

전기탈이온 시스템에서의 이온교환섬유를 통한 니켈 이온의 전기이동현상

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Migration Phenomena of Ni²⁺ Through a Cation Exchange Textile (CIET) in a Continuous Electrodeionization (CEDI)

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요 약: 전기탈이온 장치를 통한 니켈이온의 이동메커니즘이 이온교환섬유의 전기화학적 특성을 이용하여 조사되었다. 포러스 플러그 모델과 확장된 너스트-플라크 식이 니켈이온의 이동 현상의 해석을 위해서 적용되었다. 적용된 모델을 통해 전기탈이온 시스템의 성능증가는 이온교환섬유를 통해 변화되는 이동도에 기인하는 것이 아니라, 이온교환매개체의 자체 전도도에 의해 일어나는 전류 유발 효과에 의한 것으로 나타났다. 또한, 최적의 전기탈이온 공정운전이 최소화된 전기적 재생영역하에서 일어남을 본 연구를 통해 제시되었다.

Abstract: Transport mechanisms of nickel ion through a continuous electrodeionization (CEDI) were investigated in terms of electric properties of ion exchange textile (IET). The porous plug model and extended Nernst-Planck (N-P) equation were applied for the description of transport mechanism of nickel ion. The model revealed that the CEDI performance was mainly due to the induced current not accelerated mobility by IET. This study also suggested that optimal operating conditions are attained with minimized electroregeneration region.

Keywords: continuous electrodeionization (CEDI), ultrapurification, decontamination

1. Introduction

Industrial waste water often contains considerable amounts of heavy metals that would endanger public health and the environment. The removal of heavy metals from industrial waste water has received great attention in recent years in the aspect of protection of the environment. Nickel (II) ions are contained in the effluent waste water of nickel plating plant, silver refineries, zinc base casting industries and coolant water in a nuclear power plant. The nickel

concentration over tolerance limit (0.01 mg/L) in drinking water is known to cause the cancer of lungs, nose and bone in human body. Dermatitis (nickel itch) is the most frequent effects from the nickel materials such as coins and jewelry. Nickel (II) poisoning causes dizziness, headache, nausea and rapid respiration, cyanosis and extreme weakness. Thus, nickel removal from waste stream is an important issue in the environmental aspects[1].

Continuous electrodeionization (CEDI) is a novel hybrid separation process of electrodialysis (ED) and ion exchange (IX) for the removal of ionized or

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ionizable species from feed water. Ion selective membranes are placed between the electrodes like ED stack and ion exchange media such as ion exchange textile (IET) are packed in the diluate compartment for the complete removal of ions. Water dissociation on the bipolar interface in the CEDI system electrochemically regenerates the ion exchange media and enables semi-permanent use of ion exchange media. Thus, a CEDI system has been recognized as environmental friendly process and found world wide application in industries with the most demanding high purity water[2,3,4,5].

Ionic transport in a CEDI system is not well understood due to complicated inter-relationships among the ion exchange media, electrolyte solution, and ion exchange membrane. Moreover, continuous ion exchange reactions on ion exchange media makes it difficult to describe the transport mechanism of ions[3].

The purpose of this study is to investigate the transport mechanism of nickel ion through the CEDI system which suggests important design parameters of a CEDI stack. For the description of transport mechanisms, electrical characteristics of ion exchange media were investigated. The porous plug model and extended Nernst-Planck equation were employed to describe the transport phenomena of nickel ion. The transport mechanism of nickel ion in the CEDI was discussed based on the results of combined model. The results of the model may provide useful information for the CEDI stack design and operation.

2. Experimental

2.1. Preparation and Characterization of Ion Exchange Media

Ion exchange textile (IET) to be packed in diluate compartment of a CEDI system was prepared using UV-treatment. Nonwoven polypropylene textile (3 mm, Jeonbang Co. Ltd., Korea) was immersed in 3

wt.% BP (benzophenon, photo-initiator) for 2 hrs and then dried at room temperature. BP-coated IET was then irradiated with UV light (400 watt, wave length: 232~500 nm) for 5 min under nitrogen atmosphere. After UV irradiation, it was immersed in a solution containing mixed monomer composed of 25 wt.% of styrenesulfonic salt (SSS, $\text{CH}_2=\text{CHC}_6\text{H}_4\text{SO}_3\text{Na}$) and 10 wt.% of acrylic acid ($\text{CH}_2=\text{CHCOOH}$). Textile with monomer solution was further irradiated for 15 min under the same conditions. Thermal polymerization after UV irradiation was also carried out at 80°C for 6 hrs. Generated homopolymer onto PP textile was removed with distilled water (80°C) under sonification[6].

The ion exchange capacity (IEC) of IET was determined using a titration method. Three grams of IET was converted into H^+ by immersing 1 M HCl solution for 24 hrs. The sample was soaked in deionized water to remove sorbed acid. Converted ion exchange media with hydrogen form was kept in a 1 N NaCl solution to exchange the protons with sodium form. To ensure complete exchange, IET was refreshed one more times. The NaCl solutions which contained protons were mixed and titrated with 0.1 N NaOH[3].

2.2. Electric Conductivity

A flow cell was used to measure the electrical conductivity of nickel-saturated ion exchange textile. Composed of various types of nickel solution flushed through the flow cell until it reached an equilibrium with the ion exchange textile. Conductivities of solution and textiles were measured using LCZ meter (model 2321, NF electronics, Japan) at a linear velocity of $1.5 \text{ cm} \cdot \text{sec}^{-1}$. The electrical conductivity measured by flow cell, k , was determined from the following equation (1):

$$R = \frac{1}{k} \frac{l}{A} \quad (1)$$

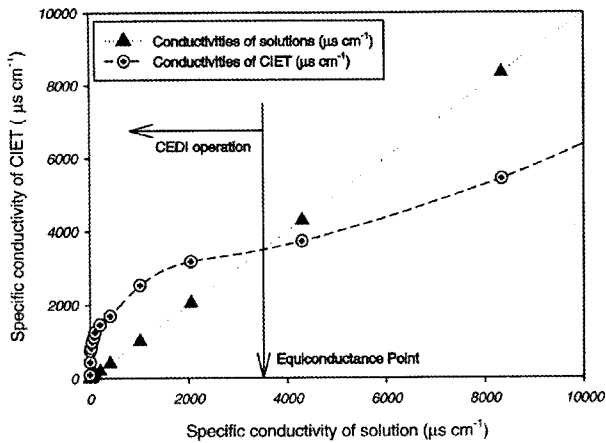


Fig. 1. Electric conductivity of IET.

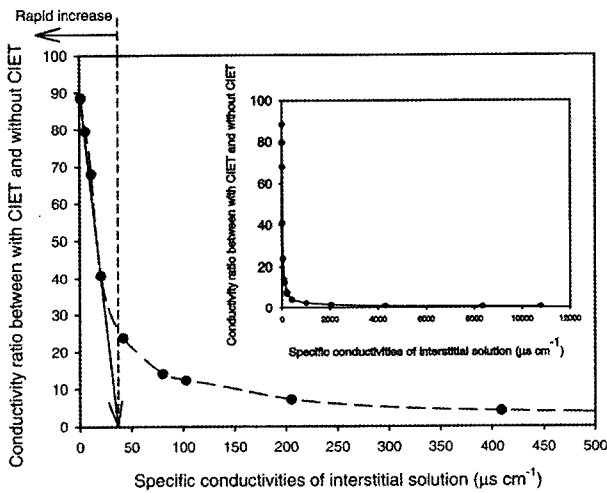


Fig. 2. Conductivity ratio of CIET to without CIET in a CEDI system.

where, l is distance between the electrodes, and A is the area of the electrodes[3,7].

2.3. CEDI Operation

A CEDI system with an effective membrane area of $2 \text{ cm} \times 10 \text{ cm}$ was used for the nickel migration experiment. The thickness of diluate compartment was 1 cm and prepared cation exchange textile was packed in diluate compartment. CMX- cation exchange membrane and AMX- anion exchange membrane (Tokuyama Soda. Co. Ltd., Japan) were used for the compartment. CEDI experiments were carried out with 1 cell pair consisting of three compartments (C,

D, and E compartments) in a constant current mode. One tenth molar H_2SO_4 solution was used as the concentrate solution and high purity water ($18.2 \text{ M}\Omega \cdot \text{cm}$) was used as feed solution in diluate compartment. The flow rate of diluate compartment (D) was $2 \text{ mL} \cdot \text{min}^{-1}$ and concentrate (C) and electrode rinsing (E) compartment was circulated at a flow rate of $5 \text{ mL} \cdot \text{min}^{-1}$. Na_2SO_4 solution of $500 \mu\text{s} \cdot \text{cm}^{-1}$ was circulated as electrode rinsing solution during CEDI operation. In this configuration, it was possible to investigate the electromigration phenomena of nickel ion through the diluate compartment[3].

3. Results and Discussion

3.1. Transport Mechanism of CEDI for the Removal of Ni^{2+}

The electrical conductivity of IET was investigated to understand the transport mechanism of nickel ion through IET. Fig. 1 shows the changes of the electrical conductivity with IET for various interstitial solutions. At zero solution conductivity, the conductivity of the IET was above zero due to the self-conductivity of IET. The specific conductivity of IET steeply increased with solution conductivity due to the bridging effect of the interstitial solution between the matrixes of IET. However, the conductivity of IET becomes lower than the solution conductivity over the equiconductance point due to the limited ion exchange capacity of IET. These results suggested that the CEDI operation is effective below the equiconductance point ($3300 \mu\text{s} \cdot \text{cm}^{-1}$) with the help of IET for the transport of nickel ion. To understand the removal mechanism of nickel ion through IET, the conductivity ratio with IET to that without IET was investigated. Fig. 2 shows the ratio of conductivities of various nickel concentrations. The ratio of conductivities was close to one at equiconductance point but it increased as feed conductivity decreases. Moreover, the steep increase of

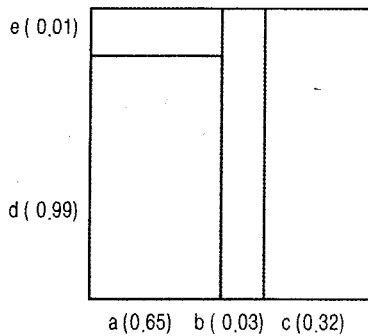


Fig. 3. Conducting pathway of nickel ions through IET.

conductivity ratio was found as feed conductivity approaches zero. The conductivity ratio also represents the ratio of induced current in a constant operation mode[3]. The result shows that the ratio of induced current increases as feed conductivity reaches zero, leading to a high removal rate in the CEDI system. This suggests that the conductivity of ion exchange media is critical parameter to achieve a high current at a low feed conductivity.

3.2. Conducting Pathway of Ni^{2+} in a CEDI System

Wyllie suggested an geometrical approach (porous plug model) for ion-exchange media where it exists irregular and discontinuous phase in the interstitial solution. The model estimates the electrochemical properties using geometrical parameters. The geometrical parameters of the model were estimated from electric conductivity shown in Fig. 1. Fig. 3 shows the conducting path of nickel through IET. Geometrical parameters (a, b, c, d, e) were determined using the porous plug model. From the model, it was possible to predict the portion of electrical conducting path way of ions through the IET[9]. The result showed that the conducting path of nickel ion through IET was mainly through IET, indicating that the IET helped the transport of nickel ion in a CEDI system. Thus, the geometry of ion exchange media in a CEDI should be designed to have high portion of "a" and "b" for the high

performances of CEDI.

3.3. Electromigration of Ni^{2+} in a CEDI

For the application of Nernst-Planck (N-P) equation into a CEDI system, the effective concentration of nickel ion in an IET was calculated. Song *et al.*, calculated the effective concentration of ion exchange textile with porous plug model from the following relation (2)[3].

$$\bar{c}_{\text{Ni}}^{\text{eff}} = \bar{c}_{\text{Ni}}^0 = \bar{c}_{\text{Ni}}^t \times \frac{\text{Total area of } b \text{ in Fig. 3}}{\text{Total area of gray block in Fig. 3}} \quad (2)$$

\bar{c}_{Ni}^t can be estimated using IEC (Ion exchange capacity) and density of IET[3]. From the above equation the effective concentration considering conducting path was found to be $0.07 \text{ mmol cm}^{-3}$. Then, N-P equation can be applied into a CEDI system to investigate the transport mechanism. Spoor *et al.* suggested a simplified transport equation in a CEDI system using N-P equation (3)[9].

$$J_{i,\text{tot}} = z_i c_i u_i^* \text{ grad } \varphi \quad (3)$$

where u_i^* is the apparent mobility including the convection conductivity. This is not the thermodynamic mobility because it contains the convective effect depending on system conditions. Apparent mobility through ion exchange textile u_i^* can be determined from the relation between the potential drop ($\text{grad } \varphi$) and the effluent flux ($J_{i,\text{tot}}$). Fig. 4 shows the relationships between the operating time and the number of moles of nickel transported into the concentrated compartment under the constant cell potential at 5.5 V.

In Fig. 4, the slope in the graph represents the flux change in the CEDI system with an effective membrane area of 20 cm^2 . The curve show linear relations at the initial operating time but the slope

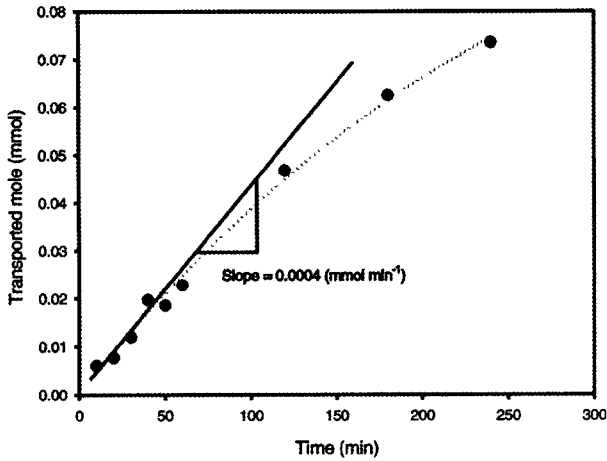


Fig. 4. Transported mole of nickel into "C" compartment with operating time.

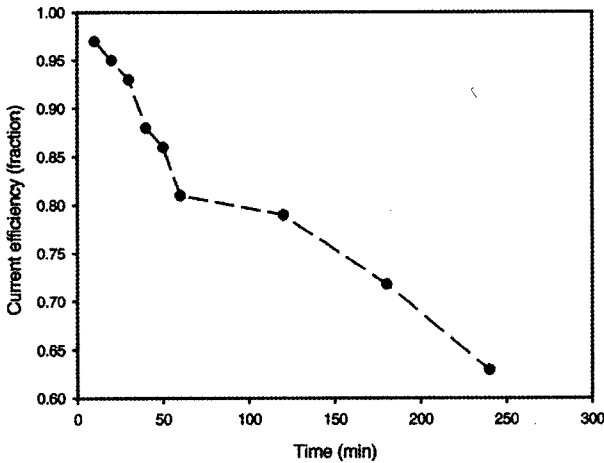


Fig. 5. Variations of current efficiency with operating time.

decreased with operating time, suggesting the constant flux was developed only in the initial stage of operation of CEDI. This result indicates that N-P equation is valid for an initial stage of operation. Also, the deviation from the linear slope after 1 hr was due to the nonhomogeneity induced by concentration change in the IET. Song *et al.* explained that the deviation was caused by the hydrogen flux due to water dissociation or proton leakage from the concentrate compartment[3]. This change disrupted the homogeneity of the ion exchange textile and made it difficult to apply the N-P equation to the

system. To confirm the applicable area of N-P equation with operating time, current efficiency (η_{Ni}) was calculated using the following equation (4):

$$\eta_{Ni} = \frac{2F(n_{Ni,c}^{t_2} - n_{Ni,c}^{t_1})}{Q^{t_2} - Q^{t_1}} \quad (4)$$

where F is the Faraday constant Q is the total applied charge until time t , n_{Ni}^t is the moles of nickel in the concentrated compartment until time t .

Fig. 5 show the time profiles of the current efficiency in terms of transport number of nickel ion during CEDI operation. The transport number of nickel ion was close to 1 at initial operating time, but it decreased with time. This result indicated that the initial applied current was used for the transport of nickel ions only but later a portion of current was used for the transport of hydrogen ion. Previously it was suggested that equation (3) is applied when the current efficiency is unity (extrapolated to time zero)[3]. Equation (3) was rearranged into equation (5) which gives the apparent mobility of nickel ion through the textile. The mobility is determined from the flux, potential gradient, and initial ionic concentration of the ion exchange textile,

$$u_{Ni}^0 = \frac{J_{Ni}^0}{z_{Ni} c_{Ni}^0 \text{ grad}\phi} = \frac{1}{z_{Ni} c_{Ni}^0} \frac{J_{Ni}^0}{\Delta E / \Delta x} \quad (5)$$

where ΔE is the potential changes in the dilute compartment Δx and the thickness of the dilute compartment in the CEDI system. From the Fig. 4 and 5, the mobility of nickel ion in a CEDI system was calculated as $4.32 \times 10^{-10} \text{ m sec}^{-1} \text{ N}^{-1}$ when IET was fully saturated with nickel ion. The calculated value of mobility through IET was much slower than the solution phase suggested from the electrochemical data. This result indicated that the removal

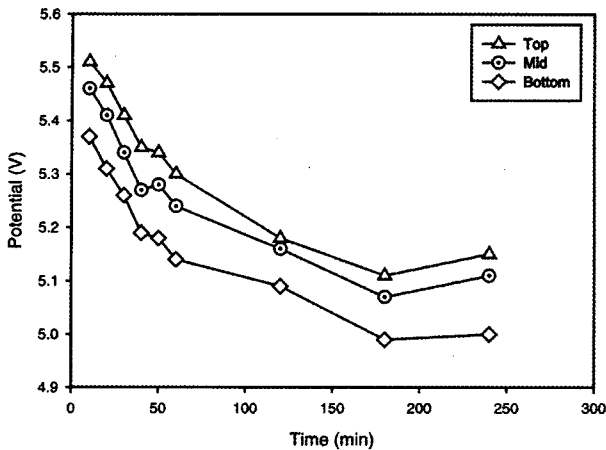


Fig. 6. Cell potential variations with operating time.

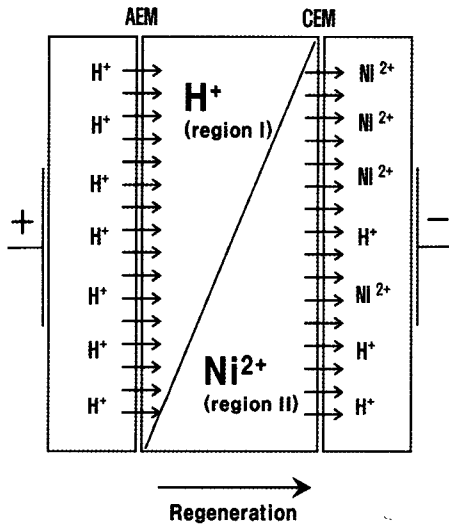


Fig. 7. Suggested removal mechanism of diluate compartment in a CEDI system.

mechanism of ions though CEDI was not dependent on the ionic mobility but other properties of IET. The transport mechanism of CEDI was mainly caused by the concentration of IET itself[2,3]. Although the mobility through IET is slower than that through the solution phase, the high concentration of counter ion induces high current and it is used for removal of ion with high performances. Thus, the IET contributed to the nickel transport in a CEDI system. From the above findings, the two important design parameters of CEDI system were suggested, the thickness and ion exchange capacity

of the media.

The thickness of diluate compartment should be reasonably thin because the mobility through IET is slower than solution phase. Secondly ion exchange capacity of IET should be high to induce a high current for low conductivity feed solution.

3.4. Removal and Regeneration in a CEDI System

Cell potential measurement in a CEDI was carried out by placing Pt electrodes in the diluate compartment. Three cell potential were measured at top, middle, and bottom parts. Fig. 6 shows the cell potential profile with operating time. The cell potential was highest at the upper part and lowest at the bottom part. All the cell potentials decreased with the operating time.

It is known that typical CEDI system expressed with two distinctive regions, referred to as the enhanced transfer and electroregeneration[10]. The ions are removed mainly in enhanced transfer region and the regeneration of ion exchange media occurs in the electroregeneration region. In the earlier study [2], the regeneration portion in a CEDI system was calculated and showed the upper part had high regeneration ratio in the upper region. Fig. 6 also explained that the regeneration occurs mainly in the upper part and removal occurs mainly in the bottom part. The decreased cell potential was caused by the regeneration of IET from nickel ion to hydrogen ion due to high conductivity of proton. Moreover, the higher cell potential of upper part indicates that the high water dissociation in the upper part by polarization in the bipolar interface. Fig. 7 shows the simplified removal and regeneration mechanism of CEDI system. The water dissociation on the bipolar interface regenerate IET as hydrogen form in the upper part and removal of nickel mainly occurs in the bottom part. The border line between region I (regeneration region) and region II (enhanced

transfer region) will move to bottom or upper region according to an operating condition. Also, the optimal operating conditions of CEDI should be determined under the conditions which minimize the electroregeneration region (region I) for the high efficiency of a CEDI.

4. Conclusion

Electric conductivity indicated that the CEDI enhanced the transport of ions more effectively at a low feed concentration, suggesting the high efficiency of CEDI at low feed conductive solution. Apparent mobility determined by the porous plug model and extended Nernst-Planck equation suggested the removal mechanism of nickel ion was not the accelerated ionic mobility but induced current due to concentration of counter ion in IET, indicating the necessity of thin thickness of diluate compartment. Removal-regeneration mechanism suggested that the optimal operating conditions are determined at the conditions which minimize the electroregeneration region. This study suggested the removal mechanism of nickel ion through CEDI suggesting the design parameter of CEDI.

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Symbols

\bar{c}_{Ni}^{eff} , \bar{c}_{Ni}^0 : Effective (initial) concentration of

nickel ion in IET considering conducting pathway of IET

\bar{c}_{Ni}^t : Total concentration of nickel ion in IET

c_i : Concentration of ion i in IET

z_i : Charge valence of ion i

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