METALLURGICAL BENEFIT OF REACTIVE HIGH GRADE ORE IN MANGANESE ALLOYS MANUFACTURING

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ABSTRACT

Worldwide, the major Manganese ores can be separated into three different types:

- *Oxidized ores (MnO2): in Australia, Gabon, Brazil,….*
- *Semi-oxidized ores (Mn2O3): in South-Africa, Australia,….*
- *Carbonated ore (MnCO3): in Ghana, South Africa,Kazhakstan….*

The other Manganese ores are less rich but can be used locally or in the neighbour countries (China, Ukraina, India…).

Since the beginning of the 20th Century, Manganese has played a big role in the steel industry process average usage ratio: 9,5 kg/mt of steel). The recent grow-up of this industry has led to an increase of Manganese ores demand. In parallel, several companies have increased their Manganese ore producing capacity.

In this presentation, we explain the link between the main Manganese ores characteristics and the key different factors for an effective and low cost Mn alloys production (HCFeMn and SiMn):

- *Chemistry*
- *Size*
- *Reactivity*

Then we will point out the advantages of Comilog ore and Sintec ® usages in various Manganese alloy metallurgical process compared with the other main ores and with the local ores.

Some advised formulations for the different kinds of furnaces and alloys will be also discussed.

1. INTRODUCTION

More than 90% of the Mn production worldwide is used in the form of ferro-alloys, mainly in the steel industry.

Mn is also essential to the chemical industry for the manufacture of batteries, fertilizers, pigments and various reactants as permanganate.

In steelmaking, overall consumption is in average 6 to 7 kgs of pure manganese per ton of steel, which means 9 to 10 kgs of manganese alloys per ton of steel.

Manganese is mainly used in steelmaking to increase steel strength and also elasticity (HSLA grades for construction and automotive industry). Another property of Manganese is to bring to steel a good resistance against abrasion (an example is the use of about 20% of Mn in steels for crushers and screens, leading to very good equipments efficiency for producing….Mn alloys!).

2. STEEL MARKET TREND

Since 2000, steel production grew from 848 million t to 1129 million t in 2005 and expected 1245 million t in 2006, which means an average growth of 6,6 % per year. Growth was particularly strong since 2003.

The growth is especially strong in China, 127 million t in 2000, 349 million t in 2005 and expected 430 million t in 2006 (35% of worldwide output). This means an annual growth rate of 22% between 2000 and 2006.

The steel industry momentum is expected to remain very favourable, thanks to the needs of some emerging countries.

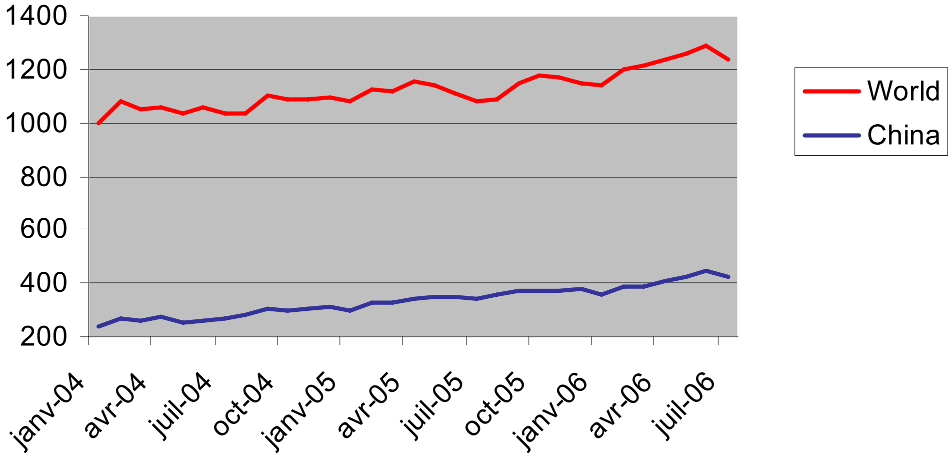

Figure 1: Steel output trend since January 2004

3. MN ALLOYS CONSUMPTION

A strong demand of steel means high level of steel production, therefore a strong demand of Mn alloys.

To feed the worldwide needs of the steel industry, more than 10 million t of Mn alloys have been used annually during the 6 last years. This is due firstly to the volum of the steel output, but the Mn unit consumption is also on a growing trend, mainly because more and more steel is produced in China where the unit consumption is higher and very different from one product to the other. The average worldwide unit consumption is estimated in 2005 at 9,8 kgs of alloys per ton of steel:

- Mainly SiMn: 5,6 kgs/mt due to China case.
- HCFeMn: 3,3 kgs/mt
- Refined: 0,9 kgs/mt.

This figure varies significantly from one region to another one the differences being related to the steel process, the quality of the used raw materials (such as iron ore grades) and the steel products grades.

4. MN ALLOYS PRODUCTION

Following the strong Mn alloys demand, the Mn alloys output has dramatically increased last years, in the same proportion than the demand. Today the main producing areas are:

- China (approx. 5,0 million mt)
- CIS (approx. 1,7 million mt)
- Europe (1,3 million mt)
- Americas (0,9 million mt)

- India (0,8 million mt)
- South Africa (0,5 million mt)

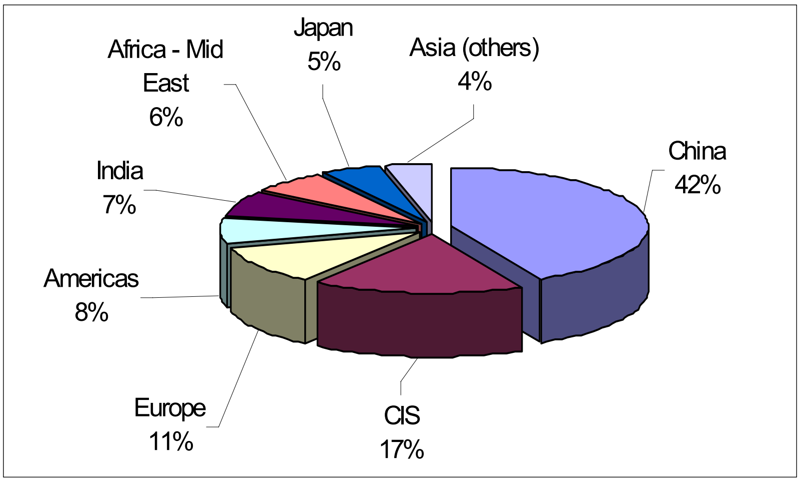

Figure 2: Manganese Ferroalloy Production by Region (as a percent of total global production, 10.7 million mt) [5]

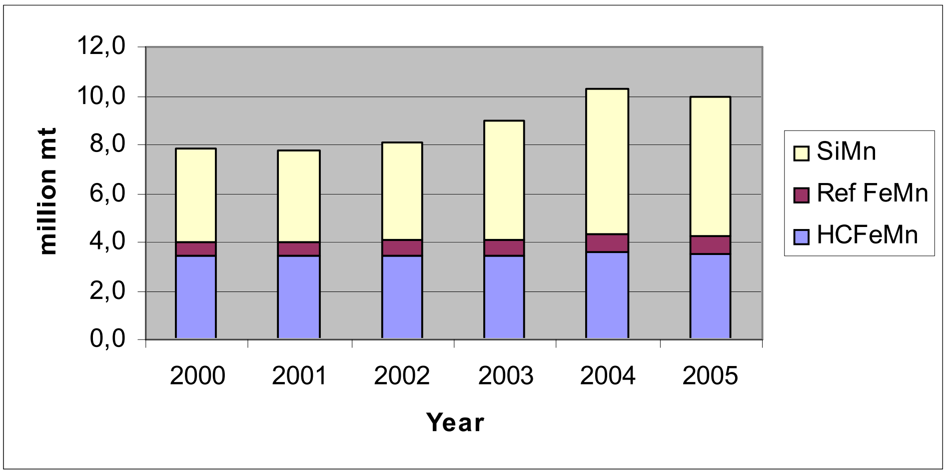

Figure 3: Global Mn Ferroalloy Production by product 2000 to 2005 - IMNI [5]

The first three production capacities are:

- Nikopol (1,2 million t)
- Eramet Comilog Manganese (0,8 million t)
- BHP-Billiton (0,7 million t)

5. MN ORES PRODUCTION

The demand of Manganese ore is mainly led by Mn alloys production: it is estimated that more than 80% of Mn ore usage goes to ferro-alloys production; the remaining 20% are dedicated to the Mn metal production and the other chemicals, in which Eramet Comilog Manganese (ECM) participates also through its subsidiary Erachem.

Lastly, a small part is coming to steelmaking industry (direct ore use in converters or pig-iron production).

In 2005, the annual output of Mn ore was about 35 million mt, i.e. approx. 1200 million dmtu.

(1 dmtu = 10 kgs of Mn). The main companies producing more than 1 million t of Mn ore are:

- BHP in South-Africa and Australia
- ECM in Gabon
- CVRD in Brazil
- PRIVAT in Ukraine
- ASSOMANG in South Africa.
- GCMC in Ghana.

The remaining part which represents more than 50% of the worldwide output is scattered in many different countries with smaller mine capacity (< 1 million mt).

China is the most spectacular example as, there, more than 1000 mines produce about 12 MT of low grade ore (i.e. 240 million dmtu), which places China at the head of the countries producing Mn ore.

The Mn content is also very different from one producer to the other: from 20% (or even lower for production of Mn metal) to more than 50%. The world average of Mn content is about 34%.

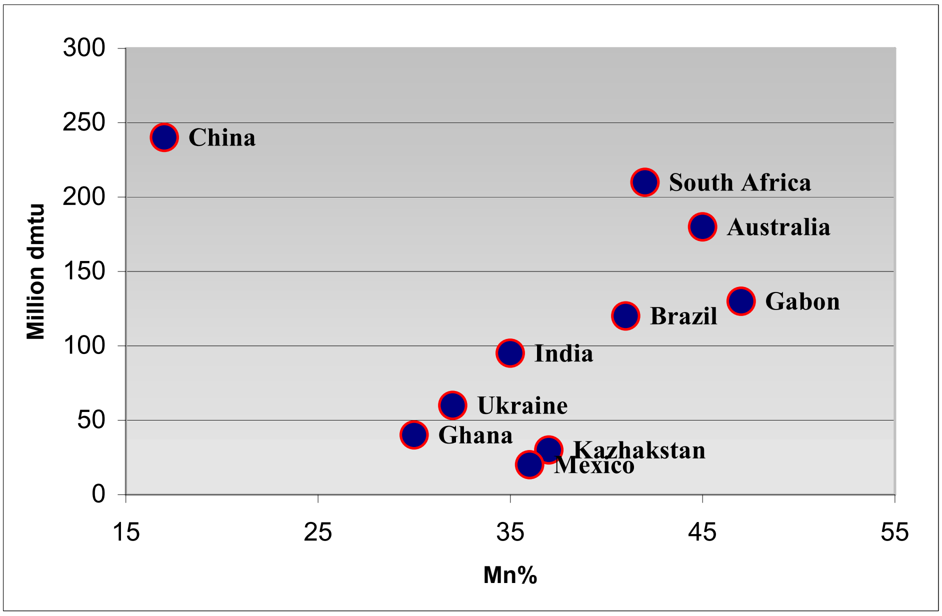

Figure 4: IMNI - 2005 top 10 Mn Ore producing Countries (in million dmtu) [5]

In the next years, the manganese ore growth should follow the high trend of steel production, then will require new mines opening or existing mines development. Already some companies (mainly BHP and ECM) have decided to push ore sales and production. However, the situation is quite complex as the ore market is also driven by economical issues like shipment and internal transportation market tightness and costs.

6. MN ORES TYPES

The next part of the presentation will be focused on Manganese alloys industry, especially on Electric Arc Furnaces, which are the main customer of Manganese ore over the world.

Indeed, some blast furnaces are still in operation (mainly in China and Russia. Only one in western countries, i.e. Mizushima in Japan), but the BF part is presently now reduced to about 20% of the world output.

6.1 Ore categories

The ores used to produce high carbon ferromanganese and silicomanganese in electric arc furnaces could be classified in 4 different types (Table 1).

Table 1: Worldwide ore suppliers

Types of ore	*Country*	*Main suppliers*
Oxidized ores (MnO_2)	Gabon	Comilog
	Australia	BHP-Billiton
	Brazil	CVRD
Semi-oxidized ores (Mn_2O_3)	South-Africa	BHP-Billiton
	South-Africa	Assoman
	Australia	CML
Semi-oxidized ores (Mn_3O_4): Sinters	Gabon	Comilog
	Australia	BHP-Billiton
	Brazil	CRVD
Carbonated ores	South-Africa	BHP-Billiton
	Ghana	GCMC

The power consumption in Mn alloys furnaces is actually linked to different factors:

- The oxidation rate of the manganese ore introduced into the furnace as the exothermicity of the pre-reduction reactions increases with the manganese oxidation degree:

$$MnO_2 + CO_{(g)} = MnO + CO_{2(g)} \qquad \Delta H_{298} = -148.14 \text{ kJ} \qquad (1)$$

$$Mn_2O_3 + CO_{(g)} = 2\ MnO + CO_{2(g)} \qquad \Delta H_{298} = -96.52 \text{ kJ} \qquad (2)$$

$$Mn_3O_4 + CO_{(g)} = 3\ MnO + CO_{2(g)} \qquad \Delta H_{298} = -50.83 \text{ kJ} \qquad (3)$$

- The decomposition of the carbonates as it is an endothermic reaction. This leads to a power consumption increase when using carbonated ores or when ore chemistry requires carbonated fluxes in the burden to balance silica in the ore:

$$MnCO_3 = MnO + CO_{2(g)} \qquad \Delta H_{298} = 115.4 \text{ kJ} \qquad (4)$$

$$CaCO_3 = CaO + CO_{2(g)} \qquad \Delta H_{298} = 178.3 \text{ kJ} \qquad (5)$$

$$MgCO_3 = MgO + CO_{2(g)} \qquad \Delta H_{298} = 101.1 \text{ kJ} \qquad (6)$$

To complete this classification and to go further in the manganese ores comparison, several ratios could be introduced. In the process, the existing elements present in the ore actually go, according to their reducibility:

- To the alloy: 100% of iron and phosphorus, 75 to 85% of manganese.
- To the slag: 100% of alumina and silica (in HCFeMn), 100% of alumina and 60 % of silica (in SiMn).

→ In consequence, the appropriate figures to evaluate P and Fe in the ore chemistry are respectively the ratios Mn/P and Mn/Fe. In the HCFeMn process, the ratio $Mn/(Al_2O_3+SiO_2)$ can also be followed up, these two elements affecting the amount of slag produced and then the performance of the furnace.

6.2 Mn/X ratios

The phosphorous content over the manganese content (Mn/P) is indeed a key factor in the HC FeMn process and in a less extends in the silicomanganese process to fulfill the quality requirements of the produced metal. In this framework the Comilog ores fit almost all the worldwide specifications (Figure 5a). The ratio of iron content over manganese content (Mn/Fe) allows a fine-tuning of the manganese composition in the final ferroalloy. The higher this ratio is the better the production control is. The Comilog ores enable particularly to control the iron content in the metal and to increase the manganese content due to a relatively high ratio (Figure 5b).

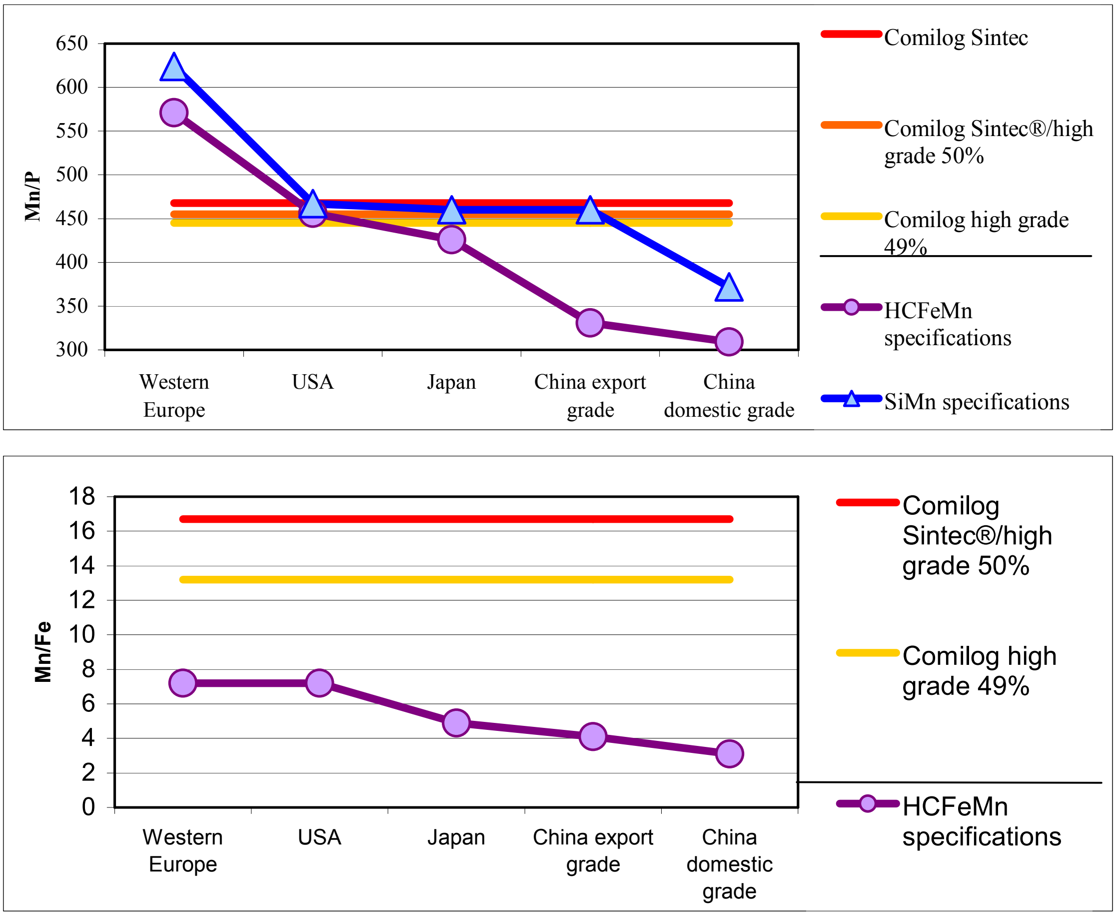

Figure 5: Compositions ratio and Ferro-alloys specification

In the HC FeMn process, the ratio of manganese mass content over the non-reducible oxides (alumina and silica) mass content Mn/(Al2O3+SiO2) drives the furnace performances as manganese yield and electric consumption.

Indeed, alumina and silica are highly stable oxides that are not reduced and then are recovered in the slag, contributing to increase the amount of slag produced (Table 2). That is to say, the higher the alumina and silica contents are in the ore, the higher the manganese losses in the slag and then the specific energy consumption are.

Table 2: Manganese yield and slag ratio for different commercial ore for 100% use

	Manganese mass content in ore, %	*Alumina and silica contents, %*	*Mn $SiO_2+Al_2O_3$*	*Slag ratio kg/mt HCFeMn*	*Total Mn yield, %*
SAR-49%	49,0	5.5	8.9	550	84*
MMA	50,5	9.5	5.3	600	97.5**
Sintec ®	58.5	13.2	4.4	650	97,0**
BHP-Australia	48.5	11.1	4.4	650	97,0**
MMR	49,0	11.3	4.3	670	96.8**
CVRD	45,0	13.1	3.4	750	96.3**

* Discard slag operation (Mn-20%) due to basic CaO+MgO contents in the ore – No slag valorisation

** Rich slag operation (Mn-30%) and subsequent valorisation of the slag in SiMn process

South-African ores suffer from high % of fluxes (10 to 15%), leading at 100% use to produce a very basic slag, then to lower the total Mn yield. At the opposite, CVRD, BHP Australia and Comilog ores are acidic ores (very low % of fluxes) and can reach a very high total Mn yield by producing rich slag (Mn 30%). Their drawback, compared with South-African ores, is the need for carbonated fluxes leading to increase a bit the power consumption. Comilog major product MMA ore is the most efficient due to highest Mn content: 50, 5 % (on dry basis).

6.3 Ore reactivity

In the electric furnace process to produce manganese alloys (see figure 6), the manganese oxides contained in the ores are prereduced by the CO gas from the bottom of the furnace. As the efficiency of these reactions affects the carbon and the energy consumptions, the ore reactivity is a main issue [1,2]. Actually, in an electric furnace the prereduction is not completely achieved and leads to MnO_x (x>1) instead of MnO, which involves a deviation of the carbon and energy consumption during the final reduction as follows:

$$MnO_x + x\,C = Mn + x\,CO_{(g)} \qquad (7)$$

Therefore, two different tests have been carried out by the CRT (Eramet R&D center) to compare the reactivity of manganese ores reproducing the conditions of pre-reduction in electric furnaces.

The first experiment consists in introducing 200g of manganese ore in the tightly closed Boris furnace (Figure 7). A gas mix (60% CO, 40% CO_2) is then introduced to react with manganese oxides, the off-gas be-

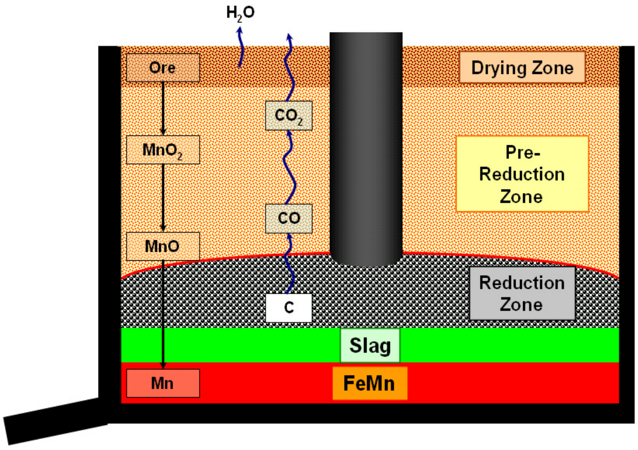

Figure 6: Ore pre-deduction and reduction in HCFeMn furnace

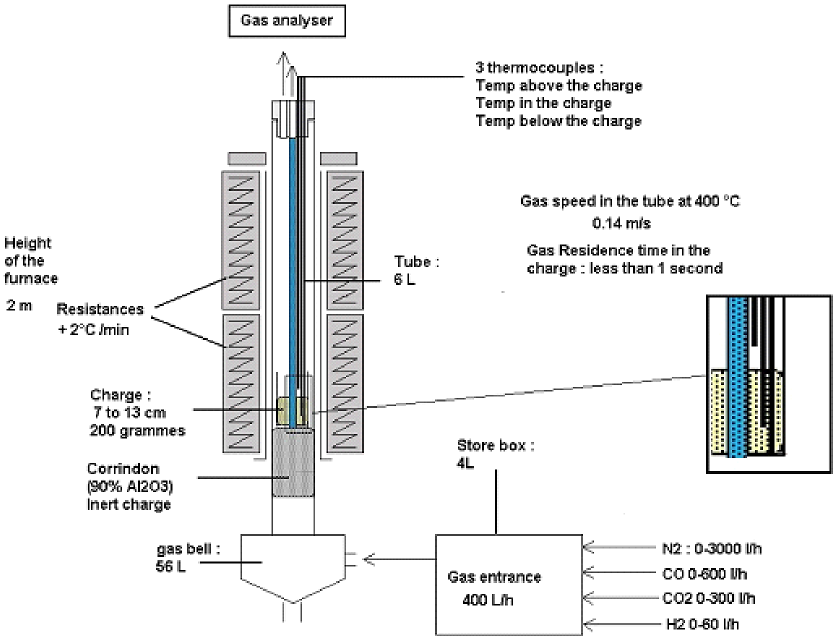

Figure 7: Boris reactivity test

ing analyzed to assess the pre-reduction rate (MnO_x reached at the end of the experiment). Reproducing industrial conditions, two different heating rates (2°C/mn and 8°C/mn) that correspond to the minimum and maximum values observed in electric furnaces are applied to reach 1100°C.

In the scope of the standard study, two ore granulometries were investigated. A small grain size is below 5mm. A medium grain size is comprised between 10 and 15mm for three different manganese ores.

Even if the pre-reduction degree reached at the end could be assessed from the gas analysis or the weight loss of the sample, the more accurate way to deduce MnO_x is the chemical analysis of the sample (%Mn, %MnO_2, %MnO).

The BHP ore is confirmed to be the less reducible one. The influence of the heating rate is all the more important with a coarse ore, except for Comilog ore. The Comilog ore is more sensitive to the granulometry than the two others.

Despite a major uncertainty of the test coming from the heterogeneity of the manganese ores studied, the results stress that *it is necessary to take into account the ore size and the heating rate when studying reducibility.*

Table 3: Reactivity results obtained with the Boris test

	2 °C/min *MnOx x =*	*8 °C/min* *MnOx x =*
Comilog small	1,00	1.11
Comilog medium	1.14	1.15
BHP small	1.22	1.20
BHP medium	1.22	1.28
Asman small	1.08	1.09
Asman medium	1.09	1.16

A second test is based on the same principle as the Boris one but enables to treat larger amount of ore (1400g) with a grain size up to 35mm. A 1400g-manganese ore sample is introduced in a horizontal tubular furnace to react with CO gas under the same conditions as in the Boris test.

If needed, the tube can rotate at a given speed all along the trial to simulate the degradation that takes place in industrial furnaces (Figure 8).

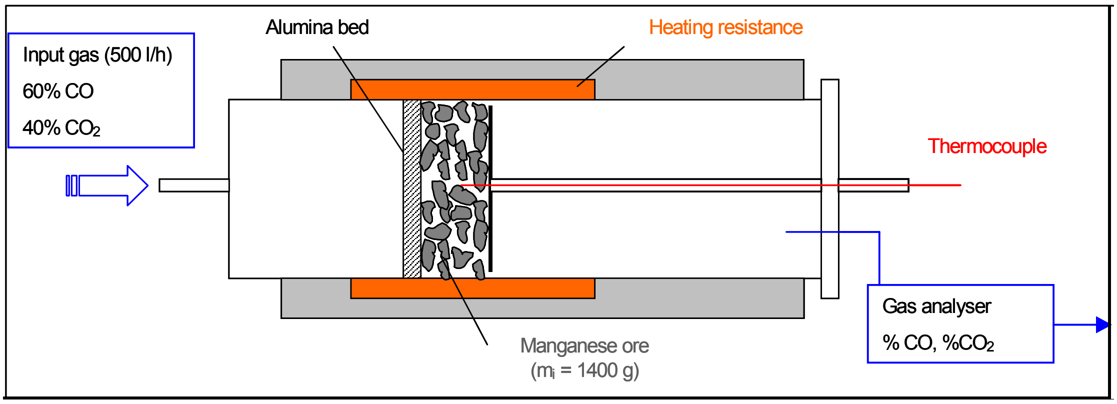

Figure 8: CORED test

In the same conditions as previously, four different manganese ores were tested changing the granulometry from [10-15mm] to [25-35mm]. The results fit with the conclusions of the Boris test concerning Comilog and BHP medium samples for a 2°C/mn heating rate (Table 4). A 2°C heating rate corresponds to standard heating conditions for Mn alloys process in electric arc furnace. For large samples, Comilog is the more reducible ore. The sensitivity to granulometry is low. The large particles are quite sensible to the heating rate.

Table 4: Reactivity results obtained with the CORED

	Comilog (MnO_x)		Asman (MnO_x)		BHP (MnO_x)		Mamatwan (MnO_x)	
Heating rate [°C/mn]	2	8	2	8	2	8	2	8
Medium [10-15 mm]	1.08	-	1.09	-	1.22	1.28	-	-
Large [25-35 mm]	1.12	1.25	1.13	1.23	1.25	1.40	-	1.11

6.4 Key differentiation factors

From the previous results and industrial tests performed in electric furnaces [3], three main parameters could be distinguished that affect the manganese ores reactivity:

- The reactivity of manganese ores in the pre-reduction is highly affected by the efficiency of the solid/gas exchange. Thus, the higher the ore porosity the more complete reactions between higher manganese oxides and CO gas
  - And then the lower carbon and power consumptions.
    The high Comilog ore reactivity stressed by the pre-reduction performed at CRT could be explained by its high porosity (Table 5). A high porosity leads to a high exchange surface with CO gas and then to a lower final pre-reduction degree (MnOx).

Table 5: Measurements from Todd and Al [4]

	%Mn	*%Fe*	*Av Ox*	*MnO_x initial*	*Porosity*	*Density*
Amapa 1	45	5.1	9.6	1.74	36	2.66
Amapa 2	56.5	3.4	15.3	1.95	12	3.97
Asman 1	44.9	14.1	7.3	1.56	1	4.26
Asman 2	53.7	6.1	9.5	1.62	0	4.45
Asman 3	55.7	6.8	9.6	1.60	0	4.57
Comilog	47.3	2.3	12.6	1.93	53	2.07
BHP 1	48.4	3.4	9.4	1.68	7	3.83
BHP 2	52.2	0.9	13	1.97	5	3.96
Wessels 1	26.1	39	5.4	1.72	6	4.52
Wessels 2	49.6	12.5	8	1.56	2	4.63
Wessels 3	46.8	6.7	6.1	1.46	9	4.06

- The high Comilog ore reactivity stressed by the pre-reduction performed at CRT could be explained by its high porosity as shown in the above table.
- The available oxygen (Av Ox) is the percentage of oxygen in ore bound to manganese above that associated with MnO, which is the maximum quantity that could be released from reaction with CO gas. The pre-reduction reactions being exothermic, the higher the available oxygen, the higher the energy released, which contributes to heat the burden in the pre-reduction zone and thus favours the reactions. From the previous table, we can stress that Comilog, Amapa and BHP ores are highly oxidised, which could lead to an important exothermic effect in the pre-reduction zone of the furnace and thus to a lower electric consumption.
- The third parameter that highly affects the ore reactivity is the grain size. As shown in both Boris and Cored pre-reduction tests, small ore particles tend to better react with CO gas than the coarse one. For a given amount of ore, the exchange surface between solid and gas is higher when using small particles, which is traduced by a lower MnOx after the pre-reduction (see Figure 9).The peak of temperature after 45 min that is only noticed in the case of small particles, traduces a higher exothermicity of the reactions and thus a higher reactivity.

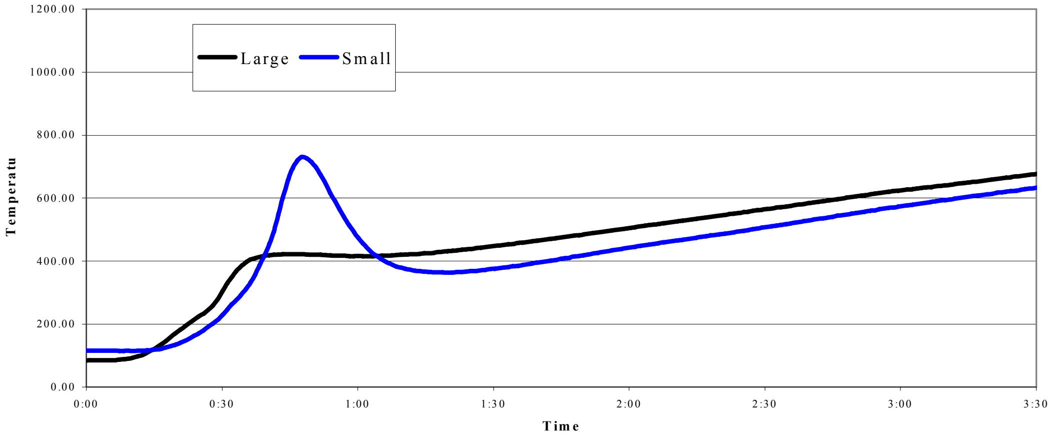

Figure 9: Temperature increase in Boris reactivity test

However, even if for a given amount of ore, small particles theoretically lead to a better reactivity than coarse ones, in practice the later enable to improve the charge permeability and thus a compromise has to be found between the two.

6.5 Burden strategy

To ensure a good burden reactivity, according to different laboratory experiments and industrial trials, small particles that well react with CO gas in the pre-reduction zone are needed. On the other hand, to remove moisture from the burden and improve the burden permeability and thus the reactivity between solid ore and CO gas, coarse particles are also needed in the burden. Therefore, to have the right size distribution concerning manganese sources introduced in the furnace, Comilog ore is a good compromise due to its spread granulometry distribution from 5 to 75 mm (See Figure 10).

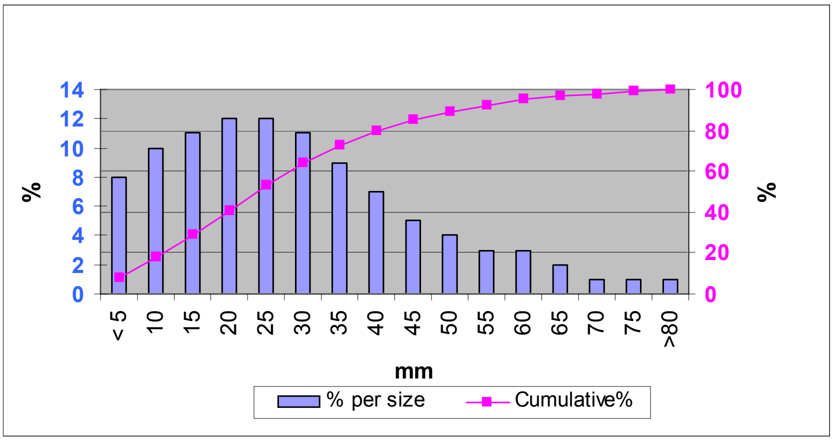

Figure 10: Comilog ore grain size distribution

In the ferromanganese and silico-manganese process the carbon consumption is directly linked to MnO_x content after pre-reduction. Thus, the better pre-reduction takes place (i.e. the lower MnO_x), the lower amount of coke is needed. From the results of Cored tests performed on large particles (i.e. [25-35mm]) with a 2°C/mn heating rate, we can calculate the non ideal carbon consumption in the scope of HC FeMn production as the amount of carbon that is needed to reduce the MnOx (x>1) to Mn:

$$m_C = \frac{(x-1)\times M_C}{M_{Mn}\times Mn_{yield}}\times 1000\times \%Mn_{alloy} \qquad \text{[kg C / mt FeMn]} \tag{8}$$

In the hypothesis of HC FeMn containing 79% of manganese and assessing a manganese yield equal to 80%, the comparison of the different ores studied leads to the following results. As the Comilog ore is the most reactive in the case considered, it leads to the lower carbon consumption during the final reduction (see Table 6).

Table 6: Non ideal carbon comsumption due to reactivity matter

	Mn %	*MnO_2 %*	*Mn_2O_3 %*	*MnO_x % Cored*	*Non ideal carbon cons. kg/tFeMn*
Comilog	50.0	75.0	3.7	1.08	15.4
BHP	48.5	72.0	4.3	1.25	48.0
Asman	49.0	33.7	38.5	1.13	24.9

The efficiency of the CO gas reaction with the manganese oxides of the ores used has impacted the exothermic effect in the pre-reduction zone and also on the energy required for the final reduction. From the performed reactivity tests, the energy consumption to produce a ton of HCFeMn was compared (see Table 7). The higher the available oxygen content and the reactivity with CO gas, the higher the exothermic effect and the lower is the energy consumption.

Table 7: Energy consumption balance due to reactivity matter

	Mn %	MnO_2 %	Mn_2O_3 %	MnO_x %	Exothermic effect KWh/t	Energy consumption kWh/t
Comilog	50.0	75.0	3.7	1.08	427	Reference
BHP	48.5	72.0	4.3	1.25	369	+ 2 %
CRVD	45.0	65.0	5.6	1.30	348	+ 4 %
Assman	49.0	33.7	38,5	1.13	164	+ 7 %

6.6 HCFeMn safety standards

In both HC FeMn and SiMn productions, recommendations could be given to fit with the different markets requirements concerning the metal chemistry (especially phosphorous content).

In order to match the phosphorous requirements, the manganese sources have to be blended.

In addition to the composition target, the specifications have to be defined to ensure safe furnace operation for both sealed and open furnaces in the HC FeMn process.

These specifications are here limited to the manganese sources load into the furnace and are based on three main parameters (see Table 8).

If the available oxygen increases in the ore blend, the furnace operation becomes less stable.

The ore grain size affects the burden permeability and specific procedures have to be established depending on the furnace category.

The zinc content is also the safety key parameter (risk of accumulation in the burden leading to bridging of the mix).

Table 8: Standards established for the use Comilog products in HCFeMn

<table>
<tr><th></th><th colspan="2">HC FeMn production</th></tr>
<tr><th></th><th>Sealed furnace</th><th>Open furnace</th></tr>
<tr><td rowspan="2">Available oxygen</td><td colspan="2">Limitation in the blend</td></tr>
<tr><td>Oxygen 12% above MnO.
Comilog ore could be blended with lower oygen containing ores such as SAR (for example)</td><td>No limitation on the use of Comilog ore</td></tr>
<tr><td rowspan="3">Ore size</td><td colspan="2">Amount of < 6mm fines</td></tr>
<tr><td><15%</td><td><25%</td></tr>
<tr><td colspan="2">Comilog content depends of the amounts of fines from Sintec ®</td></tr>
<tr><td rowspan="3">Zn content</td><td colspan="2">Ore blend content</td></tr>
<tr><td colspan="2"><0.07%</td></tr>
<tr><td colspan="2">As Comilog products contain 0,05% of zinc, this is no limitation to its use</td></tr>
</table>

6.7 Recommendations for Comilog use

In both HC FeMn and SiMn productions, recommendations could be given to fit with the different markets requirements concerning the metal chemistry (especially phosphorous content) using Comilog ore and Sintec ®.

HC FeMn production

In relation with the Comilog ore and sinter chemistry (see § 1) and to match with the phosphorous requirements, the proportions of these two manganese sources could be defined.

HCFEMN	*COMILOG ORE + SINTEC ® MAX %*	*COMILOG ORE %*	*SINTEC ® %*
P < 0,20 %	60	20/40	40/20
P < 0,25 %	80	40/60	40/20
P < 0,30 %	100	40/60	60/40

These recommendations must be considered as an optimization of Comilog ore use, they can be fine tuned according to furnace size and raw materials quality.

SiMn production

The same kind of recommendations could be given to match the phosphorous metal content.

If manganese rich slag is used to produce SiMn, the Comilog percentage in the burden is summed up in the following table:

Std SiMn	*COMILOG ORE + SINTEC ® MAX %*	*COMILOG ORE %*	*SINTEC ® %*
All grades P > 0,10 %	50	30/50	20/0

When manganese rich slag is not available, the amount Comilog products and especially sinter could be increased:

Std SiMn	*COMILOG ORE + SINTEC ® MAX %*	*COMILOG ORE %*	*SINTEC ® %*
P= 0,15 %	80	40/60	40/20
P > 0,15 %	100	40/60	60/40

7. CONCLUSION

The advantage of operating with Comilog ore is the low power consumption and thus high productivity for the same power input. First, the high oxygen content, and next, the good reactivity of the Comilog ore allows this consumption decrease. As the reduction of the higher manganese oxides are all exothermic, when reduced with CO gas, higher oxygen content in the ore will lead to lower power consumption. In addition to the oxygen content, the main factors driving the ore reactivity are the intrinsic porosity and the charge permeability. Taking into account the experiments results and these key factors, recommendations could be given to optimize the charge in both ferromanganese and silico-manganese process. Depending on the phosphorous content specification, the mix burden can include up to 100% of Comilog ore ans Sintec ®.

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