Hydrometallurgy 173 (2017) 9–14

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Recovery of sulfuric acid from a stone coal acid leaching solution by diffusion dialysis

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ARTICLE INFO

Keywords:
Diffusion dialysis
Sulfuric acid recovery
Anion exchange membrane
Stone coal
Acid leaching solution

ABSTRACT

Diffusion dialysis was employed to recover sulfuric acid from a stone coal acid leaching solution. The dialysis coefficients of H^+, V, Al, Fe, Mg, K, F, P, and S ions in a stone coal acid leaching solution for an anion exchange membrane were determined. The effects of the flow rate, flow rate ratio, and water osmosis rate as well as ion rejection on sulfuric acid recovery were investigated. The results demonstrated that the DF120-III anion exchange membrane showed a good separation performance for separating sulfuric acid from the stone coal acid leaching solution. In the diffusion dialysis process, the water osmosis rate, sulfuric acid recovery, ion rejection, water equilibrium and processing ability were taken into consideration. Controlling water osmosis was more important than obtaining a higher acid recovery. Under the optimum operating conditions of a feed flow rate of 12 mL/min and flow rate ratio of water to feed of 1–1.1, sulfuric acid recovery reached 71.12%, the water osmosis rate was controlled at approximately 14.95%, and vanadium rejection was approximately 95.50%. The rejection of impurity ions, such as Al, Fe, Mg, K, F, P, and S was approximately 99.04%, 97.37%, 98.01%, 85.12%, 98.33%, 91.16%, and 69.96%, respectively. The high rejections of F in the form of complexes and P in the form of incompletely dissociated acid were disadvantageous to the recovery of sulfuric acid. The recovered acid was able to be reused in the acid leaching process by the addition of fresh acid.

1. Introduction

In China, in addition to vanadium-titanium magnetite, stone coal is an important vanadium-bearing resource due to its vast reserves and wide distribution (Zhang et al., 2011). Currently, acid leaching of stone coal with H_2SO_4 is the most common method in vanadium metallurgical plants because of its high vanadium recovery and low pollution (Zhou et al., 2009; Ma et al., 2015; Li et al., 2009; Li et al., 2015). However, a quantity of residual free sulfuric acid is present in acid leaching solution after leaching with H_2SO_4, and the acidity of the acid leaching solution is relatively high, making it unsuitable for the subsequent extraction of vanadium. Currently, a conventional and popular method to treat the acid leaching solution is neutralization with ammonia water or lime. However, such a neutralization process will generate a large quantity of highly concentrated ammonia-nitrogen wastewater or vanadium-containing gypsum, which cause disposal problems and serious environmental pollution. Moreover, valuable resources, such as sulfuric acid, bases and a portion of vanadium, are wasted (Wei et al., 2010; Li et al., 2012; Yang et al., 2016a).

Obviously, a new method is needed to both improve the economics of the process as well as avoid the vanadium loss and environmental pollution caused by the neutralization process. Diffusion dialysis with an anion exchange membrane seems to be a desirable method due to its low energy consumption, low installation and operating costs and lack of pollution (Luo et al., 2011a). It has been widely exploited to recover acid from metal treatment wastes, such as waste streams generated in steel, metal-refining, and electroplating industries (Oh et al., 2000; Xu and Yang, 2001, 2003; Xu et al., 2009a, 2009b). However, as opposed to recovering acid from general waste acid systems, the stone coal acid leaching solution is a mineral leaching solutions that is used with the ultimate goal of separating valuable metal resources from it rather than recovering acid from it and discarding it; the residual solution will be used in the subsequent separation and enrichment process of vanadium and the recovered acid should be able to be reused in the ore acid leaching process. In this way, a closed-circuit is created, and the economic and environmental effects are remarkable.

Studies have been performed on the recovery of sulfuric acid from a stone coal acid leaching solution by diffusion dialysis. Wei et al. (2010)

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http://dx.doi.org/10.1016/j.hydromet.2017.07.005
Received 13 March 2017; Received in revised form 16 July 2017; Accepted 24 July 2017
Available online 25 July 2017
0304-386X/

investigated the effects of the sulfuric acid, $FeSO_4$ and $VOSO_4$ concentrations; flow rate; and flow rate ratio on the recovery of H_2SO_4. Acid recovery exceeded 80%. The V and Fe ion rejection levels were within 93–95% and 92–94%, respectively. Li et al. (2012) investigated the effects of the flow rate, flow rate ratio, as well as V, Al and Fe ion concentrations on the recovery of H_2SO_4 and metal ion rejection. Over an 84% H_2SO_4 recovery efficiency was achieved. The V, Al and Fe ion rejection values reached 93%, 92% and 85%, respectively. However, these authors did not conduct detailed research on the behavior of vanadium and the main impurity ions (Al, Fe, Mg, K, F, P, S), the volumetric expansion of the acid leaching solution because of water osmosis and the effects on sulfuric acid recovery. However, these factors will directly affect the subsequent separation and enrichment of vanadium as well as the utilization of the recovered acid.

Therefore, in this study, the dialysis coefficients of H^+,V, Al, Fe, Mg, Na, K, F, P, and S ions in a stone coal acid leaching solution for the anion exchange membrane were determined in a cycling type dynamic diffusion dialysis experiment to investigate the separation performance of the anion exchange membrane. Furthermore, one-pass type dynamic diffusion dialysis experiments were conducted to investigate the factors that impacted the recovery of sulfuric acid, water osmosis and ion rejection.

2. Experimental

2.1. Materials

The solution used for cycling type dynamic diffusion dialysis and one-pass type dynamic diffusion dialysis was the actual acid leaching solution generated from the stone coal direct acid leaching process. Before the experiments, the acid leaching solution was filtered through a 0.45 μm pore size filter membrane to remove suspended solids and prevent blockage of the membrane. The concentrations of various ions in the solution are listed in Table 1.

2.2. Diffusion dialysis experiments

2.2.1. Cycling type dynamic diffusion dialysis experiment

The cycling type dynamic diffusion experiment was carried out using a custom-built mini diffusion dialyzer. The diffusion dialyzer was separated by 20 sheets of an anion exchange membrane (DF120-III, Shandong, China) into dialysate cells and diffusate cells through which the feed and de-ionized water, respectively, passed in a countercurrent fashion. The effective area of each membrane for mass transfer was 0.0112 m^2 (0.56 × 0.1 × 0.2), and the total effective membrane area was 0.224 m^2. Feed (1.5 L) and de-ionized water (1.5 L) were cycled, respectively, in dialysate cells and diffusate cells by a peristaltic pump with identical flow rates of 75 mL/min. The whole experiment ran continuously for 6 h. Small amounts of samples were taken from the dialysate and the diffusate to analyze the H^+ concentration and other ion concentrations every 30 min. Due to the severe water osmosis at the late stage of the experiment, only the first six sets of data were analyzed. The schematic of the cycling type dynamic diffusion dialysis system is shown in Fig. 1.

Table 1
The chemical composition of the acid leaching solution used in the experiment.

Element	Concentration (mg/L)
H^+	1750
V	2101.81
Al	17,560
Fe	5828
Mg	4503
K	6779
F	11,244.6
P	1463
S	61,670

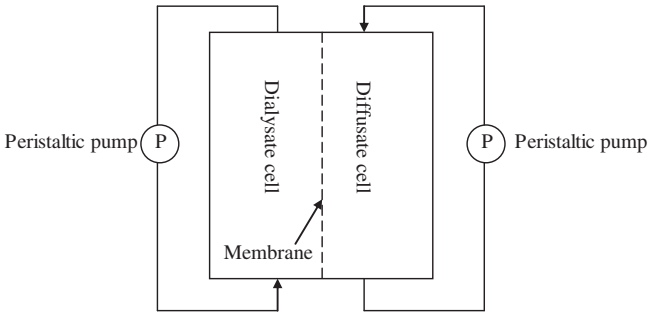

Fig. 1. The schematic of the cycling type dynamic diffusion dialysis system.

2.2.2. One-pass type dynamic diffusion dialysis experiments

One-pass type dynamic diffusion dialysis experiments were conducted using a HKY-001 diffusion dialyzer supplied by Shandong Tianwei Membrane Technology Co., Ltd. (Shandong, China). The diffusion dialyzer was separated by 19 sheets of an anion exchange membrane (DF120-III, Shandong, China) into dialysate cells and diffusate cells through which the feed and running water, respectively, passed in a countercurrent fashion. The effective area of each membrane for mass transfer was 0.08 m^2 (0.2 × 0.4), and the total effective membrane was 1.52 m^2 (19 × 0.2 × 0.4). During the tests, the diffusion dialyzer was initially fed with feed (0.7 L) and running water (0.7 L) and maintained for 2 h to reach equilibrium. Then, the test began and proceeded until a dynamic equilibrium state was reached; then, samples were taken. The schematic of the one-pass type dynamic diffusion dialysis experimental set-up is shown in Fig. 2. The DF120-III anion exchange membrane was produced from engineering polymer poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) by bromination and amination. The functional group attached on the anion exchange membrane was a quaternary ammonium group, and the physical aperture was approximately 5 nm. The membrane's lifetime is up to 5 years (Wei et al., 2010). Its characteristics are shown in Table 2 (Xu et al., 2009a; Li et al., 2012). The membranes used in all experiments were from the same production batch. All experiments were conducted at an ambient temperature of approximately 25 °C.

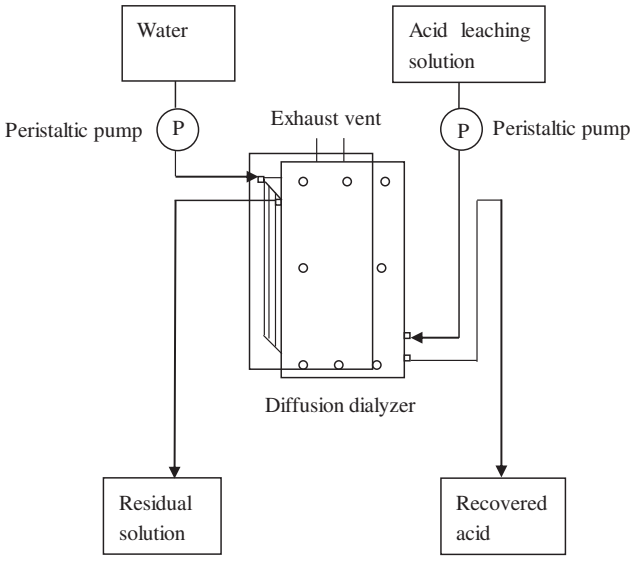

Fig. 2. The schematic of the one-pass type dynamic diffusion dialysis experimental set-up.