A Review of the Production of Ferromanganese in Blast Furnace

Conference Paper · May 2011

1 author:

Jorge Madias
Metallon
208 PUBLICATIONS   **386** CITATIONS

Some of the authors of this publication are also working on these related projects:

Project   New Steel Products View project

Project   Continuous Casting Technology View project

A Review of the Production of Ferromanganese in Blast Furnace

Jorge Madias
metallon
9 de Julio 428, B2900HGJ San Nicolas, Buenos Aires, Argentina
Phone/Fax 011 54 3461 427231
E-mail jorge.madias@metallon.com.ar

Introduction

The production of high-carbon ferromanganese in blast furnaces is reviewed, based on public literature and requests to consultants and suppliers to the industry.

The review includes an overview of the FeMn production in blast furnaces during latest decades; main features of raw materials and reductants, and its influence on the process; raw materials preparation, including sintering; design features of the blast furnaces, lining, cooling, operating practice, combination with hot metal production, offgas treatment, specific consumption of coke and Mn ore, casting practice, and a comparison with submerged arc furnaces.

Production of ferromanganese in blast furnaces

High C FeMn world production has been in the order of the 5 Mtpy in the first decade of this century. In 2008, 4.795.100 t has been produced, of which 3.419.900 t in Asia [1]. China is the largest producer, making half of the world's production. Including SiMn smelters, some 600 companies are located in China, with a large excess of installed capacity [2].

Production of High C FeMn in blast furnaces is concentrated in China, Russia, Ukraine, Poland and Japan. Blast furnaces were widely used in developed countries, up to the end of the Second World War. At that time it was common that an integrated plant destined its smaller and older blast furnace to the production of High C FeMn. One reason for this scheme was that the top gas in the FeMn blast furnace entrained excessive fines. So, the sensible heat of the top gas was not useful for air reheating in the stoves, using for the hot blast air coming from the other furnaces (those producing iron). Years later, these submerged arc furnaces (SAF) replaced blast furnaces for the FeMn production, due to having less coke consumption, longer refractory life, no need of air preheating, etc. Besides, the MnO-rich slag from High-C FeMn production in SAFs could be recovered by using it as a raw material for the production of FeSiMn.

In Russia and China the abundance of low Mn ores could have been a driver for keeping the blast furnaces running. In Japan, the decision of building an FeMn blast furnace was taken by the then Kawasaki Steel under the circumstances of the second oil crisis, to replace two SAFs with one blast furnace, in a plant supporting high electricity cost.

Those plants continuing the operation of blast furnace for this purposes, have been enhancing raw materials preparation, equipment and operating practice, in order to improve specific consumption indices and decreasing cost per ton.

Raw materials

A short discussion of raw materials, reductants and fluxes features follows.

Mn Ore. Blast furnaces are more forgiving than SAFs regarding raw material quality. It is possible to consume efficiently Mn ores with a minimum of 28% Mn.

Generally, Mn ore is composed by manganese oxides (MnO_2, Mn_2O_3, Mn_3O_4), accompanied by iron oxide, silica and other oxides. Carbonates have been processed, too; at least in Russia and China.

Attention is paid to Mn/Fe ratio. As iron oxide is fully reduced in the furnace, taking part in the ferroalloy, a low Mn/Fe ratio may imply that FeMn be below specification in Mn content. The ratio should be not less than 7.5:1. Also important is the Phosphorus content, because in the blast furnace all charged phosphorus reports to the alloy. In table 1, a typical specification of Mn ore for ferromanganese production is presented.

Mn (%)	Fe (%)	Al_2O_3 (%)	Al_2O_3+SiO_2 (%)	As (%)	P (%)	Cu+Pb+Zn (%)
48 min.	6 max.	7 max.	11 max.	0.18 max.	0.19 máx.	0.30 max.

Table 1. Typical specification for metallurgical grade Mn ore [3].

Brazil, Gabon, Australia and Russia have good quality manganese ore. Azul mine, owned by Vale S.A., located in Carajás, Pará, is the more exploited in Brazil, although there are important reserves in Corumba, Matto Grosso do Sul. Azul Mn ore chemistry is presented in table 2. Ore processing in Azul mine consists of washing, grinding and screening operations, to obtain both lumps and sinter feed, figure 1.

Mn (total)	MnO_2 (%)	Fe_2O_3 (%)	SiO_2 (%)	Al_2O_3 (%)	K_2O (%)	P_2O_5 (%)
52.0-53.0	78.8-80.0	2.5-4.2	1.4-2.0	4.3-5.0	0.8-1.2	0.20-0.22

Table 2. Chemical composition of Azul mine iron ore in Carajás, Para, Brazil [3].
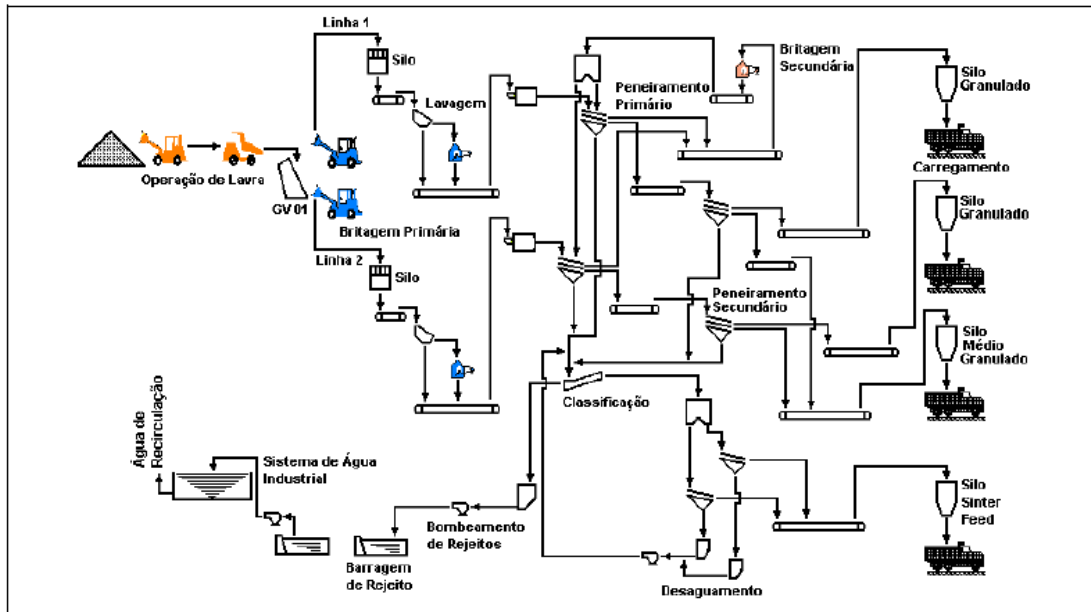

Figure 1. Scheme of Manganese ore processing at Azul mine, Carajás, Pará, Brazil [3].

402

In China and Russia, Mn ore with 30% Mn content is used, with high amount of fines. This calls for introduction of sinterplants, also utilized for the charging of submerged arc furnaces.

As an example, in table 3 the percentage of sinter used in certain Chinese plants at certain time, is detailed.

Plant	Xinyu	Saoxin	Yangkuan	Bayi	Guilin	Xinyang	Langfang	Wujing	Average
Sinter %	66.1	7.8	39.2	48.7	63.1	34.5	41.2	31.2	40.5

Table 3. Proportion of MnO sinter used in Chinese blast furnaces in 1994-95 [4].

Results obtained by agglomeration of ore fines through sintering show clear improvements in coke consumption, Mn yield and productivity. As an example, in table 4 the evolution of several indices along a year, as the proportion of sinter in the charge increased from 60 to 100%, is presented

Sinter (%)	60	70	80	90	100
Coke (kg/t)	2196	2145	2083	2075	2064
Fluxes (kg/t)	1158	978	604	526	355
Slag (kg/t)	2684	2631	2484	2473	2465
Productivity (t/m^3.day)	0.465	0.492	0.509	0.514	0.537

Table 4. Evolution of some indices with the increase of sinter in the charge, based on data taken from [4].

Reductants. Normally, coke obtained from coking coals, in conventional batteries (with recovery of byproducts or in non-recovery/heat-recovery batteries, is used. Size is 20-60 mm, as for iron blast furnaces. As a difference with submerged arc furnaces, which are flexible from the point of view of reductant type (due to less height), to our knowledge, there is no report of use of reductants other than metallurgical coke in FeMn blast furnaces. In SAFs, use of charcoal and pet coke to complement coal coke has been reported.

Two Brazilian companies producing pig iron in charcoal-based blast furnaces, that wanted to move to ferromanganese production, projected to change to coke to that purpose [5].

The injection of pulverized coal through the tuyeres, as used in iron blast furnaces, has been suggested [6]. No reports on such practice have been published, with the exception of an experimental shaft furnace developed in Japan [7]. In the Japanese blast furnace, 100 kg/t fuel oil is injected [8].

Fluxes. Slag chemistry control is required, for the slag to flow through taphole and runners; for not having high MnO; for desulfurization and for Na_2O / K_2O absorption. Limestone and dolomite are used for slag basicity management.

It is convenient to introduce part of the fluxes through sinter or with previous calcination, as lime. CO_2 generated while calcining limestone has several negative aspects [6]:

- Carbonate decomposition requires heat (the reaction is endothermic)
- Boudouard reaction between coke carbon and CO_2: $C+ CO_2=CO$ takes place, consuming both heat and carbon
- It complicates Gas distribution and operation evenness

The starting solution in China was the use of calcined lime. Yanggang applied it with immediate results: a decrease of 22% in coke consumption and an increase 33% in FeMn production [6]. Then, Xinggang started

to add dolomite in the sinterplant, instead of doing that in the furnace. Finally, most plants tended to charge a high basicity, high MgO sinter, and calcined lime in the furnace, simultaneously.

Aspects to highlight are that limestone may be overcalcined, but not semicalcined; fines must be eliminated; sinter basicity must be high (recommended value 1.7 ternary basicity).

Blast Furnace

Blast furnaces for FeMn production are generally speaking similar to those producing iron, with some differences discussed below. They tend to be smaller and less updated in technology.

In figure 2 a sketch of a blast furnace proposed by a Chinese Supplier is shown. It has an inner volume of 55 m^3, with a hearth diameter of 5 m and a height of 13 m, for a daily production of 35 t. Space required for the installation is 2000 m^2; cost including two stoves, installation for gas treatment and training of the operators is in the order of USD 3 M[9].
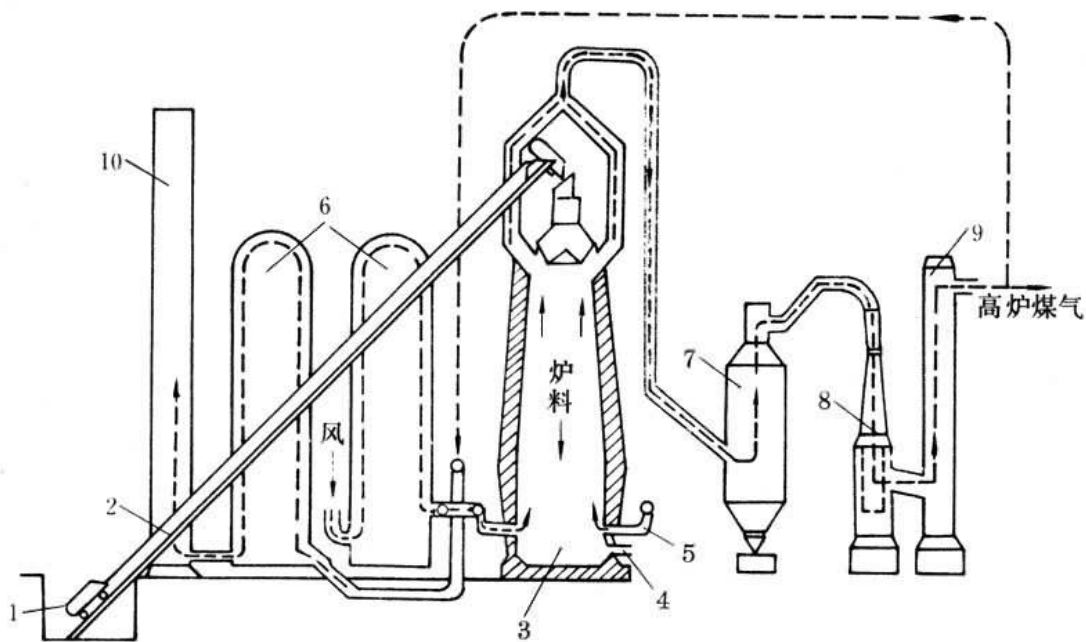
高炉冶炼流程示意图
1 料车　2 上料斜桥　3 高炉　4 铁、渣口　5 风口　6 热
风炉　7 重力除尘器　8 文氏管　9 洗涤塔　10 烟囱

Figure 2. Sketch of a blast furnace for FeMn production currently proposed by a Chinese company [9]. 1 y 2: System for charging raw materials; 3: furnace body; 4: FeMn tap hole; 5: Hot blast through tuyeres; 6: stoves; 7: gravity filter; 8: venturi; 9: gas washing tower; 10: stack.

The only FeMn Japanese blast furnace is shown in figure 3. As mentioned previously, it was introduce to replace two SAFs in a decision taken at the second oil crisis, but is still in operation. The charging system, as seen in the figure, is a bell-less top with a cardanic distribution system, instead of the bell top in the Chinese design of figure 2.
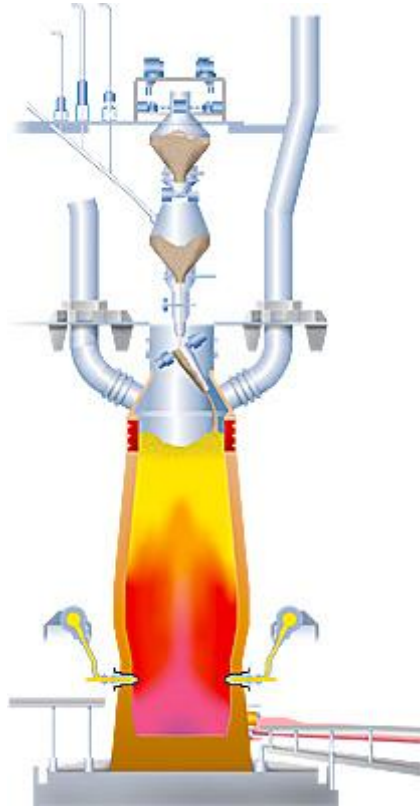
Figure 3. Cut of the FeMn blast furnace of Mizushima Ferroalloys, with bell-less top and a cardanic system for charge distribution [10].

In table 5 some FeMn blast furnaces are listed. The Chinese supplier mentions as standard size 55 m^3; 100 m^3; 175 m^3; 200 m^3 and 300 m^3. All fall within the range of 500 m3 maximum, usually taken as the range for mini blast furnaces.

Plant	Country	Volume (m^3)	Reference
Wujin Alloy Works	China	60	6
Jiang Xiniu	China	255	4
Mizushima Ferroalloys	Japan	398	10

Table 5. Inner volume of some FeMn blast furnaces.

According to references, productivity varies from 0.5 to 0.9 t/m^3.day.

Russian designs seem to differentiate FeMn from iron blast furnaces in the following features: upper shaft cooling, discussed below; sprayers for the charge, and the use of slag taphole, not common in their designs for iron blast furnaces, with much less slag volume [12].

There are important metallurgical differences between both types of blast furnaces. MnO_2 and Mn_2O_3 are reduced easily to MnO, but MnO reduction occurs only directly with C, and requires much more energy than FeO. Because of this, the reaction takes place in the lower part of the furnace. The energy needs are covered with coke consumption three times higher than that for ironmaking. Slag volumes are much higher, and generally the FeMn blast furnaces are operated with slags of higher basicity.

Gas generation is much higher too, and with more content of fines. Adiabatic flame temperature is higher; CO content and top gas temperature, are also higher. In figure 4, some of these differences are highlighted.
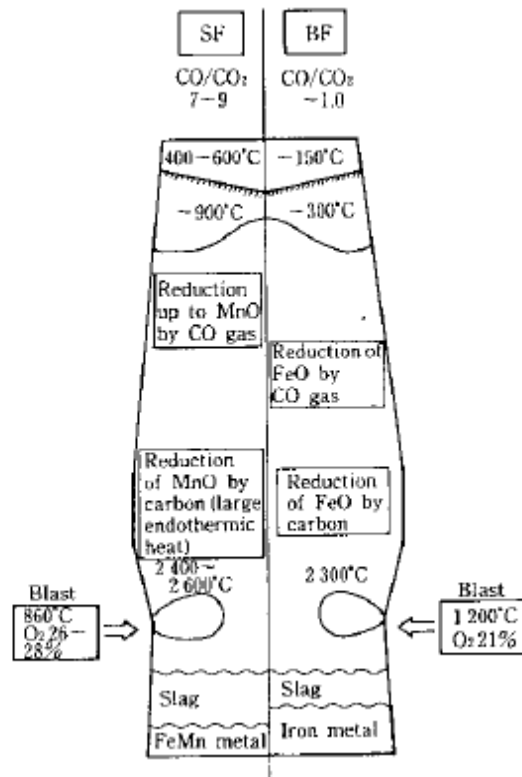

Figure 4. Comparison of metallurgical reactions, gas chemistry and temperature conditions between Mizushima Ferro-Alloy FeMn blast furnace (left) and Kawasaki Steel iron blast furnaces (right) [11].

In the following, some issues considered important for economic operation of FeMn blast furnaces are discussed.

Refractories. In general, campaigns of FeMn blast furnaces are shorter than those of iron blast furnaces. Higher temperatures favor refractory wear. The appetite of Mn for silica contained in the refractories is well known. In China, after six months of start-up, wear developed. In one or two years, more and more erosion occurred, giving place to abnormal charge distribution and operating problems. Despite efforts, campaigns were no longer of two to four years.

The solution to the problem was found in the 60s in the Yanggang plant. A furnace that was switched from Fe to FeMn started to display erosion in the belly and in the center of the upper shaft, and in two years had no lining in those zones. Bell diameter was enlarged, achieving a central distribution of gases, and the problem was overcome. This was the first FeMn furnace in China operating without lining [6].

After that, a new furnace was built, with water cooling of the full body. As this furnace had a long campaign and good production indexes, the other Chinese FeMn blast furnaces copied the design. Since then, these furnaces are designed with the standard refractories in the hearth, while the bosh is lined cooling staves and chamotte bricks. In the outer shaft and the throat, water sprays are used.

In figure 5, the design of cooling plates for the Japanese FeMn blast furnace is presented [11].
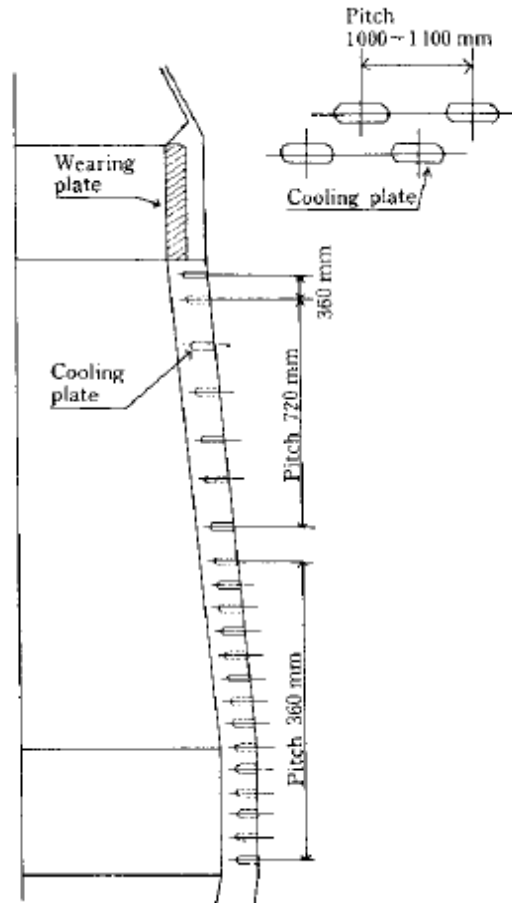
Figure 5. Cooling plates in blast furnace of Mizushima Ferroalloys [11].

These changes imply a large throat, a short bosh and a tall shaft. Belly diameter is larger and shaft angle enlarges, correspondingly with the increase in throat diameter. This coincides with the design presented in figure 2: a short furnace with large diameter, compared with usual design for ironmaking blast furnaces.

Gas cleaning. Mn ore may have big amount of fines; Mn ore sinter has low strength and may generate lot of fines, too. As a consequence, top gas entrains a high amount of fines. For economic production, it is necessary to utilize the sensible heat of the gas to preheat air blast in the stoves. As mentioned, this issue brought about that in multiple blast furnace plants, FeMn used to be produced in the smaller furnaces, using preheated air coming from the ironmaking furnaces.

In China, the FeMn blast furnace producers adopted the gas cleaning system developed by Xingang in 1963, with the help of the Maanshan Iron & Steel Design Institute. An overflow Venturi was adopted before the washing tower and a dedusting cyclone was added, too. This way, the FeMn blast furnaces became independent of the ironmaking blast furnaces [6].

Manganese recovery. The main Mn loss is to the slag. To minimize it, the slag has to have the right chemistry, the FeMn in the hearth must have high temperature and the gas distribution in the furnace must be adequate.

Generally, a good slag should have high basicity and high MgO content; Al_2O_3 content should be less than 15% to avoid $MgO.Al_2O_3$ formation, due to its high melting point. High temperature in the hearth means higher temperature in the zone where liquid metal and slags drip through coke, where most of the reduction

reaction takes place. To achieve such a high temperature, sinter must have the already mentioned features, together with a short range of softening temperature; air blast must be injected at high temperature and oxygen may be introduced through the tuyeres.

Regarding gas distribution, the aim is to have the percentage of CO_2 in the shape of a funnel [6].

In table 6, the evolution of several parameters of charging and operation along thirty years in Xingang plant is presented, as an example of the trends in specific coke consumption, Mn recovery and slag chemistry.

Ítem	1962-1964	1965-1974	1975-1979	1980-1981
% Mn in charge (%)	32.4	32.4	29.9	32.9
Specific coke consumption (kg/t)	2215	2040	1907	1722
Mn yield (%)	69.5	77.5	79.4	84.2
Si in FeMn (%)	1.10	1.01	1.07	0.99
CaO/SiO_2 in the slag	1.26	1.33	1.42	1.49
MgO in the slag (%)	3.6	6.0	5.5	9.0
Al_2O_3 in the slag (%)	n.d.	15.1	14.0	11.8
MnO in the slag (%)	14.2	9.4	8.3	4.8

Table 6. Evolution of some indexes in Xingang FeMn blast furnace [4].

These practices are limited: if slag basicity is too high, high melting point phases may precipitate in the slag, as for instance $2CaO.SiO_2$, and the benefits may be lost. Also, if hearth temperature is too high, Mn volatilization loss may increase.

Blast temperature. It is a known fact that in FeMn smelting the reduction process is direct, from the slag, in the lower part of the furnace, at high temperature (more than 1300 °C). Energy consumption is much higher than for pig iron production, and so specific coke consumption. Because of this, attention is paid to air blast temperature. In figure 6, a heat balance of a particular blast furnace is presented. In this case, 30% of the heat is supplied by the hot blast and 60% by coke combustion in front of the tuyeres.
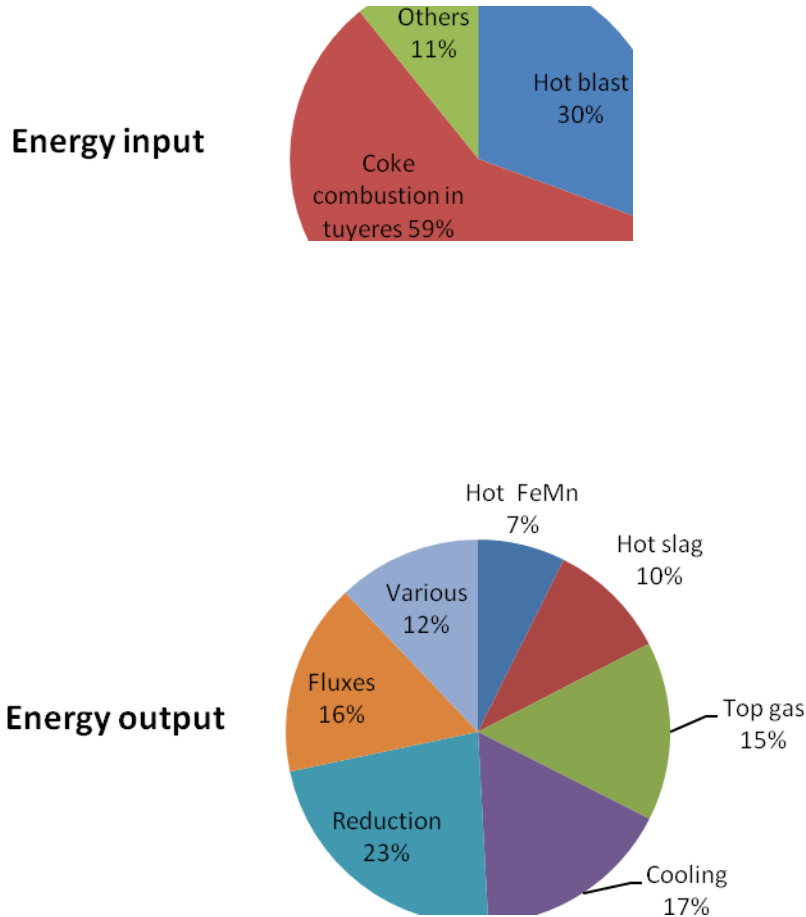
Figure 6. Heat balance of a FeMn blast furnace. Own, based on data in [13].

Normally, air is preheated at a temperature between 800 and 950 ^{o}C. A higher blast temperature should favor a better Mn recovery and smaller coke consumption. As in iron smelting blast furnaces, oxygen injection has been practiced [8, 13].

Oxygen injection gives favorable results in a low blast temperature situation (up to 950 ^{o}C), high Mn content in the charge and low/medium basicity slag. Hearth temperature increases, as well as the reduction of manganese; this brings about a higher Mn yield and smaller coke consumption. Same effect could be obtained by increasing flux consumption, if slag basicity is too low.

Instead, if preheating temperature is high (1000-1150 ^{o}C), this assures a flame temperature high enough (2260-2350 ^{o}C), although only air is being blast, and reasonable Mn yield and coke consumption. Under these conditions, oxygen injection may have negative results [13].

At pilot plant level, as high blast temperature as 1400 ^{o}C has been tested. Modifications were necessary in raw materials charged, as well as in the design and operation of the furnace, to be able to operate in uniform conditions and withdraw all the advantages of this change [13].

In general, air is heated in refractory stoves like in iron blast furnaces. An exception to this way is the Japanese blast furnace; a metallic recuperator was introduced, for continuous heat interchange (figure 7). This was probably because of lack of space, as this furnace was introduce into a building to replace two submerged arc furnaces.

Start-up. This operation may have a very important incidence in achieving a satisfactory campaign. A standard practice for many furnaces is to start producing pig iron for Foundry or Steel production; then, gradually, to increase Mn ore in the charge, up to arrive to the minimum of the standard, usually in the third day after start-up [15].

A shorter start-up procedure has been successfully tested, charging some Mn ore from the very beginning, in such a way to obtain 25% Mn at the 8th hour; 50% Mn at the 16th hour and 70-75% Mn at the 24th hour [15].
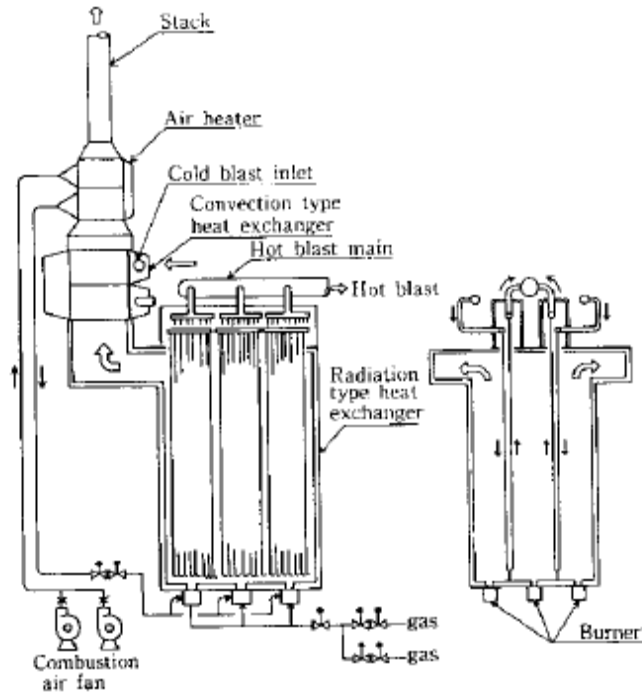

Figure 7. Metallic recuperator for heating of air blast in Japanese blast furnace [11].

Comparison with submerged arc furnaces

It is interesting to compare the use of blast furnace with the more popular submerged arc furnace, taking into account that they are the two dominant processes worldwide. In table 7 both routes are compared form the point of view of raw materials, specific consumptions, possibility of shifting to other products, metallic yield, smaller possible scale, etc.

Item	Blast furnace	Submerged arc furnace
Mn Ore	28-30% Mn possible	>35% Mn
Coke consumption (kg/t)	1500-2000	310-380
Electric energy consumption (kWh/t)	200	2400
Ore consumption	2500-3000 kg/t	
Mn yield	80 – 85 %	60 – 75%
Phosphorus content	High	Low
Slag formation (kg/t)	600-2700	600-700
Other possible products	Pig iron, FeTi, FeP	FeSi, SiMn, Si, CaSi, FeSiMgCe, CaC_2, pig iron
Flexibility to demand	Rigid (long campaign)	Good
Scale	35 t/day minimum	10 t/day mínimum

Table 8. Comparison between blast furnace and submerged arc furnace for High C FeMn production.

Conclusions

Blast furnaces continue to be used for High-carbon FeMn production, where conditions favor this route (low ore quality, availability of existing furnaces). The smaller furnace being offered currently in the market produces around 35 t/day. For even running and for product within spec, the FeMn blast furnace must operate continuously, in years-long campaigns.

In comparison with ironmaking, FeMn smelting needs higher temperature; coke consumption is much larger and much more slag is generated. Top gas needs a careful treatment due to the high amount of fines.

References

1. "Mn 2008 World Overview", The Manganese Institute, Paris, France, 2010.
2. An, H.; "Review on Production and Market of Siliconmanganese and Ferromanganese in China".
3. Alves Sampaio, J.; Calixto de Andrade, M.; Junqueira Boudort Dutra, A.; Torres Moreira Penna, M. "Manganese". Chapter 24 in Rocks and Industrial Minerals CETEM, 2005 (in Portuguese).
4. Xiong, X.; Liu, D.; "Studies on production of high carbon ferromanganese in blast furnace with high proportion of sinter and improvement in manganese recovery". The Proceedings of INFACON 8, pp. 226-231.
5. Garcia Scherer, S., private communication, August 2010.
6. Zhang, T.; "Technical progress of blast furnace ferromanganese production in China". The Proceedings of INFACON 8, pp. 247-253.
7. Kamei, Y.; Miyaza, T.; Yamaoka, H.; "Production Test of High-carbon Ferromanganese Using a Shaft Furnace with Coke Packed Bed Injected with High Oxygen Enriched Air and a Large Quantity of Pulverized Coal". ISIJ lnternational, Vol. 33 (1 993). No. 2, pp. 259-266.
8. Masukawa, M.; Shiota, T. "High productivity operation of shaft-type FeMn melting furnace". The Proceedings o INFACON 11, pp. 195-205.
9. Min Y., private communication, August 2010.
10. http://www.mizukin.co.jp/en/fe/sf.html
11. Morimoto, T.; Yoshomoto, M.; Takahashi, H.; Hamada, T.; Fukushima, N.; Sakurai, S. "Construction of shaft type ferromanganese smelting furnace". Kawasaki Steel Technical Report No. 17 October 1987 pp. 1-8.
12. Mul'ko, G.N.; Bondar', A.A.; Zaitsev, V.A.; Nitskii, E.A.; Cherkasov, E.G.; "Making ferromanganese in blast furnaces". Metallurgist, Vol. 44, Nos. 1-2, 2000.
13. Kozhemyachenko, Yu.N.; Pervushin, S.I.; Varava, V-I.; Strelets, A.I.; Vasyura, G.G.; Osadchii, V.P.; Nikolaev, K.A.; Anishchenko, Yu.V.; Shubravyi, N.S.; "Efficient blast regime in the production of blast-furnace ferromanganese. Metallurg no. 12", December 1987, pp. 9-11.