NASA CR-66323

RESEARCH, DESIGN, AND DEVELOPMENT OF AN IMPROVED WATER RECLAMATION SYSTEM FOR MANNED SPACE VEHICLES

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April 1966

Prepared under Contract No. NAS 1-4373 by
RAI RESEARCH CORPORATION
Long Island City, N.Y.

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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RESEARCH, DESIGN AND DEVELOPMENT OF AN IMPROVED WATER RECLAMATION SYSTEM FOR MANNED SPACE VEHICLES

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SUMMARY

A three-man mission requires the treatment of approximately 4.5 liters per day of urine. This study was to develop a method and prototype equipment for the recovery of the water contained in this quantity of urine while removing the salts in the form of a brine concentrate and destroying the organic components by converting them to nitrogen, carbon dioxide and hydrogen.

Accordingly, the two principal operations comprising this system are first, electrochemical conversion of the organic components and secondly, the recovery of the water by reverse osmosis separation employing a membrane stack at 1500 lbs./sq.in.

The electrochemical conversion requires 457 watt-hrs. as electrical energy for each liter of urine which is treated.

The solution which is a product of electrochemical treatment contains a small amount of available chlorine and a small amount of free acid produced as a result of anodic oxidation of ammonia or urea to nitric acid.

A neutral solution free of chlorine and oxidizable matter (COD) is produced by treating the solution with a small quantity of activated carbon and magnesium oxide. This treated solution is now in condition for reverse osmosis separation of the water.

The membrane stack which is delivered under this contract contains 10 circular membranes, 4 inches in diameter, a 3 inch diameter circle constitutes the surface which is available for reverse osmosis separation, the total area approximately 70 square inches. The capacity of this stack is 18 liters per day and while it may suffer some capacity reduction after prolonged service, the margin of safety is regarded as ample.

Potable water was produced by this unit from electrochemically treated urine. The indicated recovery is 90 per cent as a minimum. Additional membrane area may readily be incorporated in the stack simply by adding additional membrane sub-assembly modules. The stack is readily assembled and the membranes sub-assemblies removed or replaced for routine maintenance. The energy requirement for reverse osmosis separation at 1500 lbs./sq.in. forward pressure is approximately 3.5 watt-hrs. per liter of product water or 15.75 watt-hrs. for 4.5 liters daily, this is less than a watt of continuous power assuming 100% pump efficiency.

Phase separation is required for operation under zero G conditions. At the inception of this program it was considered advisable to develop a mechanical phase separator under this contract. Since that time other types of phase separators suitable for use in this system have become available. However, a phase separator developed under this program is being delivered under this contract. This unit serves as a circulating pump as well as a phase separator and possesses a capacity of 2 liters per minute of liquid and is capable of being operated in any spatial orientation and therefore, presumably, under zero G conditions. Its capacity is greatly in excess of that required for a system to treat 4.5 liters of urine daily. Consequently, a considerable scaling down is required for a flight qualifiable unit.

INTRODUCTION

Chemical Composition of Urine

Table 1 indicates the quantities of various components of human urine which are excreted daily (ref. 1).

These quantities are of course subject to a considerable degree of variation owing to the dietary variation and the variation of various metabolic processes among individuals. The system which must be designed to recover water from urine must be sufficiently flexible to permit the flexibility required to adapt its performance to these variations.

Table 1

Composition of Typical Human Urine

Constituent	Average Daily Excretion in Grams
Water	1200.0
Solids	60.0
Urea	30.0
Uric Acid	0.7
Hippuric Acid	0.7
Creatinine	1.2
Indican	0.01
Oxalic Acid	0.02
Allantoin	0.04
Amino Acid Nitrogen	0.2
Purine Bases	0.01
Phenols	0.2
Chloride as Sodium Chloride	12.0
Sodium	4.0
Potassium	2.0
Calcium	0.2
Magnesium	0.15
Sulfur, total, as S	1.0
Inorganic Sulfates as S	0.8
Neutral Sulfur as S	0.12
Conjugated Sulfates as S	0.08
Phosphate as P	1.1
Ammonia	0.7

Previous Systems

Other systems for water recovery from urine are dependent on a phase change separation method or on a method based on membranes which are selectively permeable. Among these membrane methods electrodialysis is dependent on membranes which retain the water while transferring the electrolytes under an electrical potential. Reverse osmosis, on the other hand, is dependent on membranes which are permeable to water under a pressure difference while rejecting the electrolytes.

Unfortunately, phase separation methods based on distillation require low operating temperatures and pressures, even then there occurs a considerable amount of thermal decomposition. Some of these decomposition products are distilled and contaminate the product water.

Membrane processes do not afford an adequate means of separating the water from urea and other organic components of urine. Consequently, if they are to be employed these must be combined in a system with a method which is capable of destroying or removing the organic components which, as shown in Table 1, constitute a very considerable fraction of the solids contained in urine.

Other methods which have been proposed or developed are dependent on sorption of organic components employing activated carbon. The usefulness of such methods is limited. The systems require a very large part of the sorbent carbon, which constitutes an expendable. The use of carbon or other sorbent may reasonably be considered, however, for the purpose of a final "clean up" to remove small amounts of residual substances following some other method of treatment. Chemical methods depending on oxidizing substances, e.g., calcium hypochlorite, are subject to the same considerations of weight limitations as pertain to the use of sorbents.

Present System

The system concept of this contract is based on:

1. Electrochemical oxidation to transform urea, uric acid, hippuric acid, creatinine and other organics to nitrogen, carbon dioxide and water.

2. Sorption of residual nitrogenous substances and/or chloramine derivatives using activated carbon and magnesium oxide.

3. Reverse osmosis separation of the water from chlorides, sulfates and phosphates of sodium, potassium, calcium and magnesium.

It is believed that a system based on the sequences of these three methods is capable of producing potable water feasibly at acceptable cost in terms of weight and energy requirements.

ELECTROCHEMICAL TREATMENT

Direct Oxidation with Oxygen

The direct reaction of oxygen gas with the organic components of urine should, according to thermodynamic considerations, occur spontaneously with formation of nitrogen, carbon dioxide and water as reaction products. Thus, the following reactions proceed with a considerable negative free energy change.

$$2NH_3 + 3O_2 = N_2 + 3H_2O$$

$$\Delta F^{o}_{298} = -162.26 \text{ Calories}$$

$$(NH_2)_2CO + 3O_2 = N_2 + CO_2 + 2H_2O$$

$$\Delta F^{o}_{298} = -160.52 \text{ Calories}$$

Unfortunately, these reactions do not proceed appreciably in vitro at ambient temperature in aqueous solution. That is to say the energy, or heat of activation is extremely high. Consequently, although the desired reaction is spontaneous, and even capable of generating energy the requirements for conducting the reaction at a significant and practical rate are such that energy is, in fact, required. One of the important objectives of this program is to optimize the energy requirements or the system.

Electrochemical Method

A method has been developed for the electrochemical oxidation of the organic components of urine. The cell in this method employs an anode and a cathode, each of platinized expanded titanium mesh (Exmet) separated by a polyethylene screen. Current through the cell causes the reduction to hydrogen gas at the cathode and formation of various products of oxidation in a rather complex sequence at the anode. The energy requirement and the efficiency of the electrochemical oxidation process are then dependent on the current density, the geometry of the system and the temperature. The relation of all of these to the results obtained may be better understood

from consideration of the various reactions which are known to occur.

Primary Anode Reaction.- It can be seen from Table 1 that urine contains a considerable quantity of chloride. Passage of current through the cell results in the formation of water-soluble elemental chlorine in the vicinity of the anode in accordance with the following equation:

$$2Cl^- \longrightarrow Cl_2 + 2e^- \text{ (anode)} \qquad (1)$$

Oxygen should require from considerations of reversible thermodynamics, a lower anodic potential for liberation than is required for that of chlorine. The overvoltage on a platinized surface is however sufficient to preclude liberation of atmospheric oxygen as long as there is an appreciable amount of chloride ion available.

Chlorine which is produced at the anode exists in equilibrium with hypochlorous acid produced in accordance with the following reaction:

$$Cl_2 + OH^- \longrightarrow HClO + Cl^- \qquad (2)$$

Chloride ions must migrate or diffuse to the surface of the anode in accordance with the current density and the faraday equivalence. There is a boundary layer which surrounds the anode and this layer constitutes a migration, or diffusion, barrier. The thickness of the barrier layer and the degree of resistance to migration and diffusion is dependent to geometry and degree of agitation in the cell.

If the current density is increased progressively until the concentration of chloride ions at the electrode-solution interface become very low, there is an abrupt increase in electrode potential accompanying the reaction

$$Cl^- + H_2O \longrightarrow HOCl + H^+ + 2e^- \qquad (3)$$

With further increase in current density there is an additional rise in anode potential with formation of chlorate in accordance with the following:

$$Cl^- + 3H_2O \longrightarrow ClO_3^- + 6H^+ + 5e^- \qquad (4)$$

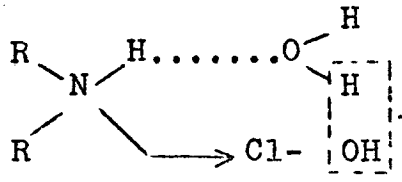
Although these equations are written as though hypochlorous acid and chlorate are all produced by reaction at the anode of chloride ions it will be understood that these reactions may occur as a sequence in progressive stages from elemental

chlorine, hypochlorous acid and finally chlorate. Formation of elemental chlorine and hypochlorous acid or hypochlorite is desirable inasmuch as these substances react with the organic components with desirable results leading to reformation of chloride ion which is then available for return to the anode and reoxidation to chlorine or hypochlorous acid in a cycle. Formation of chlorate on the other hand is wasteful both of electrical energy as well as of chloride ions which are accordingly removed or made unavailable.

Electrochemical Oxidation of Ammonia.- As shown in Table 1 the content of free ammonia in normal urine which has not undergone decomposition or hydrolysis is quite small. However, the reaction of chlorine and hypochlorite with ammonia has been studied intensively and the reactions of mono- and dichloramine and nitrogen trichloride in aqueous solutions have been a subject of considerable research. The chlorination of ammonia proceeds in a manner which is probably very similar to the reaction of chlorination of the more complex nitrogen compounds, although the reaction rates and equilibria may vary considerably. Furthermore, simple chloramines are found among the intermediate products in the more complex reaction systems.

Schestakoff (ref. 2) shows that urea may be substituted for ammonia in the Raschig synthesis of hydrazin. This reaction is discussed below.

The mechanism of formation of chloramines is as follows: (ref. 3)



$$\longrightarrow R_2NCl + 2H_2O \qquad (5)$$

where R may be an alkyl radical and an amide or a hydrogen atom. This equation indicates that the reaction of chloramine formation is one involving hypochlorous acid.

Free ammonia may react with chlorine or hypochlorite to produce mixtures of mono-, di-, and triamine. This latter which is usually called nitrogen trichloride constitutes the greater portion of the mixture at equilibrium when the pH is below 3. Between pH 3 and 5 the dichloroamine is dominant while in the range above pH 5 the monochloramine is favored (refs. 4 and 5).

The reactions of the several chloramines are as follows:

$$2NH_2Cl \rightleftharpoons NHCl_2 + NH_3 \quad (6)$$

$$2NHCl_2 \rightleftharpoons NCl_3 + NH_2Cl \quad (7)$$

In extremely alkaline solutions the equilibrium is in the direction of transforming monochloramine to hypochlorite and ammonia.

$$NH_2Cl + OH^- \rightleftharpoons NH_3 + ClO^- \quad (8)$$

The reaction sequence of sodium hypochlorite and ammonia is the basis of the Raschig process (ref. 6) of producing hydrazine on an industrial scale. In this process chlorine is passed into a dilute aqueous solution of sodium hydroxide to form sodium hypochlorite. The yield of hypochlorite is nearly quantitative if the solution is cooled to about 0°C.

In the second step of the process ammonia in excess is dissolved in the sodium hypochlorite solution and the mixture is passed through a heated reactor. An attempt is made to adjust the reaction conditions and contact time in order to maximize the yield of hydrazine. This yield is affected adversely by a number of side reactions which have also been studied. Hydrazine reacts with hypochlorite producing nitrogen gas and ammonia. Hydrazine is capable also of spontaneous decomposition forming ammonia and nitrogen as shown in the following:

$$(NH_2)_2 + 2OCl^- \longrightarrow N_2 + 2H_2O + 2Cl^- \quad (9)$$

$$3(NH_2)_2 \longrightarrow N_2 + 4NH_3 \quad (10)$$

These reactions and others resulting in loss of hydrazine yield are owing to the formation of the NH_2 free radicals which react in turn with hydroxyl ions, ammonia molecules and others. It is known that heavy metals catalyze these reactions. Glue is therefore added in the Raschig synthesis to sequester the heavy metals which may be present as impurities (ref. 7).

In the absence of chloride, ammonia is subject to anodic oxidation to nitrous acid and nitrate:

$$9NH_3 + 2H_2O \longrightarrow HNO_2 + 8NH_4^+ + 8e^- \quad (11)$$

$$10NH_3 + 3H_2O \longrightarrow NO_3^- + 9NH_4^+ + 10e^- \quad (12)$$

The former then reacts with ammonia as follows:

$$HNO_2 + NH_3 \longrightarrow N_2 + 2H_2O \quad (13)$$

Oxidation of Urea

According to Fuchs (ref. 8) the reaction of hypochlorite with urea proceeds at room temperature to the initial formation of monochlorourea:

$$NH_2 \cdot CO \cdot NH_2 + OCl^- \longrightarrow NH_2 \cdot CO \cdot NHCl + OH^- \quad (14)$$

Under acid conditions the product is relatively stable with respect to autooxidation. With an excess of hypochlorite, dichlorourea is formed by the following:

$$NH_2 \cdot CO \cdot NHCl + OCl^- \longrightarrow NHCl \cdot CO \cdot NHCl + OH^- \quad (15)$$

However, alkaline conditions appear to favor the formation of monochloroorthobicarbamid

$$NH_2 \cdot CO \cdot NHCl + OH^- \longrightarrow \begin{matrix} NH_2 \\ NHCl \end{matrix} \!\!>\!\! C \!<\!\! \begin{matrix} OH \\ O^- \end{matrix} \quad (16)$$

which reacts with additional hydroxyl to dehydrochlorinate leaving a free radical

$$\begin{matrix} NH_2 \\ NHCl \end{matrix} \!\!>\!\! C \!<\!\! \begin{matrix} OH \\ O^- \end{matrix} + OH^- \longrightarrow \begin{matrix} NH_2 \\ :N^- \end{matrix} \!\!>\!\! C \!<\!\! \begin{matrix} OH \\ O^- \end{matrix} + H_2O + Cl^- \quad (17)$$

which undergoes rearrangement:

$$\begin{matrix} NH_2 \\ :N \end{matrix} \!\!>\!\! C \!<\!\! \begin{matrix} OH \\ O^- \end{matrix} \longrightarrow NH_2 \cdot N = C \!<\!\! \begin{matrix} OH \\ O^- \end{matrix} \quad (18)$$

This undergoes hydrolysis to bicarbonate and hydrazine.

$$NH_2 \cdot N{:}C \!<\!\! \begin{matrix} OH \\ O^- \end{matrix} + H_2O \longrightarrow HCO_3^- + (N \cdot H_2)_2. \quad (19)$$

As in the case of hydrazine produced from ammonia there is decomposition to nitrogen in the presence of an excess of hypochlorite.

It is found experimentally that when urea is oxidized with hypochlorous acid the reactions end when 1.5-2.0 equivalents of HOCl are consumed instead of the maximum of 3.0 for the complete overall reaction

$$CO(NH_2)_2 + 3HOCl \longrightarrow N_2 + CO_2 + 2H_2O + 3HCl \quad (20)$$

If hypochlorite is produced from sodium chloride electrolytically the complete mixing of the anolyte results in forming sodium hypochlorite, NaOH, with the overall reaction:

$$CO(NH_2)_2 + 2NaOCl \longrightarrow N_2 + CO_2 + 2H_2O + 3NaCl \quad (21)$$

Here the reaction sequence tends to proceed somewhat farther to completion but still rather slowly and incompletely, for the reason that the carbon dioxide at ambient temperature tends to make the solution somewhat acid, approximately pH 4.

In the initial reaction of chlorine, hypochlorite or hypochlorous acid with urea, ammonia and amines to form chloramines the reaction products are alkaline and the reaction rate is favored by acid or neutral conditions. However, the subsequent dechlorination reaction is greatly favored by alkaline conditions which are in the electrolytic cell, maintained only in the vicinity of the cathode or where the catholyte solution is mixed by diffusion into the surrounding solution containing the chloramine compounds. Under these conditions the accompanying decarboxylation results in formation of carbonate and bicarbonate ions.

As the carbonate and bicarbonate produced by decarboxylation are brought into contact with the anode or as they are mixed by diffusion with the acidic anolyte solution carbon dioxide is liberated, viz.,

$$CO_3^{=} + Cl_2 + H_2O \longrightarrow HCO_3^{-} + Cl^{-} + HOCl \quad (22)$$

$$HCO_3^{-} + Cl_2 \longrightarrow CO_2 + Cl^{-} + HOCl \quad (23)$$

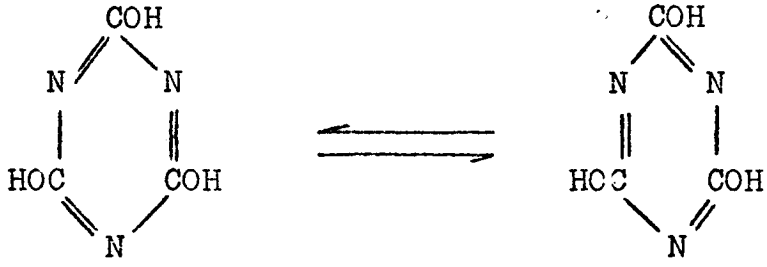
The discharge of carbon dioxide occurs readily only under the acidic conditions which prevail in the vicinity of the anode. This discharge of carbon dioxide is, in turn, a necessary condition for completion of the reaction sequence leading to destruction of the organic components.

If the electrolytic oxidation is conducted at elevated temperatures all of the reactions are accelerated as is the evolution of carbon dioxide gas. This greatly improves the efficiency of oxidation but reduces the electrochemical efficiency of hypochlorite generation and increases the extent of chlorate production.

Uric Acid, Hippuric Acid

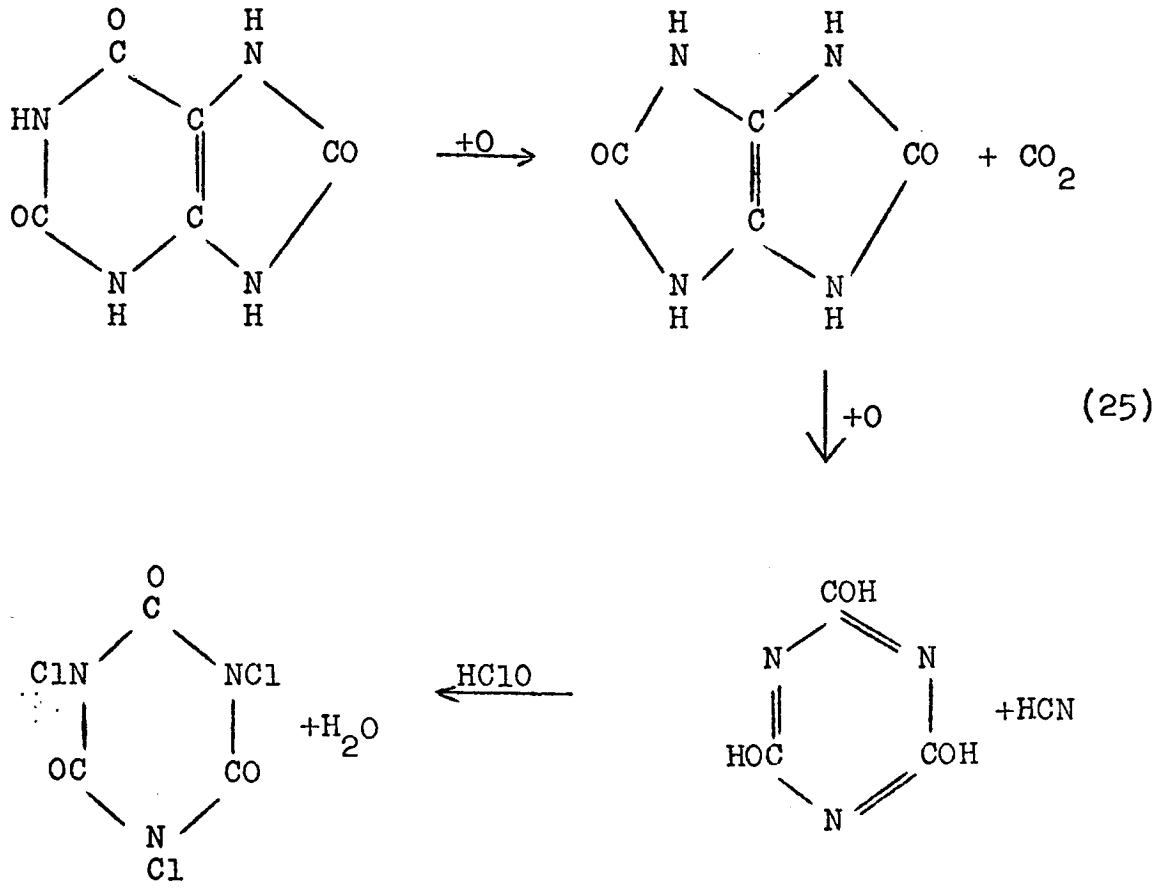
Experiments performed in the course of this study indicate that the electrochemical treatment of urine does not proceed as rapidly as that of a solution of urea. Hippuric acid (benzoyl glycine) contains a chemically resistant aryl component. Uric acid, another significant constituent of normal urine has been shown to convert to cyanuric acid by oxidation with hydrogen peroxide or permanganate (refs. 9-12). Hypochlorite oxidation in the electrochemical treatment of urine probably leads to the same products or their chloramine derivatives.

The stability of cyanuric acid is probably associated with the resonance hybrids



(24)

Oxidation of uric acid may proceed along the following lines:



(25)

The final product is cyanuric chloride, a trichloramine of isocyanuric acid. This compound constitutes a source of active chlorine in common with the other chloramines. It does not decompose readily, however, nor does it react to form hydrazine derivatives. Cyanurates are non-toxic and they are absorbed by activated carbon and rejected by cellulose acetate membranes.

Cyanurates from Urea

Cyanurates are produced from urea by deammoniation. This reaction proceeds through the intermediate formation of biuret (ref. 13).

$$2CO(NH_2)_2 \longrightarrow NH_2CONHCONH_2 + NH_3 \quad (26)$$

$$NH_2CONHCONH_2 + CO(NH_2)_2 \longrightarrow \underset{\llcorner\!\!\lrcorner}{NHCONHCONHCO} \quad (27)$$

However, a minimum temperature of 120°C. is required unless sulfuric acid is added to assist in deammoniation. It is likely that hypochlorite and anode reactions assist in promoting cyanurate formation at lower temperatures.

It is known also that formamide is oxidized by an electrochemical reaction at an anode and that cyanuric acid is produced (ref.14). This reaction takes place below 45°C. with a platinum anode.

$$3HCONH_2 \longrightarrow C_3H_3N_3O_3 + 3H_2 \qquad (28)$$

Chlorinated Substances in Gaseous Products

It has been found in this study that the electrochemical treatment of a solution containing urea and sodium chloride in the concentrations of average urine produced a gas which contained 0.036 percent by volume of a fraction which contains chlorine. This fraction showed major peaks at 61, 63, 81 and 83 molecular mass units by mass spectroscopy. From this it may be inferred that the gas contained cyanogen chloride (M.W. 61.48) and either methylene chloride (M.W. 84) or more likely dichloramine (M.W. 84). Nitrosyl chloride (M.W. 65.47) and nitryl chloride (M.W. 81.47) are possibilities.

Cyanogen chloride trimerizes to trichloroisocyanuric acid. It is possible therefore either that this substance is formed as an intermediate product from urea

$$CO(NH_2)_2 + Cl_2 \longrightarrow CNCl + H_2O + NH_2Cl \qquad (29)$$

or from trichlorocyanuric acid by depolymerization.

These were the reactions with a solution of urea and salt. Urine under the same conditions of electrochemical treatment yields a total of 0.87 percent by volume of chlorine-containing substances compared with 0.036 percent for the urea solution. Major peaks in this case were at 47, 67, 86, 101 and 116 mass units. Methyl chloride (M.W. 50.49), methylene chloride (M.W. 84.94), chlorobutadiene (M.W. 88.54) and chlorobenzene (M.W. 112.56) are among the possibilities. Nitrogen trichloride (M.W. 120.38) is undoubtedly present giving rise to a very powerful chlorine odor.

Electrode Reactions of Ammonia and Chloramines

Ammonium compounds are oxidized to nitrous acid and nitrate when aqueous solutions of these substances are subjected to electrolysis using platinum electrodes (ref. 15). Nitrous acid reacts with ammonia as well as

with urea to form nitrogen and water.

$$HNO_2 + NH_3 \longrightarrow N_2 + 2H_2O \quad (30)$$

$$2HNO_2 + CO(NH_2)_2 \longrightarrow 2N_2 + CO_2 + 3H_2O \quad (31)$$

Nitric acid is more stable except that it undergoes some re-reduction at the cathode. It is also possible that in more complex systems involving chlorine and organic nitrogen compounds the oxides of nitrogen and nitrosyl chloride and nitryl chloride may be formed.

Little is known of electrode reactions involving chloramines.

A bibliography of technical literature and patents relating to the electrochemical treatment of wastes has been accumulated (ref. 16). The investigation under this contract involved the study of platinum and lead anodes and the general feasibility of using electrochemical post treatment of sewage plant effluent. It is possible, using the methods developed, to reduce the COD by 80 percent, also ABS detergent. Although hypochlorite was generated in these tests the effect on COD of the sewage was greater than with addition of a comparable amount of hypochlorite solution.

This merely confirms the conclusion that the electrochemical treatments involve a sequence of electrode, and homogeneous solution, reactions of great complexity although the conditions of Miller and Knipe as well as the electrode configuration and other factors affecting the process were different from those of this investigation.

Electrochemical Hypochlorite Reactions

The electrochemical treatment of urine involves more than a mere combination of hypochlorite formation and the sequential reaction of this hypochlorite. Nevertheless, it is of interest to consider the experience in commercial production of electrolytic bleach and the laboratory studies that have been made to explore the effect of operating conditions.

There is an optimum electrolyte circulation rate, anode and cathode current density, temperature and electrode configuration. The highest salt concentration to the point of saturation is desirable. Allmand and Ellingham (ref. 17) summarize these conditions as follows:

1. An electrode arrangement which will permit an undisturbed diffusion layer at the anode;

2. A neutral electrolyte;

3. The strongest possible chloride solution;

4. Low temperature;

5. High anodic current density;

6. The presence of chromate, calcium or magnesium salts or other substances promoting cathode polarization;

7. Use of platinized electrodes.

By way of illustration of the effect of certain of these variables the following Table 2 which is contained in Allmand and Ellingham, and is taken from Foerster and Mueller (ref. 18) is applicable.

This data obtained under steady-state conditions after a prolonged electrolysis represents the concentrations of hypochlorite at zero current efficiency, i.e., at a stage at which further passage of electric current does not increase the yield. At the other extreme the data of Table 3 obtained from the same source as that of Table 2 indicates the effect of the variables in the range at which current efficiencies are very high.

It is well known that the current efficiency diminishes as the concentration of hypochlorite is increased. In part this is owing to reduction of hypochlorite to chloride at the cathode and also to oxidation at the anode and self oxidation of hypochlorite in solution producing chlorate. This is favored by very high temperature and acid conditions which tend to promote chlorate formation by the auto oxidation of hypochlorous acid according to the following reaction:

$$3HClO \longrightarrow ClO_3^- + 2Cl^- + 3H^+ \qquad (32)$$

On the other hand, highly alkaline conditions favor the anodic oxidation forming chlorate according to the following reaction:

$$ClO^- + 2H_2O \longrightarrow ClO_3^- + 4H^+ + 4e^- \qquad (33)$$

The effect of a high current density coupled with the

Table 2

Steady-State Concentration of Hypochlorite under Varying Conditions of Salt Concentration, Temperature and Current Density

Concentration Sodium Chloride	Temperature (°C.)	Current Density (amps./sq.cm.)	Gms. per 100 ml. Hypochlorite Oxygen*	
			Platinized*	Bright Platinum*
4.8N	13	0.017	0.61	0.34
		0.17	0.89	0.68
	50	0.017	0.31	0.17
		0.17	0.64	0.42
1.7N	13	0.017	0.48	0.28
		0.17	0.65	0.47
	50	0.017	0.23	0.15
		0.17	0.40	0.35

*1 Gm. per 100 ml. Hypochlorite Oxygen is equivalent to 1.25 N

Table 3

Effect of Temperature, Current Density, and Hypochlorite Concentration Upon Voltage, Ampere Efficiency and Power Efficiency

Hypochlorite Cell Electrolysis from Starting Solution: 280 gpl NaCl, 2 gpl K_2CrO_4 Platinized Electrodes

Temperature (°C.)	Anode Current (amps./sq.cm.)	Cell Potential (Volts)	Hypochlorite Oxygen (gm./l.)	Ampere Efficiency (%)	Power Requirement Watt hr. / gm. O_2
13	0.017	2.4	4.2	96	8.4
13	0.017	2.4	5.24	90	8.95
10	0.017	3.1	6.8	96	10.84
13	0.17	3.6	5.28	97	12.2
13	0.17	3.6	8.7	87	13.5
14	0.17	4.7	5.20	95	16.6

presence of a boundary layer at the anode surface is to favor an acid condition in the vicinity of the anode thereby reducing the tendency to anodic formation of chlorate. Because a high current density tends to produce localized overheating of the electrolyte, process efficiency is favored by providing an extended anode surface in the form of a mesh.

PRELIMINARY LABORATORY RESULTS

Conditions in the electrochemical oxidation of urine components are, as stated above, considerably more complex and it is necessary to employ semi-empirical methods of optimization. This calls for some method of assaying the solution. There are various methods measuring the effectiveness of the electro-chemical treatment. Chemical oxygen demand (COD), indophenol nitrogen and others. These methods are all subject to interpretive limitations inasmuch as they are, with the exception of Kjeldahl nitrogen, somewhat dependent upon arbitrary conditions to obtain reproducibility. The Kjeldahl method for nitrogen is in general very accurate except for the more refractory components of urine or their derivatives. Urea as well as ammonia contains nitrogen having a valency of 3. It is oxidized to elemental, or zero valency, state. Consequently, for urea or ammonia 3 Faradays are required ideally, i.e., at 100% ampere efficiency, the valency of the carbon hydrogen and oxygen of urea is not changed during the oxidation process. This is not generally the case for other nitrogen-containing compounds of urine. When these, as in the case of uric acid, contain single or double carbon-carbon bonds additional oxidation, or faraday equivalency is required beyond the 3 equivalence required for urea and ammonia. This is true also where, as in creatinine, there are amino- or imino-nitrogen. Therefore, the ampere efficiency for conversion of urine components is somewhat higher than is indicated from calculations which are made arbitrarily on the basis of Kjeldahl nitrogen determination and assumed equivalency of 3 faradays per gram-atom of nitrogen. The cell reaction for uric acid, if completely gasified, is:

$$C_5H_4N_4O_3 + 7H_2O \longrightarrow 2N_2 + 5CO_2 + 9H_2 \qquad (34)$$

It is seen that this involves 18 equivalence or faradays for 4 atoms of nitrogen, a ratio of 4.5. For creatinine the reaction is:

$$C_4H_7N_3O + 7H_2O \longrightarrow 3/2N_2 + 4CO_2 + 21/2H_2 \qquad (35)$$

Here, there are 21 equivalence or faradays required for 3 atoms of nitrogen, or a ratio of 7. The content of creatinine in normal urine is 1 gram per liter or 371 ppm as nitrogen. There are also present in urine proteinaceous substances which add further to the oxidation requirements but their effect as well as that of other oxidizable components is but very little.

At the beginning of the electrochemical oxidation the current is consumed largely in forming chloramines of urea and other substances. This reaction does not result in reducing the Kjeldahl nitrogen. The ampere efficiency is therefor low in the initial stage until the subsequent further oxidation to the ultimate products. This is shown in Table 4 in which ampere efficiency is measured in an experiment to treat 60 ml. of urine in a 75 ml. cell with an anode of platinum 37 sq.cm. in effective area.

Table 4

Decomposition of 60 ml. Urine containing 11,606 ppm N at 0.081 amps./sq.cm.

Time (hrs.)	Total Current		Nitrogen		Ampere Efficiency (%)
	Amp.-Hrs.	Faradays	ppm.	meq.	
0	0	0	11,606	146.04	14.4
0:30	1.5	.05625	10,962	137.94	51.5
1:00	3.0	.1125	8,673	109.0	32.0
2:00	6.0	.225	5,824	73.0	52.2
3:00	9.0	.3375	1,305	14.25	

As stated above the ampere efficiency is dependent on current density and it tends to be greater at higher current density up to rather high levels. However, the cell voltage increases with current density and a point is reached at which the energy efficiency is at a minimum. This is illustrated in Table 5.

The data of Table 5 would appear to indicate that current efficiency is generally improved at the higher current density.

Table 5

Ampere, and Energy, Efficiency Related to Current Density

Current		Voltage	Amp.Eff.	Energy Efficiency
Amps.	Amps./sq.cm.	(Volts)	(%)	Watts/St'd Liter
1.8	0.0333		62.5	
0.9	.0667		57.8	
0.9	.0166		51.2	
14.0	.378	6.7	85	555
7.0	.189	5.3	37	1054
3.1	.084	4.0	38	773
4.77	.130	5.26	51	762
4.77	.130	4.07	62	481
4.77	.130	3.85	81	347
0.9	.0166	3.35	51	455
0.9	.0166	3.2	58	402
	1.2		85	
	1.2		63	

Gas Composition and Process Control

The composition of the gases generated in this method of electrochemical treatment of urine varies with the operating conditions and the degree of completion of the treatment. In the initial period during which the dominant reactions are those producing chloramines the gas is predominantly hydrogen from the cathode while little gas is generated at the anode or in the solution.

At a later stage of the treatment hydrogen continues to be generated cathodically. However, nitrogen and carbon dioxide are generated by the oxidation reactions. In one pair of tests the gas generated in the cell was collected for analysis. The samples of urine in the one test and a solution of urea and sodium chloride in the other were sufficient to generate 2 liters (NTP) of gas. Each test was run long enough to collect only 1.25 liters before the gas sample tube was closed. Results are as shown in Table 6.

The ratio of nitrogen to carbon dioxide is close to unity on both tests. Subtracting the hydrogen equivalent to the oxygen we have a ratio, $H_2:N_2=2.97$ for the urea and salt solution and 3.94 for the urine. The first ratio is very nearly theoretical for urea while the high value of

the latter ratio reflects principally a considerable tie-up of nitrogen in the solution as chloramines and also to a lesser extent the higher ratio for non-urea components.

Data contained in Table 6 does not reflect the gas generated in the final period of electrochemical treatment during which the ampere efficiency tends to fall and the oxygen content tends to rise. Ultimately the gases generated are hydrogen and oxygen by the electrolysis of water. Hypochlorite reaches a constant level the value of which varies with the operating conditions. It is necessary to terminate the treatment before this point, not only to avoid wastage of power but also to avoid creating an explosive mixture.

Various control devices are available to monitor the gas composition. The selection and system design incorporating such a monitoring device are not within the scope of this study.

Table 6

Gases from Electrochemical Treatment of Urine
Concentrations in Volume Percent

Components	Urea + Salt	Urine
Nitrogen	19.5	14.7
Oxygen	1.92	8.17
Argon	.067	.10
Carbon Dioxide	19.5	14.5
Hydrogen	59	62
Chlorinated 'Hydrocarbon'	0.036	0.87

ELECTROCHEMICAL TREATMENT PROTOTYPE

This unit is constructed of glass for convenience and visibility. It is constructed for operation batchwise or continuously. Gases which are generated by the reactions of the organic constituents of urine rise and leave the cell chamber near the top. Under zero G the contents of the cell chamber require slow circulation of the contents through a phase separator which removes the gas while permitting return of the liquid to the cell chamber.

Circulation Requirements

Laboratory cell operating experience indicates that it is possible to conduct the electrochemical treatment with a volume ratio of one third gas to two-thirds liquid. The total volume of gas is approximately 60 liters measured at 60°C. and normal atmospheric pressure per liter of urine, or 270 liters per 24 hours for 4.5 liters of urine assuming 24 hour operation. This is 0.1875 liter per minute of gas, or 0.375 liter per minute of liquid recirculated.

From the standpoint of the circulation requirements and phase separation it is advantageous obviously to operate the electrochemical treatment cell at a pressure greater than that of normal atmospheric. This is, however, not within the scope of this study.

Prototype Construction

This has a capacity of 1400 ml. It consists of a glass cylinder, 12 inch high and 4 inch in its inside diameter. One end is closed and on the other end is an integral glass flange which is ground to fit a matching flange on an upper domed section which closes the cylinder. An inlet and an outlet arm are provided at the top and bottom for the flow of liquid into and out of, the cell. The upper arm serves also to vent the gases which are generated during the electrochemical treatment.

The upper domed glass section has two outlets for electrical connection to the electrodes and a central tube open at the top and closed at the bottom which serves as a thermometer well. The cell and electrode assembly are shown in Figures 1 and 2.

The electrode assembly consists of one anode and one cathode. Each is constructed of a 9"x24" rectangular piece of platinized titanium expanded sheet (Exmet). To hold these electrodes from shorting by direct contact 2 pieces, each 10"x26", of polyethylene mesh are laid so that the assembly consists of a polyethylene layer, anode, polyethylene and cathode in that order. In this assembly the two electrode layers coincide as do the polyethylene layers, the latter overlapping the former by 1/2" around the entire perimeter.

This assembly is coiled to form a 4-layer spiral which is fitted inside of the glass cylinder as shown in Figure 1 . The tabs which are spot welded to the electrodes are brought through the openings in the

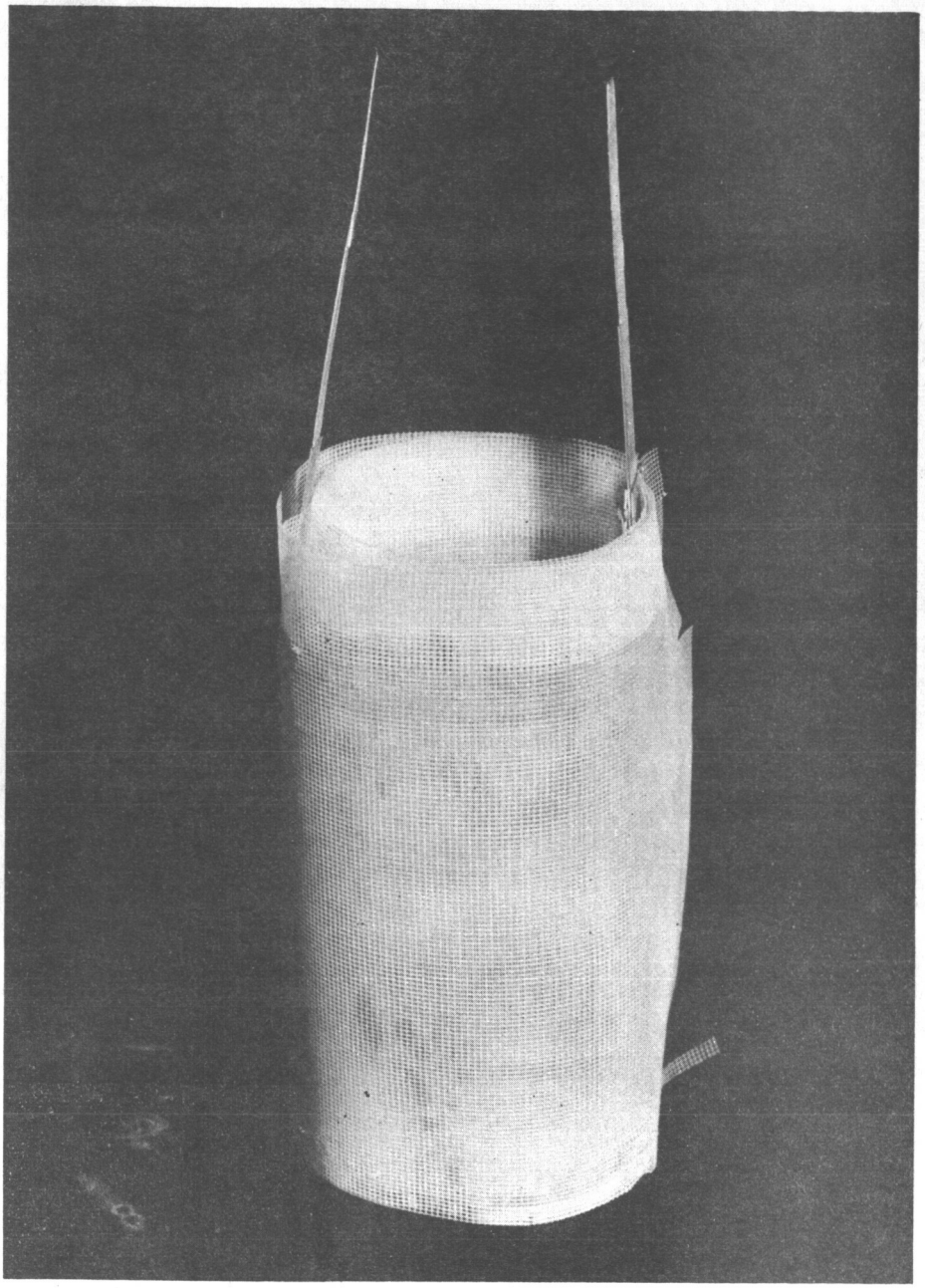


FIGURE 1. ELECTROCHEMICAL OXIDATION CELL ELECTRODE ASSEMBLY

Showing 9" x 24" platinized expanded titanium sheets and interlayers of polyethylene mesh coiled to 3-9/16" O.D. Electrical connection is by platinized titanium strips spot welded to the electrodes.

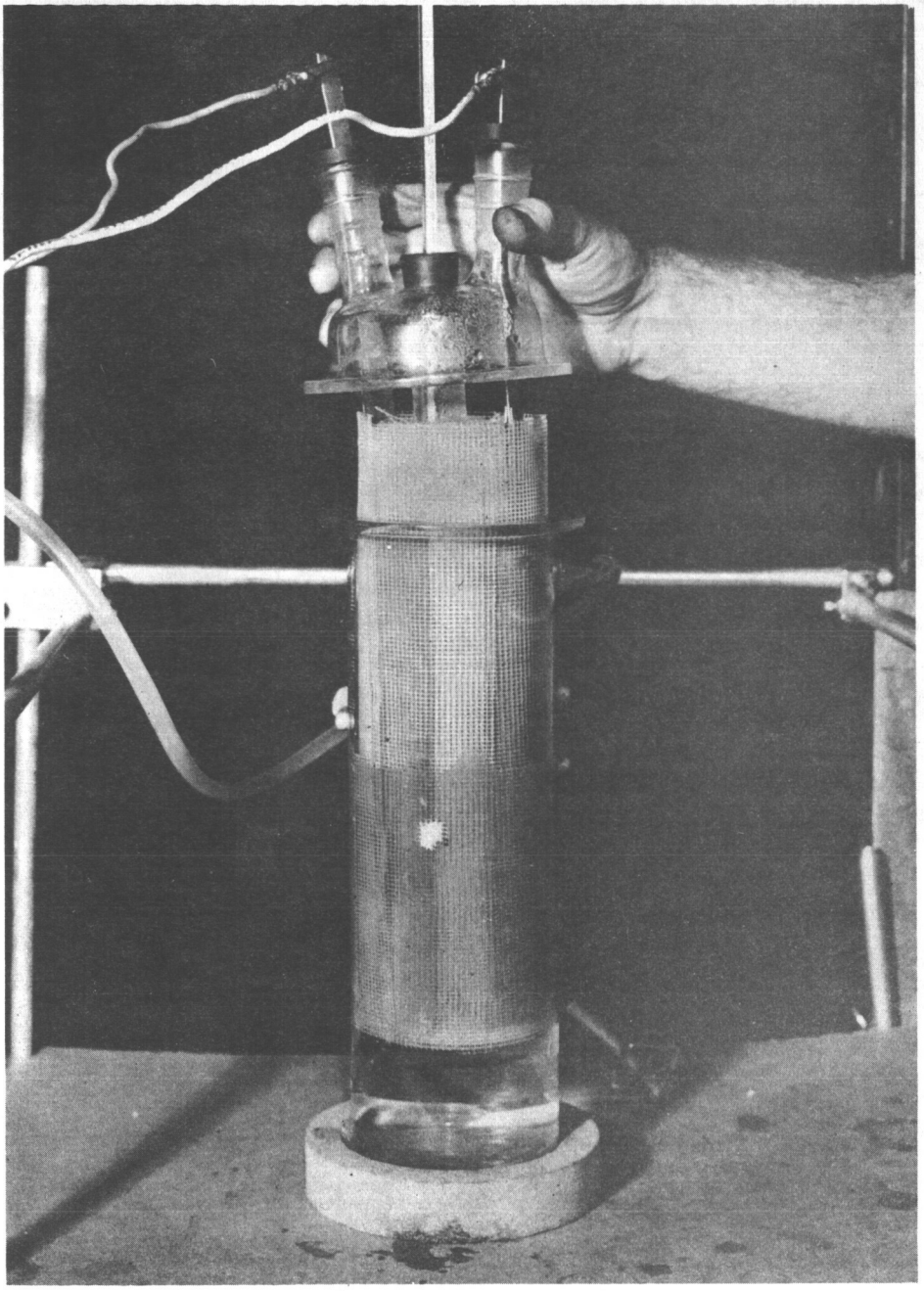


FIGURE 2. ELECTROCHEMICAL OXIDATION CELL

Electrode assembly of Figure 1 being lowered with domed upper section into the cylindrical glass lower section. Upper section has two necks for electrode connecting strips and a center thermometer well. Lower section has upper and lower tube connections.

domed upper glass section of the cell. These tabs are of platinized titanium and are 1 inch wide and 6 inches long.

Prototype Operation

The cell is charged with 1400 ml. of urine. A current of 10 amperes is passed through the cell and it is maintained until the oxygen concentration exceeds 10 percent in the gas stream which leaves the system.

The cell voltage was initially 5.4 volts. It fell rapidly and remained at 3.8 volts for most of the period. A total of 640 watt-hours were consumed, or 457 watt-hours per liter. The results are summarized in Table 7.

Table 7

Electrochemical Treatment of Urine in Prototype 1400 Ml. Treated Using 10 Amperes, 18 Hrs.

Component	Raw Urine	Treated Urine
Total Solids, ppm	ca. 50,000	-
Chloride, ppm	ca. 7,500	5,975.3
COD, ppm	ca. 60,000	nil
pH	ca. 8.0	1.20
Free Acid, ppm HNO_3	nil	2,750

Previous tests indicate that the product is sterile and free from pyrogenic compounds. The color was pale and there was no visible turbidity.

This product was treated with one gram of activated carbon to remove available chlorine and 1.2 grams of calcium oxide to neutralize the acidity. At the end of this treatment the pH was 3.6 and the solution was clear and colorless. This then constituted the feed to the reverse osmosis system.

PHASE SEPARATION

In the electrochemical treatment of urine approximately 60 liters (at 60°C. and 1 atmosphere) of gases are produced per liter of liquid. This presents no problem under earth conditions, the gas rising to escape

as bubbles which rise during the treatment. However under conditions of zero G the gas phase remains in suspension.

Although the electrolytically treated urine is ultimately clear of suspended solids the urine is initially alkaline owing to the presence of free ammonia and there is a considerable precipitation of magnesium ammonium phosphate, calcium carbonate and other substances. Ultimately these are dissolved as the electrochemical treatment approaches completion but the system must be capable of separating the gas from a liquid-solid slurry in the initial stages of treatment.

Inasmuch as the phase separation occurs, in this system, outside of the electrochemical treatment cell it is necessary to circulate a portion of the solution (and suspended solids) together with the entrained gas. A phase separator removes the gas from the recirculating stream and returns the liquid or slurry to the electrochemical treatment cell.

To estimate the volume rate of circulation which is required it is necessary to make certain assumptions with regard to the cell operation. The volume of gas which is in suspension in the cell should not exceed 50 percent of the liquid volume or 33 percent of the total volume of cell contents. If the gas volume is 60 liters per day this is 0.0417 liter per minute for the gas rate and 0.0834 liter per minute for the liquid, per liter of urine or 0.375 liter per minute for the gas, assuming that the gas volume evolution rate is constant with respect to time.

The liquid circulation capacity of the phase separator shown in Figure 4 is 2.0 liter per minute.

This apparatus was found to be operable in any space orientation including the 'upside-down' or -1G configuration, in which the shaft is oriented vertically with the wide end of the phase separator at the top.

Operating Principles

The mixture of gas and liquid, with or without suspended solids enters the phase separator and distributes around the circumferential grooved section near the feed entrance port. Centrifugal force is

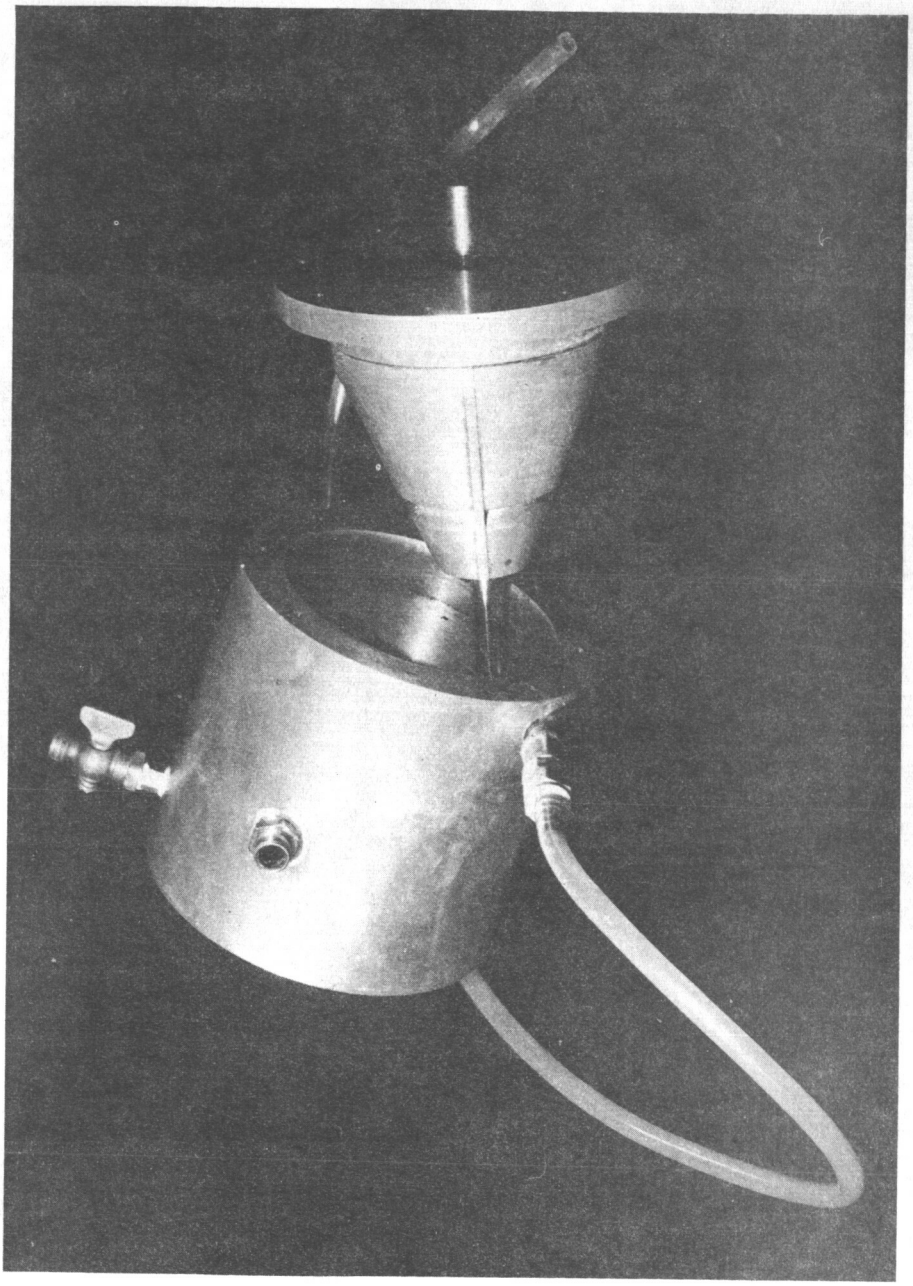


FIGURE 3 PHASE SEPARATOR

Rotatable conical inner section at top has a circumferential groove at the feed entrance in the assembled unit. Hollow conical casing at bottom has liquid discharge connection at the top, feed connection at lower center and gas outlet connection with stopcock at the bottom.

imparted by the rotation of the conical rotor. This results in a radially outward pressure upon the inner wall of the casing and a component of this pressure exerted along the elements of the cone in the direction of the wide end. If the angle of the cone is 'a' the radius distance from the axis to the casing wall at any point is 'r', and the density of the liquid is 'd', the radial force per unit of liquid is

$$F = drw^2/g \tag{36}$$

and the force component toward the wide end is

$$f = drw^2 \cos a/g \tag{37}$$

where w is the angular velocity

$$w = \pi (RPM)/30 \tag{38}$$

The liquid phase is as noted above, thus subjected to a force which causes it to separate from the gas and collect on the inner wall of the housing and to a component of force which causes it to flow toward the outlet. When flow of liquid from the outlet is throttled the liquid discharge pressure consists of the sum of that which is due to the combined force of all of the liquid between the discharge and the free surface of the liquid and the additional pressure due to the velocity head against the tangential discharge outlet. This may be computed from the following:

$$\Delta P = \frac{dw^2}{g} \cos a \int_{r_o}^{R} r.d(r \sin a) + \frac{w^2R^2.d}{2g} \tag{39}$$

$$= \frac{dw^2R^2}{2g} (\sin 2a + 1) - \frac{dwr_o^2 \sin 2a}{2g} \tag{40}$$

For conditions of throttled liquid flow the discharge pressure increases with the speed of rotation and with the radius, R, at the discharge point. This pressure is greater the smaller the radius, r_o, at the free liquid surface, i.e., the deeper the liquid pool in the separator. For maximum zero flow pressure the optimum conical angle is one for which $\alpha = 45^o$.

At the maximum flow of liquid the discharge liquid pressure is diminished by the hydraulic resistance. The phase separator is intended for operation with very

low differences of pressure. The power requirement may be estimated from the liquid discharge rate and the static pressure which is given by means of equation (40).

Based on this estimate the energy consumed by the phase separator in circulating 2 liters per minute of liquid is about 1 watt of continuous power. The circulation required is, as stated above, 0.375 liter per minute if the cell is operated at normal atmospheric pressure, requiring 0.1875 continuous watts. This assumes no loss of power due to bearing friction or motor losses.

The problem of designing a flight qualifiable phase separator is therefore one of reducing the size and weight of the apparatus; designing bearings which operate with minimum friction, and obtaining the required dynamic balance of the rotating parts. In this design the phase separator intake must be of sufficient size to avoid a pressure drop which is sufficient to cause the interior to be under negative pressure inasmuch as the gas phase cannot be expelled under these circumstances. The proportion of gas to liquid in the intake stream is of importance only in that the intake is required to be larger in size as the proportion of gas is increased.

This problem is more critical the smaller the phase separator inasmuch as there is a limitation to the space available for the feed intake port. It may then be necessary to employ multiple input ports from a circumferential manifold or its equivalent.

Operating Procedure: Phase Separator and Electrochemical Cell

With the cell assembly closed and with the phase separator in operation, urine is injected into the cell from a bladder. Air is expelled from the gas exit tube as the cell is filled until a pressure rise indicates the displacement of all of the air.

At this point the urine feed bladder is shut off and a connection is opened to a second bladder which is expandable to a volume equal to that of one half of the cell.

The electric current circuit is next closed to begin the electrochemical treatment using 7 amperes per liter of urine. Product gases are expelled from the gas exit tube while the reserve volume bladder gradually expands to its full capacity. The total time of electrochemical treatment is approximately 16 hours depending on the concentration of organics in the urine. Near the end of the treatment period the volume rate of gas expulsion and the reserve bladder expansion are diminished. The end of the electrochemical treatment is noted by a marked reduction in volume of hydrogen and a virtual disappearance of nitrogen and carbon dioxide. On the other hand, some oxygen appears and the gas composition becomes explosive. Various possibilities exist for monitoring the electrochemical treatment in the solution and/or the gas phase.

Disappearance of oxidizable organics is accompanied by the appearance of free available chlorine in the solution. This is measurable by polarographic means. Gas monitoring may be by means of thermal conductivity (sensitive to hydrogen), diamagnetic analysis (for oxygen) or by thermal analysis of a catalyst in the gas stream. Instrumental control and monitoring are not within the scope of this study.

Prevention of Explosions

Until the very end of the electrochemical treatment the gases which are generated are non-explosive. At the end of this treatment they may enter into an explosive range. The combination of oxygen with hydrogen occurs

at atmospheric temperature in the presence of a platinum surface such as that of the electrodes of the electrochemical cell.

The propagation of an explosion within the cell is not possible at atmospheric pressure if the cell is not permitted to run dry, i.e., if the interior is filled at all times with liquid or with a two phase mixture. This should be the condition which is maintained during operation except in case of a malfunction. Fail-safe control should then provide for opening the cell electrode circuit.

Safety is provided in the handling of the gases which are expelled from the electrochemical cell and phase separator by means of conventional explosion checks in the lines and by passing the gases through a palladium catalyst converter to consume any oxygen. The gas is then cooled to condense water which is recovered in a phase separator.

System Stability Analysis

A detailed system analysis is beyond the scope of this study. However, it may be seen from the foregoing that the volume of gas which is generated by the electrochemical treatment tends to vary during the period of treatment if the electrode current is constant. Under zero G conditions the rate of gas generation tends to be more nearly constant if the cell is operated at constant voltage rather than at constant current. This is for the reason that a larger volume of gas in a multiphase system within the cell means a higher cell resistance. Under constant voltage operation the current is diminished by the larger gas volume and there is a corresponding diminution of the volume rate of gas generation.

Another stabilizing influence is provided by the phase separator characteristic of a greater generation of pressure the greater the liquid volume rate or back pressure. This is provided that there is no appreciable resistance to the flow of the mixture of phases at the intake. The static, or ideal, pressure is given by equation 40. It is equal to the back pressure and hydraulic resistance. If the flow rate increases due to a variation in the process, the free liquid level approaches the liquid discharge port. This increases the absolute value of second term, d approaching the larger diameter, D. The generated pressure, ΔP is thus reduced and the flow rate is restored.

Use of Elemental Oxygen

The treatment of liquid waste materials with air or oxygen, usually under conditions of elevated temperature and pressure is termed 'wet oxidation'. Considerable study has been given to employment of this method to municipal wastes and products of primary waste treatment plants. With air oxidation, a temperature of at least 200°C., pressuresof at least 1000 psi and about one hour of treatment time (ref. 19).

Such conditions are not necessarily outside of the range of possibility for employment in life support systems but they involve formidable problems in terms of weight and energy penalties. On the other hand the use of oxygen to supplement the use of electrical energy in the electrochemical oxidation of the organic components of urine may be worthy of serious consideration.

Oxygen may be employed in two ways in this connection. It may be employed as a cathode depolarizer or to contribute in some measure to the oxidation of a portion of the organics or their products. As a depolarizer oxygen might be used to reduce the cell voltage and also the volume rate of gas generation. In this case the cathode reaction which is, in the electrochemical treatment of this study,

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \qquad (41)$$

becomes, instead,

$$H_2O + 1/2O_2 + 2e^- \longrightarrow 2OH^- \qquad (42)$$

Hydroxyl ions are produced in both reactions. The theoretical possible reduction of the cell voltage due to the depolarization with oxygen is 1.229 volt. In actuality the depolarization with elemental oxygen should reduce the cell voltage by somewhat less than this. Nevertheless, a substantial percentage reduction of power is possible, at least in theory.

In practice this is possible only by employment of a reversible oxygen electrode which is capable of reducing gaseous oxygen at a rate commensurate with the current density required in the electrochemical treatment system. Such electrodes have been designed and constructed for use in fuel cells in which the electrolyte is potassium hydroxide but they have not been adapted for use in neutral or acid solution.

With the object of determining whether a platinized sintered nickel thimble is usable as an oxygen electrode tests were performed with this electrode in an electrochemical treatment cell using a platinum anode. The oxygen electrode was prepared in a manner recommended for use in a fuel cell (ref. 20). This preparation included 'waterproofing' with paraffin wax.

The results of this test are summarized in Table 8. It is shown that oxygen does not depolarize the cathode in the cell with urine. The fact that the electrode was of the correct design and construction is confirmed by the fact that it does serve as an oxygen depolarized electrode under alkaline conditions.

Table 8

Electrochemical Treatment Cell Performance

Platinized Nickel Thimble Microporous Cathode, 6 sq.cm. Apparent Surface

Solution	Volts	Current in Microamperes	
		No Oxygen	With Oxygen
KOH 1N	2.30	100	200
	1.65	-	100
Urea + NaCl	3.35	100	120
	3.30	-	100
Urine	3.40	100	110
	3.35	-	100
KOH 1N	2.29	100	200
	1.65	-	100

Electrode Potentials

The following are reversible thermodynamic potentials from Latimer (ref. 21).

$2H_2O$	$= O_2 + 4H^+ + 4e^-$	$E^o = -1.229$	(43)
$4OH^-$	$= O_2 + 2H_2O + 4e^-$	$E^o = -0.401$	(44)
$2H_2O$	$= O_2 + 4H^+(10^{-7}M) + 4e^-$	$E^o = -0.815$	(45)
H_2O_2	$= O_2 + 2H^+ + 2e^-$	$E^o = -0.682$	(46)
$OH^- + HO_2^-$	$= O_2 + H_2O + 2e^-$	$E^o = 0.076$	(47)
$2H_2O$	$= H_2O_2 + 2H^+ + 2e^-$	$E^o = -1.77$	(48)
$3OH^-$	$= HO_2^- + H_2O + 2e^-$	$E^o = -0.87$	(49)
$2Cl^-$	$= Cl_2 + 2e^-$	$E^o = -1.3583$	(50)
$H_2O + Cl^-$	$= HClO + H^+ + 2e^-$	$E^o = -1.49$	(51)
$2OH^- + Cl^-$	$= ClO^- + H_2O + 2e^-$	$E^o = -0.94$	(52)
$3H_2O + Cl^-$	$= ClO_3^- + 6H^+ + 6e^-$	$E^o = -1.45$	(53)
$6OH^- + Cl^-$	$= ClO_3^- + 3H_2O + 6e^-$	$E^o = -0.62$	(54)
$4H_2O + Cl^-$	$= ClO_4^- + 8H^+ + 8e^-$	$E^o = -1.34$	(55)
$8OH^- + Cl^-$	$= ClO_4^- + 4H_2O + 8e^-$	$E^o = -0.51$	(56)
$H_2O + NH_4^+$	$= NH_3OH^+ + 2H^+ + 2e^-$	$E^o = -1.35$	(57)
$2NH_4^+$	$= N_2H_5^+ + 3H^+ + 2e^-$	$E^o = -1.24$	(58)
$2OH^- + 2NH_4OH$	$= N_2H_4 + 4H_2O + 2e^-$	$E^o = -0.1$	(59)
$N_2H_5^+$	$= N_2 + 5H^+ + 4e^-$	$E^o = 0.17$	(60)
$4OH^- + N_2H_4$	$= N_2 + 4H_2O + 4e^-$	$E^o = 1.15$	(61)
$NH_4^+ + 3H_2O$	$= HNO_3 + 9H^+ + 8e^-$	$E^o = -0.87$	(62)
$H_2O + CO(NH_2)_2$	$= CO_2 + N_2 + 6H^+ + 6e^-$	$E^o = -0.1$	(63)

REVERSE OSMOSIS

Membranes

The membranes used in this study were cast in accordance with Manjikian (ref. 22). They are composed of cellulose acetate having a considerable content of imbibed water in the body of the film and a dense thin outer layer. The membranes are placed so that this dense layer is 'upstream', i.e., at the higher pressure side in the apparatus. Salt rejection properties are based primarily on this layer as will be seen from the following discussion.

These membranes were developed by Loeb, Sourirajan and co-workers at the University of California, Los Angeles by semi-empirical methods (refs. 23, 24) which are based on earlier observations of Bretton and Reid (refs. 25, 26) who noted the very efficient salt rejecting characteristics of cellulose acetate membranes. There is considerable speculation regarding the specific properties and mechanism which are responsible for this unique selectivity, unequalled by any other material so far developed or tested.

It is the concensus of thosewho have contributed to the development of these materials that water is transferred by a diffusional process whereby water molecules are able to move by a make and break of hydrogen bonds with the cellulose acetate molecules. The rate of diffusion determines the production capacity and this depends on the number of hydrogen bonding sites and also on the entropy of hydration and on the energy of activation of the hydration and dehydration processes.

It is found experimentally that the rate of water transfer and the efficiency of salt rejection are not greatly dependent on the molecular weight of the cellulose acetate. The optimum acetyl content appears to lie in the range 37-39 percent. Cellophane, deacetylated cellulose acetate and ethyl cellulose are effective to some degree but they do not perform nearly as efficiently as the acetate with regard to salt rejection. Synthetic ion exchange membranes reject salt in dilute solutions but are less effective in concentrated solutions. Rejection is, in all cases, better for salts of polyvalent, than for monovalent, electrolytes and less for acids and bases than for salts (ref. 27).

Rejection of ammonia and urea is relatively poor, even

with cellulose acetate. Consequently, it is not possible to recover potable water from urine by reverse osmosis without some pretreatment to convert or remove these substances.

To obtain the requisite membrane structure and properties the cellulose acetate must be incorporated in a solution to be cast into a film and the cast film must be treated in a prescribed manner. This consists of immersing the cast film, while it is in a gel stage with retained solvent, into water at freezing temperature. The retained solvent is then leached, or dissolved, by interdiffusion with the water.

The structure of the cast film is then retained to a considerable degree during the exchange of solvent with the water although there is a considerable shrinkage in the thickness of the film in the process. Water which is retained is in some physico-chemical state which permits a diffusional transfer from a region of higher, to one of lower, activity. There is no experimental evidence to indicate, without some ambiguity, the nature of this physico-chemical state or its characteristics.

In casting the membranes there is a thin layer at the air interface which is different in structure and composition from the rest of the film. It is this face of the membrane which is 'upstream' in the reverse osmosis unit, i.e., it is facing the concentrated solution at the higher pressure while the other side of the membrane is supported to resist the pressure tending to compress the membrane.

After the cast membrane film has been immersed in cold water for one hour it is peeled from the glass plate. Loeb et al., have determined that there is a considerable improvement in the performance characteristics when the membranes are then conditioned or 'annealed' in water at elevated temperatures. In general there is a reduction of water flux rate which is greater the greater the temperature but there is an increase in salt rejection. These effects accompany a reduction of the imbibition of water in the membrane.

The component of the casting solution which is a solvent for cellulose acetate and also an imbibition, or flux-inducing, additive is formamide in this present study, following Manjikian. Other additives with comparable properties are, according to Manjikian, dimethyl-formamide, dimethyl sulfoxide, tetrahydrofurfuryl phosphate, triethyl phosphate, acetic acid and methyl-pyrrolidone. Urea, glyoxal and inorganic perchlorates

are also effective additives when combined with water and acetone.

When these membranes are employed in reverse osmosis the water flux is found to be a function of the pressure difference, the electrolyte composition and the time of operation. The osmotic pressure of the electrolyte solution is, of course, the minimum pressure at which operation is possible. The pressure in excess of this may be considered to constitute the 'driving force'. The water flux is a nearly linear function of this driving force until at a pressure of about 1000 psi there is a gradual levelling of the flux owing, it is assumed, to a compaction of the membrane.

The pressure difference across the membrane is equivalent to a difference in the thermodynamic activity if the diffusivity of water in the membrane is defined as the mass flux density per unit of activity in a centimeter of membrane thickness. Thus, if the pressure difference is 100 atmospheres above the osmotic pressure of the solution the free energy per liter, or per kilo, of water is 100 atmosphere-liters per kilo, or $100 \times 18.016 \div 1000 = 1.802$ atmosphere-liters per mole.

The equivalent activity is given by

$$\Delta \ln a = -\Delta G_p / RT \qquad (64)$$

where a is the thermodynamic activity

G_p is the molal free energy due to pressure

R is the gas law constant, 0.08205 in atmosphere-liters per degree Kelvin.

$$\text{At } 298^{\circ}\text{K}, \ \Delta \ln a, \text{ or } \ln (a/a_o) = \frac{-1.802}{0.08205 \times 298} = -0.0737$$

$$a/a_o = 1.0133$$

Diffusivities are normally calculated in units of concentration which are, for pure water, 0.0555 mole per cubic centimeter. Assume this to be the value of a_o. Then Δa, the activity difference is equivalent to

$0.0555 \times 0.0133 = 7.37 \times 10^{-4}$ moles per cubic centimeter.

Finally, the membrane thickness is assumed to be 0.015 cm. and a typical flux of a Loeb-type membrane is,

say, one gallon/(sq.ft.)(hr.), or 0.1337 ft./hr., or 1.134×10^{-3} cm./sec., or 6.28×10^{-5} moles of water/(sq.cm.)(sec.).

An average effective 'D' for this membrane is then

$$\frac{6.28 \times 10^{-5} \times 1.5 \times 10^{-2}}{7.37 \times 10^{-4}} = 1.28 \times 10^{-3} \text{ cm.}^2/\text{sec.}$$

It is reasonable to assume that the diffusivity of water within a membrane cannot exceed the coefficient of self-diffusion for pure water which is 2.8×10^{-5} cm.^{2}/sec. It is seen, therefore, that the estimated diffusivity based on the measured water flux is about 2 orders of magnitude higher than the maximum which could be assumed if the transmission is by a normal diffusion process.

This matter is discussed in Tuwiner (ref. 28) and it is noted that permeation of water through cellophane corresponds with a 'D' of 4.2×10^{-4} at 25°C. which is also much higher than the maximum value if true diffusion is the mechanism of transfer.

Commercial cellulose acetate film (DuPont 88 CA48, 0.8 mil) was found in this investigation to transmit water at a rate which corresponds to only a fraction of the normal diffusivity of water. In this case, the mean effective diffusivity is given by

$$\frac{3.77 \times 10^{-7} \times 2.02 \times 10^{-3}}{7.37 \times 10^{-4}} = 1.035 \times 10^{-6} \text{ cm.}^2/\text{sec.}$$

which is 3.7 percent of the self diffusivity of water.

Salt rejection by this cellulose acetate membrane is greater than 99 percent. It is a reasonable supposition that the flux is a true diffusion involving single molecules of water. This appears to be a necessary condition for obtaining very high salt rejection. Under these conditions the ions are brought into close proximity with the cellulose acetate molecules with which they become bound.

The Loeb membranes possess an outer 'case' or layer which is probably composed of nearly water-free cellulose acetate. Considerations which are noted above indicate that this layer, which is responsible for salt rejection, is less than one percent as thick as the total membrane.

The specific permeability of this denser layer is far less than that of the much thicker layer which supports it. As a consequence the pressure gradient is heavily concentrated in this very thin outer layer. The entire membrane is under a very intense compression.

Manjikian shows that the salt rejection increases considerably as the operating pressure is increased. This indicates a compaction. There is also a time effect; the salt rejection increases while the water flux decreases with time. Eventually these effects level off.

Finally, it may be noted that the water flux rate is diminished sharply as the electrolyte concentration is increased, an effect due probably to a concentration of electrolyte in the membrane. The rejection of polyvalent electrolytes is greater than that of the monovalent ones especially at low concentrations. This is especially noteworthy for membranes such as cellophane which are less effective than cellulose acetate in salt rejection.

The casting and post-treatment of Loeb membranes is an empirical art and all prescribed conditions must be followed without deviation. The composition of casting solution employed in this study is as follows:

Acetone	45%
Formamide	30%
Cellulose Acetate	25%

This is cast at room temperature (25°C.) on a glass plate. After 30 seconds in a horizontal position the plate and film are immersed in ice water for one hour. The membrane is then peeled from the glass and immersed in a water bath for 15 minutes at 80°C. The membrane is stored at room temperature until it is ready for use as a 4-inch diameter, die-cut circles.

The main purpose of heating the membranes is to improve the demineralizing properties. Manjikian states that some of the improvement is lost in storage for a prolonged period and regained on reheating. Heating probably reduces the size of the skin pores, consolidates the substructure, stabilizes the system and reduces the deterioration in storage.

The membranes of Manjikian are similar to the ones developed earlier by Loeb and Sourirajan which are obtained

from the following casting solution:

Cellulose acetate	23.15%
Acetone	69.50
Water	5.46
Magnesium Perchlorate	1.65
Hydrochloric Acid	.33

This must be cast at a temperature of from -11 to -8°C. instead of at room temperature and it is much more difficult to obtain membranes with reproducible properties.

With any casting solution it is extremely important to eliminate any suspended solids or incompletely dissolved gel particles. Otherwise these constitute sources of potential pinhole porosity. It is therefore recommended that the casting solution be polished by filtration through a microporous sintered metal medium before the film is cast.

The importance of maintaining the correct membrane orientation in the stack assembly cannot be too greatly emphasized. Very large differences appear in the salt rejection of a membrane depending on which side is oriented in the upstream position. The differences are greater percentagewise for those membranes which are formulated and conditioned for a high rejection with some sacrifice of product flow rate.

When the dense skin layer is upstream the entire membrane is under intense compression. In the other orientation it is only the skin layer which is under strong compression while the remainder of the membrane is under but very moderate compressive force.

Apparatus Requirements

A flight qualifiable system must be reliable, light in weight and compact. It must be resistant to corrosion and to the stresses which accompany high pressure operation. It must be capable of easy assembly and maintenance. Finally, it must possess a capability of handling a solution with suspended solids and of extracting at least 90 percent of the water in a single pass. Auxiliary equipment of the system consisting of a high pressure pump and brine bleed control must be designed for integration with the main unit of the system so that high pressure fluid is confined to the space within a single housing.

These requirements collectively have never been achieved heretofore. The system designed and constructed in this study may, however, be modified considerably for a flight qualifiable unit. Some of these modifications are, in general terms, as follows:

1. Closure of the membrane stack assembly with 12 tie bolts through holes around the periphery of the end plates is time consuming. These bolts should be eliminated and instead a self-sealing closure should be designed with a floating head and retaining ring on one end of the stack. The other end should be at the closed end of a forged hollow cylindrical vessel which encloses the stack. The wall thickness should be expanded at the open end of the forging and this end should be machined for the floating head closure.

2. The membrane pair sub-assemblies should be slightly redesigned so that they may be dropped into their appropriate positions in assembling the stack. This would be done using guide rods and peripheral holes in the spacers, gaskets and membranes.

3. Closure of the stack should be by means of a torque applied to the retaining ring which should have a hexagonal center hole which receives the hexagonal head of the closing tool. The expanded wall section should have a welded cylindrical boss which is drilled and tapped for a torque rod so that the closing torque may be applied to the retaining ring which is peripherally threaded into the wall of the forging.

4. A multistage gear pump should be mounted as an integral part of the closed end of the forging. Critical parts of this pump must be constructed with extreme precision and a very low wattage motor must be designed and constructed.

Apparatus Design of this Study

The design of apparatus in this study is intended to test fully the design principles of a membrane stack to meet the requirements set forth above with some compromise of size and weight in the interest of a much less costly and less time consuming design and construction.

The apparatus is considerably overdesigned structurally. An elaborate and detailed stress analysis is outside the scope of this study. Each of the two end plates of titanium weighs 2 pounds. The combined weight of the

spacers, membranes and other components of the stack is 0.15 pound while the twelve bolts and nuts, if of titanium, would weigh 0.5 pound. The entire assembly is therefore less than 5 pounds. This is obviously capable of being reduced markedly in a space qualifiable system.

The construction of the end plates and other parts is shown in Figure 5 while Figure 6 represents the construction of a spacer. This consists of a flat ring constructed of epoxy resin-impregnated glass fiber cloth. The thickness of the ring is 0.0254 inch. The outer diameter is 4 inches and the inside diameter 3 inches.

Bonded to the flat faces of the ring are a series of concentric flat copper rings 0.0048 inch in thickness. There are 3 of these rings on one side of the epoxy ring and two on the other. The width and spacing of these copper rings or ridges is such that when two spacers are brought together face to face the opposing copper ridges interlock with a clearance of 0.056 inch.

In each membrane pair sub-assembly there are placed between the enveloping spacer rings 2 polyethylene gaskets 0.012 inch thick, 2 layers of membrane 0.005 inch thick, 2 nylon paper layers 0.01 inch thick and a single layer of woven wire cloth 0.0036 inch thick. This combined multilayer assembly is 0.038 inch thick not including the thickness of the spacer rings. With a clearance between interlocking copper ridges of 0.056 inch there is a considerable pinching of the layers within the clearance between concentric copper ridges. This has the effect of imparting a self-centering property and also of holding a seal between the separator rings and the membranes which is watertight under 1500 pounds per square inch pressure.

The copper ridges are fabricated by employing the technique which was developed for printed circuits. The starting material is a laminate consisting of epoxy resin impregnated glass cloth with copper foil bonded to both faces. The exposed surfaces of the copper are coated with a photo resist which is exposed to light from a master transparency. Unexposed portions are washed away and the copper removed by etching in a solution of ammonium persulfate. Where the photo resist has been exposed and hardened the copper remains as an etched pattern.

Because of the methods used the pattern of concentric circular ridges is reproduced very precisely and the

method is capable of producing any number of perfectly interchangeable parts. The ultimate tensile strength of the plastic composition is 40,000-60,000 psi and the copper is bonded to conform with rigid peel strength specifications.

Concentricity of the spacer rings and the copper ridges is ensured by the self-centering property. This results in a uniform peripheral distribution of the pressure on each spacer provided that the tie bolts are tightened uniformly.

The assembly of the reverse osmosis apparatus involves the prefabrication of membrane pair sub-assemblies, one of which is shown in "A" of Figure 7. Each of these sub-assemblies consist of two parallel and concentric 4 inch diameter membranes separated by, and supported on, a base consisting of a woven wire screen and two layers of nylon paper. This sub-assembly is designed so that the pressure upon the outer faces of the membranes may be as high as 1500 psig while the hydrostatic pressure between the inside faces of the membranes is nearly zero. The differential pressure of 1500 psi compresses each membrane upon the supporting base. The water diffuses through each membrane and flows into the supporting base and then flows laterally toward the periphery of the supporting base and out of the stack.

Construction of the membrane pair sub-assembly is completed with two spacer rings, one against each of the outside faces of the two membranes. The spacer rings are concentric with the membranes and their base support and there are two polyethylene gaskets, 0.003 inch thick, one between each membrane and its opposing spacer ring. In the sub-assembly the side of a spacer ring having three copper ridges opposes a two ridge side of the other spacer.

The supporting base for the two membranes of the sub-assembly is composed of a layer of woven and sintered stainless steel screening and, on either side of the screening, a layer of nylon paper. The selection of the screening (Rigimesh K) and nylon paper was made after extensive testing and evaluation of alternatives.

When the membrane pair sub-assembly is placed in compression in the stack assembly the layers between the spacer rings are molded into a 'W'-shaped configuration. This imposes a severe strain on each layer owing to the stretch in the lateral, and the compression in the tranverse, direction. The plastic membranes and gaskets

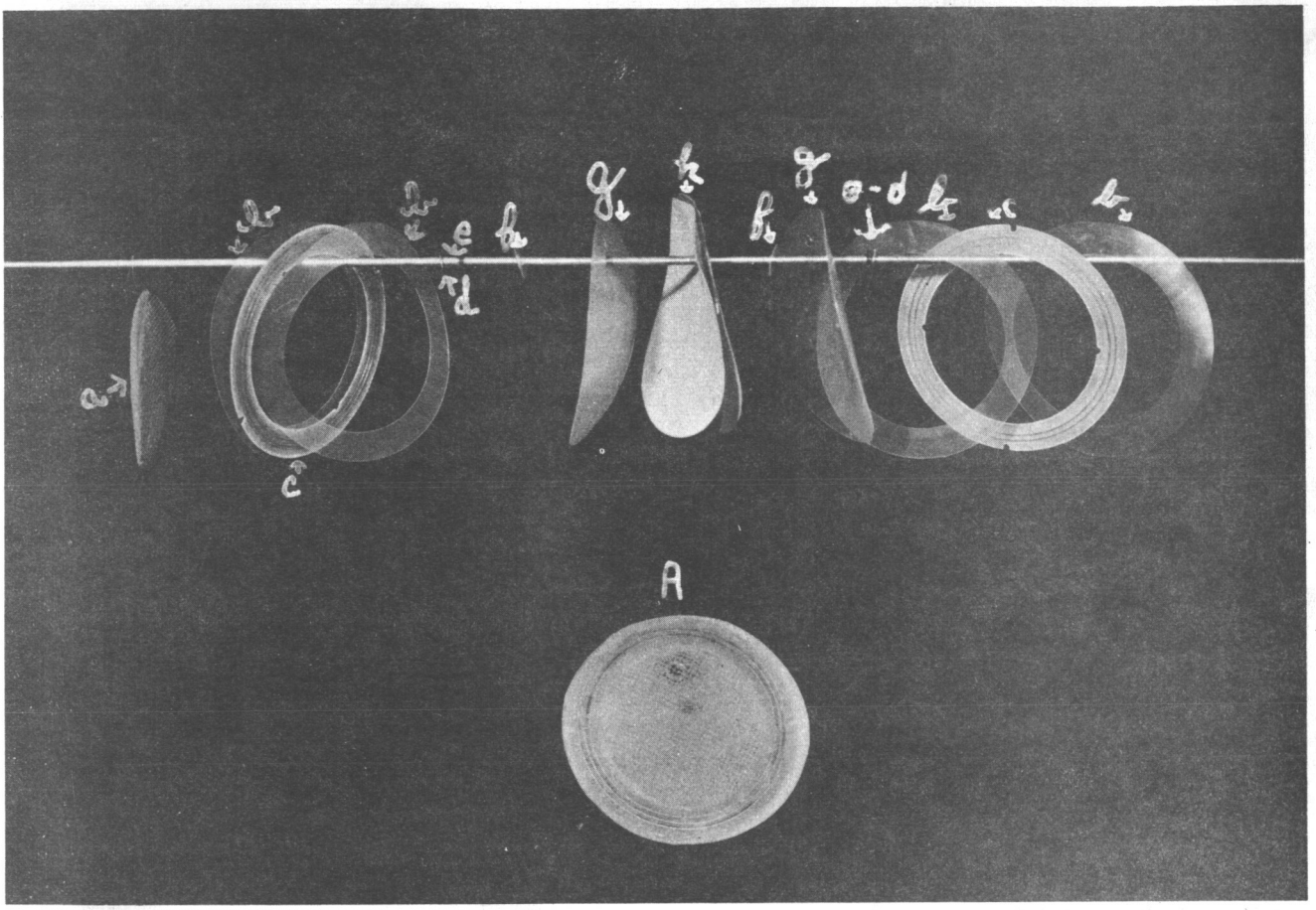


FIGURE 4 REVERSE OSMOSIS SUB-ASSEMBLY

Same as Figure 6 but with sub-assembly, A, face on showing grommet assembly through the two layers, a-a, of polyethylene screening.

and the fibrous nylon conform readily. The screening, however, is subject to considerable tensile stress radially. Despite this stress, which exceeds the yield point, the screen structure does not collapse or break and the water which is transferred by reverse osmosis flows laterally, not merely within the 3 inch diameter space inside of the spacer rings but also along that part which is subjected to stress due to compressing the membrane stack.

To satisfy the requirement for communication between the cells containing pressurized mineral-containing solution it is necessary to provide an opening through both membranes and the supporting base of each membrane pair sub-assembly. This opening permits communication between the two sides of the sub-assembly but it must avoid communication with the low pressure pure water in the space between the membranes. There must be no significant leak of the pressurized brine into the permeate water through the peripheral seal between each membrane and its contacting spacer or through the wall of the hole through the membrane pair sub-assembly.

To fabricate the pressuretight hole through the membrane pair sub-assembly the following concentric hole sizes are cut in the component layers the center of each hole 3/4 inch from the outside edge:

Woven and sintered screen	5/8 inch diameter
Nylon paper layers (2)	9/16 " "

The woven screen, with a layer of Viskon nylon paper on each side, and with the holes aligned concentrically, is assembled with two 0.012 inch thick polyethylene flat gaskets, each 13/16 inch in diameter, each with a 1/8 inch center hole. The gaskets are placed one on each outside face of the nylon paper discs and they are positioned to be concentric with the holes in the nylon paper and the screening. By means of an adhesive the gaskets are bonded to one another on the inside and to the nylon layers around the peripheries of the gaskets. Adhesive is next applied to the outer faces of the gaskets and to the opposing surface of the two membrane discs which are mounted on either side of the screen and nylon paper assembly. Finally, 9/16 inch gaskets with 1/8 inch holes are bonded to the outsides of the membranes after being positioned to be concentric with all of the holes. The adhesive is permitted to cure while the components are held together under pressure while immersed in water. The 1/8 inch holes are then punched through the membranes and sealed with a # 00 G&W grommet.

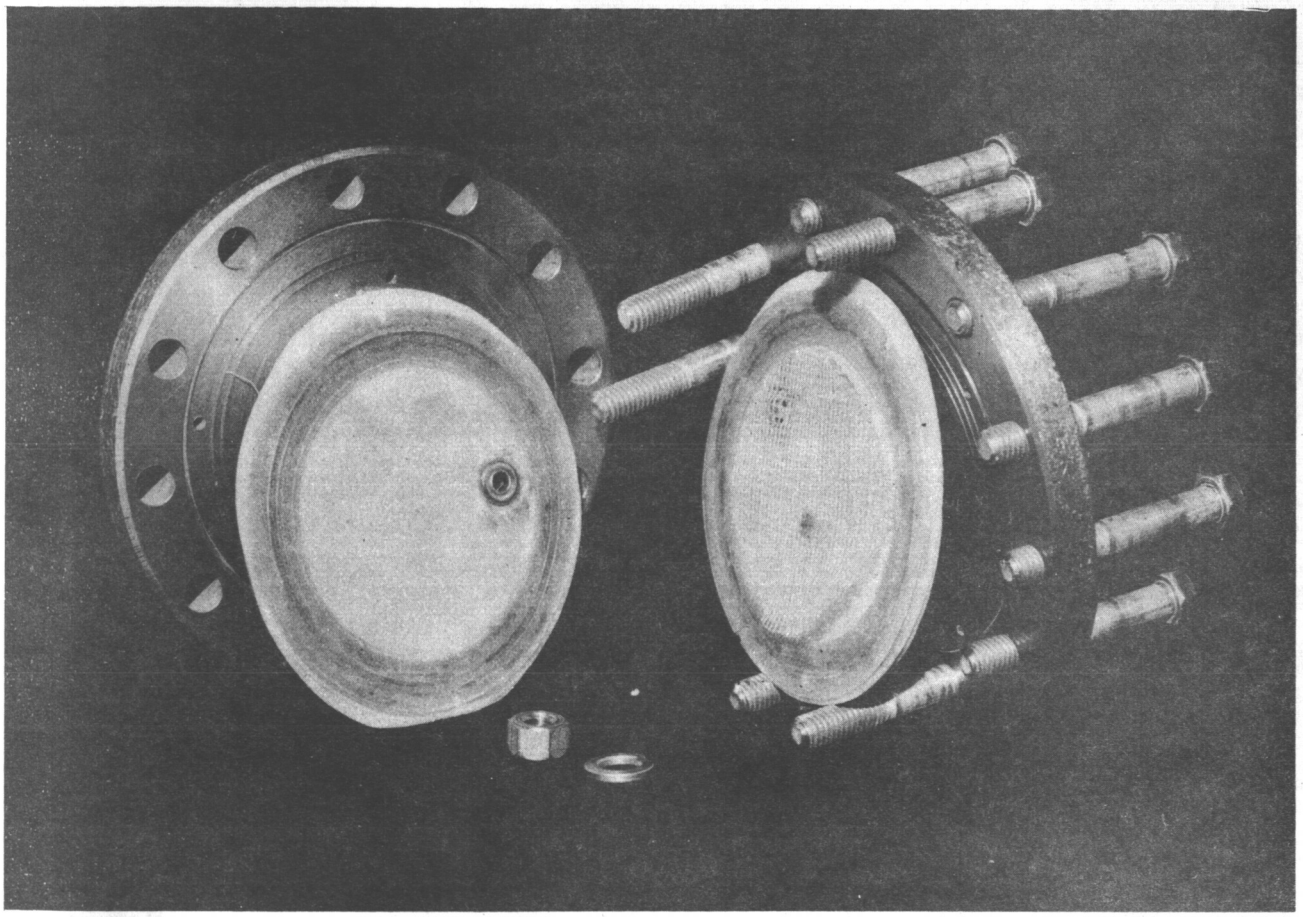


FIGURE 5 REVERSE OSMOSIS ASSEMBLY, OPEN

Titanium end flanges and two sub-assemblies.
possible to use an indefinite number of these

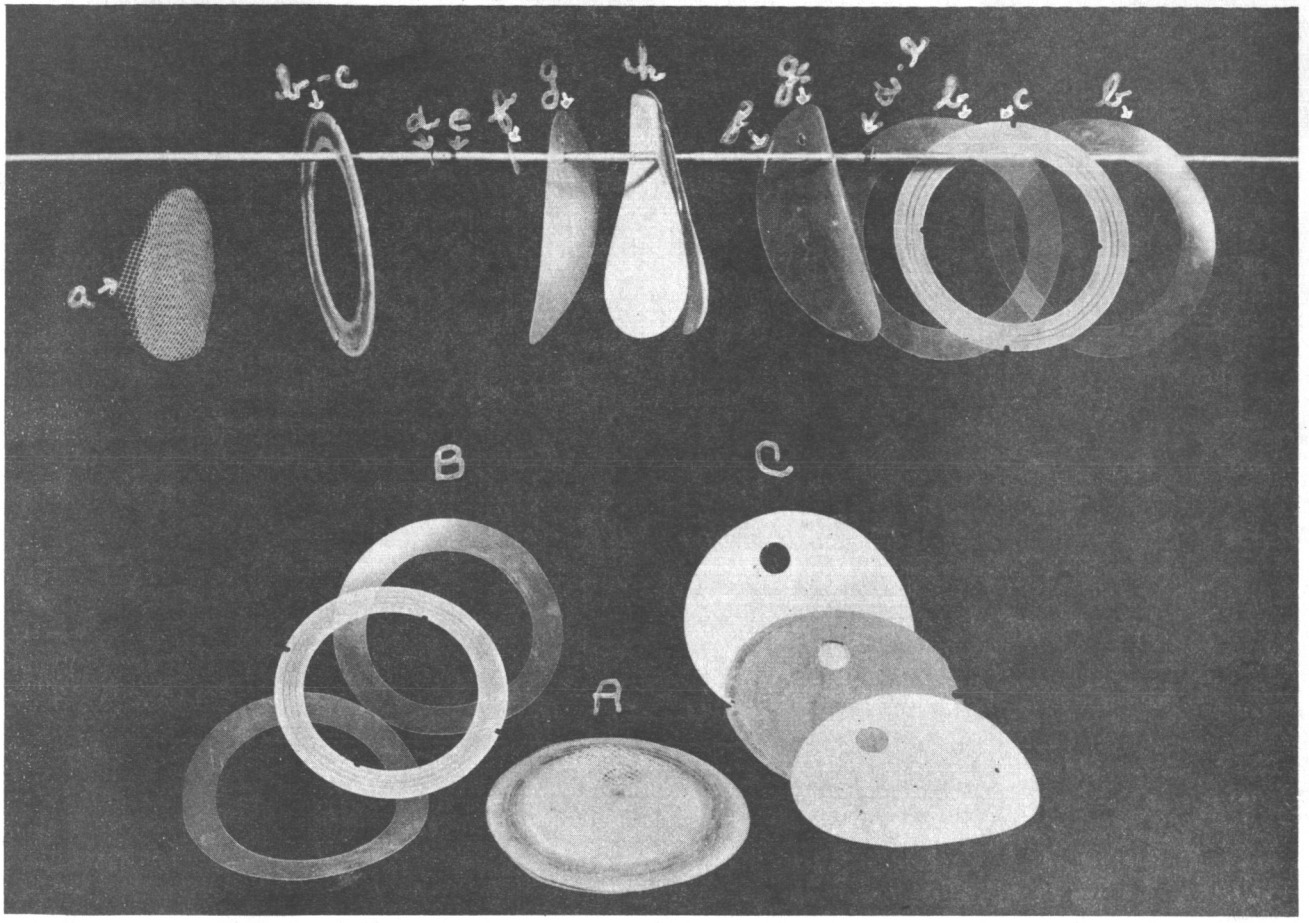


FIGURE 6 REVERSE OSMOSIS SUB-ASSEMBLY

a. Double layer of polyethylene screen
b-c Spacer ring and two polyethylene gaskets at left. At right hand end of supporting rod the same showing expanded components. Also at B, below.
d-e Grommet and quad ring. On the left is the female grommet, d, and quad ring e. At the right the quad ring is on the cylindrical section of the male grommet component.
f-f Polyethylene gaskets. These are cemented around the holes in membranes, g-g.
h. Nylon paper layers and layer of woven and centered wire screen. Expanded view in C.
A The complete sub-assembly.

The membrane pair sub-assemblies are then assembled in the stack. Figure 8 shows two of these sub-assemblies placed between the end plates. The assembled stack may contain any number of membrane pairs. One end plate contains the inlet hole for the solution feed. When the first membrane pair is inserted, it is placed so that the position of its grommet hole is diametrically opposite to the inlet hole of the end plate. The following membrane pair sub-assemblies are then placed with the grommet holes alternating diametrically. Finally, the exit hole which is in the second end plate is located diametrically opposite to the position of the grommet hole in the last membrane pair sub-assembly. This provides for an alternating flow of the feed solution as it traverses the membranes.

Two layers of 8 mesh polyethylene screen are employed to fill some of the space of the pressurized cells within the inside diameter of the spacer rings. This serves the purpose of restricting the movement of the sub-assemblies and also of preventing the lip of any grommet from touching the face of an opposing membrane and thus restricting or closing off the flow of the solution from cell to cell along the stack.

Materials Development

In the previous section apparatus is described which represents a culmination of a program of design and experimental study. Various materials and modifications have been tried to obtain the maximum performance and reliability. It is important to design apparatus and components in which there is a minimum probability of pinholes, leaks or defects which would result in contamination of the product water. Also, this apparatus must possess the capability of being assembled and disassembled for routine maintenance and repair.

Accordingly, for the design of the spacer rings an investigation was made of various possible ways of pressure molding the ridges which are employed for centering and sealing them. Vulcanized fiber board was first considered for this purpose. This material, obtainable in sheet form, may be die-cut to the required internal and external diameter specifications. The ridges might then be pressure molded. We were informed, however,

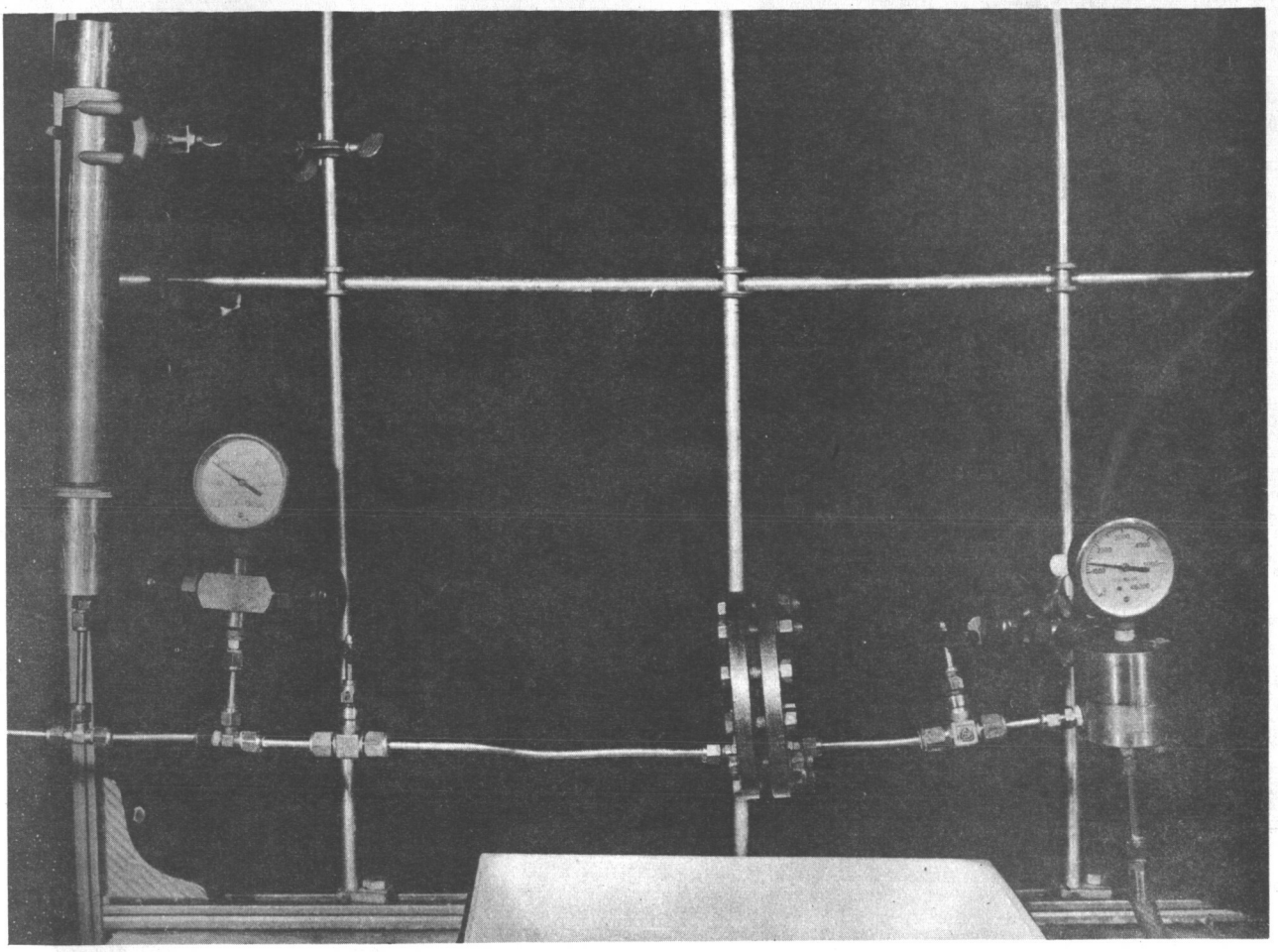


FIGURE 7 REVERSE OSMOSIS TEST ASSEMBLY

Pretreated urine is delivered from pump (not shown) through stainless steel tube. Vertical cylinder at left is accumulator. Next to right is gage to measure liquid feed pressure. Next is cell assembly. Product water is collected in pan below. Next is needle valve and back pressure regulator on extreme right.

by a firm which would have sub-contracted the manufacture of these components that the degree of upset which is required for our design is not within the limits of formability of this material. Other types of laminates were next studied but these also were found to possess undesirable limitations of dimensional tolerance or design strength.

Consideration was next given in the design of these spacer rings to providing a minimum thickness in order to favor the most compact arrangement of membranes in the stack. Opposing this requirement is that of providing the space which is required to enclose the grommets described in the preceding section without crowding the open ends of these grommets where they face the outer surface of the next membrane pair sub-assembly.

After due consideration and study the printed circuit board laminate was selected. It combines the highest design strength with the most precise concentricity and dimensional accuracy and stability. Time and other limitations precluded consideration in this study of all of the various design modifications which are possible or conceivable. It is obvious for example that there is an infinite possibility of variation of width, spacing, and number of concentric ridges of the spacers. Also, it is possible to vary at will the height of these ridges above the surface of the epoxy plastic base and it is possible also to modify the surface of the ridges by using electroplates or chemically deposited layers of, e.g., nickel or chromium.

The selection of the appropriate materials for the gaskets is extremely important to the reliability of performance of this apparatus. Various gasketing materials accordingly were tried and studied and these covered a wide range of hardness and plasticity. Included in this study were various impregnated cloth materials. It was concluded from this study that a 12-mil thickness of low density polyethylene compared favorably with any of these.

In order to obtain sufficient frictional resistance to withstand the outward force due to the hydrostatic pressure it was found necessary to employ an elastomeric adhesive between the gasket and the surface of the spacer ring. Accordingly, a considerable amount of study was given to the evaluation of various adhesives. Not only between the gasket and the spacer but also between this gasket and the membrane this adhesive is effective.

Even with the best of the adhesives studied it was found that the 3/8 inch tie-bolts between the end plates needed to be drawn rather tightly in order to provide the necessary frictional resistance for withstanding 1500 pounds/sq.in. of pressure. In any future design modification it may be advisable to consider a prebonded plastic gasket.

Considerable attention has been given to the development of adhesives to provide a satisfactory bond with cellulose acetate membranes of the Loeb-type. This is a very difficult problem owing to the fact that this membrane contains considerable imbibed moisture and undergoes considerable dimensional change accompanying any considerable change in its water content. Considerable work has been done in this area in studies sponsored by the Office of Saline Water, U.S. Department of the Interior, but the results of these investigations are unpublished at this writing. Initially in this program it was thought that the pressuretight holes in the membrane pair assemblies described in the preceding section might be obtained simply by bonding the two membranes which form the outer layers of the sub-assembly around the periphery of each hole.

Unfortunately, however, tests indicated that the adhesives and techniques which were employed did not offer any indication of success. In these tests the peripheries of the two membranes were bonded using what was essentially a solvent weld. The solvent consisted of acetone in which there was a small amount of cellulose acetate. The acetone solution was applied around the periphery of the holes on the inside faces of the membranes. The membrane surfaces were then pressed together for a period of time to permit the solvent to diffuse into the membranes leaving a bonding layer. In all cases this method was unsuccessful owing to the fact that cracks developed in the membranes outside of, but very close to, the bonded peripheral area. This was due to some nonhomogeneity of composition which developed from the bonding or perhaps from the stresses which are produced as a consequence of the nonhomogeneity of composition in the vicinity of the bond.

These results led to the development of the grommet enclosure which is described above. In this the adhesive is one which does not diffuse appreciably into the membrane layer but provides nevertheless some adhesive tendency in holding the membrane from sliding and moving in relation to the polyethylene gasket. Mechanical force

provided by the flaring of the grommet neck provides a constant pressure which serves as a mechanical means of obtaining the watertight seal which is an absolute necessity in this apparatus. This mechanical force is supplemented by the adhesive bond which is provided. In this connection it was found desirable to avoid and attempt to bond any one membrane layer to any other. Instead, all bonds are made between a membrane and a polyethylene gasket.

The adhesive which is used to bond the membranes to the polyethylene gaskets (B.F. Goodrich A 951 B Industrial Adhesive) does not penetrate the cellulose acetate more than superficially. The volatile ketone (MEK) in this adhesive is normally an excellent solvent for cellulose acetate but in the system in which this compound is applied as a synthetic rubber solution, there is little interdiffusion of the components of this solution with the substrate of water-imbibed cellulose acetate.

The mechanical properties of the membranes are not affected therefore by the application of this adhesive, deleteriously or otherwise. At the same time there is a degree of interpenetration which results in adhesion of the membrane to the gasket, normally very difficult to achieve. The adhesive bond with the membrane is not very strong but it serves, with the mechanical reinforcement of the closure, to ensure a watertight seal of the membranes to the spacer rings.

The same adhesive is used for the similar purpose of obtaining a pressuretight seal around the grommet holes. Here the mechanical reinforcement is provided by the pressure which is applied between the grommet flange and the washer by the flaring of the neck into this washer.

A number of other adhesives were tried unsuccessfully including epoxies, proprietary adhesives and a solution of cellulose acetate in acetone.

The development of the woven and sintered stainless wire screening to provide a means of lateral passage of the pure water permeate was following a program in which various alternate materials were evaluated. Woven cloth of varying type and thickness were studied but all of them were found to suffer from compaction due to cold flow under the bearing surfaces of the spacer rings. Thus they were rendered impermeable to the outward flow of water. Consequently with all of these materials there

resulted considerable back pressure on the downstream side of the membranes; they are therefore unsuitable inasmuch as they do not provide the outward peripheral flow which is required for effective collection of the product water.

In addition to this shortcoming all of the woven fiber materials were subject to a considerable bulging as a consequence of which it was impossible to obtain the open space between the membrane pair sub-assemblies to provide for the circulation of the solution from cell to cell without a considerable back pressure being developed between the liquid feed and brine discharge ports.

In an attempt to remedy this difficulty 19-mil thick sheets of tinned copper were employed as the center layer of the membrane pair sub-assemblies. Then to provide the means of passage of product water outward from the peripheries of the membrane pair sub-assemblies, cloth layers were placed on either side of the center layer of metal sheet.

This modification provided the necessary rigidity and prevented bulging of the membrane pair sub-assemblies. However, the difficulty with excessive back pressure caused by the compaction of the woven cloth remained as an obstacle to the effective use of this design modification.

Finally, various types of woven wire mesh were tried. It was found at first that these suffered a disintegration due to the severe stresses that are imposed around the area of the pressure closure. The material which was finally adopted however was found to be quite serviceable (Rigimesh K). It appears therefore that the sintering of the wire strands in this woven screening material reinforced the structure sufficiently so that it appears to be capable of withstanding the maximum stresses imposed under conditions of service in this apparatus.

Design Parameters

The spacer frames must be designed on the basis of a long cylinder under a working pressure of 1500 psi on the inside and a pressure of 0 psig on the outside. In actuality this yields a very conservative estimate of the maximum operating stress in the spacer frames inasmuch as the end plates assist in withstanding the

outward pressure particularly in a short stack.

A number of formulae have been proposed for estimating the maximum stress in the wall of a cylinder. One of these is

$$S_{max} = P_1 \left[\frac{R_o^2 + 1}{R_o^2 - 1} \right] \qquad (65)$$

where P_1 is the inside pressure, psi

R_o is the ratio of outside to inside diameter.

For the apparatus of this study, P_1 = 1500 psi and R_o = 1.333. Accordingly

$$S_{max} = \frac{1500 \times 2.775}{0.775} = 5375 \text{ psi}$$

This estimate of stress is approximate but it represents an extremely conservative allowance for a glass cloth reinforced epoxy. It is probable that the material of the spacer rings could be reduced considerably but it was considered advisable in this study to overdesign considerably and provide for refinement of the design at a later study.

An approximation may be made of the maximum stress on the titanium end plates by assuming that this is a circular flat plate uniformly loaded over a 3 inch radius and with the edge fixed. The maximum stress at the edge is

$$S_{max} = \frac{3}{4} \frac{P r^2}{t^2} \qquad (66)$$

where P is the inside pressure, 1500 psi

r is the radius, 1.5 inch

t is the plate thickness, 0.5 inch

This yields

$$S_{max} = \frac{3}{4} \times \frac{1500 \times 2.25}{0.25} = 10,130 \text{ psi}$$

This represents a very conservative allowance as in the case of spacer rings. However, again it was deemed appropriate to overdesign for this study.

RESULTS

A typical urine sample, 1.4 liters in volume, was treated by electrochemical oxidation as described on page 26. The d.c. current at 10 amperes was maintained for 16 hours during which the temperature, as indicated by a thermometer in the center well, rose from ambient to 64°C.

Considerable foaming was encountered initially as well as a considerable amount of suspended solids. Both disappeared after a few hours of operation. The voltage, which was 5.4 volts initially, fell rapidly to 3.8 volts and remained constant. The power consumption is estimated to be 457 watt-hours per liter.

The solution obtained after this treatment was then separated into potable water and brine by a single pass through the reverse osmosis system. Because of system hold up and withdrawal of samples for analysis the volume of products was only 752 ml. of which 588 ml. was product water and 164 ml. was brine. This represents a recovery of 78 percent. The brine stream contained a considerable amount of solid material in suspension owing to the concentration of the solution to the limits of solubility of some of the solute components.

The product water contained 9719 mg/l of total solids, including 2318 mg/l of chloride. The feed stream contained 26,530 mg/l of solids including 5,975.3 mg/l of chloride while the brine stream contained 17,343 mg/l of chloride and total solids which could not be determined because of solids precipitation.

The Chemical Oxygen Demand of the product water was nil when determined by the USPHS standard method of analysis.

DISCUSSION

Although the product water is relatively high in total solids and chloride it is in all other respects suitable as drinking water inasmuch as it is free of COD, pyrogens and all trace of color and odor. The brine is

comparable in concentration with sea water and much of the calcium, magnesium, phosphate and sulfate are precipitated from the stream.

If the brine is accumulated and then treated in a second pass through the reverse osmosis system the total water recovery should be very high. There is a possibility also of retreating the product water to bring the total solids to within the limits of normal drinking water.

The performance of the membranes is about as would have been anticipated from the published results of Loeb, Manjikian and Sourirajan. With the very high water recovery which is required for this system it appears that it would be advantageous to obtain better salt rejection even at some considerable sacrifice of capacity in terms of product volume per square foot of membrane.

Another factor to be considered is that a membrane of the Loeb type undergoes gradual compaction with continued use and this results in an improvement in salt rejection accompanied by a gradual decrease in capacity. The limited period of the system evaluation of this study did not permit attainment of the steady state.

It will be necessary to operate this system for a considerable period of time to estimate the effects of these factors as well as that of precipitation of some of the inorganic solute components during the operation.

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ABSTRACT FOR CONTRACTOR REPORT UNDER NAS1 4373: Research, Design, and Development of an Improved Water Reclamation System for Manned Space Vehicles, by S.B. Tuwiner

The Research and Development work promoted by Langley Research Center under this contract resulted in the construction of a laboratory prototype, urine water reclamation system that requires a relatively small quantity of expendable materials for its operation. Such a system would be desirable on space missions of medium to long term duration. It combines the techniques of electrolytic pretreatment, for removal of organic constituents, and reverse osmosis for the final separation of water from the resultant brine solution. The system can recover at least 90 percent of the available water in urine at an average cost of about 1660 joules per gram (209 watt-hrs per pound) of urine processed. An expendable requirement is activated charcoal in the amount of 3.6 grams per liter of water recovered. The recovered water may be considered potable.