267
3-10-78

sh. 1909

MLM-2503

**Development of Ultrafiltration and
Inorganic Adsorbents for Reducing
Volumes of Low-Level and Intermediate-
Level Liquid Waste: October -
December 1977**

**John W. Koenst, William R. Herald
and Raymond C. Roberts**

February 24, 1978

Monsanto

MOUND FACILITY

Miamisburg, Ohio

operated by

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company

for the

U. S. DEPARTMENT OF ENERGY

Contract No. EY-76-C-04-0053

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

PRINTED IN THE UNITED STATES OF AMERICA

Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161
Price: Printed Copy \$4.00; Microfiche \$3.00

**Development of Ultrafiltration and Inorganic
Adsorbents for Reducing Volumes of Low-Level
and Intermediate-Level Liquid Waste:
October-December 1977**

**John W. Koenst, William R. Herald
and Raymond C. Roberts**

Issued: February 24, 1978

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MOUND FACILITY
Miamisburg, Ohio 45342

operated by
MONSANTO RESEARCH CORPORATION
a subsidiary of Monsanto Company

for the
U. S. DEPARTMENT OF ENERGY

Contract No. EY-76-C-04-0053

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Abstract

The exposures of noncellulosic ultrafiltration membranes to a radioactive environment simulating up to 24 months of exposure to a β dose of $10 \mu\text{Ci}/\text{cm}^3$, a γ dose of $10^{-5} \mu\text{Ci}/\text{cm}^3$, and an α dose of $4.9 \times 10^{-3} \mu\text{Ci}/\text{cm}^3$ were completed. Exposure to β and γ radiation did not affect membrane performance. After a simulated six months of exposure to α radiation some degradation of membrane performance occurred.

Several experiments were made on a laboratory-scale reverse-osmosis unit using the product from ultrafiltration as feed. Rejection of activity ranged from 88 to 99%.

The "continuous" ultrafiltration pilot run was completed. Approximately 40,000 gal were processed in over 70 hr of operating time without shutdown for cleaning. Flux and rejection were maintained relatively steady over this period. Rejection of gross alpha ranged from 80 to 99.5% depending on the ionic content of the waste stream. Flux rates ranged from 5-8 liters/min over this period.

The engineering column tests were continued using uranium-233 with product from the ultrafiltration pilot plant. Flow rates and pH were varied in order to determine optimum operating conditions.

Membrane irradiation studies

The exposure of noncellulosic ultrafiltration membranes to a radioactive environment simulating up to 24 months of exposure to a β dose of $10 \mu\text{Ci}/\text{cm}^3$ and a γ dose of $10^{-5} \mu\text{Ci}/\text{cm}^3$ did not show any conclusive evidence of membrane degradation. Membrane performance characteristics were not reproduced identically after irradiation; however, the random nature of the changes strongly suggests no membrane degradation occurred. After exposure to an α dose of $4.9 \times 10^{-3} \mu\text{Ci}/\text{cm}^3$ for periods simulating up to 24 months of operating time, some membrane degradation was evident. Flux and rejection declined severely for 12-month and 24-month exposures. The UF membranes tested were Abcor, Inc. types HFD and HFM. Both membranes are noncellulosic and have a molecular weight cut-off of $\sim 20,000$ amu.

A summary of the UF membrane flux data before and after irradiation (β, γ) is given in Table 1. The average changes in the flux of the control membranes (membranes not exposed to β and γ irradiation) were 16% and 25.2% for the HFD and HFM membrane types, respectively. For both groups of control membranes the flux change was negative, i.e., a loss of flux occurred with time. Losses in flux of these magnitudes are not unrealistic. Particulate matter (e.g., dirt and residual Carbowax) that is likely to be in the feed stream will partially block some of the larger membrane pores, reducing the permeate flow.

The flux changes for the HFD membranes exposed to β and γ irradiation averaged -13.3% for the 6-month exposure group, -4.8% for the 12-month exposure group,

and -17.5% for the 24-month exposure group. Three observations are evident from these data. 1) In all three groups, negative changes in flux occurred. These flux losses may be attributed to polymer crosslinking due to irradiation or to partial plugging of gross pores in the membrane structure by particulates in the feed solution. 2) The changes in membrane flux performance are essentially equal to or less than changes in the control membrane performance. This suggests that irradiation had little or no effect on HFD membrane flux. 3) The losses in flux performance are nonlinear. If radiation damage had a significant effect on membrane flux, it would be expected that the flux change after 1 yr of exposure (-4.8%) would be higher than the change observed after six months of exposure (-13.3%). Therefore, again the flux changes are not attributed to irradiation.

The changes in permeate flux observed for the HFM membranes were +18.5%, +4.4%, and -5.2% for the 6-month, 12-month and 24-month exposures, respectively. The magnitudes of these changes are all below the observed change in the control membrane average flux (-25.2%). For the membranes exposed for 12 and 24 months the observed changes are small ($\sim 5\%$), and no damage due to irradiation is suspected. The flux increase of 18.2% for the 6-month exposure is not readily explainable.

Table 2 presents a summary of membrane rejection (as measured by total solids assays) before and after radiation (γ, β). The rejection for the HFD membranes decreased for each membrane grouping, including the control group. Average rejection losses were 15% following 6 months of exposure, 39.3% following 12 months of exposure, 55.3% following 24 months of

Table 1 - SUMMARY OF MEMBRANE FLUX DATA BEFORE AND AFTER IRRADIATION (γ, β)

Membrane Type	Duration of Simulated Exposure (months)	Membrane Disc Identification	Water Flux Prior to Irradiation (gal/ft ² /day)	Average Water Flux For Similar Group of Membranes (gal/ft ² /day)	Water Flux After Irradiation (gal/ft ² /day)	Average Water Flux For Similar Group of Membranes (gal/ft ² /day)	Change in Average Water Flux (%)
HFD	6	D6a	267		202		
		D6a	227		224		
		D6c	252	249	224	216	-13.3
	12	D12a	235		258		
		D12b	254		179		
		D12c	205	231	224	220	- 4.8
	24	D24a	216		168		
		D24b	283		246		
		D24c	269	255	218	211	-17.5
	0*	CD1	288		224		
		CD2	291		246		
		CD3	280	287	252	241	-16.0
HFM	6	M6a	134		157		
		M6b	83		106		
		M6c	109	109	123	129	+18.5
	12	M12a	99		134		
		M12b	99		92		
		M12c	106	101	90	106	+ 4.4
	24	M24a	89		85		
		M24b	91		96		
		M24c	147	108	123	102	- 5.2
	0*	CM1	152		119		
		CM2	157		116		
		CM3	143	151	105	113	-25.2

*Control Membranes

Table 2 - SUMMARY OF MEMBRANE REJECTION DATA BEFORE AND AFTER IRRADIATION (Y,8)

Membrane Type	Duration of Simulated Exposure (months)	Membrane Disc Identification	Total Solids Rejection Prior to Irradiation (%)	Average Rejection for Similar Group of Membranes (%)	Total Solids Rejection After Irradiation (%)	Average Rejection for Similar Group of Membranes (%)	Change in Average Total Solids Rejection (%)
HFD	6	D6a	14.6		13.7		
		D6b	16.8		8.9		
		D6c	12.7	14.7	15.0	12.5	-15.0
	12	D12a	10.8		11.2		
		D12b	6.0		1.5		
		D12c	8.4	8.4	2.7	5.1	-39.3
	24	D24a	10.0		5.5		
		D24b	11.0		4.6		
		D24c	12.5	11.2	5.0	5.0	-55.3
	0*	CD1	12.5		6.1		
		CD2	11.0		8.3		
		CD3	11.8	11.8	4.9	6.4	-45.8
HFM	6	M6a	27.0		28.4		
		M6b	34.8		36.0		
		M6c	25.8	29.2	39.4	35.8	+22.6
	12	M12a	24.6		32.2		
		M12b	32.5		32.2		
		M12c	26.7	27.9	30.6	31.6	+13.3
	24	M24a	32.7		34.4		
		M24b	37.0		34.4		
		M24c	26.9	32.2	30.4	33.1	+ 2.8
	0*	CM1	20.1		25.3		
		CM2	16.6		9.9		
		CM3	24.1	20.3	33.0	22.7	+11.8

*Control Membranes

exposure, and 45.8% for the control set. The significant loss of rejection in the control group makes any interpretation of the irradiated membrane results very speculative and of little value. Interpretation becomes even more difficult since each rejection loss was accompanied by a permeate flux loss.

Increases in total solids rejection occurred for all the sets of HFM membranes, including the control set. The membranes irradiated to simulate six months of exposure showed an increase of 22.6% in rejection. The 12-month and 24-month exposures produced respective rejection increases of 13.3% and 2.8%. The rejection for the HFM control group increased 11.8%. As was the case with the HFD membrane results, definitive conclusions cannot be drawn from these data.

Wide variations in the control membrane flux and rejection characteristics make interpretation of the performance data for the irradiated membranes difficult. The changes in the control membrane performance are greater than would be expected due to experimental error and are often inconsistent when corresponding flux and rejection changes are considered. The reasons for the control membrane performance variations are not, however, readily apparent. Overall, the fairly random results suggest that no degradation of the membranes will occur with up to 24 months of exposure to low level (γ , β) nuclear wastes.

The first phase of the alpha irradiation tests on samples of the D&M membranes has been completed. Samples of D&M membranes were exposed to an alpha concentration of $4.9 \times 10^3 \mu\text{Ci}/\text{cm}^3$ for periods that simulated 6 months, 1 yr, and 2 yr of actual

operating time. Flux and rejection of Carbowax 6000 were measured before and after irradiation of each sample. The results of these measurements can be seen in Table 3.

As can be seen, the flux with distilled water remained fairly constant before and after irradiation, whereas the flux with Carbowax 6000 dropped considerably in most cases. This decline in flux is more probably due to membrane compaction than to degradation. It can also be seen that the rejection of Carbowax increased for the samples subjected to the six-month test, but declined severely for the samples subjected to the 1-yr and 2-yr tests. Further studies will probably be necessary to determine if degradation has occurred or if the decline in rejection rate is from other causes. Dissolution of some of the membrane samples and then a viscosity test to determine the molecular weight of the polymer making up the membrane may be necessary to determine if degradation has really occurred.

Membrane pilot plant studies

Several experiments were made on a laboratory-scale reverse-osmosis (RO) unit using the product from the ultrafiltration (UF) system as feed. The results of these determinations are listed in Table 4.

As can be seen from Table 4, the gross alpha concentration of the product from the RO ranged from ~0.2 to 0.4 dis/min/ml, and rejection of activity ranged from ~88% to 99%. Rejections of conductivity from 91 to 93% were also obtained.

Table 3 - SUMMARY OF FLUX DATA BEFORE AND AFTER α IRRADIATION^a

Membrane Sample Number	Flux with Deionized Water		Flux with Carbowax 6000		% Rejection of Carbowax 6000		Time Irradiated (days)	Simulated Operating Time
	Before	After	Before	After	Before	After		
	(gal/ft ² /day)	(gal/ft ² /day)	(gal/ft ² /day)	(gal/ft ² /day)	(%)	(%)		
D-1	366.2	453.3	45.3	33.1	13.1	18.1	18	6 mo
D-2	401.0	383.6	41.8	34.9	8.1	21.8	18	6 mo
D-3	627.7	610.7	64.5	41.8	4.0	11.4	18	6 mo
D-4	732.3	610.7	68.0	38.4	11.4	1.9	35	1 yr
D-5	697.4	697.4	71.5	43.6	11.0	3.0	35	1 yr
D-6	732.3	662.6	55.8	40.1	27.1	0	35	1 yr
D-7	906.7	732.3	69.7	36.6	13.3	3.4	70	2 yr
D-8	732.3	697.4	52.3	48.8	24.7	1.4	70	2 yr
D-9	749.7	645.1	52.3	45.3	36.6	3.4	70	2 yr
M-1	226.7	697.4	52.3	20.9	19.5	8.6	18	6 mo
M-2	348.7	697.4	62.8	20.9	9.9	29.9	18	6 mo
M-3	697.4	871.8	71.5	24.4	2.4	24.7	18	6 mo
M-4	732.3	714.9	76.7	41.8	16.6	0	35	1 yr
M-5	871.8	2005.1	170.9	71.5	19.8	3.0	35	1 yr
M-6	2092.3	2266.7	174.3	69.7	13.8	0	35	1 yr
M-7	1569.2	2789.8	258.1	83.7	3.4	3.4	70	2 yr
M-8	3051.3	2789.8	200.5	43.6	3.3	7.1	70	2 yr
M-9	1918.0	2789.8	261.5	61.0	16.9	3.4	70	2 yr

^a α concentration of irradiating solution was $4.9 \times 10^{-3} \mu\text{Ci}/\text{cm}^3$.

One run was made on the RO unit using uranium-contaminated waste as feed. The feed had an activity level of 422 dis/min/ml, and the product had a level of 1.25 dis/min/ml gross alpha, for a rejection of activity of 99.7%. The rejection of conductivity was 86.6%.

The "continuous"* run that was started on the ultrafiltration pilot plant in August was continued throughout this quarter. At the time of its termination, ~40,000 gal of feed had been processed. The data for this "continuous" run are tabulated in Table 5.

As can be seen from this table, although the flux has become fairly steady (allowing for daily fluctuations due to the unit sitting idle overnight and over weekends), the rejection of activity was definitely decreasing in recent weeks. The reason for this drop in rejection of activity is not readily apparent. It could be the result of membrane degradation, or it might also be a function of the waste stream itself. Since the overall content of the waste stream varies considerably from time to time, it is nearly impossible to correlate rejections from day to day. Generally speaking, the higher the concentration of ionic material in the waste stream, the lower the rejection of activity.

In December, the "continuous" run was terminated and a thorough cleaning of the system was begun. This cleaning consisted

of flushing the system with hot (120°F) water containing detergent and enzyme for 2 to 3 hr and then flushing with clean water in order to remove the detergent. This is the first time the system has been cleaned with anything except tap water since September 1977. Since this time, 39,775 gal of feed have been run through the system and ~70 hr of operating time has been logged. The total operating time on the unit to this point is 226 hr.

From the test results, it appears that the "M" membrane has given better overall performance than the "D" membrane both in flux rates and in rejection of activity. Table 6 shows some of the properties of the D and M Membranes.

Adsorbent tests

The engineering column tests were continued using uranium-233 with product from the Ultrafiltration Pilot Plant. This enabled the system to operate on a relatively clean waste stream without the constant plugging of filters and the consequent removal of activity by filters. The resin used in the Engineering Test System were MSA-1, a strong base macroporous and ion exchange resin; MSC-1, a strong acid macroporous cation exchange resin; and XN1010, a strong acid macroporous cation exchange resin usually used for nonaqueous solutions. Flow rates and pH were varied in order to determine optimum operating conditions. The results are summarized in Table 7. The data indicate that the best results were obtained with MSA-1 at pH's from three to nine. The resins, XN1010, MSC-1, and MSA-1 were also tested in series (see Table 8). A total dissolution factor, across all three columns, of 73.5 was obtained at an

*By "continuous" run, it is not meant that the unit was run continuously around the clock, but rather that a batch was run and the unit was shut down overnight or over the weekend, but was not cleaned.

Table 4 - RESULTS OF DETERMINATIONS USING UF PRODUCT AS FEED FOR LAB SCALE R.O. UNIT

Run Number	Alpha (feed) (dis/min/ml)	Alpha (product) (dis/min/ml)	Alpha (concentrate) (dis/min/ml)	Conductivity (feed) (μ mho/cm)	Conductivity (product) (μ mho/cm)	Conductivity (concentrate) (μ mho/cm)	Rejection of Activity (%)	Rejection of Conductivity (%)
1	3.56	0.19	4.45	1620	106	2020	94.7	93.5
2	6.85	0.36	8.15	1960	178	2540	94.7	90.9
3	7.52	0.18	8.44	1660	132	2430	97.6	92.1
4	4.25	0.47	4.96	1460	109	1975	88.8	92.5
5	2.94	0.23	3.30	1710	130	2300	92.2	92.4
6	10.88	0.34	12.65	1730	149	2520	96.9	91.4
7	19.89	0.23	--	--	--	--	98.9	--

Table 5 - RESULTS OF CONTINUOUS RUNNING OF UF PILOT PLANT

<u>Total Feed Processed (gal)</u>	<u>System Flux Corrected to 77°F (25°C) (liter/min)</u>	<u>Rejection of Activity (%)</u>	<u>Suspended Solids (mg/liter)</u>	<u>Conductivity (μmho/cm)</u>	<u>pH</u>
3,000	7.6	99	30	1675	8.4
4,000	6.5	92	30	1800	8.7
5,000	7.2	98	30	1900	8.6
6,000	8.3	96	30	1770	8.4
7,000	6.2	95	30	2100	10.2
8,000	6.5	91	30	2100	10.4
9,000	5.6	91	30	1500	9.0
10,000	5.6	99	30	1750	8.7
12,000	6.4	97	30	2600	9.3
14,000	8.0	92	30	2100	9.2
16,000	5.6	91	30	2000	8.8
18,000	6.7	95	30	2050	8.4
20,000	6.4	99	30	1600	8.6
22,000	6.0	99.5	30	1600	9.1
24,000	5.5	99	30	1900	8.4
26,000	6.4	92	30	1700	9.1
28,000	7.0	90	30	2100	8.6
30,000	6.4	89	30	1950	8.6
32,000	7.1	88	30	1700	8.5
34,000	7.5	91	30	1700	8.3
36,000	5.5	80	30	2400	8.4
37,000	5.1	80	30	2400	7.8
38,000	6.6	91	30	2100	8.6
39,000	5.4	95	30	1750	8.3
40,000	5.4	90	30	1650	8.1

Table 6 - MEMBRANE PROPERTIES

<u>Membrane Type^a</u>	<u>pH Range</u>	<u>Maximum Temperature (°F)</u>	<u>Maximum Inlet Pressure (psi)</u>	<u>Tolerance of Free Chlorine</u>
HFD	3-12	185	75	None
HFM	0.5-12.5	195	75	50 ppm

^aBoth membranes have a pore size of $50 \pm 25 \text{ \AA}$.

Table 7 - ENGINEERING COLUMN TESTS USING URANIUM-233^a

Adsorbent	Flow Rate (ml/min)	pH	Feed (dis/min/ml)	Raffinate (dis/min/ml)	D.F.
MSA-1	150	9	1047	39	26.9
	150	8	935	57	16.4
	150	7	993	53	18.7
	150	3	2120	96	22.1
	100	3	1873	81	23.1
MSC-1	50	9	1057	734	1.4
	25	9	1037	712	1.5
	25	8	935	470	2.0
	25	7	993	439	2.3
	25	3	2020	302	6.7
	5	3	1888	206	9.2
XN1010	50	9	1057	392	2.7
	25	9	1037	280	3.7
	25	8	935	242	3.9
	25	7	993	221	4.5
	25	3	2020	322	6.3
	5	3	1888	258	7.3

^aUF product was used as feed

Table 8 - TYPICAL RESULTS OF ENGINEERING COLUMN TESTS IN SERIES USING URANIUM-233^a

Feed		Flow (ml/min)	Total D.F.	After 1st Column XN1010		After 2nd Column MSC-1		After 3rd Column MSA-1	
(dis/min/ml)	pH			(dis/min/ml)	D.F.	(dis/min/ml)	D.F.	(dis/min/ml)	D.F.
1956	3	100	73.5	185	10.7	118	1.6	27	4.4
2118	3	50	38.5	229	9.3	88	2.6	55	1.6

^aColumns in series XN1010+MSC-1+MSA-1. UF product was used as feed.

initial pH of three with a flow rate of 100 ml/min. Results tended to fluctuate; however, results reported in Table 8 were typical of the runs. At a pH of seven or greater, elution of the columns starts to occur.

Several new resins were obtained and tested on small columns (~1 g of resin). The results are listed in Table 9. Combinations of resins in series were also evaluated using UF product spiked with uranium-233.

Table 9 - SMALL ION EXCHANGE COLUMN TESTS USING URANIUM-233^a

Resin Type	pH	Flow (ml/min)	Feed (dis/min/ml)	Raffinate (dis/min/ml)	D.F.
MSC-1	7	2.0	780	367	2.1
200	7	2.0	780	475	1.6
MSA-1	7	2.0	780	175	4.5
IRC-50	7	2.0	780	764	1.0
XN1010	7	2.0	780	479	1.6
11	7	2.0	780	105	7.4
MSA-1	7	1.87	618	81	7.6
11	7	1.87	618	126	4.9
IRA-938	7	1.87	618	21	29.4
MSA-1	3	2.5	5035	506	10.0
11	3	2.5	5035	642	7.8
IRA-938	3	2.5	5035	446	11.3
11	2.9	2.0	13032	850	15.3
SBR-POH ^b	2.9	2.0	13032	2730	4.8
IRA-430 ^b	2.9	2.0	13032	1696	7.7
ACA ^b	2.9	2.0	13032	12380	1.1
IRA-938	2.9	2.0	13032	776	16.8
AG 1X4 ^b	2.9	2.0	13032	493	26.4
XE236 ^b	2.9	2.0	13032	596	22.9
IRA-904 ^b	2.9	2.0	13032	719	18.1
IRA-900 ^b	2.9	2.0	13032	563	23.2
MSA-1/MSA-1	7	1.87	780	87	9.0
11/IRA-938	7	1.87	780	16	48.8
MSA-1/IRA-938	7	1.87	780	11	70.9
IRA-938/IRA-938	7	1.87	780	103	7.6
11/11	7	1.87	780	59	13.2
11/MSA-1	7	1.87	780	65	12.0
MSA-1/MSA-1	3	2.5	5035	344	14.6
11/IRA-938	3	2.5	5035	358	14.1
11/MSA-1	3	2.5	5035	509	9.9
IRA-938/IRA-938	3	2.5	5035	535	9.4

^aUF product was used as feed.

^bNew resins

Distribution

EXTERNAL

TIC, UC-70 (267)

J. A. Chacon, Dayton Area Office (2)
D. W. King, Albuquerque Operations (2)
T. C. Jones, Albuquerque Operations
R. Y. Lowrey, Albuquerque Operations
G. Oertel, Division of Waste Management
T. C. Chee, Division of Waste Management
T. K. Keenan, Los Alamos Scientific Laboratory
J. O. Blomeke, Oak Ridge National Laboratory
J. A. Leary, Waste Process and Recovery
R. E. Lerch, Hanford Engineering Development Laboratory
R. K. Flitcraft, Monsanto Research Corporation
Monsanto Library, St. Louis

INTERNAL

A. G. Barnett
B. E. Baughn
W. H. Bond
W. T. Cave
J. W. Doty
T. C. Elswick
K. V. Gilbert
R. C. Herman
C. W. Huntington
L. V. Jones
J. W. Koenst (5)
B. R. Kokenge
J. R. McClain
D. L. Prosser
L. B. Stevens
R. E. Vallee
Library (10)
Publications