**Technological Development of Salt-containing Wastewater Treatment and Salts Electrolysis to Acids and Bases**

Jianbo Luo, Dongfang Niu, Xinheng Zhang*

State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai, 200237, China

Meilong Road 130, Xuhui District, Shanghai, China

(E-mail: xszhang@ecust.edu.cn)

**Introduction**

The industrial process of metallurgy usually generates large volumes of hypersaline wastewater leading to environmental pollution. Treatment of this kind of wastewater has always been a challenge to the factory. The plant produces 300,000 tons/year of wastewater containing about 75g/L Na\(_2\)SO\(_4\), 20g/L NaCl, as well as small quantity of Ca\(^{2+}\), Mg\(^{2+}\) and SiO\(_2\). On the basis of this background, we develop a process (Fig.1) to recycle the water and produce acid and base by salt electrolysis.

Fig.1 The process flow diagram of wastewater recycling

Two and three-chamber cell are usually used for salt electrolysis to prepare acids and bases\(^{1,2}\). The drawback is that current efficiency and production purity are not as good as we expect. Attempting to get a higher current efficiency and purity of acid and base, we design a four-chamber type cell (Fig.2. (b)) for salt electrolysis. Because of the Fickian diffusion driven by concentration difference, the H\(^+\) ions in the acid chamber pass through the anion exchange membrane to the salt chamber. The increase of H\(^+\) concentration in salt chamber will result in more H\(^+\) ions migrating through the cation exchange membrane to the base chamber to react with OH\(^-\), leading to a decrease in current efficiency. The “buffer chamber” can weaken the Fickian diffusion by decreasing the concentration difference between the salt chamber and buffer chamber. As a result, it prevents more H\(^+\) migration from acid chamber to base chamber, as well as Na\(^+\) migration from salt chamber to acid chamber, which is expected to improve the current efficiency and production purity.

**Results and discussion**

1. Pretreatment: Membranes in electrodialysis and electrolysis were vulnerable to damage by solid precipitating on the surface, therefore it is necessary to get rid of Ca\(^{2+}\), Mg\(^{2+}\) and SiO\(_2\)\(^-\) in wastewater (Ca\(^{2+}\) < 0.1 ppm, Mg\(^{2+}\) < 0.1 ppm, SiO\(_2\)\(^-\) < 5 ppm). In this work, precipitation process and, resin adsorption method were used to decrease Ca\(^{2+}\), Mg\(^{2+}\) and SiO\(_2\)\(^-\) contents in wastewater to 0.1 ppm,0.1ppm and 5ppm, respectively.

2. Electrolysis (ED): Two-stage electrodialysis process was used to realize desalination of wastewater in diluted tank, and salt enrichment in concentrated tank. After desalination and enrichment by ED with a current efficiency of 85%, the Na\(_2\)SO\(_4\) concentration in diluted solution was reduced to less than 0.5 g/L, and the concentrated solution increased to a higher content (230 g/L Na\(_2\)SO\(_4\), 50 g/L NaCl). The diluted water with 0.5 g/L Na\(_2\)SO\(_4\) can be reused in the production line, and the concentrated solution containing 230 g/L Na\(_2\)SO\(_4\) and 50 g/L NaCl was used to produce sulfuric acid and sodium hydroxide in the followed salt electrolysis. Wastewater treatment capacity of ED in this work is four times of that in the existing industrial ED.

3. Pre-electrolysis: The anion exchange membrane in the cell (Fig.2. (a)) is susceptible to C\(_2\)I corrosion, which will reduce the service life of anion exchange membrane. In order to remove Cl\(^-\) in wastewater, firstly we used chlor-alkali electrolysis. Cl\(^-\) was reduced to less than 5 g/L in the anode chamber, at the same time, the concentration of NaOH in the cathode chamber was increased from 20 to 25% with a current efficiency of 80~85% during the pre-electrolysis process.

4. Electrolysis: The dechlorinated solution was fed into the salt tank. The experiment was carried out with current density of 1500 A/m\(^2\) at 50 °C. First, two-chamber cell was used to test the performance of different membranes (AEM and CEM). We found that combination of AAV anion exchange membrane and Chlor-alkali cation exchange membrane showed best performance in current efficiency and prevention of migration of H\(^+\)

Table 1 AMV membrane as “AEM” in three-chamber cell

<table>
<thead>
<tr>
<th>“C” membrane</th>
<th>CMV</th>
<th>CGC</th>
<th>Chlor-alkali</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current efficiency</td>
<td>61.0%</td>
<td>49.0%</td>
<td>72.0%</td>
</tr>
</tbody>
</table>

Table 2 Chlor-alkali membrane as “CEM” in three-chamber cell

<table>
<thead>
<tr>
<th>“A” membrane</th>
<th>AMV</th>
<th>AAV</th>
<th>AHT</th>
<th>ASD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current efficiency</td>
<td>72.0%</td>
<td>73.5%</td>
<td>61.0%</td>
<td>58.2%</td>
</tr>
</tbody>
</table>

Attempting to get a higher current efficiency, the four-chamber cell was used. 20% NaOH and 25% H\(_2\)SO\(_4\) were produced in both three and four-chamber cell (Fig.2. (a), (b)). the current efficiency of base and acid in four-chamber cell (Fig.2. (b)) is 80~85%, which is 10% higher than that in three-chamber cell (table 2). Impurity Na\(_2\)SO\(_4\) content in 25% H\(_2\)SO\(_4\) is 400 mg/L in four-chamber cell and is 150mg/L in three-chamber cell. Na\(_2\)SO\(_4\) content in 25% NaOH is 400 mg/L in both three and four-chamber cell. It indicated that much purer H\(_2\)SO\(_4\) solution was obtained with four-chamber cell than that with three-chamber cell and that reported in previous studies.

High-purity H\(_2\)SO\(_4\) solution of 15 wt% which contained impurity Na\(_2\)SO\(_4\) 30 mg/L was obtained by diffusion dialysis method with more than 80% of the H\(_2\)SO\(_4\) being recovered from the 25% H\(_2\)SO\(_4\).

**Reference**

