

CHAPTER VII

Electro-deposition of manganese with selenious acid as an addition agent

The results of experiments with selenious acid as an addition agent to study the influence of different cell variables on the current efficiency of deposition of manganese, hydrogen and selenium content of deposited manganese and consumption of electrical energy per kilogram of deposited metal have been presented. Current efficiencies of the order of 90 per cent, corresponding to an energy consumption of 5 kWh per kilogram of deposited manganese, can be obtained from electrolysis of 125-50 gm of manganese sulphate, 125-50 gm of ammonium sulphate and 0.1 gm of selenious acid per litre of electrolyte in a double compartment cell between stainless steel cathodes and lead-silver anodes, with arrangement for flow of electrolyte, at a catholyte pH of 7.8, temperature of 28-30°C and at a cathodic current density of 4.8 amps/sq dm.

Cell reactions leading to the precipitation of selenium in the cathode chamber has been discussed along with hydrogen content and stripping of deposited metal.

Introduction

Technical superiority of electrolytic manganese as a manganese addition agent in special steels and non-ferrous alloys has been of late widely acknowledged. The technology of the production of this metal has been described in detail elsewhere¹⁻³. The striking discovery in the electro-deposition of manganese was the addition of sulphur dioxide to the electrolyte which made the electrolytic process commercially successful^{4,5}. Current efficiency in the deposition of manganese falls off on continued electrolysis in absence of sulphur dioxide but may be maintained for 48 hours or more with sulphur dioxide addition¹.

Recently, in Russian literatures it has been reported that selenious acid has been tried as an addition agent^{6,7} but their experiments were conducted at very low temperatures, viz 18-20°C, which is rather difficult and uneconomical in a commercial electro-winning practice, especially in tropical countries.

Besides the presence of sulphur dioxide or selenium dioxide as an addition agent in the electrolyte, the efficient deposition of manganese depends upon a combination of many other factors, such as purity of the solution, temperature, concentration of manganese and ammonium sulphate in the electrolyte, pH of catholyte, current density and rate of flow to the cell. It is not possible to consider any of these variables separately. In fact nearly all of them influence one another and the limits of one variable cannot be specified without defining other conditions very closely⁸.

This work relates to the systematic study of the influence of selenium dioxide as an addition agent in the electro-deposition of manganese from manganese ammonium sulphate solutions with regard to current efficiency, power consumption and different cell variables.

Materials and methods

Apparatus — A rectangular glass vessel 10×10×16 cm was used as the electrolytic cell. The cell containing one cathode and two anodes was furnished with two anode chambers 1.5×7.5×16 cm, made of cotton canvas, mounted on perspex diaphragms. A sectional view of the electrolytic cell is given in Fig. 3.I of Chapter III.

Electrolyte — The mode of preparation of the electrolyte was exactly the same as described in the earlier paper. A large bulk solution of about 20 litres was prepared and purified at a time and was used for all the experiments of a particular series with additions of other constituents when required. For certain series of experiments in this investigation

only, the spent liquor and catholyte from experiments of a previous series were collected together and purified, in the same manner as described earlier, after addition of manganese sulphate, prepared from electrolytic manganese, and ferrous sulphate. Any selenious acid present in the electrolyte was carried down by the ferric hydroxide precipitated during purification⁹. Selenious acid was prepared with 99.9 per cent pure selenium powder.

Analysis — Selenium: Selenium content of manganese metal was determined based on ASTM method¹⁰.

Experimental results

The results of experiments carried out with selenious acid as an addition agent to study the influence of different cell variables on the current efficiency of the process, hydrogen and selenium content of the deposited manganese are presented in Tables 7.I-7.VII.

Discussion

Before proceeding with the discussion of experimental results, certain observations made on the deposition of manganese with selenious acid as an addition agent shall be presented and the possible reactions at the cathode, as compared to those which take place with sulphur dioxide as an addition agent, will be examined.

Comparison of the properties of selenium with sulphur and the possible reactions at the cathode — In properties, selenium behaves very much like sulphur in many of its reactions, but the compounds formed with selenium are much less stable than those formed with sulphur. This difference between the stability of sulphur compounds and that of the corresponding selenium derivatives are attributed to the preference which selenium exhibits for existing as a quadrivalent element whereas sulphur as a bi- or sexavalent element¹¹.

Sulphur dioxide is an excellent reducing agent and, in dilute solutions, sulphur dioxide is oxidized even by atmospheric oxygen. In contrast to this, selenium dioxide, i.e. selenious acid anhydride, is a good oxidizing agent. Even solid selenium dioxide when exposed to air eventually becomes pink to red as a result of its reduction to elementary selenium by organic dust particles¹². Only strong oxidizing agents, such as hydrogen peroxide and potassium permanganate, are able to oxidize selenium dioxide to selenates¹². This difference in the chemical properties of sulphur and selenium dioxides are markedly seen in the electro-deposition of manganese with one of the two as an addition agent. The conditions under

TABLE 7.1 — INFLUENCE OF SELENIUM CONTENT IN THE ELECTROLYTE ON CURRENT EFFICIENCY OF DEPOSITION

7

Composition of electrolyte: 80 gm of manganese sulphate/litre
160 gm of ammonium sulphate/litre
Selenium content as given in the table

Initial pH of cell solution and feed electrolyte = 3; Flow of electrolyte = 6 cc/min
Current density = 4.2 amps/sq dm; Temperature of electrolysis: 21°C; Average pH of catholyte: 7.2-7.4; Time of deposition = 3 hr

SELENIUM ACID gm/litre	AVERAGE VOLTAGE	CURRENT EFFICIENCY %	SE CONTENT IN METAL %	HYDROGEN CONTENT cc/100 gm	STRIPPING	NATURE OF DEPOSIT	REMARKS
0.4	4.4	85.55	0.98	343	Easy	Striations and small pit- tings due to sticking of hydrogen bubbles on the cathode surface	There was precipitated Se in cathode chamber. Spent li- quor was also red in colour due to precipitated selenium
0.2	4.4	83.12	0.57	345	do	do	Slight precipitated Se in cathode chamber. Spent liquor was red in colour
0.1	4.4	81.87	0.38	305	do	Very bright, fine and smooth deposit	Very slight Se precipitation in cathode chamber. Red Se tinge in spent liquor
0.05	4.5	78.83	0.18	325	do	do	Catholyte was clear. Red Se tinge in spent liquor
0.02	4.4	73.35	0.13	284	do	Fine smooth and of a matte nature	Catholyte was clear. No red tinge in spent liquor
0.012	4.6	64.68	0.09	260	Difficult	Fine smooth	Catholyte was clear. No red tinge in spent liquor

TABLE 7.II — INFLUENCE OF AMMONIUM SULPHATE IN THE ELECTROLYTE ON CURRENT EFFICIENCY OF DEPOSITION

Composition of electrolyte: 90 gm of manganese sulphate/litre
 0.1 gm of selenious acid/litre
 Ammonium sulphate as given in the table

Initial pH of cell solution and feed electrolyte = 2.7; Flow of electrolyte = 6 cc/min
 Current density = 4.2 amps/sq dm; Temperature of electrolysis = 21°C; Time of deposition = 3 hr

AMMONIUM SULPHATE gm/litre	AVERAGE VOLTAGE	CURRENT EFFICIENCY %	SE CONTENT IN THE METAL %	AVERAGE pH	STRIPPING	NATURE OF DEPOSIT	REMARKS
162.5	4.45	79.3	0.29	7.45	Easy	Smooth fine deposit. Few pittings due to sticking of hydrogen	Red tinge in spent liquor. No red selenium precipitation in cathode chamber do
149.5	4.47	80.04	0.24	7.41	do	Smooth fine with few pit- tings at the bottom of the cathode	do
125.0	4.57	80.87	0.23	7.46	do	Smooth fine with very few pittings	do
110.4	4.64	81.85	0.31	7.48	do	Smooth fine deposit	0.005 gm of red Se in total spent liquor after washing through a sintered glass cru- cible
96.3	4.80	81.3	0.20	7.5	do	Slight nodular growths. Treeing at the edges of the cathode	Practically no pittings. Stria- tions of hydrogen evolution. Nodular growth on striation line. No red Se in cathode chamber
50.2	5.11	86.94	—	2.81	do	Two blisters one on each side of the cathode. Tree- ing	Slight red Se precipitation in cathode chamber
Nil	6.87	45.4	0.32	2.1 (Initial pH 1.7)	do	Deposit was loose and not adherent, considerable treeing has fallen in cell	Red precipitated Se in cathode chamber. No red tinge in spent liquor

TABLE 7.III — INFLUENCE OF TEMPERATURE ON CURRENT EFFICIENCY OF DEPOSITION

Composition of electrolyte: 87 gm manganese sulphate/litre
 159.5 gm of ammonium sulphate/litre
 0.1 gm of selenious acid/litre

Initial pH of cell solution and feed electrolyte: 3.4; Flow of electrolyte: 6 cc/min
 Current density: 4.2 amps/sq dm; Time of deposition: 3 hr
 Temperature of electrolysis as given in the table

TEMPERATURE °C	AVERAGE VOLTAGE	AVERAGE CATHOLYTE pH	CURRENT EFFICIENCY %	STRIPPING	NATURE OF DEPOSIT	REMARKS
18.5	4.85	7.8	80.17	Easy	Smooth fine but not very bright deposit	Minor pittings and nodular growths on the surface
27.5	4.45	7.42	87.06	Difficult	Smooth fine deposit	Very few pittings and few nodu- lar growths. Red Se preci- pitation in cathode chamber
36.5	4.13	7.20	87.19	do	Smooth, bright and fine depo- sit	No pittings nor any nodular growths. A lot of red Se pre- cipitation in cathode chamber
46.5	4.08	7.19	79.27	Very difficult	Very fine grained, smooth and bright deposit	Top portion was dissolving and deposition was taking place over that
61	3.86	7.2	63.31	do	do	Top portion was dissolving

TABLE 7.IV — INFLUENCE OF SELENIUM CONTENT IN THE ELECTROLYTE WITH RESPECT TO TEMPERATURE OF ELECTROLYSIS ON CURRENT EFFICIENCY OF DEPOSITION

Composition of electrolyte: 88 gm of manganese sulphate/litre
160 gm of ammonium sulphate/litre
Se content as given in the table

Initial pH of cell solution and feed electrolyte: 3; Flow of electrolyte: 6 cc/min
Current density: 4.2 amps/sq dm; Average pH of catholyte: 7.2-7.4; Time of deposition: 3 hr

SE CONTENT AS SELENIUM ACID gm/litre	TEMPERATURE °C	CURRENT EFFICIENCY %	STRIPPING	NATURE OF DEPOSIT	REMARKS
0.1	21	81.87	Easy	Fine smooth deposit	Very slight selenium precipitation in cathode chamber
0.05	25	80.75	Difficult	do	Extremely little selenium precipi- tation in cathode chamber
0.025	29.5	81.87	do	Fine smooth and bright deposit. Few pittings on one side of cathode	No selenium precipitation visible in cathode chamber

TABLE 7.V — INFLUENCE OF CATHOLYTE pH ON CURRENT EFFICIENCY OF DEPOSITION

Solution used: Purified spent liquor and concentration adjusted to

120 gm manganese sulphate/litre

125 gm ammonium sulphate/litre

and 0.1 gm selenious acid/litre

Initial pH of cell solution and feed electrolyte = as given in the table, Flow of electrolyte = 5 cc/min
Current density: 4.2 amps/sq dm; Temperature of electrolysis: 28.5-29.5; Time of deposition: 3 hr

CATHOLYTE pH	FEED ELECTRO- LYTE pH	VOLTAGE	CURRENT EFFICIENCY %	SELENIUM CONTENT %	HYDROGEN CONTENT cc/100 gm	STRIPPING	NATURE OF DEPOSIT	REMARKS
2.55	2.2	4.71	77.5	0.25	277	Slightly difficult	Smooth bright depo- sit. No nodular growths	Red Se precipitation in cathode chamber. Clear spent liquor
3.63	2.5	4.56	84.68	—	279	do	do	Slight Se precipitation in cathode chamber. Spent liquor had red Se tinge
4.92	4.0	4.55	86.52	—	229	Easy	do	Catholyte colour was slowly turning red
6.66 7.23	3.7* 7.2	4.64 4.68	89.37 88.89	0.30 0.28	201 —	do Slightly difficult	Smooth bright de- posit. Nodular growths on the sides and at bottom of cathode	Up to ½ hr of starting the expt there was no ap- preciable change in catholyte colour. To- wards the end it was slightly reddish. Spent liquor had red tinge
7.72	7.6	4.68	92.87	0.26	199	Easy	do	No red Se precipitation in cathode chamber.
7.96	7.75	4.73	89.76	0.25	196	do	do	Slight Mn(OH) ₂ in the feed

*Flow of electrolyte was 6 cc per minute.

TABLE 7.VI — INFLUENCE OF CONCENTRATION OF MANGANESE SULPHATE IN THE ELECTROLYTE ON CURRENT EFFICIENCY

Solution used: Purified spent liquor and concentration adjusted to manganese sulphate as given in the table
 150 gm of ammonium sulphate/litre

0.1 gm of selenious acid/litre

Initial pH of cell solution: 6.7; pH of catholyte: 6.9-7.1, Flow of electrolyte: 6 cc/min

Current density: 4.2 amps/sq dm; Temperature of electrolysis: 27-29°C; Time of deposition: 3 hr

CONCENTRATION OF MANGANESE SULPHATE IN THE ELECTRO- LYTE gm/litre	AVERAGE VOLTAGE	CURRENT EFFICIENCY %	HYDROGEN CONTENT cc/100 gm	STRIPPING	NATURE OF DEPOSIT	REMARKS
50	4.65	79.45	265.6	Easy	Smooth, bright deposit. No nodular growths	Slight red Se precipitation in cathode chamber do
75	4.90	85.43	255.7	do	do	do
100	4.69	87.36	265.7	Slightly difficult	do	Catholyte colour was turn- ing red towards the end of expt due to precipitated Se
125	4.77	89.60	224.9	Easy	Smooth bright deposit. Slight nodular growth	Red Se precipitation visible in spent liquor
150	4.75	90.55	202.1	do	Smooth bright deposit. Nodular growths were more prominent	do
175	4.67	91.03	218.9	do	do	do
200	4.73	91.98	—	do	do	do

TABLE 7.VII — INFLUENCE OF CATHODIC CURRENT DENSITY ON CURRENT EFFICIENCY OF DEPOSITION

Solution used: Purified spent liquor and concentration adjusted to 103 gm manganese sulphate/litre
 154 gm ammonium sulphate/litre
 0.1 gm of selenious acid/litre

Initial pH of cell solution = 7.2; pH of feed solution = 6.8; Flow of electrolyte = 5 cc/min.
 Catholyte pH = 7.4-7.5; Current density = as given in the table; Time of deposition = 3 hr; Temperature = 27-29°C

CURRENT DENSITY amps/sq dm	VOLTAGE	CURRENT EFFICIENCY %	ENERGY CONSUMPTION/kgm, kWh	SE CONTENT %	HYDROGEN CONTENT cc/100 gm	STRIPPING	NATURE OF DEPOSIT	REMARKS
1.48	3.86	84.18	4.474	—	—	Difficult	Smooth bright deposit. No nodular growth or treeing	Red Se precipitation in cathode chamber
1.98	4.05	85.84	4.499	—	236.8	do	do	do
2.90	4.29	88.96	4.704	0.38	209.4	Slightly difficult	do	Red Se precipitation in cathode chamber was less than the two previous experiments.
3.40	4.36	89.60	4.812	0.33	237.0	Easy	do	Se precipitation much less in cathode chamber
4.17	4.6	88.67	5.062	0.32	234.9	do	Treeing at the edges of the cathode	There was practically no Se precipitation in cathode chamber except pink to red colour of catholyte towards the end of experiment
4.86	5.19	89.28	5.674	0.34	214.4	do	do	do
5.23	5.37	87.77	5.973	0.33	231.9	do	Lot of treeing at the edges of the cathode. Not as bright as the deposits at low current densities	do
6	5.57	86.88	6.255	0.33	250.3	do	do	do

which elementary selenium precipitates in the cathode chamber can in all cases be traced to the instability of the selenium compounds and to its subsequent reduction or decomposition to elementary selenium.

Besides the two principal reactions¹³ at the cathode, viz



the possibility of the following reactions have to be considered.

In acid solution,



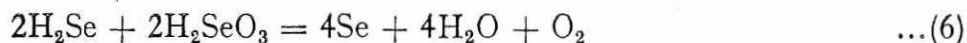
and in alkaline solutions,



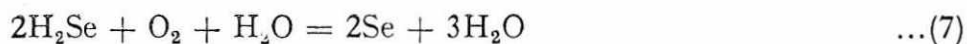
It is known that hydrogen telluride can be formed cathodically with good yields by the electrolysis of 50 per cent sulphuric acid solution with tellurium as a cathode¹², and that in strongly acid aqueous solutions of sulphur dioxide, hydrogen sulphide and polysulphides are obtained¹⁴. Similarly, in case of selenium in presence of acids, the possibility of formation of hydrogen selenide cannot be ruled out. In case of manganese deposition, when there is always a simultaneous evolution of hydrogen due to the negative electrode potential of manganese with respect to hydrogen, the possibility of hydrogen selenide formation is increased by the action of nascent hydrogen on cathodically reduced selenium¹⁵.

Hydrogen selenide is thermodynamically unstable at room temperature and, in aqueous solutions, hydrogen selenide gradually decomposes into elementary selenium¹². Above 30°C, hydrogen selenide does not exist in aqueous solutions and decomposes into selenium¹⁵.

Hydrogen selenide can also react with selenious acid in the electrolyte to form elementary selenium¹⁶.



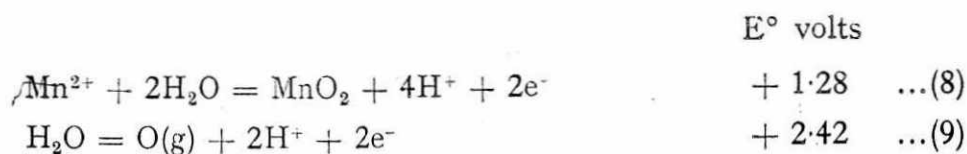
and



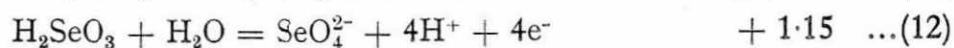
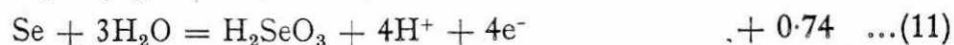
In presence of ammonium salts in the electrolyte, ammonium selenide, ammonium hydrogen selenide and ammonium polyselenide can be formed. These compounds alone have been mentioned as more stable than their sulphur counterparts¹⁵.

As in the case with sulphur, on the addition of selenium to solutions of selenide salts, the polyselenide is formed which, when acidified, decomposes to hydrogen selenide and selenium¹². During electro-deposition of manganese in presence of selenious acid, the chances of polyselenide formation exists as elementary selenium and ammonium selenide are formed. Under acid conditions, this polyselenide can decompose into hydrogen selenide and elementary selenium.

At the anode, besides the two principal reactions¹³, viz



the possibility of the following reactions¹³ have to be considered.



Any hydrogen or ammonium selenide formed at the cathode will be oxidized to selenium in the anode chamber, if not decomposed in the cathode chamber itself. The polyselenides will also be decomposed at the anode due to the strong acidity in the anode chamber. Any selenium or selenious acid present in the electrolyte can be got oxidized to selenious or selenic acid at the anode.

Some important observations with selenious acid as an addition agent —
With selenious acid as an addition agent, it was found that

- (i) selenium precipitates in the cathode chamber under the following conditions:
 - (a) at low pH values of catholyte,
 - (b) at low concentrations or in the absence of ammonium sulphate in the electrolyte,
 - (c) at higher temperatures of electrolysis,
 - (d) at low cathodic current densities of deposition,
 - (e) at high selenious acid concentrations in the electrolyte, and
 - (f) at low concentrations of manganese sulphate in the electrolyte;
- (ii) red selenium appeared in spent liquor excepting when selenium was being profusely precipitated in cathode chamber as mentioned under conditions (i) (a), (b) and (c);
- (iii) in absence of ammonium sulphate in the electrolyte, manganese deposit could not be obtained at catholyte pH values of 2.7 and

above but was obtained from the same solutions at still lower pH values with simultaneous precipitation of selenium in the cathode chamber;

- (iv) in absence of ammonium sulphate, the pH value of catholyte was not found increasing with time of deposition and was remaining constant at 2.1;
- (v) with very low concentrations of ammonium sulphate also, the pH value of catholyte was not found increasing but remained constant at 2.8; and
- (vi) with purified spent liquor, the catholyte pH was remaining constant just a little above the pH value initially taken for electrolysis.

Explanation of the experimental observations — An attempt may now be made to explain the experimental observations mentioned earlier.

- (i) (a) Precipitation of red selenium in the cathode chamber is found to be more at low pH values of catholyte. At low pH values, H^+ ions preponderate, and the selenides and polyselenides formed are decomposed early to hydrogen selenide and selenium in acid medium. On the other hand, at high pH values, H^+ ion concentration is low and formation of ammonium selenide, ammonium hydrogen selenide and polyselenide can take place which are comparatively more stable. Because of the alkalinity of the catholyte, these do not get decomposed in the cathode chamber.
- (b) At low concentrations or in the absence of ammonium sulphate in the electrolyte, the chances of forming the comparative stable ammonium selenide and ammonium hydrogen selenide are limited resulting in the gradual decomposition of hydrogen selenide. This explains that, at 50 gm per litre of ammonium sulphate concentration, there was slight red selenium precipitation in the cathode chamber while, at higher concentrations of ammonium sulphate, there was no visible precipitation of red selenium in the cathode chamber.
- (c) Selenium precipitation in the cathode chamber is found to increase with rise in temperature. While at experiments carried out at 18-20°C, with 0.1 gm/l of selenious acid, there is practically no precipitated selenium in the cathode chamber, at 28°C the colour of catholyte is definitely changing from pink to red due to precipitation of selenium. But during experiments at 36.5°C and above, there is profuse precipitation of selenium and the cathodes and hydrogen evolution could not be even seen clearly on account of the precipitate.

Aqueous hydrogen selenide does not exist above 30°C (ref 15) and at higher temperatures possibly ammonium selenide and

ammonium hydrogen selenide might also decompose to selenium which explains the precipitation at higher temperatures.

- (d) Precipitation of selenium in the cathode chamber is found to be more during low cathodic current density experiments, possibly due to reaction (4) taking place at a more negative cathode potential than reaction (3).
- (ii) Excepting under conditions explained above, there is precipitated elementary selenium in the spent liquor; it can be presumed that the cathodically formed ammonium selenides or polyselenides are being decomposed to elementary selenium at the anode. When there is precipitation of elementary selenium in the cathode, conditions are such that the selenides or polyselenides are decomposed at the cathode itself and the spent liquor is found to be clear.
- (iii) When the electrolysis was carried out in the absence of ammonium sulphate in the electrolyte at an initial pH of 2.7, no manganese metal could be obtained and there was no precipitation of red selenium in the cathode chamber. The catholyte pH rose up to 8 in a few minutes and only manganese hydroxide coating was seen on the cathode with manganese hydroxide precipitation at the bottom of the cathode chamber. When the same solution was acidified to pH 1.5, good manganese deposit was obtained though loose and poorly adherent. There was considerable precipitation of red selenium, and the whole catholyte was charged with suspended red selenium.

This can be explained on the basis that the decomposition potential of selenious acid is lowered at higher H^+ ion concentrations in the electrolyte¹⁷ and that increase in H^+ ion concentration in the electrolyte favours the formation of colloidal selenium particles in the cathode area¹⁸.

Influence of selenium content in the electrolyte on current efficiency of deposition — From Table 7.I it can be seen that current efficiency rises with increase in concentration of selenious acid, the rise being quite sharp up to a concentration of 0.1 gm of selenious acid per litre. With further increase in selenious acid concentration, the efficiency rise is steady but not so marked as up to the concentration of 0.1 gm per litre. A current efficiency of 65 per cent usually obtained with 0.13 gm of sulphurous acid per litre in pilot plant production of electrolytic manganese is obtained with as low as one-tenth of that concentration of selenious acid.

Sulphur has been mentioned to be a negative catalyst for combination of hydrogen atoms¹⁹. The high hydrogen content of manganese prepared in presence of sulphur in the electrolyte bears evidence to this. Similarly, manganese obtained with selenium as an addition agent is also

found to contain high hydrogen as seen from Table 7.I. It is quite likely that selenium also behaves like sulphur in its negative catalytic activity on the combination of hydrogen atoms. By virtue of this property, the hydrogen over-voltage increases during electro-deposition in presence of selenium. As the hydrogen over-voltage increases, efficiency of manganese deposition also increases explaining the higher current efficiency with higher selenium content in the electrolyte.

The inclusion of selenium in the deposit also increases with increase in concentration of selenious acid in the electrolyte. With increase in selenium content in the electrolyte, the hydrogen content is found to increase initially but remains practically unchanged at higher selenium concentrations. Stripping of the deposited metal is also found to bear some relationship with the selenium content in the electrolyte. At higher selenium concentrations in the electrolyte, the stripping was very easy while, at 0.0125 gm per litre, it was extremely difficult to strip off the deposited metal. It is likely that the higher the hydrogen content, the more the stress in the deposit which can presumably explain the easier stripping at higher selenium and consequently higher hydrogen contents in the deposit.

The deposits obtained with selenium were fine, smooth and bright excepting at 0.2 and 0.4 gm of selenious acid per litre when striations and small pittings due to sticking of hydrogen bubbles on the cathode surface were seen. At higher selenium concentrations, the mobility and stability of the colloidal particles are less and the tendency to agglomerate are greater which in turn impairs the quality of the deposits²⁰.

Considering the various factors and the inclusion of selenium in the deposit effecting the purity of the metal, it is felt that a concentration of 0.1 gm of selenious acid per litre would be the optimum for a good current efficiency keeping in view the lower selenium content.

Influence of ammonium sulphate in the electrolyte on current efficiency of deposition — From Table 7.II, it can be seen that current efficiency slowly increases with decrease in ammonium sulphate concentration and passes through a maximum before it falls to a minimum in the complete absence of ammonium sulphate in the electrolyte. In presence of rather high ammonium sulphate concentrations, pittings appear on the cathode due to sticking of hydrogen bubbles which partly explains the slow fall in current efficiency. Secondly, the formation of manganese ammonium sulphate co-ordination compound in the electrolyte decreases the free manganese ion concentration in the electrolyte; the higher the ammonium sulphate concentration, the less the free manganese ions at a particular concentration of manganese sulphate. On the other hand, in the complete absence of ammonium sulphate in the electrolyte, loose and poorly adherent deposits with considerable treeing are only

obtained which fall from the cathode redissolving in the electrolyte and results in a sharp fall in current efficiency.

But the slow fall in current efficiency with increase in ammonium sulphate concentration is more than counter-balanced by other significant improvements and advantages which ammonium sulphate brings in the electro-deposition of manganese. Presence of this salt not only promotes the deposition of manganese in a thick, coherent and adherent form but also permits the use of a high catholyte pH without precipitation of manganese hydroxide. Besides, as can be seen from Table 7.II, the loss in current efficiency is sufficiently made up by the increase in conductivity of the solution at higher ammonium sulphate concentrations with the resultant lowering of cell voltage and energy consumption. Considering all these factors, it is felt that an ammonium sulphate concentration of 125-50 gm per litre would be the optimum for a good and steady current efficiency.

No appreciable change is found in the selenium content of the deposited metal with varying concentrations of ammonium sulphate in the electrolyte except perhaps a slow decline with decreasing concentrations of ammonium sulphate.

Influence of temperature on current efficiency of deposition — Table 7.III shows the marked influence of temperature on current efficiency of deposition. Raising the temperature from 18.5°C to 27.5°C increases the current efficiency from 80.17 to 87.06 per cent. A similar rise can be seen at 0.025 gm per litre of selenious acid concentration (vide Table 7.I, Expt 2; and Table 7.IV, Expt 1). A current efficiency of 73.35 per cent at 21°C increases to 81.87 per cent at 29.5°C. This increased efficiency remains practically unchanged up to 36.5°C above which temperature current efficiency begins to fall.

With rise in temperature, the diffusion of manganese ions to the vicinity of the cathode, where manganese ions are being depleted owing to its being discharged on the cathode, increases. Due to this increased diffusion, manganese ion concentration in the vicinity of the cathode does not decrease, and, therefore, current efficiency remains unimpaired. But at still higher temperatures, though diffusion is faster, deposited manganese begins to redissolve and the current efficiency falls.

In Fig. 7.I, unetched surfaces of the deposits, obtained at various temperatures, are given. It can be seen that the nodular growth formation decreases as temperature is raised. The lower the temperature, the less will be the diffusion of manganese ions to the vicinity of the cathode, when the formation of nodular growth takes place from the cathode towards regions of high manganese concentration. The fine graininess of the deposits obtained at high temperatures is clearly seen from Fig. 7.I.



(1) At 18.5°C

(2) At 27.5°C

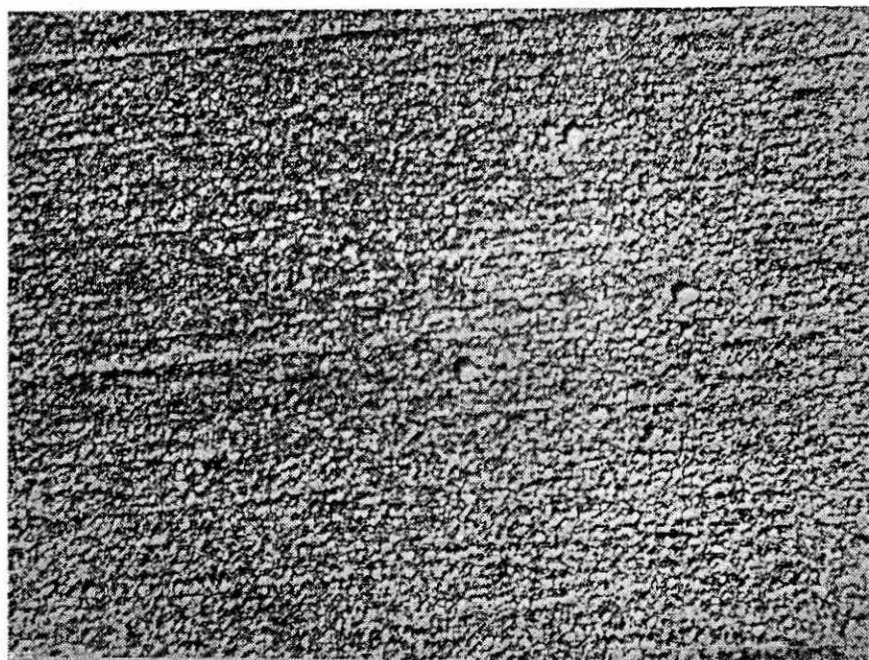
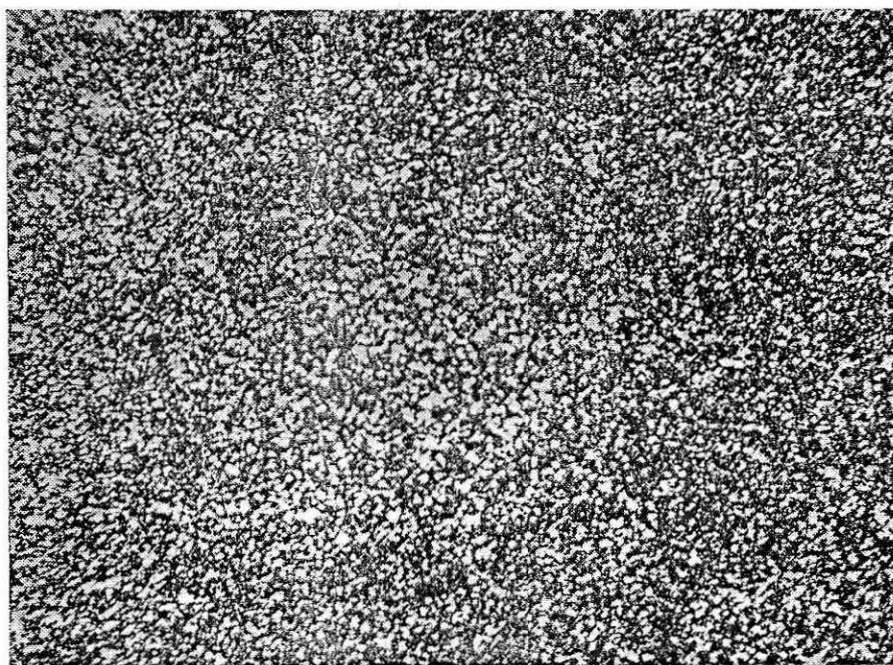


FIG. 7.I — MICRO-PHOTOGRAPHS SHOWING VARIATION IN GRAIN SIZE WITH TEMPERATURE OF ELECTROLYSIS $\times 100$



(3) At 36.5°C

(4) At 46.5°C

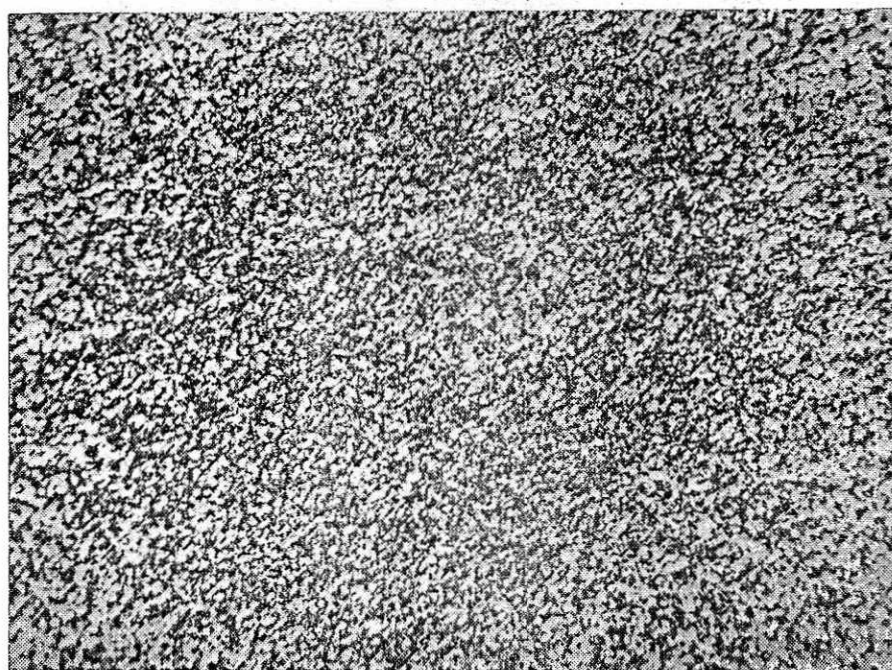
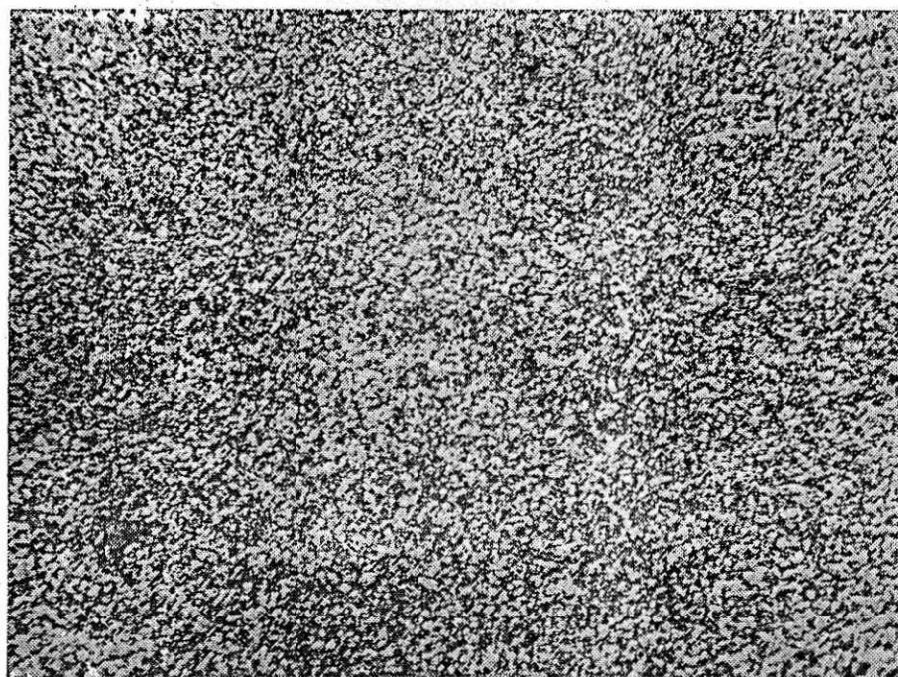


FIG. 7.I (continued) — MICRO-PHOTOGRAPHS SHOWING VARIATION IN GRAIN SIZE WITH TEMPERATURE OF ELECTROLYSIS - $\times 100$



(5) At 61°C

FIG. 7.I (continued) — MICRO-PHOTOGRAPHS SHOWING VARIATION IN GRAIN SIZE WITH TEMPERATURE OF ELECTROLYSIS $\times 100$

Stripping was easy at low temperatures, but at high temperatures stripping was extremely difficult and no metal could be collected. At higher temperatures, the rate of combination of hydrogen atoms is likely to increase resulting in a lower hydrogen content in the deposit. It has been said²¹ that with increase in temperature up to 55°C, the stress in the electro-deposits is found to decrease. These might explain lower stripping of metal from the cathode at higher temperatures, correlating the relationship of easy stripping with the hydrogen content and stress in the electro-deposit.

Influence of selenium content in the electrolyte with respect to temperature of electrolysis on current efficiency of deposition — In the preceding section, it is seen that current efficiency of deposition increases by 7.8 per cent by raising the temperature of electrolysis from 18.5 to 27.5°C. From Table 7.IV, it is interesting to note that the concentration of selenious acid can be decreased with increase in temperature of electrolysis to obtain the same range of current efficiencies. As the temperature of electrolysis is raised from 20° to 30°C, the concentration of selenious acid in the electrolyte can be reduced from 0.1 gm per litre to 0.025 gm per litre, almost to one-fourth, to obtain practically the same order of current efficiencies.

It would be of further interest to mention that while slight selenium precipitation was noted with 0.1 gm/l of selenious acid at 28°C, there was

no selenium precipitation at this temperature with 0.025 gm of selenious acid per litre. At 36.5°C also there was practically very little selenium precipitation with 0.025 gm per litre of selenious acid.

For electro-winning of manganese when the deposition is to be carried out for long hours, if 0.1 gm per litre of selenious acid concentration is used in the electrolyte, the temperature of electrolysis has to be kept at about 28°C so that the catholyte does not get fouled on account of selenium precipitation. And if the temperature of electrolysis is to be kept at 36°C, it would be advantageous to choose a selenious acid concentration of 0.025 gm per litre.

It would be interesting to mention that when the electrolyte was prepared from chemically pure reagents, but was not purified as mentioned in the experimental procedure, a uniform thick deposit of manganese could not be obtained with 0.025 gm per litre of selenious acid at 36.5°C though at lower temperatures, with the same concentration of selenious acid, uniform deposits of manganese with good current efficiencies were obtained. This indicates that, at high temperatures and at low selenium concentrations, the impurities in the electrolyte affect good deposition and efficiency. If selenium concentration is high and the temperature of deposition is low, slight impurities are not found to have much deleterious effect on obtaining thick deposits at reasonably good current efficiencies. This is because both low temperature and high selenium content increase the hydrogen over-voltage and, possibly on account of this, under these conditions good deposit of manganese is obtained. On the contrary, high temperature and low selenium content decrease the hydrogen over-voltage and when conditions are such that the hydrogen over-voltage is low, slight impurities have much deleterious effect on deposition of manganese.

Influence of pH of catholyte on current efficiency of deposition — From Table 7.V, it can be seen that current efficiency of deposition increases with increase in pH value of catholyte up to a limiting value of 7.7 and with further increase in pH, the efficiency falls down.

As the pH value is increased, the hydrogen decomposition potential becomes more negative and at more negative values, less current is consumed for discharge of hydrogen. But with further increase in pH, OH⁻ ions preponderate in the catholyte with the formation of manganese hydroxide. This precipitated manganese hydroxide at high pH values in catholyte settles on the cathode and impairs efficient deposition of manganese. A similar observation has been recorded by the authors on deposition of manganese with sulphur dioxide as an additive agent². Under otherwise similar conditions, the optimum pH value of catholyte can be increased with lowering of manganese sulphate concentration in the electrolyte and vice versa; because at a particular concentration of

ammonium sulphate, manganese hydroxide begins to precipitate from dilute solutions of manganese sulphate at high pH values while manganese hydroxide precipitates from concentrated solutions at low pH values.

During the deposition of manganese with sulphur dioxide as an addition agent under favourable conditions, a current efficiency of 65 per cent is generally obtained. The rest of the current is spent on the discharge of hydrogen thereby depleting the H^+ ion concentration in the vicinity of the cathode and increasing the pH value of catholyte as deposition goes on. On the other hand, with selenium as an addition agent a current efficiency of the order of 90 per cent is obtained and comparatively only little current is consumed for the discharge of hydrogen. Because of this low rate of discharge of hydrogen ion in the cathode chamber, the pH of the catholyte is not found to change appreciably during deposition of manganese with selenium as an addition agent. Further, even in highly acid conditions of catholyte, in presence of selenium, good current efficiencies more than that attainable with sulphur dioxide under optimum conditions, have been obtained as can be seen from Table 7.V.

Hydrogen content in the deposit appears to decrease with increase in pH value of catholyte as is seen from Table 7.V. Though at low pH values of catholyte, the hydrogen content is not found to be appreciably changing, a slow decrease in hydrogen content is observed as the pH change occurs in the higher ranges of pH . This may most likely be due to the low H^+ ion concentration in the catholyte at high pH values and high efficiency obtained at these pH values.

In this series of experiments on pH -current efficiency studies, stripping of manganese metal from the cathodes did not seem to have much correlation with the hydrogen content of the metal. Possibly, at high pH values, manganese hydroxide can be occluded in the deposit increasing the stress²² inside the deposit which results in easier stripping at higher pH values of catholyte.

Influence of concentration of manganese sulphate in the electrolyte on current efficiency of deposition — From Table 7.VI, it is seen that with increase in concentration of manganese sulphate, current efficiency increases, the increase being more marked up to a concentration of 125 gm of manganese sulphate per litre.

Presence of selenious acid in the catholyte raises hydrogen over-voltage and suppresses discharge of hydrogen. Mn^{2+} ions are, therefore, discharged at a higher current efficiency. Unless the electrolyte contains high concentration of manganese ions, current efficiency falls off due to

fast depletion of Mn^{2+} ions in the vicinity of the cathode. But the concentration of Mn^{2+} ions cannot be raised to any value unless ammonium sulphate is added in sufficient amount to prevent formation of manganese hydroxide at the high pH values of catholyte, optimum for manganese deposition. But, as discussed earlier, increase in ammonium sulphate concentration decreases the current efficiency. Further, at higher concentrations of manganese and ammonium sulphate, crystallization and loss of manganese during purification (when the pH of the electrolyte has to be raised to 7.2-7.6) take place. Considering the various factors a concentration of 125-50 gm of manganese sulphate seems to be the most suitable.

At higher concentrations of manganese sulphate in the electrolyte, nodular growths were more prominent at the edges and bottom of the cathode, where cathodic current density is high.

Influence of cathodic current density on current efficiency of deposition — From Table 7.VII, it can be seen that current efficiency increases with current density and reaches a maximum of 89 per cent at a current density of 2.9 amps/sq dm. With further increase in current density, the efficiency of deposition is not found to be appreciably changing and remains almost constant at 89 per cent up to a current density of 4.86 amps/sq dm. Above this current density, a very slow fall is noticed.

At very low current densities, it is likely that the cathode is not polarized to an extent as to enhance the steady deposition of highly electro-negative manganese and low efficiencies are obtained. At low current densities, the hydrogen over-voltage is low. At very high current densities, a lot of treeing grows up at the edges of the cathode which falls and re-dissolves in the electrolyte. This partly explains the slight fall in current efficiency at higher current densities.

The energy consumption at an optimum current density of 2.90 amps/sq dm is 4.704 kWh/kg of deposited manganese. As the current density is increased from 2.9 amps/sq dm, though the efficiency remains almost unchanged up to a current density of 4.86 amps/sq dm, the energy consumption increases from 4.704 to 5.67. At optimum current density, the cathode potential is also optimum but with further increase in current density, the applied cathode potential and the resultant cell voltage also increase requiring a higher energy consumption per kilogram of manganese.

In electro-winning of metals, if the efficiency of deposition remains unchanged, a higher current density is generally chosen for, under otherwise similar conditions, a larger output from the cell can be effected by employing a high current density.

Conclusion

Under optimum conditions of different cell variables, in presence of 0.1 gm of dissolved sulphur dioxide per litre of electrolyte, a current efficiency of the order of 65 per cent with an energy consumption of 7.8 kWh/kg of deposited manganese is generally obtained. On the other hand, current efficiencies of the order of 90 per cent, corresponding to an energy consumption of 5 kWh/kg of deposited manganese, can be obtained from electrolysis of 125-50 gm of manganese sulphate, 125-50 gm of ammonium sulphate and 0.1 gm of selenious acid per litre of electrolyte at a catholyte pH of 7.8, temperature of 28-30°C and a cathodic current density of 4.8 amps/sq dm. The metal thus obtained contains about 0.25 per cent of selenium.

REFERENCES

1. DEAN, R. S., *Electrolytic manganese and its alloys* (Ronald Press Company, New York), 1952.
2. DHANANJAYAN, N., CHAKRAVARTI, H. K. & BANERJEE, T., *J. sci. ind. Res., India*, **13B** (No. 2), (1954), 136.
3. DHANANJAYAN, N., CHAKRAVARTI, H. K. & BANERJEE, T., *Indian Construction News*, July 1960, 204.
4. SHELTON, S. M., *U. S. Bureau of Mines, R.I.*, 3322 (1936), 29; C.A. 31 (1937), 1705.
5. SHELTON, S. M., *U.S. Patent* 2,119,560, June 7, 1938; C.A. 32 (1938), 5711.
6. YANITSKI & STULPINAS, B. B., *Zhur Priklad Khim*, 1957, 30, 1776-8; C.A. 1958, 52, 7906d.
7. YANITSKI & STULPINAS, B. B., *Zhur Priklad Khim*, 1958, 31, 255-60, C.A. 1958 52, 10761f.
8. JACOBS, J. H., HUNTER, J. W., YARROL, W. H., CHURCHWARD, P. E. & KNICKERBOCKER, R. G., *Metal ind*, 1944, 65, 358-60.
9. FURMAN, N. H., *Scott's standard methods of chemical analysis*, 5th edition (D. Van Nostrand & Co, New York), 1939, Vol 1, 791.
10. A.S.T.M., *Methods for chemical analysis of metals*, *Am. Soc. for testing materials*, 1950, 94.
11. MELLOR, J. W., *A comprehensive treatise on inorganic and theoretical chemistry* (Longmans, Green & Co, London), Vol X, 1930, 746.
12. YOST, D. M. & RUSSEL, H. (Jr), *Systematic inorganic chemistry of the fifth and sixth group of non-metallic elements* (Prentice-Hall, New York), 1944, 325, 289, 291-3.
13. MOELLER, *Inorganic chemistry* (Asia Publishing House, Bombay), 1938, 286.
14. EMELEUS, H. J. & ANDERSON, J. S., *Modern aspects of inorganic chemistry* (Routledge & Kegan Paul Ltd, London), 1960, 408.
15. THORNE, P. C. L. & ROBERTS, E. R., *Fritz Ephraim's inorganic chemistry* (Interscience Publishers Inc, New York), 1949, 5th edition, 531, 539.
16. JACOBSON, C. A., *Encyclopedia of chemical reactions* (Reinhold Publishing Corporation, New York), 1956, 32, 73.

17. HIRASAWA, J. *Mining Inst. Japan*, 1956, 72, 255; C.A. 1956, 50, 16473a.
18. POLUKAROV, M. N., *Referat Zhur. Khim.* 1954, No. 42784; C.A. 1955, 49, 14525g.
19. EVANS, U. R., *An introduction to metallic corrosion* (Edward Arnold & Co, London), 1950, 144.
20. POLUKAROV, M. N., *Zhur. Obshchei Khim.*, 1948, 18, 249; C.A. 1949, 43, 950g.
21. EVANS, D. J., *Trans. Faraday. Soc.*, 1958, 54, 1086.
22. HOTHERSALL, A. W., Symposium on internal stresses in metals and alloys, *Inst. of Metals* 1948, 116.

APPENDIX

The important observations, made during the course of these investigations, may be summarized as follows:

1. The standard electrode potential value of pure alpha manganese (containing no sulphur or selenium) is less negative than that of gamma manganese and that the values for the two phases differ only very slightly, as would be expected from the thermo-chemical data of the two phases.

2. The standard electrode potentials of alpha manganese containing sulphur or selenium are more negative than those of pure alpha manganese and gamma manganese.

3. Pure alpha manganese, containing no sulphur or selenium, has a very low hydrogen over-voltage while gamma manganese has a comparatively higher over-voltage.

4. Cathode potential values for deposition of manganese in various phases increase in the following order:

- (i) Pure gamma manganese
- (ii) Alpha manganese containing sulphur
- (iii) Alpha manganese containing selenium.

5. Deposition of manganese, at current densities of the order of 4-5 amps/sq dm and at pH values around 7 from pure solutions of manganese and ammonium sulphate in the absence of reducible sulphur or selenium compounds on stainless steel cathodes, results in a non-uniform amorphous deposit for the first 8-10 seconds over which gamma manganese begins to build up.

Deposits on copper up to one minute of deposition, under the same conditions, do not show any other lines in X-ray pattern other than those of copper, after which up to 3 minutes of deposition, besides substrate pattern, broad halo at low angle indicating amorphous nature of the growing deposit is noticed.

At 5 minutes of deposition, deposits on both stainless steel and copper give all the diffraction lines of gamma manganese.

6. While deposits on stainless steel and copper cathodes in absence of sulphur dioxide in the electrolyte give distinguishingly clear diffraction lines of gamma manganese at 5 minutes of deposition, as mentioned above, in presence of 0.1 gm of sulphur dioxide per litre, no evidence for deposition of gamma manganese is found on either of the cathodes. On the other hand, deposits on copper and stainless steel, in presence of sulphur dioxide, continue to show the initial amorphous pattern up to 10 minutes of deposition, and at 15 minutes deposition both give clear crystalline pattern of alpha manganese.

7. Addition of 0.1 gm/l of selenious acid results in the deposition of crystalline alpha manganese after 1 minute of deposition on stainless steel cathodes.

8. Copper is found to have some influence in the first few layers of the deposit. Beyond that, it is found that the substrates have no directing influence on the structure of the deposit. The presence of reducible sulphur or selenium compounds alone in the electrolyte determine the ultimate structure.

9. With all other conditions of deposition like current density, pH, temperature, flow of electrolyte and even current efficiency remaining the same, on the same and similarly prepared substrates, gamma or alpha manganese can be prepared. Addition of 0.1 gm/l of sulphur dioxide or selenious acid results in the deposition of alpha manganese while in the absence of sulphur or selenium compounds, gamma manganese is obtained.

10. Gamma manganese can be deposited on alpha manganese and vice versa depending upon the absence or presence of reducible sulphur or selenium compounds in the electrolyte.

11. During deposition of gamma over alpha manganese an amorphous deposit forms initially. Because of this, the initiation of gamma manganese over alpha manganese is difficult and the current efficiency of deposition of gamma over alpha manganese is found to be lower than that on stainless steel or copper.

12. Deposited gamma manganese over alpha manganese could be stripped off from each other while alpha manganese deposited over gamma manganese could not be stripped off, the entire deposit together coming out from the cathode.

13. The electro-deposited alpha manganese in presence of sulphur or selenium contains 250-350 cc of hydrogen per 100 gm while the absolute solubility of hydrogen in alpha manganese is 21.6 cc per 100 gm at 25°C.

14. Electro-deposited gamma manganese contains 42-70 cc of hydrogen per 100 gm, almost the same amount soluble in gamma manganese within its temperature range of stability.

15. It is noticed that the effects of reducible sulphur or selenium compounds in the deposition of manganese are not primarily those of an anti-oxidant to prevent the precipitation of manganese hydroxide or to suppress the harmful effects of impurities. The presence of these compounds in the electrolyte increases the cathodic polarization with a resultant increase in the hydrogen content of the alpha deposits obtained. Both these properties have been attributed to the negative catalytic effect of sulphur and selenium on the recombination of hydrogen atoms.

16. Organic inhibitors which also increase the cathodic polarization do not yield the deposition of alpha manganese. Alpha manganese is obtained when not only the cathodic polarization is increased but also the hydrogen content of the deposit is increased. Other than group VIB elements, these effects are brought about by the use of very high current densities.

17. Increase of current density from 5 to 30 amps/sq dm prevents the formation of gamma manganese from pure solutions containing no reducible sulphur or selenium compounds and an amorphous brittle manganese containing about 550 cc of hydrogen per 100 gm is obtained.

18. The manganese initially obtained in presence of sulphur dioxide at catholyte pH values around 7, and the deposit obtained at very high current densities bear a close resemblance in that both give an X-ray powder pattern of broad halo at low angle and no back reflection lines indicating the amorphous nature of the deposit. The hardness of both these deposits is found to be similar to that of alpha manganese.

19. At pH values around 2, the initial deposit obtained in presence of sulphur dioxide shows crystalline pattern of alpha manganese instead of the amorphous pattern obtained up to 10 minutes at higher pH values of catholyte.

From these experimental facts, the following mechanism can be suggested in the deposition of alpha and gamma modifications at current densities of the order of 4-5 amps/sq dm and at catholyte pH values around 7.

1. (a) Barring the exceptions of a directing influence of an active substrate in the first few atomic layers of the deposit, manganese is initially electro-deposited

from pure solutions of manganese and ammonium sulphate in an amorphous nature. Experimental evidences indicate that this amorphous deposit resembles alpha manganese.

(b) Pure alpha manganese has a very low hydrogen over-voltage and, for this reason, it cannot be electro-deposited from pure solutions to an appreciable thickness.

(c) As soon as an initial flash layer of such extremely fine-grained (alpha) manganese is formed in about 8-10 seconds, it facilitates hydrogen discharge and hydrogen evolution takes place. This discharge of hydrogen ions makes the vicinity of the cathode more alkaline when the potential for evolution of hydrogen is raised up.

(d) The standard electrode potential of gamma manganese is only slightly more negative than that of alpha manganese, the increase in polarization due to discharge of hydrogen [as mentioned under (c)] enables gamma manganese to be deposited.

(e) Due to the higher hydrogen over-voltage of gamma manganese, gamma manganese begins to build up.

2(a) With an addition of 0.1 gm/l of sulphur dioxide to the electrolyte the amorphous nature of the initial deposit continues to build up to an increasing thickness, over which crystalline alpha manganese is obtained. This initial amorphous deposit has hardness values similar to that of alpha manganese.

This bears a close resemblance to the thick amorphous brittle manganese, having hardness values of alpha, obtained at high current densities of deposition from pure solutions of manganese and ammonium sulphate and in the absence of reducible sulphur or selenium compounds.

(b) Addition of reducible compounds of sulphur or selenium to the electrolyte not only increases the cathode potential values, but simultaneously increases the surface concentration of hydrogen atoms similarly as in the case of high current densities of deposition from pure solutions.

(c) These above two facts indicate that alpha manganese begins to build up when the cathodic polarization is raised, together with a high surface concentration of hydrogen atoms and resultant adsorption or absorption as noticed from the hydrogen contents of deposited manganese in presence of sulphur or selenium, and at high current densities from pure solutions.

(d) Besides these two important effects, presence of reducible sulphur or selenium in the electrolyte has another added advantage in that cathodically reducible or colloidal sulphur or selenium gets adsorbed on the growing borders of the crystals.

(e) The strength of bond between manganese and sulphur or selenium may be greater with a result of the adsorption of these particles on the surface and their effect on the discharge of metal ions may also be greater.

(f) After the first flash layer of amorphous (alpha) manganese takes place in 8-10 seconds after the introduction of the cathode, further deposition of alpha manganese in presence of these elements (sulphur or selenium) has to be attributed to the properties mentioned before and has to be explained presumably on the basis that a part of the hydrogen goes inside the lattice and remains as protons. At the same time, it is felt that all the hydrogen inside the deposited metal cannot be in interstitial positions and, as such, at present it could only be a speculation to attempt to a theoretical approach to the role of hydrogen in the formation of crystalline alpha deposit.