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AUSTRALIAN MINERAL DEVELOPMENT LABORATIORIES.

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MANGANESE

FIRST REPORT

BENEFICIATION REVIEW

by

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This report covers a survey of available technical information on the treatment of manganese ores undertaken at the request of the Sth. Aus. Department of Mines, and carried out under the general supervision of D.W. Read, Chief Metallurgist.

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MANGANESE.

FIRST REPORT.

BENEFICIATION REVIEW.

1. INTRODUCTION.

A survey of the literature covering methods of beneficiation for low grade manganese minerals has been made to determine world trends. As well as being a review of beneficiation methods this report contains a summary of world production and consumption of the maganese minerals.

2. WORLD PRODUCTION.

2.1. GENERAL.

Free world production of manganese in 1956 approximated 6 million tons. Major producers were - India, North and South Africa, and Brazil. The U.S.S.R., which has the worlds largest reserves of manganese ore exports approximately 300,000 tons per annum, mainly to the United Kingdom. The general feeling is that the expanding U.S.S.R. steel industry will absorb most of the future internal ore production and leave only a small surplus for export.

Sales of manganese minerals during 1958 have been lower than in previous years mainly because of the trade recession in the United States where steel production dropped thus causing an oversupply of manganese ore from countries geared to an expanding market. This position has been aggravated by the entry of Brazil as a major producing country.

The United States consumes more than one third of the free world's manganese ore but produces only two per cent of her own needs.

2.2. AUSTRALIAN PRODUCTION AND CONSUMPTION OF MANGANESE.

Australia produced 76,243 tons of metallurgical grade manganese ore in the year 1957. mainly from deposits in Western Australia.

The 1957 consumption of metallurgical grade ore was 50,582 tons. Most of this material is treated at Port Kembla and Newcastle to produce ferromanganese (approximately 65 per cent manganese), of which the Australian consumption averages 13 pounds per ton of steel produced. The balance of the Australian ore produced was exported to the United States (16,765 tons) and Japan (5,591 tons).

An additional amount (5037 tons) of ferromanganese was imported for the steel industry. The major portion was obtained from Norway with lesser amounts from the Union of South Africa, Japan and England.

Australia produced 767 tons of dioxide grade material (minimum of 75 per cent Mn) and imported 2049 tons, notably from Ghana, in the year 1957. Manufacture of dry-cell batteries absorbed approximately 90 per cent, the balance being used in the chemical, glass making and ceramic industries.

Prior to 1956, Australian reserves of manganese ore were low and exports were prohibited. To encourage exploration, the export embargo was eased in July 1956 to allow the export of up to one third of the proven ore in new deposits. Intensive prospecting, resulted in the discovery of additional ore in the Port - Marble Bar area where more than one million tons of manganese ore has been proved. No details of the grade of the deposits are available.

3. USE OF MANGANESE.

The major consumer of manganese minerals is the iron and steel industry. The main uses are:

(1) Deoxidizing and scavenging of the molten steel.
(2) Combining with sulphur to improve the working properties.
(3) As an alloying element to improve strength, toughness and the response to heat treatment in many structural steels.

Manganese is supplied to the steel industries as high grade ore, ferromanganese, spiegeleisen, silico-manganese, or silica spiegeleisen.

It is interesting to note the difference between the manganese addition to steel in the United States and in the U.S.S.R. The United States consumes 13 pounds of manganese per ton of steel while the U.S.S.R. consumes 70 pounds per ton of steel. The high U.S.S.R. consumption is necessary to overcome large amounts of sulphur present in the iron ore and coke.

Non-metallurgical uses of manganese minerals include: depolarizer in dry cell batteries, colouring agent in ceramics, decolourizing agent in glass making, and various manganese chemicals such as manganates and permanganates.

4. TREATMENT OF HIGH GRADE ORES.

High-grade ore is produced by selective mining, and simple washing to remove gangue. In some cases heavy-media and normal gravity separations are used to up-grade ores to metallurgical and chemical standards.

5. TREATMENT OF LOW GRADE ORES.

The abundant supply of high grade manganese ore is such that little interest has been taken in the development of low-grade deposits. The United States however has to rely on imported ores and is interested in developing her extensive low-grade deposits. With this aim, the U.S. Bureau of Mines has conducted a research programme into ore beneficiation and the production of manganese compounds. Reports on this work form the major portion of the current literature on manganese. Other research teams have investigated the extraction of manganese by leaching, and the electrolytic deposition of the metal.

5.1. OREDRESSING METHODS.

5.1.1. GRAVITY.

Several of the United States ores have been treated by various methods of gravity concentration. Flotation is usually effective on ores which can be concentrated by gravity methods.

5.1.2. FLOTATION CONCENTRATION.

Flotation methods which have been successful are:-

(1) Flotation with fatty acids.

(2) Flotation with an emulsion of fatty acids, fuel oil and a wetting agent.

The latter has proved to be the more successful method.

Rosenbaum, et al, (Section 7.1.3) recommended an open flotation circuit and softened make-up water for effective fatty acid flotation. Concentrates produced by this method were difficult to thicken and filter, and recovery was maintained only by the production of a large amount of low-grade middling. Rosenbaum found that oil—emulsion flotation could be operated in closed circuit and with hard water. Thickening and filtering of concentrates were easier than for those obtained by fatty acid flotation.

Only one reference to a plant treating low grade manganese ores by flotation was found. The Manganese Incorporated plant in Nevada treats ore from the Three Kids deposit by grinding and flotation with an emulsion of fuel oil and fatty acid. Large amounts of reagents are required to obtain a 2:1 ratio of enrichment from feed material assaying approximately 20 per cent manganese. Conditioning of the ground ore is very important. It has been found that for satisfactory flotation approximately 40 Kw of power per ton of ore has to be expended in pulp conditioning.

5.2. LEACHING.

Manganese ores have been leached with sulphur dioxide, sulphuric acid and/or ferrous sulphate, ammonium carbonate, nitric and hydrochloric acid and caustic soda.

5.2.1. LEACHING WITH SULPHUR DIOXIDE.

Two different methods have been developed to utilize SO_2 in the leaching of manganese.

In one, the slurry of ground ore and water is agitated with sulphur dioxide to convert the manganese to the sulphate or dithionate according to the following equations:-

$$MnO_2 + SO_2 \longrightarrow MnSO_4$$

$$MnO_2 + 2SO_2 \longrightarrow MnS_2O_6$$

The slurry is then pressure leached to convert the dithionate to sulphate and uncombined SO_2 to sulphuric acid, and also to precipitate some elements as insoluble sulphates.

$$MnS_2O_6 + \tfrac{1}{2}O_2 + H_2O \longrightarrow MnSO_4 + H_2SO_4$$

$$SO_2 + \tfrac{1}{2}O_2 + H_2O \longrightarrow H_2SO_4$$

$$RO + H_2SO_4 \longrightarrow R\ SO_4 + H_2O$$

The pregnant liquor is recovered by filtration and then concentrated by evaporation to obtain crystalbre $MnSO_4$. The $MnSO_4$ is dried and calcined with coke to produce nodules of manganese oxide. The sulphur dioxide produced is recycled.

$$2Mn\ SO_4 + \tfrac{1}{2}\ C \longrightarrow Mn_2O_3 + \tfrac{1}{2}CO_2 + 2SO_2$$

In the second method, the manganese ore is first calcined to decompose carbonates and to reduce the higher oxides. The feed then passes into an atmosphere of SO_2 and the temperature is raised to 850°C, mainly by the exothermic heat of the sulphating reaction.

At this temperature soluble manganese sulphate is formed, but iron and phosphorous remain insoluble.

After cooling and grinding, the manganese sulphate is leached from the gangue minerals by counter current decantation. The manganese is recovered from the pregnant liquor as described in the previous method.

5.2.2. SULPHURIC ACID LEACHING.

Several of the extraction processes use sulphuric acid. Various methods of recovering the manganese are practiced. Usually the manganese ore is calcined prior to leaching to reduce the higher oxides to the more soluble monoxide.

The pregnant liquor is purified by precipitation of the heavy metal ions with barium sulphide, and by aeration to remove sulphur, arsenic and organic material.

Three methods have been used to treat the pregnant liquor to recover to manganese:-

(1) Evaporation and crystallisation to recover sulphate.

(2) Electrolytic deposition to recover metal.

(3) Electrolytic deposition to recover oxide.

The method selected is determined by the product required.

5.2.3. FERROUS SULPHATE AND SULPHURIC ACID LEACHING.

Ferrous sulphate can be obtained cheaply from two sources:-

(1) Waste pickle liquor, discarded by the steel industry, containing a mixture of $FeSO_4$ and H_2SO_4 of the following composition:- 10-22 per cent $FeSO_4$ and 0.5 to 10 per cent H_2SO_4.

(2) Pressure oxidation of pyrite according to the following equations suggested by Cornelius

and Woodward:-

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4$$

$$FeS_2 + 7Fe_2(SO_4)_3 + 8H_2O \rightarrow 15\ FeSO_4 + 8H_2SO_4$$

The following method for the recovery of the manganese from the pregnant liquor has been suggested:

(1) Precipitation of the sulphate radicle as $CaSO_4$, $2H_2O$ (gypsum) by the addition of calcium chloride.

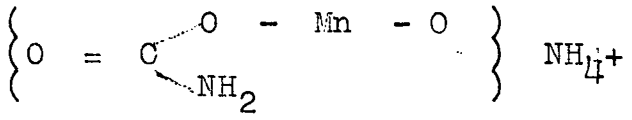
(2) Precipitaion of the iron, as an oxide, by the addition of freshly precipitated chalk.

(3) Precipitation of the manganese as hydroxide, by the addition of lime.

The remaining liquor contains mainly calcium chloride and after concentration can be re-used to precipitate sulphates.

5.2.4. <u>AMMONIA - AMMONIUM CARBONATE LEACHING</u>.

The ore is calcined to reduce the manganese to the monoxide form and is then leached in a solution of ammonia and carbon dioxide. The manganese is dissolved and held in solution as the complex



$$\left\{ O = C\begin{matrix} O - Mn - O \\ NH_2 \end{matrix} \right\} NH_4^+$$

Ammonium sulphide is added to inhibit oxidation of the manganous oxide during leaching. The slurry is filtered and the temperature of the pregnant liquor raised to break down the complex and to precipitate crystalline manganese carbonate.

Only portion of the manganese is precipitand the residual liquor is cooled and returned to the leaching stage. Ammonia gas and carbon dioxide are added as required.

5.2.5. CAUSTIC SODA LEACHING.

This method is very effective for the treatment of ores containing fine grained cryto-crystalline and opaline silica these being removed by treatment with caustic soda.

However the method is more applicable to near market grade material high in silica than to the treatment of low grade ores.

5.3. CHLORIDE VOLATILIZATION.

Hydrochloric acid gas is passed through manganese ore heated to a temperature of 950-980°C. Volatile chlorides of manganese and iron are formed and are swept from the furnace by the HCl gas stream. The chlorides are condensed and the unused HCl returned to the furnace.

The oxides of iron and manganese are then formed by hydrolysis of the chlorides in a tunnel kiln heated by burning natural gas. HCl, recovered from this operation, is concentrated and returned to the furnace.

This method has an application to refractory-type ores containing manganese silicates, which do not respond to the usual froms of acid leaching.

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7. SUMMARIES OF REFERENCES.

7.1. OREDRESSING METHODS.

(1) "How Manganese, Inc. Upgrades Complex Three Kids Ore."

Engineering and Mining Journal, Vol. 156, No. 11, November 1955.

This article covers the beneficiation methods used prior to calcining and nodulizing in rotary kilns.

The Ore - Wad with lake sediments and sandstone.

Feed - Mined material was carted and blended to give a consistant feed containing 20 per cent Mn, 1 per cent Pb, and 18 per cent moisture.

Treatment Method - The feed was crushed to minus 5 inch in a 30" x 42" jaw crusher and to minus 1/2 inch in an impact breaker working in closed circuit with a half inch screen. The crusher product was sampled and stored in bedding bins.

Grinding - Fine ore was screened at 1/4 inch, the oversize passing to two Marcy rod mills and the undersize to two Akins classifiers in closed circuit with the rod mill. Classifier overflow was pumped to four 12 inch cyclones, cyclone overflow being the feed to the conditioning plant, the underflow being returned to the rod mill. Average feed was 60 per cent minus 200 mesh.

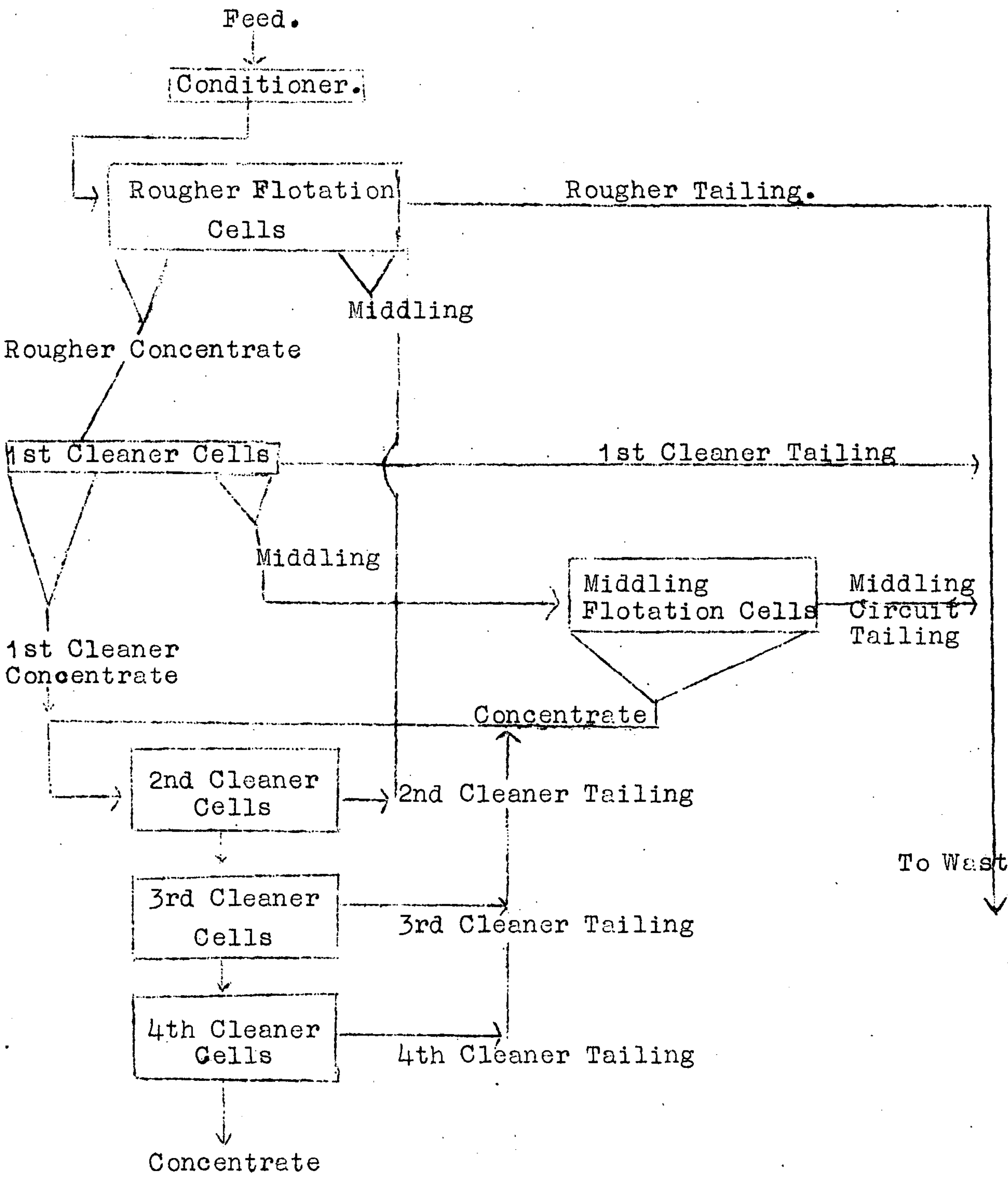
The cyclone overflow at 23 per cent solids was diluted to 19 per cent solids prior to conditioning.

Flotation reagents were:

Sulphur dioxide	9.25	lb/ton
Diesel oil	156	lb/ton
Soap skimmings	75	lb/ton
Aronite S	9.6	lb/ton

<u>Flotation</u> - Rougher flotation was carried out at 15 per cent solids and the concentrate produced cleaned four times. The flotation circuit was as follows.

<u>Flowsheet of Manganese Inc. Flotation Section</u>.



The concentrate which contains over 40 per cent manganese 23-25 per cent reagents and 28 per cent moisture was thickened and filtered. Recovery was approximately 79 per cent.

Final treatment was by calcination and nodulizing.

(2) "Agglomeration Flotation of Manganese Ore".

Min. Eng., December 1957 T.A.I.M.E. Vol. 19, No. 12.

This article is a summary of conditioning and flotation practice at Manganese Inc., Nevada.

Conditioning was carefully carried out in 20 tanks each fitted with 50 hp motors. An input of 38 kilowatt-hours per ton of solids was required for effective conditioning of the carefully blended ore. The type of conditioning, either slow-speed with long-retention time, or high-speed with short-retention time, does not affect flotation greatly, provided the energy input remai constant.

Fine grinding improved the recovery but lowered the grade and increased the power consumption. Increased reagent quantity increased the recovery, but often made the froth uncontrollable.

Experimental work showed that -

(a) Conditioning was more effective as the pulp density increased.

(b) Flotation reagents were more effective when added as an emulsion, but in the plant the pulp density in the conditioners was maintained at 20 per cent solids, and no effort made to produce good emulsions other than by mixing received during transportation about the plant.

(3) "Pilot Plant Flotation of Manganese Ore from the Maggie Canyon Deposit, Artillary Mountain Region, Mohare County, Ariz".

U.S. Bureau of Mines, R.I. 5330 April 1957.

The Ore - Main minerals are psilomelane and pyrolusite with quartz, feldspar, opal, chalcedony, volcanic ash, calcite, limonite and apatite as the gangue minerals. Barium salts present are usually chemically combined with the manganese minerals.

Grinding.- It was shown that poor recovery was caused by unfloated slime manganese oxide, whereas a poor grade concentrate was due to the ready floatability of plus 150 mesh middling particles, this indicating the importance of fine but granular flotation feed. A rod mill was found to be superior to a ball mill in the production of a granular product.

Fatty Acid Flotation - The circuit consists of grinding to approximately minus 100 mesh in a rod mill using soft water and small amounts of fatty acid (Neo-fat DE12), soda-ash and caustic soda. Pulp density was 20 per cent solids The calcite and some barite and chalcedony was floated in the rougher step. The concentrate was cleaned at 17 per cent solids using dextrin to depress the manganese oxide.

Manganese minerals were then floated from the tailing from the calcite section, concentrate low-grade middling and tailing fractions being obtained. The concentration was cleaned once. In order to obtain higher recoveries the low-grade middling was added to the concentrate, although its grade is lower than the feed value.

The use of raw or reclaimed water in the fatty acid flotation always resulted in a higher loss of manganese and lower grade concentrates. With reclaimed water the froth was also more voluminous and difficult to control and tended to dewater the flotation pulp. The tenacious froth also entrapped slime which could not be thickened effectively.

Oil Emulsion Flotation - Small amounts of the oil emulsion are added, and the calcite floated using one rougher and one cleaner stage. Tailings were conditioned with 21 lb of an emulsion consisting of fuel oil, tall oil and Oronite S (a sulphonated petroleum wetting agent)mixed in the ratio of 12:6:1.

A rougher concentrate which was cleaned once, a middling fraction which was reground with 9 lb. of emulsion per ton of solids and returned to the head of the rougher cells and a tailing fraction were obtained.

The importance of high pulp density in the conditioning of the material prior to flotation is recognised but it was not achieved due to the lack of thickening equipment.

Lowering the pH below 7 improved the flotation at the rougher stage, and pH value of 5.5 was helpful in cleaning. At this pH the froths were more heavily mineralized, contained less gangue; and handled better in the launders than when floated at the natural pH of 8.2.

(4) "Concentration of Oxides Manganese Ores from the Vicinity of Death Valley National Monument, California." U.S. Bureau of Mines, R.I. 4599.

This report covers work on ssveral United States ores namely:-

(a) McWhinney Ore: This material was of high grade (42.4 per cent Mn) and could be brought to the standard figure of 48 per cent by sintering. However flotation of the calcite from the ore, followed by sintering, produced a concentrate of 52.9 per cent. Mn with 95.9 per cent. recovery. Reagents were oleic acid and Emulsol X1.

(b) National Resources Ore: Grade 34.0 per cent. Mn. This ore contains very fine mixtures of manganese, barium and iron minerals which were impossible to separate by physical means. Crushing to 10 mesh and tabling resulted in a concentrat containing 44.1 per cent. Mn with a recovery of 71.5 per cent.

This grade was raised to 49 per cent by sintering. Flotation with an oleic acid-water emulsion, and Emulsol X1 as a coupling agent, did not produce a saleable grade concentrate. Flotation of silica with a cationic reagent lauryl amine hydrochloride, was not successful.

(c) <u>Chapin Ore</u>: The ore consisted of pyrolusite, and psilomelane occurring with tuff and limestone comglomerate. The ore assayed 12.9 per cent Mn. A high grade concentrate was recovered by tabling, but represented a recovery of only 11.1 per cent. Flotation of the table tailing was only selective to calcite and not to the other "insoluble" gangue minerals.

(d) <u>Traeger and Eckloff Ore</u>: The ore consisted of psilomelane, containing large quantities of barium, in a calcitic gangue, Recovery tabling was approximately 50 per cent. Grade of the feed and concentrate were 12 and 43 per cent. Mn respectively.

(5) "<u>A Mineral-dressing Study of Manganese Deposits of West—Central Arkansas" U.S. Bureau of Mines, R.I. 5262.</u>

This is a report on the treatment of several different ores by a variety of concentration methods similar to those reported in U.S. Bureau of Mines Reports Nos. 4985, 5022, 5024, and 5086.

(6) "<u>Utilizing Offgrade Manganese Materials from Montana" U.S. Bureau of Mines, R.I. 5255.</u>

The report deals with flotation tests carried out on the following materials.

(a) <u>Butte Mill Tailing</u>.

This tailing contained 16.2 per cent Mn. The material consisted mainly of quartz with some manganese oxide, biotite and other ferromagnesian minerals, calcite, coke and a small amount of slag. The sizing was 87 per cent minus 200 mesh. Petrographic examination showed that approximately 50 per cent of the liberated manganese was less than 18 microns.

Laboratory Testing - Oil emulsion flotation using the following flotation conditions:

(I) 70lb. of reagents per ton.

(II) 20 minutes conditioning at 40 per cent solids.

(III) Floated at 30 per cent solids for 3 minutes at a pH of 5.5.

(IV) Rougher concentrate cleaned at a pH of 5.0.

(V) Reagent combination was 6 parts of fuel oil, 6 parts of Ligro (crude tall oil) to 1 part of Oronite L (a petroleum sulphonated-type wetting agent). These reagents were made into an emulsion by first beating the active ingredients together and then adding the wetting agent and water.

Recovery was 90.4 per cent in a concentrate assaying 34 per cent Mn.

Pilot Plant Results - Concentrate grade 32.6 Mn. Recovery 90.1 per cent, Reagents used - 62 lb. of emulsion and 6.4 lb. H_2SO_4 per ton of solids.

(b) Nettie Mine Ore.

This material was a highly siliceous manganese oxide. Petrographic examination showed that the sample contained mainly quartz, some pyrolusite and small amounts of altered feldspar and calcite. Grade was 15.5 per cent Mn.

Pilot plant testing produced a concentrate assaying 36.6 per cent. Mn with a recovery of 90.8 per cent. Flotation was carried out at a pH of approximately 5.0 - 5.5, on material ground to 78 per cent. minus 200 mesh. Approximately 65 pounds of emulsion and 8.8 pounds of H_2SO_4 were required for each ton treated.

Smelting tests made on the concentrate are reported.

(7) "<u>Concentration Tests on Manganese Ores" U.S. Bureau of Mines, R.I. 4985</u>.

This report covers work on several ores namely:-

(a) <u>Rosebud Mine, Humbolt County, Nevada</u>.

<u>Ore</u>: The ore contained manganese oxide, psilomelane, in crusts and seams in a manganese stained calcite gangue. Grade was 12 per cent. Mn.

<u>Treatment:</u> Heavy liquid separation at a specific gravity of 2.9 on material crushed to minus half inch, produced a concentrate of 27.5 per cent. Mn with 81 per cent. recovery. Flotation was not successful. The suggested treatment was that the ore be reduced to minus 10 mesh, hydraulicallay classified and the fractions tabled. This was expected to produce concentrates of approximately 30 per cent. Mn. with recoveries in the order of 70 to 80 per cent.

(b) <u>Black Diable Mine, Humbolt County Nevada</u>.

<u>Ore</u>: A dense mixture of black and brown chert containing siliceous psilomelane and pyrolusite, all fine grained. Two samples were provided:-

(1) Low grade lump ore - 32 per cent. Mn.

(2) Fines from high grade ore - 27.4 per cent Mn.

The two samples were similar in manganese occurence and behaved in the same manner. Two stage jigging produced a combined concentrate of 37.8 per cent Mn, with a recovery of 80.4 per cent. It was suggested that the grade could be raised to 40 per cent Mn, with recovery of 60 per cent. Concentrates produced from this ore were very high in insoluble silica material.

(c) Bristol Silber Mine, Lincoln County, Nevada.

Ore: Fine grained manganese oxide (pyrolusite) in a calcite gangue. A negligible amount of manganese carbonate, some lead, zinc and copper sulphides and carbonates were also present. Manganese content was 12.5 per cent.

Gravity Concentration: Neither jigging nor tabling produced a satisfactory concentrate or a tailing suitable for discard.

Flotation: Flotation of the manganese minerals was not successful. Calcite was floated with oleic acid (0.20 lb/ton), 8 lb. sodium carbonate per ton to bring the pH to 12, and 3 lb. dextrin per ton as a depressant for manganese. Rougher concentrate from this test contained 27.4 per cent manganese, with a recovery of 52.8 per cent.

(d) Colorado Development Co., Riverside County, California.

Ore: The manganese minerals, pyrolusite and psilomelane, in this ore occurred in crusts and seams of a breccia, with manganese surrounding fragments of iron-stained siliceous gangue. Grade was 17 per cent Mn.

Gravity Concentrate: The ore after crushing to minus 4 mesh and screening at 10 mesh was jigged or tabled according to size. This gave a concentrate of 41.4 percent Mn with a recovery of 68 per cent.

(e) Gerberville, Humbolt County, California.

Ore: The ores were from three mines, but were similar in texture, containing psilomelane and pyrolusite finely disseminated in quartz and iron stained silicates.

Gravity Concentration: Jigging and tabling were tried but did not indicate a satisfactory concentrate.

Flotation: Desliming with a loss of 25 per cent Mn was necessary befor flotation. The concentrate contained 32 per cent manganese but represented only 34 per cent recovery.

(f) Greenville, Plumas County, California:

Ore: The manganese occured as a very fine grained, siliceous psilomelane in a cherty gangue. Grade was 33 per cent Mn.

Treatment: Jigging and tabling gave a concentrate of 40 per cent Mn, representing a recovery of 55 per cent. This concentrate contained approximately 12 per cent SiO_2 and Al_2O_3.

(g) Lower California, Mexico

Ore: Lumps of vein material about 3 inches thick of massive homogenous manganese and iron oxide, showed little gangue of any kind and contained 32.9 per cent manganese, 14.4 per cent iron and 22 per cent insoluble.

Flotation: No concentration of manganese minerals was made.

Magnetic Separation: Some slight concentration was made in the non-magnetic fraction. Most of the iron reported in the magnetic fraction.

(8) "Concentration of Oxide Manganese Ores from North-Eastern Nevada (Cariglia - Vietti. Berning Rud Parker Deposits)" - U.S. Bureau of Mines, R.I. 5023.

This report contains similar information to that found in U.S. Bureau of Mines reports numbers 4985, 5086, and 5024. The ores treated contained pyrolusite, psilomelane and braunite. Interesting information is given for a method in which the ground ore was treated by tabling, and the tailing floated. The table concentrate and the flotation concentrate were then retabled to remove gangue coated with a fine layer of manganese minerals.

(9) "Concentration of Oxide and Silicate Manganese Ores from the Vicinity of Winnemucca, Pershing County, Nevada. U.S. Bureau of Mines, R.I. 5022.

This report covers ore dresssing treatment of three ores from the above mentioned district.

(a) Pollard Canyon Ore:

Ore: Samples were of two similar ores containing pyrolusite, psilomelane, braunite, and minor amounts of other manganese minerals in a siliceous gangue. Grades were 25 and 47 per cent Mn respectively. The low grade sample contained relatively coarse aggregates of manganese minerals in a matrix of very fine quartz grains and chalcedony through which manganese minerals were scattered and diffused, thus giving cloudy appearance to the gangue minerals.

Oredressing Treatment: Jigging and tabling proved successful on the low grade ore, and high grade ore was hand picked to meet the 48 per cent Mn limit. Flotation was not satisfactory, due to the presence of braunite and the intimate association of the manganese minerals and silica.

(b) Victory Lode:

Ore: The manganese oxides largely occur as particles of pyrolustie and psilomelane, in the 48 to plus 270 mesh size range, uniformly distributed through a quartzite, chert, and limestone gangue. Part of the manganese minerals could be liberated at sizes suitable for tabling, but optimum liberation would require extremely fine grinding. Manganese liberation was complicated by the occurrence of manganese oxides as shells surrounding silica grains and as grains locked with calcite.

Head assay was 8.4 per cent Mn.

Oredressing Treatment: Tabling recovered approximately 40 per cent of the manganese in a concentrate that could be sintered to over 44 per cent Mn. The intimate association of calcite and manganese minerals made selective flotation of these minerals unsatisfactory.

(c) Pink Lady Property.

Ore: Hard and siliceous, the principal consituents being silica and rhodonite with minor amounts of black manganese oxide intimately associated with the silica. The black manganese oxides were between 400 and 800 mesh. Head assay was 14.8 per cent Mn.

Chemical examination indicated that the highest grade possible would only be 29.2 per cent Mn. Tabling produced a concentrate of 27 per cent Mn with a recovery of 35.1 per cent. Flotation produced a concentrate of 24.9 per cent. Mn with only 10.7 per cent. recovery.

(10) "Laboratory Recovery of Manganese Carbonate from the Martin Mine. Independence County, Arkansas," U.S. Bureau of Mines, R.I. 5086.

This article covers the recovery of manganese by various oredressing methods.

Ore: Major constituent was limestone contaminated with manganese. The main manganese minerals were carbonates, which varied a good deal in colour-the pink variety containing the largest proportion of manganese. The rhodechrosite had some of the manganese replaced by iron. Head grade was 10.7 per cent Mn.

Much of the manganese carbonate was freed from the limestone at 14 mesh, but grinding to 100 or 150 mesh was necessary for complete liberation. Gangue minerals were iron oxide, iron oxide stained siliceous material, colophanite, barite, pyrite, clay, quartz and glauconite.

Concentration Methods: After a good deal of preliminary work, the experimental work was divided into two parts:-

Part 1. MAGNETIC PRECONCENTRATION PLUS FLOTATION.

The ore was crushed to minus 10 mesh, sized and the sized fractions produced treated on a crossbelt magnetic separator. The combined magnetic fractions assayed 25.6 per cemt.

Mn representing a recovery of 75.6 per cent. This concentrate was ground to pass a 100 mesh screen and used in the flotation tests.

Flotation was carried out in zeolite-softened water with the following reagents - (reagents given in pounds per ton) Sodium hydroxide - 1.25, tetrasodium pyrophosphate - 1.25, refined tall oil collector - 0.96 and a synthetic frother 0.05). After a rougher float and three cleaning stages, a concentrate containing 28.7 per cent Mn, 2.1 per cent Fe and 2.5 per cent acid insoluble was obtained, representing a recovery of 54 per cent of the manganese.

Attempts to increase the recovery of manganese in the flotation test resulted in a flotation concentrate, which on sintering, assayed 40.7 per cent Mn.

Part 2. Combined Gravity and Magnetic Preconcentration Plus Flotation.

The ore was crushed to minus half inch and screened on four and ten mesh for heavy media testing, at densities between 2.9 to 2.65. Material sinking at the higher density was classed as the concentrate, while particles floating at the higher density and sinking at one of the lower levels was classed as a middling. The concentrate assayed 26.8 per cent Mn. (48.7 per cent recovery) and the tailing assayed 3.4 per cent manganese.

The middling produced assaying 9.5 per cent Mn and containing 39.9 per cent Mn, was combined with the primary minus 10 mesh fraction and passed through the magnetic separator for a recovery of 20.7 per cent at a grade of 25.3 per cent Mn.

The combined magnetic and heavy media concentrate which assayed 26.4 per cent Mn, 5.6 per cent Fe, 6.3 per cent insoluble, and 0.40 per cent P, was ground to pass a 100 mesh screen and then floated in zeolite-softened water using sodium hydroxide and tetrasodium pyrophosphate - 1.0, refined tall oil - 0.96 and synthetic frother - 0.05 lb./ton of feed. The concentrate which was produced after a rougher and three cleaner stages of flotation contained 30.0 per cent Mn representing a recovery of 47.7 percent. Sintering gave a product assaying 41.4 per cent Mn, 4.6 per cent Fe, 3.8 per cent acid insoluble, 1.1 per cent Al_2O_3 and 0.28 per cent P.

Attempts to increase recovery of manganese in the flotation stage resulted in an increased amount of phosphorous in the concentrate, the maximum allowable phosphorous content of metallurgical grade manganese concentrate being 0.30 per cent P.

(11) "Beneficiation of Oxide Manganese and Manganese - Silver Ores from Southern Arizona." U.S. Bureau of Mines, R.I. 5024.

The article discussed the treatment of several manganese - silver ores.

(a) Patagonia Group

Ore: Manganese minerals present were pyrolusite psilomelane, manganity, wad and braunite, mostly as hard compact, high grade material. However the wad was fine and soft and a source of slime. The ore assayed approximately 20 per cent Mn.

High intensity magnetic separation upgraded the manganese minerals. It was also helpful in the removal of porous manganese minerals from the tailing produced by gravity separation. The silver was removed by a choridizing roast before sintering.

(b) Tombstone Group

Ore: These were complex, medium to low grade ores containing appreciable amounts of silver and small amounts of lead and zinc. Pyrolusite and psilomelane were the chief manganese minerals present, with other manganese minerals in minor quantities, As the ores grouped here vary a good deal, they are treated individually.

(b1) Oregon Mine - The ore assayed 31.6 percent Mn. Best results were obtained by magnetic or gravity concentration. Recoveries above 80 per cent were obtained and, in the case of the magnetic test, a concentrate of over 57 per cent manganese (after sintering) was produced. Flotation was also effective, but the recovery of valuable minerals was lower.

(b11) Contact Mine - The ore assayed 14.6 per cent Mn. It was fine grained and proved diffficult to concentrate in the normal manner. Concentrates of approximately 30 per cent Mn were obtained but recoveries were usually low. High-grade products were obtained only by a reducing roast of the concentrates produced by other methods of treatment. High-intensity magnetic-separation of crude ore gave the best results, over 71 percent of the manganese being recovered in a product that would sinter to 39 to 40 per cent Mn.

(bIII) Comet Mine - The ore assayed 10.1 percent Mn and was not amenable to oredressing methods of beneficiation because of a complex association of manganese with gangue minerals, principally calcite. Calcining of the ore followed by an attritioning grinding and screen sizing recovered 68.3 per cent of the manganese in a product assaying 23.6 per cent Mn and 8.4 per cent insoluble.

(c) Baboquivari and Cavoti Claims

Ore: These ores were similar in texture but varied greatly in manganese content. Major manganese minerals were pyrolusite, psilomelane and braunite, deposited in gashes and fractures in an andesite rock.

Results on the individual members of this group were:

(cI) Baboquivari, Lot A

The ore was stage-ground to pass 65 mesh, tabled, and the tabled concentrate floated to produce a manganese concentrate which after a reducing roast was treated in a low intensity, wet magnetic separator to remove iron. The non-magnetic fraction assayed 57.5 per cent Mn representing a recovery of 53 per cent.

(cII) Baboquivari, Lot B

Ore dressing methods were not successful in concentrating this ore.

(12) "Separation Plant for Manganese Ore at Indian Mine" The Mining Jnl. July, 16th 1954.

A waste dump of manganese material was retreated by heavy media separation to produce a high grade manganese concentrate.

(13) "Concentration of Manganese Ores from Pinti and Kani Counties Southern Utah," U.S. Bureau of Mines, R.I. 4551.

Ores containing 14 and 7 per cent Mn, respectively were treated by gravity and flotation methods, gravity concentration being the most successful. Flotation with oleic acid and Emulsol X-1 produced low grade concentrates due to the manganese oxide occuring as coatings on the gangue.

(14) "Concentration of Manganese Ores from the Tintie District Eureka, Juab County, Utah" U.S. Bureau of Mines, R.I. 4545.

A report of gravity and flotation test work. Flotation was fairly successful using a mixture of oleic acid and Emulsol X-1.

(15) "Rhodesian Firm Opens Mangabolt District for Large Scale Mining" Mining World, May 1957.

This report covers the opening of a new manganese mine and mill in the Rhodesian Mangabolt district.

Run of mine ore was screened and the oversize crushed. Washing was carried out in a trommel, the oversize passing to condentrate storage and the undersize to a second washing trommel. The oversize from this second trommel, before being discarded, was hand picked to recover manganese minerals. The undersize was jigged to produce a final concentrate and a tailing product.

(16) "High Grade Manganess Source Grows in Cuba". Eng. Min Journal, Volume 155, No. 9. September 1957.

Logwashing and heavy media separation are used to produce a high grade manganese concentrate. No details of operating conditions are given.

(17) "Preliminary Concentration Test on Manganese Ore from Gebore, New Guinea" C.S.I.R.O. Melbourne, August, 1958.

Litte information other than the petrological examination of the ore, and the results of one tabling test are given.

(18) "To Float Low-Grade Manganese Ore" Eng. Min. J. Volume 157, No. 5, May 1956.

Flotation tests were carried out on low grade manganese ore from the Sherman Valley Area, Pennsylvania.

Ore: Manganese minerals present in the ore were cryptomelane (possibly KMn_8O_{10}) with minor amounts of pyrolusite and psilomelane but wad and black manganiferous clay occurred in some of the altered ore beds. The gangue minerals consisted of clay, quartz, goethite, limonite, calcite, orthoclase and carbonates with lesser amounts of sericite, zircon and tourmaline.

Sodium dihydro - orthophosphate, or sodium silicate as depressants with hexyl alcohol as a frother were found to be suitable reagents.

The collector could be either sodium oleate, oleic acid, reagent 708, tall oil, ore emulsions of soap, fuel oil and Oranite S.

The optimum pH value for rougher circuit was found to be 8.0 but this was raised to between 8.3 and 9, depending on the amount of iron present in the cleaning stages.

The experimental work indicated that the amount of iron present in the ore controlled the concentration of manganese. The authors believe that the high pH and large amounts of depressants required to depress the geothite and limonite also depressed the cryptomelane.

Magnetic separation of the flotation concentrate proved ineffective as both goethite and cryptomelane are weakly magnetic.

(19) "Process for Concentrating Oxidised Ores by Means of Froth Flotation" British Patent 460,072 January 20th 1937.

This patent covers the application of complex polyacids of tin, tungsten, vanadium, germanium and molybdenum, to the flotation of some oxide minerals. The polyacids are stated to be activators for these minerals.

An example of the flotation of pyrolusite given was:-

An oxidized manganese ore (pyrolusite with silicate gangue) was wet crushed to 65 mesh (U.S.A. Standard) with o.1 kg sodium stannate and 0.3 kg sodium vanadate per ton of ore. The pulp was treated with 2.5 kg quebracho bark to depress the gangue. Flotation was conducted at 35°C. with 0.75 kg stearic acid and 0.05 kg amul xanthate as collectors and 0.03 kg terpinol as frothing agent.

No indication as to the grade of ore, concentrate produced or the recovery is given.

(20) "<u>Development of the low - grade Manganese Ores of Cuba" Metal Mining Milling Methods, A.I.M.E. 1943.</u>

A description of mining and milling operations of the Cuban Mining Company where a mixture of manganese minerals of various type, hardness and grade is treated. Major minerals (in order of extent) which occur in a volcanic tuff are:-

Pyrolusite
Psilomelane
Manganete
Wad (rarely seen)

Three grades of ore were recognised, the assays being:-

Grade of Ore	Assays %				
	Mn.	SiO_2.	Fe.	CaO.	Al_2O_3.
High	21.2	31.0	4.6	6.2	10.5
Medium	19.3	30.8	4.6	4.3	11.0
Low	16.6	35.0	4.1	4.9	12.0

Feed - The grade of mill feed is not uniform owing to the irregular replacement of the tuffs by manganese minerals.

Mineral Beneficiation

Crushing - The ore is crushed to -3/8" in three stages and then ground in a rod mill.

Flotation - Flotation is carried out in normal M.S. cells using a mixture of fatty acids and gas oil as the main collectors.

The amounts of collectors and other reagents used are:-

Ore	Reagents per Ton of Ore					
	Fatty Acid lb.	Gas Oil gals.	Caustic lbs.	Quebracho lb.	Lime lb	Fuel Oil gals.
High	19.1	12.4	5.6	1.5	7.6	1.3
Medium	24.3	16.3	8.3	2.9	9.6	1.6
Low	17.4	10.9	5.8	1.9	5.9	1.2

A rougher concentrate and a scavenger concentrate were taken, the latter being returned to the head of the rougher cells.

The rougher concentrate was treated in a hydraulic classifier to remove a high grade coarse product. The fine fraction was treated in the cleaner and recleaner banks of the flotation cells. The recleaner tailings were thickened and returned either to the rod mill or to the head of the rougher cells.

The coarse fraction from the rougher concentrate and the recleaner concentrate were dewatered prior to passing to the nodulizing kiln. Slimes leaving the dewatering drag conveyor were treated separately, the concentrate being thickened before adding to the feed to the nodulizer.

Flotation Reagents. Flotation reagents were added to following extra points.

Rod Mill	7 per cent of whole.
Rougher Flotation cell	19 per cent of whole.
Cleaner Flotation Cell	2 per cent of whole.

Alternative Treatment.

Hard dense ore was treated in a separate plant by jigging. Concentrates of 40 - 44 per cent Mn. can be produced in this way. All reject products that carry manganese were treated in the flotation plant.

Mill water was treated to maintain a constant hardness and amount of soluble salts in the return water.

(21) "A Mineral-dressing Study of Manganese Deposits of the Batesville District, Ark." U.S. Bureau of Mines, R.I. 5301.

This report contains summaries of work carried out on 14 different ores. As the materials tested varied considerably it is considered that general trends of concentration methods could not be drawn. This report should be studied in full as it contains much useful data that cannot be reduced with any safety.

(22) "Investigation of Cuyuna Iron-Range Manganese Deposits, Crow Wing County, Minnesota, Progress Report 1" U.S. Bureau of Mines, R.I. 5400, 1958.

This article included details of heavy media and flotation testing of ores found in the Cuyuna Range area. Heavy media testing was not successful.

Flotation of Carbonate Ores.

The ground ore was floated under the following conditions:

Desliming - Not required.

Pulp Dispersion - With sodium carbonate, sodium hydroxide, or sodium metasilicate.

Collectors - Most selective collector was Neo-Fat 92-04 (oleic acid). Up to 30 per cent of oleic acid could be replaced by cheaper resin acids.

It was found that stage addition of the collectors improved both grade and recovery, and emulsification of the fatty acid collector improved recovery, grade, and the structure of the froth.

7.2 LEACHING.

(1) "From Low grade Domestic Ores, High Grade Manganese Oxide" Chemical Engineering, January 1954.

This article describes a sulphuric acid leaching process for the production of electrolytically deposited manganese dioxide.

After grinding, the ore was calcined to convert the manganese oxides into the soluble manganous form. The material was then leached with sulphuric acid.

After filtering, the pregnant liquor was treated either with barium sulphide or by adjusting the pH to precipitate the metallic impurities. Colloidal sulphur, arsenic, iron and sundry organic materials were precipitated by aeration.

Carbon rods were used as electrodes in the electrolysis of the purified solution. When the oxide deposit was of sufficient thickness the rods were crushed and the manganese dioxide separated from the carbon by jigging and then dried at a temperature below 350°C to produce gamma phase battery active MnO_2.

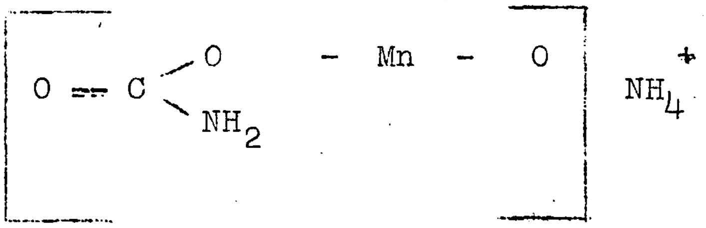
(2) "New Commercial Process for Electro-winning Manganese" J. Electrochem. Soc., Volume 104, No 6 June 1957.

Manganese ores are smelted to produce ferro-manganese and a manganese rich slag. The slag was ground and leached with spent electrolyte and acid at pH 4.4. The slurry at pH 6.6 was then treated with ammonia to precipitate most of the impurities. After filtering, the pregnant liquor was passed to the electrolytic cell for deposition.

(3) "Manganese from Low Grade Ores by the Ammonium Carbonate Process" Jnl. of Metals. June 1957.

This article describes pilot plant scale testing of the Dean-Leute ammonium carbonate process.

The manganese oxides were reduced, by calcining in a reducing atmosphere, to the monoxide (MnO), which was then leached by a solution of ammonia and carbon dioxide. The manganese was held in solution as the complex ammonium salt shown below.



Ammonium sulphide was added to prevent any oxidation of the complex during leaching.

After filtration, the manganese was precipitated by heating the clear pregnant solution to 65°C. This reduced the ammonia concentration from 18 to 10 mols/litre so precipitation well formed crystals of rhodochrosite.

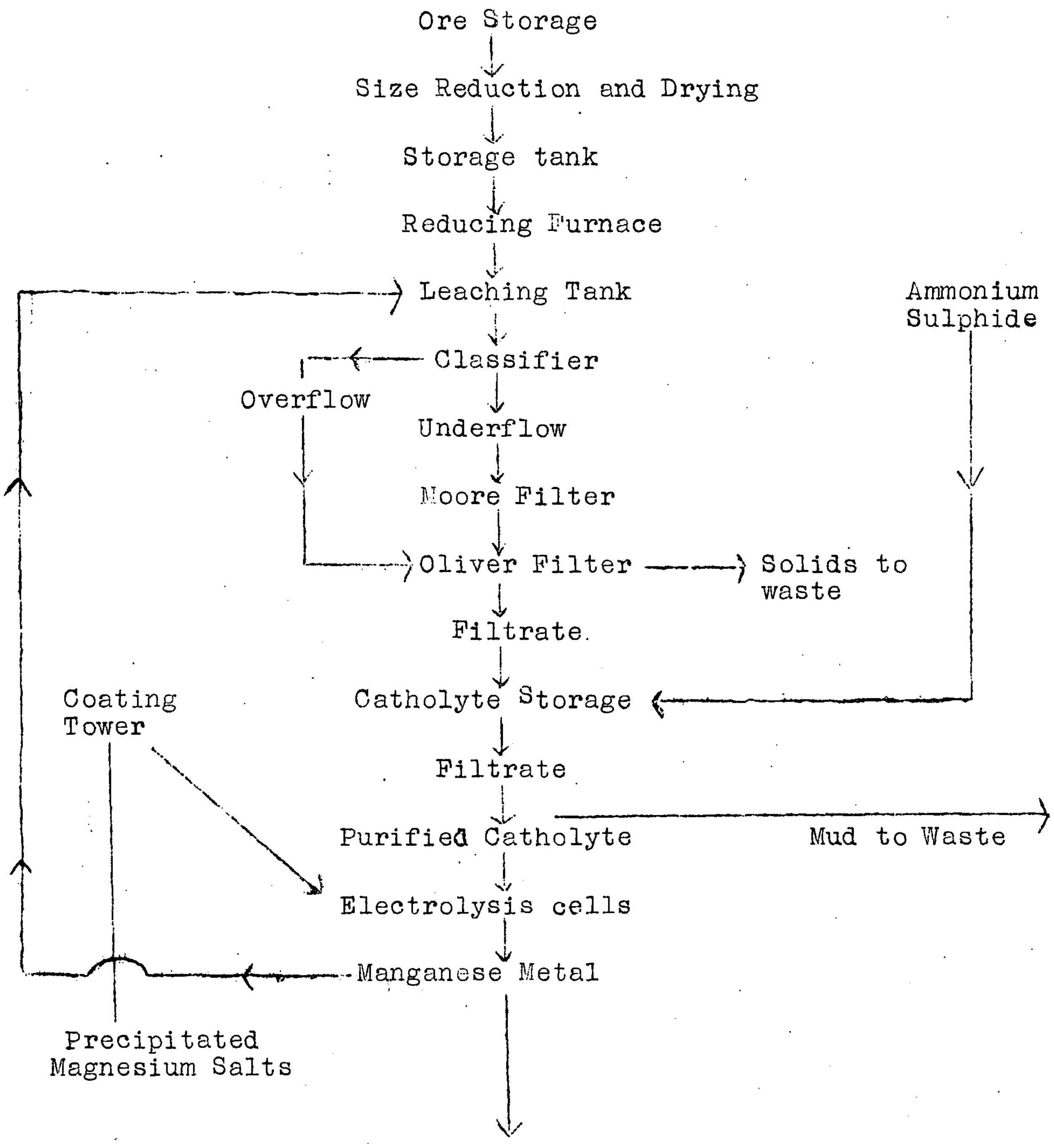
The manganese carbonate was converted into the various manganese oxides by calcination.

(4) "A Decade of Electrolytic Manganese" J. Electrochem. Soc. Volume 94, No. 5, Nov. 1948.

This report covers many of the general problems associated with the production and marketing of electrolytic manganese.

The ore was roasted in an electric resistance furnace to produce a soluble monoxide and was then leached with spent anolyte. Treatment of the ore and pregnant liquor is shown in the flowsheet.

Flowsheet.



The following difficulties were encountered:-

(1) High negative value of manganese with respect to hydrogen.

(2) High current losses in heating solutions and evolution of cathodic hydrogen.

(3) Large quantities of the ammonium sulphate buffer were required for conductivity and prevention of manganese dioxide precipitation in the cell.

(4) The active nature of the manganese metal causing re-solutioning which was especially noted in times of power failure.

(5) Higher than usual electrolytic power consumption.

(6) The careful roasting required to reduce the manganese ore to the divalent manganese.

(9) The solutions were extremely corrosive. This means a diaphragm cell must be used.

(10) Close temperature control must be maintained to prevent precipitation of salts from the saturated pregnant solution.

5. "Commercial Production of Electrolytic Manganese" J. Electrochem, Society Volume 94, No 5, November 1948.

This describes the same process covered in the proceding article. Some useful information on the general properties of manganese are included.

6. "Leaching Process Recovery of Manganese from Low Grade Ores" Chem. Eng. Prog. March 1950, Volume 46, No 3.

The preparation of manganese oxides by the leaching of low grade ores, is described using pickle liquor containing between 0.5 to 10 per cent H_2SO_4 and 10 to 22 percent ferrous sulphate by weight. The probable reactions for the leaching are:

$$MnO_2 + 2FeSO_4 + 2H_2SO4 \longrightarrow MnSO_4 + Fe_2(SO_4)_3 + 2H_2O$$

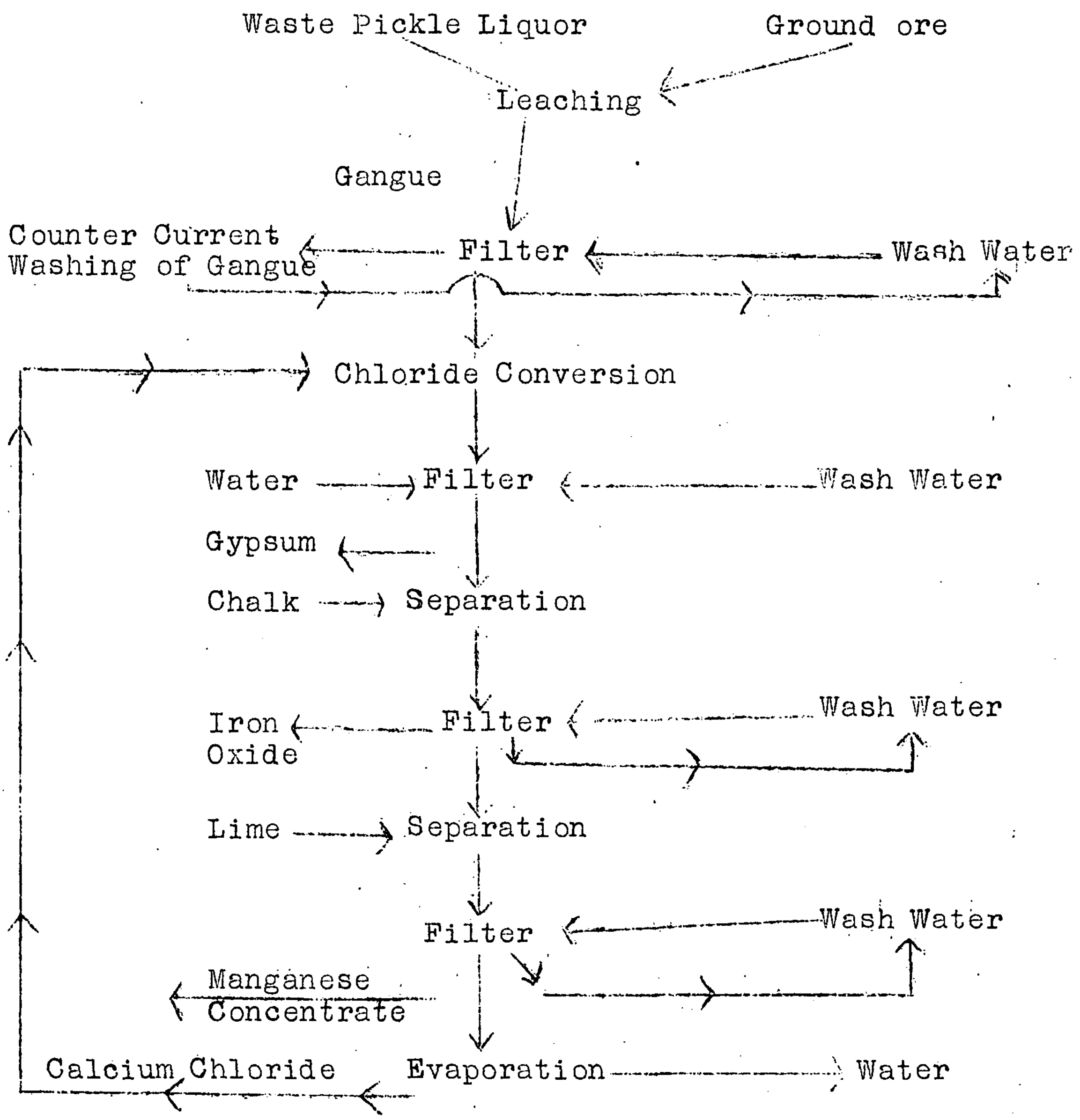
$$Mn_2O_3 + 2FeSO_4 + 3H_2O \longrightarrow 2MnSO_4 + 2Fe(OH)_3$$

Manganese dissolves quickly at normal temperature and pressure. The solution of magnesium sulphate was treated with $CaSl_2\ 2H_2O$ (gypsum). The iron was precipitated by freshly precipitated chalk and aeration of the solution, and the manganese precipitated with lime.

After concentration, the remaining liquor, (a dilute solution of calcium chloride) can be recycled to precipitate the sulphate radical.

The flowsheet of this process is shown below:

FLOWSHEET.



(7) "Upgrading Domestic Manganese Ores by Leaching with Caustic Soda" Min Eng., April 1953.

This report covers the leaching of silica from manganese ores to increase the grade of manganese. Ores containing fine (crypto-crystalline) silica and opaline silica were leached successfully. The article deals with settling and filtering of the leach liquor and the regeneration of the caustic soda.

The extent to which these interesting methods can be used depend on the type of silica present. Minerals such as gypsum can cause a cyclic build up of sodium sulphate.

8. "How U.S. BM Metallurgists are Solving the Manganese Shortage" Eng. Min. Journal, Vol 155, No. 11 November 1954.

A report on the high temperature sulphating process for the treatment of an carbonate slate ore from the Cuyuna Range, Minnesota. The ore contains 7 per cent Mn and 27 per cent Fe.

The slate was crushed to produce the major amount of material in the $-\frac{3}{4}$ to $+\frac{3}{8}$ inch fraction which was combined with the pellets formed from the minus $\frac{3}{8}$ inch material after grinding to 65 mesh, and fed to the vertical shaft kiln.

In the kiln, the ore was first calcined below 480°C and then heated in an atmosphere of sulphur dioxide at 880°C to form water soluble manganese sulphates. Water soluble compounds of iron and phosphorous are not formed. Approximately 1.5 times the theoretical amount of SO_2 to combine with the manganese was required.

After passing through the sulphating zone the ore was held in the kiln to cool before discharging. Kiln discharge was ground in a ball mill and leached using counter-current decantation. The pregnant solution was concentrated by evaporation and the precipitated manganese sulphate was calcined to the oxide. The sulphur dioxide formed was recycled.

The final product containing more than 60 percent Mn representing a recovery of 74 to 84 per cent.

(9) "Pressure Leaching of a Manganese Ore" Part 1 - Kinetic Aspects, PartII - Leaching Aspects. Proc Aust Inst Min Met. No. 185 March 1958.

This report covers leaching of manganese ores with ferrous sulphate and sulphuric acid produced by the pressure oxidation of pyrite.

The following overall reaction applies:

$$4MnO_2 + 4FeS_2 + 13O_2 + 4H_2O \rightarrow 4MnSO_4 + 4H_2SO_4 + Fe_2O_3$$

This equation can be split into two parts, namely:-

(1) The oxidation of pyrite.

$$2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4$$

$$FeS_2 + Fe_2(SO_4)_3 \longrightarrow 3FeSO_4 + 2S$$

$$FeS_2 + 7Fe_2(SO_4)_3 + 8H_2O \longrightarrow 15FeSO_4 + 8H_2SO_4$$

(2) The reaction of manganese dioxide with the ferrous and hydrogen ions.

$$MnO_2 + 2Fe^{++} + 4H^+ \longrightarrow Mn^{++} + 2Fe^{+++} + 2H_2O$$

Some of the ferrous ions are oxidized by the gaseous oxygen according to the equations -

$$4Fe^{++} + O_2 + 4H^+ \longrightarrow 4Fe^{+++} + 2H_2O$$

$$2Fe^{+++} + 2H_2O \longrightarrow Fe_2O_3 + 6H^+$$

Optimum leaching conditions were at pressures of 25 to 90 pounds per square inch and a temperature of approximately 140° C.

High grade 51 per cent Mn ore was used and in some instances complete extraction of the manganese was obtained.

Points emphasised in the report are:

(1) The manner in which the process can be carried out.

(2) Both the oxidation of the pyrite and the reaction between the ferrous and hydrogen ions take place in one vessel.

(3) Ores containing only manganese as the valuable metal may need a favourable combination of circumstances for successful economic appliciation of this process. It is believed that the process may be suitable for treating wads containing cobalt and nickel.

(10) <u>"Extraction of Manganese Oxide from Low Grade Manganese Ore at Pernatty Lagoon". Sth Aust Department of Mines Met. Branch, Report No. 63 January 1954</u>.

The report describes leaching of Pernatty Lagoon manganese ore with waste pickle-liquor. A detailed description of the leaching method is given with the results of various tests made to precipitate the iron and manganese from the pregnant solution. It was interesting to note that gypsum was a by-product and it was hoped to find a market for this material to reduce the production costs of the manganese concentrate.

Grade and recovery by this method were 60 and 85 per cent respectively.

Costs estimates are included.

(11) "Manganese Concentration from Low Grade Domestic Ore" Industrial Eng. Chem Vol 43, No 7 July 1951.

This article deals with the development of a nitric acid leaching process.

The ore, ground to minus 60 mesh, was heated in a reducing atmosphere to convert the higher oxides of manganese to manganous oxide, the iron oxides present being reduced to ferro-ferric oxides. Leaching with nitric acid, at normal temperature and pressure, dissolved the manganese but not the iron oxides, silica, alumina, and phosphorous.

Barium, calcium, and lead salts were precipitated by adding small amounts of H_2SO_4. By omitting this step calcium nitrate can be produced as a by-product for sale as a fertilizer.

The high manganese solution was concentrated and decomposed in the presence of air at a temperature of 200°C, according to the equation.

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

The manganese dioxide, purified by washing, was then dried.

A typical product assayed 60 per cent Mn representing a recovery of about 95 per cent. Recovery of nitric acid depended on the amount of soluble nitrate products formed during leaching, and with ores containing only small amounts of sodium, potassium, magnesium and zinc, the recovery of nitric acid has been high.

A high grade iron ore was obtained by magnetic treatment of the insoluble residue.

7.3. CHLORIDE VOLATILIZATION.

(1) "Development of Chloride Volatilization Process For Manganese Ores from Arroostook County, Maine" Progress Report U.S. Bureau of Mines, R.I. 5281.

A process involving chloride volatilization is being developed to recover the manganese contained in the silicate type ores found in the Maple Horey Mountain deposit. Average content of the ore is:

Mn	10.8	per cent.
Fe	26.8	per cent.
SiO_2	22.0	per cent.
Al_2O_3	5.6	per cent.
CaO	4.2	per cent.
P	1.0	per cent.

The process consisted of a roasting step in which metal chlorides, produced by treating the ore with hydrochloric acid gas are volatilized and swept from the reaction zone to a condenser, followed by a conversion step in which the reagent was regenerated and the condensed chlorides converted to oxides.

For siliceous manganiferous ores and plant residues, chloride volatilization had several important advantages:-

(1) High recoveries were possible from refractory ores.

(2) Preliminary treatment other than crushing and

grinding was not required.

(3) The reagent may be regenerated and recycled.

(4) Phosphorous, if present, remained in the residue.

(5) Sulphur contamination of the product was minimized. Unfortunately a large proportion of the iron was volatilized and a purification step was necessary to achieve the proper manganese - iron ratio required for ferromanganese production.

The three important unit processes were:-

(1) Roasting and chloridization.

(2) Hydrolysis of the chloride product.

(3) Regeneration of the hydrochloric acid gas.

1. Roasting and Chloridization.

The broken ore was heated to 950° - 980°C and swept by hydrochloric acid gas. Ninety per cent of the manganese and 60 to 100 per cent of the iron was converted to volatile chlorides. The gas flow must be large enough to remove the metal chlorides as they are formed. Chlorides remaining in the charge fused the ore particles together and made handling difficult.

The volatile chlorides were condensed and the unused HCl dried and passed back into the furnace.

2. Hydrolysis of the Chloride Product.

The chlorides can be converted to oxides by hydrolysis in a tunnel kiln fired with natural gas. By careful control of temperature, the iron can be converted before the manganese. The soluble manganese chloride can then be leached from the iron oxides and recovered by crystallization.

By raising the temperature and increasing the retention time of the chlorides in the kiln almost complete hydrolysis of the chlorides was possible.

3. Regeneration of the Hydrochloric Acid.

The dilute acid collected from the exhaust gases of the tunnel kiln can be concentrated by boiling first at reduced pressure to remove water, and then at atmospheric pressure to boil off nearly pure HCl gas.

7.4 MISCELLANEOUS REFERENCES.

(1) "Examination of Manganese Ore from Tamworth District , N.S.W.", C.S.I.R.O. Ore Dressing Investigation, No. 496.

Mineragraphic examination of a rhodonite ore from N.S.W.

(2) "U.S. Research on Manganese Ores and Slags". The Mining Journal, May 20th 1955.

This article, condensed from a report by the Emergency Procurement Service, contains references to various articles already covered in this literature survey. It is of no real interest apart from the general summation of data.

(3) "Manganese Mining at Immi, French Morocco" The Min. J. July, 23rd, 1954.

High grade manganese ore (40 per cent) mined by underground methods was treated by hand picking (to discard a low grade tailing), Birtley pneumatic tables, and screening.

concentrates assayed approximately 55 per cent Mn.

(4) "Manganese Dioxide for Primary Batteries". Chem. Trade Journal and Chem. Eng. September 21st, 1956.

An interesting article covering the extraction and uses of manganese. Common leaching methods are listed, and the electrolytic deposition of MnO_2 and Mn is discussed. Particular attention is given to the production of manganese oxides for primary batteries. The difficulties in measuring the effectiveness of the different batches of manganese minerals are pointed out and it states that X-ray diffraction work is replacing the old method of determining reactivity by the measurement of bulk density and MnO_2 content.

(5) "Manganese: Major Strategic Metal" The S.A. Min. Eng. J. March 28, 1958, (South Africa).

A general converage of manganese minerals and the uses of manganese, with particular attention to the manufacture of ferromanganese and other iron manganese compounds. The starting of a new industry in South Africa to produce ferromanganese for export to dollar areas is the main theme.

(6) "Manganese and Chrome Ore Outlook" Min. Eng., Aug 1958 T.A.I.M.E. Vol. 10 No. 8.

The article covers the uses and output of manganese and chrome ore. U.S. consumption of manganese is approximately 13 lb. per short ton of steel production but with iron ores and cokes having higher sulphur content, consumption may rise to 70 lb. per short ton, as in the Russian steel industry.

Free world supply of manganese in 1956 was 6 million tons. This is expected to rise to 9 million tons per year in 1970. Major free-world supplies come from India, South Africa and the new major producer, Brazil Russia supplies approximately 350,000 tons per annum, mainly to U.K. and Western Europe.

7. "Mining Journal, Annual Review, 1958.

This report indicates that the supply of manganese available in 1958 is far in excess of the world consumption. However it assumes that world steel production in 1980 will be three times that of the 1956 figure. This indicates an expanding market for manganese minerals.

8. "Experimental Electric Smelting of Manganese Ore" Part II Production of Iron, Silico-Spiegeleissen and Portland Cement from Low Grade Ore. The Canad. Min. Met. Bull., May, 1958, Trans fol LX1, 1958.

The ore treated assayed approximately 30 per cent. Fe, 4-5 per cent. Mn and 50 per cent. SiO_2. It was obtained from Steep Rock Iron Mines, Ontario as overburden being removed to expose the high grade iron ore. The ore was smelted to produce iron-low manganese and a slag rich in manganese.

The slag after being colled, crushed and passed through a magnetic separator to recover prills of iron, was recharged to the furnace and a new slag and the silicospiegeleisen produced. The slag from this second stage, mixed with limestone and alumina, was fired in a rotary kiln to form a portland-cement-type clinker. Overall recovery of manganese and iron were 65 per cent. and 93 per cent. respectively. The silico-spiegeleisen contained 63 per cent. of the manganese.

A small three electrode electric furnace was used.

9. "Electrodeposition of Gamma Manganese." J. Electrochem. Soc. Volume 94, No. 2. August, 1948.

Interesting information on the deposition of manganese by electrolytic means.

10. "Domestic Chrome and Manganese Ore can be Upgraded and Utilized" Min. Eng. April, 1953.

General summary of treatment methods and sources of these ores in the United States.

11. "Minerals in the Development of Australia" Issued by the Economic Society of Australia and New Zealand.

(Abstract) Manganese: Australia's known resources of manganese ore have always been small. However, recent exploration in the north-west of Western Australia is adding to known reserves, which are now estimated at 685,000 tons of high grade ore. The major resources in N.S.W. and S.A. have been worked out, so the steel industry is now dependent on deposits in Western Australia. The bulk of the dioxide-grade production for Australia is mined in N.S.W. : 490 tons of this ore were produced in 1956. The Horseshoe deposits in W.A. are the most important deposits of metallurgical grade ore in the Commonwealth. Several other large deposits of ore have been reported from the North-west district.

There has been a yearly production of manganese ore in Australia since 1882. A record output of 25,681 tons was achieved in 1957. Known reserves in Australia are insufficient to supply the iron and steel industry for more than one or two decades and export of manganese ore is therefore strictly controlled. The estimated domestic consumption of dioxide-grade is about 3,000 tons annually of which about 90 per cent is used in themanufacture of dry cells. Imports of dioxide grade manganese ore, mainly from India, were 2,049 tons in 1957. Imports of ferromanganese, chiefly from Norway, were 7,339 tons in 1956.

12. "<u>The Concentration of ,hiature Manganese Ore</u>" <u>Chemical Abstracts, Vol. 52, No. 1, 199 (i)</u>.

(Abstract) It is recommended that (1) a combination of settling, electromagnetic and electrical separation, mechanical separation and flotation. (2) a combination of heavy suspension, and electromagnetic and electrical separation, or (3) a variation of both 1 and 2 be used for the concentration of the different ores of the Chieatura Basin.

13. "<u>Deoxidation of Steel with Manganese" Chemical abstracts, Vol. 52, 211f.</u>

(Abstracts) Steel de-oxideized with manganese only, contains inclusions inthe form of globules consisting of a blank outer layer of FeO and an inner portion having the composition SiO_2 15 and Mn 85 per cent. It is thought that Mn and FeO only react in a silicate melt, and thus the presence of Si is necessary. When deoxidizing steel with a constant amount of Si in the metal the amount of inclusions did not increase with the increased addition of manganese. In simultaneous de-oxidation of Fe with different amounts of Si and Al, aluminium silicate is not formed in Fe, but Al_2O_3, is formed in all cases. With the addition of FeO, Si and Al, the silicates were formed with the predominance of Al_2O_3.

Inclusions in steel de-oxidized by a mixture of FeO 0.5-1.0 Si

0.2 per cent are Mn silicates. Inclusions in steel deoxidized with 0.2 per cent Si, and 0.02 per cent Al are Al_2O_3. The absence of Mn silicate in steel deoxidized with Si and Al only, throws a doubt upon the existence in the steel of FeO and MnO. The ironic theory of slag structure is used to explain the passive behaviour of Mn in Fe as deoxidizer when Si is absent.

16. "Manganese-bismuth Alloys for Permanent Magnets" U.S.S.R. 102,993, June 25th, 1956. Chemical Abstracts Vol. 52, 5276e.

(Abstract) Manganese and bismuth are melted together in an open furnace in the presence of substances, such as NH_4Cl and $ZnCl_2$, which are capable of forming volatile chlorides with manganese and bismuth oxides to provide a protective atmosphere for the melt.

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