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Electrolytic manganese metal from chloride electrolytes. I. Study of deposition conditions

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Results of beaker scale and large laboratory scale experiments on the deposition of manganese from chloride electrolytes are reported for conditions where chlorine is the secondary anode product.

Manganese concentration in the catholyte was found to be the most significant variable, with higher manganese levels (to 33 $g\,Mn\,l^{-1}$) resulting in higher current efficiency (65–70%) and lower power consumption (5·5 $kWh\,kg^{-1}$). Temperature (30–60°C) and current density (1·0–2·0 $kA\,m^{-2}$) had opposing effects on current efficiency and power consumption. In the ranges studied, lower temperatures and higher current densities gave rise to increases in current efficiency and power consumption.

The literature on the electrowinning of manganese from chloride electrolytes is reviewed and the anomalies in previous reports discussed.

1. Introduction

Manganese metal is used in certain grades of steel [1], particularly in special steels such as the low carbon stainless steel grades (e.g. 200 series), and in non-ferrous alloys in conjunction with aluminium and zinc [2]. In addition, manganese-copper alloys are currently being promoted for vibration reduction [3]. World consumption of electrolytic manganese metal is currently about 60 000 tonne per year, most of which is produced by electrolysis of $MnSO_4$ solutions [4]. There are, however, potential advantages in producing electrolytic manganese metal by the electrolysis of $MnCl_2$ solutions, such as [5]:

(1) Lower cell potential reduces power consumption by approximately 25%;
(2) a greater manganese strip can be used (about 2 × strip from sulphate electrolytes), thereby decreasing the size of the solution preparation plant and the amount of pumping; and
(3) higher current densities can be used (2–3 × sulphate current densities), thereby decreasing the size of the electrolysis plant.

Potential disadvantages are:

(1) Ammonia is destroyed at the anode in large amounts (approximately 0·3 tonne per ton of Mn) and must be replaced;
(2) the small amount of chlorine formed at the anode must be removed and destroyed.

The overall process is outlined in Fig. 1. This process is the chloride analogy of the conventional commercial sulphate process [6]. The process shown in Fig. 1 is cyclic, the majority of the acid required for leaching being generated in the electrolysis step. In situations where, per tonne of chlorine, the value of chlorine is greater than hydrochloric acid it could be feasible to operate a non-cyclic process whereby chlorine is generated as the major anode product and an external source of acid is used for leaching and anode supply. This configuration is clearly most suitable for integration with a process using chlorine and producing hydrochloric acid as a by-product (for example, organic chlorination).

Much of the work reported in the literature on electrowinning of manganese from chloride electrolytes, especially by Russian workers, has

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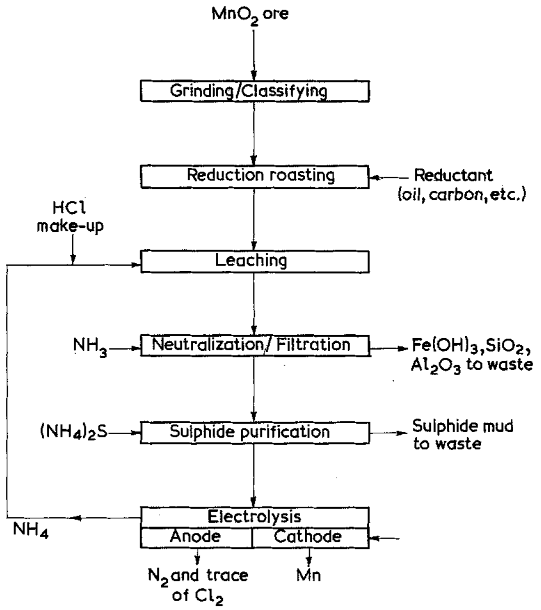

Fig. 1. Production of electrolytic manganese using aqueous chloride electrolyte.

been aimed at determining appropriate operating conditions for electrolysis where chlorine is the primary anode product.

The overall process shown in Fig. 1 consists of a number of steps, such as, ore roasting, leaching, purification and electrolysis. MnO_2 is roasted in conventional sulphate plants and no change in existing technology is required for this step. Leaching of reduced ore with hydrochloric acid and purification of the leach solution are both straightforward operations for which standard technology is adequate. It is in the literature on the electrolysis of manganese from chloride electrolytes that many inconsistencies and contradictions appear. Moreover, it is the electrolysis step which involves the largest capital outlay and is the dominant component of the overall operating cost. As a result, the electrolysis step, appropriate to a process of the type shown in Fig. 1, has been studied here in some detail.

2. Experimental

Electrolysis experiments were carried out on two scales:

(1) Beaker scale laboratory experiments (10^{-3} m^2 electrode areas)–this scale is suitable for initial screening experiments, a large number of runs being possible within a comparatively short time;

(2) large scale laboratory experiments ($0{\cdot}05\ m^2$ electrode areas)–these experiments reduce the importance of edge effects, enable longer deposition periods to be studied and are a better approximation to practical operation.

2.1. *Initial beaker scale experiments*

A series of preliminary experiments were performed in 600 ml beakers using a graphite block as the anode and a strip of 1·6 mm thick 316 stainless steel as cathode. Electrode faces were 30 × 150 mm long, and were coated with contact adhesive, except for a 25 × 40 mm active plating area at the lower end. The graphite anode was 12·5 mm thick. Anolyte and catholyte compartments were provided by dividing the beaker into two equal volume compartments with a vertical sheet of canvas, fixed with 'Silastic'* to the sides and bottom of the beaker. Power was supplied from a 20 V, 20 A laboratory power supply (Hewlett Packard 6264B DC Power Supply) operating in the constant current mode. Anolyte and catholyte solutions were prepared from AR grade laboratory chemicals and the initial pH was adjusted, usually to 6·0. No attempt was made to control the pH as deposition was continued for only 1 h. SO_2 ($0{\cdot}2\ g\,l^{-1}$) was added to the catholyte in all experiments. Solutions were added to the two compartments simultaneously. The electrodes were then inserted and power supplied. The operations were performed in a fume cupboard and no special facilities were provided for gas collection. Deposition was continued for 1 h, after which time the cathode was removed, immersed in a 5% solution of potassium dichromate, washed with distilled water followed by alcohol, dried and weighed. Current efficiency and power consumption were then calculated.

2.2. *Laboratory scale experiments ($0{\cdot}05\ m^2$ electrode area)*

The cell was basically a perspex box, 300 mm wide by 180 mm high and 290 mm long. The cell was divided vertically by a diaphragm, of either canvas

* Dow Corning Corporation.

or a very porous polypropylene weave. The cathode was usually a sheet of 316 stainless steel, although a titanium cathode was also used in a few experiments. The dimensions of the cathode were marginally larger than the inside dimensions of the perspex cell. The anode was a 25 mm thick sheet of graphite of the same dimensions as the cathode. Both cathode and anode were located in slots machined into the side of the perspex cell.

Separation between the anode and cathode was approximately 30 mm, with the diaphragm midway between the faces of the two electrodes. In both cases, the electrodes were supported approximately 5 mm above the base of the cell. Manganese concentration in the catholyte was maintained approximately constant ($\pm 2\,g\,l^{-1}$ Mn) by periodic additions of manganese as crystalline $MnCl_2 \cdot 4H_2O$. Solution from the large volume behind each electrode was circulated through a peristaltic pump into the spaces between the diaphragm and electrode faces and then under the bottom edge of the electrodes back into the large holding volume behind the electrodes. This circulation from the large (stirred) holding space behind the electrodes gave a more uniform concentration across the face of the electrodes, and permitted ready addition of manganese chloride in crystal form to maintain the manganese level.

pH was maintained in the catholyte by the addition of acid via a peristaltic pump controlled by a comparator unit receiving the input of a combination glass/pH electrode. SO_2 ($0{\cdot}2\,g\,l^{-1}$) was added to the catholyte in all experiments.

A 0–100 A continuous, constant current power supply (0·1% stability) was used in the laboratory cell experiments.

3. Results

Possible electrode reactions in chloride electrolytes containing NH_4Cl and corresponding standard potentials (25°C) are as follows:

Cathode	E_0(V)
$Mn^{2+} + 2e^- \longrightarrow Mn$	($-1{\cdot}18$)
$2H^+ + 2e^- \longrightarrow H_2$	(0)

Anode	E_0 (V)
$2NH_4^+ \longrightarrow N_2 + 8H^+ + 6e^-$	($+0{\cdot}275$)
$2Cl^- \longrightarrow Cl_2 + 2e^-$	($+1{\cdot}36$)
$Mn^{2+} + 2H_2O \longrightarrow MnO_2 + 4H^+ + 2e^-$	($+1{\cdot}23$)

The overpotential for hydrogen evolution, together with a low concentration of hydrogen ions (pH 6), enables manganese to be deposited at the cathode, despite the large difference in the standard potentials. Similarly, at the anode, the overvoltage for the electrochemical oxidation of ammonium ions, together with the high concentration of hydrogen ions (approx. $1\,mol\,l^{-1}$), results in the oxidation of chloride ion to chlorine being the dominant anode reaction [7]. While chlorine is the primary anode product, reaction with ammonium ions occurs according to the equation,

$$2NH_4^+ + 3Cl_2 \longrightarrow N_2 + 8H^+ + 6\,Cl^- \qquad (1)$$

and nitrogen is the observed gaseous anode product. Manganese ions almost certainly participate in this reaction [7].

A series of experiments was run to determine the amount of chlorine evolved under typical conditions of electrolysis. For this purpose, a hood was constructed of perspex to fit over the laboratory scale cell. The gases generated were collected and the chlorine content determined.

The results are shown in Fig. 2.

Jacobs *et al.* [5] found that the anode gas, generated from what is likely to have been a similar anolyte, but probably with only 16 g $Mn\,l^{-1}$, 'contained less than 1% chlorine'. Mulin and Zaretskii [8] and Lisov *et al.* [7] report anolyte gas compositions for a variety of anolyte compositions and conditions. These authors, however, worked with either much higher mixed chloride levels or pure acid and do not report data for anolytes in a comparable range to those in the present work.

The conclusion from these experiments is that, although chlorine evolution can be reduced to a small level, it would be necessary to collect and scrub the anode gases before discharge.

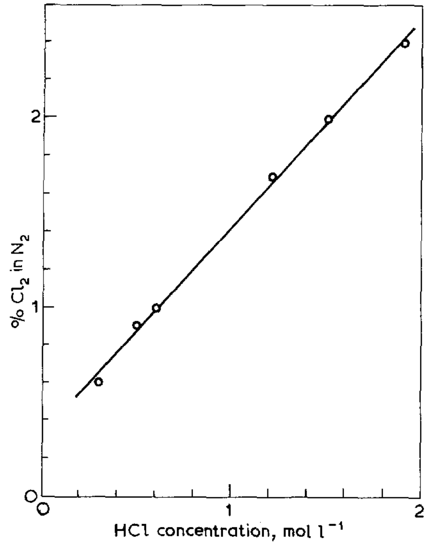

Fig. 2. Variation of chlorine evolution at anode with hydrochloric acid concentration in anolyte.

3.1. *Beaker cell results*

On the basis of the literature available and some preliminary experiments, four variables were selected for more detailed study. A 3^4 factorial design was drawn up with the variables investigated being current density, (1·0, 1·5 and 2·0 kA m^{-2}), temperature (30, 40 and 50°C), manganese level (22, 27·5 and 33 g l^{-1}) and ammonium chloride concentration (100, 125 and 150 g l^{-1}). For this series of experiments, four beaker 'cells' were run simultaneously.*

All experiments were performed with 0·2 g SO_2 l^{-1} in a pH 6 catholyte solution, and current efficiency and power consumption determined for each experiment. The current efficiency for all conditions was found to be 73 ± 10% (2σ) and the power consumption was 4·7 ± 0·7 kWh kg^{-1} (2σ).

An analysis of the variance of the data showed that:

(1) *High Current Efficiency* was favoured by (in descending order of significance)
high Mn^{2+} levels (33 g/l)
high current density (2·0 kA/m^2)
low temperature (30°C)
low NH_4 Cl levels (100 g l^{-1}).
However,

(2) *Power Consumption* was lowest for
high Mn^{2+} (33 g l^{-1})
low current density (1·0 kA m^{-2})
high temperature (50°C)
and medium NH_4 Cl levels (125 g l^{-1}).

Table 1. Results of canonical correlation analysis

Original variables	*Canonical variables*	
	1	*2*
Current efficiency	0·75	−0·62
Power consumption	0·67	0·78
Current density	0·79	0·21
NH_4Cl concentration	−0·35	0·17
Temperature	−0·50	0·12
Mn^{2+} concentration	0·05	−0·96
Canonical root	0·969	0·591
Significance level	1%	1%

As there were two response variables the results were also examined using canonical correlation techniques [9]. The particular advantage of this technique is that it indicates how a set of prediction variables may influence simultaneously more than one criterion variable. Table 1 summarizes the results of this analysis.

The dominance of the manganese level in the second canonical variate is consistent with the results of the analysis of variance which also indicated that manganese level was highly significant for both response variables. In the range studied increasing manganese level results in the desired simultaneous increase in current efficiency and a decrease in power consumption.

A second observation, from the first canonical variate, is that increased current density tends to increase current efficiency at the expense of increased power consumption, again consistent with the conclusions from the analysis of variance.

A similar, but less pronounced, effect occurs with temperature.

3.2. *Laboratory cell results (0·05 m^2 electrode area)*

A number of experiments were conducted to verify the preliminary findings on the beaker scale. A two level partial factorial experiment was performed with the same factors studied as for the

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* The tabulated data are available from the authors.

*Table 2. Experimental results on laboratory scale cell**

Experiment No.	*Current density* (kA m^{-2})	*Temperature* (°C)	*Catholyte composition* *Mn* (g l^{-1})	*Catholyte composition* *NH_4Cl* (g l^{-1})	pH	*Mn efficiency* (%)	*Power consumption* (kWh kg^{-1})
L1	1·5	50	22	120	6·2	63·3	6·2
L2	1·5	60	22	130	6·0	58·6	5·9
L3	2·0	60	22	120	6·0	58·3	6·7
L4	2·0	50	22	130	6·0	60·3	6·7
L5	1·5	60	33	120	6·0	62·6	5·9
L6	1·5	50	33	130	5·0	62·6	6·0
L7	2·0	50	33	120	6·0	67·1	5·8
L8	2·0	60	33	130	6·0	59·5	6·4

* 0·05 m^2 electrode area, 2 h deposition; anolyte composition Mn 22 g l^{-1}, NH_4Cl 120 g l^{-1}, HCl 40 g l^{-1}, SO_2 0·2 g l^{-1}.

beaker scale experiments. Results of these experiments are shown in Table 2.

Conventional analysis of the results in Table 2 shows that:

(1) *High Current Efficiency* was favoured by
high Mn^{2+} level (33 g l^{-1})
low NH_4 Cl level (120 g l^{-1})
low temperature (50°C).

(2) *Power Consumption* was lower for
high Mn^{2+} level (33 g l^{-1})
low current density (1·5 kA m^{-2}).

The conclusions are consistent with the results obtained in the beaker scale experiments except that current density did not appear as a significant variable affecting current efficiency in the range used in the laboratory scale experiments.

Theoretically, current efficiency would be expected to increase with increasing current density, as was found in the beaker scale. There are, however, a number of differences between the experiments performed on the beaker scale and the large laboratory scale, other than scale differences. Deposition time in all beaker scale experiments was 1 h, whilst in the laboratory scale cell deposition was continued for 2 h. The fact that current density showed no significant effect on the laboratory scale may be due to the fact that deposition in the second hour was onto a poorer (less even) surface.

Secondly, the conclusions from the laboratory scale experiments were based on the results of 8 experiments compared to 162 (2 x 3^4) in the beaker scale.

A number of further experiments were performed on the laboratory scale cell, apart from those which formed the partial factorial series. An experiment was performed with 33 g Mn l^{-1} in both anolyte and catholyte (50°C, 120 g NH_4Cl l^{-1} and 0·2 g SO_2 l^{-1}, 1·5 kA m^{-2}) as experiments with catholyte composition of 33 g Mn l^{-1} in the partial factorial series were run with 22 g Mn l^{-1}, in the anolyte. In this experiment a current efficiency of 69·5% was achieved with a power consumption of 5·4 kWh kg^{-1}. A similar experiment with a Ti cathode (but 22 g Mn l^{-1} in anolyte) gave a current efficiency of 70% and a slightly lower power consumption (5·1 kWh kg^{-1}).

An experiment using the conditions of Experiment L6 in Table 2, but with pH of 6·0 and no acid addition to the anolyte, was run for 5 h. The acid level in the anolyte was allowed to rise to 1 mol l^{-1} and maintained at this level by addition of concentrated ammonium hydroxide. In this run a cathode current efficiency of 63% and a power consumption of 6·1 kWh kg^{-1} were obtained.

4. Discussion

Previous work on the production of Mn metal by electrolysis of $MnCl_2$ solutions is summarized in Table 3. For comparison, the ranges of variables covered in the current work are also shown. These results may be compared with the nominal conditions used in the standard sulphate route [6]:

Current efficiency	60–65%

Table 3. Electrodeposition of manganese from chloride electrolytes

Reference	*[5]*	*[17, 18]*	*[12]*	*[11]*	*[10]*	*[13]*	*[15]*	*[19]*	*[14]*	*[16]*		*Current work*
Current efficiency (%)	64–67	70	–	60	51	78	60–70	80	79	76	50–80	60
Cell voltage (V)	3·5–3·6	–	–	3·6	3·8	3·8	–	–	–	6·5	–	–
Power consumption (kWh kg^{-1})	5·3	–	–	5·8	7·3	4·8	–	–	–	8·3	4·1–5·5	5·8–6·7
Duration (h)	48–60	60	36–48	7	12	24	8–24	8	24	–	1	2
Current density (A m^{-2})	480–540	540	480–540	480–540	465	1007	1000	1000	800	480–540	1000–2000	1500–2000
Temperature (°C)	40	30	35–40	35	30–36	30	–	20	45	35	30–50	50–60
Catholyte Composition												
Mn (g l^{-1})	14–16	12	35–50	–	18	82	75	50	35	10–15	22–33	22–33
NH_4Cl (g l^{-1})	95–105	100	120–130	110	120	200	200	110	200	Formamide	100–150	120–130
SO_2 (g l^{-1})	0·1	0·2	0·1	–	0·3	–	–	None	0·2–0·35	–	0·2	0·2
pH	7·0–7·4	4·5–6·0	–	–	7·0–7·4	0·3	1·3	–	7·5	7·5	–	5–6
Anolyte composition	Spent catholyte	–	30% HCl	Satd. NaCl	20–30% NaCl	175 g l^{-1} Mn 12·5 g l^{-1} HCl	200 g l^{-1} HCl	–	70–100 g l^{-1} HCl	90–100 g l^{-1} NH_4Cl pH = 2·5		22 g l^{-1} Mn 120 g l^{-1} NH_4Cl 40 g l^{-1} HCl
Anode product	N_2	N_2	Cl_2	Cl_2	Cl_2	Cl_2	Cl_2	–	Cl_2	N_2	N_2	N_2
Electrode materials												
Cathode	S.S., Ti	Ti	S.S., Ti	S.S.	S.S.	Fe	Ti	S.S.	Ti	S.S., Ti	S.S.	S.S.
Anode	Graphite	Graphite	Graphite	Graphite	Graphite	Pt on Ti	Graphite	Graphite	Graphite	Graphite	Graphite	Graphite
Diaphragm	Vinyon	–	Vinyon	Vinyon 1424N	Porous Ceramic	Ceramic	Asbestos	PVC	Porous PVC	Fritted Glass	Canvas	Canvas
Scale of cell	Pilot	(Patent)	(Patent)	Small	Laboratory	Laboratory	Large lab.	Small	Laboratory	Laboratory	Small	Laboratory

Cell voltage	5·1 V
Power consumption	7·9–8·8 kWh kg^{-1}
Current density	430–650 A m^{-2}
Temperature	45°C

A detailed comparison of the present work with previous studies is difficult as most previous studies have been oriented to the production of chlorine as the primary anode reaction product. For the production of chlorine, a high chloride ion level in the anolyte is required and the manner in which this chloride ion is provided, e.g. operation with a high level of manganese chloride, can affect the deposition of manganese at the cathode. As a result, comparison of cathode performance between cells with different anode products is often difficult.

Of the 'chlorine' papers, the work of Aravamuthan and Gopal [10] is of little interest as they report two electrolysis experiments, both of rather poor efficiency (51 and 60%, the higher efficiency corresponding to the experiment in which the catholyte was stirred throughout the electrolysis). Aravamuthan and Gopal have drawn heavily on the work of Jacobs *et al.* [5] in determining cathode conditions, the difference being solely the anolyte composition which was 20–30% NaCl at pH 2.

Similarly, the patents of Sakowski [11] and Olin Mathieson [12] provide little extra information from the early work of Jacobs *et al.* [5] as the conditions listed in both patents with regard to materials of construction, temperature, current density and catholyte composition are essentially the same as Jacobs *et al.* [5]. The difference again lies in the use of hydrochloric acid or alkali or alkaline earth chlorides as the anolyte to produce chlorine.

Kooi and Louissen [13] use similar cathode conditions to those reported by Russian workers (i.e. high manganese concentrations in the catholyte) and their patent is basically concerned with defining the anode conditions to yield good efficiency with respect to chlorine, with minimal formation of manganic ion. The point is made that if an alkali or alkaline earth chloride is used in the anolyte, these ions tend to diffuse through the diaphragm and contaminate the catholyte and provision must be made in the process for their removal. Mixtures of HCl and $MnCl_2$ are, therefore, recommended as anolyte.

Typical of the Russian work are the papers by Gamali *et al.* [14] and Zaretski and Mulin and coworkers [15]. In both cases hydrochloric acid was used as the anolyte and high yields of chlorine (>97%) were obtained. Gamali *et al.* [14] determined optimum conditions for electrolysis and considered the problem of operating an overall hydrometallurgical scheme. The preferred conditions were: 800 A m^{-2}, 200 g $NH_4Cl\,l^{-1}$, 35–40 g Mn l^{-1} 45°C. At higher current densities, lower temperatures, and lower contents of ammonium and manganese chlorides, dendrites appear, while at 55°C a coarse-grained deposit was obtained.

The conditions used by Zaretski *et al.* [15] were quite similar, the most notable difference being a somewhat higher composition of manganese (75 g Mn l^{-1}) in the catholyte.

Turning to the papers which deal with situations where nitrogen is the primary anode product, the work of Qazi and Leja [15] involves electrolysis from nonaqueous media and is therefore of limited interest, particularly in view of the high power consumption. Dean's patents [17, 18] are directed entirely at behaviour at the anode of either a diaphragm or single compartment cell and are concerned with the use of antioxidant compounds to prevent oxidation of sulphide ion at the anode [18] and control of pH by addition of manganese carbonate [17].

The work of Jacobs *et al.* [5] is a thorough examination of the technical aspects of the various steps in a process of the type shown in Fig. 1 with particular attention to the electrolysis step. The effects of the more significant operating variables as found in the present study are compared with the findings of Jacobs *et al.* [5] and other researchers in the following paragraphs.

4.1. *Manganese level*

In the present work, on both the beaker scale and the laboratory scale, manganese level (varied in the range 22 to 33 g l^{-1}) was found to be the dominant variable. In this range highest current efficiency and lowest power consumption occurred at the highest manganese level.

This finding is consistent with the observation of Yurev and Mozhaev [19] that 'the influence of manganese content in the solution on cathode efficiency is most pronounced at low Mn concentration (up to 30 g l^{-1}). With a further increase in manganese concentration (to 110 g l^{-1}) the cathode efficiency increases only slightly'. Yurev and Mozhaev [19], however, were attempting to produce essentially sulphur free manganese and therefore did not use any additives and produced a deposit of γ Mn. Zaretskii *et al.* [15] found that current efficiency continued to increase slowly up to 75% at 80 g Mn l^{-1}.

Similarly, Stender and Loshkarev [20] found that for current densities in the range 500–2000 A m^{-2}, cathode efficiency (range 73–85%) increased with increasing manganese level (range 15–72 g l^{-1}) in the catholyte, the increase being particularly marked up to 30 g l^{-1}.

Jacobs *et al.* [5] found that the current efficiency increased from 60·3% at 12 g Mn l^{-1} to 70·5% at 16 g Mn l^{-1}, but that at higher manganese concentrations the deposits tend to crack and fall off the cathode.

There were three significant differences in experimental conditions between the work of Jacobs *et al.* [5] and most other workers i.e. the scale of operations, deposition time and source of electrolyte. Jacobs *et al.* [5] operated with an active plating area of the electrode of 0·155 m^2 per face compared to beaker and small laboratory scale experiments with electrode areas from 10^{-3}–0·05 m^2 per face. Whilst it is well known that it is difficult to achieve the same efficiency on a commerical scale electrode as obtained on the laboratory scale, the size differences alone seem unlikely to have given rise to the quite different performances on the two scales.

The deposition time, would seem to be potentially much more important. Current efficiency is not constant throughout the time manganese is deposited and tail off effects towards the end of the plating time can be significant. This effect appears quite a reasonable explanation for the 10–15% differences in current efficiencies obtained in short duration experiments compared to the much longer times used by Jacobs *et al.* [5] as, inevitably, gravimetric measurement of current efficiency results in an average current efficiency over the plating period.

However, these differences do not explain the effect of the manganese deposit cracking and falling into the cell above manganese levels of only 16 g Mn l^{-1}.

Perhaps the most significant difference between the work of Jacobs *et al.* [5] and others lies in the fact that Jacobs *et al.* performed their electrolysis experiments with purified leach solutions instead of synthetic solutions prepared from laboratory chemicals. Using a smaller cell with an electrode area of 0·05 m^2, Jacobs *et al.* did find that deposits produced from catholyte solutions with more than 5 mg Pb l^{-1} tended to crack, and that zinc of around the same concentration also tended to produce brittle deposits. However, prior to electrolysis on the pilot scale, the leach solutions were subjected to a sulphide purification, which, it is reported, reduced the levels of these impurities well below these limits.

4.2. *Current density*

At a fixed nominal current density, the current efficiency decreases as the deposit grows. In the present work, with short deposition times on the small scale, increased current density led to higher current efficiency and higher power consumption. In the few laboratory scale (0·05 m^2 area) experiments, the effect of current density on current efficiency was not significant at the 95% significance level. In these experiments lower power consumption (around 6·0 kWh kg^{-1}) was again associated with lower current density.

In similar experiments, Yurev and Mozhaev [19] found essentially no change in current efficiency for current densities from 1–2·5 kA m^{-2}. The beaker scale results of Stender and Loshkarev [20] also showed that current efficiency reached a plateau value around 1·0 kA m^{-2}. In both cases, however, high current efficiencies were obtained (~80% compared to 60–70% in the present study).

Jacobs *et al.* [5] studied current densities in the range 0·35–0·7 kA m^{-2} and concluded that 'manganese can be deposited over a wide range of current density with only a slight variation in current efficiency'. However, power consumption increased progressively as the current density was increased, and at the upper end of the current density range, a significant reduction in current efficiency occurred. Gamali *et al.* [14] also working with purified leach solutions, experimented over a similar narrow and lower range of current density (0·59–1·0 kA m^{-2}) and arrived at 0·8 kA m^{-2} as optimum for their conditions.

4.3. *pH*

Because manganese is so electropositive with respect to hydrogen, efficient deposition requires that the pH of the catholyte be as high as can be conveniently maintained without being too close to the point where manganese precipitates as the hydroxide. In the preliminary experiments in the present work, it was found that current efficiency was not particularly sensitive to pH in the range of pH 6–7·4. As a result, a pH of approximately 6 was used, as this was easily maintained.

Jacobs *et al.* [5] found a very much stronger dependence on pH. In their experiments, a 7–10% drop in current efficiency occurred with a change of pH from 7·4–7·0.

With a manganese concentration of 37 g l^{-1} in a very pure catholyte solution, Stender and Loshkarev [20] observed a lesser dependence of current efficiency on pH. For current densities in the range 0·5–1·5 kA m^{-2}, no significant difference in current efficiency was found when depositing from pure catholytes at pH 5·9–7. At current densities of 2–4·0 kA m^{-2}, solutions of pH 1 and 5·9 exhibited essentially identical constant current efficiencies (around 80%), but for pH 7 solution the current efficiency dropped with increasing current density. The drop in efficiency was attributed to formation of hydroxides, (also found by Jacobs *et al.* [5]).

Other Russian work was quoted by Stender and Loshkarev [20] as having established that high current efficiencies could be maintained over the pH range of 1–7 [21].

Zaretskii *et al.* [15] also report no problems in obtaining satisfactory current efficiencies when working with catholytes of pH between 1 and 5.

4.4. *Temperature*

Beaker scale experiments indicated that the effects of increasing temperature on current efficiency and power consumption were both in the same direction, with high current efficiency being favoured by lower temperatures (30°C). On the laboratory scale, experiments were performed at 50 and 60°C and the current efficiency was again higher at the lower temperature. At these temperatures, temperature did not appear as a significant variable (95% level) influencing power consumption.

Gamali *et al.* [14] found that dendritic deposits tended to occur below 45°C, and that above this temperature deposits were coarse grained.

Yurev and Mozhaev [19] found a particularly strong dependence of current efficiency on temperature (80% at 20°C dropping to 25% at 50°C). The effect may have been more pronounced in Yurev and Mozhaev's experiments because of the absence of SO_2 additions which results in the manganese being deposited in the γ form.

Jacobs *et al.* [5] report little effect of current density on current efficiency up to 40°C. A 3% drop in efficiency occurred on raising the temperature to 45°C.

It would seem that temperature is one area where results of various workers are most consistent. Lower temperatures have consistently been found to give higher current efficiencies. The temperature chosen is governed by the compromise between increased current efficiency favouring lower temperatures and the cost of cell cooling, which tends to favour operation at high temperature. A temperature of 40–45°C appears to be a reasonable compromise.

4.5. *Ammonium chloride level*

Ammonium chloride concentrations in excess of 120 g l^{-1} appear to have little effect on cathode current efficiency (present results, Yurev and Mozhaev [19], Jacobs *et al.* [5]), although Gamali *et al.* [14], and several other Russian workers [15] prefer much higher levels (~200 g l^{-1}).

The lower limit of concentration of ammonium chloride below which efficiency is significantly reduced is quoted to be between 75 g l^{-1} [5] and 100 g l^{-1} [19].

4.6. *General comment on literature*

Numerous inconsistencies appear in the literature on electrowinning of manganese from chloride electrolytes. Because of the scale, time of deposition (48–60 h) and the detailed examination of process variables, the major work in the area is still the pioneering work of Jacobs *et al.* [5]. However, the anomaly of a practical upper limit on manganese concentration in the catholyte of only 16 $g l^{-1}$ has not been observed by any subsequent workers and may have resulted from undetected impurity levels or a synergistic effect of impurities at lower levels than was critical for any individual element.

In a commercial plant, with nitrogen as the primary anode product, manganese concentrations in the range 10–30 $g l^{-1}$ would normally be chosen. Future studies should be aimed at determining whether a manganese concentration limit exists for electrolytes prepared from ore using the dissolution and purification schemes proposed for the commercial plant.

The critical dependence of current efficiency on pH, not found by other workers, and the dependence on current density determined by Jacobs *et al.* [5] are probably both related to the effects of impurities and the low manganese level.

If impurities in the electrolyte are the cause of the problems, it is diffucult to see how impurities could be economically reduced below the levels reported by Jacobs *et al.* [5].

5. Conclusions

The results of the small and laboratory scale cells indicated that conditions leading to highest efficiencies and lowest power consumptions are, to some extent, conflicting. Where such conflict occurs, conditions chosen must ultimately be determined by the economics of production. This, however, is not a simple choice. For example, low current density in the ranges studied led to low power consumption and hence low operating costs. However, high current density leads to higher production per cell. Hence, fewer cells are required and a lower capital cost plant results.

An analysis of the capital costs in the cell room shows that doubling the current density in the chloride route results in a 20% reduction in capital cost compared to the sulphate route, after allowing for the reduced number of cells, increased busbars (to carry the higher currents) and Cl_2 collecting and absorbing equipment.

Satisfactory catholyte conditions for practical electrolysis of manganese from chloride electrolytes as suggested by the results of the present study are as follows:

Assumptions:	Leach solution of 55 $g\,Mn\,l^{-1}$ minimum as catholyte feed solution
Catholyte:	25 $g\,Mn\,l^{-1}$ 125 $g\,NH_4Cl\,l^{-1}$ 0·2% SO_2 alkali impurities to their solubility limit
Current density	1–1·5 $kA\,m^{-2}$
Temperature	40–45°C
pH	6
Anolyte	spent catholyte together with 1 M HCl (approximate).

In beaker and laboratory scale experiments current efficiencies of 65–70% and power consumption of 6 $kWh\,kg^{-1}$ were achieved with these conditions.

These conditions are consistent with the findings of Jacobs *et al.* [5] with the notable exceptions of the higher manganese concentration in the catholyte (25 $g l^{-1}$ compared to 16 $g l^{-1}$), the higher current density (1·0–1·5 $kA\,m^{-2}$ compared to 0·5 $kA\,m^{-2}$) and the lower pH (6 compared to 7·4).

Lower power consumption, higher current efficiencies and reduced sensitivity to impurities can be obtained using additives, other than SO_2, and this is the subject of a companion paper.

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