Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Studies on Electrodialytic Separation of Radionuclides from Effluent Streams

V. Ramachandhran[a]; B. M. Misra[a]
[a] DESALINATION DIVISION, BHABHA ATOMIC RESEARCH CENTRE, BOMBAY, INDIA

To cite this Article Ramachandhran, V. and Misra, B. M.(1985) 'Studies on Electrodialytic Separation of Radionuclides from Effluent Streams', Separation Science and Technology, 20: 7, 623 — 632
To link to this Article: DOI: 10.1080/01496398508068243
URL: http://dx.doi.org/10.1080/01496398508068243

SEPARATION SCIENCE AND TECHNOLOGY, **20**(7 & 8), pp. 623-632, 1985

Studies on Electrodialytic Separation of Radionuclides from Effluent Streams

V. RAMACHANDHRAN and B. M. MISRA

DESALINATION DIVISION
BHABHA ATOMIC RESEARCH CENTRE
BOMBAY 400085, INDIA

Abstract

Electrodialytic separation of radionuclides present in trace concentrations in effluent streams using ion-exchange membranes has been investigated. Separation of trace constituents by electrodialysis (ED) involves studying the polarization problems and the resulting loss of efficiency due to increasing ohmic resistance of the dilute solutions. Polarization problems arising in handling solutions having trace ionic concentration were analyzed and the effects of various parameters (such as flow rate, boundary layer thickness, and feed temperature) were investigated. Optimization of a suitable ED system in terms of varying intermembrane distances, effect of solute concentration on performance, and percent separation of radionuclides at different trace concentrations was attempted.

INTRODUCTION

Separation of trace radionuclides from effluent streams generated from various nuclear installations is important from the point of view of environmental safety. The presence of radionuclides at the trace level makes their separation complicated. Conventional separation methods (e.g., chemical precipitation, ion exchange, and evaporation) are practiced in several countries. Techniques such as electroflotation (*1*), bacterial decontamination (*2*), and fixation in biomasses (*3*) are also reported to yield reasonable separation efficiencies. The reverse osmosis process has recently been suggested for possible application (*4-6*). Electrodialysis (ED), an electromembrane process involving ion-exchange membranes as semipermeable barriers, has been successfully applied for a variety of separation applications from desalination of sea and brackish waters to

0149-6395/85/2007-0623$3.50/0

effluent treatment. Attempts have also been made (*7–12*) to investigate the electrodialysis process for radionuclides removal. Handling of dilute solutions in the electrodialysis process involves several problems, particularly polarization at membrane solution interfaces and loss of separation efficiency due to increasing specific resistance in the dilute region.

Polarization at the membrane–solution interface occurs in the electrodialysis process. This arises primarily due to the difference in the transference numbers of ions in solution and in the membrane phases. Ions move faster in the membrane phase than in the solution phases, and with the passage of current the ions tend to concentrate on the exit side of the membranes whereas the concentration drops at the entering side. Such a polarization tendency is opposed by diffusion and physical mixing. The concentration of ions on the entering side of the membranes drops to zero with increasing current density. Beyond this limiting current density, H^+ and OH^- ions form as a result of water splitting and permeate through the membranes. Such a situation is detrimental to the life of the membranes in addition to being a waste of power.

An expression for the limiting current density, i_c, can be obtained under steady-state conditions where the combined ionic and diffusive flux through the solution in the boundary layer equals the ionic flux through the membrane:

$$i_c = \frac{C_b D F Z_+}{\delta(\bar{t}_+ - t_+)} \tag{1}$$

where Z_+ = valency
D = diffusivity
C_b = bulk concentration
t_+ and $\bar{t}_+$ = cationic transference number in solution and membrane phases, respectively
F = faraday constant
δ = boundary layer thickness

Experimentally, it has been found (*13*) that the boundary layer thickness (δ) is inversely proportional to the velocity of the solution (v) in the electrodialysis apparatus along the membrane surface and intermembrane distance (d):

$$\delta = K/vd \tag{2}$$

where K is a constant depending on the hydrodynamics of the flow conditions.

Equation (1) indicates that limiting current density is directly proportional to the bulk concentration and solute diffusivity and inversely proportional to the boundary layer thickness. If other parameters are kept constant, limiting current density is proportional to bulk concentration. For dilute solutions, polarization becomes a severe problem because the limiting current density is very low. Polarization studies have been reported (*14*) for interpolymer anion-exchange membranes by following pH changes. In this paper, electrodialytic performance with respect to the separation of radionuclides from dilute saline feeds and some aspects of concentration polarization are studied.

EXPERIMENTAL

Cation-exchange membranes were synthesized by *in situ* polymerization of freshly synthesized (*15*) phenol sulfonic acid and G.R. grade formaldehyde solution using the procedure described elsewhere (*16*). Various electrochemical properties were evaluated to characterize the membranes and are presented in Table 1. The electrodialysis apparatus (Fig. 1) used in our studies was based on the plate and frame concept. Commercially available cation- and anion-exchange membranes from Ionics, Inc., Cambridge, Massachusetts, were used in most of the studies. The polarization phenomena was investigated by studying the voltage-current characteristics of the cell under different flow rates and different feed temperatures. Studies on the optimization of suitable electrodialysis apparatus were carried out using different laboratory test cells having varying intermembrane distances. A.R. grade sodium chloride was used for evaluating the dependence of solute concentration in a dilute region on the performance. The performance was evaluated in terms of solute flux and power consumption. Percent separation in the case of radionuclides was evaluated from the ratio of feed and effluent radioactivities. Analysis of the electrolytes was carried out by conductance measurements. Radioactivity measurements were made using γ-ray spectrometry.

TABLE 1
Electrochemical Properties of Cation-Exchange Membranes

Moisture content (%)	27.82
Cation exchange capacity (equiv/g (wet))	0.809
Resistance (in 0.1 N KCl) (ohm · cm^2)	14.44
Membrane potential (measured in 0.1 N/0.01 N Kcl (mV))	105
Cation transference number, $\bar{t}_+$	0.89

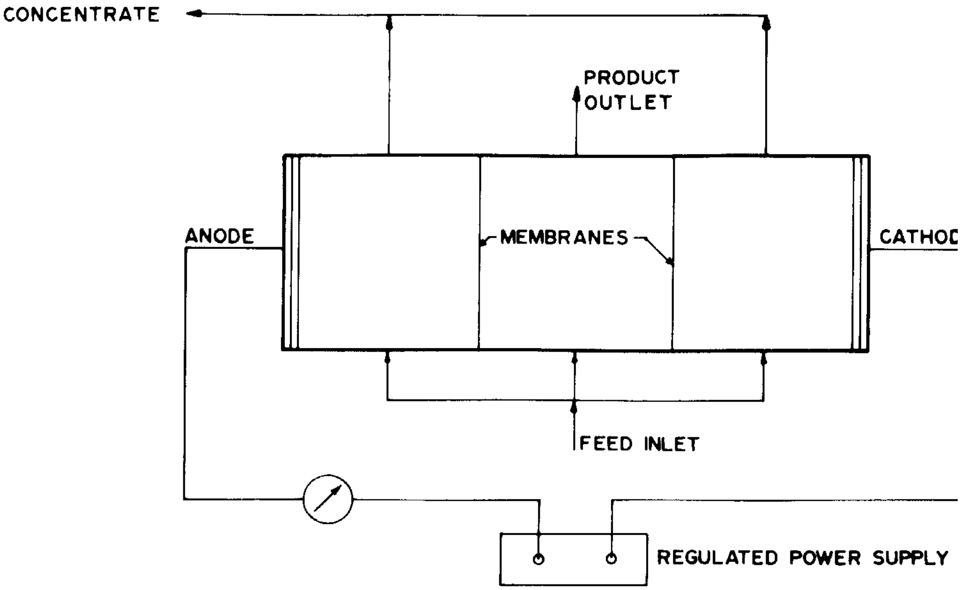

FIG. 1. Electrodialysis experimental setup.

RESULTS AND DISCUSSIONS

Electrodialysis Performance for Low Solute Concentrations

The effect of feed concentration on ED performance was evaluated in the range of 100 to 1000 ppm by using sodium chloride. A 3-compartment ED cell having a 2-cm channel width was used. All experiments were carried out under dynamic conditions using a steady flow rate of 3.0 mL/min. The results, shown in Fig. 2, indicate that as the feed concentration decreases, the solute flux decreases.

It is worthwhile to compare reverse osmosis and the electrodialysis process in dilute concentration ranges. In reverse osmosis, solute separation increases and reaches a maximum at about 10^{-4} *M* concentration (*5*) and declines subsequently when the solute concentration is increased from tracer levels. It appears that solution properties dominate beyond this maxima wheras at lower concentrations the membrane properties dominate. This means that separation of radionuclides from radioactive effluent streams is more efficiently accomplished at the trace level by reverse osmosis.

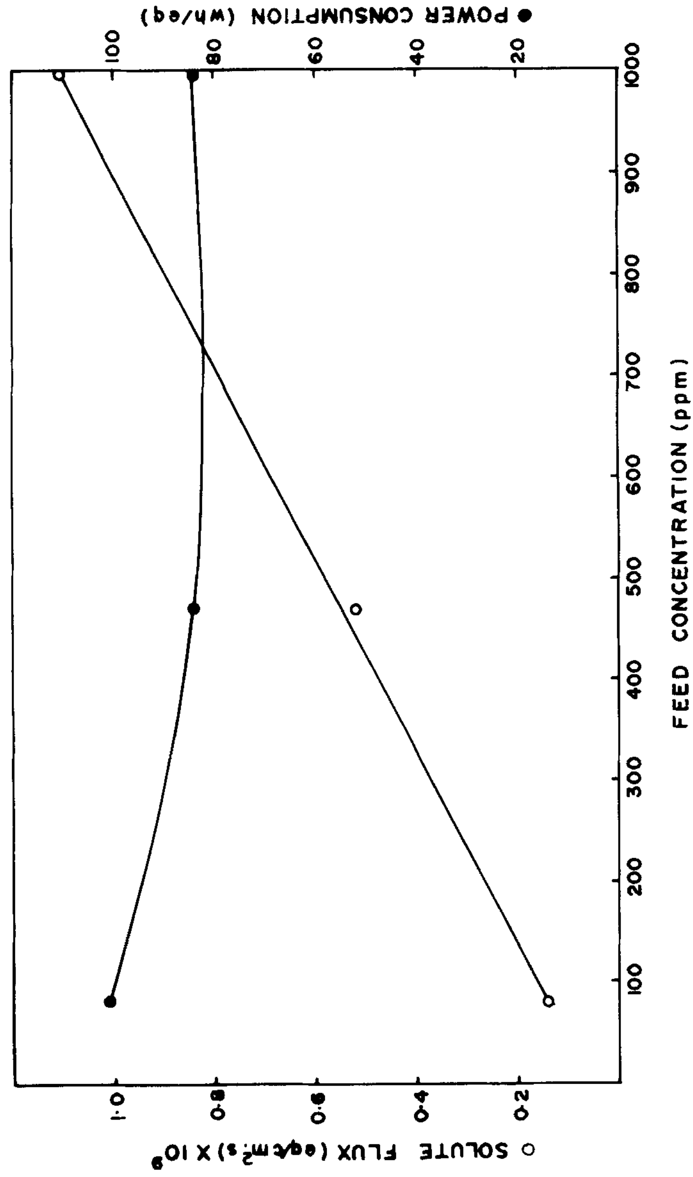

FIG. 2. Effect of feed concentration on electrodialysis performance in dilute region.

TABLE 2
Separation of Different Radioactive Feeds by ED[a]

Sample	Feed activity (μCi/mL)	Separation (%)
1	8.13×10^{-3}	95.2
2	1.15×10^{-3}	83.4
3	3.58×10^{-4}	72.5

[a] Flow rate = 0.3 mL/min; feed contains 1000 ppm NaCl.

Such a typical maxima in solute separation behavior with concentration is not noticeable in the electrodialysis process. Solute separation measured in terms of solute flux decreases with a decrease in solute concentration due to the increasing electrical resistance of the solution. Power consumption is also observed to increase dramatically below a 500-ppm feed concentration. At higher concentrations, power consumption remains steady. The sudden increase in power consumption below a 500-ppm concentration may be due to polarization problems.

The performance data collected for different feed effluents with varying amounts of radionuclides from 3.5×10^{-4} to 8.1×10^{-3} μCi/mL are shown in Table 2. The results indicate that the decontamination efficiency and percent activity separation improve with an increase in the activity level of the feed stream. A similar result is obtained in the case of reverse osmosis studies, indicating the potential of concentrating the radioactivity to a very significant extent by repeated recycling of the concentrate and feed streams. The improvement in the separation of trace radionuclides with an increase in tracer activity in the presence of a significant inactive solute load clearly points out that, apart from electrical resistance criteria, other solution parameters, such as the availability of trace solute ions near the membrane–solution boundary, also play a significant role.

The problem of high resistance of the electrolyte at low concentrations, as in the case of separating radionuclides from effluent streams, can also be countered by filling the dialysate compartment with a mixed bed of strong ion-exchange resins. By this means the concentration range over which electrodialysis is feasible can be extended since the electrical conductivity of a dilute electrolyte solution in the presence of ion-exchange resins is largely that of the resin itself. A two-step decontamination process for radioactive effluents using a similar approach has been reported (*12*). Recently, electrodialytic decontamination of "spent" ion-exchange resins in the primary heat transport purification system of CANDU-type reactors has been reported (*17*).

Electrodialysis Performance with Different Membrane Spacings

The performance of a 3-compartment electrodialysis cell having different intermembrane spacings was evaluated. Cells having 2 cm, 6 mm, and 3 mm channels were fabricated and tested. The experiments were carried out using a feed concentration of 1000 ppm sodium chloride. All the experiments were carried out under dynamic conditions using a steady flow rate of 3.0 mL/min. The results obtained are shown in Table 3.

The resistance of the cell pair is comprised of resistance of the membranes and that of the concentrating and depleting streams. A typical membrane resistance is in the region of 3–20 ohm · cm^2, and the specific resistance of the electrolyte solutions normally encountered far exceeds this value. Hence, the resistance of the cell is largely attributable to the depleting stream. One way of reducing the resistance is to resort to extremely low spacings between the membranes. The results shown in Table 3 indicate that reducing intermembrane distance reduces the power consumption and improves the solute flux.

Effect of Flow Rate on Polarization

The effect of feed flow rate on polarization was studied in a 3-compartment electrodialysis apparatus having 6 mm intermembrane spacings. Sodium chloride (100 ppm) was used as the feed, and the flow rate was adjusted from zero to 1.0 mL/min. Polarization was studied in terms of voltage–current characteristics. The results are shown in Fig. 3. The results indicate that at higher flow rates the voltage–current characteristics remain linear, indicating the absence of polarization effects. At lower flow rates the potential difference tends to increase drastically, indicating the setting in of polarization. Polarization is seen to be much too severe at a zero flow rate.

TABLE 3
Performance under Different Intermembrane Distances

Sample	Intermembrane distance (mm)	Solute flux (equiv/cm^2 · s)	Power consumption (W · h/equiv)
1	20	1.4×10^{-10}	329.1
2	6	2.9×10^{-10}	101
3	3	1.1×10^{-9}	73.7

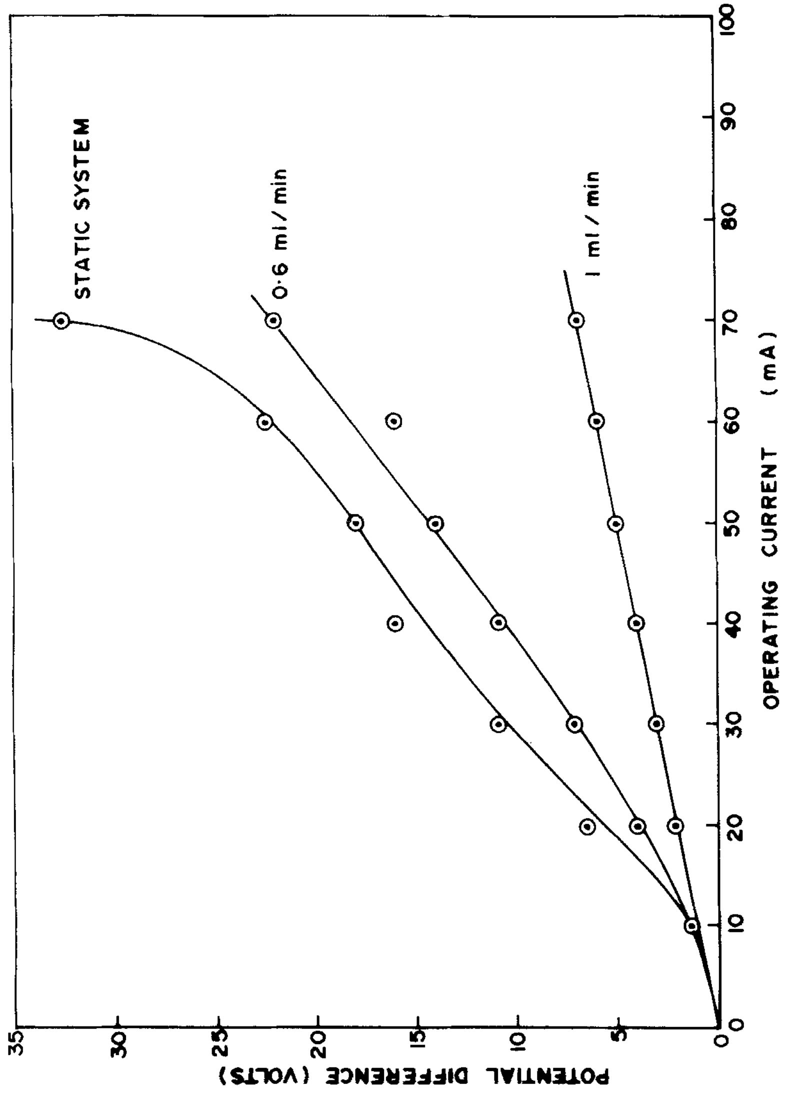

FIG. 3. Effect of flow rate on polarization.

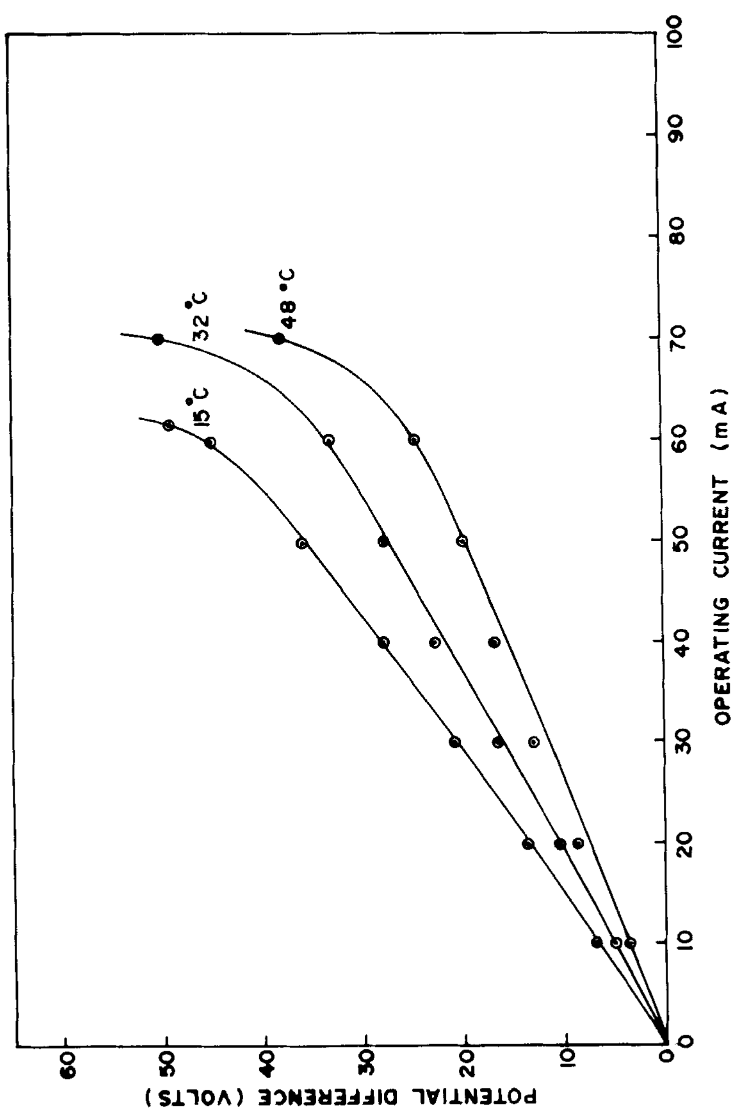

FIG. 4. Effect of feed temperature on polarization.

Effect of Feed Temperature on Polarization

The effect of temperature on polarization was studied with a 100 ppm sodium chloride feed maintained at different temperatures by using a themostated water bath. The voltage-current characteristics are shown in Fig. 4. The results indicate that at lower temperatures polarization is noticed at the early stages where the voltage begins to increase. Polarization is also observed to occur at progressively higher temperatures, although its onset is slightly delayed. It appears that increasing the flow rate is more effective in eliminating polarization than is increasing the feed temperature. It is noted that increasing the feed temperature improves the current characteristics by decreasing the specific resistance of the solution. This results in a faster removal of solute species. Hence, increasing the flow rate and slightly increasing the temperature not only improves performance, but solves polarization problems.

Acknowledgment

The authors wish to acknowledge Dr M.P.S. Ramani, Head, Desalination Division, for his kind encouragement and keen interest in this work.

REFERENCES

1. F. Kepak and J. Kriva, *Waste Manage. Res. Abstr.*, *6*, 42 (1971).
2. K. R. Price, *Nucl. Sci. Abstr.*, *26*, 2644 (1972).
3. S. Bonotto et al., *Proceedings of the International Symposium on Impacts of Radionuclide Releases into the Marine Environment*, Vienna, IAEA-SM-248/165, 1980.
4. V. Ramachandhran and B. M. Misra, *J. Appl. Polym. Sci.*, *27*, 3427 (1982).
5. V. Ramachandhran and B. M. Misra, *Ibid.*, *28*, 1641 (1983).
6. V. Ramachandhran and B. M. Misra, *Ibid.*, *30*, 35 (1985).
7. M. S. Seal and R. A. Presok, ORNL cf-55-5-171.
8. L. F. Coleman and J. R. Eliason, BN 102-72, 1965.
9. C. V. Rauzen et al., *Proc. 4th Int. Conf. Peaceful Uses of At. Energy*, *11*, 387 (1971).
10. I. A. Sobolev et al., *Waste Manage. Res. Abstr.*, *8*, 40 (1973).
11. M. Ito and M. Nishidoi, JAERI Report 1012, 1960.
12. W. Walters, D. Weiser, and C. Marek, *Ind. Eng. Chem.*, *47*, 61 (1955).
13. J. R. Wilson, *Demineralization by Electrodialysis*, Butterworth, London, 1960.
14. V. K. Indusekhar and N. Krishnaswamy, *Desalination*, *48*, 267 (1983).
15. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Wiley-Interscience, New York, 1961, p. 306.
16. N. Lakshminarayanaiah, *Transport Phenomena in Membranes*, Academic, New York, 1972, p. 14.
17. B. R. Nott, *Proceedings of the International Symposium on Water Chemistry and Corrosion Problems in Nuclear Power Plants*, Vienna, IFEA-SM-264/32, 1983.

Received by editor March 14, 1985