

ELECTROWINNING ZINC FROM CHLORIDE MELTS IN BIPOLAR CELL^①

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ABSTRACT Molten salt electrolysis of zinc chloride has been studied and optimum conditions of electrolysis have been found out. Highly efficient bipolar cell has also been successfully designed. Thus the lowest power consumption in the world, 1.77 kW·h/kg Zn, has been achieved. More than 40 pct of dc electricity can be saved compared with current commercial electrolysis of aqueous solution of zinc sulphate.

Key words: zinc molten salt electrolysis bipolar cell

1 INTRODUCTION

In order to reduce the air pollution due to sulphur dioxide, and to reduce the cost and energy requirement for zinc production, a molten chloride electrolysis preceding a leaching process has been developed^[1-3] in Reno Research Center, U. S. Bureau of Mines in 1970 s' and 80 s'. Numerous papers covered physical and chemical properties of zinc chloride and its mixtures^[4, 5] have been published.

Although energy consumption of 2.6 kW·h/kg Zn^[1] was achieved in monopolar cells of lab. scale, energy consumption of pilot plant was 4.6 kW·h/kg Zn in monopolar cells and 3.75 kW·h/kg Zn in bipolar cells respectively^[3], both are higher than the typical value of 3.15 kW·h/kg Zn required by the present commercial electrowinning of zinc from aqueous solution of zinc sulphate^[6]. This is unreasonable because the molten salt electrolysis of zinc chloride should be the one of lower power consumption for its smaller decomposition voltage and polarization, and for its higher current efficiency and electrolyte conductivity compared with those of aqueous solution electrolysis of zinc sulphate. Based on our study

on the bipolar cells^[7], we are sure that the application of bipolar cell to molten salt electrolysis of zinc chloride in order to reduce dc electricity required is promising.

2 EXPERIMENTAL PROCEDURE

ZnCl₂-NaCl-KCl ternary system was used as electrolyte, in which the concentration of ZnCl₂ was 35 mol.-% ~ 45 mol.-% in equal molar NaCl-KCl. All salts used were A. R. grade reagent supplied from BDH Chemical Ltd. In order to avoid hydrolysis of zinc chloride and to remove product of hydrolysis, a closed cell and dried hydrogen chloride were used. The desired amount of salt mixture was put into the cell and melted under flowing hydrogen chloride. The HCl was bubbled through the melt for 40 min before electrolysis. The HCl was taken from HCl cylinder, dried by two columns of molecular sieves.

When electrolytic current was off, dried hydrogen chloride was maintained inside the cell to minimize the reaction of zinc chloride with moisture and oxygen in the air. A zinc collector was used to minimize the effect of residual water contained in zinc chloride, be-

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cause only the taken out amount of salts in the zinc collector and the consumed amount of zinc chloride during electrolysis have to be added to the cell.

In order to save time, labour and materials, a monopolar cell was used to find out the optimum conditions of electrolysis. Then, a bipolar cell with three bipolar electrodes was used to confirmed the optimum conditions from the monopolar cell.

Current and cell voltage were measured by digital multimeters, respectively. Temperature was controlled and measured by Chromel-Alumel thermocouple.

Experiments were arranged according to an orthogonal array in which 3 factors with three levels each are contained. The selected factors and their levels for experiments are listed in Table 1. Every experiment was repeated once more for better accuracy of data.

Table 1 The selected factors and their levels

Factors	Level 1	Level 2	Level 3
Current density $D_c / A \cdot cm^{-2}$	0.2	0.3	0.4
Electrode spacing S / cm	1.5	2.5	3.5
Concn. of $ZnCl_2$ $C / mol. - \%$	35	40	45

3 EXPERIMENTAL RESULTS AND THEIR VARIANCE ANALYSIS

3.1 Monopolar Cell

Experimental data of monopolar cell are shown in Table 2 and the variance analysis of them was carried out in an IBM pc/AT.

The variance analysis showed that current density was found to be the most significant factor affecting power consumption, electrode spacing the second significant one, both in the confidence level of 99 pct, and concentration of zinc chloride the non-significant one. The smaller the current density and electrode spacing in the range of levels selected, the lower the power consumption.

The similar effects of selected factors on

Table 2 Results of monopolar cell

No.	Power consumption $/kW \cdot h \cdot kg^{-1}$		Cell voltage $/V$		Current efficiency $(\%)$	
	1st	2nd	1st	2nd	1st	2nd
	1	1.885	1.876	2.204	2.129	95.9
2	1.864	1.853	2.220	2.204	96.8	97.5
3	1.974	2.023	2.331	2.350	96.8	95.2
4	2.116	2.121	2.457	2.470	95.6	95.5
5	2.085	2.102	2.489	2.464	97.9	96.1
6	2.166	2.196	2.552	2.547	96.6	95.3
7	2.302	2.246	2.629	2.655	93.6	96.9
8	2.394	2.340	2.795	2.773	95.7	97.1
10	2.350	2.366	2.823	2.805	98.5	97.2

cell voltage were observed from the variance analysis. Again, the most significant one was current density, in confidence level of 99 pct, the second was electrode spacing, in confidence level of 95 pct, and concentration of zinc chloride had no significant effect. The smaller the current density and electrode spacing, the lower the cell voltage.

All selected factors at the selected levels showed no significant effect on current efficiency. In other words, the power consumption of molten salt electrolysis of zinc chloride containing melts mainly depended on cell voltage. A favourable point of bipolar cell against monopolar cell is its low cell voltage. If a bipolar cell with high current efficiency can be designed, molten salt electrolysis of zinc chloride with low power consumption can be achieved.

The optimum conditions were found to be current density $0.2 A/cm^2$, electrode spacing 1.5 cm, concentration of zinc chloride 40 mol.-% in equal molar KCl-NaCl melt. Fuming was observed in experiments of higher concentration of zinc chloride, while operational difficulties would be caused in experiments with lower concentration.

Using the optimum conditions, the lowest power consumption in the world, $1.881 kW \cdot h/kg Zn$, on molten salt electrolysis from chloride melts in a monopolar cell was obtained, and more than 40 pct of dc electricity

for electrolysis could be saved compared with the present commercial electrolysis of aqueous solution of zinc sulphate.

3.2 Bipolar Cell

Using the optimum conditions from monopolar cell, four times of experiments in a bipolar cell were carried out. Average values of experimental data of the bipolar cell with four compartments are listed in Table 3.

Table 3 Measured data in a bipolar cell with four compartments

No.	Av. CE (%)	Av. CV /V	Av. PC / kW·h·kg ⁻¹ Zn
1	97.1	2.09	1.76
2	95.9	2.08	1.78
3	95.9	2.07	1.77
4	94.7	2.04	1.77
Av.	95.9	2.06	1.77

note: $T = 773\text{ K}$; $C_{\text{ZnCl}_2} = 40\text{ mol.-%}$;

$D_c = 0.2\text{ A/cm}^2$; $S = 1.5\text{ cm}$;

CE = Current Efficiency; CV = Cell Voltage;

PC = Power Consumption

As expected, the power consumption were lower in bipolar cell than that in monopolar cell, but the differences were not so large. When the cells are extended, the differences would be much more significant. This will be discussed in detail below.

4 DISCUSSION

4.1 Purification of Zinc Chloride

In the early stage of electrowinning zinc from zinc chloride containing melts, many difficulties were encountered. When no measures were taken to avoid hydrolysis of zinc chloride and small open cell were used, very low current efficiency, poor coalescence of zinc deposited, sludge formation, and corrosion of the cell etc. were found very serious. In this work, all these problems have been overcome by full purification of molten salts and very good results were obtained. Similar results in the continuous electrolysis of pilot plant with use of simply purified zinc chloride^[3] and the

results of the glass corrosion^[8] have also shown the importance of the purification of molten salts.

4.2 Electrode Design

In the point of view of hydrodynamics, vertical electrodes should be the best ones for gas escaping. The increase of resistance in electrolyte and of cell voltage should be the minimal. In fact, this has been shown by Murphy^[9].

The vertical electrodes were tested by Haver *et al*^[1], but given up soon and then horizontal flat plates were used as electrodes which were found to be the worst for gas escaping^[9], and very high cell voltage was resulted as observed in experiments of pilot plant^[3].

4.3 A Comparison With Aqueous Solution Electrolysis of ZnSO₄

Compared with the present commercial electrolysis of aqueous solution of zinc sulphate, fused salt electrolysis of zinc chloride can save a lot of energy, as listed in Table 4.

Table 4 A comparison of energy requirements

Items	Aqueous solution	Fused salts	Amount saved
Emf	2.036 V ^[6]	1.572 V ^[10]	0.464 V
Polarization			
Cathodic	-0.062 V ^[6]	-0.062 V*	0 V
Edditives	-0.001 V ^[6]	0 V**	0.001 V
Anodic	0.840 V ^[6]	0.020 V ^[11]	0.820 V
Edditives	-0.216 V ^[6]	0 V**	-0.216 V
IR drop			
In electrolyte	0.594 V ^[6]	0.219 V*	0.375 V
In anodic mud	0.15 V ^[6]	0 V*	0.15 V
On electrodes		0.33 V**	-0.33 V
Cell Voltage	3.467 V ^[6]	2.203 V**	1.264 V
Cur. efficiency	90 % ^[6]	96 %**	6.7 %
Energy required	3.158 kW·h/ kg Zn ^[6]	1.881 kW·h /kg Zn**	1.277 kW·h /kg Zn

* Estimated values by this work

** Measured values by this work or no additives

It can be seen from Table 4 that the energy saving of fused salt electrolysis from zinc chloride was found to be 40 pct as high as the

energy required by the aqueous solution electrolysis of zinc sulphate. However, one should note that the data for aqueous solution electrolysis were taken from commercial electrolytic cells, but those for molten salt electrolysis from a cell of lab scale. When the electrolytic cell is extended to a commercial scale, the power consumption would increase to some extent due to the following factors;

(1) For molten salt electrolysis, the IR drop in electrodes of a monopolar cell of commercial scale can be as high as 1~1.5 V, which are 3~4 times of that of this work. However, the average IR drop in electrodes for a compartment of a bipolar cell of commercial scale, U_m , can be evaluated by

$$U_m = [1.5 + (n - 1) \times 0.03]/n$$

where n is the number of the compartments of a bipolar cell. For $n \geq 9$, U_m is less than 0.2 V. Thus the cell voltage of a monopolar cell would increase significantly due to the increase on IR drop of electrodes, as the cell is extended to a commercial scale. But such an increase on IR drop of electrodes of a bipolar cell, is minimized, which is about 0.1 V.

(2) The IR drop in electrolyte would increase in both mono- and bipolar cells due to increasing of bubble fractions of anodic gas in the electrolyte, but this IR drop in molten electrolyte would not be larger than that in aqueous solution because of the higher conductivity of molten salts. In other words, for molten salt electrolysis of commercial scale, this IR drop would increase at the most by 0.3~0.4 V compared with this work.

It has been shown from above analysis that if molten salt electrolysis of zinc chloride is extended to commercial scale, the amounts

on energy saved would be quite different between monopolar and bipolar cells. Monopolar cell would be operated at almost the same cell voltage but a bit higher current efficiency compared with aqueous solution electrolysis of zinc sulphate, so the energy saving would not be much. While bipolar cell would be operated at lower cell voltage by 1 V and higher current efficiency by a few per cents compared with aqueous electrolysis of zinc sulphate. The power consumption of 2.0~2.1 kW·h/kg Zn can be expected in commercial scale, so that should be very attractive.

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