rates (in the range of 1 lb/man hr), power requirements are low enough that comparison of these three approaches on a formal penalty basis will not show significant differences.

Figure 5 shows schematically a waste water recovery device, now under development, which utilizes a spray condenser for the dual purpose of generating the pressure lift required for condensation and for providing a g-insensitive condensation mechanism. Water is recirculated by a small pump through the spray condenser where it provides a heat sink and sufficient ejector action to condense the waste water vapor. The condenser outlet water is circulated through a heat exchanger which furnishes heat to the waste water evaporator, from which the flow is divided, part returning to the spray condenser, part being drawn off as product. The evaporator is batch-type, packed with a sponge-like material for g-insensitivity. The key to successful operation of the cycle is getting enough pressure lift out of the spray condenser to condense the vapor.

Preliminary distillation tests, conducted in glassware, have been successfully run at a temperature of $157^\circ F$, with 90 per cent recovery of a product which when filtered with activated charcoal met the U.S. Public Health standards for drinking water[3].

The following conclusions may be drawn regarding water management:

1. Manned space missions of duration from a few days to a few weeks, using a hydrogen-oxygen APU (fuel cell or heat engine) can operate at water parity (that is, consumption equal to production) by recovery of APU water and approximately 50 per cent of the exhaled and perspired water. Recovery of fecal water, water from urine, or wash water waste (the latter budgeted at 3.0 lb/man day) is not necessary in this case. The use or non-use of LiOH for CO_2 removal does not materially change this picture.

2. Manned space missions too long for use of a hydrogen-oxygen APU (and therefore requiring solar or nuclear power) will operate under rigorous water management discipline. Water must be kept not only on board the vehicle, but within the consumption-recovery cycle. Water parity can be obtained in this case without recovery of fecal water, if slightly more than 90 per cent of the exhaled and perspired water vapor is recovered, together with 90 per cent of the waste water, including water from urine.

3. Water balance must be considered as a constraint on the design of related equipment, such as CO_2 removal equipment which concurrently separates water and CO_2 and is subsequently regenerated by venting both water and CO_2 overboard. Such a CO_2 removal system may or may not be applicable to missions with by-product (APU) water, depending on the amount of overboard water loss; it will almost certainly not be applicable to long missions which have no by-product water.

CO_2 Management

The human CO_2 production (nominally 2.25 lb/man day) must be removed in a way that avoids excessive CO_2 concentrations in the breathing atmosphere. Figure 6 shows representative human tolerance curves for CO_2 in terms of allowable concentration versus time duration. Curve A is the desirable standard for normal operation. Curve B sets emergency limits, consistent with maintaining astronaut performance at a functional level[4].

The many different ways of removing CO_2 from a space vehicle atmosphere can be combined into four basic processes, listed here in order of increasing complexity:

1. Open-cycle

2. Non-regenerable

3. Regenerable

4. O_2-recoverable

The open-cycle system, in which CO_2 is simply purged overboard by a relatively high ventilation rate, has a definite place in backpack or emergency breathing systems. Such systems will be important for many manned space missions. In spite of its high ventilating flow rates, the open-cycle system has been found to be optimum for a backpack emergency life support system of as long as 4 to 5 hours duration, in comparison with a non-regenerable CO_2 absorbent such as LiOH. The open system has the definite advantage of greater tolerance of leakage than the system using LiOH, an important consideration in suit-backpack applications.

The non-regenerable systems are mainly chemicals of two types: metal oxides or hydroxides, and superoxides. LiOH has been successfully used for CO_2 removal in the Mercury project. Its stoichiometry is predictable. Utilization efficiency is 90 per cent or better, requiring about 1.2 lb LiOH per lb of CO_2 absorbed.

As previously mentioned, LiOH evolves water when absorbing CO_2. If the evolved water cannot be credited to the system (and typically it

cannot, because LiOH will be used on missions where the water balance is not critical) there is incentive to consider Li_2O. Tests on CO_2 absorption with Li_2O are now in progress. If Li_2O proves successful it will result in a 37.5 per cent weight saving, since (at 90 per cent efficiency) only 0.76 lb Li_2O per lb of CO_2 will be required. Unfortunately, there will not be a corresponding volume saving. Li_2O is about 30 per cent less dense than LiOH.

By comparison, superoxides, such as NaO_2 or KO_2, absorb CO_2 and water vapor and produce oxygen, according to reactions such as:

$$2NaO_2 + CO_2 = Na_2CO_3 + 1.5\ O_2$$

$$2NaO_2 + 2CO_2 + H_2O = 2NaHCO_3 + 1.5\ O_2$$
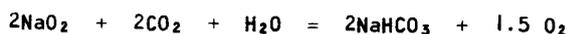
Ideally, the relative rates of these reactions should be controlled to maintain an $O_2 - CO_2$ balance with man's metabolism. For example, for a respiratory quotient of 0.82, the proper over-all reaction would be:

$$2NaO_2 + 1.23\ CO_2 + 0.23\ H_2O$$
$$= 0.77\ Na_2CO_3 + 0.46\ NaHCO_3 + 1.5\ O_2$$
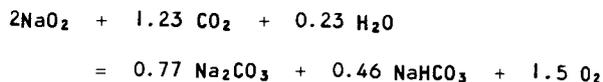
A simple material balance based on the above reaction shows that NaO_2 appears to be reasonably competitive with LiOH on a weight basis:

$$\frac{2NaO_2 - 1.5\ O_2}{CO_2} = 1.18$$

$$\frac{2LiOH}{CO_2} = 1.09$$

Detailed comparisons, reported elsewhere, show that NaO_2 is actually non-competitive with LiOH for CO_2 removal, even when NaO_2 is credited with the O_2 produced, and LiOH is not credited with the water produced[5]. Also, it appears infeasible to rely solely on chemical reaction with CO_2 to produce breathing oxygen; the process is too vulnerable to leakage, repressurization requirements, and unbalance in $O_2 - CO_2$ ratio. For this reason, the superoxide would have to be used as a supplemental oxygen source. On this basis, the superoxide loses its primary potential advantage, namely that of eliminating a separate oxygen supply. In short, superoxides are non-competitive with LiOH for CO_2 removal, when evaluated on an overall basis.

Typically, regenerable CO_2 systems utilize a process which is reversible by exposure to vacuum. The process must be periodic, to avoid the sealing problems inherent in a rotary regenerator. In simplest form, as shown in Figure 7, the device contains two sorbent beds with interconnecting valving to permit regeneration of one bed by exposure to vacuum, while the other is sorbing CO_2. Practical devices are somewhat more complex.

LiOH is unsuitable as a regenerable absorbent, since it requires excessive temperature for its regeneration. A survey of all common metal oxides and hydroxides has not yet led to any that are proven satisfactory as regenerable absorbents. In this connection, Ag_2O is of particular interest. The O_2 dissociation pressure vs temperature curve for Ag_2CO_3, shown in

Figure 8, suggests the possibility of absorption of CO_2 by Ag_2O at a temperature near $50°F$ and vacuum desorption at a temperature near $175°F$, both temperatures being within the range of temperatures available from the ECS. The decomposition of Ag_2O to Ag and O_2 during vacuum desorption of the Ag_2CO_3 is suggested by the dissociation pressure of O_2 over Ag_2O, but there is some evidence that the rate of decomposition of Ag_2O is slow enough not to cause trouble. Tests of Ag_2O were not successful in achieving practical CO_2 absorption rates, even at gas concentration of CO_2 in excess of 50 per cent[6]. Apparently the reaction of Ag_2O with CO_2 proceeds until the oxide surface is covered with Ag_2CO_3, after which it becomes very slow. Clearly, a way of improving the reaction rate is needed. If Ag_2O can be brought close to its potential performance in absorbing CO_2, and if it proves stable under vacuum desorption, it deserves serious consideration as a regenerable absorbent, since it has no affinity for water vapor.

The synthetic zeolites (molecular sieves or microtraps) are good regenerable adsorbents. They show good dynamic efficiency, are stable, and can be regenerated by adiabatic exposure to vacuum. Unfortunately, they adsorb water preferentially to CO_2, so that water must be removed rather completely in advance of CO_2 adsorption. The subsequent processing of the removed water has an important effect on the water balance, as already noted.

Regenerable adsorbent systems tend to use more power than the best proved non-regenerable system, (LiOH), because of the pressure drop associated with flow through the extra equipment which processes water vapor and CO_2, and (in some schemes) because of the need for heat to carry out the regenerative process. (Development of a regenerable substance like Ag_2O, specific to CO_2 and unaffected by water vapor would materially reduce the power consumption of the regenerable CO_2 system.)

Figure 9 shows schematically a regenerable CO_2 system using a molecular sieve as a CO_2 adsorbent, with vacuum regeneration. The process gas is predried by a silica gel adsorbent bed, which is periodically regenerated by the dry, essentially CO_2-free, effluent gas. Heat is required to aid in regeneration of the silica gel. This system retains the water vapor (temporarily adsorbed in the silica gel) in the system; this feature is essential for long missions with a tight water balance.

Missions in the 300 to 500-hour class will be characterized by chemical APU's with relatively high power penalties (of the order of 600 lb/kw), at least until a solar or nuclear APU is available. For such missions, the high power consumption of the system of Figure 9 places it at a distinct disadvantage compared to the non-regenerable LiOH absorbent.

Figure 10 is a photograph of a regenerable CO_2 system now under development. The same system is shown schematically in Figure 11. The design objective of this device is to be competitive with the non-regenerable LiOH for missions in the 300 to 500 hour class, which, with a chemical APU, are characterized by high power penalties and available by-product water. The system of Figure 10

has therefore been designed to minimize power consumption, at the expense of water recovery. This system differs from the system in Figure 9 in two ways:

1. Silica gel is regenerated by vacuum desorption rather than by purging.

2. Heat is provided for regeneration of the vacuum-exposed silica gel bed by conduction from the other silica gel bed, which is absorbing water.

Heat is transferred between the two silica gel beds by virtue of their being located on each side* of a conventional plate-fin heat exchanger. In essence, the water adsorbed in the silica gel on one side of the heat exchanger releases heat which is partly transferred to the gas flowing through the silica gel on the same side of the exchanger, and partly transferred to the vacuum-exposed silica gel bed on the other side. Calculations have shown that about 80 per cent of the heat released from the active bed is conducted to the vacuum-exposed bed, with only 20 per cent being transferred to the gas.

The two molecular sieve beds are also packed into two sides of a heat exchanger, primarily for convenience in packaging.

Existing valves, linked by Teleflex cable, were used for flow switching in this development unit. It may be desirable to vacuum-desorb the water vapor from both ends of the silica gel bed; the present valve arrangement provides for desorption of both water vapor and CO_2 through the same valve. One such valve is located between the silica gel and molecular sieve beds on each side of the unit.

Design conditions for the unit are shown in Table 5. Preliminary tests are now being run to measure the completeness of vacuum desorption of silica gel. If silica gel does not vacuum desorb adequately, one of the molecular sieves will be tried as a water adsorbent.

Table 5 shows a water loss of 1.52 lb/man day by vacuum desorption of the silica gel. This water loss is quite tolerable if a chemical APU is on board, thereby providing a by-product water source. The system has a lower power consumption than the purge-regenerated system of Figure 9 for two reasons:

1. Process gas flows through only two beds (one silica gel, one sieve). Hence pressure drop is reduced.

2. No external heat is required to regenerate the silica gel bed.

Another process of regenerative CO_2 removal is by freeze-out. Temperatures in the range of 225^0R are required to give adequately low CO_2 partial pressure. Given the availability of cryogenic fluids stored on the vehicle, either for atmosphere storage or for APU fuel, the potential exists for a heat sink which is both

*In heat exchanger terminology, "side" refers to a set of parallel flow passages taken together, as hot-side face area.

cold enough and adequate in capacity. The problem of water management is similar to that with the adsorbents, since water ice must be precipitated either upstream or together with the CO_2.

Figure 12 shows schematically a typical CO_2 freeze-out system, consisting of four thermally linked flow passes, numbered for identification. During the operating mode shown, process gas from the vehicle atmosphere, containing both CO_2 and water vapor, flows into pass 2 where it is cooled by heat transfer to both pass 1 and pass 3. Both the water vapor and CO_2 from the process gas freeze out on the surface of pass 2. The gas leaving pass 2 is essentially dry and has a CO_2 partial pressure well under 1 mm Hg. This gas is mixed with makeup LOX from storage, and the mixture flows to pass 1. The LOX, admixed with the cold, dry, nearly CO_2-free process gas provides part of the heat sink for pass 2. Discharge gas from pass 1 is returned to the space vehicle atmosphere. The remainder of the heat sink for pass 2 is provided by sublimation to vacuum of the CO_2 and H_2O vapor in pass 3. Pass 4 is inactive.

The complementary operating mode reverses all valve positions from those shown in Figure 12, making pass 1 inactive, pass 2 open to vacuum for desorption of water vapor and CO_2, pass 3 the receiver of inlet gas, and pass 4 the regenerative pass.

Figure 13 shows the performance potential of a regenerative freeze-out system using subcritically stored metabolic oxygen as a heat sink. The ordinate is the ratio of oxygen required to effect freeze-out to the metabolic oxygen. The abscissa is total pressure, which controls the total quantity of gas circulated. Operation below an ordinate of 1.0 is essential if the system is to work on metabolic oxygen alone. This is possible for pressures up to 7 psia, 70 per cent CO_2 recovery, and 3.8 mm Hg partial pressure of CO_2. In practice, supplemental oxygen (and possibly nitrogen) will be used by the ECS for leakage makeup, providing a performance margin.
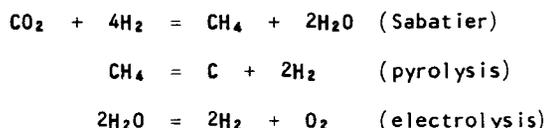
Cryogenic hydrogen is an excellent heat sink for CO_2 freeze-out, if available. A space radiator heat sink is also feasible. A small, oriented radiator panel is required. The radiator sink would be used for long missions where cryogenic APU fuel is not available, being precluded by the use of solar or nuclear power, and where the supply of stored oxygen is limited by the existence of an oxygen-recoverable CO_2 cycle. In such a case, the CO_2 freeze-out system would give up its CO_2 to the O_2-recovery system. The tolerability of water-ice admixed with the CO_2-ice depends on the mechanics of the O_2-recovery system; if a mixture is not tolerable, the H_2O and CO_2 can be frozen out separately at different temperature levels, and therefore recovered separately.

Long space missions, greater than about 2000 hours, will require such large quantities of metabolic oxygen that it will become economical to recover O_2 from CO_2. Such missions will have solar or nuclear power at reasonable penalties, probably in the range of 200 to 500 lb/KW. The theoretical minimum power available for regeneration of O_2 from CO_2 is given by the free energy of formation of CO_2, which is 1.13 KWh/lb CO_2 or 1.55 KWh/lb O_2. Practical processes can be

expected to consume several times the theoretical minimum energy.

Clearly, power from a chemical APU (fuel cell or heat engine) which produces no more than about 1.0 KWh/lb of fuel consumed, is not attractive for regeneration of O_2, with a power requirement no less than 1.55 KWh/lb. O_2 recovery is therefore definitely tied to missions with solar or nuclear power available.

Direct thermal or electrolytic decomposition of CO_2 has been extensively studied, with only limited progress toward a system useful in a space vehicle. As an alternate, processes producing intermediate products have been considered. A promising example is the hydrogenation of CO_2 by the Sabatier process, followed by pyrolytic decomposition of methane and electrolysis of water. The reactions are:

$$CO_2 + 4H_2 = CH_4 + 2H_2O \quad \text{(Sabatier)}$$

$$CH_4 = C + 2H_2 \quad \text{(pyrolysis)}$$

$$2H_2O = 2H_2 + O_2 \quad \text{(electrolysis)}$$

The sum of these reactions gives the desired end result:

$$CO_2 = C + O_2$$

Except for a small initial and makeup supply, the required hydrogen would be regenerated by the process. Similarly, the intermediate products, methane and water, would be decomposed as shown.

Use of the water in the Sabatier reaction to augment the space vehicle water supply is not recommended, nor does it appear advantageous to use methane as fuel for a chemical APU.

The Sabatier reaction has a favorable equilibrium (99 per cent conversion of CO_2 at 400°F; 95 per cent at 640°F). Catalysis of the reaction is necessary for any practical reaction temperature; catalyst development is naturally aimed at a reasonable reaction at a low temperature, where the equilibrium is favorable relative to competing side reactions, such as:

$$CO_2 + 2H_2 = C + 2H_2O$$
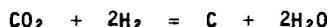
(This is the reverse of the commercial water gas reaction used to produce hydrogen from coal and steam. This reaction, catalyzed, proceeds from left to right at about 1000°F.)

Methane spontaneously pyrolyzes at 1600°F or higher. The reaction is substantially complete at 2000°F. Reaction at lower temperatures is is desirable for space applications. In particular, it would be desirable to pyrolyze methane at a temperature low enough to absorb the heat produced by the Sabatier reaction:

$$CO_2 + 4H_2 = CH_4 + 2H_2O + 1640 \text{ Btu/lb } CO_2$$

$$CH_4 = C + 2H_2 - 830 \text{ Btu/lb } CO_2$$
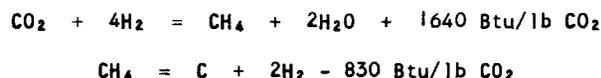
The Sabatier reaction has plenty of heat available, but for this heat to have a chance of being used to pyrolyze methane, the temperature would have to be at least 600°F, with some sacrifice of completeness of CO_2 conversion. Even at this temperature, the equilibrium conversion of CH_4 to C and H_2 is less than 10 per cent. To make the CH_4 pyrolysis complete at 600°F, carbon would have to be continuously removed. Process-development tests of low-temperature pyrolysis of methane are planned as a supplement to test work recently completed on the Sabatier reaction[7]. The latter will be briefly summarized in the next few paragraphs. It is of course not essential that the heat to pyrolyze methane be obtained from the Sabatier reaction, but it is desirable to do so.

The Sabatier reaction will not work in the presence of appreciable oxygen because of the preferential reaction with hydrogen to form water. Thus, space vehicle atmospheres, with only about 1 per cent CO_2 content, cannot be hydrogenated. It is necessary to work with relatively pure CO_2. In the test work reported in Reference 7, CO_2 was obtained by desorption of a molecular sieve bed (Linde type 5A). Rather than desorb the sieve by the usual process of exhausting to low pressure (which in this case would require a pump) the CO_2 was removed by purging with hydrogen at 300°F. Approximately 75 per cent desorption was obtained in a once-through process. Complete desorption of CO_2 from the sieve is unnecessary.

The advantage of H_2-purge desorption is the power saved. Figure 14 shows typical power requirements for pumping CO_2 (temperature = 100°F) from a desorption pressure of 0.05 mm Hg to the pressures shown. The disadvantage of H_2-purge desorption is the variable composition of the purge gas, which was found to have an unfavorable effect on the completeness of the Sabatier reaction.

In a typical run on purge gas, 85 per cent conversion of the CO_2 to CH_4 was obtained at 600°F in one pass through the reactor, with a nickel catalyst. The effect of the unconverted CO_2 on the subsequent processing (especially pyrolysis) has not been investigated. Hopefully, small percentages of CO_2 would be tolerable, passing through the process and being recycled to the sieve inlet with the produced hydrogen.

CO formation should be avoided on principle. This is one of the best reasons for keeping the temperatures reasonably low, since CO formation is thermodynamically favored at high temperatures.

Figure 15 shows the elements of a complete, steady-flow, O_2 recovery system using H_2-purge desorption of the sieve bed, a catalytic reactor for the Sabatier process, a cooler-condenser to separate the water produced, an electrolyzer for the water, and a pyrolyzer for the methane.

The major power requirement would be for the gas blowers and for the electrolysis of water. Figure 16 compares the theoretical energy requirement for electrolysis of water with that achieved by actual electrolytic cells. Efficiencies of 50 to 80 per cent are typical. O_2 is drawn from the electrolytic cell and returned to the breathing system. The hydrogen from the electrolytic cell is dehumidified, combined with the hydrogen from CH_4 pyrolysis, and returned to the desorbing sieve bed.

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Work to date on the Sabatier reaction has gone a long way toward establishing its feasibility for O_2 recovery in space ECS, but substantial development of the process remains.

Certain ion exchange resins absorb CO_2 from gas streams. Since these resins can be regenerated electrically, the materials can be used in regenerable CO_2 removal systems using the fundamental process of electrodialysis. Cationic and anionic exchange membranes which are permeable to ions of opposite charges are placed in contact with the ion exchange resin bed. These membranes, which are essentially the ion exchange resins in film form, provide the means for CO_2 removal from the resin bed.

Operation of an electrodialysis removal system involves absorption of the CO_2 in a basic ion exchange resin bed to form carbonate ions:

$$2(R^+ + OH^-) + CO_2 = (2 R^+ + CO_3^=) + H_2O$$
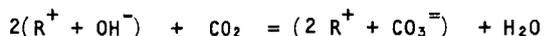
As shown in Figure 17, the carbonate ions migrate from the absorption bed through an anionic membrane into an adjacent reaction bed. Hydrogen ions migrate into this reaction bed through a cationic membrane on the opposite side of the reaction bed. The hydrogen ions and carbonate ions react to liberate CO_2 and H_2O:

$$CO_3^= + 2H^+ = H_2O + CO_2$$
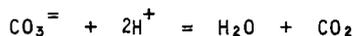
Hydrogen and oxygen are generated at the cathode and anode, respectively. The ratio of the gas generation rate to the CO_2 removal rate depends upon the internal arrangement of the cell. If the cell is designed primarily for CO_2 removal, it will have a relatively large number of removal passages per pair of electrodes. If the cell is to be used in an oxygen recovery system, the electrode area will be sized to provide the required O_2 flow while removing the CO_2. Of course, increased O_2 production will involve increased power consumption over that needed for CO_2 removal alone. The theoretical power required for CO_2 removal alone is 65 watts/man. Present prototype electrodialysis cells require approximately 350 watts/man. There is reason to believe that the power consumption can be reduced to less than 100 watts/man. Because of the continuous flow and static nature of the process, electrodialysis may be used to advantage for long-duration space missions.

Table VI contains recommended ECS elements for missions of length 3, 30, 300, 1000, and 3000 hours. The 3 and 30 hour missions are assumed to carry 1 man; the other missions are assumed to carry 3 men. Recommended power source is included in the table together with a power penalty figure. Power selection is included because of its effect on ECS element selection. The quoted penalty range for solar-nuclear power (200-500 lb/kw; 100-300 lb/kw) reflects a range of system advancement status and also a range of power levels, as shown.

Weights of expendables produced and consumed per man are shown for the mission lengths indicated. These quantities are the theoretical calculated minima; for example, the O_2 shown is metabolic O_2 only. Where closed cycles are used for O_2 or H_2O recovery, the numbers in parentheses

reflect an arbitrarily selected inventory for makeup and emergencies. Where total water utilization differs from the makeup quantity required, because of partial water recovery, both numbers are shown. For example, on a 1000-hour mission, the total water utilized is 460 lb/man, of which all but 75 lb/man is provided by water recovery.

There are few surprises in the table. The longest mission shown (3000 hours) is clearly in the stored food and stored solid waste regime. (The latter would probably be dehydrated to save volume.) Only the 3000 hour mission, of those shown, utilizes oxygen recovery.

Acknowledgment

References

1. "Development of Analytical Cooling Design Techniques and Procedures for Airborne Electronic Equipment," C. H. LaFranchi, AiResearch Report L-9033-R; Progress Report, NADC Contract N62269-1353.

2. "How to Select an Adequate Cooling System," A. L. Johnson, Electronics, Oct. 20, 1961.

3. "Waste Water Recovery System," F. Fujimoto; AiResearch Report L-9099-MR; Progress Report, Contract AF33(657)-7252 for Aerospace Medical Laboratory, ASD

4. Data received from Department of Aerospace Medicine and Bioastronautics, the Lovelace Foundation.

5. "Atmospheric Control Systems for Space Vehicle," J. Rousseau; AiResearch Report SS-716-R. To be published by ASD in T & A series.

6. "Analytical Methods for Space Vehicle Atmosphere Control Processes--Part 2," C. S. Coe, J. Rousseau, A. Shaffer; AiResearch Report SS-595-R, to be published by ASD in T & A series.

7. "Space Vehicle Atmospheric Control Study: Investigation of Integrated CO_2 Hydrogenation Systems," R. F. Rydelek; AiResearch Report SS-712-R, to be published by ASD in the T & A series.

8. "Low Temperature Absorption of CO_2 by Molecular Sieves," G. Christensen and J. R. Wenker; AiResearch Report SS-715-R. To be published by ASD in T & A series.

9. "Contaminant Freeze-out Study for Closed Respiratory Systems," AiResearch Report SS-596-R. Technical Documentary Report No. MRL-TDR-62-7. C. C. Wright; Prepared for Aerospace Medical Laboratories, ASD, under Contract AF33(616)-7768.

10. "Problems and Progress in Providing an Earth Environment for Manned Space Flight," J. N. Waggoner, W. L. Burriss; ARS Space Flight Report to the Nation, October 1961.

11. "Problems Associated with Environmental Control in Manned Spacecraft with Mission Durations up to Two Weeks," J. N. Waggoner, W. L. Burriss; J. ARS (in press).

TABLE I HUMAN MATERIAL BALANCE

CONSUMED	LB/MAN DAY	PRODUCED	LB/MAN DAY
FOOD	1.80	CO_2	2.25
OXYGEN	2.00	WATER VAPOR (EXHALED & PERSPIRED)	5.70
		WATER (URINE)	3.25
		WATER (FECAL)	0.30
DRINKING WATER	8.00	SOLID WASTE (URINE + FECAL)	0.30
WASH WATER	3.00	WASH WATER	3.00
TOTAL	14.80	TOTAL	14.80

BASED ON:
1. AVERAGE METABOLIC LEVEL ANTICIPATED IN SPACE FLIGHT.
2. RESPIRATORY QUOTIENT (CO_2 PRODUCED/O_2 CONSUMED) =.82.
3. 50-50 SPLIT OF SENSIBLE AND LATENT COOLING LOAD.
4. ARBITRARY WASH WATER ESTIMATE.

TABLE III SPACE VEHICLE WATER BALANCE

CONSUMED	LB/MAN DAY	PRODUCED	LB/MAN DAY
HUMAN	11.0	HUMAN	12.25
		BY-PRODUCT SOURCES	
		LiOH	0.90
		$H_2 \vert O_2$	8.00
		TOTAL	21.15

BASED ON:
1. $CO_2 = 2.25$; $2 LiOH + CO = Li_2 CO_3 + H_2O$

2. APU POWER = .33 KW/MAN DAY (AVERAGE)
SFC = 1.00 LB/KW HR

TABLE II HUMAN WATER BALANCE

CONSUMED	LB/MAN DAY	PRODUCED	LB/MAN DAY
DRINKING WATER	8.00	WATER VAPOR (EXHALED & PERSPIRED)	5.70
WASH WATER	3.00	WASTE WATER (URINE & WASH)	6.25
TOTAL	11.00	FECAL WATER	0.30
		TOTAL	12.25

BASED ON WATER QUANTITIES OF TABLE I. EXCESS OF 1.25 LB REPRESENTS WATER TAKEN IN WITH FOOD (0.25 LB) AND METABOLIC WATER (1.00 LB).

TABLE IV SPACE VEHICLE WATER BALANCE FOR VARIOUS RECOVERY SOURCES

		PRIMARY WATER RECOVERY SOURCES			
		VAPOR (EXHALED AND PERSPIRED) WASTE (URINE AND WASH) FECES	VAPOR (90%) WASTE (90%)	VAPOR (90%)	NONE
BY-PRODUCT WATER RECOVERY SOURCES	APU AND LIOH	10.1	8.6	3.0	-2.1
	APU	9.2	7.7	2.1	-3.0
	LIOH	2.1	0.6	-5.0	-10.1
	NONE	1.2	-0.2	-5.9	-11.0

POSITIVE NUMBERS DENOTE WATER SURPLUS, LB/MAN DAY
NEGATIVE NUMBERS DENOTE WATER DEFICIT, LB/MAN DAY

TABLE V

OPERATING CONDITIONS, REGENERABLE CO_2 SYSTEM

ATMOSPHERE MOLECULAR WEIGHT	MW	=	30
INLET PRESSURE	P_1	=	7.0 psia
INLET TEMPERATURE	T_1	=	45 ^0F
INLET HUMIDITY	γ_1	=	0.013 lb/H_2O lb atmosphere (saturated)
OUTLET HUMIDITY	γ_2	=	0
AVERAGE INLET CO_2 CONCENTRATION	Y_1	=	0.0207 lb/lb atmosphere
INLET CO_2 PARTIAL PRESSURE	p_1	=	5.0 mm Hg
AVERAGE OUTLET CO_2 CONCENTRATION	Y_2	=	0.0021 lb/lb atmosphere
OUTLET CO_2 PARTIAL PRESSURE	P_2	=	0.5 mm Hg
CO_2 REMOVAL RATE	Y	=	7.5 lb/day (3 men)
CO_2 REMOVAL RATE	Y	=	0.313 lb/hr
ATMOSPHERE FLOW RATE	W	=	16.8 lb/hr
WATER LOSS	L	=	0.19 lb/hr
WATER LOSS	L	=	4.56 lb/day (3 men)
WATER LOSS	L	=	1.52 lb/man day
SILICA GEL BED WEIGHT	X	=	3.0 lb silica gel (per pass)
MOLECULAR SIEVE BED WEIGHT	Z	=	3.3 lb zeolite (per pass)
SILICA GEL BED	ΔP	=	3.73 psf
MOLECULAR SIEVE BED	ΔP	=	7.90 psf
DESIGN CYCLE TIME (BOTH BEDS)	θ	=	20 min

TABLE VI

RECOMMENDED ECS ELEMENTS

MISSION DURATION, HOURS	POWER SOURCE AND PENALTY, LB/KW / ESTIMATED POWER LEVEL	HEAT SINK	ATMOSPHERE SOURCE		CO2 REMOVAL	CO2 RECOVERY AND O2 REGENERATION	H2O REMOVAL	H2O RECOVERY FROM ATMOSPHERE	FOOD MANAGEMENT	WASTE MANAGEMENT INCLUDING H2O RECOVERY FROM WASTE	TOTAL WATER CONSUMED (DRINKING, FOOD PREPARATION, WASH)	TOTAL EXPENDABLES CONSUMED (NOT INCLUDING POWER PENALTY)	TOTAL EXPENDABLES PRODUCED AND STORED
			OXYGEN	NITROGEN									
3	BATTERIES 60 LB/KW — 50 W	CRYOGENIC O_2	CRYOGENICALLY STORED (8 LB), SET BY COOLING LOAD	NONE	OPEN CYCLE VENTILATION BY O_2	NONE	COOLER-CONDENSER-SEPARATOR	NONE (ALL CONDENSED WATER IS RE-EVAPORATED)	NONE	NONE	NONE	(8 LB)	NONE
30	H_2-O_2 APU; 300 LB/KW — 1 KW	WATER (7.5 LB) + CRYOGENIC O_2 AND H_2 AS AVAILABLE	CRYOGENICALLY STORED (2.5 LB)	NONE	LIOH (3.4 LB)	NONE	→	→	STORED (22 LB)	STORED (3.8 LB)	(10 LB)	(25.6 LB)	(3.8 LB)
300	H_2-O_2 APU; 600 LB/KW (SOLAR-NUCLEAR APU WHEN AVAILABLE: 200-500 LB/KW) — 2 KW	RADIATOR + CRYOGENIC O_2 AND H_2 AS AVAILABLE	CRYOGENICALLY STORED (25 LB)	CRYOGENICALLY STORED; QUANTITY DEPENDS ON LEAKAGE AND REPRESSURIZATION REQUIREMENTS	LIOH (34 LB)	NONE	→	PARTIAL RECOVERY	STORED (22 LB)	STORED (85 LB)	140 LB; PARTIALLY MET BY WATER RECOVERY; WATER INVENTORY: (35 LB)	(117 LB)	(85 LB)
1000	H_2-O_2 APU; 1200 LB/KW (SOLAR-NUCLEAR APU WHEN AVAILABLE: 200-500 LB/KW) — 5 KW	→	CRYOGENICALLY STORED (85 LB)	→	REGENERABLE: MOLECULAR SIEVE OR FREEZE-OUT	NONE	COOLER-CONDENSER-SEPARATOR, WITH FURTHER WATER REMOVAL PRIOR TO CO_2 PROCESSING	POTENTIAL RECOVERY WITH CHEMICAL APU, NEARLY COMPLETE WITH SOLAR-NUCLEAR APU	STORED (75 LB)	WATER RECOVERY AS NEEDED FOR WASTE WATER. STORAGE OF FECAL WASTE AND URINE RESIDUE (42 LB)	460 LB; PARTIALLY MET BY WATER RECOVERY; WATER INVENTORY: (75 LB)	(150 LB)	(42 LB)
3000	SOLAR-NUCLEAR APU; 100-300 LB/KW — 10 KW	RADIATOR	STORED AS GAS FOR MAKEUP AND EMERGENCIES (75 LB)	STORED AS GAS; LEAKAGE MUST BE LOW (75 LB)	→	SABATIER + CH_4 PYROLYSIS + H_2O ELECTROLYSIS	→	AS COMPLETE AS POSSIBLE	STORED (225 LB)	WATER RECOVERY FROM WASTE WATER, DEHYDRATION OF FECES TO SIMPLIFY STORAGE (105 LB)	1400 LB; PARTIALLY MET BY WATER RECOVERY; WATER INVENTORY: (150 LB)	(325 LB)	(105 LB)

NOTE: Weights in parentheses indicate theoretical minimum quantity of indicated expendables consumed or produced per man for the mission length indicated. System selection is based on 1 man for the 3 and 30 hour missions, 3 man for longer missions.

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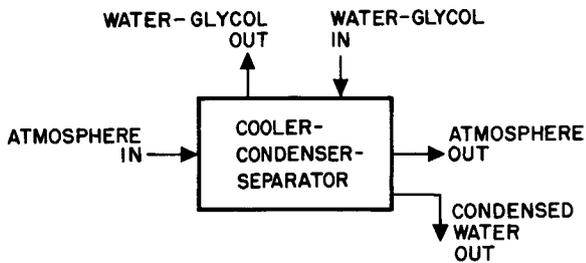
FIGURE I. COOLING, DEHUMIDIFYING, AND WATER RECOVERY PROCESS
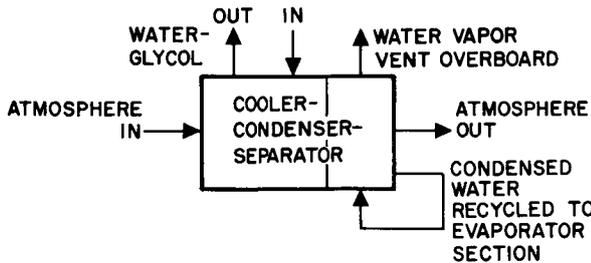
FIGURE 2. COOLING AND DEHUMIDIFYING PROCESS

FIGURE 3. Integral Cooler--Condenser--Water Separator

FIGURE 4. WASTE WATER RECOVERY SCHEMES
a. Available Heat Source and Sink

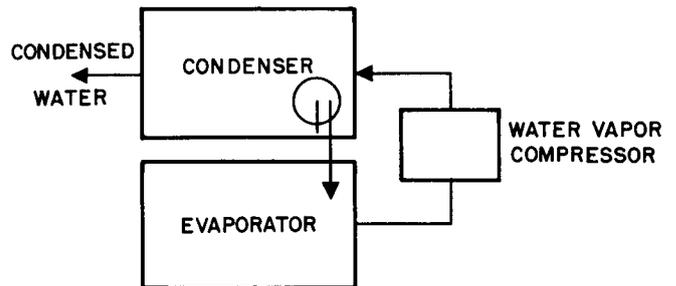
FIGURE 4. WASTE WATER RECOVERY SCHEMES
b. Vapor Compression

FIGURE 4. WASTE WATER RECOVERY SCHEMES
c. Thermoelectric
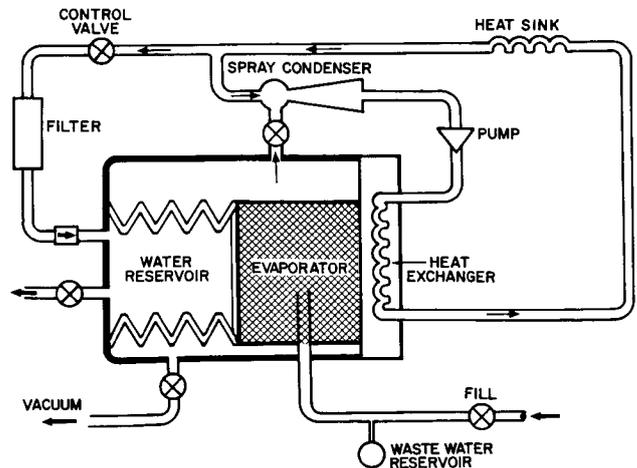
FIGURE 5. SCHEMATIC DIAGRAM
WASTE WATER RECOVERY SYSTEM

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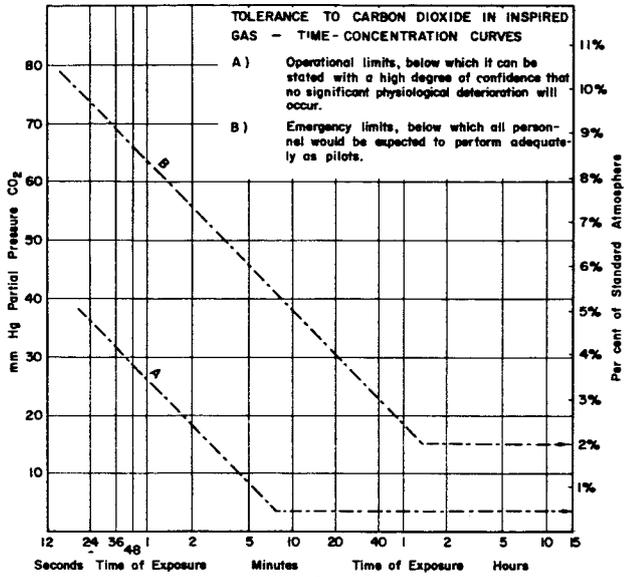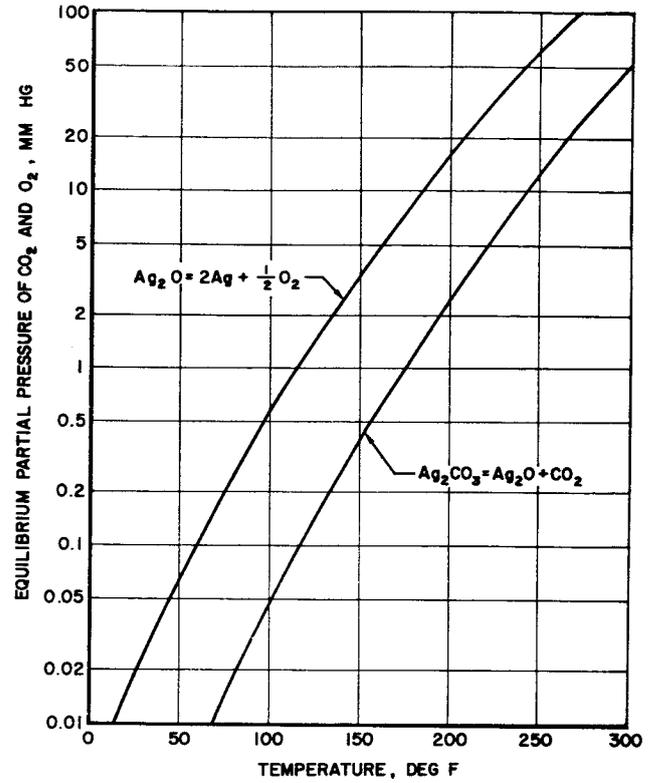
FIGURE 6.

FIGURE 8. EQUILIBRIUM PARTIAL PRESSURES
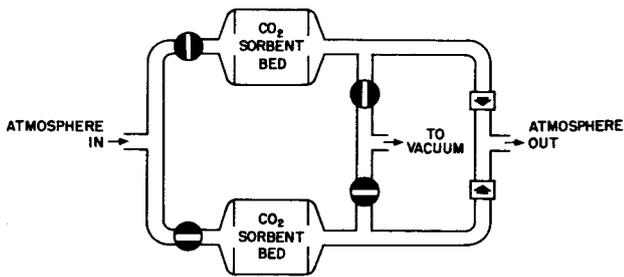
FIGURE 7. SIMPLIFIED REGENERABLE CO_2 SORBENT SYSTEM
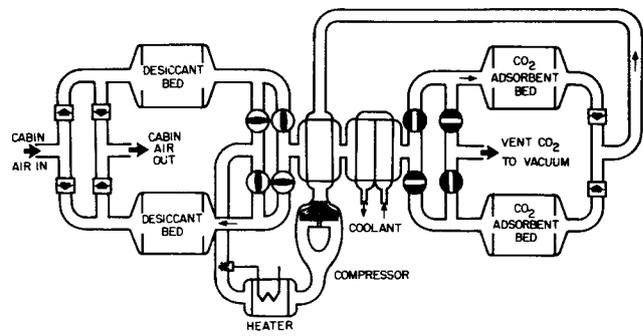
FIGURE 9. RECUPERATIVE CYCLE REGENERABLE CO_2 REMOVAL SYSTEM

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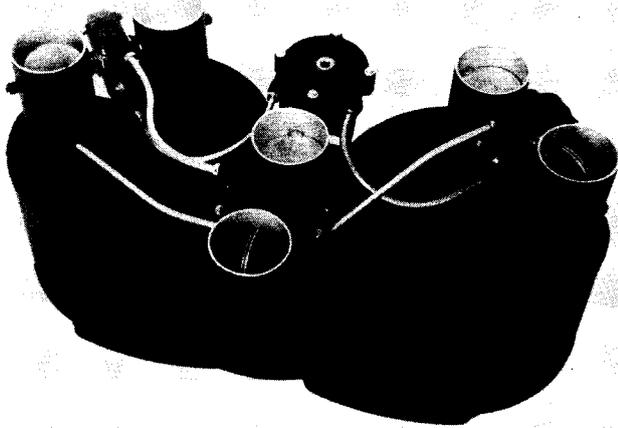
Figure 10.   Regenerable CO_2 Removal System
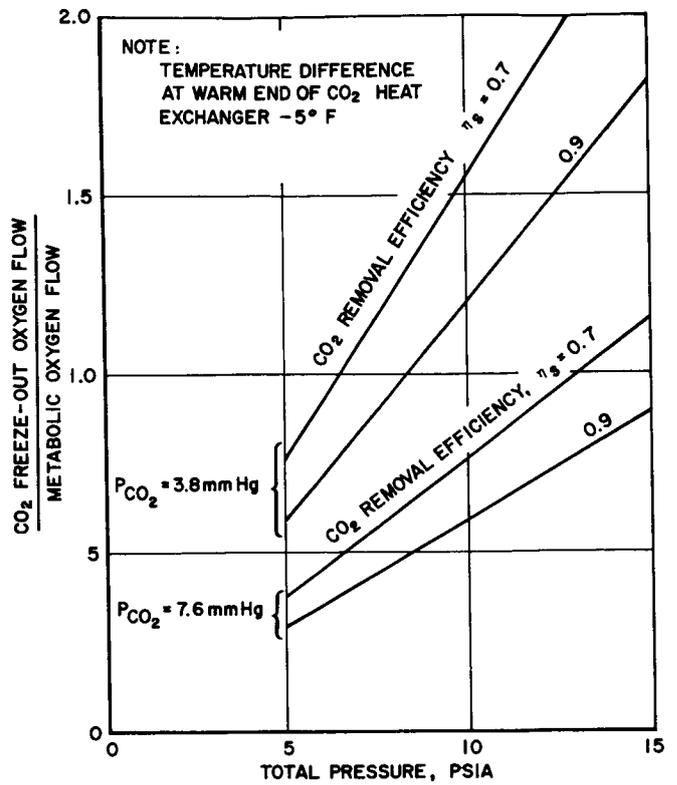
FIGURE 13. PERFORMANCE OF CO_2 FREEZE-OUT SYSTEM
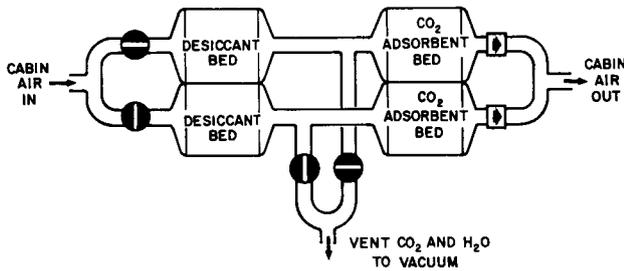
FIGURE II. REGENERABLE CO_2 REMOVAL SYSTEM WITH
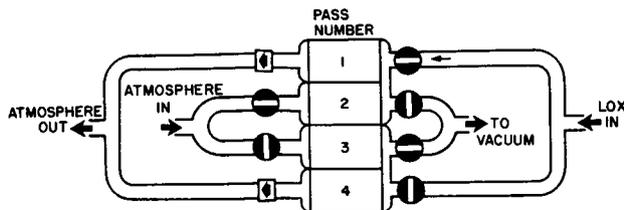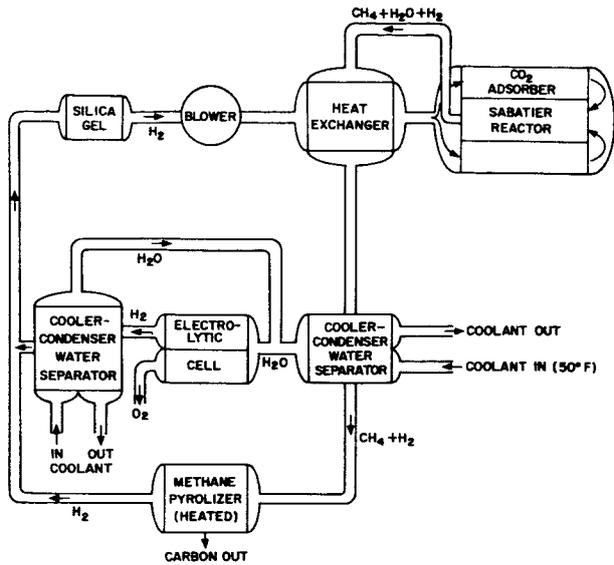VACUUM DESORPTION OF CO_2 AND H_2O

FIGURE 14. PUMPING POWER FOR DESORPTION
OF REGENERABLE ADSORBENT

FIGURE 12. REGENERABLE CO_2 FREEZE-OUT SYSTEM

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FIGURE 15. O_2-RECOVERABLE CO_2 PROCESSING SYSTEM
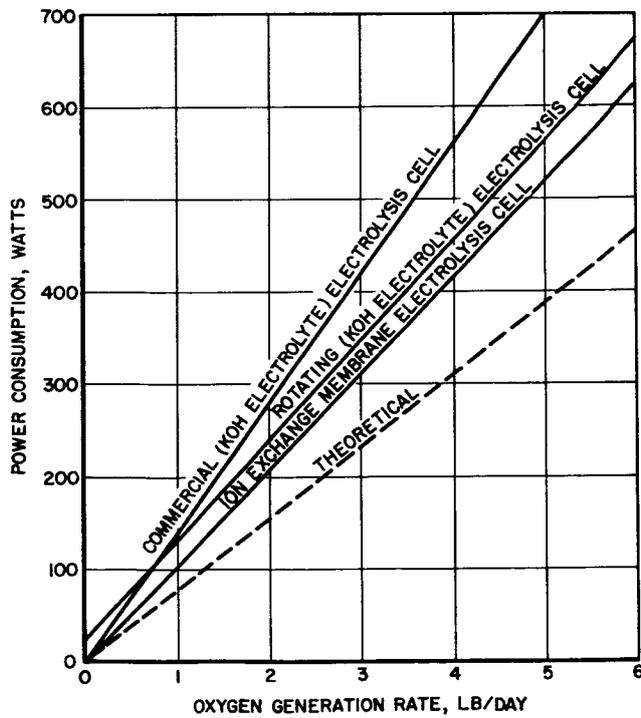
FIGURE 16. POWER REQUIRED FOR ELECTROLYSIS
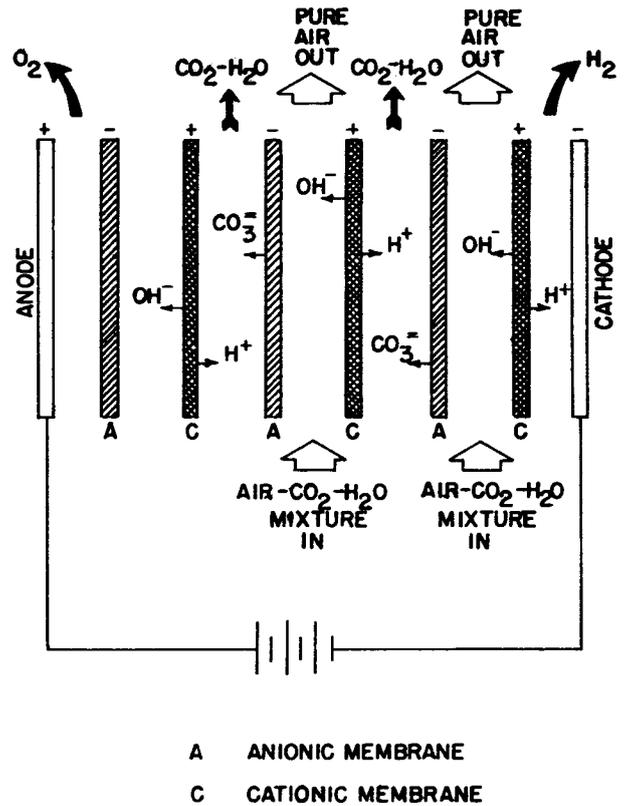OF WATER

A   ANIONIC MEMBRANE

C   CATIONIC MEMBRANE

FIGURE 17. ION EXCHANGE ELECTRODIALYSIS UNIT FOR
CONTINUOUS CO_2 REMOVAL