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

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

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

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Abstract

Ultrafiltration (UF) membranes have demonstrated 90-98% rejection of gross alpha in laboratory tests. In the treatment of laundry wastes, rejection of activity ranged from 98-99.9% gross alpha. The pilot UF system was installed and started up. Flux decline curves and volume reduction performance were determined. Volume reductions of 210:1 were achieved at flux rates of 1.1 gal/min (system is rated at 2-3 gal/min, 90% recovery) at activity rejection of 99.94% gross alpha.

Adsorbent studies demonstrated capacities in excess of 10^9 dis/min/g for uranium-233 and in excess of 10^8 dis/min/g for plutonium-238. Construction and start-up of the Engineering Test Facility has been completed.

Ultrafiltration

During the month of April, the final work on the bench-scale ultrafiltration (UF) system was completed. Typical results obtained from this bench-scale system showed that the Mound Waste Disposal Facility influent (ranging in activity levels from 50 to 3,000 dis/min/ml gross alpha) could be decontaminated to levels that were generally much less than 7 dis/min/ml gross alpha. Several samples of the incinerator scrubber solution were also passed through this system, but little if any decontamination occurred because of the ionic nature of the contaminants in this solution.

Laboratory tests demonstrated that UF is uniquely suited to treat Mound problem waste streams such as floor drains, contaminated shower waste, laundry wastes, and combined waste. The UF membranes tested on the Mound combined waste stream produced a low-level activity product. The laboratory modules had molecular weight (MW) cut-offs ranging from 7000 to 80,000 MW. These membranes demonstrated a rejection of gross alpha 90-98% with a product of ~7 dis/min/ml gross alpha. The UF laboratory modules decontaminated "hot" laundry wastes to less than background. Rejection of activity ranged from 98-99.9% gross alpha, yielding a product containing <<0.1 dis/min/ml. In treating a mostly ionic contaminated waste stream from plutonium contaminated floor drains, the membranes exhibited rejections ranging from 85 to 88% gross alpha. This was certainly better than would be expected using very open membranes to treat dissolved ionic activity.

The UF pilot system was shipped to Mound on April 22, 1977, by Abcor Inc. Prior to shipment, all system components were checked out and shakedown tested. During the week of May 9, 1977, Abcor personnel assisted Mound Liquid Waste Treatment Technology personnel in start-up of the UF pilot system. The membranes were conditioned using detergent solutions and initial water flux measurements were taken. These data are given in Table 1.

Table 1 - INITIAL CHARACTERIZATION OF ULTRAFILTRATION PILOT SYSTEM

Membrane Type	Initial Water Flux at 77°F (gal/ft ² -day)
HF D	151
HF M	258

The pH of the pilot system and conductivity probes were calibrated, and concentrate bleed rates were measured at various timer settings and two different outlet pressures. Operating procedures were reviewed for batch, feed-and-bleed, and total recycle modes of operation and for system cleaning.

On May 19, the UF system went "hot" for the first time (See Figures 1 and 2). For the first two weeks, several batch runs were made, and data were collected mainly to determine flux decline with time (a function of suspended solids concentration). (See Figures 3, 4, and 5).

Experiments were conducted in which the feed solution was concentrated to 5:1 and 10:1, respectively. In both cases

FIGURE 1 - Front view of the Ultrafiltration Pilot Plant showing control panel, pumps, and piping.

FIGURE 2 - Side view of the Ultrafiltration Pilot Plant showing tubular membrane banks.

FIGURE 3 - Flux decline curves for Ultrafiltration System with <10 mg/liter suspended solids [corrected to 77°F (25°C)].

FIGURE 4 - Flux decline curves for Ultrafiltration System with ~70 mg/liter suspended solids [corrected to 77°F (25°C)].

FIGURE 5 - Flux decline curves for Ultrafiltration System with ~200 mg/liter suspended solids [corrected to 77°F (25°C)].

it was noted that although the flux declined from ~3 gal/min to ~1.5 gal/min throughout the course of the run, the activity of the product remained virtually constant.

On June 9, the system was put through a cleaning cycle for the first time. To accomplish this cleaning, ~40 gal of tap water were added to the cleaning tank and heated to 100°-120°F with steam. Then about 700 g of detergent and 100 g of enzyme (used to remove organic fouling) were added and recirculated through the system for about 2 hr. After that, the system was rinsed several times to remove residual detergent, and the total flux rate was determined using tap water. The flux, after cleaning, was ~7 gal/min. This compares to ~10 gal/min which was obtained before the system went "hot".

A series of tests was conducted using sodium phosphate or laundry detergent as additives to the feed. First raw feed was run and data were collected. Then, sodium phosphate or laundry detergent was added at a concentration of 0.5 g/gal of feed. After the feed was allowed to sit for several hours, the solution was run, and the results were compared to the original run using raw feed. The results of these experiments showed that in some cases the additives reduced the activity of the product by as much as 50%; but, in most cases, little if any reduction in the activity of the product occurred.

From June 21 to June 30, a series of experiments was conducted using the continuous mode, in which the concentration of the feed was increased to 200:1. (200:1 volume reduction). The original feed for

this run had an alpha level of 91.0 dis/min/ml and a suspended solids content of 70 mg/liter with a total flux of 2.2 gal/min. The permeate activity level at the beginning of this run was 3.1 dis/min/ml for the "D" membrane and 2.8 dis/min/ml for the "M" membrane. At the conclusion of the test at 200:1 volume reduction, the feed had an alpha level of 900 dis/min/ml with a suspended solid concentration of 3500 mg/liter, and the total flux had dropped to ~1.1 gal/min. One item of interest is that although the alpha concentration of the feed increased from 91 to 900 dis/min/ml and suspended solids increased from 70 mg/liter to 3500 mg/liter, the activity of the product decreased from 3.1 dis/min/ml to 0.64 dis/min/ml for the "D" membrane and from 2.8 dis/min/ml to 0.55 dis/min/ml for the "M" membrane. These results indicate that the membranes may actually reject activity more effectively after they become fouled. These results also show that the membranes perform at least as well on highly concentrated feed as on dilute feed. (See Table 2).

Another fact noted during the first six weeks of operation of the system is that there has been little difference in the overall performance of the two types of membranes (D & M) being tested. Both show similar flux rates and also similar activity rejection characteristics.

Material composition of membranes will determine some of the operating limitations as shown in Table 3.

Membrane life is being demonstrated through laboratory tests and pilot plant demonstrations. The permanent flux and rejection decline of the UF pilot system will be measured and compared to initial flux and rejection rates. Samples of membranes will be radiated at MIT Research Reactor (γ, β) and tested for changes in flux and rejection as well as physical properties. Also, samples of membranes will be radiated at Mound (α) and tested for changes in membrane performance.

Table 2 - RESULTS OF 200:1 VOLUME REDUCTION

Volume Reduction	Product		Alpha Level (dis/min/ml)			Suspended Solids (mg/l)	Temp. (°F)	pH
	D Membrane (gal/min)	M Membrane (gal/min)	D Membrane Product	M Membrane Product	Concentrate			
1:1	1.05	1.15	3.1	2.8	91	70	73	8.2
10:1	0.91	0.96	3.1	2.7	585	-	86	8.4
50:1	0.66	0.68	2.3	2.5	639	600	90	8.2
100:1	0.63	0.63	2.8	2.5	719	1600	89	8.4
150:1	0.61	0.61	0.9	0.9	901	2800	93	8.6
200:1	0.56	0.55	0.64	0.55	937	3500	94	8.4

Table 3 - MEMBRANE OPERATING LIMITATIONS

Membrane	Temperature (°C)	pH Range	Free Chlorine Tolerance
HF D	85	3-12	None
HF M	90	0.5-12.5	50 ppm

The expected dosages of β and γ radiation in various waste streams have been estimated to be $10 \mu\text{Ci}/\text{cm}^3$ and $10^{-5} \mu\text{Ci}/\text{cm}^3$, respectively. These values were transmitted to MIT Research Reactor personnel for irradiation of the pretested membrane samples.

The membrane samples were submitted for testing on June 10, 1977. They were treated with tritiated water at dosages to simulate 6, 12, and 24-month exposures to the waste stream. These irradiated membrane discs were returned to Abcor on June 24 for various modes of testing.

Bench-scale tests were started with flat sheets of the D and M membranes in an Amicon test cell to determine the membrane rejection of a 10% Carbowax 6000 solution in water. Flux rates and rejection rates using Carbowax solution are being determined before and after alpha radiation. On the membrane samples tested so far, however, rejection of the Carbowax has been very low (~10%). This low rejection makes comparisons difficult.

Inorganic Adsorbents

The small laboratory columns (0.7 cm diameter) tests are being continued. The following results have been obtained. (See Table 4) 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 2 ml/min for uranium-233. These experimental column tests will continue until breakthrough data are obtained.

Isotherms were run on several inorganic adsorbents. A summary of the data is given in Table 5. Also, sodium titanate (NaTi_2O_5), as developed by Sandia Laboratories, is being tested and compared to previously evaluated inorganic adsorbents. Tests will be run on all these inorganic adsorbents at pH 4, 7, and 10 as time permits.

Tests on the small laboratory columns were also continued, using untreated waste solutions. Waste solution was collected before entry into the waste processing

Table 4 - LABORATORY COLUMN TESTS

Isotope	Adsorbent	Total Adsorbed (dis/min)	Decontamination Factor
233U	MSC	1.12×10^9	42
	XN1010	1.12×10^9	38
	200	1.12×10^9	42
238Pu(+6)	MSC	4.29×10^8	39
	XN1010	4.27×10^8	20
	200	4.29×10^8	16
238Pu(+4)	MSC	4.28×10^8	32
	XN1010	4.29×10^8	17
	200	4.27×10^8	32

Table 5 - ADSORBENT ISOTHERM TESTS

Adsorbent	Isotope	Initial Conc. (dis/min/ml)	Adsorbent Conc. (g/ml)	Kd	pH
Titanium Phosphate	^{233}U	5382	3.9×10^{-4}	1.6×10^2	10
	$^{238}\text{Pu}(+4)$	15974	8.4×10^{-5}	1.67×10^5	10
Zirconium Phosphate	$^{238}\text{Pu}(+4)$	19669	8.49×10^{-5}	7.25×10^4	10
	$^{238}\text{Pu}(+4)$	20350	8.8×10^{-5}	6.34×10^2	7
Ammonium Molybdenum Phosphate	$^{238}\text{Pu}(+4)$	19641	9.7×10^{-5}	1.8×10^2	10
Bone Char (minus carbon)	^{233}U	18160	1.0×10^{-4}	2.29×10^3	10
Bone Char (with carbon)	^{233}U	18058	9.6×10^{-5}	4.17×10^3	10
Bone Char ($<75 \mu\text{m}$)	^{233}U	14406	9.2×10^{-5}	5.7×10^3	10

facility and filtered through a $1 \mu\text{m}$ filter. The filtered solution was spiked with polymeric plutonium to give a total alpha concentration of 20,000 dis/min/ml. Resins IRC-50, SBR-POH, IRA-938, XE270, 11, HCR-WA, XN1010, 200 and MSC all yielded decontamination factors (DF) of approximately 6. Bone Char gave a DF of 10 using the same solutions. The columns were not run long enough to obtain breakthrough data.

Several resins were converted using CaCl_2 to the Ca^{+2} and Cl^{-1} forms before being used in the small columns. Resins XN1010, 200, MSC, SBR-POH, IRC-50, and IRA-938 were converted in this manner and yielded a 7% increase in the amount of activity adsorbed from solution.

Construction and checkout were completed on the Engineering Test Ion Exchange system on June 1, 1977. A problem with the transfer pump and piping to the feed tank delayed the start of the first test.

Waste solution was filtered through $100\text{-}\mu\text{m}$ filters before entering the feed tank on June 10, 1977, and the first run was started on June 16, 1977. The three, 2-in. diameter columns were filled with bone char (column A), IRC-50 (column B), and 200 (column C) to a height of 20 in. The feed solution alpha activity was increased to 20,000 dis/min/ml and pH was adjusted to 7. This feed solution was then filtered through a $10\text{-}\mu\text{m}$ filter before being pumped through the columns. After two days the $10\text{-}\mu\text{m}$ filter was reducing the feed alpha activity from 20,000 to 500 dis/min/ml. This could be caused by a combination of several things. First, plutonium could be adsorbed onto suspended solids ($<100 \mu\text{m}$), on algae, and on bacteria, which could be filtered out. Secondly, the polymerization of plutonium into large molecules in pH 7 solution could also cause the activity to be filtered from the solution.

The entire 1700 liters of feed was then filtered through the 10- μ m filter, bypassing the columns, back to the raffinate tank. The solution was then transferred back to the feed tank, and 30% H_2O_2 was added to kill bacteria. The alpha concentration was increased from 400 to 21,000 dis/min/ml, and a second run was started using the same three columns.

However, the 10- μ m filter still removed most of the alpha activity from the solution. The most promising approach to this problem is to pump the product from the UF to the feed tank. This solution contains all the ionic species found in WD waste but no solid material to adsorb the plutonium in solution.

An alternative approach will be used until piping from UF to feed tank is completed. The feed material will be filtered through a 1- μ m filter before being pumped into the feed tank. This should significantly decrease the amount of solids in solution.

At present, the product from the ultrafiltration system is being considered as feed solution for the engineering test columns. This solution would contain no suspended solids but yet contain most of the ionic species found in waste streams. This solution would then be spiked with different isotopes before obtaining data for polishing of product from the UF system.

Even with these problems with the feed solution, this system gave a total DF of 100 at a feed rate of 130 liters/min. A larger DF could be achieved at a slower feed rate and increased bed height.

These additional parameters will be investigated in the next quarter.

Conclusions

Laboratory tests at Mound demonstrated that UF is uniquely suited to treat problem waste streams such as floor drains, contaminated shower waste, laundry wastes, and combinations of these wastes. These membranes demonstrated a gross alpha rejection of 90-98% with a product of ~7 dis/min/ml gross alpha. The UF laboratory modules decontaminated "hot" laundry wastes to less than background. Rejection of activity ranged from 98-99.9% gross alpha. The pilot UF system was installed and started up. The system went "hot" on May 19, 1977. Numerous experiments have been run on the pilot plant. Flux decline was measured as were system performance and volume reduction. Volume reductions of 210:1 were achieved at flux rates of 1.1 gal/min at a product concentration of 0.60 dis/min/ml gross alpha (this is a rejection rate of 99.94%). Membrane radiolysis studies are under way. Membranes will be radiated (α , β , γ), and degradation will be measured.

Adsorbent studies are continuing. Small columns have demonstrated capacities exceeding 10^9 dis/min/g for uranium-233 and 10^8 dis/min/ml for plutonium-238. Isotherms are being developed for various inorganic adsorbents, including sodium titanate ($NaHTi_2O_5$). Construction and check-out of the Engineering Test Ion Exchange System was completed on June 1, 1977. The system went "hot" on June 16, 1977.

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