

# Beneficiation of manganese ore fines for the production of battery grade $MnO_2$

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## INTRODUCTION

Though India is a leading producer of manganese ore, it is importing battery grade manganese dioxide to meet the domestic requirements. The total consumption of manganese dioxide by the 10 to 12 units of battery industry for the production of 1,214 million pieces of batteries per annum was around 21,521 tonnes in 1981-82. In 1980, the import of battery grade  $MnO_2$  was more than 50% of the total requirements of the industry. So attempts have been made by Manganese Ore India Ltd. (MOIL) to beneficiate the "Dongribuzurg," ore fines in collaboration with other organisations for the production of the battery grade manganese dioxide. As a part of the programme of help to sister organisations the Mineral Technology Laboratories of Atomic Minerals Division, Hyderabad, have taken up this work. Beneficiation tests were carried out on three different grades of samples analysing 45% Mn, 40% Mn, and 36% Mn.

The mineralogy of the sample is quite complex. The petro-mineralogical study of these samples indicate the presence of pyrolusite, cryptomelane, braunite, hollandite, jacobsite, sitaprite and vredenburgite as the manganese ore minerals. Pyrolusite and cryptomelane, which form bulk of the ore, are intimately associated with cryptocrystalline silica and often contain remnants of braunite. Pyrolusite (white), cryptomelane (grey) and cryptocrystalline silica (black) form alternate bands (Plate-1). These minerals are often intimately associated (Plate-2). Remnants of braunite also occur alongwith pyrolusite and cryptomelane (Plate-3). Pyrolusite in

the form of very fine powder is also seen as rims around the gangue minerals (Plate-4). It can thus be seen that  $SiO_2$  is intimately associated with Mn in many of these minerals and poses a challenging problem in beneficiation.

Vredenburgite exsolved to jacobsite and hausmanite (Plate-5) gives rise to complex assemblages. Hausmanite sometimes forms euhedral crystals in a mass of pyrolusite and cryptomelane with remnants of braunite and traces of hollandite in them. Jacobsite is also present as a separate mineral. Thus jacobsite and hausmanite behave similarly as vredenburgite in magnetic separation and when picked up with other manganese minerals increase the iron content of the concentrate. Because of intimate association of cryptocrystalline silica with manganese minerals the sample has to be crushed to very fine sizes and higher recoveries may not be possible even at very fine grind due to the presence of vredenburgite.

Gravity concentration methods are not suitable, as the concentration criteria is not high. Flotation is not efficient at fine sizes. The other concentration method that can be utilised in this case is magnetic separation which depends on the magnetic susceptibilities of the ore and gangue minerals.

Size analysis of the low grade sample at different mesh of grind indicated that there is no preferential concentration of Mn values in any particular size (Table-1).

Wet low intensity magnetic separation of the samples as such and samples ground to

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various MOG have shown that complete liberation of the manganese minerals from the gangue does not take place even at fine sizes, as is evident from mineralogy. Grinding to finer sizes results in higher slime losses (Table-2).

Several flowsheet tests were carried out by varying conditions to formulate a final flowsheet (Table-3).

The response of the three samples to the final flowsheet with the concentrates assay is shown in Table-4.

A composite sample was prepared by mixing all samples in equal proportions and its response to the final flowsheet and other tests were studied.

The recommended flowsheet is given in Figure-1.

#### Conclusion :

From the mineralogical data it can be inferred that the separation of Fe, Mn & SiO<sub>2</sub> into Fe, Mn & SiO<sub>2</sub> bearing individual species is quite difficult and the recoveries will be low. The manganese values are intimately associated with the gangues. Before subjecting to magnetic separation desliming is essential to get rid of surface coatings of the particles or else they behave differently in the magnetic field and

reduce the recoveries. Grinding of the sample is required for further processing of the ore in the roll magnetic separators as it is not feasible to carry out the magnetic separation of the sample as such. The high grade sample has responded positively to the final flowsheet test with a recovery of 50% and the maximum losses of 30% of Mn values are associated with the slimes which further on wet high intensity magnetic separation raises the recovery to 70%. The recoveries with the medium and low grade samples are low because of their high Fe and SiO<sub>2</sub> contents. Though in some flowsheet tests required grade is obtained at appreciably high recovery values, the products are not acceptable because of high iron content. In view of the product specifications only 40% recovery was obtained at +80% MnO<sub>2</sub>.

#### Acknowledgements :

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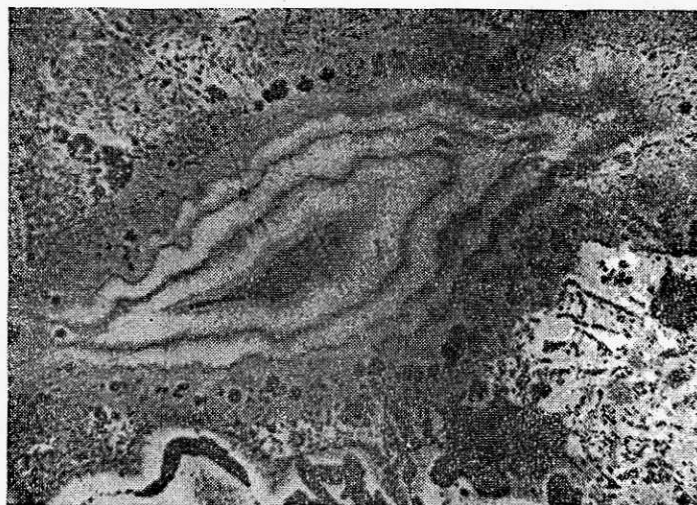


Plate No. 1 : Alternate bands of pyrolusite (white) cryptomelane ( grey ) and cryptocrystalline silica (black) as vug fillings ( X 500 )



Plate No. 2 : Pallets of pyrolusite, cryptomelane and silica ( X 500 )



Plate No. 4 : Pyrolusite rimming the gangue minerals ( X 500 )



Plate No. 3 : Remnants of braunite (Br.) in pyrolusite and cryptomelane  
Br = Braunite ( X 500 )

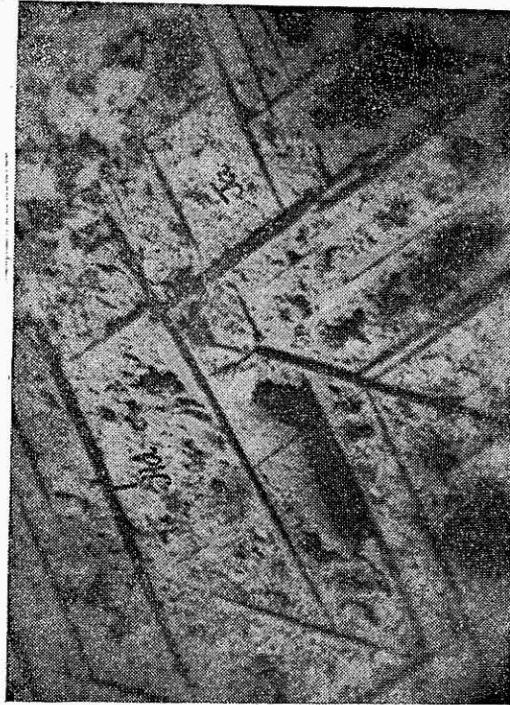
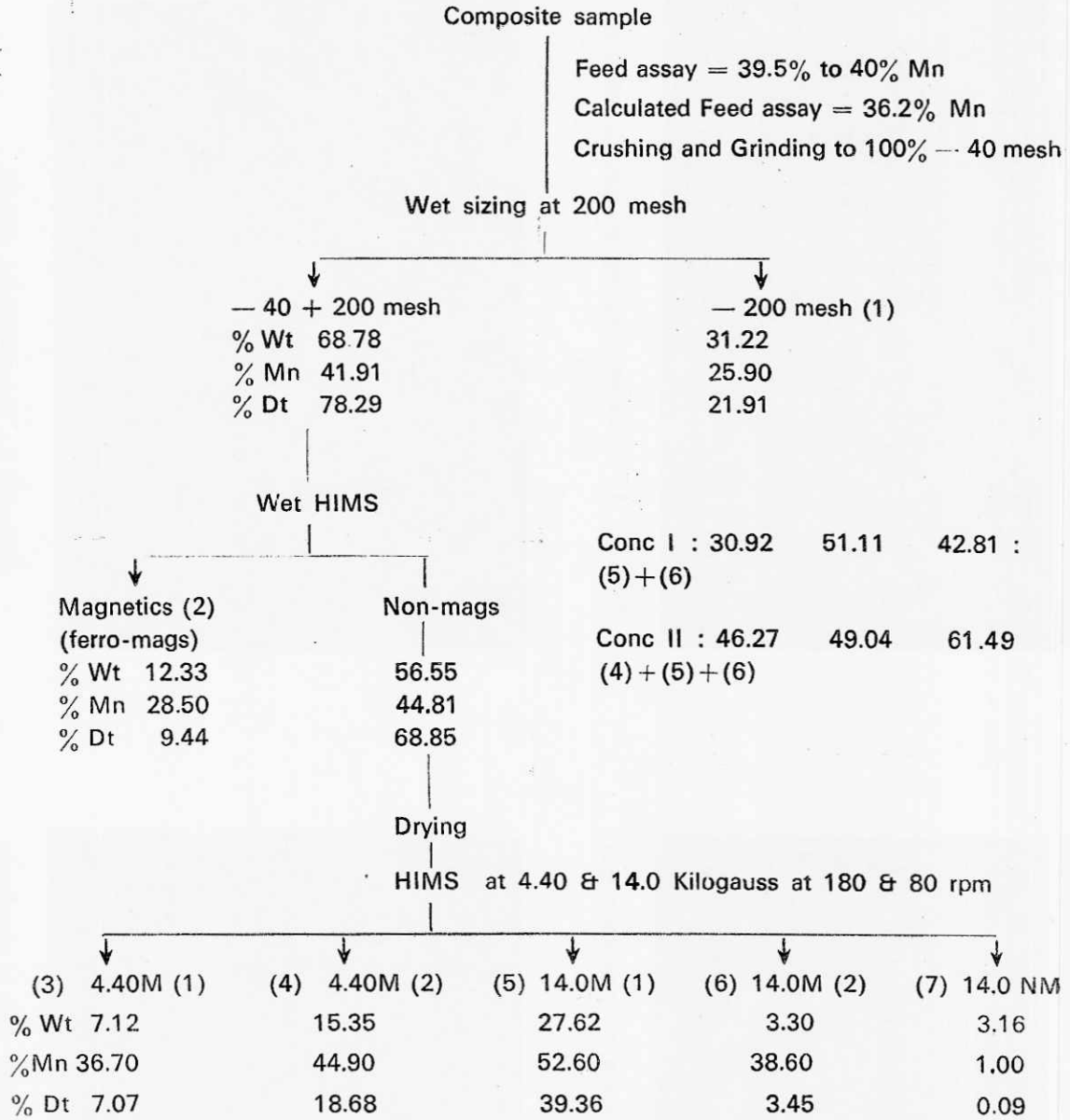


Plate No. 5 : Vredenburgite, etched  
Ha = Hausmanite, Ja = Jacobsite  
( X 900 )

Figure — 1

Recommended Flow-Sheet



HIMS : High Intensity Magnetic Separation.

M : Magnetic

NM : Non-magnetic



**Table — 1 : Distribution of Mn content in products at various mesh of Grind.**  
**Sample No. 2 DROM —3 mm (MCS 1004)**

Size in mesh	ROM				— 20				— 40				— 60				— 100			
	% Wt	% Mn	% D	% D	% Wt	% Mn	% D	% D	% Wt	% Mn	% D	% D	% Wt	% Mn	% D	% D	% Wt	% Mn	% D	
— 3mm + 20	33.23	41.20	38.31																	
— 20 + 40	17.68	34.40	17.02	24.74	43.50	27.73														
— 40 + 60	12.10	35.70	12.09	17.68	40.96	18.65	26.02	40.75	28.25											
— 60 + 100	9.83	31.70	8.72	14.15	37.30	13.60	20.92	37.53	20.94	28.0	41.97	30.16								
— 100 + 140	5.93	28.70	4.76	10.09	34.45	8.95	13.78	36.33	13.35	19.0	38.44	18.75	29.0	38.54	29.15					
— 140 + 200	8.09	30.40	6.88	8.59	36.96	8.18	11.22	34.89	10.44	15.0	36.42	14.02	22.0	38.44	22.05					
— 200	13.14	33.20	12.21	24.75	35.90	22.89	28.06	36.10	27.02	38.0	38.00	37.07	49.0	38.02	48.80					
Total	100.00	35.73	99.99	100.00	38.80	100.00	100.00	37.50	100.00	100.0	38.08	100.00	100.0	38.35	100.00					

**Table — 2 : Distribution of Mn in magnetic and non-magnetic fractions at various mesh of grind.**

Product	R. O. M.				— 20				— 40				— 60				— 100			
	% Wt	% Mn	% D	% D	% Wt	% Mn	% D	% D	% Wt	% Mn	% D	% D	% Wt	% Mn	% D	% D	% Wt	% Mn	% D	
Magnetics	17.00	30.09	13.36	16.66	29.04	12.46	15.30	28.00	11.42	14.50	33.79	12.58	9.00	26.29	6.17					
Non-Magnetics	67.80	42.80	75.73	58.59	42.84	64.65	56.64	40.75	61.56	47.50	41.30	50.36	42.00	41.12	45.03					
Slime	15.20	27.50	10.91	24.75	35.90	22.89	28.06	36.10	27.02	38.00	38.00	37.06	49.00	38.20	48.80					
Total	100.00	38.30	100.00	100.00	38.80	100.00	100.00	37.50	100.00	100.00	38.96	100.00	100.00	38.35	100.00					

**Table — 3 : Results of flowsheets tested on a composite sample (39.5% Mn)**

Sl. No.	Flowsheet details	Conc.			Remarks
		Wt%	Mn%	Recovery%	
1.	Crushing and grinding to 100% —40 mesh LIMS and HIMS	37.32	47.54	44.30	Specified grade not obtained. Magnetic between 4.4 and 14 kilogauss. Magnetics upto 14 kilogauss. Grade and Fe specifications do not confirm.
		56.50	45.22	63.80	
2.	Crushing and grinding to 100% —40 mesh, dry sizing at 100 and 200 mesh followed by LIMS and HIMS of +200 mesh products separately.	29.92	49.68	36.70	Mixture of both the sized products between 4.4 and 14 kilogauss. Poor recovery. Mixture of both the sized products magnetic at 14 kilogauss.
		46.31	47.65	54.50	
3.	Crushing and grinding to 100% —40 mesh wet sizing at 200 mesh LIMS and HIMS of +200 mesh Product only.	30.92	51.11	42.80	Magnetics between 4.4 and 14 kilogauss Fe 3.07%. Although recovery is more Fe content is more than 4%.
		46.27	49.04	61.50	
4.	Crushing and grinding to 100% —40 mesh and WHIMS.	66.67	44.80	76.40	Product does not conform, to specifications.

**Table — 4 : Details of samples response to recommended flowsheet (Fig. 1)**

Sample		Conc.			Remarks		
		% Wt.	%MnO <sub>2</sub>	%Chemical Recovery			
Sample No. 1	DROM+3 mm	62.73	82.84	71.22	Fe. 3.38	SiO <sub>2</sub>	6.27
Sample No. 2	DROM—3 mm	32.72	76.50	44.08	Fe. 3.84	SiO <sub>2</sub>	7.70
Sample No. 3	DROM—3 mm	36.07	79.61	47.28	Fe. 5.66	SiO <sub>2</sub>	5.64
Composite sample		30.92	86.12	42.81	Fe. 3.07	SiO <sub>2</sub>	7.06

## DISCUSSION :

**Dr. I. G. Thapar**

*Question 1* : What is the practice abroad for reducing silica content in manganese ore ?

*Author* : The practice abroad for reducing silica content in manganese ore are those of log washing, jigging and wet tabling. These practices remove fine cryptocrystalline silica and quartz, but silica present in the ore mineral itself as a constituent is inseparable by physical beneficiation.

*Question 2* : What are the harmful effects of presence of silica in upgraded Mn ore ?

*Author* : In this case beneficiation is attempted to produce battery grade manganese dioxide. Excess silica in this concentrate affects the battery quality.

**B. Banerjee, N. M. L.**

*Question 1* : What is the origin of the ore ?

*Author* : The ore is formed from manganiferous solution or gel and has stable phases under NTP conditions. The presence of vredenbugite in the sample indicates the temperature to be 500—700°C with slow cooling. These have been subjected to surficial oxidation condition resulting in the concentration of more pure MnO<sub>2</sub>—forms in the form of pyrolusite and cryptomelane.

*Question 2*; Whether vredenbugite exhibited any inter growth ?

*Author* : Intergrowth of jacobsite and hausmanite is seen in vredenbugite.

*Question 3* : To study the intergrowth of jacobsite and hausmanite whether any etching test is done there. What was the etching reagent used and the time given for etching ?

*Author* : Etching test was done on vredenbugite and after etching the hausmanite lamellae appeared to be more prominent. The etching reagent was hydrofluoric acid and the time given for etching was one minute.