

PRODUCTION OF MANGANESE AND MANGANESE
DIOXIDE - PILOT PLANT INVESTIGATIONS(*)

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Investigations on production of electrolytic manganese and electrolytic manganese dioxide were initiated in this laboratory in 1950 for the utilisation of low-grade manganese ores. Basic data for the two processes were collected by 1953 and the processes developed were covered by patents. Before the processes could be handed over for commercial exploitation, it was thought necessary that the processes should be tried on a comparatively larger scale of a pilot plant to find the soundness of the processes, to visualise the relative sizes of various equipment, materials of construction, relative effects of different stages of the processes, working conditions, quality of products and a preliminary idea about cost, i.e., in short to find how far the conditions and data found in laboratory scale experiments were applicable on a large scale. A beginning in the establishment of a pilot plant was made in 1954.

PILOT PLANTS FOR MANGANESE AND MANGANESE DIOXIDE:

The processes for production of electrolytic manganese and manganese dioxide have already been carried out on pilot plant scales producing 32 lbs of manganese and 5 lbs of manganese dioxide per day respectively. Except for very specialised equipment, such as acid resisting pumps, filters and generator, all other equipment including the design of cells were made with the help of laboratory staff. At the pilot plant, first four of the following sections of the process were kept common for manganese and manganese dioxide.

(a) Crushing and Grinding of Ore:

The manganese ores which have been received for use in the pilot plant have sizes between 2" - 4". Experiments carried out in connection with ore dressing investigations in this laboratory have shown that ores having sizes of about 1" can be satisfactorily reduced with coke oven gas. But it has been found that leaching becomes very inefficient and time-consuming unless the ore is finely ground. Therefore, grinding to -35 mesh precedes reduction.

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(b) Reduction of ground ore:

A horizontal rotary kiln furnace has been used for reduction of ore. The kiln is about 20 ft. long and 6" in diameter. It is externally heated with coke oven gas and through a different circuit, gas is passed into it at the delivery end for reducing the ore. The furnace temperature has been kept between 500°C - 600°C so that major part of the iron is reduced to the stage Fe_3O_4 which is insoluble in dilute sulphuric acid. This control of temperature is important. It has been found that unless the reduced ore is cooled down to 100°C or less, atmospheric air rapidly reoxidises the ore. Even otherwise, the mass of reduced ore is superficially reoxidised in a short while, which penetrates deeply with time. It is not practicable to store the finely ground reduced ore without costly arrangement or storing the same in a closed container for more than 24 hours without reoxidation of a substantial part of manganese.

(c) Leaching of reduced ore:

Leaching operations have been carried out in wooden tanks, lined with lead. The leaching tanks are filled up with spent liquor from electrolytic cells containing about 30 gms of sulphuric acid per litre and mixed up with additional quantities of sulphuric acid and ammonium sulphate if necessary. Reduced ore is added in calculated amount and the liquid is vigorously stirred. The pH of the solution is brought up to 2. After settling, the liquid is transferred to a separate vessel for next operation.

Leaching usually takes about an hour for completion. However, rate of stirring plays an important role. A two stage leaching with counter current principle has been found more efficient and has given better recovery of manganese from the reduced ore. Recovery of manganese from the ore is intimately connected to the chemical constitution of the ore. Iron content does not in fact affect recovery of manganese at the leaching stage but iron consumes a large quantity of sulphuric acid which is not very practicable to recover.

(d) Purification of leach liquor and preparation of feed electrolyte:

Purification of leach liquor is done in two stages. First stage removes mainly iron, arsenic, phosphorus and second stage removes nickel, copper, etc.

To remove iron, air is bubbled through leach liquor and its pH is raised to 6-7 by addition of ammonia. Ferric hydroxide precipitates out. This ferric hydroxide carries down all phosphorus and arsenic. Ferric hydroxide is a voluminous precipitate and entraps a large volume of the solution. Filtration in the pilot plant has been carried out in a rubber lined pressure filter satisfactorily. It is felt, however, when dealing with large volumes of electrolyte and variable amounts of iron, a drum filter fitted with scrappers

will be a useful adjunct to the pressure filter. This double stage filtration will help in recovering most of the entrapped electrolyte with ferric hydroxide and permit smooth operation of the pressure filter to obtain a clear filtrate.

The filtered liquid, after removal of iron, is sent directly to sulphide precipitation tank to remove nickel, copper, cobalt, etc. In presence of high concentration of manganese sulphate at comparatively high pH the possibility of formation of manganese sulphide exists. As soon as sulphide is added either as hydrogen sulphide or as ammonium sulphide, voluminous precipitation of manganese sulphide takes place which reacts later with nickel or copper salts. This reaction can be considerably speeded up by vigorous stirring and additions of a little kaolin powder. In the pilot plant experiments kaolin powder has been first added under stirring followed by ammonium sulphide solution.

After settling, the liquor is filtered through a pressure filter. For transport of liquid at this stage rubber and plastic rotary diaphragm pumps have been found satisfactory.

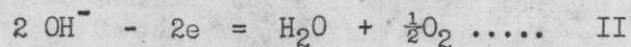
The filtered solution from this stage is sent to electrolyte preparation tank. After a complete analysis of the liquor, suitable additions are made to obtain a feed having the following composition.

Manganese sulphate	...	100 gm/l
Ammonium sulphate	...	150 gm/l
Sulphur dioxide	...	0.1 to 0.2 gm/l
Iron	...	Test negative with sulphocyanide.
Nickel	...	Test negative with dimethyl glyoxime.

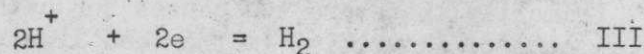
Separate tests for copper and cobalt have not been found necessary in practice.

(e) Electrolysis:

The overall principal reactions that occur during electrolysis are



The side reactions with the above are mainly the following:-



It will be noted from the above that the products of reaction II at the anode is injurious for reaction I at the cathode. Therefore anode and cathode compartments are kept separate by diaphragms.

The cell consists of a wooden tank reinforced with angle iron. There is a small box attached to the bottom of the tank. Three openings on the bottom of the tank allow flow of liquid from the tank to the box. Three anode diaphragm frames are vertically placed over the three openings such that liquid from the diaphragms directly enters the small box which has a swan neck delivery to spent electrolyte launder. The cell is also fitted with cooling pipes on two sides, which help to control the temperature of the cell.

CELL CHARACTERISTICS AND THEIR CONTROL:

The general conditions for normal functioning of the cell are as follows:

Temperature	30°C
pH	8
C.D.	33 Amp/sq.ft
Voltage	4.8 - 5 V.

During long duration of pilot plant experiments each of these variables was allowed to deviate, from these normal values to understand how far such deviations could be allowed without spoiling the bath irrevocably. It was found temperature upto 40°C could be tolerated for short periods. pH of catholyte could go up to 8.5. But under such abnormal conditions rate of output diminished.

It was noticed that if circulation of electrolyte in various cathode compartments was better, pH control was easier. Further, cells of larger capacity were found more stable in pH values than smaller cells. Exactly similar observations were recorded for temperature. The composition of electrolyte plays an important role on stable and uniform functioning of the cell. The concentration of sulphur dioxide if allowed to rise much above 0.1 - 0.2 gm per litre, the sulphur content of deposited metal goes up.

Cathodes going black, cracked deposit, trees, unusual rise of temperature in catholyte, low pH in catholyte, high pH in catholyte, unusual accumulation of manganese dioxide in the anode diaphragm are the common difficulties met with during long term running of the cells.

Primarily there are two causes for cathodes going black. Firstly, presence of impurities in the feed liquor. Impurities concerned are generally iron, nickel and cobalt. Second cause is

inadequately cleaned and prepared cathode surfaces. Proper polishing of cathode coupled with electrolytic cleaning in a alkaline cleaning bath usually prevents such troubles.

Cracked deposits are very serious from the view point of smooth operation of the cells. If cracks develop it is found that evolution of hydrogen becomes very high and pH of the catholyte starts shooting up to high values. Mere replacement of the cathode does not rectify the trouble. Causes have been located in the feed composition. In a similar way excessive treeing in the deposit is caused by wide variation in the manganese sulphate content of the catholyte.

Rise in temperature of the bath is usually associated with dissolution of deposited metal for reasons indicated above. However, loose electrical contact anywhere in the electrode connection system will also cause similar difficulty.

Low pH of the catholyte under otherwise optimum operating conditions, indicates punctured anode diaphragm or similar source of leakage of anolyte into cathode chamber. Often such leakages can be prevented by raising the feed rate, but this will naturally cause a lower strip from the feed. It is generally necessary to cut out the cell for overhaul and repair. High pH value in the catholyte will naturally indicate loss of hydrogen from the electrolyte. This may be caused by conditions which either prevent deposition of metal or cause dissolution of the metal. As indicated earlier these conditions concern the composition of catholyte, feed electrolyte and preparation of cathode surface. It is obvious that to prevent this difficulty it will be necessary to arrange effective check on the regeneration side.

Production of large amounts of manganese dioxide results in choking up the outlet from the cells, bulging out of canvas diaphragms, requirement of higher hydrostatic pressure head in the catholyte chamber besides loss of manganese from the electrolyte. For prevention of this difficulty the well known practice of using 1% silver lead alloy helps a great deal. The position becomes more satisfactory if the anodes are first coated with an adherent deposit of manganese dioxide by a suitable pre-treatment.

The table below gives some typical average data to determine the optimum hours of deposition on a cathode when the cells are run for two or three weeks.

TABLE I

Composition of feed solution:	100 gms of manganese sulphate per litre.
	150 gms of ammonium sulphate per litre
	0.2 gm of SO ₂ per litre.
Average strip from solution:	58 gms of manganese sulphate per litre.

C.D. - 29 Amp/per sq.ft.

Contd.....6.

Hrs of deposition.	Average Voltage.	Average Temp.	Average pH.	C.E.
18	5.1	30°C	8.2	66.8%
24	5.15	29.5°C	8.5	64.1%
44	5.05	31.5°C	8.2	63.23%
50	5.1	30.5°C	8.4	59.99%

MANGANESE DIOXIDE CELL:

Working conditions for the manganese dioxide cells are somewhat more exacting as far as materials of construction are concerned. The cells are to work at 85° - 90°C containing an electrolyte which is highly acidic. The cell which has been used in actual experiments consists of a jacketted mild steel tank, lined inside with lead. Steam is introduced or produced in the jacket to heat the contents of the lead lined inner tank. Cathodes and anodes are placed in wooden frames so that they are securely kept in positions. The entry of feed and outflow of electrolyte to and from the cell are maintained in a manner similar to that of a manganese metal cell. All the difficulties that arise in operating manganese dioxide cell are mostly from maintenance of high temperature. These are

- (1) Evaporation of water from the electrolyte.
- (2) Deposition of crystals on the upper parts of the cell, electrodes and accessory parts.
- (3) Sulphuric acid carried mechanically by the vapour from the cell into atmosphere.

To a limited extent, these difficulties are controllable by partly covering the cell, and providing good ventilation in the cell room. In other respects manganese dioxide cell offers many advantages when compared to manganese metal cell. The advantages are -

- (1) It does not require close control of pH
- (2) It does not need replacement of electrodes every day or every two days.
- (3) Nothing similar to "Cathodes going black", "abnormal variation in pH", or "failure of anodes" occurs.

One set of anodes works for about three weeks and builds up thick deposit of manganese dioxide on them. This is detached from the anodes and washed to remove entrapped sulphuric acid and manganese sulphate.

TABLE II

Typical data on C.D - C.E. relationship
of a manganese dioxide cell.

Days of run	Average voltage.	Current Density Amps/sq.ft.	Average temp.	Anode spacing.	Concn. of MnSO ₄	C.E.
15 days	2.75 V	12.5	85°C	3.3"	175 gms/l	89.2%
15 days	2.6 V	10	85°C	3.3"	180 gms/l	94.6%
15 days	2.5 V	7.5	85°C	3.3"	178 gms/l	98.4%

PROPOSED PILOT PLANTS WITH HIGHER CAPACITIES:

From the foregoing description it is evident that

- (1) the two processes are fundamentally sound.
- (2) low grade ores are generally suitable but it is necessary to work with ore of substantially constant composition to obtain uniform conditions for regeneration process.
- (3) The designed cells are satisfactory.
- (4) The two process are in a position to be considered for commercial exploitation.

In order to meet the heavily increased demands for electrolytic manganese for research projects now under active investigation at the National Metallurgical Laboratory, the rate of production is being stepped to 100 lbs/day for manganese metal and manganese dioxide both in the Pilot Plant.

LAYOUT OF THE 100 LBS/DAY PLANT:

The plant is housed in a bay measuring 82' x 27' and in a covered corridor measuring 30' x 14'. Part of the bay has a raised platform, measuring 24' x 27'. The covered corridor houses raw materials and rotary reduction furnace. There is no plant for crushing the ore which is to be done in ore dressing pilot plant bay.

MOVEMENT OF MATERIALS & OPERATIONAL DESCRIPTION:

The ground ore will be received at the covered corridor together with other raw materials such as sulphuric acid, ammonium sulphate, etc. The ground ore will be taken on to the hopper to feed

the rotary furnace. The rotary furnace has a capacity to produce 30 lbs of reduced ore per hour accounting for about 720 lbs of reduced ore per day. The plant will normally require about 450 lbs of ore daily if the ore contains 25% manganese, or less, if the ore is richer.

The reduced ore from the furnace will then be taken to the bay by manual labour and taken on the platform by a bucket elevator. There are two leaching tanks, each provided with stainless steel stirrers, having a capacity to hold 1400 litres and measuring 4' x 4'4" (high). This capacity of a reactor permits treating the total quantity of spent liquor which will be collected in 8 hours when the cells are functioning and also provides for margin. The capacity of this unit determines the capacities of all other tanks which take part in subsequent treatment of the leach liquor. Each of the four reservoirs for finished liquor has a dimension of 5' x 5'.

Two leaching tanks will be functioning in two stages in series and in counter current principle. Freshly reduced ore will first meet the liquor which has already been treated with ore at a previous stage and passed through the filter in one of the Reactor tanks. The leach liquor with sludge after this stage will go to a settling tank and thence the clear liquid goes to a rich liquor storage tank on the platform. The sludge will pass from settling tank to a second reactor tank to react with fresh spent electrolyte. The liquid with sludge passes through a filter. The sludge goes to waste while the liquid goes to the first Reactor tank.

From the rich liquor tank, the solution passes to the iron precipitation tank where air and ammonia will be used to precipitate iron together with arsenic, phosphorus, etc. After completion of the reaction, the liquid and precipitate will be pumped to filter feed tank on the platform and filtered through a pressure filter. The filtrate from this filter will next go to another filtrate storage tank from where the liquid goes to nickel precipitation tank which is fitted with a stirrer. After sulphide precipitation is complete, the liquid will be pumped up to filter feed tank on the platform from where the liquid will go through final filtration through another pressure filter. The liquid is delivered in the electrolyte preparation tank. It is to be treated with ammonium sulphate, sulphuric acid and sulphur dioxide to obtain the requisite composition for feed liquor. After this conditioning and subsequent analysis, the liquor is pumped to respective reservoirs and feed tanks. There are two reservoirs and one feed tank separately for manganese and manganese dioxide cells on the platform. The rest of the regeneration plant is common for both manganese and manganese dioxide cells which will be worked in alternation.

On the two sides of the central platform, cells for manganese and manganese dioxide have been laid out with accessory equipment. A rectifier with an output of 3000 amp between 0-10 V has been installed to supply sufficient electrical energy necessary to produce about 100 lbs of manganese metal per day. The D.C. output is carried through copper bus bars to the electrolytic cells. Space by the side of the rectifier has been kept reserved for a cooling unit having a

capacity of about 10 tons of refrigeration per day. The cooling plant will be used to cool water for circulation in the coils inside manganese cells. The feed electrolyte to the cell will be transported from the feed tank on the platform through polythene pipes. The spent liquor from the cell will be taken to an underground tank, from which it will be pumped to Reactor tanks.

Space around the electrolytic cell will be utilised for polishing of electrodes, removal of metal from cathodes and similar other works. These will be done manually.

On the opposite end of the bay, an electrode boiler having a capacity of 1000 lbs of satd. steam per hour has been installed. This boiler will meet the demand for steam from manganese dioxide cell which has been estimated to be about 250 lbs per hour. Manganese dioxide cells will be supplied with low voltage power from a rectifier having a capacity of 2000 amp at 0-7 V. The designed cell is a jacketted m.s. tank, and fitted with steam coils and will have a production capacity of 100 lbs of manganese dioxide per day. Feed electrolyte for the manganese dioxide cell will be transported to it from the feed electrolyte tank on the platform through lead pipes. The spent liquor will be collected in an underground tank from which it will be pumped to reactors.

EQUIPMENT FOR THE 100 LBS/DAY MANGANESE AND
MANGANESE DIOXIDE PLANTS

Rubber lined pumps	2	Nos.
Stainless steel acid resisting pumps	6	"
acid resisting filters	3	"
Electrode steam boiler	1	"
Refrigerating unit	1	"
Rectifier, 3000 amps, 10 V	1	"
Rectifier, 2000 Amps, 7 V	1	"
Manganese dioxide cell	2	"
Manganese metal cell	2	"
Reactor vessels	5	"
Intermediate storage tanks	5	"
Settling tank	1	"
Feed tanks	2	"
Finished electrolyte storage tank	4	"
Rotary reduction furnace	1	"

Overall design and installation of the plant have been completely undertaken at the National Metallurgical Laboratory.

Quality of the product obtained from Pilot Plant

Composition of electrolytic manganese:		Composition of electrolytic manganese dioxide	
Manganese	... 99.94 to 99.97%	MnO ₂	... 90.4%
Heavy metals	... less than 0.01%	Mn	... 58.0%
Sulphur	... 0.01 - 0.02 %	H ₂ O	... 3.3%
Hydrogen	... 0.02% Max.	Pb	... 0.10%
		Fe	... 0.1%

The electrolytic manganese from pilot plant has been satisfactorily used to introduce manganese in nickel-free stainless steel, coinage alloys, manganese brasses and bimetallic strips. Leclanche type dry cells have been fabricated in the laboratory for the purpose of testing the manganese dioxide from pilot plant. The tests have proved satisfactory in comparison with imported electrolytic manganese dioxide. Samples were sent to one Indian dry cell manufacturer and one foreign manufacturing firm. They have reported the product to be satisfactory after continuing tests for 6 and 3 months respectively.

COST OF PRODUCTION ON COMMERCIAL SCALE:

Estimates of cost for both the items have been made and it has been shown that under Indian conditions cost of production of electrolytic manganese and manganese dioxide will be about Rs. 1500/- and Rs. 600/- respectively which compare well with foreign market prices.

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