*Desalination and Water Treatment*
www.deswater.com
doi: 10.1080/19443994.2013.808789

52 (2014) 401–406
January

Taylor & Francis
Taylor & Francis Group

# Application of nanofiltration membrane and ethyleneimine oligomer mixture for selective separation of Strontium from a simulated nuclear waste solution

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Received 10 April 2012; Accepted 24 April 2013

ABSTRACT

Efficient radioactive waste management calls for maximum volume reduction and selective separation of elements from a radioactive waste solution. Ethylenimine (EI) oligomer mixture and GE Osmonics nanofiltration membrane has been used for selective strontium separation from an aqueous synthetic nuclear waste solution. Effect of concentration of EI, presence of cesium and sodium ions in strontium rejection, and effect of feed pH on strontium rejection, volume reduction, and permeate flux has been studied.

*Keywords:* Nanofiltration; Strontium removal; Ethylenimine; Volume reduction

## 1. Introduction

The nuclear industry generates a broad spectrum of high-, low- and intermediate-level liquid wastes. These liquid wastes produced in semi-batch or batch operation vary continuously in volume, radioactivity, and chemical composition. Treatment methods for low-level wastes (LLWs) have widely utilized the same conventional processes found in industrial and municipal water treatment. Conventional methods for treatment of LLW include evaporation, chemical precipitation, and ion exchange. Evaporation is a costly and energy-intensive process. This is suitable to handle very low volumes of LLW. Chemical treatment is less expensive; however, it is a batch process. Moreover, this technique is suitable only for wastes with very low activities. Ion exchange process can be used as a continuous process for treating wastes of different activities. However, its efficiency depends on the presence of other inactive ions in the waste solution. Also, it generates secondary solid wastes which needs safe disposal [1]. Therefore, these methods have associated drawbacks, which make satisfactory processing of LLWs difficult.

In recent decades, various membrane separation processes have been developed and utilized in the field of water purification, and more recently in the treatment of various process and waste liquors. Some of the membrane processes are capable of removing both dissolved and particulate contaminants. These processes include reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and micro filtration. It has

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*Presented at the DAE—BRNS Biennial Symposium on Emerging Trends in Separation Science and Technology (SESTEC 2012) Mumbai, India, 27 February–1 March 2012*

been demonstrated that pressure-driven reverse osmosis can be successfully employed for the removal of radioactive substances [2]. A combination of RO and membrane distillation (MD) technique was used to treat liquid radioactive wastes in Poland [3]. However, RO has an inherent disadvantage of very high operating pressures. UF, on the other hand, operates at low pressures. Also, UF has poor retention factors for inorganic solutes. Separation of metals using UF membranes with MWCO 1,000 after adsorption on titanium hydroxide particles has been reported for very dilute aqueous solutions [4]. Similarly, hybrid methods using UF/complexing agent has been studied elsewhere for radioactive waste processing [5–9]. Use of NF and complexation by polyacrylic acid has also been reported [10]. However, the effect of cesium ions on strontium retention has not been reported. Liquid membrane process using D2EHPA as a low molecular weight carrier has been used for sr recovery from strongly alkaline waste in Hanford. This technology is simple, safe, and economical. However, third phase formation has been observed in the lab-scale experiments and it requires addition of a modifier to prevent this phenomenon [11].

The most recent membrane separation technique is NF. The properties of these membranes lie between nonporous RO membranes and porous UF membranes. NF membranes have advantages like high retention, low operating pressure, and higher permeate flux. Also, these membranes posses a fixed charge on its surface developed by dissociation of functional groups [12]. This electrostatic property of the membrane permits monovalent ions to pass through, while retaining multivalent ions. These properties of the NF membrane and the selective complexation of strontium ions with ethylenimine oligomer mixture (EI) has been utilized in this work to selectively reject strontium from a simulated waste solution. The operating conditions for selective rejection of strontium, maximum volume reduction, and permeate flux has also been devised.

## 2. Objective

To develop operating conditions for selective removal of strontium greater than 99% from a typical nuclear waste (intermediate-level waste) solution using NF membranes. The selective rejection of strontium needs to be achieved with maximum volume reduction factor (VRF), which is ratio of initial and final waste volumes, without affecting the permeate flux and at reasonably low operating pressures.

## 3. Experimental

The experimental setup consisted of feed tank of 25 L capacity. A positive displacement diaphragm pump of capacity 8 L/h and head 24 kg/cm$^2$ was used to circulate the simulated feed in the circuit. A microfilter of 5 μ pore size is used to remove any suspended solids in the feed. A NF membrane of GE Osmonics make (model No. HL1812T) is used for the strontium-removal studies. A schematic flow diagram of the setup is shown in Fig. 1. The permeate and reject lines of the membrane are routed back to the feed tank to ensure constant feed composition during the initial parametric studies. Finally, after the parameter optimization studies, the permeate and reject streams are segregated to study the volume reduction. Detailed specification of the setup is listed in Table 1. The strontium concentrations in the feed and permeate streams were analyzed using an atomic absorption spectrometer (AAS) of Analytikjena make (novAA 300). Estimates made using AAS carried an uncertainty of about 5%. The experimental procedure typically involved feed preparation, feed conditioning,

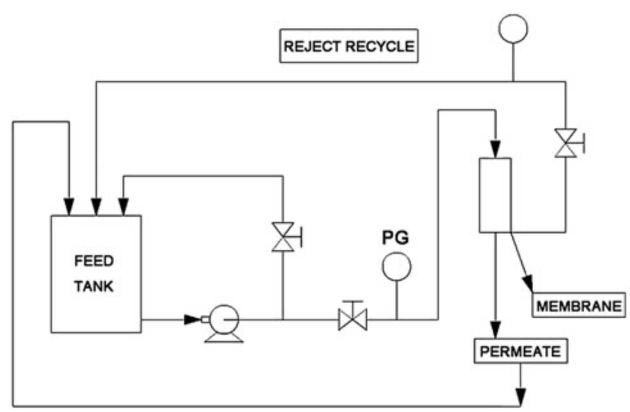



Fig. 1. Experimental setup for strontium removal studies.

Table 1
Detailed specifications of the experimental setup

| No. | Item name | Description |
|---|---|---|
| 1 | Feed tank | 25 L capacity PVC |
| 2 | Pump | Positive displacement diaphragm pump flow rate = 8 L/h Head = 24 kg/cm$^2$ |
| 3 | Microfilter | 5 μ prefilter |
| 4 | Nanofilter | GE osmonics TFC NF membrane Polyamide 100–300 Da 95% Rejection for $MgSO_4$ |
| 5 | Pressure gauges | 0–6 kg/cm$^2$ |

membrane separation, flux measurement, sampling, analysis by AAS, water rinsing, and pure water flux measurement to check the integrity of membrane.

### 3.1. Membrane characterization

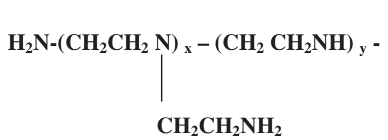
The first set of experiments was done to characterize the NF membrane. The pure water flux and rejection for strontium were studied using demineralized (DM) water as feed medium. Here, the system was operated at various pressures. The permeate flux was measured at regular intervals for all operating pressures up to 2 kg/cm$^2$.

### 3.2. Strontium rejection experiments using only NF membrane

A feed stock solution of 200 L containing about 14 mg/L of strontium was prepared by dissolving strontium nitrate in DM water. The final pH of the solution was typically in the range of 6.8–7.0. The simulated waste solution will also contain some sodium. In order to understand the effect of sodium on flux and strontium rejection, the pH of the feed stock solution was not altered during the course of the experiments initially. Experiments were done in batches of 10 L of feed solution. Initially, only the NF membrane was used to study the rejection characteristics for strontium. The permeate fluxes were measured for various operating pressures as before. Permeate samples were also drawn at regular intervals and analyzed for strontium using AAS. The effect of operating pressure on pure water flux, permeate flux with strontium in feed solution, and the rejection of strontium was studied.

### 3.3. Experiments with EI oligomer mixture as a complexing ligand

Since the permeate flux and rejection of strontium was not significant in the previous experiments, subsequent experiments were carried out using strontium feed treated with a complexing agent. An organic ligand EI oligomer mixture of molecular weight (Mn = 423) was used as the complexing ligand for strontium. EI oligomer mixture is a commercially available macromolecule with 25% primary, 50% secondary, and the remaining 25% teritiary amine groups.




EI also exhibits good water solubility and chemical stability. During pretreatment experiments, the ligand and feed solution were put in circulation mode before plugging the NF membrane in the circuit for separation. The conditioning time required for effective strontium complexation was estimated in circulation mode with and without stirrer.

### 3.4. Optimization of EI concentration

Initial experiments were done to study the effect of concentration of EI on strontium rejection and permeate fluxes. Accordingly, different concentrations of EI were taken (1–5 g/L of feed solution). The resultant slurry was put in circulation mode. The reject back pressure valve was throttled in such a way that the operating pressure stabilized at about 2.2 kg/cm$^2$. Permeate samples were collected every hour at this pressure. The permeate flux and the percent rejection of strontium was evaluated after analyzing the strontium concentration in the permeate of each experiment. The conditioning time needed for the ligand to complex with strontium was also estimated.

### 3.5. Effect of competing ions like cesium and sodium

The above feed solution containing strontium was also spiked with cesium and sodium to study its effect on strontium rejection and permeate flux. It was found that strontium was selectively rejected from the feed containing strontium, cesium, and sodium. Both cesium and sodium appeared in the permeate. The results are shown in Table 3. The concentrations of strontium, cesium, and sodium in the reject were obtained from the final material balance.

### 3.6. Effect of feed pH on strontium rejection and VRF

After optimizing, the EI concentration the effect of feed pH on rejection of strontium and volume reduction was studied. The feed pH was varied between 5 and 12. The effect of pH on permeate flux was also studied. In order to obtain explicit results for each parameter, the membrane is rinsed with DM water after each experiment. The pure water flux was also measured after each experiment to rule out the possibility of fouling of membrane.

## 4. Results and discussions

Since the design pressure for the NF membrane is 6 kg/cm$^2$, the operating pressure for the NF membrane was in the range of 2.0–2.5 kg/cm$^2$. The pure

Table 2
Effect of EI concentration on strontium rejection and permeate flux

| Sl no. | EI concentration (g/L) | Flow rate (mL/min) | | Average permeate flux ($L/m^2 h$) | Feed sr (mg/L) | Permeate sr concentration (mg/L) | % sr rejection |
|---|---|---|---|---|---|---|---|
| | | Permeate | Reject | | | | |
| 1 | 0 | 148.3 | 1.7 | 22.25 | 8.5 | 8.0 | 5.89 |
| 2 | 1 | 82.25 | 71.0 | 12.34 | 14.0 | 4.8 | 65.7 |
| 3 | 2 | 82.0 | 71.8 | 12.3 | 14.0 | 4.5 | 67.8 |
| 4 | 3 | 64.25 | 84.5 | 9.64 | 14.0 | 4.2 | 70.0 |
| 5 | 4 | 61.5 | 87.5 | 9.22 | 14.0 | 4.0 | 71.4 |
| 6 | 5 | 53.75 | 90.75 | 8.1 | 14.0 | 3.2 | 77.1 |

water flux was found to be 22.5 $L/m^2$.h at this operating pressure. It can be seen from Fig. 2 that the maximum strontium rejection by the NF membrane alone was only 36% at 0.6 $kg/cm^2$ pressure. The permeate flux at this pressure was 6 $L/m^2$ h.

Since the flux and rejection were not significant, experiments were done by adding EI oligomer mixture as a complexing ligand, followed by membrane separation. During complexation with ethylenimine, the bivalent strontium ion binds with the lone pair of electrons of the nitrogen present in the imine functional group of the ligand and thereby increases its ionic size greater than the membrane molecular weight cut-off, viz. 100–300 Da. Experiments with varying ligand concentrations were conducted to obtain the optimal ligand concentration required for complexation. It was observed that for a feed solution containing 14 mg/L of strontium and with 2 g/L of EI added to it, the permeate flux was 12.3 $L/m^2$ h and the strontium rejection was 67.8%. The concentration of the complexing ligand EI was optimized to be 2 g/L. Beyond this optimal concentration, there was no significant enhancement of flux and strontium rejection. The effect of EI concentration on permeate flux and strontium rejection is shown in Table 2 and plotted in Fig. 3.

Also, as shown in Fig. 4 and it was found that by circulation, the conditioning time for complexation of the ligand with strontium is about 5 h.

Subsequent experiments were done to study the effect of cesium and sodium ions in the feed solution. As shown in Table 4, these ions do not significantly affect the permeate flux. For the same operating conditions and ligand concentrations, it was seen that strontium was selectively rejected up to a maximum of 96%.

The above experimental procedure was carried out to find the effect of feed pH on strontium rejection, VRF and permeate fluxes. It was observed that all the three parameters were maximum at pH 10.8. The

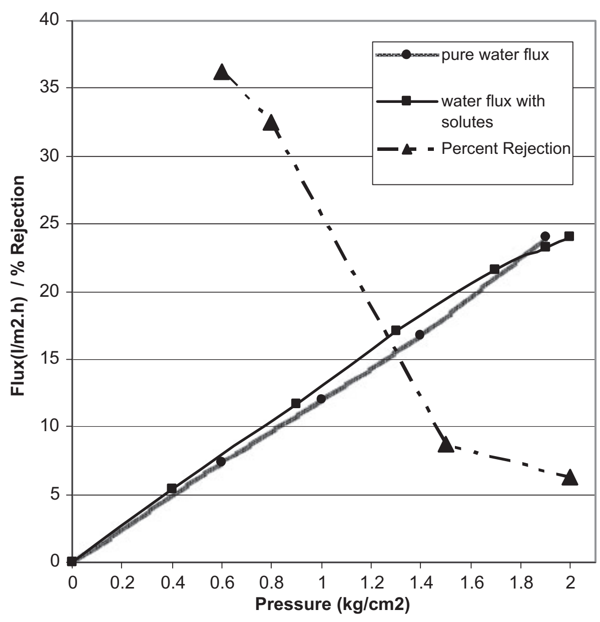



Fig. 2. Effect of trans-membrane pressure on permeate flux and strontium rejection.

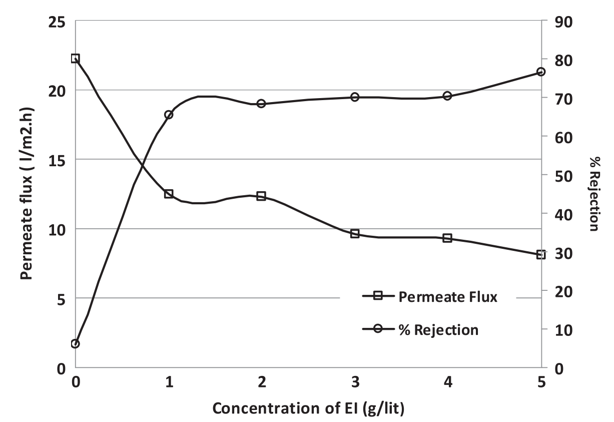



Fig. 3. Effect of ethyleneimine concentration on strontium rejection and permeate flux.

Table 3
Effect of cesium and sodium on strontium rejection

| Sl no. | EI concentration (g/L) | Feed concentration (mg/L) | | | Permeate concentration (mg/L) | | | % Rejection | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Sr | Cs | Na | Sr | Cs | Na | Sr | Cs | Na |
| 1 | 0 | 8.5 | 0 | 0 | 8.0 | 0 | 0 | 5.88 | – | – |
| 2 | 1 | 14.0 | 24.2 | 0 | 4.05 | 16.9 | 0 | 80.3 | 52.5 | – |
| 3 | 2 | 14.0 | 24.2 | 0 | 0.98 | 18.1 | 0 | 95.2 | 49.1 | – |
| 4 | 3 | 14.0 | 24.2 | 0 | 1.18 | 16.7 | 0 | 94.2 | 53.1 | – |
| 5 | 1 | 14.0 | 15.0 | 26.0 | 1.8 | 15 | 26.5 | 91.3 | 32.0 | 31.0 |
| 6 | 2 | 14.0 | 15.0 | 26.0 | 0.82 | 16 | 28.5 | 96.0 | 27.3 | 25.0 |

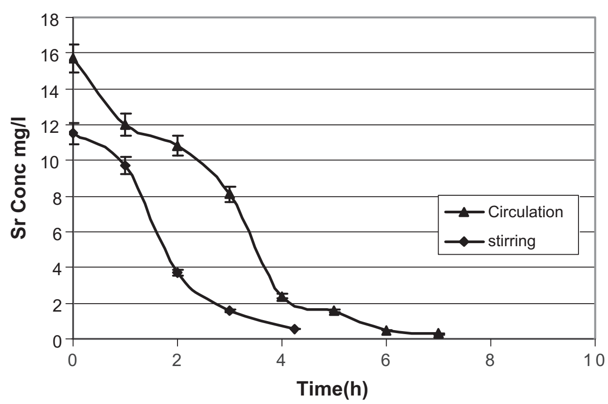



Fig. 4. Conditioning time for strontium complexation in circulation with and without stirring.

Table 4
Flux variation with feed composition at operating pressure of 2–2.5 $kg/cm^2$

| Sl no. | Feed composition (mg/L) | EI concentration (g/L) | Permeate flux ($L/m^2 h$) |
|---|---|---|---|
| 1 | Sr—14.2 | 1 | 12.4 |
| | | 2 | 12.0 |
| | | 3 | 9.6 |
| | | 4 | 9.2 |
| | | 5 | 8.0 |
| 2 | Sr—14.2/Cs—15.0 | 1 | 16.6 |
| | | 2 | 14.9 |
| | | 3 | 12.0 |
| 3 | Sr—14.2/Cs—15.0/Na—26.0 | 1 | 16.8 |
| | | 2 | 13.1 |
| | | 2 | 15.0 |

effect of feed pH on strontium rejection is shown in Fig. 5. It was found that 98% strontium rejection was possible at feed pH of 10.8. Also, significant rejection of strontium was observed at pH 5.8.

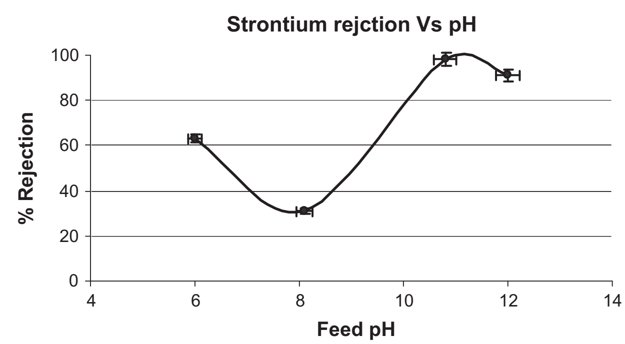



Fig. 5. Effect of feed pH on strontium rejection.

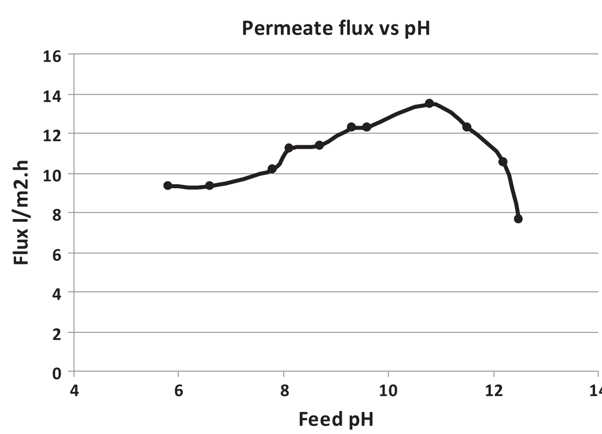



Fig. 6. Effect of feed pH on flux.

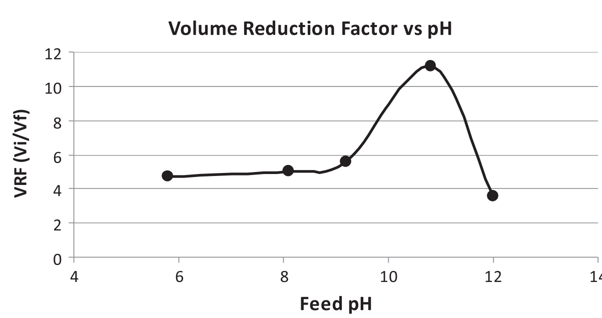



Fig. 7. Effect of feed pH on VRF.

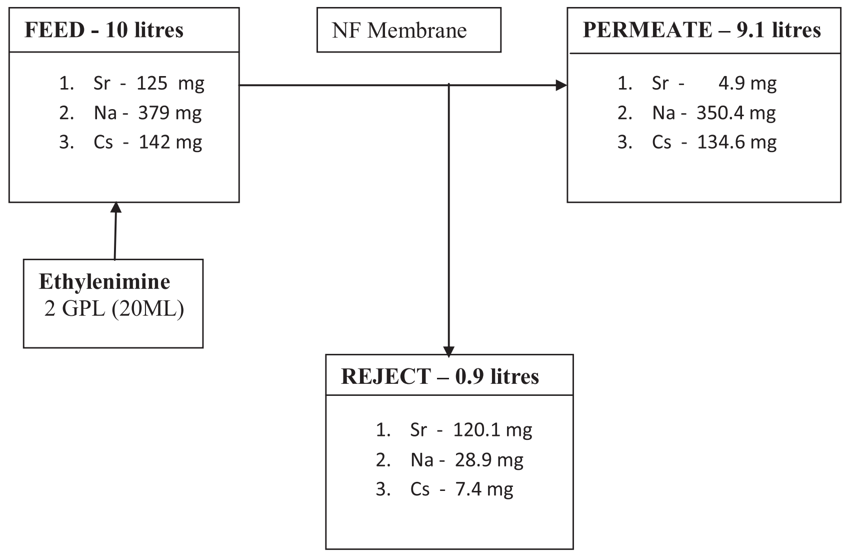



Fig. 8. A typical material balance chart.

Subsequently, the rejection of strontium decreases at pH between 5.8 and 9.2. At these pH values, the $H^+$ ion does not allow the complexation of strontium with EI. However, the $H^+$ ions form a charge barrier at the membrane surface, which causes the strontium rejection by charge exclusion at pH 5.8. The permeate flux measurements were made for various pH values and the maximum flux of $13.5\,L/m^2\,h$ was also obtained at pH 10.8 and is shown in Fig. 6. The flux reduction at acidic and alkaline pH is attributed to the rise in osmotic pressure due to addition of acid or alkali for pH variation. Similarly, a maximum VRF of 11.1 was obtained for the same feed pH of 10.8. The variation of VRF with pH is shown in Fig. 7. The reduction in solvent flux at other pH values also has a direct effect on VRF.

A typical material balance diagram is shown in Fig. 8. It can be seen that 96% of strontium in the feed solution is concentrated in the reject stream and 4% in the permeate stream, whereas 93% sodium and 95% cesium is in the permeate stream and only the rest appears in the reject stream.

## 5. Conclusion

From the above experimental results, it can be inferred that when the simulated waste solution is complexed with optimal concentration of EI oligomer mixture and passed through a NF membrane, strontium can be selectively rejected and isolated from the rest of the ions present in the initial waste solution. The permeate flux is largely affected by ligand concentration. The presence of sodium and cesium ions not only has a negligible effect on the overall permeate flux, but also enhances the selective rejection of strontium. Also, a significant VRF has been achieved using NF membranes.

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