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**Evaluation of Ultrafiltration Membranes
for Treating Low-Level Radioactive
Contaminated Liquid Waste**

John W. Koenst and Raymond C. Roberts

March 31, 1978

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Miamisburg, Ohio

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U. S. DEPARTMENT OF ENERGY

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Introduction

Under funding from the DOE Division of Waste Management (DWM) [formerly the ERDA Division of Nuclear Fuel Cycle and Production (DNFCP)], Mound Facility developed and demonstrated separation methods for removing radionuclides from process streams at the source, that is, prior to introduction into general waste streams. As part of this program, Mound Facility investigated lower cost alternatives for use in 1980 fuel reprocessing and waste solidification plants, evaluating the processes within the nuclear fuel cycle that contribute to low-level and intermediate-level waste, and determining the feasibility of using such separation concepts as ultrafiltration, reverse osmosis, and inorganic adsorbents in process designs to reduce waste generation. In this report, which summarizes work done through April 1977, we will examine the concept of ultrafiltration, since inorganic adsorbents were discussed in a previous report [1].

Ultrafiltration, or the process of filtering with membranes, shows great promise in the area of waste treatment since membranes will treat and concentrate various process streams without pretreatment. This method could conceivably replace coagulation/sedimentation, evaporation, spray ponds, percolation, and solidification and storage tanks at nuclear fuel reprocessing plants.

Reverse osmosis/ultrafiltration consists of pressurizing (in the case of reverse osmosis, above the osmotic pressure) an aqueous solution and bringing it in contact with a semipermeable membrane. This semipermeable membrane rejects phosphates, radioactive species, and other dissolved or suspended solids. The solution that passes through the membrane is the

product or permeate. The concentration of solutes in the permeate is lower than that in the feed and, hence, the permeate tends to be very low in radioactivity, in the case of radioactive process streams, and low in dissolved solids. The solution that remains is enriched in solutes and is called the blowdown. The blowdown stream will have its volume reduced to the point that it can be treated by techniques such as evaporation and/or solidification.

Without needing pretreatment (some filtering may be required for reverse osmosis), reverse osmosis/ultrafiltration has the advantage of achieving a decontamination factor (DF) in the range of approximately 10^2 to 10^3 , and a volume reduction (VR) ratio in the range of 3:1 to 9:1 where,

$$DF = \frac{\text{activity of feed}}{\text{activity of product}} \text{ and}$$

$$VR = \frac{\text{volume of feed stream}}{\text{volume of concentrate blowdown stream.}}$$

However, using ultrafiltration on industrial type wastes, volume reductions in the range of 14:1 to 200:1 have been reported. Hence, similar results are expected on radioactive process streams.

In summary, then, reverse osmosis/ultrafiltration offers the following benefits in processing radioactive waste streams:

- High DF's with both alpha and gamma type contaminants in radioactive process streams.
- Significant (200:1) volume reductions without the addition of chemicals to the waste stream, thus decreasing or eliminating chemical sludge as a waste by-product.
- Much smaller water treatment facility, because replacement of a clarifier/

coagulation process with a reverse osmosis/ultrafiltration unit could reduce area by a factor of approximately 70:1.

In addition, ultrafiltration systems are both versatile and economical and will separate hard-to-handle process streams quickly, easily, and with minimal maintenance. Additional advantages include:

- Mechanical stability and chemical resistance, allowing operation on feeds over a wide range of temperatures, pH's, and pressures.
- Reliability over a long life, resulting in less downtime and lower maintenance cost.
- Low pumping energy and conservation process heat since no cooling of the feed solution is required.
- Separation of particles, colloids, and emulsions whose particulate diameters are as small as 10 to 50 Å compared to diameters of a few microns for conventional filtration. Separation of larger polymer molecules in the range of 10,000 to 50,000 mol wt can also be achieved.

Already, in the chemical process industries, ultrafiltration has proven to be a valuable tool in the separation of dissolved or suspended materials from various liquid streams. Some typical applications have been:

- Removal of oil and dirt from hot-alkali detergent solutions used to clean auto bodies and other metal items before painting or coating.

- Separation of stabilized oil/water emulsions, without any need for emulsion breakers.
- Recovery and concentration of paint pigment from electropainting rinse waters, or of textile size from aqueous effluents.
- Pretreatment of reverse osmosis or ion exchange feed streams to take out troublesome algae and other particulate and colloidal matter.
- Clear-water recovery from paper mill streams (such as black liquors, and rolling mill coolants) and from laundry dry streams.

Ultrafiltration favorably compares with such processes as distillation, centrifugation and vacuum evaporation. The latter techniques consume more energy than ultrafiltration does which can make them almost twice as costly.

Ultrafiltration is uniquely suited to treat problem waste streams from reprocessing plants. These waste streams include floor drain waste, which will be evaporated and/or solidified; hot shower waste, which will be sent to the sanitary sewer and consequently to spray ponds that could contaminate the environment; and laundry wastes, for which no treatment is presently defined.

The modular construction of membrane systems enables an ultrafiltration system to treat waste streams at the source of contamination. The modular units could be situated throughout the plant as an integral part of various processes thereby eliminating the need of a large, complex facility that has to treat a combined waste stream before it leaves the processing plant.

A membrane acts as a barrier to the flow of molecular or ionic species. Osmosis is defined as the spontaneous transport of a solvent from a dilute solution to a concentrated solution across an ideal semipermeable membrane, which impedes passage of solute but allows solvent flow. Solvent flow can be reduced by exerting pressure on the concentrated solution side of the membrane. At the osmotic pressure, equilibrium is reached and the amount of solvent which passes in each direction is equal. The osmotic pressure is a property of the solution only, provided the membrane is truly semipermeable. If the pressure is increased above the osmotic pressure on the concentrated solution side of the membrane, the flow reverses. Pure solvent will then pass from the concentrated solution into the less concentrated solution. This phenomenon is the basis of reverse osmosis treatment of water and wastewater.

Reverse osmosis is considered by some to be similar to the filtration process because both processes involve removing a liquid from a mixture by passing it through a device that retains the other components of the mixture. Because of this comparison, the reverse osmosis process has also been termed hyperfiltration. However, there are at least three important differences between reverse osmosis and filtration. First, the osmotic pressure, which is very small in ordinary filtration, plays an extremely important role in reverse osmosis. Second, filter cakes with low moisture are not feasible in reverse osmosis because the solution osmotic pressure increases with the removal of solvent. Third, filters separate mixtures primarily on the basis of size, whereas; the semipermeability of desalination, reverse-osmosis membranes is significantly dependent

upon such factors as: ionic radius and hydrated radius of solute species, solubility in membrane materials, effects of hydrogen bonding, and the polar nature of solute species.

Membrane ultrafiltration, as reverse osmosis, is dependent on a pressure driving force and a membrane that is permeable to some components in a liquid solution or mixture and impermeable to others. The two processes, ultrafiltration and reverse osmosis, differ because ultrafiltration is not impeded by osmotic pressure and can be effected at low pressure differences of 0.5-7 atm. Ultrafiltration is usually applicable for separation of solutes above a molecular weight of 500 amu, which have small osmotic pressures.

Reverse osmosis is applicable for materials of lower molecular weight. However, a continuum exists whereby osmotic pressure plays a larger role as the molecular size decreases at constant concentration by weight. The upper molecular weight limit for ultrafiltration is usually defined as 500,000 amu. Above that molecular weight size, separation occurs by conventional microporous filtration.

Both reverse osmosis and ultrafiltration membranes are subject to fouling which tends to reduce membrane flux and may also decrease membrane rejection. There are five distinct types of fouling that may occur in membrane processes. These are:

- Inorganic
- Ferric
- Particulate
- Proteinacious
- Organic

Of the five types of fouling that may occur, it is expected that the first three will occur in radioactive process streams.

Theory

Of the comparatively low-energy desalination processes using semipermeable membranes, only in the reverse osmosis process does the treatment interface require the transport of purified product water and not pollutants. Whereas conventional wastewater treatment processes require a multitude of steps to remove wastewater constituents, the reverse osmosis process requires fewer operations to perform a superior treatment.

If the wastewater contains less than 500 mg/liter of dissolved solids, it is necessary to only remove the suspended solids to make the water potable. The membrane process generally referred to as ultrafiltration can easily perform that type of separation. Ultrafiltration is a separation process using membrane filters whose average pore diameter is less than that of conventional filters. Typically, ultrafiltration units will readily pass water, solvents, and electrolytes, while retaining larger dissolved and suspended solids such as proteins or other organic and inorganic polymeric molecules. Ultrafiltration differs from reverse osmosis, which normally refers to separation of substances such as salts with molecular weights within one order of magnitude of the solvent in that the relatively high molecular weight of the retained species makes osmotic pressure differences across the membrane negligible so that low pressures are adequate to obtain high flux rates.

Standard reverse osmosis can be applied directly to wastewater, as demonstrated by Hauck and Sourirajan [10], to remove both suspended and dissolved solids in one operation. However, since the suspended solids tend to foul the membranes used in

the high-pressure operation, it might be desirable to use an ultrafiltration process to remove the suspended solids before going to reverse osmosis. Systems of this type (ultrafiltration preceding reverse osmosis) have been operated on cheese whey.

Low-pressure ultrafiltration is still in the preliminary stages of development as a unit process in municipal waste and water treatment. Recently, this membrane process has attracted attention as a promising method for treatment of radioactive wastewaters. Data on the separation or the removal of radioactive solutes are needed to evaluate the potential application of ultrafiltration systems in radioactive wastewater treatment. Ultrafiltration has the potential of making possible the economic treatment of at least some radioactively contaminated wastewaters.

Experimental

Experiments were performed on radioactive waste solutions received at the Waste Disposal (WD) Facility at Mound Laboratory to determine whether ultrafiltration would be a suitable method of removing radioactive contamination from this wastewater. These experiments were performed with Romicon hollow fiber ultrafiltration modules of different sizes, as shown in Table 1.

In all cases, the WD influent used in these experiments was prefiltered through a 1- μ filter. This was done to prevent plugging the small modules by the large amount of suspended solids (up to 200 mg/liter) found in these waste solutions. This should in no way affect the results obtained in these tests since anything removed by a 1- μ filter would certainly have been removed by any of the ultrafiltration modules.

Table 1 - ULTRAFILTRATION MODULES USED IN EXPERIMENTS

<u>Module Designation</u>	<u>Cutoff (mol wt)</u>	<u>Fiber i.d. (mils)</u>	<u>Effective Area (ft²)</u>
GM-80	80,000	20	2.5
XM-50	50,000	45	1.1
PM-30	30,000	43	1.0
PM-10	10,000	20	1.8
PM-5	5,000	20	1.8
AM-2	2,000	43	1.0

As a first step, several runs were made using WD influent and passing it through various modules. This influent is a mixture of alpha - contaminated waste from showers, laboratory drains, janitorial work, decontamination activities, and the laundry, all from plutonium processing areas at Mound Facility.

As shown in Table 2, rejection of radioactive contamination by all the modules was high (90 to 97.7%). The variation in rejection from run to run is probably accounted for by the variation in content of the WD influent from day to day and by the amount of complexing and polymerization that occurs. It should be noted here that for each run a separate sample from a common stock solution was passed through each module. No solution was passed through more than one module. At the conclusion of each run, the stock solution was discarded and a fresh batch was obtained for the next run.

The rejection of conductivity was found to be very low in most cases. This was not unexpected since the modules have a relatively high molecular weight cutoff and cannot be expected to remove much ionic material unless it is greatly affected by complexing or polymerization.

The next step was to obtain samples of two of the components of the total WD influent and run them through the modules. First, alpha-contaminated laundry waste was run and secondly, a sample of the decontamination water from the PP Building was run.

As shown in Tables 3 and 4, radioactivity and conductivity were more completely removed from the alpha-contaminated laundry wastewater than from the PP Building decontamination water because most of the material in the laundry wastewater was in a colloidal or complexed form whereas the decontamination water contained a much higher percentage of ionic material.

Next, several runs were made using WD influent plus varying concentrations of additives, such as cationic polyelectrolytes, anionic polyelectrolytes, non-ionic polyelectrolytes, EDTA, sodium phosphate, laundry detergent, and citric acid. All of these samples were processed with the same module (PM-5) at a pH of 7.5 to 7.8. The results of these experiments showed that none of the additives had any noticeable effect on the rejection of radioactivity or conductivity in any of the influent solutions used.

Table 2 - REJECTION OF RADIOACTIVITY^a BY THE ULTRAFILTRATION MODULES

Run No.	Initial Levels	Levels After 1 μ -Filter	Levels After GM-80	Levels After XM-50	Levels After PM-30	Levels After PM-10	Levels After AM-2
1	2200	205[90.7%]	-	96[95.6%]	60.5[97.3%]	50.9[97.7%]	-
2	133.6	68.5[48.7%]	10.2[92.4%]	9.5[92.9%]	7.1[94.7%]	-	-
3	316	160[49.4%]	31.6[90.0%]	34[89.2%]	21.1[93.3%]	14.4[95.4%]	10.4[96.7%]

^aAlpha radiation levels are given in dis/min/ml.

Percent rejection is shown in brackets [].

pH of all solutions ranged from 7.5 to 8.5.

Table 3 - REJECTION OF RADIOACTIVITY^a AND CONDUCTIVITY FROM LAUNDRY WASTE SOLUTION^b

<u>Treatment</u>	<u>Alpha Radiation (dis/min/ml)</u>	<u>Conductivity (μmhos)</u>
None	50	1700
1- μ Filter	13[74%]	1700[0%]
CM-80	0.7[98.6%]	1610[5.3%]
XM-50	1.0[98.0%]	1300[23.5%]
PM-30	2.5[95.0%]	850[50%]
PM-10	0.1[99.8%]	690[59.4%]
AM-2	<0.1[>99.8%]	400[76.4%]

^aPercent rejection in brackets [].

^bSolution pH = 8.3.

Table 4 - REJECTION OF RADIOACTIVITY^a AND CONDUCTIVITY FROM DECONTAMINATION WATER^b

<u>Treatment</u>	<u>Alpha Radiation (dis/min/ml)</u>	<u>Conductivity (μmhos)</u>
None	1440	1400
1-μ Filter	400 [71.4%]	1400 [0%]
GM-80	229 [84.1%]	1250 [10.7%]
XM-50	211 [85.3%]	1300 [7.1%]
PM-30	210 [85.4%]	1300 [7.1%]
PM-10	166 [88.5%]	1300 [7.1%]

^aPercent rejection in brackets [%].

^bSolution pH = 7.3.

Table 5 - AVERAGE FLUX RATES OF THE ULTRAFILTRATION MODULES

<u>Column Size</u>	<u>Flux Rate (ml/min/ft²)</u>
AM-2	65
PM-5	111
PM-10	135
PM-30	171
XM-50	184
GM-80	250

In the final test, the pH of the WD influent was raised in stages from 8 to 11. There seemed to be an increase in the rejection of radioactivity as the pH increased; but at the present time, there is insufficient data to verify that hypothesis. Also, precipitation of insoluble hydroxides occurs as the pH approaches 9.5 to 10.

All of the experiments were fed through the modules at an inlet pressure of 20 to 25 psig, and the blowdown rate was 2400 to 3300 ml/min. The flux rate varied according to the molecular weight cutoff of the modules used, and an average flux rate for each module is shown in Table 5.

Summary

A series of experiments were performed on WD influent using Romicon hollow fiber ultrafiltration modules with molecular weight cutoffs ranging from 2,000 - 80,000. The rejection of conductivity was low in most cases. The rejection of radioactivity ranged from 90 - 98%, depending on the membrane type and on the feed concentration. Typical product activity ranged from 7 to 100 dis/min/ml of alpha radiation. Since feed concentrations changed daily, results were not consistent. In some cases, a slight problem of leakage across the headers of the module added to the inconsistency.

Experiments were also performed on alpha-contaminated laundry wastewater. Results ranged from 98 to greater than 99.8%, depending on the membrane type. This yielded a product concentration of less than 0.1 dis/min/ml of alpha radiation. Tests on PP-Building decontamination water yielded rejections of 85 to 88% alpha radiation depending on the membrane type.

These experiments show that the ability to remove radioactivity by membrane is a function of the contents of the waste stream because the radioactivity in the wastewater is in various forms: ionic, polymeric, colloidal, and absorbed onto suspended solids. Although removal of suspended or colloidal material is very high, removal of ionic material is not as effective. Alpha-contaminated laundry wastewater proved to be the easiest to decontaminate, whereas the low-level PP-Building decontamination water proved to be the most difficult to decontaminate. Decontamination of the WD influent, a combined waste stream, varied considerably from day to day because of its constantly changing makeup.

The WD influent was also treated with various substances, such as polyelectrolytes, complexing agents, and coagulants, to determine if these additives would aid in the removal of radioactive material from the various wastewaters by complexing the ionic species. At the present time, none of the additives evaluated has had much effect; but experiments are continuing.

As a general conclusion, then, some solutions decontaminate better than others. In all cases, greater than 90% rejection of radioactivity was obtained; and in some cases, greater than 99% rejection was achieved. Also, in all cases, rejection of suspended solids and colloid material was nearly complete, resulting in a clear product solution.

Bibliography

1. J. W. Koenst and W. R. Herald, Evaluation of New Macroporous Resins for Removal of Uranium and Plutonium from

- Waste Streams, MLM- 2320 (Dec. 20, 1976) 8 pp.
2. J. W. Koenst and D. E. Blane, Evaluation of Coagulant Aids at High pH, MLM-2240 (April 30, 1976) 7 pp.
3. J. W. Koenst and D. E. Blane, "Chemical Coagulation of Radioactive Wastes at High pH," MLM-2263 (OP), presented at the 3rd ERDA Environmental Protection Conference, Chicago, Ill., September 23-26, 1975.
4. J. W. Koenst et al., Wastewater Renovation Using Semipermeable Membranes, Final Report, Office of Saline Water, Department of Interior (1974).
5. J. W. Koenst et al., Reverse Osmosis Sand Logs for Sea Water, Final Report, Office of Saline Water, Department of Interior (1974).
6. J. W. Koenst et al., "The Design of a Reverse Osmosis Membrane Assembly Segment Suitable for Seawater Desalting," presented at the 3rd OSW Conference on Reverse Osmosis, Las Vegas, Nevada, 1972.
7. J. W. Koenst et al. "The Treatment of PWR Nuclear Process Wastes Using Membrane Systems," presented at the Purdue Industrial Waste Conference, 1973.
8. J. W. Koenst et al. The Design of a Reverse Osmosis Membrane Assembly Segment Suitable for Seawater Desalting, Final Report, Office of Saline Water, Department of Interior (1971).
9. A. R. Hauck and S. Sourirajan, "Performance of Porous Cellulose Acetate Membranes for the Reverse Osmosis Treatment of Hard and Wastewaters," Environ. Sci. and Technol., 3, 1269 (1969).
10. A. J. Wiley, G. A. Dubey, J. M. Holderby and A. C. F. Ammerlaan, "Concentration of Dilute Pulping Wastes by Reverse Osmosis and Ultra Filtration," Water Pollut. Control Fed., 42:8, part 2, R279 (1970).
11. A. J. Wiley, A. C. F. Ammerlaan, and G. A. Dubey, "Application of Reverse Osmosis to Processing of Spent Liquors from the Pulp and Paper Industry," TAPPI, 50:9, 455 (1967).
12. A. C. F. Ammerlaan and A. J. Wiley, "The Engineering Evaluation of Reverse Osmosis as a Method of Processing Spent Liquors of the Prepared Paper Industry," presented at the AIChE Meeting, New Orleans, La., Mar. 1967.
13. U. Merten and D. T. Brag, "Reverse Osmosis for Water Reclamation," Proceedings for the 3rd International Conference on Water Pollution Research, abstracted in J. Water Pollut Control Fed., 38 397 (1966).
14. P. J. Bennett, S. Narayarian, and E. Hindin, "Removal of Organic Refractories by Reverse Osmosis," Proceedings of the 23rd Industrial Waste Conference, Purdue Univ., Ext. Ser. 132, 1968, p. 1000.
15. E. Hinden, P. J. Bennett, and S. S. Narayarian, "Organic Compounds Removed by Reverse Osmosis," Water and Sewage Works, 116 466 (1969).
16. E. Hinden and P. J. Bennett, "Water Reclamation by Reverse Osmosis," Water and Sewage Works, 116 66 (1969).

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