



Recovery of sulfuric acid from waste aluminum surface processing solution by diffusion dialysis

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Abstract

Diffusion dialysis with anionic ion exchange membranes was employed to recover sulfuric acid from the waste acid solution of aluminum surface processing plant. Experiments were conducted to examine the dialyzer performances under various operating conditions, including feed flow rates, sulfuric acid concentration in the feed solution, temperature and number of pieces of ion exchange membrane. Diffusion dialysis was found very efficient for this purpose. Based on the test results, optimum operating conditions of these variables were identified. Preliminary economic evaluation of the process indicated that diffusion dialysis is highly viable for sulfuric acid recovery due to its short payback period. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Aluminum surface finishing has been a rapidly growing industry in many countries around the world for the past decade [1]. The products involved in this industry include aluminum cables and wires, structural materials, electric capacitors, etc. The aluminum finishing industry invariably produces a large amount of waste acid solution. Depending on specific type of aluminum surface finishing, the waste acid may contain sulfuric acid, hydrochloric acid, phosphoric acid, additives along with appreciable amount of dissolved aluminum. A typical waste acid solution is that generated in either the aluminum window sash anodizing or the etching of aluminum foil for high-power

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Table 1
Properties and specifications of the Asahi Type T-O Dialyzer

Item	Specifications
Membrane type	Anion ion exchange
Total effective area of membrane	0.326 m ²
Number of membrane sheet	19
Dimension of membrane sheet	10 cm (W) × 17.2 cm (L) × 0.16 cm (T)
Dimension of dialyzer stack	35 cm (W) × 35 cm (L) × 55 cm (H)
Dialyzer flow capacity	10 l/h
Bursting strength	2 kg/cm

an overhead tank which was equipped with water jacket for temperature control. The stock acid solution then went through the Asahi dialyzer (Model T-O with Selemion DMV, Asahi Glass, Tokyo, Japan). Deionized water in the storage tank was preheated to the same temperature of the stock acid solution, then pumped to an overhead tank and finally entered the Asahi dialyzer. The properties and specifications of the Asahi dialyzer are given in Table 1. During a test run, a significant amount of sulfuric acid and a smaller amount of aluminum ion in the feed solution diffused through the anionic ion exchange membrane to the deionized water. The deionized water containing those sulfuric acid and aluminum ion was collected at one outlet of the dialyzer as diffusate which can be reused by mixing this solution with high concentration sulfuric acid to bring the H₂SO₄ content to the level required by the aluminum surface finishing process. In fact when appropriately operated, the anionic ion exchange membrane was capable of rejecting a majority of aluminum ion in the feed solution and letting through a large portion of sulfuric acid. The feed solution came out from the other end of the dialyzer as the rejection solution (dialyzate). The diffusion dialysis was run at 1 atm pressure with a temperature kept between 10 and 40°C to maintain the integrity of the anionic ion exchange membranes for a long test life.

After a test run was started, samples were taken from the dialyzate and diffusate once every 30 min for determination of sulfuric and aluminum ion concentrations until the final steady state was reached which was achieved in approximately 4 h, as will be seen later. The total amounts of diffusate and dialyzate along with the sulfuric acid and aluminum ion concentrations in these two solutions were determined. The sulfuric and aluminum ion concentration were measured by the standard methods [4] using a Metrohm auto burette (Model 716 Titrino, Metrohm, Switzerland). The total acid concentration was defined as the sum of all cations (H⁺ and Al³⁺ concentrations in the present case) that can react with OH²⁻. H⁺ ion concentration alone was considered as the free acid. Accordingly, the percent acid recovery (AR), acid loss (AL) and aluminum ion removal (AIR) were, respectively, defined as follows:

$$AR(\%) = \frac{(\text{Total acid conc. in the diffusate})(\text{Diffusate flow rate})}{(\text{Total acid conc. in the feed solution})(\text{Feed solution flow rate})} \quad (1)$$

$$AL(\%) = \frac{(\text{Total acid conc. in the dialyzate})(\text{Dialyzate flow rate})}{(\text{Total acid conc. in the feed solution})(\text{Feed solution flow rate})} \quad (2)$$

AIR(%)

$$= \frac{\text{Aluminum ion conc. in the feed solution} - \text{Aluminum ion conc. in the diffusate}}{\text{Aluminum ion conc. in the feed solution}} \quad (3)$$

The three parameters were employed to assess the efficiency of a diffusion dialysis process. It should be noted that the aluminum ion concentration in the dialyzate was observed in all instances to be higher than that in the feed solution. Hence, it would be a good feedstock for aluminum ammonium sulfate (ammonium alum) recovery [1].

3. Discussion and results

3.1. The Donnan equilibrium of diffusion dialysis

According to Wallace [5], the diffusion dialysis was caused mainly by the concentration difference of ions across the membrane. The ion concentration difference established across the membrane was known as the Donnan equilibrium [5] which is mathematically represented by

$$(a_i/\bar{a}_i)^{1/Z_i} = \text{constant} \quad (4)$$

where a_i and \bar{a}_i are the ion activities in the solution and membrane, respectively, and Z_i is valence of ion electric charge. For the dialysis system considered in the present study, the above equation can be rewritten as [6]

$$(a_{H^+}/\bar{a}_{H^+}) = (a_{Al^{3+}}/\bar{a}_{Al^{3+}})^{1/3} \quad (5)$$

in which a_{H^+} and $a_{Al^{3+}}$ are the hydrogen and aluminum ion activities in the solution, respectively. The two ion activities in the solution were related to their activity coefficients (γ) by $3.93 \gamma_{H^+}$ and $0.97 \gamma_{Al^{3+}}$ [6] and the two activity coefficients in turn were found equal to 0.1 and 0.29. Hence Eq. (5) becomes

$$\bar{a}_{Al^{3+}} = 0.29(\bar{a}_{H^+})^3 \quad (6)$$

Since the hydrogen ion activity (a_{H^+}) in the membrane is less than 1, the aluminum ion activity is much less than 1 according to Eq. (6), implying that the dialyzer membrane strongly favors the hydrogen ion passage. This offers logical explanation for the efficient sulfuric acid recovery discussed in Section 3.2.

3.2. Effects of operating variables on the dialyzer performances

Once a test run was started, it would take a little while the diffusate and dialyzate flow rates as well as all concentrations in these two exit streams to stabilize. The three curves in Fig. 2 show the acid recovery, aluminum ion removal and free acid in the diffusate. The general trends clearly indicate that it took approximately 4 h for all those parameters to reach a steady state. In fact, the corresponding parameters in the dialyzate

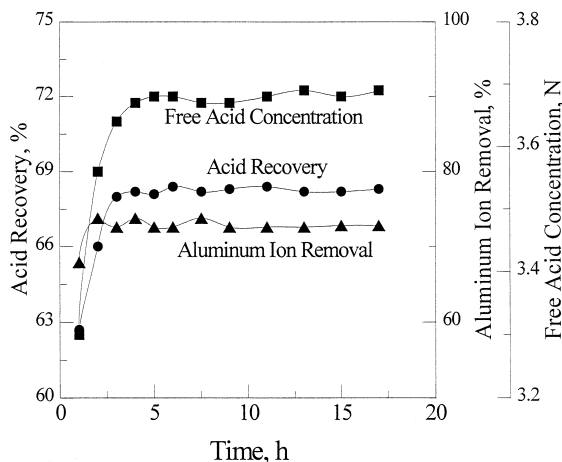


Fig. 2. Dialyzer performance as a function of time with 1.48 l/h m² feed solution flow rate, 1.02 l/h m² deionized water flow rate, 3.82 N initial free acid concentration, 1.0 N initial aluminum ion concentration and 25°C.

depict the same results. Hence, 4 h or slightly longer from the beginning of each test run can be considered as the steady state. The results demonstrated in the following figures represent the steady state data for all test runs.

The inlet flow rates of the feed solution and deionized water were important operating variable of a dialysis process. By maintaining a 1:1 ratio of these two flow rates, the effect of flow rate on the steady state performances of the Asahi dialyzer is demonstrated on Fig. 3. It is noted in this figure that the acid recovery increases slowly with an increase in the flow rate and reaches a maximum at 2.4 l/h m². Beyond that flow rate, there is a rapid decrease in the acid recovery. At or below 2.4 l/h m² flow

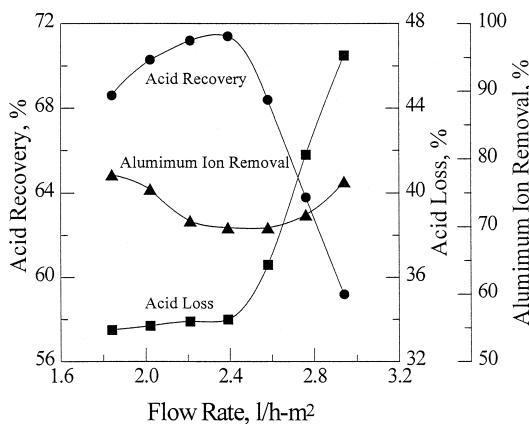


Fig. 3. Effect of flow rate on the dialyzer performance with 4.05 N initial free acid concentration, 1.03 N initial aluminum ion concentration and 25°C.

rate, the acid loss remains relatively flat and beyond that, a rapid increase in the acid loss is observed. It is also seen in this graph that the aluminum ion removal remains at a relatively low level at 2.4 l/h m² feed solution flow rate and a feed solution flow rate below 2.2 l/h m² or above 2.8 l/h m² appears to be more favorable.

At initial 10 g/l aluminum ion concentration and 200 g/l sulfuric acid concentration, the free acid and aluminum ion concentrations in the feed solution were equivalent to 4.05 N and 1.03 N, respectively, and the total acid concentration, as the sum of the two free acid and aluminum ion concentrations, is equal to 5.08 mg/l. The test results reveal that the variations of free acid and aluminum ion concentrations with feed flow rate in either the diffusate or dialyzate is surprisingly small. The average free acid and aluminum ion concentrations in the diffusate are 2.36 ± 0.2 N and 0.25 ± 0.04 N, respectively, while those in the dialyzate are 1.52 ± 0.13 N and 1.05 ± 0.04 N, respectively. Although the free acid concentration in the diffusate is about 44% lower than that required in the production line (4.2 N), the 0.25 N aluminum ion concentration is sufficiently low to warrant the reuse of the diffusate in the production process. In this case, make-up addition of sulfuric acid to elevate the free acid concentration to 4.2 N is necessary. The low free acid and reasonably high aluminum ion concentrations of the dialyzate enables this solution for aluminum ammonium sulfate recovery, as mentioned earlier. Considering the overall performances in terms of the acid recovery, aluminum ion removal and acid loss as well as the free acid and aluminum ion concentrations in the diffusate and dialyzate, it can be concluded that a feed flow rate between 2 and 2.4 l/h min would be deemed as optimum for the present dialyzer module.

In Fig. 3, the ratio of feed solution and deionized water flow rates was deliberately kept at the same, but in practical applications, the two flow rates could be different. In Fig. 4, the deionized water flow rate was kept constant at 2.02 l/h m², but the feed solution flow rate was varied between 1.66 and 2.28 l/h m². The acid recovery in the diffusate decreases slowly as the feed solution flow rate is increased up to 2.02 l/h m² and beyond that, there appears to be a rather rapid decrease of the acid recovery, leading

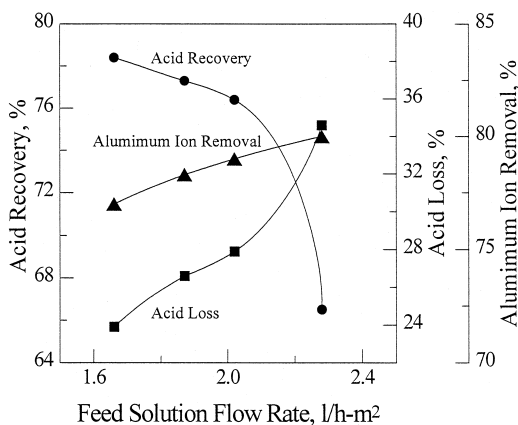


Fig. 4. Effect of feed solution flow rate on the dialyzer performance with 2.02 l/h m² deionized water flow rate, 4.05 N initial free acid concentration, 1.0 N initial aluminum ion concentration and 25°C.

to a correspondingly rapid increase in the acid loss. In contrast, the aluminum ion removal is seen in this figure to have relatively small variation. Hence, for a dialysis operation with variable feed solution flow rate, a better results will be realized by keeping the feed solution flow rate below the deionized water flow rate. Fig. 5 demonstrates the results for the other case with constant feed solution flow rate at 1.49 l/h m^2 and variable deionized water flow rate between 0.9 and 2.76 l/h m^2 . The general trends of Fig. 4 was seen to be preserved for the acid recovery, acid loss and aluminum ion removal curves in Fig. 5. The acid recovery decreases and the acid loss increases slowly in Fig. 5 for deionized water flow rate below 1.47 l/h m^2 . Above that flow rate, the acid recovery decreases sharply. Therefore, for optimum performances, the deionized water flow rate must be kept at or below the constant feed solution flow rate.

A situation that could be also encountered in industrial practice is that the feed solution could get diluted and the sulfuric acid concentration in this solution becomes lower than 200 g/l considered in the above figures. Test runs were performed in the present work by lowering the initial sulfuric acid concentration to below 100 g/l . Fig. 6 shows the acid recovery, acid loss and aluminum ion concentration removal as a function of the feed sulfuric acid concentration. The acid recovery is still kept at an excellent level between 82% for 20 g/l initial sulfuric acid concentration and nearly 90% for 100 g/l . For the same range of initial sulfuric acid concentration, the acid loss varies from 17.5 to 25.1% which is still not excessive. The aluminum ion removal shows a rather small variation between 35.3 and 38.5% . Hence, the diffusion dialysis remains equally effective regardless of the much lower initial sulfuric acid concentration level in the feed solution.

In the above test runs, the inlet temperatures of both the feed solution and the deionized water were maintained at 25°C . It would be of practical interest to ascertain whether the operating temperature will affect the dialysis performances. To do so, the inlet temperatures were controlled to between 10°C and 40°C . Fig. 7 compares the acid recover, acid loss and aluminum ion removal at various inlet temperatures. This figure

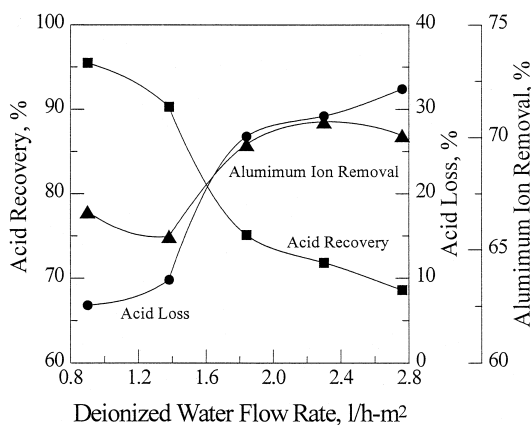


Fig. 5. Effect of deionized water flow rate on the dialyzer performance with 1.49 l/h m^2 feed solution flow rate, 4.05 N initial free acid concentration, 1.0 N initial aluminum ion concentration and 25°C .

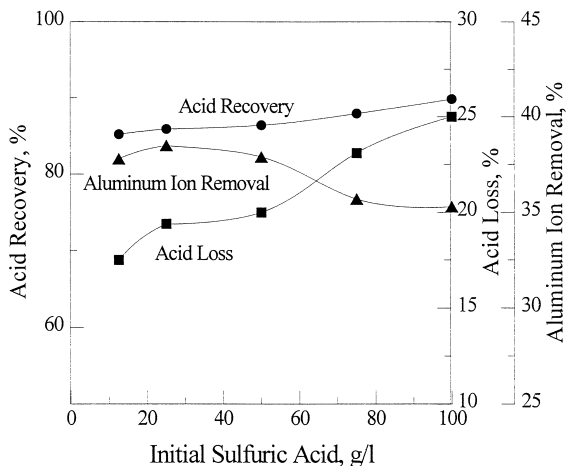


Fig. 6. Effect of initial sulfuric acid concentration in the feed solution on the dialyzer performance with 1.47 l/h m² feed solution flow rate, 3.2 l/h m² deionized water flow rate, 1.0 N initial aluminum ion concentration and 25°C.

reveals that the effect of the inlet temperature is very small with a slightly better acid recovery and aluminum ion removal being realized at a low inlet temperature. According to the manufacturer of the dialysis module, an operating temperature above 40°C is to be avoided because a higher temperature above 40°C would shorten the life of the anionic ion exchange membrane. In industrial practices, the waste acid solution from a production line usually has a temperature much higher than 40°C. Therefore, a cooling system is definitely necessary to lower the feed solution preferably to 25°C or lower in order to maximize the life of the ion exchange membrane.

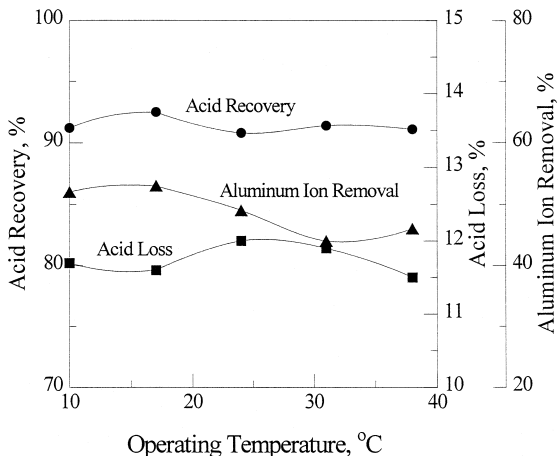


Fig. 7. Effect of operating temperature on the dialyzer performance with 1.5 l/h m² feed solution flow rate, 1.24 l/h m² deionized water flow rate, 5 N initial free acid concentration and 0.97 N initial aluminum ion concentration.

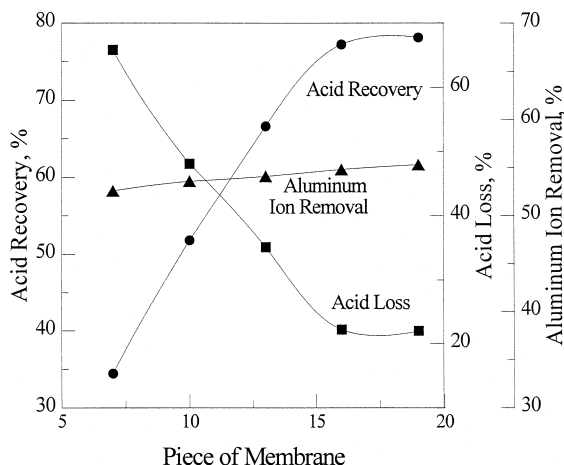


Fig. 8. Effect of the piece of ion exchange membrane on the dialyzer performance with 1.45 l/h m^2 feed solution flow rate, 0.78 l/h m^2 deionized water flow rate, 3.93 N initial free acid concentration and 0.97 N initial aluminum ion concentration.

Another variable worth considering is the piece of anionic ion exchange membranes in the Asahi dialyzer. The original Asahi dialyzer came with 19 pieces of membrane. Because the module could be easily disassembled, the effect of the piece of membrane on the dialysis performance was relatively easily explored by reducing the piece of membrane down to as few as 7 from 19. The results were displayed in Fig. 8 which shows the acid recovery, acid loss and aluminum ion removal as a function of the piece of membrane. It is clear that the effect of the piece of membrane on the acid recovery and acid loss is quite drastic. The acid recovery increases sharply as the piece of membrane is increased from 7 to 17 and the acid loss decreases considerably also in this piece range of membrane. At 17 pieces of anionic ion exchange membrane, both parameters tends to level off. Hence, 17 pieces of anionic ion exchange membrane is considered as the optimum for the Asahi dialysis module. The effect of the piece of membrane on the aluminum ion removal is seen to be relatively small with an average of 54.1% for the piece range between 7 and 19.

3.3. Preliminary economic evaluation of diffusion dialysis process

The test results shown in the previous figures have indicated that the diffusion dialysis is an efficient system for recovering sulfuric acid from the waste aluminum acid solution. However, the economic viability of the sulfuric acid recovery process needs to be assessed. Fig. 9 displays the material balance for a steady state run for a plant processing 1000 tons/month of aluminum product. The material balance was computed based on a typical test results using the Asahi dialyzer. The capital investment cost for the dialyzer handling the waste acid solution was estimated to be US\$1 250 000. Assuming an interest rate of 8% and with a linear 10 y depreciation of the equipment, the annualized capital investment cost amounts to US\$270 000/year. The operating

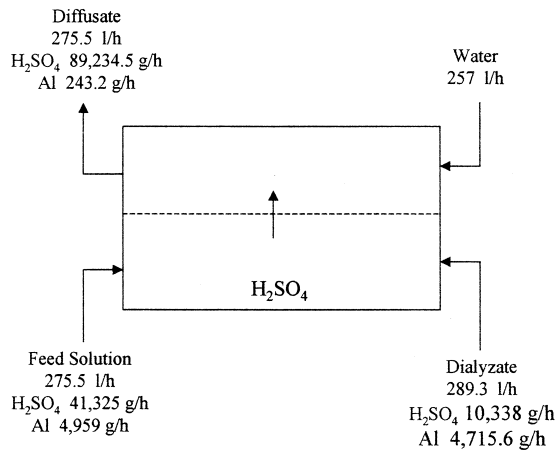


Fig. 9. Material balance for a 1000 tons/month aluminum surface processing plant.

costs of dialysis include the membrane replacement, power, maintenance, manpower costs. The membrane replacement was estimated to be about US\$15 000 and the other cost items was assumed to be 50% of that. Hence, the total operating cost comes to US\$22 500/year. The total system cost is the sum of the two cost items or US\$292 500/year.

The benefits realized in the preset dialysis operation stem primarily from saving of chemicals (H₂SO₄ and NaOH). Based on the material balances shown in Fig. 9, the annual savings in H₂SO₄ and NaOH were calculated to be 223 and 182 tons/year, respectively. Hence the cost savings of these two chemicals were US\$114 000/year and US\$165 600/year, respectively, based on the current sale prices for these chemicals. Finally, the total savings were then the sum of the two saving items or US\$279 600/year. The payback period was found to be slightly less than 1.05 years which is the ratio of the total system costs and total savings. Such a short payback period has demonstrated that the diffusion dialysis system is high attractive economically.

4. Conclusions

Experimental investigations were conducted to examine the system performances of a commercial dialysis module in recovering sulfuric acid from waste acid solution of aluminum surface processing industry. Test runs results have indicated that the dialysis module is very efficient for this purpose. The experimental results reveal the following.

(1) The dialysis module took approximately 4 h from the beginning of a test run to reach a steady state.

(2) For the same flow rate ratio of feed solution and deionized water, an optimum performance of the dialysis module was realized by maintaining both flow rates between 2 and 2.4 l/h m². For the cases with variable feed solution flow rate or deionized water

flow rate, better performances of the dialyzer module were obtained by keeping the variable flow rate below the constant counterpart.

(3) The concentration level of sulfuric acid in the feed solution was observed to have little influence on the dialyzer performances, implying the dialyzer module is equally effective for high and low sulfuric acid concentration in the feed solution.

(4) The operating temperature of feed solution and deionized water between 10°C and 40°C was found to have relatively little effect on the dialyzer performances. Hence, an operating temperature at 25°C or below was recommended in order to maximize the life of the anionic ion exchange membrane in the dialysis module.

(5) Tests of the effect of the piece of anionic ion exchange membrane on the system performances have revealed that 17 pieces of membrane are the optimum. Below this number of membrane piece, there is a sharp decrease in the acid recovery and a sharp increase in the acid loss also. With more 17 pieces of membrane, improvement in the dialyzer performances becomes marginal.

(6) Preliminary economic evaluation of the dialysis system has indicated that a payback of slightly over a year can be realized for the capital investment and operation of the system. Such a short payback period renders the system highly attractive.

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