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Electrolytic manganese metal from chloride electrolytes. II. Effect of additives

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Results of beaker scale and large laboratory scale experiments on the deposition of manganese from chloride electrolytes using selenium based additives are reported. High cathode efficiencies (85–90%) were obtained at moderate selenium levels (0·03–0·06 $g\,l^{-1}$). Selenium pick-up in the deposit was lower when selenium was added as the selenate [Se(VI)].

A cost/benefit analysis of selenium additions is presented.

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1. Introduction

In all conventional (sulphate) electrolytic manganese plants sulphur dioxide is used as an additive to the catholyte. The effects generally attributed to the presence of a small amount of SO_2 (typically 0·1–0·2 $g\,l^{-1}$) are:

(i) deposition of manganese in the brittle α-phase rather than the ductile γ-phase [1–3]

(ii) increase in current efficiency to around 60% [2, 3], independent of the nature of the cathode metal [3]

(iii) change of crystal size and structure of the deposit [3, 4]

(iv) reduction of the deleterious effects of impurities [4, 5]

(v) increase in H_2 overvoltage [6, 7]

(vi) inhibition of oxidation of Mn^{2+} to MnO_2 at the anode [8].

Clearly, some of the above effects are interrelated, to the point of being cause and effect (e.g. increase in hydrogen overvoltage and the increase in current efficiency).

Numerous theories have been advanced to explain the effect of SO_2 additions but a thorough understanding of the exact mechanism by which additives affect the electrolysis does not appear to have been developed at this stage. From a practical viewpoint the main effects are that SO_2 additions permit deposition of brittle (i.e. easily removed) α-manganese at reasonable efficiencies (60%).

The advantages listed above for sulphite additions are also attainable, to a greater or lesser extent, with most other Group VIB elements [3]. In particular, it is widely reported that selenium is a more effective additive than SO_2 [3, 9–11] especially with respect to current efficiency, efficiencies of 80 to 90% being easily achieved with selenium additions.

The other advantages attributed to the presence of sulphite additions apply equally to selenium. Reduction of the deleterious effects of impurities is particularly marked with selenium additives.

Although the mechanism by which additives increase current efficiency is not well understood, the most widely accepted hypotheses postulate some deposition of a derivative of the additive on the cathode surface. This leads to contamination of the manganese metal product. In the case of sulphite additions in a conventional sulphate plant, with 0·1 to 0·2 g SO_2 l^{-1}, this is not a problem. Typical sulphur levels in the product are around 0·03% [12, 13], the majority of which appears to be the result of cathodic reduction of sulphate rather than sulphite [13]. With the same amounts of SO_2 added to chloride electrolytes, sulphur levels in the metal product also appear to be acceptably low. Jacobs *et al.* [14] do not report quantitative data on the level of sulphur but merely indicate the purity of the metal to be at least 99·9%. They do indicate that the majority of the impurity was sulphur, suggesting that sulphur pick up is possibly more significant from chloride electrolytes.

The advantages of using selenium compounds, however, are at the cost of selenium inclusion in the product at significantly higher levels [10, 15] than the sulphur levels with SO_2 addition. With sulphate or chloride media, the amount of selenium reported in the metal depends primarily upon the level of selenium in the catholyte [10, 15], with one study [10] finding a linear relationship. In addition, selenium pick-up has been found to depend on the valence of selenium in the additive [15–17], the operating conditions [10, 17] and on the presence of secondary additives [19, 20], such as hydroxylamine sulphate.

The minimum level of selenium required in the catholyte to increase the current efficiency to around 80% or more is of the order of 0·05 g l^{-1} Se [10]. Unfortunately, at this level, selenium pick-up is in excess of 0·1% [10]. In commercial operations, inclusion of selenium in the deposit at this level negates the advantage of higher current efficiency and SO_2 is therefore used exclusively in practice.

The work reported in the present paper was undertaken with the aim of determining electrolysis conditions under which the selenium pick-up in the metal could be kept below 0·1%, whilst maintaining a high current efficiency (>80%). An attempt was also made to establish the significance of a number of operating variables on selenium pick-up, current efficiency and power consumption. The work forms an extension of an earlier study by the authors [18] performed with chloride electrolytes.

2. Experimental

Electrolysis experiments were performed on two scales. Preliminary screening experiments were performed with cells consisting of 600 ml beakers divided by a canvas diaphragm into anolyte and catholyte compartments as described previously [18]. The electrode plating area in these cells was 10^{-3} m^2. In all beaker scale experiments, the deposition period was 1 h. No attempt was made to maintain or control cell conditions other than current flow and temperature, and consequently levels of Mn and Se quoted are initial values. Experiments were carried out with anolyte and catholyte compositions of 20–60 and 20–100 g Mn l^{-1}, respectively, at various concentrations of selenious acid. With these experiments, the amount of deposit which could be recovered was inadequate for convenient analysis of selenium in the metal. The majority of experiments were therefore performed on a large laboratory cell with electrodes of 0·05 m^2 plating area.

The large laboratory cell was also described in the earlier study [18]. In order to simulate potential plant conditions the manganese level was maintained at 40 ± 2 gl^{-1}. To achieve this control, catholyte samples were taken and analysed for manganese (volumetrically) every 20 min as before [18] and periodic additions of crystalline $MnCl_2 . 4H_2O$ were made to maintain the concentration. Selenium was added as either crystalline selenious acid or ammonium selenate.

No rapid analytical method was available for selenium determinations and no control on selenium was therefore attempted in the early laboratory cell experiments. In later experiments (Table 4) a solution of selenious acid or ammonium selenate was prepared and added to the catholyte continuously via a peristaltic pump in an attempt to maintain the selenium level in solution roughly constant. The rate of addition to replace the selenium used was estimated from experience of depletion rates in earlier experiments. Catholyte pH was controlled by automatic additions of ammonia solution through a peristaltic pump activated via a pH control unit. A portion of the deposited manganese, sampled by

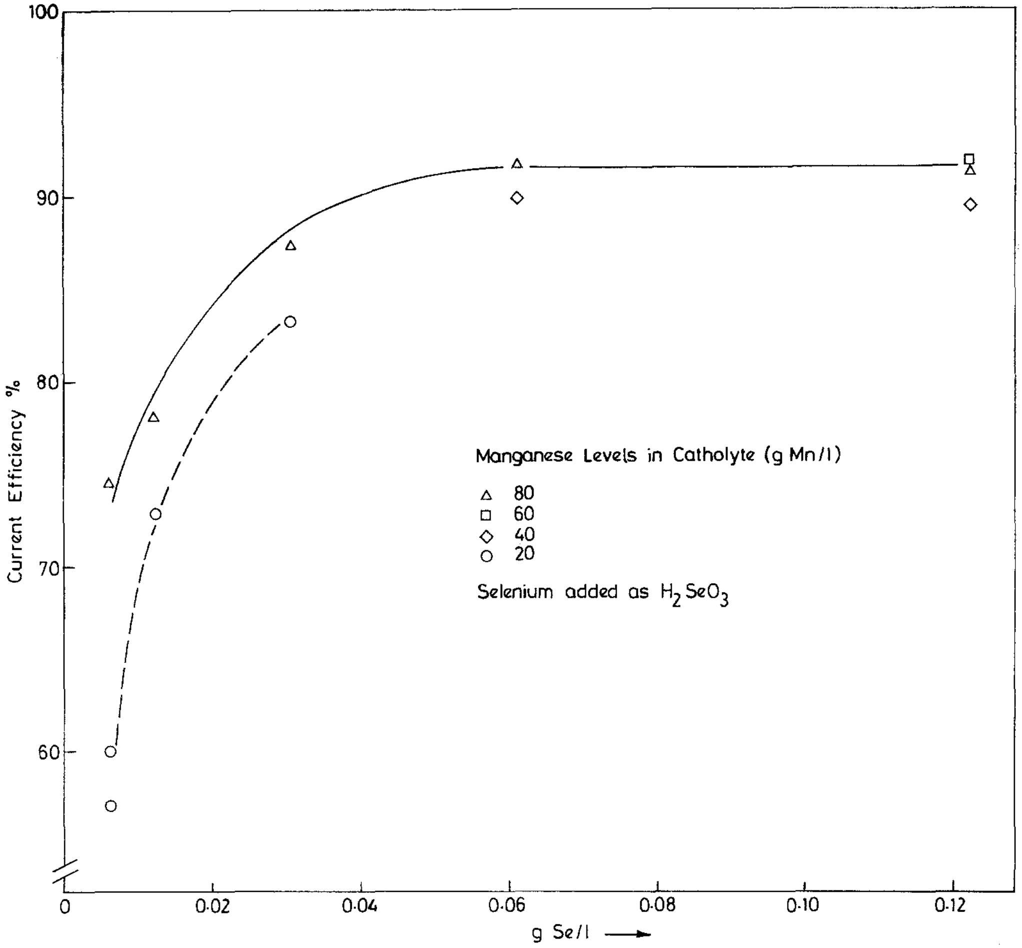

Fig. 1. Variation of current efficiency with initial selenium (IV) concentration in catholyte.

flaking off a section of the deposit, was analysed for selenium.

The analytical procedures for determining selenium in the catholyte and in the deposit were as follows:

(a) Se(IV) in solution – a yellow complex with 3,3′-diaminobenzidine hydrochloride is formed in a solution buffered to pH 2·5, and, after adjustment to pH 6·5, the complex is extracted into toluene and the coloured extract measured spectrophotometrically.

(b) total Se in solution – determined by X-ray fluorescence spectrometry using 5 ml aliquots and synthetic solution calibration standards. Se(VI) was determined by difference [(b) – (a)].

(c) total Se in deposit – determined by X-ray fluorescence spectrometry (Siemens SRS XRF spectrophotometer) on samples ground to -76μ under petroleum spirit. 1 g samples were briquetted with boric acid binder and the total selenium obtained by direct analysis of the briquette. A conservative estimate of the precision of the selenium analysis is ± 0·002%.

3. Results

3.1. *Preliminary Screening Experiments (Beaker Scale)*

To confirm the literature reports of improved current efficiencies with selenium additions a series of beaker scale experiments were carried out. The results of the experiments are shown graphically in Fig. 1.

As can be seen from Fig. 1, current efficiency

Table 1. Selenium Addition Experiments(1) *– Series I (Electrode Area 0·05 m^2)*

Run No.	*Primary Additive* Se(IV) ($g\,l^{-1}$)	Se(VI) ($g\,l^{-1}$)	*Secondary Additive* *(NH_2OH).HCl* ($g\,l^{-1}$)	*Current Efficiency* (%)	*Se Pick-up in Deposit* (% Se)
1(2)	0·06	–	–	88	0·190
2	0·03	–	–	85	0·092
3	0·03	–	–	75	0·063
4	0·012	–	–	74	0·032
5	0·06	–	0·1	85	0·259
7	0·03	–	0·01	86	0·124
9	–	0·06	0·05	88	0·129
10	–	0·06	0·01	91	0·126
11	–	0·03	–	84	0·088
12	–	0·03	0·05	85	0·093
13	–	0·03	0·01	91	0·074

(1) Standard experimental conditions:
Catholyte: 40 $g\,l^{-1}$ Mn, 120 $g\,l^{-1}$ NH_4Cl, pH 6
Anolyte: 20 $g\,l^{-1}$ Mn, 120 $g\,l^{-1}$ NH_4Cl, 1 mol/l HCl
Temperature: 40° C
Current Density: 1·5 kAm^{-2}
Diaphragm: Polypropylene

(2) This run was performed with the following changes: Catholyte: 33 $g\,l^{-1}$ Mn, Anolyte: 22 $g\,l^{-1}$ Mn
Temperature: 50° C

initially increases rapidly with increased selenium level to a plateau value of about 90% at selenium concentrations above 0·06 $g\,l^{-1}$. Current efficiency also increases with increased Mn level, although this effect becomes less pronounced at high selenium levels. Very low efficiencies were obtained from solutions with less than 0·005 g Se l^{-1}.

A comparison of the current efficiencies shown in Fig. 1 with those previously reported for SO_2 [18] (0·2 $g\,l^{-1}$) shows that an increase in current efficiency of 15–20% was achieved with selenium levels above 0·06 g Se l^{-1}. Power consumption was reduced by a similar percentage.

3.2. *Laboratory Scale Experiments*

Series I. An initial series of experiments with the large laboratory cell was conducted to determine:

(a) The general levels of selenium in the deposit when depositing from chloride solutions and a preliminary indication of the variation with initial selenium levels in the catholyte.

(b) What differences resulted from adding selenium in the (VI) rather than the more common (IV) valence state, and

(c) What effects secondary additives had on the deposition process.

The results of the experiments are summarised in Table 1. From these results the following conclusions can be drawn:

(a) Selenium pick-up in the deposited manganese was of the order of 0·1%, with as much as 0·25% being observed in some cases.

(b) With selenium alone, the valence state of the selenium added appeared to have essentially no effect on either the current efficiency or selenium pick-up in the metal (cf runs 2 and 11), but,

(c) When the secondary additive NH_2OH.HCl was used, selenium added in the (VI) valence state resulted in only half as much selenium in the product as was observed with similar conditions when selenium was added as Se(IV). (cf runs 5 and 10, and 7 and 13).

(d) At the particular levels used, the addition of NH_2OH.HCl appeared to increase the selenium pick-up with Se in the (IV) state (initially at 0·06 $g\,l^{-1}$), compared to the pick-up from corresponding solutions of selenium alone.

Series II. A second series of experiments were carried out to obtain information on the sensitivity of the effects observed to variations in operating parameters. An attempt was made to establish the relative importance of a number of the

Table 2. Selenium Addition Experiments – Series II (Se(VI) + $NH_2OH.HCl$)

			Run Conditions					*Results*			
Run	*(Nominal) pH*	*(Variation)*	*C.D.* ($A\,m^{-2}$)	*Temp.* (° C)	*Se*(VI) ($g\,l^{-1}$)	*Mn*(II) ($g\,l^{-1}$)	*$NH_2OH.HCl$* ($g\,l^{-1}$)	*Efficiency* %	*Power* $kWh\,kg^{-1}$	*Se Pick-up %* *Substrate*	*Dendrites*
S/32	6·0	(± 0·2)	1500	40	0·03	40	0·005	81·2	4·46	0·092	0·097
S/20	4·0	(3·5 ± 0·5)	1500	40	0·015	55	0·01	78·8	4·93	0·070	0·050
S/30	4·0	(± 0·5)	1500	50	0·03	40	0·01	82·1	4·30	0·065	0·092
S/21	6·0	(± 0·2)	1000	40	0·03	55	0·01	85·9	3·94	0·102	0·097
S/22	6·0	(± 0·3)	1000	50	0·015	40	0·01	78·9	4·29	n.d.	0·063
S/26	4·0	(3·5 ± 0·5)	1000	50	0·03	55	0·005	84·8	3·75	n.d.	0·094
S/23	4·0	(3·5 ± 0·5)	1000	40	0·015	40	0·005	82·5	4·08	n.d.	0·068
S/25	6·0	(± 0·1)	1500	50	0·015	55	0·005	77·8	4·71	n.d.	0·064
S/33	2·0	(2·0–3·0)	1500	40	0·03	40	0·01	82·6	4·56	0·084	0·097
S/13	6·0	(± 0·5)	1500	40	0·03	40	–*	87·0	4·44	0·102	0·086

n.d. not determined; * 0·1 g $C_2H_5OH\,l^{-1}$ was used in this experiment in place of $NH_2OH.HCl$

operating variables on current efficiency, power consumption and selenium pick-up. In view of the results of the earlier experiments it was felt selenium (VI) with hydroxylamine was the most appropriate additive combination. An experimental design of the Plackett Burman [21] type was planned with the six variables studied being current density, pH, Mn(II) level, temperature, Se level (as Se(VI)), and $NH_2OH.HCl$ level.

The levels of selenium and hydroxylamine hydrochloride were chosen with the view of minimizing the selenium inclusion. With the exception of manganese concentration, which was considerably higher than would normally be encountered in a plant, the remaining variables were typical of anticipated operating conditions.

The results of the experiments and the statistical analysis are shown in Tables 2 and 3 respectively. In Table 3 the variables are listed with the corresponding 'Effect'. In this experimental design the relative significance of the 'Effect' of a variable is directly proportional to the absolute value of the 'Effect'. On this basis the significant variables (in decreasing order of importance) are as follows:

(i) *High Current Efficiency* is favoured by
- a) higher selenium levels (0·03 $g\,l^{-1}$)
- b) lower current density (1·0 $kA\,m^{-2}$)

and, in the ranges studied, appears relatively insensitive to

temperature	(40–50° C)
pH	(4–6)
Mn level	(40–55 $g\,l^{-1}$)
$NH_2OH.HCl$ level	(0·005–0·01 $g\,l^{-1}$)

Table 3A. Results of Analysis of Plackett-Burman Design [21] Table Entries are the Effects of each Variable on the Responses

Variable / *Response*	*pH* (A)	*Current Density* (B)	*Temp.* (C)	*Se level* (D)	*Mn level* (E)	*Hydroxyl amine level* (F)	*Dummy* (G)
Current Efficiency	−1·1	−3·05	−1·2	+4·0	+0·65	−0·15	−1·15
Power Consumption	+0·085	+0·585	−0·09	−0·39	+0·05	+0·115	+0·10
Selenium pick-up*	+4·3	−4·8	+0·3	+34	−3·8	−5·3	−4·2

* Effect × 10^3 for Se in loosely bound dendritic portion of deposit.

Table 3B. Second Order Interactions Confounded with Primary Variable Effects for Plackett-Burman Design with N = 8

	Primary Variable	*Second Order Interactions*		
pH	A	BF	CD	EG
Current Density	B	AF	CG	DE
Temperature	C	AD	BG	EF
Selenium Level	D	AC	BE	FG
Manganese Level	E	AG	BD	CF
($NH_2OH.HCl$) Level	F	AB	CE	DG
Dummy	G	AE	BC	DF

(ii) *Lower Power consumption* is associated with
a) lower current density ($1{\cdot}0\,kA\,m^{-2}$)
b) higher selenium level ($0{\cdot}03\,g\,l^{-1}$)
with the remaining variables appearing to have little effect compared to the above variables

(iii) *Lower levels of selenium in the deposit* are associated predominantly with
a) lower selenium levels ($0{\cdot}015\,g\,l^{-1}$)

Three problems need to be mentioned before extrapolating these conclusions to other situations.

From a purely statistical viewpoint, when interpreting highly fractionated designs it is important to identify the specific interactions, especially second order interactions, which are aliased with the primary variables. For the present case these aliases are shown in Table 3B. From an examination of this table it is suggested that in view of the fact that selenium level (variable D) is a dominant variable (see Table 3A) the large dummy effect, G, is more likely to be a measure of a real interaction (in this particular case probably DF), than an estimate of experimental error. This would seem even more likely to be the case here as D and F (selenium and hydroxylamine levels, respectively) are the two most significant variables when considering selenium pick-up.

Secondly, because the cell was a batch cell with no provision for input of fresh catholyte, the selenium levels quoted were initial concentrations. In view of the large circulating volume of solution in the catholyte and anolyte (approximately 8 l of each) it was thought that selenium levels in solution would not be markedly lowered throughout the deposition (2 h). Later experiments where the catholyte was sampled throughout the run and subsequently analysed indicated that this was not the case. The results of a number of these experiments are shown in Fig. 2. As a result, the levels of selenium quoted are strictly initial levels. Clearly, average levels of selenium in solution during the run were very much lower.

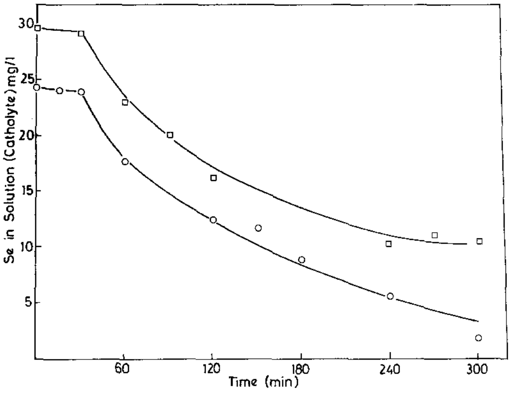

Fig. 2. Variation of selenium concentration in catholyte with time. Catholyte – $40\,g\,l^{-1}$ Mn, $120\,g\,l^{-1}$ NH_4Cl $0{\cdot}01\,g\,l^{-1}$ $NH_2OH.HCl$; Anolyte – $20\,g\,l^{-1}$ Mn; current density – $1500\,A\,m^{-2}$; ○ 40° C, □ 50° C; overall current efficiency is 70% in each case.

A further problem concerned the sampling of the manganese for analysis. The nature of the deposit varied somewhat, particularly the proportion of loosely bound dendritic material in the deposit. Only a relatively small quantity of sample was required to determine selenium (< 1 g was adequate) and in the early experiments (Table 1) no attention was paid as to whether the samples analysed were dendritic in origin or were obtained from the substrate. Partway through the second series of experiments (Table 2) it was discovered that sometimes significant differences occurred in selenium levels in the substrate and any dendrite material. These differences varied in magnitude and sign.

Samples of the dendritic material were obtained in all experiments in Table 2 but the substrate was difficult to remove and in some early experiments samples were not obtained. The analyses of the variables affecting selenium pick-up is therefore strictly an analysis of effects on selenium inclusion in the dendritic material.

The conclusions from the early experiments (Table 1) are also affected by the uncertainty as to the origin of the sample analysed. Consequently, with the benefit of the results of Series I and II a third series of experiments were performed with more controlled conditions.

Series III. In these experiments the cathode was pretreated with sodium silicate to permit more ready sampling of the substrate and an attempt was made to maintain the selenium level in solution constant by continuous addition of an appropriate solution of selenium via a peristaltic pump.

Unlike the situation with manganese, where rapid volumetric determination permitted accurate determination of manganese addition requirements, selenium addition requirements could only be estimated from experience with previous experiments. No feedback control was possible during an experiment. The result of this was that selenium level still varied substantially in some cases.

The manganese concentration in these experiments was reduced to more realistic levels typical of anticipated operation with a 'flow through anode-box' type cell in a commercial unit (i.e. 25 g Mn l^{-1} in both anolyte and catholyte).

Two pairs of experiments were performed with controlled selenium levels. In the first pair selenium was added as ammonium selenate [Se(VI)] with and without hydroxylamine. In the second, selenious acid was used [Se(IV)] with and without hydroxylamine. The four experiments were repeated without sodium silicate pretreatment to establish the effects of this pretreatment on power consumption and current efficiency.

The results are shown in Table 4. The conclusions from these results are:

(1) Selenium pick-up in the substrate is dependent on the valence of the selenium in the additive.

(2) Selenium inclusion in the dendrite formations with Se(VI) appears to be higher than in the underlying substrate. This effect was not observed with selenium (IV).

(3) The valence of the selenium does not appear to have a pronounced effect on current efficiency or power consumption.

(4) Pretreatment of the electrode with sodium silicate raised the power consumption by approximately 5–10% and also reduced current efficiency marginally (3–5%).

(5) The conclusion (b) from the results of Table 1, that the valence state of selenium had no effect on selenium pick-up, is not consistent with the conclusion from the results in Table 4. The latter results are more reliable and the earlier con-

Table 4. Se additive experiments – Series III

Run No.	*Se Conc* (mg l^{-1}) *Se*(IV)	*Se Conc* (mg l^{-1}) *Se*(VI)	*$NH_2OH.HCl$ Conc* (mg l^{-1})	*Se Added* (g)	*NH_3 Added* (ml)	*Current Efficiency* (%)	*Power Consumption* (kWh kg^{-1})	*Se Pick-up Dendrite* (%)	*Se Pick-up Substrate* (%)
S46		30–28	10	0·189	150	87·8	4·28	0·120	n.d.
S47		47–31		0·164	115	84·9	4·38	0·135	n.d.
S48	29–19		10	0·129	109	83·6	4·48	0·120	n.d.
S49	27–12			0·176	104	83·8	4·49	0·140	n.d.
S50	27–11		10	0·186	103	83·8	4·38	0·140	n.d.
S51*		31–24	10	0·124	105	84·6	4·43	0·110	0·070
S52*		29–24		0·132	102	80·7	4·79	0·114	0·078
S53*	26–11			0·125	92	77·7	4·93	0·130	0·137
S54*	24–21		10	0·168	92	79·9	4·76	0·129	0·138

* cathode treated with sodium silicate.

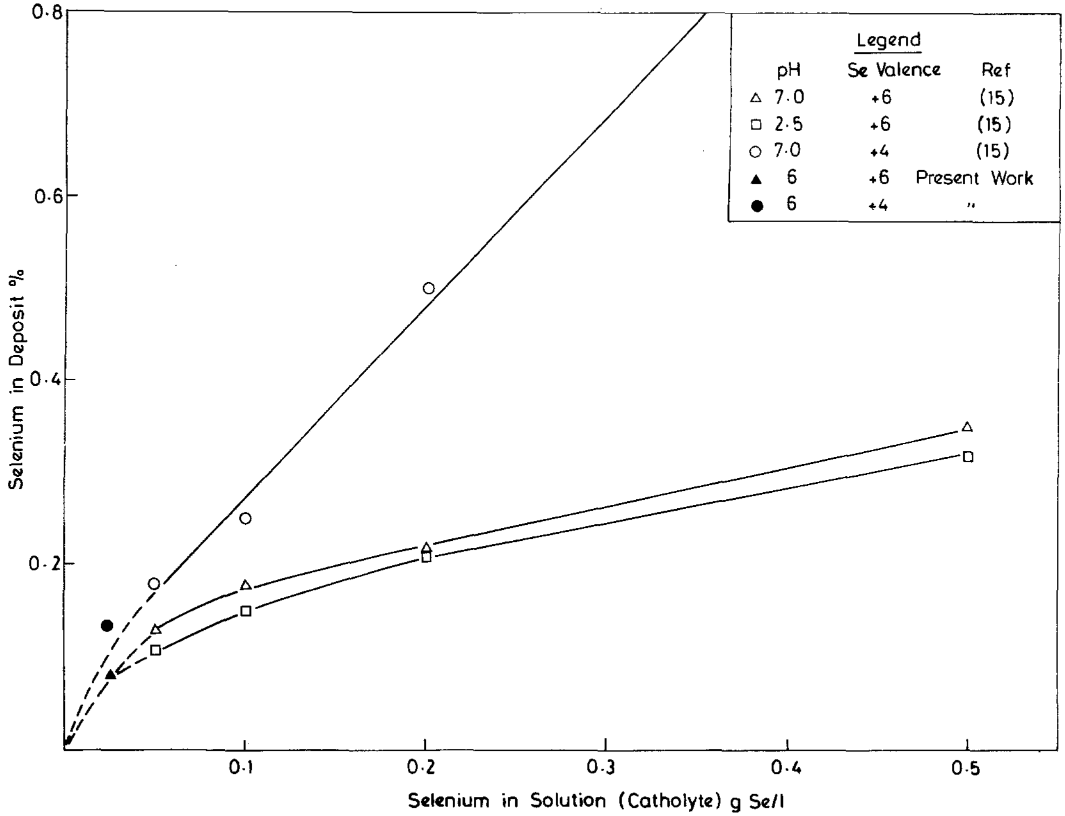

Fig. 3. Level of selenium in deposit as a function of selenium concentration in catholyte.

clusion is thought likely to be the result of analysis of dendrite material rather than substrate deposit. In the light of the results in Table 4, the conclusion (c) from the results of Table 1 appears to be generally true for the substrate with or without hydroxylamine.

4. Discussion

In comparing the present results with previous researches the most obvious disparity concerns the synergistic effect of selenious acid and hydroxylamine sulphate in sulphate electrolytes reported by Amino and co-workers [19, 20]. These workers found only 0·0014% Se deposited in the manganese with these additives. With chloride electrolytes and the corresponding chloride additive in the present study this effect was not observed with either selenious acid or ammonium selenate. Apart from the use of sulphate electrolytes the only notable apparent difference between the work of Amino *et al.* [19, 20] and the present work is possibly current density. In view of the deposition times of 64–72 h it is thought likely that the current density used by Amino *et al.* was very low, approximately 200 A m^{-2}. Current density in normal sulphate practice is approximately 500 A m^{-2}.

Without hydroxylamine additions the present results are consistent with previous workers' results with sulphate electrolytes [15]. Fig. 3 shows the results of Klungeviciute *et al.* [15] with sulphate electrolytes. The appropriate results of the present study (Table 4) are also plotted on the same graph. The two studies are obviously consistent and suggest that the anion has no influence on the effects of the additives.

While Stulpinas and Stasonaite [17] found that the selenium level in the deposit varied in a complex manner with the level of manganese and ammonium ions in solution, no such effects were found in this study.

Contamination of the product metal is not the only problem associated with the use of selenium additives. Ultimately, any choice of additive is governed by an economic balance.

Neglecting potential advantages resulting from better deposits with selenium additives, the minimum requirement for selenium to be considered would be for the increased current efficiency and hence power saving, together with the reduction in capital charges, to balance the increased price of the additive.

To estimate the economics, some assumptions about selenium usage are required. Making the assumptions that:

(i) a selenium concentration of $0{\cdot}05\,\mathrm{g\,l^{-1}}$ is used and that

(ii) all the selenium is consumed in the electrolysis stage either via inclusion in the metal or by reduction to colloidal selenium, and

(iii) the Mn strip is $30\,\mathrm{g\,l^{-1}}$,

a usage of 1·67 kg Se/tonne of manganese produced would result.

The operating cost savings resulting from the increased current efficiency (assuming 65% and 85% for current efficiencies with SO_2 and Se respectively) is approximately \$10–\$12/tonne manganese (assuming power costs \$0·007–0·008 $\mathrm{kWh^{-1}}$). The saving in capital charges would represent a further \$5–\$10/tonne Mn. A total saving of around \$20/tonne manganese would therefore be expected when using selenium.

A cost benefit analysis indicates that the addition of selenium to increase current efficiency is only warranted if the price of selenium, in an appropriate soluble form, was less than \$12 $\mathrm{kg^{-1}}$ of contained Se for an electricity charge of \$0·007 $\mathrm{kWh^{-1}}$. If the charge for electric power was increased to \$0·015 $\mathrm{kWh^{-1}}$, the breakeven cost for contained selenium would be approximately \$20 $\mathrm{kg^{-1}}$.

5. Conclusions

The use of selenium additives [either as Se(IV) or Se(VI)] instead of sulphur dioxide in the electrowinning of manganese from chloride electrolytes increases the cathode efficiency by 15–20%. A similar result has been found by other workers using sulphate electrolytes [15].

Increased cathode efficiency was favoured by higher selenium levels ($0{\cdot}03\,\mathrm{g\,l^{-1}}$) and lower current density ($1{\cdot}0\,\mathrm{kA\,m^{-2}}$), but is relatively insensitive to temperature (in the range 40–50° C), pH (4–6), manganese level ($40–55\,\mathrm{g\,l^{-1}}$) and hydroxylamine hydrochloride level ($0{\cdot}005–0{\cdot}01\,\mathrm{g\,l^{-1}}$).

The selenium level in the deposit increases with increasing selenium concentration in the catholyte but is lower when selenium is added as the selenate [Se(VI)] rather than as selenious acid [Se(IV)]. The valence of the selenium addition does not have a pronounced effect on either current efficiency or power consumption. No dependence of selenium pick-up on the concentration of manganese and ammonium ions in the catholyte was observed.

The very low selenium pick-up (0·0014% Se) reported by Amino and coworkers [19, 20] for manganese electrowinning, using sulphate electrolytes and selenious acid and hydroxylamine sulphate additives, could not be obtained using chloride electrolytes. However, the present study has defined operating conditions which lead to acceptably low (<0·1%) levels of selenium in the deposit.

From a consideration of the operating and capital cost savings due to the increased current efficiency for manganese deposition using selenium as additive, a break even cost for contained selenium in the additive of \$20 $\mathrm{kg^{-1}}$ can be calculated for an electricity cost of \$0·015 $\mathrm{kWh^{-1}}$.

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