

CORRIGENDUM

Specification No. 65646.

The following misprints in the above specification should be corrected :—

PROVISIONAL SPECIFICATION

1. Page 1, Line 6, of title of provisional specification, *after* "METAL" *add* " FROM MANGANESE CHLORIDE BATHS
2. „ Line 6, *for* " APPLICATION " *read* " UTILIZATION '.
3. „ Column 1, Line 2, *after* " metal " *add* " from manganese chloride baths ".
4. „ Line 3, *for* " application " *read* " utilisation ".
5. „ Line 29, *for* " chloride " *read* " chlorine ".
6. „ Line 56, *for* " by product " *read* " by-product ".
7. „ Column 2, Line 2 from bottom, *for* " hydrochloric " *read* " hydrochloric acid ".
8. „ 2, Column 1, Line 23, *for* " 2 " *read* " 3 ".
9. „ Column 1, Line 23, *for* " minute " *read* " Second ".
10. „ Column 2, Line 54, *for* " chlorinstion " *read* " dechlorination ".
11. „ 3, Column 1, Line 18, *for* " advantages " *read* " are the advantages ".

COMPLETE SPECIFICATION.

12. Page 3, Column 2, Line 10, *for* " catholyte " *read* " catholyte, ".
13. „ Line 27, *for* " solutions " *read* solutions as catholyte and a 30% solution of sodium chloride .
14. „ 5, Column 1, Line 6, *for* " call " *read* " cell ".
15. „ Line 11, *for* " 1/2 " *read* " 1/4 ".
16. „ Line 20, *for* " SO₂ " *read* " SO₂O-3 "
17. „ Line 25, *for* " hours " *read* " hour ".
18. „ Line 31, *for* " Cathod " *read* " Cathode ".
19. „ Line 31, *for* " 40-0 " *read* " 48-0 ".
20. „ Line 41, *for* " circulation " *read* " circulation ; ".
21. „ Last line, *for* " section " *read* " suction ".
22. „ Column 2, *delete* " for ".
23. „ Line 7, *for* " sodium " *read* " stationary sodium ".
24. „ Line 26, *for* " chloride " *read* " chlorine ".
25. „ Line 38, *for* " production " *read* " production ".

B. N. ATRISHI,
Deputy Controller of Patents & Designs.

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.
 Specification No. 65645. Application No. 65646, dated 29th October 1958. Complete
 Specification left on 22nd July 1959. (Application Accepted 25th February 1960.)

PROVISIONAL SPECIFICATION.

IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF MANGANESE METAL WITH SPECIAL REFERENCE TO THE APPLICATION OF LOW GRADE MANGANESE ORES.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OLD MILL ROAD, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

THIS IS AN INVENTION BY V. ARAVAMUTHAN AND S. GOPAL, BOTH OF THE CENTRAL ELECTRO-CHEMICAL RESEARCH INSTITUTE, KARAIKUDI, INDIA, BOTH INDIAN CITIZENS.

The following specification describes the nature of this invention.

Introduction.

This invention relates to improvements in or relating to the production of manganese metal with special reference to the application of low grade manganese ores.

It is very well known that mixtures of manganese and ammonium chloride solutions can be electrolysed in a two-compartment (diaphragm) cell to get manganese metal and this method is more advantageous than electrolysing manganese-ammonium sulphate solutions owing to the comparatively low energy requirements. However, in the chloride process, a heavy loss of ammonia occurs, in the form of nitrogen due to the interaction of anodic chlorine with ammonium chloride solutions in the anode compartment. The elimination of ammonium chloride loss without sacrificing the quality of the metal, current and energy efficiencies, will introduce greater economies in the process of electrowinning of manganese from chloride solutions.

Novelty in the present invention.

The most important detail of the present invention relates to the use of continuous flow of a 30 per cent. solution of chlorine free sodium chloride in the anode compartment instead of the conventional anolyte of the manganese chloride bath. The above said change not only helps to eliminate the loss of ammonium chloride usually associated with the electrolysis of manganese-ammonium chloride solutions but also serves (a) to maintain a catholyte pH steady between 7 and 7.4 and (b) to recover chlorine as free chlorine. This change enables the electrolysis to be conducted at 30° C. without any loss in current and energy efficiencies. The cell voltage is 3.5 and very bright metal deposits are obtained. A 60 per cent. current efficiency is realised. Medium porous diaphragms made of porcelain, etc., are employed.

Advantages of the invention.

The electrowinning of manganese, employing manganese-ammonium chloride solutions as catholyte and a continuous flow of 30 per cent. solution of chlorine free sodium chloride as anolyte in a two compartment cell, as described in the present invention, will serve—

- (1) to produce manganese metal from low grade manganese ores by a cyclic process economically. Briquettes, containing mixtures of low grade manganese ore and a cheap fuel like lignite is chlorinated. The mixed manganese and ferric chlorides are collected, dissolved in water and double decomposed with a mixture of manganous oxide and magnetic oxide of iron obtained in the conventional roast-reduction process. Pure manganese chloride solution for use as catholyte cell-feed is obtained. The anodic chlorine is used again in the process;
- (2) to convert hydrochloric acid to chlorine. Hydrochloric acid obtained as a by product in organic chlorinations; in the production of sodium sulphate from sodium chloride and sulphuric acid, etc., can be employed to decompose low grade manganese ores with the liberation of chlorine. The mixed ferric and manganese chlorides, resulting in the above said reaction, is double decomposed with a mixture of manganous oxide and magnetic oxide of iron obtained in the conventional roast-reduction process. Pure manganese chloride solution, thus obtained, is employed

as catholyte cell-feed. Chlorine is recovered as a valuable by-product;

- (3) to recover chlorine from ferric chloride. Ferric chloride obtained as a by-product in the chlorination of ores like ferruginous bauxite, chromite, ilmenite, mixed sulphide ores, etc., or obtained by reacting low grade iron ores with the hydrochloric acid, etc., can be double decomposed with a mixture of magnetic oxide of iron and manganous oxide obtained by the conventional roast-reduction process. The resulting pure manganese chloride is employed as a catholyte cell-feed. Chlorine is obtained as a valuable by-product;
- (4) to couple the utilisation of chloride waste pickle liquor from Iron and Steel Industries. The ferrous chloride pickle liquor is treated with chlorine evolved at the anode in the electrolysis of manganese-ammonium chloride solutions. The resulting Ferric chloride is then treated, as described in (3).

In all the said processes, the residue left after the leaching of manganese chloride can be reduced to get magnetic oxide of iron which can be magnetically separated and used as a source of high grade iron ore. This procedure will serve to introduce greater overall economy in the electrowinning of manganese metal from low grade manganese ores;

- (5) to couple the ammonia-soda process or sodium or potassium sulphate manufacture from gypsum or anhydrite. Ammonium chloride obtained as a by-product either in the ammonia-soda process or resulting in the double decomposition of ammonium sulphate (obtained from gypsum or anhydrite) with sodium or potassium chloride is reacted with a mixture of manganous oxide and magnetic oxide of iron obtained by the conventional roast-reduction process. Ammonia for use again in the processes is expelled, with the simultaneous production of manganese chloride for use as catholyte cell-feed. Chlorine is obtained as a valuable by-product. Thus, the chlorine content of sodium or potassium chloride employed in the production of sodium carbonate, sodium sulphate or potassium sulphate is recovered as free chlorine.

The following are the typical data obtained on a laboratory scale for the production of manganese chloride from low grade ores and also for electrowinning of manganese by the new procedure.

TYPICAL LEACHING EXPERIMENTS.

(A) Leaching experiment with hydrochloric acid :

Quantity of ore taken .	500 gms. Treated in two batches of 287 gms. and 213 gms.
Volume of acid used .	7 litres of 10 per cent. hydrochloric acid (4 & 3 litres respectively). Calculations were made thus to determine the quantity of hydrochloric acid required. Manganese requiring 4 hydrochloric acid; Iron requiring 2 hydrochloric and 10 per cent. excess for alumina etc.

Price : TWO RUPEES.

Time taken for reaction	Boiling for 3 hours in each case.
Total volume of leach liquor.	4.2 litres containing a mixture of manganese and ferric chloride.
Manganese estimated in the leach.	30.2 gms. per litre
Manganese present in the ore.	199 gms.
Leaching efficiency with respect to manganese.	80.6 per cent.
pH of the solution	1.5

(B) Direct chlorination of the ore:

50 gms. of the ore (-60 mesh to +100 mesh size) was mixed with 50 gms. of air dried lignite (-40 mesh) and compressed at 1 ton per square inch pressure for one minute at laboratory temperature. 25 briquettes were produced.

The amount of the lignite taken was twice the theoretical amount required to get iron oxides and manganese oxides reduced, with the expulsion of carbon monoxide, dioxide and other gases. The rate of chlorination was about 2 ccs per minute. The briquette size was about 5/8" diameter and 1/4" height. It was heated in a nichrome wire wound silica tube furnace of about 1 1/2" diameter and 1 1/2 ft. long. The temperature of chlorination was between 700-800° C. The chlorination was conducted for 1 1/2 hours. Ferric chloride was volatilised and condensed in the portions far away from the furnace and manganese chloride in portions somewhat nearer. The manganese chloride from the condenser and also from the furnace was dissolved in water and made up to one litre. The manganese was estimated to be 15.5 gms. per litre. This gives a leaching efficiency of 77.87 per cent. with respect to manganese. The volume of water employed can be even reduced to 200 cc to get a concentrated solution of manganese chloride. From the residue the entire manganese is leached out as manganese chloride by treatment with 10 per cent. hydrochloric acid. The manganese chloride solution containing some ferric chloride can be reacted with the calcine and the strength of the manganese chloride solution can further be increased without any trouble.

(C) Leaching of the calcine with the leachate from (A) or (B):

Quantity of the ore taken.	1000 gms. of the ore in -60 to +100 mesh size.
Quantity of charcoal	200 gms. of -60 mesh size.
Reducing vessel	Mild steel drum provided with screw stopper in the lid of the drum 5" internal dia. and 10" height. Heated by a coal flame.
Time of reduction	45 minutes at 700° C.
Weight of the calcine	800 gms.

The calcine was slowly added with stirring to the mixture of manganese and ferric chloride solutions in (A) or (B) till the pH rose to 5.5. The time of leaching was 1 1/2 hours. The amount of calcine consumed was 600 gms.

This contained $\frac{600}{800} \times 398 = 298.5$ gms of manganese. The temperature rose from 28 to 38° C. The volume of the solution was 4800 cc. The manganese in the solution was estimated to be 72.6 gpl. The weight of the manganese leached from the calcine was 188.0 gms which corresponds to 62.99 per cent. leaching efficiency.

The above leaching efficiency is low as the manganese chloride hold-up in the residue is not taken into account and which is leached as a dilute solution by boiling with water. Greater leaching efficiencies have been possible if leachate from (A) or (B) is kept at 85-90° C. and the calcine is added with periodical stirring. Hence a leaching efficiency of 80 per cent. with respect to manganese is possible, a fact confirmed while dealing with gram lots.

(D) Electrolysis:**4 hours continuous electrolysis.**

Electrolytic vessel	Pitch lined wooden tank of the following dimensions. 8 1/2" x 8 1/2" x 5" (ht).
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Cathode	Stainless steel 7" x 2" x 1/32" (thick).
Anode	Graphite 7" x 2" x 1/8" (thick).
Current passed	6 amps. total 24 amp. hrs.
Current Density	43.2 amps/sq. ft.
Bath voltage	3.6 (average).
Catholyte	3500 cc containing: Mn 18 gpl. NH ₄ Cl 120 gpl. SO ₂ 0.3 gpl.
Anolyte	4000 cc of 20-30 per cent. solution of chlorine-free sodium chloride solution circulated into two porous pots each holding 500 cc at any time.
Temperature	30-36° C.
Inter electrode distance	Anode to Anode is 3 1/2"
pH of the catholyte	7 to 7.2
pH of the anolyte	4.5 after electrolysis.
Level of the anolyte	1" above the level of catholyte at any time.
Nature of the deposit	Very good. Stripping was good.
Weight of metal obtained.	13.6 gms.
Current efficiency	55.2 per cent.
12 hours continuous electrolysis.	
Current passed	6 amps. total 72 amp. hrs.
Current density	43.2 amps/sq. ft.
Bath voltage	3.8 (average).
Anode chambers	Same Coors' medium porous pots. (The difference between the previous experiment and this consists in covering the porous pots with perspex and sucking off the chlorine). Instead of 500 cc of sodium chloride, 650 cc were maintained in each porous pot.
Catholyte	The volume was 3800 cc. A continuous feeding of the feed electrolyte 58 Mn gpl, 120 NH ₄ Cl gpl and 0.2 SO ₂ gpl was maintained.
Temperature	30-36° C. (cooling coils were employed)
Catholyte pH	7.0 to 7.4.
Anolyte pH	2.0 at the end of 12 hours. Vigorous chlorination would prevent the pH coming to 2.0 in the anode compartment. This was not possible as dechlorination was effected by only boiling in a beaker.
Nature of the deposit	Very good. Stripping was good.
Weight of the metal	37.8 gms.
Current efficiency	51.22 per cent.
6 hours continuous electrolysis.	
Current passed	6 amps. total 36 amp. hrs.
Current density	43.2 amps/sq. ft.
Bath voltage	3.50 volts.
Anode chambers	Same as in previous experiment. Used 30 per cent. NaCl solution.
Catholyte	The volume was 3800 cc. A continuous feeding of the feed electrolyte 58 Mn gpl, 120 NH ₄ Cl gpl and 0.2 SO ₂ gpl, was maintained. The catholyte was being stirred through out the electrolysis.
Temperature	30° C.-36° C.
Catholyte pH	7.0 to 7.4.
Anolyte pH	8.0 at the end of 6 hours.

Nature of the deposit . . . Very good. Stripping was good.
 Weight of the metal . . . 22.0 gms.
 Current efficiency . . . 59.6 per cent.

The following are among the noteworthy features of the process:

(1) A process for the production of manganese metal from chloride baths wherein sodium chloride is employed as anolyte and chlorine is obtained as a valuable by-product.

(2) A current efficiency of not less than 60 per cent. at a cell voltage of 3.5 when electrolysis is conducted, as described in (1) at a temperature of 30° C. Stainless steel cathodes, medium porous diaphragms made of porcelain and the like and graphite anodes are employed in the two compartment cell.

(3) The following advantages of the process described in (1):

(a) Pure manganese metal can be obtained electrolytically from low grade manganese ores by a cyclic process.

(b) The conversion of hydrochloric acid to chlorine can be coupled with the utilisation of low grade manganese ores for the production of pure manganese metal.

(c) The recovery of chlorine from ferric chloride can be advantageously combined with the electrowinning of manganese metal from low grade ores.

(d) The utilization of waste chloride pickle liquor from Iron and Steel Industries can be coupled with the electrowinning of manganese metal and the hydrochloric acid initially employed for pickling can be ultimately obtained as free chlorine, and

(e) Ammonia-soda process or the production of alkali metal sulphates from gypsum or anhydrite through the intermediate production of ammonium sulphate can be coupled with the electrowinning of manganese metal from low grade manganese ores. Thus, chlorine can be obtained as a by-product in the manufacture of alkali metal sulphates and sodium carbonate.

R. BHASKAR PAI.

Patent Officer,

Council of Scientific & Industrial Research.

Dated this 15th day of October, 1958.

COMPLETE SPECIFICATION.

IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF MANGANESE METAL FROM MANGANESE CHLORIDE BATHS WITH SPECIAL REFERENCE TO THE UTILIZATION OF LOW GRADE MANGANESE ORES.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OLD MILL ROAD, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (XXI OF 1860).

THIS IS AN INVENTION BY VEERARAGAVA ARAVAMUTHAN AND SUBRAMANIA GOPAL, BOTH OF THE CENTRAL ELECTRO-CHEMICAL RESEARCH INSTITUTE, KARAIKUDI, INDIA, BOTH INDIAN CITIZENS.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

Introduction.

It is very well known that mixtures of manganese and ammonium chloride solutions can be electrolysed in a two compartment (diaphragm) cell to get manganese metal and this method is more advantageous than electrolysing manganese-ammonium sulphate solution owing to the comparatively low energy requirements. However, in the chloride process, a heavy loss of ammonia occurs in the form of nitrogen due to the interaction of anodic chlorine with ammonium chloride solutions in the anode compartment. The elimination of ammonium chloride loss without sacrificing the quality of the metal, current and energy efficiencies, will introduce greater economies in the process of electrowinning of manganese from chloride solutions.

To avoid the loss of ammonia in the anode compartment, the use of a 30 to 33 per cent. hydrochloric acid solution, an alkali metal chloride or alkaline earth chloride solution as anolyte has been suggested. The anolyte is circulated and fortified as per the above and similar processes. These processes refer to the use of vinyon and like diaphragms. Although these processes refer to the elimination of loss of ammonium chloride, in the anolyte compartment yet the catholyte compositions disclosed in these processes differ from those employed by the U. S. Bureau of mines and the stripping of manganese from the catholyte as per these processes is about 15 grams per litre whereas in U. S. Bureau of mines method, a stripping of 40 grams of manganese per litre have been successfully achieved on a semi-pilot plant scale.

Novelty in the present invention.

One of the important advantages claimed in the electrowinning of manganese from the chloride bath is that the maximum depletion of manganese that can be achieved during electrolysis is nearly twice in comparison with the sulphate process, viz., 40 grams of manganese per litre in the case of chloride bath and about 20

grams of manganese from sulphate bath. In our process not only we were able to achieve a depletion of 40 grams of manganese per litre but also employed a stationary anolyte thereby introducing greater economies and ease of operation.

The anolyte was a 30 per cent. solution of sodium chloride contained in a porcelain diaphragm. The chlorine was continuously sucked off and electrolysis was conducted for six hours with a stationary anolyte. The temperature of catholyte cell voltage, current density, nature of deposit etc., remain the same, in all the methods under reference (a cell voltage of 3.5; a cathode current density of 40-45 amps. per square foot; a current efficiency of about 60 per cent., a temperature of 30-36° C.) and hence the advantages of our process are very easily compared with the other methods.

In addition the overall economy in the production of manganese from low grade manganese ores via chloride bath has not so far been recorded in literature in a manner similar to the one described in the specification.

In brief, the invented process for the production of manganese metal consist in electrolysing manganese-ammonium chloride solutions (catholyte) and wherein sodium chloride is employed as anolyte with production of chlorine as valuable anode product.

The electrowinning of manganese, employing manganese-ammonium chloride solutions as stationary anolyte in a two compartment cell, as described in the present invention, will serve—

(1) to produce manganese metal from low grade manganese ores by a cyclic process economically. Briquettes containing mixtures of low grade manganese ore and a cheap fuel like lignite is chlorinated. The mixed manganese and ferric chlorides are collected, dissolved in water and double decomposed with a mixture of manganous oxide and magnetic oxide of iron obtained in the conventional roast-reduction process. Pure manganese chloride

solution for use as catholyte cell-feed is obtained. The anodic chlorine is used again in the process;

(2) to convert hydrochloric acid to chlorine. Hydrochloric acid obtained as a by-product in organic chlorinations; in the production of sodium sulphate from sodium chloride and sulphuric acid, etc., can be employed to decompose low grade manganese ores with the liberation of chlorine. The mixed ferric and manganese chlorides, resulting in the above said reaction, is double decomposed with a mixture of manganous oxide and magnetic oxide of iron obtained in the conventional roast-reduction process. Pure manganese chloride solution, thus obtained is employed as catholyte cell-feed. Chlorine is recovered as a valuable by-product;

(3) to recover chlorine from ferric chloride. Ferric chloride obtained as a by-product in the chlorination of ores like ferruginous bauxite, chromite, ilmenite, mixed sulphide ores, etc., or obtained by reacting low grade iron ores with the hydrochloric acid, etc., can be double decomposed with a mixture of magnetic oxide of iron and manganous oxide obtained by the conventional roast-reduction process. The resulting pure manganese chloride is employed as a catholyte cell-feed. Chlorine is obtained as a valuable by-product;

(4) to couple the utilisation of chloride waste pickle liquor from Iron and Steel industries. The ferrous chloride pickle liquor is treated with chlorine evolved at the anode in the electrolysis of manganese-ammonium chloride solutions. The resulting ferric chloride is then treated, as described in (3).

In all the said processes, the residue left after the leaching of manganese chloride can be reduced to get magnetic oxide of iron which can be magnetically separated and used as a source of high grade iron ore. This procedure will serve to introduce greater overall economy in the electrowinning of manganese metal from low grade manganese ores;

(5) to couple the ammonium-soda process or sodium or potassium sulphate manufacture from gypsum or anhydrite. Ammonium chloride obtained as a by-product either in the ammonium-soda process or resulting in the double decomposition of ammonium sulphate (obtained from gypsum or anhydrite) with sodium or potassium chloride is reacted with a mixture of manganese oxide and magnetic oxide of iron obtained by the conventional roast-reduction process. Ammonia for use again in the process is expelled, with the simultaneous production of manganese chloride for use as catholyte cell feed. Chlorine is obtained as a valuable by-product. Thus, the chlorine content of sodium or potassium chloride employed in the production of sodium carbonate, sodium sulphate or potassium sulphate is recovered as free chlorine.

The following are the typical data obtained on a laboratory scale for the production of manganese chloride from low grade ores and also for electrowinning of manganese by the new procedure.

TYPICAL LEACHING EXPERIMENTS.

(A) Leaching experiment with hydrochloric acid.

Quantity of ore taken . . . 500 gms. Treated in two batches of 287 gms and 213 gms.
Volume of acid used . . . 7 litres of 10 per cent. hydrochloric acid (4 & 3 litres respectively). Calculations were made thus to determine the quantity of hydrochloric acid required. Manganese requiring 4 hydrochloric acid; Iron re-

quiring 2 hydrochloric acid and 10 per cent. excess for alumina etc.

Time taken for reaction	Boiling for 3 hours in each case.
Total volume of leach liquor	4.2 litres containing a mixture of manganese and ferric chloride.
Manganese estimated in the leach	38.2 gms. per litre.
Manganese present in the ore	199 gms.
Leaching efficiency with respect to manganese	80.6 per cent.
pH of the solution	1.5.

(B) Direct chlorination of the ore.

50 gms of the ore (-60 mesh to +100 mesh size) was mixed with 50 gms of air dried lignite (-40 mesh) and compressed at 1 ton per square inch pressure for one minute at laboratory temperature. 25 briquettes were produced.

The amount of the lignite was twice the theoretical amount required to get iron oxides and manganese oxides reduced with the expulsion of carbon monoxide, dioxide and other gases. The rate of chlorination was about 3 cc per second. The briquette size was about $\frac{3}{8}$ " diameter and $\frac{1}{4}$ " height. It was heated in a nichrome wire wound silica tube furnace of about $1\frac{1}{2}$ " diameter and $1\frac{1}{4}$ ft. long. The temperature of chlorination was between 700-800° C. The chlorination was conducted for $1\frac{1}{4}$ hours. Ferric chloride was volatilised and condensed in the portions far away from the furnace and manganese chloride in portions somewhat nearer. The manganese chloride from the condenser and also from the furnace was dissolved in water and made up to one litre. The manganese was estimated to be 15.5 gms per litre. This gives a leaching efficiency of 77.87 per cent. with respect to manganese. The volume of water employed can be even reduced to 200 cc to get a concentrated solution of manganese chloride. From the residue the entire manganese is leached out as manganese chloride by treatment with 10 per cent. hydrochloric acid. The manganese chloride solution containing some ferric chloride can be reacted with the calcine and the strength of the manganese chloride solution can further be increased without any trouble.

(C) Leaching of the calcine with the leachate from (A) or (B).

Quantity of the ore taken	1000 gms of the ore in -60 to +100 mesh size.
Quantity of charcoal	200 gms of -60 mesh size.
Reducing Vessel	Mild steel drum provided with screw stopper in the lid of the drum 5" internal dia. and 10" height. Heated by a coal flame.
Time of reduction	45 minutes at 700° C.
Weight of the calcine	800 gms.

The calcine was slowly added with stirring to the mixture of manganese and ferric chloride solutions in (A) or (B) till the pH rose to 5.5. The time of leaching was $1\frac{1}{4}$ hours. The amount of calcine consumed was $800 \text{ gms. This contained } \frac{600}{800} \times 398 = 298.5 \text{ gms of manganese. The temperature rose from 28 to } 38^\circ \text{ C. The volume of the solution was 4800 cc. The manganese in the solution was estimated to be 72.6 gpl. The weight of the manganese leached from the calcine was 188.0 gms which corresponds to 62.99 per cent. leaching efficiency.}$

The above leaching efficiency is, low as the manganese chloride hold up in the residue is not taken into account and which is leached as a dilute solution by boiling with water. Greater leaching efficiencies have been possible if leachate from (A) or (B) is kept at 85-90° C. and the calcine is added with periodical stirring. Hence a leaching efficiency of 80 per cent. with respect to manganese is possible, a fact confirmed while dealing with iron low.

Electrolysis.

Data pertaining to typical reproducible electrolytic experiments both with a circulating and stationary anolyte are given.

	Anolyte in circulation	Stationary Anolyte
Cell	Pitch-lined wooden tank 8½" x 8½" x 5" height	Pitch-lined wooden tank 8½" x 8½" x 5" Ht.
Cathodes	Stainless steel 7" x 2" x 1/32" thick	Stainless steel 8½" x 2½" x 1/32" thick
Anodes	Graphite 7" x 2" x ½" thick	Graphite 8½" x 2½" x ½" thick
Duration of Electrolysis	6 hours	6 Hours
Current passed	6 amps Total 36 amp. Hrs.	10 amps. Total 60 amp. Hrs.
Catholyte	3800 c. c. Mn: 18 Gpl NH ₄ Cl 120 Gpl SO ₂ 0.3 Gpl. Stirring employed	3700 c. c. Mn: 18 Gpl NH ₄ Cl 120 Gpl SO ₂ 0.3 Gpl. Stirring employed
Anolyte	30% sodium chloride solution circulated at the rate of 2 litre/ hours (Chlorine sucked off)	1200 c. c. of 30% sodium chloride solution 600 c. c. in each anode compartment. (Chlorine sucked off)
Feed concentration:	Mn: 58 Gpl NH ₄ Cl 120 Gpl SO ₂ 0.2 Gpl Fed at the rate of 100 c. c. per Hr.	Mn: 58 Gpl NH ₄ Cl 120 Gpl SO ₂ 0.2 Gpl Fed at the rate of 150 c. c. per Hr.
Cathod current density:	43.2 amps/sq. ft.	40.0 amps/sq. ft.
Bath Voltage	3.5 V	3.5 V
Catholyte pH	7.0 to 7.4	7.0 to 7.4
Temperature	30° to 36°C	30° to 36°C
Nature of Deposition:	Very Good	Very good
Weight of metal	22.0 gms	37.0 gms
Current efficiency	59.6%	60.2%

It is clear that stationary anolyte is as effective as continuous anolyte circulation for large scale work porcelain plates PVC or microporous rubber sheets fitted into grooves in frames of wood treated with chlorinated rubber paint and the like can be employed as rectangular anolyte chamber with provision for chlorine section also.

This would facilitate including for any desired number of anode compartments with facilities for replacing the anode chambers at any time with ease.

We claim:

1. A process for the production of manganese metal which consists in electrolysing manganese-ammonium chloride solutions (catholyte) and wherein sodium chloride is employed as anolyte with the production of chlorine as valuable anode product.

2. A process as claimed in Claim 1 wherein a current efficiency of not less than 60 per cent. at a cell voltage of 3.5 is achieved when electrolysis is conducted, as described in (1) at a temperature of 30° C., and stainless steel cathodes, medium porous diaphragms made of porcelain and the like and graphite anodes are employed in the two compartment cell.

3. A process as claimed in Claim 1 wherein pure manganese metal is obtained electrolytically from low grade manganese ores by a cyclic process.

4. A process as claimed in any of the preceding claims wherein the conversion of hydrochloric acid to chlorine is coupled with the utilisation of low grade manganese ores for the production of pure manganese metal.

5. A process as claimed in any of the preceding claims wherein the recovery of chloride from ferric chloride is combined with the electrowinning of manganese metal from low grade ores.

6. A process as claimed in any of the preceding claims wherein the utilisation of waste chloride pickle liquor from iron and steel industries is coupled with the electrowinning of manganese metal and the hydrochloric acid initially employed for pickling is ultimately obtained as free chlorine.

7. A process as claimed in any of the preceding claims wherein ammonia-soda process or the production of alkali metal sulphates from gypsum or anhydrite through the intermediate production of ammonium sulphate is coupled with the electrowinning of manganese metal from low grade manganese ores, whereby, chlorine is obtained as a by-product in the manufacture of alkali metal sulphates and sodium carbonate.

R. BHASKAR PAI,

Patents Officer,

Council of Scientific and Industrial Research.

Dated this 20th day of July, 1959.