A molten salt electrolytic process for recovering chlorine and ammonia from ammonium chloride. I.

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Various electrolytic methods were examined for recovering chlorine, hydrogen and ammonia from by-product ammonium chloride produced in the ammonium chloride–soda process. Two methods, one based on an aqueous electrolysis and the use of an ion exchange membrane, and the other employing a molten metal cathode were considered possible. This series of papers aims at a detailed description of the latter process, which seems more interesting from the viewpoint of industrial exploitation. This paper briefly reviews the other electrolytic processes before describing the principle of the molten salt process and the study of the reaction between ammonium chloride and liquid metals.

1. Introduction

The ammonium chloride–soda process for producing soda-ash shown in Fig. 1, is a very effective process, due to its high sodium chloride utilization. In this process ammonia is one of the main raw materials, whereas the ammonium chloride by-product is not particularly valuable. Since chlorine is widely used for the chlorination of organic compounds it seems advantageous to recover chlorine, ammonia and hydrogen from the ammonium chloride and to recycle the ammonia to the ammonium chloride–soda process. Electrolytic processes seemed interesting for this purpose, and this paper outlines a suitable ammonium chloride electrolysis process and provides the basic data required for its design.

2. Preliminary studies

Some preliminary studies were carried out to find the most suitable electrolytic process for our purpose.

2.1. *Aqueous solution electrolysis with diaphragm cell*

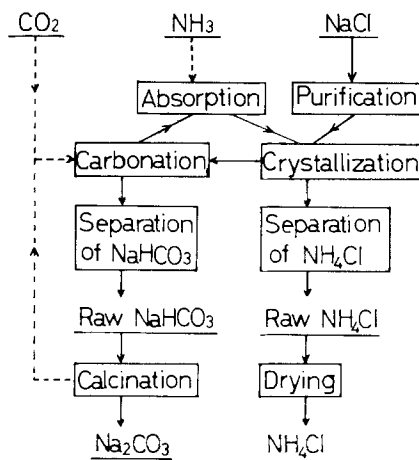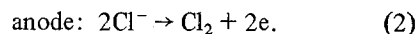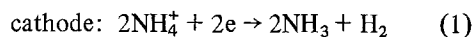When an aqueous solution of ammonium chloride

Fig. 1. Block diagram of ammonium chloride–soda process.

is electrolyzed, chlorine, ammonia and hydrogen are the expected products,

$$\text{cathode: } 2NH_4^+ + 2e \rightarrow 2NH_3 + H_2 \quad (1)$$

$$\text{anode: } 2Cl^- \rightarrow Cl_2 + 2e. \quad (2)$$

Unfortunately, many side reactions can occur (Reactions 3–8) even if a diaphragm is used between the anode and the cathode, and the current efficiency is reported to be only about 10–45% in earlier studies [1, 2].
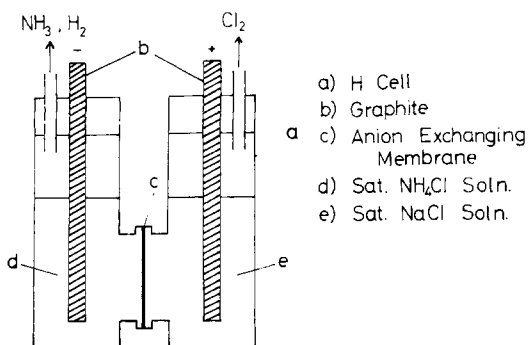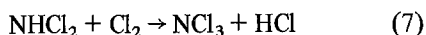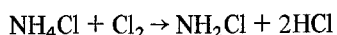
Fig. 2. Ion exchange membrane cell (25° C).

$$NH_4Cl + Cl_2 \rightarrow NH_2Cl + 2HCl \quad (3)$$

$$3NH_2Cl \rightarrow N_2 + NH_4Cl + 2HCl \quad (4)$$

$$4NH_2Cl \rightarrow N_2 + 2NH_4Cl + Cl_2 \quad (5)$$

$$NH_2Cl + Cl_2 \rightarrow NHCl_2 + HCl \quad (6)$$

$$NHCl_2 + Cl_2 \rightarrow NCl_3 + HCl \quad (7)$$

$$8NHCl_2 \rightarrow 3N_2 + 2NH_4Cl + 7Cl_2. \quad (8)$$

Therefore, this process requires some ingenious technological developments (e.g. effective bulk flow of raw material ammonium chloride solution) before it could be commercially successful.

2.2. Aqueous solution electrolysis with ion exchange membrane

When an anion exchange membrane was used to avoid the side reactions (see cell in Fig. 2), chlorine gas is obtained from the anode compart-

ment and ammonia from the cathode compartment, almost quantitatively, although the resistance of the membrane was found to be rather high. This process may therefore be possible if a high quality membrane is developed in the future.

2.3. Molten salt direct electrolysis

Ammonium chloride is a solid at room temperature and it sublimes at 340° C. However, it forms a liquid phase when mixed with other chlorides [3]. The possibility of direct electrolysis of such a molten salt was examined using several types of cell as shown in Fig. 3.

In cell 1, graphite electrodes were used for both cathode and anode. In cell 2, a skirt was used to separate the cathode and anode, and a nickel cathode was used to lower the hydrogen overvoltage and prevent zinc deposition.

Cell 3 was almost the same as cell 2, except that a graphite cathode was again used since no zinc deposition is possible from a LiCl–NH_4Cl molten mixture. Table 1 shows the current efficiencies obtained by constant current electrolysis with such cells. Chlorine evolved at the anode reacts with ammonium chloride according to Equation 3, to produce monochloramine (NH_2Cl), which decomposes further according to Reaction 4; hydrogen chloride was obtained as a by-product according to the following total reaction:

$$2NH_4Cl + 3Cl_2 \rightarrow N_2 + 8HCl. \quad (9)$$
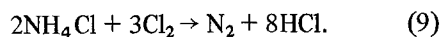
The current efficiency for hydrogen chloride

a) Graphite
b) Pyrex Holder
c) Pyrex Beaker
d) Nickel
e) Electrolyte
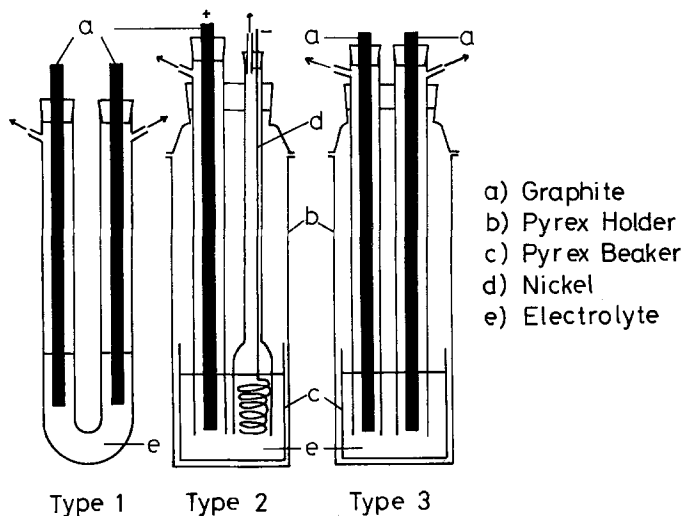
Type 1   Type 2   Type 3   Fig. 3. Electrolytic cells.

Table 1. Current efficiency

| Run	Electrolyte	Cell	Temperature ($^{\circ}$ C)	Current (A)	Current efficiency (%)		
					Cl_2	HCl	NH_3
1	$NH_4Cl–ZnCl_2$	1	280	0.7	21	5	–
2	$NH_4Cl–ZnCl_2$	1	270	1.0	18	14	–
3	$NH_4Cl–ZnCl_2$	1	270	1.0	27	9	–
4	$NH_4Cl–ZnCl_2$	1	250	1.0	19	5	–
5	$NH_4Cl–ZnCl_2$	2	260	1.0	5	8	–
6	$NH_4Cl–LiCl$	3	320	1.0	–	86	83

evolution given in Table 1 was calculated according to Equation 9, When $NH_4Cl–ZnCl_2$ was used as an electrolyte, both hydrogen chloride formation and zinc deposition were observed. Only a small amount of ammonia was obtained, perhaps due to the high solubility of ammonia in this melt. In the $NH_4Cl–LiCl$ system, ammonia was obtained with a current efficiency of more than 83%, which might be explained by the lower solubility of ammonia in the electrolyte. While the results shown in Table 1 might be interesting, they do not permit the design of a practical cell.

2.4. Molten metal cathode method

This method is a modification of our molten metal cathode method of recovering chlorine from hydrogen chloride [4]. Ammonium chloride reacts with a molten metal, forming ammonia, hydrogen and a metal chloride, and the metal chloride dissolves in the electrolyte, where it may be electrolyzed to produce chlorine and the metal. For example, when zinc is used as a reducing agent, ammonia, hydrogen and zinc chloride are produced according to the following:

$$2NH_4Cl + Zn \rightarrow 2NH_3 + H_2 + ZnCl_2. \quad (10)$$
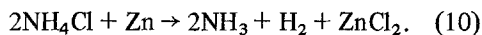
Ammonia and hydrogen gas are removed from the system, and the zinc chloride dissolves into the electrolyte, where it is electrolyzed according to the equation

$$ZnCl_2 \rightarrow Zn + Cl_2. \quad (11)$$
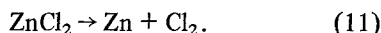
Zinc is recovered on the molten zinc cathode and reacts further. A molten metal seems the most suitable reducing agent because of:

(a) the effective contact with the ammonium chloride gas;

(b) the absence of dendrite formation on the cathode, and hence the constant cell geometry;

(c) its good electrical contact with the current feeder.

Fig. 4 shows a scheme for this process. The possibility of this process from the voltage balance viewpoint was already confirmed by the authors [4] with the cell shown in Fig. 5 (e.g. terminal voltage of 2.0 V at 30 A dm^{-2} at the cathode). The current efficiencies at both anode and cathode were found to be more than 90%. This process seems very promising because of the high reaction rate due to the gas–liquid three-dimensional reaction and because of the undivided electrolysis cell.

The above experiments show that the aqueous solution electrolysis with an anion exchange membrane and the molten metal cathode method seem promising. In addition to these methods, the direct ammonium chloride gas electrolysis using a
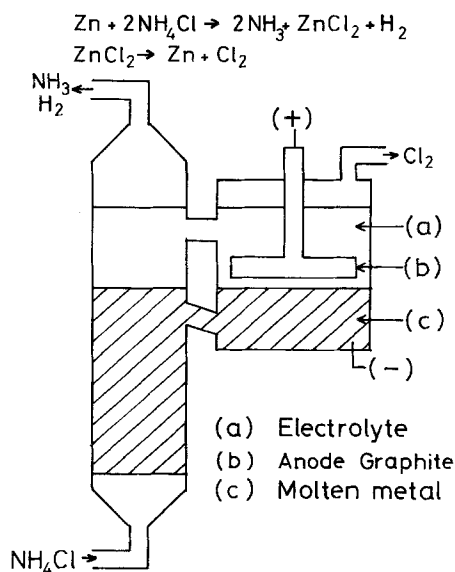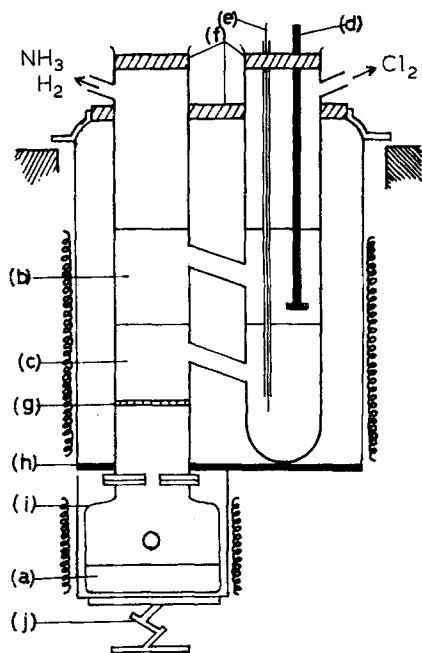

Fig. 4. Diagram of electrolytic cell.

(a)	Solid NH$_4$Cl	(f)	Silicon rubber
(b)	Electrolyte(LiCl-KCl)	(g)	Glass filter
(c)	Molten metal	(h)	Asbest
(d)	Anode (graphite)	(i)	NH$_4$Cl feeding
(e)	Cathode lead		beaker
	(stainless steel)	(j)	Jack

Fig. 5. Experimental cell with NH$_4$Cl sublimation chamber. Cell temperature 450° C, sublimation chamber temperature 34° ~ 38° C.

gas diffusion type electrode, and a direct molten salt electrolysis using an ion selective permeable ceramic membrane such as β-alumina, might also be possible. In this paper the molten metal cathode method will be examined further.

3. Reaction between ammonium chloride and liquid metal

For the design of the electrolytic cell a quantitative understanding of the reaction between the ammonium chloride and the liquid metal is very important. Hence in this section, quantitative experimental results and some discussion of this reaction are reported.

3.1. *Experimental method and results*

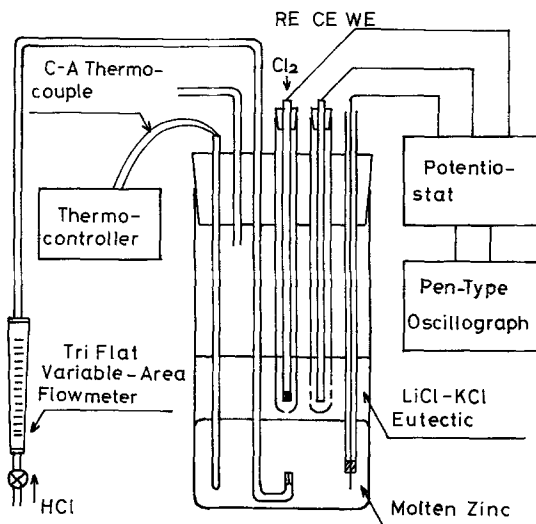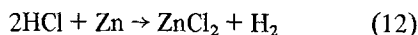The basic study of this gas–liquid reaction was carried out in the experimental column shown in Fig. 6.

Fig. 6. Experimental column.

Hydrogen chloride was chosen as a model reactant gas. When the hydrogen chloride gas was bubbled through the top hole of the pyrex glass capillary into the liquid zinc, this gas bubble grows and simultaneously reacts with the liquid zinc. It then leaves the capillary, rises and the reaction continues. The rate of this reaction was measured and plotted in Fig. 7. This reaction is

$$2HCl + Zn \rightarrow ZnCl_2 + H_2 \qquad (12)$$

The hole diameter was set as 0.25 mm, when stable gas bubbling was obtained. In order to

HCl Gas Flow Rate (ml / min at 450°C)

Height of Zinc; o: 2·5cm, ●:5cm, ▲:10cm

—— :Calculated Curves with
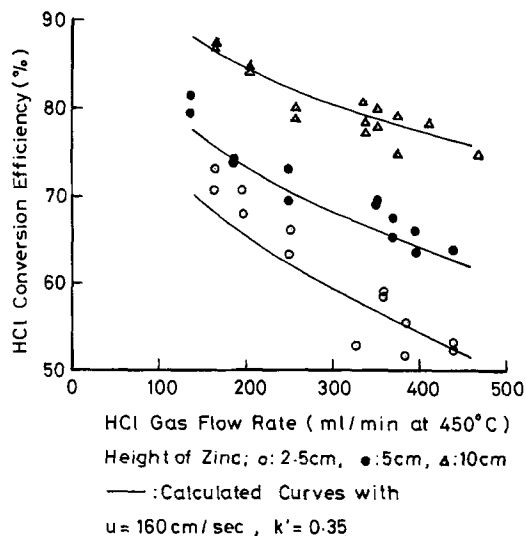
u = 160 cm/sec , k'= 0·35

Fig. 7. HCl conversion efficiencies under various conditions.

avoid a concentration change of zinc chloride during the experiment, a potentiostatic electrolysis was carried out to electrolyze zinc chloride to produce zinc and chlorine.

3.2. Reaction model

To analyze such data, the reaction model shown in Fig. 8 is effective.

Let us write n_1 for the number of moles of hydrogen chloride and n_2 for the hydrogen gas product. Then, during the time between 0 and τ, where τ is the time required for the complete bubble growth, the following equation holds.

$$\frac{dn_1}{dt} = \Phi - kpS. \tag{13}$$

Here, Φ is the feed rate of hydrogen chloride gas through the capillary, S, the surface area of bubble, p, the partial pressure of hydrogen chloride, and k is the rate constant for Reaction 11. After the bubble leaves the capillary, i.e. $\tau \leqq t$, the following equation holds:

$$\frac{dn_1}{dt} = -kpS \tag{14}$$

Furthermore, surface area S is related to the bubble volume V by

$$S = \alpha V^{2/3} \tag{15}$$
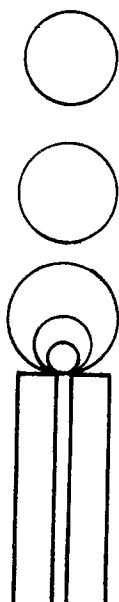
where

$$\alpha = (36\pi)^{1/3}$$

Fig. 8. Reaction model.

$$n_1 + 2n_2 = t\Phi \tag{16}$$

and if we can assume ideal gas model for both hydrogen chloride and hydrogen, the following equation holds, where P is the total pressure.

$$PV = (n_1 + n_2)RT \tag{17}$$

Taking into account Equation 15, Equation 13 is rewritten as

$$\frac{dn_1}{dt} = \Phi - k'n_1(n_1 + t\Phi)^{-1/3} \tag{18}$$

and Equation 14 is rewritten as

$$\frac{dn_1}{dt} = -k'n_1(n_1 + t\Phi)^{-1/3}. \tag{19}$$

Here, k' is the constant

$$k' = k\alpha(2p)^{1/3}(RT)^{2/3}.$$

This apparent rate constant k' can be obtained by a trial and error method for solving the differential equations, Equations 18 and 19, in which the bubble rise rate u should be included and this value is also estimated by a trial and error method.

Thus, assuming a value of k', numerical solution of Equations 18 and 19 gives an n_1 value as a function of the time as shown in Fig. 9.

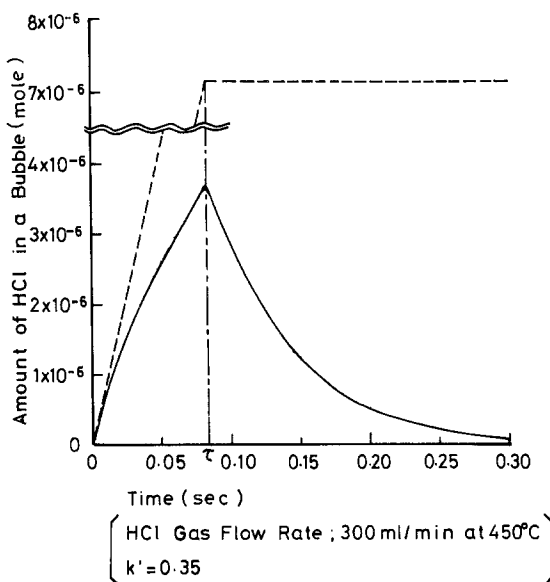Assuming now the value of u, the hold-up time of bubble τ' is expressed as

$$\tau' = h/u$$

Fig. 9. Theoretical relationship between time and amount of HCl in a bubble.
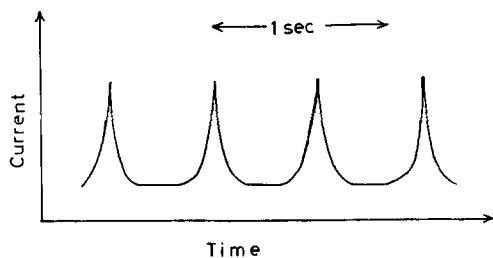
Fig. 10. Current–time curve under potentiostatic conditions.

Table 2. Conversion efficiency ratio experimental: theoretical (height of zinc 5 cm)

Flow rate of HCl (ml min^{-1})	Partial pressure of HCl	
	1 atm	1/16 atm
150	1.02	1.05
330	1.03	1.16

where h is the height of liquid metal. And the total amount of hydrogen chloride at the time $(\tau + \tau')$ can be read graphically; i.e. the efficiency of hydrogen chloride conversion can be calculated. Such a procedure was repeated until the most suitable combination of k' and u is found, i.e., the calculated n_1 value and experimentally obtained n_1 value coincide. The values found were $k' = 0.35$ and $u = 160$ cm s^{-1} and using these values the lines are drawn in Fig. 7. The agreement between the observed and calculated values is reasonable. The τ value, necessary for the above calculation is obtained as follows. During the potentiostatic electrolysis, the liquid metal–molten salt interface is stirred rapidly at the moment when the bubble goes from the liquid metal phase into the molten salt phase, and a sudden current change was observed as shown in Fig. 10.

The peak-to-peak time corresponds to the time τ (see Fig. 11). From this figure, the τ value at various hydrogen chloride feed rates can be obtained.
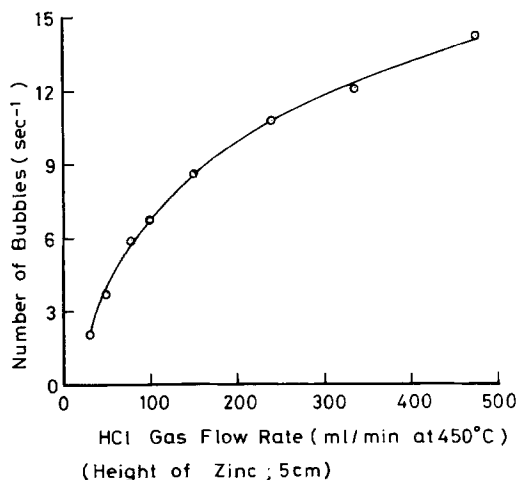
3.3. Partial pressure dependence of k' and u values

By diluting the hydrogen chloride gas with argon gas, the dependence of k' and u values on the partial pressure of the hydrogen chloride gas was examined.

Table 2 shows the ratio of experimental to calculated conversion efficiency ratio when the same value of k' and u as above were assumed. Fairly good coincidence is observed and the constancy of k' and u values at various partial pressures of hydrogen chloride was confirmed.

3.4. Experiment using ammonium chloride gas

At our experimental temperature of $450°$ C, ammonium chloride dissociates to ammonia gas and hydrogen chloride gas, and if it can be regarded as a mixture of ammonia and hydrogen chloride gas, the expected conversion efficiency is shown in Fig. 12.
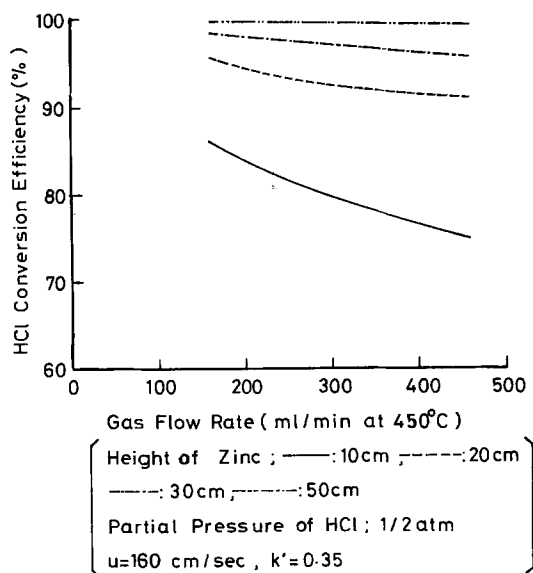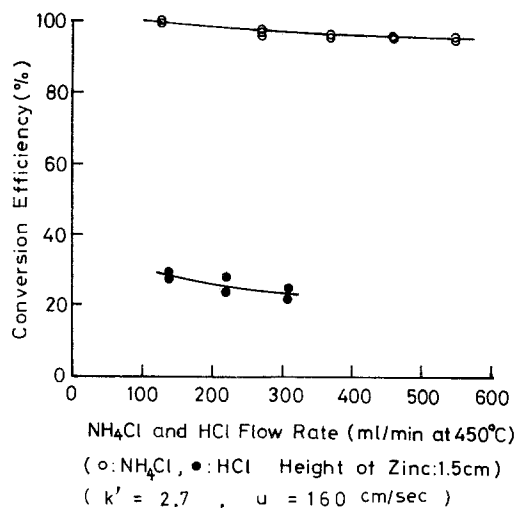

Fig. 11. Number of bubbles at various HCl gas flow rates.

Fig. 12. Calculated HCl conversion efficiency.

Fig. 13. NH_4Cl and HCl conversion efficiency.

Table 3. Dimensions for reaction column

Cell capacity	100 A
Conversion efficiency	99.6%
Flow rate at 450° C	7.381 min^{-1}
Number of bubbling centres	25
Height of zinc	50 cm

In fact, the experimental data shown in Fig. 13, lead to larger k' values. This large difference may arise because the hydrogen chloride does not dissolve into the metal chloride produced and the low mass transfer of hydrogen chloride through this chloride film may cause a low k' value. On the other hand, ammonium chloride can dissolve in the chloride easily and the mass transfer rate might be accelerated if this were to happen.

4. Conclusions

From the above experimental results and discussion, it can be seen that the molten metal cathode method for recovering chlorine and ammonia from ammonium chloride is promising. As an example of the basic data required for scaling-up this process, some dimensions of the reaction column are summarized in Table 3, for a 100 A bench scale electrolytic cell. Here, an ammonium chloride conversion efficiency of 99.6% is assumed.

Acknowledgement

References

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[2] C. B. F. Young and E. G. Lundstrom, Trans. Electrochem. Soc. 81 (1942) 175.
[3] K. Hachmeister, Z. Anorg. Chem. 109 (1919) 145.
[4] S. Yoshizawa, Z. Takehara, Y. Ito and A. Yamano, Denki Kagaku 39 (1971) 331.