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Studies on the Reverse Osmosis Treatment of Uranyl Nitrate Solution

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Abstract

The aqueous effluent generated in uranium processing, particularly in the nuclear fuel fabrication step, contains mainly uranium nitrate. This requires treatment before discharge into the environment to meet stringent standards. This paper presents the performance of cellulose acetate membranes with regard to rejection of uranium under reverse osmotic conditions for feed concentrations up to 200 mg/L of uranium, which corresponds to the levels normally prevalent in the effluents. The use of additives like the disodium salt of ethylenediaminetetraacetic acid and sodium sulfate for the improvement of reverse osmosis performance of the above membranes was also investigated. In the light of the experimental results, the suitability of reverse osmosis for the decontamination of uranium effluents is discussed.

INTRODUCTION

Membrane processes, particularly reverse osmosis (RO) and ultrafiltration (UF), have been found to be very useful in recent years in the treatment of aqueous effluents (*1*) in addition to their predominant role in desalination (*2*) and the food processing industries (*3*). Reverse osmosis, an inherently simple operation with built-in flexibility for adopting a combination of membranes and module configurations, has good potential for various separation applications in the process industry. Because it is an ambient temperature rate-governed process, it is ideally suited for adoption in the nuclear industry, particularly for effluent treatment.

Uranium processing, which represents the first phase of the nuclear fuel cycle, generates effluents containing uranyl nitrate, ammonium diuranate, ammonium fluoride, etc. The major constituent is uranyl nitrate with con-

centrations ranging up to 200 mg/L. The effluents require treatment before discharge in order to meet environmental standards.

The present practice involves conditioning of the effluent to pH 9 followed by passing it through a lime column to remove the uranium species. The process is costly due to the requirement for chemicals and because the sorbed uranium cannot be easily recovered. The membrane processes are particularly attractive because they can divide the initial effluent into two streams: the permeate stream with low concentrations of uranium, suitable for discharge, and the concentrated stream containing sufficiently higher concentrations of uranium, permitting economic recovery. In addition, the reverse osmosis process can bring down the concentration of nitrates, unlike the lime treatment process where only the uranyl species is adsorbed to the permissible level of discharge and a denitrification step may have to be adopted. A complexation–ultrafiltration technique (*4*) is currently being studied for the concentration or decontamination of heavy metal ions. To understand the separation characteristics of uranyl nitrate species under the conditions of reverse osmosis and hence to extend the system to decontamination applications, experiments were conducted using cellulose acetate membranes with varying porosities.

EXPERIMENTAL

Cellulose acetate membranes were prepared in-house by following a method described elsewhere (*5*). Membranes of varying performance characteristics were prepared by annealing at 83, 75, 70, and 65°C (designated as CA-1, CA-2, CA-3, and CA-4, respectively). Unannealed membranes were also used and were designated as CA-5. Sheet membranes were assembled in a 4-plate module system. Each module accommodated 6 sheets of membrane with an effective membrane area of 0.244 m^2. Analar grade chemicals were used for the experiments, and the solutions were prepared in demineralized water.

A schematic diagram of the experimental system is shown in Fig. 1. The feed was initially prepared in a 100-L capacity tank. A high-pressure triplex pump was used to circulate the solution through the modules. The pressure was adjusted by using back-pressure regulators (BPR) for the individual modules. The flow rates were maintained at equal levels of about 5 L/min by appropriate adjustment of the valve positions. The permeate flow rates and reject flow rates were physically measured by using a stopwatch and calibrated vessels. The time and volume measurement were so chosen as to keep the measurement errors to less than 1%. The pressures were maintained at 40 ± 1 bars. Due to the inherently different fluxes of the membranes, minor variations were observed in the recovery of the modules. However, it was found that these variations did not affect the performance of the modules to any significant extent. The pHs of the solutions

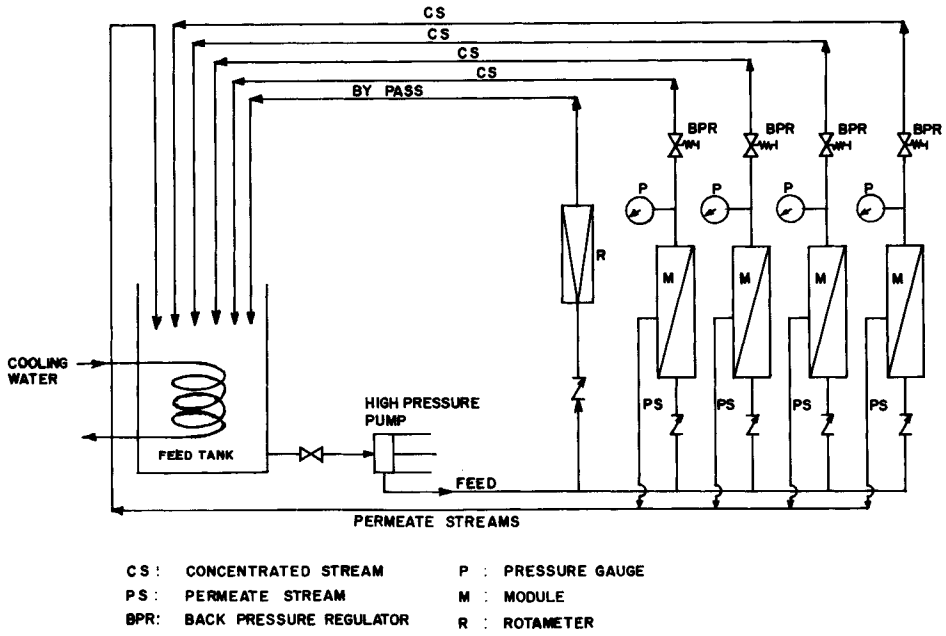

FIG. 1. Schematic diagram of experimental setup.

were always within the range of 4 to 5.5, in keeping with the operating pH range of cellulose acetate membranes.

The concentrated streams and the permeate streams were led to the feed tank itself so as to maintain the same overall concentration throughout the course of a particular measurement. Measurements were made after allowing the membranes to stabilize. Normally, one batch of experiments lasted about 2 h. Feed was cooled by using chilled water to maintain a constant temperature. As the same feed was used for all the modules simultaneously, the comparisons can be considered to be under identical conditions.

Uranium concentrations were measured by using Arsenazo III complexation and observing the absorption at 550 nm, following the method of Gharat and Murthy (*6*). Concentrated samples were diluted and then measurements were made.

RESULTS AND DISCUSSIONS

Characterization of the Membranes

Basic characteristics of the membranes determined are pure water permeability and membrane constant and their reverse osmosis perform-

ance; namely, percent solute rejection and water flux at 4 MPa pressure for a 3000 mg/L sodium chloride solution.

The above parameters are defined as

$$A = PWP/(S \cdot 3600 \cdot P) \quad (1)$$

$$SR = (1 - C_P/C_F) \cdot 100 \quad (2)$$

$$N_B = 1.44 \cdot E + 04 \cdot PR/S \quad (3)$$

where A = membrane constant (cm/s·atm)
PWP = pure water permeability (cm^3/h)
S = membrane area (cm^2)
P = applied pressure (atm)
SR = percent solute rejection
C_P, C_F = permeate and feed solute concentrations
N_B = water flux (m/d)
PR = permeate rate (L/min)

As given in Table 1, the membranes used exhibit a maximum of 94% solute rejection for CA-1 and a minimum of 10% for CA-5, while the permeate water fluxes ranged from 0.70 to 4.70 m/d. Membrane constants are expressed in cm/s · atm in order to enable comparison with membranes reported in the literature. The average pore sizes of the membranes were estimated to correspond to their membrane constants as reported in our earlier studies (*7*).

TABLE 1
Reverse Osmosis Performance of the Membranes[a]

Membrane type	Percent solute rejection	Permeate water flux (m/d)	Membrane constant (cm/s·atm) × 10^5	Average pore radius (Å)
CA-1	94.0	0.70	2.170	18.8
CA-2	84.0	1.36	4.196	21.9
CA-3	40.0	2.16	6.728	25.7
CA-4	25.3	2.77	8.540	28.5
CA-5	10.0	4.70	14.071	36.9

[a]Feed concentration = 3000 mg/L NaCl, 29°C, membrane area = 0.244 m^2, operating pressure = 4 MPa.

Effect of Feed Concentration on Membrane Performance

Uranyl nitrate solutions with uranium concentrations ranging from about 20 to 200 mg/L were used as feed, and the RO performance was measured in terms of percent solute rejection and permeate water flux. The measurements for all the modules were made at stabilized and identical conditions.

The variation of the percent solute rejection as a function of the feed concentration is shown in Fig. 2. The percent solute rejection of uranium has been found to increase with increasing feed concentration for all the membranes. Predictably, the higher porosity membranes exhibited lower

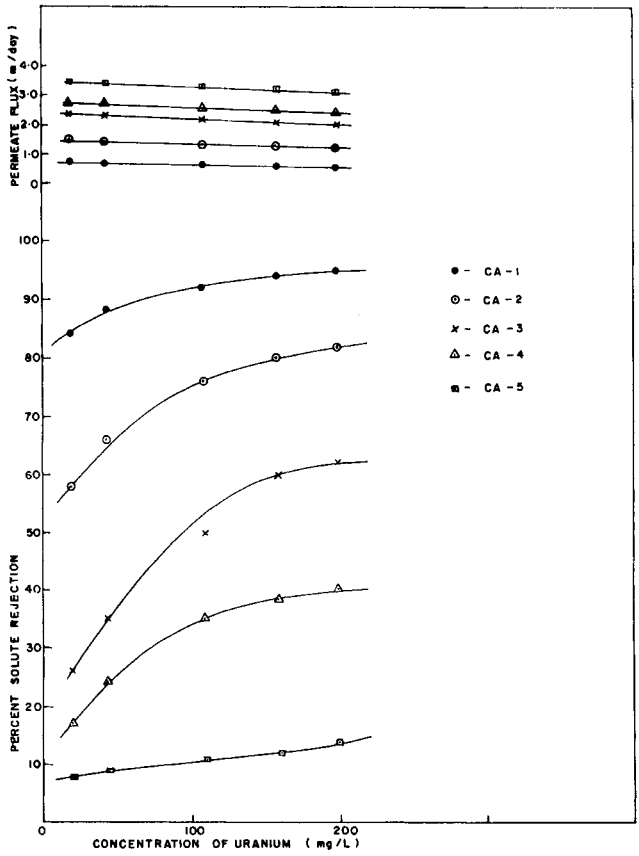

FIG. 2. Variation of solute rejection and permeate flux with feed concentration for different types of membranes.

solute rejection and higher permeate fluxes for the same concentrations. The rate of increase in solute rejection with feed concentration was found to be maximum for membranes with an average porosity of about 25 Å, as seen in Fig. 3. The increase in the case of tighter membranes was nevertheless significant. For porous membranes, the increase was only marginal.

The change in solute rejection with feed concentration is somewhat unique in the case of uranyl species. Similar observations for higher concentrations of mixed effluent streams were reported by Ging Ho Hsiue et al. (*8*) for FT-30 membranes. In reverse osmosis, one normally encounters decreasing solute rejection with increasing feed concentrations. For extremely dilute solutions, a maximum occurs in the percent solute rejection

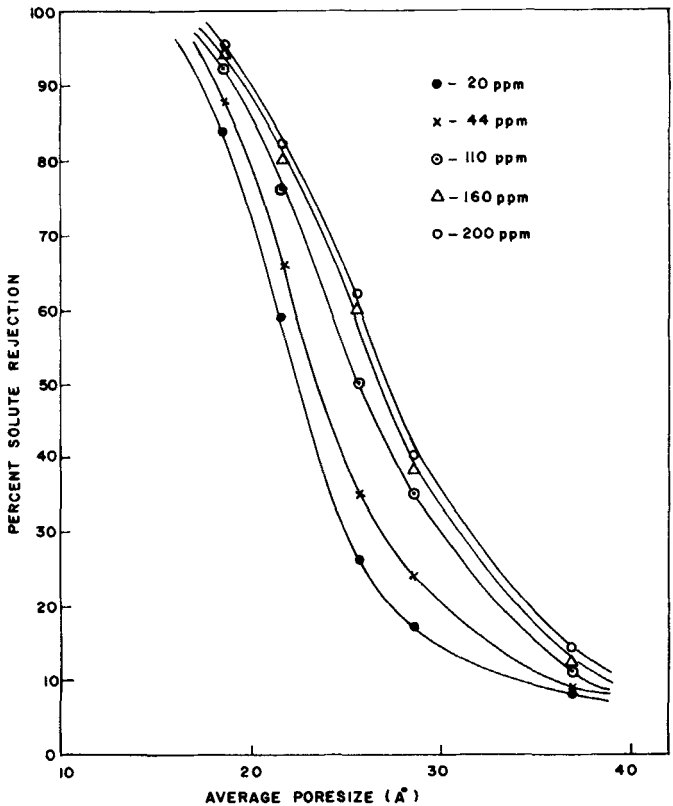

FIG. 3. Variation of percent solute rejection of uranyl nitrate with pore size of CA membranes for various feed concentrations.

versus feed concentration behavior, marking the dominance of solution properties over the membrane properties of reverse osmosis separation (*9*).

Water transport across the membrane under reverse osmosis is governed by the equation (*10*)

$$N_B = A(P - \Pi_{xA2} + \Pi_{xA3}) \tag{4}$$

where Π_{xA2} and Π_{xA3} refer to the osmotic pressures of the boundary layer and permeate solutions, respectively. The solute flux (N_A) across the membrane is described by

$$N_A = (D_{AM}/K\delta)(C_{A2} - C_{A3}) \tag{5}$$

where $(D_{AM}/K\delta)$ is the solute transport parameter, and C_{A2} and C_{A3} refer to the concentrations of the boundary and permeate solutions.

With increasing feed concentration, C_{A2} and, hence, Π_{xA2} increase. On the other hand, the increase in C_{A3} and Π_{xA3} is marginal. For a given applied pressure, N_B decreases and N_A increases with increasing feed concentration. Thus the permeate concentration is a direct function of N_A and an inverse function of N_B. Solute rejection, as per the definition given earlier, is directly dependent on the solute flux. Hence, a decrease in solute rejection with increasing feed concentration is expected. Contrary observations lead us to believe that the state of uranium species in the dissolved phase may change with increasing concentration, probably due to the formation of anionic complexes or the aggregation of uranium species. As can be seen from our earlier papers (*7*, *11*) and that of Matsuda and Kamizawa (*12*), membrane behavior is different beyond a pore size of about 25 Å. Perhaps the preferential sorption of water on the membrane surface is not controlling for larger pore sizes. The observations clearly indicate that any change in conditions for the improvement of membrane performance under reverse osmosis conditions should be attempted up to an average porosity of about 25 Å and not above. The variation of the permeate water flux for the above membranes is shown in Fig. 2, and it is in keeping with the general observations encountered in reverse osmosis.

Effect of Additives on U Separation by Reverse Osmosis

Since the membranes exhibit relatively poor solute rejections at lower concentrations, direct RO processing sometimes may not yield dischargeable concentrations even after two stages. For instance, an effluent concentration of 200 mg/L uranium operating at 90% recovery would lead to a permeate concentration of about 20 mg/L. A second stage RO unit for

the first stage permeate would lead to about 3 to 4 mg/L U in the permeate under similar considerations. In practice, the permeate concentrations may be somewhat higher because solute rejection is lower at lower concentrations. Since the desirable limit of uranium is less than 1 mg/L in the effluents, it is imperative to explore the feasibility of improving solute rejections by suitable pretreatment of the feed.

Literature indicates that sulfate ions are capable of forming sulfato anionic complexes (*13*) of the type $[UO_2(SO_4)_2]^{2-}$, $[UO_2(SO_4)_3]^{4-}$, etc. in acidic media. This has been exploited in the recovery of uranium from sulfate leach liquors using solvent extraction processes. Moreover, sulfates as counterions are highly rejected compared to nitrates. Alternately, EDTA is known to form 1:1 molar complexes with a variety of metal ions and is a commonly used commercially available complexing agent. The spatial structure of its anion has six donor atoms which enable it to satisfy the coordination number of six, frequently encountered among metal ions. The general reaction with EDTA can be represented as

$$M^{n+} + H_2Y^{2-} \rightarrow MY^{(n-4)+} + 2H^+ \quad (6)$$

where H_2Y^{2-} stands for the EDTA ion in solution. This indicates that the stability of the complex is higher at higher pHs. Because the stability constants are very high for lanthanides and actinides, stable complexation is possible even at lower pHs (*14*). For uranyl ions the reaction may be represented as

$$(UO_2)^{2+} + H_2Y^{2-} \rightarrow [(UO_2)Y^{2-}] + 2H^+ \quad (7)$$

Based on these considerations, studies were carried out to investigate the effect of addition of sodium sulfate and EDTA. The feed concentration of uranium in the studies was limited to 50 mg/L. At higher uranium concentrations the solute rejection is inherently high. Besides, at higher concentrations the amount of additives required, and hence the cost, would be too high for economic processing.

For a feed concentration of about 44 mg/L uranium, experimental measurements were made using EDTA at 1:1 and 1:2 molar ratios to evaluate the efficacy of reverse osmosis separation. The feed pH levels were not adjusted, and they were in the acidic range between 4 to 6 depending on the uranium concentration. As can be seen from Table 2, addition of EDTA significantly increased the solute rejection of all the membrane systems. The ability to reject EDTA by cellulose-based membranes has been reported by Thamm and Staude (*15*). Even though excess EDTA helps to improve solute rejection, the actual benefits are only marginal.

TABLE 2
Effect of EDTA Addition on U Removal by Reverse Osmosis[a]

Membrane type	Percent solute rejection		
	Feed without additive	Feed with 1:1 EDTA	Feed with 1:2 EDTA
CA-1	88.0	99.0	99.3
CA-2	66.0	88.0	91.2
CA-3	34.6	75.0	80.8
CA-4	24.0	42.3	59.6
CA-5	9.0	31.2	50.0

[a]Feed concentration = 44 mg/L U, 29°C, membrane area = 0.244 m^2, operating pressure = 4 MPa.

Sodium sulfate has also been found to improve the solute rejection of the membrane systems with respect to uranium, as can be seen from Table 3.

The general improvement observed for all the membranes is attributed to the formation of sulfato anionic complexes. The observed water fluxes are marginally lower than those observed for the corresponding pure solution.

The porous membranes (CA-3,CA-4, and CA-5), even though they show improved performance with the additives, do not give solute rejection values significant enough for practical utility as far as the dissolved uranyl nitrate solutions are concerned. However, they underline the effect of additives in the improvement of performance. Of the two additives studied, EDTA has been found to be superior in all respects.

TABLE 3
Effect of Na_2SO_4 Addition on U Removal by Reverse Osmosis[a]

Membrane type	Percent solute rejection		
	Feed without additive	Feed with 1:1 Na_2SO_4	Feed with 1:2 Na_2SO_4
CA-1	88.0	98.5	98.8
CA-2	66.0	84.0	87.4
CA-3	34.6	50.0	72.0
CA-4	24.0	42.6	50.0
CA-5	9.0	24.0	30.0

[a]Feed concentration = 44 mg/L U, 29°C, membrane area = 0.244 m^2, operating pressure = 4 MPa.

TABLE 4
Comparison of Performance of CA and Polyamide Membranes[a]

Membrane type	Percent solute rejection			
	Feed with EDTA		Feed with Na_2SO_4	
	1:1	1:2	1:1	1:2
CA-1	99.0	99.3	98.5	98.8
Desal II	98.7	99.3	96.7	96.8
DDS	98.7	99.3	97.0	97.8

[a]Feed concentration = 44 mg/L U, 29°C, membrane area = 0.244 m^2, operating pressure = 4 MPa.

Experiments were carried out with identical feed solutions using commercially available polyamide membranes like Desal and DDS in order to have a comparative evaluation. These membranes exhibited better solute rejection compared to CA-1 for uranyl nitrate solutions without any additives. However, with the addition of EDTA and Na_2SO_4, the performance of CA-1 was found to be better, as seen in Table 4. Perhaps the relatively poor rejection of virgin solution with respect to CA-1 can be traced to the inherently poor nitrate rejection characteristics of cellulosic membranes.

CONCLUSIONS

The studies indicate that membrane processes, particularly reverse osmosis, have a potential for the concentration/decontamination of uranyl solutions. In order to reduce the permeate concentrations to less than 1 mg/L, a two-stage reverse osmosis would be better, with the second stage operating with additives, preferably EDTA. It is well established that additives improve membrane performance. The performance of cellulose acetate membranes has been found to be on par with commercially available polyamide membranes when additives are used.

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