USE OF COMILOG ORE IN FERROMANGANESE PRODUCTION

M. Tangstad[1], P. Calvert[2], H. Brun[1] and A.G. Lindseth[1]

[1] Eramet Norway, P O Box 82 N-3901 Porsgrunn, Norway; E-mail: Merete.Tangstad@eramet-mn-no.com
[2] Eramet Marietta, P O Box 299 Marietta, Ohio 45750, USA; E-mail: Paul.Calvert@eramet-mn-us.com

ABSTRACT

In 1999, Eramet bought the ferromanganese plants in Porsgrunn and Sauda (Norway) and Marietta (USA). With an ownership in the Comilog mine, the plants will operate with a high amount of Comilog ore. The properties of Comilog ore are reviewed and compared to a number of industrial operations. Important ore properties are chemical and mineralogical analyses, CO reactivity and mechanical strength. The advantage of Comilog ore is its contribution to lower energy and coke consumption. However, special precautions must be taken regarding the amount of fines and water introduced in the furnace, as Comilog ore is more porous compared to other Mn ores.

1. INTRODUCTION

1.1 Overview of HC FeMn process

HC FeMn is produced industrially in electric arc furnaces, where the energy is supplied by electric energy, or in blast furnaces, where the energy is supplied by carbon combustion. The optimal properties of the raw materials are almost the same, as are the chemical reactions. The following only discusses FeMn production in the electric arc furnace.

The raw materials for the production of HC FeMn may be divided in the following groups:

- **Mn sources** which will mainly be Mn ores. There are also some by-products, containing large amounts of manganese oxides that are circulated into the process.
- **Carbon sources** are often coke from the blast furnace coke production, as this coke combines high mechanical strength with low CO_2 reactivity. The carbon sources could also be coal or charcoal or a mix of the above. This is mostly a matter of price and cost.
- **Flux agents** are added to obtain certain slag characteristics, such as a specific viscosity. Dolomite or limestone is frequently used to increase the chemical activity of MnO to obtain a higher Mn yield. However, this will increase the total amount of slag which must be taken into consideration.
- **Iron sources** are used to obtain a certain Mn/Fe ratio in the product if the Mn-sources have a high Mn/Fe ratio.

As the raw materials move down in the furnace they will gradually be heated in a reducing atmosphere. Under ideal conditions that is when there is sufficient depth of mix from the electrode tip to the mix surface, the main reactions will be as shown in Figure 1. The main reactions in the ore, will be the prereduction of the higher manganese oxides (MnO_x, $x>1$). The prereduction reactions with CO gas are all exothermic, and thus the higher oxidation level of the ore will give lower energy consumption.

The final prereduction step is the reduction of Mn_3O_4:

$$^{1}/_{3}\, Mn_3O_4 + {}^{1}/_{3}\, CO = MnO + {}^{1}/_{3}CO_2 \qquad \Delta H^\circ_{298} = -16.9 \text{ kJ} \qquad (1)$$

Above about 800°C the highly endothermic Boudouard reaction will be active:

$$^{1}/_{3}\, C + {}^{1}/_{3}\, CO_2 = {}^{2}/_{3}\, CO \qquad \Delta H^\circ_{298} = 57.5 \text{ kJ} \qquad (2)$$

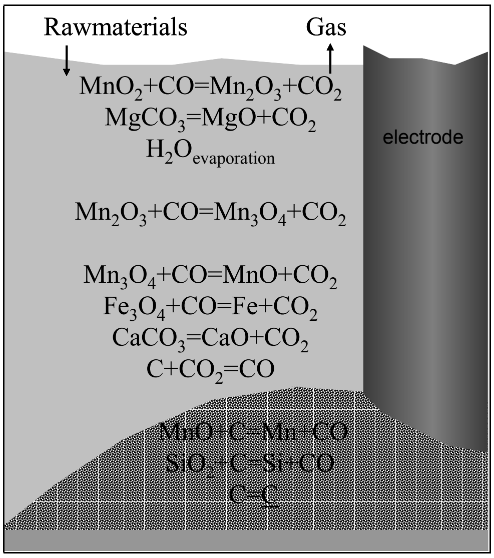

Figure 1. Overview of the main reactions in the HC FeMn process

When the reactivity of the ore is low, and the reduction of Mn_3O_4 (1) occurs at a high temperature, the resultant CO_2 will react according to the Boudouard reaction (2). The energy consumption of the process will thus increase together with an increase in the total carbon consumption and a decrease in the CO_2/CO ratio in the off gas.

As the prereduced charge enters the high temperature area, the ore and flux agents will melt down and flow into a coke layer situated next to and below the electrodes. In this high temperature area the main reaction in the HC FeMn process will be the reduction of MnO to Mn-Fe-C saturated metal. Minor amounts of Si will enter the metal. How much will depend on the slag chemistry and temperature. The gangue elements, such as Al_2O_3, MgO, CaO, BaO will stay in the slag phase. As the MnO content in the slag is determined by the slag chemistry and temperature, higher basicity, that is a higher $(MgO+CaO)/(SiO_2+Al_2O_3)$ ratio, will give lower MnO content in the slag.

Table 1. Mineral Composition of Mn-ores.

Manganese ore	Manganese ore	Mineral name	Chemical formula
Groote Eylandt ore (BHP)	Pyrolusite and Cryptomelane	MnO_2 and KMn_8O_{16}, respectively.	Tetravalent (Mn^{4+}) and mixed (Mn^{2+} and Mn^{4+}), respectively.
Asman ore	Braunite II	$7(Mn,Fe)_2O_3\cdot CaSiO_3$	Mixed (Mn^{2+} and Mn^{3+})
Comilog ore	Pyrolusite and Cryptomelane	MnO_2 and KMn_8O_{16}, respectively.	Tetravalent (Mn^{4+}) and mixed (Mn^{2+} and Mn^{4+}), respectively.
Mamatwan ore	Braunite, Hausmannite, Hematite and Manganite.	$3(Mn,Fe)_2O_3MnSiO_3$, Mn_3O_4, Fe_2O_3, MnOOH, respectively.	Mixed (Mn^{2+} and Mn^{3+}) and trivalent (Fe^{3+} and Mn^{3+}).
Wessel WH	Braunite II, Hausmannite, Hematite, Manganite and Calcite.	$7(Mn,Fe)_2O_3\cdot CaSiO_3$, Mn_3O_4, Fe_2O_3, MnOOH, $CaCO_3$, respectively.	Mixed (Mn^{2+} and Mn^{3+}) and trivalent (Fe^{3+} and Mn^{3+}).
Wessel W1	Bixbyite, Hausmannite, Hematite, Manganite and Calcite.	$(Mn,Fe)_2O_3$, Mn_3O_4, Fe_2O_3, MnOOH, $CaCO_3$, respectively.	Trivalent (Fe^{3+} and Mn^{3+}) and mixed (Mn^{2+} and Mn^{3+}).
Amapa ore	Cryptomelane	KMn_8O_{16}	Mixed (Mn^{2+} and Mn^{4+})
Gloria ore	Rhodochrosite	$MnCO_3$	Mn^{2+}

Table 2. Chemical analyses of manganese ores analysed at Eramet Norway Sauda (wt%, dry)

Manganese ore	Mn/Fe	H_2O	XH_2O	Mn	MnO	MnO_2	Fe_2O_3	FeO	SiO_2	Al_2O_3	MgO	CaO	BaO	K_2O	P	CO_2
Comilog MMA	18.5	8.7	5.4	50.5	3.2	76.0	3.9		4.0	5.5	0.3	0.2	0.2	0.70	0.11	0.1
Comilog MMD	9.5	9.0	5.6	44.5	3.3	66.1	6.7		7.7	7.2	0.0	0.1	0.2	0.75	0.09	0.1
Comilog MMR	13.9	9.0	4.9	48.5	2.8	73.4	5.1		5.0	6.1	0.1	0.1	0.3	0.75	0.11	0.1
Comilog MMS	12.0	9.0	6.5	46.5	4.4	68.2	5.5		7.7	7.5	0.0	0.0	0.1	0.75	0.085	0.1
Comilog Sinter	16.7	1.5	0.4	58.5	59.6	19.7		4.5	7.0	6.5	0.0	0.1	0.3	0.75	0.12	0.0
Asman 48	5.1	0.9	0.5	51.3	37.9	34.7	14.3		5.5	0.4	0.7	4.3	0.4	0.0	0.04	0.8
Amapa Sinter	5.1	1.0	0.6	49.1	45.7	18.6		12.5	7.6	7.6	0.5	0.8	0.3	0.3	0.10	0.0
Amapa Miudo 40	3.3	10.0	2.3	41.3	22.4	38.0	18.0		5.9	8.1	0.1	0.3	0.3	0.8	0.11	3.5
Mamatwan	8.2	1.0	0.3	37.8	29.8	23.4	6.6		4.0	0.5	3.5	14.7	0.0	0.0	0.02	17.0
Gloria	7.8	0.4		39.1	31.3	23.6	7.2		5.7	0.3	3.8	12.7	0.1	0.0	0.02	15.4
Groote Eylandt	11.6	2.7		48.8	2.6	73.9	6.0		6.9	4.2	0.1	0.1	0.3	2.0	0.09	0.5
CVRD sinter	11.5	0.6		54.5	52.0	22.5		6.1	5.4	8.7	0.5	1.9	0.3	1.4	0.11	0.2
Wessel 38%	3.2	1.2		42.3	27.8	32.8	18.9		4.9	2.5	1.0	6.0	0.3	0.1	0.04	3.6
Wessel 50%	5.0	0.9		50.2	36.1	35.2	14.5		3.6	0.4	1.0	5.6	0.3	0.1	0.04	2.6

2. ORE PROPERTIES

2.1 Analyses and mineralogical composition

The chemical analyses and the mineralogical composition of some major Mn-ores are shown in Table 1 and Table 2.

There are several important issues regarding the chemical analyses of an ore:

- **Oxygen content**
    - As mentioned, the reduction of the higher manganese oxides with CO are exothermic reactions. Thus, higher oxygen content in the ore will lower the energy consumption. For a specific charge with oxygen content given by $MnO_{1.7}$, the calculated power consumption was 2174 kWh/ton alloy [1]. With the same charge, but with an oxygen content given by Mn_3O_4, the power consumption increased to 2514 kWh/ton alloy. Comilog ore is one of the ores with high oxygen content and will thus give lower energy consumption compared to other low oxygen ores and sinters under the assumption of equal degree of prereduction.
    - In closed furnaces the oxygen content in the ore may be a safety factor and special precautions have to be taken if one operates with high oxygen ores.
- **Mn content**
    - Ores with a high Mn content, such as Comilog, Groote Eylandt, Asman and Wessel 50, may give a low slag/metal ratio which will lower the power consumption. A high Mn content combined with low SiO_2 and Al_2O_3 levels is especially beneficial regarding the Mn yield of the process. But it is shown that Comilog gives a higher Mn yield than Groote Eylandt, as it will give a lower Mn content in the final slag at similar basicities.
- **Mn/Fe ratio**
    - The Mn/Fe ratio in the ore mix will determine the Mn/Fe ratio in the metal together with the slag basicity. This means that if the ore has a higher Mn/Fe ratio, a metallurgist has a larger degree of freedom in mixing the charge. As an example, inexpensive iron sources can be added if Groote Eylandt ore or Comilog ore are used, as these two ores have high Mn/Fe ratios.

- **Mn/P ratio**
  - The Mn/P ratio in the ore will determine the P content in the final product. As many customers demand low P content, this must be controlled by using low P ores. In this respect, the South African ores are especially beneficial. Eramet Norway uses about 60% Comilog ore at present due to P requirements given by the market.
- **Potassium**
  - Higher potassium may contribute to a higher lining wear as well as a higher rate of the Boudouard reaction. The increased rate of the Boudouard reaction will increase the energy- and carbon-consumption. The Comilog ore is quite favourable, compared to CVRD and Groote Eylandt as far as the alkalis are concerned.

There are also other issues regarding the chemical analyses, for example, the amount of trace elements. Also the environmental limits differ between nations, but this issue will not be further addressed here.

2.2 Prereduction

In the industrial manganese reduction process, the consumption of energy and carbon is determined by the reactivity of the ore, that is, how much of the oxygen will be released at high temperatures. This is already discussed in the previous section "Overview of the HC FeMn process". Seven laboratory investigations were reviewed [2] to determine which ores would give the lowest consumption of carbon and energy. The results are summarized in Table 3. In all the laboratory studies, Groote Eylandt and Comilog were found to be the most reactive ores. Groote Eylandt is best in some investigations, Comilog in others. However, there are major uncertainties in these studies. The largest one is the inhomogeneity of the ore. Each type of ore has different qualities, and even within one quality two different lumps may have differences in reactivity. Despite this, Groote Eylandt and Comilog stand out as the most reactive ores in all the studies. This can be explained by the fact that the reduction of bixbyite, which both Comilog and Groote Eylandt will be reduced to, is faster than the reduction of braunite ores like Assmang, Wessel and Mamatwan, see Berg [3].

Table 3. Summary of the order of reactivity [2]

Investigation	**Sørsdal lump**	**Sørsdal pellet**	**Todd et al.**	**Beck**	**Stalheim**	**Ruud**	**Berg**	**Wasbø**
High reactivity	GE	GE	Com	Com	Com /GE	GE	GE	Com
	Com	Tem.S.	GE(?)	GE		Glo		Asm
	Gh.C.	Com	Am			Com		GE
	Tem. S.	Wes	Asm	(Asm)		Asm	Asm	
	Wes	Gh.C.	Wes					
Low reactivity	Mam	Mam						

Com-Comilog, Gh.C.-Ghana Carbonate, Tem.S.-Temco Sinter, Wes-Wessel, Mam- Mamatwan, Am-Amapa, Asm-Assmang, Glo-Gloria, GE - Groote Eylandt

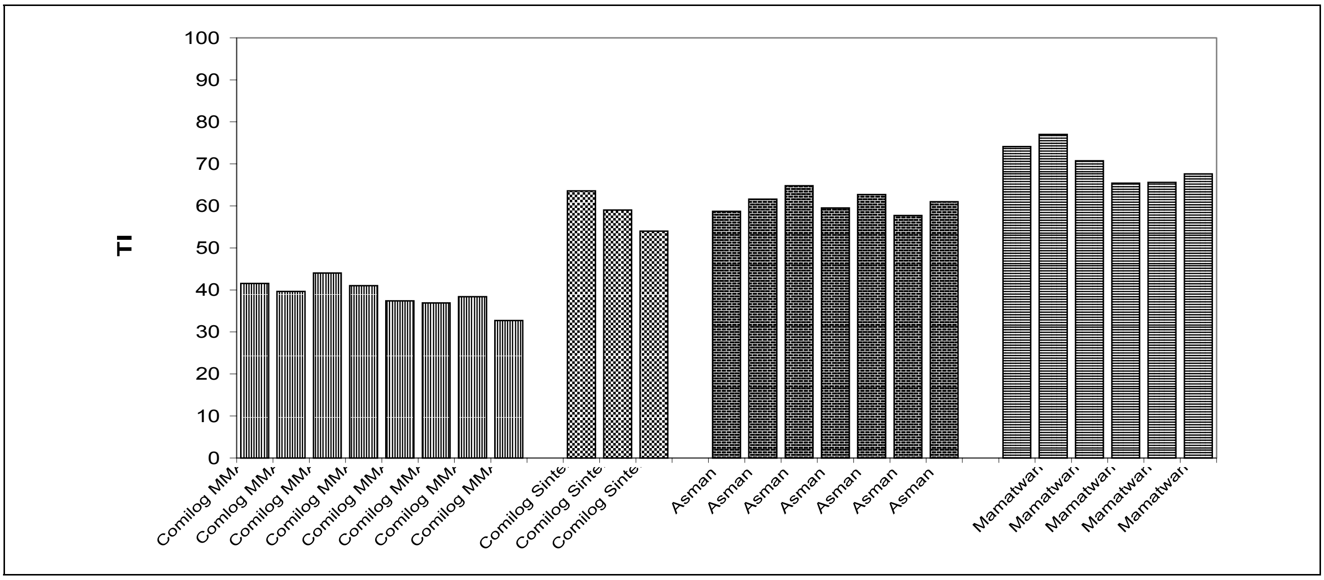

Figure 1. Mechanical strength given by tumbling index (TI) after heating and tumbling

Table 4. Ore data used by Todd et al. [4]

	%Mn	%Fe	Av. Ox	x (MnOx)	Porosity	Density g/cc
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
Asman38-1	44.9	14.1	7.3	1.56	1	4.26
Asman46-1	53.7	6.1	9.5	1.62	0	4.45
Asman50-1	55.7	6.8	9.6	1.6	0	4.57
Comilog-5	47.3	2.3	12.6	1.93	53	2.07
BHP-2	48.4	3.4	9.4	1.68	7	3.83
BHP-3	52.2	0.9	13	1.97	5	3.96
Wessel-3	26.1	39	5.4	1.72	6	4.52
Wessel-4	49.6	12.5	8	1.56	2	4.63
Wessel-5	46.8	6.7	6.1	1.46	9	4.06

Table 5. Mn ore density and porosity [5]

Ore	**Density**	**Apparent density**	**Porosity**
Comilog (MMR, lump):	3.75-3.78	1.93-2.61	30.4-48.9%
Comilog (MMA, lump):	3.56-4.32	2.34-3.02	30.2-34.2%
BHP	4.04-4.28	3.74-3.94	7.7-7.8%
Comilog (MMR, crushed):	4.57	3.93	14.0%
Comilog (MMA, crushed):	4.32-4.34	3.28-3.83	11.4-24.4%
BHP (crushed)	4.21-4.25	3.89-4.02	5.5-7.8%

2.3 Mechanical strength

When investigating the mechanical strength, there are two aspects that are important:

1. How the ore behaves when it is transported to the furnace, which is in a cold state.
2. How the ore behaves in the furnace, which is at high temperatures in a CO/CO_2 atmosphere.

Laboratory studies found that, in general, ores are much more fragile when heated in a reducing atmosphere, compared to being heated in inert or oxidizing atmospheres. Some laboratory tests have been done to study the mechanical strength of different ores in reducing atmosphere. Here 10-15mm ore particles were heated to 1100°C in a 70%CO 30%CO_2 atmosphere. The particles are then tumbled in a Hannover drum and sieved. The size fraction after heating and tumbling will show the strength of the ore in the furnace. The size distribution of three different ores and Comilog sinter is shown in Figure 1. Compared to Mamatwan and Asman, Comilog has a lower mechanical strength during heating and reduction as it gives a higher amount of fines. This is probably the large porosity of the Comilog ore as shown in Table 4 and Table 5. The high porosity will also increase the ability to retain water, and a higher amount of water will generally follow the Comilog ore and Amapa ore compared to others, as also seen in Table 2.

2.4 Electrical resistivity and viscosity of various slags

It is not clear how the electrical properties and the viscosity of the slag affect the reaction mechanisms in the furnace. When the metal and slag is tapped, low viscosity is preferred to get a satisfactory metal and slag separation, but inside the furnace this correlation is not that obvious. We will now discuss the electrical resistance and the viscosity of three slags, and briefly discuss the possible consequences in industrial operation.

Comilog ore, like Groote Eylandt and Amapa, contain small amounts of basic oxides. When they are smelted with a low slag/metal ratio, the slag will be acid. There is also the possibility of adding fluxes, although it will give an extra cost in flux agents and higher power consumption. Table 6 shows slag analyses for three different slags, two of which are based on 100% Comilog ore, and one based on a mix of various ores. As the total amount of acid oxides (SiO_2+Al_2O_3) increases, the viscosity raises as does the electrical resistivity in the slag as shown in Figure 3. This may lead to a higher temperature for two reasons, first, the electrode tip will be deeper in the furnace and next, if the slag flow rate in the furnace is low, more energy will be transferred into the slag, until it reaches the viscosity where it flows freely.

Table 6. Three cases with different slag composition

	Comilog + Fe	Comilog + dolo+Fe	Low Alumina slags
MnO	47.0	39.0	39.0
SiO_2	18.0	17.0	25.0
CaO	2.1	9.7	17.0
MgO	0.5	6.1	7.0
Al_2O_3	28.5	24.9	12.0
LB=(MgO+CaO)/SiO_2	0.1	0.9	1.0
slag/alloy -ratio	0.36	0.41	0.7

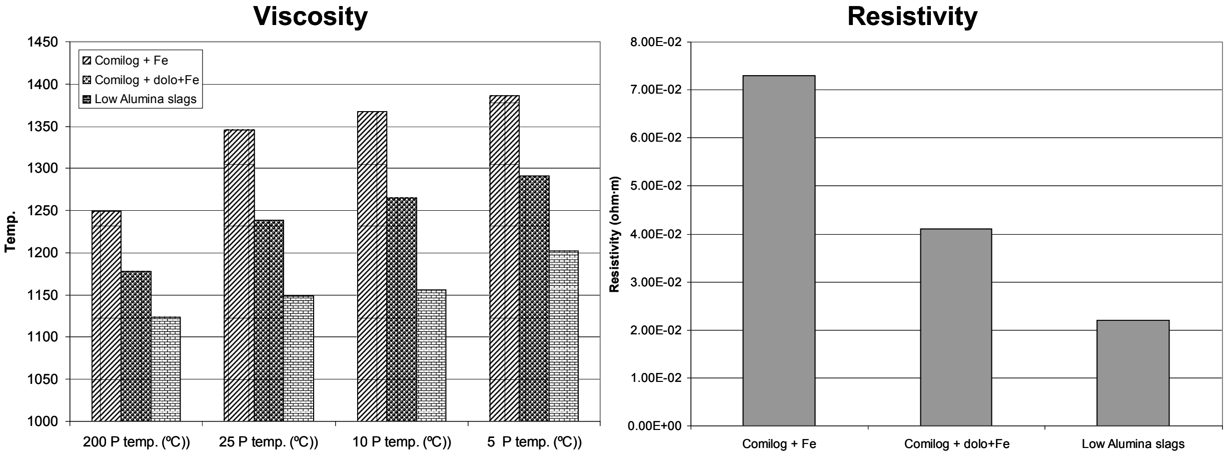

Figure 2. Viscosity and slag resistivity at 1500°C (Resistivity data based on Seger et al. [6])

3. INDUSTRIAL EXAMPLES OF USE OF COMILOG ORE

We will now consider the use of Comilog ore in industrial HC FeMn furnaces. It will show that low power consumption may be achieved due to a high oxygen content, a high degree of prereduction, a low slag/metal ratio both due to a high Mn content in the ore and a relatively low MnO content in the final slag as a high Al_2O_3 content in the slag will give a higher temperature. As an example of this, one of the industrial cases from the mid 1980's will be used in this paper, as in that period several trials were performed with high amount of Comilog ore in the charge.

3.1 Union Carbide - Beauharnois 1985 [7][8]

In 1985, a 6 month trial was done in the 34MW closed furnace to use a high amount of Comilog ore in production. The Comilog ore was sieved at 6 mm and dried to 4-5% water. The Comilog fines and coke fines were used to produce sinter. In addition to the Comilog ore and sinter, coke and a minor amount of briquettes were added. A summary of the operating results are shown in Table 7 and the slag and metal chemistry is shown in Table 8.

The Comilog trial was successful for several reasons. The power consumption was low and the tonnage high due to:

- High oxidation content of the ore
- Good prereduction
- Low slag/metal ratio due to a) a high Mn content in the ore and b) due to a good Mn yield
- Good Mn yield due to a relatively low MnO content in the slag despite the low basicity. This is believed to be caused by a higher temperature due to the use of a high alumina slag.

Table 7. Operating numbers - 6 months trial (Beauharnois)

Operating Load	33.3 MW	
Operating Time	98.9%	
Production	395.5 Mt/Day	
Power Cons.	2000 kWh/t alloy produced	
Power Cons.	2152 kWh/t alloy smelted	
Electrode Cons.	6.6 kg/t (3.3 kg/MWh)	
Carbon Cons.	306 kg/t reduced alloy (excl. electrodes)	
Mn Recovery	81.5%	
Comilog in blend	100%	
	Comilog Ore	78%
	Sinter	22% (from Comilog Ore fines)

Table 8. Slag and metal chemistry (Beauharnois)

Alloy Chemistry		Slag Chemistry			
Mn	78.7	Mn	33.1	Slag/Alloy ratio	0.46
Si	0.8	MnO	42.7	(CaO+MgO)/SiO2	0.20
Fe	12.7	SiO_2	18.3		
P	0.19	Al_2O_3	28.2		
C	6.7	CaO	2.8		
		MgO	0.98		
		BaO	1.2		
		K_2O	3.3		

The furnace was operated very well in this 6 month period, which can be seen both from the high operation time (98.9%), the low electrode consumption (6.6 kg/t alloy) and the low C consumption of 306 kg/t smelted alloy (electrode consumption not included).

The Si content in the metal is determined by the slag-metal equilibrium ($2MnO+Si=Mn+SiO_2$), and when the Mn content in the slag becomes very low, the Si content in the metal will be high as shown in Table 8.

Table 9. Metal and slag analyses from furnace 12 Eramet Marietta (July-December 2002)

Alloy chemistry		**Slag chemistry**			
Mn	79.5%	Mn	29.7%	Mn. Recovery	82.3%
Cr	0.01%	MnO	38.3%	Comilog in blend	100%
Si	0.35	SiO_2	20.7%	MMA	51.1%
Fe	12.3%	Al_2O_3	22.8%	MMD	35.4%
As	0.2%	CaO	7.7%	Sinter	11.5%
P	0.24%	MgO	5.1%	MMR	6.0%

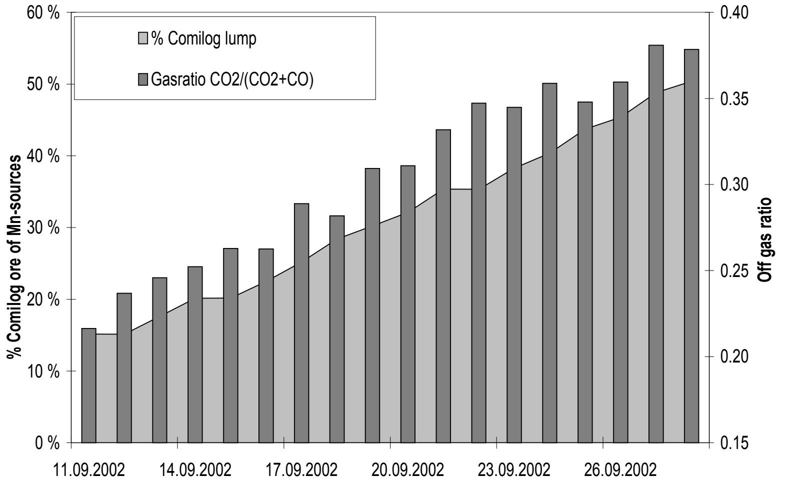

Figure 4. Increase of gas ratio with increasing Comilog ore content (ENS)

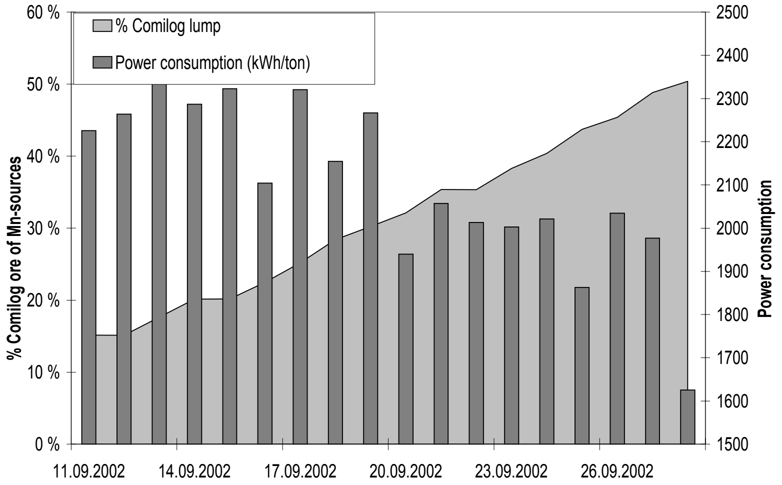

Figure 5. Decrease of power consumption with an increase of Comilog ore (ENS)

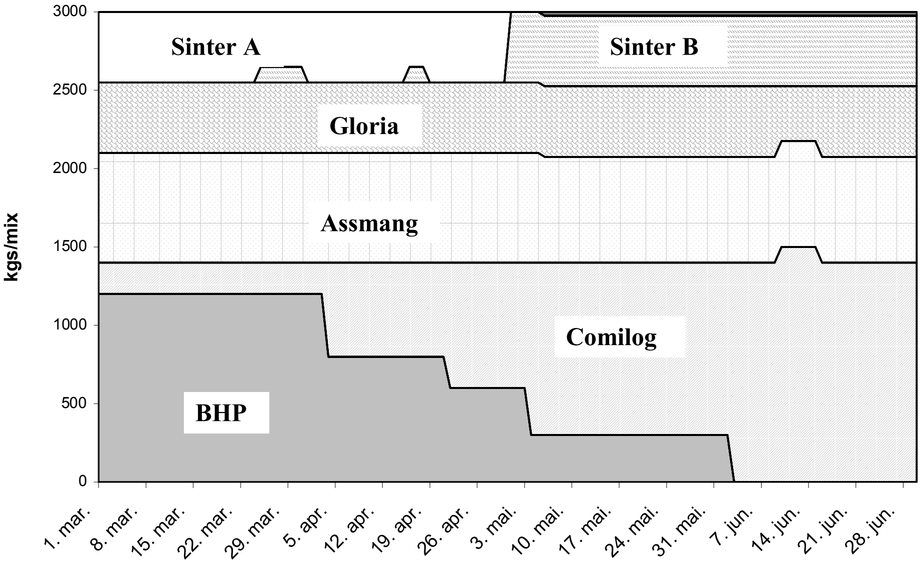

Figure 6. Manganese sources during transfer from Groote Eylandt to Comilog on frnc.11 Eramet Norway Porsgrunn.

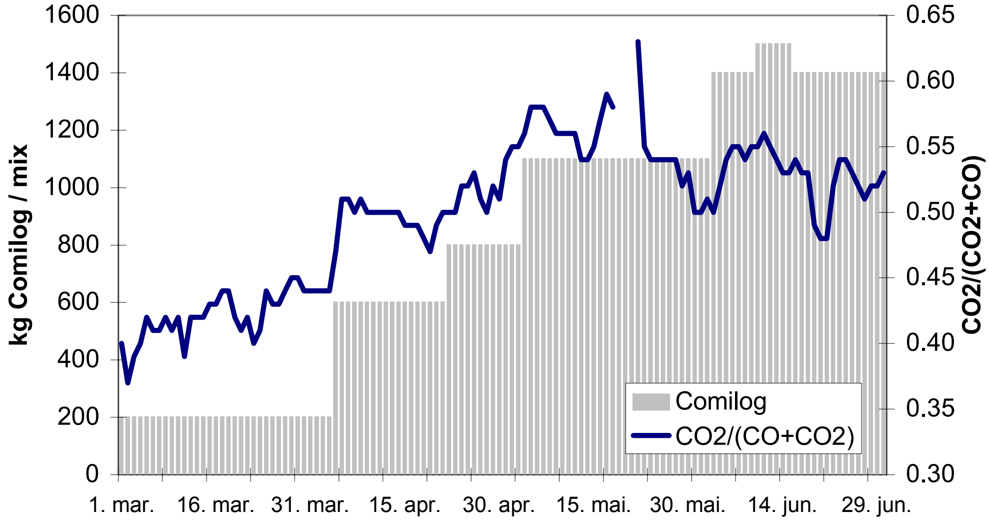

Figure 7. Off gas analyses with increasing amount of Comilog ore substituting Groote Eylandt.

3.2 Use of Comilog ore at Eramet plants

In an open furnace at Marietta about 90% Comilog ore and 10% Comilog sinter were used. The ore were not sieved or dried, as was done at Beauharnois. In addition to these manganese sources, coke, dolomite and metallic materials were added. Dolomite is added to lower the Si content in the metal. At the same time it will lower the MnO content in the slag. The relative low MnO content and a higher addition of metallic material, will give an even better Mn recovery compared to the Beauharnois operation described above.

The next example is from one of the closed Norwegian furnaces, frnc. 12 at Eramet Norway Sauda. It is aimed at a lower P content in the metal and thus Comilog ore is mixed with other manganese sources. The Comilog ore is increased from 15% to 50%, on behalf of low oxygen Mn sources. The gas ratio will increase in this period (Figure 4) due to a higher oxygen content, which will decrease the power consumption as shown in Figure 5. However, the degree of prereduction was low during this period, which shows that the furnace must be in good condition to obtain a high degree of prereduction.

The last industrial example is from frnc. 11 at Eramet Norway Porsgrunn, and will show the effect of a better degree of prereduction of Comilog ore compared to Groote Eylandt ore which both has good reactivity according to laboratory scale tests. The Comilog proportion was increased from below 10% up to 37% and was substituted for the Groote Eylandt ore, which has very similar properties. Although the total oxygen content of the charge did not change, the degree of prereduction changed from a medium level to a high level. It is very rare that such a high degree of prereduction has been seen industrially, and this example is therefore used although it was also shown at Infacon 9 [2].

Based on operating results in Beauharnois when operating with high levels of Comilog ore, it was also concluded that Groote Eylandt ore did require approximately 7% higher carbon consumption and 5% additional power consumption as compared to Comilog ore [9]. A higher carbon- and power- consumption was also noted in Marietta. This is due to the higher porosity of Comilog ore compared to Groote Eylandt ore.

4. CONCLUSION

The advantage of operating with Comilog ore is that it will give low power consumption and thus a high tonnage for the same power input. The main reasons for this are first, the high oxygen content, and next, the good reactivity of the Comilog ore.

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. When using Comilog ore with an oxygen content of $MnO_{1.7}$ compared to Mn_2O_3 ore or Mn_3O_4 ore, the power consumption will be reduced in the order of 150kWh/tonne and 350kWh/tonne alloy respectively.

Both laboratory scale experiments and industrial operation showed that Comilog ore has a high reactivity. This is due to the mineralogy of the ore and the high porosity. A good prereduction may decrease the power consumption in the order of 100 kWh. With a good reactivity, the carbon consumption per ton alloy will decrease, which will improve the overall cost. The high porosity also affects the mechanical strength of the ore, and Comilog ore is relatively friable. However, it is shown that this is not a decisive issue. Eramet has been operating both today and previously with close to 100% Comilog ore in the charge with good results.

When using Comilog ore, a low slag/metal ratio may be achieved for two reasons. First, the Mn content in the ore is high, and accordingly the amount of gangue minerals will be low. The second reason is that the MnO content in the slag is relatively low when operating with low basicity. It is believed that this is due to a higher temperature when operating with a high alumina slag. The high Mn/Fe ratio of the ore will increase the numbers of freedom in the operation, and may lead to reduced costs by enabling low price iron sources to be used.

A new sintered ore, produced by Comilog in Gabon, and named “Sintec” could give an efficient complement or alternative for Comilog ore. “Sintec” will have the same characteristics regarding the low slag volume and the high Mn/Fe ratio. It may also improve the permeability in the charge, and thus improve the degree of prereduction.

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