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TREATMENT METHODS FOR MANGANESE ORES

(A.M.D.L. Report No. 169)

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Introduction

This report covers a review of the literature on the recovery of manganese, and was carried out as part of a wider programme of research into beneficiation of Western Australian manganese ores.

The report has been issued in the Bureau Record series so that an adequate dissemination of the results of this work may be made through the Bureau's open file system. It has not been altered in any way.

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AUSTRALIAN MINERAL DEVELOPMENT LABORATORIES

REPORT AMDL-169

BUREAU OF MINERAL RESOURCES

PROJECT 2/1/2

TREATMENT METHODS FOR MANGANESE ORES

by

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L. Wallace Coffer. Director

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1. INTRODUCTION

The Bureau of Mineral Resources has sponsored a programme of research into the beneficiation of manganese ore from Pilbara, Western Australia. The first stage of the investigation involved a detailed mineralogical examination of a suite of ore specimens from Western Australia. The second stage calls for a review of the literature on the recovery of manganese and the preparation of a bibliography. The present report covers the second stage of the investigation, and was compiled to be read in conjunction with another report, yet to be issued, giving the results of the mineralogical examination.

2. SUMMARY

The methods that have been reported for the beneficiation of manganese ores and the extraction of manganese are described and discussed and a bibliography is added. The limited information at present available indicated that it is unlikely that Pilbara manganese ores can be beneficiated by physical methods, with the possible exception of magnetic separation following a reducing roast. Of the chemical methods discussed, leaching with ammonium carbonate after reduction of the ore appears on paper to be the most satisfactory. Leaching with sulphur dioxide has the advantage that no preliminary reduction of the ore is necessary, and might be a satisfactory process if very cheap lime and sulphur dioxide were freely available.

3. ORE-DRESSING METHODS

Muskett and Tasker (1960) examined low-grade manganese ores from Pilbara and found that they were not amenable to concentration by magnetic or electrostatic separation, or by flotation. After a reducing roast, however, the ores could be upgraded by magnetic separation. The ores were reduced by heating in hydrogen for 2.25 hours at 560-580°C, and the results are summarised in Table 1.

TABLE 1: BENEFICIATION OF PILBARA MANGANESE ORES

No.	Sample	Original Ore Assay % Mn	Fe	Acid Insol.	Concentrate Assay % Mn	Recovery % Mn
1.	Balfour Downs Main deposit	31.1	13.2	17.9	46.9	70.0
2.	Pisolites and fragments, near Balfour Downs	13.7	20.0	37.6	38.6	78.4
3.	Ripon Hills	32.9	24.6	6.8	53.9	53.4

Fander (1961) examined 5 samples from Ripon Hills. They consisted principally of haematite, pyrolusite and cryptomelane, all three very fine-grained, the mineral particles being usually less than 10 microns in size. He concluded that upgrading would present considerable and perhaps insurmountable difficulties in view of the very fine-grained nature of the ore.

4. HYDROMETALLURGICAL METHODS

4.1 Leaching with Sulphuric Acid

Manganese dioxide ores cannot be leached directly with sulphuric acid, but must be reduced to convert the dioxide into soluble lower oxides. This may be done by roasting in a reducing atmosphere in a rotary kiln. If the reduction is successfully controlled so that all the dioxide is reduced, high recoveries of manganese, of the order of 98 per cent, may be obtained by leaching with dilute sulphuric acid. The leach liquor is purified by adjustment of the pH with lime and aeration to precipitate iron. Several methods are available for the recovery of manganese from the purified leach liquor:

1. Evaporation and crystallisation of $MnSO_4$. The $MnSO_4$ may then be decomposed to produce a high grade manganese oxide sinter and SO_2 by heating at about 1000°C.
   The sintered product is probably a mixture of oxides (MnO_2, Mn_2O_3, Mn_3O_4 and MnO). By heating $MnSO_4$ with 5-10 per cent of carbon at about 900°C in a gas low in oxygen all the sulphate is decomposed and over 99 per cent of the sulphur is evolved at SO_2. When $MnSO_4$ is roasted in the absence of carbon at 1000°C about 10 per cent of the sulphur is evolved as SO_3.
2. The solubility of $MnSO_4$ decreases as the temperature is raised, hence $MnSO_4$ can be recovered by heating the pregnant liquor under pressure. The solubility varies from 40 per cent $MnSO_4$ at 20°C to 0.5 per cent at 200°C, so that $MnSO_4$ is precipitated by heating under pressure to about 195°C. Since the solubility at 100°C is 27 per cent, $MnSO_4$ can also be recovered from a concentrated solution by heating to the boiling point. The precipitated $MnSO_4$ is decomposed as under (1).
3. Electrolysis of the sulphate solution. Manganese dioxide may be deposited on carbon anodes, which are then crushed. The dioxide is separated by jigging and dried below 350°C to produce gamma-phase battery grade MnO_2. Alternately, the manganese may be recovered as pure metal by cathodic deposition from a solution containing ammonium sulphate. The electro-winning of manganese has been described in a series of papers by Jacobs (1944-51), and more recently by Carosella and Fowler (1957).

The ground reduced ore is leached to a pH of 4.4 with anolyte and make-up sulphuric acid. The slurry is treated with ammonia to pH 6.6 to precipitate most of the impurities. The neutralised slurry is then filtered and the residue washed with water to recover soluble manganese. The pregnant liquor is treated with a small amount of hydrogen peroxide to oxidise and precipitate the residual iron. The precipitate is filtered from the solution and sulphur dioxide is added to the solution before it enters the electrolytic cells. The presence of sulphur dioxide is essential for successful electrodeposition. The anolyte produced in the cells is returned to the leaching circuit. The composition of the cell solutions is shown in Table 2.

TABLE 2: ANALYSIS OF CELL SOLUTION g/1

	Feed	Anolyte
Mn	32 - 34	10 - 12
$(NH_4)_2$ SO_4	120 - 140	120 - 140
SO_2	0.30 - 0.50	-
H_2SO_4	-	36 - 44

Magnesium is not removed from the pregnant solution by the purification treatment described, and if any is present in the ore it will accumulate in the anolyte. It may be removed from the circuit when necessary by cooling the anolyte in a continuous vacuum crystalliser, when a complex Mg, Mn, $(NH_4)_2$ SO_4 crystallises out. After removing the salt, the solution is returned to the leaching circuit.

The cathodes are made of Hastelloy Alloy C (a nickel alloy), the anodes are 99 per cent Pb, 1 per cent Ag. The anodes are drilled with holes to increase the current density and minimise the production of MnO_2 by anodic deposition. The cathode current density is 45-50 amp/sq ft, the anode current density 81-90 amp/sq ft, and the cell voltage 5.0 - 5.3. After deposition for 24 hours the cathodes are dipped in dichromate solution (1 per cent) to prevent oxidation of manganese. They are then washed and dried and stripped by striking with a rubber mallet. The power consumption is 6 kw hr/lb of manganese.

4.2 Leaching with Ferrous Sulphate and Sulphuric Acid

This process eliminates the reductive roasting necessary for sulphuric acid leaching, since reduction is effected by the ferrous ion:

$$MnO_2 + 4H^+ + 2Fe^{2+} = Mn^{2+} + 2Fe^{3+} + 2\,H_2O \quad \ldots\ldots\ldots (1)$$

or

$$MnO_2 + 2H_2SO_4 + 2\,FeSO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2H_2O \quad \ldots (2)$$

Hydrolysis of ferric sulphate liberates sulphuric acid, and in theory leaching could be effected with ferrous sulphate alone without the addition of acid:

$$MnO_2 + 2Fe^{2+} + 2\,H_2O = Mn^{2+} + \tfrac{4}{3}\,Fe\,(OH)_3 + \tfrac{2}{3}\,Fe^{3+} \quad \ldots . (3)$$

or

$$MnO_2 + 2\,FeSO_4 + 2H_2O = MnSO_4 + \tfrac{4}{3}\,Fe(OH)_3 + \tfrac{1}{3}\,Fe_2(SO_4)_3 \,(4)$$

Equation (4) shows that more sulphuric acid could still be obtained by hydrolysis of the residual ferric sulphate. This acid would not leach MnO_2, but it could leach MnO, and for ores containing MnO the best theoretical utilisation of $FeSO_4$ is shown by:

$$MnO_2 + MnO + 2\,FeSO_4 + 3\,H_2O = 2\,MnSO_4 + 2Fe\,(OH)_3 \qquad (5)$$

Equation (5) shows that 1 lb of ferrous ion is required per lb of manganese; the minimum quantity of iron required to leach ore in which the manganese is all present as dioxide would be double this.

Dolezal and Fuller (1959) have described the acid-ferrous sulphate leaching of various low grade manganese ores. The ferrous sulphate for leaching MnO_2 was obtained by leaching ores containing both $MnCO_3$ and $FeCO_3$ with sulphuric acid. The following results were obtained with a black oxide ore:

Head Sample	%
Mn	8.3
Acid soluble Mn	0.4
Fe	27.8
SiO_2	39.6
CO_2	0.25

Mn extraction, 93.8 per cent.

Reagent consumption, lb/lb of Mn leached,	H_2SO_4	3.21
	Fe^{2+}	1.87

Leaching time, 120 min.

Temperature was not a critical factor. Leaching with ferrous sulphate alone was also successful, but a long leaching time was required; 92.2 per cent extraction was obtained with a 10 hour leach at 70-75°C. Although acid requirements are higher than for a reduced ore (since acid must be allowed for preparation of $FeSO_4$), this disadvantage is partly compensated for in that a reducing roast is not required. The authors do not expect acid-ferrous sulphate leaching to lower the cost of producing manganese.

4.2.1 Waste Pickle Liquor Process

Hoak and Coull (1950) used waste pickle liquor for leaching low grade ores. Their ore contained 15 per cent Mn, mostly present as dioxide, and was ground to minus 50 plus 100-mesh. The average composition of the pickle liquor was 15 per cent $FeSO_4$, 5 per cent free H_2SO_4 by weight, and this extracted 98 per cent of the manganese in 30 minutes. Grinding finer than minus 100 plus 200-mesh was not essential for complete extraction. 84 per cent extraction could be obtained with ferrous sulphate alone. 95 per cent of the iron and 5 per cent of the manganese were precipitated by raising the pH of the leach slurry to 4.2 by the addition of precipitated chalk. Manganese was precipitated from the pregnant liquor by lime slurry at pH 9.5 (Fe^{3+} can be completely precipitated at a pH of about 3.5, Fe^{2+} begins to precipitate at 5.5 and Mn^{2+} at 8.5.) The manganese precipitate was dried and roasted for 1-hour at dull red heat, when a product containing 64.5 per cent of manganese was obtained. Leaching of 48 tons of ore containing 15 per cent Mn required 75,000 gallons of pickle liquor of average composition. In this process there is high consumption of CaO and $CaCO_3$, but the problem of shipping the pickle liquor to the mine is the most serious disadvantage. The process was developed principally as a means of utilising waste pickle liquor. The authors say nothing about contamination of the product with calcium sulphate.

4.2.2 Calcium Chloride Process

Hopkins (1954) applied the pickle liquor process to the extraction of manganese from low grade Pernatty Lagoon ore. This is a wad ore of average grade 24 per cent Mn. The pickle liquor used contained 13 per cent $FeSO_4$ and 5 per cent free H_2SO_4 by weight. The ore was ground to minus 60-mesh and leached at 70°C, when up to 98 per cent of the manganese was extracted. In order to obtain a product substantially free from sulphur, and hence suitable for the manufacture of ferromanganese, sulphate was precipitated by the addition of calcium chloride. Without this step calcium sulphate will be precipitated with manganese and will appear in the final product. After precipitation of sulphate, iron was oxidised by aeration and removed by addition of precipitated chalk slurry to pH 4.2. 98 per cent of the iron and not more than 5 per cent of the manganese were precipitated in this way. Slaked lime slurry could not be used as a precipitant because it precipitated excessive amounts of manganese, probably due to localised increase in pH. Manganese was precipitated from the purified chloride liquor by addition of finely ground lime slurry to pH 9.5. The filtrate containing calcium chloride was concentrated by evaporation for recycle. The precipitate was roasted for 1-hour at 600°C to give a product containing 61 per cent Mn. Manganese recovery was 85 per cent. Hopkins estimated the production cost at £29 per ton of manganese nodules for a plant treating 20 tons of ore per day. Apart from the difficulty of transporting the pickle liquor, this process suffers from the fact that ultimately all of the leach liquor must be evaporated.

4.3 Leaching with Ammonium Sulphate

The Bradley ammonium sulphate process is described in U.S. Patents 1,889,021; 1,937,508; 1,947,457; 1,951,341; 2,074,013. Manganese is reduced to MnO and Fe_2O_3 is reduced to Fe_3O_4 by a reducing roast. The calcine, which must be kept away from air to prevent re-oxidation, is agitated with ammonium sulphate liquor at about 88°C. MnO dissolves to form $MnSO_4$ with the generation of ammonia, which is recovered. Manganese can be recovered from the sulphate liquor by one of the methods already described (crystallisation, electrolysis, precipitation with lime). Apart from the question of sulphur recovery, which is common to all the sulphate processess, a chief obstacle has been the difficulty of recovering the ammonia.

4.4 Leaching with Sulphur Dioxide

4.4.1 Calcium Chloride Process

Dean (1934) suspended ground ore in water and leached with SO_2 gas to extract manganese as $MnSO_4$. Calcium chloride was added to the slurry to precipitate $CaSO_4$ and form $MnCl_2$ solution, which was separated from $CaSO_4$ and the insoluble portion of the ore by filtration. Lime was added to the filtrate and the mixture was agitated with air to precipitate oxides of manganese and regenerate calcium chloride. The precipitate was calcined and the calcium chloride solution recycled. Ravitz (1946) modified the process by suspending the ore in calcium chloride solution, so as to extract manganese and precipitate $CaSO_4$ in one step. He also omitted the air agitation after addition of lime as unnecessary. When the process was carried through a series of cycles it was noted that the concentration of dithionate ion in the cycled solution gradually increased and the chloride content gradually decreased (owing to soluble losses in the leach residue and precipitate.) Finally calcium chloride became virtually completely replaced by calcium dithionate, the quantity of dithionate ion formed during the leach being more than enough to make up the loss of dithionate in filtering. The calcium chloride process thus developed into the calcium dithionate process described by Ravitz (1946, 1949).

4.4.2 Dithionate Process

A slurry of ore in an excess of calcium dithionate solution is treated with gas containing SO_2 and O_2. $MnSO_4$, MnS_2O_6, H_2SO_4 and $H_2S_2O_6$ are formed. The sulphate ion formed is immediately precipitated as $CaSO_4$ by reaction with the CaS_2O_6 present. After separation of the solids the solution contains MnS_2O_6, CaS_2O_6 and a small quantity of $H_2S_2O_6$. It is treated with slaked lime to precipitate $Mn(OH)_2$ and regenerate CaS_2O_6. The precipitate is filtered off and nodulised or sintered and the calcium dithionate solution is recycled.

The ore, which contained 13-18 per cent Mn mostly as pyrolusite and psilomelane, was crushed to minus 10-mesh, mixed with barren calcium dithionate solution and ground to minus 65-mesh. The slurry, of pulp density 65-70 per cent solids, was diluted with calcium dithionate solution (180 - 200 g S_2O_6/l) to 20-25 per cent solids for leaching. Leaching was done in 3 conical vessels with SO_2 diluted with air to simulate waste smelter gas (3 per cent SO_2). The gas entered near the apex of the conical bottom. The temperature in the first vessel rose to 40°C due to the heat of reaction. From the last leaching vessel the slurry flowed to a similar vessel in which it was aerated to remove any unreacted SO_2. Dithionate in the final slurry was 200 - 250 g/l. Manganese extraction was 85-95 per cent. 2.0 - 2.5 lb of SO_2 were introduced per lb of manganese extracted and 60-70 per cent of the SO_2 introduced were absorbed. The theoretical consumption of SO_2 per lb of manganese extracted would be 1.16 lb if all the SO_2 formed $MnSO_4$ and 2.33 lb if all the SO_2 formed dithionate. The final pH of the leach slurry was generally less than 1.0. Slaked lime was added to raise the pH to about 3.5 and precipitate any iron extracted. The amount required was 0.2 - 0.4 lb of CaO per lb of manganese extracted. The slurry was filtered and the pH of the filtrate adjusted to about 9 with slaked lime to precipitate $Mn(OH)_2$. This required 1.1 - 1.3 lb of CaO per lb of manganese extracted (the theoretical quantity is 1.02). The $Mn(OH)_2$ filter cake usually contained about 50 per cent of water. The final sintered product contained 60-63 per cent Mn. Part of the barren calcium dithionate solution was used to slake the lime and the rest was evaporated to the desired concentration and returned to the head of the circuit.

2.0 - 4.0 per cent of the manganese were precipitated in the neutralisation step, and 0.6 - 1.5 per cent were lost as soluble manganese in the washed tailing, so that recovery was about 96 per cent of the extraction. Total loss of dithionate in filtering the tailing and the $Mn(OH)_2$ precipitate was 15-20 lb per ton of ore, but more than enough was generated to make up for this loss.

Zinc could be removed from the pregnant solution by adjusting the pH to 6.9 with lime, dissolving the precipitate in sulphuric acid, adding calcium dithionate to precipitate sulphate, and reprecipitating the zinc with lime. At least 85 per cent of the zinc can be removed in this manner as a 60 per cent product (after calcining), with a loss of less than 1 per cent of manganese.

Water enters the system as free and combined water in the ore, water vapour in the leaching gas and wash water for tailing and precipitate. It leaves as water vapour in the exit gas, free and combined water in the tailing and precipitate, and water driven off in the evaporator. The average quantity of water used for washing the tailing and precipitate filter cake was 2.6 tons, and the average quantity evaporated was 1.3 tons per ton of ore. Ravitz however believed that adequate washing could be obtained with a total of about 2 tons of water under suitable conditions, in which case only about 0.6 - 0.7 ton of water per ton of ore would have to be removed in the evaporator.

Back, Ravitz and Tame (1952) have examined the effect of ore and SO_2 feed ratios, concentration of SO_2, rate of agitation, temperature, pH, cell design and the addition of certain reagents on the rate of dithionate formation.

This process requires slightly more than 1 lb of lime per lb of manganese recovered, and the sulphur dioxide cannot feasibly be recovered. A cheap source of SO_2, such as waste smelter gas, is therefore necessary.

4.4.3 Crystallisation Process

The sulphur dioxide process described by Vedensky (1946) envolves suspension of the ore in water, leaching with SO_2, recovery of $MnSO_4$ - MnS_2O_6 crystals by evaporation, thermal decomposition of the crystals into MnO and SO_2 - SO_3 gas, nodulising the oxide, and recycling the gases to the leach. During the leaching it was found necessary to prevent the pH of the slurry from rising above 3.5, otherwise insoluble $MnSO_3$ was formed and lost in the tailings. Separation of $MnSO_4$ liquor from the leach was difficult because the fine slimes formed during leaching do not readily flocculate, settle or filter. Washing efficiency was 97.4 per cent with 6 thickeners. Manganous oxide slurry was added to the pregnant solution to raise the pH to about 5.5 and precipitate iron and aluminium. Manganous oxide was prepared by reducing calcined $MnSO_4$, mixed with 7-13 per cent of fine coal, in a roasting kiln. The degree of reduction, as measured by solubility in excess of sulphuric acid, was greater than 98 per cent. The reduced oxide was well ground and pumped to the neutralising plant.

Roasting produces both SO_2 and O_2

$$3\,MnSO_4 = Mn_3O_4 + 3\,SO_2 + O_2$$

The roasting temperature was 1090 - 1200°C.

At this temperature the equilibrium $SO_3 = SO_2 + \frac{1}{2}O_2$ lies so far to the right that very little SO_3 ever forms. Dithionate salts began to decompose at lower temperatures to sulphate and SO_2. Ring formation in the kiln caused difficulties. This was due to the presence of alkali salts, which form a low melting (700 - 800°C) eutectic with $MnSO_4$; this later solidified as the temperature rose and SO_2 was driven off. Make-up SO_2 for leaching was supplied by burning elemental sulphur.

It was necessary to nodulise the calcine to increase physical strength, reduce the quantity of fines and complete the conversion of $MnSO_4$ to oxide. The temperature varied between 1310 and 1430°C, depending on the amount of alkali present, which acted as a flux. Some sulphur remained in the nodules in the form of alkali sulphate. This was removed by spraying the storage piles with water from a hose.

A typical analysis of leached nodules was:

	%
Mn	64.8
S	0.25
Fe	0.56
P	0.01
SiO_2	2.82

This process was operated at Las Vegas in a large scale plant which treated 1000 tons a day of 20 per cent Mn ore from the Three Kids mine. The plant ran for about a year and closed down in September, 1944. It demonstrated that high grade manganese nodules can be produced from low-grade ores by the sulphur dioxide process on a large scale, but at a non-competitive price, owing to the expensive evaporation and decomposition equipment and the large quantities of heat required.

The process described by Vedensky has been modified by Allen (1954) by the introduction of two new factors, a high temperature autoclaving step and a sintering operation. The ore, which contained 20.2 per cent Mn, 22.9 per cent Fe, 19.6 per cent SiO_2 and 3.9 per cent Al, was ground to minus 80-mesh and slurried with twice its weight of water. A stream of air containing about 7 per cent of SO_2 was passed through the slurry until the amount of SO_2 absorbed was approximately 1.4 times the weight of manganese present, giving a mole ratio of sulphur to manganese in the slurry of about 1.2. Manganese extraction during the leaching step was 72-85 per cent, iron extraction 0.5 - 5 per cent. The reacted slurry was heated in a stirred autoclave at 230°C under a pressure of 600 lb per sq in. gauge for 2 hours to oxidise dithionate. Free SO_2 is oxidised to H_2SO_4, which increases the extraction of manganese. After autoclaving, manganese extraction was 89-98 per cent, iron extraction 2.4 - 10.4 per cent.

The pregnant liquor was separated from the tailings and concentrated in an evaporator to obtain crystals of $MnSO_4$. The crystals were separated by filtration and the mother liquor returned to the evaporator to maintain a magma density of approximately 40 per cent solids by weight and a liquid phase of 60 per cent H_2SO_4. In the range 40-70 per cent, and preferably 55-60 per cent H_2SO_4, $MnSO_4$ crystals grow to a size at which they are readily filterable. The filter cake, which contained about 13 per cent of H_2SO_4, was mixed with powdered coal and powdered recycled oxide and sintered to produce the final product.

$$2\ MnSO_4 + \tfrac{1}{2}\ C = Mn_2O_3 + \tfrac{1}{2}\ CO_2 + 2\ SO_2$$

The sinter was rough ground and screened to furnish a plus quarter inch hearth layer. The balance was ground to minus 50-mesh to furnish the recycled oxide. The SO_2 produced in the sintering would be recycled and the loss made up by burning pyrite.

The estimated cost of a plant to produce 100,000 tons of manganese as sintered oxide per year was 16½ million dollars. The direct operating cost would amount to 41.33 dollars per ton of manganese, excluding all mining, ore dressing, transport and amortisation costs. The total cost, assuming delivery of concentrates at 30 cents per unit of manganese and amortisation at 17.5 per cent per year, would be about 100 dollars per ton.

4.4.4 Ammonia Precipitation Process

Another variant of the sulphur dioxide leaching process is described by Ketzlach (1950). The ore, ground to minus 65-mesh, is treated with sulphurous and sulphuric acids at a temperature of 60°C. The addition of sulphuric acid is necessary in the treatment of oxide ores which contain a substantial proportion of divalent manganese. In the treatment of ores in which most of the manganese is present as dioxide no addition of sulphuric acid is necessary. The reason for this is that sulphurous acid dissolves Mn (IV) to produce manganous ions, which act catalytically in the presence of air to oxidise portion of the sulphurous acid to sulphuric acid. Enough sulphuric acid is produced in this way to leach small quantities of Mn (II). Ketzlach claims that the formation of dithionate is prevented by maintaining an oxygen to sulphur dioxide ratio of about 4. The $MnSO_4$ solution is purified from iron, aluminium and silica by heat, aeration and addition of ammonia to pH 5.2, as described by Allen (1948). Approximately 2 per cent of the manganese is lost in the precipitated impurities. The purified pregnant liquor is essentially a solution of $MnSO_4$ with some $(NH_4)_2SO_4$. Manganese is precipitated as an oxide product, in which 70-80 per cent of the manganese is in the dioxide form, by addition of ammonia and air under pressure (Moulton 1949). Suitable conditions were:

1. An ammonia concentration above 3N,
2. A partial pressure of oxygen above 10 psi absolute
3. Temperature 25°C or less.

A typical product contained 77.9 per cent MnO_2, 11.5 per cent MnO, 10.2 per cent water of hydration. After the manganese precipitate has been separated, excess of ammonia is stripped from the solution by steam and the solution is evaporated to recover ammonium sulphate.

For treatment of 90,000 tons of ore (27 per cent Mn) a year with 90 per cent recovery, equivalent to annual production of 37,700 tons of manganese oxides containing 58 per cent Mn, and 50,700 tons of ammonium sulphate, the manganese oxide production cost was estimated at 0.358 dollar per long ton unit of manganese and the ammonium sulphate cost at 43.57 dollars per ton. These costs include amortisation of an 800,000 dollar investment in four years, but the manganese oxide cost does not include mining or freight of the ore. The raw material costs have been taken as 23.75 dollars per ton for sulphur and 110 dollars per ton for anhydrous ammonia. The ore treatment is the type that does not require sulphuric acid.

This process takes as raw materials a low grade manganese ore, sulphur and anhydrous ammonia, and produces from them two products, a manganese oxide and ammonium sulphate, of which the latter is the more valuable.

4.4.5 Percolation Leaching

Bender and Rampacek (1957) studied leaching of manganese ores with sulphur dioxide. The procedure consists of alternate upward passage of SO_2 through an agglomerated charge of moist coarse ore and downward percolation of wash solutions to remove soluble manganese. Ore crushed to minus 1-inch screen or finer is mixed with enough water or calcium dithionate solution to distribute and cement the fines to the coarser particles and yield a moist permeable ore bed containing 9-25 per cent moisture. Reaction of SO_2 to produce $MnSO_4$ and MnS_2O_6 releases considerable heat. When SO_2 escapes from the charge introduction of the gas is stopped and the charge is allowed to absorb the unreacted SO_2.

The manganese salts are washed from the ore bed by downward percolation with water or dithionate solution to reactivate the bed. The leach solution can be evaporated to crystallise $MnSO_4$, or treated by the dithionate process.

Large scale tests were made on 220 lb charges in 8-inch diam. x 9 ft high earthenware columns. The ores were agglomerated with water in a cement mixer before being charged to the columns. In the initial cycle the heat of reaction was high and the temperature rose to 70-100°C, the hot zone progressing steadily upward through the bed. Water rather than barren solution was used in the first leaching stage to minimise cementation of the charge by the precipitation of gypsum. When 40-50 per cent of the total manganese had been removed barren dithionate solution was introduced. The pregnant liquor had approximately the same dithionate concentration as the barren dithionate solutions used for leaching and washing. Subsequent precipitation of manganese from the pregnant liquors with lime therefore permitted recovery of a barren solution that could be used to wash new charges without evaporation. 2.3 lb of SO_2 were added per lb of manganese recovered.

The pregnant solution was aerated to convert any free SO_2 to acid and oxidise Fe^{2+}. After aeration, solutions containing more than 20 g of manganese per litre were diluted with barren liquor to reduce the manganese content to about 20 g per litre while maintaining the S_2O_6 at about 100 g per litre. The diluted solution was neutralised to pH 5.5 with lime slurry, prepared by slaking 1 part of pulverised quick lime with 1 part of water and diluting the thick paste with barren dithionate solution. 0.3 lb of dry lime (95 per cent CaO) was added per lb of manganese recovered. Impurities such as Fe, Al_2O_3, and P_2O_5 were precipitated with the gypsum and 0.4 per cent of the manganese was lost during the neutralisation. The slurry was filtered and the precipitate washed with barren dithionate solution.

The manganese was precipitated from the purified solution by addition of lime slurry to pH 9.0. Consumption of dry lime was 1.2 lb per lb of manganese precipitated. The precipitated pulp was heated to 60°C, filtered and washed at 60-65°C with 5.9 tons of water per ton of dry solids. The product was dried at 110°C. The principal impurities were calcium sulphate and magnesium (derived from the lime). The dry precipitate was pelleted by mixing and rolling with 4.5 per cent of petroleum coke and 30.5 per cent of water. The pellets were heated at 1200°C for 30 minutes when hard compact nodules were obtained. Coke appears to be necessary to get rid of sulphur. Recovery of manganese in the nodules was 94 per cent. Analysis of the liquors and products is shown in Table 3.

TABLE 3: PERCOLATION LEACHING WITH SO_2.
Analysis of Liquors and Products

Liquors	pH	Mn g/l	S_2O_6 g/l	SO_4 g/l	S g/l	Fe g/l	Al_2O_3 g/l	SiO_2 g/l	MgO g/l	CaO g/l	P g/l
Aerated pregnant solution	1.1	30.4	89.6	22.9	-	0.55	1.42	0.35	0.45	-	0.21
Diluted - ditto -	1.2	19.0	93.5	4.9	-	0.40	0.58	0.33	0.20	-	0.14
Neutralised "	5.4	17.6	93.6	2.6	-	0.05	0.05	0.15	0.63	-	0.01[x]
Barren solution after precipitation	8.9	0.0	92.5	1.4	-	0.05[x]	0.25	0.29	0.57	-	0.01[x]
Products		%	%	%	%	%	%	%	%	%	%
Precipitate dried at 110°C	-	59.0	-	-	0.67	0.18	0.35	1.2	2.29	1.26	0.032
Precipitate nodulised at 1200°C	-	64.6	-	-	0.06	0.23	0.53	1.6	2.63	2.86	0.058

[x] Less than.

4.4.5 Heap Leaching

Heap leaching was also investigated. A mixture of air and sulphur dioxide containing 15 per cent of SO_2 was introduced through a jet at the bottom of a small pile of ore (800 lb). The gas was added at the rate of 1 lb of SO_2 per hour for 20-hours after which some loss of SO_2 from the top of the pile was noted. Percolation washing with water then began. At the next sulphating stage the SO_2 in the gas mixture was increased to 53 per cent, and alternate treatment with gas and water and dithionate wash solutions was carried on for an additional 10 days. The recovery of manganese was 82.8 per cent. The poorest leaching occurred in the surface layers. Much higher recoveries might be obtained in large scale heap leaching, since the surface would represent a much smaller proportion of the whole.

Farnham, Stewart and DeLong (1961) applied the percolation leaching process to a zinc-bearing pyrolusite intimately associated with a fine grained chalcedonic quartz and haematite, which contained 22.4 per cent Mn, 5.6 per cent $CaCO_3$ and 0.28 per cent Cu. Treatment of minus quarter inch feed recovered 98 per cent of the manganese during a 16 day leach. Consumption of SO_2 was 5 lb per lb of manganese recovered. They concluded that it is doubtful whether the ore could be treated profitably by this method at the present market value of manganese.

4.5 High Temperature Sulphating Process

Ashton and Moffitt (1960) have described this process. The ore is calcined below 480°C in a vertical shaft kiln to decompose carbonate and reduce the higher oxides. It is then heated in an atmosphere of SO_2 at 880°C, mainly by the heat of the exothermic sulphating reaction. An excess of 50 per cent of SO_2 is required over that needed to sulphate the manganese. The kiln discharge is ground and leached and the leach liquor evaporated to crystallise $MnSO_4$. The crystals of $MnSO_4$ are calcined to oxide and the SO_2 recycled.

4.6 Leaching with Nitric Acid

Nossen (1951) has described a nitric acid cycle for the extraction of manganese. The ore, usually containing about 20 per cent Mn, is crushed and ground to minus 60-mesh and fed to a reducing kiln, where manganese is reduced to MnO and iron to Fe_3O_4 (insoluble in nitric acid). The reduced ore is leached with nitric acid in stainless steel equipment, sulphuric acid being added to precipitate barium, calcium and lead. The temperature in the leaching vessels rises to 80-90°C and the leach is finished within an hour. After filtration the insoluble residue is washed and the wash solution is used to dilute the nitric acid for the next leach.

The $Mn(NO_3)_2$ solution, which may contain some Na, K, Mg, and Zn, is concentrated in an evaporator and decomposed in the presence of air at 200°C.

$$Mn(NO_3)_2\ H_2O + \tfrac{1}{2}\ O_2 = MnO_2 + 2HNO_3$$

The decomposition takes place on the surface of an internally heated rotary drum inside the stainless steel decomposition unit. This drum dips into a pan filled with concentrated $Mn(NO_3)_2$ solution and is covered with a layer of the solution. The MnO_2 is removed from the drum by a knife and discharged on a chute to the outside. Nitric acid leaves with the air which is sucked through the system, and is condensed to a liquid containing about 50 per cent HNO_3. The air is then washed with water to remove residual HNO_3. The MnO_2 leaving the decomposition unit is washed to remove soluble impurities, dried and nodulised to produce a product containing 60 per cent Mn.

Manganese recovery was 85-90 per cent from Cuyuna ores. These are dense ores containing 10-13 per cent Mn, 25-40 per cent Fe and 15-30 per cent SiO_2, in which iron and manganese are intimately associated. The manganese product contained 88.0 per cent MnO_2, 5.32 per cent MnO, 1.67 per cent CaO, 0.31 per cent MgO, 0.04 per cent Fe_2O_3 and 0.91 per cent NO_3. A marketable product containing 50-60 per cent Fe was extracted from the insoluble residue. For metallurgical use the manganese product must be nodulised. It can also replace chemical grade ore, and since it contains gamma MnO_2, may be suitable for battery use.

A production rate of 100 tons of finished product per day required HNO_3 replacement of about 10 tons (68 per cent) per day. Cost of H_2SO_4 equivalent to the soluble impurities was 1-4 dollars per ton of finished product. Theoretical heat consumption per ton of finished product from ore containing 20 per cent Mn and 20 per cent Fe is 2,738,000 k. cal = 11,000,000 Btu (equivalent to 3220 kwhr). If an average heat efficiency of 65 per cent is assumed, heat consumption would be 16,900,000 Btu (equivalent to 4950 kwhr) per ton of finished product (60 per cent Mn). This includes heat for reduction, concentration (evaporation), decomposition, drying and nodulising. The estimated processing cost, based on 1951 prices, and excluding the cost of mining and transportationof the ore to the mill, is 30 dollars per ton of finished product (60 per cent Mn).

4.7 Leaching with Hydrochloric Acid

Jacobs and others (1951) developed an electrolytic process based on HCl leaching which was successfully applied to various types of ore. The principal problem in changing from one ore to another is modification of the solution preparation to ensure removal of all impurities.

The ore was crushed and ground to 95 per cent minus 35-mesh and subjected to a reducing roast to reduce MnO_2 to acid soluble MnO. The calcine was leached with spent cell electrolyte containing 16 g Mn, 60-90 g NH_4Cl, and 50-78 g HCl per litre. Enough calcine was added to give the final desired manganese concentration (usually 56-58 g per litre). Manganese extraction averaged 96-98 per cent with final pH 2.5 - 3.0. The pH was then raised to 6.5 by the addition of ammonia, which is the most desirable neutralising agent as ammonia has to be added to replace nitrogen losses at the anode. The residue was separated by filtration and discarded. The leach liquor contained 100 g of NH_4Cl and 56-60 g of Mn per litre. The theoretical HCl requirement for leaching manganese is 1.33 lb per lb of Mn, but about 1.6 lb are required in practice.

The leach liquor must be purified before electrolysis. Impurities such as Co, Ni, As, Cu, Pb, Fe, and Mo were removed by passing H_2S or adding sodium or ammonium sulphide and filtering. Aeration must be avoided during precipitation. The solution after filtration still contained colloidal sulphur and sulphides. These were removed by adding 0.1 g of iron as $FeCl_3$ per litre and aerating. The precipitate of ferric hydroxide acted as a collector for the colloidal sulphur and sulphides. About 1 hour was required for the complete precipitation of the iron and 0.5 - 1.0 g of Mn per litre was also precipitated. The solution was clarified by filtration and was then ready for electrolysis.

The anodes were of graphite, packed into a Formica frame. Each anode was enclosed in a No. 1 Vinyon cloth bag or diaphragm, which was connected by a rubber tube to a common spent-electrolyte or anolyte compartment beneath the electrolytic cell. The cathodes were of 316 stainless steel and were suspended in a common electrolyte or catholyte. The purified electrolyte was fed to the catholyte compartment of the cell. The solution, depleted of manganese, flowed through the diaphragms into the anode compartments, thence into the common anolyte compartment beneath the cell, and then up through a riser and out through the side of the cell at any desired height. The height of the anolyte discharge determined the catholyte solution level in the cell.

Optimum Conditions for Electrolysis

Feed solution	Mn	56-60 g/l (in the form of $MnCl_2$)
	NH_4Cl	95-105 g/l
	SO_2	0.1 g/l
Current density	45-50 amp/sq ft	
Temperature	40°C	
Time of deposition	48-69 hr	
Current efficiency	64-67 per cent	
Cell potential	3.5 - 3.6 v	

Ammonium chloride was decomposed at the anodes and nitrogen was quantitatively discharged, together with some chlorine (less than 1 per cent of the total gas discharged). The anode reaction products can be accounted for by assuming that the anode reaction is essentially an oxidation of NH_4^+ to N_2:

$$Cl' = Cl + e$$

$$\frac{1}{3}NH_4^+ + Cl = \frac{1}{6}N_2 + \frac{4}{3}H^+ + Cl'$$

$$\frac{1}{3}NH_4^+ = \frac{1}{6}N_2 + \frac{4}{3}H^+ + e$$

The theoretical N_2 loss is 0.18 g per amp hr - 0.31 g of NH_3 lost per gram of manganese deposited on the cathode at 70 per cent current efficiency. For best results the catholyte pH should be 7.4. The decomposition of NH_4^+ produces H^+, hence NH_3 must be added continuously to the catholyte to maintain the desired pH and make up the loss of nitrogen.

The presence of SO_2 is essential for successful electrodeposition. From solutions containing no SO_2 or non-sulphate sulphur compounds, manganese was deposited as the gamma form, which is ductile. The presence of more than 0.05 g of SO_2 per litre caused manganese to be deposited in the brittle alpha form at much better current efficiency. To reduce adhesion of manganese to the cathodes, they were dipped in dilute sodium silicate solution and washed. Manganese could then be recovered by flexing or rapping with a rubber mallet. Titanium cathodes were found to be much superior, as they did not corrode above the solution line and manganese did not adhere to them.

Sodium, potassium, magnesium and calcium have no effect on electrodeposition up to the limit of solubility. It is necessary however to have some control over their removal, or they will build up to the point where crystallisation will occur. Calcium can be removed by adding sulphate to the leach. No method of controlling magnesium was found; addition of ammonium bifluoride is suggested as a possibility.

The purity of the product exceeded 99.9 per cent. The principal impurity was sulphur, derived from the added SO_2. The authors conclude that the chloride process has the following advantages over the electrolytic sulphate process:

1. Reduction of power consumption by about 25 per cent, owing to the lower cell potential.
2. Greater recovery of manganese from the feed solution. Hence the solution preparation plant needs to be only half as large as for the sulphate process.
3. Reduced cost of handling cathodes, owing to longer time of deposition.
4. No deposition of MnO_2 at the anode.

and the following disadvantages:

1. More corrosive solutions, which require expensive materials for construction.
2. Loss of nitrogen (equivalent to nearly $\frac{1}{3}$ lb of NH_3 per lb of Mn deposited), and the necessity of adding NH_3 to each cell to control the catholyte pH.
3. Ventilation of cells to remove chlorine.
4. Cost of Vinyon diaphragms, which are necessary because of the high acid concentration but are more expensive than the cotton diaphragms used in the sulphate process.
5. Lack of an assured method for the control of calcium and magnesium contents.

They express the opinion that the chloride process would be more difficult and expensive to operate than the sulphate.

4.8 Leaching with Caustic Soda

The object of this is to beneficiate manganese ores by the removal of silica. Perkins (1957) found that the optimum conditions for leaching were 1-hour contact time, 60-70 per cent solids, 100 lb of NaOH per ton of concentrate and a temperature of 95°C at atmospheric pressure. He treated 22 tons of a flotation concentrate (86 per cent minus 200-mesh) with the following result:

	After Ignition at 1200°C					
	Mn %	SiO_2 %	Al_2O_3 %	CaO %	BaO %	Na_2O %
Before leaching	41.5	17.7	2.2	2.9	9.8	0.23
After leaching	43.7	11.1	2.6	3.1	11.7	1.10

The fine concentrate obtaind would not be acdeptable without sintering or nodulising. Roasting of the concentrate in air at 600°C to remove flotation oil did not effect the extraction of silica.

The sodium silicate solution obtained contained 40 g of Na_2O (= 52 g NaOH) and 66 g of SiO_2 per litre. NaOH was recovered from this by adding a slurry of quick lime containing 1 mole of CaO for each mole of SiO_2. The mixture was agitated at 20°C for 2 hours and filtered.

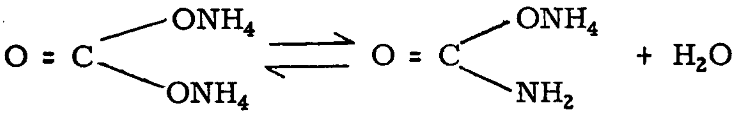
The precipitate was washed by repulping with water and filtering. A typical filtrate contained 23 g of NaOH and 0.5 g of SiO_2 per litre. After one repulp washing step the precipitate contained 6.0 per cent NaOH, 25 per cent Ca and 36 per cent SiO_2. The final recovered NaOH solution represents the original leach liquor, plus wash of the tailings, plus water from the quicklime slurry, plus the final wash of calcium silicate. The volume may be estimated as 2 tons per ton of concentrate. To obtain 50 per cent NaOH for re-use in leaching nearly 2 tons of water would have to be evaporated per ton of concentrate.

Lundquist (1953) reported the results of laboratory experiments. The best result from an ore containing 31.7 per cent Mn and 21 per cent SiO_2 was a concentrate containing 46 per cent Mn. The method was most effective for the treatment of ores that consisted almost entirely of cryptocrystalline or metacolloidal silica carrying the manganese minerals. Ores containing quartz or silicate minerals were much more refractory.

Liquors containing more than 75 g of SiO_2 per litre could not be regenerated with lime because they formed thick muds that would not flow readily. The slimy nature of the calcium silicate precipitate precluded the use of thickeners except for very dilute slurries. The total loss of NaOH in treating 1 ton of ore was estimated as 65 lb, excluding the loss by build up of impurities in the leach liquor. About 30 lb of this were lost in the ore tailings and could not be recovered by additional washing.

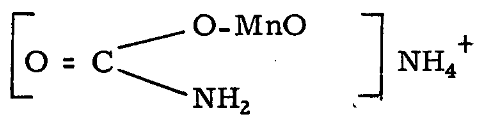
4.9 Leaching with Ammonium Carbonate

This process, described by Dean (1952), was applied to the treatment of low grade ores by Welsh and Peterson (1957). The reduced ore is leached in a solution of ammonia (18 moles per litre) and carbon dioxide (3 moles per litre). The mechanism of the extraction is thought to be as follows: ammonium carbonate loses a molecule of water to form ammonium carbamate



$$O=C\begin{smallmatrix}ONH_4\\ ONH_4\end{smallmatrix} \rightleftharpoons O=C\begin{smallmatrix}ONH_4\\ NH_2\end{smallmatrix} + H_2O$$

and the carbamate ion forms a soluble complex with MnO



$$\left[O=C\begin{smallmatrix}O\text{-}MnO\\ NH_2\end{smallmatrix}\right]NH_4^+$$

which is decomposed by heat into NH_3 and $MnCO_3$. Dean found that with a high grade ore pregnant solutions containing at least 80 g of Mn per litre could be obtained with 10-15 minutes' leaching, together with more than 90 per cent extraction.

Since FeO is also dissolved by the leach liquor, the ore reduction must be controlled to maintain iron as insoluble Fe_3O_4, while manganese is all reduced to MnO. The conditions necessary for reduction have been described by Dean and others (1934) and by DeVaney (1952).

The formation of the carbamate complex gives off heat sufficient to raise the temperature of the reacting slurry about 0.3°C for each gram of manganese leached per litre. Careful control is necessary to hold the temperature of the reacting slurry within proper limits, since too high a temperature causes the precipitation of $MnCO_3$ in the slurry. Reducing conditions must be maintained to ensure maximum leaching efficiency. This may be done in two ways:

1. By the presence of the ferrous complex, which acts as a mild reducing agent. The iron is removed as ferric hydroxide.
2. By addition of ammonium sulphide, usually of the order of 0.1 per cent or less.

Manganese is recovered by heating the solution with live steam to 55-64°C. Well crystallised $MnCO_3$ separates containing more than 46 per cent Mn (theoretical 47.8 per cent). Impurities are chiefly water and ammonia, which are removed by calcining. During the precipitation of $MnCO_3$ the NH_3 concentration is reduced from 18 to 10 moles per litre. Only portion of the manganese is precipitated and the residual liquor is cooled and returned to the leaching stage. Ammonia and carbon dioxide are stripped from the spent ore slurry with steam in a 6 tank slurry still to which the slurry passes from the thickener.

The process was applied to Cuyuna Range ores containing 9-10 per cent Mn, mostly pyrolusite, and 25-28 per cent Fe, mostly haematite. The extraction efficiency was at least 70 per cent. The pelletised product (Mn_3O_4) contained 63 per cent Mn, 3 per cent SiO_2, 1 per cent Fe. The discharge slurry (about 60 per cent solids) contained about 0.5 g of NH_3 per litre of liquid phase. The plant treated 200 tons of raw ore per day and the NH_3 loss was less than 300 lb per day, ie. about 20 lb of NH_3 per ton of manganese recovered.

5. PYROMETALLURGICAL METHODS

5.1 Chloride Volatilisation

MacMillan and Turner (1954, 1956) tested 3 chloridising reagents, chlorine, calcium chloride and hydrochloric acid, and selected hydrochloric acid as the most satisfactory from the point of view of temperature requirement, reactivity, ease of regeneration and overall efficiency. They then developed a process for the extraction of manganese from ores in which it is present in the form of difficulty soluble silicates. The process should work equally well for open-hearth slags and oxide type ores.

The ground ore was introduced at the top of the chloridising reactor and heated at 950-980°C. HCl gas, introduced at the bottom, was passed through the ore. If the temperature rose above 1000°C the ore tended to soften and become sticky. The volatile chlorides formed were swept from the reactor by the HCl gas stream and condensed and the unused HCl was returned to the reactor. The original ore contained 10.8 per cent Mn, 26.8 per cent Fe and 22.0 per cent SiO_2 and the ore residue after chloridisation contained 1.28 per cent Mn, 18.2 per cent Fe and 42.1 per cent SiO_2; 88 per cent of the manganese and 32 per cent of the iron were volatised as $MnCl_2$ and $FeCl_2$ respectively.

The mixed chlorides ($MnCl_2$ + $FeCl_2$) are completely hydrolysed in an atmosphere of steam above 600°C. This may be accomplished by heating the dry chlorides in the combustion products of a gas containing a high proportion of hydrocarbons, such as natural gas. Hydrochloric acid was recovered from the combustion gases, which were passed through the kiln countercurrent to the chloride charge, by a condenser and a scrubbing tower. Solutions which contained up to 27 per cent HCl, with recoveries of 75 per cent of the total chlorine content of the charge, were recovered in the condenser. The hydrolysed product contained 39.9 per cent Mn, 25.3 per cent Fe, 2.17 per cent Cl and 1.66 per cent SiO_2.

The chloride product may be upgraded by selective hydrolysis of the $FeCl_2$, which is completely hydrolysed at 350°C in the vapours from boiling solutions containing 22 per cent of HCl (corresponding to 34 per cent of HCl inthe vapour). Under these conditions less than 1 per cent of the $MnCl_2$ was hydrolysed. A water leach and filtration readily separated the $MnCl_2$ from the iron product (Fe_2O_3, according to the authors, but if this is to be produced air must be admitted with the HCl vapours during the hydrolysis). $MnCl_2$ may then be crystallised as $MnCl_2$ $4H_2O$ and hydrolysed with natural gas to oxide with recovery of HCl as above. The hot gases from the $MnCl_2$ hydrolysis could be used for the $FeCl_2$ hydrolysis, thus effecting a heat economy.

5.1.1 Recovery of HCl

Gaseous HCl containing not more than 5 per cent of water was considered best for the chloridisation furnace. This can be obtained by distillation of the condensate from the hydrolysis kiln. The amount of HCl in the azeotropic mixture of water and HCl increases as the boiling point of the mixture decreases. Thus at a pressure of 760 mm of mercury the azeotrope contains 20.2 per cent HCl; at a pressure of 200 mm it contains 22.3 per cent, and at 100 mm 22.9 per cent. Hence by distillation of the azeotropic mixture produced at one pressure at a lower pressure, pure water may be condensed by using a fractionating column with the top maintained at the temperature at which water boils under the existing pressure. If the acid concentrate produced at the lower pressure is fractionated at a higher pressure, HCl is produced. By using a low pressure still at 250 mm of mercury and a high pressure still at 760 mm, the two stills being coupled for continuous working, an HCl fraction containing more than 99 per cent HCl and a water fraction containing 0.1 per cent HCl were obtained. The theoretical minimum heat required to distill 1 lb of HCl gas from 4.95 lb of 20.2 per cent aqueous HCl is 21,379 Btu.

5.2 Lime Clinkering

This, known as the Sylvester process, has been described by Ruppert (1952). Limestone is mixed with low-grade manganese ores or open-heath slags in the proportion of 3 moles of CaO to each mole of P_2O_5 plus 2 moles of CaO to each mole of SiO_2 present. The mixture is fired under oxidising conditions to about 1360°C. After cooling, the clinker is finely ground and subjected to magnetic separation; most of the manganese, iron, aluminium and magnesium go into the magnetic fraction; the non-magnetic fraction consists for the most part of phosphorus-containing dicalcium silicate. The magnetic product may be reduced with carbon to spiegeleisen, the aluminium and magnesium being eliminated as a slag; or a partial reduction with a deficiency of carbon might be accomplished, removing most of the iron and leaving a slag rich in manganese, which could subsequently be reduced to ferromanganese.

The ore tested by Ruppert contained 11.4 per cent Mn, 26.6 per cent Fe, 24.3 per cent SiO_2, 0.7 per cent P. Very fine grinding of the clinker was necessary to approach liberation of the oxide phase from the silicate phase. Grinding to minus 325-mesh followed by magnetic separation gave only a rougher concentrate, which had to be reground before final separation. The final concentrate contained 15-16 per cent Mn, 0.1 - 0.2 per cent P. This was treated in two ways:

1. To produce spiegeleisen. The concentrate was mixed with one tenth of its weight of carbon black and heated for 1 hour in a covered graphite crucible at 1600°C in an induction furnace. Towards the end of the reduction Al_2O_3 in amount equal to 2 per cent of the concentrate taken was added to fluidise the slag.
   Analysis of the products was:

	Mn %	Fe %	P %
Spiegeleisen	25.9	64.9	0.38
Slag	6.1	3.9	0.03

Recovery of manganese from the concentrate in the spiegeleisen was 83 per cent.

2. To produce ferromanganese. The concentrate was heated with carbon black (12.5 parts of carbon per 100 parts of concentrate) for 8 hours at 1410°C.
   The product was wet ground to liberate iron shot and the metal was separated from the slag in a magnetic separator.
   Analysis of the product was:

	Mn %	Fe %	P %
Metallic fraction	4.9	87.1	0.30
Manganese rich slag	19.0	12.5	0.17

The manganese rich slag was then heated with carbon black (6 parts per 100 parts of slag) at 1600°C for 1 hour in the induction furnace. Shortly before the end of the reduction 3.5 parts of Al_2O_3 and 0.8 parts of fluospar per 100 parts of slag were added for fluidising purposes. Analysis of the products was:

	Mn %	Fe %	P %
Ferromanganese	51.7	35.3	0.19
Slag	2.9	4.2	0.04

The recovery of manganese in the first stage was 88 per cent, in the second 90 per cent, an overall recovery of 79 per cent of the manganese in the original magnetic concentrate.

6. NOTE ON USES, GRADES, SPECIFICATIONS AND PRICES

Schneider (1959) states that about 95 per cent of the world's output of manganese ore are used by the steel industry, 3 per cent by the dry-battery industry, and 2 per cent by the chemical industry. Manganese is important in the steel industry because it is the cheapest material known for desulphurisation and dephosphorisation. Manganese metal (95.5 per cent pure) is made in electric furnaces by a submerged-arc process and is more costly than electrolytic manganese; both are used in place of low-carbon ferromanganese to reduce the carbon content of stainless steels and thus to eliminate the need of a carbon stabiliser.

Electrolytic manganese is used by the non-ferrous industries, particularly the aluminium industry and the brass industry, for the production of alloys (e.g. manganese bronzes).

6.1 Metallurgical-grade Ore

Most of the manganese consumed by the steel industry is in the form of high-carbon ferromanganese. For making ferromanganese, the manganese: iron ratio should be 7 or more. High silica is undesirable because it increases the quantity of slag, which is attended by manganese loss. Zinc, tin, lead and copper even in small amounts are deleterious, and sodium and potassium should be practically nil. General specifications for metallurgical-grade ore are as follows:

%		
48	Mn	minimum
7	Fe	maximum
8	SiO_2	"
0.15	P	"
6	Al_2O_3	"
1	Zn	"

The ore should be in hard lumps of less than 4 inches and not more than 12 per cent should pass a 20-mesh screen.

Ferromanganese contains approximately 80 per cent Mn. Spiegeleisen, which contains approximately 25 per cent Mn, is produced in a blast furnace in the same manner as ferromanganese, and makes possible the use of manganiferrous iron ores and other low-grade materials. Its use appears to have declined, or to be declining.

6.1.1 Battery-grade Oxide

MnO_2 occurs in two well crystallised forms: tetragonal, (pyrolusite-beta MnO_2), and orthorhombic (ramsdellite). Between these is a series of phases not well crystallised. Battery quality MnO_2 has structures that occur in this series, known as gamma, gamma-rho and rho. The gamma and gamma-rho are the most desirable. It also has a large proportion of anhedral particles (irregular particles with no smooth or straight edges). Lundquist (1957) quotes the following specifications for battery grade MnO_2:

	%	
Available oxygen as MnO_2	85.0	minimum
Total Mn	58.0	"
Total alkali metal	0.5	maximum
Total alkaline earth metals	0.5	"
SiO_2	0.5	"
Moisture	3.0	"
Bulk density	18	g/cu in. min.
Morpholygy	anhedral	
X-ray diffraction pattern	gamma	

Another very important factor is the shelf life, which can only be determined by experience. MnO_2 prepared by anodic deposition has the requisite high bulk density and desirable structural features and gives an excellent performance. Copeland and others (1947) described the preparation of high-grade battery quality MnO_2 by oxidation of precipitated $Mn(OH)_2$ in water slurries. They found that the concentration of NaOH should be in the range 0.03 - 3.0 and that $Mn(OH)_2$ should be oxidised before it had time to stabilise by aging.

Lundquist (1957)was unable to prepare MnO_2 suitable for use in batteries from $Mn(OH)_2$ slurries obtained in the dithionate process. Cole and others (1947) reported the preparation of gamma MnO_2 by roasting pyrolusite and leaching the roasted product with dilute sulphuric acid. Lundquist found that roasting 600°C transforms the original crystal structure into a gamma-rho structure, and leaching removes the Mn_2O_3 formed, but only a 50 per cent recovery of Mn is made in the final product.

6.2 Prices

The following are taken from the Mining and Chemical Engineering Review, May 15, 1961 (p. 13).

Metallurgical ore	£12 per ton f. o. b.	Geraldton
Battery grade	£30 per ton f. o. b.	N. S. W. Railway-siding for 75% MnO_2
	£35 per ton c and f.	Sydney for Queensland ore 75-80 %.

(U.K. Stg. 5/8 - 5/11 per unit, 46 % ore c. i. f. European ports).

7. DISCUSSION

7.1 Ore Dressing

The information available suggests that Pilbara manganese ores would not be amenable to ore-dressing methods of concentration, owing to the very fine-grained natured of the ore. It is however possible that a marketable product could be obtained by magnetic separation following a reducing roast.

7.2 Chloride Volatilisation

In this process hydrochloric acid is recovered by distillation of aqueous solutions under different pressures. This would require special equipment owing to the very corrosive nature of the solutions. The minimum theoretical heat requirement is 21,379 Btu per lb of HCl gas recovered (MacMillan and Turner, 1956). If the chloride product is assumed to contain 2 moles of $MnCl_2$ per mole of $FeCl_2$, 2 lb of HCl are required for the recovery of 1 lb of manganese. On this basis, the minimum theoretical quantity of coal (at 12,000 Btu per lb) required for HCl recovery is 3.55 tons per ton of manganese recovered. If a heat efficiency of 65 per cent is allowed, this becomes 5.5 tons. Heat is also required for heating the reactor, hydrolysing the $FeCl_2$, evaporating the $MnCl_2$ leach liquor, and sintering or nodulising the final product. The total coal consumption would therefore exceed 6 tons per ton of manganese recovered. It appears that this process could not be successful unless a cheap source of fuel or power were available.

7.3 Lime-clinkering

Among the disadvantages of this process are the very fine grinding (finer than minus 325-mesh) of the clinker necessary for successful magnetic separation and the high temperatures (1600°C) required for reduction of the magnetic concentrate. To obtain ferromanganese of 52 per cent Mn from an ore containing 25 per cent SiO_2 the consumption of materials per ton of manganese recovered in the ferromanganese was:

10	tons of limestone,
1.8	ton of carbon
460	lb of alumina
105	lb of fluospar

These results were obtained in laboratory tests and no claim is made that they are translatable to large scale practice or that the tests were made under optimum conditions. Hence only a rough assessment of the process can be made from the available data. It would however, appear unlikely that it could be economically applied at Pilbara, owing to high power requirements, high limestone and coke consumption, and the low grade of the final product.

7.4 Leaching with Caustic Soda

It is unlikely that a saleable product could be produced from Pilbara ores by this method. No iron is removed and quartz and silicate minerals are refractory to attack by caustic soda. Recovery of caustic soda from the leach liquors by treatment with lime is not easy owing to the slimy nature of the calcium silicate precipitate, which makes separation difficult. Further, the recovered caustic soda solution must be concentrated before it can be re-used, and this involves the evaporation of about 2 tons of water per ton of concentrate. The loss of caustic soda is about 65 lb per ton of ore treated. The process might have some application in the case of ores that can be raised to an acceptable market specification by the removal of a small amount of silica.

7.5 Leaching with Sulphuric Acid

A reducing roast, in which reducing gases are passed over the heated ore, is necessary to reduce higher oxides of manganese to MnO before leaching. The leach liquor, after purification by treatment with lime, is a nearly pure solution of $MnSO_4$, the treatment of which depends on the final product desired. Electrolysis of the solution can be made by yield either battery grade MnO_2 or manganese metal. These are expensive products of high purity for which the market is likely to be very limited. It seems reasonable to suppose that if large deposits of low grade manganese ores are to be treated by chemical methods for the recovery of manganese, metallurgical grade oxide must be the product aimed at. It also seems likely that the general principle will apply, that a chemical process can only be economical if there is practically no consumption of chemicals, or if the chemicals used can be recovered. There are several methods for the recovery of manganese as an oxide product from $MnSO_4$ solution. The solution may be evaporated to obtain crystals of $MnSO_4$, which are then decomposed by roasting in a kiln. This method requires a large consumption of heat, since all the leach liquor must be evaporated. It also consumes sulphuric acid, though it is possible that much of this could be recovered by feeding the gases from the $MnSO_4$ roaster to a sulphuric acid plant.

$MnSO_4$ may also be separated by heating the solution to about 195°C under pressure. Very little information is available about this process, which has perhaps not been tried except as a laboratory experiment. Heat consumption should be much less than in the evaporation process, but capital cost and running expenses might be high. Manganese may also be recovered from the $MnSO_4$ solution by precipitation with lime. It is however first necessary to precipitate the sulphate ion, otherwise the product will be contaminated with calcium sulphate. Sulphate may be precipitated with calcium chloride or calcium dithionate, after which manganese is precipitated as hydroxide and sintered to produce the final product. Calcium chloride or calcium dithionate may be recovered for re-use, but only at the cost of concentrating the filtrate from the manganese precipitate by evaporation. Sulphuric acid is not recovered, and lime consumption is high.

7.6 Leaching with Ferrous Sulphate and Sulphuric Acid

This has the advantage over leaching with sulphuric acid that reduction of the ore is unnecessary, since reduction is effected by the ferrous ion. The consumption of acid however is great, if ferrous sulphate is obtained by leaching ores containing $FeCO_3$ or by dissolving scrap iron. The alternative is the use of waste pickle liquor, but even if adequate supplies of this were available, the cost of transport to Pilbara would be prohibitive. The problem of recovering manganese from the leach liquor is the same as that already discussed in connection with sulphuric acid leaching.

7.7 Leaching with Sulphur Dioxide

The dithionate process consumes 2 - 2.5 tons of sulphur dioxide (= 1 - 1.25 tons of sulphur) and rather more than 1 ton of quick lime per ton of manganese recovered. It also requires the evaporation of about 1 ton of water per ton of ore treated in order to recover the calcium dithionate solution for re-use. To operate the process successfully a very cheap source of sulphur dioxide, such as waste smelter gas, would be necessary.

The crystallisation process described by Vedensky (1946), in which manganese is recovered from the pregnant liquor by evaporation and thermal decomposition of the $MnSO_4$ - MnS_2O_6 crystals with recycle of sulphur dioxide, requires expensive evaporation and decomposition equipment and large quantities of heat. It has been tried on a large scale at Las Vegas, perhaps the only chemical process for the recovery of manganese to be so tried, and was abandoned as un-economic. Allen's modification of this process (1954) introduces an autoclaving step, in which the leach slurry, after reaction with sulphur dioxide, is heated with air under pressure to oxidise dithionate to sulphate. Evaporation and thermal decomposition of $MnSO_4$ are still called for. The total production cost was estimated in 1954 as 100 dollars per ton of manganese recovered. It is unlikely that this process would be economic at Pilbara.

In Ketzlach's modification of the sulphur dioxide leaching process (1950), manganese is precipitated from the pregnant liquor with ammonia and ammonium sulphate is recovered from the filtrate by evaporation. The success of this process depends on the ready availability of elemental sulphur and anhydrous ammonia, and of a market for ammonium sulphate, which is in fact the major product.

A modification of the dithionate process, using percolation or heap leaching, avoids the necessity of concentrating the calcium dithionate barren solution by evaporation and can be applied with very simple equipment. Consumption of sulphur dioxide and quick lime is much the same as in the original dithionate process. Sulphur dioxide leaching has the advantage over most other leaching processes that no preliminary reduction of the ore is necessary, and of the sulphur dioxide processes surveyed, the percolation leaching method appears to be the best. It requires however a cheap source of sulphur dioxide, since sulphur is not recovered.

7.8 High Temperature Sulphating Process

This process leads to a pregnant liquor containing $MnSO_4$, from which the recovery of manganese has already been discussed. It may have some advantages over sulphuric acid leaching in that sulphur dioxide produced by thermal decomposition of $MnSO_4$ could be recycled directly to the reactor without the necessity of conversion to sulphuric acid. Since sulphation requires an excess of 50 per cent of SO_2, it would be necessary to recycle the effluent gases fromthe reactor. This process is subject to the same disadvantages as the other sulphate processes: recovery of sulphur dioxide requires evaporation of the pregnant solution; if manganese is precipitated from the solution without evaporation, lime and sulphur are consumed.

7.9 Leaching with Ammonium Sulphate

This method requires reduction of the ore, and leads to a pregnant liquor containing $MnSO_4$, from which manganese may be recovered by the methods already discussed. It combines the disadvantages of the other sulphate processes: like the sulphuric acid leaching process, it requires preliminary reduction of the ore; like the other sulphate processes, it requires evaporation of the leach liquor, if sulphur is to be recovered, or alternatively, the precipitation of manganese with loss of sulphur and consumption of lime. To these disadvantages the process adds one peculiar to itself, the difficulty of recovering ammonia. It therefore appears that both sulphuric acid and sulphur dioxide are preferable to ammonium sulphate as leaching agents.

7.10 Leaching with Nitric Acid

This requires reduction of the ore. Capital cost would be high as specialised stainless steel equipment is necessary. Although nitric acid is recovered, losses are appreciable, and may exceed 400 lb per ton of manganese recovered, so that, if the process were applied at Pilbara, it would be necessary to install a nitric acid plant. Concentration of the leach solution by evaporation is necessary, and heat consumption is therefore high, exceeding 1 ton of coal (at 12,000 Btu/lb) per ton of manganese recovered.

7.11 Leaching with Hydrochloric Acid

Here again a reducing roast is necessary, and manganese must be recovered electrolytically from the chloride solution, so that, by recycling the anolyte, the consumption of hydrochloric acid may be reduced to a minimum. The consumption of ammonia is large, nearly one third of a pound per pound of manganese deposited. This ammonia cannot of course be recovered, since it is oxidised to nitrogen. A product of high purity is obtained, but if it is desired to produce electrolytic manganese a leaching method leading to $MnSO_4$ would almost certainly be preferable, chiefly owing to the large consumption of ammonia in the chloride method.

7.12 Leaching with Ammonium Carbonate

This requires a carefully controlled reduction of the ore. The leaching reagents, ammonia and carbon dioxide, are both recoverable without any evaporation being necessary, and elaborate equipment is not required. Manganese is recovered in a product of fairly high purity without the need to concentrate the leach liquor by evaporation, and without the consumption of any reagents. Loss of ammonia is about 20 lb per ton of manganese recovered. This method should be applicable to a wide variety of ores, and is on paper the most attractive of the processes examined in this report.

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