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Recovery of H_2SO_4 from waste acid solution by a diffusion dialysis method

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Abstract

A diffusion dialysis method using anion exchange membrane was used to recover H_2SO_4 from waste sulfuric acid solution produced at the diamond manufacturing process. Effects of flow rate, operation temperature, and metal ion concentration on the recovery of H_2SO_4 were investigated. The recovery of H_2SO_4 increased with the concentration of H_2SO_4 and operation temperature. It also increased with the flow rate ratio of water/H_2SO_4 solution up to 1, above which no further increase was observed. The flow rate did not affect the rejection of Fe and Ni ions. About 80% of H_2SO_4 could be recovered from waste sulfuric acid which contained 4.5 M free-H_2SO_4 at the flow rate of 0.26×10^{-3} $m^3/h\,m^3$. The concentration of recovered H_2SO_4 was 4.3 M and the total impurity was 2000 ppm. Preliminary economic evaluation has revealed that the dialysis system is highly attractive one that has payback period of only few months.

Keywords: Sulfuric acid recovery; Diffusion dialysis; Waste; Fe; Ni

1. Introduction

Sulfuric acid (H_2SO_4) solution has been widely used in chemical and metal industries for various surface treatments as electrolysis, electroplating, and acid pickling because of its relative inexpensiveness compared with other acids [1,2]. As a result, large amounts of waste sulfuric acid solution have been generated causing environmental problems. The waste sulfuric acid solution contains valuable metals as Fe, Ni, and Co and so on. It is thus required to develop an alternative method to recover sulfuric acid and valuable metals, simultaneously.

The waste sulfuric acid solution can be treated by various methods as cooling, evaporation, distillation, thermal decomposition, solvent extraction and membrane separation [3–6]. Among them, the membrane separation methods have been favored due to its lower energy consumption and the cleaner nature. One of the membrane separation methods is a diffusion dialysis (DD) using membrane. The technology has been commercialized in aluminum anodizing process, pickling of secondary steel products, aluminum foil etching process and etching of stainless steel. In the diffusion dialysis method using membrane, there are many advantages such as low energy consumption, simple plant, continuity operation, stable and easy operation, low installation cost, and low operating cost.

In this study, a diffusion dialysis method using anion exchange membrane was suggested for recovering H_2SO_4 from waste sulfuric acid solution containing metal ions which was generated from diamond manufacturing plants. The effects of H_2SO_4 concentration, flow rate, temperature, and metal ion concentration on the recovery of H_2SO_4 were investigated using a continuous contactor.

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Table 1
Chemical composition of sulfuric acid waste used in the experiment

Element	Composition (ppm)
Fe	52,000
Ni	18,000
Na	611
Zn	66
Ca	55
Mg	105
Co	6
Ti	11
Mn	3
Al	11

Table 2
Properties and specifications of the Asahi Type T-0b Dialyzer

Item	Specifications
Membrane type	Strong basic anion exchange
Total effective area of membrane (m^2)	0.327
Number of membrane sheet	19
Distance between membranes (cm)	0.19
Dimension of membrane sheet	16 cm (W) × 24 cm (L) × 0.16 cm (T)
Dimension of dialyzer stack	20 cm (W) × 30 cm (H) × 13.5 cm (L)

2. Experimental

2.1. Materials

The solutions for diffusion dialysis experiment using anion exchange membrane were sulfuric acid solution prepared with agent grade chemicals, $H_2SO_4 + NiSO_4$ solution, and waste sulfuric acid solution generated from an industry. The free H_2SO_4 concentration in the waste sulfuric acid solution was 4.5 M and the metal ion concentration contained in the solution is listed in Table 1.

2.2. Procedure

Anion exchange membrane (CI type, Selemion DSV from Asahi Glass Co.) was used for diffusion dialysis. The experimental apparatus is described in Fig. 1. The properties and specifications of the Asahi dialyzer are given in Table 2. The recovery of sulfuric acid was determined by measuring the sulfuric acid and metal ion concentrations at a regular interval.

It was reported that it took 2 h to reach the steady state via transient period [10,11]. In our experiment, the specimen was taken after 3 h at which the steady state was obtained. When the operation is stopped, all liquid in the device are removed and filled with deionized water.

The concentration of H_2SO_4 was determined by titration using 0.1 M NaOH solution using phenolphthalein as an indicator. The concentration of the metal ions in the solution was analyzed by Inductively Coupled Plasma Spectrometer (Labtest 3000).

2.3. Performance of diffusion dialysis

In order to find the preferential diffusion for each run, the separation factor should be known. The separation factor (S) with respect to one species over another is given as the ratio of dialysis coefficients (U) of the two species present in the solution and can be calculated by the following formula [7–9]

$$U = \frac{M}{A\,\Delta C_{\mathrm{lm}}} \tag{1}$$

where M is the amount of component transported in moles/h, A the effective area in square meters, and ΔC the average

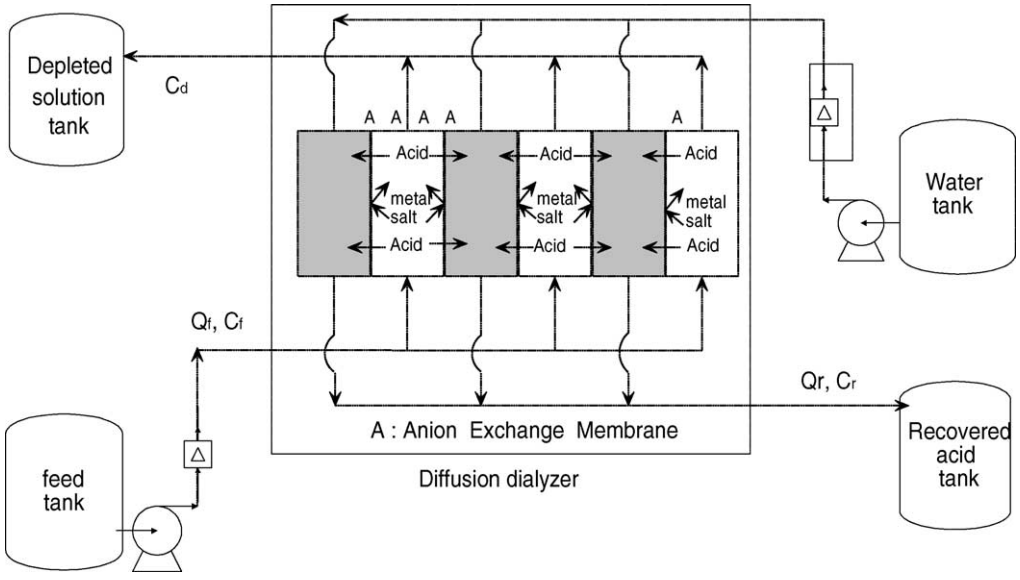

Fig. 1. Diagram of the diffusion dialyzer.

concentration between the two chambers in moles per cubic meters and defined as below [7–10]

$$\Delta C_{\mathrm{lm}} = \frac{C_{\mathrm{f}} - C_{\mathrm{r}} - C_{\mathrm{d}}}{\ln[(C_{\mathrm{f}} - C_{\mathrm{r}})/C_{\mathrm{d}}]} \quad (2)$$

here C is acid concentration.

Subscript f represents feed, r recovered acid and d depleted solution (dialysate).

It should be noted that $(C_{\mathrm{f}} - C_{\mathrm{r}} - C_{\mathrm{d}}) \neq 0$ because of the volume changes that occur in the cell chambers caused by water transport through the membrane during the experiment [7].

$$R\,(\text{recovery}\,\%) = \left(\frac{Q_{\mathrm{r}}C_{\mathrm{r}}}{Q_{\mathrm{f}}C_{\mathrm{f}}}\right) \times 100 \quad (3)$$

where Q is volumetric flow rate.

The separation factor was defined as the ratio of the dialysis coefficient for acid to that for metal salt ($U_{\mathrm{acid}}/U_{\mathrm{salt}}$) in this study.

3. Results and discussion

3.1. Performance of diffusion dialysis

The recovery of H_2SO_4 by diffusion dialysis using anion exchange membrane was conducted using pure H_2SO_4 solution prepared with agent grade chemicals, $H_2SO_4 + NiSO_4$ solution, and waste H_2SO_4 solutions generated from an industry.

Fig. 2 shows the variation of H_2SO_4 recovery with flow rate when the flow rate ratio of pure 3.0 M H_2SO_4 and water was 1. As can be seen in the figure, the recovery shows a sharp decrease with the flow rate. At the flow rate below 0.3×10^{-3} m^3/h m^2, the recovery of H_2SO_4 was over 90%, while at the flow rate of 1.0×10^{-3} m^3/h m^2, that was about

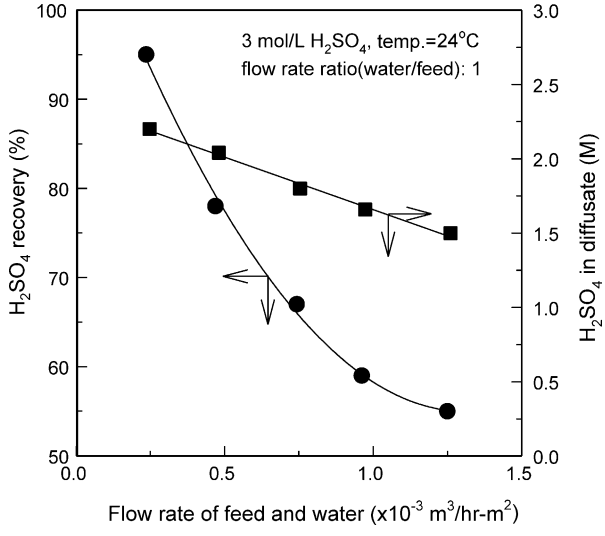

Fig. 2. Effect of flow rate on the recovery of H_2SO_4 from pure 3 M H_2SO_4 solution at 24 °C.

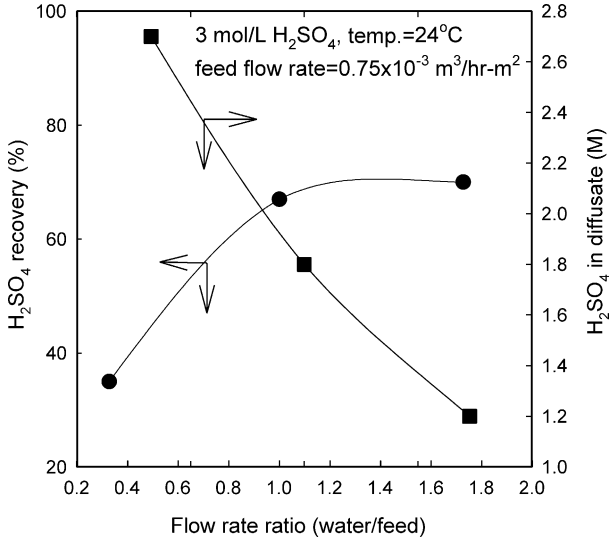

Fig. 3. Effect of flow rate ratio (water/feed) on the recovery of H_2SO_4 from pure 3 M H_2SO_4 solution at 24 °C.

60%. The recovery decreases because the surface area of membrane is constant even though the flow rate is varied.

The effect of water flow rate when the acid (pure 3.0 M H_2SO_4) flow rate was constant is shown in Fig. 3. In all figures, the arrows indicate the corresponding axis. As shown in the figure, the concentration of recovered H_2SO_4 shows a sharp decrease with the water flow rate. The recovery of H_2SO_4 was about 67% at the flow rate of 0.75×10^{-3} m^3/h m^2, above which it was almost constant. Moreover, the concentration of H_2SO_4 recovered becomes low as the flow rate increases. Thus, the optimum flow rate must be determined by considering the H_2SO_4 recovery and the concentration of the recovered H_2SO_4.

The concentration of waste H_2SO_4 solution generated from industries is quite different and the effect of the concentration of H_2SO_4 on the recovery of that was investigated. Fig. 4 shows the variation of H_2SO_4 recovery with the concentration of H_2SO_4 when the flow rate of water and H_2SO_4 solution were constant at 0.75×10^{-3} m^3/h m^2, respectively. As shown in the figure, the recovery of H_2SO_4 decreased with increasing the concentration of H_2SO_4 in the solution. This is because the contact area between the membrane and H_2SO_4 solution is finite, and the diffusion coefficient decreases as the solution viscosity increases with H_2SO_4 concentration. In other experiments to recover each acid from HCl, HNO_3, and H_2SO_4 by a diffusion dialysis method, it was reported that the recovery of H_2SO_4 was the lowest among the acids because of the highest viscosity of H_2SO_4 solution. At the concentration of 3.0 M H_2SO_4, the recovery was 65%, which agrees with the results by Oh et al. [10]

The recovery of H_2SO_4 increases with operation temperature. Fig. 5 shows the effect of operation temperature on the recovery of H_2SO_4. This can be explained by the fact that diffusion coefficient increases with operation temperature.

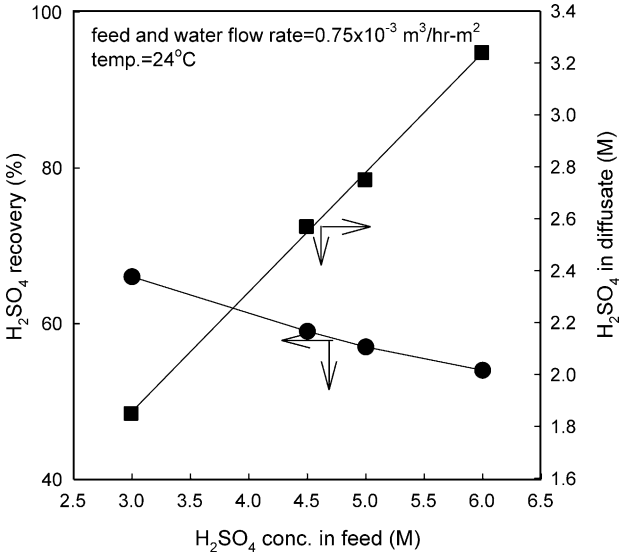

Fig. 4. Effect of H_2SO_4 concentration on the recovery of H_2SO_4 at 24 °C.

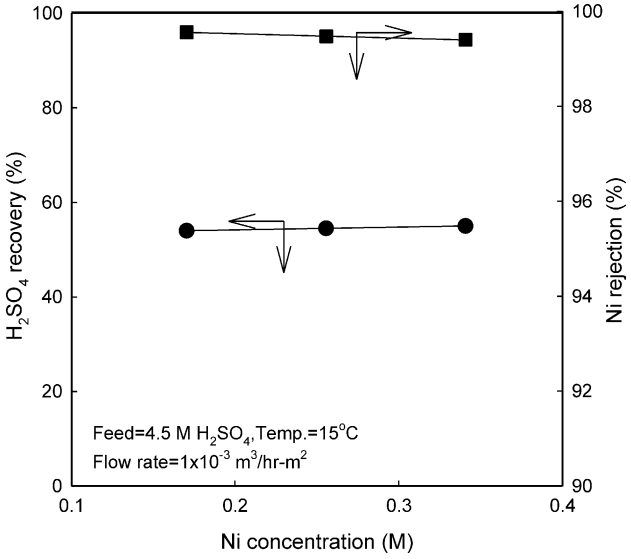

Fig. 6. Effect of Ni concentration on the recovery of H_2SO_4 from pure 4.5 M H_2SO_4 solution containing Ni at 15 °C.

Fig. 6 shows the effect of Ni^{2+} on the recovery of H_2SO_4 from 4.5 M H_2SO_4 solution containing 0.15–0.35 M Ni^{2+}. The flow rate and temperature of the solution were 1.0×10^{-3} m^3/h m^2 and 15 °C, respectively. The recovery of H_2SO_4 was almost constant regardless of Ni^{2+} concentration in the solution. The diffusion dialysis of Ni^2 decreased slightly with concentration, and the rejection ratio of Ni^{2+} is 99.3% at 0.35 M Ni^{2+}.

The recovery decreased sharply with the flow rate. Fig. 7 shows the effect of flow rate on the recovery of H_2SO_4 from H_2SO_4 solution containing 0.34 M Ni^{2+}. It can be seen that the rejection ratio of Ni^{2+} increases slightly with increasing flow rate. As the flow rate increased from 0.26×10^{-3} to 1.00×10^{-3} m^3/h m^2, the recovery of H_2SO_4 decreased from 78% to 55%, while the rejection of Ni^{2+} increased about 1%.

Figs. 8 and 9 show the recovery of H_2SO_4 from waste sulfuric acid. The concentration of the waste sulfuric acid was about 6 M H_2SO_4 involving 4.5 M free H_2SO_4, which contained 5.2% Fe and 1.8% Ni. As can be seen in the figures, the recovery decreased sharply with the flow rate. This agrees with the results shown in Fig. 7. As the flow rate increased from 0.26×10^{-3} to 1.00×10^{-3} m^3/h m^2, the recovery of H_2SO_4 decreased from 80% to 57%. While the rejection of Ni and Fe was independent of the flow rate. The rejection of Ni and Fe was 96% and 99%, respectively. Because the amount of Fe was higher than that of Ni in used H_2SO_4 solution,

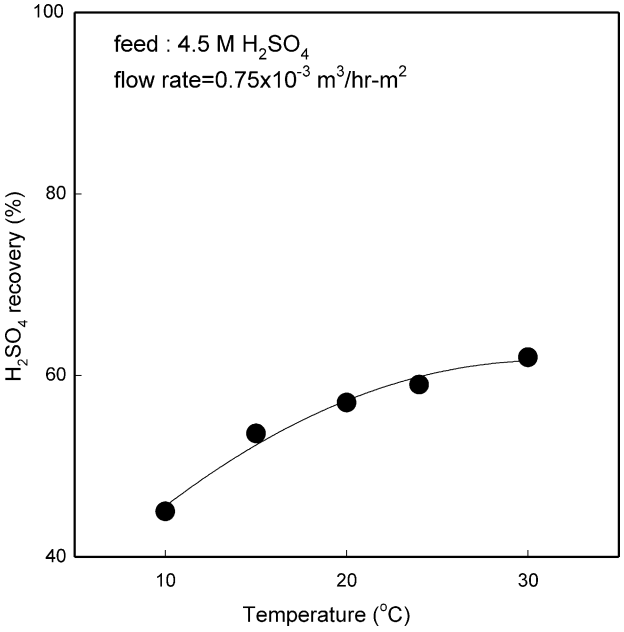

Fig. 5. Effect of the operating temperature on the recovery of H_2SO_4 from pure 4.5 M H_2SO_4 solution.

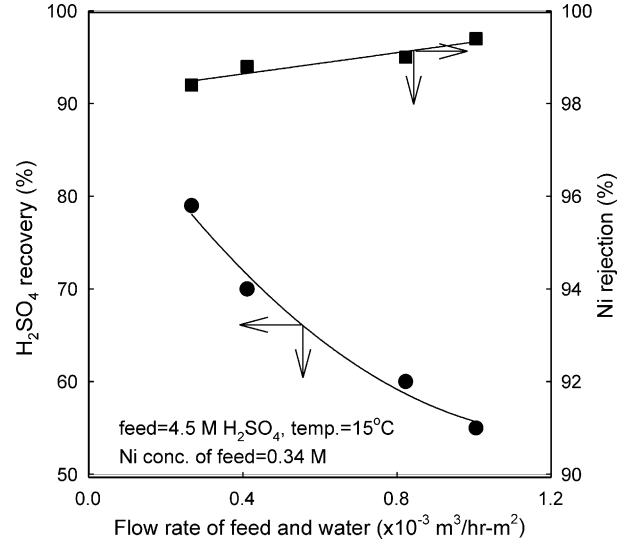

Fig. 7. Effect of flow rate on the recovery of H_2SO_4 from pure 4.5 M H_2SO_4 solution containing Ni at 15 °C.

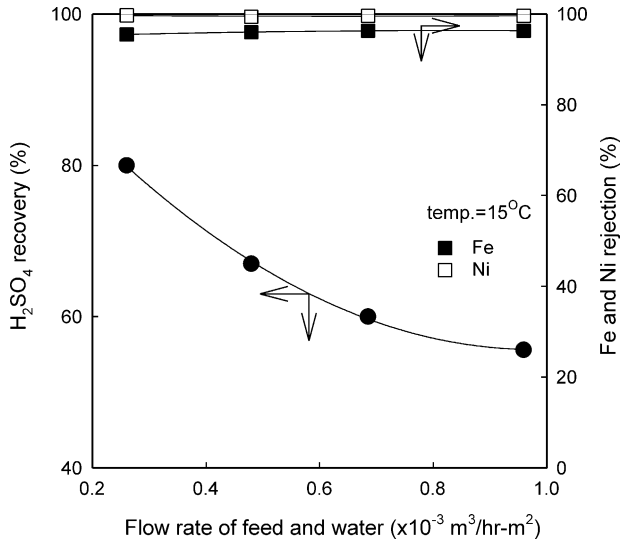

Fig. 8. Effect of flow rate on the recovery of H_2SO_4 from H_2SO_4 waste at 15 °C.

more Fe was diffused towards recovered acid. The recovered H_2SO_4 by diffusion dialysis increased with flow rate. Also, the purity of H_2SO_4 was independent of the flow rate and was 99.8% constantly.

The effect of flow rate on separation factor is shown in Fig. 10. The separation factor of Fe by H_2SO_4 was 15–18 and that of Ni was 140–270. This suggests the excellent separation of Ni along with moderate separation of Fe. It was confirmed that the recovery process using H_2SO_4 acid from diamond manufacturing plants does not affected by the presence of other metal ions. It was also confirmed that the recovered acid could be reused by adjusting its concentration to initial value.

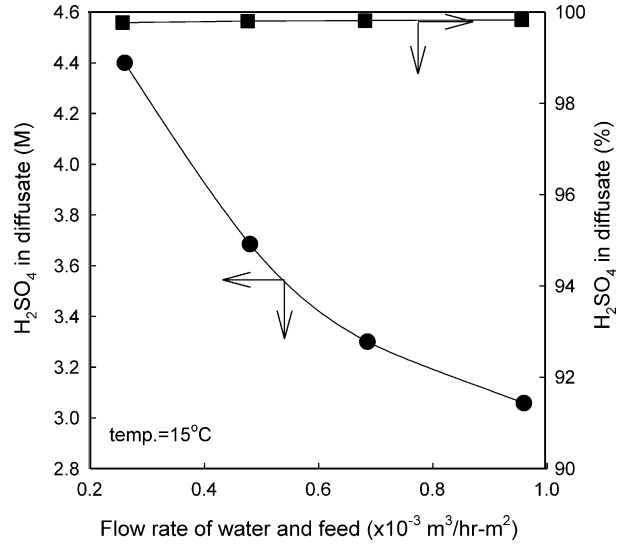

Fig. 9. Effect of flow rate on the concentration and purity of H_2SO_4 recovered from H_2SO_4 waste at 15 °C.

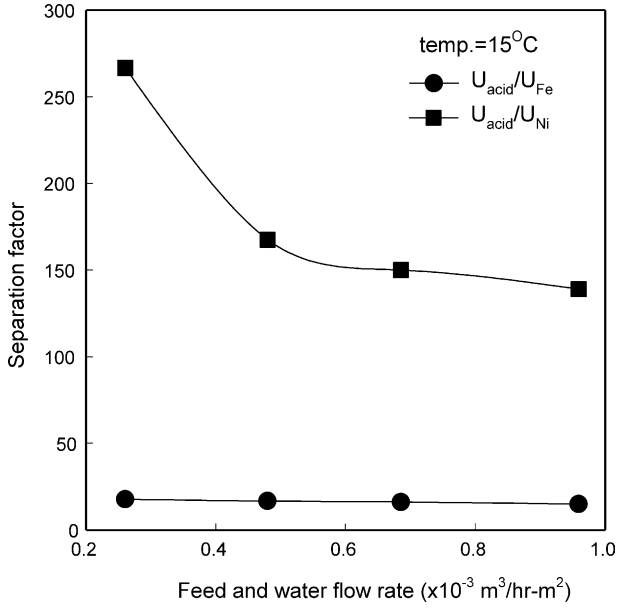

Fig. 10. Effect of flow rate on the separation factor at 15 °C.

3.2. Economic evaluation

The experimental results in previous figures have demonstrated that the diffusion dialysis is an efficient system for recovering sulfuric acid from the waste solution. Nevertheless, the economic viability of the process should be assessed for practical applications. This evaluation is being used in a diamond manufacturing plant in Korea.

Fig. 11 summarizes the material balance for a steady state run of a plant processing 10 tonnes/day of waste solution. The capital investment cost for the dialyzer was estimated to be US$ 500,000. Based on the material balances shown in Fig. 11, the annual savings in (H_2SO_4 and NaOH) were calculated to be 1323 and 1079 tonnes/year, respectively. The cost savings of these two chemicals were US$ 105,840/year and US$ 269,750/year, respectively, based on the current sale prices for these chemicals. This indicates

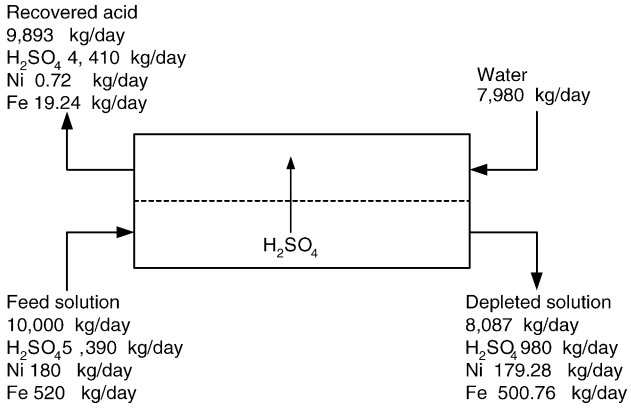

Fig. 11. Material balance for a 10 tonnes/day waste processing plant.

Table 3
The economic analysis for the industrial diffusion dialysis runs in a diamond manufacturing plant (10 tonnes waste acid/day) (unit: kg/day, US$)

	Water input	Feed	Depleted solution	Recovered acid
H_2SO_4	–	5390	980	4410
H_2O	7980	4610	7107	5430

The reduced NaOH for neutralization

$$H_2SO_4 + 2NaOH = Na_2SO_4H + 2H_2O$$

$$\frac{4410}{98.08} \times 2 \times 40 = 3597$$

The annual save amount of acid (annual operation day = 300)

H_2SO_4: $4410 \times 300 = 1{,}323{,}000$

NaOH: $3597 \times 300 = 1{,}079{,}100$

Saving acid values on recovery operation

H_2SO_4: $1{,}323{,}000 \times 0.08\$/kg = 105{,}840\$$

Less value of NaOH

$1{,}079{,}100 \times 0.25\$/kg = 269775\$$

Total receiving benefits

$105{,}840 + 269{,}775 = 375{,}615$

Investment

Diffusion dialysis unit (150 effective area in m^2): 300,000

Auxiliary (pump, circuit, valve and tank): 150,000

Power, labor and others: 50,000

Total: 500,000$

Write-off (investment-recovered) period

$$\frac{500,000}{375,615} \times 12 = 15.97 \text{ months}$$

that the major economic benefits stem primarily from saving of chemicals (H_2SO_4 and NaOH). Eventually, the total savings which are the sum of the two savings items are calculated to be US$ 375,590/year. The results were also listed in Table 3.

After introducing a diffusion dialyzer, the net benefit due to the saving of chemicals can attain as high as 0.37 million dollars per year. The investment can be recovered within 16 months. As we known, diffusion dialysis is very simple in operation and energy saving and can run automatically without any maintenance. The plant run shows the membrane's life can exceed 5 years, so one such dialyzer can bring about 1.35 million dollars profits besides the significant environmental benefits.

4. Conclusions

In this study, a diffusion dialysis was carried out in a continuous reactor to recover H_2SO_4 from waste sulfuric acid solution using anion exchange membrane. The results are summarized as follows.

(1) The recovery of H_2SO_4 was enhanced with the flow rate ratio of water/H_2SO_4 solution up to 1, above which no further increase was observed.
(2) The flow rate and Ni concentration affected neither the diffusion dialysis of Ni nor the recovery of H_2SO_4. The rejection of Fe was smaller than that of Ni in diffusion dialysis of H_2SO_4 from used H_2SO_4 solution.
(3) About 80% of H_2SO_4 was recovered from used H_2SO_4 solution at the flow rate of $0.26 \times 10^{-3}\,m^3/h\,m^2$. The concentration of recovered H_2SO_4 was 4.3 M and the total impurity was 2000 ppm.
(4) Preliminary economic evaluation of the dialysis system revealed the investment-recovered period is about 16 months.

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