Parameters Affecting the Production of High Carbon Ferromanganese in Closed Submerged Arc Furnace

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ABSTRACT

This study has been performed to investigate the different parameters affecting on the production of high carbon ferromanganese in closed submerged arc furnace. The analysis of industrial data revealed that using manganese ores with low Mn/Fe ratio necessitates higher amount of Mn-sinter in the charge. Using Mn-blend with higher Mn/Fe ratio reduces the coke consumption and this leads to reducing the electrodes consumption. The recovery of Mn ranges between 70 and 80 %. Much higher basic slag has slight effect on Mn- recovery. However, as slag basicity increases, the MnO- content of slag decreases. The manganese content of produced HCFeMn depends mainly on Mn/Fe ratio of Mn-blend. For obtaining HCFeMn alloy containing minimum 75%Mn, it is necessary to use Mn-blend with Mn/Fe ratio of higher than 6. A model for determination of the amount and composition of off-gases has been derived based on the chemical composition and material balance of the input raw materials and the produced alloy and slag. By using this model, the amount of off-gases was found to increase by increasing both Mn-blend and coke consumption.

Key words: *Ferromanganese, closed Furnaces, carbothermic reduction, Slag basicity*

1. INTRODUCTION

At Sinai Manganese Company (SMC), Abu Zenimam, standard high-carbon ferromanganese (HCFeMn) for the domestic and exported markets is smelted in 21 MVA three phase submerged electric arc furnace as closed top unit. The closed top submerged arc furnace has the following advantages comparing with open furnace: less power consumption, kwh/ton and higher productivity. On the other hand, the requirements for ore used in closed top

furnace are more restricted, e.g. free oxygen must be less than 10% and less friable ore. Otherwise, crust may be formed leading to occurrence of explosion.

The proper economic production of ferromanganese performance will be improved by selecting the proper raw materials suitable for the closed top submerged arc furnace, applying the best material balance for the raw materials and enhancing the smelting condition. The result will be lower consumption of raw materials, reduced specific energy consumption, good furnace operation, higher alloy quality and lower production cost. Thus, it is of prime importance to examine the different parameters affecting on the production of high carbon ferromanganese in closed submerged arc furnace.

2. EXPERIMENTAL PROCEDURE

In the high carbon ferromanganese making process at SMC, different local manganese ores and imported manganese sinter are blended along with the reducing agent (coke) and flux materials (dolomite and limestone) are mixed outside of the furnace (often called charge mix). The different raw materials components are weighed out based on chemical analysis of the ores, sinter, fluxes and coke and on the desired composition of alloy and slag. It is desired to obtain standard high carbon ferromanganese alloy containing at least 75% Mn and minimum content of phosphorus.

The raw materials mix is transported to hoppers above the furnace from where it is fed by gravity through chutes passing through the furnace cover.

In the submerged arc furnace, the electrodes are buried deep in the furnace burden and the reduction reaction takes place near the tip of the electrodes. The current flow between electrodes creates the intensive heat needed for the high temperature and energy required for the reduction reactions.

Charge mix is added periodically and the metal and slag are collected during tapping at appropriate intervals (often at 30 Mw). Produced slag and metal are tapped from the same tap-hole.

3. RESULTS & DISCUSSION

3.1 Statistical Analysis of Collected Data

The real operating data for producing high carbon ferromanganese at SMC were collected and statistical analysis of collected data has been conducted to evaluate the different parameters affecting on the production process.

The material balance for producing one ton high carbon ferromanganese has been calculated and an example of the material balance is summarized in **Table 1.**

The electric are steelmaking furnace operates as a batch melting process producing batches of molten steel known "heats". Thus, it is easy to determine the input and output of every heat.

On the other hand, the closed top submerged arc furnace for producing high carbon ferromanganese operates by continuous process. The charge mix is added periodically and the metal and slag are collected during tapping at appropriate materials (often every power consumption of 30Mw). Consequently, the tapped metal and slag are not the output of input charge mix especially when changing the charge materials composition or if the charge mix is subjected to modification. For that reason, the material balance calculations were done for periods of one month, or periods of some operations days working with constant charge mix.

Table 1: Material balance for producing one ton of HC-FeMn alloy

Raw materials	Kg	MnO_2	MnO	Fe	Fe_2O_3	SiO_2	Al_2O_3	CaO	MgO	Na_2O	BaO	P_2O_5	C	CO_2	CO	H_2O
Mn-ore1	976	458.4	206		118.6	83.3	24.4	26.4	13.7	3.416	27.13	2.235				7.12
Mn-ore2	392	166.7	78.8		68.99	43.1	9.016	8.04	3.53	1.254	5.88	0.763				2.55
Mn-sinter	653	130.6	382		42.9	50.4	25.47	1.96	1.18	2.612	2.612	1.137				4.83
Dolomite	245				2.132	11.9	3.185	72	46.8					107		1.27
Limestone	140				0.742	5.74	1.022	72.2	0.98					58		0.56
Coke	458.3		0.34		7.975	23.9	17.01	1.55	0.13			0.033	394			4.58
Electrodes	16.9												16.9			
Elect.casing	0.708			0.708												
Sum	2882	755.7	667	0.71	241.3	218	80.1	182	66.3	7.28	35.62	4.17	411	165		20.9
Kmol		8.69	9.4	0.013	1.51	3.64	0.79	3.25	1.64	0.117	0.232	0.029	34.2	3.76		1.16
Products	Kg	Mn	Fe	MnO	FeO	SiO_2	Al_2O_3	CaO	MgO				C	CO_2	CO	H_2O
FeMn	1000	752	173										70			
Slag	690			129.9	5.87	182	80.05	185	63.8							
Gases	1024													278	725	20.9
Losses	168															
Sum	2882	752	173	129.9	5.87	182	80.05	195	53.8				70	278	725	20.9
Kmol		13.67	3.09	1.83	0.08	3.03	0.78	3.48	1.35				5.83	6.32	25.9	1.16

Metal composition (%)						Slag composition (%)							Gas composition (kmol)		
Mn	Fe	C	P	Si		MnO	FeO	CaO	MgO	SiO_2	Al_2O_3		CO_2	CO	H_2O
75.2	17.3	7	0.18	0.18		18.8	0.85	26.8	9.2	26.3	11.6		6.32	25.9	1.16

3.2 Effect of Different Parameters

3.2.1 Raw Materials

3.2.1.1 Mn- Ores

Blends of local manganese ores and imported manganese sinter are used at SMC for producing the high carbon ferromanganese. The local manganese ores are law and medium grades with Mn/Fe ratio ranges between 3 and 5.5.

Manganese to iron ratio is very important in the ferromanganese production process. Mn /Fe weight ratio of 7.5 is required for production standard ferromanganese alloy with 78 % Mn

[1]. Furthermore, the local manganese ores vary widely in their content of manganese, iron, silicon, alumina, lime, magnesia, potassium and sodium oxides, barium oxide and phosphorus.

Mixtures of two Mn- ores are usually used to be blend with Mn-sinter. The charged Mn-ores mixture amounts to 890 - 1890 kg per ton produced alloy (average 1375 kg/ton) with Mn/Fe ratio ranges between 3.3 and 5.5 (average 4.08).

3.2.1.2 Mn-Sinter

Mn-sinter is suited for use in ferromanganese furnaces, since it is mechanically strong and thermally stable, allowing the gas to disperse evenly throughout the preheating and pre-reduction zone. Moreover, the requirements for ore used in closed top furnace are more restricted, i.e. excess oxygen must be less than 10 %. To adjust this vital parameter in closed top furnaces, excess oxygen, Mn-sinter is used in the charge mix. Excess oxygen is defined as the difference between the actual amount of oxygen chemically bounded to manganese and the theoretically amount of oxygen assuming the total amount of manganese being present in the monoxide MnO state.

At SMC, Mn-sinter is used to increase the Mn-Fe ratio of the blend and reduce the excess oxygen. Mn-sinter has a higher Mn /Fe ratio ranges between 9.3 and 12.6, and the charged amount ranges between 385 and 870 kg per one ton produced ferromanganese alloy (average 642 kg/ton). This amount represents 22 to 45% of the Mn- blend (average 32.2%).

By adding Mn –sinter into the Mn–ores mixture, the Mn /Fe ratio of Mn-blend increases to 4.5 – 6.4 (average 5.4) and the Mn-blend amounts to 1745 - 2430 kg per ton produced ferromanganese alloy (average 1998 kg/ton).

Furthermore, addition of Mn-sinter reduces the excess oxygen, **Figure1**. As Mn/Fe ratio of local Mn-ores increases, the Mn-sinter weight per one ton produced HCFeMn decreases, **Figure 2**, and Mn-sinter% in the Mn-blend decreases, **Figure 3** .
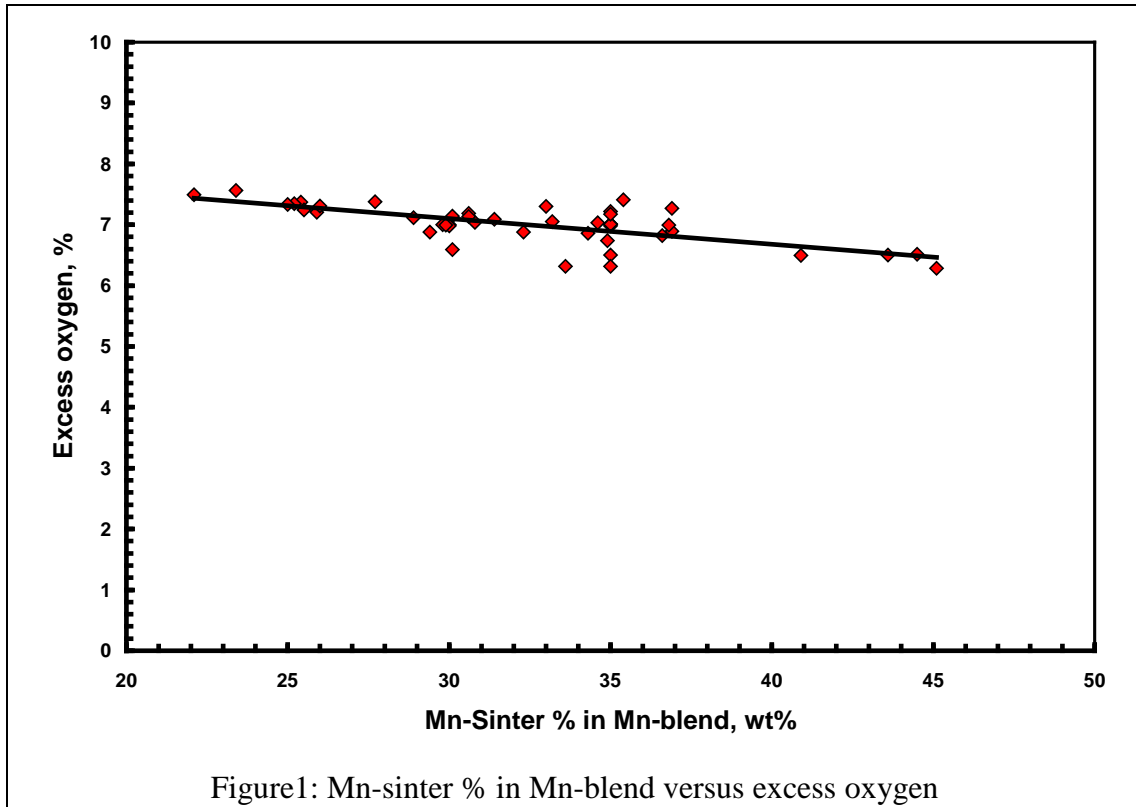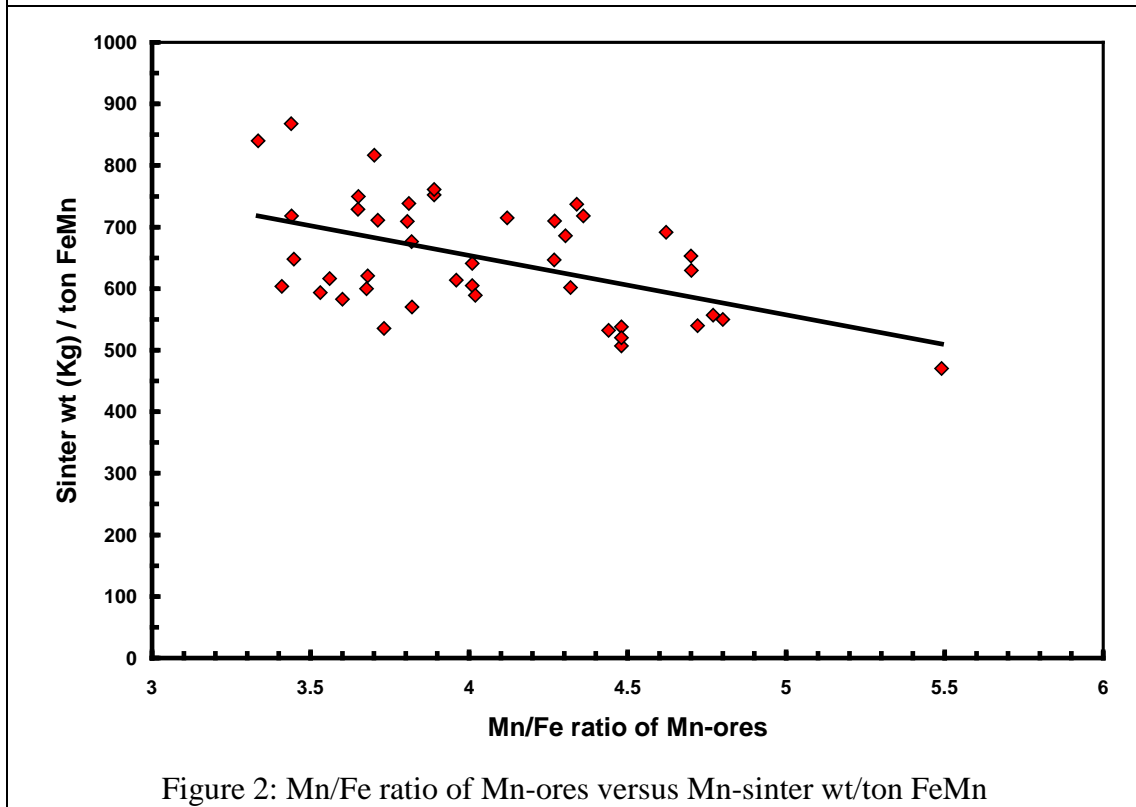
Figure1: Mn-sinter % in Mn-blend versus excess oxygen

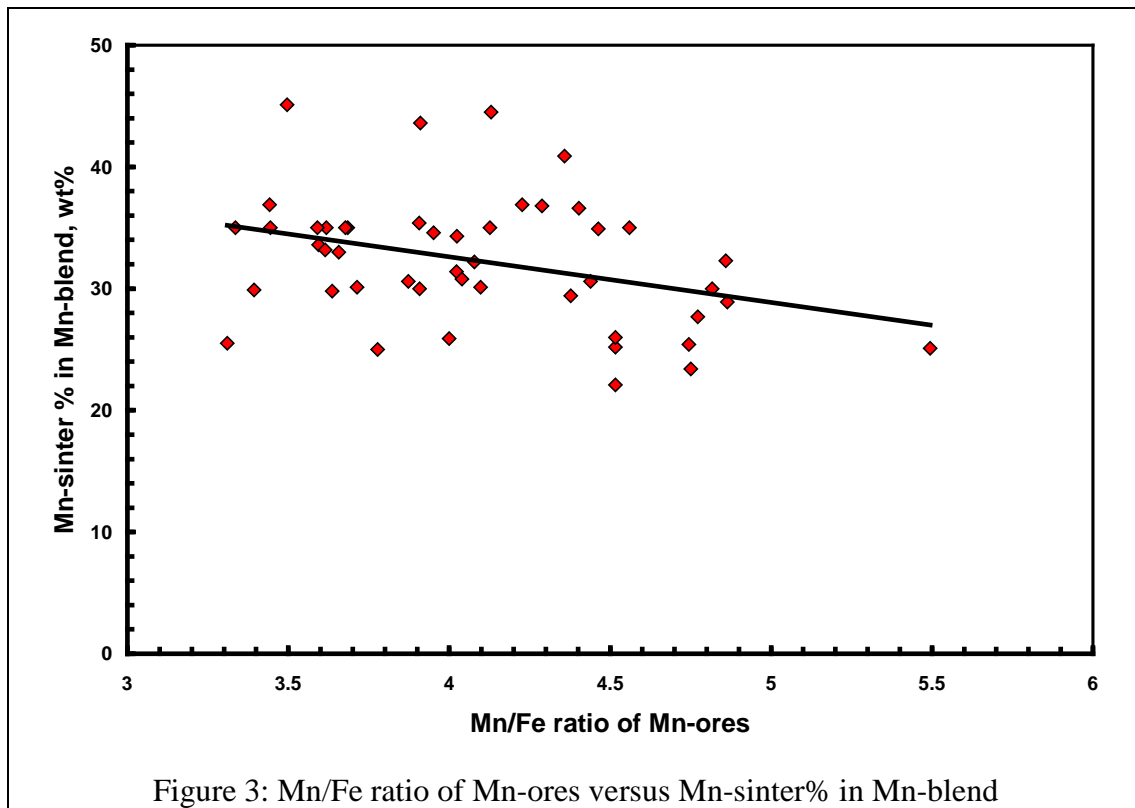Figure 2: Mn/Fe ratio of Mn-ores versus Mn-sinter wt/ton FeMn

Figure 3: Mn/Fe ratio of Mn-ores versus Mn-sinter% in Mn-blend

3.2.1.3 Reducing Agent

Coke is added as a source of carbon for ore reduction. The interior of a furnace producing high carbon ferromanganese consists of two main zones with different characteristics: the low temperature pre-reduction zone, and the high temperature coke bed zone. As the raw materials move down in the pre-reduction zone, the higher oxides of manganese are pre-reduced in solid state to Mn_3O_4 and preferably further to MnO by CO gas formed in the crater zone. The extent of the simultaneously running Boudouard reaction ($CO_2+C = 2CO$) is responsible for the variation in carbon. After further reheating, the pre-reduced ore and added fluxes start melting at temperatures of about $1250^{o}C$ to $1300^{o}C$. The coke remains solid, so below this area there is a permanent coke bed [2]. The melting together of ores and fluxes and reduction of MnO dissolved in the slag phase take place in the coke bed. The coke bed starts approximately at the tip of the submerged electrodes. It constitutes a permanent reservoir of coke. The relative amount of coke in the charge mix determines whether the coke bed increases, decreases or stable in size. In addition to being the chemical reductant it is also the heating element of the process where the electric current runs and ohmic energy is produced. The coke consumption ranges between 400 - 550 kg/ton HCMnFe (average 462 kg/ton).

The coke consumption increases as the Mn-blend weight increases, **Figure 4**, and Mn/Fe of the Mn-blend decreases, **Figure 5**.
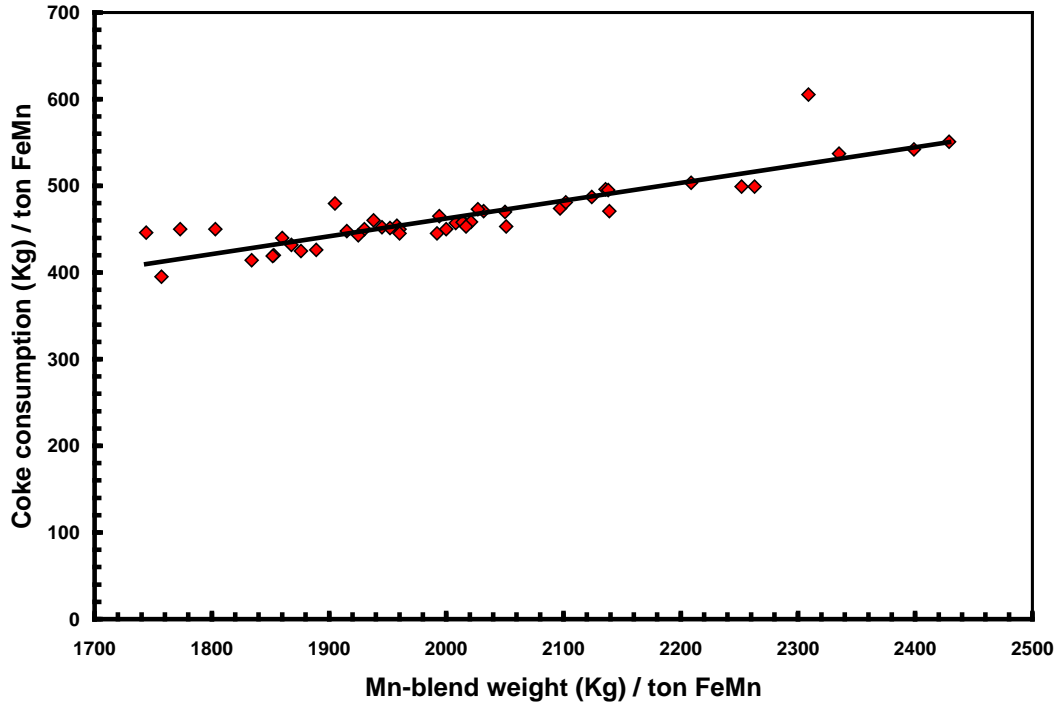
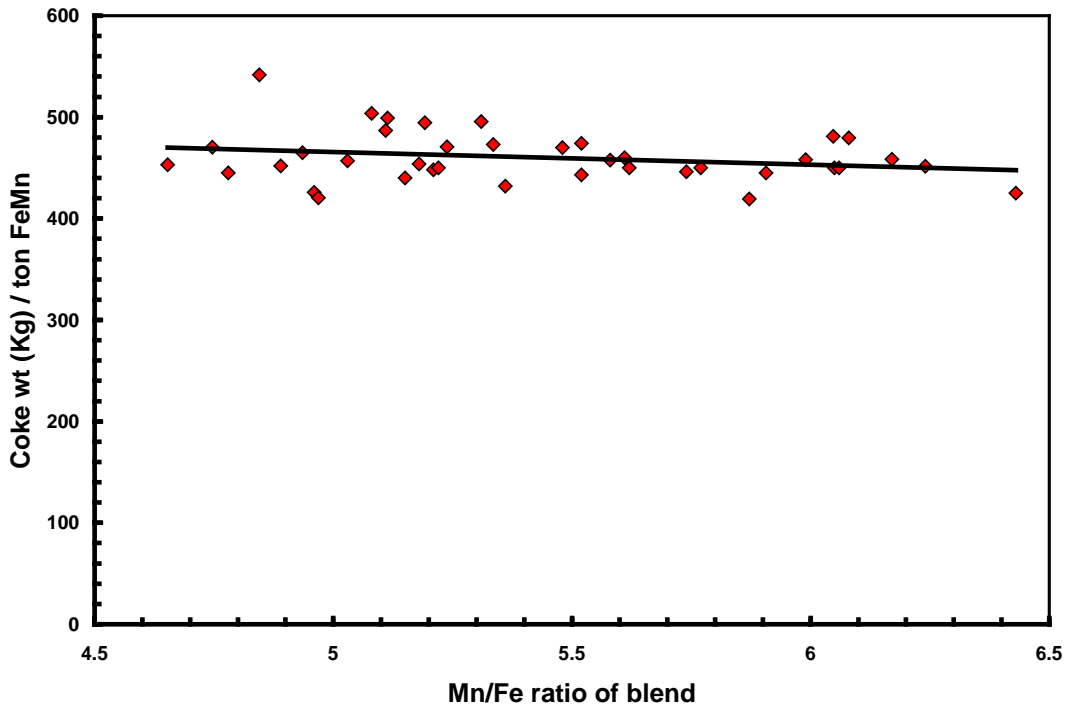Figure 4 : Mn-blend weight per ton FeMn versus coke consumption

Figure 5: Mn/Fe ratio of Mn-blend versus coke consumption

3.2.1.4 Flux Materials

Limestone and dolomite are used as flux materials. These basic fluxes are added to give the slag suitable chemical properties, smelting temperature and viscosity in order to secure good furnace operation and a high manganese recovery [1].

The amount of added limestone and dolomite depends on the required CaO and MgO to attain the specific slag basicity.

The flux consumption per ton HCFeMn ranges between 200 and 450 kg (average 340 kg). About two third of this amount is dolomite and the other third is limestone.

The flux consumption is correlated with the basicity and SiO_2 content of Mn-blend, **Figures 6-8** . As the silica amount or percent in Mn-blend increase, the flux addition increases. On the other hand, as the basicity of Mn-blend increases, the flux addition decreases.
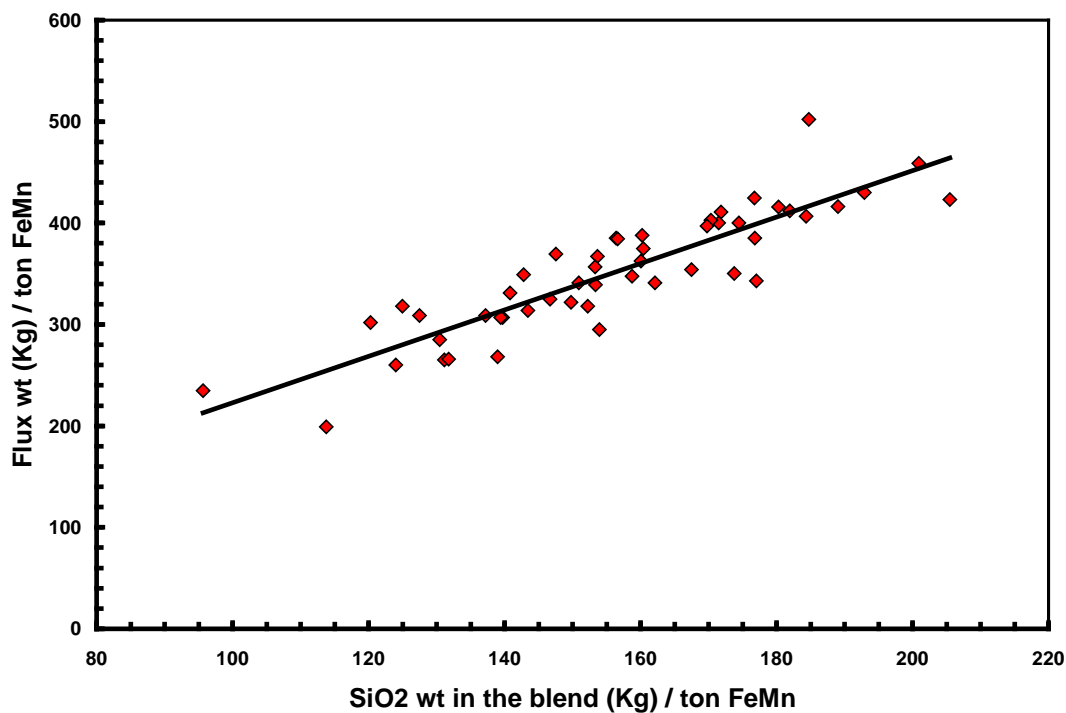
Figure 6: SiO_2 weight in Mn-blend per ton FeMn versus coke consumption
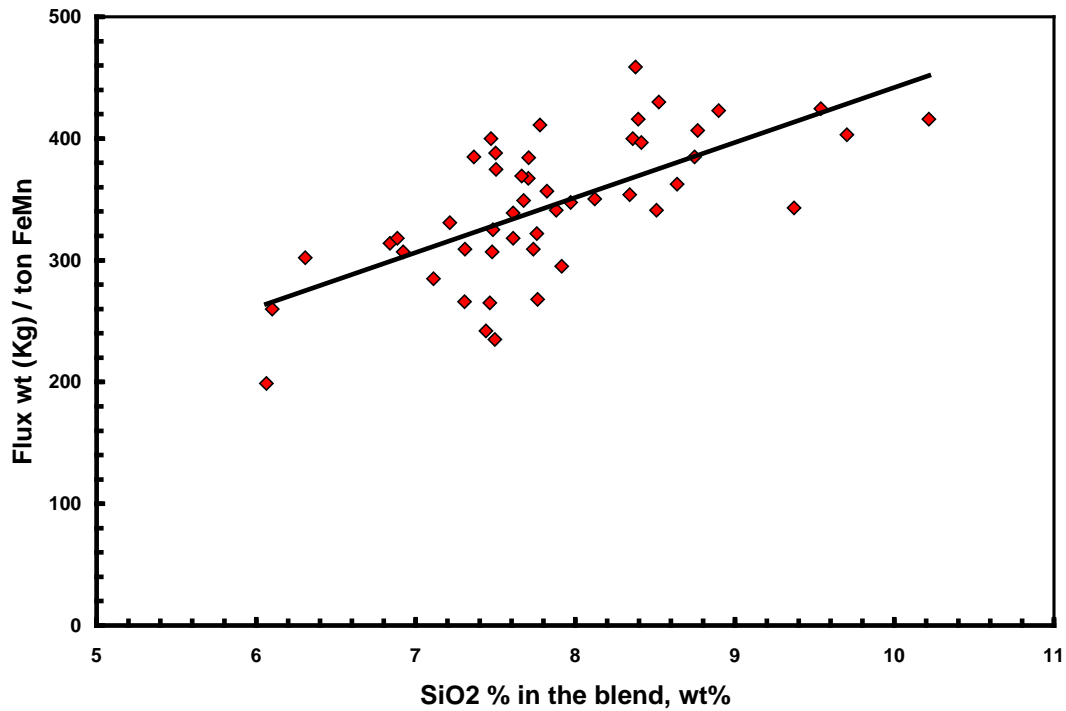
Figure 7 : SiO$_2$ % in Mn-blend versus flux consumption per ton FeMn
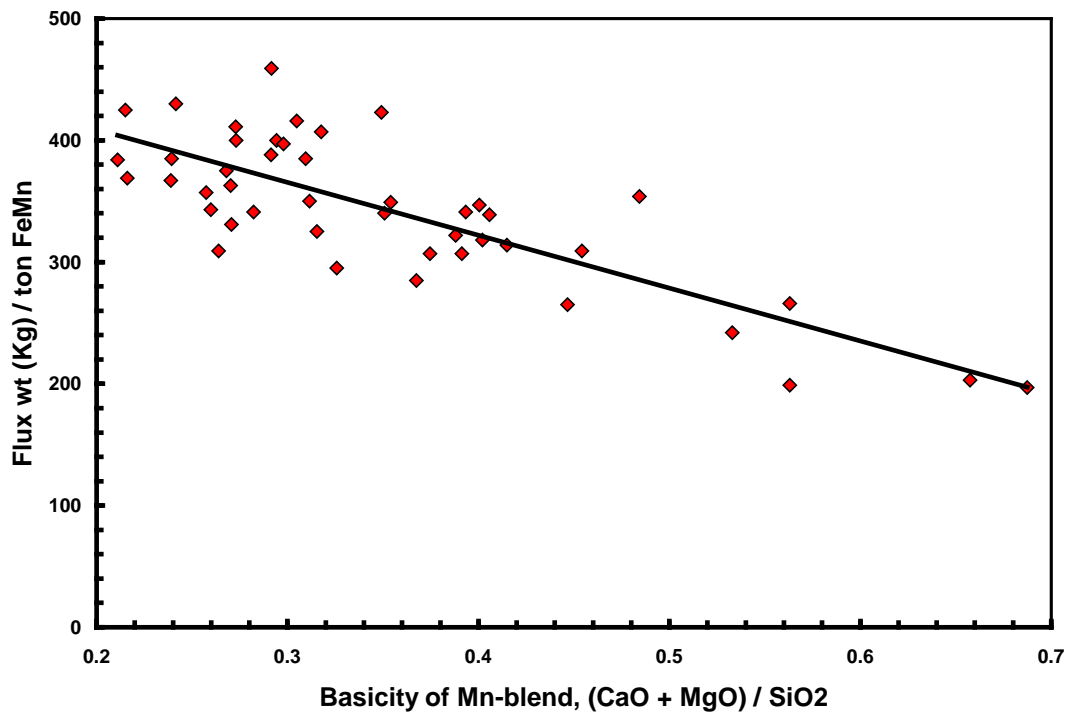
Fig.8: Basicity of Mn-blend versus flux consumption per ton FeMn

3.2.2 Electrodes

The electrodes of three-phase electric furnace are made of carbonaceous material, and they consumed during normal production. The consumption is usually large near the tip of the

electrode where the temperature is high and the reactants are more active. To keep the electrode tip at the same position it is therefore necessary to prolong the electrode regularly. The electrodes consumption per ton HCFeMn ranges between 8 and 37 kg (average 17.5 kg). The electrodes consumption increases as the coke consumption per ton HCFeMn increases, **Figure 9**.

3.2.3 Electrodes Casing

Electrodes casing is a low carbon steel and is consumed with the consumption of electrodes. The electrodes casing consumption ranges between 0.4 and 1.3 kg / ton HCFeMn (average 0.6 kg/ton
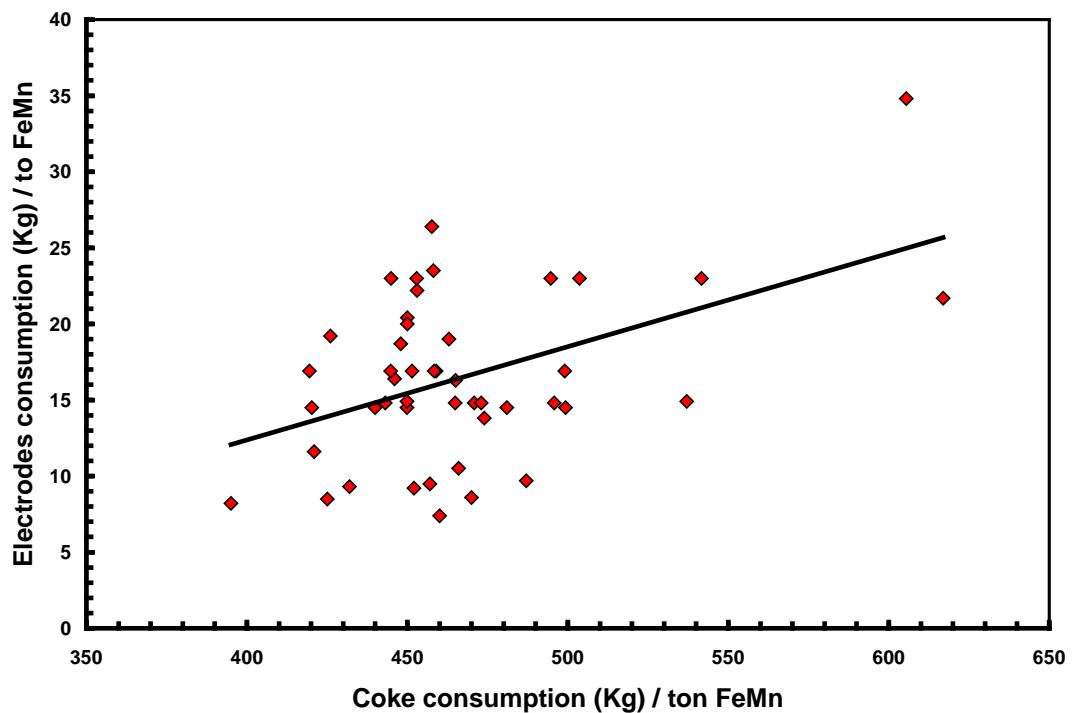
Figure 9: Coke consumption versus electrodes consumption per ton FeMn

3.3. Products

3.3.1 High Carbon Ferromanganese

The quality of high carbon ferromanganese depends mainly on the content of manganese and phosphorus. The phosphorus content of standard HCFeMn is $\leq$ 0.2 %. Most of the phosphorus in the ore remains in the finished product. The recovery of phosphorus is high (average 98%) and decreases with increasing the slag basicity as shown in **Figure 10**. However, due to the relatively low phosphorus content of Mn-blend, the phosphorus content in the produced HCFeMn is low of average 0.18 %. The recovery of Mn ranges between 70 and 80 % (average 75 %). In smelting of high carbon ferromanganese, manganese recovery was found to increase by increasing slag basicity **[3-10]** and decreasing slag viscosity [5,6].

Figure 11 illustrates slight effect of much higher basic slag on Mn- recovery. In the range of the basic slag used, the negative higher viscosity of much higher basic slag **[11]** hinders the positive effect of increasing the activity of manganese oxide in the slag melt due to existing of higher content of basic oxides CaO and MgO. The manganese content of produced HCFeMn depends mainly on Mn/Fe ratio of Mn-blend as shown in **Figure 12**.

For obtaining HCFeMn alloy containing minimum 75%Mn, it is necessary to use Mn-blend with Mn/Fe ratio of higher than 6.

The recovery of iron is higher than the recovery of manganese. Its average is about 96%. In the range of basic slag used, slag basicity has insignificant effect on iron recovery, **Figure 13**. The silicon content in the metal is very low (average 0.18 %) as a result of high slag basicity and low operating temperature, leading to low Si recovery of only 2 %, **Figure 14** .
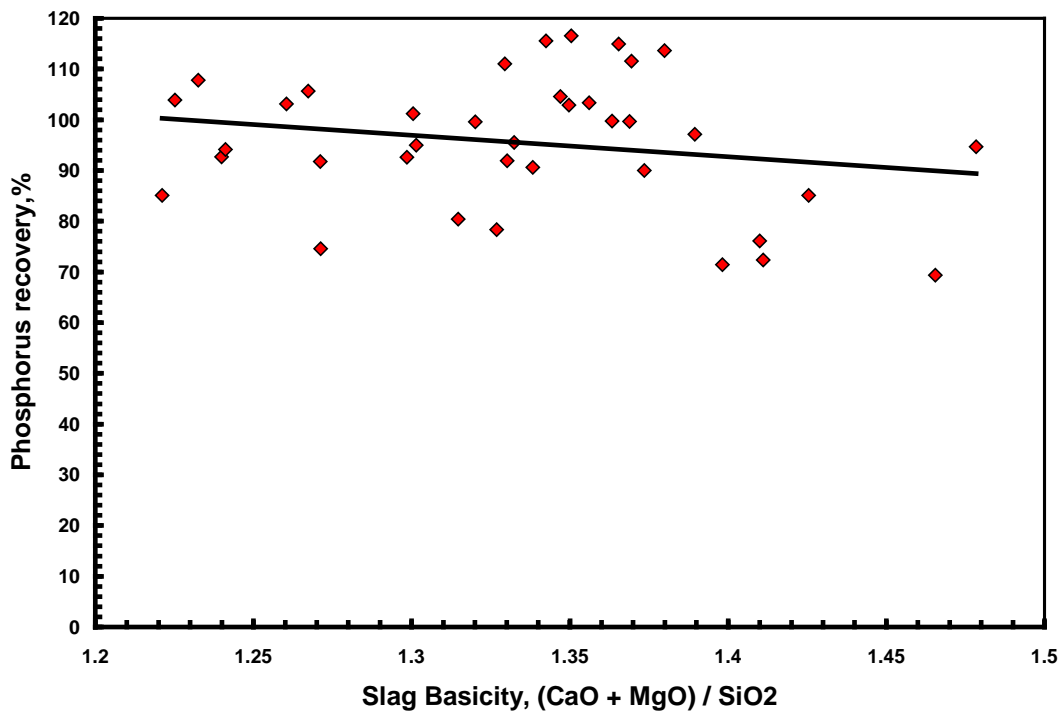
Figure 10: Slag basicity versus phosphorus recovery
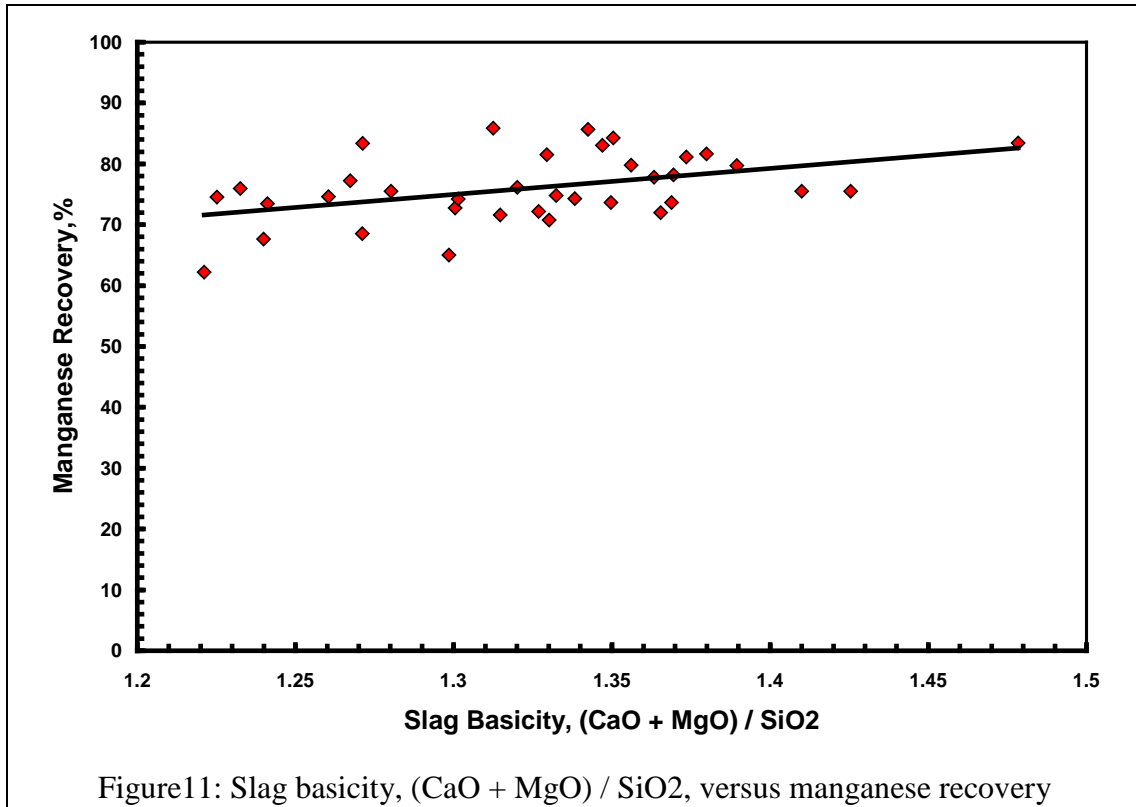
Figure11: Slag basicity, (CaO + MgO) / SiO2, versus manganese recovery
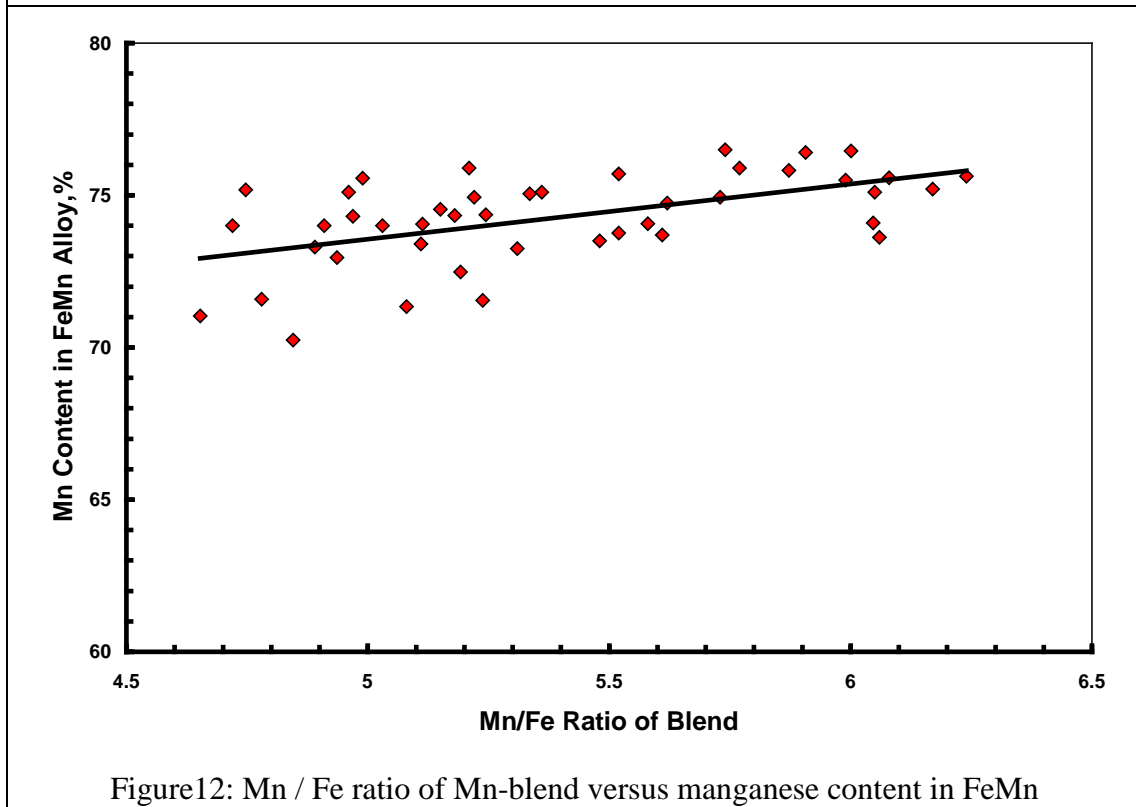

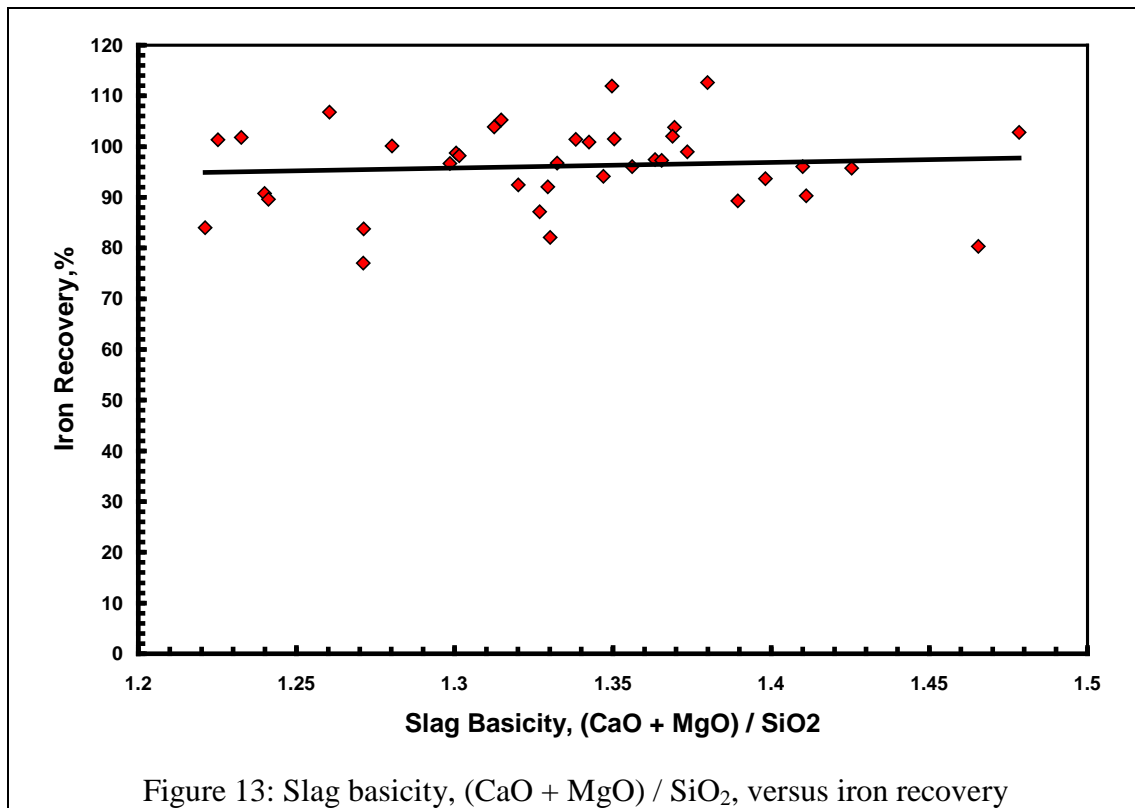Figure12: Mn / Fe ratio of Mn-blend versus manganese content in FeMn

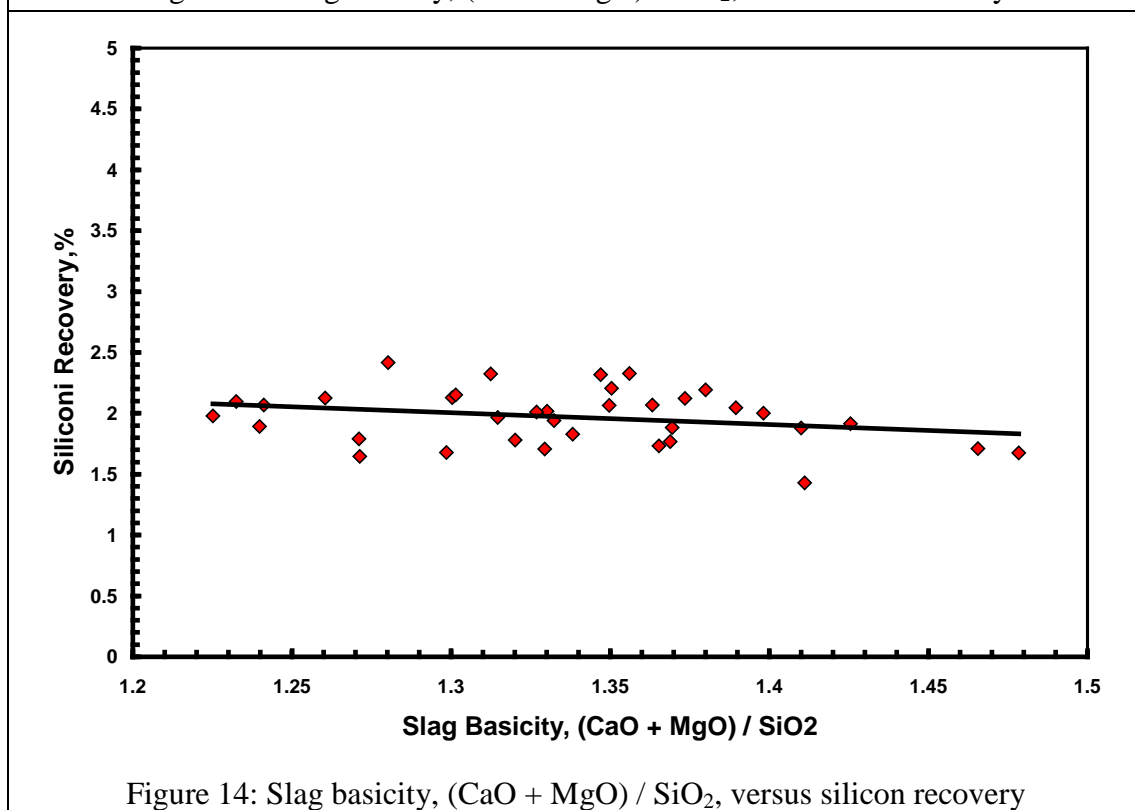Figure 13: Slag basicity, $(CaO + MgO) / SiO_2$, versus iron recovery

Figure 14: Slag basicity, $(CaO + MgO) / SiO_2$, versus silicon recovery

3.3.2 Slag

Besides manganese and iron oxide, the manganese ores contain SiO_2, Al_2O_3, CaO, MgO, Na_2O, BaO and P_2O_5. Coke ash also contains SiO_2, Al_2O_3 and smaller amount of CaO and

MgO. In addition, CaO- and MgO- containing fluxes (dolomite and limestone) are added to the raw materials mixture. These oxides will end up in the slag phase.

Most of iron oxides are reduced while Mn-oxides are partially reduced from the slag to form the metal phase. Less SiO_2 is reduced because silicon is more stable than MnO_2. Even more stable oxides are CaO, MgO and Al_2O_3. These oxides are considered to be irreducible, and they maintain their mutual ratio in the slag during the reduction process. The amount of slag produced per ton HCFeMn ranges between 460 and 940 kg (average 661kg).

The amount of slag weight depends on the amount of Mn-blend, **Figure 15** . This can be attributed to increase of gangue materials and irreducible oxides which enter the slag phase.

In addition, limestone and dolomite are added in the charge mix to adjust the slag basicity. The formula of mass ratio (CaO+MgO)/ SiO_2 is often used to express the slag basicity. As much amount of limestone and dolomite are added the produced slag weight increases, **Figure 16**.

During the period of collected data, high slag basicity is used to increase the manganese recovery. The MnO–content of slag ranges between 16 and 28% (average 20%) depending primarily on slag basicity, **Figure 17**. As slag basicity increases, the MnO- content of slag decreases.
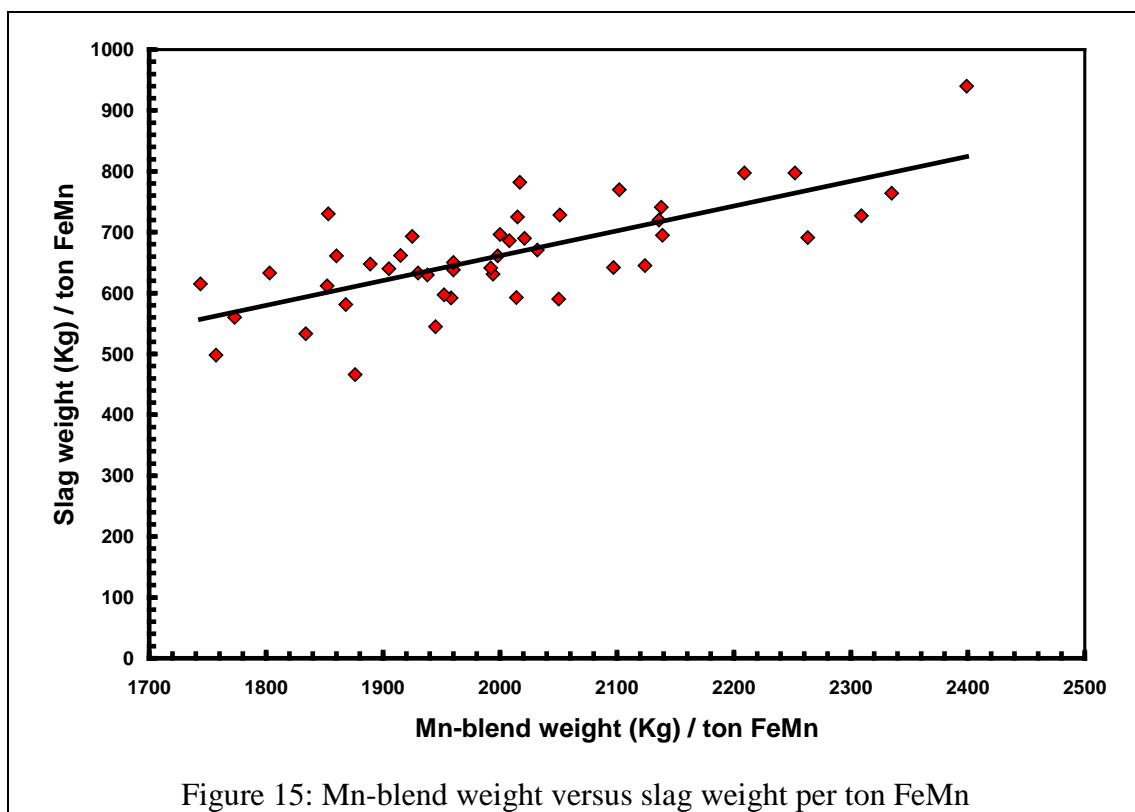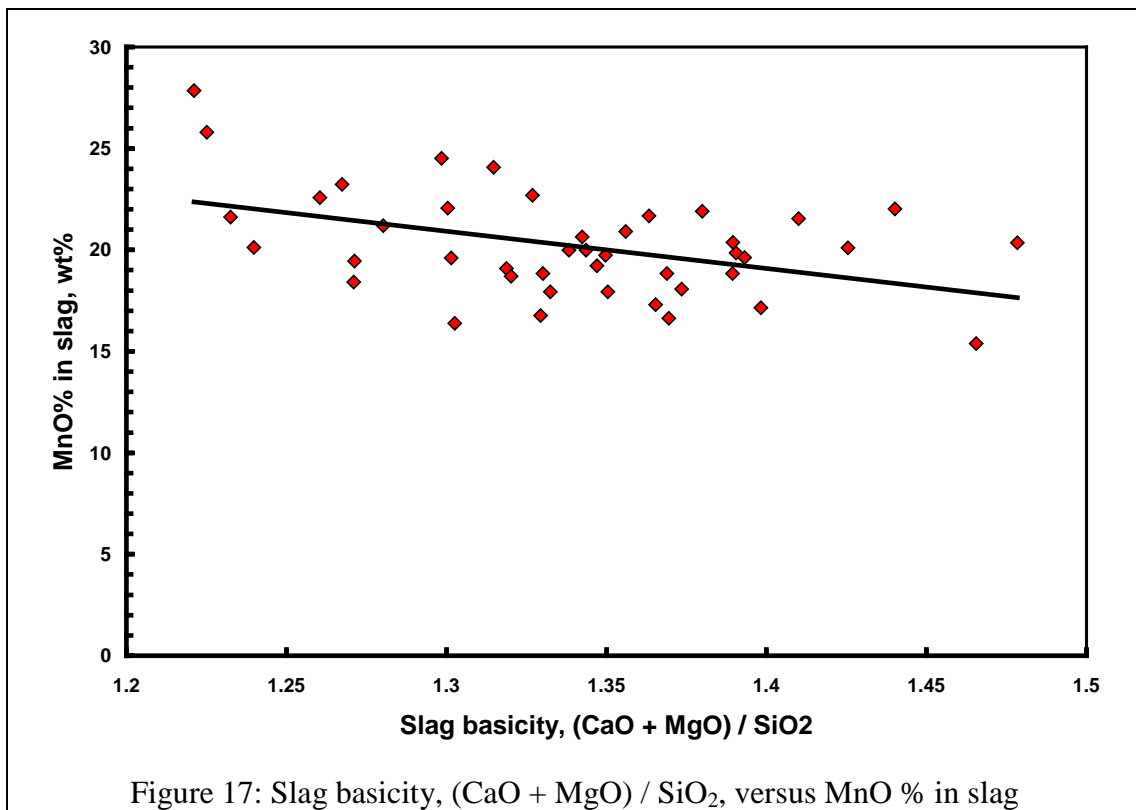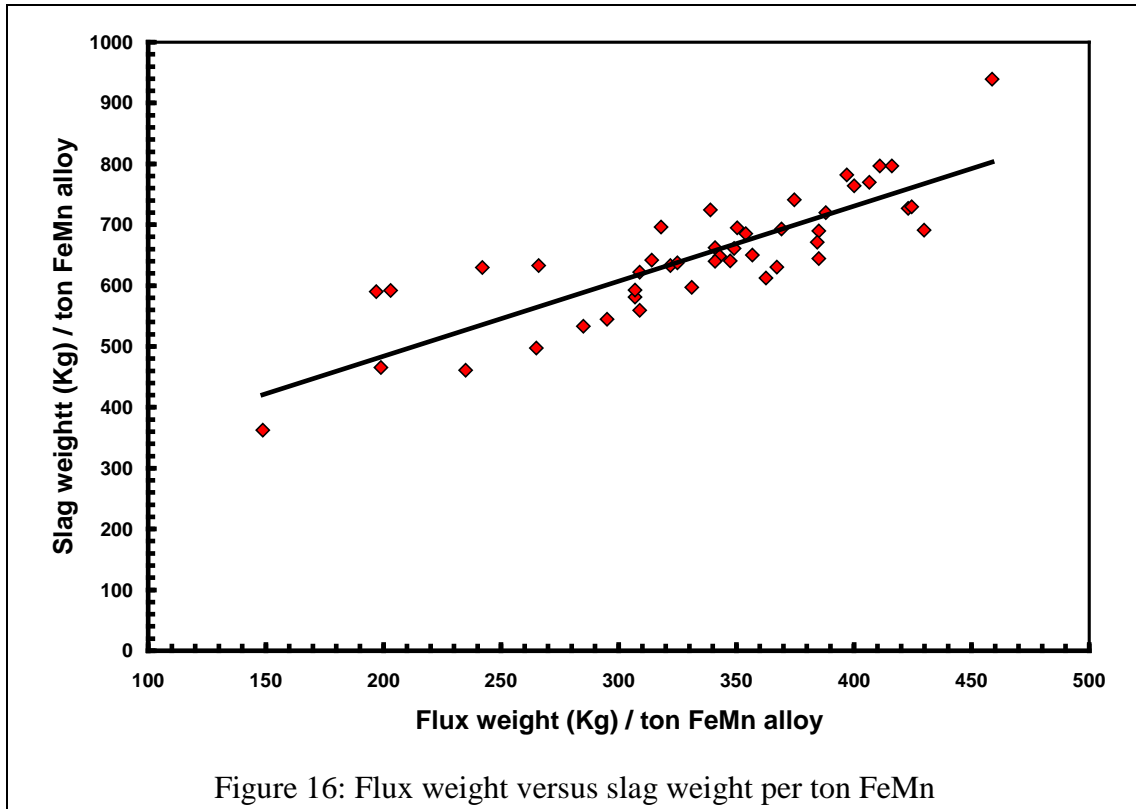

Figure 15: Mn-blend weight versus slag weight per ton FeMn

Figure 16: Flux weight versus slag weight per ton FeMn

Figure 17: Slag basicity, (CaO + MgO) / SiO$_2$, versus MnO % in slag

3.3.3 Gases

The amount and analysis of the gases leaving the furnace is not available at SMC due to unavailability of measuring devices. Assumptions have been made in order to calculate the amount and composition of the gases. It is assumed that the temperature of the gases at the furnace top, which is in excess of $200^{o}C$, being high enough for evaporation of moisture from charge as soon as the materials fall into the furnace. Evaporation of moisture is very rapid. Thus, all $H_2O_{(l)}$ enters the furnace leaves as $H_2O_{(g)}$ with the off-gas.

The other constituents of gas phase are CO and CO_2. By determining the amount of carbon and oxygen in gases, the amount of CO and CO_2 can be calculated.

The carbon amount in CO and CO_2 mixture in off-gas can be calculated by subtraction the carbon contained in the produced HCFeMn from the sum of carbon contained in the added coke, fluxing materials and consumed electrodes,

$$\mathbf{C_{\{CO+CO2\}} = C_{(Coke)} + C_{(electrodes)} + C_{(flux)} - C_{(alloy)}} \qquad \textbf{(1)}$$

The oxygen amount in CO and CO_2 mixture in off-gas can be calculated by subtraction the oxygen contained in the produced slag from the oxygen contained in the raw materials (local Mn-Ores, Mn-Sinter, limestone, dolomite and coke ash),

$$\mathbf{O_{\{CO+CO2\}} = O_{(Raw\ materials)} - O_{(slag)}} \qquad \textbf{(2)}$$

The sum of carbon and oxygen in (CO +CO_2) mixture equals the sum of CO and CO_2 in off-gas:

$$\mathbf{C_{\{CO+CO2\}} + O_{\{CO+CO2\}} = \{CO + CO_2\}\ in\ gases} \qquad \textbf{(3)}$$

Consequently, the total weight of gases can be calculated:

$$\mathbf{Gases\ weight = CO + CO_2 + H_2O} \qquad \textbf{(4)}$$

Carbon / oxygen ratio is calculated and correlated with $CO_2/ (CO+CO_2)$ as shown in **Fig (18)**. The following equation is fitting this relation:

$$\mathbf{CO_2 / (CO+CO_2)\ wt\ ratio = -266.67\ (C/O) + 200} \qquad \textbf{(5)}$$

The amount of gases per one ton HCFeMn ranges between 855 and 1316 kg (average 1016 kg). The $CO_2 / (CO+CO_2)$ wt ratio ranges between 0.05 and 0.45 (average 0.25)

Figures (19 -21) reveal increasing the amount of gases per one ton HCFeMn by increasing both Mn-blend and coke and sum of Mn-blend and coke, respectively. This can be attributed to the higher oxygen and carbon in the charge mix.
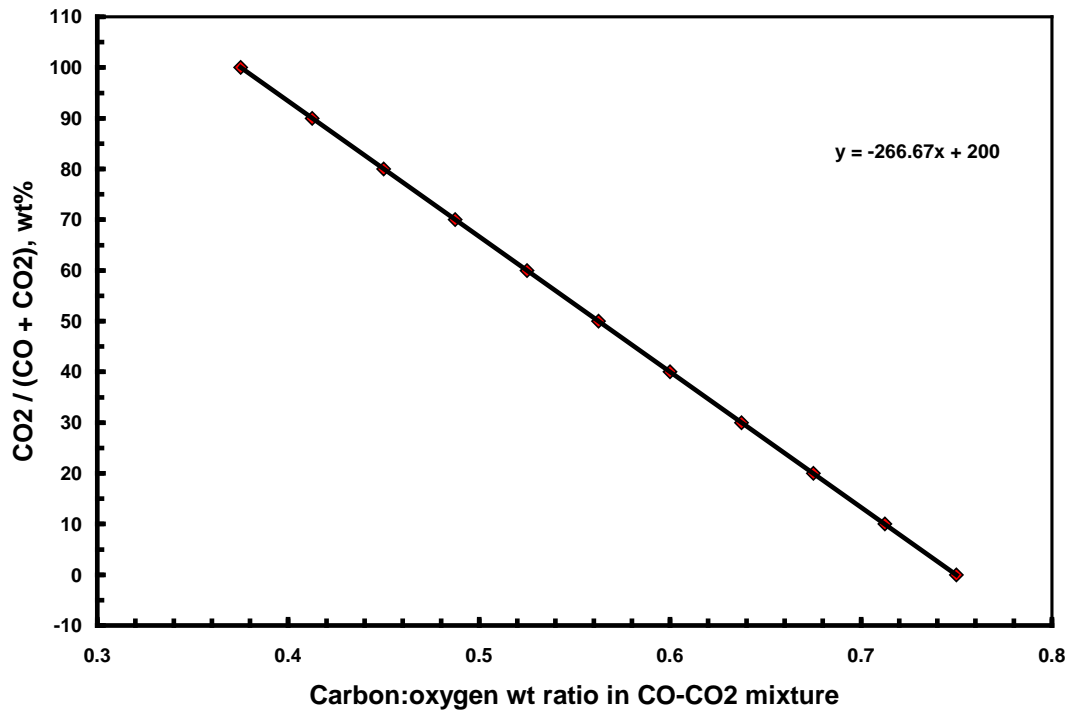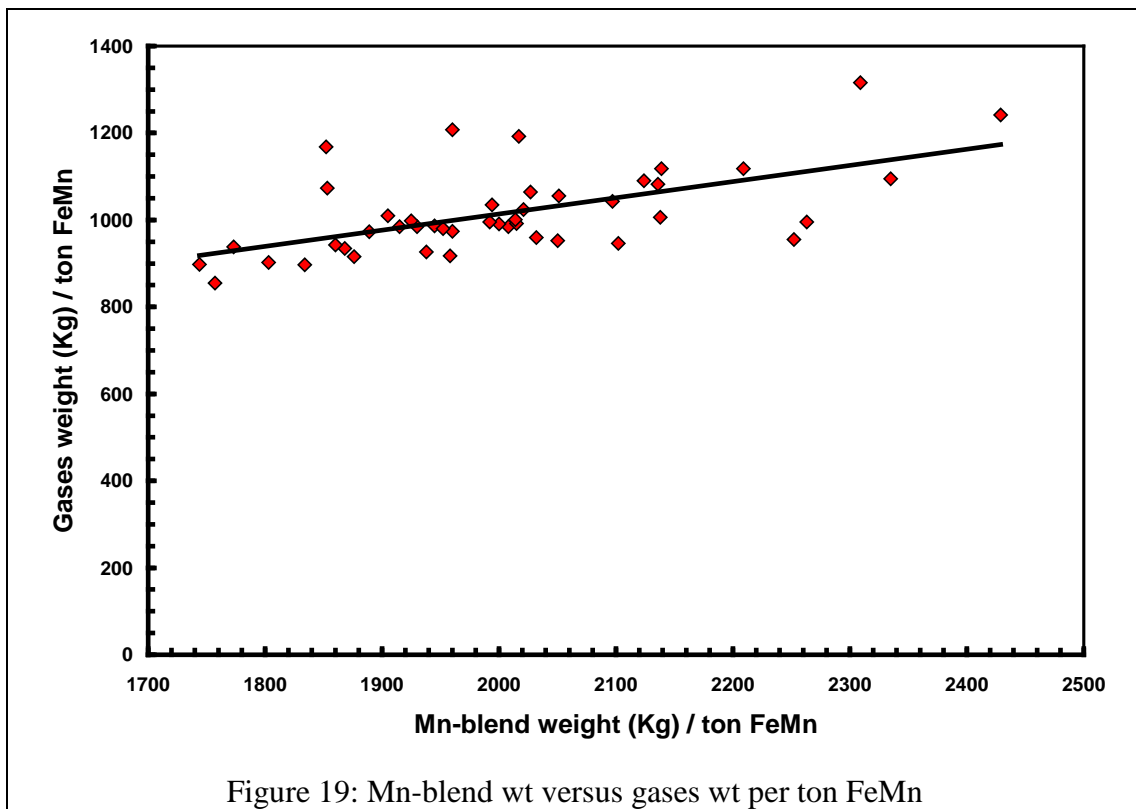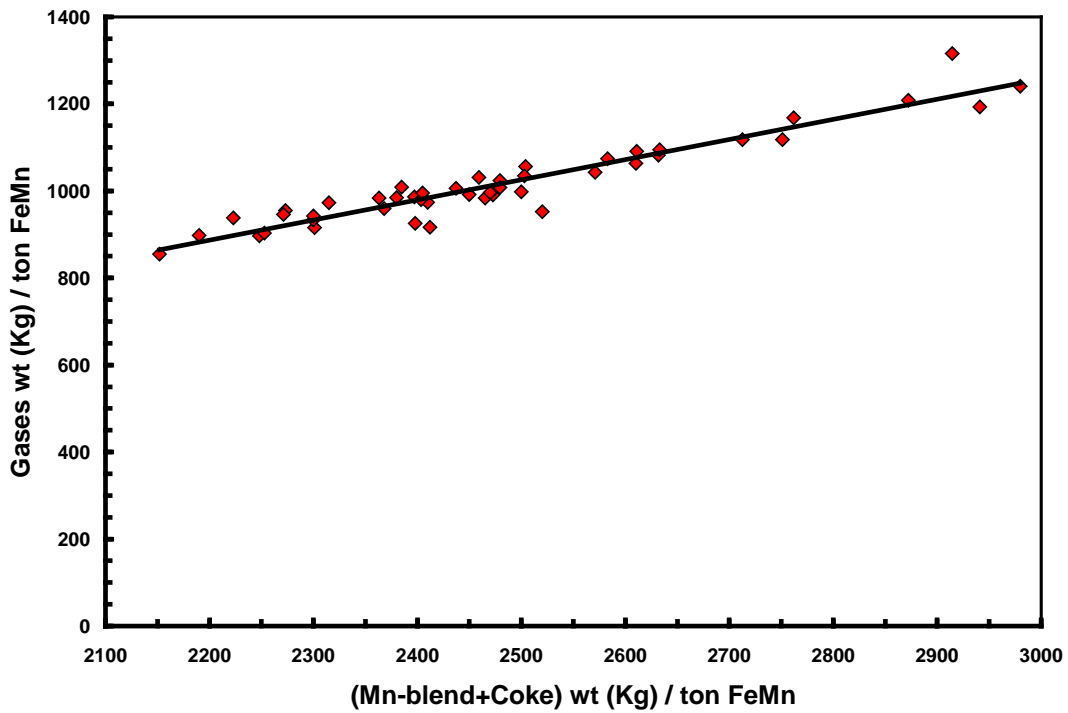
Figure18: Carbon: oxygen ratio versus CO_2 % in $CO - CO_2$ mixture

Figure 19: Mn-blend wt versus gases wt per ton FeMn

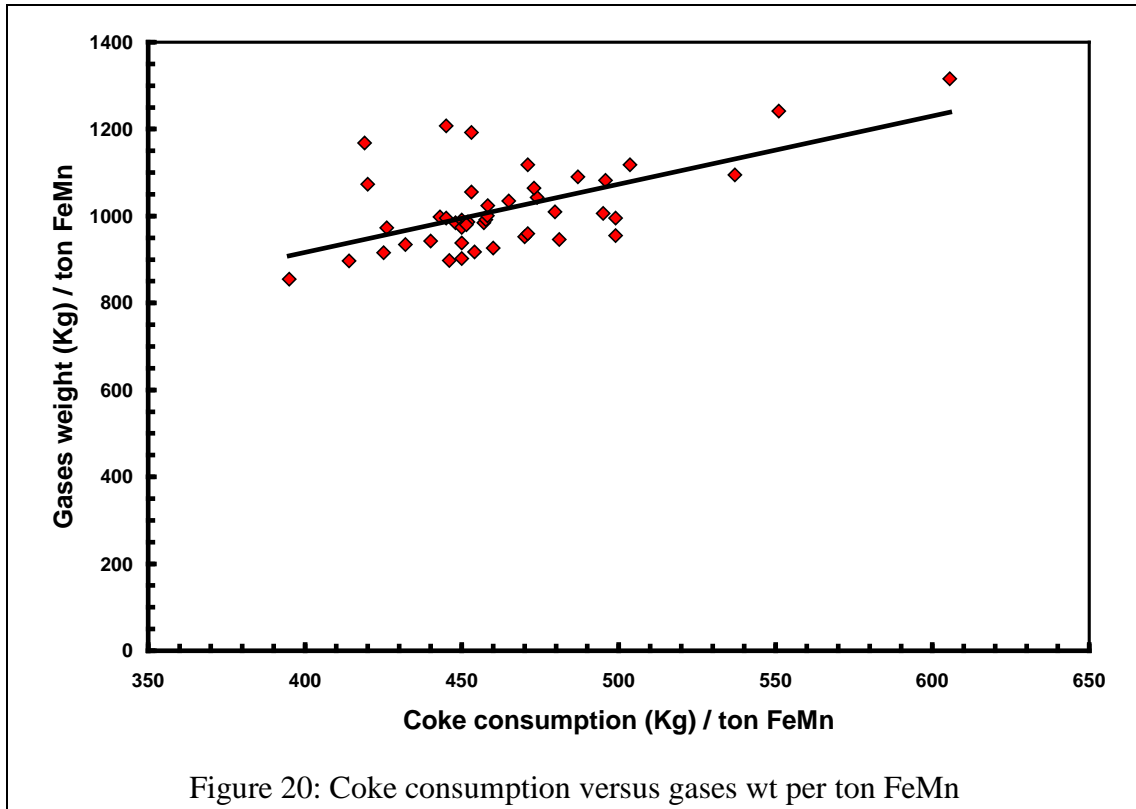Figure 20: Coke consumption versus gases wt per ton FeMn

Figure 21: Sum of Mn-blend and coke wt versus gases wt per ton FeMn

3.3.4 Losses

From material balance calculations, weight losses up to 350 kg per one ton produced HCFeMn has been detected (average 162 kg). The average weight losses represent about 5.5% of the charge mix. These weight losses could be attributed to materials losses in handling and charging process, dust leaving the furnace with the off-gas, weight errors and metal lost in slag and in crushing to the suitable sizes.

4. CONCLUSIONS

From the results of analysis of industrial data for producing HC-FeMn in closed submerged arc furnace, the following conclusions can be deduced:

- As Mn/Fe ratio of local Mn-ores increases, the Mn-sinter weight per one ton produced HCFeMn decreases, and Mn-sinter% in the Mn-blend decreases.
- The coke consumption increases as the Mn-blend weight increases and Mn/Fe of the Mn-blend decreases.
- As the silica amount or percent in Mn-blend increase, the flux addition increases. On the other hand, as the basicity of Mn-blend increases, the flux addition decreases.
- The electrodes consumption increases as the coke consumption per ton HCFeMn increases.
- Most of the phosphorus in the ore goes to the finished product. The recovery of phosphorus is high of about 98% and slightly decreases with increasing the slag basicity. For producing standard HCFeMn containing ≤ 0.2 % P, charging of Mn-blend with low phosphorus content is required.
- The recovery of Mn ranges between 70 and 80 %. Much higher basic slag has slight effect on Mn- recovery. The negative higher viscosity of much higher basic slag hinders the positive effect of increasing the activity of manganese oxide in the slag melt due to existing of higher content of basic oxides CaO and MgO.
- The manganese content of produced HCFeMn depends mainly on Mn/Fe ratio of Mn-blend. For obtaining HCFeMn alloy containing minimum 75%Mn, it is necessary to use Mn-blend with Mn/Fe ratio of higher than 6.
- The recovery of iron is higher than the recovery of manganese. Its average is about 96%. In the range of basic slag used, slag basicity has insignificant effect on iron recovery.
- The silicon content in the produced alloy is very low (average 0.18 %) as a result of high slag basicity and low operating temperature, leading to low Si recovery of only 2 %.
- The amount of produced slag depends on the amounts of Mn-blend and fluxing materials.
- The MnO–content of slag depends primarily on slag basicity, as slag basicity increases, the MnO- content of slag decreases.

- A model for determination of the amount and composition of off-gases has been derived based on the chemical composition and material balance of the input raw materials and the produced alloy and slag.
- The amount of off-gases increases by increasing both Mn-blend and coke amounts.
- In the production process, about 5.5% of the charge mix weight is lost due to materials losses in handling and charging process, dust leaving the furnace with the off-gases, weight errors and metal lost in slag and in crushing to the suitable sizes.

ACKNOWLEDGEMENT

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