Studies on suitability of high grade manganese ore of Bahadurgatta area, Chitradurga District, Karnataka in the manufacture of electrolytic manganese dioxide

*** M. R. Patil, * R. Nijagunappa, ** S. Prakash, *** R. R. Dixit, and * B. Somasekar.**

INTRODUCTION :

Manganese is one of the most widely distributed elements in the earth's crust. Manganese does not occur in nature in metallic form, but only in combination, usually in the form of oxide, hydroxide, carbonate, and silicate. Besides, it is an important raw material in iron and steel industry, finds use in the manufacture of chemicals and dry cells in the form of manganese dioxide. The Indian manganese dioxide ores are reported to be mostly of pyrolusite and cryptomelane and are devoid of gamma or delta form. The high grade MnO_2 of our country is unsuitable for battery manufacture because of the lack of α—MnO_2 phase in the mineral composition. Hence, the high grade ores of indigenous origin are blended with imported ore to bring them to suitable specificiations, which then give fairly satisfactory results.

In view of these problems the present investigation includes the studies on suitability, preparation, and other physical and chemical parameters of indigenous pyrolusite and cryptomelane variety of ore from Bahadurgatta area, which may be suitable for battery manufacture. The investigation is mainly concerned with the studies on suitability and preparation.

EXPERIMENTAL RESULTS :

(1) Liberation Studies :

The natural high grade manganese ore of Bahadurgatta area is subjected to liberation study, on representative samples of various size fractions.

Table — 1 : Liberation Studies

Sl. No.	Size	Total No. of particles counted	Free	Locked	Degree of liberation
1.	—22 mesh	50	12	38	24.00
2.	—44 mesh	76	25	51	32.89
3.	—60 mesh	46	22	24	47.83
4.	—100 mesh	44	31	13	70.45
5.	—150 mesh	62	47	15	75.81
6.	—200 mesh	89	75	14	84.27

From the liberation studies (Table—1) it is found that the degree of liberation increases as the size of the ore decreases.

* *Dept. of Geology and Mineral Processing, Gulbarga University, P. G. Centre, Nandihalli - Sandur 583119.*

** *Regional Research Laboratory, Bhubaneswar.*

*** *S. E. S. College, Sandur - 583119.*

(2) Chemical analysis :

Representative manganese ore sample from Bahadurgatta area is subjected to major and trace element analysis by wet chemical analysis and atomic absorption spectrophotometer. Trace elements were determined by semi-quantitative spectro-chemical analysis. Also, the manganese samples obtained by J. K. batteries, Bhopal were analysed in order to compare the chemistry with that of Bahadurgatta ore. Since the samples from J. K. Batteries are of battery grade, these are taken as standard for comparison in terms of specifications. The results of the chemical analysis are given in Table — 2.

Table — 2 : Chemical Analysis :

Constituents	Bahadurgatta ore wt. %	J. K. Batteries wt. %
MnO_2	81.65	90.0894
Fe_2O_3	6.15	1.8219
SiO_2	7.10	—
Al_2O_3	0.28	—
P_2O_5	0.02	—
Cu	0.005	0.005
Pb	0.002	0.001
Ni	0.008	0.0005
Co	Less than 0.030	0.005
As	Less than 0.01	—
Sb	Less than 0.002	—
Bi	Less than 0.002	—
Cr	0.002	—
V	0.003	—
Mo	Less than 0.0005	—
Ca	Less than 0.0005	—
Ag	Less than 0.0001	$<$0.0001
La	0.006	—
Y	0.002	—
Zr	Less than 0.002	—
Ba	0.060	—
Sr	Less than 0.050	—
Li	0.060	—
Cd	Less than 0.10	—
Moisture	0.1756	1.14

(3) Sieve analysis :

Sieve analysis has been carried out for the various fractions of the manganese ore of Bahadurgatta area and their MnO_2 and Fe_2O_3 contents were determined. The results of the sieve analysis are given in Table—3.

Table—3 : Sieve analysis of manganese ore of Bahadurgatta area.

Sl. No.	Size in mesh	MnO_2 wt.%	Fe_2O_3 wt.%
1.	—22 + 44	74.5529	7.5475
2.	—44 + 60	75.9517	8.4102
3.	—60 + 100	80.4406	6.2874
4.	—100 + 150	81.6150	5.4570
5.	—150 + 200	84.5708	5.6149
6.	—200 + 270	86.1369	4.0198
7.	—270	88.3333	5.7584

Flotation :

Representative sample of high grade manganese ore from Bahadurgatta area was crushed in jaw crusher followed by roll crusher. The product from the roll crusher was subjected to grinding in a ball mill.

Flotation technique was employed in order to upgrade the ore. pH was varied to a constant feed size of –60+100mesh. Oleic acid is used as a collector (2ml.) and pine oil is used as a frother (1 ml.) at pH 7. By this technique, the ore was upgraded from 80.4 wt.% MnO_2 to 85 wt.% at pH 7, whereas, at pH 8 the same feed was upgraded to 89 wt.% .

Tabling :

Tabling is carried out on —60 + 100 mesh feed size ore. The product assay obtained is very encouraging particularly with respect to SiO_2 , which is reduced from 7.1 wt.% to 2.1 wt.%. Further, the MnO_2 was upgraded from 80.4% to 86.5 wt.% with 75—78% recovery.

However, Fe_2O_3 content did not change appreciably by tabling.

Reduction roast :

The iron content of Bahadurgatta manganese ore when compared with the standard sample needs reduction in order to suit the specification. The iron in the ore is present in the form of hematite (Fe_2O_3) which is feebly magnetic and cannot be separated easily by magnetic separation. The magnetising reduction study is carried out in order to reduce Fe_2O_3 to Fe_3O_4 with solid carbon. The reduction study is done at 650—700°C for a period of 1 to 2½ hours. The increase in the magnetic susceptibility mainly depends upon the amount of Fe_2O_3 present in the ore and on the amount of Fe_2O_3 converted to Fe_3O_4 after the reduction. The magnetic susceptibilities of the ore before and after the reduction were determined by using E-Mettler (Zurich) standard balance. The magnetic susceptibility of the natural high grade ore of Bahadurgatta is found to be 3.149 prior to the reduction and was increased to 5.411 after the reduction.

Structural transformations :

X-ray studies were conducted using Sieman's Kristalloflex X-ray set up with a camera of 57.3 mm dia. with Cr-Kα radiation and exposure time of five hours. The principal crystal form of the natural ore was found to be of pyrolusite type (β—MnO_2). As the chemical and thermal treatment of the ore is responsible for the structural alteration in the ore, heat treatment was carried out on the ore at different temperatures and it was found that in the range of 650°–780°C, the colour of the ore has changed from black to reddish brown.

It is understood that the MnO_2 on heating at about 650°—720°C, has decomposed to form mangenese (III) oxide i. e., Mn_2O_3 .

$$4MnO_2 \xrightarrow{650°-720°C} 2\,Mn_2O_3 + O_2$$

The formation of Mn_2O_3 at 650°—720°C is responsible for the change in the structure from one phase to another. The change in the chemical composition at the above temperature is an evidence of the alteration in the structure.

In the present investigation, the manganese ore of Bahadurgatta was subjected to Differential Thermal Analysis and the thermograms obtained show an endothermic peak at 645°C. A detailed study of endothermic peak shows that the structural transformation of MnO_2 commences at 544°C. and the total transformation in the structure to the α — Mn_2O_3 has taken place at 645°C, and the transformation of the structure has been completed at 715° ± 10°C. Therefore, the authors are of the opinion that the total transformation of β—MnO_2 to α—Mn_2O_3 taken place at about 715° ± 10°C. Further work on the transformation of α—Mn_2O_3 to α — MnO_2 is under progress.

Conclusions :

1) The MnO_2 content in the Bahadurgatta ore is appreciable (81.7 wt.%) but, lower when compared to that of the standarad sample presented by J. K. Batteries (90.1 wt.%). By the flotation technique the MnO_2 content was improved by about 8%. Tabling can be applied for reducing SiO_2 appreciably (7 to 2%). Reduction roasting is favourable for reducing iron content.

2) The most harmful impurities like Sb and As are almost equal to the amount in E. M. D. and their presence is extremely low to consider them to be harmful.

3) From the present investigation, the authors are of the opinion that the manganese ore from Bahadurgatta is amenable for the treatment and conversion to E. M. D.

DISCUSSION :

S. S. Sheelavantar
I. S. M., Dhanbad

Question 1 : What are the conditions you have maintained in flotation operation ? What pH you are maintaining during flotation ? In which form did you add the oleic acid as a collector ?

Author : Conditions are used as follows :

i) Feed size .. —60+100 mesh

ii) Pulp density .. 25%

iii) Amount of collector used (Oleic acid) .. 2 ml

iv) Frother added Dow frother (improved) .. 1 ml

v) pH maintained .. 7 and 8

vi) Conditioning & collection time. .. 3 minutes.

S. T. Kulkarni
MMCL, Bombay

Question 1 : What is liberation size of MnO_2 ?

Author : Liberation size of MnO_2 is $-60+100$ mesh. In this size we get good recovery also.

Question 2 : What is liberation size of SiO_2 ?

Author : At same size.

Question 3 : How many cleanings are done and at what pulp density ?

Author : 5 to 6 cleanings at 40% pulp density.