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S. Prabhakar[a]; B. M. Misra[a]; S. B. Roy[b]; A. M. Meghal[b]; T. K. Mukherjee[b]
[a] DESALINATION DIVISION BHABHA ATOMIC RESEARCH CENTRE, BOMBAY, INDIA [b] URANIUM & RARE EARTHS DIVISION BHABHA ATOMIC RESEARCH CENTRE, BOMBAY, INDIA

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Reverse Osmosis Separation of Radiocontaminants from Ammonium Diuranate Effluents

S. PRABHAKAR and B. M. MISRA
DESALINATION DIVISION

S. B. ROY, A. M. MEGHAL, and T. K. MUKHERJEE
URANIUM & RARE EARTHS DIVISION

BHABHA ATOMIC RESEARCH CENTRE
BOMBAY 400085, INDIA

ABSTRACT

A reverse osmosis process has been found to be effective for the separation of radiocontaminants from ammonium diuranate effluents in a uranium metal plant. Pilot-plant-scale experiments were conducted using cellulosic membranes in a plate module system and actual plant effluents containing more than about 40,000 ppm of ammonium and nitrate species and having radiocontaminants corresponding to specific activities of about 10^{-3} Ci/m^3 beta/gamma emitters. The results indicated that more than 95% by volume of the treated effluents were within disposal limits, while the remaining contained the concentrate, which can be treated for possible containment.

INTRODUCTION

Reverse osmosis (RO) and ultrafiltration (UF) are two pressure-driven membrane separation processes which find increasing application in the nuclear industry (1). These processes are currently being used in the treatment of radioactive laundry and laboratory effluents (2). The efficacy of cellulose-acetate-based membrane systems for the decontamination of low and intermediate level radioactive effluents was demonstrated with volume reduction factors of about 20 and decontamination factors of about 20 (3). Parametric studies carried out by Hsiue et al. (4) and Chen et al.

TABLE 1
Characteristics of the Effluents

Description	Raffinate filtrate	Ammonium diuranate filtrate
α-Activity (Ci/m^3)	10^{-6} to 10^{-5}	10^{-6} to 10^{-5}
β-Activity (Ci/m^3)	10^{-6} to 10^{-5}	10^{-4} to 10^{-3}
Uranium concentration (mg/L)	<100	<100

(5) with respect to uranium fluoride effluents (UFE) using reverse osmosis have clearly indicated the potential application of the process. Laboratory studies on uranyl nitrate solutions have also pointed out that cellulose acetate membranes can efficiently separate uranium species from its solutions (6). During the processing of natural uranium by the ammonium dicarbonate precipitation route, two main streams of liquid effluents are generated with characteristics as given in Table 1. Uranium and its β-γ emitting daughter products are the main radionuclides present in the effluent streams.

The pure uranyl nitrate solution obtained after extraction from the mother liquor is treated with ammonia, and the ammonium diuranate (ADU) precipitates:

$$2UO_2(NO_3)_2(l) + 6NH_3(g) + 3H_2O(l) \rightarrow (NH_4)_2U_2O_7(s) + 4NH_4NO_3(l) \quad (1)$$

After filtration of the ADU precipitate, the solution (ADUF) contains radiocontaminants associated with uranium and its daughter products, and significant quantities of ammonium nitrate. In this context, reverse osmosis offers a means for decontaminating the radioactive effluents by concentrating the activity in smaller volumes and making the larger volumes suitable for direct disposal. Because RO is primarily a rate-governed process, the holdup volume is less. In addition, the possibility of recovering commercially useful ammonium nitrate exists by using a second-stage reverse osmosis. Therefore, pilot-scale experiments were conducted to assess the suitability of the process for large-scale adoption.

METHODS AND MATERIALS

The experimental scheme is shown in Fig. 1. The supernatant portion of the ammonium diuranate (ADU) filtrate was transferred to the feed tank after sufficient cooling. Chemicals and sulfuric acid were manually added based on the experimental conditions. They were thoroughly mixed

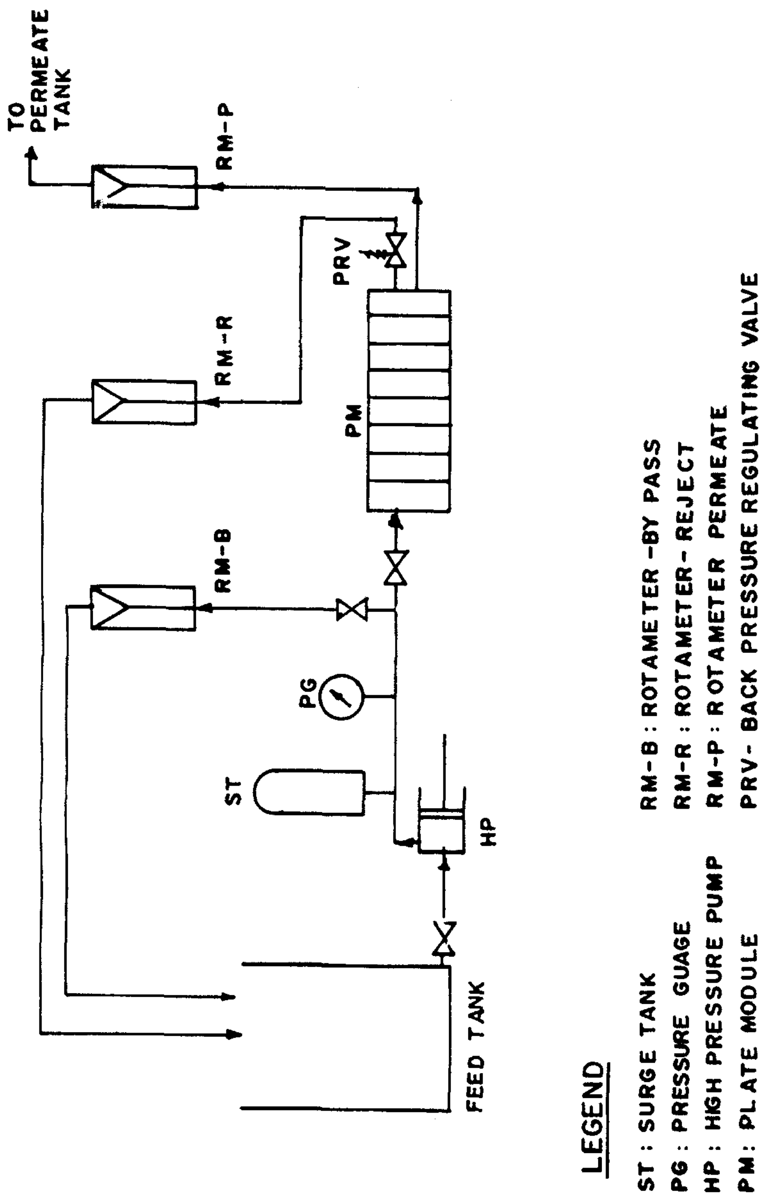

FIG. 1 Experimental setup with plate module.

by recirculating the contents of the tank using the feed pump and a bypass provision. The experiment was conducted in a batch mode. The feed thus prepared was pumped at high pressure through the module or modules connected in series. The pressure was adjusted using a backpressure regulating valve (PRV). The permeate streams were separately collected, and the concentrate stream was sent back to the feed tank. Rotameters of the requisite ranges were connected on-line in the concentrate and permeate streams to help regulate the flow rates. Manual flow measurements were made periodically for the more precise data required for performance analysis. The time of collection of the sample was so chosen as to keep the measurement error less than 2%. Every set of flow data was recorded along with the feed temperature to enable normalization of the results for analysis. Three modules containing cellulose acetate membranes with varying performance characteristics were connected in series to assess the relative performance under near-identical conditions. The feed rate was between 2.5 to 3 L/min. Since the permeate rates were much lower, the average concentrations of the feed in the three modules were within narrow statistical limits. The pressure drops were also insignificant. These modules were connected in increasing order of permeate rates, so that the possible error was minimized. Other experiments to assess the reverse osmosis characteristics were made with individual modules.

During the course of the experimental work, three sets of cellulose acetate membranes were prepared in-house and annealed at three different temperatures (75 to 81°C) in order to determine distinct membrane characteristics.

The performance characteristics of the modules used during the experiments are given in Table 2.

The uranium analysis was carried out using AAS, and radioelements were estimated as gross β-γ and α activities using standard counters. Necessary precautions were taken with respect to counting time, sample volume, etc. to minimize statistical errors. Background counts of the

TABLE 2
Standard Performance Characteristics of Reverse Osmosis Modules Used in Studies [test solution: sodium chloride (2000 ppm)]

	Module type		
	CA1	CA2	CA3
Membrane constant (m/s bar × 10^8)	7.23	16.78	28.92
Solute rejection (%)	92.5	88.0	82.5
Permeate flux (m/d)	0.235	0.55	0.95
Operating pressure (bars)	40	40	40

counter were measured periodically and accounted for before the gross activities were estimated.

The experiments were conducted by recirculating the concentrate. Various performance indicators, such as volume reduction factor (*VRF*), decontamination factor (*DF*), percent solute rejection (*SR*), percent recovery (*R*), etc., were calculated as follows.

$$VRF = \frac{\text{initial volume of the feed in the tank}}{\text{volume of the concentrate left in the tank after the experiment}}$$

$$DF = \frac{\text{initial specific activity}}{\text{permeate specific activity}}$$

$$SR = \left[\frac{(\text{feed concentration of tds}) - (\text{permeate concentration of tds})}{\text{initial concentration of tds}}\right] \times 100$$

tds corresponds to total dissolved solids ‡

$$R = \left(1 - \frac{1}{VRF}\right) \times 100$$

RESULTS AND DISCUSSION

Theoretical Considerations

The production of ammonium diuranate (ADU) from pure uranyl nitrate solution generates ammonium nitrate as a by-product. The ADU filtrate contained about 40,000 ppm ammonium nitrate besides small amounts of dissolved and suspended uranium and its daughter products, corresponding to a mother liquor concentration of about 0.2 M uranyl nitrate. Economic treatment and safe disposal of the effluent demands a decontamination factor of at least 10 with a volume reduction factor of more than 10. This corresponds to a minimum solute rejection of 90% at more than 90% water recovery for reverse osmosis. At first glance, reverse osmosis as a possible process to meet such demands, particularly at higher feed concentrations, does not seem reasonable. However, our laboratory studies indicated that both ammonium and nitrate species are poorly rejected by cellulose acetate reverse osmosis membranes, as seen in Table 3, compared to sodium chloride. The solute rejection of ammonium nitrate was also found to decrease with increasing concentration.

The permeate flux (N_B) in reverse osmosis is given by

$$N_B = A[P - (\pi_{X_{A2}} - \pi_{X_{A3}})] \tag{2}$$

TABLE 3
Reverse Osmosis Performance of Membranes for Ammonium Nitrate[a]

Membrane type	Pressure (bar)	Sodium chloride SR (%)	Sodium chloride Flux (m/d)	Ammonium nitrate SR (%)	Ammonium nitrate Flux (m/d)
Cellulose acetate (high flux)	40	81.4	0.98	32.9	1.1
Cellulose acetate (low flux)	40	90.5	0.42	43.0	0.5
Polyamide	40	93.5	0.86	80.0	0.9

[a] Feed flow rate: 2.5 L/min. Membrane area: 0.74 m^2. Concentration of NaCl ≈ 2000 ppm. NH_4NO_3 ≈ 10,000 ppm.

where A = membrane constant (m/s·bar)
P = operating pressure (bar)
$\pi_{X_{A2}}, \pi_{X_{A3}}$ = osmotic pressure of boundary layer and permeate streams with solute mole fractions X_{A2} and X_{A3}, respectively

For a solute with high rejection, the permeate concentration would tend to zero. Thus:

$$X_{A3} \rightarrow 0 \quad \text{and} \quad \pi_{X_{A2}} - \pi_{X_{A3}} \cong \pi_{X_{A2}} \tag{3}$$

As the recovery increases, the bulk solute concentration and hence X_{A2} increase. The recovery would then be limited by the value of $\pi_{X_{A2}}$ approaching the operating pressure P.

On the other hand, for a poorly rejected solute like ammonium nitrate, the permeate concentration of solute would be significant, and hence

$$\pi_{X_{A2}} - \pi_{X_{A3}} < \pi_{X_{A2}} \tag{4}$$

Since the permeate concentration is considerable, the rise in the bulk concentration of the feed (X_{A1}) as well as the boundary layer concentration (X_{A2}) with recovery would be less. Moreover, the solute rejection decreases with increasing concentration, thereby always keeping the term ($X_{A2} - X_{A3}$) much less than P. Under these conditions, one can theoretically go up to a concentration where the osmotic pressure of the feed would approach the operating pressure, subject to the limitations of scaling and fouling. Accordingly, the volume reduction factor or recovery would not be a critical design step as long as the permeate quality is maintained within the desired limits. The high solubility of ammonium nitrate and the absence of scaling components make it theoretically feasible to attain high recoveries. If radioactive contaminants are selectively removed, then it is possible to use RO for the decontamination of ADU effluents despite the high concentrations of the total dissolved solids.

Decontamination Studies

The uranyl concentration in the feed was less and the permeate streams contained less than the dischargeable limits in all experiments. Therefore, no attempt was made to analyze the experimental data or its implications with respect to uranium. The results were therefore analyzed with respect to the radiocontaminants which were critical constituents for the environmental discharge of the treated effluents.

Performance of Cellulose Acetate Membranes

As described in the Experimental Section, three modules with distinct performance characteristics were connected in series in order to collect data under identical conditions. The membrane performance as measured in terms of the overall decontamination factors with reference to the corresponding feed specific activities at different points of time is given in Table 4.

CA-1 performs better than CA-2, which in turn is better than CA-3 with respect to decontamination. The permeate rates, on the other hand, are highest for CA-3 and lowest for CA-1. As reported in Table 2, the membrane constants as well as the standard solute rejections of these membranes under reverse osmosis conditions indicate that the decontamination mechanism may be akin to a reverse osmosis solute rejection mechanism.

The *VRF* increases with the progress of the experiment as more permeate is withdrawn from the fixed volume of the feed, which is concen-

TABLE 4
Overall Decontamination and Volume Reduction Factors of CA Membranes in Reverse Osmosis (initial feed volume: 408.6 L)

Feed specific activity	Permeate volume (L)			*VRF*	Overall decontamination factors			
	CA1	CA2	CA3		CA1	CA2	CA3	Combined
1.80	—	—	—	1	55.4	41.7	31.9	45.1
2.50	13.5	66	111	1.9	42.3	31.5	23.7	33.0
2.93	25.5	106	201	5.0	26.2	36.1	18.8	27.0
9.93	29.0	123	244	32.4	17.9	14.8	22.0	18.6

trated. It can be seen that the overall decontamination factor decreases with increasing *VRF*. This imposes a design condition whereby one has to choose a *VRF* corresponding to a fixed *DF*. The fixation of *DF* is governed by the feed specific activities and the allowable limits of the dischargeable streams.

Figure 2 presents the rejection of ammonium nitrate as a function of its concentration for all three membranes. The ammonium nitrate rejection is in the order CA1 > CA2 > CA3. However, the rejection drops more rapidly with increasing concentration for CA1. This behavior is due to the relatively high solute build up at the membrane interface for the high rejecting membrane, resulting in more solute passage. It appears that with still higher ammonium nitrate concentrations, the rejection might be identical for all the membranes. This suggests the suitability of using moderately porous membranes for such systems. Of the three membranes studied, CA2 appears to have an average *DF* of about 25, corresponding to a *VRF* of 15, which is reasonable for large-scale adoption. The radiocontaminants of the solution are essentially due to the daughter products of uranium, such as thorium, protoactinium, etc., which are multivalent cations in solution. The addition of polyelectrolytes leads to sequestering of these

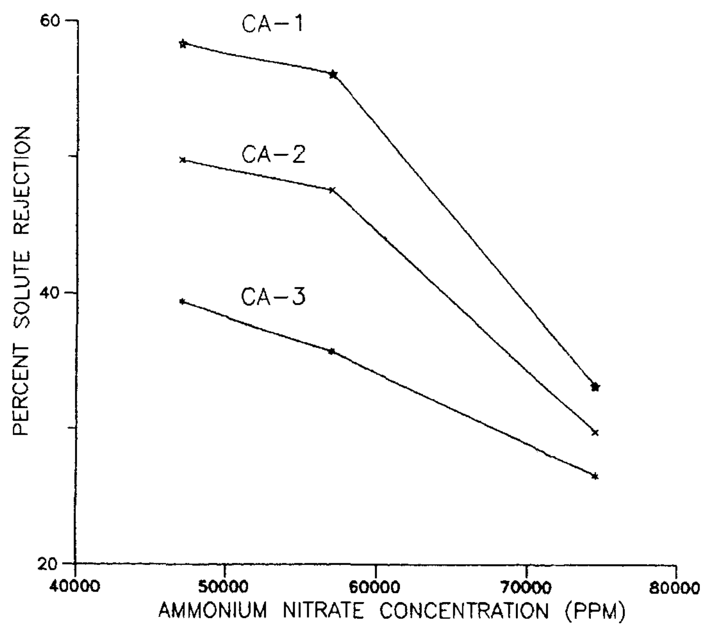

FIG. 2 Behavior of ammonium nitrate solution under reverse osmosis conditions.

TABLE 5
Performance of CA Membranes with FLOCON-100 (Pfizer) (initial feed volume: 387 L)

Feed sp. act. (10^{-3} Ci/m^3)	*VRF*	*DF*	Perm. sp. act. (10^{-6} Ci/m^3)	Perm. rate (L/min)		
				CA1	CA2	CA3
1.06	1	198	5.34	0.08	0.26	0.45
1.67	2.67	186	6.14	0.064	0.208	0.398
3.21	5.23	173	7.11	0.054	0.172	0.372
6.00	7.60	167	7.53	0.040	0.140	0.312
18.77	51.60	160	7.96	0.030	0.096	0.234

active species. Polyelectrolytes, basically high molecular weight compounds, do not pass through the membranes. Table 5 shows that the decontamination factor improved significantly with the use of polyelectrolytes (FLOCON-100, Pfizer).

It is therefore suggested that in the presence of highly inactive ammonium nitrate concentrations, it may be preferable to use a moderately rejecting membrane which has a *DF* of around 100 and optimum permeate flux rates. Nanofiltration membranes in the presence of polyelectrolytes could possibly provide still better performance, and studies of these are in progress in our laboratory.

CONCLUSIONS

Experimental studies have shown that:

1. Reverse osmosis with cellulosic membranes can be used for the decontamination of radioactive streams containing high concentrations of ammonium nitrate.
2. The addition of sequestering chemicals leads to the required decontamination factors and high volume reduction factors.

Further studies are in progress to establish the design criteria for similar systems.

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