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EXTRACTION OF MANGANESE OXIDE FROM LOW GRADE MANGANESE ORE AT PERNATTY LAGOON

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FROM
LOW GRADE MANGANESE ORE AR PERNATTY LAGOON

SUMMARY

1. The ore consists of clay, limonite pyrolusite and psilomelane, thoroughly mixed and carries quartz, barytes and gypsum crystallized in cavities. The average grade is 24 per cent manganese.

2. Beneficiation by gravity methods, by flotation or magnetic seperation was unsatisfactory.

3. The possibility of hydro-extraction of the ore was investigated and leaching with Ferrous Sulphate (waste Pickle Liquor) was selected for trial.

4. Overall recoveries of 85 per cent of manganese were obtained in a product assaying 60 per cent manganese.

5, Capital cost of a plant to supply 2000 tons per year of metallurgical grade manganese oxide would be approximately £158,000

6. The cost of producing this material, after allowance of credit for gypsum and precipitated iron oxide is approximately £28 per ton.

GENERAL

Exposed pockets of high grade manganese ore are almost completely mined out in the area adjacent to Pernatty Laggoon. It is possible that a drilling programme would outline a considerable tonnage of low grade ore with some small areas of high grade material.

Tests by simple mineral dressing methods, such as jigging tabling or flotation, were carried out with a view to producing metallurgical grade manganese ore from low grade material. If this had been successful the more expensive drilling programme would have been justified.

When the mineral dressing was abandoned, it was decided to review the literature on hydr-extraction. Manganese oxide is one of the strategic minerals essential in the production of steel. In a national emergency, supplies could be obtained from Pernatty area by simple excavation. Leaching with ferrous sulphate to obtain high grade manganese oxide was therefore tested in five pound lots.

SAMPLE

The material submitted by the Mining Branch was mostly from dumps of the present workings. A 100 pound sample obtained by coning and quartering, was reduced to one quarter inch sizing.

Examination showed this to consist of black plastic earthy wad, with some haematite and crystals of gypsum. Screened factions were very difficult to examine petrologically, though the presence of pyrolusite and psilomelane was established.

After leaching in HCl, the following gangue minerals remained:-

Clay Felspar Biotite Chlorite
Quartz Barytes Muscovite Hornblende
Limonite Haematite

A screen analysis of material dried at 250°F was made. and a second analysis made on material crushed to 10 mesh. There appeared to be some concentration in the harder pieces, which constituted the coarser faction, but these were obviously still heterogenous, so that only a limited upgrading in this manner would be possible.

TABLE NO 1

Screen analysis after crushing to 1/4 inch

Mesh	%Wt.	%Mn.	%Distribution
plus 1/4"	39.1	29.1	46.1
6	17.8	26.0	18.4
10	13.3	23.8	12.9
18	13.3	21.1	11.4
minus 18	16.5	16.7	11.2
Feed	100.0	24.7	100.0

TABLE NO 2

Screen analysis after Crushing to 10 mesh

Mesh	%Wt.	%Mn	% Distribution
plus 22	34.6	29.6	43.5
44	23.7	23.2	23.5
60	13.2	20.0	11.2
100	7.2	18.1	5.5
200	7.6	18.6	6.0
minus 200	13.7	17.7	10.3
Feed	100.9	23.5	100.0

MINERAL DRESSING TESTS

Tests on small samples were made in standard laboratory mineral dressing equipment. By tabling, a recovery pf 25 per cemt was made, with product assaying 38 per cent manganese. By jigging, 38 per cent was recovered in a product assaying 38 per cent manganese. Flotation was attempted with several reagent comninations all, of which failed to give any selectivity for the manganese oxides. Reduction roasting followed by magnetic containing 50 per cent of the manganese in the feed.

None of the concentrates is of marketable grade. a brief summary of the tests by each method follows:-

1. Tabling

A forty pound sample was crushed to 22 mesh and deslimed. The sands were tested on the laboratory Wilfley Table. The table concentrate assayed 38 per cent manganese and gave 25 percent recovery.

TABLE NO 3

Treatment on Wilfley Table

		Assay %			Distribution %		
Material	%Wt	Mn	Fe	Sio$_2$	Mn	Fe	SiO$_2$
Slime	54.4	17.3	11.2	14.4	37.6	56.9	66.0
Table feed	45.5	33.8	10.1	8.4	-	-	-
Conc.	16.6	38.0	7.2	5.8	25.1	11.2	8.2
Middlings	18.6	34.3	11.2	9.0	25.3	19.4	14.4
Tails	10.3	29.4	13.1	12.4	12.0	12.5	10.9
	100.0	25.2	10.7	11.7	100.0	100.0	100.0

2. Jigging

A ten pound sample was crushed to six mesh and treated in a laboratory Denver jig. The concentrate assayed 38 per cent manganese with a recovery of 38 per cent

TABLE No. 4

Treatment in Denver Jig

		Assay %			Distribution %		
Material	%Wt	Mn	Fe	SiO$_2$	Mn	Fe	Si02
Jig Conc.	28.6	37.9	8.2	4.0	38.5	19.4	8.9
Tailing	71.4	24.3	13.8	16.4	61.6	81.6	91.1
Feed	100.0	26.0	11.2	11.9	100.0	100.0	100.0

2. Flotation

Five hundred gram lots were tested after grinding with tap water in stainless steel ball mills. On each test there was over ten per cent loss in weight due to sloution of gypsum. This has caused an apparent discrepancy in the tailings assays.

In no case ising anionic of cationic collectors was tjere any selective seperation of the manganses minerals. Prior removal of the slime made no improvement,

TABLE NO 5

Treatment by Flotation

Test	Products	%Wt.	%Mn.	%Distb.	Reagents
a.	Conc. 1	4.0	15.0	2.2	0.5 lb/ton R 801 removed 1st conc.
	Conc. 2	8.2	17.3	5.1	0.75 lb/ ton R801 with sod. silicate removed 2nd conc.
	Tailing	87.8	29.2	92.7	
	Feed	100.0	27.6	100.0	
b.	Conc 1.	7.6	18.5	5.1	2.0 lb/ton Oleic acid removed 1st conc.
	Conc. 2	9.2	19.6	6.5	1.0 lb/ton Oleic acid removed 2nd conc.
	Tailing	83.2	29.3	88.4	
	Feed	100.0	27.5	100.0	
c.	Conc. 1	6.0	23.1	4.7	1.0 lb/ton Amine 320 0.5 lb/ton H_2SO_4 removed 1st conc.
	Conc.	5.2	22.0	3.9	Some addition again removed 2nd conc.
	Tailing	88.8	30.3	91.4	
	Feed	100.0	29.4	100.0	
d.	Conc.	10.6	23.3	8.8	Ground in ball mill with 4 lb/ton acid sludge, 8 lb/ton Fuel oil, 4 lb/ton Teepol 4 lb / ton H_2SO_4.
	Tailing	89.4	28.6	91.2	
	Feed	100.0	28.0	100.0	
	Slime	41.2	24.8	35.5	Pulp deslimed and sands floated with Oleic acid
	Conc.	8.2	23.8	6.8	
	Tailing	50.6	32.8	57.7	
	Feed	100.0	28.8	100.0	

4. Magnetic Seperation

A fifty gram sample of minus 10 mesh ore was roasted above red heat in an atmosphere of coal gas for one hour.

By roasting alone ore grade increased from 24 to 29 per cent manganese. Three fractions were made with a hand magnet. Further tests carried out with larger samples and using a Wethrill type seperator did not produce any better results.

TABLE No 6

Magnetic Seperation

Material	%Wt.	Assay %			Distribution %		
		Mn	Fe	SiO_2	Mn	Fe	SiO2
Highly Magnetic	10.2	14.6	37.2	11.6	5.1	25.5	7.2
Slightly Magnetic	42.0	25.0	18.3	17.6	35.7	51.2	45.6
Magnetic Tailing	47.8	36.2	7.3	16.2	59.2	23.3	47.2
Feed	100.0	29.4	14.9	16.4	100.0	100.0	100.0

HYDROMETALLURGICAL METHODS

Considerable expenditure has been undertaken by the U.S. Bureau of Mines in an effort to establish a method for treatment of low grade manganese deposits not amenable to simple mineral dressing. Many methods have been suggested and several taken to pilot scale operations. A brief survey of the provcesses available is given below:-

1. Ammonia Solution

Leaching with ammonia and ammonium carbonate permits ready extraction from reduced ores. The manganese is precipitared from solution by heatinf to transform the carbanate to carbonate. A commercial plant is using this process is now being built at Crosby Minnesota by the Manganese Chemical Company.

2. Nossen Process

Nitric acid is used to dissolve the manganese. The economical operation of this process depends upon the regeneration of nitric acid. The U.S. Bureau of Mines us currently building a pilo t plant to operate the process.

3. Blast Furnace Process

Manganese bearing material is smelted in a blast furnace to produce high manganese pig iron. The pig iron is then partially oxidized in a converter to produce a manganese rich slag.

4. Solution with Sulphurous and Sulphuric Acid

Manganese Products Incorporated has developed a mixed acid leaching process for recovery of low grade, intermediate manganese ores. The process ghas been carried through pilot plant equipment and extended to the production of Ammonium sulphate.

5. Waste Pickle Liquor Process

This process involves leaching of manganese ore with waste pickle liquor. It has been designed to operate partly continuously and partly on a batch basis, but as yet has not received any commercial acceptance.

6. The Cyclic Chloridation Process

The Armour Research Foundation of Chicago is developing a cyclic chloridaztion process and a pilot plant is being built.

7. Electrolytic Manganese.

A process has been developed by the U.S. Bureau of Mines in their pilot plant at Boulder City, Nevada. The process consists of leaching ore after a reducing roast with sulphuric acid and ammonium sulphate. The solution is filtered from residue, and purified of iron, arsenic cobalt and nickel, After addition of glue and sulphur dioxide the solution is electrolized in a lead lined wooden cell.

Manganese metal of 99.8 per cent purity is deposited for power consumption of 3.6 KW hour per pound of manganese. Spent electrolyte is recycled with addition of fresh sulphuric acid.

DESCRIPTION OF FERROUS SULPHATE PROCE$S

The method using ferrous sulphate as the solvent was chosen for further trial because small quanitities of waste pickle liquor are available from British Tube Mills and General Motors Holden. The process appeared the best under South Australian conditions. Following is a desćription of the process and the intial tests made to check whether it could be used on ore from Pernatty Lagoon. The reactions of dissolution of the ore, and precipitation of the manganese oxide are described:

1.Descruption of Process

Manganese forms a series of oxides whose basicity decreases as the valence of the manganese increases. The monoxide resembles calcium oxide in basicity, and the heptoxide is an acid anhydride with as strongly acidic properties as perchloric acid. The dioxide has weakly basic or acidic properties, depending upon conditions.

An appreciation of this range of basicity is essential to an understanding of the hydrometallurgy of manganese.

A consideration of the chemistry of manganese, discloses that a common chemical, ferrous sulphate, could be used to win manganese from its ores. Ferrous sulphate has the chemical properties of stong reducing agents and strong acids, and this combination affords a made to order reagent for the purpose. The compound is available in large quantities in every steel making plant as a component of pickling liquor, a waste material from the essental operation of removing oxide scale from certain steel products by immersing them in dilute sulphuric acid.

Composition of waste pickle liquor usually falls within the range of 0.5 - 10 per cent free H_2SO_4, and 10 - 22 per cent ferrous sulphate by weight.

Commerical acceptance of the pickle liquor process would not only provide means for recovering manganese from low grade ores, but would also solve a difficult waste disposal problem. Usually due to its corosiveness it must be neutralized or stored in lagoons, and either of these expedients is costly and wasteful.

The above situation provided the basis for the development of a process for producing an oxide concentrate low in impurities, and containing better than 60 per cent manganese. The process will yield pure manganese sulphate or chloride, where there are the preferred manganese compounds. No liquied waste is produced and a secondary polution problem is thereby avoided.

Four principal operations are involved.:

1. Ground ore is leached with pickle liquor and the sulphate solution is seperated from the gangue.
2. The sulphate is converted to chloride solution, by addition of calcium chloride, and the precipitated calcium sulphate is filtered off.
3. The optimum proportion of iron is seperated from the pregnant solution by differential precipitation with chalk slurry.
4. Manganese is precipitated from the solution with high grade lime slurry.

The precipitate is filtered off, whashed and dried as product, and the calcium chloride sloution remaining is concentrated for reuse.

2. Ore Leaching

Manganese ore frim the low grade dumps at Pernatty Lagoon was used in studying the leaching reactions Head assay was approximately 23.4 per cent manganese.

Several scale leaches at room temperature were carried out in half gallon bottles agitating on the laboratory rolls, using minus 100 mesh ore. Leaching time was varied from one to four hours but in each case very low extractions were obtained.

Leaching was then carried out on minus 60 mesh ore at various temperatures and various pickle liquor concentrations and it was found that up to 98 per cent extractions sould be obtained at a temperature of 160°F. The volume of pickle liquor required depended upon the ferrous sulphate content.

This temperature could easily be obtained of the pickle liquor was used promptly after it is discharged from the pickle vats where its temperature is 180°F to 220°F.

3. Reactions which take place in Leaching

Ferrous sulphate can act as a strong acid and as a powerful reducing agent. It has been pointed out that manganese monoxide ~~in~~ is a strong base, and, as ferrous sulphate can act as a strong acid, these two compounds will react as follows:

$$MnO + H_2SO_4 = MnSO_4 + H_2O$$

$$MnO + FeSO_4 = mnSO_4 + Fe(OH)_2$$

Also since feerrous sulphate can act in a dual capacity it can provide the acid as well as the reducing power, required in the manganese dioxide reaction. In addition ferric iron has a strongly tendency to form basic sulphates, and this tendency in creases with the concentration of the reactants. A consideration of these facts, suggested the possible reaction:

$$MnO_2 + 2FeSO_4 + 2H_2O = MnSO_4 + Fe(OH)\ SO_4 + Fe(OH)_3$$

Similarly for the sesquioxide,

$$MnO.MnO_2 + 3FeSO_4 + 3H_2O = 2MnSO_4 + Fe(OH)\ SO_4 + Fe(OH)SO_3 + Fe(OH)_2$$

The reactions that acually occur are undoubtly more complex than might be assumed from the sumplified equations above. For example tje amounts of basif ferric sulphate and ferric hydrate that form will depend on the concentration of free sulphuric acid, and a small amount of free acid would precent the formation of ferrous hydrate.

The whole leaching operation involves a complicated group of raactions, all seeking conditions of equilibrium.

Physical characteristics of the residues vary as the concentration and composition of the leach liquor is changed. Seperation of the residues from the extracts is an important step, and the consumption of leach liquor should be adjusted to yield a residue that will filter or settle at the highest possible rate.

It has been found thst the presence of a small amount of free acid improves the settling rate, and the filtering rat4 of the residues, This may be due to the solution of ferric hydrate formed as a result of the complex of reactions that occur.

No general principles can be set down for achieving the desired result in every case, because of variations in the gangeu material associated with different ores. For this reason a series of trial extractions is recommended to establish the optimum leach liquor composition for any particular ore. In general an average pickle liquor of 15 per cent $FeSO_4$ and 5 per cent free H_2SO_4 by weight will effect relatively complete extraction of manganese, from common low grade ores, and will result in a residue that will settle fairly well.

4. Conversion of Sulphates to Chlorides

Where it is desired to recover manganese in a form adopted to the manufacture of ferrO-manganese it is desirable that the product be substantially free from sulphur, It is not possible to precipitate , manganese from a sloution of its sulphate with a cheap alkaline material, e.g. lime, because the co-precipitated calcium sulphate would contaminate the product. This difficulty can be largely overcome by converting the sulphates in solution to chlorides, Conversion is carried out by addition of calcium chloride to the extract and the precipitated calcium sulphate can be reocvered as the dihydrate in a pure form by filtration. It is a by-product of low value whose principal commercial ise is in the manufacture of gypsum plaster and wall board.

Conversion to sulphates to chlorides does not eliminate sulphate contamination entirely. Calcium sulphate is appreciaby soluble (2 gms / litre in distilled water) and its solubility is increased by the presence of hydrochloric acid. produced by any sulphuric acid in the originial extractm or by hydrolysis of ferric chloride.

This procedure however, reduces the sulphur in the final product to a low value.

5. Seperation of Iron from Manganese

When the objective of the process is the preparation of pure manganous sulphate (or chloride), complete seperation of iron is essential. Where the recovery of manganese oxides for manufacture of ferro-manganese is required the concentrate should contain not less than 50 per cent manganese and the manganese iron ratio should not be less than 9:1 Complete seperation of iron is not necessary in this case but the degree of removal will be a function of removal cost versus value of product. Premiums are paid for manganese contents in excess of the minimum specified for any grade.

Where a manganese extract contains iron, and this will usually be the case speration of the iron as a relaticely pure oxide would be advantageous for enrichment of blast furnace dust prior to sintering, or for use a s a pigment in the paint industry.

Several methods for making this seperation were investigated but differential precipitation of the iron proved to be effectice and reasonably east to control. Ferric iron can be precipitated completelt at a pH of about 3.5 the actual value depends some what on the presence of the other dissolved salts. Ferrous iron begins to precipiatate at pH 5.5 and the higher the pH the more rapidly it can be oxidized to the ferric state by aeration.

Manganese on the other hand does not ordinarly begin to precipitate until the pH is raised to about 8.5 This favourable combination of properties procided a sound means for seperating iron from manganese in solution

Seperation of the iron from the manganese ions in extract will be more nearly complete if all the iron is in the ferric state. When an alkaline agent is added to a solution of ferric and manganous chlorides some manganese generally will be precipitated with the iron even though the average pH of the mixture is well below the point at which mangenses begins to precipitate, This phenomenon presunably results even tough agitation if provided, from small localized areas of high pH. The effect is particularly noticeable where the aklakine material is realtively insoluble, e.g. lime or calcium carbonate. This circumstance emphasizes the necessity for precipitating most of the iron in the ferric state if excessive loss of manganese is to be avoided.

Where a large proportion of the iron in the ferrous state it will be apparent that, as the average pH of the mixture is increased, localizied areas of high pH will tend to precipitate increasing quantities of manganese. Also the pH at which manganese begins to precipitate, is lower than the pH at which ferrous iron can be completely precipitated In practice however, extractions can be made that the concentratu ion of ferrous iron in the extract is low.

Where much ferrous iron is present it is desirable to aerate the mixture during the iron removal step to oxidize the ferrous iron to ferric state, and thus permit the operation to be carried out at the lowest possible pH/ Although any manganeous hydroxide precipitated through localized increase in pH, should redissolve, when the pH is agian lowered, it does not do so because it oxidizes rapidly to an insoluble compound such as mnO.OH

Development of this step, dusclosed that slaked lime slurry was unsatisfactory as a precipitant because of its tendency to precipitate excessive amounts of manganese.

Despite vigourous agitation it was impossible to dispense the lime slurry rapidly enough to prevent local increases of thepH above the manganese precipitation point.

Precipitated chalk slurry however, served the purpose well because it cannot of itself, raise the pH much above eight. By adding the chalk slowly (Clarkson Reagent Feeder) and providing rapid agitation 98 per cent of the iron and no more than 5 per cent of the manganese can be precipitated if the average pH of the mixture is not allowed to rise above 4.2

If mangananese sulphate, or chloride, is the desired product the iron must be completely removed from solution, before crystallization of the salt. Manganese sulphate can be prepared in a state of high purity by tresting the clear extract from the gangue filter, with sufficient calcium carbonate, as just described. Manganous chloride can be similarly prepared by precipitating the iron from the filtrate from the chloride conversion step. The relatively high value of these salts permits a substantial loss of manganese in the iron removal step, without significantly affecting the economics of the process.

If an appreciable amount of manganese were precipitated with the iron hydrate, it could be recovered by recycling the precipitate.

6. Production of Oxide Concentrate

Manganese concentrates intended for the manufacture of ferremanganese should contain the highest possible proportion of manganese.

This means, in effect that manganese monoxide should be the predominent compound in the concentrate, because it contains the highest percentage of manganese of any of the oxides of that element. The purified extract is principally a solution of manganeous and calcium chlorides.

Manganese is precipitated as a hydrated oxide, by adding high calcium lime slurry (finely ground) until the pH rises to 9.5

During tje precipitation it is desirable to exclude air as far as possible, to avoid oxidation of the monoxide to dioxide, thereby diluting the concentrate with oxygen. Concentrates produced in thus manner filter readily. The filtrate consists essentially of calcium chlroide wich can be concentrated for re-use in the chloride conversion step.

A typical product from the process in the laboratory starting with a 24 per cent manganese ore, contained 56.0 per cent manganese. Roasting the product for one hour at a dull red heat raised its manganese content to 60.7 per cent manganese. Even higher figures up to 65 per cent manganese could have been attained if the calcium oxide assay had been kept below one per cent.

7. Flow Sheet.

A schematic flow sheet is shown in figure 1 Counter-current stage decantation is indicated as a means for recovering values from the gangue because a procedure of this general nature was used in developing the process in America.

Slurries from the leaching operations are sometimes difficult to settle and filter. These properties can be improved by pH adjustment, and a continuous decanter and sludge thickener would handle most slurried satisfactorily in practice. The method indicated for working the other precipitates would be practical because these materials can be filtered and washed without difficulty.

The process has been designed to operate partly continuously and partly on a batch basis. Duplicate reaction tanks should be provided, to be charged alternatively on a one hour cycle.

Each tank would then discharge alternately to the respective filter which would operate continuously This is a flexible design that would permit adjustment at cycle time to reaction rate.

This design has t e merit of compactness, simplicity and relatively low cost.

Note:- Process is covered by U.S. Patent 2,462,499, issued February, 22nd 1949

EXPERIMENTAL LEACHING RESULTS

A series of tests was conducted to observe the effect of pressure, temperature, liquor composition and liquor colume on the efficiency of extraction.

The tests are described in the following parapgraphs with tabulation of the metallurgical balances.

1. Preliminary Tests.

In the early experimental stage, quite a few small scale leaches were carried out on 25 gram samples of minus 60 mesh ore, with varying amounts of waste pickle liquor atrroom temperature.

Leaching was carried out in half gallon bottles on the laboratory rolls varying the leaching time. The pickle liquor used in these tests assayed 7.4 per cent $FeSO_4$; 6.6 per cent H_2SO_4 which was all that there was available from the British Tube Mills at the time.

Chloride conversion iron and manganese precipitations from the pregnant solutions were done by hand in small conical 2000 c.c. flasks. The finely divided chalk for iron precipitation and high grade lime for manganese precipitation were added in the dry state.

Results from these experiments were very poor, due to the low ferrous sulphate content of the pickel liquor and localized areas of high p H formed on the addition of the chalk hand causing high manganese losses. Satisfactory aeration fro oxidation of the ferrous iron to ferric iron could not be obtained and e xcess lime was always found present in the manganese concentrates.

Assay figures for the manganese concentrates varied anything from up to 10 to 15 per cent and it was decided to try an alternative method.

Pressure leaching of the ore was first tried to see of the excess ferrous iron could be oxideized to the ferric state under pressure, and this facilities its removal from the pregnant solution at a sufficiently low pH value, so as not to bring down any manganese from the solution.

2. Pressure Leaching

A mild steel autoclave with overall outside dimensions 1ft 8 inch diameter by 4 ft 3 inch high and inside diameter 9ft 4 in was used.

A small laboratory type, stainless steel pachuca vessel was made in the laboratory workshop. Overall dimensions of the vessel being 9 inch inside diameter and 3 feet in length the air lift consisting of a 3/8 inch air pipe inside a 1½ inch diameter pipe, also constructed of stainess steel.

The pachuca was constructed so that it could be used inside the autoclave for pressure leaching, or set up in a special stand in the laboratory for ordinary leaching.

A five pound sample of minus 60 mesh ore was leached with three and one half gallons of pickle liquor assaying 9 per cnet $FeSO_4$; 6 per cent H_2SO_4; for one hour at 120 lb/sq. in. in the pachuca autoclave.

In order to keep the pulp agitated in the pachuca, air was beld off continuously, by means of a small 1/4 inch needle valve.

After leaching, the normal procedure of filtration of the gangue chloride conversion iron removal and manganese precipitation was carried out, this time using chalk slurry and high grade lime slurry respectively,

Results showed that a very poor extractiob of manganese from the residue was obtained (assay residue 11.5 per cent Mn). and that considerable trouble was still experienced in the iron oxidation step at a low pH.

All the iron was precipiatated at a p H of 5.0 after approximately twenty four hours agitation time in the pachuca bringing down appreciable quantities of manganese with it.

Analysis of manganese concentrates gace 31.5 per cent manganese and after heatinf to dull red heat, was raised to 36.5 per cent manganese.

Results are shown in Table No 7.

Pressure leaching was abandoned in favour of testing the effect of temperature on extraction efficiency.

Table No 7

Results of Pressure Leaching

Product	%Weight	Fe	Mn	Recovery
Residue	65.2		11.5	36.7
Gypsum ppt.	132.6		0.9	5.9
No 1 Fe ppt.	70.5		5.3	17.3
No 2 Fe ppt.	13.9		2.3	1.6
Mn Conc.	25.1	1.1	31.5	38.5
Feed	100.0		23.4	100.0

3. Effect of Temperature upon Leaching.

Fresh pickle liquor for these experiments was obtained from General Motor Holdens assaying approximately 13 per cent $FeSO_4$; 6 per cent H_2SO_4. Twenty five gram samples of minus 60 mesh ore were leached in 500 c.c. beakers at 140°F with varying amounts of pickle liquor.

TABLE No .8

Variation in Volume of Leach Liquor

Wt Ore Grams	Vol of pickle Liquor	Temp Leaching	Time	Residue Assay % Mn	Extraction %
25	250 ccs.	140°F	2 hrs.	3.3	93.4
"	300 "	"	"	2.4	95.3
"	350 "	"	"	0.7	98.6
"	400 "	"	"	1.1	97.7

These results showed that very good extractions could be obtained by heating alone.

Following these results a steam heated leach was made on a five pound sample of minus 60 mesh ore in the pachuca with approximately 14 litres of 13 per cent $FeSO_4$ pickle liquor.

Steam was generated by means of aportable kerosene heated stema degreaser at 50 lb/ sq. in and passed through a one half inch copper coil around the outside of the pachuca. This gave very poor heat exchange taking over an hour to heat the pulp to a maximum of 130°F Leaching was carried out at this temperature for one hour, thus giving a total leaching time of two hours.

Poor results were again obtained shown in Table No 9 so further steam leaching was abandoned, until a one inch mild steel jacket had been been welded to the outside of the pachuca. This jacket was then lagged and provision made for steam entry and steam exit, and also fot bypassing se Figure 2. Also two fresh samples of pickle liquor were obtained for leaching from the British Tube Mills.

TABEE NO 9

Extraction at 130°F in Pachuca Tank

Sample	Weight %	Assay Mn	Recovery %
Residue	60.4	13.5	58.0
Iron ppt	153.5	0.3	3.2
Mn Conc.	23.1	23.7	38.8
Feed	100.0		100.0

The two pickle liquors obtained from the British Tube Mills assayed as follows:

a. From J.E. Tank No 2 inside hot strip mill

21.7 per cent $FeSO_4$: 8.0 per cent H_2SO_4

b. <u>From outside Tank</u>

12,0 per cent $FeSO_4$: 2.5 per cent H_2SO_4

A series of 25 gram leaches at 140°F were carried out in beakers in the laboratory varying the addition of both pickle liquors respectively in order to find the optimum ration of pickle liquor to ore for efficient extraction of the manganese.

Very good extractions were attained with these liquors probably die to the high ferrous sulphate content in (a) and the low acid concentration in (b)

Results are shown below in Tables 10 and 11.

TABLE No 10

<u>Pickle Liquor with High Ferrous Sulphate and Acid Content</u>

Wt. Ore grams	W.PL Assay %	Volume Pickle Liquor	Leaching. Temp	Time	Res) Assay %Mn	Extraction %
25.0	21.7 $FeSO_4$	250 ccs.	140°F	1hr	1.7	93.4
"	8.0 H_2SO_4	300 "	"	"	1.5	94.6
"	"	350 "	"	"	1/4	95.1
"	"	400 "	"	"	0.77	98.2

TABLE No 11

<u>PICKLE LIQUOR WITH LOW ACID CONTENT</u>

Wt. Ore grams	W.P.L. Assay %	Volume Pickle Liquor	Leach. Temp	Time	Res. Assay % Mn	Extraction %
25.0	12.0 $FeSO_4$	250 ccs	140°F	1hr	5.9	63.1
"	2.5 H_2SO_4	300 ccs	"	"	4.1	75.9
"	"	350 ccs	"	"	1.3	93.2
"	"	400 ccs	"	"	1.1	95.4

Larger scale leaches, suing each of these pickle liquors in turn were made on minus 60 mesh ore in the stainless steel pachuca, with the aid of steam heating.

Pickle liquor additions were based on results shown in Tables No 10 and 11.

1. Leaching with Liquor assaying 2117% $FesO_4$: 8.0% H_2SO_4

A five pound sample was leached in the pachuca with 22.7 litres of pickle liquor at an average temperature of 160°F for duration of one and one half hours.

With the new steam jacket, heat transfer was much more efficient and it was found that most of the steam from the degreaser had to be bypassed to keep the temperature at 160°F. After leaching the gangue was filtered off and washed thoroughly in the laboratory pressure fulter.

After the chloride conversion step, the pregnant solution was aerated strongly in the pachuca, adding high grade chalk slurry slowly with the aid of a Clarkson Reagent Feeder to precipitate iron as ferric hydrate. The pH value was kept between 3.5 and 4.5 until all the feerrous iron had been oxidized to the ferric state and precipitated.

Iron removal was still very slow, but a much better degree of control could be obtained than by the previous method of hand addition of chalk slurry. When the pH began to rise rapidly, removal of most of the iron was indicated. Total aeration time was approximately 44 hours, and the iron precipitates were filtered off in three stages.

For manangese precipitation high grade calcium lime slurry (over 70 per cent available CaO) was added, also be means of the reagent feeder until the pH was 9.5 to 10.0 All the manganese was precipitated in just over an hour, then filtered washed and dried in the usual manner.

The concentrates were then roasted at 600°C for one hour to raise the manganese content. Results showed that considerable excess CaO was present in the concentrates (over 12 per cent) which could be prevented in practice, by more careful addition of lime.

Assay of unroasted manganese concentrates - 37.5% Mn

Assay of roasted manganese concentrates - 51.5%

The metallurgical accounting is shown below

TABLE No 12

Extraction with Strong Pickle Liquor

Sample	%Weight	CaO	Fe_2O_3	Mn	Recovery %
Residue	94.4			0.88	4.2
Gypsum ppt.	85.8			1.16	5.0
No 1Fe_2O_3 ppt	117.0			0.76	4.5
No 2 Fe_2O_3 ppt	103.0			0.14	0.7
No 3 Fe_2O_3 ppt	39.8			0.77	1.5
Roasted Mn Conc.	32.5	12.7	0.33	51.5	84.2
Feed	100.0			20.0	100.0

It can be seen that if the CaO figure had been kept low the manganese content of the concentrate could easily have been raised to 60 per cent manganese

2. Leaching with 12.0 per cent $FeSO_4$: 2.5 per cent H_2SO_4

Three pounds of ore was leached in the pachuca with 19.1 litres of pickle liquor for one and one half hours at an average temperature of 160°F. After leaching and filtration of the gangue the same procedure as for (1) was adopted for treatment of the pregnant solution.

This time in the iron removal step, all the iron was precipitated in a total aeration time of thirteen hours, as against fourty four hours in the previous experiment. pH control was kept between 3.5 and 4.5 during oxidation of the iron.

This acceleration in the iron removal step was probably due to the low sulphuric acid concentration in the pickle liquor than previously and also a greater degree of control pH that was obtained, after the experience of the first leach using the reagent feeder.

After the manganese precipitation step it was noticed that the concentrates contained traces of small lumps of CaO so that concentrates were screened through an 80 mesh screen prior to filtration drying and roasting.

Moisture loss on roastin concentrates at 600°C for one hour was 7.8 per cent.

Analysis of the unroasted concentrates was 56.0 per cent Mn : 4.8 per cent CaO

TABLE NO 13

Extraction with Low Acid Liquor

Sample	%Weight	SiO_2	Assay % CaO	Fe_2O_3	Mn	Recovery %
Residue	139.0				0.26	1.4
Gypsum ppt.	111.0				1.10	5.3
Fe_2O_3	178.0				0.87	6.7
Roasted Mn Conc	33.1	0.31	5.2	0.34	60.7	86.6
Feed	100.0				29.9	100.0

The manganese concentrate from this experiment was assayed for MnO and MnO_2 content, with the following results

MnO 44.3 per cent

MnO_2 41.7 per cent

ESTIMATION OF COSTS

Any estimation of costs at this stage of the investigation can do no more than indicate the order of costs involved.

The scale of operations would at present be limited to the 10,000 gallons a week of leach liquor available in Adelaide. However, there is the possibility of 15,000 gallons a day after evaporation of dilute liquor from the uranium extraction plant at Port Pirie. and further quantities frim a steel works which may be erected at Whyalla. Both these latter sources are 150 miles closer than Adelaide to pernatty Lagoon.

It is not likely that the product would be satisfactory for either chemical grade, or battery grade manganese since the oxide is a mixture of MnO and MnO_2. The requirements for ferr-manganese are approximately 7,500 tons per year. The assumed scale of operation for this estimate is 2,000 tons per year of product, requiring a treatment rate of approximately 20 tons of ore perday. This assumes 40,000 gallons per day of leach liquor .

Other raw material requirements are, powdered limestone 5,000 tons per year, and high grade lime, 1,000 tons per year Both these materials are readily available in South Australia. Calcium chloride at the rate of several tons per year would be needed to make up the chloride circuit.

By-products from the operation are high grade gypsum powder, 6,000 tons per year, and precipitated iron oxide 10,000 tons per year. Some credit should be allowed for these products. The gypsum is probably worth £1 per ton. There is a market for imported pigment grade oxide in Australia of 2,000 tons per year. This could be made relatively easily from the precipitate produced in thus process. The precipitate would be worth, as made, approximately £10 per ton for this purpose. The remainder could be sintered for steel production and would be valued at only 10 shillings per ton. This makes average to be obtained for the precipiated iron £2-8-0 per ton.

1. Estimate of Capital Requirements

Capacity of Plant equal to 20 tons of ore per day

Crushing and grinding section	£22,000
Leaching section	25,000
Purification and Precipitation	40,000
Boilers, evaporators and Nodulizing Kiln	20,000
Buildings	15,000
General expenses	10,000
Contingencies - 20%	26,000
	£158,000

2. Estimated Operating Costs

Cost per ton of concentrate

Ore delivered from mine to Pt. pirie	£6.
Power at 2.2 pence per unit	4
Leach liquor on site	0.2
Calcium Chloride	0.3
Calcium Carbonate	1.3
Lime	1.0
Steam	9.0
Maintenance and General Supplies	2.0
Labour	3.5
Supervision Sales	1.0
General	1.0
Contingencies - 20%	2.0
	£32.2

3. Cost per ton of Product

2,000 tons of product per year

Depreciation of Capital 10%		£7.6
Interest on Capital 5%		3.8
Cost of Operating Plant		32.2
		£43.6
Value of Gypsum	£3.0	
Value of Precipitated iron	12.0	15.0
Approximate cost of manganese nodules		£28.6

18/1/54
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