

# RECENT RESEARCHES ON THE DRESSING OF LOW-GRADE MANGANESE ORES IN INDIA

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## Abstract

A case for the conservation of mineral wealth of India by banning selective mining has been made out. The necessity of beneficiating low-grade manganese ores is emphasized. Results obtained on several ores of different types are given and their beneficiation methods have been indicated. Exhaustive beneficiation tests have shown that enrichment to about 48 per cent Mn can be obtained with good recovery. Garnet can be removed by electrostatic separation. Fundamental studies on the flotability of manganese mineral or garnet to effect concentration are being conducted to examine the possibilities of flotation method of concentration.

**M**INERAL industry plays an important part in the economy of any industrialized nation. With the increasing industrialization of India, mineral production has been showing a steady increase in recent years, the total value of the minerals produced during 1951 being estimated at over Rs. 1,05,86,00,000, as compared to Rs. 83,41,00,000 for the previous year. Coal accounts for about 50 per cent of the total, but it is followed by manganese ore with 17 per cent by value and with a production of 12,83,929 tons in 1951. Except for a small quantity used up by the indigenous iron and steel industry, manganese ore is at present mostly exported in the raw state.

Proper conservation of the mineral wealth requires that all workable low-grade ores should be concentrated and utilized, if possible, instead of working only the higher grade deposits. The First Five Year Plan of the Government of India correctly lays emphasis on this aspect and calls for a systematic study by various organizations of the

country's reserves of the strategic minerals, and development of suitable methods for concentration of low-grade ores to enable such deposits to be exploited. It is also stressed that the policy regarding the important minerals of India, e.g. mica, manganese and chromite, which are at present mined largely for export, should be to convert them into finished or at least semi-finished products for export purposes. Beneficiation of metallic ores, as well as non-metallic minerals, which is a primary requisite to the proper conservation of the mineral wealth, has been entrusted to the National Metallurgical Laboratory, in collaboration with the Indian Bureau of Mines. The latter with its field staff is to arrange for representative samples for test purposes to be sent to the National Metallurgical Laboratory and this Laboratory is to undertake detailed test work alone or jointly with the Bureau of Mines to find out whether the ore can be concentrated to a marketable grade and, if so, to work out the most economical method for the purpose to recommend suitable machinery and to undertake, when required, continuous test work in the small pilot plant of the Laboratory.

Up to the present, only the higher grade deposits of manganese ore have been worked. Nevertheless, not all the manganese ore exported conforms to the metallurgical standard given below:

GRADE	ASSAY, PER CENT				
	Mn	Fe	SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub>	P	Cu+Pb+Zn
Standard	48.0	6.0	11.0	0.12	—
Minimum	40.0	16.0	15.0	0.30	1.0*

\*Not less than 0.25 per cent Cu.

For every ton of high-grade ore (over 48 per cent Mn) produced and marketed, it is estimated that about 1 ton of low-grade ore has also to be mined which generally goes to the dumps as it has no market. Due to the present very heavy overseas demand for the commodity, even low-grade ores of about 35 per cent Mn are temporarily being exported. Even so a 35 per cent Mn ore fetches only about Rs. 35 per ton as compared to about Rs. 155 for a 48 per cent grade. There is thus in the case of manganese ores a special case for the implementation of the policy laid down by the Planning Commission in respect of the utilization of low-grade ores.

Manganese ores in general are not very easy to concentrate due to the large variety of manganese minerals which may be present and to the difficulty encountered in eliminating certain types of gangue minerals which often occur. Flotation, which has revolutionized the mineral industry in the field of many metallic and of some non-metallic minerals, like phosphates, graphite and fluorospar, has not yet developed to the stage when it can be applied with success to all types of manganese ores for want of reagents which would effect selective flotation of manganese minerals. In fact, the only ores of manganese which are comparatively easy to float are the carbonate ores which are not common in India. The oxide ores float well with fatty acid, but the presence of interfering gangue slimes and soluble salts, as well as of gangue minerals like iron oxide and garnet which are common in Indian ores, presents a difficult problem. In most cases good recovery may be obtained with a deslimed feed, but a high-grade concentrate is difficult to obtain. Flotation of siliceous gangue minerals employing cationic reagents is possible, but its application would be limited due to the high cost of the reagent and the availability of the cheaper tabling method that could be employed for treating such ores.

As manganese ore is a low-priced commodity, any treatment to be worked out for the concentration of the low-grade ores must be

cheap and should not normally involve more than two separating processes. This is particularly true because the concentrate from the milling plant will be in the form of powder which will finally need sintering or pelletizing to make it suitable for metallurgical purposes or for marketing. Moreover, although there are a few large producers of manganese ores in India, the remaining production comes from small mines which cannot afford to have costly plants for upgrading their low-grade ores. The requirements of these producers have, therefore, to be kept in view when testing possible concentration methods.

The National Metallurgical Laboratory, which started functioning towards the end of 1950, has already done a fair amount of work on the dressing of a large variety of Indian low-grade ores, including manganese ores. The results of research reported below are those obtained by the staff of the Ore-dressing & Mineral Beneficiation Division of the Laboratory working either alone or jointly with the staff of the Indian Bureau of Mines.

The work so far done has shown that the low-grade manganese ores in India can be divided into the following categories from the mineral-dresser's point of view:

- (i) Ores which contain principally quartz or other light gangue minerals
- (ii) Ores containing appreciable quantities of garnet
- (iii) Ores high in iron
- (iv) Ores high in phosphorus
- (v) Ores combining features (i) to (iv) or selections thereof.

For each of the categories of ores (i) to (iv) a treatment for elimination of the gangue concerned should be able to be specified, but the treatment becomes more complex with the presence of gangue from other categories, as in (v). Ores falling under category (i) are the easiest to concentrate by gravity methods—jigging, tabling, heavy-media separation (when conditions are favourable), etc. They occur in some parts of Madhya Pradesh, Western India, Orissa and South India.

Separation of garnet from manganese ores (category ii) is somewhat difficult, because the specific gravity difference is small and the magnetic properties of garnet and manganese minerals are also somewhat similar. Flotation is not yet a success for the separation of garnet, but it has been found in the National Metallurgical Laboratory that electrostatic separation does effect a good separation and is perhaps the only method that could be employed with success. This type of ore is common in Madhya Pradesh and in the area near Visakhapatnam. Category (iii) of ore, viz. high in iron, occurs mostly in Orissa and in some parts of Madhya Pradesh, South India and Bombay. Separation of ferruginous gangue from manganese minerals is usually very nearly impossible by ordinary ore-dressing methods, and is especially so when they have nearly the same magnetic susceptibility, but separation is possible in some cases by giving a reducing roast to convert the iron oxide to the magnetic state and following this by magnetic separation for the removal of magnetic oxide of iron. Alternative methods of concentration include matte smelting and sulphating by heating with  $\text{SO}_2$  or ammonium sulphate, as well as thermal methods to reduce the iron to the metallic state and bring the manganese into the slag. High-phosphorus ores (iv) are common in the Madhya Pradesh and Bombay. Reduction of the phosphorus content to the metallurgical grade is comparatively easy when it is present in the form of apatite, or other phosphorus mineral, that is freed by a coarse grind. This, however, is seldom the case, and phosphorus is almost invariably intimately associated with the manganese minerals. The results obtained in the National Metallurgical Laboratory, with some of the samples tested, are given below:

1. *Sample from Kachidhana Mines, Madhya Pradesh*—The sample as received assayed Mn, 41.6;  $\text{SiO}_2$ , 14.6; Fe, 8.46 and P, 0.2 per cent. The manganese minerals present were braunite, psilomelane and pyrolusite, the gangue minerals being jaspery quartz, iron-stained

quartz and some garnet. This sample thus falls roughly into category (i) being a medium grade manganese ore containing silica as the principal gangue. The silica starts to be liberated at a coarse grind, viz. about 10 mesh, and liberation is complete at about 35 mesh.

Jigging followed by tabling, as well as straight tabling, has yielded concentrates of about 48 per cent Mn with recoveries of 70 per cent and over. As the garnet content in the ore is low, it has not affected the grade of concentrate though most of it has come into the concentrate. Straight soap flotation at a pH of about 8.5 has yielded a concentrate of about 47 per cent Mn with a recovery of 74 per cent. This is a fairly simple ore and, due to the high silica content, gravity as well as flotation has given good results so far as manganese concentration is concerned. The ore does not really fit category (i); it is rather phosphoric. The phosphorus is intimately associated with the manganese minerals as well as with the gangue. Phosphorus in the concentrate is almost the same as in the original ore, viz. 0.19 per cent.

2. *Sample from Mansar Mines, Madhya Pradesh*—The sample as received assayed Mn, 32.67;  $\text{SiO}_2$ , 27.48; Fe, 10.13 and P, 0.46 per cent. The manganese minerals present were essentially braunite with a fair amount of psilomelane and a little pyrolusite, and the gangue minerals were quartz, mica, barite, apatite, rhodonite and calcite. The high silica in the ore present as quartz and the absence of garnet indicated that the manganese content of the ore should be comparatively easy to concentrate, but the phosphorus content is very high (0.46 per cent), present as apatite.

Most of the manganese minerals in the ore were fortunately found to be magnetic. Jigging followed by tabling as well as straight tabling have both yielded concentrates of over 48 per cent Mn, with recoveries of about 68 per cent, but high in phosphorus, viz. about 0.25 per cent. As the manganese minerals are magnetic and the phosphorus

is mainly present in apatite, a good amount of the phosphorus could be eliminated as a non-magnetic residue. The magnetic portion when tabled yielded a high-grade concentrate assaying about 49 per cent Mn with a recovery of about 65 per cent. Phosphorus in this concentrate was only 0.16 per cent. Magnetic separation followed by flotation of the magnetic product yielded a concentrate assaying 48.5 per cent Mn, and 0.13 per cent P with an overall recovery of 63 per cent.

The magnetic portion of the ore containing almost all the manganese could also be floated, using controlled addition of fatty acid, where by a first froth high in phosphorus could be removed and the manganese subsequently floated by further addition of collector.

3. *Sample from Shivrajpur Syndicate, Bombay* — A sample of low-grade manganese fines produced from the underground mines of the Shivrajpur Syndicate Ltd. assayed Mn, 36.5; Fe, 10.25;  $Al_2O_3$ , 6.94;  $SiO_2$ , 19.07 and P, 0.38 per cent. Psilomelane was the predominant manganese mineral with minor amounts of pyrolusite and braunite. The gangue minerals present were quartz, decomposed feldspar, limonitic clay, and ochre. Silica and phosphorus were high but iron comparatively low. Gravity separation was indicated for elimination of silica, because a good amount of the manganese minerals was free even in the coarsest size received. Jigging of the coarse size followed by tabling of the fines yielded a concentrate assaying 46.3 per cent Mn (0.28 per cent P) with a recovery of 74.5 per cent. When heated to about 900°C., the grade of the concentrate was found to improve to about 51 per cent.

As heating improves the grade by 4-5 units, higher recovery is to be aimed at during gravity treatment, in spite of a lower grade, because sintering will presumably have to be done with fine products. A concentrate of grade about 48 per cent Mn could be obtained with a recovery of 75 per cent by straight tabling. This concentrate should improve in grade to over 52 per cent by sintering.

The phosphorus in the gravity concentrate was high and it was intimately associated with the manganese minerals so that further reduction by magnetic separation or flotation could not be effected.

4. *Sample from Tirodi Mines, Madhya Pradesh* — The sample as received assayed Mn, 27.39;  $SiO_2$ , 33.4; Fe, 17.4 and P, 0.36 per cent. The principal manganese minerals in the ore are braunite and psilomelane with small amounts of pyrolusite and vredenburkite. Garnet and quartz are the main gangue minerals. The high silica content suggested gravity methods of separation, but gravity concentrates were always found to be of low grade (40 per cent Mn) due to contamination with garnet. As manganese minerals were found to be magnetic, the ore ground to -20 mesh was passed through a magnetic separator, yielding three products, viz. strongly magnetic, feebly magnetic and non-magnetic. The strongly magnetic product, which was high in iron, had to be ground to -100 mesh to remove vredenburkite, a low-manganese and high-iron-bearing mineral. The feebly magnetic fraction containing large amounts of garnet had to be passed through electrostatic separator for elimination of garnet. The above operations yielded a combined concentrate of grade 45.41 per cent Mn and 0.27 per cent P and low iron with a recovery of 51 per cent manganese. Heating of the concentrates close to the sintering temperature raised the grade to over 48 per cent Mn. As braunite was the predominant manganese mineral in the ore, the concentrates were rather high in silica. Phosphorus in the concentrates could not be brought down to the metallurgical grade due to its intimate association with the manganese minerals.

5. *Sample from Kharsawan Mineral Concerns, Madhya Pradesh* — A sample of manganese ore from Messrs Kharsawan Mineral Concerns Ltd., Barajamda, was received from the Director, Indian Bureau of Mines, to develop a cheap method of eliminating silica from the ore so that small mine owners

could make use of this method for concentrating high-silica manganese ores. The sample as received assayed Mn, 36.18; Fe, 6.44 and  $\text{SiO}_2$ , 27.23 per cent. The sample contained quartz as the principal gangue and it appeared to be free at a coarse grind. It was crushed to  $-10$  mesh and screened into three products, viz.  $-10 + 20$ ,  $-20 + 48$  and  $-48$  mesh. The three fractions were tabled separately. The concentrates obtained from the above tabling operation were mixed and found to assay 47.37 per cent Mn with a recovery of 66.7 per cent. The recovery could be improved in practice by careful grinding without production of too much slime.

As the ore is fairly soft, crushing to the above size can be done by small mine owners in a *chakki* with the help of a pair of bullocks. Hand-screening could be employed and only a shaking table would require to be installed which would cost about Rs. 10,000-12,000. Though not very efficient, this method of concentration could be employed by small operators on a modest scale with small capital, but only when the ore is soft and has siliceous gangue.

6. *Sample from Garbhum Dumps, Chipurupalle, Madras* — The sample of ore assayed Mn, 25.82; Fe, 10.89; P, 0.13 and  $\text{SiO}_2$ , 25.16 per cent. The manganese minerals present were psilomelane and wad, the gangue minerals being quartz, limonite, garnet and gypsum. It was interesting to observe that the garnet was present only in the  $-20$  mesh fraction of the ore. Rejection of this  $-20$  mesh fraction, followed by jigging of the coarse product ( $-6 + 20$  mesh), yielded a concentrate assaying 48.25 per cent Mn with a recovery of 28.2 per cent. When the jig tailing was crushed to  $-14$  mesh and again jigged, it produced more concentrates yielding a total recovery of about 60 per cent in a concentrate of grade 48 per cent Mn. In another test, comprising tabling of the ore followed by electrostatic separation for separation of garnet, a concentrate assaying 47 per cent Mn was obtained with a recovery of 70 per cent.

This is yet another type of sample which appears to be complex from the point of mineral dressing because of the presence of garnet.

*Ores High in Iron* — An ore high in iron was received from the Tata Iron & Steel Co. Ltd. It assayed Mn, 26.8; Fe, 28.8 and  $\text{SiO}_2$ , 6.67 per cent. The silica was present as fine quartz and clayey matter and could be separated by washing with water and wet classification or screening of the fines to yield a washed product containing about 2.5 per cent  $\text{SiO}_2$ . Straight magnetic separation was not successful in separating the iron from the manganese minerals at 10 mesh. Reduction roast at about  $550^\circ\text{C}$ . was found to convert readily most of the iron to the magnetic form which could be removed by a magnetic separator. By this method using washed ore, concentrates of grades between 59 and 62 per cent Mn (Fe varying from 7.5 to 3.5 per cent) could be obtained with recoveries ranging from about 66 to 50 per cent respectively. The results obtained with unwashed ore were not as good as those obtained with washed ore. By another combination of ore-dressing methods, involving no thermal reduction, a concentrate assaying 47 per cent Mn and 9 per cent Fe was obtained with a manganese recovery of 65 per cent. Flotation tests are also contemplated to see whether the manganese minerals can be selectively floated from the ferruginous minerals.

A reference is invited in this connection to a paper recently read before the Mining, Geological & Metallurgical Institute of India by Dr. P. K. Ghosh and others on the 'Beneficiation of Low-grade Manganese Ores of Orissa'. Out of the eleven samples tested by them on a laboratory scale, two were low in iron, but the rest were high, ranging from about 11 to 45 per cent. Reduction roast at  $600^\circ\text{C}$ . employing coal gas, followed by magnetic separation for removal of iron, has been reported to yield high-grade concentrates assaying between 50 and 62 per cent Mn with good recoveries, except in the case of three of the samples. The results reported are

interesting and it is our intention to proceed along these lines, but using cheaper reducing agents.

Work is also in process in the Research Laboratories of the Tata Iron & Steel Co. Ltd. on the concentration of ores high in iron.

### Conclusion

The time has come when suitable measures should be taken in the interests of conservation of mineral wealth to ban selective mining, and the manganese mining industry in India, in particular, ought to start beneficiating their economically workable low-grade ores *in situ*, as well as that lying in dumps. Steps have been taken to do detailed test work with low-grade ores from various parts of India and a good start has been made by the National Metallurgical Laboratory jointly with the Indian Bureau of Mines to collect detailed information about the characteristics of the various types of ores, from the point of view of mineral dressing.

Almost all the samples tested so far have been capable of concentration to about 48 per cent Mn with fairly good recoveries by the conventional ore-dressing methods. It has been found that garnet, which is present in the ores derived from the gondite and kodurite series, viz. in the Madhya Pradesh and Visakhapatnam areas, can be successfully separated from the manganese minerals by electrostatic separation, which is new in the beneficiation of manganese ores. It remains to be seen to what extent flotation can be employed for beneficiating manganese ores in general, and separation of garnet in particular.

Till more selective reagents are available, it is felt that flotation will only have a limited scope in India in this field. Work is, however, in progress in the National Metallurgical Laboratory from the fundamental aspect, by measurement of contact angle on the surfaces of garnet and manganese minerals, to determine whether suitable conditions can be laid down for the selective flotation of garnet from

the manganese minerals, or vice versa. The economics of the process, if new reagents are involved, will have to be watched closely.

It is gratifying to learn that the Central Provinces Manganese Ore Co. Ltd. is installing two heavy-media plants for treating their boulder deposits which are amenable to this treatment and one of the plants has perhaps already started operations by now. Throughout the work at the National Metallurgical Laboratory, the requirements of the small mine owners are being kept constantly in view during laboratory testing, so that when a simple siliceous ore or other type requiring simple treatment is encountered, the concentration of such ores could be done by them with equipment improvised locally as far as possible, though they may not be very efficient. It should also be borne in mind that a considerable proportion of the manganese ore produced in India is not capable of treatment in simple plant, and yet comes from small operators who cannot afford to put up costly milling and sintering plants. It may thus be necessary for the Central Government to make arrangements to put up custom mills in centrally located places, where the small mine owners can get their ores concentrated and sintered. The custom mills may be suitably designed to treat single type of ores occurring in a restricted locality.

With more and more information being made available to the industry about the characteristics of the different low-grade manganese ores in India, it is hoped that more beneficiation plants will be installed in due course for the benefit of the industry and the country at large.

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