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Hydrochloric acid recovery from rare earth chloride solutions by vacuum membrane distillation

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Abstract: The possibility of the recovery of hydrochloric acid from rare earth (RE) chloride solutions was first experimentally studied by batch vacuum membrane distillation (VMD). The recovery by continuous VMD was also studied to devise methods that enabled the operation of VMD setup in a stable condition as well as to increase the membrane-operating life The results indicated that HCl separation with RE by VMD was possible, and the recovery ratio of 80% could be achieved by batch VMD. In continuous VMD, when the temperature of circular solutions, circular rate, and downstream pressure was 62-63°C, 5.4 cm/s, and 9.33 kPa, respectively, the HCl concentration in circular solutions and the processing capacity per membrane area were obtained. The mathematical results were in accordance with the experimental ones.

Key words: membrane separation; hydrochloric acid recovery; vacuum membrane distillation; rare earth; mathematical stimulation

1. Introduction

The system of P204 or P507-HCl to achieve RE separation was generally adopted in China. Since high concentration of hydrochloric acids was used to strip RE, HCl concentration in stripping solutions was thereby very high, which usually reached 2-6 mol/L. As to those high concentration of hydrochloric acids in stripping solutions, the traditional means was to neutralize it using alkali, or to recover it by diffusion dialysis [1-2]. In addition, there were reports concerning HCl recovery by high-temperature evaporation [3-4], electrodialysis [5], solvent extraction [6], and so on. However, RE metallurgical plants were usually unwilling to use these methods because of their various disadvantages.

As a promising separation technique, vacuum membrane distillation (VMD) had been widely studied for concentrating solutions containing non-volatile substance [7-8], gas separation [9-10], or volatile organic components' removal [11-12]. Since VMD could be carried out at low temperature to make full use of low-cost waste heat, the application of VMD in the metallurgical industry could be very attractive.

The possibility of HCl separation with RE by batch VMD was first experimentally studied in this article. Batch means caused shrinkage of the membrane because of the frequent changes in temperature and feed constitutes in the actual membrane-separation process, which inevitably led to the shortening of the membrane-operating life; however, by continuous means it was possible to avoid or decrease this influence [13]. The recovery by continuous VMD was also studied to devise methods that enabled the operation of VMD setup in a stable condition as well as to increase the membrane-operating life.

2. Experimental

2.1. Batch VMD

The experimental apparatus, characteristics of the membrane, and feed solutions used in this study can be found in Refs. [11,14].

Fig. 1 shows how HCl and RE concentrations

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change in batch VMD process. The experimental conditions were as follows: membrane area 0.012 m^2, feed volume 2 L, and initial concentrations of RE and HCl were 0.45 and 2.7 mol/L, respectively.

Fig. 1 indicates that the RE concentration in feed solutions increased continuously during the process, and HCl concentration initially increased and then started to decrease when RE and HCl concentrations were concentrated to some degree. This was due to the existence of RE chloride and its "salt effects" [14-15], and hence it was possible to achieve HCl recovery from RE chloride solutions by VMD.

Table 1 shows the experimental results. The experimental conditions were: membrane area 0.021 m^2, initial volume of feed solution 5 L, temperature 62-63°C, downstream pressure 8-10 kPa, initial concentrations of RE and HCl were 0.305 mol/L and 5.171 mol/L, respectively.

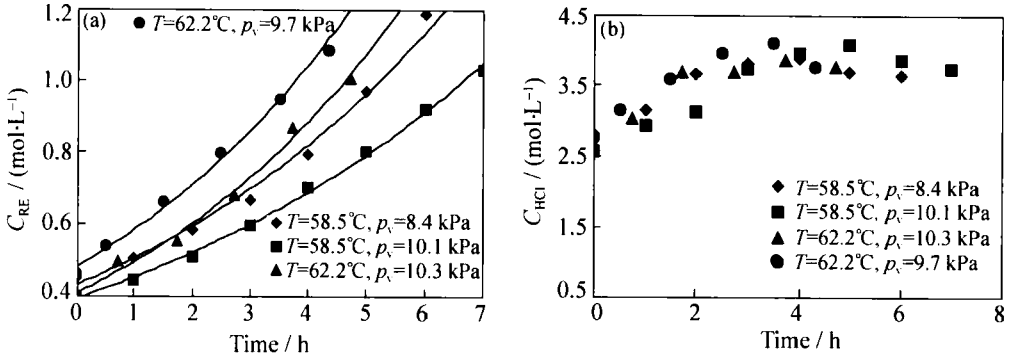

Fig. 1. RE (a) and HCl (b) concentrations over time at different conditions.

Table 1. Experimental results of HCl recovery

Time / h	Feed solutions		Distillate			Recovery ratio / %
	C_{HCl} / (mol·L^{-1})	C_{RE} / (mol·L^{-1})	V / mL	C_{HCl} / (mol·L^{-1})	C_{RE} / (mol·L^{-1})	
2.00	5.259	0.353	675	5.018	0.0011	13.1
3.50	5.069	0.390	1140	5.341	0.0015	23.6
5.15	4.919	0.451	1680	5.535	0.0019	36.0
6.65	4.723	0.529	2145	5.718	0.0020	47.4
8.15	4.383	0.629	2605	5.824	0.0022	58.7
9.65	3.840	0.776	3055	5.949	0.0024	70.3
11.65	3.163	1.131	3635	5.964	0.0029	83.8

From Table 1, it can be seen that the RE concentration in distillate was very slim, and pure acids were obtained in the permeate side. Furthermore, the recovery ratio of hydrochloric acid was as high as 80%. Hence HCl recovery from the RE chloride solutions by VMD was feasible.

2.2. Continuous VMD

The continuous VMD experimental apparatus was different from batch VMD, as shown in Fig. 2. During the experimental process, a certain feed solution was used as circular solution, and its volume was 2 L. The temperature and circular rate were 62-63°C and 5.4 cm/s, respectively, and the pressure in the permeate side was 9.33 kPa. The feed solutions flowed from the elevated tank at a certain flow rate into the circular solutions tank, which expressed the processing capacity of the experimental setup. Overflowing solutions were discharged from the circular solutions tank, which served as processed solutions. RE and HCl concentrations were frequently measured to keep constant RE concentration in circular solutions. The volumes of both overflowing solutions and distillate were measured at the