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# A STUDY ON TRIPLE-MEMBRANE-SEPARATOR (TMS) PROCESS TO TREAT AQUEOUS EFFLUENTS CONTAINING URANIUM

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## ABSTRACT

An effective process incorporated with the novel membrane separation technology was developed to recover uranium from the filtrate effluent of uranium dioxide conversion processes. The prominent feature of the process is that it utilizes separation characteristics of three different types of membranes as follow: separation of uranium species from effluent of high fluoride content by ultrafiltration membrane, separation of uranium species from effluent of low fluoride content by reverse osmosis membrane, precipitation of uranium species with hydrogen peroxide, and filtration of uranium bearing precipitates by microfiltration membrane. The process is simple and feasible for treatment of liquid waste containing both soluble and suspended uranium species. The recovery of uranium can achieve 95% and the treated effluents meet the current environmental standards.

## INTRODUCTION

The effluent from uranium dioxide conversion process can be classified into two different categories: uranium nitrate effluent (UNE) from the purification process and uranium fluoride effluent (UFE) from the conversion process of uranium hexafluoride to uranium dioxide. The composition of the uranium containing effluent (UE) is very complicate and depends on the process conditions. The major components in UE are uranyl, nitrate, ammonium, carbonate and fluoride ions. The UE is radioactive, toxic and corrosive. If it is released without proper treatment, not only the environment will be polluted, but also the valuable uranium is wasted.

Treatment of uranium containing effluent with reverse osmosis (RO) membrane in the Institute of Nuclear Energy Research (INER) started in 1985(1,2). It has been found that uranyl ion and the coexisting species such as nitrate ion and ammonium ion can be rejected from UNE at pH 2-10 with a feed back reverse osmosis process. The influences of the composition, chemical properties and pH values for both UNE and UFE on reverse osmosis process have been investigated(3). It shows that uranium can be recovered from effluent of low fluoride and ammonium concentration. The present work is then focused on the separation of uranium from effluent of high fluoride and ammonium concentration.

Because of great variations in quantity and quality of UE, a compact unit capable to handle various kinds of UE is desired. The compact unit consists of an ultrafiltration (UF) membrane, a RO membrane, and a microfiltration (MF) membrane. It is called TMS, abbreviation of triple-membrane-separator. Effluents according to its properties can be directed through different membranes and be treated more effectively. Laboratory information and data are presented for this test unit.



## EXPERIMENTAL

### Membrane Elements

The UF membrane used in this study is FilmTec's NF-40. The membrane possesses performance characteristics between RO and conventional UF. It exhibits a high rejection of divalent ions. The RO membrane is FilmTec's FT-30 with a pore diameter of 325 Å. Both the FT-30 and the NF-40 membranes are made in spiral wound module. The MF membrane is SM-11806, made by Sartorius GmbH, West Germany. The pore size of the membrane is 0.45 $\mu$m.

## Procedures

A schematic diagram of the TMS test unit is shown in Figure 1. It consists of one high pressure pump and three membrane elements. Investigations were carried out at operating pressures consecutively increased from 0.69 to 6.9 MPa. The total operation period was about 80 minutes. The concentrate stream which consists of the impermeated flow through the membrane elements and the by-passed flow through the safety valve when the operation pressure is too high (>7 MPa) was fed back to the feed tank continuously. The samples of the corresponding concentrate stream and the permeate stream were collected simultaneously. The flow rates were recorded for both the permeate and the concentrate. After each experiment, FT-30 and NF-40 membrane were washed by demineralized water at 0.69 MPa for 30 minutes. The collected concentrate was precipitated and filtered by MF membrane in 50 liter batch.

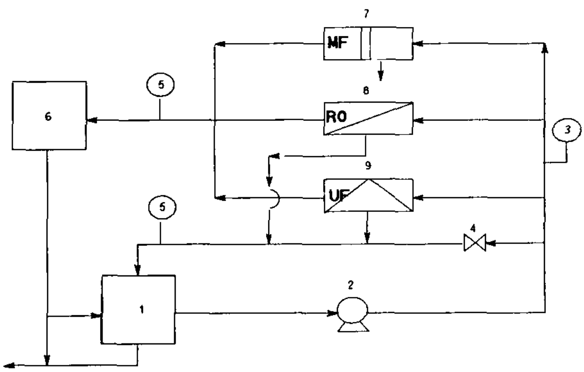


**Figure 1** Schematic diagram of TMS test unit: (1) feed tank; (2) high pressure pump; (3) pressure gauge; (4) safety valve; (5) rotameter; (6) permeate tank; (7) MF membrane module; (8) RO membrane module; (9) UF membrane module.

## Analysis

The nitrate ion was analyzed with ion-pair chromatography, the fluoride ion with an ion selective electrode, and the uranyl ion with polarographic measurement. The ammonium ion concentration and the solution pH were determined by titration.

## RESULTS AND DISCUSSION

### Characterization Tests on NF-40 Membrane Elements

A series of experiments was done to characterize the performance of the element at various conditions of pressure and feed concentration. The influences of pressure on permeate flux are shown in Figure 2. The permeate flux increased linearly as the pressure increased when the properties of feed stream were kept constant. The permeate flux decreased as the concentration of feed stream increased.

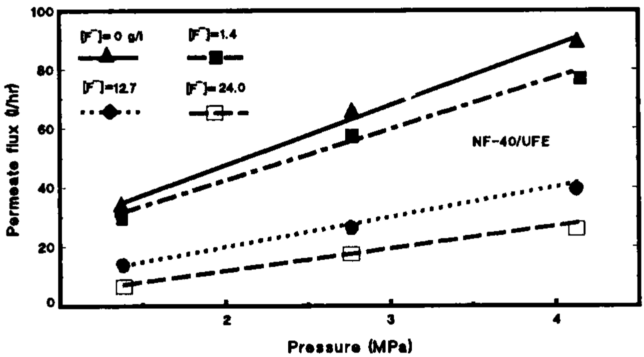


**Figure 2.** Permeate flux vs. operating pressure.

The influences of the feed concentration and pressure on rejection ratio are shown in Figure 3. The solute rejection ratio is defined as:

$$R_j = (1 - C_p / C_f) \times 100 \%$$

where $C_p$ and $C_f$ are the solute concentration in the permeate and feed, respectively. Figure 3 shows the rejections of fluoride ion and ammonium ion. The rejections increase as the operating pressure increases. When the pressure was raised from 0.69 to 4.14 MPa, their rejections increased by about 10%. When the feed concentrations were changed from $[F^-]$=6.3 g/l, $[NH_4^+]$=7.9 g/l, $[U^{+6}]$=0.22 g/l to $[F^-]$=39.1 g/l, $[NH_4^+]$=40.5 g/l, $[U^{+6}]$=1.08 g/l, the rejections of fluoride ion and ammonium ion decreased by about 15%. The rejection ratios of fluoride ion and ammonium ion were below 40% and roughly equal to each other. The rejections of uranium were between 97% and 99.9%. This indicates that uranium can be easily separated from effluent by the NF-40 membrane under these operating conditions.

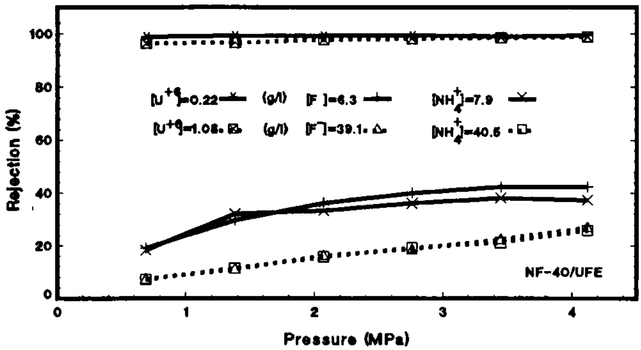


**Figure 3.** Rejection vs. operating pressure.

In the treatment of UFE, the concentrate stream was recycled and sequentially concentrated by NF-40 membrane and until the concentration of uranyl ion in the permeate reached a low limit. The volume reduced ($V_c/V_i$) and the feed concentration increased ($C/C_i$) are plotted in Figure 4. The volume of effluent is reduced to 28% of its original value. The concentration ratio of uranyl ion, fluoride ion and ammonium ion in the effluent are 3.4, 1.4 and 1.2, respectively. Therefore, 95% of uranium, 39% of fluoride ions and 33% of ammonium ions were retained in the concentrate.

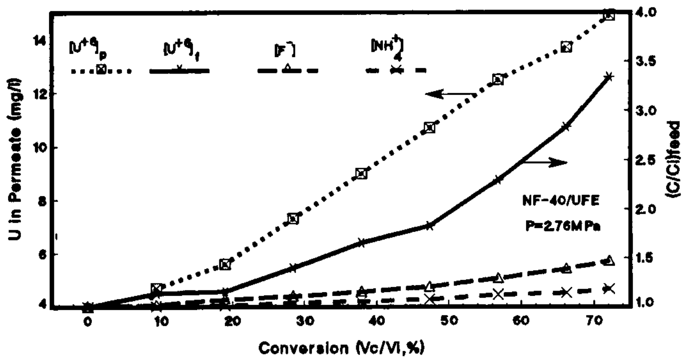


**Figure 4.** Effect of conversion on various parameters.

**Characterization Tests on FT-30 Membrane Elements**

The relation between the permeate flux and the feed fluoride concentration is shown in Figure 5. The permeate flux decreased as the fluoride concentration increased. When the feed fluoride concentration was raised to 25 g/l, the permeate flux decreased to a minimal. Because the fluoride concentration in UFE is usually over 25 g/l, FT-30 membrane is not applicable to treatment of UFE.

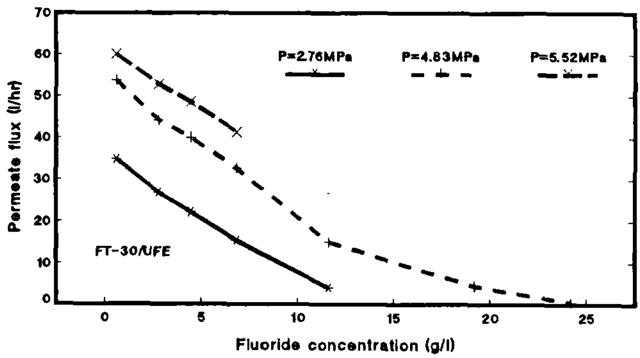


**Figure 5.** Permeate flux vs. fluoride concentration in feed.

Figure 6 shows the effects of pressure and feed concentration on the permeate flux of FT-30 membrane in treating UNE. The permeate flux decreases linearly as the feed concentration increases. When the ammonium ion concentration of feed changes from $[NH_4^+]=0.4$ M to $[NH_4^+]=3.1$ M, the average permeate flux decreases about 30%.

Figure 7 shows the rejection ratios of solutes in UNE. When the concentrations of feed change from $[U^{+6}]=0.21$ g/l, $[NO_3^-]=0.04$ M, $[NH_4^+]=0.45$ M to $[U^{+6}]=0.92$ g/l, $[NO_3^-]=0.27$ M, $[NH_4^+]=3.10$ M, the rejection ratios of uranium ion keep higher than 99%. The rejection ratios of ammonium ion and nitrate ion increase from 9% to 20% and 82% to 89%, respectively. This suggests that uranium can be recovered from UNE with FT-30 even at high ammonium ion concentration.

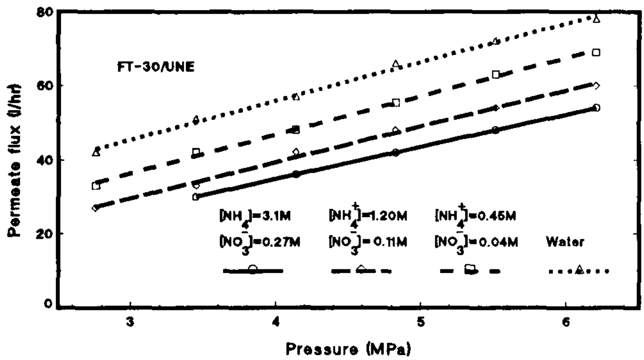


**Figure 6.** Permeate flux vs. operating pressure.

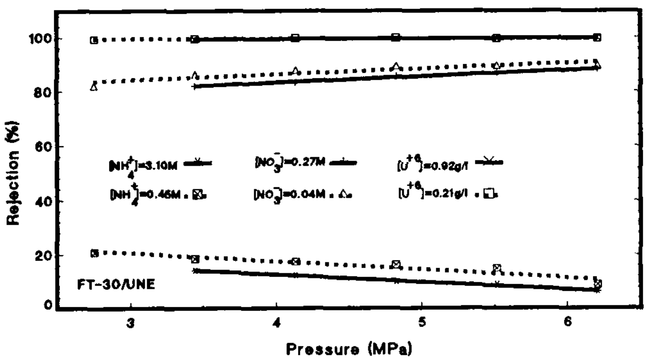


**Figure 7.** Rejection vs. operating pressure.

## Precipitation of Uranium and Characterization Tests on MF Membrane Elements

The precipitation of uranium from waste stream of low uranium concentration by hydrogen peroxide has been used for many years(4). In this study, about twenty times stoichiometric amount of hydrogen peroxide was used to precipitate uranium at pH=9 and T=50 °C. It was found that the mole ratio of $[NH_4^+]/[F^-]$ does not affect much the particle size of precipitates but the aging is the dominant factor in particle size control. With one hour aging, the precipitates obtained have the average particle size greater than 0.8 $\mu$m. Because the pore size of MF membrane is 0.45 μm, the precipitates can be then easily retained. The results of MF were shown in Table 1. The filtration was carried out at 0.2 MPa. The filtrate contains uranium less than 1 mg/l. The uranium cake can be recycled back to the uranium conversion process.

Table 1. Results of TMS process on UE treatment

| Run No. | | 1 | 3 | 4 | 10 | 11 | 13 |
|---|---|---|---|---|---|---|---|
| Source | | UNE* | UNE* | UFE* | UFE* | UFE** | UFE** |
| pH | | 7.82 | 8.80 | 10.02 | 9.20 | 8.22 | 8.20 |
| $U^{+6}$(mg/l) | | 214 | 240 | 154 | 292 | 471 | 1550 |
| $F^-$ (g/l) | | -- | -- | 25.0 | 48.1 | 57.2 | 43.7 |
| $NH_4^+$ (M) | | 4.12 | 0.4 | N.A. | N.A. | 4.6 | 3.4 |
| $NO_3^-$ (M) | | 0.31 | 0.40 | -- | -- | -- | -- |
| $CO_3^=$ (M) | | -- | -- | -- | -- | 3.76 | 6.37 |
| Activity | α | 1.55 | 1.75 | 1.37 | 3.29 | 7.8 | 38 |
| ($10^{-5}$ μCi/ml) | β | 2.19 | 10.7 | 14.2 | 12.0 | 34.0 | 759 |
| U in UF con. | | -- | -- | 693 | 876 | 942 | 2930 |
| U in UF per. | | -- | -- | 9 | 10 | 12 | 14 |
| U in RO con. | | 6741 | 7920 | -- | -- | -- | -- |
| U in RO per. | | 1 | 1 | -- | -- | -- | -- |
| $H_2O_2$ adding(v%) | | 1.5 | 1.5 | 2 | 2 | 2 | 2 |
| pH of Ppt. | | 9.1 | 9.0 | 9.1 | 9.1 | 9.0 | 9.0 |
| Temp. (°C) | | 50 | 50 | 50 | 50 | 50 | 50 |
| Particle size(μm) | | 0.8 | 1.0 | 0.8 | 1.8 | 1.0 | 1.2 |
| U in MF filtrate | | 0.5 | 0.5 | 0.3 | 0.9 | 0.7 | 0.9 |
| Total U recovery(%) | | >99 | >99 | >97 | >95 | >96 | >95 |

* ADU conversion process ** AUC conversion process



**TMS Process**

Figure 8 shows the process of effluent treatment. The UFE is first treated by UF membrane. The uranium in UFE is retained in the concentrate. Most of ammonium ion and fluoride ion will pass with the permeate. The UNE is directly fed to the RO membrane module. Most of the ammonium ion will pass through the membrane with permeate. The uranyl ion and the nitrate ion are retained in the concentrate. Concentrates from both the UF and the MF are fed to a precipitation tank and the uranium is precipitated by hydrogen peroxide at controlled pH and temperature. The solution with fine precipitates of uranium is filtered by MF membrane. The recovery of uranium for the whole process can reach values of 95% for UFE and 99% for UNE. Table 1 shows the results of treatment of two different uranium bearing effluents. The filtrates of MF and the permeates from both the UF and the RO membrane can satisfy prevailing environmental standards. The process has been tested to treat the effluents from INER's Uranium Conversion Test Facility for eight months and 120 $m^3$ was treated. It is found that the performance of FT-30 and NF-40 membranes did not have evident changes.

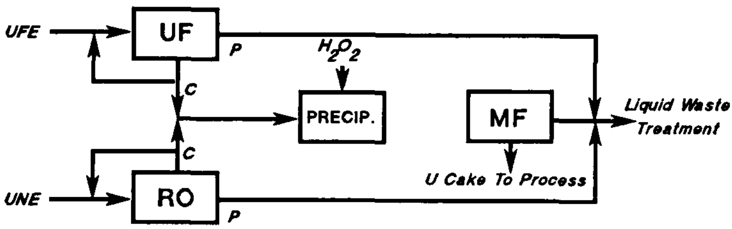


**Figure 8.** Uranium recovery process (TMS).



## CONCLUSIONS

Uranium can be easily separated from effluents by both NF-40 membrane and FT-30 membrane. FT-30 membrane has greater rejection ratio of uranium and less permeate flux, comparing with NF-40 membrane. The UFE is better treated with NF-40 membrane, while UNE can be treated using FT-30 membrane to increase the uranium recovery. Uranium retained in the concentrates can be precipitated by hydrogen peroxide at controlled pH and temperature. The solution with fine precipitates of uranium is filtered by the MF membrane. The recovery of uranium for the whole process can achieve 95% for UFE and 99% for UNE. The treated effluents meet the current environmental standards.

## ACKNOWLEDGEMENTS

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