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

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

February 9, 1978

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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

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Abstract

The ultrafiltration (UF) pilot system is being evaluated at Mound Facility. The effect of pressure drop, temperature, and pH of the feed on system performance has been studied. The system has been run through a number of cleaning cycles including tap water flush, enzyme soak, detergent wash, and citric acid/oxalic acid wash. A continuous run was started on waste from the Waste Processing Facility; at the time of this report, approximately 11,500 gal had been processed. Studies to determine the effect of (α , β , γ) radiation on membrane characteristics were initiated this quarter and will be completed next quarter.

The small laboratory column tests were completed. Isotherms were run on several inorganic adsorbents, including titanium phosphate and sodium titanate. Tests were continued on the Engineering Test Ion Exchange System. Waste solution from the Waste Processing Facility spiked with plutonium-238 and ultrafiltration product spiked with uranium-233 were used as feeds.

Ultrafiltration

During the month of July, a series of experiments were started on the pilot ultrafiltration system in order to determine the effect of changing the operating pressure drop (ΔP) across the system on membrane flux and rejection of activity. The system was operated at an inlet pressure (IP) of 50 psi. The outlet pressure (OP) was varied from 15 to 35 psi, thereby producing ΔP 's (IP-OP) from 15 to 35 psi. The results of these tests showed that flux was greater at lower ΔP 's (Table 1).

Table 1 - RELATIONSHIP OF FLUX WITH ΔP

Average Flux Corrected to 77°F (gal/min)	ΔP (psi)
1.32	15
1.20	20
1.09	25
1.03	30
0.99	35

Although the flux rate is somewhat higher at a low ΔP , the recirculation rate and, therefore, the amount of turbulence within the membrane tube are also lower. This would most probably lead to faster fouling of the membrane surface. (A ΔP of 15 psi yields a recirculation rate of 18 gal/min, whereas a ΔP of 35 psi gives a recirculation rate of 32 gal/min.) The ΔP appeared to have very little effect on the rejection of activity.

A series of runs was made at an elevated temperature (110°F) in order to determine the effect of temperature on membrane performance. Flux rates were much higher at elevated temperatures (They ranged from 1.6 to 3.5 gal/min); however, rejection of α activity was lower, ranging from 90 to 95% instead of the 99% usually obtained at lower operating temperatures. All the elevated temperature runs were made at a ΔP of 25 psi.

In the next series of runs, the pH of the feed solution was raised to pH 10 or pH 11 with the addition of NaOH. Although the elevation of pH reduced the activity remaining in the permeate by about 50% (on the average), the metal hydroxide precipitate formed caused rapid fouling of the membranes and a very rapid flux decline. (Flux dropped from 2.8 gal/min to 1.2 gal/min in the first 3 hr of operation, and down to ~0.85 gal/min after two days of operation).

After the elevated pH runs were completed, it was necessary to thoroughly clean the system. Washing with detergent and enzymes did little to improve flux; therefore, the unit was cleaned with a 0.5% solution of citric acid followed by a 0.5% solution of oxalic acid. This succeeded in removing the heavy metal hydroxide fouling the membrane surface. After a final detergent wash and water rinse, flux had recovered to ~5.5 gal/min (using tap water). This compares to 10 gal/min when the system was new and 7 gal/min after the first major cleaning.

During the month of August, a continuous run of the ultrafiltration pilot plant was started. The system was run continuously at a ΔP of ~25 psi using waste from the Waste Processing Facility containing about 25 to 30 mg/liter of suspended solids. The system flux at the beginning of this experiment was ~1.85 gal/min (corrected to 77°F). This flux quickly declined to about 1.2 to 1.3 gal/min as the first 600 gal were processed by the system. The flux very slowly declined to 0.95 gal/min by the time 2400 gal had been run. At this point, the system was flushed with 200 gal of tap water and allowed to sit over a four-day period. When the system was started up again, the flux, using tap

water, had recovered to ~4.5 gal/min. When continuous running was resumed, the initial flux was ~3.0 gal/min. This flux rate rapidly declined to about 2 gal/min and then leveled off.

Periodic flushes with tap water maintained the flux near this level for a long period of time. After 5,000 gal had been run, flux was still about 1.9 gal/min, and after 7,000 gal a flux of ~1.6 gal/min was still being obtained. Since that time, the flux has slowly declined. At the present time, ~11,500 gal have been processed and the flux is still in the 1.2 to 1.3 gal/min (corrected to 77°F) range (see Table 2 and Figure 1).

One interesting fact that has come to light during the course of this continuous run is that the "M" membranes have performed better than the "D" membranes. The difference in performance of the two types of membranes has increased as the run progressed. At the present time the "M" membrane accounts for ~60% of the total permeate produced and also is 30 to 40% better in the rejection of activity.

Studies have been initiated to determine the effect of alpha bombardment on the membranes. Samples of both the "D" and "M" membranes have been characterized as to flux with H₂O, flux with 10% Carbowax 6000 solution, and rejection of Carbowax 6000. These samples will then be exposed to a solution containing 1.08×10^4 dis/min/ml α activity for periods that will simulate six months, 1 yr, and 2 yr of operating time. The membrane sample will then be recharacterized as to H₂O flux, Carbowax 6000 flux, and rejection of Carbowax. These results will then be compared to the results obtained before α irradiation.

Table 2 - FLUX DECLINE DURING CONTINUOUS OPERATION

Total Throughput (gal)	Flux Corrected to 77°F (gal/min)
0	1.85
500	1.10
1,000	1.10
1,500	1.10
2,500	1.00
3,000	3.00 ^a
3,500	2.25
4,000	2.10
4,500	2.15
5,000	2.10
6,000	2.20
7,000	1.90
8,000	1.65
9,000	1.60
10,000	1.40
11,500	1.25

^a Run was interrupted for a week and system was flushed with water.

FIGURE 1 - Flux history during continuous processing. Peaks show flux recovery after cleaning or shutdown periods. Dotted line shows general trend of flux decline.

The assessment of membrane mechanical properties following exposure to β and γ irradiation will be completed next quarter. The experiments employed to evaluate pre- and post- irradiation properties entailed dissolving each membrane in an appropriate solvent and measuring the resultant solution viscosities. These viscosity measurements were then used to compute the polymer molecular weights which were then compared to the original molecular weights.

A new type of membrane was obtained in tubular form. The membrane material is polysulfone and was manufactured on an experimental basis at our request. This membrane is currently designated as Type WRP and has a molecular weight cutoff of approximately 5000. Some difficulties occurred in casting the WRP membranes in 0.5 in. diameter tubes. As a result, membrane performance characteristics have not been uniform. Two tubes will be tested next quarter on contaminated solution from the Waste Processing Facility. One membrane has a low water flux (2.6 gal/ft²/day) and moderate solids rejection (63.8%), and the other has a high water flux (93.6 gal/ft²/day) and low solids rejection (34.8%). These data were taken at 75 psig inlet pressure, 50 psig outlet pressure, and 3-4 gal/min circulation rate at 80°F. The rejection data were measured with a 2% Carbowax 6000 solution. The variations in performance are attributable to the developmental nature of the casting procedure with this particular membrane formulation; that is, the viscosity of the WRP casting solution is approximately an order-of-magnitude lower than the viscosity of typical tubular membrane casting solution. These membranes should, however, provide sufficient data to assess the applicability of Type WRP membranes for processing of low-level nuclear waste water.

Inorganic Adsorbents

The small-laboratory-column (0.7-cm diameter) tests were completed. The results are tabulated in Table 3. The feed solution to these columns is approximately 20,000 dis/min/ml at a rate of 2 ml/min for all plutonium-238 and a feed solution of 40,000 dis/min/ml at a rate of 20 ml/min for uranium-233. Breakthrough was achieved for the tests with uranium-233.

Isotherms were run on several inorganic adsorbents. A summary of the data is given in Table 4. Also, sodium titanate (NaTi_2O_5), as developed by Sandia Laboratories, is being tested and compared to previously evaluated inorganic adsorbents.

Tests on the Engineering Test Ion Exchange System were continued from last quarter. Waste solution from the Waste Processing Facility was used as feed to the system. The waste solution was filtered through a 10- μm filter and spiked with plutonium-238. The bed volume of each column is ~ 1000 ml (50 mm diameter x 50.8 cm height). A summary of the data is given in Table 5. Decontamination factors as high as 98 were obtained using feed concentrations of $\sim 20,000$ dis/min/ml gross alpha; with feed concentrations of ~ 1000 dis/min/ml gross alpha, decontamination factors (DF) dropped to ~ 10 .

Tests were started using ultrafiltration product from the ultrafiltration pilot plant to feed the Engineering Test Ion Exchange System. The feed was spiked with uranium-233 and fed to three different adsorbents. The results are given in Table 6. As can be seen, the MSA-1 resin yielded a maximum DF of 237 while the XN1010 and MSC-1 yielded DF's of <10 .

Table 3 - LABORATORY COLUMN TESTS

Isotope	Adsorbent	Total Activity Adsorbed (dis/min)	Wt. of dry Resin (g)	D.F.
^{233}U	MSC	1.80×10^9	1.0	1.26 ^a
	XN1010	1.80×10^9	1.0	1.32 ^a
	200	1.80×10^9	1.0	1.33 ^a
$^{238}\text{Pu}(+6)$	MSC	7.88×10^8	0.5	95
	XN1010	7.85×10^8	0.5	63
	200	7.87×10^8	0.5	34
$^{238}\text{Pu}(+4)$	MSC	8.10×10^8	0.5	28
	XN1010	8.11×10^8	0.5	21
	200	8.09×10^8	0.5	20

^aBreakthrough.

Table 4 - ADSORBENT ISOTHERM TESTS

Adsorbent	Isotope	Initial Conc. (dis/min/ml)	Adsorbent Conc. (g/ml)	Equilibrium Adsorption Coefficient Kd	pH
Titanium Phosphate $\text{Ti}_3(\text{PO}_4)_4$	^{233}U	20,208	7.89×10^{-7}	2.18×10^7	2.4
		20,208	3.94×10^{-4}	4.80×10^5	1.5
		20,208	7.889×10^{-4}	6.9×10^5	2
		16,213	3.94×10^{-4}	4.8×10^4	7
		5,832	3.9×10^2	1.6×10^2	10
Zirconium Phosphate $\text{Zr}_3(\text{PO}_4)_4$	^{233}U	19,619	4.42×10^3	1.12×10^3	3.2
		23,462	4.42×10^3	7.37×10^2	4.1
		18,648	8.86×10^2	3.48×10^2	7.5
		18,648	9.11×10^3	1.69×10^4	9.6
Sodium Titanate NaHTi_2O_5	^{233}U	4,186	1.02×10^4	4.16×10^4	9.8
		19,759	1.0×10^4	5.39×10^1	1.3
		19,759	5.0×10^2	4.49×10^1	3.4
		23,672	2.5×10^2	2.56×10^3	6.5
Sodium Titanate NaHTi_2O_5	$^{238}\text{Pu}(+6)$	24,986	1.0×10^4	1×10^2	5.9
		15,701	1.0×10^4	6.95×10^3	9.2
	$^{238}\text{Pu}(+4)$	10,446	1.01×10^4	1.39×10^4	9.8
		24,601	1.0×10^4	2.5×10^3	6.5
Ammonium Molybdo- phosphate	$^{238}\text{Pu}(+4)$	17,630	9.7×10^6	3.57×10^2	4.3
		19,641	9.7×10^6	1.82×10^2	9.3
	$^{238}\text{Pu}(+6)$	19,999	9.7×10^6	2.57×10^3	4.3
		19,035	9.7×10^6	1.04×10^2	7.0
Zirconium Phosphate $\text{Zr}_3(\text{PO}_4)_4$	$^{238}\text{Pu}(+4)$	19,669	8.49×10^6	7.25×10^3	9.7
		20,350	8.84×10^6	6.3×10^1	4.9
	$^{238}\text{Pu}(+6)$	22,920	4.4×10^2	3.17×10^1	2.0
Titanium Phosphate $\text{Ti}_3(\text{PO}_4)_4$	$^{238}\text{Pu}(+4)$	19,791	8.84×10^5	1.6×10^0	3.0
		15,974	8.41×10^6	1.67×10^4	9.4
		11,731	7.89×10^5	6.3	4.5
		19,083	7.89×10^4	1.02×10^2	3.9
	$^{238}\text{Pu}(+6)$	19,573	7.89×10^5	1.15×10^1	3.0
		18,700	7.89×10^5	5.3×10^2	4.4
		23,322	7.89×10^5	8.3×10^0	3.5

Table 5 - RESULTS FROM THE ENGINEERING TEST ION
EXCHANGE SYSTEM WITH COMBINED WASTE-PLUTONIUM-238

Resin	One Bed Volume Weight (g)	Isotope	Flow Rate (ml/min)	Initial Feed		Product (dis/min/ml)	Temp. (°F)	DF
				pH	Alpha (dis/min/ml)			
200	881.4	Pu	26	6.7	655	71	78	9.2
			112	7.4	379	47	78	8.1
			47	6.8	3763	217	68	17.3
			42	6.8	2586	66	68	39.2
XN1010	482.2	Pu	60	6.9	847	448	70	1.9
			60	6.9	1522	424	70	3.6
			60	7.1	663	141	70	4.7
			60	7.1	1294	195	70	6.6
			30	6.6	966	269	70	3.6
IRC-50	753.3	Pu	143	6.7	655	55	78	11.9
			127	7.1	1281	41	78	31.2
			135	6.4	45	14	80	3.2
			130	6.6	21482	386	76	55.7
			130	6.8	20035	204	76	98.2
			60	6.8	3763	171	85	22.0
			43	6.8	1267	190	86	6.7
Bone Char >32 mesh	806	Pu	112	6.7	655	63	76	10.4
			72	7.1	1281	46	76	27.9
			135	6.5	22	5	76	4.4
			130	6.6	21482	308	76	69.8
			47	6.9	3763	273	83	138
			27	6.9	2586	70	85	36.9
MSC-1	813.3	Pu	60	6.9	1522	403	76	3.8
			60	6.1	361	212	76	1.7
			60	8.0	1427	404	76	3.5
			30	6.8	650	174	76	3.7
			30	8.2	793	134	76	5.9
MSA-1	727	Pu	60	6.9	847	137	76	6.2
			60	6.1	425	103	76	4.1
			60	8.0	1427	160	76	8.9
			60	7.1	1294	186	76	7.0
			30	6.6	966	82	76	11.8
			30	7.7	929	119	76	7.8

**Table 6 - RESULTS FROM THE ENGINEERING TEST ION EXCHANGE
SYSTEM WITH ULTRAFILTRATION PRODUCT-URANIUM-233**

<u>Resin</u>	<u>One Bed Volume Weight (g)</u>	<u>Isotope</u>	<u>Flow Rate (ml/min)</u>	<u>Initial Feed</u>		<u>Product (dis/min/ml)</u>	<u>Temp. (°F)</u>	<u>DF</u>
				<u>pH</u>	<u>Alpha (dis/min/ml)</u>			
MSA-1	719	U	50	7.2	538	6	72	89.7
			100	7.5	877	7	70	125.3
			100	7.5	950	4	68	237.5
			150	8.5	1054	23	70	45.8
			150	7.6	1043	22	71	47.4
MSC-1	804.7	U	50	7.2	538	477	72	1.13
			100	7.7	1436	240	70	6.0
			100	7.5	931	162	71	5.8
			100	8.9	1204	912	72	1.3
			50	7.6	1043	694	71	1.5
XN1010	470	U	50	7.2	538	190	72	2.8
			100	7.5	877	109	70	8.1
			100	7.5	931	119	71	7.8

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