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

Experimental Studies on Electrodeionization for the Removal of Copper Ions from Dilute Solutions

Shan Guan[a]; Shichang Wang[a]
[a] Chemical Engineering Research Center, Tianjin University, Tianjin, China

To cite this Article Guan, Shan and Wang, Shichang(2007) 'Experimental Studies on Electrodeionization for the Removal of Copper Ions from Dilute Solutions', Separation Science and Technology, 42: 5, 949 — 961
To link to this Article: DOI: 10.1080/01496390701193751
URL: http://dx.doi.org/10.1080/01496390701193751

Separation Science and Technology, 42: 949–961, 2007

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390701193751

Experimental Studies on Electrodeionization for the Removal of Copper Ions from Dilute Solutions

Shan Guan and Shichang Wang
Chemical Engineering Research Center, Tianjin University,
Tianjin, China

Abstract: The purpose of this study is to investigate the ability of electrodeionization to remove copper ions from dilute solutions without chemical regenerations. Experiments were carried out in a bench-scale stack using a feed solution containing about 50 mg/L of copper. It was demonstrated that electrodeionization operated in either the "enhanced transfer" or the "electroregeneration" regime. In the "electroregeneration" regime, the process was able to produce a pure water product containing non-detectable concentrations of copper, while CuO scale was found on the surface of anion exchange membranes. With optimal conditions, a steady and continuous process can be achieved.

Keywords: Electrodeionization, copper ions, ion exchange resin, ion exchange membrane, scaling

INTRODUCTION

For the purification of dilute heavy-metal process liquids such as electroplating rinsewaters, ion exchange is a conventional method. Although it is able to achieve effective removal of heavy-metal ions, ion exchange is a discontinuous process which requires chemical regeneration cycles providing saline effluents (1). Therefore current interest exists for the development of a new technology which is more convenient and needs no chemical regenerations.

Received 28 September 2006, Accepted 27 December 2006

Address correspondence to Shichang Wang, Chemical Engineering Research Center, Tianjin University, Tianjin 300072, China. Tel.: +86(22)27404347; Fax: +86(22)27404757; E-mail: jiswang@tju.edu.cn

Electrodeionization(EDI) is a novel separation process combining ion exchange resins and ion exchange membranes. In recent years, EDI has been widely accepted as a competitive technology for the production of ultrapure water (2, 3) In many cases ion exchange has already been replaced by the EDI process. Because EDI is capable of achieving a high extent of deionization coupled with a low volume concentrate stream without the use of chemical regenerants, it becomes a potentially viable technology for the recovery of heavy-metal-ion containing wastewaters. Some research on the removal of heavy-metal ions use special designed EDI stacks, which the dilute compartment is composed of two cation exchange membranes, and cation exchange resin is filled in the dilute compartment (4–8). The process only enhances the transport of cations, so it is not able to produce high purity water. Moreover, the process relies on a recirculating acid stream to provide regenerating ions. The stack is complex and the operation needs extra power consumption. Other researchers use conventional EDI stacks, which the dilute compartment is composed of a cation exchange membrane and an anion exchange membrane, and is packed with a mixture of cation and anion exchange resin (9–13). The process enhanced the transport of both cations and anions to achieve high purity water without net chemical additives.

The conventional EDI process operates in two regimes (2): at high salinity, the resins in the dilute streams remain in the salt forms, and efficiencies are derived from the resin-enhanced electrical conductivity of the dilute compartments; at low salinity, water splitting occurs in the dilute compartments and the resins are converted to the hydrogen and hydroxide forms, and deionization is consistent with a model of a continuously regenerated mixed bed ion-exchange column. These regimes are defined as the "enhanced transfer" regime and the "electroregeneration" regime, respectively. In this work, a mixed-bed EDI was used to remove copper ions from dilute solutions. Cation resin in the dilute compartments was in Cu^{2+} form prior to the tests and the occurrence of electroregeneration can be distinguished by conducting a mass balance of copper ions. The process with electroregenerated copper ions operated in the "electroregeneration" regime, while an operation without electroregeneration was in the "enhanced transfer" regime. The performances of different regimes were investigated and discussed.

EXPERIMENTAL

Equipment Description

The experimental set-up is illustrated in Fig. 1.

Figure 2 is a schematic representation of the laboratory EDI stack. It was a two-stage stack, with three cell pairs in each stage. The dilute compartment

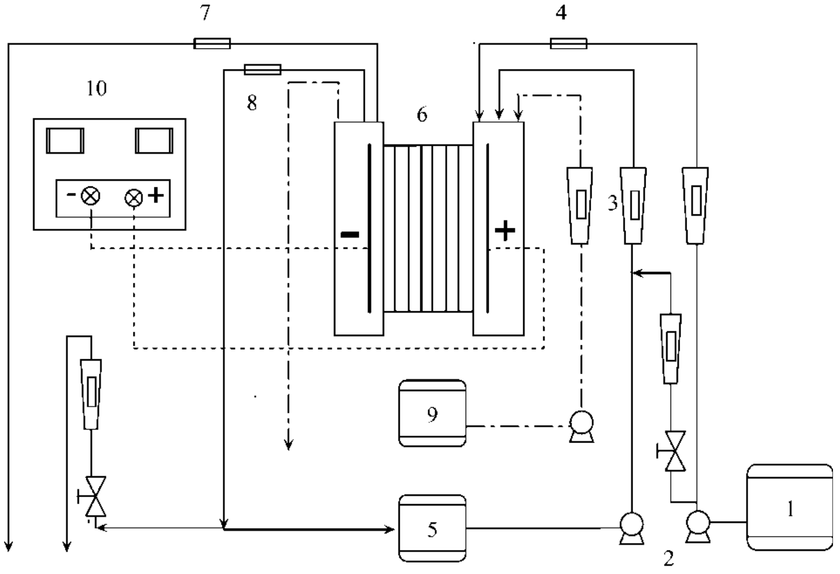

Figure 1. Experimental set-up 1. Feed tank 2. Pump 3. Flow meter 4. Conductivity cell 5. Concentrate tank 6. EDI stack 7. Conductivity cell 8. Conductivity cell 9. Electrolyte tank 10. Power supply.

was composed of a cation exchange membrane (CM) and an anion exchange membrane (AM). Each membrane had an effective area of 135 cm^2. The thickness of the dilute compartment (D) was 3 mm. A mixture of cation and anion exchange resin was filled in the dilute compartment. The thickness of the concentrate compartment (C) was 0.8 mm. The concentrate compartment was filled with thin woven non-conducting screens.

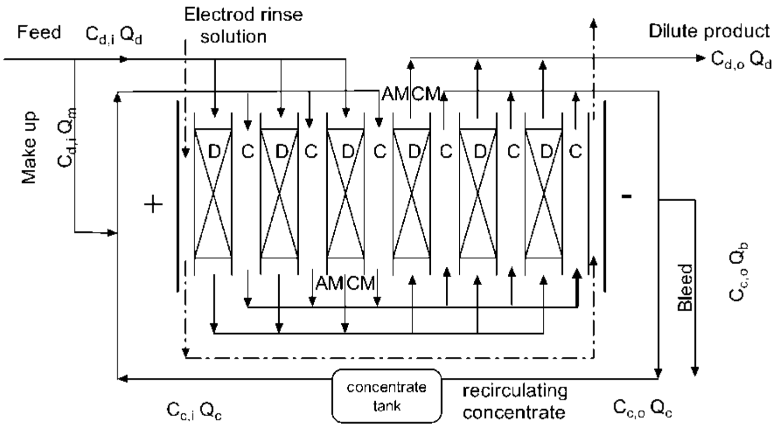

Figure 2. The EDI stack and the flow diagram.

Cation exchange membrane and anion exchange membrane were heterogeneous ion exchange membranes used for EDI (Shanghai Shanghua water treatment material Co., Ltd., China). Macroporous type strong acidic cation exchange resin D072 and macroporous strong basic anion exchange resin D296 (The chemical plant of Nankai University, China) were used to fill the dilute compartments. The volume ratio of the anion resin to the cation resin was 50:50. Cation exchange resin and cation exchange membranes were converted to Cu^{2+} form, and the anion exchange resin and anion exchange membranes were converted to SO_4^{2-} form before they were installed into the EDI stack.

Operating Conditions

In this work, stack voltage was set as the only parameter to control operating regimes. Two tests were carried out with constant voltages of 7.5 V and 15 V, respectively.

The feed was a $CuSO_4$ solution containing about 50 mg/L of copper, which was acidified with sulfuric acid to a pH of 3.0. It was introduced into the dilute compartments with a flow rate of 7.5 L/h.

Another $CuSO_4$ solution recirculated in the concentrate compartments with a flow rate of 1.24 L/h. The concentrate tank had a capacity of 1L. For the 15 V test, the initial concentration and pH of the solution in the concentrate tank were identical to the feed solution. For the 7.5 V test, initial copper concentration of 700 mg/L and pH of 2.35 were used to make the process approach its steady state as soon as possible. The flow rate of the bleed stream was 0.36 L/h, equal to the flow rate of the make up stream added to the recirculating concentrate stream.

The electrode rinse solution was 0.1% Na_2SO_4. Its flow rate was 1.6 L/h.

Analysis of Copper Ion Concentration

The copper concentration was determined by flame atomic absorption using a WFX130 system (Beijing Rayleigh Analytical Instrument Corp., China).

RESULTS

Enhanced Transfer Regime

The mass balance of the system is given by:

$$N_{in} + N_r = N_{out} + N_k + N_s \tag{1}$$

where N_{in} is the amount of Cu^{2+} introduced to the system at any moment, N_r is the amount of Cu^{2+} regenerated from the stack, N_{out} is the amount of Cu^{2+}

carried out from the system, N_k is the amount of Cu^{2+} migrating into the cathode compartment, N_s is the amount of Cu^{2+} remaining in the stack as scale.

In the 7.5 V case, no scaling was observed. Equation 1 can be rearranged as:

$$N_r = N_{out} - N_{in} + N_k \tag{2}$$

Knowing the concentrations and flow rates of all the streams (Fig. 2), one can deduce the amount of copper ions regenerated from the stack:

$$\begin{aligned} N_r &= (C_{d,o}Q_d + C_{c,o}Q_c + C_{c,o}Q_b) - (C_{d,i}Q_d + C_{c,i}Q_c + C_{d,i}Q_m) + N_k \\ &= [(C_{c,o} - C_{c,i})Q_c + (C_{c,o}Q_b - C_{d,i}Q_m)] - (C_{d,o} - C_{d,i})Q_d + N_k \\ &= N_C - N_D + N_k \end{aligned} \tag{3}$$

where N_C is the amount of Cu^{2+} gained by concentrate compartments at any moment, N_D the amount of Cu^{2+} removed from the dilute stream at any moment, $C_{c,i}$ is Cu^{2+} concentration of the recirculating concentrate stream introduced into the stack, $C_{c,o}$ is the concentration of the recirculating concentrate stream flowing out the stack, $C_{d,i}$ is the concentration of the feed solution, $C_{d,o}$ is the concentration of the dilute product stream. Q is the flow rate. Subscript d denotes the dilute stream, c the recirculating concentrate stream, m the make up stream, b the bleed stream.

The permselectivity of anion exchange membrane was about 90%. Cu^{2+} migrated through the anion exchange membrane into the adjacent cathode compartment. Some of these copper ions deposited on the cathode, others remained in the electrode rinse solution. Therefore an average value of 23 mg/h for the amount of Cu^{2+} migrating into the cathode compartment, N_k, was obtained.

The variation of copper flux is shown in Fig. 3. It can be seen that there is a gap between the curves representing N_C and N_D, which is the amount of

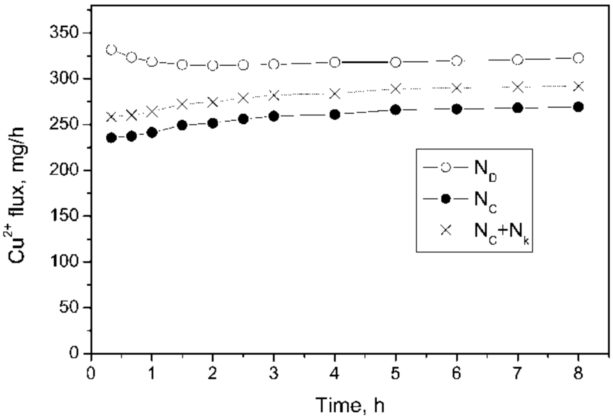

Figure 3. Copper flux as a function of time for a test operated in the "enhanced transfer" regime. Stack voltage was 7.5 V.

Cu^{2+} gained by the concentrate compartments and the amount of Cu^{2+} removed from the dilute stream, respectively. After the average value of N_k is added, the value of $N_C + N_k$ is still smaller than that of N_D through the entire test. According to Equation(3), it is concluded that no electroregeneration took place and the process operated in the "enhanced transfer" regime.

The stack current over time shown in Fig. 4 reflects the variation of the ohmic resistance of the stack. At the beginning of the test, the salt concentration of the interstitial solution in the dilute compartments was high, thus the stack resistance was small. After the voltage was applied, a relative high initial current was achieved. As ions were removed from the dilute compartments, the resistance increased rapidly and the current dropped sharply to the lowest value. Then ions accumulated in the concentrate compartments, resulting in the decrease of the stack resistance and the slow increase of the current. The current remained steady after 5 h. It can be seen that the contribution of concentrate compartments to the stack resistance was not so important as that of dilute compartments.

The variation of the removal efficiency of copper ions is also depicted in Fig. 4. After the test was started, the removal efficiency rose rapidly to the highest value of about 91%. Then it declined to about 86% at 2 h. After 2 h it increased slowly and a value greater than 88% was obtained at the end of the test. It is evident that this variation corresponded with the variation of current. The increase of current enhanced the ion transport, hence improved the removal efficiency of copper ions.

In Fig. 5, the pH of the dilute stream rose from 3.09 at the beginning of the test to 3.79 at 2 h, indicating the increase of H^+ removal. The variation of pH after 2 h was contrary to the variation of the removal efficiency of copper ions. While the removal of Cu^{2+} was increasing, the pH of the dilute stream gradually declined to 3.67 at the end of the test. The reason was that ions

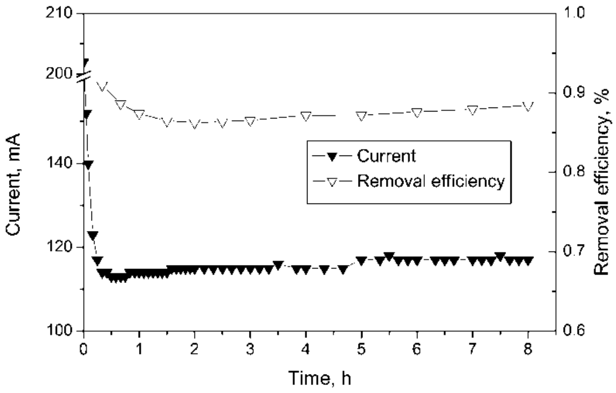

Figure 4. Current and removal efficiency as a function of time for a test operated in the "enhanced transfer" regime. Stack voltage was 7.5 V.

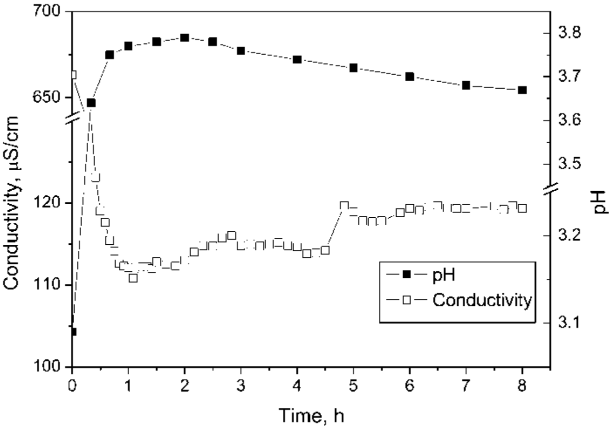

Figure 5. pH and conductivity of the dilute stream as a function of time for a test operated in the "enhanced transfer" regime. Stack voltage was 7.5 V. Initial conductivity was 663 μS/cm.

accumulated in the concentrate stream (Fig. 6) and proton leakage of anion exchange membranes was enhanced (14).

The increase of H^+ concentration led to the increase of the conductivity of the dilute stream. From Fig. 5, it can be seen that the conductivity increased from 110.8 μS/cm at 1 h to about 120 μS/cm at the end of the test.

The variation of Cu^{2+} concentration and pH of the bleed stream is shown in Fig. 6. It is noted that there was only slight increase of Cu^{2+} and H^+ concentration after 4 h, indicating that the process approached a steady state.

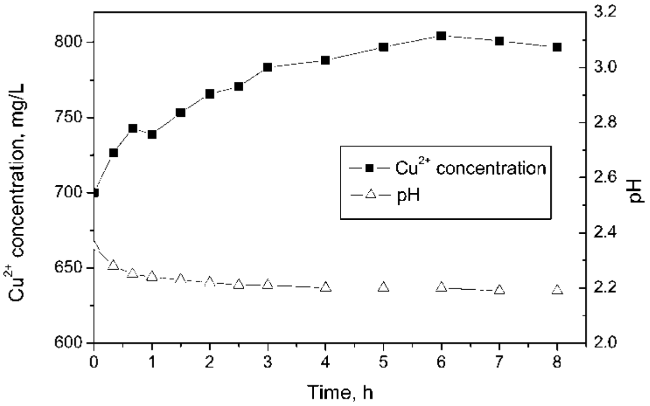

Figure 6. Cu^{2+} concentration and pH of the bleed stream as a function of time for a test operated in the "enhanced transfer" regime. Stack voltage was 7.5 V.

The stack was disassembled after the test was completed. No color change of the resins in the dilute compartments was observed and no scaling occurred on the surface of the concentrate side of anion exchange membranes.

Electroregeneration Regime

In the 15 V test, scaling occurred on the surface of anion exchange membranes. From Equation (1), the amount of copper ions regenerated from the stack is determined by:

$$\begin{aligned} N_r &= N_{out} - N_{in} + N_k + N_s \\ &= [(C_{c,o} - C_{c,i})Q_c + (C_{c,o}Q_b - C_{d,i}Q_m)] - (C_{d,o} - C_{d,i})Q_d \\ &\quad + N_k + N_s = N_C - N_D + N_k + N_s \end{aligned} \tag{4}$$

The variation of copper flux of the 15 V test is shown in Fig. 7. It is noted that even if the Cu^{2+} remaining in the stack as scale, N_s, and the Cu^{2+} migrating into the cathode compartment, $N_{k,}$ were not counted in, more copper ions were gained by concentrate compartments than those removed from the dilute stream at some moments. The presence of regenerated copper ions means that the 15 V test operated in the "electroregeneration" regime.

In Fig. 7, the amount of copper ions regenerated from the stack achieved its highest value at 2.5 h, but dropped rapidly later. This was due to the occurrence of scaling, in which some of the copper ions were retained in the stack as scale. The concurrence of scaling and electroregeneration may be the primary reason for the fluctuation of the copper flux after 4 h.

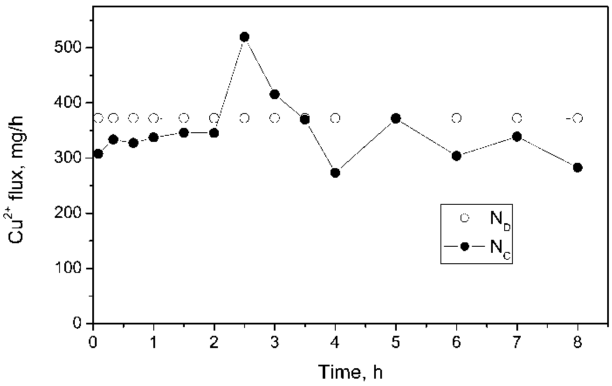

Figure 7. Copper flux as a function of time for a test operated in the "electroregeneration" regime. Stack voltage was 15 V.

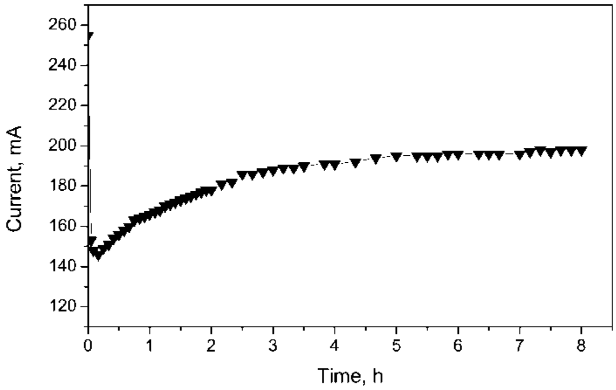

Figure 8. Current as a function of time for a test operated in the "electroregeneration" regime. Stack voltage was 15 V.

From Fig. 8, it can be seen that the variation of current is similar to that of the 7.5 V test. However, the current was substantially higher in the 15 V case, which enhanced the removal of copper ions.

In the 15 V test, Cu^{2+} concentration of all the samples of the dilute stream was non-detectable by flame atomic absorption spectrometry (AAS). Assuming the Cu^{2+} concentration was equal to the detection limit of the AAS analysis, which was 0.008 mg/L, the removal efficiency was greater than 99.9% through the entire test.

Conductivity was used to represent the purity of water, as shown in Fig. 9. After the voltage was applied, the conductivity of the dilute product dropped

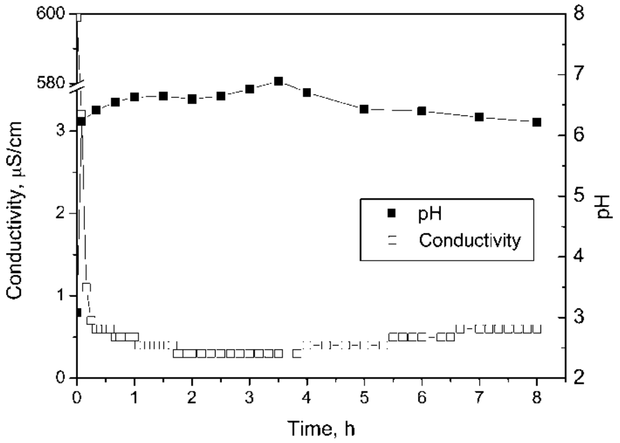

Figure 9. pH and conductivity of the dilute stream as a function of time for a test operated in the "electroregeneration" regime. Stack voltage was 15 V. Initial conductivity was 599 μS/cm.

sharply from 599 μS/cm to less than 1 μS/cm in several minutes. At about 2 h, the conductivity achieved the lowest value of 0.3 μS/cm. Then it slowly increased to 0.6 μS/cm at the end of the test. The reasons for this were: Firstly, proton leakage of anion exchange membranes was enhanced, which was demonstrated by the decrease of pH of the dilute stream after 3.5 h in Fig. 9; Secondly, ion transport was hindered due to the scale formation on the surface of anion exchange membranes.

The variation of pH and Cu^{2+} concentration of the bleed stream is shown in Fig. 10. From 2.5 h to 3 h, a drop of Cu^{2+} concentration was observed, indicating the occurrence of scaling in the stack.

After the test was completed, the stack was disassembled. It was found that near the outlets of the dilute compartments of the second stage, cation resin changed its color to brown and anion resin changed to yellow, while other cation resin in the same compartment remained green and the anion resin remained white. This suggested that cation and anion resin were converted to the hydrogen and hydroxide form, respectively.

Black CuO scale was observed on the surface of the concentrate side of anion exchange membranes in the second stage, as shown in Fig. 11. The shape of the scale coincided with the dimensions of the screens filled in the concentrate compartments.

Ionic depletion at resin/membrane and resin/resin interfaces in the dilute compartments resulted in water splitting:

$$H_2O \longrightarrow H^+ + OH^-$$

On the surface of the concentrate side of the anion exchange membranes, high pH regions were present due to the flux of OH^- ions resulting from water splitting. Such regions were also the areas where Cu^{2+} accumulated due to the

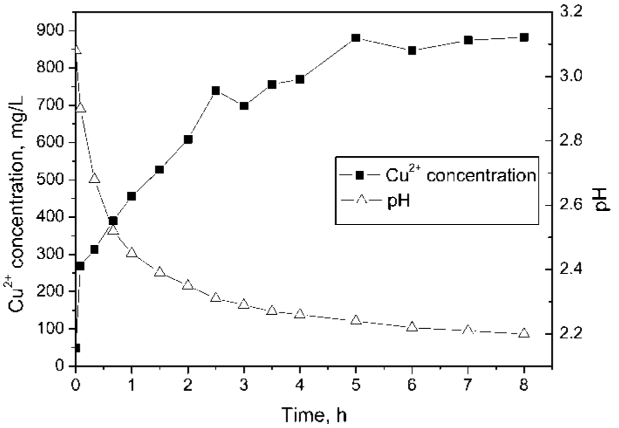

Figure 10. Cu^{2+} concentration and pH of the bleed stream as a function of time for a test operated in the "electroregeneration" regime. Stack voltage was 15 V.

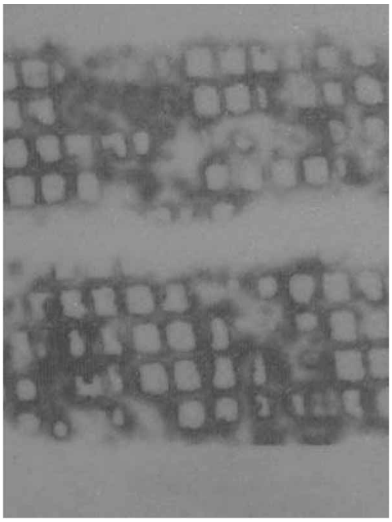

Figure 11. Scale on the surface of the concentrate side of anion exchange membranes for a test operated in the "electroregeneration" regime. Stack voltage was 15 V.

existence of the diffusion layer. At the contact points between anion membranes and the screens, the turbulence of the liquid was weak. If the ionic product was greater than the solubility product constant of $Cu(OH)_2(Ksp = 5.6 \times 10^{-20})$, precipitation occurred:

$$Cu^{2+} + 2OH^{-} \longrightarrow Cu(OH)_2 \downarrow$$

At the same time, H^+ combined with OH^- to form water:

$$H^{+} + OH^{-} \longrightarrow H_2O$$

The precipitation further decomposed to form CuO due to localized reaction heat:

$$Cu(OH)_2 \longrightarrow CuO + H_2O$$

Scaling first occurred at the contact points between anion membranes surface and the screens. Then it tended to expand on membranes surface. Scaling had several negative effects on the process and should be prevented, so the stack configuration with screens in the concentrate compartments was not suitable for this application. From Fig. 11, it can be seen that no scaling occurred at other areas on the membranes surface, indicating the effectiveness of keeping a low pH on the concentrate side for the prevention of scaling. Therefore, appropriate stack configurations along with optimized operating conditions can prevent scaling and thus achieve a continuous and steady EDI process.

CONCLUSIONS

In this paper, it was demonstrated that the EDI process for the removal of copper ions also operated in the "enhanced transfer" regime and the "electroregeneration" regime, similar to its application for ultrapure water production. For feed solutions with copper concentrations of about 50 mg/L, the EDI process operating in the "electroregeneration" regime was able to produce a pure water product containing non-detectable concentrations of copper. The results suggest that EDI is a potentially viable technology for dilute copper-containing wastewater recovery. In localized regions on the surface of the concentrate side of anion exchange membranes, OH- ions resulting from water splitting combined with copper ions to form $Cu(OH)_2$ precipitation. This precipitation further decomposed to form black CuO scale. With the control of scaling, a steady and continuous EDI process can be achieved.

REFERENCES

1. Helfferich, F.G. (1962) *Ion Exchange*; Mcgraw Hill: NewYork.
2. Ganzi, G.C., Wood, J.H., and Griffin, C.S. (1992) Water purification and recycling using the CDI process. *Environmental Progress*, 11 (1): 49–53.
3. Wang, J.Y., Wang, S.C., and Jin, M.R. (2000) A study of the electrodeionization process—high-purity water production with a RO/EDI system. *Desalination*, 132: 349–352.
4. Basta, K., Aliane, A., Lounis, A., Sandeaux, R., Sandeaux, J., and Gavach, C. (1998) Electroextraction of Pb^{2+} ions from diluted solutions by a process combining ion-exchange textiles and membranes. *Desalination*, 120: 175–184.
5. Spoor, P.B., terVeen, W.R., and Janssen, L.J.J. (2001) Electrodeionization 2: The migration of nickel ions absorbed in a flexible ion-exchange resin. *J. Appl. Electrochem.*, 31: 1071–1077.
6. Spoor, P.B., Koene, L., terVeen, W.R., and Janssen, L.J.J. (2002) Electrodeionization 3: The removal of nickel ions from dilute solutions. *J. Appl. Electrochem.*, 32: 1–10.
7. Spoor, P.B., Koene, L., and terVeen, W.R. (2002) Continuous deionization of a dilute nickel solution. *Chemical Engineering Journal*, 85: 127–135.
8. Spoor, P.B., Grabovska, L., Koene, L., Janssen, L.J.J., and terVeen, W.R. (2002) Pilot scale deionization of a galvanic nickel solution using a hybrid ion-exchange/electrodialysis system. *Chemical Engineering Journal*, 89: 193–202.
9. Spoor, P.B., terVeen, W.R., and Janssen, L.J.J. (2001) Electrodeionization 1: Migration of nickel ions absorbed in a rigid, macroporous cation-exchange resin. *J. Appl. Electrochem.*, 31: 523–530.
10. Semmens, M.J., Dillon, C.D., and Riley, C. (2001) An evaluation of continuous electrodeionization as an in-line process for plating rinsewater recovery. *Environmental Progress*, 20: 251–260.
11. Guan, S., Wang, J.Y., and Wang, S.C. (2004) Purification and concentration of acid copper electroplating rinsewater by the continuous electrodeionization process. *Journal of Chemical Industry and Engineering* (China), 55: 166–167.

12. Kyeong-Ho Yeong and Seung-Hyeon Moon (2003) A study on removal of cobalt from a primary coolant by continuous electrodeionization with various conducting spacers. *Separation Science and Technology*, 38: 2347–2371.
13. Kyeong-Ho Yeong, Jung-Hoon Song, and Seung-Hyeon Moon (2004) A study on stack configuration of continuous electrodeionization for removal of heavy metal ions from the primary coolant of a nuclear power plant. *Water Research*, 38: 1911–1919.
14. Lorrain, Y., Pourcelly, G., and Gavach, C. (1997) Transport mechanism of sulfuric acid through an anion exchange membrane. *Desalination*, 109: 231–239.