

Influence of Operating Conditions on the Performances of a Continuous Electrodeionization with Cation Exchange Textile (CEDI-CET)

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Abstract: The transport and removal characteristics of cobalt ions were investigated in a continuous electrodeionization with cation exchange textile (CEDI-CET). It was shown that the removal properties of cobalt ions are strongly dependent on the operating parameters such as temperature, flow velocity, and the solution pH. The transport and removal of cobalt ions was mainly related to the sorption on the surface and the convection and electro-migration through the ion exchange medium. In this study, the CEDI-CET showed good process performance for the removal of metal ions compared with the conventional CEDI with resins.

Keywords: *continuous electrodeionization (CEDI), cation exchange textile (CET), cobalt, process performance*

1. Introduction

Chemical and physical separation processes such as ion exchange and cartridge filter system have been applied for the removal of cobalt ions in the primary coolant of a nuclear power plant. They have disadvantages, however, due to low recovery efficiency and environmental problems to effluents [1]. In order to overcome these problems, ion exchange membrane process such as continuous electrodeionization (CEDI) system was successfully applied in order to remove cobalt ions in synthetic solution at similar conditions of a primary coolant system in a nuclear power plant [2,3]. In the previous studies, the CEDI application showed the excellent removal performance for cobalt ions, showing the feasibility of CEDI as an alternative of ion exchange resins in a nuclear power plant [4,5]. The CEDI process, a novel hybrid separation process combining electrodialysis and ion exchange process, is

applied on a large scale, as an alternative to the ion exchange process [6-8]. This technology minimizes the problems such as polarization phenomena on the boundary layer on the membrane surface and chemical regeneration of ion exchange resins, respectively, in the electrodialysis and ion exchange processes [9-11].

In the enhanced transfer regime of a CEDI system, ion transport is enhanced by increasing active surface area of the ion exchange surface per membrane area under fixed feed conditions [12]. Therefore, it is desired to minimize the regenerated resin fraction since water dissociation results in a loss of electrical current efficiency. In addition, the removal characteristics through ion exchange media should be understood in order to increase the process performance of a CEDI system. It is well known that the parameters such as the operation parameters are directly related to the process performance of CEDI [8]. However, the influence of the operation parameters on the process performances in a CEDI system was rarely reported due to the complicated electrochemical properties in the

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Table 1. Basic Characteristic Values for the Cation Exchange Media

Parameters*	Cation exchange textile	Cation exchange resin
Ion exchange capacity (meq/g-dried medium)	2.2	4.6
Density (g/cm ³)	0.58	0.87
Fraction of the active conducting pathway	0.10	0.09

*Data referred from [2].

system consisting of ion exchange media, electrolyte solution, and ion exchange membrane [13]. The objective of this study is, thus, to investigate the removal behavior of cobalt at the different experimental conditions for the effective application of CEDI system. The influence of the operation parameters on cobalt transport behavior was investigated in order to optimize the CEDI with cation exchange textile (CEDI-CET) process.

2. Experimental

2.1. Characteristics of the Cation Exchange Textile

Commercially available ion exchange membranes, NEOSEPTA[®] CMX and AMX, (ASTOM Co., Japan) were employed as cation and anion exchange membranes, respectively. Cation exchange textile (CET) was prepared by the UV irradiation in our laboratory as a cation exchange medium in the CEDI-CET system [2]. Characteristic values of the CET were compared with those of available cation exchange resins, IRN 77 (Rhom & Hass Co.) and the results are shown in Table 1. The fraction of the active conducting pathway is similar for both cation exchange media in the table, indicating the ion transport mechanism is not different between two cation exchange media during CEDI process [2,3].

Sorption of cobalt ions on surface of the cation exchange textile was conducted at various pH values in order to investigate sorption capacity as a function of the solution pH. After the textile was equilibrated in

an acidic solution for 1 day in the presence of 0.17 mM cobalt ions, an equivalent fraction in the textile was estimated based on the concentration of cobalt ions in the solution. Cobalt concentration was analyzed using an inductively coupled plasma (ICP) spectrophotometer, Thermo Jarrel Ash IRIS/AP.

2.2. CEDI Operation for the Removal of Cobalt Ions

For the CEDI-CET operation, the experimental setup was prepared using the stack configuration with the cation exchange textile in the diluate compartment, as shown in Fig. 1. The influence of the operation parameters (temperature, flow velocity, and feed solution pH) on the process performances was investigated in the CEDI operation at a constant current density of 6.5 A/m² with an effective membrane area of 50 cm². Cobalt nitrate (Co(NO₃)₂ · 6H₂O) solution of 0.17 mM was supplied to the diluate compartment. A Na₂SO₄ solution of 1,000 μS/cm was circulated to electrode rinse compartment. One hundredth molar H₂SO₄ was circulated as concentrate solution to prevent the cobalt precipitation on the surface of the membrane and the resins. The flow velocity of the diluate solution was set to 13.3 cm/min, meanwhile both the concentrate and electrode rinsing solutions maintained at 57.1 cm/min. The transport and removal of cobalt ions were investigated in the CEDI-CET and the results were compared with those of the CEDI with IRN 77 under the identical experimental conditions.

3. Results and Discussion

3.1. Influence of Operation Conditions on the CEDI-CET Performances

3.1.1. Effect of Operation Temperature

The CEDI-CET was operated at the controlled temperature of 20, 40, and 60°C in order to observe the influence of temperature on the process performance. Fig. 2 shows the effects of operation temperature on the removal efficiency in the CEDI system. The time required for the cobalt removal efficiency of 80% was

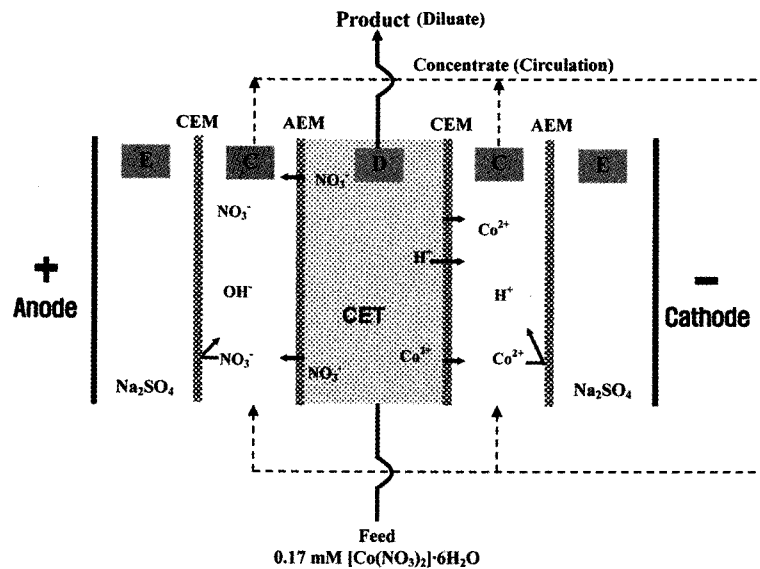


Fig. 1. Stack configuration of the CEDI-CET system (CET: cation exchange textile, C: concentrate compartment, D: dilute compartment, E: electrode rinse compartment, AEM: anion exchange membrane, and CEM: cation exchange membrane).

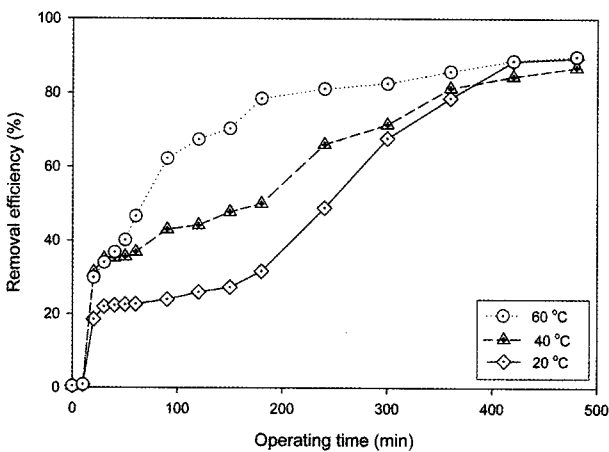


Fig. 2. Influence of operating temperature on the removal rate in the CEDI-CET.

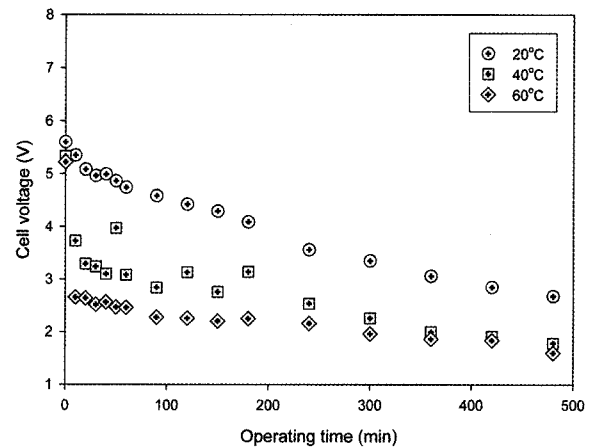


Fig. 3. Influence of operating temperature on the cell voltage in the CEDI-CET.

determined to 370 min, 360 min for the feed temperature of 20 and 40°C, respectively. The highest removal rate was observed at the operation temperature of 60°C, showing the 80% removal efficiency at the operation time of 210 min. Increase in the removal efficiency of cobalt is due to increase in exchange rate at higher temperature. It is reported that ion exchange rate of ion exchange media is dependent on operational temperature and that the rate increases by about 4 to 8% per degree centigrade, respectively [14].

A high removal rate of ionic species results in low

resistance or voltage drop during the CEDI operation. Fig. 3 shows the voltage variation with operating time at different feed temperatures. As the temperature increased, the cell voltage drop or the cell resistance decreased in the figure. The CEDI operation at 60°C shows the lowest cell voltage among examined temperatures due to the increasing rates of ion exchange or ion transport. In the practical point of view, however, the process should be operated at lower temperature than 60°C to minimize degradation of ion exchange media during the operation.

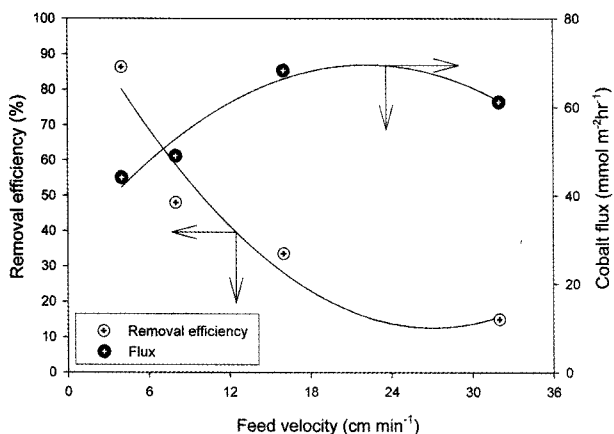


Fig. 4. Effect of feed velocity on the performances of CEDI-CET at the elapsed time of 240 min.

3.1.2. Effect of the Feed Flow Rate

Generally, it is of importance to investigate the influence of the flow rate on the process performance. With increasing retention time in the compartment, the removal efficiency increased. Fig. 4 shows the removal efficiency and the transport rate per unit membrane area (or flux) of cobalt ions. The removal efficiency of cobalt ions decreased with increasing feed velocity due to decrease in the retention time. Meanwhile, the cobalt flux to concentrate compartment increased up to the feed flow velocity of 16 cm/min with increasing velocity, then showing similar value as 65 mmol/m²hr at higher velocities than 16 cm/min. This result can be understood by the water dissociation effect in a CEDI

system, which is proportional to the thickness of a diffusion boundary layer of an ion exchange membrane [15]. The increasing feed flow velocity decreases the thickness of the boundary layer, thus decreasing the water dissociation. Therefore, the cobalt flux increases with increasing flow rate.

The feed flow rate can also affect the dispersion of the exchange zone front in the diluate compartment [14]. The developed length of the exchange zone front shortens at a low flow rate due to the strong preference of exchange medium, as illustrated in Fig. 5. Meanwhile, the dispersion of the exchange zone front becomes dominant due to the reduced preference of ion exchange media at a high feed velocity. Therefore, the dispersion of the exchange zone front reaches the outlet of the CEDI system, decreasing the removal capacity.

3.1.3. Effect of the Solution pH

When the cobalt nitrate solution (Co(NO₃)₂ · 6H₂O) is dissolved in the water, the electrolyte consists of four types of cobalt species, Co²⁺, Co(OH)⁺, Co(OH)₂, and Co(OH)₃⁻. In the following three equations, the reaction in water phase occurs at different pH value according to the equilibrium constant, K:

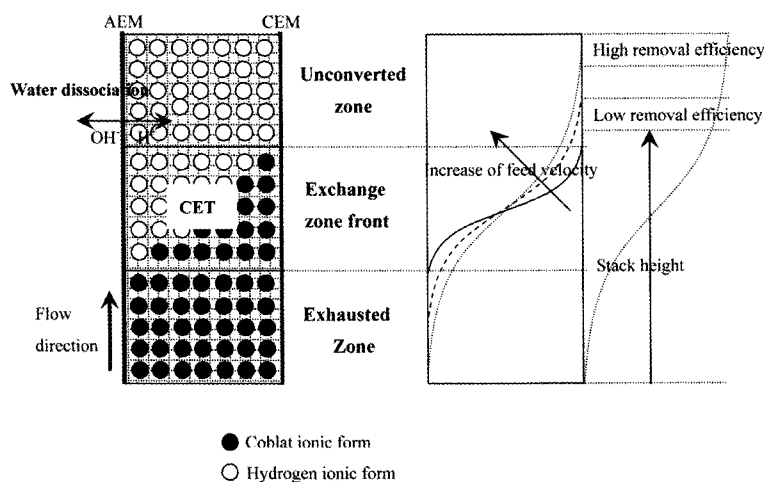
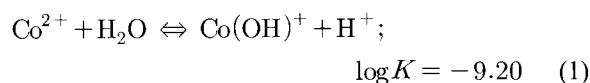
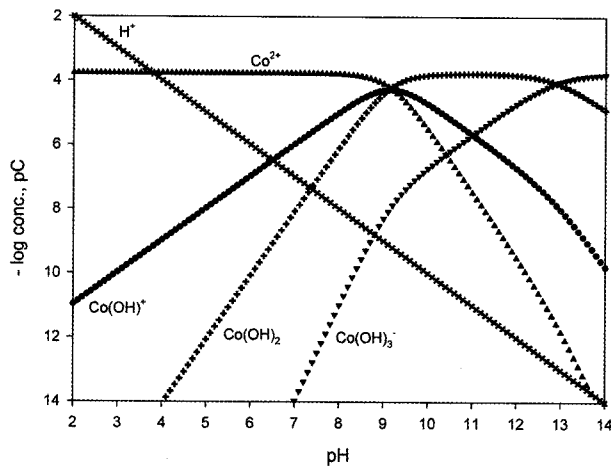


Fig. 5. Influence of the distribution in the exchange zone front on CEDI performance.



(a) pC-pH diagram in the presence of cobalt ions

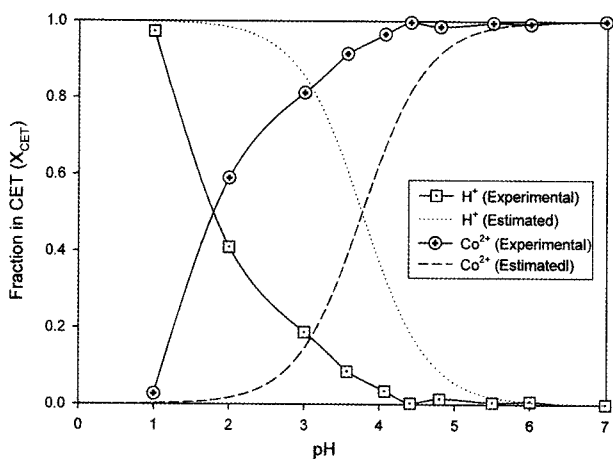
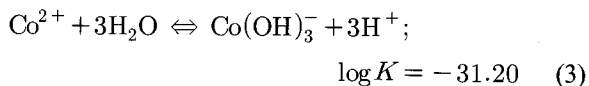
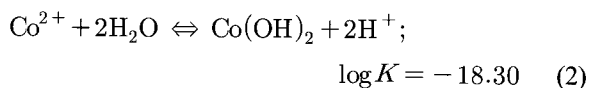
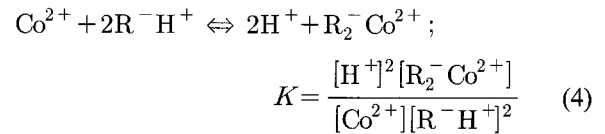
(b) Fraction of cobalt in the CET with solution pH variations
Fig. 6. Effect of the solution pH on the behavior of cobalt ions.

Fig. 6(a) shows the calculated pC-pH diagram for hydroxocobalt (II) complexes for 0.17 mM of cobalt nitrate solution using the equations from 1 to 3. The diagram shows that cobalt is a major ion species at the pH range between 2 and 7. In the acidic condition, the equilibrium is mainly caused by the concentration of cobalt and protons in a solution phase. If the proton

generation is considered in a CEDI system under electric field, the equilibrium for an ion exchange medium in a CEDI system can be expressed in the following equation 4.



In order to investigate the influence of the solution pH on the cobalt sorption on the surface of the cation exchange textile, the sorption equilibrium experiment of cobalt ions on the textile was conducted. Fig. 6(b) shows the sorption ability of the textile as a function of the solution pH using the fraction of cobalt in the textile. In the figure, the dashed line represents the distribution of cobalt ions in the solution, which was obtained by the relationship between cobalt and proton from the pC-pH diagram in Fig. 6(a). Meanwhile, the solid line represents the sorption equilibrium of cobalt ions as a function of the solution pH bases on the sorption experimental results. The figure shows that more amount of cobalt ions exist in the textile than in the solution under the acidic condition due to ion exchange capacity of the textile. From the results, the fraction of cobalt ion in the CET increases with increasing the solution pH, showing the estimated value of 95% when the solution pH is higher than 4. These results indicate that the sorption of cobalt ions on the surface of CET becomes dominant at a higher pH than 4.

The sorption capability of ion species on the surface of an ion exchange media increases the removal rate or efficiency in the CEDI process. Fig. 7 shows the removal efficiency of cobalt ions as a function of the solution pH. As shown in the figure, the removal efficiency notably increased up to higher than 90% when the solution pH values were higher than 4. The results imply that the removal mechanism of CEDI is mainly based on the sorption between solution and ion exchange media as well as electro-migration under the electric field.

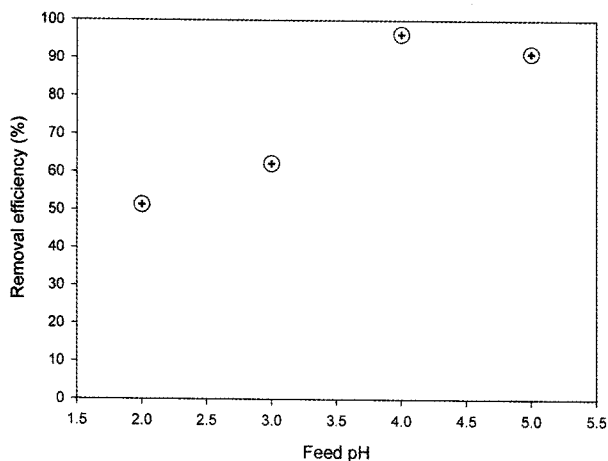


Fig. 7. Removal efficiency of cobalt ions as a function of the feed solution pH.

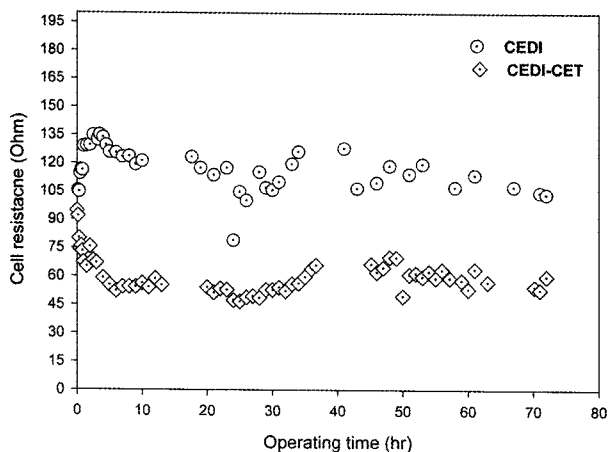


Fig. 8. Cell resistance change of the CEDI processes with different ion exchange media.

3.2. Transport and Removal of Cobalt Ions in the CEDI-CET

3.2.1. Removal of Cobalt Ions in the CEDI-CET Operations

The CEDI process performances in terms of the removal efficiency of cobalt, the current efficiency, and the power consumption were compared between ion exchange media and cation exchange resins. Fig. 8 shows the results of the cell resistance at a constant current density of 6.5 A/m². In the CEDI-CET process, the cell resistance was lower than the result of the resin, related to the water dissociation on the textile surface.

Table 2 summarizes changes in the removal effi-

Table 2. Process Performances in the CEDI Operations with Different Ion Exchange Media

	CEDI-CET	CEDI
Removal efficiency of cobalt ions (%)	98.5	99.2
Current efficiency (%)	16.8	17.2
Power consumption (Wh/L)	0.11	0.23
Ion exchange medium	Cation exchange textile	Cation exchange resin

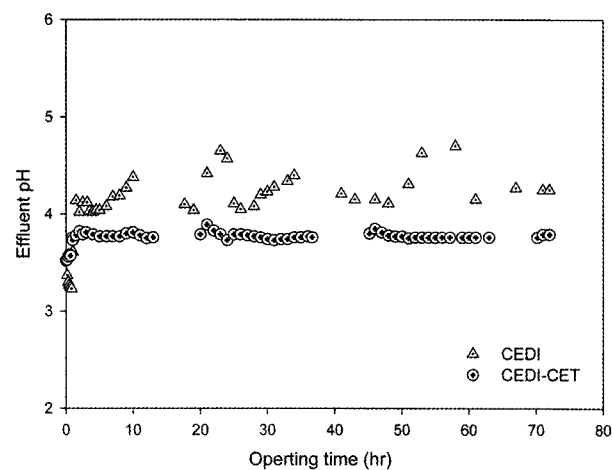


Fig. 9. Effluent pH values in diluate solutions for the CEDI processes.

ciency of cobalt ions, the current efficiency and the power consumption to produce 1 L of water. In the results for both CET and resins, the removal efficiency and the current density were similar. Considering the power consumption, the CET showed an estimated power consumption of about 0.1 Wh/L, much lower than that with resin. These results indicate that the CEDI-CET was more effective than the CEDI [13].

3.2.2. Water Dissociation Mechanism for the CEDI

Fig. 9 shows the pH changes during the CEDI operations with CET and cation exchange resins. In the figure the pH change was different between two cation exchange media. The effluent pH maintained stable values of about 3.8 in the CEDI with CET. Meanwhile, the pH value in the effluent for the CEDI with resins showed variation between 4 and 6. Different pH

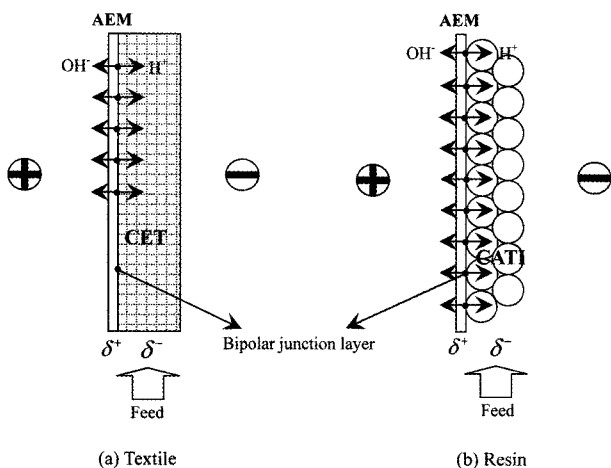


Fig. 10. Water dissociation mechanisms occurring in the interface between anion exchange membrane and ion exchange media.

change is related to the water dissociation mechanism. That is, the more amount of water dissociation in the CEDI-CET resulted in constant pH values compared with the conventional CEDI.

Different aspects of water dissociation can be explained by the different contact pattern between membrane and exchange media during the CEDI process [16]. Fig. 10 shows the different water dissociation mechanisms occurring in the interface between a membrane and ion exchange media. When the anion exchange membrane contacts to cation exchange resin, a bipolar junction layer forms only on the contact regions. However, a larger area of the bipolar junction layer can form on the surface when an anion exchange membrane contacts to the textile. A larger area of the bipolar junction layer generates more amount of water dissociation in the interface between membrane and the textile. The high water dissociation capability of the textile results in a low pH value in the diluate compartment. In the case of the conventional CEDI with ion exchange resins, the amount of the water dissociation will be less than CEDI-CET due to a small area of the bipolar junction layer [17].

3.3. Consideration on Transport and Removal Mechanism of Cobalt Ions

In order to investigate the transport and removal

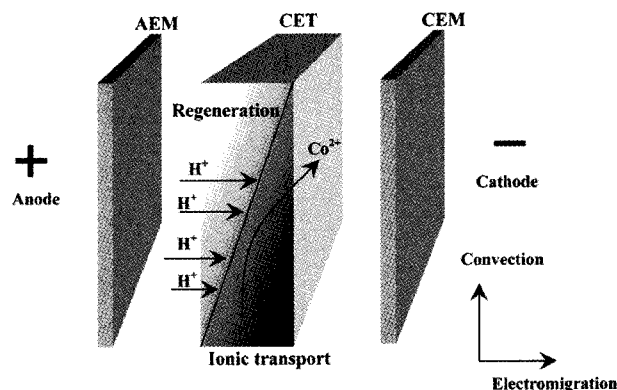


Fig. 11. Suggested transport mechanism of cobalt ions transport in the CEDI-CET system.

characteristics of cobalt ions, the stack was disassembled and the color change was observed after the CEDI operation at the operating current of 6.5 A/m^2 . Fig. 11 shows the color changes of the CET after CEDI operation for 72 h. As shown in the figure, the contact area of CET with the AEM became white because of the hydrogen ionic form of the CET but the contact area with CEM turned red due to the cobalt ionic form of CET.

The existence of a distinct line in the cation exchange textile indicates that the removal characteristic of cobalt ion is affected by the combined effects of convection and electro-migration as shown in the figure. The electric field enhances the movement of cobalt ions to the cathodic site. Meanwhile, the convection increases the movement of cobalt ions to the upper region due to the feed velocity. As a result, the combined effects of electric field and convection phenomena enhanced the transport of cobalt ions in the boundary of the electro-regeneration and ionic transport regime [18]. If the convective force is dominant, the line will move upward. It will move downward when the electric field effect is dominant. Thus, the optimal operating conditions of CEDI with minimized electro-regeneration region (or maximized ionic removal region) can be achieved by controlling flow rate (convection) or applied potential (electric field).

4. Conclusions

In this study, the influence of the operation parameters on the transport and removal of cobalt ions were investigated in the CEDI-CET system with cation exchange textile in the diluate compartment. The removal efficiency of cobalt ion increased with increasing temperature and decreasing flow velocity. The feed solution pH showed higher process performance at higher pH than 4, which is related to sorption equilibrium. In addition, the performances of the CEDI system were also dependent on the water dissociation and ionic transport of the CEDI system. The CEDI-CET operation showed lower cell resistance compared with the results of CEDI due to different water dissociation mechanism occurring on the interface between the anion exchange membrane and the textile.

In the transport and removal mechanism of cobalt ions, the combined effects of electric field and convection phenomena enhanced the transport of cobalt ions in the boundary of the electro-regeneration and ionic transport regime in the presence of the ion exchange textile. The CEDI-CET results showed the feasibility for the application in the removal of metal ions with different operation parameters.

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