Zero discharge process for foil industry waste acid reclamation: Coupling of diffusion dialysis and electrodialysis with bipolar membranes

Jin-Xia Zhuang [a], Qing Chen [a], Shun Wang [a], Wei-Ming Zhang [a,*], Wei-Guo Song [b,*,1], Li-Jun Wan [b], Kun-Song Ma [c], Chun-Nian Zhang [c]

[a] College of Chemistry & Materials Engineering, Wenzhou University, Wenzhou 325000, PR China
[b] Beijing National Laboratory for Molecular Sciences (BNLMS), and Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China
[c] Yangzhou Hongyuan Electronic Co., Ltd., Gaoyou 225600, PR China

ARTICLE INFO

ABSTRACT

A zero discharge process was proposed to totally recover both acid and aluminum resource from the waste acid in foil industry. Diffusion dialysis (DD) was coupled with electrodialysis with bipolar membranes (EDBM) in this process, in which most of the free acid was first recovered by DD; and the resulting waste dialysate was further basified by EDBM, recovering aluminum resource and the rest of free acid. Through this process, all components in waste acid were recovered as valuable chemicals, resulting in zero discharge of dangerous effluents. This process is profitable in terms of cost analysis and significantly reduces the environmental burden of foil industry, enabling the foil industry to be more cost-effective, more environmental friendly and more sustainable.

1. Introduction

The electrolytic capacitor is one of the most utilized electronic components in modern electronic devices, and the global market for electrolytic capacitors has grown steadily. Chemosynthesis aluminum anode foil is the most important and valuable part in these capacitors. To produce aluminum anode foil, fresh acids (typically HCl, H_2SO_4, HNO_3 or various mixtures of them) are used to etch the smooth aluminum foil surfaces, and consequently large amount of waste acids, which contain the remaining free acids and soluble aluminum species, are produced. In a typical process for low voltage anode foil production, for example, the compositions of the resulting waste acids are 4.70 mol/L H^+, 6.48 mol/L Cl^- (Al^{3+} for balance), resulting in about 150 m^3 of waste HCl per day. This waste acid must be properly treated before discharge and significantly increases the cost of the products. Thus it will be both economically and environmentally advantageous to completely recover the free acids and aluminum species from the waste acid.

In recent years, diffusion dialysis (DD) has been a very successful membrane separation process to recover free acid from waste

acid by concentration gradient [1]. Many efforts were made in various plants including titanium white,[2,3] pickling, [4] metal-refining, [5–8] and foil industries [9–13]. DD process has two desirable features: high efficiency and low operation cost. However, a large amount of waste salt solution (namely the dialysate) is generated during the process. Typically researchers only focused on the recovered free acid, which is economically valuable, and made efforts to increase the recovery ratio and concentration. Very few attentions were paid to dealing with the residual dialysate solutions in DD process. However, the dialysate solution contains salts and a considerable amount of free acid (typically 10–20%) from original waste acid feed. The disposal of this waste solution remains an environmental problem, which deters the wide implement of DD in the foil industry. Because of the growing public concern for the environment and tightening environmental regulations, the foil industry is seeking an integrated solution to minimize waste generation during the recovery of free acid, and the ultimate goal is an affordable zero discharge process [14].

Recently we designed and built an integrated electrolysis system to produce polyaluminum chloride (PAC) with ultra-high basicity and even aluminum chlorohydrate (ACH) from aluminum chloride [15]. This process is very cost-effective to deal with the waste dialysate solution after HCl recovery by DD. However, chlorine gas is generated in the electrolysis process. Furthermore, this process is not capable of dealing with waste salt solution after H_2SO_4 and HNO_3 recovery. Hence alternative approaches are needed. EDBM is

an electro-membrane process combining the conventional electro-dialysis (ED) and bipolar membranes [16]. It can convert the salt into corresponding acid and base without producing other salt [17–23]. Pratt et al proposed a process to increase the basicity of PAC by EDBM [24]. Thus we envisioned that coupling DD process with EDBM may be a viable route to realize total recovery of free acids and not produce new pollutants [25,26].

In this study, we designed an integrated process to recover free acids as well as aluminum resources directly from foil industry waste acids. The process is capable of recovering more acid than the total free acid in original waste acid. In addition, valuable pure aluminum salt or polyaluminum is produced. The system consists of conventional DD and EDBM modules. Original waste acid feed and pure water were pumped through the DD stack to produce the first part of recovered acid (the diffusate) and the waste salt solutions (the dialysate); then the dialysate and another receiving stream (preferably the diffusate from DD process) were pumped through the EDBM stack to recover the rest of free acid and produce polyaluminum solutions directly from the aluminum species in the waste, resulting in zero discharge of pollutions from foil industry waste acids.
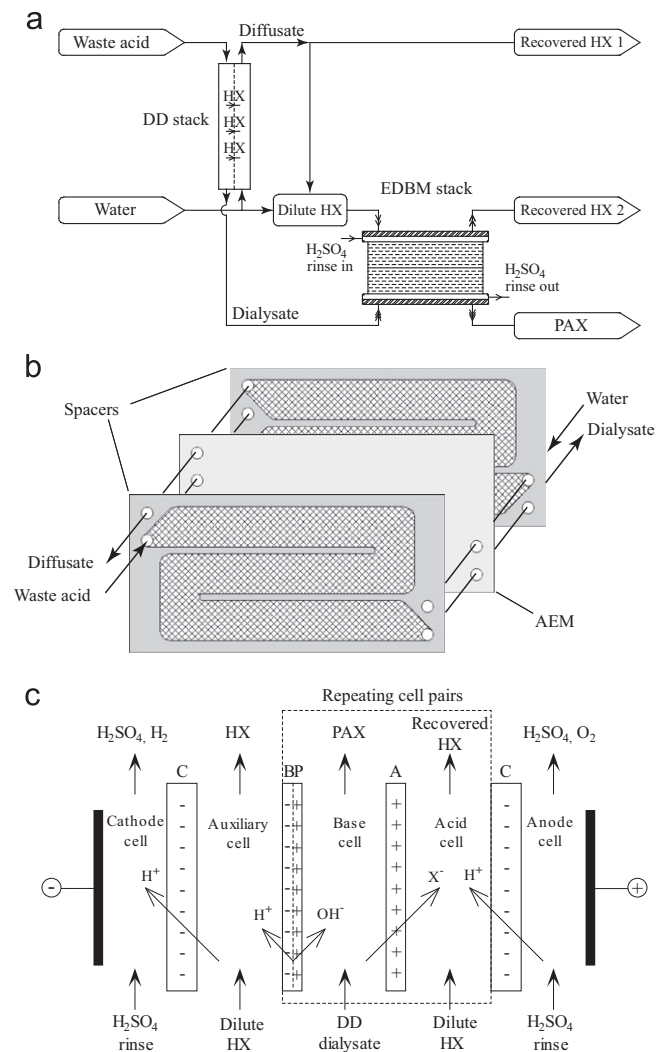
2. Experimental

2.1. Equipment setup

The simplified diagram of the integrated system is illustrated in Fig. 1a. The DD and EDBM stacks were newly designed and home made in our lab (Fig. 1b and c). These stacks are equipped with the same kind of spacer with a dimension of 260 mm (length) $\times$ 130 mm (width) $\times$ 0.9 mm (thickness). The spacer consists of polyethylene (PE) sheet and polypropylene (PP) turbulence accelerating mesh net, with tortuous path flow geometry of 33 mm (width) $\times$ 567 mm (length), i.e. 187 cm^2 of effective area, as shown in Fig. 1b.

The DD stack comprises three hydraulic stages with a 170 cm flow path. There are five spacers for waste acid and five spacers for water streams in each stage. The stack is equipped with 27 anion exchange membranes (AEMs, DF-120, from Shangdong Tianwei Membrane Technology Co., Ltd. China), two inter-stage PE sheets, and 30 turbulence accelerating spacers. The parameters of the AEMs are well documented in the literature [9,10]. They have a thickness of 0.30 mm, and the area resistance is less than 4 Ω cm^2 in 0.1 M NaCl solution. The total membrane area of AEMs is 0.91 m^2 and the effective area is 0.50 m^2. The details of the DD testing system and stack can be found in Supporting Information. The DD stack is operated in a total counter-current flow mode, as shown in Fig. 1b. The waste acid and water streams are driven by a multi-channel metering pump (BT-100, from Baoding Longer Precision Pump Co., Ltd, China), and the flow of each stream can be adjusted between 0 L/h (LPH) and 1.8 L/h.

The arrangement of EDBM stack is shown in Fig. 1c. It is a two-compartment configuration stack with total co-current flows. Heavy cation exchange membranes (CEMs, Selemion CMD, from Asahi Glass Engineering Co., Ltd, Japan) are positioned adjacent to the electrodes. These heavy CEMs are thick (0.4 mm), mechanically strong ($>$ 0.9 MPa burst strength) and durable for chemical contaminations, which are essential for the membrane adjacent to an electrode compartment. Consequently, an extra auxiliary cell is employed for proper function of the stack. The bipolar membranes (BPs, Fumasep FBM, from FuMA-Tech GmbH, Germany), AEMs (Selemion AMT, from Asahi Glass Engineering Co., Ltd, Japan), and adjacent turbulence accelerating spacers form nine repeating cell pairs in the stack. H$_2$SO$_4$ is chosen as the electrode rinse, and it supplies H$^+$ ions to conduct the current in

Fig. 1. Simplified flow diagram of the recovery system (a), illustrations of the DD stack (b) and EDBM stack (c). HX, free acid in waste acid (HCl, H$_2$SO$_4$, HNO$_3$ or the mixture); PAX, polyaluminum; A or AEM, anion exchange membrane; C, cation exchange membrane; BP, bipolar membrane.

the heavy CEMs. All streams in the EDBM stack are driven by a four-channel metering pump (LEAD-2, from Baoding Longer Precision Pump Co., Ltd, China), and the flow rate of each stream is adjustable between 0 L/h and 24 L/h. The details of the EDBM system can be also found in the Supporting Information.

2.2. Operation procedures

Since the waste HCl is the biggest issue in foil industry, waste HCl solution is the main subject in this study. Field analysis indicates that the waste solution is a mixture of 4.70 mol/L HCl and 0.59 mol/L AlCl$_3$ solutions, with trace amounts (ppm level) of impurities such as Fe^{3+} and Cu^{2+}. So simulated waste acid containing 4.70 mol/L HCl (by 37% concentrated HCl, AR, from Sinopharm Chemical Reagent Co., Ltd., China) and 0.59 mol/L AlCl$_3$ (by AlCl$_3 \cdot 6$H$_2$O, AR, from Sinopharm Chemical Reagent Co., Ltd., China) was used in the following tests. Reverse osmosis (RO) water ($<$ 15 ppm TDS) was used as the water supply throughout this study. All experiments were conducted at ambient temperature about 25 °C.

The DD stack was flushed offline with RO water in co-current flow mode first to purge all trapped air before operation. Typically, 20 L simulated waste HCl and 20 L water were filled in PE tanks as stock

solutions, which were pumped through the DD stack, respectively in counter-current mode as shown in Fig. 1a and b. The flow rates of waste acid and water are identical in all experiment, which were controlled between 0.25 L/h and 1.25 L/h. During the operation, graduated cylinders were used to collect and measure the amount of resulting diffusate and dialysate; and the samples were taken at a pre-determined interval.

The DD dialysate and dilute HCl were then pumped through the EDBM stack as shown in Fig. 1c. The dilute HCl comes from the DD diffusate and RO water. The EDBM is running in batch mode. In a typical operation, 2.0 L DD dialysate, 2.0 L dilute HCl, and 1.0 L H_2SO_4 rinse (0.10 mol/L) were cycled, respectively. Parameters such as pH and temperature in dialysate tank, current and voltage of the EDBM stack were automatically recorded by a home-built controlling system [15].

2.3. Analytical methods

The total Al concentrations in samples were determined by the ferron photometric assay [15]. The H^+ and Cl^- concentrations were analyzed by an automatic potentiometric titrator (ZD-2, from INESA Scientific Instrument Co., Ltd, China) with standard Na_2CO_3 (0.05 M) or $AgNO_3$ (0.05 M) solutions.

The free acid recovery ratio η_H and Al^{3+} leakage ratio η_{Al} in DD process are calculated by the formula: [9]

$$\eta_i = \frac{C_{di}Q_d}{C_{fi}Q_f} = \frac{C_{di}Q_d}{C_{di}Q_d + C_{ri}Q_r} \tag{1}$$

where C_{fi}, C_{di}, and C_{ri} are the concentrations of species i (H^+ or Al^{3+} here) in feed acid, diffusate solution and residual dialysate solutions. Q_f, Q_d, and Q_r are flow rates of the corresponding solutions, respectively.

The cumulative current efficiency η in EDBM process is determined by the amount of free H^+ generated in EDBM recovered acid stream shown in the following formula:

$$\eta = \frac{[H^+]_t V_t - [H^+]_0 V_0}{Q_t} \tag{2}$$

where V_0 and $[H^+]_0$ are the volume and free H^+ concentrations in recovered acid stream on initial state. V_t and $[H^+]_t$ are the volume and free H^+ concentrations in recovered acid stream at sampling point. Q_t is the cumulative charge transferred in mol electrons at the same point.

The basicity of the polyaluminum in basified dialysate is calculated as following: [15,24]

$$\text{Basicity} = \frac{3Al_t - [X^-]}{3Al_t} \tag{3}$$

where Al_t is the total aluminum concentration in product solution, and $[X^-]$ is the concentration of counter anions X^- (Cl^-, NO_3^-, $\frac{1}{2}SO_4^{2-}$ or the mixture).

3. Results and discussion

3.1. DD process modeling

In this study, the inlet flow rates of feed waste acid as well as water in the DD stack were kept the same. Such ratio is usually optimized in many practical industrial plate-and-frame DD stacks. The counter-current flows in the stack maximize the concentration gradient, which is helpful for the mass transfer. The free acid (HX) diffuses across the AEMs from the waste acid stream to the water stream, as shown in Fig. 1a. When the water stream comes out of the stack, it contains HX and small amount of aluminum salt as diffusate. The feed acid stream loses most of the HX while keeps most of the waste aluminum salt as dialysate. During this diffusion process, some of the water molecules in water stream migrate to waste acid stream because of the osmosis effect. So the flow rate of dialysate is always larger than the original waste acid stream, and the flow rate of diffusate is always smaller than the water stream. The experimental data in Table 1 indicate that the total flow rate of the inlet flows (water+feed acid) and that of the outlet flows (diffusate+dialysate) keep nearly the same in all tests.

The inlet flows (water or feed acid) were controlled in the range of 0.25 L/h –1.0 L/h, and the mass transfer in DD stack varied as the flow rates changed. As shown in Table 1, the $[H^+]$ decreases in diffusate and increases in dialysate stream as the inlet flow increases, indicating a lower η_H. The reason is that higher inlet flow rates lead to shorter diffusion time and insufficient mass transfer. The variation of aluminum leakage ratio η_{Al} is a little bit more complex; it decreases first and then increases again as shown in Table 1. Since H^+ and Al^{3+} ions in both diffusate and dialysate streams come from the original waste acid, a mathematical model can be established from three independent parameters (delta flow ratio, $[H^+]$ and $[Al^{3+}]$ in the dialysate are selected here) to describe the DD process. Experimental data fit this model very well, as shown in Supporting Information. An Excel worksheet is also composed from the model above. DD operation parameters such as diffusate/dialysate flow rates and compositions are calculated automatically according to the inlet flow input. This worksheet is enclosed in Supporting Information.

Salt effect is observed in the DD tests. When inlet flow rates are lowered than 0.50 L/h, the $[H^+]$ in recovered acids are higher than 4.70 mol/L, which is the same as the free acid concentration in original waste acid. The aluminum chloride in the waste acid provided extra driving force for such mass transfer [1,27]. The salt effect observed here indicates that the stack design is successful and ensures excellent mass transfer.

3.2. DD cost analysis

The DD process model indicates that lower inlet flow rates are favored for H^+ recovery ratio. However, low inlet flow rate means large DD stack is needed, which increases the capital cost. So

Table 1
Experimental data of DD process at different inlet flow rates.

Inlet flow /LPH	Dialysate			Diffusate			Delta flow ratio [a] (%)	η_H (%)	η_{Al} (%)
	Flow/LPH	$[Al^{3+}]$/M	$[H^+]$/M	Flow/LPH	$[Al^{3+}]$/M	$[H^+]$/M			
0.253	0.300	0.446	0.23	0.206	0.075	5.44	18.7	94.1	10.3
0.373	0.425	0.468	0.27	0.321	0.067	5.10	13.8	93.5	9.7
0.503	0.552	0.495	0.38	0.453	0.051	4.76	10.0	91.2	7.7
0.626	0.702	0.489	0.62	0.551	0.048	4.55	12.0	85.2	7.2
0.750	0.887	0.462	0.95	0.614	0.054	4.37	18.2	76.0	7.5
0.875	1.140	0.410	1.17	0.609	0.079	4.56	30.4	67.7	9.4
1.001	1.377	0.390	1.32	0.626	0.088	4.61	37.5	61.3	9.3

[a] Delta flow ratio=(Water-diffusate)/Water=(Dialysate-feed)/feed.

there is a trade-off for inlet flow rates, and many related efforts have been made to minimize the price of the recovered acid. In most previous works the residual dialysate is waste effluent without cost considerations at all [9]. The residual acids in the dialysate need further treatment to avoid environmental pollution. The treatment charge for the residual free acid in the dialysate should be considered in the overall costs. As the inlet flow rates increases, more waste acid can be treated; but the residual free acid concentration in dialysate stream increases too, which increases the treatment cost remarkably.

Available options for free acid disposal in the dialysate include lime or $NH_3 \cdot H_2O$ neutralization, and the cost is acceptable. The actual cost depends on the facilities and chemicals used, which approximates the price of industrial HCl (~\$0.007/mol) itself. It may be more appropriate to evaluate the economics of the DD process with this extra cost under consideration. The rest of the cost estimation is similar to that of previous works [9]. The effective areas of membranes are calculated by the flow intensity as well as the waste acid flow rate in the full-scale system. The flow rates and compositions of the diffusate and dialysate are obtained from the process model. We can easily calculate the amount of HCl recovered in the diffusate and residual HCl in the dialysate; the former is profit while the other is extra charge. The pay-off period depends on the total cost and net saving. Details of the cost estimation is described in Supporting Information, in which a excel worksheet is composed to supply detailed costs at different inlet flow rates.

The pay-off period at different inlet flow intensities is presented in Fig. 2. It decreases when inlet flow intensity increases from 0.5 L/h/m^2 to 1.25 L/h/m^2, which means that the recovered acid accounts more in this range. It increases as the flow intensity increases further, because the neutralization cost is too high in this stage. The most cost-effective inlet flow intensity is 1.25 L/h/m^2 (i.e., 0.625 LPH inlet flow rates for the lab DD system), and all investment can be recovered within 241 days. It is very attractive on economics. Fig. 3 presents the mass balance at this optimized flow intensity. The industry is able to reclaim 130.58 m^3 free acid (~4.596 mol/L) per day, and the corresponding waste is 169.42 m^3 dialysate (0.482 mol/L Al^{3+}, 0.619 mol/L H$^+$) per day according to the process model. These predicting compositions accord well with the experimental data in Table 1.

3.3. Basification of DD dialysate by EDBM

The DD process is economically attractive to recover free acid from the waste acid in the foil industry, while the waste dialysate needs to be neutralized and discharged. A better strategy is converting the remaining chemicals in the dialysate into useful
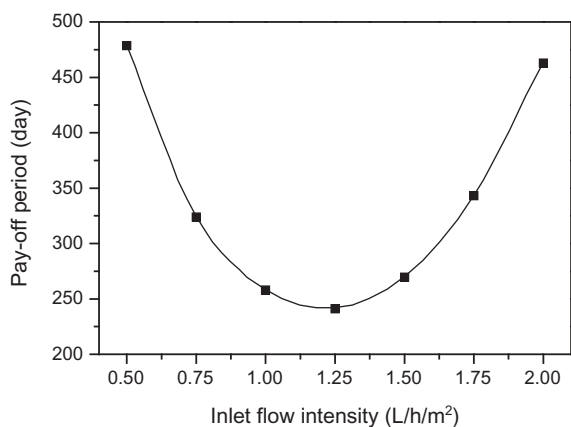

Fig. 2. Dependence of DD pay-off period upon inlet flow rate intensity.
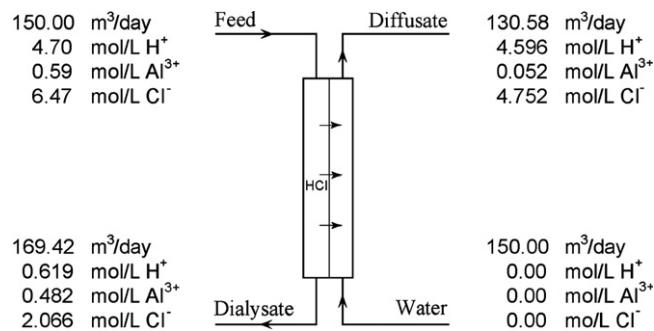

Fig. 3. DD material balance at the optimized inlet flow rate intensity of 1.25 L/h/m^2.
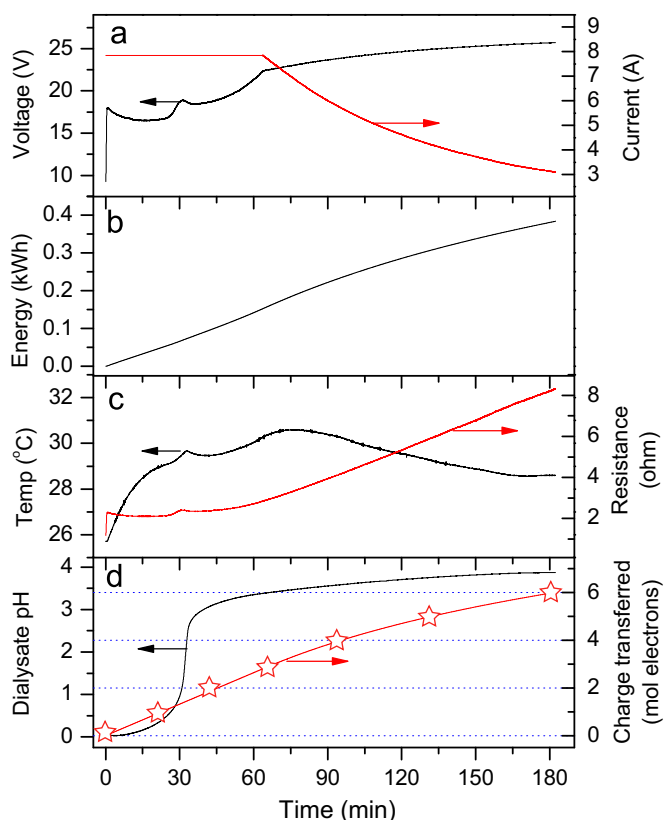
products. The raw materials in foil industry (Al foils and fresh acids) are highly purified, which makes it possible to basify the waste dialysate to produce pure AlCl$_3$ or polyaluminum solutions by EDBM.

As described in Table 1, after the DD process, the waste DD dialysate at optimized flow rate (~0.625 LPH) is a mixture of 0.489 mol/L AlCl$_3$, and 0.62 mol/L HCl. This mixture was the feed solution in EDBM process. Another 2 L of highly dilute HCl (~0.05 mol/L) receiving solution was obtained by mixing RO water and 22 mL of diffusate (~4.55 mol/L HCl). Dilute HCl is used as starting solution because of its better conductivity than pure water, which is helpful to reduce the initial energy consumption. The basification principles and detailed configurations of the EDBM stack are presented in Fig. 1c, and the photograph of the EDBM system in this study can be found in Supporting Information.

3.3.1. On-line monitoring of EDBM process

During the basification process, several parameters, including temperature/pH of the dialysate solution, voltage/current of the stack, were monitored on-line, and meanwhile samples were taken for off-line analysis. The data profiles from on-line sensors and transducers are represented in Fig. 4. The EDBM stack was operated basically in a constant voltage (~25 V) mode, and the current was limited within 8 A. As shown in Fig. 4a, the voltage output drops to 16–18 V at first because of the current limitation; and then the voltage increases. The temperatures of all three solutions were maintained nearly constant by tap water heat-exchangers. The temperature of the dialysate solution is recorded and illustrated in Fig. 4c. The ambient temperature is 26 °C during the basification process; and the solution temperature rises to 30.5 °C first due to the Joule heat and then falls to 28.5 °C when the current decreases. As plotted in Fig. 4c, the resistance of the stack increases continuously, from 2 Ω to about 8 Ω. Since there are no large variations of solution temperatures, the stack resistance increases for the following reasons. First, the Cl$^-$ concentration decreases in the dialysate stream, which increases the stack resistance (see Fig. 1c for details) remarkably. Second, the water splitting generates plenty of OH$^-$ on the anode surfaces of the BP membranes, which might cause Al(OH)$_3$ scaling on the same surfaces and increase the stack resistance. This scaling is a killer for long-term stability of the EDBM stack. Fortunately, the residual free acid in the dialysate is a natural cleaner for the newly formed Al(OH)$_3$ scaling by dissolving the scaling formed in previous running. The stack resistance in the subsequent repeating process returns to about 2 Ω again, indicating that the scaling risk is not an issue here.

As shown in Fig. 4d, the pH of the dialysate solution increases during the basification process. The pH change pattern looks like a titration curve of the same dialysate. The initial dialysate contains plenty of free acids and the pH is about 0.2. During the EDBM process, the free acid is neutralized first and the pH increases. As

Fig. 4. On-line data profiles during the EDBM basification process: (a) stack voltage and current curves; (b) cumulative stack energy consumption curve; (c) dialysate solution temperature and stack resistance curves; (d) dialysate pH and cumulative charge transferred curves, the sampling points are marked as ☆ symbols herein.

all free acids are consumed, the pH increases from about 1.5 to 2.5, which agrees well with that of pure $AlCl_3$ solution with similar concentration. After that, the Al^{3+} ions are partially neutralized to form polyaluminum chloride (PAC), and the pH increases slowly again as the basicity of PAC increases, which is very similar to that in our previous work [15].

The energy consumption in this process can be readily calculated from current and voltage curves of the stack, which is represented in Fig. 4b. The charge transferred in mol electrons is calculated by current and cell-pair number of the stack and the result is illustrated in Fig. 4d. The maximum charge transferred is 6.0 mol electrons in this study, and samples are taken in both HCl and dialysate tanks when charge transferred reaches every 1.0 mol electrons. The sampling points are marked as star symbols (☆) in Fig. 4d. H_2SO_4 rinse samples were also taken before and after the test.

3.3.2. Off-line sample analysis

The solution volume increases in the HCl tank and decreases in dialysate tank (Fig. 5a). These volume variations are mainly caused by electro-osmosis [17]. As shown in Fig. 1c, when Cl^- ions move through the AEMs, they drag water molecules from dialysate chambers to HCl chambers. Another minor reason is the water consumed by the bipolar membrane. These volume variations are linear vs. the charge transferred in the stack.
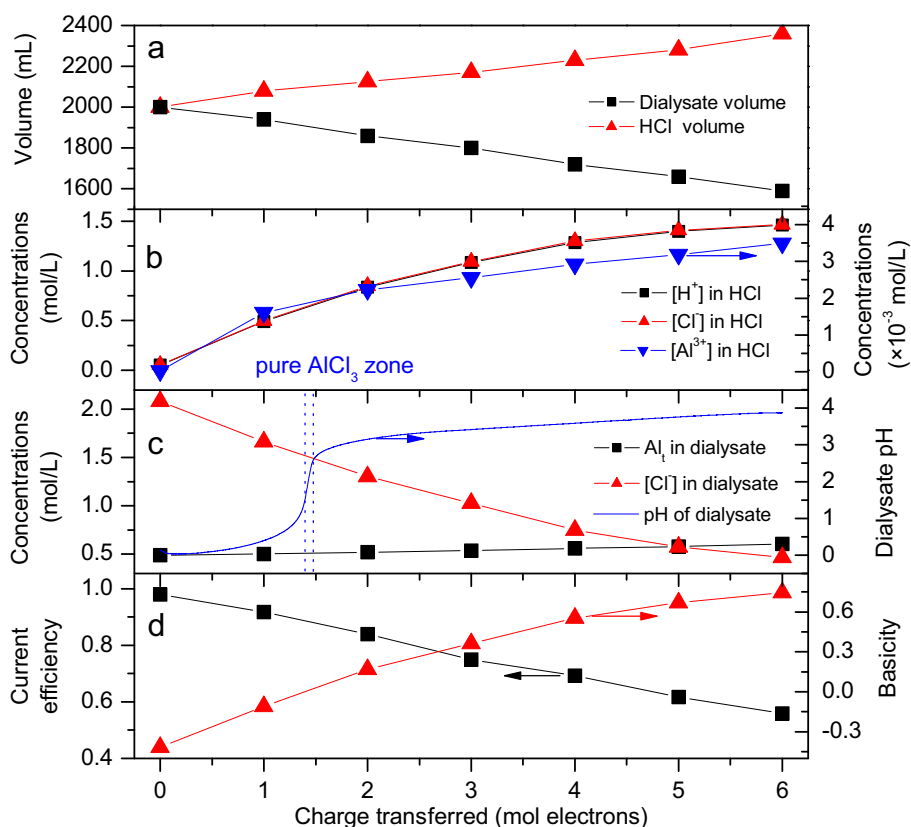
The concentrations of all ions (including H^+, Cl^-, and Al^{3+}) in HCl samples are quantitatively analyzed, and the final results are plotted in Fig. 5b. Concentration of $[H^+]$ and $[Cl^-]$ is nearly the same in all samples, indicating that it is nearly pure HCl. $[Al^{3+}]$ determined by ferron assay further validate the high purity of the HCl obtained, which increases from 0 to about 3.49×10^{-3} mol/L. Meanwhile $[H^+]$ increases from 0.05 mol/L to 1.46 mol/L, which means that the Al^{3+} ions account 0.7% maximum of all cations in HCl stream. The Al^{3+} leakage from dialysate to HCl chambers is negligible in this study.

The total Al concentration (Al_t) and $[Cl^-]$ are determined in all dialysate samples, which are shown in Fig. 5c. The Al_t increases slightly from 0.49 mol/L to 0.605 mol/L, and the $[Cl^-]$ decreases remarkably from 2.08 mol/L to 0.465 mol/L. The total amount of aluminum in dialysate stream is basically constant during the study since very little leakage occurs; the increase of Al_t is due to solution volume shrinkage. The basicity of the polyaluminum can be calculated by Eq. (3) according to Al_t and $[Cl^-]$ here, which increases from −41.5% to 74.4% as plotted in Fig. 5d. Basicity below zero means that there are extra free H^+ ions in the solution. The corresponding pH curve is also plotted in Fig. 5c. The polyaluminum pH increases as the basicity increases, and there is a steep rise near basicity value of 0 on the pH curve. This signal is an indicator for pure $AlCl_3$ solution formation. The pure $AlCl_3$ zone in this study is marked out in Fig. 5c, and the corresponding charge transferred is 1.37 mol electrons. This basification endpoint can be easily monitored by pH changes, which enables pure $AlCl_3$ recovery possible in real systems. High basicity polyaluminum is also available in this process, which is a highly value-added chemical and is widely used as flocculants for potable water and wastewater treatment, catalysts, and cosmetics [15].

The rates of $[H^+]$ increase in the HCl stream and that of $[Cl^-]$ decrease in the dialysate stream slow down as the charge transferred goes up in Fig. 5b and c, which means that the efficiency degrades. The cumulative current efficiency is determined by Eq. (2), and plotted in Fig. 5d. The initial current efficiency is quite high, and then decreases quickly as the free acid concentration increases. The current efficiency is mainly hindered by the back-diffusion of the free acid (HCl here). As shown in Fig. 1c, the $[H^+]$ rises in acid cells and falls in base cells under electric forces. While the H^+ ions in acid cell tend to diffuse back to base cell by H^+ concentration gradient, which is a reversal of basification process. Unfortunately the H^+ and anions are able to migrate through AEMs, which is helpful in the DD process while harmful here. In this study thick and strong Selemion AMT AEMs (0.22 mm thickness, 0.7 MPa burst strength) are carefully selected to reduce the HCl back-diffusion. During the last period of the experiment, the $[H^+]$ in the HCl stream increases slowly, which should retain the current efficiency. But the stack current decreases due to $[Cl^-]$ depletion and possible initial $Al(OH)_3$ scaling, which delays the EDBM process and aggravates the back-diffusion of free acid. So the current efficiency keeps falling during this stage. The efficiency completely depends on wrestle of these two above competitive processes, and higher current density in EDBM process is helpful to enhance H^+ ions migration, which increases the current efficiency. The current density here is 43 mA/cm² (8 A for 187 cm²), which is limited by the capacity of DC power supply used. The efficiency has a good chance to increase when higher current density (such as 100–200 mA/cm², which is achievable in EDBM process) is involved. AEMs with high mechanical strength, low solution leakage, and low H^+ back-diffusion are favored in this study. Furthermore, the system performance should increase if low resistant H^+ blocking layers are attached on these thick AEM surfaces.

The volume and composition of H_2SO_4 rinse remained stable during the basification process. Theoretically only about 6 mL water is consumed in one single batch, so the rinse volume change is negligible (∼0.6%). Cl^- and Al^{3+} ions in H_2SO_4 rinse samples are not detected in titration and photometric assay after one running, which means that the Cl^- and Al^{3+} leakages to rinse are small. The

Fig. 5. Off-line sample analysis results during the EDBM basification process: (a) variations of dialysate and HCl volumes; (b) variations of ion concentrations in HCl stream; (c) total aluminum and Cl$^-$ ion concentrations of dialysate. Corresponding pH curve is also presented here, where pure AlCl$_3$ zone is marked on the steep rise of the pH curve; (d) dialysate basicity and cumulative current efficiency.

rinse can be reused in such batch-mode EDBM process for many times, with just a small quantity of pure water for makeup.

Pratt et al. proposed a similar process to produce high-basicity PAC with EDBM, [24] but their design is not able to cope with our situation. They used AlCl$_3$ solution as base cell stream and KCl solution as acid cell stream. KOH was added continuously to KCl stream to maintain [H$^+$] low (≤ 0.1 mol/L). The additional alkali would neutralize the recovered free acid and produce extra salt effluents.

3.4. EDBM cost analysis

Typically the total cost of an electrodialysis based process involves the investment for the equipment, the maintenance cost, and the energy cost [16]. The cost of EDBM process usually suffers from high prices of BP membranes. It is widely recognized to estimate the total equipment cost from membrane prices before implement of real projects. The total energy required in real system consists of power of pumps, controllers, and the stacks. Among them stack power is much higher than others, which is commonly used instead of the total power.

A cost model is established as an Excel worksheet and attached in Supporting Information. The target basicity of recovered poly-aluminum is specified as input parameter. The degree of EDBM basification (represented by the charge transferred in lab stack here) can be readily calculated from the target basicity. And then all other parameters such as energy consumption, flow rate of dialysate treated in lab system are calculated from the charge transferred. In this study, parameters in full scale system are obtained by scale up the lab system to required capacity. Key parameters and final overall cost for the EDBM process are automatically computed in the cost model worksheet.

The cost analysis indicates that this basification process is cost-effective itself in addition to the environmental benefits. For example, we can recover pure AlCl$_3$ and HCl from the DD dialysate. The target basicity of recovered polyaluminum (actually AlCl$_3$ here) is 0.0%, and the overall cost is $13.62 per cubic meter of dialysate according to the cost model. The corresponding material balance chart is illustrated in Fig. 6. Since the waste DD dialysate has been completely treated and reclaimed as valuable raw materials (AlCl$_3$ + HCl here), there is no neutralization cost for the waste dialysate and then save $4.38 per cubic meter of dialysate. Further profits are obtained from the recovered materials. The value of the recovered HCl is $4.26 per cubic meter of dialysate. So the cost for recovering AlCl$_3$ is $4.98 per cubic meter of dialysate, namely $42.4 to recover 1 t of AlCl$_3 \cdot 6$H$_2$O. The market prices of AlCl$_3 \cdot 6$H$_2$O is much higher than that, meaning that the EDBM process will make extra profits under current conditions, besides valuable environmental impacts.

This basification process can also produce high quality poly-aluminum from the same waste DD dialysate. Al(OH)$_2$Cl and HCl will be recovered when the target basicity is 66.7%, for another example. The corresponding mass balance chart is also shown in Supporting Information. The overall cost is $57.38 per cubic meter of dialysate. Similar to the above example, the cost for recovering polyaluminum is $660 for 1 t of Al(OH)$_2$Cl $\cdot 2$H$_2$O. That cost is much higher than AlCl$_3$ reclamation for several reasons. First, high target basicity means more charge transferred, and longer process time is needed. Larger stack is involved to treat the same dialysate, which increases the cost. Second, high target basicity means more HCl recovered. Consequently the H$^+$ back-diffusion increases and the current efficiency decreases, which raises the cost further. Third, higher target basicity means more ion depletion and higher risk of Al(OH)$_3$ scaling in the stack, which lower
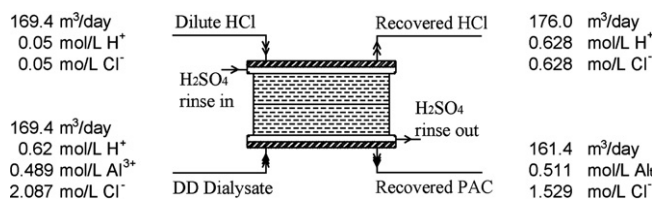
Fig. 6. EDBM mass balance for pure $AlCl_3$ and HCl reclamation.

the stack current. Consequently the process time is further extended; larger stack and higher cost are involved.

In this study, polyaluminum with 74.4% basicity is obtained without reducing the process stability. Higher basicity products (theoretically highest basicity is 83%) will be difficult because of extremely high cost and highly risk of irreversible scaling. It is worthy to note that the polyaluminum recovered here are instinctively clean products without impure ions and by-product salts, which boosts their value especially in high-end applications such as portable water treatment, catalysts and cosmetics. The cost of these recovered polyaluminum (such as $660 for 1 t of $Al(OH)_2Cl \cdot 2H_2O$) is still cost-effective according to our previous work [15].

4. Conclusions

Waste acids with high concentration in the foil industry increase the final product costs and pollution risks to the environment. A combined system was designed to solve such problem using DD and EDBM. The system recovered most of the free acid by DD, and the process and cost model were established for better understanding the DD process. Flow intensity in DD stack was optimized to maximize the productivity, which is adopted in real systems. The DD dialysate was further treated by EDBM basification process, with polyaluminum (or pure aluminum salt) and another portion of free acid as recovered products. Process and cost models of EDBM process indicate that it is cost-effective in addition to the environmental benefits. The coupling operation here is able to convert the waste acids to valuable chemicals completely, resulting in zero pollutant discharge. HCl acid was completely treated as an instance in this study, and this technology is able to deal with other waste acids such as H_2SO_4, HNO_3 and various mixtures of them. This new zero discharge process is able to make the foil industry more cost effective, more environmental friendly and more sustainable.

Acknowledgment

Appendix A. Supporting information

Details of DD test system setup, DD process modeling, DD cost modeling, EDBM system setup, EDBM process modeling and EDBM cost modeling are represented as Microsoft Excel worksheets in Supporting Information.

The supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.memsci. 2013.01.016.

References

[1] J. Luo, C. Wu, T. Xu, Y. Wu, Diffusion dialysis-concept, principle and applications, J. Membr. Sci. 366 (2011) 1–16.

[2] T. Xu, W. Yang, Industrial recovery of mixed acid ($HF+HNO_3$) from the titanium spent leaching solutions by diffusion dialysis with a new series of anion exchange membranes, J. Membr. Sci. 220 (2003) 89–95.

[3] X. Tongwen, Y. Weihua, Sulfuric acid recovery from titanium white (pigment) waste liquor using diffusion dialysis with a new series of anion exchange membranes—static runs, J. Membr. Sci. 183 (2001) 193–200.

[4] M. Regel-Rosocka, A review on methods of regeneration of spent pickling solutions from steel processing, J. Hazard. Mater. 177 (2010) 57–69.

[5] C. Wei, X. Li, Z. Deng, G. Fan, M. Li, C. Li, Recovery of H_2SO_4 from an acid leach solution by diffusion dialysis, J. Hazard. Mater. 176 (2010) 226–230.

[6] Y.-C. Lai, W.-J. Lee, K.-L. Huang, C.-M. Wu, Metal recovery from spent hydrodesulfurization catalysts using a combined acid-leaching and electrolysis process, J. Hazard. Mater. 154 (2008) 588–594.

[7] A. Agrawal, K.K. Sahu, An overview of the recovery of acid from spent acidic solutions from steel and electroplating industries, J. Hazard. Mater. 171 (2009) 61–75.

[8] W. Li, Y. Zhang, J. Huang, X. Zhu, Y. Wang, Separation and recovery of sulfuric acid from acidic vanadium leaching solution by diffusion dialysis, Sep. Purif. Technol. 96 (2012) 44–49.

[9] X. Zhang, C. Li, H. Wang, T. Xu, Recovery of hydrochloric acid from simulated chemosynthesis aluminum foil wastewater by spiral wound diffusion dialysis (SWDD) membrane module, J. Membr. Sci. 384 (2011) 219–225.

[10] X. Zhang, C. Li, X. Wang, Y. Wang, T. Xu, Recovery of hydrochloric acid from simulated chemosynthesis aluminum foils wastewater: an integration of diffusion dialysis and conventional electrodialysis, J. Membr. Sci. 409-410 (2012) 257–263.

[11] S.H. Lin, M.C. Lo, Recovery of sulfuric acid from waste aluminum surface processing solution by diffusion dialysis, J. Hazard. Mater. 60 (1998) 247–257.

[12] J.-Y. Kim, C.-H. Shin, H. Choi, W. Bae, Recovery of phosphoric acid from mixed waste acids of semiconductor industry by diffusion dialysis and vacuum distillation, Sep. Purif. Technol. 90 (2012) 64–68.

[13] J. Xu, D. Fu, S. Lu, The recovery of sulphuric acid from the waste anodic aluminum oxidation solution by diffusion dialysis, Sep. Purif. Technol. 69 (2009) 168–173.

[14] M.E. Goldblatt, K.S. Eble, J.E. Feathers, Zero discharge: what, why, and how, Chem. Eng. Prog. 89 (1993) 22–27.

[15] W.-M. Zhang, J.-X. Zhuang, Q. Chen, S. Wang, W.-G. Song, L.-J. Wan, Cost-effective production of pure Al_{13} from $AlCl_3$ by electrolysis, Ind. Eng. Chem. Res. 51 (2012) 11201–11206.

[16] H. Strathmann, Electrodialysis, a mature technology with a multitude of new applications, Desalination 264 (2010) 268–288.

[17] J.S. Jaime-Ferrer, E. Couallier, P. Viers, M. Rakib, Two-compartment bipolar membrane electrodialysis for splitting of sodium formate into formic acid and sodium hydroxide: modelling, J. Membr. Sci. 328 (2009) 75–80.

[18] F. Zhang, C. Huang, T. Xu, Production of sebacic acid using two-phase bipolar membrane electrodialysis, Ind. Eng. Chem. Res. 48 (2009) 7482–7488.

[19] Y. Wang, X. Zhang, T. Xu, Integration of conventional electrodialysis and electrodialysis with bipolar membranes for production of organic acids, J. Membr. Sci. 365 (2010) 294–301.

[20] M.T. de Groot, R.M. de Rooij, A.A.C.M. Bos, G. Bargeman, Bipolar membrane electrodialysis for the alkalinization of ethanolamine salts, J. Membr. Sci. 378 (2011) 415–424.

[21] M.D. Eisaman, L. Alvarado, D. Larner, P. Wang, B. Garg, K.A. Littau, CO_2 separation using bipolar membrane electrodialysis, Energy Environ. Sci. 4 (2011) 1319–1328.

[22] M.D. Eisaman, L. Alvarado, D. Larner, P. Wang, K.A. Littau, CO_2 desorption using high-pressure bipolar membrane electrodialysis, Energy Environ. Sci. 4 (2011) 4031–4037.

[23] Y. Wang, N. Zhang, C. Huang, T. Xu, Production of monoprotic, diprotic, and triprotic organic acids by using electrodialysis with bipolar membranes: effect of cell configurations, J. Membr. Sci. 385-386 (2011) 226–233.

[24] W.E. Pratt, J.J. Stevens, P.G. Symons, Polyaluminum Chloride and Aluminum Chlorohydrate, Processes and Compositions: High-Basicity and Ultra High-Basicity Products, US. Patent 7846,318 (2010).

[25] R.-H. Xiong, W. Cai, A.P. Shapiro, C.-Q. Zhang, J.M. Silva, Z.-J. Xia, W.-M. Zhang, Method for Removing Ionic Species from Desalination unit, US. Patent 20100242995 (2010).

[26] J.-Y. Xia, R.-H. Xiong, W. Cai, Z.-J. Xia, C.-Q. Zhang, J.M. Silva, W.-M. Zhang, Desalination System and Method, US. Patent 20110024354 (2011).

[27] Z. Palatý, H. Bendová, Separation of $HCl+FeCl_2$ mixture by anion-exchange membrane, Sep. Purif. Technol 66 (2009) 45–50.