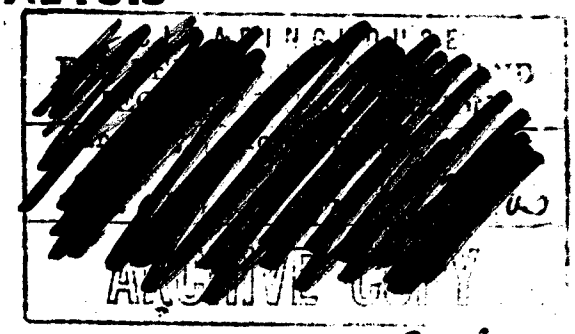
OCD WORK UNIT NO. 3215B

ADVANCED STUDY OF MILK DECONTAMINATION BY ELECTRODIALYSIS



OCTOBER 1965

POSTATTACK RESEARCH DIVISION
OFFICE OF CIVIL DEFENSE
DEPARTMENT OF DEFENSE
WASHINGTON, D.C. 20310

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

PREPARED UNDER CONTRACT NO. OCD-PS-64-281
BY THE
RESEARCH DIVISION OF IONICS, INCORPORATED
WATERTOWN, MASS. 02172
JOHN L. GREATOREX, WERNER GLASS, AUTHORS

ADVANCED STUDY OF MILK DECONTAMINATION BY ELECTRODIALYSIS

OCD Work Unit No. 3215B

October 1965

Postattack Research Division, Office of Civil Defense

Department of Defense, Washington, D.C. 20310

Prepared Under Contract No. OCD-PS-64-281 By John L. Greatorex And Werner Glass

Research Division, IONICS, INC., Watertown, Mass. 02172

SUMMARY

A five gph electrodialytic milk decontamination test plant was built and operated. Previous research, also sponsored by the Office of Civil Defense, had established that radioactive contamination can be removed by flushing cations through a layer of milk. The cations leaving the milk include the radioactive species such as Sr-90 and Cs-137. The milk itself flows in a constrained path between a pair of cation-selective membranes. The cation motion - from a salt make-up solution, through the milk and into a waste solution - is induced by a DC electric field. It had been shown that the cation composition of the treated milk could be controlled by suitable selection of the composition of the salt make-up stream.

The present work was aimed at further defining operating parameters in the electrodialytic removal of radionuclides from milk. The parameters to be studied were membrane life, effect of time on current efficiency and cleaning technique.

After the initial debugging expected with any test plant, operability was excellent. Approximately 8,000 lbs of milk were treated. Decontamination averaged 90%. The ion-selective membranes showed no decrement in performance following an initial drop from 90% current efficiency to 82% during the first 50 hours of operation. (Current efficiency is defined as the ratio of net equivalents of salts flushed through the milk to the total equivalents of electric current.)

A suitable *in situ* method of cleaning the membrane stack was developed: consecutive rinses of water, 5% NaOH, warm (150°F) water, 5% HCl and water. The chemical costs of this cleaning method come to about 0.03¢/ gallon milk. Bacteria counts always remained below the 50,000 per ml USPHS standard. The appearance and taste of the treated milk was very similar to that of the raw milk.

Rat-feeding and vitamin-analysis tests conducted by independent laboratories showed that the electrodialytically decontaminated milk was nutritionally indistinguishable from untreated milk.

ADVANCED STUDY OF MILK DECONTAMINATION

BY ELECTRODIALYSIS

OCD Work Unit No. 3215B

Distribution of this Document is Unlimited

October 1965

Postattack Research Division
Office of Civil Defense
Department of Defense
Washington, D.C. 20310

Prepared under Contract No. OCD-PS-64-281
by the
Research Division of Ionics, Incorporated
Watertown, Mass. 02172
John L. Greatorex, Werner Glass, Authors

TABLE OF CONTENTS

TABLE OF FIGURES

TABLE OF TABLES

1.0 SUMMARY

A five gph electrodialytic milk decontamination test plant was built and operated. Previous research, also sponsored by the Office of Civil Defense, had established that radioactive contamination can be removed by flushing cations through a layer of milk. The cations leaving the milk include the radioactive species such as Sr-90 and Cs-137. The milk itself flows in a constrained path between a pair of cation-selective membranes. The cation motion - from a salt make-up solution, through the milk and into a waste solution - is induced by a DC electric field. It had been shown that the cation composition of the treated milk could be controlled by suitable selection of the composition of the salt make-up stream.

The present work was aimed at further defining operating parameters in the electrodialytic removal of radionuclides from milk. The parameters to be studied were membrane life, effect of time on current efficiency and cleaning technique.

After the initial debugging expected with any test plant, operability was excellent. Approximately 8,000 lbs of milk were treated. Decontamination averaged 90%. The ion-selective membranes showed no decrement in performance following an initial drop from 90% current efficiency to 82% during the first 60 hours of operation. (Current efficiency is defined as the ratio of net equivalents of salts flushed through the milk to the total equivalents of electric current.)

A suitable in situ method of cleaning the membrane stack was developed: consecutive rinses of water, 5% NaOH, warm (150°F) water, 5% HCl and water. The chemical costs of this cleaning method come to about 0.03¢/gallon milk. Bacteria counts always remained below the 50,000 per ml USPHS standard. The appearance and taste of the treated milk was very similar to that of the raw milk.

Rat-feeding and vitamin-analysis tests conducted by independent laboratories showed that the electrodialytically decontaminated milk was nutritionally indistinguishable from untreated milk.

2.0 INTRODUCTION

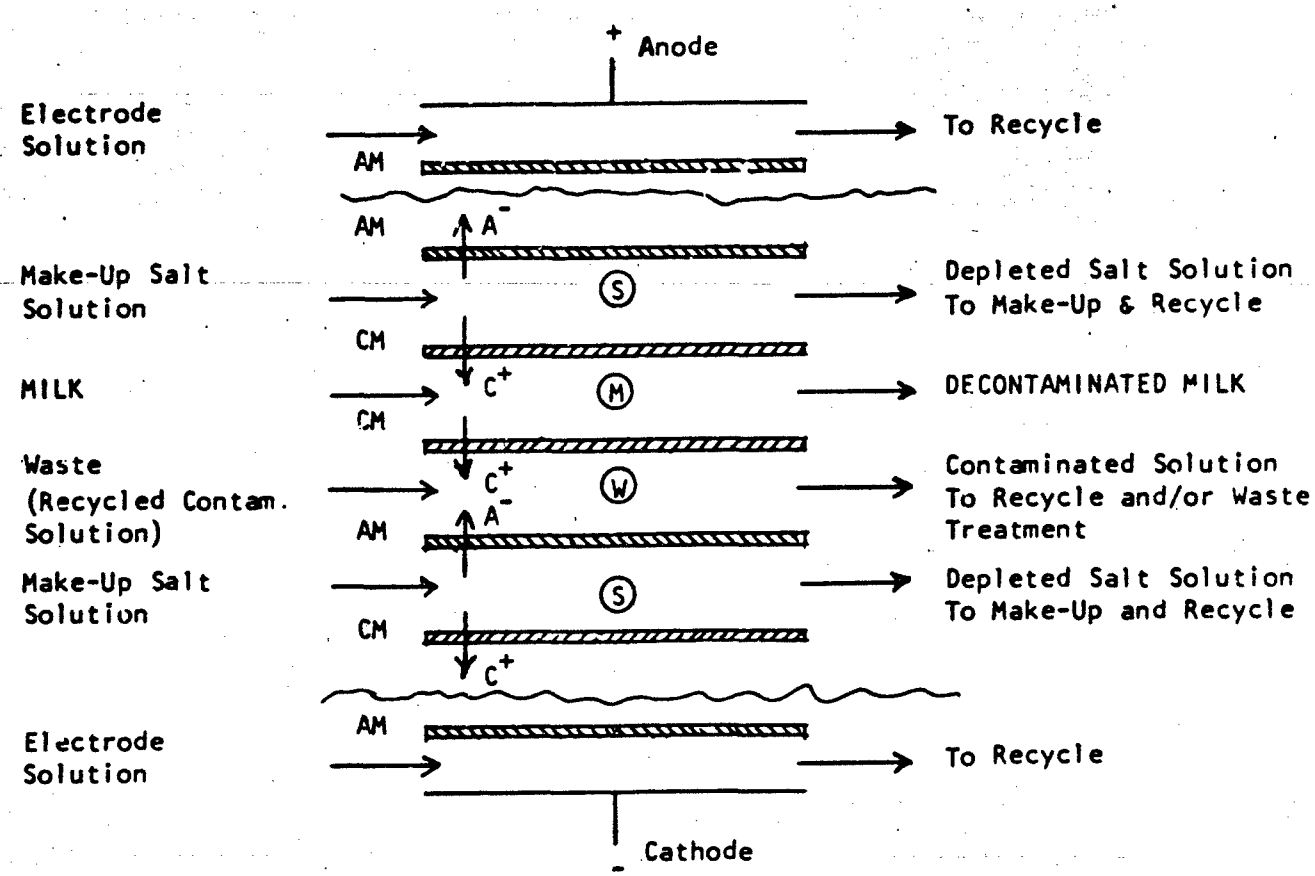
The removal of radionuclides from milk could be desirable in selected post attack situations. It may also become desirable if nuclear device testing in the atmosphere were resumed and if the resulting fall-out raises the radionuclide level in milk above the acceptable peace time limits. The Office of Civil Defense has sponsored research on the development of an electrodialytic process for the removal of radionuclides from milk. The results of the first phase of this work, in which process feasibility was demonstrated and data were obtained to permit the design of a full scale plant, are reported in the Final Report OCD-OS-62-206, (AD429-917) available for qualified requestors from the Defense Documentation Center, Cameron Station, Alexandria, Virginia.

The second phase of the work, reported on here, involved the construction and operation of a scaled-up test unit capable of 90% Sr-90 removal from 5 gallons of milk per hour. Cleaning procedures and the effect of operating time on ion selective membrane performance were investigated. In addition, the results of feeding studies using electrodialytically decontaminated milk and carried out with in-house funds prior to the start of the present contract are also included.

Preceding Page Blank

FIGURE 1

Membrane Cell Configuration for Milk Decontamination



KEY:

AM = Anion Transfer Membrane

CM = Cation Transfer Membrane

A^- = Any Anion Present in Solution

C^+ = Any Cation Present in Solution

(S) = Make-Up Solution Cell

(M) = Milk Cell

(W) = Waste Solution Cell

3.0 BACKGROUND INFORMATION

3.1 Process Description

Electrodialytic decontamination of milk is a process to introduce radioactive - free cations into a milk stream and simultaneously to remove cations at an equal rate from the same milk stream thereby diluting any cation radioactivity in the milk. In its simplest form the mechanism is to pass cations in and out of the milk through cation permeable membranes under the influence of an electric field. (It should be noted here that cation permeable membranes will pass almost no anions and vice versa for anion permeable membranes). This selective flushing of cation results in a decontaminated milk product.

Figure 1 shows the configuration of typical components for a milk decontamination stack and the ionic mechanism of decontamination. In the configuration, cations are shown to travel from the make-up solution stream into the milk stream through a cation transfer membrane under the influence of an electric field, and cations in the milk stream simultaneously are shown to travel through a cation transfer membrane into the adjacent waste stream under the influence of the same electric field. The relative cation concentrations (i.e., amounts of Na, Ca, etc.) are planned to remain the same in the milk. Electrode solution is passed into the compartments adjacent to the electrodes and is unaffected by the decontamination going on in the rest of the stack.

3.2 Previous Contract Work

The following points were established under the previous contract to the Office of Civil Defense (OCD-OS-62-206):

- The general feasibility of the process was clearly established.
- Data were obtained to permit design of a full scale unit.
- The loss of organics such as lactose was shown to be less than 1%.
- The total cost of removing 90% of the Sr-90 and substantially all the Cs-137 will be of the order of 3/4¢ per quart.

- Adjustment of the pH could be easily accomplished in a manner developed by the Department of Agriculture, i.e. by the controlled addition either of acid or of potassium hydroxide.
- The laboratory process was carried out successfully with the milk remaining below 50°F at all times.
- The cationic composition of the treated milk could be controlled by varying the relative concentration of cations in the make-up salt solution.

3.3 Scope of Present Work

This study was initiated to further define operating parameters in the electrodialytic removal of radionuclides (particularly Cs-137 and Sr-90) from milk. The most important parameter to be studied was ion-selective membrane life and the mode of decrement of performance. Based on extensive experience in the demineralization of whey by electrodialysis (a similar operation to the decontamination of milk) the most likely effects of long term operation were expected to be a decrease in the Faraday efficiency of the ion-selective membranes and an increase in operating voltage at a constant current density. These effects would tend to increase the electrical energy requirement per unit quantity of milk or to decrease the production capacity of a given decontaminating unit.

Another parameter to be observed under this contract was cleaning technique. It had become evident from the previous research sponsored by OCD and from laboratory and industrial experience with the electrodialytic demineralization of whey that an effective cleaning technique was essential to prevent fouling of the membranes and to keep bacteria levels well within USPHS standards.

3.4 Additional In-House Work

In the interim between the end of Contract OCD-OS-62-206 and the start of Contract OCD-PS-64-281, Ionics electrodialytically decontaminated enough milk to permit rat-feeding studies and vitamin analyses by independent laboratories. The results of these studies, which were aimed at checking the nutritive qualities of electrodialytically decontaminated milk, are also presented in this report. These studies were preliminary in nature and were not intended to constitute full-scale qualification tests.

4.0 EXPERIMENTAL PROGRAM

An electrodialytic milk decontamination pilot plant was constructed. A photograph of the unit is shown in Figure 2. A schematic process flow sheet is shown in Figure 3.

4.1 Description of Pilot Plant and Process Flow Sheet

The unit was designed to decontaminate a batch of milk at a time. Batch sizes up to 20 gallons could be handled (nearly all runs were made on 20 gallon batches.)

The milk-in-process was held in a 20 gallon stainless steel tank. From there it was circulated by a Moyno sanitary pump through the electrodialytic decontamination stack. The stack itself consisted of 60 three-compartment cells with an active area of 33 sq. in. per compartment. A central anode and two terminal cathodes were used so that half of the total current would flow through the upper 30 cells and half through the lower 30 cells. The direct current itself was obtained from a rectifier mounted under the supporting table top and equipped with a suitable high and low range switch and a variable transformer input to permit maintaining the desired DC output.

Make-up and waste salt solutions were circulated through the stack by Eastern centrifugal pumps. These salt solutions also passed through stainless steel cooling coils immersed in an ice-bath. The salt solutions were thus maintained at a low temperature (below $40^{\circ}F$). The stack itself served as a "heat exchanger" in which the I^2R losses generated in the milk were removed by heat transfer through the membranes into the salt solutions. This eliminated any need for an external sanitary milk heat exchanger.

A slightly elevated tank holding concentrated salt solution (2.5N) was provided along with an in-line conductivity meter and controller in the "make-up solution" stream. When the controller called for additional salt (which had been depleted from the make-up solution by electrodialytic transfer to the milk) then a solenoid would open and the concentrated

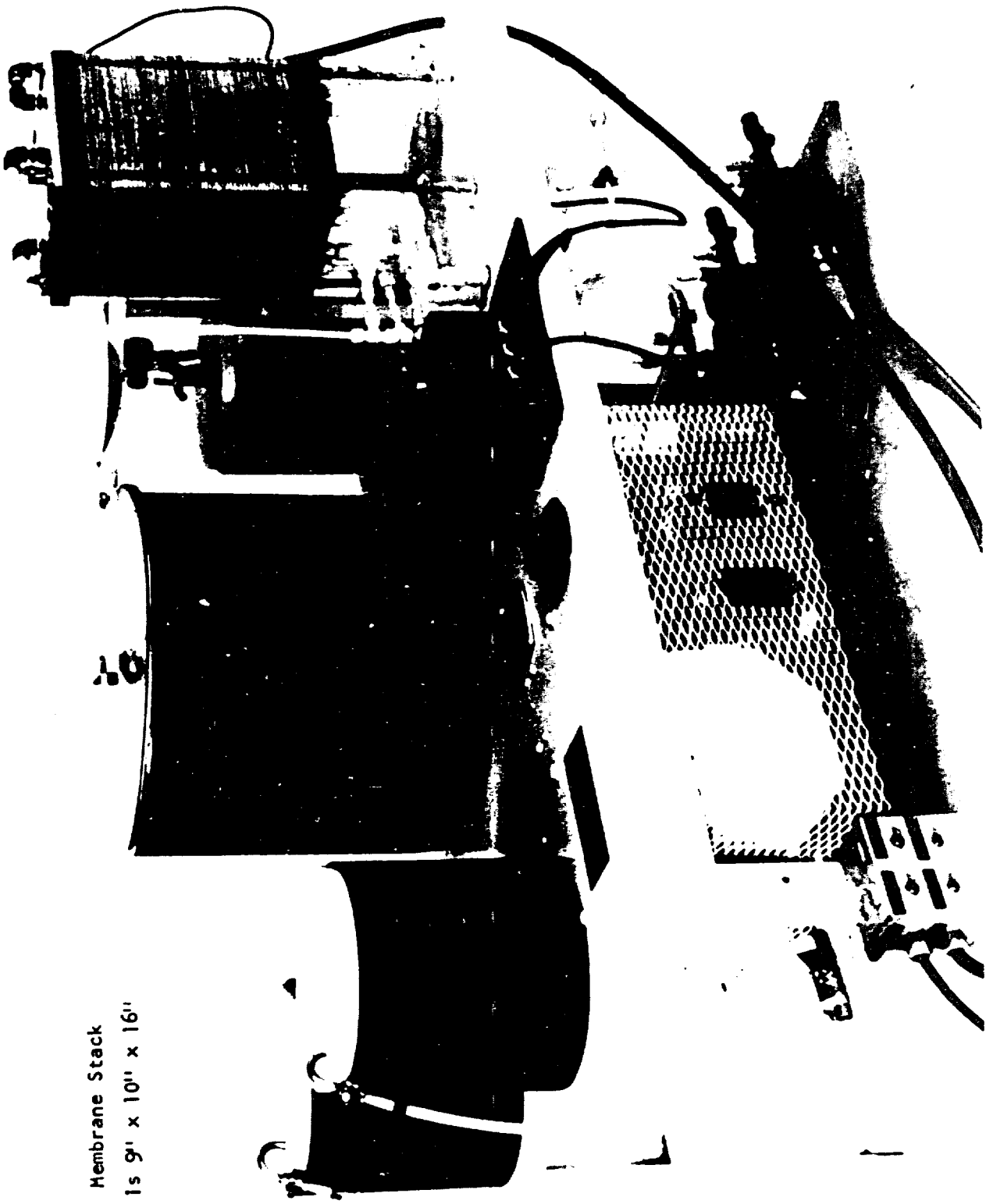
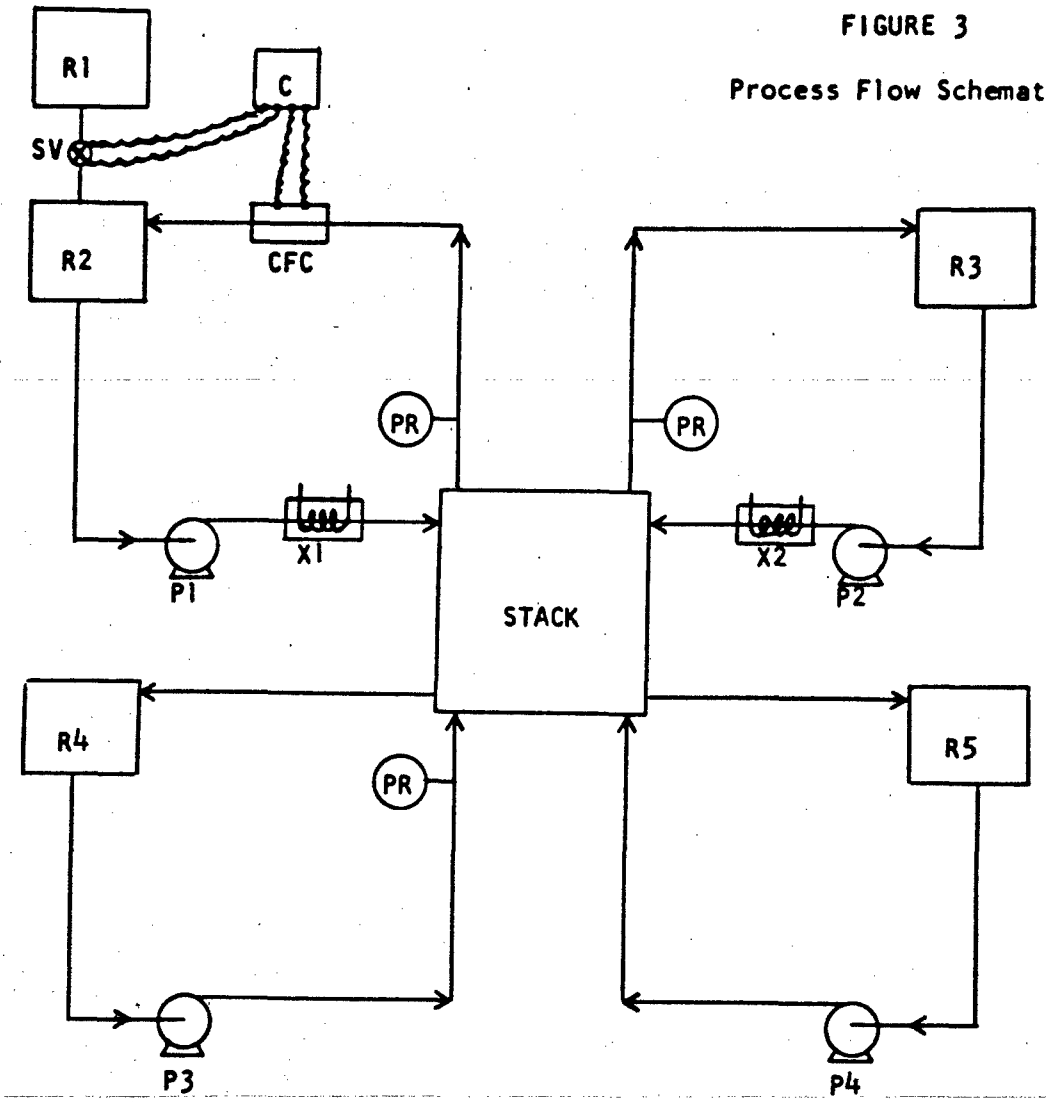


Figure 2

Milk Decontamination Unit

FIGURE 3

Process Flow Schematic



LEGEND

CFC - Conductivity Flow Cell
C - Conductivity Controller
SV - Solenoid Valve
R1 - Concentrated Salt Reservoir
R2 - Make-Up Salt Reservoir
R3 - Waste Salt Reservoir
R4 - Milk Reservoir
R5 - Electrode Solution Reservoir
X1 - Make-Up Heat Exchanger
X2 - Waste Heat Exchanger
PR - Pressure Gauges
P1 - Make-Up Pump
P2 - Waste Pump
P3 - Milk Pump
P4 - Electrode Solution Pump

solution could flow by gravity into the make-up solution tank until the desired make-up concentration (0.1N) was reached.

A "feed and bleed" system was provided for the waste salt solution. Water was fed in continuously and waste solution bled out to maintain a constant salt concentration of approximately 0.2N. This part of the plant was added after initial operation with intermittent manual dilution of the waste salt solution had proven unsatisfactory from the point of getting steady current efficiency and cell voltage data.

4.2 Operation of the Test Plant

Emphasis was placed on (a) demonstrating operability of the test plant (b) determining the Faraday current efficiency and the voltage requirements of the cells as a function of operating time and (c) demonstrating cleaning techniques that would permit continued operation while maintaining USPHS standards on bacteria levels.

4.2.1 Typical Run

A typical batch run would proceed as follows:

a) Milk Preparation

Twenty gallons of cold raw milk are placed in the insultated stainless steel tank and stirred with a motorized stirrer. The stirrer speed is kept low to prevent foaming. Citric acid (1.5 Molar) is added slowly until the pH of the milk has dropped to 5.2. About 1.5 liters are required per 20 gallons of milk.

b) Hydraulic Start-Up

Ten liters each of "Waste Solution", "Make-up Solution", "Concentrated Make-up Solution" and "Electrode Solution"are placed in their respective reservoirs. Composition of these solutions is given in Table 1. All pumps are turned on simultaneously and the flow rates of all circulatory streams determined. Approximate flow rates are 6.0 liters per minute

Table I

Solution Compositions

Concentrated Make-Up Solution:

1450 gms NaCl
1640 gms $CaCl_2 \cdot 2H_2O$
277 gms $MgCl_2 \cdot 2H_2O$

} in 20 liters of water

Waste Solution (for start-up purposes):

Dilute 400 cc of Conc. Make-Up Solution to 10 liters

Make-Up Solution (for start-up purposes):

Dilute 400 cc of Conc. Make-Up Solution to 10 liters

Electrode Solution:

10 liters of 0.2N sodium acetate adjusted to a pH of 4.0 with acetic acid

Citric Acid Solution:

1.5 liters of 1.0 molar citric acid

Potassium Hydroxide Solution:

1.5 liters of 3.0N KOH

Acid Cleaning Solution:

10 liters of 5% HCl

Base Cleaning Solution:

10 liters of 5% NaOH

for milk, 7.5 liters per minute for the waste and make-up streams and 1.0 liter per minute for the electrode stream. (Flow rates significantly below these indicated gas-bound pumps. The pumps would be freed of gas before proceeding.)

c) Conductivity Controller Start-Up

The conductivity dial is set at 6000 mho/cm after which the controller is turned on and allowed to warm up for 1 minute. The dial is then adjusted to give the maximum dark segment in the electric eye. The reading should be about 6000 mho/cm. (Any significant deviation from 6000 mho/cm means that either the controller is out of order or, more likely, that a mistake has been made in making up the salt solution). This setting - of approximately 6000 mho/cm - is maintained throughout the run.

d) D. C. Power Start-Up

With the range switch in the "Low" position, the AC power is turned on and the Variac adjusted until a current of 8.0 amps. is attained. If the maximum Variac setting is reached before the current is 8.0 amps, the Variac is set back to zero, the range switch set on "High" and the Variac adjusted again to give 8.0 amps.

e) Decontamination

The Variac setting is adjusted as required during the run to maintain the DC current at 8.0 amps. Four hours operation at 8.0 amps correspond to 90% removal of *in vivo* Sr-90 decontamination of a 20 gallon batch. Smaller batches need correspondingly shorter times or lower currents to achieve the same degree of decontamination. At the end of the run, all pumps, the DC power and the conductivity controller are turned off.

f) Readjustment of Milk pH

During the run the milk has been depleted in potassium content. Adjustment of the pH and K levels is carried out with 3 Molar KOH until the milk is back to its original pH (6.6 to 6.8).

4.2.2 Cleaning Methods

A review of commercial dairy cleaning agents revealed that most powders contained various combinations of oxidant, quarternary ammonium detergent, wetting agent, a basic agent to saponify fats and proteins and an emulsifier. From past experience most oxidants, emulsifiers and wetting agents tend to foul ion exchange membranes. It is also known that caustic in dilute solution is compatible with ion exchange membranes and will also both saponify and act as a bactericide. It was therefore decided to use a caustic wash followed by acid to neutralize and remove the slimy film left by the caustic.

4.2.3 Bacteria Measurement

Direct microscopic bacteria counts were made of the milk at the start and at the end of the run according to the procedure described in American Public Health Association Standard Methods for the Examination of Dairy Products, 11th Ed., p.85, 1960.

4.3 Holdup Time and Volume Considerations

The electrical current in the stack flows through the milk as a stream of cations. This cation stream washes out the unwanted radioactive species. In order to obtain a given degree of decontamination, a specified number of ampere-seconds must be passed through each milliliter of milk. The previous research performed under Contract OCD-OS-62-206 established that 30 amp-secs/ml were required to obtain 90% decontamination.

In a continuous once-through system the time (θ seconds) required to pass these 30 amp-secs/ml through the milk will depend only on the current density (i,amp/cm^2 of flowpath area) and the flow-path thickness (t,cm).

Thus:

$$\theta = 30t/i$$

In the work reported on here t was 0.1 cm and i was 0.019 amp/cm^2 leading to a value of 159 seconds for θ. The actual in-stack time that would be required would thus be under 3 minutes in a once-through system. However, it is desirable to maintain the milk velocity at approximately 25 cm/sec to obtain good mass-transfer conditions at the milk/membrane interface. A once-through system would thus necessitate a flow path approximately 159 x 25 cm or nearly 40 meters long. This is impractical especially in the laboratory where the "standard" electrodialysis laboratory stack has a flow-path length of 384 cm. (In commercial applications flow paths 20 meters long are currently in use.) The total required flow path length of 40 meters is therefore obtained by operating batch-wise and recycling the milk through the laboratory stack. The actual time spent in the stack, θ, is still low - on the order of a few minutes - however, the process time for the entire batch, T, will now depend on the size of the batch selected for treatment.

Thus:

$$T = \theta \, (v/h)$$

where v is the volume of the milk in the whole batch and h is the milk holdup volume in the stack. The 20-gallon batches of milk treated in the work reported correspond to a ratio of batch to holdup volumes of almost 100/1. The batch process time was thus four hours. The laboratory equipment could just as well have been run with 10 gallon batches at 2 hours/batch or 1 gallon batches at 0.2 hours/batch.

In commercial practice it would probably be preferable either to run continuously on a once-through basis or, if running batch, to run with as large a batch as practical. It was for this latter reason that a 20 gallon, 4-hour batch system was selected for the laboratory study as these long milk process times would put a severe tests on the system as far as bacterial growth was concerned. Smaller batches with shorter batch process times would have provided a less severe test of the sanitary aspects of electrodialytic decontamination.

5.0 RESULTS OF THE EXPERIMENTAL PROGRAM

The data obtained in the 49 runs made during this program are summarized in Table 2 and also presented in Figures 4 and 5.

5.1 Membrane Life

Daily runs were made and both total stack voltage and the Faraday current efficiency of the decontaminating membranes determined. The Faraday current efficiency is defined as the ratio of the net equivalents of salt transferred through the milk to the electrochemical equivalent of the applied current. This ratio is less than unity because (a) some back-diffusion does occur and (b) the ion-selectivity of the membranes is not 100%, i.e., cation membranes do allow a small fraction of the current to pass through them as anions and vice versa.

Two suites of membranes were used during this work. Suite #1 failed after only a few hours of operation due to improper cleaning. Suite #2 was tested for the remainder of the work. Figure 4 shows the variation of total voltage applied to the stack as a function of Suite #2 membrane life expressed in totalized amp-hrs/ft^2. The early dip in the stack voltage is not considered significant due to the fact that until about 500 amp-hrs/ft^2 the waste salt stream dilution was controlled manually. After this period continuous "feed and bleed" control was installed and there seem to be only minor variations in the total stack voltage until the end of the testing period at 2800 amps-hrs/ft^2. Further life testing is suggested in order to determine whether long-term voltage increases occur which would necessitate membrane replacement.

Figure 5 shows the variation of current efficiency of the decontaminating cation membrane with membrane life in the same units of totalized amp-hrs/ft^2. During the period until 1200 amp-hrs/ft^2 there appears to be a slight decline in current efficiency. However, for the last 1600 amp-hrs/ft^2 of operation there seems to be a very constant response in net salt transferred through the milk stream to the current applied. This constant value of 82%

FIGURE 4

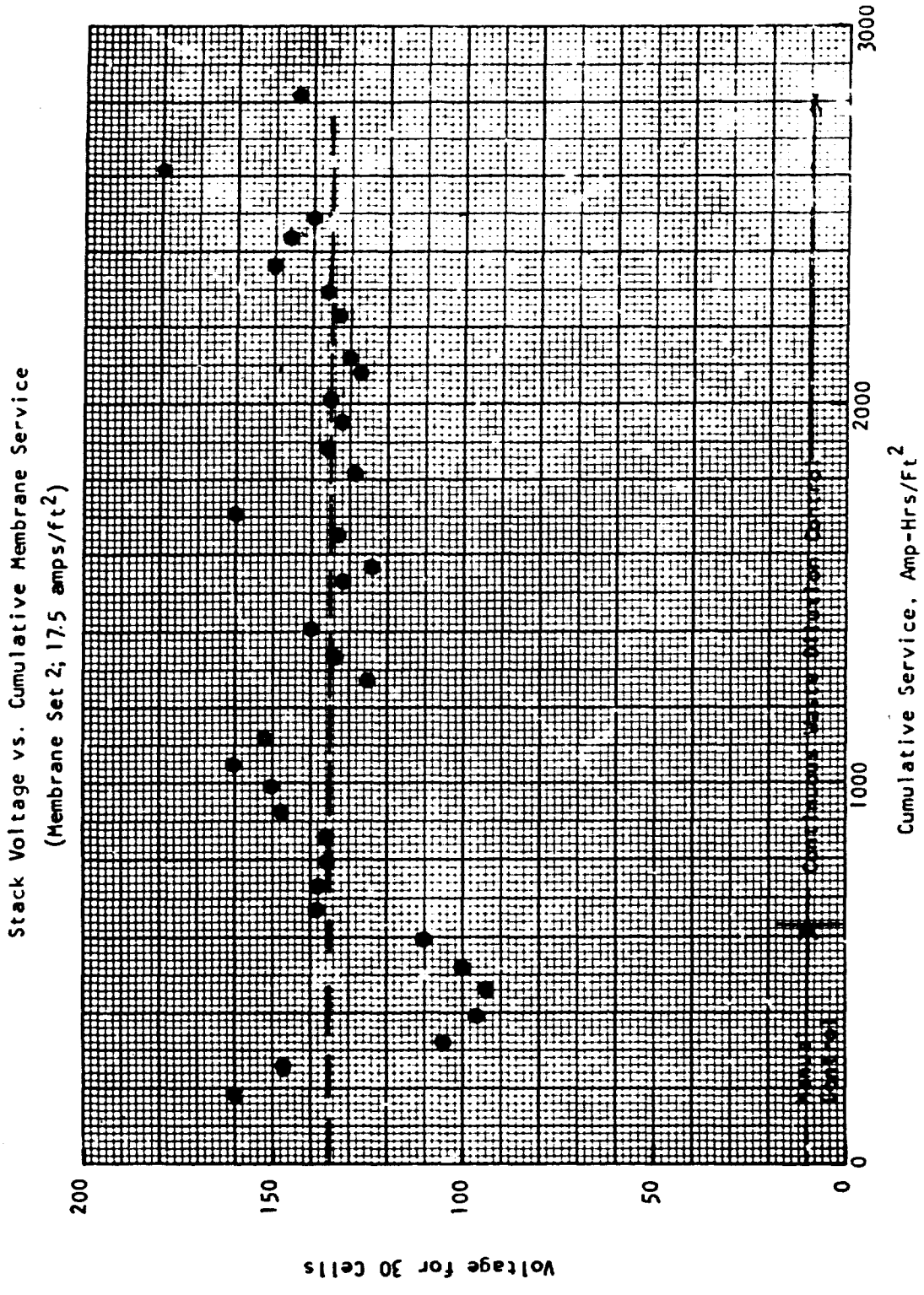

Stack Voltage vs. Cumulative Membrane Service
(Membrane Set 2; 17.5 amps/ft²)
Voltage for 30 cells
200
150
100
50
0
0
1000
2000
3000
Cumulative Service, Amp-Hrs/Ft²

Table 2

Summary of Milk Decontamination Runs-17.5 amps/ft^2, 90% Sr-90 Removal

Run No.	Membrane Set	Cum. Wt. of Milk (lbs)	Cumulative Service (amp-hrs/ft^2)	Feed Volume Concentrated Make-Up (ml)	Stack Voltage (Volts)	Current Eff. (%)	Milk Temp. (°C)
1	1	42	--	--	-	--	--
2	1	85	35	--	-	--	--
3	1	127	70	--	-	--	--
4	1	210	150	--	-	--	--
5	1	380	200	--	-	--	9.5
6	1	550	280	--	-	--	10.3
7	2	720	100	--	-	--	9.0
8	2	890	180	--	160	--	10.5
9	2	1060	260	--	147	--	9.2
10	2	1230	324	7,200	105	72.0	7.5
11	2	1400	396	10,900	96	--	7.8
12	2	1570	460	7,700	94	79.5	7.9
13	2	1740	524	7,300	100	74.5	7.6
14	2	1930	588	--	110	--	7.3
15	2	2100	668	14,350	138	92.5	8.3
16	2	2270	732	14,000	138	91.5	9.5
17	2	2440	796	--	136	--	8.7
18	2	-	-	--	-	--	5.3
19	2	2610	860	13,270	136	87.5	8.5
20	2	2780	924	13,140	148	85.5	10.4
21	2	2950	988	13,400	150	88.0	9.0
22	2	3120	1052	13,800	160	90.0	9.2
23	2	3290	1116	13,300	152	87.5	9.3
24	2	3360	1148	9,750	-	--	10.3
25	2	3430	1196	11,500	-	83.0	10.0
26	2	3600	1212	--	-	--	7.6
27	2	3770	1276	12,000	125	81.0	8.5
28	2	3940	1340	11,300	134	81.5	9.5
29	2	4110	1404	11,300	140	81.5	9.3
30	2	4280	1408	11,500	130	82.0	9.0
31	2	4450	1532	11,600	132	83.5	9.2
32	2	4620	1588	10,900	125	79.5	8.5
33	2	4790	1652	11,300	133	80.0	9.8
34	2	4960	1708	9,600	160	--	10.0
35	2	5130	1756	--	-	--	9.5
36	2	5300	1820	11,600	128	83.0	10.5
37	2	5470	1884	11,300	136	81.0	10.0
38	2	5640	1948	11,000	132	79.0	9.5
39	2	5810	2012	11,500	135	82.5	9.2
40	2	5980	2076	12,000	127	86.5	10.0
41	2	6060	2108	6,200	130	--	9.5
42	2	6230	2172	11,000	-	--	9.5
43	2	6400	2236	11,500	133	83.0	10.0
44	2	6580	2300	11,000	136	80.0	10.2
45	2	6750	2364	10,600	150	77.0	10.6
46	2	6920	2428	11,000	146	80.0	10.3
47	2	7080	2492	11,000	140	80.0	10.5
48	2	7420	2620	--	180	--	9.2
49	2	7940	2812	33,700	144	81.5	9.7

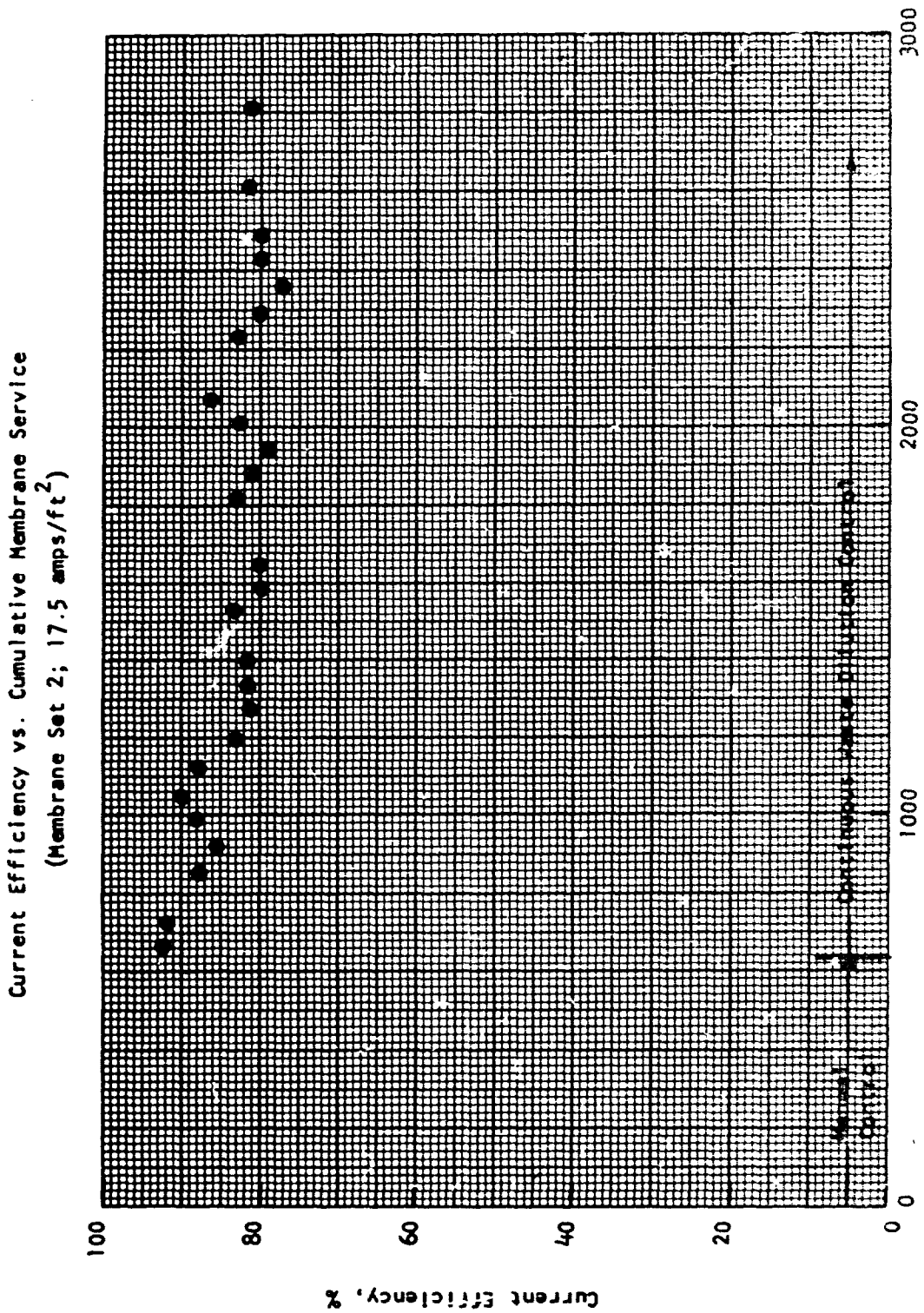
is well above the point at which it is necessary from an economic point of view to replace the suite of membranes. Further testing should be carried out to see if at some point the current efficiency of the membranes actually deteriorates and the membranes would have to be replaced.

Two problems were encountered in the early stages of membrane life testing and should be included here as a guide to future studies. It became evident that some alterations needed to be made in the original apparatus. The first problem encountered was that occasionally small bits of extraneous matter caused blocked cells and hence, high stack voltage. A particle 1/16" in diamter can block a cell and cause this cell to become entirely demineralized causing a high resistance spot. This was eliminated by filtering the raw feed milk through a 40-mesh stainless steel screen. The second problem to arise was the fact that manual dilution of the waste salt streams caused fluctuations in the current efficiency data that were too large for accurate monitoring of membrane performance. This condition was corrected after about the first 500 amp-hrs/ft^2 of a total 2800 amp-hrs/ft^2 of this test resulting in much more reliable data after that period.

5.2 Cleaning Procedures

As a result of experience in the electrodialytic treatment of whey the first attempt at cleaning the membrane stack by *in situ* methods utilized NaOH (5%) and HCl (5%). The actual procedure was to flush with tap water for 20 minutes, circulate 5% NaOH for twenty minutes, (about 1 gallon for 10 ft^2 of membrane was used), 20 minutes tap water flush, circulate 5% HCl for 20 minutes (also about 1 gallon for every 10 ft^2 of membrane) and a 20 minute tap water flush as a final rinse. Initially considerable deposition of butter fat was encountered. Attempts were made to use a solvent to remove the deposit. It was then found that warm water, 150°F, would melt the fat deposit and float it out of the stack. This was a much cheaper approach to the problem and warm water was then used in the second water flush. It was not used in the first water flush due to the possibility of denaturing the milk protein and thereby causing a worse problem.

FIGURE 5


Current Efficiency vs. Cumulative Membrane Service
(Membrane Set 2; 17.5 amps/ft²)
Current Efficiency, %
100
80
60
40
20
0
0
1000
2000
3000
Cumulative Service, Amp-Hrs/Ft²
Manual Continuous Water Dilution Control
Control

The total cleaning procedure thus took approximately two hours. This would be an unreasonable time if stack-cleaning had to be done after every four hours of operation. To see whether longer intervals between stack cleaning were practical, Run 48 was carried on for 8 hours and Run 49 for 12 hours. No increase in bacteria count was noted at the end of these runs, showing that 12 hour stack operation between cleaning intervals is acceptable. In the commercial sanitary electrodialysis of whey, standard practice is to clean the stacks after every 16 hours of operation.

Figures 4 and 5 show that practically no decrement in membrane life resulted from this method of cleaning. The cleaning costs of technical NaOH and HCl is about 0.3 mil/gallon based on a cleaning ratio of 1 gallon each of 5% acid and base for every 10 ft^2 of membrane active area. This cost is about half that of similar caustic type commercial dairy cleaning agents on a per pound basis.

5.3 Bacteria

A bacteria count was made of the fresh raw milk and the decontaminated product milk from each run. In no case was there any build-up of bacteria. The direct microscopic counts were always below 50,000 per ml, the USPHS standard. This excellent result can be attributed to two factors. The first is the fact that the NaOH wash solution in the stack both acts as a bactericide and removes food material from potential bacterial growth. The other is that the milk process temperature is kept below 50°F, thereby depressing bacterial growth. The four-hour hold-up in the system at the process temperature does not result in significant bacterial growth. Runs 48 and 49 which consisted respectively of 2 and of 3 consecutive 4-hour runs, i.e., of 8 and 12 hours exposure to milk, also showed satisfactorily low bacteria counts.

5.4 Cation Distribution

The product milk from Runs 32 and 33 were examined for cation distribution at the beginning and at the end of the run. This represents about 1600 amp-hrs/ft^2 of membrane life at this time. The product milk tested had been readjusted to pH 6.6 with KOH. The results are given in Table 3.

Table 3				
Cation Distribution in Milk				
	Ca^{++} Meq/L	Mg^{++} Meq/L	Na^{+} Meq/L	K^{+} Meq/L
Run #32 Feed Milk	16.3	5.5	8.7	10.9
Run #32 Product Milk	18.1	10.5	11.9	10.0
Run #33 Feed Milk	16.3	5.5	7.6	10.8
Run #33 Product Milk	18.1	7.3	10.7	9.5

These data show that (a) the ratio of magnesium and sodium to calcium in the make-up solution was higher than needed and (b) that the total salt concentration in the waste stream should have been lower to minimize salt build-up in the milk stream. No particular effort had been made to maintain the cation distribution in the milk. Previous research under OCD-OS-62-206 had established that this could be done by suitable adjustment of the make-up salt stream.

5.5 Nutritional Tests

Samples of untreated milk and of the same milk after electrodialytic decontamination were submitted to the U.S. Public Health Service Laboratory in Winchester, Massachusetts for radiological analyses. Additional samples were freeze-dried by the M.I.T. Department of Food Technology and submitted to the Food and Drug Research Laboratories, Maspeth, L.I., New York for nutritional analyses and feeding tests with white rats. Results are presented in Tables 4, 5, 6 and 7. The data show that there is no significant nutritional difference between treated and untreated milk. The control of the ash content was not quite as good as it could have been as these early decontamination runs were made without automatic control of the make-up and waste salt solution concentrations.

Table 4		
Ionic Analyses of Fluid Milk*		
Ionic Species	Decontaminated	Untreated
Calcium, g/l	1.51	1.57
Magnesium, g/l	0.17	0.11
Sodium, g/l	1.05	0.38
Potassium, g/l	1.08	1.65
Phosphate, g/l	1.52	1.86
Chloride, g/l	1.96	1.05
Citrate, g/l	0.30	0.10
Total of Above, g/l	7.58	6.73

*Analyses by Ionics, Incorporated

Table 5		
Analyses of Milk Solids*		
Component	Content Per Gram of Protein	
	Decontaminated	Untreated
Proteins, gm	1.00	1.00
Carbohydrates, gm	1.72	1.49
Fats, gm	1.17	1.11
Ash, gm	0.33	0.22
Total Solids, gm	4.23	3.83
Moisture, gm	0.09	0.06
Caloric Value, cals	21	20
Calcium, mg	59	41
Phosphorus, mg	31	30
Ascorbic Acid, mg	67	96
Thiamine Hydrochloride, mg	8	8
Riboflavin	112	98

*Analyses by Food and Drug Research Laboratories

Table 6		
Radioanalyses of Fluid Milk*		
	Decontaminated	Untreated
Strontium-90/Calcium, pc/g	2.7	25.7
Cesium-137/Potassium, pc/g	6.5	196.0
Strontium Decontamination, %	89.5	- - -
Cesium Decontamination, %	96.7	- - -
*Analyses by U.S. Public Health Service Winchester Labs.		

Table 7			
Feeding Tests*			
	Decontaminated	Untreated	Casein
Mean 4-week Gain, gm	107	111	100
Mean Food Intake, gm	318	337	293
Mean Protein Intake, gm	31.8	33.7	29.3
Protein Efficiency Ratio**	3.36	3.29	3.41
Protein Quality Value***	98.5	96.5	100

*Tests by Food & Drug Research Labs., Maspeth, L.I., N.Y.
Casein Reference Standard

**PER = (Four week Gain)/(Protein Intake)

***PQV = 100 (PER)/(Casein PER)

5.6 Taste Tests

A dozen persons tasted the decontaminated and the untreated milk without knowledge of which sample they were tasting. This can not be considered adequate but it was interesting to note that most people found the decontaminated milk to be indistinguishable from the untreated milk.

6.0 CONCLUSIONS

1. The electrodialytic decontamination plant was found to be eminently operable.

2. The membrane life testing of an electrodialysis milk decontaminator proceeded to 2800 amp-hrs/ft^2. At the end of this period the membranes were still in good shape. Unfortunately the membrane replacement rate cannot be predicted under this program except to say they will last for at least the above mentioned 2800 amp-hrs/ft^2. Further testing must be carried out to establish the membrane replacement rate.

3. A suitable <u>in situ</u> method ofcleaning the membrane stack was developed in the early stages of the program. It consists of rinsing alternately with cold water, 5% NaOH, warm water, 5% HCl, and cold water. The chemical costs of this cleaning method are about one-sixth that of equivalent commercial dairy cleaning agents: approximately 0.03¢ per gallon of decontaminated milk. Bacteria counts remained below 50,000 per ml in all cases.

4. Rat-feeding and vitamin-analysis tests showed that the electrodialytically decontaminated milk was nutritionally indistinguishable from untreated milk. Very limited taste tests indicated that no particular taste problem exists.

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Ionics, Incorporated Watertown, Massachusetts	UNCLASSIFIED
	2b. GROUP N/A

REPORT TITLE

ADVANCED STUDY OF MILK DECONTAMINATION BY ELECTRODIALYSIS

DESCRIPTIVE NOTES (Type of report and inclusive dates)

Final Report July 1964 - May 1965

AUTHOR(S) (Last name, first name, initial)

Greatorex, John L.
Glass, Werner

REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
October 1965	24	2

CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
OCD-PS-64-281	
PROJECT NO. Work Unit No. 3215B	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

AVAILABILITY/LIMITATION NOTICES

Qualified Requesters may obtain copies of this report from DDC.

SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
None	Postattack Research Division Office Of Civil Defense, Washington, D.C.

ABSTRACT

A five gph electrodialytic milk decontamination test plant decontamination test plant was built and operated. Parameters studies were membrane life, effect of time on current efficiency and cleaning technique. After the initial debugging expected with any test plant, operability was excellent. Approximately 8,000 lbs of milk were treated. Removal of radioactive Sr-90 and Cs-137 averaged 90%. The ion-selective membranes showed no decrement in performace following an initial drop from 90% current efficiency to 82% during the first 60 hours of operation. A suitable *in situ* method of cleaning the membrane stack was developed: consecutive rinses of water, 5% NaOH, warm (150°F) water, 5% HCl and water. The chemical cost of this cleaning method come to about 0.03¢/gallon milk. Bacteria counts always remained below the 50,000 per ml USPHS standard.

FORM 1473

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Decontamination Milk Electrodialysis Ion-Washing Strontium-90 Postattack						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS), (S), (C), or (U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.