The recovery of chlorine from by-product hydrogen chloride
Part 2: molten metal cathode method

S. YOSHIZAWA, A. TAKEHARA, Y. ITO and K. OKA

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto, Japan

Received 27 April 1971

A new method of recovering chlorine from by-product hydrogen chloride is proposed and developed. According to the reaction $\text{Me} + 2\text{HCl} = \text{MeCl}_2 + \text{H}_2$ (Me = Metal) hydrogen chloride is reduced to give hydrogen and metal chloride. Gaseous hydrogen was drawn out from the reaction system and the metal chloride dissolved in the electrolyte, where it was electrolysed to give chlorine and metal using molten metal as a cathode. The metal was recovered on the cathode in a molten state and re-used for the former reaction. Bench scale tests were also carried out, where zinc was used as a molten metal cathode and the cell capacity was about 50 A. The cell voltage was 6.5 V at 50 A (working temperature 560°C, distance between anode and cathode 5 mm) and in this case, the ohmic loss was about 70%. The current efficiency was about 90% (anodic current density 200 A/dm$^2$) when the working temperature was 500°C and electrode distance between anode and cathode was 18 mm.

This method seems very promising on the basis of the above-mentioned data.

Introduction

In Part 1 (p. 245), the direct electrolysis of hydrogen chloride gas using a molten salt as the electrolyte was reported. We would propose another new method, in which two successive reactions occur; i.e. chemical reduction of hydrogen chloride by molten metal followed by electrolysis of the metal chloride formed. This method has not only the advantages described previously but also the following merits.

1. A diaphragm is not necessary, which is the main cause of ohmic loss.

2. A gas diffusion-type electrode is not necessary. These need delicate care in order to get a continuous and most effective gas flow rate, to prolong the life-time of the electrode.

Method and apparatus

Hydrogen chloride gas is bubbled into a molten metal which is in the form of a pool on the bottom of the cell under the molten salt of lithium chloride (58 mol%) - potassium chloride (42 mol%), resulting in the reaction,

$$\text{Me} + 2\text{HCl} = \text{MeCl}_2 + \text{H}_2$$ (1)

where Me = Metal.

Hydrogen is drawn out from the reaction system as a gas, and the metal chloride produced dissolves in the molten salt electrolyte. It is electrolysed there, with the molten metal acting as the cathode.

Metal is recovered on the cathode in a molten state according to the reaction.

$$\text{MeCl}_2 = \text{Me} + \text{Cl}_2$$ (2)

and re-used as the reactant for the reaction (1).

Compared to other indirect electrolysis methods using aqueous solutions, the reaction rate of the reaction part is very much higher owing to the high temperature and also to the gas-liquid reaction involved, so that much more current can be obtained for the same electrolytic...
Graphite is used as an anode. Fig. 1 shows the experimental cell. Fig. 2 shows the principle of a reaction part.

**Zinc as a molten metal cathode**

*Reaction between zinc and hydrogen chloride*

Fig. 3 shows the relationship between hydrogen chloride gas flow rate and hydrogen evolution rate, when the apparatus shown in Fig. 2 is used. The conversion efficiency of hydrogen chloride to hydrogen is calculated according to the equation

$$Zn + 2HCl = ZnCl_2 + H_2$$

(3)

and summarized in Table 1.

**Table 1. Conversion efficiency of hydrogen chloride to hydrogen**

<table>
<thead>
<tr>
<th>HCl gas flow rate (ml/min)</th>
<th>H_2 evolution rate (ml/min)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>33.0</td>
<td>7.7</td>
<td>46.7</td>
</tr>
<tr>
<td>65.0</td>
<td>13.3</td>
<td>40.9</td>
</tr>
<tr>
<td>125.0</td>
<td>18.7</td>
<td>29.9</td>
</tr>
<tr>
<td>185.0</td>
<td>21.8</td>
<td>23.6</td>
</tr>
<tr>
<td>240.0</td>
<td>25.0</td>
<td>20.8</td>
</tr>
<tr>
<td>325.0</td>
<td>30.7</td>
<td>18.8</td>
</tr>
</tbody>
</table>

Hydrogen evolution rate increases as the supplying rate of the hydrogen chloride gas increases, but conversely the conversion efficiency decreases. In order to increase this efficiency, the method of supplying gas must be improved. In our experiment, the stirring of the solution is also...