

INDIAN MANGANESE ORE INDUSTRY AND SCOPE FOR ITS DEVELOPMENT

B. R. NIJHAWAN

Deputy Director, National Metallurgical Laboratory, Jamshedpur

Abstract

In this short paper are reviewed the reserves of Indian manganese ores and their quality. Emphasis has been laid on different possibilities of their exploitation for the manufacture of ferro-alloys in this country and export of the latter in preference to that of raw unprocessed manganese ores. Mineral upgrading by ore-dressing methods of low-grade manganese ores has been referred to, followed by the possibilities of their thermal beneficiation for the production of ferro-manganese. In this connection the efforts of countries deficient in manganese mineral to tap all possible sources of manganese, such as recovery from steel slags, manganiferous iron ores, etc., have been discussed.

Introduction

EXCLUDING Russia, India probably ranks as the world's largest supplier of high-grade manganese ore. Next in order lie the high-grade manganese ore deposits of the African continent on the Gold Coast and in South Africa and also those of Brazil. The incessant demands for manganese ore made by overseas markets in U.S.A. and Europe have been largely met by the export from this country of raw unprocessed ore of high grade — a rather uneconomic proposition, even though India earned nearly Rs. 21 crores through the export of 1.4 million tons of manganese ore during 1952. Most recent estimates figure the reserves of high-grade manganese ores in India at about 60 million tons against the previously accepted figure of 25 million tons, with much greater reserves of the sub-standard grades of these ores. The sub-standard grades have hitherto been chiefly neglected or wholly discarded and the advisability of imposing statutory restrictions for the mining of high as well as low-

grade ores in a certain ratio appears a national necessity. The indigenous manufacture of exportable grades of ferro-manganese in place of large shipments of raw ore should be regarded as of utmost national importance. This could be supplemented by the commercial production of electrolytic manganese and manganese dioxide. Initially the fullest possible scientific and industrial exploitation of this national mineral asset should be attempted.

Forms and Uses of Manganese

The different forms and grades in which manganese finds applications in metallurgical industries are the electrolytic manganese, low and high-carbon ferro-manganese, medium and high-carbon ferro-manganese, standard ferro-manganese, spiegel or spiegeleisen, silico-manganese, silico-spiegel, etc. Typical analyses of these are given in Table 1.

Silico-manganese can be made in different grades, but the grade that satisfied almost any requirement contains 65-70 per cent Mn, 17-20 per cent Si, 1.5 per cent C (max.). Silico-spiegel, a product of the blast furnace, contains 17-22 per cent Mn and 6-12 per cent Si (guaranteed) besides carbon 1.3 per cent, phosphorus 0.07 per cent and balance iron. Silico-ferro-manganese is the name applied to it when higher in manganese such as 60-80 per cent Mn, 20-25 per cent Si, with varying percentages of carbon, iron and aluminium.

Manganese is one of the most important raw materials of metallurgical industries, the iron and steel industry being wholly dependent upon it in one form or the other. About

TABLE 1

	Mn, %	Fe, %	C, %	Si, %	P, %	S, %	
Standard ferro-manganese	78-82	12-16	6-8	1.0 max.	0.30-0.35 max.	0.05 max.	
Low-carbon ferro-manganese	1	90	—	0.07 max.	1.0 max.	0.06 max.	0.05 max.
	2	80-85	—	0.10 max.	1.0 max.	0.20 max.	0.05 max.
	3	80-85	—	0.20 max.	1.0 max.	0.20 max.	0.05 max.
	4	80-85	—	0.30 max.	1.0 max.	0.20 max.	—
	5	80-85	—	0.50 max.	1.0 max.	0.20 max.	—
	6	80-85	—	0.75 max.	7.0 max.	0.25 max.	—
Medium-carbon ferro-manganese	80-85	—	1.50 max.	1.5 max.	—	—	
Spiegeleisen or spiegel (alloy of iron and manganese)	1	16-19	—	6.5 max.	3.0 max.	—	—
	2	19-21	—	6.5 max.	3.0 max.	—	—
	3	26-28	—	6.5 max.	1.0 max.	—	—
Electrolytic manganese	99.98	0.001 max.	0.004	nil	—	—	
Manganese metal thermit	95-98	2-2.5	0.06-0.20	1-1.5	—	—	

96 per cent of the manganese ore produced annually is used for metallurgical industries, the balance finding use in dry batteries, chemical, ceramic, glass and paint industries. Manganese ores used in the making of dry cells should contain 80-85 per cent of MnO_2 , less than 1 per cent iron and be free of such electro-negative metals such as Cu, Ni, Co and As.

The functions of manganese in steel-making in which it is used to the extent of about 95 per cent of its total production are three-fold: (1) deoxidation of steel, (2) control of carbon content commonly known as recarburization, and (3) for alloying purposes in different amounts to improve hot-workability and mechanical properties. In greater amounts from 11 to 13 per cent manganese is used in Hadfield austenitic manganese steels, manganese-rich stainless steels, etc. In low-alloy structural steels it materially improves the mechanical properties in relation to its transition temperature ranges from ductile to brittle failure. This is achieved by increasing the manganese-carbon ratio in the steel.

Manganese also plays an important part in certain non-ferrous alloys, although its

consumption in these fields represents an exceedingly small proportion of its total utilization. Such uses include the alloys, manganese, bronze, nichrome, monel metal, german-silver, manganin, duralumin, invar, E-alloy, K.S. Piston alloy, etc. In non-ferrous alloys, however, the conventional ferro-alloys of manganese cannot be employed in view chiefly of their iron contents. Until recently manganese from thermit process or by carbon reduction could be used where iron only was chiefly undesirable. Thermit process, however, is very expensive and carbon-reduced manganese contains fairly high carbon contents. This is where electrolytic manganese 99.98 per cent pure has come into the forefront being of extremely high purity and less costly than thermit manganese. Owing to its present high cost of production, it cannot replace ferro-alloys in all ferrous metallurgical uses of manganese. But in the manufacture of non-ferrous alloys and certain types of manganese-rich low-carbon austenitic stainless steels the electrolytic manganese can hold its own both in respect of cost factors and the quality of the final product it goes to make.

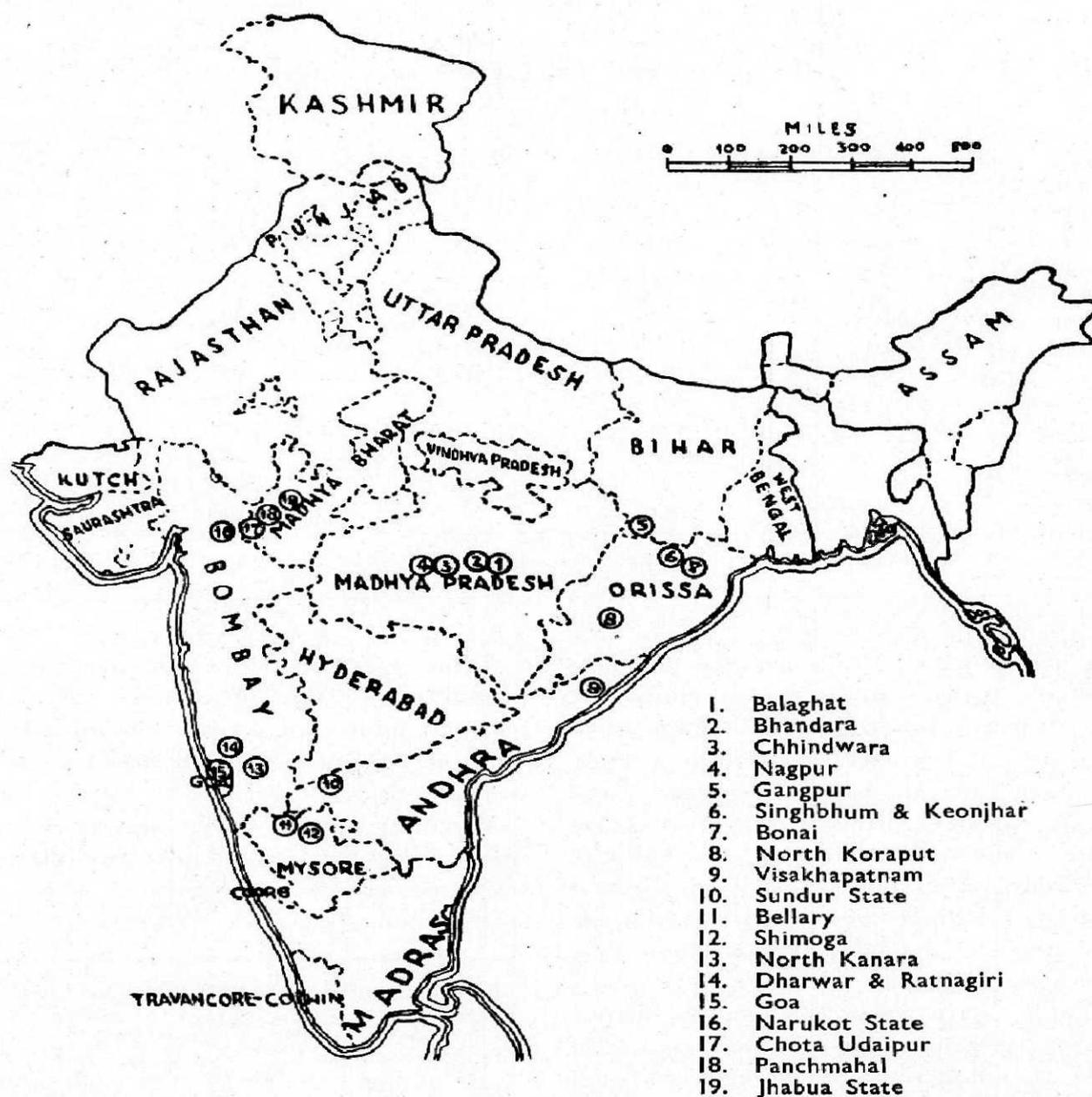


FIG. 1 — MAP SHOWING MANGANESE ORE LOCALITIES IN INDIA

Indian Reserves of Manganese Ores

The locations of manganese ore deposits in India are shown in the map above.

Deposits at present being worked are in Singhbhum (Bihar); Panchmahal

(Bombay); Balaghat, Bhandara, Chhindwara, Nagpur (Madhya Pradesh); Indore (Madhya Bharat); Visakhapatnam, Sundur (Madras); Shimoga (Mysore State); Bonai, Keonjhar, Koraput (Orissa), Patna State and Banswara (Rajasthan). Ore supplies are

TABLE 2 — WORLD MANGANESE ORE PRODUCTION AND STOCKS

(Thousands of long tons)

YEAR	STEEL OUTPUT	Mn ORE OUTPUT	Mn ORE REQUIRED	Mn ORE SURPLUS APPROX.	CUMULATIVE SURPLUS APPROX.
1924	77256	2282	1866	416	416
1925	88756	2628	2143	485	901
1926	90931	3196	2196	1000	1901
1927	98781	3497	2386	1111	3012
1928	109789	3038	2651	387	3399
1929	118208	3780	2855	925	4324
1930	93430	3458	2256	1202	5526
1931	68031	2278	1643	635	6161
1932	50012	1269	1208	61	6222
1933	67081	1797	1620	177	6399
1934	80797	2918	1951	967	7366
1935	97887	4035	2364	1671	9037
1936	124794	5266	3014	2252	11289
1937	135317	6024	3268	2756	14045
1938	107157	5116	2588	2528	16573
1939	132857	5000	3208	1800	18400
1940	143430	5000	3464	1500	19900

abundant. Madhya Pradesh alone produces more than 70 per cent of the ore mined in India. Further investigation of manganese ore deposits in Bombay, Kalahandi district, Bonai, Gangpur, Mayurbhanj (Orissa) and Balaghat district formed part of the programme of the Geological Survey of India in recent years and there have been reports that the G.S.I. have recently discovered extensive deposits in Balaghat (Madhya Pradesh), Kalahandi and Bihar.

In Table 2 are given the world's output figures of steel and manganese ore from 1924 to 1940, the manganese ore required for each year's steel output (at an average rate of consumption of 54.1 lb. of manganese ore per ton of steel made), the surplus of production over the indicated consumption need and the cumulative total of the surplus. The indicated use of 54.1 lb. of manganese ore per ton of steel made appears high. The average consumption of manganese per ton of steel is about 12-15 lb. It is a matter of speculation if the shown cumulative surplus did in fact accumulate.

Table 3 gives the annual manganese ore production of India up to 1950. The corresponding figures of production for 1951 and 1952 are about 1.28 and 1.4 million tons respectively.

Table 4 gives the estimated Indian reserve of manganese ores in relation to world resources.

TABLE 3 — MANGANESE ORE

YEAR	MINE	DOMESTIC	EXPORTS
	PRODUCTION	CONSUMPTION	
	Tons	Tons	Tons
1940	368918	82690	737735
1941	791269	103146	568980
1942	757269	85181	712424
1943	595365	47858	151621
1944	370980	43619	171276
1945	209583	54807	476447
1946	252916	54064	597677
1947	451034	78106	367750
1948	528876	51877	613907
1949	645825	79264	600204
1950	882929	69325	808221

TABLE 4

COUNTRY	PER CENT OF WORLD PRODUCTION	RESERVES OF MANGANESE ORE (million tons)
U.S.S.R.	50	250-600
Tchiaturi	—	100-150
Nikopol	—	100-400
Various	—	50
India	20	At least 150
Gold Coast	10	„ „ 13
Brazil	5	„ „ 45
South Africa	5	Probably more than 1000

The price of high-grade manganese ore before World War II varied from Rs. 15 to 20 per ton at ports as against the prevailing price of Rs. 100-200 per ton at any one time. The prices also vary according to grade, rising sharply for every unit of manganese, above, say, 45 per cent. There has been a marked tendency, therefore, to pick and choose the ore that fetched lucrative prices, the inferior grades being relegated to the background. The general trend of prices which Indian ore fetched in the dollar area until recently is given below:

Quality % Mn	Price in dollar/ton
46-48 ...	46
43-44 ...	38
42 ...	34
38-40 ...	26
32-26 ...	14

Ores with 48 per cent Mn and over are regarded as first grade, with 45-48 per cent Mn

as second grade and below 45 per cent Mn as third grade. A recent specification dated January 8, 1953, concerning manganese ores issued by the U.S. Bureau of Mines (General Services Administration) sets forth the following chemical requirements for delivery to national stock piles in U.S.A.:

<i>By weight (dry basis)</i>	
	%
Manganese (Mn)	40.0 min.
Iron (Fe)	16.0 max.
Silica plus alumina (SiO ₂ plus Al ₂ O ₃)*	...
Phosphorus (P)	0.30 max.
Copper plus lead plus zinc (Cu plus Pb plus Zn) †	1.00 max. †

Comparison of average chemical analyses of some of the important manganese deposits of the world is given in Table 5.

The Mn-Fe ratio of manganese ores of four major world production centres is: U.S.S.R., 40-60; India, 5.5-7.5; Gold Coast, 10-13; and Brazil, 12-13.

In India, it is roughly computed that for every ton of high-grade manganese ore mined, there remains discarded at the mine site over 1-2 tons of low-grade ore. High-grade manganese ore is generally handpicked by mass labour from the manganese ore burden after blasting in open-cast mining, leaving the low-grade manganese ore with small prospects of commercial utilization at the mine face. Deposits of high-grade manganese

*No limit specified, but material over 15 per cent will be purchased in exceptional cases only.

†Of which not more than 0.25 per cent may be copper.

TABLE 5

	Mn, %	Fe, %	SiO ₂ , %	P, %
Madhya Pradesh (India)	48-56	7.8-2	4.5	0.09-0.13
Orissa (India)	45-54	6-9	3-4	0.03-0.15
Georgia (U.S.S.R.)	52	0.8	0.2	0.18
Nikopol (U.S.S.R.)	38-46	1.0	12.0	0.12
Gold Coast (Africa)	48-52	4-6	3.5	0.1 max.

ores in India are not inexhaustible. It is, therefore, necessary in national interests to develop ways and means for the commercial utilization of low-grade manganese ores. It has been reported that one single large producer-exporter of manganese ore in Madhya Pradesh has accumulated over six million tons of such low-grade ores at the mine face over the past decades lying as waste. Large dumps of ore wastes have likewise been accumulated in close proximity of other mines. This material, which so far has been deemed useless, has got to be turned into a national asset by all possible scientific methods at our disposal. To the Indian mine owner selective mining to meet the quality requirements of foreign buyers is comparatively easy as a result of cheap mass labour available for handpicking the richer grade.

Manganese ore with a manganese content below 30 per cent is not exportable. Because of the leaching effect of heavy monsoon rains upon manganese ore, top layers of manganese deposits are gradually deteriorating in their metallic manganese content which is wandering down to lower layers.

To convert reject low-grade ores into high grade, simple upgrading operations will have to be undertaken. We are fortunate in this respect inasmuch as contaminating elements are often easily separable. Many of our manganese ores are metallic oxides contaminated mostly with silica and alumina, with a little calcium and magnesium oxides, constituents which lend themselves to water treatment, gravity separation and in some cases to flotation processes, so that by the well-developed methods of washing, water-sizing or classification, jigging, etc., major parts of unwanted components can be separated. The aim is to get at a concentrate of exportable quality depending upon the chemical and physical structure of the ore; in most cases a simple flow sheet of upgrading operations can be evolved. Usually, ores in reject and weathered dumps may not require extensive crushing, but should the

contaminating impurities run through the ore in a fine network, crushing would be necessary, following which one of the many different types of washing machines might give spectacularly good results. On the basis of relevant data concerning the analyses and mechanical structure of impurities, further water-concentration methods like jigging, gravity separation, etc., might be most usefully employed. Metallic oxide particles of fine structure may entail flotation operations. Extreme fines of manganese concentrates may eventually be used in powder form for chemical purposes. In this case, however, the dioxide content of the concentrates has to be raised to at least 80 per cent MnO_2 or above to meet accepted standards. Another aspect of upgrading is the possibility of making commercial use of separated main contaminants like silica and alumina. These might, after suitable purification, be employed for refractories or put to other electro-metallurgical uses. The manganese-iron ratio can be improved by magnetic separation of the magnetic oxides of iron following reduction-roast treatments. Work on upgrading of low-grade manganese ores is being conducted at the National Metallurgical Laboratory.

Ferro-manganese Manufacture

The necessity of manufacture of ferro-manganese in India instead of exporting raw unprocessed manganese ores has been discussed on different platforms several times during the last two decades. Manganese is a 'must addition' in the manufacture of all steels, without which steel usually cannot be made. It is a conditioning as well as an alloying element. It is added as ferro-manganese of high or low-carbon grade depending upon the steel being made (Table 6).

The metallurgical functions of ferro-manganese in general are:

1. As an essential constituent of certain cast irons.

TABLE 6

	Mn, %	Si, %	C, %	P, %	Fe, %
High-carbon standard ferro-manganese	78-82	0.5-1.5	6-8	0.35 max.	15-19
Low-carbon standard ferro-manganese	80-85	1.0 max.	0.3 max. to 1.0 max.	0.15-0.25	Balance

2. As a desulphurizing agent in iron-making.

3. As a deoxidizing and recarburizing agent in steel manufacture.

4. As an alloying element in various alloy and special steels.

It needs emphasis that without manganese no iron and steel industry can really function. It may be interesting to remember that if the Third World War comes, the most important material on which the war efforts of a country will depend may well not be uranium or thorium or the hydrogen bomb, but again 'manganese', because without manganese no steel can be made, and without steel no war can be fought. Of the four major steel producers in the world, viz. U.S.A., U.S.S.R., U.K. and Germany, only U.S.S.R. has huge reserves of manganese ores, the other three have to depend mostly on external resources. Next to U.S.S.R., India is most favourably situated as regards adequate reserves of manganese for her steel industry. During the last fifty years India has exported 35-40 million tons of manganese ore of mostly high grade, chiefly derived from Madhya Pradesh. It is a natural thought, therefore, that if the western countries could manufacture ferro-manganese from our ores, why the ferro-alloy could not be made in India and exported as such. It has to be made clear that due to high iron content and other properties of Indian manganese ores and high phosphorus contents of our metallurgical coals, it is not possible in India to manufacture standard grades of ferro-manganese in the iron blast furnace, which is, of course, the cheapest process at present. The indigenous production of ferro-manganese for export

markets has not been taken up so far, as the Indian ferro-alloy contains a high percentage of phosphorus with a relatively lower manganese content in comparison with the standard grade used abroad. The following are the compositions of high-carbon ferro-manganese made in India and the quality used in America:

	Indian Fe-Mn, %	'Standard' Grade Fe-Mn, %
Manganese	70-75	78-82
Carbon	6-8	7.5 max.
Phosphorus	0.5-0.6	0.35 "
Sulphur	0.027	0.05 "
Silicon	0.550	1.24 "

The high phosphorus content in the Indian product is mainly due to the high phosphorus (ash) content in the Indian coke. The following table shows the difference in the quality of coke used in India compared to that used by a ferro-manganese producer in America:

	India, %	America, %
Phosphorus	0.18-0.25	0.01-0.012
Iron	1.25-2.30	0.75-0.850

The average Indian ore (oriental mixture) has the following approximate composition:

Mn, %	Fe, %	SiO ₂ , %	Phosphorus, %
48-52	6-8	8	0.10

The manganese-iron ratio is about 7:1 against the Caucasian ore ratio of 60:1, Gold Coast 10:1 and Brazil 12:1.

This quality manganese ore together with the coke that is being used does not give a ferro-manganese of desired analysis for the export market. The trouble lies in the chemical analysis of the coke over which there can be little control. By careful selection of ore resources, it is possible to get manganese ore of lower phosphorus content from Madhya Pradesh, i.e. having about 0.09 per cent phosphorus maximum. The most serious drawback, however, is the Indian coke, which has an average phosphorus content of 0.2 per cent and an iron content of 1.2-5 per cent. Over 2.25 tons of coke are required to produce a ton of ferro-manganese in an iron blast furnace and the phosphorus introduced in the ferro-alloy derived from the coke alone would be about 0.4 per cent. It may be pointed out that the iron content of the Indian coke, as well as the low manganese iron ratio in the Indian manganese ores, dilutes the ferro-manganese thus lowering the final manganese content in the ferro-alloy made. Approximately 0.4 per cent (66 per cent) out of the 0.5/0.6 per cent phosphorus contained in the Indian ferro is derived from the coke. The crux of the problem is, therefore, to find a metallurgical coke with a much lower phosphorus content. Although India does not have coals with very low ash, the most suitable grade available are the Giridih and Laikdih coals, which have phosphorus contents of about 0.01/0.05 per cent and could be utilized for making the right type of metallurgical coke for ferro-alloy manufacture. In the 'blend' used by foreign manufacturers of ferro-manganese, the manganese-iron ratio is not less than 10:1. Where coke of low phosphorus content is available as in the U.K., the Indian manganese ore is used straight for the production of ferro-manganese without blending. In the U.S.A. high-grade manganese ore is blended not because the Fe-Mn ratio is high in the Indian ore, but because the American iron ore used for ferro-manganese manufacture is high in sulphur and phosphorus compared to iron ores employed for

the purpose in Europe. The Japanese use an ore with 33 per cent manganese and 0.05 per cent phosphorus and smelt it in electric furnaces, producing a ferro-manganese of over 70 per cent manganese and 0.14 per cent phosphorus contents. About 3 tons of this ore are used per ton of ferro-manganese made by the Japanese.

Briefly, the factors that govern the making of standard grades of ferro-manganese acceptable for export are:

(a) *Manganese ore*

1. The manganese-iron ratio should be as high as possible.
2. The phosphorus content should not exceed 0.1-0.13 per cent.
3. The silica and alumina contents should not exceed 8 and 10 per cent respectively.

(b) *Coke*

1. The fixed carbon content should be 77 per cent minimum.
2. The iron and silica contents should be 1 and 10 per cent maximum respectively.
3. The phosphorus content should be 0.065 per cent maximum.

There are several ways in which the problem of making a ferro-manganese of the 'standard' grade could be tackled in India:

1. The quality of the metallurgical coal could be improved by washing and/or by blending with other low-phosphorus coals.
2. The use of Assam coal which contains low phosphorus.
3. Manufacture in electric furnace.

With the type of coke now used regularly in the production of pig iron, it is not possible to manufacture a high-grade ferro-manganese in the blast furnace. Giridih coal has a low phosphorus percentage of 0.02 per cent, but it is not always used for metallurgical purposes. If the coke from this area is exclusively utilized for the production of ferro-manganese, it will be possible to produce ferro-manganese of the required standard. By trying out various blends of Jamadoba coal

and other grades such as Bararee, it may be possible to produce a coke with fixed carbon of 75 per cent, iron $\frac{1}{2}$ per cent, silica about 10 per cent and phosphorus 0.064 per cent. The manganese ores from the Ukwa and Bhaweli mines in Madhya Pradesh contain about 0.08 per cent phosphorus and these ores may be stocked separately and utilized for the high-grade ferro manufacture. Sufficient technical data may now be available on the advantage to be derived from washing of coals. Regarding Assam coals, high cost of transport would rule out their use. It is often asked as to why, if the Indian steel industry is in a position to make use of indigenous ferro-manganese containing 0.5/0.6 per cent phosphorus, the American and other western steel-producing countries do not wish to take this grade of ferro-manganese. Ferro-manganese is added to the liquid steel after it has been 'refined' and is generally added in the ladle for purposes of deoxidation and alloying. The foreign manufacturers of ferro-manganese have been able to produce a low-phosphorus ferro-alloy by blending manganese ores from different parts of the world, thus enabling them to get an alloy with as low a phosphorus content (0.3-0.35 per cent max.) as possible. When they can obtain this product of better quality, naturally they would not accept a relatively inferior quality such as Indian ferro-manganese made in the blast furnace.

The higher phosphorus contents of Indian blast furnace-made standard ferro-manganese also affect the range of high-manganese steels, such as of Hadfield manganese austenitic types which can be successfully made. Whilst with the Indian standard ferro-alloy it is relatively easy to make Hadfield steels with 12-14 per cent Mn, 1.1-1.25 per cent C, 0.1 per cent phosphorus (max.) for different applications such as jaw-crushers, etc., made to A.S.T.M. Designation A. 128-33 and other specifications, the same does not always apply in case of Hadfield steels required for tramway rails points and crossings, where the phosphorus is preferably below 0.056-

0.06 per cent with the same manganese and carbon contents, even though the maximum specified limit is 0.1 per cent phosphorus. However, with the use of basic electric arc furnace for making these types of manganese steels, some dephosphorization can be successfully attempted even with ferro-manganese containing high phosphorus above 0.35 per cent.

Manufacture of Ferro-manganese in Electric Furnace

The electric furnace used for the production of ferro-manganese is similar to those used for ferro-silicon and ferro-chrome, although the ferro-manganese furnace may have a closed top to utilize the gaseous products. The raw materials used are 40/50 per cent manganese ore, coke or charcoal for reduction, steel scrap and a suitable flux. The advantages of the electric furnace are in that the manganese recovery is higher than that of the blast furnace; the alloy can be made with a low phosphorus and carbon contents and the loss of manganese in the slag is also considerably lower. The electric furnace method of manufacturing ferro-manganese would be of particular interest to India to eliminate most of the phosphorus in the ferro derived from the coke. In the electric furnace about 1500 lb. coke is used against the 2.25 tons in the blast furnace for the production of 1 ton of ferro-manganese. Since over 60 per cent of the phosphorus in the ferro-manganese made in blast furnace comes from the coke, the manufacture of ferro-manganese in the electric furnace is of topical interest to India. In the electric furnace about one-third of the coke used in the blast furnace is required for purposes of reducing the ore. If coke of suitable quality is not available, then any other suitable form of 'carbon' could be employed. The cost of electric power is the most important factor, as a ton of ferro-manganese would require about 3500 units for the 7 per cent carbon grade of the ferro-alloy. The price

of the electric furnace product is much higher than the ferro made in blast furnace. Canada, U.S.A. and Norway are some of the countries where ferro-manganese is made in the electric furnace. Of these Canada and Norway make ferro-manganese mainly for export from imported manganese ores. U.S.A. makes the alloy chiefly for her internal consumption.

As there are several hydro-electric projects under construction in India and manganese ore of suitable quality is available in Madhya Pradesh, Bihar, Orissa and Mysore, it should be possible to establish a plant for the production of ferro-manganese by the electric furnace, say, near the Hirakud or D.V.C. area. To couple this ferro-alloy plant with the new steel plant being set up by the Government of India appears to be an admirable object.

It should be pointed out that the demand within the country for low-carbon ferro-manganese is very small and the ferro-manganese produced would, therefore, have to be mostly exported. Doubts are often expressed as to foreign market for ferro-manganese, but these have no basis when it is realized that U.S.A. imported over 46,000, 103,000 and 120,000 tons of ferro-manganese in 1949, 1950 and 1951 respectively from Norway, France and Canada. If steel production in U.S.A. reaches 150 million tons during the next 10-15 years as expected, the corresponding manganese ore (46 per cent grade) consumption would amount to 2.5 million tons. Only India has to produce the acceptable grades of ferro-manganese or at least standard ferro-manganese grade for the latter to be exportable to overseas markets.

Thermal Beneficiation of Low-grade Manganese Ores for Ferro-alloy Manufacture

Attempts have been made in America¹ to concentrate low-grade manganese materials in a blast furnace to produce manganese-rich pig iron followed by partial oxidation of the pig iron in a converter to obtain a manganese-

rich slag which is subsequently used for the production of ferro-manganese. In another method² oxides of iron and manganese in the ore are separated by fixing the acids such as silicates and phosphates with bases like CaO through manipulating a suitable $(\text{CaO}-3\text{P}_2\text{O}_5)/\text{SiO}_2$ ratio thereby retaining the iron and manganese as free oxides. This is accomplished through roasting the crushed material at 1380°C. in a rotary kiln, followed by magnetic separation. By this method it is claimed that 95 per cent of the Fe, Mn and Mg oxides can be recovered, and can subsequently be utilized for the manufacture of spiegeleisen.

A new method of recovering manganese from hitherto worthless steel slags is being devised by the American Steel Industry in co-operation with the United States Bureau of Mines, resulting in synthetic manganese ore containing 55-63 per cent of manganese. Studies and experiments have revealed that what has been considered worthless slag piles from open-hearth furnaces can produce synthetic manganese ore of a considerably higher grade than most natural ores. And, in the conversion of this slag, sufficient iron is recovered to pay for most of the cost of processing. In 1949, under the supervision of Dr. Russell C. Buehl, Supervising Engineer of the Metallurgy Section, Bureau of Mines, a tiny pilot plant blast furnace was constructed at Pittsburgh, Pennsylvania. The natural content of the slag on the waste piles ranges from 7 to 12 per cent of manganese. The original furnace was a failure, in that the metal froze at the tapping level and could not be restored by more oxygen and higher heat. Finally, the entire lower portion of the furnace was enlarged and rebuilt. The first metal tapped from the rebuilt pilot furnace contained 21-24 per cent of manganese, 3-4 per cent of carbon, 0.8-4 per cent of silicon, and 3-4 per cent of phosphorus, the remainder iron. The next problem was how to refine further so that the metal could be obtained virtually free of phosphorus. It was solved

by incomplete blowing in a Bessemer-like converter, producing a high-manganese slag containing 55-63 per cent of manganese. The phosphorus remained with the iron. The next step in the experiment — the design of a converter with four times the capacity of the old one — is now being completed, which will bring the pilot plant operation closer to full-scale production. The final economics of the process will depend upon the selling price of the recovered iron and on the market price of manganese, excluding, of course, the potential advantages to be gained in times of war emergencies.

India's resources of low-phosphorus high-grade manganese ores and of low-phosphorus coals, as is quite obvious by now, are limited, whereas those of low-grade manganese ores are relatively far more abundant. Bearing this in mind some experiments on the thermal beneficiation of low-grade manganese ores have been conducted in the National Metallurgical Laboratory³. The object of this treatment lies in the treatment of low-grade manganese ores through suitable thermal technique aiming at the production of an enriched manganese slag and iron as a by-product in the first stage followed by smelting of the enriched manganese slag preferably in an electric furnace of Soderberg type. On commercial scale the possibility of a combination of acid Krupp-Renn rotary kiln during the first stage to produce an enriched manganese slag followed by the use of basic Stuzelberg rotary furnace to smelt the manganese-rich slag in the second stage may be considered.

Concerning the commercial aspects of this problem and reckoning on an approximate average export sale price of Rs. 140 per ton of high-grade manganese ore, a million tons of which are currently exported from this country, the inflow of foreign exchange amounts thereby to about 14 crores a year. But if, after conversion of the high-grade manganese ores into exportable grades of ferro-manganese (containing phosphorus below 0.3 per cent), these million tons of high

grade manganese ores were to yield about 350,000 tons a year of ferro-manganese, it should fetch, at the current price of the latter, about 28-30 crores of rupees a year. The economic benefits accruing thereby are evident, apart from the fact that suitable methods for the utilization of low-grade manganese ores at present chiefly discarded through thermal beneficiation would also be evolved and be one of the greatest economic assets to the country. This thermal method for the production of ferro-manganese from low-grade manganese ores, as stated before, may be through a combination of acid Krupp-Renn rotary kiln process and basic Stuzelberg rotary furnace process or Soderberg electric furnace smelting of the intermediate enriched manganese slag. This problem in India requires serious and integrated examination for the utilization of low-grade manganese ores on the one hand and making the best use of high-grade manganese ores for production of exportable grades of standard ferro-manganese on the other. This should also lead to the conservation of our high-grade manganese ores and their utilization to the best national advantage. The successful evolution and utilization of a thermal process for the above purposes should prove to be of great potential both in peace and in times of war.

Preliminary experiments for the thermal beneficiation of low-grade manganese ores conducted at the National Metallurgical Laboratory have provided useful clues for pursuing the work on pilot plant scale. Further elucidating its principle, this method is based on studies of free energy of the oxides of manganese, iron and phosphorus and thermodynamic factors involved in their reduction under optimum conditions of temperature and basicity. This has to be achieved through a two-stage process consisting of (a) first stage, to be worked under acid conditions and at low temperatures to produce a high-phosphorus iron leaving manganese, as far as possible, in the slag, (b) second stage, using phosphorus-free, manganese-

enriched slag from the first stage to produce a manganese-rich iron alloy of very low phosphorus content. The byproduct of high-phosphorus iron from the first stage would be a useful byproduct for use in foundry as such or subsequent steel-making. Further study of the above subject on a pilot plant scale is expected to prove to be of considerable national and economic potential, if systematically persevered with.

It would not be out of place to further outline the strenuous efforts being made in countries deficient in manganese resources, like the U.S.A. and Australia, to explore alternative sources of manganese such as the recovery of manganese from steel slags of which there are unlimited huge stocks. In Australia, at the Broken-Hill Proprietary Company Limited, work is underway on the recovery of manganese from open-hearth run-off and final steel slag by means of pyro-metallurgical operations to yield a ferro-silico-manganese containing about 70 per cent manganese. Typical analysis of open-hearth slag so treated above is:

	<i>Per cent</i>
FeO	... 24.12
Fe ₂ O ₃	... 4.23
MnO	... 31.00
P ₂ O ₅	... 2.07
SiO ₂	... 21.00
CaO	... 13.10
MgO	... 2.20
Al ₂ O ₃	... 2.28

Reduction of the slag is undertaken in a two-stage process:

1. Under acid conditions to produce a high-phosphorus iron leaving manganese, as far as possible, in the slag.
2. Using phosphorus-free, manganese-enriched slag from the first stage to produce a manganese-rich alloy and a slag virtually free of phosphorus and metallic oxides.

Two-stage process is necessary to avoid reversion of manganese and phosphorus. During the first stage, reduction of oxides of

iron and phosphorus is carried out under highly acidic conditions and at low temperatures. The acid charge performs two functions, viz. by forming more stable silicates of manganese it assists in the retention of manganese in the slag, thereby contributing to the expulsion of phosphorus through alloying with iron. The first stage metal is of the order of: iron, 91 per cent; manganese, 0.4 per cent, and phosphorus, 4 per cent. In the second stage takes place the reduction of manganese-rich slag at considerably higher temperatures and highly basic conditions, yielding a ferro-silico-manganese alloy of about 70 per cent manganese, 16 per cent iron, 0.3 per cent phosphorus, 11 per cent silicon and 3.6 per cent carbon. This process in Australia has not yet been wholly standardized and vigorous pilot plant research is in progress utilizing mostly open-hearth run-off slags, although suitable mixtures of run-off and final slags may also be utilized. The cost of producing manganese-iron alloy through this two-stage process will naturally be higher than that involved in direct reduction of high-grade manganese ores in a single-stage reduction, but it is by no means prohibitive. And in case of an emergency shutting off overseas supplies of high-grade manganese ore, the benefits to be derived from this process are self-evident. Incidentally, the byproduct iron obtained from the first stage can be usefully employed for foundry purposes or for steel-making through basic Bessemer or basic open-hearth processes. The use of final slag obtained from the second stage for cement manufacture could also be a useful proposition.

Extensive work has also been carried out jointly by the U.S. Bureau of Mines and Minnesota School of Mines on the selective reduction of iron and manganese contained in the Minnesota manganese iron ores for the separation of manganese therein and its concentration into an iron-manganese alloy of standard ferro-manganese analyses (Bulletin No. 12 of the University of Minnesota). The principle of all these methods aiming at

the recovery of manganese in the form of a suitable ferro-alloy from steel slags, low-grade manganese ores, or manganiferous iron ores is identical and has to be applied through two-stage reductions.

The most recent work of Union Carbide Inter-National Company and Electro-Metallurgical Company on the development of an electrolytic process for the manufacture of ferro-manganese forms the subject-matter of most recent applications for patent rights in the U.S.A. and full particulars thereof will be available only at the latter part of this year.

The importance of the need to economize in the use of available manganese supplies in countries deficient in manganese may be gauged by the efforts of Iron and Steel Committee of the Organization for European Economic Co-operation (O.E.E.C.). Their report on this subject has been published a few months back. It includes outlines of a process now in use in Germany whereby an increased yield of manganese in the production of ferro-manganese in blast furnaces may be procured by control of the composition of the slag. This consists in reducing the iron in the iron ores containing manganese, whilst most of the manganese remains in the slag. The resulting slag is then treated in the blast furnace for conversion into ferro-manganese.

It will also be not out of place to mention investigations initiated by the Tata Iron & Steel Co. Ltd.⁴ on the possibilities of making ferro-manganese in a German low-shaft furnace. The process appeared to offer the following advantages:

1. The use of low-phosphorus non-coking coal, considerable reserves of which are available in India.
2. The possibility of using a wider range of manganese ores.
3. The manufacture of the alloy in separate self-contained units.

Experiments were made in Germany in a low-shaft furnace operating on the Humboldt principle, where raw materials are briquetted

prior to charging in the low-shaft furnace. These trials showed that it was possible to produce an alloy low in phosphorus, although excessive oxidation losses of manganese in the slags reduced the manganese content of the alloy to 60-70 per cent. Further trials, however, have shown the possibilities of cutting down these oxidation losses in the slags through suitable additions.

Another front on which the problem is being tackled at the National Metallurgical Laboratory which, whilst having no direct relation to the production of ferro-manganese, does aim at the utilization of quite inferior grade of manganese ores through electrolytic processes for the production of MnO_2 and Mn of high purity. Similar work is also in progress at the Central Electro-Chemical Research Institute, Karaikudi.

The use of manganese in non-ferrous alloys such as manganese bronze, monel metal, E-alloy, manganin, duralumin, etc., or as a coating to provide corrosion and abrasion resistance to steel and non-ferrous metals is not being discussed in this paper. It will also be not possible in this paper to discuss the multitude of uses to which electrolytic manganese can be put to in preference to different grades of ferro-manganese for use in metallurgical industries.

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Discussions

DR. H. SCHRADER (Director, Scientific Researches, Tisco Control & Research Laboratory, Jamshedpur)

I have listened with interest the paper on Indian Manganese Ore Industry and Scope for Its Development. The paper is very interesting. I would

further like to emphasize that in all methods aiming at the upgrading of manganese ores whether by ore-dressing or thermal beneficiation, one of the most important points to be borne in mind is the adequate dephosphorization of upgraded material or the ferro-alloys. Mere increase in the manganese-Fe ratio will not serve the purpose.

Author's Reply

Dr. B. R. Nijhawan thanked Dr. H. Schrader for his remarks and stated that he fully agreed with him that phosphorus reduction in the manganese ore was an important aspect of upgrading operations particularly if blast furnace smelting of ferro-manganese were to be employed in India using high-phosphorus cokes. In case of electric smelting of ferro-manganese, higher phosphorus content of the manganese ores could be accepted.

MR. P. P. BHATNAGAR (National Metallurgical Laboratory, Jamshedpur)

It appears to me that the problem of high phosphorus can best be solved by resorting to chemical methods. Amongst the methods may be men-

tioned the sulphur-dioxide-in-roaster-gas treatment of the ore either at low or high temperature or chlorination of the ore. These would yield pure MnO_2 which could be sintered and used for reduction. As regards the dephosphorization of ferro-manganese, no attention seems to have been paid in this country. Successful experiments have been reported on dephosphorization using magnesium metal.

Author's Reply

Dr. B. R. Nijhawan stated that apart from the chemical approach of dephosphorization, thermal and ore-dressing techniques can effectively lower the phosphorus contents. As I have said before, the question of phosphorus reduction assumes importance if blast furnace smelting is to be resorted to, using Indian cokes.

I may also point out here that with Indian metallurgical coke Tatas have made ferro-manganese containing 0.5-0.6 per cent phosphorus from Indian manganese ores and have most effectively utilized it for steel-making. The question of phosphorus contents of the ferro-alloy needs examination in proper perspective on the whole.

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