**Separation Science and Technology**
Publication details, including instructions for authors and subscription information:
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# A Study on Removal of Cobalt from a Primary Coolant by Continuous Electrodeionization with Various Conducting Spacers

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**To cite this Article** Yeon, Kyeong-Ho and Moon, Seung-Hyeon(2003) 'A Study on Removal of Cobalt from a Primary Coolant by Continuous Electrodeionization with Various Conducting Spacers', Separation Science and Technology, 38: 10, 2347 — 2371

**To link to this Article: DOI:** 10.1081/SS-120021628

**URL:** http://dx.doi.org/10.1081/SS-120021628

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 10, pp. 2347–2371, 2003

# A Study on Removal of Cobalt from a Primary Coolant by Continuous Electrodeionization with Various Conducting Spacers

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## ABSTRACT

The production of high purity water in the primary coolant of a nuclear power plant was investigated using a CEDI process with three ion-conducting spacers, i.e., ion-exchange resin (IX), an immobilized ion-exchange polyurethane resin (IEPU), and an ion-exchange textile (IET). The spacers were characterized by varying experimental conditions, e.g., dosage of adsorbent, pH of the solution, contact time, and the porous-plug model. The CEDI stack was assembled as a bed layered with the cation-exchange and anion-exchange materials. The stack configuration was designed to prevent a reaction between the metal ions and hydroxide ions. The performance of the CEDI operation with the layered bed showed

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DOI: 10.1081/SS-120021628 0149-6395 (Print); 1520-5754 (Online)

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more than 99% removal of the ions at a current efficiency ranged from 18 to 24%. In this study, the feasibility of using the CEDI in operations for the removal of heavy metals present at very low concentrations was successfully demonstrated.

*Key Words:* Ion-conducting spacer; Ion-exchange resin; Ion-exchange polyurethane; Ion-exchange textile; Continuous electrodeionization.

## INTRODUCTION

Ion exchange is the most widely used process for purifying the primary coolant in pressurized water reactor-type nuclear power plants due to its high decontamination efficiency, simplicity, and ease of operation. Since the method is nonselective in removing radionuclides and nonradionuclides, there is a large volume of waste. Volume-reduction technology has not yet been developed for the management of this radioactive waste. The waste has usually been stored for lengthy time periods in the nuclear power plant itself, or has been solidified into a radioactive resin waste by cementation. To prevent the generation of solid wastes, a continuous electrodeionization (CEDI) process was studied in search of a method to purify a primary coolant using synthetic solutions under various experimental conditions.[1]

CEDI is a hybrid separation process that removes ionized species from liquids using electrically active media and an electrical potential activating ion transport. The electrically active media, such as ion-exchange resin, in CEDI devices may function to alternately collect and discharge ionized species, or to facilitate the transport of ions continuously by ionic or electronic substitution mechanisms. This system does not require chemicals to regenerate the ion exchange resin or to concentrate the wastewater. In a CEDI system, the ion-exchange resin bed plays a major role in the reduction of the high electrical resistance in the diluate compartment, while the ion-exchange membranes lead to depletion and concentration of the solutions in the diluate and concentrate compartments, respectively.[2–5]

The production of high purity water in the primary coolant of a nuclear power plant was investigated using a CEDI process with ion-conducting media, such as ion-exchange resin. The ion-exchange resin was introduced into the ion-depleting compartments of the electrodialysis (ED) stack, and has been used to reduce the electrical resistance of the stack since ED cannot be applied economically to treat dilute solutions due to their high electrical resistances.[6–10] However, packing the resin beads in the compartment and assembling the stack is laborious work, while attaining a free-flowing solution is difficult because the resin beads are driven downward by gravity in the diluted compartment, as shown in Fig. 1.[11] Nevertheless, a resin-packed ED stack has recently been developed by Millipore Corporation (Billerica, MA, USA),[13] and is now commercially available from U.S. Filter (Warrendale, PA, USA) as industrial units.

In this study, we compared ion-conducting materials for use in CEDI stacks. IEPU was prepared using a blending method that produces immobilized resin beads by allophanate/biuret cross-linking of flexible polyurethane foam,[13] while IET was prepared by the radiation grafting of styrenesulfonic acid or trimethylammonium chloride onto polypropylene nonwoven fabric.

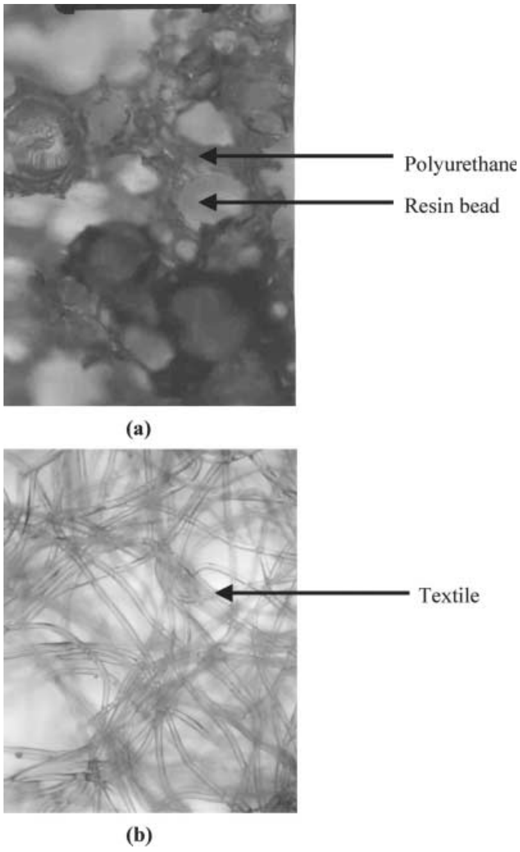

*Figure 1.* Photograph of IEPU (a) and IET (b) (40-fold magnification).

## EXPERIMENTAL

### Preparation of Immobilized Ion-Exchange Resin with Polyurethane (IEPU)

Figure 2 shows the schematic illustration for the synthesis of polyurethane foams containing resin beads. IRN77 and IRN78 (nuclear grade resin, Rohm and Haas) were used as cation and anion exchange resins in this study. A four-neck flask, equipped with a condenser, a mechanical stirrer, a nitrogen inlet adapter, and a dropping funnel, was initially charged with toluene diisocyanate ($2,4 = 80\%$, $2,6 = 20\%$) under saturated nitrogen and at a constant temperature of 110°C. Polypropylene glycol (PPG, Mn = 1000) was slowly added and the reaction was allowed to proceed until the theoretical isocyanate content, 10%, was attained. The isocyanate content was determined using the di-n-butylamine method. Polyurethane prepolymers, 200 g (27.9% of the total weight), was mixed with 19.5-g deionized water (2.7% of the total weight), 450-g ion-exchange resin (62.8% of the total weight), 32.5-g glycerol (4.5% of the total weight), and 15-g L-5614 silicone surfactant (2.1% of the total weight) at an agitation speed of 4000 rpm for

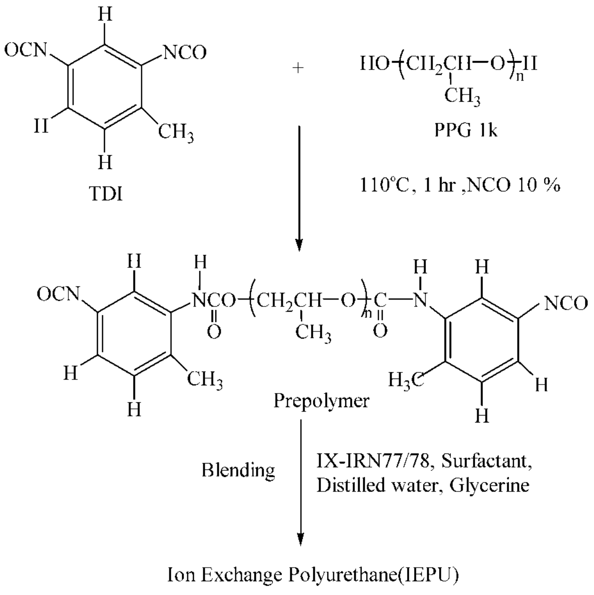

***Figure 2.*** Synthesis of the ion-exchange polyurethane.

10 seconds. Then, the polyurethane prepolymer was poured into a warm mold and placed into an oven at 40°C for 24 hours. The IEPU beads were soaked in distilled water for 30 minutes at 40°C. IEPU requires the homogeneous rearrangement of its polymeric bonds through water conditioning because the foam does not experience stress-free conditions after preparation. The resulting immobilized polyurethane cation- and anion-exchange resins are referred to as CIEPU (cation-exchange polyurethane) and AIEPU (anion-exchange polyurethane), respectively, while CIEPU-IRN77 refers to an IRN77 resin immobilized with the polyurethane cation-exchange resin.

## Preparation of Ion-Exchange Textile

A nonwoven polypropylene textile (Chonbang Co., LTD, South Korea, Model: LP200) was used as a base polymer for grafting. The initial area of the base film for the CEDI stack experiments was 10 × 10 cm. Sodium styrenesulfonate (SSS, $CH_2{=}CHC_6H_4SO_3Na$) and vinyl benzyl trimethyl ammonium chloride (VBTAC, $CH_2{=}CHC_6H_4CH_2N(CH_3)_3Cl$) were used without further purification. The reaction scheme for introduction of ion-exchange groups onto the polypropylene (PP) textile by the radiation-induced graft polymerization (RIGP) technique is shown in Fig. 3. The reaction conditions are summarized in Table 1. The $\gamma$-rays from $Co^{60}$ sources were used to irradiate the preweighed PP textiles at an exposure rate of 4.51 kGy/h to a total dose of 30 kGy under a nitrogen atmosphere at ambient temperatures. The irradiated PP textiles were then immersed in a solution containing monomers of SSS or VBTAC. After grafting, the textile was repeatedly immersed in the corresponding solvent to remove the residual monomer and homopolymer. The resulting cation- and anion-exchange textiles are referred to as CIET and AIET, respectively.

## Characterization of Ion-Conducting Media

The cation-exchange resins IRN77 (M/s. Rohm and Haas, France S.A), CIEPU and CIET, as ion-conducting media, were characterized by their ability to remove cobalt ions. A 500-mg $dm^{-3}$ stock solution of Co(II) was prepared by dissolving 2.4705 g of $Co(NO_3)_2{\cdot}6H_2O$ in 1000 mL of distilled water. This solution was diluted as required to obtain standard solutions containing 10 to 150 mg $dm^{-3}$ of Co(II). One hundred milliliters of a Co(II) solution at a desired concentration and pH were transferred to 300-mL reagent bottles. The pH of the solutions was adjusted with 0.1 N hydrochloric acid or

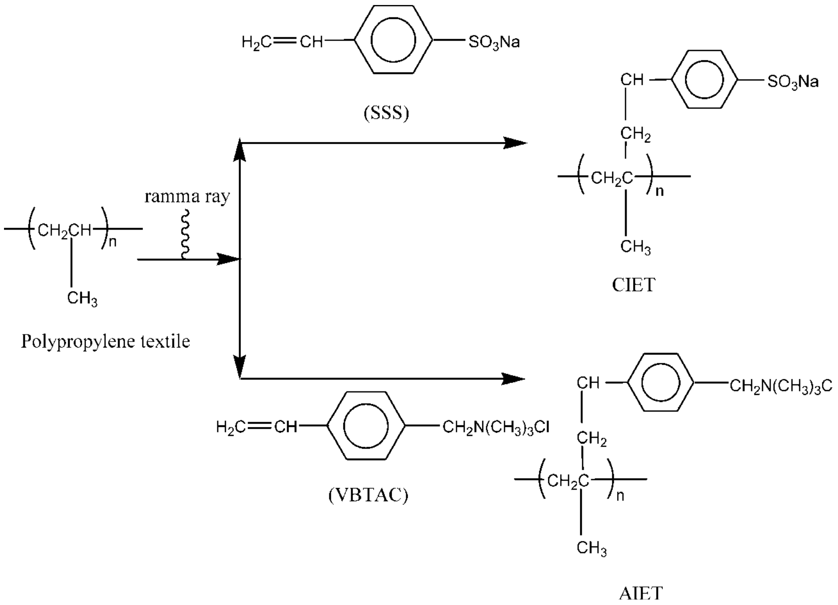

***Figure 3.*** Synthesis of the ion-exchange textile.

dilute sodium hydroxide solutions. Known amounts of ion-conducting media were then added to these solutions. The solutions were agitated for a predetermined period at 25 ± 1°C in a shaking incubator (Model SI-900R Jeio Tech, Korea). The media was then separated and the filtrate was analyzed to

***Table 1.*** Reaction conditions of radiation-induced cografting for preparing ion-exchange textile.

| | Cation-exchange textile | Anion-exchange textile |
|---|---|---|
| Monomer concentration | SSS 1.0 M | VBTAC 0.6 M |
| Solvent | Water | Methanol/DMF |
| Temperature (°C) | 70 | 70 |
| Reaction time | Over 24 hr | Over 24 hr |

DMF = dimethylformamide, SSS = sodium styrenesulfonate, VBTAC = vinyl benzyl trimethyl ammonium chloride.

determine its cobalt content with an inductively coupled plasma spectrophotometer (Sci-Tek Instruments, Model Thermo Jarrel ash IRIS/AP UK). Adsorption isotherm studies were carried out with different initial concentrations of Co(II) while maintaining the resin dosage at a constant value. To study pH effects, $10\,\mathrm{mg\,dm^{-3}}$ of Co(II) and a media dosage of $500\,\mathrm{mg}\ 100\,\mathrm{mL^{-1}}$ were used. To correct any adsorption of Co(II) to the containers, control experiments were carried out without media addition. It was found that there was no adsorption by the container walls. In addition, all mixing vessels were kept sealed throughout the duration of each isotherm test to minimize volume loss due to evaporation.

A flow cell was used for measurement of the electrical conductivity of the media when saturated with a solution of cobalt nitrate. As shown in Fig. 4, the media were placed between a pair of platinum electrodes. The feed solution was circulated through the flow cell until it reached a steady state with the packed resin. The top pair of electrodes was used to measure the conductivity of the solution using an LCZ meter (Model 2821, NF Electronics, Japan), and the bottom pair of electrodes was used to measure the conductivity of the solution and the IEPU. The electrical conductivity of the ion-exchange polyurethane foam was measured using a LCZ meter with the flow cell at 1.5 cm/sec. The feed solution was circulated through the flow cell until it reached equilibrium with the packed resin. The cell constant was calculated using a solution having a known $k$ value, while the LCZ meter provided the resistance, $R$. Therefore, $k$ can be determined from the equation:

$$R = \frac{1}{k}\frac{l}{A} \tag{1}$$

where, $l$ is distance between the electrodes, and $A$ is the area of the electrodes.

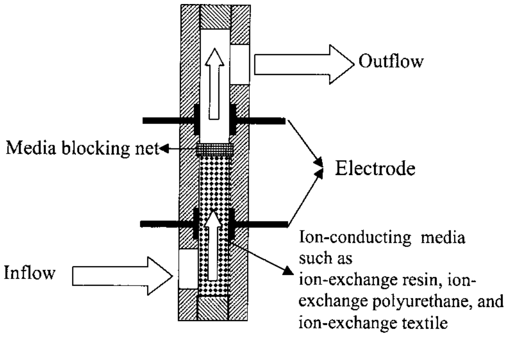

*Figure 4.* Schematic representation of the flow cell.

If the value of $k$ is known for a standard solution of a reference electrolyte, $l/A$ (the cell constant) can be calculated from the observed resistance. Once the cell constant is determined, the conductivity of any electrolyte can be calculated from the measured resistance using this equation. The cell constant of the flow cell was obtained for each electrode pair using a frequency of either 1 kHz or 100 kHz.

The permeability of the media in the CEDI module was calculated from the equation:

$$\text{Permeability} = \frac{J \times L}{\Delta P} \tag{2}$$

where, $J$ is the flux, $L$ is the thickness of the media, $\Delta P$ is the pressure difference across the media. The permeability test was carried out to measure the hydraulic resistance of the media in the CEDI module in the presence of ion-exchange membranes.

## CEDI Stack Operation

A single cell pair of the module (1-cell laboratory CEDI unit) was used while purifying the synthetic primary coolant water. A silicon block with a thickness of 0.95 cm was placed between the ion-exchange membranes to confine the resin beads in the diluted compartments. Figure 5 shows the cell configuration of the CEDI stack. The stack, with an effective membrane area of 50 $\text{cm}^2$ per cell, was assembled as a layered bed. In the layered bed, cation-exchange media was placed in the bottom so as to prevent a reaction between the cobalt ions and hydroxide ions since the metal ions would be removed before contacting with the anion-exchange media. A DC power supply (Agilent Technologies, HP-IB series 6674A, USA) was used for the CEDI module operation. The ratio of the anion to cation-exchange resins was varied to observe the pH change. A 0.34-mN cobalt nitrate solution was used with the various resin bed ratios in the diluted compartment. Prior to CEDI operations, the counter ions in the media were substituted by cobalt (cation exchange) and nitrate ions (anion exchange) since it was assumed that ion exchange alone could remove ions without an electrical field. The feed solutions were pumped through the diluted compartment at a flow rate of 5 mL/min. The concentrated solution and electrode solutions were circulated at flow rates of 5 mL/min and 30 mL/min, respectively. The conductivity and pH of the inlet and outlet solutions of the diluate and concentrate were measured at predetermined time intervals.

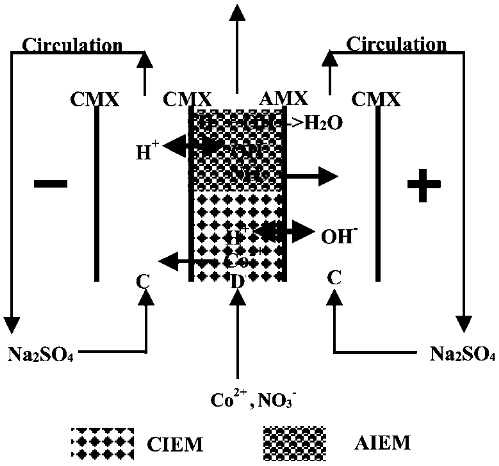

*Figure 5.* Layered bed configuration in the diluted compartment. CMX: cation exchange membrane, AMX: anion exchange membrane, C: concentrate, D: diluate, CIEM: cation-exchange media, AIEM: anion-exchange media.

## RESULTS AND DISCUSSION

### Characterization of Ion-Conducting Media

Effects of the pH on the Removal of Co(II)

Figure 6 presents the effect of the pH on the removal of Co(II) by IRN77, CIEPU-IRN77, and CIET. These media are effective in removal of Co(II) over a pH range of 2 to 8. For comparison, a precipitation curve at the different pH values in the absence of resins is shown in Fig. 6. Precipitation of Co(II) began at pH 8.5. The result indicates that at any pH, the removal of the metal cation by adsorption is much greater than by hydroxide precipitation. Adsorption of the metal cation on the adsorbent depends on the nature of the adsorbent surface and species distribution of the metal cation. For all media tested, an increase in the pH to a value of greater than 8 results in a decrease in the adsorption, because of the formation of the hydroxocomplex of cobalt, $Co(OH)_2$.[14,15] Hence, in all subsequent studies, the experiments were performed in a solution at pH 5.3.

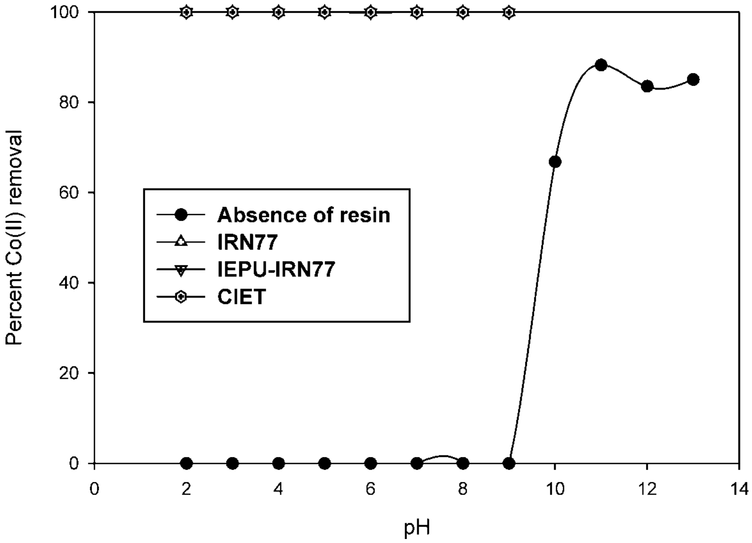

*Figure 6.* The effect of pH on the adsorption of Co(II) on the IRN77, IEPU-IRN77, CIET. Conditions: initial Co(II) concentration = 10 mgl$^{-1}$; equilibrium time = 24 h; and media dosage = 1000 mg 100 ml$^{-1}$.

## Effects of Media Dosage on the Removal of Co(II)

Figure 7 shows the removal of Co(II) as a function of media dosage, i.e., the quantity of IRN77, CIEPU-IRN77, and CIET. The media dosage was varied from 0.025 to 0.700 g and equilibrated for 24 hours. For the quantitative removal of 100 mg dm$^{-3}$ of Co(II) in 100 mL, a minimum dosage of 150 mg IRN77, 500 mg CIEPU, and 6000 mg CIET are required. The results show that a minimum dosage, of 1.5 g/L of IRN77 is needed for the maximum removal of Co(II), which is 3.3 times lower than that of CIEPU. In Figs. 6 and 7, IRN77 in CIEPU refers to the quantity of IRN77 in the CIEPU since it was prepared using a polyurethane binder and the IRN77 ion-exchange resin by allophanate/biuret cross-linking. The ion-exchange capacity of the IRN77 in CIEPU media is similar to the IRN77 media based on the resin dosage. This may be due to the composition of IRN77 in CIEPU, with a final mixture ratio of 70% IRN77 and 30% prepolymer. Experimental results revealed that the Co(II) removal efficiency increases up to the optimum dosage, beyond which the removal efficiency did not change with the media dosage.[16,17]

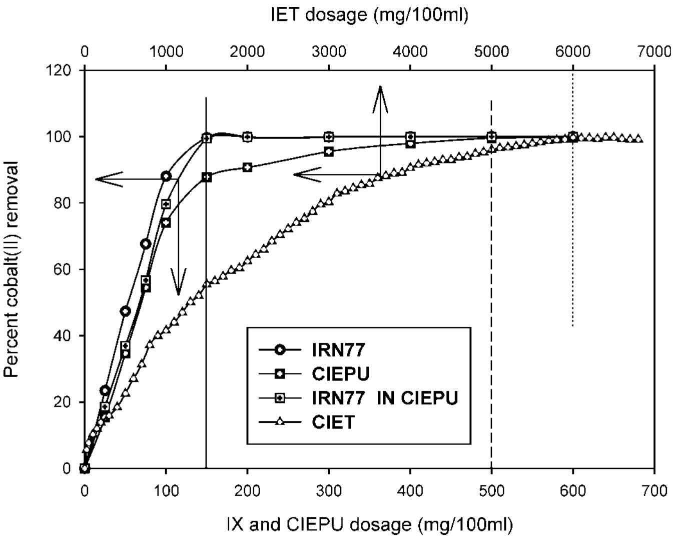

***Figure 7.*** The effect of media dosage on the adsorption of Co(II) on the IRN77, IEPU-IRN77, CIET. Conditions: initial Co(II) concentration = $100\,\text{mgl}^{-1}$; equilibrium time = 24 h; and pH = 5.3.

## Effects of the Contact Time on the Removal of Co(II)

Figure 8 shows the effects of the contact time on the removal of Co(II) by IRN77, CIEPU-IRN77, and CIET. The removal rate increased with time and reached equilibrium within 4 hours for IRN77, 5 hours for CIEPU, and 0.1 hours for CIET for an initial Co(II) concentration of $100\,\text{mg}\,\text{dm}^{-3}$. The time to reach equilibrium was independent of the initial concentration. The metal uptake versus time curves are single, smooth, and continuous, leading to saturation, suggesting a possible monolayer coverage of the metal ions on the surface of the adsorbent.[18]

## Adsorption Isotherm

Removal of the cobalt ions can be expressed mathematically in terms of adsorption isotherms. Three commonly cited isotherms are the linear, Langmuir, and Freundlich types. The simple linear isotherm is frequently assumed even though it rarely occurs.

$$q = K \cdot y \tag{3}$$

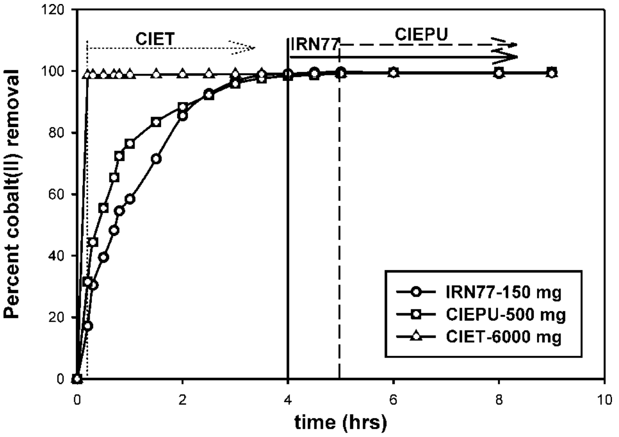

*Figure 8.* The effect of contact time on the removal of Co(II) on the IRN77, IEPU-IRN77, CIET. Conditions: initial Co(II) concentration $= 100\,\mathrm{mgl^{-1}}$; IRN77/CIEPU/CIET dosage $= 150/500/6000\,\mathrm{mg100\,ml^{-1}}$, and pH $= 5.3$.

where $q$ is the concentration in the adsorbent and $y$ is the concentration in the solution. The isotherms for the various materials are shown in Fig. 9. From this figure, the data for IRN77 and CIEPU fit the Langmuir isotherm the best, in part due to the fact that the ion-exchange resin has a limited number of sites that are subject to chemical equilibrium.[19]

The Langmuir equation, below, was applied to the adsorption equilibrium for the three different media,

$$(C_e/q_e) = 1/(Q_o b) + C_e/Q_o \tag{4}$$

where $C_e$ is the equilibrium concentration ($\mathrm{mg\,dm^{-3}}$), $q_e$ is the amount adsorbed at equilibrium ($\mathrm{mg\,g^{-1}}$), and $Q_o$ and $b$ are the Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The adsorption capacity is the number moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface. The adsorption energy is a constant representing the energy of interaction with the surface. The linear plots of $C_e/q_e$ vs. $C_e$ shows that the adsorption obeys the Langmuir model for both media (Fig. 10). $Q_o$ and $b$ were determined from the Langmuir plots and the values are summarized in Table 2. The high specific conductivity is favored by a high concentration of the fixed ionic group, and a higher value for $b$ indicates a lower affinity for cobalt. The maximum adsorption capacity, $Q_o$, was amount of adsorbed Co(II) per unit weight (g) of adsorbent. The adsorption capacity of IEPU, 110 mg/g, corresponds to an ion-exchange

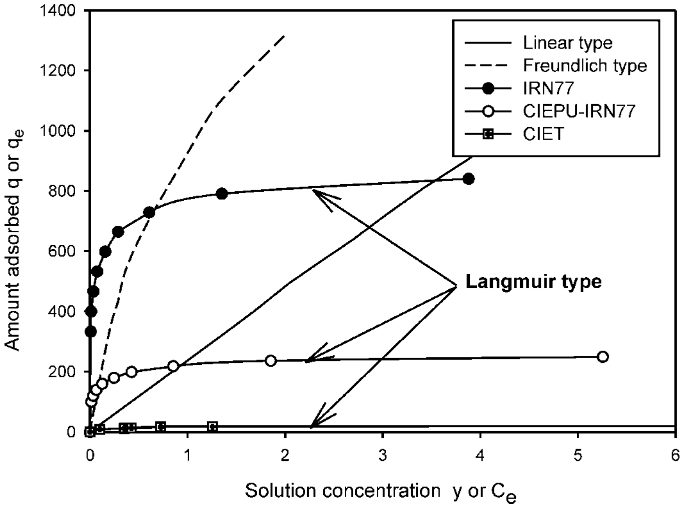

*Figure 9.* Adsorption isotherm for Co(II) with IRN77, CIEPU-IRN77, and CIET. Conditions: initial Co(II) concentration = 0 ~ 100 mgl$^{-1}$; IRN77/CIEPU/CIET dosage = 150/500/6000 mg 100 ml$^{-1}$, pH = 5.3).

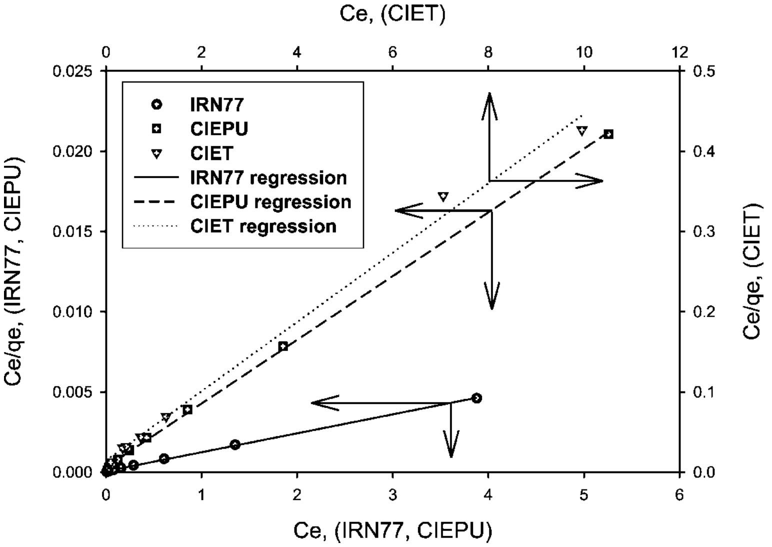

*Figure 10.* The Langmuir adsorption isotherm for Co(II) with the IRN77, CIEPU, and CIET systems.

***Table 2.*** Adsorption capacity and energy from Langmuir adsorption isotherm.

| Ion-exchange media | Adsorption capacity Qo, mg/g | Adsorption energy b, dm$^3$/mg |
|---|---|---|
| IRN77 | 126.85 | 12.00 |
| CIEPU | 110.00 | 13.33 |
| CIET | 23.15 | 3.00 |

capacity of 3.7 meq/g. The CEDI system with IEPU may have a higher electrical resistance than the CEDI system with IRN77 due to its lower adsorption capacity and higher adsorption energy. Even though the capacity of IRN77 and IEPU was higher than that of IET, the adsorption energy of IET was lower. Therefore, IET has a high selectivity for cobalt and transport through the IET is faster than that through IRN77 and IEPU.

The essential characteristics of the Langmuir isotherm is its expression as a dimensionless constant, separation factor, or equilibrium parameter, $R_L$, which is defined by,

$$R_L = 1/(1 + bC_o) \tag{5}$$

where $b$ is the Langmuir constant and $C_o$ is the initial concentration of Co(II).[20] The $R_L$ values indicate a favorable adsorption of Co(II) onto IRN77, CIEPU, and IET media under the conditions investigated in this study. $R_L$ values for IRN77, CIEPU, and IET media were 0.077, 0.071, 0.25, respectively.

## Reversible Adsorption Kinetics

The kinetics of sorption describe the solute uptake rate, which in turn governs the residence time of the sorption reaction. It is one of the more important characteristics in defining the efficiency of sorption. Hence, in the present study, the kinetics of cobalt removal has been investigated to understand the behavior of the two different adsorbents. The adsorption of cobalt from an aqueous solution follows reversible first-order kinetics, as when a single species is adsorbed on a heterogeneous surface. The heterogeneous equilibrium between the cobalt solution and the ion-exchange resin may be expressed as,

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \tag{6}$$

where $k_1$ = forward reaction rate constant, $k_2$ = backward reaction rate constant.

$$k_C = \frac{X_e}{A - X_e} = \frac{k_1}{k_2} \tag{7}$$

$$\ln(1 - U_t) = -(k_1 + k_2)t = -kt \tag{8}$$

where $k_C$ is the equilibrium constant, $k$ is the overall rate constant, and $A$ is the initial concentration of cobalt.

$$\frac{C_{A(O)} - C_{A(t)}}{C_{A(O)} - C_{A(e)}} = \frac{x}{X_e} = U_t \tag{9}$$

$C_{A(0)}$ = initial concentration of cobalt.

$C_{A(t)}$ = the concentration of cobalt present at any time t.

$C_{A(e)}$ = the concentration of cobalt present at equilibrium.

$x$ = the amount transferred from liquid phase to solid phase at any time t.

$X_e$ = the concentration of cobalt adsorbed at equilibrium.

where $U_t$ is the fractional attainment of cobalt at equilibrium.[21] This value was calculated by measuring the cobalt adsorption onto the resins at a given time between 1 and 24 hours. In the present study, initial concentrations of cobalt was in the range of 50 to 150 mg dm$^{-3}$. Using the kinetic equations, the overall rate constant along with the forward and reverse reactions were calculated. For instance, by plotting ln[$1 - U_t$] vs. $t$, the overall rate constant $k$ for a given concentration of cobalt was calculated from the slope of the linear portion of the graph, while, by using Eqs. (7) and (8), the equilibrium constant $k_C$, and both the forward and reverse rate constants, $k_1$ and $k_2$, were calculated. The results are listed in Table 3. From these results, the forward rate constants, corresponding to the removal of cobalt from the solution, were much greater than the reverse rate constants, namely the desorption process.[22]

To assess the nature of the diffusion process responsible for adsorption of Co(II) on IRN77, CIEPU, and CIET, the coefficients of the process were calculated. If film diffusion is the rate-determining step in the adsorption of Co(II) onto their surfaces, the value of the film diffusion coefficient ($D_f$) should be in the range of $10^{-6}$ to $10^{-8}$ cm$^2$ sec$^{-1}$. If pore diffusion is the rate-limiting step, the pore diffusion coefficient ($D_p$) should be in the range of $10^{-11}$ to $10^{-13}$ cm$^2$ sec$^{-1}$.[23] Assuming spherical geometry for the sorbent,

***Table 3.*** Rate constants for the removal of Co(II) with IRN77, CIEPU, and CIET system.

| Sl. No | Name of the media | Co(II) concentration (mg dm$^{-3}$) | Overall rate constant $k = k_1 + k_2$ (h$^{-1}$) | Forward rate constant $k_1$(h$^{-1}$) | Backward rate constant $k_2$(h$^{-1}$) |
|---|---|---|---|---|---|
| 1 | IRN77 | 50 | 1.4626 | 1.4624 | 0.0002 |
| 2 | | 100 | 1.2376 | 1.2364 | 0.0012 |
| 3 | | 150 | 1.3111 | 1.2932 | 0.0179 |
| 4 | CIEPU | 50 | 1.0019 | 0.9998 | 0.0021 |
| 5 | | 100 | 0.5670 | 0.5584 | 0.0086 |
| 6 | | 150 | 0.5388 | 0.5120 | 0.0268 |
| 7 | CIET | 50 | 147.0 | 145.1537 | 1.8463 |
| 8 | | 100 | 115.7 | 114.1612 | 1.5388 |
| 9 | | 150 | 105.8 | 98.7756 | 7.0244 |

the overall rate constant of the process can be independently correlated to the pore diffusion coefficient and film diffusion coefficient in accordance with their respective expressions,[21]

$$\text{Pore diffusion coefficient} \quad D_p = 0.03 \times \frac{r_o^2}{t_{1/2}} \tag{10}$$

$$\text{Film diffusion coefficient} \quad D_f = 0.23 \times \frac{r_o \partial}{t_{1/2}} \times \frac{\bar{c}}{c} \tag{11}$$

where $r_o$ is the radius of the adsorbent (0.0325 cm for resin bead, 0.0010 cm for textile), $\partial$ is the film thickness ($10^{-3}$ cm), $\bar{c}$ is the amount adsorbed, and $c$ is the initial concentration.[24] Employing the appropriate data and the respective overall rate constants, the pore and film diffusion coefficient for various concentrations of Co(II) were calculated for each cation exchange media. The results are presented in Table 4. It is evident that the removal of Co(II) follows the film diffusion process since the coefficient values are between $10^{-6}$ and $10^{-8}$ cm$^2$ sec$^{-1}$, regardless of the media used.

Optimizing the deionization performance of CEDI devices entails optimization of the deionization rate per unit effective membrane area. For the deionization of wastewater using ion-exchange resins, the transfer rates of ions in the depleting stream are primarily controlled by film diffusion. Therefore, improvements in ion transport can be made by increasing the active surface area of ion-exchange surface per unit membrane area for given feed conditions and flow velocities, and at operating voltages that do not result in substantial electrochemical reaction products. In this case, the term active

***Table 4.*** Diffusion coefficient for the removal of Co(II) by IRN77, CIEPU, and CEIT system.

| Sl. No | Name of the resin | Co(II) concentration ($mg\,dm^{-3}$) | Film diffusion coefficient ($cm^2\,sec^{-1}$) | Pore diffusion coefficient ($cm^2\,sec^{-1}$) |
|---|---|---|---|---|
| 1 | IRN77 | 50 | $4.38173 \times 10^{-9}$ | $1.85771 \times 10^{-8}$ |
| 2 | | 100 | $3.70464 \times 10^{-9}$ | $1.57193 \times 10^{-8}$ |
| 3 | | 150 | $3.87462 \times 10^{-9}$ | $1.66528 \times 10^{-8}$ |
| 4 | CIEPU | 50 | $2.99578 \times 10^{-9}$ | $1.27256 \times 10^{-8}$ |
| 5 | | 100 | $1.67302 \times 10^{-9}$ | $7.20170 \times 10^{-9}$ |
| 6 | | 150 | $1.53417 \times 10^{-9}$ | $6.84352 \times 10^{-9}$ |
| 7 | CIET | 50 | $6.80862 \times 10^{-10}$ | $2.82828 \times 10^{-8}$ |
| 8 | | 100 | $5.67462 \times 10^{-10}$ | $2.22607 \times 10^{-8}$ |
| 9 | | 150 | $2.59037 \times 10^{-9}$ | $2.03559 \times 10^{-8}$ |

surface area is defined as the area both available to liquid flow and with an uninterrupted conductive path along the ion-exchange resin to the membrane for deionization.[4]

## Porous-Plug Model

Wyllie suggested an approach for ion-exchange beds where the distribution of the resin particles constitutes an irregular and discontinuous phase and the liquid is regarded as a continuous one.[25] The model estimates the electrochemical properties from empirical and geometrical parameters. This “porous-plug” model is based on the principle that the electrical current passes through three different paths within the media. The first path is alternating layers of foam and interstitial solution; the second is the bridge connecting foam particles or sections which are in contact with each other; and the third is the channel through the interstitial solution (Fig. 11).

The parameters of the model were estimated in this study to predict the electrochemical properties of the media.[26,27] The equation for the porous-plug model is based on the geometrical configuration of the media. From Fig. 12, the constants *a*, *b*, *c*, *d*, and *e* were calculated (Fig. 13). These values depend little on the particle size and the nature of the electrolyte. Although the experiments cannot be compared directly with other ion-exchange media, we can predict the portion of electrical current passing through the three different paths in the ion flux.

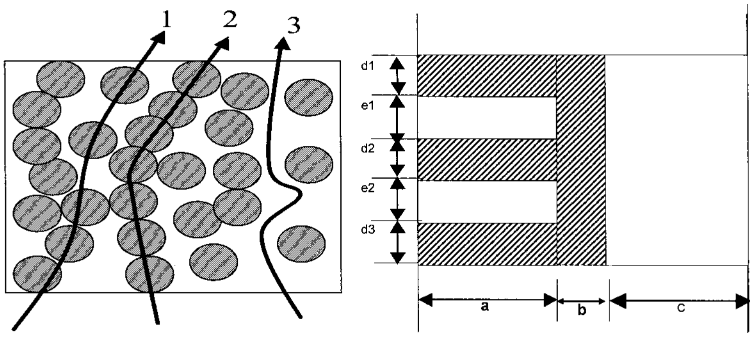

*Figure 11.* The "porous-plug" model. Left: schematic representation of the three paths which the current can take. Right: the simplified model consisting of three conductance elements in parallel. The geometrical parameters d and e are given by d1 + d2 + d3 = d, and e1 + e2 = e. From Spiegler. K.S., Yoest. R.L., and Wyllie. M.R.J.

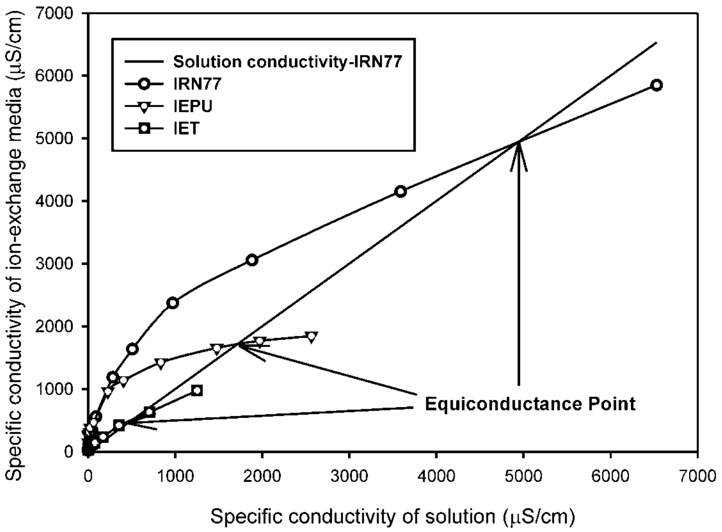

*Figure 12.* Specific conductivity of the ion conducting media versus that of the solution when in equilibrium with $Co(NO_3)_2$.

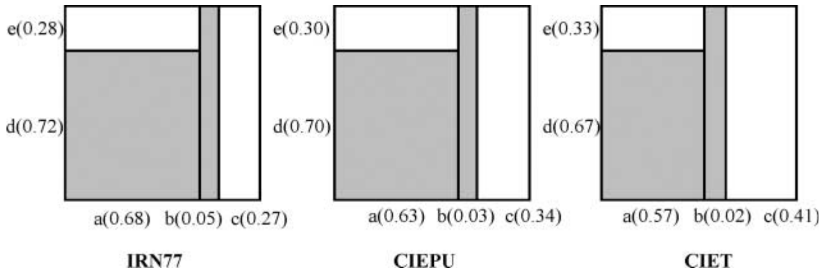

***Figure 13.*** Ratio configuration for conductance through the solid phase and the solution phase based on the porous-plug model; gray blocks are solid phases and white blocks are solution phases.

As shown in Fig. 12, the specific conductivities, $\bar{k}$, of the media were 550, 1800, and 4900 μS/cm for CIET, CIEPU, and IRN77, respectively. The results indicate that IRN77 is electrically more conductive than the others when under the influence of an electrical potential. The value for CIEPU was predicted to be in the range of 3000 to 3500, about 70% of IRN77, since it is composed of 70% IRN77. The polyurethane enclosing the IRN77 resin beads in CIEPU increases the electrical resistance by more than 2.7-fold, as shown in Fig. 1(A). The conductivity of ion-conducting media is not constant but depends on the concentration of the fixed ionic group (i.e., the ion-exchange capacity). The ion-exchange capacity of IRN77, CIEPU, and CIET is 4.2, 3.7, and 1.0 mEq/g, respectively. Moreover, the equiconductance point allows one to predict the concentration range where the media would be most efficient in the CEDI process. In a system consisting of a dilute ionic solution in contact with ion-conducting media, ionic transfer driven by an electrical potential will occur almost exclusively through the ion-conducting media, not through the water. The ease of ion transfer can be used to determine the electrical resistivity of the system. While the porous-plug model illustrates the pattern of the ionic flux, the conductivity of the resin bed is an important operating variable to maximize the total ionic flux.

Figure 13 shows the rectangular configuration of the media. It illustrates the configuration of the ratio between the solid and solution portions of the media, both horizontally and vertically. In this figure, current flows in the vertical direction. Gray-filled blocks account for the solid phase. White blocks correspond to the solution phase. From the left, they include transfer through the solution and solid phases alternatively, the solid phase alone, and the solution phase alone, respectively.

Most of the current passes through a mixture of the media and solution phases in the ion-conducting media. Thus, the ion-conducting media are electrically more conductive than the solutions to be treated. Also, the ion-conducting media significantly reduce electrical resistance and increase the available surface area for ion exchange. It is desirable to use such electrically conductive media as IRN77, IEPU, and IET, during treatment of dilute solutions with a CEDI operation.

### Permeability of the Media Through CEDI Module

If the diluate compartment is packed with resin beads and the feed solution is driven upward in the compartment, maintaining a low pressure and attaining a freely flowing solution is difficult. Therefore, a permeability test was carried out to measure the hydraulic resistance of the media in the CEDI module in the presence of ion-exchange membranes and media.

The permeability of the media is a function of pore size, void volume, or porosity, thickness, and asymmetry. The media permeability has a significant impact on the design of CEDI modules and systems as well as on process economics.[28,29] For ion-conducting media, permeabilities decrease with decreases in the pore size or void volume, or an increase in thickness. The permeability was determined using the CEDI module and the results are summarized in Table 5. The CIEPU is the cation-exchange polyurethane consisting of 70% IRN77. The permeability of CIET was higher than those of the others due to its low density, as shown in Fig. 1.

### CEDI Operation with a Vertically Layered Bed

Previous studies employed a CEDI filled with mixed-bed ion exchange resins for high purity water production.[2–4] However, such a CEDI configuration cannot treat solutions containing metal ions effectively because of the precipitation of metal hydroxides. The metal ions precipitate as a result

***Table 5.*** Permeability of the IRN77, CIEPU, and CEIT systems.

| | CIET | CIEPU | IX(IRN77) |
|---|---|---|---|
| Density (g/cm$^3$) | 0.31 | 0.65 | 0.87 |
| Permeability (l/m · hr · bar) | 36,000 | 12,800 | 9,000 |

of a reaction with hydroxide ions that are present in the CEDI stack. To improve the performance of the CEDI device, it is necessary to prevent precipitation. In this study, a CEDI system packed with a layered bed was employed with sequential layers of cation and anion exchange media, as shown in Fig. 5. The ion-exchange media bed was divided into two parts. The bottom portion contained cation-exchange media to remove cations actively, while the top contained the anion-exchange media for pH adjustment. The stack configuration with a layered bed prevented precipitation between the metal ions and hydroxide ions. The volume ratio of the media bed was 3:2 (cation:anion media) to balance out the anion and cation exchange ratios.

Removal of the cobalt ions reached 99%, as shown in Fig. 14. The pH of the diluted compartment was between 6.8 and 8.0. Also, the pH of the concentrated compartment was maintained between 3 and 4. The removal rate increased with time and reached a steady state (i.e. 99% removal) within 30 minutes for IRN77, 50 minutes for CIEPU, and 10 minutes for CIET for an initial Co(II) concentration of 10 mg dm$^{-3}$. Although IET has a lower ion-exchange capacity, its rate constant is very high because of the faster exchange kinetics due to the absence of crosslinking. Therefore, a CEDI process with IET performed effectively by

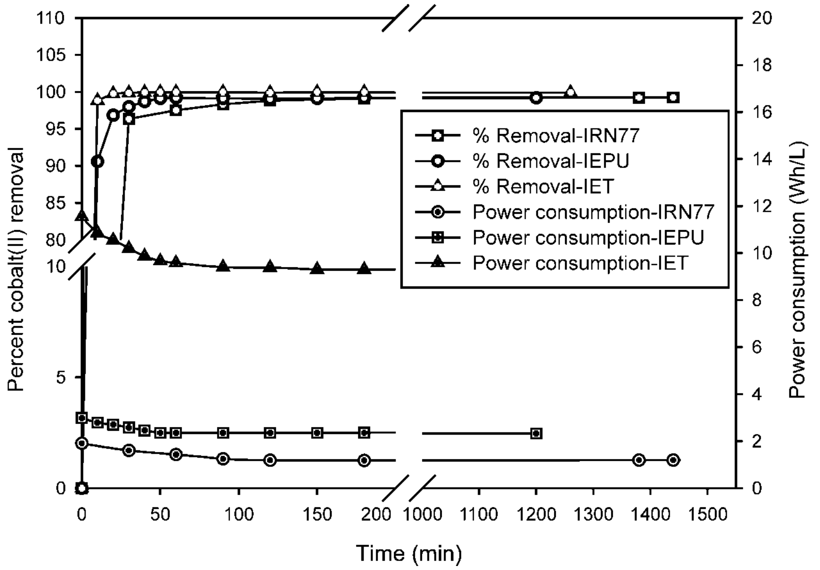

*Figure 14.* Variations in percent Co(II) removal and power consumption over time dependent upon the spacer used.

transport from the diluate compartments to concentrate compartments in the stack.

The energy necessary for the ion transfer is directly proportional to the total current flowing through the stack and the voltage drop between the two electrodes in a stack. The electrical current needed to desalt a solution is proportional to the number of ions transferred through the ion-exchange membranes from the feed stream to the concentrated brine. Thus, the operating cost increases with increasing energy consumption. The power consumption was 1.2 Wh/L for IRN77, 2.4 Wh/L for IEPU, and 9 Wh/L for IET. The current efficiency ranged from 18 to 24% with a current density of 15 A/m$^2$. Since the power consumption depends on the ion-exchange capacity of media, the power consumption of IET was higher than those of the others, as shown in Fig. 14.

The performance of the CEDI with a layered bed was demonstrated with an ion removal greater than 99% and a current efficiency of 20%. The results show that for an inlet conductivity of 40 μS/cm, a linear velocity of 4.17 cm/sec, an applied current density of 15 A/m$^2$, and an outlet conductivity of 1.0 μS/cm was obtained while preventing precipitation. In all cases, the resistivity of the water treated in the laboratory CEDI unit was greater than 1 MΩcm, which meets the guidelines for water fed to the reactor coolant system.

## CONCLUSION

The removal of cobalt ions was investigated using a CEDI process packed with ion-exchange resin, ion-exchange resin immobilized with polyurethane and an ion-exchange textile as the ion-conducting spacer. Even though all of the media removed cobalt effectively, the ion-exchange textile was better than the others as an ion-conducting spacer in terms of its faster exchange kinetics and the overall cobalt removal rate. The CEDI process with the ion-exchange textile enhanced the transport of cobalt from the diluate compartments to the concentrate compartments in the stack. It was found that CEDI is a process in which the primary sizing parameter is the transport through the media, not the ionic capacity of the media. However, the operating cost of IET was higher than that of the others since the power consumption depends on the ion-exchange capacity. Therefore, the most desirable ion-conducting spacer for the CEDI system may be an ion-exchange textile that has a high ion-exchange capacity since it has higher fixed ionic groups and faster exchange kinetics. Further studies on IET synthesis to increase its ion-exchange capacity are in progress.

## ACKNOWLEDGMENT

The authors gratefully acknowledge the nuclear technology program at the Korea Institute of Science and Technology Evaluation and Planning (KISTEP) for the financial support to carry out this work.

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Received September 2002