

NRL Report 5995

UNCLASSIFIED

DIAPHRAGMS FOR THE SULFATE CYCLE ELECTROLYTIC CELL

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September 17, 1963



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Washington, D.C.**

CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
EXPERIMENTAL TECHNIQUES	2
EXPERIMENTAL SCREENING OF COMMERCIAL TEXTILES AND PAPERS	4
GLASS PAPER DIAPHRAGMS	4
MIXED FIBER DIAPHRAGMS	5
TREATED ASBESTOS	6
MICROPOROUS RUBBER	6
SUMMARY	12
REFERENCES	12

ABSTRACT

The study of diaphragms for the sulfate cycle electrolyzer included (a) the screening of commercially available textiles, papers, and porous materials for their capability to be utilized as diaphragms, (b) the development of techniques and equipment for the realistic evaluation of candidate diaphragms, (c) the development of new combinations of fibers and resins to give improved service as diaphragms in the cell, and (d) the determination of the service life of candidate diaphragms in miniature cells which reproduce the physical, chemical, and electrical atmospheres of the full-scale cell.

Of the hundreds of materials included in this study, one form of commercially available microporous rubber was without question the material of choice for use as a diaphragm. From continuous electrolyzing runs in the miniature cells lasting 125 days, this material was shown to fulfill the stringent requirements and provide the required solution flow rate, temperature, pressure, and normality of anolyte and catholyte.

PROBLEM STATUS

This is a final report on this phase of the problem; work on other phases of the problem is continuing.

AUTHORIZATION

NRL Problem C05-17
Projects RR 001-01-43-4701 and SF 011-08-02-3335

Manuscript submitted July 12, 1963.

DIAPHRAGMS FOR THE SULFATE CYCLE ELECTROLYTIC CELL

INTRODUCTION

The sulfate cycle system has been intensively studied at this Laboratory (1-3) for its potential use in nuclear submarines for generating oxygen and removing carbon dioxide. The problems inherent in the development of a practical system have been evaluated from the laboratory to the pilot plant scale. The initial studies were completed in 1959 of the three main components of the system: the electrolyzer, the carbon dioxide absorber, and the carbon dioxide desorber. It was evident that the most critical problem was the requirement of diaphragms for the electrolyzer. In 1960, a separate laboratory study of diaphragms was initiated with the ultimate objective of developing appropriate diaphragm materials and proving, on a laboratory scale, their feasibility for proposed submarine use in the sulfate cycle cell.

These diaphragm studies have included: (a) the design and fabrication of special laboratory-sized equipment required in the studies, (b) the screening of commercially available porous materials which were considered capable of withstanding the chemical environment of the cell, (c) the preparation of experimental hand sheets containing various fibers, resins, and mixtures for evaluation as diaphragms, and (d) a number of continuous operating runs in miniature cells of candidate diaphragms to determine their service life expectancy.

The physical and chemical properties required of the diaphragms can be deduced from a brief review of the cell and its operation. The electrolyzer contains three chambers: the anode, the cathode, and the central or supply chamber. Anode and cathode diaphragms provide the compartmentation. The cell is a flow type in that the electrolyte (18% Na_2SO_4 solution) fills the central chamber and flows through the diaphragms and perforated metal electrodes and drains off the outer, free surface of the metal electrodes to be collected from the bottom of the anode or cathode chamber. Fresh electrolyte is furnished the supply chamber and held at constant liquid pressure at a value depending on the solution flow rate desired, the diaphragm porosity, the concentrations of electrolytically produced acid and alkali, and the temperature. Electrolysis of the flowing solution produces oxygen and sulfuric acid at the anode and hydrogen and sodium hydroxide at the cathode. The gases are collected through vents in the top of the anode and cathode compartments. For the desired operating conditions the anolyte and catholyte contain in addition to excess sodium sulfate a concentration of about 5% H_2SO_4 or 5% NaOH . The operating temperature is held below 50°C to prevent excessive corrosion of the lead anode.

The diaphragms are required to perform three functions: (a) they serve to provide at constant liquid pressure the desired solution flow rate to the electrodes, (b) by providing a constant solution flow rate they prevent the back diffusion of acid or base into the central chamber, and (c) in a similar fashion by providing a flow and pressure gradient they prevent a back flow and undesired mixing of hydrogen and oxygen produced at the electrodes. The physical and chemical properties required of the diaphragms are stringent and include: (a) dry strength sufficient to enable storage, handling, and insertion into the cell, (b) wet strength sufficient to insure service life measured in months, (c) permeability to provide and maintain the desired solution flow rate at liquid pressures up to 100 inches of water and temperatures up to 50°C , (d) chemical resistance to 18% sodium sulfate solution, (e) chemical resistance to 5% H_2SO_4 for the anode diaphragm and 5% NaOH for the cathode diaphragm, and (f) resistance to the electrolytic oxidizing or reducing atmospheres at the electrodes.

The diaphragms used in the exploratory studies (1) of electrolytic cell operation consisted of three sheets of asbestos paper, electrolytic grade. Although diaphragms of this material were useful for these short experiments, it was evident that asbestos diaphragms would not be practical for the proposed submarine use of the cell. The difficulties with asbestos included: (a) very low wet strength, (b) lack of acid resistance as evidenced by disintegration of anode diaphragms after only a few hours service, and (c) excessive liquid permeability which precluded the use of liquid pressures higher than about 20 inches of water. Higher pressures were desired to prevent back diffusion of acid, alkali, or gases into the feed compartment.

In the initial studies devoted to diaphragms, major emphasis was given to the development of a practical anode diaphragm material. However, cathode diaphragms were included in the studies in the hope that the same material could be used for both diaphragms to simplify the problems in the proposed submarine use of the cell.

EXPERIMENTAL TECHNIQUES

In order to study the performance of diaphragms, it was necessary to fabricate equipment especially designed for the purpose. The initial studies involved a screening of commercially available materials by use of an apparatus to measure the liquid flow rate through samples as a function of pressure and time. The apparatus designed for these screening studies is illustrated in Fig. 1. The original device was constructed of brass, since distilled water was used for the test liquid. A later model was fabricated from stainless steel to permit the use of sodium sulfate solutions which were acidified or made basic to reproduce more accurately the chemical environment of the electrolytic cell. The percolation apparatus has three main parts: (a) a chuck with an integral collecting funnel and perforated metal plate for holding the sample, (b) a standpipe to contain the test liquid, and (c) a lock ring to secure the chuck and standpipe. A sample 2-1/2 inches in diameter was required which provided an exposed area 2 inches in diameter (3.14 sq in.). The sample was supported on a plate perforated to the same free area (about 25%) as the electrode to be used on the electrolytic cell. The height of liquid above the sample, and hence the pressure, was variable up to the height of the standpipe (18 inches). In these studies, the liquid level in the pipe was held constant by use of a demand, gravity feeder.

The simple apparatus described above was sufficient to provide quantitative and reproducible flow rate data of value for screening materials. However, it was recognized that more realistic performance data were needed to guide the developmental studies and that such information could only be obtained by reproducing the operating conditions and environment of the electrolytic cell.

A number of miniature electrolytic cells patterned after the cell used in the exploratory studies (1) were designed and constructed. These miniature cells are about 1/10 the size of the full-scale cell. This size was selected to allow diaphragms to be cut from the 6-inch-diameter experimental hand sheets made in the paper laboratory.

The design of these miniature cells is illustrated in Figs. 2 and 3. The cells were fabricated from 1/2-inch Lucite to simplify construction and to allow visual inspection during operation. The three chambers of the cell are nominally 4 x 4 inches in overall dimension. The internal dimension of each chamber is 3 x 3 x 3/4 inch. Both the anode and cathode chambers were fitted with a top vent for release of gas and a bottom tube for withdrawal of solution. An S-shaped glass tube was connected by a rubber union to the bottom tubes of each of these outer compartments. A liquid seal was thus maintained to force the gases generated at the electrodes out the top vents. The central chamber was furnished with four tubes. The two opposing ones on front and back at the bottom of the chamber were used for feed supply and drain. One of the two top vents was used as an access for a glass thermometer while the other was used as a pressure tap. The

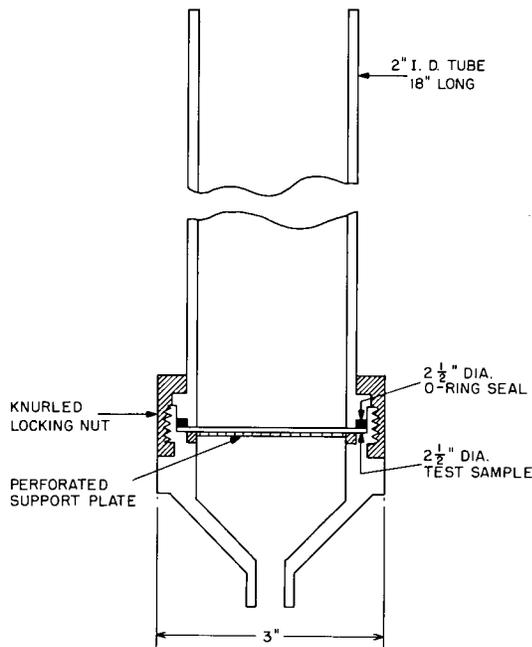


Fig. 1 - Percolation apparatus

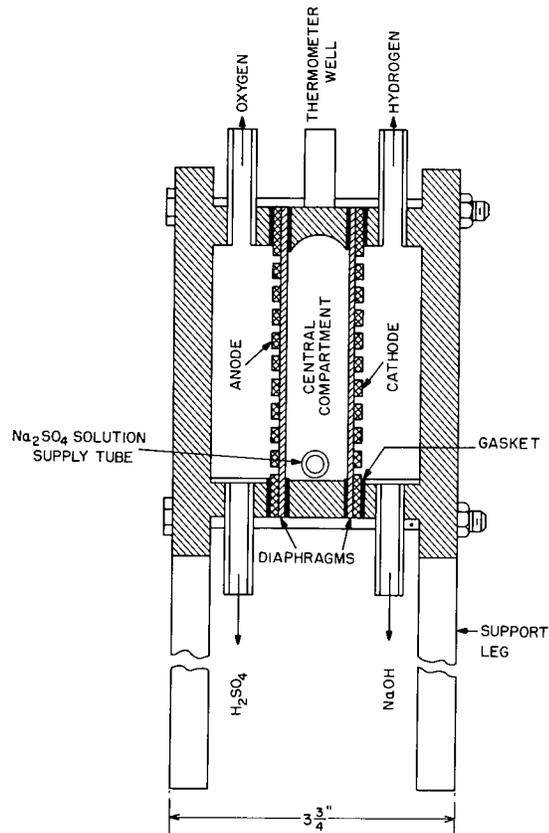


Fig. 2 - Miniature sulfate cell - sectional view

electrodes used for the cells were fabricated from 1/8-inch lead (or lead-silver alloys) for the anode and 1/16-inch stainless steel (No. 304) for the cathode. Each electrode is nominally 4 × 4 inches with an exposed area of 3 × 3 inches. The electrodes are perforated in a staggered pattern by 189 holes (1/8 inch in diameter) contained within the exposed area. The diaphragms were cut to 3-1/2 × 3-1/2 inches and stepped gaskets used to seal the diaphragms and electrodes in the cell. The whole assembly was held together by four symmetrically located bolts.

The sodium sulfate solution was supplied to the central compartment by means of the bottom inlet. For the early studies, the solution pressure was held constant by means of a constant-gravity device (4). This system was modified in later runs in which pressures up to 100 inches of water were required. For the later studies, the solution was supplied to the cell by air displacement from 18-liter polyethylene bottles. Air was used to pressurize the stock bottle and thus provide a constant, regulated hydrostatic pressure of feed solution in the central chamber. Although the system was capable of pressurizing the feed solution to 200 inches of water, the highest pressure generally used was of the order of 50 inches. This system replaced the gravity feed system, since recirculation of the sulfate solution was not required for these studies, the air pressure technique was simpler and had the added advantage of providing a rapid means for changing the hydrostatic pressure in the cell.

Nine miniature cells were constructed and a facility established wherein six cells could be operated simultaneously. Four of the six stations were fully instrumented to

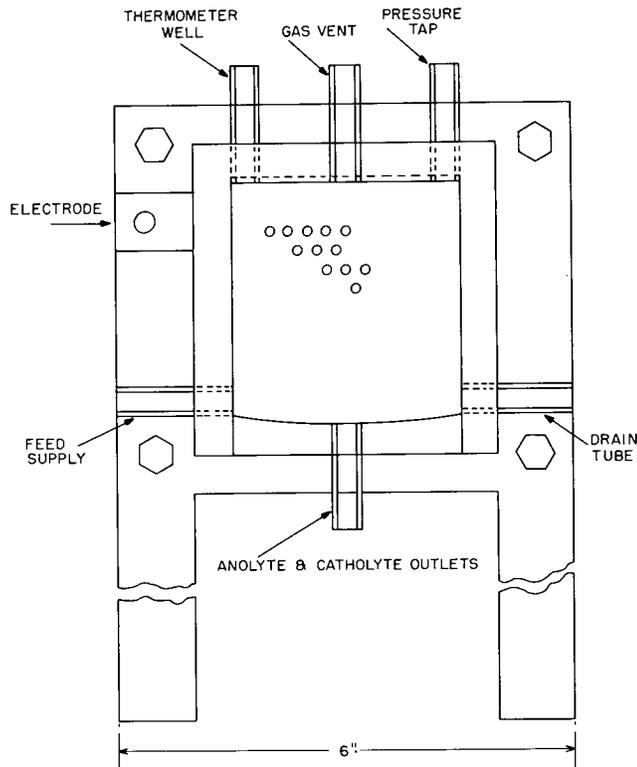


Fig. 3 - Miniature sulfate cell - side view

provide complete evaluation of cell operations. The other two cells were used on standby and for liquid flow studies of assembled cells without electrolysis.

EXPERIMENTAL SCREENING OF COMMERCIAL TEXTILES AND PAPERS

The initial studies involved a screening of commercially available materials which were considered capable of withstanding chemical degradation in service. Textiles and papers containing or composed entirely of Teflon, Dacron, Orlon, polyethylene, and polypropylene were examined as to their capability of providing the liquid permeation rate desired. In this work, liquid flow as a function of differential pressure and time was determined using the apparatus previously described. Distilled water and 18% sodium sulfate solution were used as test liquids. The desired flow rate through the 2-inch-diameter sample was 1 milliliter per 8-inch head per minute. The maximum thickness of diaphragm was set at 0.060 inch although about 0.040 inch was preferred to reduce the electrical resistance of the cell. None of the commercially available materials of this type, which included different weaves, thicknesses, and compositions, satisfied the requirements. Fiber swelling of Dacron and Orlon as evidenced by the diminution of flow at constant pressure as a function of time precluded the use of these materials. The desired flow rate could not be obtained with Teflon fabrics, mixed Teflon and Dacron fabrics, porous polyethylene papers, polypropylene scrim, or laboratory-prepared paper of Teflon fiber mixed with other fibers.

GLASS PAPER DIAPHRAGMS

Concurrent with the screening of commercial materials, three laboratory studies were initiated to develop new combinations of materials for use as diaphragms. The first

approach was the use of fine-fiber glass paper treated with Teflon and silicone emulsions. It was expected that these inert substances would partially plug the pores of the paper and thus provide the desired percolation rate. Glass paper providing an initial flow of 200 ml/min under the test conditions was treated with these emulsions and sheets having the desired flow rate of 1 ml/min were obtained. The emulsion-treated sheets were found, however, to be only surface treated in that the paper, acting as a filter, prevented the penetration of the emulsion particles. Microscopic and wetting studies of the internal layers showed them to be essentially free of the additives. These studies also showed that the low flow rate was obtained by blocking all but a small area of the paper. The tensile strength of the treated sheets was five times that of the original glass paper due to the bonding by the additives. Nevertheless, diaphragms composed of three such sheets easily and quickly ruptured (within 48 hours) when evaluated in the miniature cell. It was evident that once the central, untreated layers of the paper became thoroughly wet with solution, the thin, surface treated layer did not have sufficient strength to prevent failure.

These data indicated that surface treatment alone was not sufficient and that the burst strength of the diaphragm may be more indicative of serviceability than tensile strength. Attempts were made to provide a uniform distribution of the additives by treating glass fibers in the beater prior to formation into a sheet. Although hand sheets were prepared in this manner, the sheets did not have sufficient strength to insure that the method could be scaled up for use of the miniature paper machine. The tensile strength of the wet sheet was too low for it to be carried across the pressing and drying sections of the paper machine. It was also evident that even a glass fiber paper of the "hard" borosilicate type did not have sufficient chemical resistance to be used in this service. It was therefore concluded that the use of emulsion-treated glass fiber paper for use as a diaphragm was not promising and was not considered further.

MIXED FIBER DIAPHRAGMS

The second approach was the study of mixed sheets of hydrophobic and hydrophilic fibers. The desired flow rate would be achieved by adjustment of the proportion of these fibers in the sheet. The normal beating of the fibers before sheet formation would insure uniformity of the paper. Fine-fiber polypropylene, prepared by use of this Laboratory's fiber machine (5), was selected as the hydrophobic fiber of choice. A commercially available polyester fiber, Acrilan, was selected for the hydrophilic fiber because of its ability to fibrillate under extensive beating to provide added strength to the final sheet. Studies showed that eight hours of beating in the paper beater and a heat treatment of the final sheet for 30 minutes at 150°C provides a sheet with adequate strength for use as a diaphragm. Diaphragms consisting of three sheets of this paper, each 0.020 inch thick and containing 65% polypropylene and 35% Acrilan by weight, were found to provide the desired flow rate. Three sheets were used per diaphragm to reduce the effects of pinholes or non-uniformity of the paper.

Although diaphragms with adequate strength and the desired flow rate have been prepared using these composite sheets, one factor is believed to limit their practicability. Since this type depends on the wetting properties of the solution to limit flow, the difficulty arises of insuring the absence of wetting agents in the original solution or a change in surface tension from contaminants. The first case was observed in that one diaphragm under test in the miniature cell lost control when the supply solution was changed. Subsequent investigation revealed that a wetting agent was present in the fresh stock solution, as the surface tension was only 42 dynes/cm. Although methods are available for detection and monitoring the surface tension of the sodium sulfate solution, the practicability of a diaphragm based on the wetting properties of fibers was seriously questioned and this approach also abandoned.

TREATED ASBESTOS

The third approach which was intensively studied was the treatment of asbestos paper with a commercially available ketone-soluble fluorine resin. The resin used was Viton, which is a copolymer of hexafluoropropylene and vinylidene fluoride. A solution of this polymer in 95% methyl ethyl ketone and 5% methyl isobutyl ketone (MIBK) was used to treat the papers. Microscopic studies showed that the use of 5% MIBK improved the film formation by increasing the drying time by a twofold factor. The sheets to be treated were immersed for one minute in the solution then removed at a constant rate by use of a motorized pulley. The rate of removal was adjusted to prevent excessive runoff. The treated paper was heat cured at 300° F for 3 hours. Longer treatment time in the bath did not give additional weight gain. However, redipping in the same solution or one of higher or lower concentration did increase the total weight gain. It was thus possible to use a few solutions and by multiple treatment obtain a gain in weight over a wide range. The solutions used contained 5, 35, 50, and 70 grams of Viton per 1000 ml of mixed solvent.

Since the untreated asbestos paper provided the desired solution flow rate at a pressure differential of 8 inches of water the initial objective was to add sufficient Viton to provide increased strength without seriously reducing the flow properties. It was necessary to modify the requirement, as it was shown that to increase the wet tensile strength by a tenfold factor required the use of 4.5% Viton by weight. Using two such asbestos sheets per diaphragm required the application of a hydrostatic pressure of 50 inches of water to obtain the required solution flow rate of 2 ml/min. The higher pressure requirement of treated asbestos diaphragm was not considered detrimental in that it would help prevent the back diffusion of electrolytic products into the feed chamber.

Three hundred sheets (4 × 4 inches) of 20-mil asbestos paper, electrolytic grade, were treated with Viton. A third of these sheets was used to determine wet tensile strength and burst strength as a function of weight percent of Viton. The remaining two hundred sheets were used as diaphragms in experiments using the miniature cells. In all, some 50 continuous runs were accomplished to determine the service life expectancy of treated asbestos paper diaphragms. In no case was it possible to exceed 150 hours continuous duty before serious defects in cell operation occurred. Although, this service life is approximately three times the life of untreated asbestos paper diaphragms, it was woefully short of the minimum acceptable service life of three months. Two types of failure occurred. In the first the diaphragms would expand into the feed chamber and eventually rupture. In the second, where perforated cover sheets of polypropylene or Lucite were used to prevent distortion, the solution flow rate would decrease to unusable values after a week of continuous service. The same type of swelling of asbestos was noted in the untreated sheets but was accompanied by a rapid disintegration of the diaphragm. The effect of the binder was merely to increase the time to failure. It became evident that treated asbestos could not provide a practical diaphragm for use in this type of electrolytic cell.

MICROPOROUS RUBBER

The continuing studies of porous material indicated that one type of a commercially available microporous rubber did provide the desired solution flow rate at 50 inches of water pressure. Although two sheets per diaphragm were required, this again was not a deterrent. The use of two sheets would minimize nonuniformity of porosity. It was expected that this type of material should serve in the acidic environment of the anode since it is used commercially as a battery separator in acid batteries. The sensitivity of microporous rubber to the oxidizing atmosphere at the anode and its serviceability in the alkaline environment of the cathode were the main questions to be resolved.

Microporous rubber is prepared by extracting a soluble additive from a sheet of a cured mixture of the elastomer and additive. In the type used in this study, the soluble

additive is silica gel and the capillary structure which provides the porosity is obtained by extraction with hot acid solutions. The resulting sheet is readily wet with water, has high tensile strength, and though brittle, can be handled with ease.

The initial experiments with microporous rubber entailed a number of short runs in the miniature cells. The longest continuous operation during the exploratory tests was seven days. After this period, the cells were dismantled and all components examined to determine any changes. It was evident that very little change had occurred except for the corrosion and loss in weight of the lead anodes.

With the successful completion of this series of short-term runs, a number of continuous duty trials was initiated to determine the operational life of these diaphragms in the miniature cells. For this study, three cells were assembled using two microporous rubber sheets per diaphragm. The only difference in the cell assembly was in the composition of the anodes. In order to gain further insight into the problem of anode corrosion, three types of anodes were used. In cell 1-3, a pure lead anode was used, while for cell 2-5, a lead-silver alloy containing 1% silver was utilized. The silver content of the lead-silver alloy used for the anode in cell 3-7 was 0.1%. Each anode was identical in design and construction, and contained 189 holes (1/8 inch in diameter) in the active area of 3 x 3 inches to provide the desired open area. The cathodes used in these cells were fabricated in a similar manner from No. 304 stainless steel. One difference in the cathode design was that the holes were countersunk on the outside surface to allow a more even discharge of the hydrogen gas formed in the exposed surface of the holes.

The dc power for the cells was furnished by use of constant voltage power supplies rated at 10 amperes at 36 volts. The voltage was continuously variable over the range but was maintained for these runs between 5 and 6 volts to achieve a current of about 3 amperes.

This current in the miniature cells results in a current density of about 50 amperes per square foot, which is the order of magnitude expected to be used in the pilot plant cell. This was the maximum rating which could be maintained in the cells to prevent the solution temperature from exceeding 45°C, since it was known that higher temperatures would cause excessive corrosion of the anodes.

For these continuous studies, the anolyte and catholyte were collected in polyethylene bottles. The volume of each solution was measured daily and analyzed for acid and alkali. Fresh solution was supplied to the stock bottles each day without interrupting the operation of the cell.

The three cells were operated continuously for 125 days, at which time the runs were terminated. Each of the cells was operating in a completely satisfactory manner at cutoff, but they were secured at this time since all the desired objectives had been achieved.

The main variables—solution pressure and temperature, cell voltage and current, and anolyte and catholyte flow rate are plotted as a function of time in Figs. 4-6 for the three cells. A summary of the operational data obtained from the cells during these runs is contained in Table 1. The data are average values over the 125-day runs. Except for minor variations in the average values, the cells performed in identical fashion.

The two independent variables were the pressure and voltage. The objective was to provide a total solution flow rate of 6 ml/min for both the anode and cathode. The maximum temperature permitted was 45°C. The solution flow rates and temperature were maintained within these set values for the duration of the 125 days in each cell by continuous monitoring of these variables with occasional manual adjustment of pressure and voltage.

The pressure of 100 inches used for the first ten days in cell 1-3 and for one day in cell 2-5 was shown not to be required to initiate operation, as evidenced in the third cell.

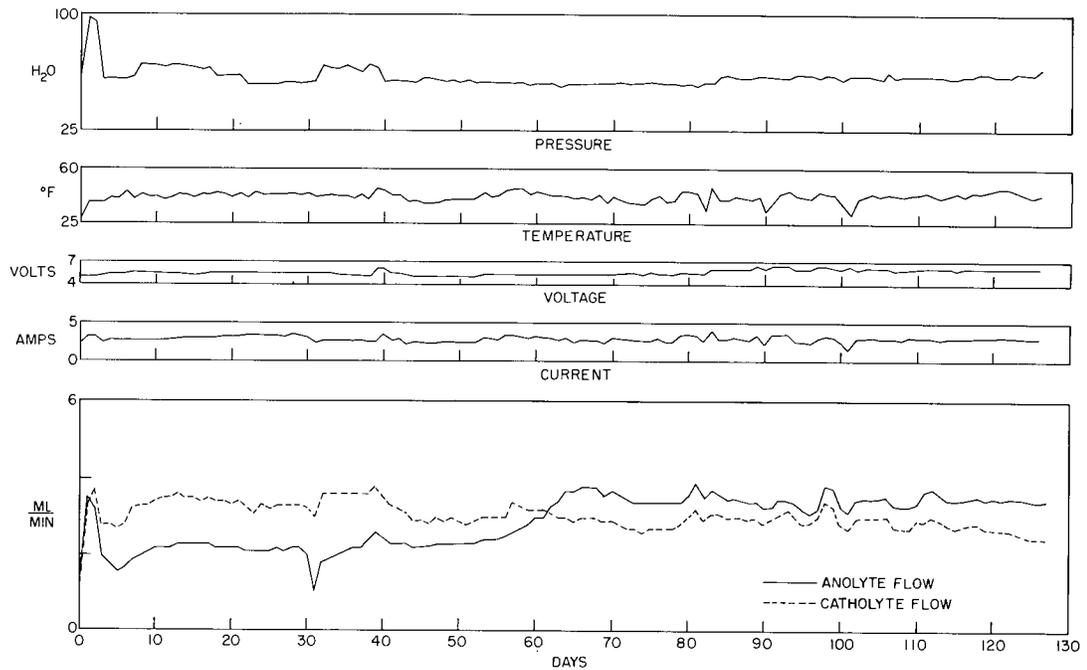


Fig. 4 - Main variables as function of time (Cell 1-3)

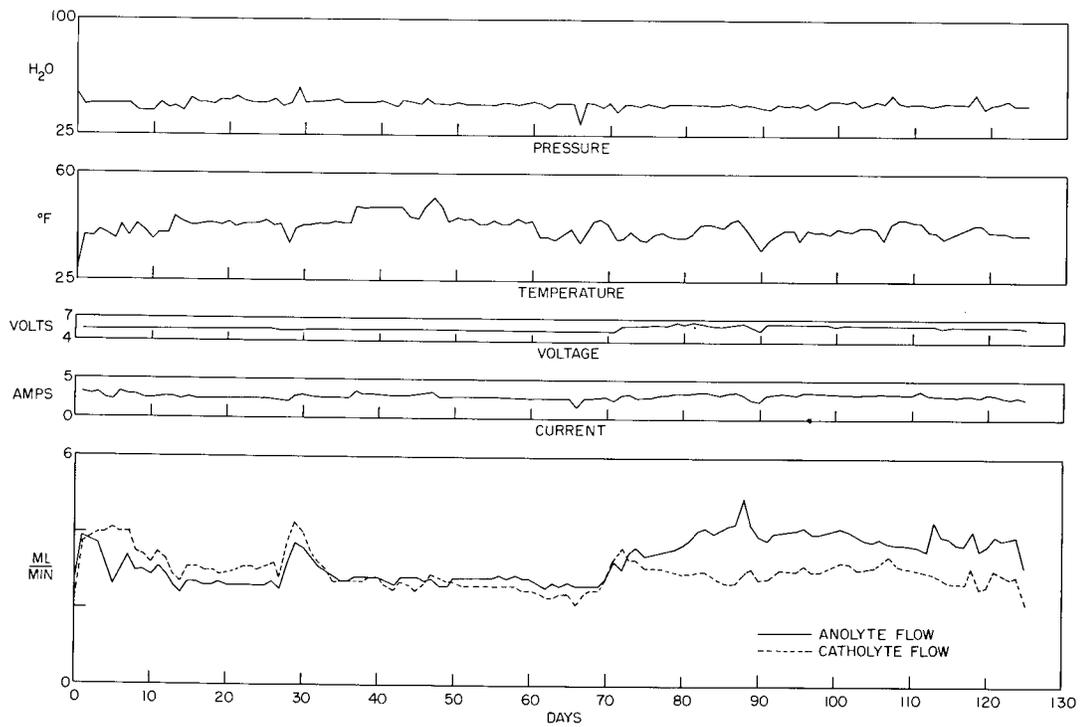


Fig. 5 - Main variables as function of time (Cell 2-5)

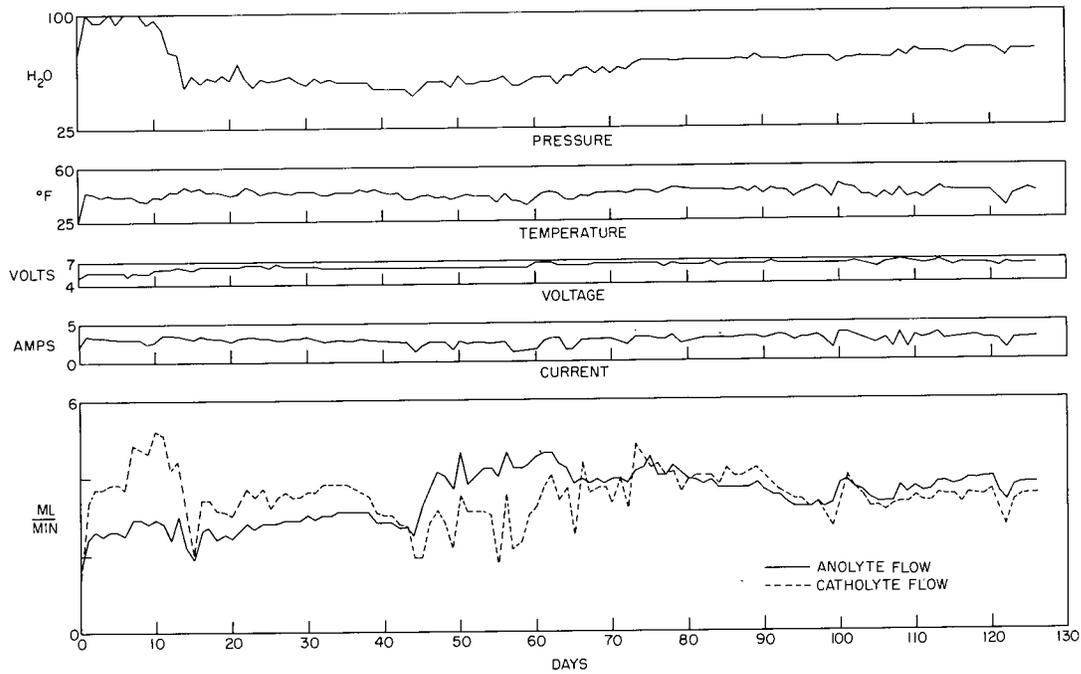


Fig. 6 - Main variables as function of time (Cell 3-7)

Table 1
 Summary of Average Values of Operational Variables of Electrolytic Cells Using Microporous Rubber Diaphragms

Cell No.	Duration (hr.)	Anolyte flow (cc/min)	Catholyte flow (cc/min)	Temp. (°C)	Pressure (in. H ₂ O)	Current density (amp/ft ²)	Anolyte normality (eq/liter)	Catholyte normality (eq/liter)
1-3	3015	3.4	3.5	41.7	65	44.2	0.49	0.49
2-5	3000	2.9	3.0	42.2	60	46.2	0.60	0.62
3-7	3005	3.3	3.0	41.9	45	46.9	0.59	0.66

in all three runs, initiation of cell operation occurred smoothly and equilibrium conditions of temperature and flow rate were established within 2 hours of startup.

After securing the runs, the cells were dismantled and the diaphragms and electrodes examined to determine the effect of the 3000 hours operation on physical properties. The changes in weight of the critical components are summarized in Table 2. With regard to the cathode, it is evident that only a minor loss in weight in the stainless steel electrode resulted. The reason for the relatively higher values for the electrode of cell 2-5 is not known. It is believed that the difference in the loss of weight of the anodes is significant and indicates that a lead alloy containing 1% silver does provide a measure of corrosion resistance.

Table 2
Weight Loss of Diaphragms and Electrodes from 125-Day Operation
of Miniature Cells

Cell No.	Weight Loss (percent)					
	Anode Diaphragms		Cathode Diaphragms		Anode	Cathode
	Sheet 1	Sheet 2	Sheet 1	Sheet 2		
1-3	20.0	25.0	24.4	23.2	14.6	0.64
2-5	16.2	35.7	17.7	19.1	4.6	3.0
3-7	20.2	35.0	19.6	20.1	14.5	0.04

The loss in weight of each sheet of the microporous rubber diaphragms after 3000 hours service is also listed in Table 2. The sheets labeled "Sheet 1" designate those sheets which were exposed to the feed chamber. Those labeled "Sheet 2" are those which were in contact with the metal electrodes. It is evident that each sheet had lost weight. Those in contact with the anodes had a significantly greater weight loss.

Examination of the sheets revealed that those in physical contact with the metal anodes were deformed. All other sheets of both anode and cathode diaphragms were visually unchanged. The No. 2 anode sheets had adopted a waffle pattern. Measurement of the thickness of the sheets showed that the area of the sheet in physical contact with the metal electrode was thinner than the portion of the sheet at the location of the hole in the electrode. The thickness of all the sheets of both anode and cathode diaphragms at the end of the 125-day exposure are recorded in Table 3. The original thickness of the sheets used is nominally 50 mils. The values recorded in Table 3, except for those of the No. 2 anode sheets are average values of eight readings taken over the area exposed in the cell. For the No. 2 anode sheets, two thicknesses are recorded; those labeled B in Table 3 are the average value of the thickness at the hole sites, while those labeled A are the average value of the thickness of the sheet which was in contact with the electrode.

It is apparent that the weight loss indicated in Table 2 and the partial reduction in thickness indicated in Table 3 are related and are the results of the extraction of additional silica from the microporous sheet during the exposure to the chemical solutions in the cell and the oxidizing environment at the lead anode.

Table 3
 Thickness of 50-Mil Microporous Rubber Sheets
 After 125-Day Operation of Miniature Cells

Cell No.	Anode Diaphragms			Cathode Diaphragms	
	Sheet 1 (mils)	Sheet 2		Sheet 1 (mils)	Sheet 2 (mils)
		A* (mils)	B† (mils)		
1-3	46.4	33.8	46.6	45.4	45.1
2-5	49.5	26.8	47.5	49.5	49.0
3-7	48.8	26.7	48.0	48.1	48.6

*A-Thickness of areas of sheet in physical contact with metal electrode.

†B-Thickness of areas of sheet not in physical contact with metal electrodes.

The weight loss due to further extraction of silica was investigated in corollary studies. It was shown that the maximum amount of silica that could be leached from the commercial microporous rubber was 30% by weight. This was achieved in 48 hours with 2N NaOH at 70°C. The time to reach this limit for 2N H₂SO₄ and 18% sodium sulfate solution was much greater in that a weight loss of 5% was obtained in 48 hours with these solutions. The duration of exposure of 3000 hours in the miniature cells at temperatures not exceeding 45°C was sufficient to remove approximately two-thirds of the extractable silica. This reduction is evidenced by the values of weight loss of the No. 1 sheets of the anode and both sheets of the cathodes. The loss in weight approximates 20%. This weight loss has very little influence on thickness since these sheets were reduced in thickness by about 4%.

The additional loss in weight for the No. 2 sheets of anodes in all three runs is ascribed to oxidation in that, the areas of the sheet not in contact with the metal electrode had the same order decrease in thickness as all the other samples, and the No. 2 sheet of the anode of cell 1-3 had the lowest weight loss and smallest change in thickness at the sites where oxidation could occur.

The change in weight due to the loss of silica and the reduction in thickness of the sheet in contact with lead anodes would be expected to increase the porosity of the sheet as additional channels would be opened in the material or existing ones shortened in length. This is also consistent with the experimental results of the 125-day cell runs. It was observed that initially to achieve the desired solution flow rate, a hydrostatic pressure of 100 inches was required, while after 125-days operation, the required pressure for the three cells was 75, 65, and 45 inches. Although additional silica was being extracted from the microporous rubber during the continuous operation of 125 days, the increase in porosity was still not beyond control by a reduction in the hydrostatic pressure maintained in the cell. The only evidence of degradation in the rubber matrix itself from the exposure to either the chemical environment of the anode or cathode was the effect on the No. 2 anode sheets. Thus, it is concluded that this type of diaphragm would be practical for the proposed use in the sulfate cycle electrolyzer. Microporous rubber diaphragms with reduced porosity, with all the extractable silica removed by a pretreatment such as outlined above and physically spaced to prevent contact with the metal anode would be required for use in the full scale cells. Each of these modifications is considered to be minor in nature and could readily be incorporated into the full scale cell.

SUMMARY

The study of diaphragms for the electrolyzer of the sulfate cycle system has involved (a) the screening of commercially available fabrics, papers, and porous materials in regard to their physical and chemical properties and suitability for use as diaphragms, (b) the development of new combinations of fibers and fiber treatment to improve their potential use in the cell, and (c) the determination of the service life expectancy of candidate diaphragms in miniature cells which reproduce the environment of the sulfate cycle electrolyzer.

It has been shown from continuous 125-day runs in these miniature cells that diaphragms comprising two sheets of 50-mil microporous rubber meet the stringent requirements and are capable of giving continuous duty service life measured in months. All cells used for the long runs operated with no difficulty and give satisfactory service in regard to maintenance of solution flow rate, temperature, pressure, and normality of anolyte and catholyte. It is evident that, of the hundreds of types of materials studied, only microporous rubber had the strength and durability to be considered for use in the proposed application of this system in nuclear submarines. However, microporous rubber sheets with lower porosity than that available for these studies would be needed. In addition, all extractable silica must be removed from the microporous rubber by a more stringent pretreatment to insure the successful use of this material in the electrolyzer of the sulfate cycle system.

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