

## CHAPTER IV

### Addition agents, hydrogen content and structure of electro-deposited manganese

The effect of various addition agents on the structure and hydrogen content of electro-deposited manganese has been studied. With the exception of boric acid, only cathodically reducible compounds of group VIB elements S, Se and Te prevent the formation of gamma manganese and facilitate the deposition in alpha modification. Addition of organic inhibitors or polarizing agents, which increase cathodic polarization, do not yield 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.

## Introduction

The solubility of hydrogen in the various allotropic modifications of manganese has been exhaustively studied by Sieverts<sup>1</sup> and Potter<sup>2</sup> and the results of both group of workers were, in general, in close agreement. Both Sieverts and Potter agree that the solubility of hydrogen in alpha manganese decreases up to 500°C and then increases with increasing temperature up to gamma → delta transformation. The absolute solubility of hydrogen at particular temperatures in alpha, beta and gamma modifications are given in Table 4.I.

TABLE 4.I — ABSOLUTE SOLUBILITY OF HYDROGEN IN ALPHA, BETA AND GAMMA MANGANESE

PHASE	STRUCTURE AND TYPE <sup>3,4</sup>	TEMPERATURE RANGES OF STABILITY <sup>5</sup> °C	HYDROGEN CONTENT <sup>1,2</sup>	
			Tempera- ture °C	cc/ 100 gm
Alpha	Complex cubic A12	Up to 725	24	21.6
			500	11.4
Beta	Complex cubic A13	725-1095	745	23.4
Gamma	Face-centred cubic A1	1095-1134	1100	41.3
Delta	Body-centred cubic A2	1134-1245	—	—

On the other hand, it is seen that the electro-deposited alpha manganese obtained in presence of sulphur or selenium contains high hydrogen, about 250-350 cc per 100 gm, and the electro-deposited gamma manganese is found to contain 42-70 cc per 100 gm (ref 6). It is interesting that the complex cubic alpha manganese with 58 atoms in the unit cell, whose absolute solubility for other metals is practically very little, can take up so much of hydrogen while the simple face-centred tetragonal electro-deposited manganese, whose solubility for other metals is considerably high, takes up only 42-70 cc per 100 gm under the same current efficiencies of deposition. Sulphur and selenium have been mentioned as negative catalysts for combination of hydrogen atoms to form molecules<sup>7</sup>. Hence, it can be understood that the presence of these negative catalysts in the electrolyte in the case of alpha deposition tends to increase the concentration of hydrogen atoms at the cathode surface resulting in a high absorption of hydrogen by manganese. It was felt desirable to examine whether the high hydrogen content obtained in presence of sulphur or selenium in the electrolyte or any of its related properties is responsible for the deposition of manganese in complex and stable alpha manganese. Hence, it is intended to study in this work the structure and hydrogen

content of deposited manganese in presence of trace amounts of various addition agents, such as

- (i) negative catalysts for hydrogen re-combination,
- (ii) different sulphur compounds,
- (iii) oxidizing agents in presence of selenium,
- (iv) organic inhibitors,
- (v) non-metallic elements, and
- (vi) polarizing agents,

in order to examine whether any correlation exists between the structure and hydrogen content of the deposit and the polarizing property of the addition agent.

### Materials and methods

The electrolytic cell used for the deposition and the mode of preparation of electrolyte were exactly the same as described in the earlier paper. In all cases, the electrolyte and conditions of experiments were such that, but for the addition of each addition agent, good deposits of gamma manganese could have been easily obtained. For each addition agent either guaranteed reagent of that salt was used or was prepared by known methods from spectrographically pure metals supplied by Johnson Mathey & Co Ltd, London.

*Hydrogen determination* — The absolute solubility of hydrogen in manganese is minimum at 500°C (ref 1 & 2), and by heating the specimen, at this temperature and in high vacuum, practically all the hydrogen can be made to diffuse out of the sample. The hydrogen content in electro-deposited manganese was determined based on this vacuum heating and extraction principle.

Sample for hydrogen determination was taken from random sites of the deposit and the surfaces were cleaned with benzene followed by acetone for any greasy matter. About 0.5-1 gm of the sample, depending upon the hydrogen content, was usually taken. The specimen was heated at 500°C in a vacuum heating and extraction assembly set up by Banerjee<sup>8</sup> in National Metallurgical Laboratory. The assembly is a modified form of the design by Newell<sup>9</sup>. The gas liberated was collected in inverted mercury tubes with the aid of a Toepler pump.

The collected gas was analysed for hydrogen in an Ambler's gas analysis apparatus. The gas was led into the calibrated bulbs of known volume in the Ambler's apparatus and the pressure was read on the manometer. The value was further checked by passing oxygen and

reading the pressures of the combined gases and after reaction between them at known volumes.

From the pressure known at a known volume of hydrogen, the volume of hydrogen at NTP was calculated.

### Results of experiments

Results of experiments on the structure and hydrogen contents of manganese deposits obtained in the presence of various addition agents have been presented in Tables 4.II to 4.VII.

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TABLE 4.II — STRUCTURE AND HYDROGEN CONTENT OF DEPOSITS OBTAINED IN PRESENCE AND ABSENCE OF SELENIOUS OR SULPHUROUS ACID IN THE ELECTROLYTE ON CATHODES OF COPPER AND STAINLESS STEEL

Composition of electrolyte: 65-70 gm manganese sulphate per litre and 135-40 gm ammonium sulphate per litre. Addition agent as indicated in the Table

Initial pH of feed electrolyte and cell solution: 7.3  
 Flow of electrolyte: 10 cc/min  
 Current density: 4.6 amps/sq dm  
 Temperature of electrolysis: 28-30°C  
 Time of deposition: 2 hr

ADDITION AGENT PER LITRE	CATHODE MATERIAL	AVERAGE VOLTS	CURRENT EFFICIENCY %	SULPHUR OR SELENIUM CONTENT IN THE DEPOSIT %	STRUC- TURE	HYDRO- GEN CONTENT cc/ 100 gm
Nil	Copper	5.1	67.35	Not de- tected	Gamma	70
Nil	Stainless steel	5.25	73.72	do	Gamma	42
0.013 gm of sele- nious acid	do	5.3	64.68	0.13 Se	Alpha	260
0.13 gm of sul- phurous acid	do	5.2	63.48	0.07 S	Alpha	231

*Remarks* — It is seen that gamma manganese contains 42-70 cc of hydrogen while alpha manganese prepared from baths containing sulphur or selenium contains 231-60 cc of hydrogen per 100 grams.

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TABLE 4.III — ADDITION AGENTS AND HYDROGEN CONTENT

I. Group VB and VIB elements generally known as negative catalysts for  $H+H=H_2$  reaction

Conditions of deposition: Same as in Table 4.II

ADDITION AGENTS PER LITRE	TIME OF DEPOSITION hr	AVERAGE VOLTS	CURRENT EFFICIENCY %	STRUCTURE	HYDROGEN CONTENT OF DEPOSIT (cc/100 gm)	REMARKS
Sulphur as 0.15 gm of $SO_2$	2	5.5	63.75	Alpha	273	—
Selenium as 0.1 gm of selenious acid	3	—	85.43	do	325	—
Tellurium as 0.1 gm of telluric acid (prepared $H_2O_2 + H_2SO_4 + HNO_3$ ) (ref 11)	2	5.2	26.02	Alpha and amorphous, ie very fine-grained	598	—
Bismuth as 0.1 gm of bismuth oxide	$\frac{1}{2}$	5.3	—	—	—	Black deposit
0.05 gm arsenic as sodium arsenite	$\frac{1}{2}$	—	—	—	—	Deposit at edges only
0.05 gm phosphorous as sodium hypophosphite	$\frac{1}{2}$	5.5	65.77	Gamma	84	—

*Remarks* — It is noticed that addition of cathodically reducible compounds of group VIB elements, viz sulphur, selenium and tellurium, results in the deposition of alpha manganese with high hydrogen content.

Of group VB elements, phosphorus does not deter the deposition of gamma manganese, while arsenic and bismuth are found to be deleterious in the deposition of manganese.

TABLE 4.IV — ADDITION AGENTS AND HYDROGEN CONTENT

## II — Sulphur compounds

Conditions of deposition: Same as in Table 4.II

ADDITION AGENTS PER LITRE	TIME OF DEPO- SITION	AVERAGE VOLTS	CUR- RENT EFFI- CIENCY %	STRUC- TURE	HYDRO- GEN CONTENT cc/ 100 gm	REMARKS
Dithionic acid 0.4 gm	2 hr	5.0	65.55	Gamma	36.1	Sulphide sulphur not detected in 6 gm sample
Thiourea 0.332 gm	2 hr	5.1	68.89	Alpha	160.0	Very adherent bright deposit
Sodium formalde- hyde sulphonylate	20 min	5.25	65.31	do	—	Deposit was too adherent but not uniform
<i>o</i> -Tolylthiourea 0.26 gm	2 hr	5.2	63.43	do	230.5	Very bright deposit

*Remarks* — Addition of dithionic acid has no effect on the structure of deposited manganese to that obtained from pure electrolytes, but addition of cathodically reducible sulphur compounds, such as thiourea and *o*-tolylthiourea, results in the deposition of alpha manganese.

### Discussion of experimental results

*Negative catalysts for hydrogen re-combination* — Phosphorous, arsenic, bismuth, sulphur, selenium and tellurium have been mentioned as negative catalysts for hydrogen recombination<sup>10</sup>, ie for the reaction  $H + H \rightleftharpoons H_2$ . Anions  $SO_4^{2-}$  and  $PO_3^{2-}$  being in a high degree of oxidation and stability are not reduced at the cathode and have no influence on the process of hydrogen penetration, but lower oxides such as sulphur dioxide and oxides and oxidized anions of other elements mentioned, give by cathodic reduction free elements and hydrides<sup>10</sup>. Phosphorous was added as sodium hypophosphite, arsenic as sodium arsenite, sulphur and selenium as dioxides and tellurium as telluric acid.

As seen from Table 4.III, addition of phosphorous did not prevent formation of gamma manganese. On 30 minutes of deposition a current efficiency of 65 per cent was obtained with a hydrogen content of 84 cc per 100 gm of metal.

With arsenic, there was practically no deposit on the cathode except at the edges where the current density is higher in comparison with other

TABLE 4.V — ADDITION AGENTS AND HYDROGEN CONTENT

## III. Oxidizing agents in presence and absence of selenium

Conditions of deposition: Same as in Table 4.II

ADDITION AGENTS PER LITRE	TIME OF DEPO- SITION hr	AVERAGE VOLTS	CURRENT EFFI- CIENCY %	STRUC- TURE	HYDROGEN CONTENT OF DEPOSITED METAL (cc/100 gm)
Selenium as 0.1 gm of selenious acid and 4 gm of ammonium per sulphate	2	5.3	88.67	Alpha	184
Selenium as 0.1 gm of selenious acid and 0.05 gm of cerium as ceric sulphate	2	5.3	88.0	do	195
Ammonium persulphate 10 gm	2	5.0	50.0	Gamma	50.6

*Remarks* — Addition of strong oxidizing agents such as 10 gm/l ammonium persulphate to the pure electrolyte does not prevent the formation of gamma manganese. Nor the addition of oxidizing agents to the electrolyte containing selenium hamper the deposition of alpha manganese.

parts. Jacobs<sup>12</sup> has mentioned that the presence of 0.024 gm of arsenic per litre of electrolyte is deleterious in deposition of manganese even in presence of sulphur dioxide.

Bismuth addition also brings a deleterious effect on the deposition of manganese. In presence of bismuth, only a black deposit was obtained as is usually obtained in the presence of impurities like nickel, cobalt, zinc, iron, etc, in the electrolyte. The structure of black powdery deposit usually obtained in presence of impurities is explained later.

Thus, it is seen that the negative catalytic elements (for hydrogen recombination) of group VB do not initiate the deposition of alpha manganese and further it is found that with the exception of phosphorus group VB elements are deleterious in the deposition of manganese.

On the other hand, sulphur and selenium in group VIB prevent the formation of gamma manganese and facilitate the deposition of alpha manganese with good current efficiencies. Of these two, selenium is found to have more powerful effect. Even as little as 0.008 gm of selenium

gives the effect of 0.05 gm of sulphur with a current efficiency of 65 per cent, the current efficiency increasing to the order of 90 per cent with a selenium content of 0.05 gm per litre of electrolyte. As seen from Table 4.II, alpha manganese prepared in presence of 0.008 gm of selenium per litre of electrolyte as an addition agent contains 260 cc of hydrogen per 100 gm which increases to 325 cc per 100 gm at a selenium concentration of 0.06 gm per litre and remains around the range of 350 cc per 100 gm up to 0.25 gm per litre of selenium<sup>13</sup>. With increasing sulphur content in the electrolyte, though the hydrogen content is raised to 350 cc, the current efficiency of deposition does not increase as is the case with selenium.

Similar to sulphur and selenium, addition of tellurium to the electrolyte prevents the formation of gamma manganese and alpha manganese is obtained. The hydrogen content with tellurium is found to be higher than the other two, about 598 cc per 100 gm. But the current efficiency of deposition is very poor, only about 26 per cent. The X-ray patterns of deposit obtained with tellurium as an addition agent immediately after deposition and after one month's ageing at room temperature shows only the very intense diffraction lines of alpha manganese and they were extremely faint but for the high intensity line of 'd' value 2.099Å which was broadened and diffused. No back reflection pattern was obtained on examination of deposited metal with cathode. This indicates that with increasing hydrogen content in presence of tellurium, the grain size of the deposits falls below the range to be diffracted by X-rays. On ageing at room temperature the faint lines are found to be a little clear from the background but neither strong nor sharp.

Tellurium dioxide is only slightly soluble in water and telluric acid had to be used for addition of tellurium to the electrolyte. Telluric acid was prepared with tellurium of purity > 99 per cent. The mode of preparation of telluric acid had also its own influence in the deposition of manganese. Telluric acid prepared in dissolving tellurium in  $H_2O_2$  and conc  $H_2SO_4$  and addition of  $HNO_3$  (ref 11) gave better results than telluric acid prepared with  $KOH + H_2O_2 + HNO_3$  (ref 14) and  $HNO_3 + PbO_2$  (ref 15). In all cases of telluric acid addition, the hydrogen evolution was found to be negligible, yet the current efficiency of manganese deposition was low. This requires further investigation in future.

It is seen that the effect of group VIB elements on the efficient deposition of alpha manganese is in the order selenium, sulphur and tellurium, though the hydrogen content of the deposit in equal amount of the addition agent falls in the order of Te, Se and S. With regard to tellurium, from his studies on electrolytic charging of nickel, Smialowsky<sup>16</sup> says that the effect of this addition agent was irreproducible and the irreproducibility of results was probably due to the fact that tellurium hydride,

which evidently is the active poisoning compound, is highly sensitive to experimental conditions, such as temperature, presence of reducing and oxidizing agents, light, etc. He continues to say that a great number of experiments were performed, but no clear conclusion could be drawn from them, as was also felt during this investigation.

*Sulphur compounds* — The effect of various sulphur compounds on the structure of the deposit and hydrogen content is given in Table 4.IV. It has been reported that a manganese electrolyte circuit to which sulphur dioxide is added, will contain dithionate<sup>17</sup> and, according to Dean<sup>18</sup>, other compounds of sulphur, such as dithionates, xanthates and sulphides, can be used in place of sulphites for deposition of alpha manganese. It is seen from Table 4.IV that dithionic acid addition up to 0.4 gm per litre of electrolyte results only in the deposition of gamma manganese with 36.1 cc of hydrogen per 100 gm. No sulphide sulphur could be detected in a 6 gm sample of this deposit by the evolution method<sup>19</sup>. It shows that dithionic acid cannot be cathodically reduced and it is understandable from the absence of sulphide sulphur in the deposit. Schlain<sup>20</sup> has also experimented with 5 gm per litre of dithionic acid but has obtained only gamma manganese. Dithionic acid was prepared by the standard established method<sup>11</sup>.

Addition of sulphonylic acid as sodium formaldehyde sulphonylate resulted in very adherent deposit of alpha manganese. Addition of thiourea and *o*-tolylthiourea gave excellent deposits of very bright and adherent alpha manganese. These experiments show that when there is presence of cathodically reducible sulphur compound in the electrolyte, however long the chain of organic molecule attaching to sulphur might be, the result is the deposition of alpha manganese. Thiourea, as is reported, decomposes at the cathode giving hydrogen sulphide<sup>10,16</sup>. In presence of thiourea in the electrolyte, the hydrogen content of the deposit decreases to 160 cc per 100 gm. The very adherence and brightness of the alpha deposit shows much promise for thiourea as an addition as well as brightening agent for manganese plating baths.

*Oxidizing agents* — The effect of oxidizing agents in presence and absence of selenium on the structure and the hydrogen content has been presented in Table 4.V. It is seen that 10 gm per litre of ammonium persulphate has no deleterious effect on the deposition of manganese, and gamma manganese is obtained with a hydrogen content of 50.5 cc per 100 gm. On the other hand, additions of ammonium persulphate or other strong oxidizing agents, such as ceric sulphate, in presence of selenium do not deter the deposition of alpha manganese. Only the hydrogen content of the deposit in presence of selenium and oxidizing agents is found to be decreased to 184.95 cc per 100 gm from a value of 325 cc.

TABLE 4.VI — ADDITION AGENTS AND HYDROGEN CONTENT

## IV. Organic inhibitors

Conditions of deposition: Same as in Table 4.II

ADDITION AGENTS PER LITRE	TIME OF DEPOSITION hr	AVERAGE VOLTAGE	CURRENT EFFICIENCY %	STRUCTURE	HYDROGEN CONTENT OF DEPOSITED METAL cc/100 gm	REMARKS
Triamylamine 0.11 gm	2	5.05	68.31	Gamma	99.93	Very adherent. A very thin layer of white undercoat Mn was seen on stripping gamma Mn
Triethanolamine, 3 cc	$\frac{1}{2}$	—	54.34	do	48.6	—
Paraformaldehyde, 0.1 gm	1	5.35	73.68	do	26.62	Excellent deposit, not very adherent
Benzaldehyde	$\frac{1}{2}$	5.5	—	—	—	Black slimy coat. Benzaldehyde precipitated MnO <sub>2</sub> . It was twice filtered
Dimethylamine benzaldehyde, 0.05 gm	$\frac{1}{2}$	5.1	57.19	Gamma	123.6	Deposit was rather loose, not adherent. Amorphous coat was practically absent
Dimethylamine benzaldehyde, 0.1 gm	2	5.4	51.56	do	62.8	do
Glycerol, 25 cc	2	5.4	60.71	do	100	—
Glycerol, 10 cc	2	—	69.28	do	45.6	—

*Remarks* — Addition of organic inhibitors have no effect on the structure of deposited manganese to that obtained from pure electrolytes.

Sulphur dioxide as an addition agent in the electrolyte for manganese deposition has been discussed as an anti-oxidant to prevent the precipitation of manganese hydroxide at the  $pH$  attained in the catholyte<sup>21</sup>. No strong oxidizing agents can be tried along with sulphur dioxide as it is itself oxidized quickly. Above experiments with oxidizing agents in presence and absence of selenium clearly indicate that the primary effect of sulphur dioxide addition is definitely not that of a reducing agent. The current efficiency of 88 per cent obtained with selenium in presence of these oxidizing agents show that oxidizing agents do not have any particular deleterious effect on the current efficiency of deposition.

*Organic inhibitors : polarizing agents* — The effect of organic inhibitors on the structure and hydrogen content of the deposit has been presented in Table 4.VI. It is seen that the deposits obtained on the addition of any of these organic inhibitors were gamma manganese and that these inhibitors had no effect on the structure of deposited manganese to that obtained from pure solution in their absence. The hydrogen content varied from 26.62 cc per 100 gm with paraformaldehyde to 123.6 cc per 100 gm with dimethylamine benzaldehyde. The deposits obtained with paraformaldehyde and dimethylamine benzaldehyde were not very adherent with the cathode and could be stripped off easily in one piece and no thin layer of undercoat manganese was observed on the cathodes. This observation is similar to that of Schlain's<sup>20</sup> results that the gamma manganese obtained by him could be stripped off easily in sheets. Schlain, in his work, though used electrolytic manganese for preparing manganese sulphate solution, used only commercial quality ammonium sulphate. It has to be considered that impurities will have their own influence on cathodic polarization.

The mechanism of the action of these inhibitors is still not clearly understood<sup>22-28</sup>. In pickling of steel in presence of inhibitors, it is believed that "these inhibitors function by being adsorbed on the metal surface to form a fairly well-organized and oriented film, which serves to increase the polarization for hydrogen evolution by increasing the hydrogen over-voltage, concentration polarization and by introducing a high transfer resistance between the solution and metal surface".

With paraformaldehyde, it is seen that a current efficiency of 73.68 per cent is obtained with a hydrogen content of 26.62 cc per 100 gm. Presumably paraformaldehyde increases the hydrogen over-voltage by slowing down the discharge of hydrogen ions as seen from the low hydrogen content in the deposit compared to the hydrogen content in gamma manganese in absence of paraformaldehyde.

It is seen from Table 4.VI that addition of glycerol from 2.5 to 10 cc per litre had no effect on the structure of deposited manganese, gamma manganese being deposited in each case. However, according to Moiseev<sup>29</sup>

TABLE 4.VII — ADDITION AGENTS AND HYDROGEN CONTENT: MISCELLANEOUS ADDITION AGENTS

Conditions of deposition: Same as in Table before

ADDITION AGENTS PER LITRE	TIME OF DEPO- SITION hr	AVERAGE VOLTAGE	CURRENT EFFI- CIENCY %	STRUCTURE	HYDROGEN		REMARKS
					CONTENT OF DEPOSITED METAL	CONTENT OF METAL	
Boric acid 15 gm	$\frac{1}{2}$	5.78	2.2	Alpha	—	cc/100 gm	There was only an initial deposit which gave an X-ray pattern of alpha manganese
Germanium 0.04 gm	$\frac{1}{2}$	5.58	—	Gamma	49.24		A pinkish coat of germanium took place on the cathode. Manganese deposit was observed at those areas where there was no germanium deposit
Sodium stearate 0.1 gm	1	5.6	47.66	do	46.91		—
Zinc (0.05 gm of zinc as zinc sulphate)	$\frac{1}{2}$	—	65.94	do	40.00		No flow of electrolyte
0.05 gm of zinc as zinc sulphate	$\frac{1}{2}$	—	—	A black slimy coat at most portions of the cathode. At top portion alone, white ductile gamma manganese	—		With flow of electrolyte, gamma at top portion. X-ray data of black slimy coat indicates alpha, beta and oxides of manganese (Vide Fig. 4.I and Table 4.VIII)
0.025 gm zinc and 0.025 gm arsenic	$\frac{1}{2}$	5.6	—	Uniform black slimy coat	—		For X-ray data, Vide Fig. 4.I and Table 4.VIII

*Remarks* — It is noticed that addition of 15 gm per litre of boric acid to the pure electrolyte results in the deposition of alpha manganese.

addition of glycerol to the electrolyte suppressed the formation of gamma manganese. Moiseev<sup>29</sup> had employed a high current density of 30 amp/sq dm and such observations have been made and is discussed in the next paper under the effect of current density.

*Other addition agents* — Table 4.VII gives the effect of miscellaneous addition agents.

It is found that addition of 15 gm per litre of boric acid gives diffraction lines of alpha manganese. It is interesting that other than those of reducible sulphur and selenium compounds, boric acid was the only addition agent which resulted in the deposition of alpha manganese. But unfortunately enough, boric acid gives only an initial coat of manganese and further deposition does not take place though hydrogen evolution continues to be far less. As seen from Table 4.VII, 45 minutes of deposition has given only a current efficiency of 2.2 per cent.

With germanium, gamma manganese deposits were obtained only at the bottom side of the cathode, the other portions being covered with a very thin grayish red coat of presumably germanium which seemed to catalyse hydrogen evolution very much. It is interesting to mention that a flash layer of germanium is only obtained<sup>30</sup> in the electro-deposition of germanium and the inability of continuing the deposition has been attributed to the extremely low hydrogen over-voltage of germanium as compared to other metals, "so that the minute you get a flash coating, you could not continue the deposition, you had hydrogen evolution instead".

With 0.05 gm of zinc as zinc sulphate addition, a black slimy coat was only obtained on most part of the cathode. At the top alone, where the inflow of feed electrolyte has less access, there was bright white ductile metal. It is a well-known fact in electrolytic manganese pilot plants that when impurities like nickel, cobalt, iron and similar other impurities are present in the solution, even in presence of SO<sub>2</sub>, a black slimy coat is generally obtained, which facilitates hydrogen evolution, and further deposition of manganese is completely arrested. It would be recalled that with bismuth addition also in this investigation, a similar black slimy coat was obtained. The X-ray powder pattern of the black deposit along with that of beta manganese is given in Fig. 4.I and the calculated 'd' values are given in Table 4.VIII. The values indicate that the deposit contains alpha and beta manganese and oxides of manganese. A similar observation has been recorded by Jan Kaloc<sup>31</sup>. During pilot plant experiments on electrolytic manganese when 0.001-0.0015 gm of beryllium per litre of electrolyte was present in the solution, a black film was obtained which completely prevented deposition of manganese. According to Jan Kaloc, the black film on X-ray examination showed beta manganese along with beryllium and beryllium oxide.

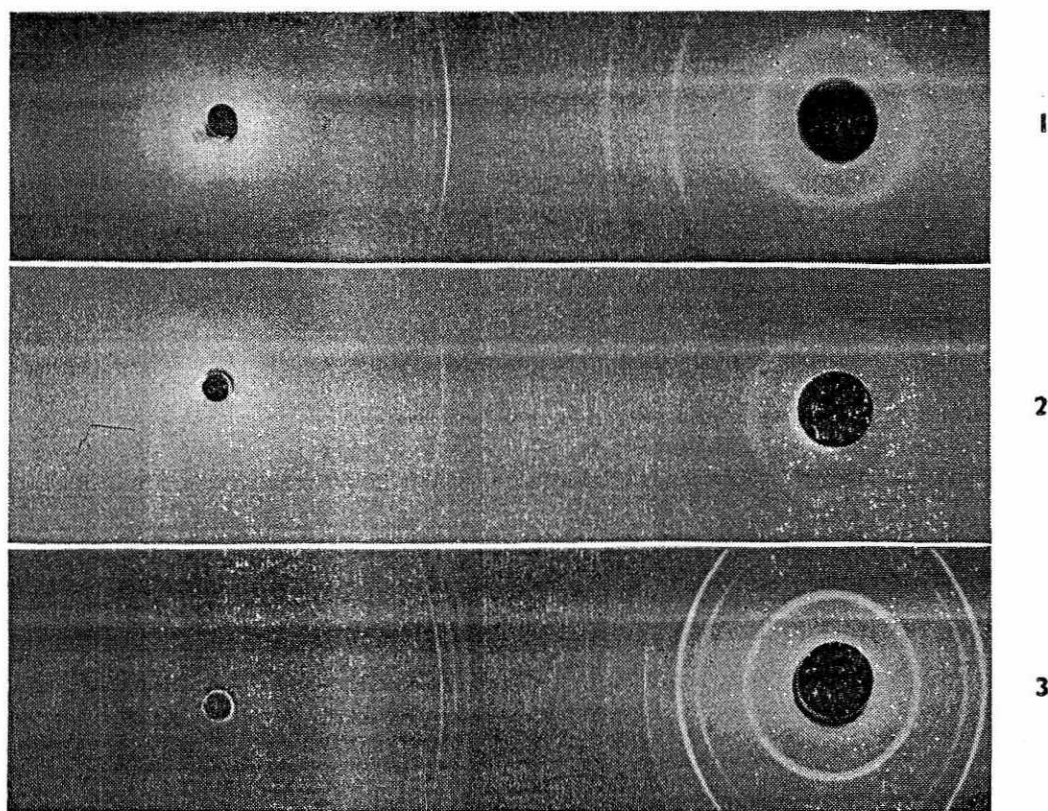


FIG. 4.I — X-RAY POWDER PHOTOGRAPHS OF DEPOSITS OBTAINED IN PRESENCE OF ZINC, AND ZINC AND ARSENIC (IN ORDER OF SEQUENCE)

Deposit obtained (1) in presence of zinc, (2) in presence of zinc and arsenic, and (3) beta manganese

Most elements have practically zero solid solubility in alpha manganese and considerable solubility in gamma manganese. Gamma manganese can take 36 per cent zinc in solid solution. The question is why then addition of zinc, as low as 0.05 gm per litre, deters the deposition of gamma manganese. It is seen that addition of 0.05 gm of zinc per litre lowers the cathode potential. Though the zinc content in the immediate vicinity of the cathode would get discharged primarily, the fresh arrival of feed electrolyte fluctuates the cathode potential and presumably deters the formation of gamma manganese. It is seen that at the top alone, where the inflow of feed electrolyte had less access, there was bright white ductile metal. It is interesting to mention that with no flow of electrolyte and 0.05 gm of zinc, coherent deposits of gamma manganese were obtained, hydrogen content being 40 cc per 100 gm of metal.

Even with copper, which is soluble to the extent of 18 per cent in gamma manganese, it is seen from Schlain's<sup>20</sup> work that with 60 mg or more of copper per litre of electrolyte, little or no metallic manganese was obtained. The current efficiencies dropped from 62.3 per cent, with no

TABLE 4.VIII—CALCULATED 'd' VALUES FROM X-RAY PHOTOGRAPHS OF DEPOSITS OBTAINED IN PRESENCE OF ZINC, AND ZINC AND ARSENIC

X-ray examination: 6 cm camera with Cr radiation

BETA MANGANESE		WITH ZINC		WITH Zn & As		ALPHA MANGANESE	
VW	2.816						
VW	2.565						
		MS	2.374*	VVW	2.392		
		MS	2.209*	W	2.218	W	2.222
VS	2.099*	VS	2.094*	VS	2.108	VS	2.096*
		VW	2.028				
S	1.993*						
MS	1.900					S	1.902
						S	1.819*
MS	1.686*					MS	1.747*
		MS	1.622*	W	1.624		
						MS	1.602
VW	1.598					W	1.528
		W	1.509				
MS	1.488					W	1.484
MS	1.411	VVW	1.434			W	1.445
		MS	1.376*	MS	1.380		
VW	1.346						
						MS	1.313
						MS	1.286*
VS	1.239*						
		S	1.256	MS	1.254	MS	1.261*
S	1.216*					S	1.213*
		W	1.191			S	1.192*
VS	1.173*	VS	1.169*	S	1.172	S	1.171
S	1.156*						
						MS	1.137*

VVW = very very weak, VW = very weak, W = weak, MS = medium strong, S = strong, and VS = very strong.

\*Lines of  $K_{\beta}$  radiation corresponding to the same interplanar spacings were present in the diffraction pattern as no filter was used.

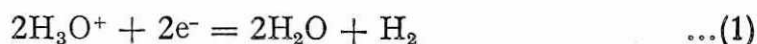
copper added to the feed solution, to 43.4 per cent with 30 mg/l when the deposit contained 0.17 per cent of copper.

Similarly, even in presence of sulphur, trace amounts of these elements in the electrolyte hamper the deposition of alpha manganese and only a black slimy coat is obtained. Here also it may be due to the fluctuation in cathode potential values and the fact that alpha manganese cannot take up any of these elements in significant quantity in solid solution. And once the black powdery deposit is formed, it catalyses hydrogen evolution quickly and even deposited manganese at any other part

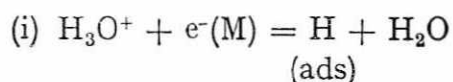
of the cathode begins to dissolve anodically forming a local couple with the black film.

With 0.025 gm of zinc and 0.025 gm of arsenic per litre, a uniform black slimy coat was obtained which also gave a similar X-ray pattern (vide Table 4.VIII and Fig. 4.I).

The overall reaction for hydrogen evolution may be represented by<sup>32</sup>



which is generally assumed to consist of at least two stages.



leaving the other possible mechanism such as the discharge of hydrogen ions on adsorbed hydrogen atoms.



The first stage in reaction (2) is the discharge of the hydrogen ions on the surface of the cathode, resulting in the formation of adsorbed hydrogen atoms. The second stage in reaction (2) is the combination of the adsorbed hydrogen atoms to form hydrogen molecules. Either of these stages can be a slow one and may be the rate determining step in overall reaction (1). Due to slowness of either of the two stages, the cathodic evolution of hydrogen occurs at potentials more negative than the reversible potential given by the Nernst formula.

Experiments with different addition agents and the hydrogen content of alpha and gamma manganese obtained therefrom show that the presence of reducible sulphur or selenium compounds in the electrolyte increases the hydrogen over-potential by slowing down the second stage in reaction (2), namely the combination of hydrogen atoms to form molecules. The hydrogen content of deposited alpha manganese strongly suggests this view. Addition agents, like paraformaldehyde, presumably increase the hydrogen over-voltage by slowing down the first stage in reaction (2), when only gamma manganese is obtained as seen from the low hydrogen content in presence of paraformaldehyde. Though both sulphur group and organic inhibitors like paraformaldehyde increase the hydrogen over-voltage, ie cathodic polarization by different methods, in the presence of the former alpha manganese is obtained, while in presence of the latter gamma manganese with an increased current efficiency is obtained.

If cathodic polarization is the only resultant effect of reducible S or Se compounds in the deposition of alpha manganese, the addition of pure

organic polarizing inhibitors should also have yielded alpha manganese. But it is not found to be so in practice. This shows that polarization is not the only property of sulphur group of elements which effects the deposition of manganese in alpha modification but something more, most likely the hydrogen content or some other resultant effect of sulphur addition.

That increase in polarization and the hydrogen content are the major effects which result in alpha manganese deposition on addition of reducible sulphur or selenium compounds can be clearly seen in the next paper on the effect of current density on structure of electro-deposited manganese. At very high current densities of deposition, formation of gamma manganese is prevented and amorphous manganese, having hardness of alpha, is obtained with high hydrogen content.

### Conclusions

With the exception of boric acid, it is found that only cathodically reducible compounds of group VIB elements, sulphur, selenium and tellurium, prevent the formation of gamma manganese and facilitate the deposition in alpha modification. The presence of strong oxidizing agents in the electrolyte or long chain organic molecules attaching to the reducible compound has no influence in the deposition of alpha manganese in presence of reducible selenium or sulphur compounds. The electro-deposited alpha manganese in all cases contain more hydrogen than gamma manganese prepared in presence of many addition agents, though the absolute solubility of hydrogen in alpha manganese is only about half of that in gamma manganese.

It has been suggested that it is not only the polarization property of the sulphur group of elements as an addition agent in the electrolyte that effects the deposition of manganese in alpha modification, but also the high hydrogen content of the deposit obtained in presence of these addition agents.

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