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Separation and recovery of sulfuric acid from acidic vanadium leaching solution by diffusion dialysis

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ABSTRACT

Diffusion dialysis with anion exchange membranes was employed to recover sulfuric acid from acid leaching solution generated in vanadium producing process. The effects of flow rate, flow rate ratio, V, Al and Fe ions concentration on the recovery of H_2SO_4 and metal ions rejection were investigated. The results have proved that sulfuric acid permeates well through the membrane used, while the vanadium ions are efficiently rejected. Over 84% H_2SO_4 recovery efficiency could be achieved by controlling the flow rate of 0.21×10^{-3} $m^3/h\ m^2$, flow rate ratio of 1.1–1.3 at 25 °C. V, Al and Fe ions rejection could reach to 93%, 92% and 85%, respectively.

1. Introduction

Vanadium is an important rare metal which has been widely used in ferrous and non-ferrous alloys to improve its hardness, tensile strength, and fatigue resistance. In China, there are two important vanadium resources, one is the vanadium titano-magnetite, and the other is carbonaceous shale, also called stone coal. The vast amount of stone coal deposits has made this black shale an important vanadium resource [1]. Currently, the acid leaching for vanadium extraction from stone coal has received considerable attention because it can achieve the high vanadium recovery [2]. However, the large quantity of residual free sulfuric acid after the leaching process need to be treated to fit the pH value in the range of 1.5–2.5 for the following solvent extraction of vanadium [3]. A conventional and popular method for disposal of this acid leaching solution is neutralization by NaOH or CaO. However, a large amount of sludge generated during the neutralization process would result in serious losses of valuable vanadium due to adsorption. Moreover, the residual free sulfuric acid that can be reused in acid leaching process is also lost, which causes the waste of the acid [4–6].

At present, some methods except for the neutralization by alkali have been developed for the recovery of inorganic acids including sulfuric acid from other processing waste water such as cooling, distillation, evaporation, ion exchange, solvent extraction, electrohydrolysis and diffusion dialysis [7–11]. Among them, the diffusion dialysis with anion exchange membrane is an attractive acid recovery method due to its low operating cost, high effectiveness in purifying the wastewater, low installation and operating cost and environmentally friendly nature [12–14]. But more importantly, the diffusion dialysis method can be used in the separation of sulfuric acid and the salts from their mixtures with high proton permeability and metal rejection [15–19].

In this study, a diffusion dialysis method with anion exchange membrane was used for sulfuric acid recovery from acid leaching solution generated from vanadium extraction plant. The optimum operating conditions were investigated.

1.1. Principle of diffusion dialysis

Diffusion dialysis is a membrane separation process in which the transport of selective ions is driven by the concentration gradient over an ion-exchange membrane, with observation of Donnan criteria of co-ion rejection and preservation of electrical neutrality [20,21]. The diffusion dialyzer for acid recovery consists of multitude of compartments, which are made of gaskets and anion exchange membranes by alternative distribution. One meshlike separator is clamped by two gaskets, and all the compartments can be enhanced in this way. The membranes allow acids to permeate but remain metal ions. The separation of H_2SO_4 from its feed solution is illustrated in Fig. 1 to describe the principle of the diffusion dialysis. As shown in Fig. 1, the H_2SO_4 and the containing metal salts in the feed solution tend to transport through the membrane to the water side due to the concentration difference. The SO_4^{2-} ions are permitted to permeate, but the metals in the feed solution are hard to pass through the anion exchange membrane. As for the H^+ ions, although

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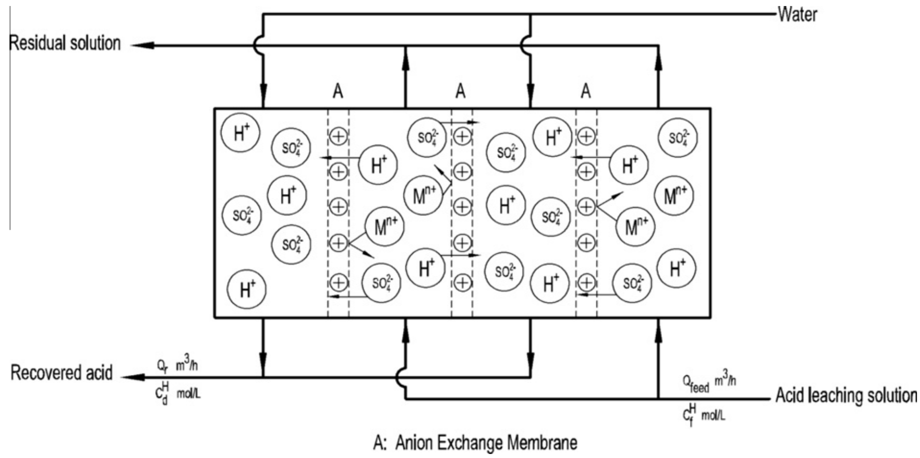

Fig. 1. Illustration of the diffusion dialysis principle.

the membrane is positively charged, they have higher competition in diffusion than metal ions because of their smaller size, lower valence state and higher mobility. Hence, they can diffuse along with the SO_4^{2-} to meet the requirement of electrical neutrality in solution [22].

2. Experimental

2.1. Experimental set-up

The schematic diagram of the experimental apparatus used in this study is shown in Fig. 2. A self-assembly diffusion dialyzer is separated by 40 sheets of anion exchange membrane (DF120, Shandong, China), and contains 40 diffusate cells and 40 dialysate cells, through which the feed and tap water pass in counter current direction. The dimension of each membrane effective for mass transfer is 200 mm × 400 mm, and the total membrane area is 3.2 m^2. The polymer membrane DF120 is based on poly (2,6-dimethyl-1,4-phenylene oxide). Its properties and specifications are shown in Table 1 [4,21].

2.2. Materials

The solutions for diffusion dialysis experiment using anion exchange membranes were prepared from the analytical grade H_2SO_4, $VOSO_4$, $Al_2(SO_4)_3$ and $FeSO_4$ reagents obtained from domestic chemical reagents companies, or the actual sulfuric acid solution generated from a stone coal roast-leaching process. The free H^+ concentration was around 2.4 mol/L in one actual acid leaching solution containing 4.2 g/L V_2O_5. The other metal ions concentrations in the solution are listed in Table 2.

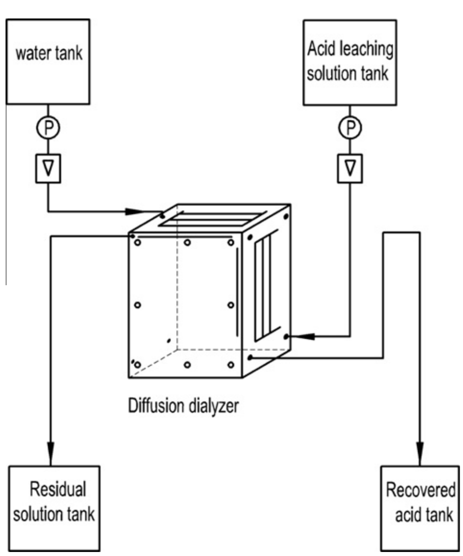

Fig. 2. Experimental set-up for diffusion dialysis.

2.3. Diffusion dialysis test

Fig. 3 shows the flow chart of separating and recovering sulfuric acid in vanadium producing process by diffusion dialysis. Acid leaching is one of the key steps in the vanadium extraction from stone coal. The diffusion dialysis technology can solve the problems of H_2SO_4 separation and recovery.

At the beginning of each experiment, the compartments of diffusion dialyzer were fed fully with feed acid solution and tap

Table 1
The properties and specifications of DF120 anion exchange membrane.

Item	Specifications
Materials	BPPO[a] amination and crosslinking
Water content (%)	42.34
Thickness (mm)	0.20–0.23
Transference number of ions in membrane	0.98
Membrane area resistance (Ω cm^2)	3.5–4.0
Ion exchange capacity (mmol/g)	1.7–1.9
Burst strength (MPa)	>0.9

[a] BPPO is brominated poly(2,6-dimethyl-1,4-phenylene oxide).

Table 2
The chemical composition of the acid leaching solution used in the experiment.

Element	Concentration (g/L)
V	4.20 (V_2O_5)
Al	13.75
Fe	6.64
Mg	0.63
K	0.41
Na	0.14
Ti	0.11
Ca	0.077
Ba	0.028
P	0.54
Si	0.33