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Recovery of H_2SO_4 from an acid leach solution by diffusion dialysis

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ABSTRACT

Diffusion dialysis with a series of anion exchange membranes was used to recover H_2SO_4 from an acid leach solution produced during the vanadium manufacturing process. The effects of sulfuric acid, $FeSO_4$ and $VOSO_4$ concentration, flow rate and flow rate ratio on the recovery of H_2SO_4 were investigated. The results showed that sulfuric acid permeated well through the membranes used, while metal ions were efficiently rejected. The recovery of H_2SO_4 increased as the sulfate concentration of the feed increased and the flow rate ratio of water to feed increased. More than 80% of the H_2SO_4 could be recovered from the leach solution which contained 61.7 g/L free H_2SO_4, 11.2 g/L Fe and 4.60 g/L V at a flow rate of $0.19 \times 10^{-3}\ m^3/h\ m^2$. V and Fe ion rejection were within 93–95 and 92–94%, respectively. A preliminary economic evaluation revealed that an investment in this process could be recovered within 27 months.

1. Introduction

Pressure acid leaching is an effective technique for extracting vanadium from black shale because it results in a high amount of metal recovery without emitting harmful gasses [1]. However, the leaching process is usually accomplished by large quantities of acid solution containing 60–90 g/L H_2SO_4, 4–6 g/L V and other metal ions such as Fe, Mg, etc. Generally, about 120 m^3 of acid solution will be produced for every ton of vanadium that is processed. A conventional and popular method to treat the acid solution is neutralization by ammonia water ($NH_3 \cdot H_2O$) [2,3]. The pH is adjusted to about 2.5 and vanadium is then recovered by solvent extraction. This neutralization process, however, generates highly concentrated ammonia-nitrogen wastewater and results in a serious disposal problem. Additionally, valuable sulfuric acid is lost during the neutralization process which could otherwise be recovered for future reuse. Industry is now giving serious consideration to the recovery of acid from leach solutions as it makes economic and environmental sense.

Several methods other than direct neutralization have been developed for the recovery of sulfuric acid and other acids from industrial wastes and these include distillation [4,5], solvent extraction [6,7], ion exchange techniques [8], electrohydrolysis [9,10] and diffusion dialysis [11,12]. The diffusion dialysis is an attractive acid recovery method because it is characterized by high proton permeability and strong salts rejection [13–15]. Another advantage of diffusion dialysis is its low energy consumption and easy operation during processing [11,16]. These properties promote the use of diffusion dialysis for the recovery of various acids. Jeong et al. [17] investigated the recovery of H_2SO_4 by diffusion dialysis from waste sulfuric acid that was generated at diamond manufacturing plants. Lin and Lo [18] conducted an extensive study on the recovery of H_2SO_4 from simulated acid solution by diffusion dialysis and Palatý and Žáková [16,19,20] have done a great deal of work on the separation of sulfuric acid from a sulfate acid system by diffusion dialysis. However, different waste acid systems will have different diffusion performance. The aim of this paper is to determine the optimum operating conditions for the recovery of sulfuric acid from an actual acid leaching solution that was generated from a vanadium hydrometallurgical plant. We investigated the effect of various operating variables on the diffusion performance using a continuous contactor. The recovered acid is therefore expected to be reused in the leaching process.

2. Experimental

2.1. Materials

The solution used for the diffusion dialysis experiment was a sulfuric acid solution prepared with analytically pure chemicals, a $H_2SO_4 + FeSO_4$ solution, a $H_2SO_4 + VOSO_4$ solution and actual acid solution that was generated from a black shale pressure acid leaching process. The free sulfuric acid in a typical acid leaching solution was 61.7 g/L and the concentrations of various metal ions in the solution are listed in Table 1.

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Table 1
Chemical composition of the acid leach solution used in the experiment.

Element	Concentration ($g L^{-1}$)
V	4.60
Fe	11.20
Mg	2.84
K	0.43
Na	0.083
As	0.09
Ca	0.116
P	2.03
Si	1.42

2.2. Apparatus

The anion exchange membranes used were DF120-I and DF120-III (Shandong Tianwei Membrane Technology Co., Ltd., China.) and a HKY-001 diffusion dialyzer was used for diffusion dialysis. We used 40 sheets of the anion exchange membrane. The total membrane area was 3.2 m^2. The peristaltic pump used to control the deionized water and the feed solution flow rate was supplied by Changzhou Co., Ltd., Zhejiang. The experimental apparatus and the principles of diffusion dialysis are shown in Fig. 1.

A previous report indicated that 2 h is required to reach equilibrium after initially filling the apparatus with feed solution and deionized water [21]. In our experiment, the test began after 2 h at which time a dynamic equilibrium state was obtained.

The concentration of free sulfuric acid was determined by titration using 0.1 M NaOH with phenolphthalein as an indicator. The Fe concentration was determined by potassium dichromate titration using sodium diphenylamine sulfonate as an indicator and the V concentration was determined by ferrous ammonium sulfate titration using 2-(phenylamino)-benzoic acid as an indicator. Other elemental analyses were carried out at the analysis test center of the Panzhihua iron and steel research institute, Sichuan, China.

The total acid recovery ratio E was calculated using the following equation:

$$E = \frac{Q_r C_r^H}{Q_f C_f^H}$$

where Q_r is the flow rate of the recovered acid, Q_f is the flow rate of the feed. C_r^H is the H_2SO_4 concentration in the recovery solution and C_f^H is the H_2SO_4 concentration in the feed.

The metal ions rejection ratio R was calculated as follows:

$$R = \frac{Q_r C_r^M}{Q_f Q_f^M}$$

where C_r^M and C_f^M are the metal ions concentrations in the recovered solution and feed, respectively.

3. Results and discussion

3.1. Choosing the type of anion exchange membrane

We used two anion exchange membranes, DF120-I and DF120-III, as supplied by the manufacturer. To determine which one is more efficient, we carried out a dialysis test using a synthetic acid solution under predetermined operational conditions. The feed was prepared using $FeSO_4$, $VOSO_4$ and sulfuric acid which were based on the actual leaching solution. Results of the H_2SO_4 recovery and metal ions rejection at different times are shown in Table 2.

The acid recovery ratio for the DF120-I membrane was slightly higher than that for the DF120-III membrane. It was also shown that after 2 h of running the test a steady state for acid recovery was reached. However, metal ions rejection for the DF120-III membrane was found to be higher than for the DF120-I membrane under the same operating conditions. This results from the different flux of the two membranes. For our test, the low rejection indicates that more metal ions accumulated during the leaching process and, therefore, the recovery of vanadium will be reduced over the whole flow sheet. From these results it is clear that the DF120-III membrane should, therefore, be favored for industrial applications.

3.2. Effect of H_2SO_4 concentration on diffusion performance

Concentrated H_2SO_4 is often used in hydrometallurgy processes to extract valuable metals from various ores. Leaching solutions usually contain various concentrations of free sulfuric acid dependent on different operating conditions. Experiments were carried out to investigate the performance of diffusion dialysis for H_2SO_4 recovery using various acid concentrations. Fig. 2 shows the acid recovery of H_2SO_4 at a fixed flow rate. The recovery ratio decreases as the concentration of sulfuric acid increases in the feed. The recovery was more than 90% at a H_2SO_4 concentration in the feed of lower than 100 g/L and it was 86% when the H_2SO_4 in the feed reached 150 g/L. This decrease in the acid recovery at higher concentrations may be caused by dehydration of the membrane as

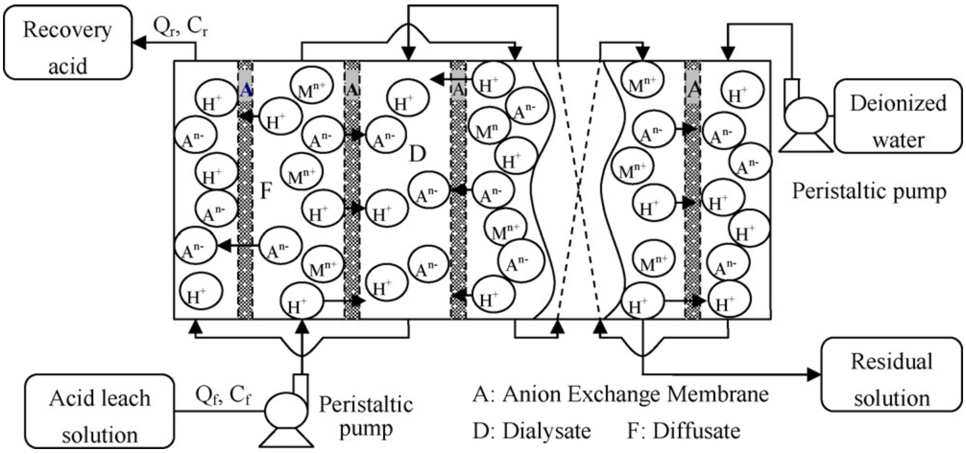

Fig. 1. Diagram of the diffusion dialyzer.

Table 2
The diffusion performance of the DF120-I and DF120-III membranes.

Membrane type	Time of samples obtained	Acid recovery ratio (%)	V rejection ratio (%)	Fe rejection ratio (%)
DF120-I	2 h	86.4	83.5	82.7
	4 h	87.1	84.8	83.1
	6 h	87.3	84.2	82.8
DF120-III	2 h	82.3	94.6	94.3
	4 h	83.2	95.1	94.5
	6 h	83.1	95.4	94.8

Operational conditions: feed flow rate of 0.19×10^{-3} m^3/h m^2; flow ratio of water to feed of 1.05; free H_2SO_4, V and Fe concentrations in the feed were 62.1, 5.0 and 12.2 g/L, respectively.

well as osmotic water transport. The increased acid concentration leads to a decrease in membrane swelling followed by membrane dehydration thus resulting in increased friction resistance to ion transport [22]. In addition, the transport characteristics of H_2SO_4 may be governed by diprotic acid ionization. From the ionization constants of H_2SO_4, the dominant species is the monovalent HSO_4^-. The negative charge of HSO_4^- is less than that of the SO_4^{2-} ion and this leads to higher friction resistance than for SO_4^{2-} under the same operating conditions. Therefore, H_2SO_4 recoveries decrease with an increase in the acid concentration of the feed.

3.3. *Effect of metal ions on diffusion performance*

During the acid pressure leaching process, many metal oxides (such as vanadium oxides and iron oxides) are dissolved in the leach solution. To recover purified acid in the diffusion dialysis process, the metal ions must be rejected by the ion exchange membranes. The effect of $FeSO_4$ and $VOSO_4$ concentrations on sulfuric acid recovery and metal ions rejection are shown in Figs. 3 and 4.

The results in Fig. 3 show that the rejection increases as the $FeSO_4$ concentration increases. The permeability of Fe ion was influenced by the ionic strength and the concentration gradient. Increasing the concentration of metal ions caused a decrease in mobility in the membrane because of the rejection of co-ions. In contrast, an increase in the concentration gradient enhances the membrane's permeability. Therefore, the net increase in Fe ion permeability is as a result of the interaction of the two above-mentioned factors [23].

The behavior of vanadium ions during diffusion was similar to that of $FeSO_4$ as shown in Fig. 4. Nevertheless, vanadium has less of an effect on the ionic strength than ferrous ion does because of its low concentration in the leach solution resulting in a small increase in H_2SO_4 recovery. It is interesting that the recovery of H_2SO_4 increases slightly after the addition of $FeSO_4$ and $VOSO_4$ within the salt concentrations investigated. The reason is that the addition of salt ions containing the same anion as that of the acid promotes the diffusion of protons.

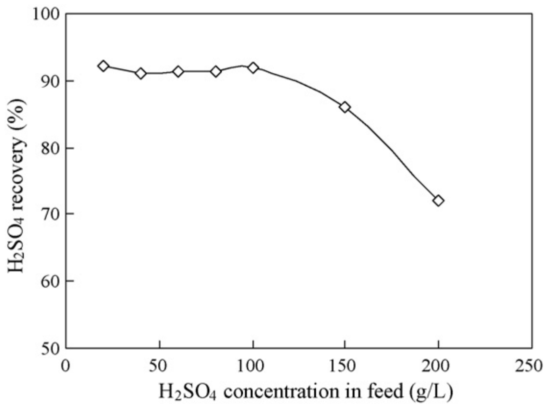

Fig. 2. Effect of the sulfuric acid concentration on the recovery of H_2SO_4.

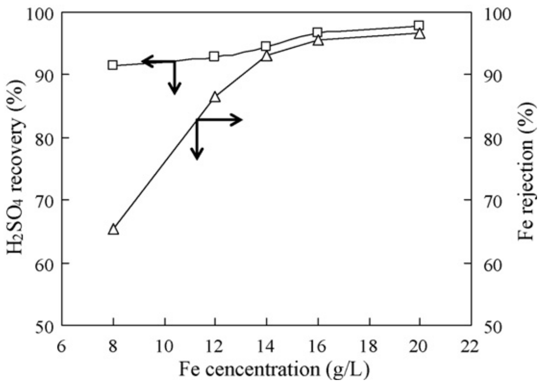

Fig. 3. Effect of the Fe concentration on the recovery of H_2SO_4 from a pure 65 g/L H_2SO_4 solution containing Fe at 20 °C.

3.4. *Effect of flow rate on the diffusion dialysis performance of the leach solution*

To optimize the operating conditions, several tests were conducted with an actual acid solution at ambient temperature (20 °C). Fig. 5 shows how H_2SO_4 recovery varied and the metal ions rejection with flow rate when the flow rate ratio of water to feed was 1.0. From this figure, we observe that the Fe^{2+} and VO^{2+} cations rejection increased while the recovery of H_2SO_4 decreased as the flow rate increased. At a flow rate of less than 0.16×10^{-3} m^3/h m^2, the recovery of H_2SO_4 was over 88% while at a flow rate of 0.3×10^{-3} m^3/h m^2 it was about 72%. The Fe and V ions rejection increased from 91.5 to 95% and 94 to 97.5%, respectively. During diffusion dialysis, the surface area of the membrane is constant and as the flow rate is

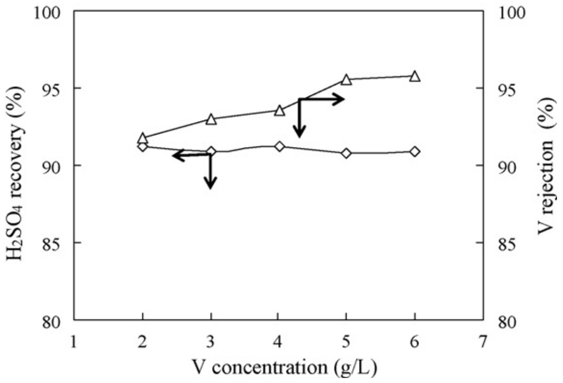

Fig. 4. Effect of the V concentration on the recovery of H_2SO_4 from a pure 65 g/L H_2SO_4 solution containing V at 20 °C.

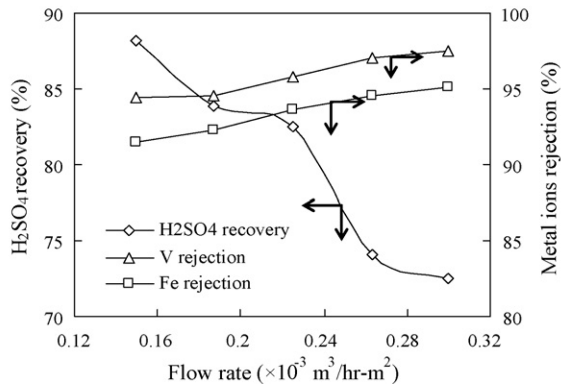

Fig. 5. Effect of the flow rate on the recovery of H_2SO_4 from the leach solution at 20 °C.

increased, the retention time becomes shorter for the feed passing through the dialysis unit. Protons do not have sufficient time to permeate through the anion exchange membrane and this result in a decrease in permeability of both sulfuric acid and metal ions. Because the membrane's aperture size is constant, the smaller ions can permeate through the anion exchange membrane more easily at the same effective nuclear charge number. Therefore, VO^{2+} cation rejection is slightly higher than Fe ion rejection under the same conditions.

3.5. *Effect of the flow rate ratio (water/feed) on the diffusion dialysis of the leach solution*

The effect of the flow rate ratio (water/feed) on H_2SO_4 recovery and metal ions rejection at a constant feed solution flow rate of 0.19×10^{-3} m^3/h m^2 is shown in Figs. 6 and 7. From these figures, the recovery of H_2SO_4 shows a sharp increase as the water flow rate increases. As the flow rate ratio was increased from 0.8 to 1.6, the recovery increased from 66.8% to about 87%. The concentration of the H_2SO_4 in the recovered solution decreased from 49 to 36 g/L and the V and Fe ions rejection decreased from 97 to 90% and 96 to 89%, respectively. As the water flow rate was increased, the concentration of H_2SO_4 in the diffusate decreased. Therefore, an increasing concentration difference between the dialysate and the diffusate resulted in an increase in the driving force for the diffusion of protons. Therefore, more protons penetrated the anion exchange membrane to end up in the diffusate. When the flow rate ratio exceeded 1.0, the recovery increased slowly. However, the concentration of H_2SO_4 showed an obvious decrease. Thus, the optimum flow rate should be determined by considering both the H_2SO_4 recovery and the concentration of H_2SO_4 in the recovered acid.

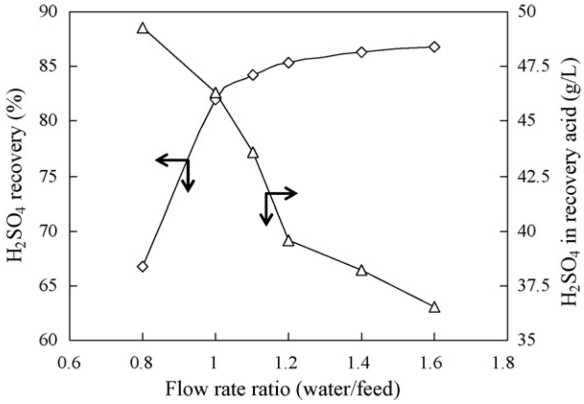

Fig. 6. Effect of the flow rate ratio on the recovery of H_2SO_4 from the leach solution at 20 °C.

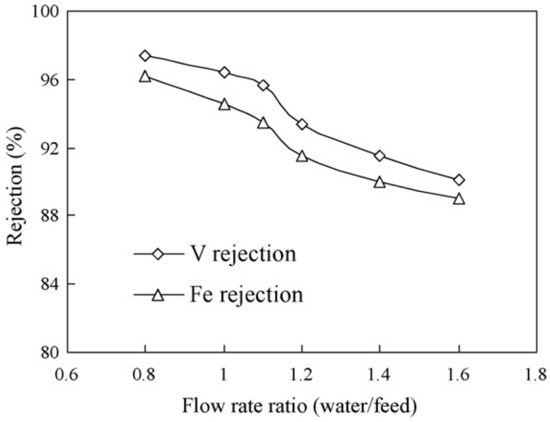

Fig. 7. Effect of the flow rate ratio on metal ions rejection from the leach solution at 20 °C.

3.6. *Preliminary economic evaluation*

The preliminary test results shown in the previously mentioned figures demonstrate that diffusion dialysis is an efficient system for the recovery of H_2SO_4 from an acid leach solution. The process economics evaluation is based on the H_2SO_4 recovery flow sheet from vanadium material processing using pressure acid leaching (Fig. 8). Currently, free H_2SO_4 in the leach solution is neutralized by $NH_3{\cdot}H_2O$ to adjust the pH to about 2.5 and this is followed by the solvent extraction of vanadium. Conventional neutralization treatments consume a large amount of ammonia water and also waste plenty of recyclable resources. Furthermore, the highly

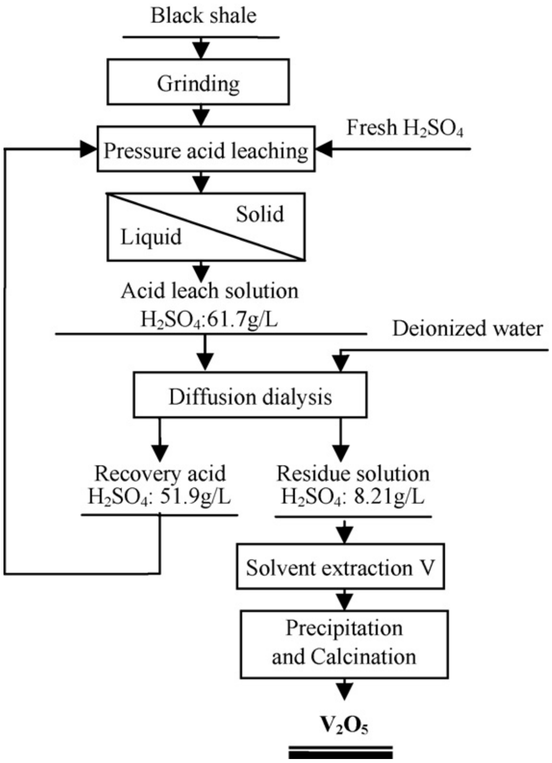

Fig. 8. H_2SO_4 recovery flow sheet for vanadium material processing using diffusion dialysis.

Table 3
Chemical composition of the recovered acid and the residual solution in the experiment.

Compositions	Recovered acid ($g L^{-1}$)	Residual solution ($g L^{-1}$)
H_2SO_4	51.90	8.21
V	0.27	4.31
Fe	0.65	10.40
Mg	0.052	2.56
K	0.060	0.365
Na	0.014	0.058
As	0.02	0.07
Ca	0.002	0.111
P	0.10	1.55
Si	0.056	1.19

Table 4
An economic analysis of the industrial dialysis runs in a vanadium hydrometallurgical plant.

Saving	Investment
Saving acid on recovery operation: 4680 t × 60$/t = 280,800$	Diffusion dialysis unit: 1,354,319$ Membranes replacement: 300,000$
Less value of ammonia water: 8118 × 65$/t = 527,670$	Other cost items (pump, power, labor, etc.): 150,000$
The total saving: 808,470$/year	The total investment: 1,804,319$
Write-off (investment-recovery period): 1,804,319/808,470 = 2.2 years	

concentrated ammonia-nitrogen wastewater will result in serious environmental pollution.

By incorporating diffusion dialysis, the free sulfuric acid contained in the acid solution can be recovered and recycled in the flow scheme after the addition of fresh acid. The chemicals found in the recovered acid and in the residual solution are listed in Table 3.

For the steady state run of a vanadium plant that processes 300 m^3/d of acid leach solution, the annual recovery of H_2SO_4 is estimated to be 4680 t/year (annual operation day: 300), based on the chemical compositions listed in Table 3. In addition, the annual savings in ammonia (20 wt.%) is 8118 t/year. The saving on acid is 4680 t × 60$/t = 280,800$. The less value of the ammonia water used is 8118 × 65$/t = 527,670$. The cost savings for these two chemicals is based on their current price. The total savings are 808,470$/year. These results are listed in Table 4.

As shown in Table 4, the net benefit because of these savings can reach 0.81 million dollars per year. The investment can, therefore, be recovered in 2.2 years. The membrane's lifetime is up to 5 years so the incorporation of dialyzers in hydrometallurgical processes can increase profits by up to 2.24 million dollars. More important, benefits will arise from the reduced environmental pollution caused by ammonia.

4. Conclusion

In this study, diffusion dialysis was carried out to recover sulfuric acid from an acid leach solution. The experimental results show that the DF120-III anion exchange membrane should be favored for industrial process purposes because it leads to a high amount of acid recovery and high metal ions rejection. The optimum operating conditions for this process are: a feed flow rate of 0.19×10^{-3} $m^3/h\,m^2$ and a flow rate ratio of water to feed of 1.0–1.1. Under these optimum conditions, 84% of the free H_2SO_4 can be recovered. There is only about 8 g/L H_2SO_4 left in the residual solution and 52 g/L H_2SO_4 in the recovered acid solution. In addition, H_2SO_4 recovery was found to decrease with an increase in sulfuric acid concentration in the feed and an increase in the flow rate. Fe^{2+} and VO^{2+} cations rejection increased as the sulfates concentration increased in the feed.

An economic evaluation of the dialysis system was based on an industrial diffusion dialyzer supplied by Shandong Tianwei Membrane Technology Co., Ltd. This evaluation indicated that a payback time of 27 months can be realized for the capital investment. If the diffusion system is operated for 5 years, an increased profit of 2.24 million dollars can be realized.

Acknowledgments

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