JOURNAL OF APPLIED ELECTROCHEMISTRY 3 (1973) 103–112

An investigation into the recovery of zinc from zinc chloride-sodium chloride mixtures by electrolysis

D. J. FRAY*

Research Department, Imperial Smelting Corporation Ltd, Avonmouth, U.K.

Received 14 July 1972 and in revised form 4 October 1972

The electrolysis of zinc chloride-sodium chloride mixtures to yield zinc and chlorine has been examined. The optimum electrolyte composition was found to extend from 75% to 60% zinc chloride. In order to obtain the maximum current and energy efficiencies, it was found necessary to use horizontal electrodes with perforations to allow easy escape of the electrolysis products.

1. Introduction

As part of a general programme of examining possible ways of extracting zinc, the electrolysis of zinc chloride has been investigated. In the early nineteen hundreds, Ashcroft [1] and Lacell [2], using multiple couple cells, electrolysed zinc chloride on a tonnage basis but found that silica accumulated in the melt, the electrodes were attacked and the current efficiency fell off after a few days' operation. These effects can be explained by the poor grade of zinc chloride used and the presence of zinc oxide. The chloride also contained substantial amounts of water, which when electrolysed gave off oxygen at the anode causing attack on the graphite. Generally, the difficulties experienced during the electrolysis are mainly created by the following properties of zinc chloride: hygroscopic behaviour, high vapour pressure, low electrical conductivity and high capacity for dissolving other salts.

Threlfall [3] also used multiple couple cells consisting of several graphite plates arranged so that they were isolated from one another. The voltage for each pair of plates reached a value of 2·4 V at the current density used (0·095 A cm^{-2}) and the electrolytic efficiency attained a maximum of 90% [1]. However, by far the most successful results on a pilot plant scale were obtained by the same investigator using a zinc chloride which had been thoroughly dehydrated, and robust wedge-shaped carbon anodes which engaged hard carbon cathodes. These cells were run for approximately 1 year yielding zinc at 4·536 kWh kg^{-1} with an electrochemical efficiency of 89%. At the end of this time, the cells were dismantled and found to be in near perfect condition.

On a laboratory scale, Kammel [4] electrolysed mixtures of zinc chloride in sodium chloride and potassium chloride and attained current efficiencies of 97–99% between 620°C and 720°C. In order to operate at such a high temperature, it was necessary to maintain the zinc chloride content below 40%, otherwise losses of zinc chloride would occur due to vaporization and, also, the dissolution of the deposited zinc would greatly decrease the electrolytic efficiency. According to Lorenz [5], the efficiency can be improved by increasing the distance between the electrodes, by means of a higher anode/cathode ratio, and by raising the current density to an optimum value which depends on the prevailing electrolytic conditions. Generally, as stated by Delimarskii and Markov [6], a rise in temperature leads to a drop in current efficiency due to increases in the solubility of the metal in the salt, lower viscosity and faster diffusion processes all

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* Now with the Department of Metallurgy and Materials Science, University of Cambridge, Cambridge, U.K.

resulting in increased chance of reaction between the products.

There is good agreement between the decomposition potentials calculated for cells of the type

$$Zn_{(l)}/ZnCl_2/Cl_2$$

and the experimentally determined decomposition voltage. On the addition of alkali halide, the decomposition voltage increases due to the reduced activity of the zinc chloride. Kammel [4] showed that at constant $ZnCl_2$ mole fraction, KCl lowers the zinc chloride activity more than NaCl probably because of its stronger tendency to form compounds with $ZnCl_2$. Overall, the $ZnCl_2$ decomposition voltage is more and more increased by adding to the bath LiCl, NaCl and KCl in that order. With regard to $ZnCl_2$-NaCl melts, there appear to have been no direct investigations into the variation of $ZnCl_2$ decomposition voltage with NaCl content in favourable concentration ranges of the electrolyte. Activity determinations by Yang and Hudson [7], and Flengas and Ingraham [8] were wholly confined to other salt mixtures with a $ZnCl_2$ content of 15 wt %. Bloom, Spurling and Wong [9] have determined the activities of $ZnCl_2$ in $ZnCl_2$-NaCl mixtures and showed that the system had strong negative deviations from Raoult's law. Using this data, together with the standard free energy of formation of zinc chloride, it is possible to calculate the decomposition potential for any melt composition.

As well as increasing the decomposition potential, the addition of alkali halides increases the conductivity of molten zinc chloride. Pure molten zinc chloride has a very low conductivity; Duke [10] measured 0·09 cm Ω^{-1} at 500°C and Eid [11] has studied the conductivity of NaCl-KCl-$ZnCl_2$ mixtures over a range of temperatures. Unfortunately, similar studies have not been performed on the $ZnCl_2$-NaCl system and, therefore, it is not possible to estimate the electrolyte composition which would give the highest energy efficiency.

It is advantageous to use sodium chloride instead of the other alkali halides as it would be cheaper and more readily available if the process were to be operated on an industrial scale. However, as it appeared that insufficient information was available to assess the likely current efficiencies and cell performances using a mixture of NaCl-$ZnCl_2$, it was decided to attempt a laboratory study of the electrolysis of the above salt mixture to obtain the optimum electrolyte composition and to examine the factors which control the energy efficiency. This information would be of considerable use in the design and construction of electrolytic cells.

The melting point of $ZnCl_2$ is 319°C and, on the addition of NaCl, the melting point of the mixture falls to 262°C at 67 wt % $ZnCl_2$. The melting point then rises nearly linearly up to the melting point of NaCl. In order to produce liquid zinc, it is necessary to work at temperatures greater than 419°C. As there are no technical advantages of working at very high temperatures due to increased volatility of $ZnCl_2$, increased heat losses and faster rate of attack of refractories, it was considered advisable to restrict the temperature of electrolysis to about 500°C. In order to allow an adequate difference between the melting point and the temperature of operation in case of slight variations in heat input, only mixtures melting below about 475°C (55% NaCl) have been investigated.

2. Experimental Procedure

Very pure $ZnCl_2$ was not available commercially so that technical grade zinc chloride of composition

0·01% Al	0·5% Ca	0·002% Cd	0·001% Cu
0·01% Fe	0·2% Mg	1% Na	0·01% Pb

had to be used. These figures are an average as the composition varied slightly with each batch. The sodium chloride used throughout these experiments was Analar grade.

As was mentioned in the introduction, one of the problems of electrolysing impure $ZnCl_2$ is the presence of oxide and water. The technique used to remove both these impurities was to bubble dry hydrogen chloride through the melt. The hydrogen chloride was taken from a gas cylinder, dried in concentrated sulphuric acid, passed into the fused salt and then through a cold trap to condense any volatile chlorides that might be formed and, finally, absorbed in sodium hydroxide solution. After about 4 h, the melt was considered sufficiently dry and the melt was then freed of excess hydrogen chloride by bubbling dried argon through the melt.

The zinc chloride melt was purified considerably by adding 99·99% zinc and stirring occasionally for 3 h. The final analysis was 1·0% Na, 0·001% Cd, 0·0001% Cu, 0·003% Fe, 0·001% Pb and 0·51 Ca.

The electrical circuit was very simple with the power from the mains supply being fed to a d.c. Mobile Rectifier set (Harmsworth, Townley and Co., Manchester). The d.c. current then passed directly into the cell and to check the accuracy of the ammeter, the potential drop across a shunt of known resistance was measured using a Cambridge potentiometer.

The Pyrex cell used for the electrolysis is shown in Fig. 1. The lid, which has 'Quickfit' multi-sockets, was clamped by a spring clip to a flanged two-litre beaker. The open socket shown in the diagram is for the escape of chlorine evolved during the electrolysis. The chlorine passed through a Liebig condenser to condense any zinc chloride vapour and then into an absorption unit. This unit contained calcium carbide which reacted with the chlorine in accordance with the equation

$$CaC_2 + Cl_2 = CaCl_2 + 2C.$$

Experimentally it was found that the reaction is strongly exothermic and virtually 100% efficient. It was found that in order for the reaction to proceed, the calcium carbide must first be heated to 200°C. With a flowrate of 1 l min^{-1}, the temperature quickly rose to 500°C, where the heat of reaction alone was sufficient to maintain this temperature. At no time were chlorine fumes detected passing out of the tube.

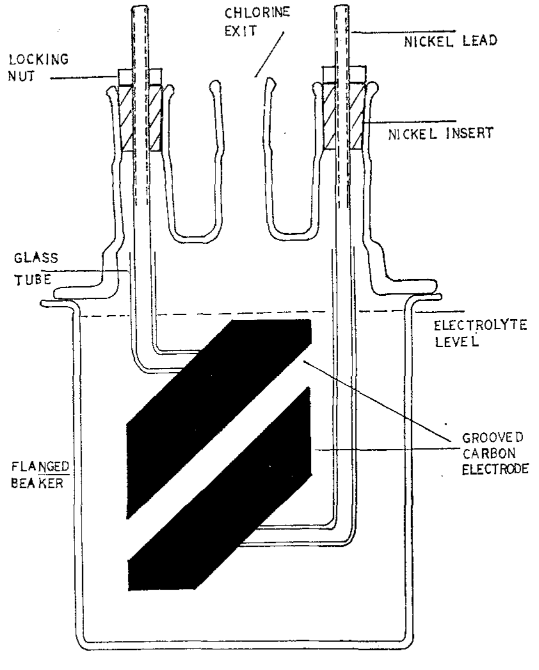

Fig. 1. Schematic diagram of cell.

The electrodes, except where otherwise stated, were made from high density amorphous carbon. The leads to the carbon blocks consisted of nickel rods, which were insulated from the electrolyte by Pyrex glass tubes sealed with alumina cement. All the vertical and 45° electrodes had a continuous series of tapered grooves cut in the faces to facilitate the escape of the reaction products. The grooves were about $\frac{1}{2}$ cm deep and $\frac{1}{2}$ cm across at the face of the electrodes. The current densities were calculated ignoring the increase in surface area due to the grooves. In the case of the vertical electrodes (7·6 cm × 6·35 cm × 3·8 cm) the surface area varied due to differences in the electrolyte level. The 45° cathode (7·6 cm × 9·51 cm × 3·8 cm) was slightly larger than the 45° anode (7·6 cm × 6·35 cm × 3·8 cm) and for the calculation of the current density the average surface area of 60·3 cm^2 was taken.

After melting and drying the electrolyte, the electrodes were introduced into the electrolyte and adjusted to give the correct depth of immersion and electrode spacing. The current was controlled by the rectifier and the electrolysis was allowed to proceed for a known time. The temperature in the furnace was maintained by a Kelvin Hughes controller operating a mercury on-off switch. The control thermocouple was maintained between the electrolysis cell and the furnace tube. Calibration showed that the temperature indicated on the controller was the true temperature. During a run, the temperature of the electrolysis cell varied by 8°C and using this simple experimental arrangement, it did not seem possible to improve on this figure. It was noticed that during the electrolysis sufficient heat was generated so that rarely was power applied to the furnace windings. When the current was switched off, there was always a residual voltage of about 1·7 V registered on the voltmeter measuring the potential across the electrodes.

After the electrodes were withdrawn, the salt layer was decanted from the metal. If some of the metal was inadvertently carried over with the zinc chloride, the salt was dissolved in water and the metal recovered. Any metal adhering to the cathodes was scraped off and added to the metal collected at the bottom of the electrolysis cell, which was then washed thoroughly, to remove any salt, and dried. The current and energy efficiencies were calculated as shown below.

The energy efficiency of the cell is defined by

$$\frac{D_0}{V_c}\frac{I_p}{I_c}\times 100\%$$

where D_0 is the decomposition potential, which for $ZnCl_2$ at 500°C is taken as 1·572 V, V_c is the cell voltage, I_p is the current calculated from the weight of zinc produced and I_c is the cell current. At lower temperatures the decomposition voltage was calculated using the formula given by Wachter and Hildebrand [12]. The formula was derived from data obtained between 500°C and 600°C but as the work of Wachter and Hildebrand is considered to be the most accurate, only a small error will be introduced by using the formula outside its temperature range. The current efficiency is defined by

$$\frac{I_p}{I_c}\times 100\%$$

In the case where a molten cathode was used, a similar procedure was adopted except that the weight of metal initially added was recorded. Although the chlorine was collected as a chloride, no check was made on the anode current efficiency.

3. Results

3.1. *Determination of optimum electrolyte composition*

In order to obtain the range of compositions over which the highest efficiencies are obtainable, electrolysis was carried out with different electrolyte mixtures using bulky vertical electrodes; the results are shown in Table 1.

3.2. *Variation of voltage with current*

The voltage dependence on the current passing through the electrolyte can be calculated from the decomposition potential and the resistance of the melt. However, for zinc chloride-sodium chloride melts, neither of these parameters has been accurately measured. In order to vary the current, a Variac was inserted between the mains supply and the rectifier. Several runs were

Table 1. Variation of voltage with electrolyte composition. Bulky grooved vertical electrodes; electrode spacing 1·8 cm; temperature 500°C.

Melt composition (% $ZnCl_2$)	*Voltage (V)*	*Current (A)*	*Current* density ($A\ cm^{-2}$)*	*Current efficiency (%)*	*Energy efficiency (%)*
85	5·22	40·45	1·25	81·3	24·5
80	4·81	40·45	1·565	84·9	27·8
75	4·41	41·53	1·176	72·5	25·8
70	3·56	42·05	1·305	72·1	31·8
67	4·44	40·17	1·25	84·5	29·9
67	4·30	40·36	1·25	83·5	30·5
65	3·71	42·0	1·305	81·2	34·4
60	4·01	40·23	1·249	58·9	23·1
60	4·15	40·55	1·26	84·4	32·0
57·5	4·89	40·05	1·248	65·10	20·9
55	7·36	40·05	1·248	38·5	8·2

* The current density varies for the same number of amperes due to slight variations in electrolyte level.

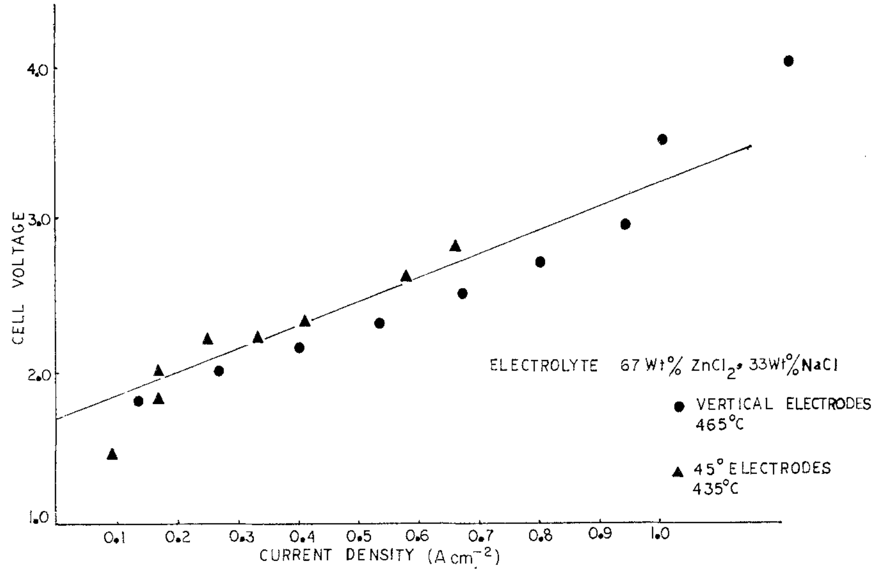

Fig. 2. Cell voltage versus current density.

performed using different electrodes and the results are shown in Fig. 2.

3.3. *Electrode arrangement to give maximum energy efficiency*

The electrolyses shown in Table 2, using large grooved electrodes held parallel at 45° to the horizontal, gave current efficiencies of the order of 60–80% and energy efficiencies around 35%. This results in an energy consumption of approximately 4·41 kWh kg^{-1} of zinc. Kammel [4] using horizontal electrodes, obtained high-current efficiencies of nearly 100% at 620°C. This is surprising as the solubility of Zn in $ZnCl_2$ is increased with increase in temperature and therefore it would be anticipated that the chance of the back reaction occurring between zinc and chlorine is likely to be enhanced. In an attempt to increase the energy and current efficiencies, it was decided to attempt to repeat the method of Kammel. The use of horizontal anode and cathodes had little effect on the efficiencies (Table 3) so twenty 0·6 cm diameter holes were drilled in the anode to facilitate the escape of chlorine (Table 4). Again, no apparent change in the efficiencies was observed. According to Lorenz [5] and Kammel [4] the efficiency of the electrolysis increases with increase in electrode gap and, also, increase in the ratio anode area/

Table 2. Cell characteristics using 45° grooved carbon electrodes. Electrolyte composition 67 wt % $ZnCl_2$, 33 wt % NaCl; temperature 450°C.

Electrode spacing (cm)	*Current (A)*	*Voltage (V)*	*Current density ($A\ cm^{-2}$)*	*Current efficiency (%)*	*Energy* efficiency (%)*
1·0	51·0	2·66	0·846	52·0	31·4
2·0	53·6	2·82	0·889	75·0	42·8
2·0	68·9	3·51	1·143	78·6	36·0
2·0	51·3	3·33	0·851	74·5	35·9
2·0	69·0	3·48	1·144	69·5	32·1

* Decomposition potential of $ZnCl_2$ taken as 1·607 V at 450°C.

Table 3. Cell characteristics using horizontal carbon anode, 7·62 cm square and 1·9 cm thick, and zinc cathode. Electrolyte composition 67 wt % $ZnCl_2$, 33 wt % NaCl; temperature 500°C.

Area of zinc cathode (cm^2)	*Area of carbon anode* (cm^2)	*Electrode spacing* (*cm*)	*Current* (*A*)	*Voltage* (*V*)	*Current density on anode* ($A\ cm^{-2}$)	*Current efficiency* (%)	*Energy efficiency* (%)
127	58	2·0	51·2	6·3	0·883	76·3	19·0
127	58	2·0	61·0	6·25	1·052	76·4	19·2

Table 4. Cell characteristics using horizontal carbon anode with chlorine escape holes. Electrolyte composition 67 wt % $ZnCl_2$, 33 wt % NaCl; temperature 500°C.

Area of zinc cathode (cm^2)	*Area of carbon anode* (cm^2)	*Electrode spacing* (*cm*)	*Current* (*A*)	*Voltage* (*V*)	*Current density on anode* ($A\ cm^{-2}$)	*Current efficiency* (%)	*Energy efficiency* (%)
127	58	2·0	57·8	6·7	0·997	78·5	18·4

Table 5. Cell characteristics using small liquid zinc cathode. Electrolyte composition 67 wt % $ZnCl_2$, 33 wt % NaCl; temperature 500°C.

Ratio of anode area: cathode area	*Electrode spacing* (*cm*)	*Current* (*A*)	*Voltage* (*V*)	*Current density on anode* ($A\ cm^{-2}$)	*Current efficiency* (%)	*Energy efficiency* (%)
1·1	2	55·4	6·93	0·955	72·5	16·4

Table 6. Characteristics of cell with perforated anode and low electrolyte level. Electrolyte composition 67 wt % $ZnCl_2$, 33 wt % NaCl; temperature 500°C.

Area of zinc cathode (cm^2)	*Area* of carbon anode* (cm^2)	*Electrode spacing* (*cm*)	*Current* (*A*)	*Voltage* (*V*)	*Current density on anode* ($A\ cm^{-2}$)	*Current efficiency* (%)	*Energy efficiency* (%)
127	58	2·4	44·24	6·13	0·763	91·1	23·4
127	58	2·4	42·3	7·00	0·729	83·8	18·8
127	58	2·25	44·20	5·4	0·762	83·5	24·3
127	58	2·0	45·00	5·4	0·776	84·9	24·7
127	58	2·0	45·00	5·3	0·776	84·3	25·0
127	58	1·7	43·00	6·36	0·741	88·1	21·8
127	58	1·7	45·00	5·00	0·776	89·0	28·0
127	58	2·0	43·9	3·41	0·757	93·0	42·9
127	58	2·75	41·5	5·25	0·716	92·0	27·5
127	58	2·75	42·57	4·63	0·734	95·9	32·6

* Ignoring surface area of the holes.

Table 7. Characteristics of cell with perforated anode and cathode. Electrolyte composition 67 wt % $ZnCl_2$, 33 wt % NaCl; temperature 500°C.

Area of carbon cathode (cm²)*	*Area* of carbon anode (cm²)*	*Electrode spacing (cm)*	*Current (A)*	*Voltage (V)*	*Current density on anode A cm⁻²*	*Current efficiency (%)*	*Energy efficiency (%)*	*kW h kg⁻¹ Zn*
58	58	2·0	44·5	3·29	0·767	95·6	45·7	2·82
58	58	2·0	45·15	2·82	0·778	91·7	51·1	2·51
58	58	2·0	45·1	2·92	0·776	90·1	48·5	2·66

* Ignoring surface area of holes.

cathode area. In order to investigate this suggestion, the zinc cathode was held in a small beaker beneath the anode. As this gave no improvement in current efficiency (Table 5), it was decided to lower the level of the melt to just below the top of the perforated anode in order to have minimum contact of chlorine with the electrolyte (Table 6). This was effective and in order to reduce the back reaction still further, the zinc was removed from the cathode as soon as it was formed by drilling holes in a horizontal carbon cathode (Table 7).

On an industrial scale, it may not be possible to operate with holes drilled in the anode and, therefore, attempts were made to use porous anodes. Initially it proved very difficult to attach the porous electrode and the first runs were carried out by screwing the nickel lead directly into the anode but, after a short while, the thread in the porous carbon failed. The problem was eventually overcome by securing the nickel lead into a small wedge-shaped piece of the amorphous carbon which then slotted into the softer graphite. This procedure, however, led to higher voltage losses, as is shown in Table 8.

4. Discussion of Results

From Table 1 it can be seen that there is a large range of compositions over which the voltage across the cell is a minimum. This extends from approximately 25% NaCl to 40% NaCl and shows that accurate control of the electrolyte composition is not necessary. On the addition of NaCl to pure $ZnCl_2$ the conductivity decreases considerably but, at the same time, the decomposition potential for $ZnCl_2$ increases due to the reduced activity of $ZnCl_2$. Table 1 shows that opposing effects of increased decomposition potential and decreased resistance results in a minimum in the voltage which extends over a reasonable range of composition.

The variation of voltage with current density is essentially linear (Fig. 2) and extrapolating the plot to the ordinate gives a decomposition voltage of 1·7 V for the 67% $ZnCl_2$:33% NaCl

Table 8. Characteristics of cell with porous anode material. Electrolyte composition 67 wt % $ZnCl_2$, 33 wt % NaCl; temperature 500°C.

Area of zinc cathode (cm²)	*Area of carbon anode (cm²)*	*Electrode spacing (cm)*	*Current (A)*	*Voltage (V*	*Current density on anode (A cm⁻²)*	*Current efficiency (%)*	*Energy efficiency (%)*
127	58	2·5	43·36	3·89	0·748	87·2	35·2
127	58	1·8	42·1	4·47	0·726	93·43	32·9
127	58	1·8	41·33	4·76	0·713	95·95	31·6
127	58	1·9	44·3	4·93	0·764	87·52	27·9
127	58	2·0	44·95	4·33	0·775	89·6	32·5

mixture. This voltage is higher than the decomposition potential given by Wachter and Hildebrand [12] as the zinc chloride has an activity of less than unity in the salt mixture. Calculation shows that a value of 1·7 V is to be expected. Some preliminary work using electrodes giving the same surface area but being much thinner gave a non-linear plot. This was originally thought to be due to Cl_2 sweeping away the electrolyte from the anode but the work of Heppenstall and Shutt [14] has shown that this effect does not occur until a current density of 10 A cm^{-2} is reached. By decreasing the resistance of the anodes by increasing the thickness, this anomaly disappeared. This demonstrates the dangers of working on too small a scale where extraneous effects become apparent. No other work has been performed on this particular composition but Kammel, using equimolar NaCl–KCl mixtures at 700–900°C with up to 50 wt % $ZnCl_2$, found similar decomposition potentials. The slope of the plot gives a rough estimate of the conductance of the melt. This figure is found to be 1·2 Ω^{-1} cm^{-1} for the 67 wt % $ZnCl_2$ mixture at 500°C which can be compared with the value obtained by Kammel at 500°C for a 55 wt % $ZnCl_2$, 25 wt % NaCl and 20 wt % KCl mixture of 1 Ω^{-1} cm^{-1}. In both cases, the melts were saturated with zinc but this has been shown by Emons and Tantz [14] not to affect the conductance.

When the current was switched off, the voltmeter registered a residual voltage of 1·7 V, which is approximately the same as the decomposition potential and was thought to be due to the back e.m.f. of the cell

$$Zn_l/ZnCl_2/Cl_2$$

Kammel observed similar values of residual voltage.

The most important fact arising from the measurements shown in Table 2 is the poor current efficiencies attained during the electrolysis. Compared with the runs with the bulky vertical electrodes, the 45° electrodes do not give such good current efficiencies. This may be because the electrolysis products do not escape from the electrodes quite so readily. From the measurements reported in Table 2, the best current efficiency was 78% with an average efficiency of 73%. The current efficiency can be increased by increasing the electrode spacing but, unfortunately, due to the larger IR drop in the melt, the energy efficiency did not increase correspondingly. Rotinyem *et al.* [15] have shown that increasing the interelectrode spacing beyond 1 cm had little effect on the current efficiency. Comparing these data with other measurements using $ZnCl_2$, it is found that Kammel [4] obtained about 98% whilst Lacell [2], who used a very impure melt, attained, on average, about 75%. Similarly, Threlfall [3], using large wedge-shaped electrodes, obtained current efficiencies of 89·3% over 1 year's operation.

The current losses found in the electrolysis of fused salts are usually associated with mechanical losses at the electrodes, dissolution of metal in the fused salt and combination of the electrolysis products into the original salt. According to Delimarskii and Markov [7] no concentration polarization occurs, except at very low concentrations. As was mentioned in the experimental section, care was taken to collect all the zinc deposited. The solubility of zinc in zinc chloride is low—Gregorzyk found 0·8 wt % [16] whilst Corbett [17] observed 0·21 wt % at 450°C by measuring the weight loss of a known mass of zinc in the melt. Instead of sampling as the previous authors had done, Van Norman [18] calculated the solubility from chronopotentiometric measurements and found it to be an order of magnitude lower. None of these workers examined the solubility in the NaCl–$ZnCl_2$ eutectic, but Kammel stated, without citing any experimental evidence, that the solubility was very much smaller. However, during electrolysis the zinc is deposited as fine droplets on the electrodes and with the agitation of the melt by the chlorine evolution it is likely that some zinc is entrained in the chloride. In order to investigate this, weighed zinc and the eutectic mixture were vigorously stirred together and allowed to settle and the weight of zinc redetermined. A sample of the salt after electrolysis was also taken, solidified and the amount of zinc determined by reacting the zinc rejected during solidification with hydrochloric acid and measuring the volume of hydrogen evolved. Using this method, it was found that there was 1·4 wt % in the salt, which compared well with the 1·3 wt % obtained using the weighing method.

It should be emphasized that this is almost certainly not the true solubility but the likely entrainment of zinc in the eutectic mixture. If the low efficiency was due solely to the solubility effect, it is anticipated that the second electrolysis would give a greater efficiency due to the melt already being saturated with zinc. As this did not happen, it is concluded that the low efficiency is probably due to the chlorine reacting with the dissolved zinc and/or the zinc deposited on the cathode. The negligible effect obtained by drilling holes in the anode indicated that the low current efficiency was not due to the evolved chlorine sweeping close to the surface of the cathode. Altering the position of the anode to give minimal contact between the chlorine and the melt and removing the zinc quickly from the cathode gave current efficiencies in excess of 90%. Porous anodes were equally as effective but, in these experiments, additional voltage losses were incurred due to the method of connecting the electrode lead to the porous anode. On an industrial scale, this problem could probably be easily overcome.

It is somewhat difficult to reconcile the results of this work and the previous work of Kammel, who found virtually 100% efficiency using a liquid pool of zinc and a solid horizontal anode with similar anode to cathode spacing to that used in these experiments. The results given in Table 1 are very similar to those obtained by Threlfall using blocks of carbon with the electrode surfaces at 23° to the vertical with electrode spacing of 2·5 cm in an electrolyte of 80% $ZnCl_2$, 20% NaCl at 490°C operating with a current density of approximately 0·35 A cm^{-2}. By altering the design of the electrodes, higher current efficiencies have been obtained, indicating that these results are consistent. All the electrolysis studies were carried out using the same vessel and it is possible that at these rates of chlorine evolution, severe turbulence was set up in the electrolyte causing the deposited zinc to be swept into the circulating electrolyte and eventually into contact with the evolved chlorine. Another possible explanation, which is even less likely, is that, by working with Kammel's electrolyte composition, the current efficiency becomes nearly 100%. However, there is no indication of this from Table 1.

5. General Discussion

Using the laboratory cell, the optimum electrolyte was determined to be between 25 and 40% NaCl. It was found that the current efficiency and energy efficiency could be increased slightly by increasing the separation of the electrodes but the largest improvement was brought about by drilling holes in the electrodes allowing the electrolysis products to be readily removed from their deposition sites. With this small cell, it was found that with some of the thinner electrodes, the IR drop in the electrodes is an appreciable part of the total IR drop and, therefore, the current efficiency is a more meaningful measure of the efficiency working of the cell than the energy efficiency.

The results shown in Table 7 demonstrate that presentable current efficiencies can be attained using relatively high-current densities. If current densities such as these were used in practice, this would have the effect of reducing the size of the cell for a given output of zinc.

The lowest energy consumption (average 2·84 kWh kg^{-1}) was obtained using perforated anodes and cathodes. On larger cells, provided porous carbon can be used, this figure could probably be reduced further due to decreased resistance in the electrodes and leads. The usual electrolytic process for extracting zinc is the electrolysis of zinc sulphate solution with a current density of 0·08 A cm^{-2} and an average energy consumption of approximately 3·31 kWh kg^{-1}. Utilizing the much higher current densities obtained electrolysing zinc chloride, both the overall cell size and energy requirement should be reduced. There are, however, the usual complications introduced by operating at high temperatures with corrosive melts and gases compared with the electrolysis of aqueous solutions below 100°C.

Acknowledgements

Thanks are due to Mr R. J. Shaw who carried out the majority of the electrolysis experiments and to the Imperial Smelting Corporation Ltd for permission to publish this paper.

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