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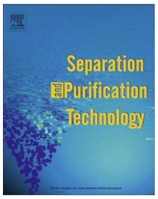

Separation of alumina alkaline solution by electrodialysis: Membrane stack configuration optimization and repeated batch experiments

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ABSTRACT

Alumina alkaline solution containing NaOH and $NaAl(OH)_4$ is separated by electrodialysis (ED), which uses self-prepared anion exchange membrane AM-QP-30. The stack arrangements and number of repeating units are optimized to achieve high alkali recovery ratio and low energy consumption. Meanwhile, repeated batch experiments (RBEs) are carried out to investigate the effect of erosion on membrane stability.

The optimal membrane stack configuration is three repeating units configuration. The membrane fouling can be effectively eliminated by acid cleaning during the RBEs. The ED performances are stable and excellent. For instance, the alkali recovery ratio (η_{OH^-}) can reach up to 64.9–68.5% and the energy consumption can be reduced to 7.29–7.65 kW h/kg. The performance of AM-QP-30 membrane is superior to commercial FQB membrane in consideration of the lower mass loss ratio, stable ED performances and morphology after erosion. As a result, the ED process is feasible and stable to separate the alumina alkaline solution.

1. Introduction

The Bayer process, which was developed and patented by Karl Josef Bayer 110 years ago, has become the cornerstone of the aluminum production industry worldwide [1]. It involves the digestion of crushed bauxite in concentrated sodium hydroxide (NaOH) solution at high temperature, during which process the majority of the aluminum containing species are dissolved as sodium aluminate ($NaAl(OH)_4$) (reaction (1)) [1–3]. After separation of the insoluble residue, the alumina alkaline solution containing $NaAl(OH)_4$ and NaOH is cooled and aluminum trihydroxide (gibbsite; $Al(OH)_3$) is precipitated by seeding with external gibbsite (reaction (2)) [2,3]. The $Al(OH)_3$ precipitate is then removed and washed prior to calcination (reaction (3)) [3], while the residual caustic solution, also called mother liquor, can be returned to the circuit.

$$\text{Bauxite digestion}: Al(OH)_3(s) + NaOH(aq) \rightarrow Na^+Al(OH)_4^-(aq) \qquad \text{(reaction 1)}$$

$$\text{Gibbsite precipitation}: Na^+Al(OH)_4^-(aq) \rightarrow Al(OH)_3 \downarrow + NaOH(aq) \qquad \text{(reaction 2)}$$

$$\text{Calcination}: 2Al(OH)_3(s) \rightarrow Al_2O_3(s) + 3H_2O \qquad \text{(reaction 3)}$$

The procedures of seeding and precipitation are complex and costly, and need long time for stirring. Besides, the presence of high concentration NaOH retards the precipitation of $Al(OH)_3$ [4,5]. Accordingly, the yield of $Al(OH)_3$ is insufficient, and the purity of alkali in the mother liquor is relatively low, which is disadvantageous to its circuit use. Hence, the NaOH and $NaAl(OH)_4$ in the alumina alkaline solution need to be separated before the procedures of seeding and precipitation.

Electrodialysis (ED) is a type of technology which arranges ion-exchange membranes alternately in a direct current field [6]. Anions and cations can migrate through the membranes toward the anode and the cathode, respectively [7]. Accordingly, ED has been widely used for separating or concentrating acids, bases, salts or organic ions [8–11]. Our previous report has shown that ED was effective to separate NaOH and $NaAl(OH)_4$ from the alumina alkaline solution [12]. However, the separation efficiency was still insufficient due to three main reasons. Firstly, the alkali recovery ratio was only 48.0% and the energy consumption was as high as 12.43 kW h/kg under the optimal conditions. Secondly, repeated

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Nomenclature

Codes	full name or meaning
ED	electrodialysis
DD	diffusion dialysis
QPPO	quaternized poly(2,6-dimethyl-1,4-phenylene oxide)
PVA	polyvinyl alcohol
AEM	anion exchange membrane
CEM	cation exchange membrane
IEC_A	anion exchange capacity
IEC_C	cation exchange capacity
EDTA-Na	disodium ethylenediamine tetraacetic acid
PAN	1-(2-pyridylazo)-2-naphthol
M_L	mass loss ratio
η_{OH^-}	OH^- recovery ratio
$\eta_{Al(OH)_4^-}$	$Al(OH)_4^-$ leakage ratio
α_k	caustic ratio
η	current efficiency
E	energy consumption

batch experiments (RBEs) were not investigated due to the inadequate long-term stabilities of the membranes. The commercial anion exchange membrane (AEM) FQB tended to be eroded in ED process, as reflected by the color change from white to black after 4 h running. Finally, fouling from $Al(OH)_3$ precipitate was serious. The hydrolysis of $Al(OH)_4^-$ in the feed could generate obvious $Al(OH)_3$ precipitate on the membrane surface which was close to the cathode chamber. The fouling would not only enhance membrane electrical resistance and energy consumption, but also shorten membrane life [13]. Hence, stable AEMs are required, and the $Al(OH)_3$ precipitate needs to be eliminated during repeated ED running.

The separation efficiency is affected critically by ED membrane stack configuration. The previous study [12] utilized only two repeating units membrane stack. The number of repeating units may need to be enhanced to achieve higher separation efficiency, since increase of the repeating units can improve the potential difference across the membrane stack [14]. Nevertheless, the capital costs and the internal resistance through the stack are also increased [15–17]. Hence, the stack configuration should be optimized to balance cost and separation efficiency.

The RBEs can be investigated by using stable AEMs. Previous work of our laboratory demonstrated that the AEMs based on quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (QPPO) and polyvinyl alcohol (PVA) showed excellent performances, since they could combine the advantages of PPO (high stability and mechanical strength) and PVA (high flexibility and excellent permeability for acid and alkali) [18]. The superiority of this kind of membrane for diffusion dialysis (DD) process has been revealed [18,19]. In this work, QPPO-PVA membrane will be prepared through modified procedures for further enhancing of the swelling resistance and stabilities. The obtained membrane, designated as AM-QP-30, will be used together with the commercial cation exchange membrane (CEM) FSB membranes for ED. Firstly, membrane stack configurations are optimized. Secondly, RBEs are carried out with the optimal membrane stack configuration. Finally, membrane stability and fouling behavior are investigated during RBEs. The stability and long-term running performances will be compared with those of reference membrane FQB.

2. Experimental

2.1. Preparation of anion exchange membrane AM-QP-30

The AM-QP-30 membrane was prepared according to procedures modified from our previous work [18]. Quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (QPPO)/SiO_2 solution was synthesized from the sol–gel reaction of QPPO, tetraethoxysilane (TEOS) and monophenyl triethoxysilane (EPh) in dimethyl formamide (DMF). The QPPO/SiO_2 solution (2.1 kg solute, 9.5 L) was dropped into 70 °C, 9.2 wt% and 6.8 L PVA solution within 3 h. The mixture was continued to stir at 70 °C for 20 h, and finally a casting solution was obtained.

PET fibers (thickness of 0.105 mm) and a casting device by Shandong Tianwei Membrane Technology Corporation of China were used for the casting process. The fibers were firstly immersed in the casting solution, then rolled out, and finally heated from 50 to 105 °C. The obtained membrane with area of $1.2 \times 40\ m^2$ was further heated from 90 to 130 °C, and kept at 130 °C for 8 h. The heat treatment was enhanced as compared with previous conditions (130 °C for 4 h [18]).

The support of PET fibers and the enhanced heat treatment would elevate membrane swelling resistance. Besides, as the membrane was prepared by a casting device, its thickness was stable at ~0.15 mm. The membrane contained both $-N(CH_3)_3Br$ and $-OH$ groups and the main properties were measured and listed in Table 1.

2.2. ED membranes and solutions

The cation exchange membranes (CEMs) for all the experiments were FSB membranes and would not be specifically explained in the following sections. The anion exchange membrane (AEM) could be AM-QP-30 or FQB membrane. Both FSB and FQB membranes were based on fluorinated polymers and kindly supplied by Hefei Chemjoy Polymer Materials Co. Ltd., China. Their main characteristics were listed in Table 1. All the chemicals used in the study were of analytical grade. Deionized water was used.

Three kinds of solutions, each with the volume of 500 mL, were used in each ED running. The feed solution containing NaOH and $NaAl(OH)_4$ was prepared by a chemosynthesis method as described previously [12]. The concentrations of NaOH and $NaAl(OH)_4$ were 1.50–1.57 mol/L and 0.80–0.83 mol/L correspondingly. The initial recovery solution was 0.1 mol/L NaOH, and the electrode rinse solution was 0.5 mol/L Na_2SO_4.

Table 1
Properties of cation-exchange membrane FSB and anion-exchange membranes FQB and AM-QP-30.

Membrane	FSB	FQB	AM-QP-30
Thickness (μm)	~150	~150	~150
[a]IEC_C (mmol/g)	~1.8	–	–
[a]IEC_A (meq/g)	–	~1.6	0.7–1.0
[b]Water uptake (%)	70	48	22
[c]Area resistance ($\Omega\ cm^2$)	~2.3	~2.1	~3.5
[d]Transport number (%)	~0.89	~1.0	~0.92

[a] Cation-exchange capacity (IEC_C) and anion-exchange capacity (IEC_A) are determined in meq/g in Cl^- and Na^+ form, respectively.

[b] Water uptake is determined by equation of g_{H2O}/g_{dry}.

[c] Area resistances of anion exchange and cation exchange membranes are measured as Cl^- and Na^+ form in 0.5 mol/L NaCl at 25 °C, respectively.

[d] Transport number is measured by the electromotive force (EMF) method using Ag/AgCl electrodes [20].