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Production of Sulfuric Acid and Ammonia Water from Ammonium Sulfate Using Electrodialysis with Bipolar Membrane and Ammonia Stripping

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Abstract: The feasibility of producing sulfuric acid and ammonia water from ammonium sulfate was investigated by an integrated process including ammonia stripping (AS) and electrodialysis with bipolar membrane (EDBM). It was suggested that the production of sulfuric acid using ammonia stripping-electrodialysis with bipolar membrane (ASEDBM) was effective in obtaining high concentration of sulfuric acid compared with EDBM alone. AS was carried out over pH 11 and within the range of temperatures, 20°C~60°C. Sodium sulfate obtained using AS was used as the feed solution of EDBM. The recovery of ammonia increased from 40% to 80% at 60°C due to the increased mobility of ammonium ion. A pilot-scale EDBM system, which is composed of two compartments and 10 cell pairs with an effective membrane area of 200 cm^2 per cell, was used for the recovery of sulfuric acid. The performance was examined in the range of 0.1 M~1.0 M concentration of concentrate compartment and of 25 mA/cm^2~62.5 mA/cm^2 of current density. The maximum current efficiency of 64.9% was obtained at 0.1 M sulfuric acid because the diffusion rate at the anion exchange membrane decreased as the sulfuric acid of the concentrate compartment decreased. It was possible to obtain the 2.5 M of sulfuric acid in the 62.5 mA/cm^2 with a power consumption of 13.0 kWh/ton, while the concentration of sulfuric acid was proportional to the current density below the limiting current density (LCD). Thus, the integrating process of AS-EDBM enables to recover sulfuric acid from the wastewaters containing ammonium sulfate.

***Keywords**: ammonia stripping, electrodialysis, bipolar membrane, ammonium sulfate, sulfuric acid*

1. Introduction

Caprolactam is an important organic chemical material that is mainly used in the manufacture of Nylon 6 fibers. Ammonium sulfate is formed as a byproduct in a neutralization step. Currently the byproduct was concentrated using reverse osmosis (RO) to be used as a fertilizer, and the permeate water is recycled for domestic use. In general, ammonium sulfate concentrated by RO is 4%~5% and it is further concentrated to 20% if it is used as fertilizer[1]. However, the operating cost increases as the target concentration increases in the RO process due to the osmotic pressure built up on the membrane surface[2-4]. To overcome the drawback, a feasibility of electrodialysis (ED) process was studied to concentrate the ammonium sulfate in RO retentate[1,5-7]. Even though the concentrated ammonium sulfate is a fertilizer, it is more environment-friendly and economical to recover the sulfuric acid and ammonia to be used in the manufacturing process.

The EDBM technology is an environment-friendly technology with a wide-ranging potential for application. A bipolar membrane (BM) is a kind of composite membrane that consists of a layered ion-exchange structure composed of a cation selective membrane (with negative fixed charges) and an anion selective mem-

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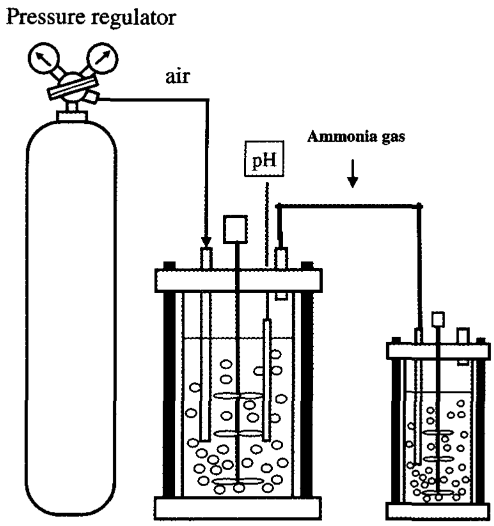

Fig. 1. Ammonia stripping apparatus.

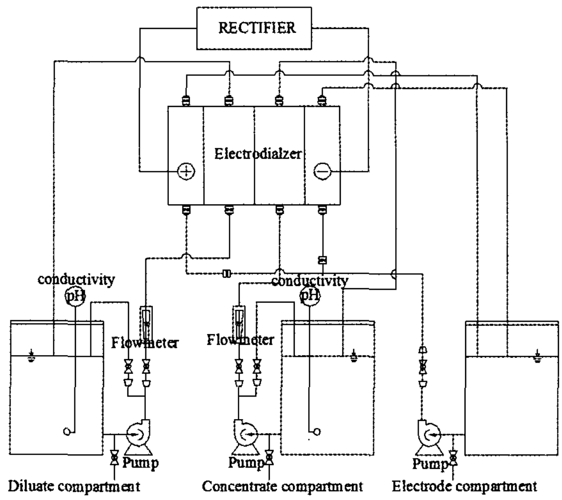

Fig. 2. Schematic diagram of batch EDBM stack.

brane (with positive fixed charges)[8,9]. In particular, water dissociation based on a BM technology is promising in electrodialysis industries due to its superiority to conventional water electrolysis. The energy consumption for electrolysis process is 198.5 kJ/mol, while for electrodialytic water dissociation it is only 79.9 kJ/mol [10]. This low energy consumption is further advantageous in reducing cooling load. Due to the advantages, BM and its related technology have found many applications in production and separation, environmental conservation such as environmental engineering, chemical production, energy sources, bioengineering, etc.

In this study, an integrated process of AS-EDBM was investigated to make sulfuric acid and ammonia water from ammonium sulfate of 40 wt%. In principle EDBM of ammonium sulfate may generate ammonia and sulfuric acid. However the process efficiency is significantly low due to the low conductivity of ammonium hydroxide. AS was performed at various temperatures and EDBM performance was presented according to current density and the concentration of sulfuric acid in the concentrate compartment.

2. Experimental

2.1. Ammonia Stripping

Ammonia was extracted continuously from the tower. The equilibrium equation for ammonia in water by the relation:

$$NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O, \quad pK_a = 9.3 \qquad (1)$$

The speciation of the ammonia in water is a function of pH, the fraction of the dissolved ammonia in the ammonium form increasing with the solution pH. At ambient temperature and pH 7, the reaction shifts to the left and only ammonium ions are present. As the pH is increased above 7, the reaction is driven to the right and the fraction of dissolved ammonia gas increases up to pH 10.5~11.5. Essentially all of the ammonium is converted to ammonia gas[11]. The ammonia stripping process (Figure 1) consists of: (1) raising the pH of the water values in the range of 10.8 to 11.5 (pH 11) with 5 N sodium hydroxide to 40 wt% ammonium sulfate solution, (2) formation and reformation of water droplets in a stripping tower, and (3) providing gas-water contact and droplet agitation by circulation of large quantities of gas through tower. The effect of temperature on stripping performance was investigated in the range of 20~60 °C.

2.2. Electrodialysis with Bipolar Membrane

The EDBM stack supplied by Tokuyama Company (model TS-2-10, Japan) was used with 10 cell pairs.

Table 1. Characteristic Properties of the Neosepta AMX Anion-exchange and Neosepta BP-1 Bipolar Membranes[12]

Properties	AMX	Properties	BP-1
Electric resistance ($\Omega \cdot cm^2$)[a)]	2.5~3.5	Water splitting Voltage[c)]	0.9~1.7 V
Thickness (mm)	0.16~0.18	Water splitting Efficiency[d)]	>0.98
Exchange capacity (meq/g dry membrane)	1.4~1.7	Burst strength	0.4~0.7 MPa
Water content[b)]	0.25~0.30	Thickness	0.17~0.26 mm
Characteristics	High mechanical strength		

[a)] Equilibrated with 0.5 N NaCl solution at 25°C, [b)] Equilibrated with a 0.5 N NaCl solution, [c)] Measured between 1 N NaOH and 1 N HCl, 10 A/dm^2, 30°C, [d)] Potential drop across the "NEOSEPTA® BP-1"

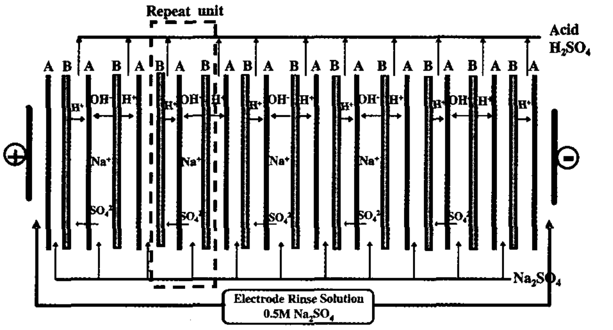

Fig. 3. EDBM stack configuration (A: anion exchange membrane, B: bipolar membrane).

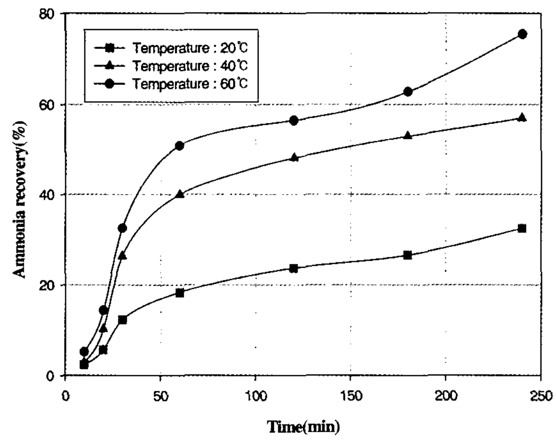

Fig. 4. Effect of ammonia stripping on temperature.

Effective membrane area was 200 cm^2 per cell. Solutions were pumped through the cell compartments continuously from recirculation tanks (Figure 2). The compartment gap was about 0.75 mm and the flow rate was 3 L/min per cell (linear velocity, 6 cm/sec).

The ion-exchange membranes used in this study was BP1 bipolar membrane (Tokuyama Soda, Japan) and AMX anion-exchange membrane (Tokuyama Soda, Japan). Table 1 gives some of their physicochemical properties.

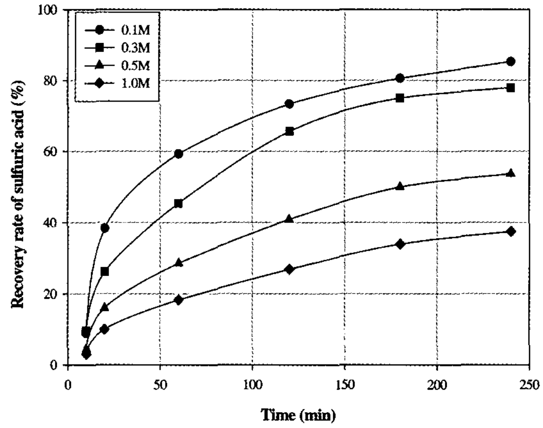

Fig. 5. Effect of recovery rate of sulfuric acid on concentration of concentrate compartment at current density of 25 mA/cm^2.

Figure 3 illustrates the stack configuration of two-compartment EDBM. While three-compartment EDBM is used for relatively high solution conductivity, two-compartment EDBM can be made up for the limitation in low solution conductivity such as ammonium sulfate and sodium acetate. EDBM experiments were carried out at various concentration of sodium sulfate (0.1~1.0 M) and current densities (25.0~62.5 mA/cm^2).

3. Results and Discussion

3.1. Effect of Ammonia Stripping on Temperature

Figure 4 illustrates the variation in ammonia recovery in the ammonia stripping as a function of temperature. The ammonia recovery at pH 11.25 was directly

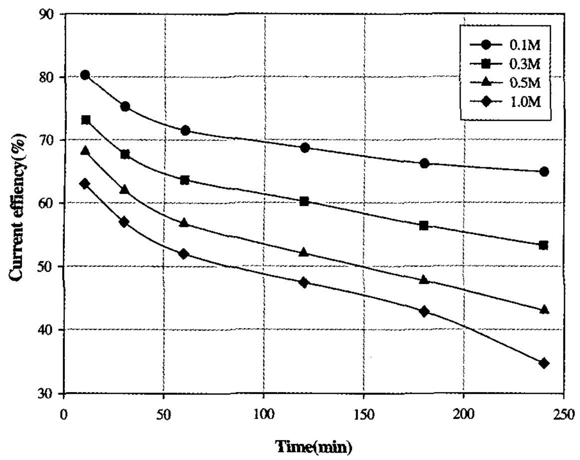

Fig. 6. Variation of current efficiency according to the different concentration of the concentrate compartments.

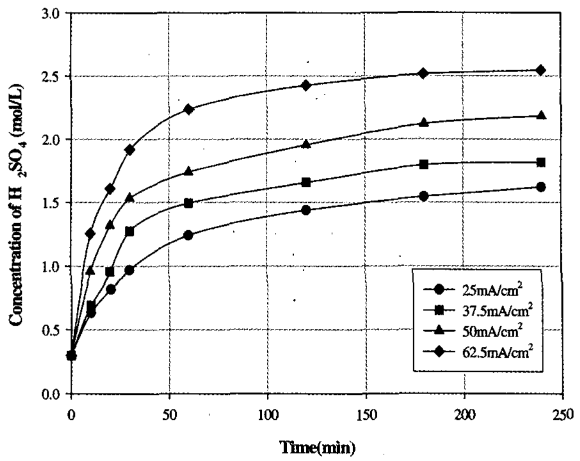

Fig. 7. Effect of concentration of sulfuric acid on current density.

dependent upon solution temperature. The rate of reaction from ammonium ion into ammonia gas increases with temperature. By increasing the solution temperature, the recovery of ammonia increased due to the increased mobility, and was improved into 40% for 20°C, 60% for 40°C, and 80% for 60°C.

3.2. Effect of Recovery Rate of Sulfuric Acid on Concentration of Concentrate Compartment

Figure 5 represents the variation recovery rate according to the concentration of sulfuric acid in the concentrate compartment solution as a function of operating time at a current density of 25 mA/cm^2. As the concentration of sulfuric acid in the concentrate compartments increases, the recovery rate decreases because the Donnan exclusion effect for hydrogen ion on the anion-exchange membranes decreases. The effect of recovery rate on the concentration of the concentrate compartment was investigated in the range of 0.1 M~1.0 M. The recovery rate increases as the concentration of the concentrate compartment decreases. The weak selectivity of the anion-exchange membrane towards protons appears real despite the selection of a specific anion-exchange membrane. This proton leakage increases with the acid concentration. Also, the recovery of sulfuric acid decreased as the concentration of the concentrate compartment increases due to the increased concentration gradient between diluate and concentrate.

The current efficiency is directly related to the product concentration, as shown in Figure 6. The current efficiency was defined as the ratio of the current that transfers salt to the total amount of applied current[13]:

$$\zeta = \frac{2(c_t V_t - C_0 V_0)F}{iANt} \times 100(\%) \qquad (2)$$

in which ζ is the current efficiency (fractional), c_0/c_t is the feed/product concentration at time 0/t (mol/L), F is the *Faraday* constant (96,500 C/eq), V_0/Vt is the solution volume at time 0/t (L), i is the current density (A/cm^2), A is the effective membrane area (cm^2), N is the cell pairs. The current efficiency of the EDBM was 64.9% for 0.1 M concentrate, 53.3% for 0.3 M concentrate, 43.1% for 0.5 M concentrate, 34.7% for 1.0 M concentrate. It was known that the current efficiency of EDBM is generally affected by the properties of the anion-exchange membrane. The loss in efficiency is mainly due to the leakage of protons.

3.3. Effect of the Concentration of Sulfuric Acid on Current Density

Current density is the more important characteristic in determining the operating and membrane cost in the EDBM process. As the current density is increased, initial installation cost can be reduced due to the increased

Table 2. Power Consumption for Desalting of 1.7 M Sodium Sulfate Solution

Current density (mA/cm^2)	Power consumption (kwh/ton)
25.0	3.6
37.5	7.9
50.0	8.8
62.5	13.0

flux.

The effect of current density was carried out in the range of 25 ~ 62.5 mA/cm^2 for 240 minutes (Figure 7). The concentration of sulfuric acid increased with as the current density increased and measured as 1.6 M for 25 mA/cm^2, 1.8 M for 37.5 mA/cm^2, 2.1 M for 50 mA/cm^2, and 2.5 M for 62.5 mA/cm^2. However, the concentration was 0.62 M, 0.72 M, 0.80 M, and 0.82 M if it re-concentrates the ammonium sulfate in RO retentate using EDBM. Therefore, it was effective in concentrating the sulfuric acid with ammonia stripping than without.

Under an electrical field, ions are transported through the membranes accompanying the solvent. This phenomenon is called electroosmosis and the number of water molecules bound to a single ion is referred to as the hydration number of the ion[14]. The volume changes in both the feed and concentrate as observed in EDBM due to the electroosmosis, and the increased amount of concentrate was measured at 150 mL, 218 mL, 302 mL, and 437 mL for 25, 37.5, 50, and 62.5 mA/cm^2, respectively. Because of electroosmosis, volume change was proportional to current density. Also, current efficiency was considered under limiting current density, and was 70%, 80.4%, 96.5%, and 99.9% for 25 mA/cm^2, 37.5 mA/cm^2, 50 mA/cm^2, and 62.5 mA/cm^2, respectively. The higher is the current density, the higher is the current efficiency due to the competition between diffusion phenomena depending on residence time and migration depending on current density[15].

3.4. Effect of Power Consumption on Current Density

The major factors that determine the performance of an EDBM process are the current efficiency and the power consumption. High current efficiency leads to a reduction in the membrane area and low power consumption resulting in reduction in the operating cost[16].

Table 2 represents the power consumption for desalting of 1.7 M sodium sulfate solution. The power consumption linearly increased from 3.6 to 13.0 kwh/ton with increasing current density in the range of 25 mA/cm^2 ~ 62.5 mA/cm^2.

4. Conclusions

The integrated process of ammonia stripping and electrodialysis with bipolar membrane (ASEDBM) enables to recover sulfuric acid and ammonia from the wastewaters containing ammonium sulfate because it was suggested that the production of sulfuric acid using ASEDBM was effective in obtaining a high concentration of sulfuric acid compared with EDBM alone. The EDBM of ammonium sulfate may generate ammonia and sulfuric acid. However the efficiency of the process is significantly low due to the low conductivity of ammonium hydroxide.

The ammonia recovery at pH 11.25 using ammonia stripping was directly dependent upon solution temperature, and the recovery was improved from 40% to 80% in the range of 20°C ~ 60°C due to the increased mobility of ammonium ion. Sodium sulfate obtained using AS was used as the feed solution of EDBM. A pilot-scale EDBM system, which is composed of two compartments and 10 cell pairs with an effective membrane area of 200 cm^2 per cell, was used for the recovery of sulfuric acid. The current efficiency of the EDBM was 64.9% for 0.1 M concentrate, 53.3% for 0.3 M concentrate, 43.1% for 0.5 M concentrate, and 34.7% for 1.0 M concentrate because the diffusion rate at the anion exchange membrane decreased as the sulfuric acid of concentrate compartment decreased. It was possible to obtain the 2.5 M of sulfuric acid in the 62.5 mA/cm^2 with a power consumption of 13.0 kWh/ton, while the concentration of sulfuric acid was proportional to the current density below the limiting current density (LCD). The main factors that affect the current efficiency are the concentration of ammonium sulfate. In particular, the current efficiency of EDBM stack is generally affected by the properties of the anion-exchange membrane and the loss in efficiency is mainly due to the leakage of protons. If the current density is higher, the current efficiency is also higher due to the competition between diffusion phenomena depending on the residence time and migration depending on current density. The study successfully demonstrated that an integrated process of ammonia stripping and electrodialysis with bipolar membrane can be employed in the production of sulfuric acid and ammonia water from ammonium sulfate.

Acknowledgements

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