BENEFICIATION OF FERRUGINOUS MANGANESE ORE

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It has been pointed out by Wadia[1] that the reserves of high quality manganese ores in India are fast depleting and that it is essential to utilize the poor quality ores by beneficiating them. A number of beneficiation methods for manganese ores are known but the suitability of any method depends largely upon the nature of the impurities present in the ore under investigation. Previous work in this laboratory involved highly siliceous ores[2] which were amenable to froth flotation and highly ferruginous ores[3] which required leaching with dilute acids. The ore employed for this work was from Keshapur Mines, Shimoga, Mysore State. It contained oxides of iron as the major impurity as can be seen from the results of analysis given in Table I. Trials involving magnetic separation, froth flotation and chlorination methods for its beneficiation have been carried out and the results obtained are presented in this paper.

ANALYTICAL

The analysis of the ore employed for this work was carried out by the methods indicated below:

Total manganese was determined by the Volhard's method as modified by Fischer.[4] Available MnO_2 was estimated by the well-known oxalic acid method. Silica, iron oxide, alumina and calcium oxide were estimated by the usual methods. Magnesia was estimated with 8-hydroxyquinoline. Phosphorus was estimated colorimetrically as recommended by Kitson and Mellon[5] by absorption measurements at 480 mμ, employing a Coleman Spectrophotometer for the purpose. The results obtained are given below in Table I.

EXPERIMENTAL

Magnetic separation

This process depends on the conversion of the non-magnetic hæmatite to magnetite by reduction with carbon, hydrogen or carbon monoxide at medium temperatures. At the temperature of reduction of hæmatite, however, pyrolusite also gets converted into lower oxides. In the subsequent

TABLE I

Analysis of the ferruginous manganese ore

Constituent	Percentage
MnO_2	58·35
Fe_2O_3	31·60
SiO_2	4·31
Al_2O_3	1·20
CaO	1·52
MgO	1·71
Moisture	1·23
Phosphorus	0·05
TOTAL	99·97

Mn = 36·87

magnetic separation of the two oxides, advantage is taken of the difference in their magnetic permeability.

It was found from preliminary experiments, that when the particle size of the reduced ore was between 40 and 60-mesh (Tylor standard), the magnetic separation was poor due to interlocking of the two oxide particles, whereas when the particle size was −100 mesh, much of the manganese was entrained in the magnetic fraction. Hence for magnetic separation, the particle size of the crushed ore was maintained between − 60 and + 100 mesh.

In the first set of experiments, the effect of time and temperature on the roasting of the ore with charcoal as the reducing agent was studied employing the ore analysing 33% Mn and 26·4% Fe. The crushed ore was mixed with charcoal (10%) having 80% fixed carbon. The mixture was then briquetted under pressure and dried at 110° C. in an air oven. A weighed quantity (80–100 g.) of the briquettes was placed in a nickel boat, which was subsequently introduced into a horizontal electrically heated tubular furnace made of silica. The furnace was closed at one end and the other end was connected with a water-seal to prevent atmospheric oxidation of the reduced ore. The furnace temperature was regulated by a variac and read by a calibrated thermocouple. The charge in the furnace was allowed to react for definite periods, after which the electric current was cut off and the mass in the furnace allowed to cool in an inert atmosphere. The mass was then taken out, weighed and ground in a porcelain pestle and mortar and passed on a Denver laboratory type magnetic separator. The magnetic field was maintained constant by passing a current of one ampere through the magnetic coil. The results obtained are given in Table III. In the magnetic separation, it was invariably noticed that there was some loss of material during the passage of the belt through the magnetic separator. The percentage recoveries noted in the table are calculated on the basis of the material that was recovered after passing through the separator.

TABLE II

Effect of temperature of reduction on the magnetic separation of the manganese ore

Briquettes taken = 85 g.
% charcoal in the briquettes = 10
Particle size of the feed to the magnetic separator = $-60+100$

Expt. No.	Temp. of reduction	Time of reduction	% loss in weight	% of non-magnetic fraction	Composition of non-magnetic fraction		% of magnetic fraction	Compositio of magn fraction	
	°C.	hrs.			Mn %	Fe %		Mn %	Fe
1	500	1	13·5	52·0	38·5	18·0	48·0	29·5	[illegible]
2	600	1	17·5	45·4	44·6	8·9	44·6	30·0	[illegible]
3	600	2	18·5	35·0	51·7	7·3	65·0	27·0	[illegible]
4	700	1	23·1	64·0	44·5	22·3	36·0	25·1	[illegible]

The results given in Table II show that roasting at 600° C. helps to give a non-magnetic fraction with higher ratio of Mn to Fe.

Experiments were then conducted to roast the manganese ore in presence of coke at about 1100° C. in a forge. About 250 g. of the ore (– 20 mesh) was mixed with powdered coke and the mixture was heated in a fireclay crucible for 4 hours. The charge was then cooled, crushed to – 60 and + 100 mesh and subjected to magnetic separation as before. In these experiments the recovery of the non-magnetic fraction varied between 40–50%. The results of the experiments conducted are given in Table III.

The results show that roasting of the ore between 1000–1100° C. in presence of coke does not help effectively in magnetic separation of manganese and iron.

TABLE III

Effect of high temperature roasting on magnetic separation of the manganese ore

Ore taken = 250 g.
Temp. of roasting = 1000 to 1100° C.
Time of heating = 4 hours
Size of the feed for magnetic separation = −60+100

Expt. No.	% coke mixed with the ore	Analysis of the roasted ore		Analysis of non-magnetic fraction		Analysis of magnetic fraction	
		Mn %	Fe %	Mn %	Fe %	Mn %	Fe %
1	20·0	30·3	30·3	32·0	15·6	29·1	36·5
2	38·2	29·7	26·8	14·7	12·1	30·0	31·9
3	52·5	21·4	21·1	17·2	7·7	25·3	41·6

Experiments were tried to see if reduction of the ore by hydrogen at medium temperatures could be of help in the magnetic separation of manganese and iron. For this purpose, a vertical tubular furnace was employed. In this furnace, the powdered manganese ore (− 60 + 100) was kept in a silica tube (½″ diameter) closed at the bottom and provided with a side arm at the top for the exit of the gases. The top of the silica tube was fitted with a rubber stopper carrying a thin silica tube (4 mm. diameter) through which hydrogen was passed. The ore was kept in a state of agitation by the bubbling of hydrogen. The reduced ore was cooled, weighed and subjected to magnetic separation. The results of the experiments are given in Table IV.

The results given in Table IV show that the temperature of reduction has very little influence on the Mn: Fe ratio in the magnetic fraction.

The non-magnetic fraction was reduced for a further period of one hour in the current of hydrogen at the respective temperatures employed in the previous set of experiments, cooled and again passed over the magnetic separator. The recoveries in the magnetic and non-magnetic fractions were almost equal. The results are recorded in Table V.

The results given in Table V show that reheating of the non-magnetic portion in hydrogen enhanced the percentage of manganese in the final product.

TABLE IV

Effect of hydrogen reduced ore on the magnetic separation

Ore taken = 50 g.
Time of reduction = 1 hour
Composition of the ore = 30·9% Mn and 24·03% Fe

Expt. No.	Temp. of reduction °C.	% loss during reduction	% of non-magnetic fraction	Composition of non-magnetic fraction		% of magnetic fraction	Composit of magnet fraction	
				Mn %	Fe %		Mn %	Fe
1	750	11·1	80	37·3	23·2	20	19·8	4
2	600	11·8	75	39·3	24·0	25	25·9	4
3	450	12·2	72	39·3	23·5	28	20·9	4

TABLE V

Effect of further reduction by hydrogen on the non-magnetic fraction during magnetic separation

Time of reduction in H_2 = 1 hour

Expt. No.	Temp. of roasting °C.	Composition of non-magnetic fraction		Composition of magnetic fraction	
		Mn %	Fe %	Mn %	Fe %
1	750	54·2	8·6	24·4	38·5
2	600	54·0	12·5	24·4	36·8
3	450	54·0	11·7	24·4	34·3

DISCUSSION

It is difficult to visualise the mechanism of reduction of the various oxides in the ferruginous manganese ore because the system is complicated by the presence of more than one oxide. The results of Table II, however, indicate that at 600° C., there is a fair amount of separation of manganese and iron. At this temperature, it is likely that hæmatite is converted into magnetite. It has been found by Krupkowski[6] that pure Fe_2O_3 is reduced by charcoal to Fe_3O_4 at 610° C. with liberation of heat. Pyrolusite also gets converted into Mn_3O_4 at much lower temperature (530° C.). The difference in the magnetic properties of Fe_3O_4 and Mn_3O_4 helps in the separation of the two constituents. It is difficult to say why separation was retarded at 700° C. At higher temperatures (1000–1100° C.), the separation is negligible (Table III). This is perhaps due to the formation of either ferrous oxide or a mixed oxide containing Fe and Mn.

Hydrogen reduction of the ore for one hour did not help much in the separation of iron and manganese. When the non-magnetic fraction was further reduced, reasonably good separation was effected. It is seen in Tables IV and V, that there is not much variation in the yield due to temperature (450–750° C.) of reduction. Rode[7] has studied the reduction of Fe_2O_3 with hydrogen and finds that Fe_3O_4 is formed first but the reduction of Fe_3O_4 to FeO is doubtful. It is likely that the formation of the magnetic oxide appears to be mostly responsible for improved separation of Mn and Fe.

FROTH FLOTATION

In these laboratories, Bhrany and Rao[2] have standardised conditions for beneficiation of low grade manganese ore, containing siliceous matter as a major gangue material, by the froth flotation method. These authors have recommended the use of 0·5 lb. of oleic acid as collector for pyrolusite, 0·6 lb. of sodium silicate as depressant for silica and 0·2 lb. of eucalyptus oil as frother per ton of the ore. They have also observed that a pulp density of 30% solids, with a pH of 9·5 was found to be advantageous in flotation of pyrolusite.

The above conditions were not suitable to float the pyrolusite from the Keshapur ferruginous ore, employed for this work. Efforts were, therefore, made to study the effect of alternative activators and depressants[8] on the flotation of the ore.

Experimental

Pine oil.—0·1% pine oil in alcohol was employed as frother.

Oleic acid.—0·1% alcoholic solution was used as collector. Sodium thiosulphate, sodium acetate, sodium salicylate, sodium silicate and sodium sulphide were used in flotation circuit in 0·1% aqueous solution.

Flotation cell.—The flotation cell used was similar to that described by Leaf and Knoll.[9] The cell consisted of a sintered glass filter (150 ml. capacity) fitted to a suction flask, which was in turn connected to an air cylinder through a mercury manometer. A copper trough, coated with paraffin wax and having a spout was fitted near the top of the cell to collect the mineralized froth. The pressure of the compressed air, when bubbled through the cell, was read by the manometer. The pulp was kept in motion by a mechanical stirrer during flotation.

Procedure

45 g. of powdered ore (– 60 + 100 mesh) was mixed with 150 ml. water in a glass stoppered bottle kept on a shaking machine to get a uniform pulp. The necessary depressant or activator (2 lb./ton) was added to the pulp and its pH was adjusted between 9·5 and 10 by addition of 10% sodium carbonate solution or 1N HCl. The pulp was allowed to condition for 5 minutes after which 120 ml. of it was transferred to the cell. The stirrer was set in motion and air was blown into the cell from the cylinder at a pressure of 6·0–6·5 cm. of mercury. The collector (total 2 lb./ton in three lots) was added and the pulp allowed to condition for a minute. Pine oil (2 lb./ton) was then added and the froth coming out was collected. As the froth got depleted in the cell, fresh amounts of the pulp, and the collector and if necessary, the frother were added. This process of addition was continued till all the pulp was transferred to the cell. Flotation was continued till the froth coming out had very little mineral in it. The froth was filtered, the residue dried and analysed for manganese and iron. Similarly, the tailings were filtered, dried and analysed for the same constituents.

During the process of flotation, it was found that the float varied between 10 and 15% of the feed. In Table VI, only the ratio of manganese to iron in the float as well as the tailings is given.

It is seen from the table that sodium sulphide is found to be comparatively a better reagent for flotation of manganese ore. Hence, its effect was studied in a greater detail.

Some experiments were tried to see if the above reagents could help the flotation of manganese in the reduced ore by H_2 at 600° C. It was found that there was no beneficial effect of reducing the ore. Experiments were also conducted employing cresylic acid replacing pine oil as frother but with no advantage. Sodium metaphosphate, triethanolamine and dimethyl aniline were tried in the flotation circuit, but did not improve the results. The results are given in Table VII. The process of flotation was the same as above.

The results of Table VII show that 0·2% sodium sulphide gives a float having the ratio of manganese to iron as 4·53.

TABLE VI

Effect of anionic depressants on the differential flotation of ferruginous manganese ore

Amount of pulp taken = 150 ml.
Pulp density = 30%
pH = 9·5 to 10
Depressant added = 2 lb./ton
Pine oil added = ,,
Oleic acid = ,,
Ratio of Mn to Fe in the feed = 1·15 : 1

Reagent	Mn/Fe ratio in the float	Mn/Fe ratio in the tailings	% of feed floated
Sodium thiosulphate ..	1·79	0·95	n.d.
Sodium acetate ..	1·54	1·01	n.d.
Sodium silicate ..	2·10	1·03	8
Sodium salicylate ..	2·38	0·98	11
Sodium sulphide ..	2·45	0·90	15

TABLE VII

Effect of concentration of sodium sulphide during flotation of ferruginous manganese ore

Amount of pulp taken = 150 ml.
Pulp density = 30% solids
Ratio of Mn/Fe in the pulp = 1·15 : 1
Pine oil added = 2 lb./ton
Oleic acid = ,,
Time of conditioning = 5 mins.

% of sodium sulphide added to the pulp	pH	Mn/Fe ratio in the float	Mn/Fe ratio in the tailings
0·1	10·7	2·45	0·97
0·2	10·9	4·53	0·95
0·3	11·1	1·98	1·00
0·4	11·1	1·98	1·00

Effect of pH in presence of 0·2% sodium sulphide was studied. The pH adjustment was made by addition of 1N HCl or 10% sodium carbonate solution as mentioned earlier.

TABLE VIII

Effect of pH in presence of 0·2% sodium sulphide on the flotation of manganese ore

Amount of pulp taken = 150 ml.
Pulp density = 30% solids
Sodium sulphide added = 0·2% of the ore.

Pine oil added = 2 lb./ton.
Oleic acid added = ,,
Ratio of Mn/Fe in the pulp = 1·15 : 1.

pH	Mn/Fe ratio in the float	Mn/Fe ratio in the tailings
9·0	1·18	1·14
9·5	2·45	0·97
10·0	2·55	1·00
10·5	3·90	1·01
11·0	4·53	0·95

It was found during the flotation experiments that as the pH increased the quantity of float decreased. The float obtained at pH 9 was about 15% of the feed, while at pH 11·0 it was only about 8%. The increase in pH beyond 11·0 decreased the ratio of Mn to Fe in the float. The results show that with the increase in pH from 9–11, there is a gradual increase in the ratio of Mn to Fe in the float.

Discussion

The results indicated in this section show that the ratio of manganese to iron in the float could be increased; but they are not of commercial value on account of small percentage of the float that is obtained during flotation of the ferruginous manganese ore. Since oxides of manganese and iron have similar properties, it is difficult to obtain reagents which could be employed satisfactorily in the differential flotation.

A much intensive work is needed to find out proper reagents which could help in the differential flotation of ferruginous manganese ore.

CHLORINATION

The importance of the chlorination of manganese ores will be evident because of lack of indigenous nickel for the manufacture of stainless steel in India and the possibility of replacing nickel by manganese to some extent for such purposes. This would require that manganese should be obtained in a pure form, such as could be obtained by electrolysis of aqueous solution of manganese chloride under suitable conditions. This idea gave rise to the development of the process of chlorination of low grade manganese ore at these laboratories. Another object of chlorination of the ore is to save sulphuric acid, for the manufacture of which India depends on foreign imports of sulphur. The third object of this method is the utilisation of chlorine from the electrolytic alkali industry, which cannot be expanded unless chlorine is utilised in a profitable way. It was further thought that direct chlorination will be more advantageous than hydrochloric acid leaching because iron could be sublimed off as ferric chloride from manganese chloride that is formed at the temperature of chlorination. This would help in obtaining iron-free manganese chloride.

Very little information is reported in literature regarding chlorination of manganese ore. Hayek[10] reported that in the absence of carbon, efficiency of chlorination of precipitated manganese dioxide was 6%, 20% and 42% at 320° C., 400° C. and 500° C. respectively.

Experimental

Since chlorination was carried out at temperatures not exceeding 550° C., the reaction tube (1" diameter) employed consisted of pyrex glass. Two receiver bulbs acted as traps for ferric chloride vapour coming from the reaction tube. Chlorine from the cylinder was dried over sulphuric acid and passed across a flow meter containing sulphuric acid.

The ferruginous manganese ore from Keshapur mines was crushed to—200 mesh and mixed with charcoal (containing 80% carbon) and briquetted using 1% aqueous ferric chloride solution as binder. The briquettes were dried at 110° C. to drive off the moisture, and employed for chlorination.

The chlorination proceeds according to the following reactions:

$$MnO_2 + C + Cl_2 \rightarrow MnCl_2 + CO_2 \qquad (1)$$

$$2Fe_2O_3 + 3C + 6Cl_2 \rightarrow 4FeCl_3 + 3CO_2 \qquad (2)$$

The chlorine employed was much in excess of that needed stoichiometrically for chlorination of the oxides.

20 g. of the briquettes were taken in a porcelain boat which was introduced in a reaction tube, kept in an electric furnace. The briquettes were heated to the desired temperature and dry chlorine gas (4 litres/hour) was passed through the charge for 1½ hours. During the chlorination ferric

chloride sublimed and collected in the two traps and the exit gases were allowed to escape into a chimney. At the end of the reaction, the combustion tube was cooled, the residue extracted with water and made up to a suitable volume. Aliquots were employed for the analysis of manganese and iron. The ferric chloride in the receivers and in the tube was also estimated for iron. The efficiency of chlorination both for iron and manganese was computed. The residue after water extraction was dissolved in concentrated hydrochloric acid and the solution was analysed for the two elements to find out the amount of unreacted ore The values by both the methods agreed well. The results obtained are given in Table IX.

TABLE IX

Chlorination of manganese ore

Weight of briquettes taken = 20 g.
Time of chlorination = 1½ hours
Rate of chlorine passed = 4 litres/hour
Analysis of the ore: MnO_2 = 58·35% and Fe_2O_3 = 31·6%
Carbon in charcoal = 80%

Temp. of chlorination °C.	Charcoal in briquettes %	Chlorination of Mn %	Chlorination of Fe %
350	5	55	51
	10	83	75
	15	85	75
450	5	65	56
	10	90	74·5
	15	95	85
550	5	85	83·5
	10	100	100
	15	100	100

The results given in the above table indicate that manganese and iron both get chlorinated *in toto* at 550°, when the charcoal in the briquettes is 10% and above. It is also seen that there is very little differential chlorination of manganese and iron in the ore. Analysis of the residue, however, indicated very little of $FeCl_3$ with the residue at 450° C. and 550° C., while at 350° C., nearly 30% of the $FeCl_3$ formed remained with the residue.

DISCUSSION

Calculations based on equations 1 and 2 indicate that 14·5% charcoal (80% C.) is necessary to reduce oxides during chlorination. When the temperature is raised to 550° C., it has been found (Table IX) that even 10% carbon is sufficient for complete chlorination of the mineral. This indicates that at elevated temperatures part of the chlorination can proceed even in the absence of carbon as noticed by Hayek.[10]

GENERAL CONCLUSION

Although the investigations described in this paper are preliminary in character, yet they indicate the possibility of beneficiation of the manganese ore by magnetic separation. But in this case, the reduction involves the use of hydrogen which may prove expensive when the process has to be employed on a large scale. Although chlorination effects practically complete separation, yet the commercial development of this method would depend upon the requirement of large quantities of manganese chloride for industrial purposes. The recovery by froth flotation being very low, the method is not feasible for commercial exploitation.

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