PRODUCTION OF MANGANESE ALLOYS WITH ORE FROM CARAJÁS

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ABSTRACT

This paper intends to give an outline of the preliminary results obtained by three (3) stage tests with Carajás manganese ore to produce HCFeMn by the rich slag process, using a 250 KVA electric furnace pilot type.

In the first stage, 100% manganese ore was used, and in the second stage a blend of 50% ore and 50% sinter.

The obtained rich-slag of approximately 36% MnO was mixed with ore to produce FeSiMn.

INTRODUCTION

Serra dos Carajás (Carajás Mountain Ridge) is known today as the Brazilian biggest native mineral reserve, and the whole area has, actually, being reckoned as the real mining ore Province of Brazil.

By 1971, during geological searches by CVRD in the area, a large manganese natural deposit has been found, and its prospective studies revealed a mining ore field of about 65 million tons.

Carajás settlement is situated in the Southern part of the State of Pará. The climate is tropical, warm and humid. The drought season runs from July to October, and the temperature, during this period, varies between 19° and 31°C, with an average 2,000mm rainfall.

The manganese mine has being exploited by CVRD at the rate of 700,000 t/year, and the production is shipped to Ponta da Madeira by a 890 km modern railway (FIGURE 1).

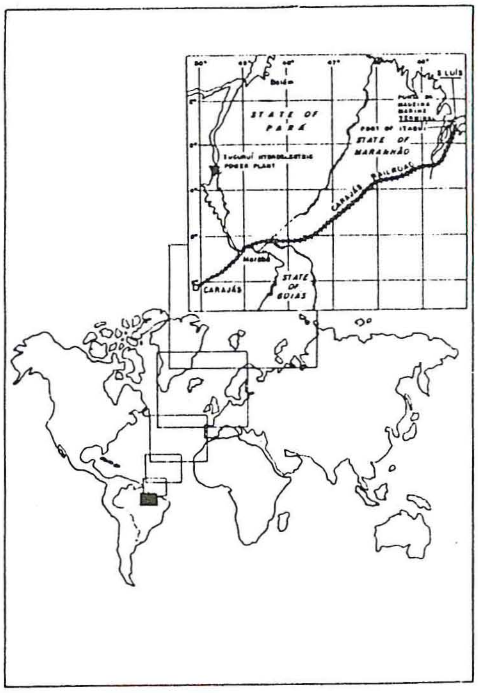


FIGURE 1 - LOCATION OF SERRA DOS CARAJÁS

Since 1978 the CVRD studies and research programmes to process the Carajás manganese ore, revealed that there are two distinct workable products: one ranging from 1/4" to 3"; and the other from 100 mesh to 1/4" (sinter feed).

The bench scale, pilot scale and industrial scale tests with the sinter feed, reached sensible results making possible to come to a sinter type with physical and chemical satisfying characteristics.

Later, further bench scale and pilot scale tests, utilizing the Carajás manganese ore and the sinter, showed a possibility to produce HCFeMn and FeSiMn.

Today's prospectives are encouraging. Several Brazilian and European alloy industries are already making use of the Carajás manganese ore, and various industrial plant projects for the area are in progress, entirely based on the exclusive application of the Carajás manganese ore.

RAW MATERIALS

- CARAJÁS MANGANESE ORE AND SINTER

  The 6 to 75mm manganese ore went under crushing and screening operation to be reduced to a 6 to 25mm range, so that its granulometry could be proper for pilot scale trials.

TABLE I shows the typical chemical composition of Carajás manganese ore.

X-ray diffraction studies showed that the principal components of this ore are cryptomelane, pyrolusite, goethite, todorokite, gibbsite and kaolinite.

In relation to sinter, its granulometry was between 6 to 20mm, and its typical chemical composition is also shown in TABLE I.

- **IRON ORE AND FLUXES**

TABLE II shows the iron ore and fluxes chemical composition , and its respective granulometry range, used in pilot scale trials.

TABLE I - TYPICAL COMPOSITION OF CARAJÁS MANGANESE ORE AND SINTER

	Mn (%)	Fe (%)	SiO_2 (%)	Al_2O_3 (%)	CaO (%)	MgO (%)	K_2O (%)	Na_2O (%)	P (%)	Granulometry (mm)
Mn Ore	46.09	3.63	2.54	9.60	0.25	0.20	1.46	0.10	0.08	6 - 25
Sinter	50.83	6.52	5.16	12.53	0.55	0.32	1.17	0.06	0.07	6 - 20

TABLE II - TYPICAL COMPOSITION OF IRON ORE AND FLUXES

	Fe (%)	Mn (%)	SiO_2 (%)	Al_2O_3 (%)	CaO (%)	MgO (%)	P (%)	Granulometry (mm)
Iron Ore	67.96	0.05	1.20	1.03	0.17	0.05	0.03	6 - 20
Limestone	0.22		1.08	-	53.48	0.32	-	10 - 20
Quartzite	0.27		98.10	0.53	-	0.80	-	10 - 20
Dolomite	-	-	0.12	0.90	29.44	19.96	-	10 - 20

- **RICH-SLAG MANGANESE**

A mixture of manganese ore and rich-slag, originated from the HCFeMn production,was used to produce FeSiMn.

TABLE III shows the rich-slag chemical composition and its granulometry.

TABLE III - CHEMICAL COMPOSITION OF THE RICH-SLAG

Mn (%)	Fe (%)	SiO_2 (%)	Al_2O_3 (%)	CaO (%)	MgO (%)	K_2O (%)	P (%)	Granulometry (mm)
27.93	0.18	19.00	21.87	15.13	4.95	1.50	0.03	6 - 20

- **REDUCTANT**

Charcoal was the reductant used in the pilot scale trials. Its selection was due to its general utilization by the national ferroalloy industry; due also to the fitness of its metallurgical characteristics, and because it is a renewable material.

TABLES IV and V show respectively the composition of the charcoal and its ashes.

TABLE IV - CHARCOAL COMPOSITION USED AS REDUCTANT (DRY BASIS)

Fixed Carbon (%)	Volatile Matter (%)	Ashes (%)
74.90	18.10	7.00

TABLE V - CHEMICAL COMPOSITION OF THE CHARCOAL ASHES

Mn (%)	Fe (%)	SiO_2 (%)	Al_2O_3 (%)	CaO (%)	MgO (%)	K_2O (%)	Na_2O (%)
1.16	0.63	1.05	0.69	51.40	6.55	15.66	1.89

EXPERIMENTAL PROCEDURES

The trials to produce HCFeMn and FeSiMn from Carajás manganese ore, started with a theorectical study of the various charge compositions that could be used.

The percentage of Al_2O_3, the slag composition, and the quantity of ore in the mixtures,ore -sinter and ore-rich slag, were varied.

The mixtures defined by those studies were tested in a bench scale (30 KVA furnace), in order to estimate the charges to be used in pilot scale.

In this scale,approximately 20 days were expended for each stage. The tapping operation of the furnace was carried out every two hours; and every 12 hours, samples of alloy and slag were taken out to determine its respective chemical composition.

During each stage, the parameter alterations were achieved according to slag/metal ratio; to alloy and slag composition; to off-gas temperature; and the furnace conditions.

EQUIPMENTS

All the trials to produce HCFeMn and FeSiMn from Carajás ore, were carried out using an electric three phase, closed, rotative, pilot furnace. Some of its characteristics can be seen in the following TABLE VI.

TABLE VI - SUBMERGED ELECTRIC ARC FURNACE, PILOT TYPE, CHARACTERISTICS

TRANSFORMER CAPACITY	-	250 KVA
FREQUENCY	-	60 HZ
GRAPHITE ELECTRODE DIAMETER	-	178 MM
CRUCIBLE DIAMETER	-	1000 MM
CRUCIBLE DEPTH	-	850 MM
SHELL DIAMETER	-	1600 MM
SHELL DEPTH	-	1580 MM
SECONDARY VOLTAGE	-	11,6 TO 46 V
TAPS NUMBER	-	16

This pilot furnace is operated by the conventional method to produce manganese alloys.

FIGURE 2 shows the tapping during trials with 100% Carajás manganese ore.

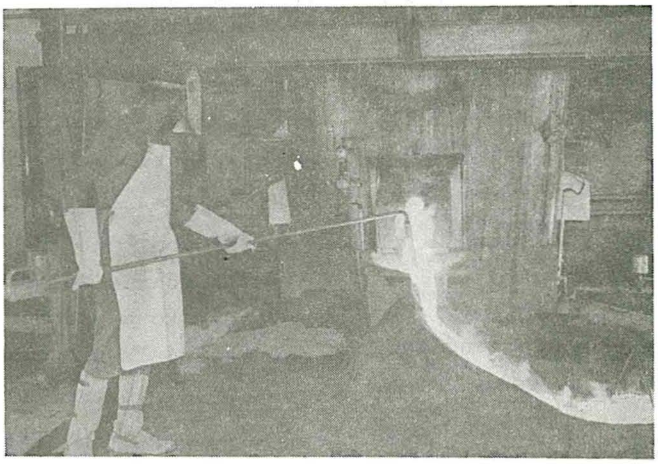


FIGURE 2 - HCFeMn TAPPING DURING TRIALS WITH 100% CARAJÁS MANGANESE ORE.

TRIALS COMMENTS

- FIRST STAGE-HCFeMn PRODUCTION WITH 100% CARAJÁS MANGANESE ORE

When only Carajás manganese ore (≈9.5% Al_2O_3) is used, it is advisable to obtain a larger percentage of Al_2O_3 in the slag.

At the same time, basic requirements (like liquidus temperature and viscosity) have to be fulfilled.

According to the conventional way to produce HCFeMn, the final slag composition should have a liquidus temperature of at least 1350°C to ensure that the alloy temperature is sufficiently high, but it should have less than 1500°C to minimize fume loss.

The viscosity must be low to produce swift slag-metal separation; easy tapping and adequate handling operations.

In relation to melting temperature, Gupta[1] results, showed that for a fixed CaO/SiO_2 wt ratio, if the Al_2O_3 content increases, the melting temperature will also increase, and will be more accentuated if the MgO content in the slag is higher.

Reffering to viscosity, the results obtained by Gupta[1] showed that an increase in alumina content, increases the viscosity of the slag.

Results obtained by Woollacott[2]

considering the system SiO_2-Al_2O_3-CaO--MgO-MnO (to 10 mole percent Al_2O_3), showed that SiO_2 exerts great influence on the viscosity. Thus, the viscosity is increased as the SiO_2 content increases at a constant ratio of the basic-oxide components (MnO-MgO and CaO). Futher, to a fixed CaO to MnO ratio, the viscosity is dependent primarily on the silica content; while the proportion of MgO shows only a minor influence.

Another secured result was that, increasing the MnO content the viscosity at all the SiO_2 and MgO levels investigated decreases.

Chubinidze[6] experiments pointed out that a decrease in the viscosity occurs, when the MnO content varies from 5 to 20% in the slag, taking into account the MnO-CaO-SiO_2 system at 10% Al_2O_3.

A literature review [7] showed that enough data is available for typical slags produced by either the rich-slag or discard slag process. There is, however, a lack of data concerning slags of high MnO and Al_2O_3 contents.

Another inference of the Al_2O_3 presence in the Carajás manganese ore is its link to the slag weight, during the HCFeMn production process.

In practice, one should try to obtain minor specific weights of the slag, in order to avoid high consumption of raw materials and energy.

FIGURE 3 illustrates this outcome, showing that the different percentages of Al_2O_3 in the slag affect the slag specific weight and the energy consumption in a way that, whereas the Al_2O_3 percentage in the slag increases, the amount of those parameters decrease

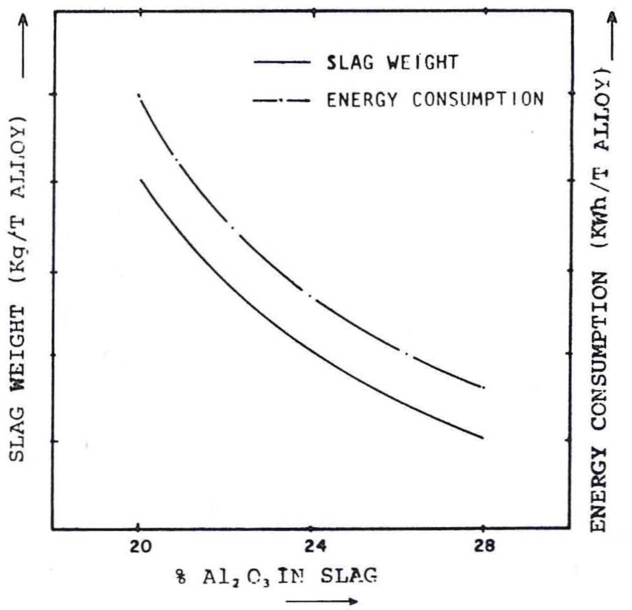


FIGURE 3 - SLAG WEIGHT AND ENERGY CONSUMPTION AGAINST % Al_2O_3 IN SLAG.

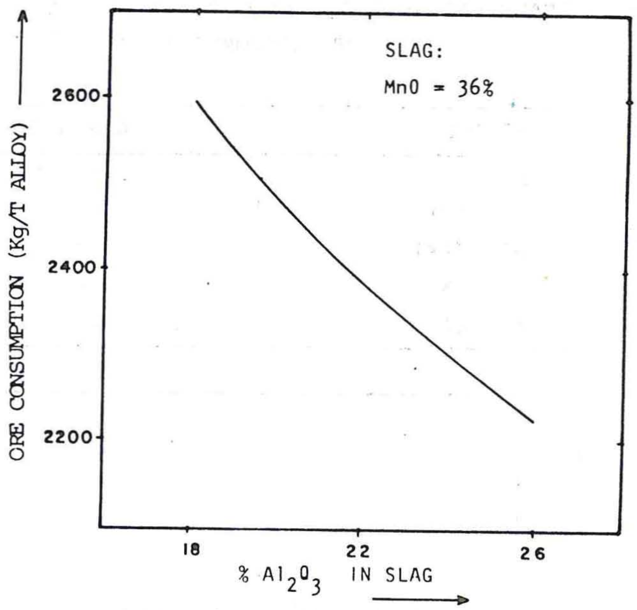


FIGURE 4 - ORE CONSUMPTION AGAINST Al_2O_3 PERCENTAGE IN SLAG

To verify the influence of Al_2O_3 percentage in the slag, regarding the ore consumption, several balances were performed, and its results are summarized in FIGURE 4. This figure shows that to a major percentage of Al_2O_3 in the slag, there will be a minor consumption of ore per ton/alloy.

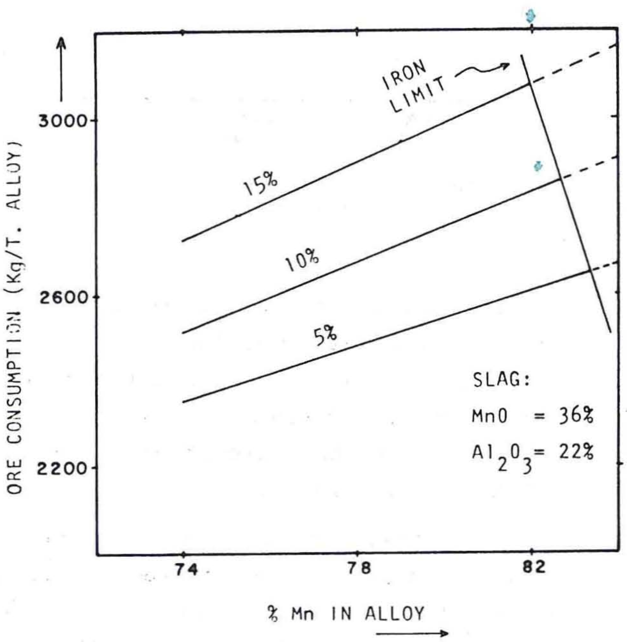


FIGURE 5- ORE CONSUMPTION AGAINST Mn PERCENTAGE IN ALLOY ACCORDING TO THE VARIOUS LOSSES

FIGURE 5 presents a variation of the specific consumption of ore in relation to the manganese percentage in alloy, according to the various losses of this element. This figure shows that the use of 100% Carajás ore (because of its high Mn/Fe ratio), enables to reach up to 82% of Mn; to 15% losses; to a slag of MnO 36%, and Al_2O_3 22%.

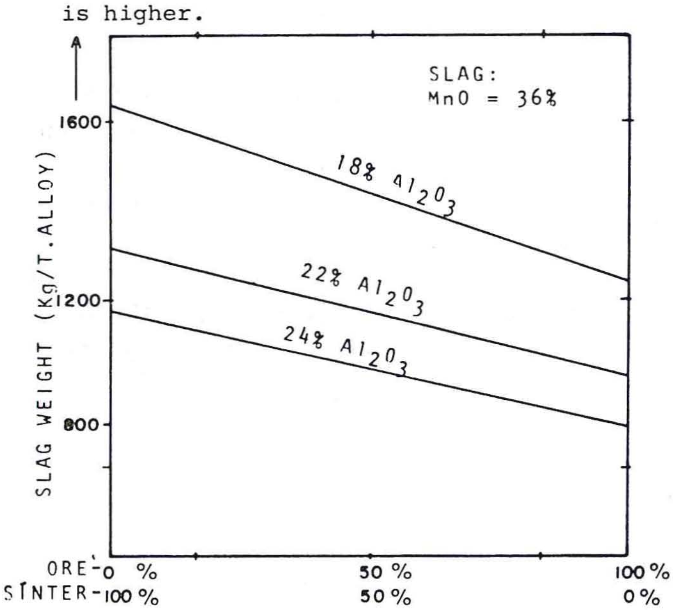
The above considerations, and the results of bench scale tests (30 KVA furnace) enabled to define a slag with 22% Al_2O_3; approximately 5% MgO; 36% MnO; and a CaO/SiO_2 wt ratio from 0.85 to 0.90, to be used at pilot scale trials.

The HCFeMn composition meets the Brazilian NBR 5911 specifications as shown in TABLE VII.

- SECOND STAGE - HCFeMn PRODUCTION WITH COARSE MANGANESE AND SINTER

Several balances were done to evaluate the influence of the sinter percentage in the mixture manganese ore-sinter. The results are summarized in FIGURES 6 AND 7.

FIGURE 6 shows that increasing sinter percentage in the mix, causes the slag weight to increase, because of its high Al_2O_3 percentage. And the other effect shown, is that to a fixed percentage of sinter, the slag weight will decrease when the Al_2O_3 percentage is higher.



FUGURE 6 - SLAG WEIGHT AGAINST % SINTER TO VARIOUS Al_2O_3 LEVELS IN SLAG.

TABLE VII - BRAZILIAN NBR 5911 HCFeMn STANDARD COMPOSITION

ELEMENT (%)	CLASS A-2
Mn	74,1 - 78
C (MAX)	7.5
Si (MAX)	2.0
P (MAX)	0.40
S (MAX)	0.04

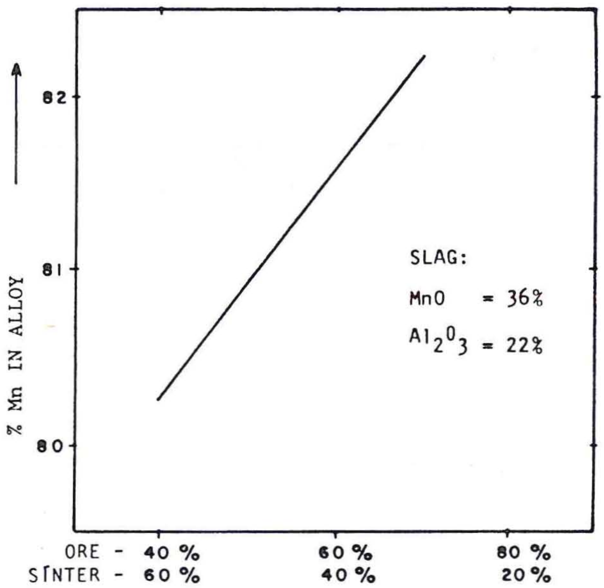


FIGURE 7 : % Mn IN ALLOY AGAINST % SINTER IN THE MIX

Figure 7 shows the manganese content in the alloy as a function of the quantity of sinter in the mix. It can be seen that the manganese content decreases when the percentage of sinter in the mix is higher.

In this stage, the trials were carried out using a mix of 50% manganese ore, and 50% sinter, keepping up the same slag and alloy specifications defined in the first stage.

- THIRD STAGE - FeSiMn PRODUCTION WITH MANGANESE ORE AND RICH-SLAG

For this trials, the available data and the bench scale (30 KVA furnace) results were used to choose the slag composition.

The MnO and Al_2O_3 contents were, respectively 10% and 23%, and the $(CaO + MgO)/SiO_2$ wt ratio near 0.65.

TABLE VIII - BRAZILIAN NBR 5904 FeSiMn STANDARD COMPOSITION

ELEMENT (%)	FeSiMn / 16-20
Mn	65,0 - 70,0
Si	16,1 - 20,0
C (MAX)	2.5
P (MAX)	0.25
S (MAX)	0.04

For the alloy, the Brazilian NBR 5904 standard specification was used (TABLE VIII).

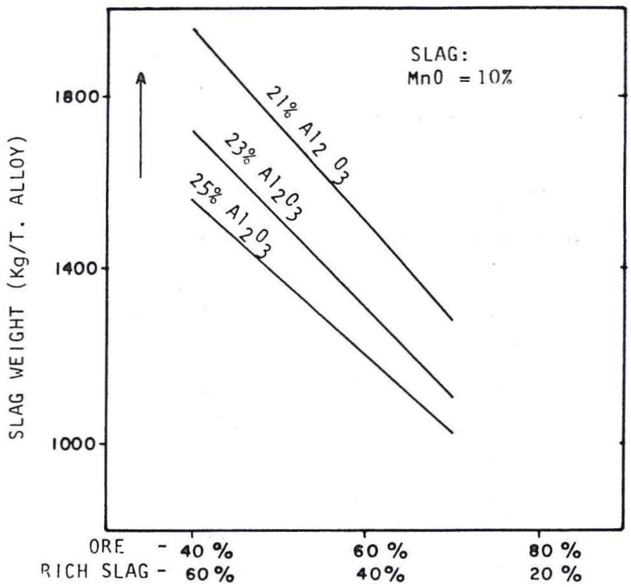


FIGURE 8: SLAG WEIGHT AGAINST ORE PERCENTAGE ACCORDING TO VARIOUS Al_2O_3 LEVELS.

To evaluate the influence of the rich-slag quantity in the mixture, several balances were done, and the results are summarized in FIGURE 8.

This figure shows that, to a major quantity of rich-slag corresponds a higher weight of produced slag.

The weight increases in proportion to the decrease of Al_2O_3 in the slag.

All the above considerations enables to define a mix with 40% rich-slag and 60% Carajás Manganese Ore.

TRIALS-OPERATIONAL DATA

The results obtained in pilot scale trials, for the production of HCFeMn and FeSiMn using Carajás ore are given bellow:

- STAGE DATA

  1st - HCFeMn production with 100% coarse manganese

  2nd - HCFeMn production with 50% coarse manganese and 50% sinter

3rd - FeSiMn production with 60% coarse manganese and 40% rich-slag.

- CHEMICAL ALLOYS COMPOSITION

ELEMENTS (%)	STAGES		
	1	2	3
Mn	74.94	75.10	65.74
Si	0.15	0.20	16.28
P	0.12	0.10	0.05
S	0.01	0.01	0.01
Fe	17.93	17.81	16.07

- CHEMICAL SLAGS COMPOSITION

COMPONENTS (%)	STAGES		
	1	2	3
MnO	36.30	35.80	10.66
SiO_2	19.02	19.10	38.30
Al_2O_3	21.30	22.44	23.12
CaO	15.20	15.05	18.41
MgO	4.90	5.00	6.60

- OPERATING CHARACTERISTICS

RAW MATERIALS CONSUMPTION (KG/T.ALLOY)	STAGES		
	1	2	3
Carajás Mn Ore	2465	1180	1300
Mn Sinter	-	1180	-
Mn Rich-Slag	-	-	870
Iron Ore	138	95	163
Limestone	153	160	79
Dolomite	250	251	182
Quartzite	155	130	700
Charcoal	505	476	580
Carbon	360	340	405
Slag weight (kg/T.alloy)	1130	1160	1450
Slag to metal ratio	1,13	1,16	1,45
Slag temp. (°C)	1360	1370	1460

- ELECTRICAL CHARACTERISTICS

	STAGES		
	1	2	3
Energy consumption (KWh/T.alloy)	3100	2950	4210
Secondary voltage-V	16,0	18,5	21,0
Secondary amperage-A	3950	3500	3400
Current density (A/cm^2)	15,5	14,2	13,71
Furnace load - KW	180	186	207
Electrode consumption (Kg/T.alloy)	19	16	32

GENERAL CONCLUSIONS

- The pilot scale trials, using Carajás manganese ore, showed that it is possible to produce HCFeMn by the rich-slag process, employing either 100% Carajás ore, or sinter-ore mixtures.

- To produce FeSiMn, the HCFeMn slag was used, and its mixture with manganese ore permitted to obtain the alloy according to the Brazilian standard specifications.

- Using sinter during the HCFeMn production, the consumption of carbon and energy was inferior to the 100% manganese ore trials.

- The possibility of employing higher percentages of Al_2O_3 in the slag than the ones used in our trials may result in securing lighter specific weights of the slag, less comsumption of raw materials and energy.

  Further studies in that line will have to be done in order to optimize the process.

- Due to the high Mn/Fe ratio found in the Carajás manganese ore, it is recommended to mix it with other manganese ore having lower Mn/Fe ratios and lower gangue, in order to produce standard HCFeMn.

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