A Strategy for utilisation of low grade high phosphorus manganese ores in the production of high carbon ferro manganese

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ABSTRACT

A two step process is outlined to utilise low grade high phosphorus ores containing Mn 31-35%, Fe 11-13%, SiO_2 8-10%, P 0.35% to 0.5%, whereby in the first step, smelting is carried out in an Electric furnace to produce High MnO containing slag with equivalent Mn 45 to 50% which can be used as synthetic high grade ore and is almost free from phosphorus and iron. The metal obtained is "Spiegeleisen" containing 14 to 18% Mn and 1.5 - 2.0% phosphorus.

In the second step the high manganese slag from the first step is blended with additional quantities of low and medium grade manganese ores and smelted to produce high grade High carbon ferro manganese and a discard slag containing about 16.0% Mn. The smelting trials carried out at FACOR is briefly mentioned.

Introduction

Gradual depletion of High grade Manganese ores has taken place in India due to export of High grade ores during earlier years of mining activities in India and subsequently domestic utilisation of high grade ores only in the production of High carbon ferro manganese during the last two decades. Considerable difficulties are being faced by Ferro manganese producers in procuring requisite quantities of High grade manganese ores for feeding existing furnaces and this difficulty will increase further as more and more ferro manganese plants are established to meet the growing demand with expansion in steel making capacity. The demand of High carbon ferro manganese by 1990 is estimated as 3,80,000 tonnes including an export of 100,000 tonnes. With 90% capacity utilisation of the furnaces the production capacity for high carbon ferro manganese should be 4,20,000 tonnes. The present installed capacity and production of high carbon ferro manganese in India is indicated in Table - 1.

For the production of high carbon ferro manganese, the manganese content of the ore should be 45.0% minimum, with a minimum Mn/Fe ratio of 6.0 and phosphorus 0.16% max, taking into consideration that the carbon reduc-

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TABLE—1

Installed capacity of high carbon ferro manganese plants in India

Sl. No.	Name of the ferro alloy producer	Number of furnaces	Transformer rating of smelting furnaces (KVA)	Production Capacity per annum. (tonnes)
1	Tata Iron & Steel Co. Joda (Orissa)	2	9000 (each)	30,000
2	Jeypore Sugar Co. Ltd., Rayagada (Orissa)	1 1	3600 7500	24,000
3	Universal Ferro Alloys & Allied Chemicals Ltd, Tumsar (Maharashtra)	2 2	9000 (each) 16500 (each)	36,000 60,000
4	Khandelwal Ferro Alloys Ltd., Kanhan (Maharashtra)	2	9000 (each)	36,000
5	Maharashtra Electro-smelt Chandrapur (Maharashtra)	1	33000	48,000
6	Electro Metallurgical Works (P) Ltd., Dandeli (Karnataka)	1 1	4600 1200	16,000
7	Visvesvaraya Iron & Steel Ltd., Bhadravati (Karnataka)	2	1500 (each)	2,800
8	Ferro Alloys Corporation Ltd., Shreeramnagar (Andhra Pradesh)	3	7500 (each)	45,000
	Additional licensed capacities granted by Government	—	—	
9	M. O. I. L. Balaghat.			60,000
	TOTAL			3,57,800

tants namely steel plant cokes contain P to an extent of 0.16 to 0.18%. Also physical character of lumpiness is to be ensured. The size of manganese ores should be hard and lumpy with $-50+6$ mm, For the production of 4,20,000 tonnes of high carbon ferro manganese, the requirement of manganese ores of the requisite grade would amount to 1.05 million tonnes per annum.

The total estimated reserves in India in 1971 was about 108 million tonnes of which about 60% are of medium and low grade ores Table - 2. Also more than about 50% of manganese ores are of high phosphorus content. Most of the ores cannot meet the phosphorus limit of 0.16% max required for high carbon ferro manganese production. Since enough quantities of high grade ores from single source are not available to meet the requirements of high carbon ferro manganese production, several ore types containing high Mn/Fe ratio with high and low P, low Mn/Fe ratio with low phosphorus, high silica ores and low silica ores are blended to obtain an average composition required for feeding to high carbon ferro manganese furnaces.

Apart from the chemical composition, it is known that for each tonne of manganese ore mined an equal quantity of ore fines are generated at the mine head. Also due to friable nature of many manganese ores especially in Eastern Region considerable amount of fines are generated during mining, transport and handling of manganese ore. Since the fines as

TABLE—2

Ore reserves in millions of tonnes

	Block-1 Madhya-pradesh Maha-rashtra Gujarat	Block-2 Orissa Andhra-pradesh	Block-3 Karna-taka	Total
Proved	7.22	0.15	0.29	7.66
Indicated	24.12	4.81	3.81	32.74
Inferred	13.66	40.19	14.11	67.96
Total	45.00	45.15	18 21	108.36
High GR	36.00	6.77	1.82	44.59
Low GR	9.00	38.38	12.41	63.79

such cannot be utilised in the electric furnaces these are required to be beneficiated and agglomerated into lumpy form as briquettes, sinters or pellets for their use in the production of high carbon ferro manganese.

Beneficiation Studies on Mn Ores :

Voluminous investigations on several manganese ores have been undertaken during the last two decades to drive home the importance of mineral beneficiation by various research centres like National Metallurgical Laboratory[2], Jamshedpur, Indian Bureau of Mines[3], Nagpur, Regional Research Laboratory, Bhubaneswar and other places. Very useful flow sheets have been evolved for several type of manganese ores.

The salient features of such investigations are enumerated hereunder :

The low grade manganese ores from different parts of India could be broadly classified into four groups for the purpose of mineral beneficiation.

1. Simple Ore Types : These ores are amenable to concentration by simple ore dressing methods such as gravity, high intensity magnetic separation or flotation processes.

2. Ferruginous ore types : These can be upgraded by magnetising reduction roast followed by magnetic separation. Most of the ferruginous ores of Orissa are amenable to this treatment.

3. Garnetiferous ore types : These types of ores are amenable for treatment by electrostatic separators or flotation.

4. Complex ore types : These ores require combination of two or three treatment methods depending on the gangue minerals present.

Though the physical beneficiation methods enumerated above have shown that several low grade manganese ores can be upgraded to improve the manganese to iron ratio, the phosphorus content in most of the ores could not be brought down. Till this date, no solution has been found for removal of phos by mineral beneficiation techniques. It has been shown by investigations at National Metallurgical Laboratory and Indian Bureau of Mines that if phosphorus is present as apatite mineral, this could be separated. However, in most of the ores, phosphorus is present intimately in the manganese oxide crystal lattice and therefore, by employing ore dressing methods phosphorus could not be brought down. FACOR too once had set up facilities for beneficiation of low grade manganese ores available in Srikakulam District, Andhra Pradesh. The beneficiation plant consisted of crushing, sizing, washing jigging, grinding, tabling, magnetic separation and flotation units. The plant was operated for a period of five years and the observations were as follows : (1) To achieve required manganese to iron ratio in ores it was found that the recovery of the mineral was too low, (2) Even after flotation the phosphorus content could not be brought down below 0.19%, (3) it was found that operation of the plant for beneficiation was uneconomical, considering that the fine concentrates obtained required further agglomeration steps.

Hydrometallurgical method :

Several investigations have been done at Regional Research Laboratory, Bhubaneswar[4,5] to decrease phosphorus content in manganese ores by hydro-metallurgical method.

These studies show that the phosphorus content of some high phosphorus manganese ores of Southern Orissa and Andhra Pradesh can be decreased by alkali-roast at 800°-850°C and subsequent leaching with water at 80° - 90°C. Phosphorus in manganese ore samples from Madhya Pradesh and Maharashtra region could be brought down by leaching in dilute mineral acids[6] like H_2SO_4, HCL or HNO_3. It may be noted that though several investigations as cited above have shown encouraging results in certain types of ores on laboratory scale, the alkali consumption is high. The recovery of manganese and the extent of phosphorus removal are low and the feasibility and economic viability of the process on Pilot plant has not been established.

Moreover, any method adopted to upgrade manganese ores by physical beneficiation and chemical leaching methods requires crushing and grinding the ores to a fine size of minus 100 mesh and therefore the beneficiated and upgraded ores cannot be directly fed to Electric Smelting Furnaces and requires agglomeration by briquetting sintering or pelletising and such steps as crushing, grinding, to a fine particle size and adoption of physical and hydro-metallurgical beneficiation methods would add appreciably to the capital cost and operating cost. In most of the ore types techno-economic viability of the processes are yet to be established.

Pyrometallurgical treatment :

Pyrometallurgical method of beneficiation whereby the high iron and phosphorus content of low grade ores are selectively reduced with carbon at high temperatures either in Rotary Furnaces or Electric Furnace is considered as another approach to utilise high phosphorus low grade manganese ores. Numerous investigations have been reported in the literature [7-13] with the object of making synthetic manganese ore (high MnO slag) by preferentially reducing and eliminating the iron and phosphorus through the molten spiegel. The slag contains high manganese oxide with 55 to 70% with very little iron and very low phosphorus of less than 0.03%. This high MnO slag can be used either in the production of silico manganese or high carbon ferro manganese. Typical examples of such pyro metallurgical method are the New Castle two stage process [15,18] and Strategic UDY process[14].

The New Castle or Broken Hill process consists of two stages in which open hearth slag containing 10-25% Mn and 1.5% P was reduced under acid conditions in the first stage in an electric furnace, such that manganese and silica in the charge were retained in the slag while the iron and phosphorus were reduced into the metal. The initial smelting operation was usually carried out within a temperature range of 1100 - 1500°C. Hosking and Gregory reported an optimum temperature of 1430°C with a base/acid ratio of 1 04. In the second stage, the synthetic ore of first stage was smelted with coke and limestone to produce high carbon ferro manganese containing upto 70% Mn at a temperature of 1600 - 1650°C with a slag base to acid ratio exceeding 1.5%.

In the strategic UDY process, ferruginous manganese ores and low grade ore concentrates containing manganese between 10 to 15 per cent were utilised. In the first step, ore was mixed with coke and flux, preheated and practically reduced at 1100 - 1200°C prior to smelting. Smelting was carried out at 1300-1600°C to reduce iron and P leaving a high MnO containing slag. The phosphorus alloyed with iron was oxidised in a succeeding smelting operation to produce low phosphorus pig iron. The synthetic slag of the first step was used for the production of silico manganese and high carbon ferro manganese. The two step smelting process was also attempted for utilising Sandur ferruginous manganese ores with low phosphorus content in pilot plant scale at Electromisk A/S, Oslo, at the instance of M/s. Sandur manganese and Iron Ores Pvt. Ltd., India. In the first stage low grade ferruginous ore with Mn 28-35%, Fe 21-23%, SiO_2 1-2%, Al_2O_3 6-8% and 0.03 - 0.05% P was smelted in a 2000 kv furnace to produce a high MnO slag with 54% Mn and spiegeleisen with 12% Mn and 0.2% P. In the second stage, high Mn slag from stage one together with additional low grade ore was smelted to produce standard ferro-manganese with 76.0% Mn and 0.10% P.

The selective reduction of iron has been the aim of these investigations to utilise ferruginous low grade manganese ores having low Mn to iron ratio. However, FACOR proposes to adopt this method for the utilisation of high phosphorus containing low grade manganese ores, available in Srikakulam-Vizag districts and low grade ore from Orissa, taking advantage of selective reduction of phosphorus also along with iron during smelting.

Two step process for producing high carbon ferro manganese :

In principle, in the first step, low grade high P manganese ore is smelted in an electric submerged arc furnace under acid conditions with carbon as reducing agent to produce spiegeleisen which will contain 14 to 20% Mn, 1.0% silicon, 6-7% carbon and 1.0 to 2.0% P. The slag will contain most of the manganese as manganese silicates with 45 to 55.0% Mn, 14-18% SiO_2, 1.0% Fe and P 0.03% max.

In the second stage the high manganese containing slag which can now be called synthetic manganese ore will be blended with further quantities of low grade high P manganese ores and other manganese ores and smelted in another electric submerged arc furnace to produce high carbon ferro manganese. Since SiO_2 content of this blend will be high, due to high silica content in the first step slag the low MnO slag practice will be adopted whereby standard high carbon ferro manganese and a discard slag containing about 15% Mn will be produced.

To establish the feasibility of the process, a few years back, smelting campaigns were undertaken at FACOR to produce spiegeleisen and synthetic manganese ore by two step method on industrial production scale in one of their furnaces producing high carbon ferro manganese.

The furnace shell is 7050 mm dia and is lined with high duty fireclay, silicon carbide and carbon tamping paste. Furnace hearth dia and height are 5080 mm and 2185 mm respectively. Three soderberg self baking type electrodes with diameter of 1050 mm are located on the apexes of an equilateral triangle. The distance between the centre of electrodes is 2670 mm The electrodes have pneumatic slipping devices to provide electrode slipping of maximum 100 mm.

The charge comprising of low grade high phosphorus maganese ores, iron ore or mill scale or steel scrap and coke, was smelted, by the heat supplied through the three self baking electrodes and the products were tapped, through tapholes at bottom of the furnace at regular intervals. The metal, spiegeleisen and high manganese slage were tapped together and separated suitably by collecting into pans which were arranged in cascades. When solidified, the metal and slag were lifted from the pans by means of a 10/3 ton. E. O. T. Crane. Metal and slag were sized and weighed. Very valuable data were collected during the campaign for smelting of low grade high phosphorus manganese ores and the process was found suitable for adoption on large scale. The salient data are presented in Table-3. In the second step, High manganese slag or Synthetic manganese ores blended with low grade high phos manganese ore and low grade ores were smelted alongwith reductants and flux in the same submerged electric arc furnace for production of High carbon ferro manganese.

Discussion of results

1. Low grade ores were found quite satisfactory for production of spiegeleisen and high manganese slag. However depending on

TABLE—3

Data on production of high manganese slag and spiegeleisen in 7.5 MVA furnace at FACOR

ITEM	Campaign - I	Campaign - II
A. 1. Low grade Mn Ore (i) Mn 35.5%, Fe 12.8%, SiO_2 9.5%, P.O. 28%, Al_2O_3 7.0%, CaO 1.5% MgO 3.5% BaO 3.8%	1600 kg	—
2. Low grade ore (ii) Mn 40%, Fe 12%, SiO_2 6%, P. O. 3%, Al_2O_3 5.5%, CaO 2.0% MgO 3.0%, BaO 3.0%.	—	1500 kgs
3. Coke F. C. 70% P. O. 16% Ash 28.0%	220 kgs	250 kgs
4. Quartz. SiO_2 98%	—	100 kgs
5. Steel scrap Fe, 97% P 0.03%	150 kgs	350 kgs
6. Electric power/tonne of slag	1400 kwh	1500 kwh
7. Electrode paste	10 kgs	10 kgs
8. Quantity of speiegel produced	400 kgs	600 kgs
9. Quantity of High Mn slag	1000 kgs	1000 kgs
B. SPIEGEL ANALYSIS IN PRECENT		
Mn	20.0	18.0
P	0.94	0.6
Si	0.19	0.2
C	6.5	6.5
S	0.004	0.01
C. SLAG ANALYSIS IN PERCENT		
MnO (Mn)	53.3 (41.29)	55.0 (42.60)
FeO	3.6	2.45
SiO_2	17.2	20.8
Al_2O_3	12.7	10.0
CaO	1.86	3.0
MgO	5.40	5.0
BaO	5.90	5.0
P	0.07	0.05

chemical composition of low grade ores available, it was necessiated to use mill scale or steel scrap to obtain desired Mn and P contents in spiegeleisen

2. The slag volume per tonne of spiegeleisen was about 2.5 tons. Due to this high volume and high MnO content carbon lining of the furnace corroded severely. It is essential to tap the slag at frequent intervals to avoid severe erosion of refractory lining.

3. Slag composition was adjusted to have good fluidity for better/slag metal separation. The SiO_2 content should be kept 18.0% minimum.

4. Smelting trails for production of High carbon ferro manganese using high manganese slag were quite satisfactory. The power consumption was 3700 KWH due to increase in slag volume per tonne of High carbon ferro manganese. It is found that 75 kwh extra power is required for every 100 kg increase in slag volume per tonne of metal.

5. The production of high Mn containing slag by selective reduction of Iron and P was found feasible on industrial smelting trails.

6. In order to bring down the cost of this synthetic Mn ore, it is necessary to make use of spiegeleisen obtained which amounts to 0.4 tonnes per each tonne of Synthetic ore. Sale of by-product spiegeleisen is essential in order to make the Pyrometallurgical process economical.

Uses of spiegeleisen :

Since spiegeleisen contains 14 to 20% Mn, 6 to 7% carbon Si-1% max it could find use as source of Mn for alloying purposes as well as for deoxidation. Prior to the advent of L. D. and other B. O. F. Processes of steel making, it was extensively used in open hearth furnaces for blocking the heats.

However with the modern steel making process, such early blocking steps for working out the heats are not required and moreover high P input will not be permissible. Now its uses are limited to foundries only.

Moreover, the spiegeleisen produced by two step process making use of low grade high phosphorus ores contains 1.5 to 2.0% P and therefore it cannot be used and therefore recourse has to be made to convert it into saleable by products like alloy steel/special steels.

It is proposed that the spiegeleisen can be selectively oxidised with air or oxygen to recover manganese as high manganese slag, and the balance metal blown to produce steel. In this regard Pilot plant investigations at U. S. Bureau of Mines have been reported by M. B. Royer and R. C. Buehl[15]. In their experiments they made use of spiegeleisen produced by smelting low grade manganese ore and open hearth flush slags in an experimental blast furnace[19]. The spiegeleisen contained on an average Mn 15 - 23%, Si 1 - 3% P 2 - 5%, C 2.4 - 3.5% and balance iron.

The experiments were done in a basic converter of 227 kg capacity. The metal was blown with air through a 1.5" diameter tuyere arranged to impinge the blast tangentialy on to the vessel bottom. The air blowing rate was 250-300 Ft^3/minute at 3-5 lbs/in^2. The converter was preheated to about 1480°C before molten spiegeleisen was taken into it. The initial series of thirty blows indicated that if the Mn content was odixised to less than 4% in the metal, the required grade of the high Mn slag with Mn/P and Mn/Fe ratio of 300 : 1 and 8 : 1 could not be achieved. Therefore. they adopted the cyclic process in which the high Mn slag of the first blow was refined by further treatment with fresh spiegeleisen. The procedure consisted first to oxidise the Mn to approximate 1% residual Mn in the metal, tap the metal and retain the slag in the vessel.

To the retained slag in the vessel, containing 10% Fe and 1.0% P, fresh spiegeleisen was added and blowing was done which reduced iron and P to a low value. This procedure enabled to produce a fluid slag with very little entrapped metal and high Mn/Fe ratios and high Mn/P ratio. In order to make the slag fluid it was necessary to add quartz, ferro silicon or alumina. The slag was then discharged and the metal retained in the convertor for a further blow to low Mn content after which the cycle was continued. The high Mn slag contained Mn 52-54%, Fe 0.9% to 2.0%, P 0.03 - 0.05% and SiO_2 18.0 to 23 0% while the metal contained Mn around 1.0% and P 3 to 4% and 3.0% carbon.

A similar approach to recover Mn & P from spiegeleisen is contemplated in our proposed process to make use of low grade high P ores. Since by smelting low grade high phosphorus ores, each 100 tonnes of ore will yield 60 tonnes of slag with high Mn content and 15 tonnes of spiegeleisen it is proposed that the spiegeleisen is to be converted into value added saleable product. Since the time the initial work on blowing spiegeleisen with air cited in the literature in 1952, it is to be emphasized that considerable changes and technological innovations have taken place in blowing techniques like L. D., V. O. D., A. O. D., L. W. S. and Q.B.O.F. And therefore it is thought that it will not be difficult to adopt one of these modern B. O. F. Processes or Q. B. O. F. technique to recover Mn, P and Fe separately from the spigeleisen.

However to adopt such processes the heat balance is to be matched and it is considered that a heat size of 4-5 tonnes per batch will be minimum capacity for such processes. In order to get 4 to 5 tonnes of spiegeleisen per heat, it is essential that the furnace be operated to make available 4 to 5 tons of spiegeleisen every two hours. Blowing the spiegeleisen in stages, it is envisaged that the spiegeleisen be selectively oxidised under suitable temperature in the first stage under acid condition to oxidise Mn as high MnO containing slag. This slag can be recycled to the production of high carbon ferro manganese. In the second stage the balance molten iron is subjected to further blow by oxygen or oxygen and other inert gases, to oxidise carbon and phos. The dicalcium phosphate slag formed can find use as a fertiliser.

The metal which is free from phosphorus. carbon and Mn can be alloyed as required to produce Ingots or castings. Thus the high phosphorus spiegeleisen can be converted to value added products such as (1) High manganese slag which can be recycled for use in production of High carbon ferro manganese. (2) Dicalcium phosphate slag can find use as a fertiliser and (3) Steel Ingots can be marketed with no difficulty.

As already indicated the technical feasibility of the Pyrometallurgical process for the production of High manganese slag and High carbon ferro manganese using HIgh manganese slag had already been established at FACOR.

Regarding Technical Feasibility of the Process for blowing of spiegeleisen it can be seen that considerable research work had been under taken abroad and were proved successful. However FACOR have taken steps for establishing the parameters for design of equipment for blowing of spiegeleisen to be adopted on Industrial scale. Annual requirements of raw material for HC Fe-Mn Plant to be operated on a combination of two step and oxygen blowing process and the products annually expected to be produced from such a process are shown in Table - 4.

Regarding the economic viability of the proposed process of utilising low grade high phosphorus manganese ore it was already mentioned that the proces will be economically viable if high phosphorus spiegeleisen is converted to value added products· However, high capital requirements are envisaged due to installation of equipment facilities for additional smelting furnaces and converters. In order to compensate for the increased depreciation and over head costs and to make the over all process economically viable, it is essential to instal facilities for production of a minimum of 1,00,000 tonnes of high carbon ferro manganese in large capacity furnaces.

Conclusion :

Adoption of two step pyrometallurgical process in conjuction with blowing of spiegeleisen will enable the use of low grade high phosphorus manganese ores of Andhra Pradesh and other regions in the production of high carbon ferro manganese and economic viability of the process is possible on large scale. It is possible to conserve the high grade mangaese ores to meet the growing need for production of high

TABLE– 4

Annual requirements of raw materials for high carbon ferro manganese plant to be operated on a combination of two step and oxygen blowing process.

Sl. No.	Type of raw material	Chemical Specification (Percentage)		Annual Qty. required (M. Tons.)
1	Local low grade high phosphorus Manganese ores	Mn	33	1,00,918.00
		Fe	12	
		SiO_2	9.5	
		P	0.5	
2	Local medium grade High phosphorus manganese ores.	Mn	42	18,200.00
		Fe	11	
		SiO_2	5	
		P	0.3	
3	Blend of other Mn ores from Orissa, Maharashtra and Madhya Pradesh	Mn	43-45	1,58,700.00
		Fe	6.68	
		SiO_2	7.01	
		P	0.15	
	Total Mn ores required			2,77,818.00
4	Pearl coke	F.C.	68-72	66,735.00
		Ash	26-30	
		P	0.16	
5	Non-coking coal	F. C.	40-45	27,300.00
		Ash	15-20	
		P	0.02	
6	Limestone	CaO	52	51,730.00
		SiO_2	3	
	Products annually expected to be produced			
1	Export grade FeMn	Mn	78-80	35,000.00
		P	0.25 max	
		Si	1.5 ,,	
		C	8 ,,	
2	Standard Grade Fe Mn	Mn	74-75	70,000.00
		P	0.35	
		Si	1.5	
		C	8 max	
3	Low carbon steel	Mn	0.1	10,641.00
		Fe	99.9	
		P	0.045	
		C	0.04	
4	Dicalcium phosphate	CaO	30.23	2,191.00
		P_2O_5	24.5	
5	Fe Mn discard slag	MnO	20-22	87,635.00
		(Mn	16-17)	

carbon ferro manganese in the coming decades or for production of value added export grade ferro manganese.

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