USE OF CHARCOAL IN SILICOMANGANESE PRODUCTION

B. Monsen[1], M. Tangstad[2] and H. Midtgaard[3]

[1]SINTEF Materials Technology, N-7465 Trondheim, Norway. E-mail: Bodil.Monsen@sintef.no
[2] Eramet Norway AS, co. SINTEF Materials Technology, N-7465 Trondheim.
E-mail: merete.tangstad@eramet-mn-no.com
[3]Tinfos Jernverk A/S, Post box 246, N-4491 Kvinesdal, Norway. E-mail: HMI@tinfos.no

ABSTRACT

The increased attention towards reducing emissions of fossil CO_2 due to its potential global warming effect has resulted in a focus on renewable resources, as charcoal. Since charcoal is produced from growing wood it does not contribute to global warming.

This paper gives a brief review of consequences of and reasons for using charcoal in the silicomanganese (SiMn) production. Results are presented from practical SiMn smelting experiments, on a pilot scale, using charcoal as reduction material and comparing with coke. As slag- and CO_2-reactivity are important for furnace performance these features have also been measured.

1. INTRODUCTION

From a global reference, CO_2-emissions from a process using charcoal combined with hydropower should be very small if there is a balance between the carbon in the process and the growth of the trees used to produce the charcoal. Charcoal is manufactured from wood by carbonisation in large kilns or retorts [1][2]. By-products are pyroligneous liquid and gases. The yield of the different reaction products varies with wood species and process parameters, for example heating conditions. Larger particle sizes and slow heating favour the formation of charcoal.

Brazil is the world's largest charcoal producer and produces 6.4 million tonnes yearly, 25% of the world's charcoal production [1]. Brazil has tradition for and long experiences in using charcoal in the production of ferroalloys. The main reason is that charcoal has been produced successfully from cultivated eucalyptus wood, at low costs competitive to import of coke and coal. During the past 10 years there has been a change both in producers and towards larger furnaces. Presently CVRD owns most of the ferromanganese (FeMn) and silicomanganese (SiMn) production in Brazil.

The Norwegian production of ferroalloys is well above one million tonnes per year and includes FeMn, SiMn, silicon (Si) and ferrosilicon (FeSi). Recently CVRD bought Elkem's ferrochromium plant at Mo i Rana, and started production of manganese alloys during the summer 2003. Norwegian producers are ERAMET Norway, Tinfos Jernverk, Elkem ASA, Fesil ASA, Finnfjord Smelteverk A/S and Globe Norge Hafslund Metall. This industry is at present responsible for about 3 million tonnes of $C0_2$-emissions [3] which come from fossil carbon, mainly coal and coke used as reductants in the smelting processes. In Norway SiMn is produced in covered furnaces, using coke as reducing agent. The SiMn industry in Norway has no experience in using charcoal and at the moment we do not believe that there are process benefits by using charcoal. Charcoal is not produced in Norway, and by importing charcoal (from Brazil, for instance) the price more than doubles due to the transportation, resulting in high charcoal costs compared to the imported coke. However, because of possibilities for process improvements, charcoal and wood chips are used to a small extent in the production of Si and FeSi. South America and Asia have been the main charcoal suppliers.

In 2002 the Norwegian Ferroalloy Producers Research Association (FFF) launched a 3-year research project called "Environmental friendly reduction processes" aiming to reduce CO_2 emissions. Central participants are SINTEF and NTNU together with the industry representatives. Sub-goals are to identify consequences of and reduce costs connected to increased use of charcoal, and optimise or develop charcoal processes with high carbon yield and/or high purity.

Both in Norway and in Brazil, the electric power supply is based on hydropower, which has very low CO_2-emissions. A recent mapping has shown that the specific CO_2-emissions are about 1.25 t CO_2/t metal for FeMn and SiMn production in Norway [3], and come mainly from the coke. Specific CO_2-emissions from typical Norwegian ferroalloys production have also been published previously [4][5]. This paper focuses on consequences of using charcoal in production of SiMn, reflecting the possibilities for CO_2-reductions for this industry in Norway, while other papers focus on the same for Si/FeSi [6][7].

The Kyoto agreement commits the industrialised world to reduce the emissions of fossil CO_2. It is most probable that Norwegian industry will be allowed to emit a certain percentage of its normal rate of emissions free of charge while emissions exceeding this level must be bought as emission quotas on the open market. At present no one knows what will be the cost if/when you have to buy CO_2 quotas in the future.

2. PROPERTIES OF REDUCTANTS FOR SiMn PRODUCTION

Typical chemical analyses and other properties of charcoal compared to metallurgical coke for SiMn/FeMn production, are compared in Table 1. There are major differences between charcoal and coke; usually charcoal has a lower fixed carbon content and much higher content of volatile matters, while ash is rather low compared to coke. Ash composition of charcoal depends strongly on the soil where the trees have grown, and if fertilisers have been used. Charcoal has also a substantial lower mechanical strength. Its compressive strength is dependent on fibre direction, being 3-4 times higher in the direction parallel to wood fibre than radial to the fibre [6]. Further charcoal has a very high electrical resistance, low volume weight, and high CO_2- and SiO-reactivity compared to coke.

Table 1. Typical properties for charcoal compared to metallurgical coke (special qualities in brackets).

Specification		Unit	Charcoal	Coke
Fixed carbon (%)		%	65 – 85 (90-94)	86-88 %
Volatile matter (%)		%	15-35 (5-9)	≤1
Ashes		%	0.4-4	10-12
Ash composition:	SiO_2	%	5-25	25-55
	Fe_2O_3	%	1-13	5-45
	Al_2O_3	%	2-12	13-30
	P_2O_5	%	4-12	0.4-0.8
	CaO	%	20-60	3-6
	MgO	%	5-12	1-5
	K_2O	%	7-35	1-4
Compressive strength	[8]	kg/cm^2	10-80	130-160
Volume weight		kg/m^3	180 -350	500-550
Electrical resistance		ohm·m	high	low
CO_2-reactivity	AC-method		3-4	0.1
CO_2-reactivity	NTNU/SINTEF[11][12]		Medium-high	Low-medium
Slag-reactivity 1600°C	SINTEF [10]		(see below)	(see below)
SiO-reactivity	SINTEF [9]	ml SiO (g)	200-1100	1500-2000

2.1 Slag-reactivity

Thermo-weight experiments with slag/charcoal and slag/coke have been carried out at 1600 °C for 60-90 minutes in CO atmosphere [10]. Heating was also carried out in CO atmosphere and took about 50 minutes. Crucibles of the reductants were made from selected large pieces. A synthethic slag was made and filled to the rim into the crucibles (with equal inner diameter). The crucibles were put inside an alumina crucible, which again were hanging in the thermo-weight.

The results showed that charcoal and coke slag reactivity was equally good, the SiMn metal produced contained 20%Si in all 4 experiments. Referring to Figure 1, the rate of reaction was equal too, if the reductants had been calcined at 1600 °C for 3 hours prior to the experiments. However, the rate of weight loss was faster for coke if a lower calcination temperature (1200 °C) was used, as shown in Figure 2, mainly due to ash reactions (the coke has a high ash content).

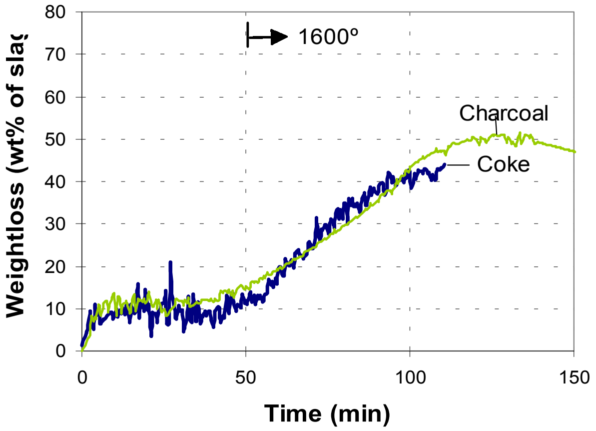


Figure 1. Slag-reactivity at 1600°C for charcoal and coke precalcined at 1600°C.

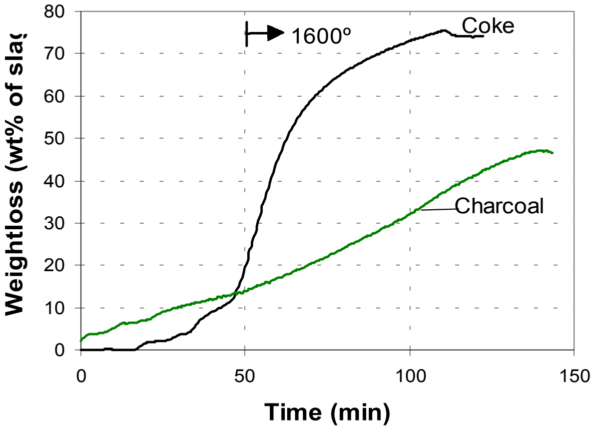


Figure 2. Slag-reactivity at 1600°C for charcoal and coke precalcined at 1200°C.

The two most important slag-reactions causing the weight-loss are shown in formulas (1,2). The carbon source can also be silicon carbide. In addition iron oxide in the slag is reduced to iron in the metal.

$$(SiO_2)_{slag} + 2C = Si_{metal} + 2CO_{(g)} \tag{1}$$

$$(MnO)_{slag} + C = Mn_{metal} + CO_{(g)} \tag{2}$$

2.2 CO_2-reactivity

Charcoal is more reactive towards CO_2 than coke according to the AC method. This test is carried out in CO_2 atmosphere at elevated temperature. A highly reactive material will have a high reactivity number, reflecting a high rate of the Boudouard reaction (3).

$$CO_2 + C = 2CO \tag{3}$$

A high rate of this reaction is undesirable in SiMn/FeMn production according to energy consideration [19], because the Boudouard reaction to CO in the upper part of the furnace will increase both coke and power consumption.

It can be argued that the CO_2-reactivity test should be carried out in an atmosphere close to furnace atmosphere. In a covered furnace the atmosphere will be reducing. Hence, NTNU/SINTEF developed a CO_2-reactivity test which is carried out in an atmosphere of 75% CO and 25% CO_2 (3-4 Nl/min). The method is described and discussed elsewhere [11][12][21]. Results from this test carried out at 1000°C for 10 or 20 g samples, are shown in Figure 3 and Figure 4.

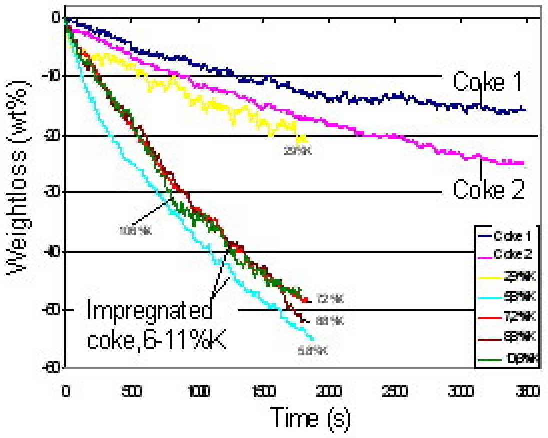


Figure 3. CO_2-reactivity at 1000 °C of coke and K-impregnated coke [21].

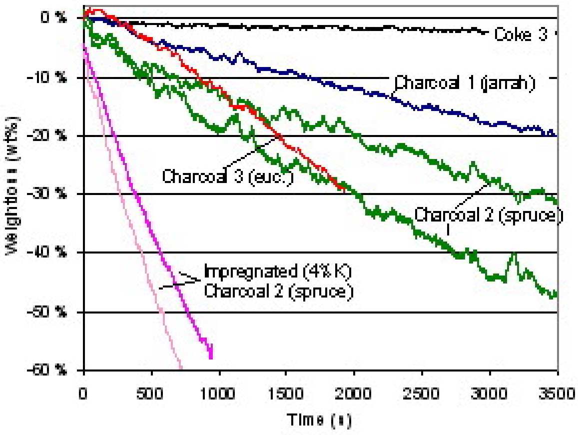


Figure 4. CO_2-reactivity at 1000°C of charcoal, coke and K-impregnated charcoal.

It is seen that the weight-loss is approximately the same for Charcoal 2 (made of Norwegian spruce) and Charcoal 3 (made of eucalyptus from Brazil.) Compared to Coke 3 these charcoals have a higher CO_2-reactivity, losing 20-30% of their weight during half an hour, compared to only 2% for Coke 3. However, there is a span in reactivity for the cokes. Cokes 1 and 2 are more reactive, comparable to Charcoal 1which was made from jarrah (Australian, dead wood).

Potassium is a catalyst for the Boudouard reaction, and enters the furnace as components of the manganese ore and to a smaller extent also as a component of the coke. Alkalis are known to accumulate and re-circulate in the furnace, and may condence on the coke in the upper parts. For this reason, CO_2-reactivity of K-impregnated coke has been carried out [11][21]. The results are here compared to K-impregnated charcoal (of Norwegian spruce). It is clearly seen that potassium speeds up the Boudouard reaction several times. K-impregnated coke is more reactive than Charcoal 2 (spruce), but less reactive than K-impregnated charcoal.

2.3 SiO-reactivity

The SiO reactivity test at SINTEF is carried out at 1650°C according to standard procedure that is well described in the literature [9]. The reactivity number indicates the amount of SiO gas passing the actual sample without reacting. Hence, a low reactivity number indicates a high reactive material. Charcoal is much more reactive towards SiO gas than coke. The actual reaction is shown in formula (4), but its importance for SiMn production is questionable.

$$SiO\ (g) + 2C\ (s) = SiC\ (s) + CO\ (g) \tag{4}$$

3. EXPERIENCE FROM USING CHARCOAL IN A PILOT FURNACE

Silicomanganese has been produced in five pilot scale experiments during 2001-2003 with three different reductants with large variations in CO_2 reactivity [13][14]. The reductants were industrial coke, reactive coke and charcoal, with increasing CO_2 reactivity (AC method) at about 0.1, 0.5-1 and 3-4 respectively. The aim was to produce SiMn with 18% silicon and see if any significant difference was found in the coke-bed by using different reductants.

3.1 Raw materials and charge composition

Analysis of the raw materials is shown in Table 2 and the charged composition in Table 3. The amount of ore and HC FeMn slag is the same in all experiments, 35 kg ore and 15 kg HC slag in each charge.

Table 2. Raw material analysis (wt%), the reductants are on a dry basis.

	Comilog ore	**HC FeMn slag**	**Quartz**	**Industrial coke**	**Reactive coke**	**Charcoal E_1**	**Charcoal E_2**
MnO_2	74.1			0			0
MnO	2.0	36.04	0.38	0.05			0.01
Fe_2O_3	5.7	0.00	0.20	1.37	1.0	0.03	0.02
CaO	0.2	13.64	0.12	0.40		0.61	0.19
MgO	0.1	4.21	0.03	0.17		0.15	0.03
BaO	0.2	0.98	0.01	0.01		-	-
Al_2O_3	6.10	11.78	1.09	3.43		0.06	0.01
TiO_2	0.2	0.56	0.15	0.22		0.003	0.001
SiO_2	5.60	20.87	92.61	6.46	1.0	0.13	0.10
P_2O_5	0.30	0.00	0.01	0.09		-	0.02
K_2O	0.80	2.00		0.13		0.41	0.03
FixC	0.00	0.42		87.47	94.8	80.0	81.3
Met Mn		2.70					
Met Fe		0.52					
CO_2	0.10						
Volatiles				0.2	2.1	18.6	18.3
SUM	95.24	93.72	94.60	100.0	98.9	100.0	100.0

Table 3. Charge composition (kg, wet), based on 35kg ore and 15kg HC slag in each charge.

Run no	Starting cokebed (kg)	Charged materials	Moisture (%)	Charge 1 (kg)	Charge 2 (kg)	Charge 3 (kg)	Charge 4-11 (kg)	
1	5	Industrial coke Quartz	13	11.5 0	12 6.5	13 11	13.5 13	
2	3	Reactive coke Quartz	2	10 0	10.5 6.5	11.5 11	12 13	
3	5	Charcoal E_1 Quartz	5	11.5 0	12 6.5	13 11	13.5 13	
4	5	Charcoal E_2 Quartz	7	11.5 0	11.5 6.5	12.5 11	13.0 13.3	12.5 12.5
5	3	Charcoal E_2 Industrial coke Quartz	7 0	5.5 4.8 0	6 5.2 6.5	6.3 5.5 11	6.6 5.7 13.3	

The experiments started with 3-5 kg coke-bed to have close to the same start volume of the coke-bed. The amount of coke in the charge is calculated to give an off gas composition of $CO/(CO+CO_2)$ close to 1 and the amount of fixed carbon added is the same in the experiments 1-3. In experiments 4-5 the electrode tip position was set 5 cm lower, and therefore the amount of fixed carbon in the charge was somewhat reduced in order to reduce the volume of the coke-bed. In experiment 5 the reductants are 50% coke and 50% charcoal on a fixed carbon basis.

The composition of the charge was changed during the first 3 charges. Trying to avoid a build-up of a quartz-bed, quartz was not added to the first charge. Gradually the amount of quartz was increased in charge 2-3, and for charge 4-11 the total amount of SiO_2 in the charge is about the same in all runs. Some quartz (and charcoal) was withdrawn from charge 7-11 in run 4 due to a viscous slag and difficult furnace operation.

The content of the charge was based on assumed slag and metal composition, 35% MnO, 25% SiO_2, and 1.8% Si for the first charge. For charge 2-11 was assumed a slag composition of 20% MnO and 40% SiO_2, while the metal was assumed to increase from 8% Si, to 15% Si, and for charge 4 - 11 it was assumed to stay at about 18% Si. The ratio of slag to metal should be 0.8 for charge 4-11. Even though 0.8 kg quartz was withdrawn from charge 7- 11 in run 4, the metal was assumed to reach 16.8% Si.

3.2 Pilot furnace and furnace operation

The 150 kW single electrode furnace at SINTEF/NTNU is shown in Figure 5 (max 80 V, max 6 kA). The lining is designed with respect to an excavation technique developed by B. Heiland at NTNU/Eramet [15], inspired by a method described by Anda et al. [16]. During excavation the outer lining of silica sand can be easily removed.

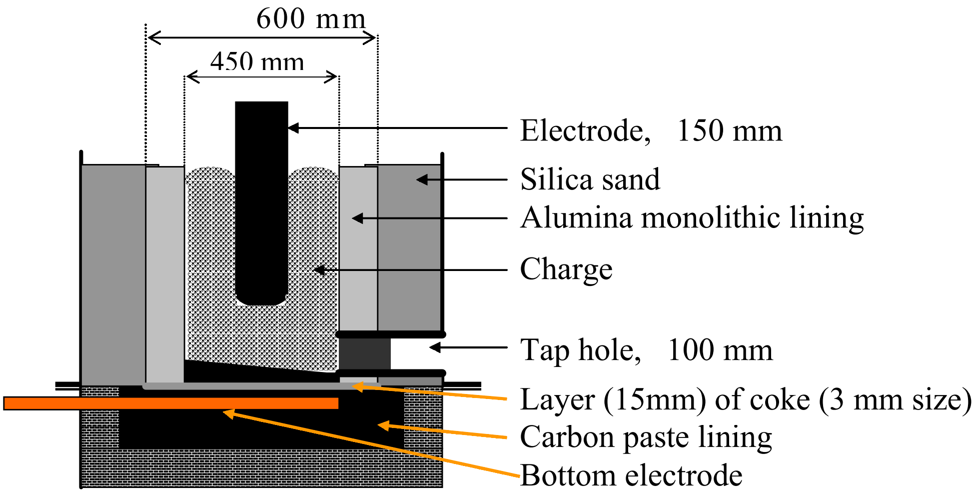


Figure 5. Sketch of pilot scale furnace.

The furnace is filled near to the rim with epoxy (40 l) and after hardening, the electrode can be cut. Because the coke layer in the bottom is serving as a slipping layer, the furnace is taken away in one piece and a cross section plate of the furnace is sawed out for further studies. Samples are cored from the excavation plate for microprobe investigations.

The furnace was preheated for 100 kWh on a coke-bed before charging was started. A load of 150 kW was aimed for once charging started (average load in the range 144-151 kW was obtained in the different runs) and tapping was carried out every 80 kWh (8 taps). The furnace was shut down 50 kWh after the last tap.

The electrode tip was set to 20cm above the bottom in run 1-3. As the electrode position was fixed, changing the voltage controlled the load. In an effort to increase the temperature, and thus increase the % Si in the metal produced, the electrode tip position was lowered to 15 cm in run 4-5. The experimental conditions are presented in Table 4.

Table 4. Furnace operation during stable production (average numbers for tap 4-8).

Run no.	**Electrode tip position**	**Current (kA)**	**Voltage (V)**	**Load (kW)**	**Resistance (m·ohm)**	**Power consumption (kWh/kg metal)**	**%Si in metal (see ch. 3.3)**
1	20 cm	3.9	39	152	10	5.0	18.8
2	20 cm	3.0	50	146	17	4.2	17.3
3	20 cm	2.1	67	138	36	3.5	11.4
4	15 cm	2.1	72	151	36	3.8	13.5
5	15 cm	2.1	71	148	35	3.6	12.9

The resistance in the coke-bed increases when charcoal is used as reductant instead of coke. This increase is believed to be an effect of the charcoal itself and not due to quartz in the coke-bed. Minor amounts of quartz were found on the excavation plate, but not enough to give the high resistance of 36 m·ohm compared to 10-17 m·ohm using coke. This is however a major uncertainty as just a small layer of quartz may stop the current paths completely. Surprisingly the resistance was at the same high level in the last run when a 50-50 mixture of charcoal and coke was used in run 5.

The industrial coke (run 1) and the reactive coke (run 2) did not give a significant difference in the total resistance. However, the resistance was unstable with reactive coke due to quartz in the coke-bed. The quartz was observed on the excavation plate, and could indicate a lower degree of reduction and/or a lower temperature.

Furnace resistance will increase with amount of slag in the furnace, and is not only dependent on reductants. Referring to Table 5, the slag weights are higher in the charcoal experiments (run 3-4), and in run 5. Hence, furnace resistance will also increase because of a higher level of slag in the furnace. In run 4 the power was partly lost after tap 3 (only 80 kW was obtained at maximum voltage) due to a very high resistance in the furnace. The weight of tapped slag was low in tap 3 (only 14 kg, because the slag had not been properly tapped). However, the situation was stabilised and the aimed load obtained from tap 5, after the charge composition had been slightly changed by reducing the amounts of quartz and charcoal.

Table 5. Weights (kg) of slag and metal. (run 5*: some raw materials were tapped along with the slag)

Tap no.	**Run 1**			**Run 2**			**Run 3**			**Run 4**			**Run 5***		
	Slag	**Metal**	**S/M**	**Slag**	**Metal**	**S/M**	**Slag**	**Metal**	**S/M**	**Slag**	**Metal**	**S/M**	**Slag**	**Metal**	**S/M**
1	34	12	2.8	30	13	2.3	28	12	2.4	31	13	2,3	33	12	2.8
2	29	19	1.6	23	20	1.1	23	20	1.2	21	29	0,7	19	26	0.7
3	26	20	1.3	22	18	1.2	22	23	0.9	14	22	0,6	32*	32	1.0
4	19	15	1.2	22	21	1.1	33	26	1.3	24	23	1,0	26*	22	1.2
5	16	19	0.9	17	16	1.1	18	18	1.0	29	18	1,6	16	18	0.9
6	17	18	0.9	20	23	0.9	46	24	1.9	21	20	1,1	34*	23	1.5
7	24	10	2.5	14	18	0.8	32	19	1.7	23	22	1,1	28	21	1.4
8	11	18	0.6	20	17	1.1	23	26	0.9	18	22	0,8	33*	27	1.3
SUM	175	131	1.3	167	147	1.1	225	168	1.34	182	169	1,1	223	180	1.2

As can be seen from Table 4, the average power consumption (averaged for tap 4-8) is the highest when industrial coke is used (5.0 kWh/kg), followed by reactive coke, and charcoal (3.5-3.8 kWh/kg). These differences are mainly reflecting the dissimilar silicon levels of the metal produced in the 5 runs.

3.3 Chemical analysis of metal and slag

The metal and slag analyses are shown in Table 6, Figure 6 and Figure 7. Run 3-5 with charcoal or a 50/50 mixture of coke and charcoal deviate from the coke experiments (run 1-2) with a lower %Si in the metal. The manganese reduction is however higher, which leads to a higher metal production in these runs. With equal amounts of energy supply, the energy will mainly be used for reduction of MnO and/or SiO_2. The more Mn that is reduced, the less energy remains for reduction to Si. The high charcoal reactivity can be the reason why more manganese has been reduced.

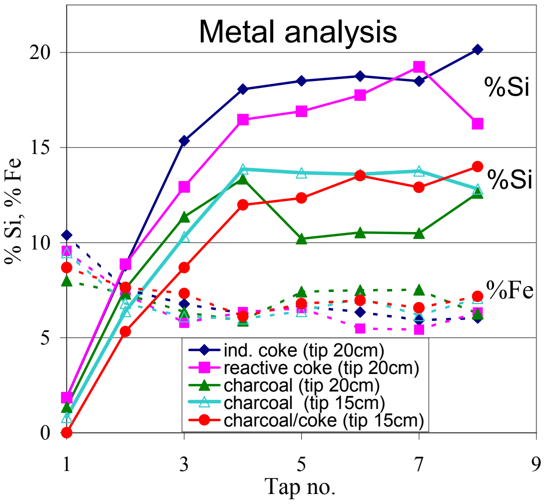


Figure 6. %Si and %Fe in tapped metal.

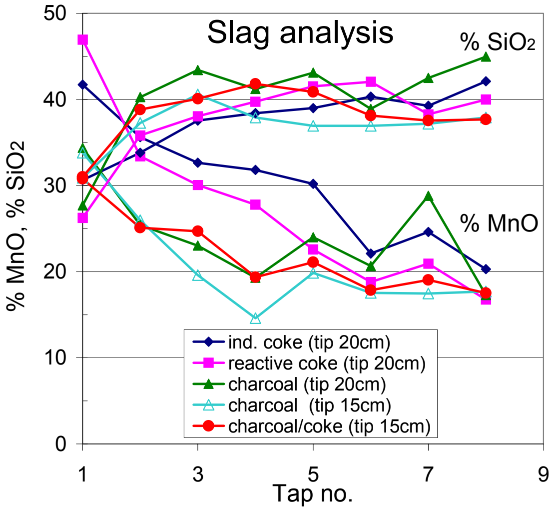


Figure 7. %MnO and $\%SiO_2$ in tapped slag.

Table 6. Metal and slag composition, average analysis of the last taps (tap number 4-8).

Metal	**Run1**	**Run2**	**Run3**	**Run4**	**Run5**
Mn	73,1	74,0	77,6	76,0	76,5
Si	18,8	17,3	11,4	13,5	12,9
Fe	6,3	6,0	6,9	6,5	6,7
C	1,2	1,9	3,3	3,1	3,0
P	0,2	0,2	0,2	0,3	0,4
Ti	0,2	0,3	0,2	0,2	0,2
Sum	99,7	99,7	99,7	99,7	99,7

Slag	**Run 1**	**Run 2**	**Run 3**	**Run 4**	**Run 5**
MnO	25,8	21,4	22,0	17,4	19,0
SiO_2	39,8	40,3	42,1	37,4	39,2
Al_2O_3	17,4	21,2	20,5	29,7	26,3
CaO	8,7	9,8	8,1	8,2	8,2
MgO	3,8	2,6	3,3	3,5	3,5
K_2O	2,2	2,5	2,0	2,1	2.0
BaO	0,9	1,0	0,8	0,8	0.8
Sum	98,7	98,8	98,9	99,1	99.0

Although the silicon level in the metal is on an average 1.5% higher when industrial coke (run 1) is used compared to reactive coke (run 2), the MnO content in the slag is around 4.4% higher as well. The total reduction of both MnO and SiO_2 is of course important.

The results of the two charcoal experiments (run 3-4) indicate that lowering the electrode tip position with 5cm has increased the temperature in the coke-bed. Hence the silicon content in the produced metal increases from 11.4% to 13.5% as an average for tap 4-8. However, the aimed level of 17-18% Si is not reached.

The basicity of the slag is defined by formula (5), being around 0.3 for all runs. The R-value, referring to formula (6), in the raw materials should be equal to the R-value in the tapped slag as MgO, CaO and Al_2O_3 is not reduced, and should therefore ideally be constant, approximately 0.7 in all taps. However, as shown in Figure 8, this is not so. In some experiments the R-value is higher at the first tap. This is probably due to the fact that the HC slag will melt down prior to the Comilog ore.

$$B = (\%MgO + \%CaO) / \%SiO_2 \qquad (5)$$

$$R = (\%\,MgO + \%\,CaO) / \%Al_2O_3 \qquad (6)$$

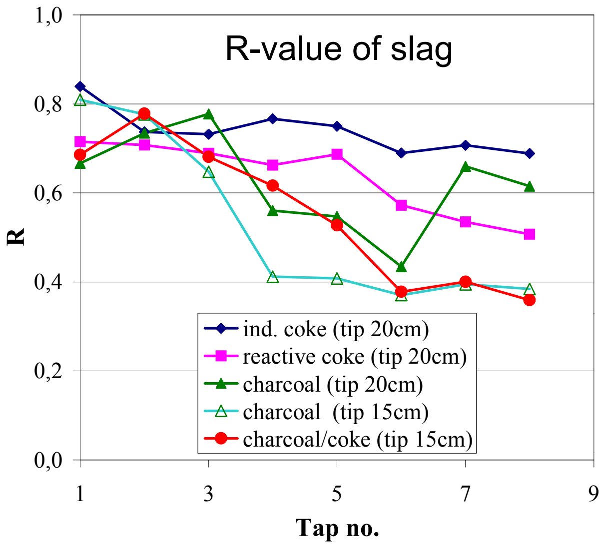


Figure 8. R value of tapped slag.

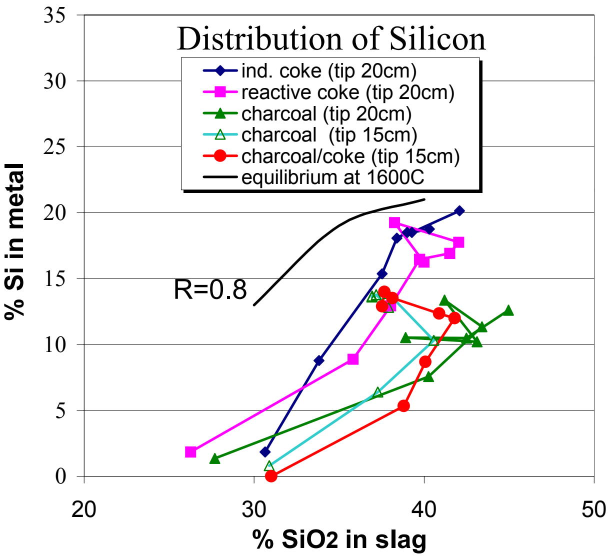


Figure 9. Si-distribution between slag and metal.

Run 4 and 5 with a 5cm lower electrode tip position have R-values far off from the expected, especially towards the end of the experiments. This is clearly a result of a 10% higher Al_2O_3-content in the slag, due to dissolution of the lining. This was observed both from the slag analyses and from the excavation plates. It was also verified by carrying out a material balance for run 4, finding that 13-16 kg of alumina lining has been dissolved in the slag. A higher temperature close to the lining at a 5cm lower electrode position can be the reason for alumina contents reaching 30% towards the end of these two runs. Provided a reduction to 20% MnO and 40% SiO_2 the Al_2O_3-content should be 20%.

In Figure 9 we see how silicon is distributed between the metal and the slag, compared to equilibrium at 1600 °C. At equally high content of SiO_2 in the slag, run 1 with industrial coke has the highest %Si in the metal, followed by reactive coke in run 2. For equal electrode tip position of 20 cm, the industrial coke run has probably the highest temperature in the reduction zone, followed by the reactive coke and the charcoal. However, by lowering the electrode tip position by 5 cm in run 4 and 5, the temperature in the reduction zone seem to increase nearly to about the same level as the industrial coke. This can also be due to a lower R-value, but a higher temperature is logical due to the observed increased wearing/dissolution of the lining. If more quartz had been added towards the end of run 4 and 5 the silicon content in the metal may have increased.

3.4 Excavation

A short description of the special excavation technique used was given in section 3.2. A photo of the excavation plate from run 4 is shown in Figure 10 as an example. Figure 11 shows the different zones which this plate can be divided into, together with the position of the 18 samples cored out from the plate and prepared for further studies.

A pure black glassy slag layer (6cm thick) is found at the bottom (only observed in this run). Above is a “coke”-bed filled with green slag, the charcoal has probably floated up towards the end of the run because the charge-pressure was too low. Above we find a coke-bed with some metal and slag, reaching up on the electrode (probably higher up than during the run because the charcoal has floated up afterwards). The metal is found at the bottom in the previous carbon lining and has about the same composition as the last tap (76% Mn, 13% Si, 7% Fe, and 3% C).

In run 5 we kept on charging after the run was stopped to ensure that the charge-pressure was maintained during cooling, preventing particles to float up. The excavation plates from run 4 and 5 look rather similar, and current paths are easily observed. We find a few small islands of melted quarts in the coke-bed filled with slag, which will increase the furnace resistance. The shape of the coke-bed is equal, but it does not reach high up on the electrode in run 5.

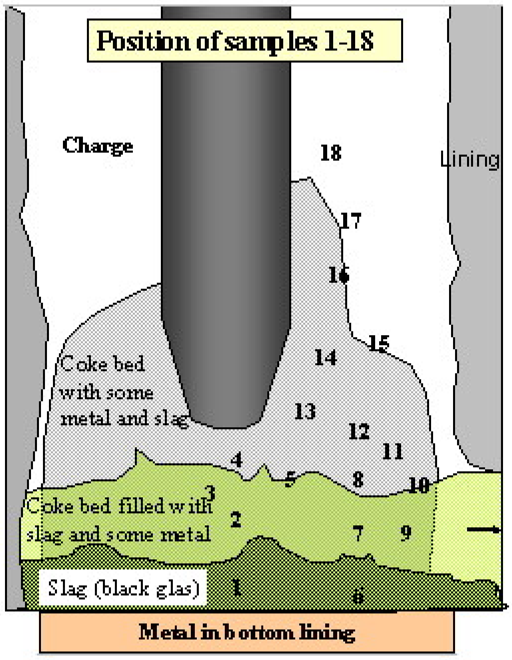


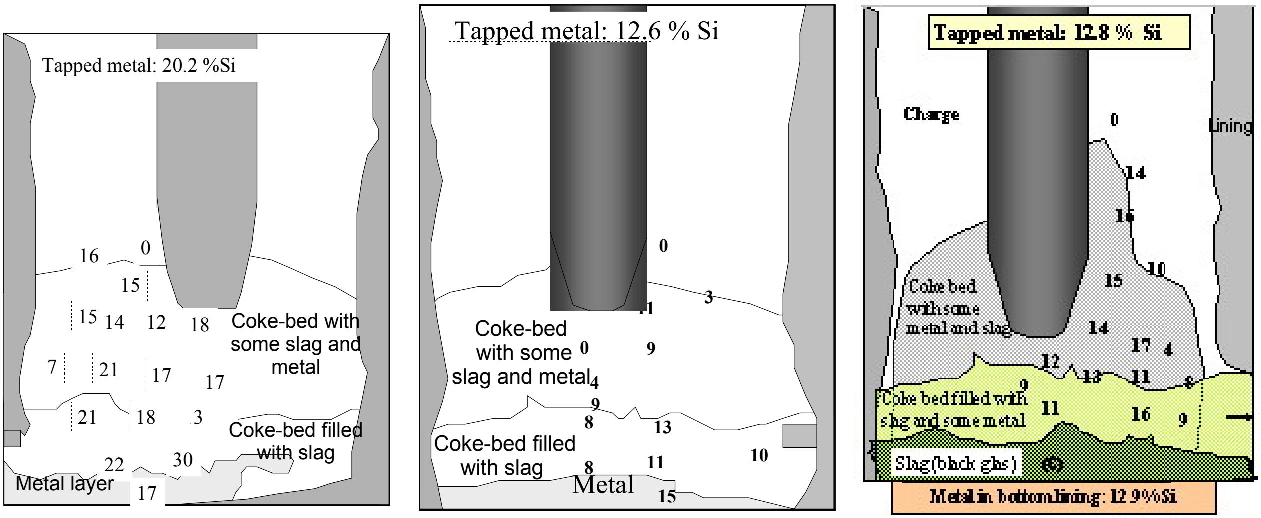
Figure 10. Excavation plate from run 4 (charcoal).

Figure 11. Furnace zones and samples, run 4.

By measuring the electrode length before and after the runs we find that 2cm of the electrode were consumed in run 4 and 5. It is reasonable to believe that the electrode consumption has been the same in previous runs too. Another similar observation in these two runs is that the upper part of the bottom lining (4-5cm) has been consumed, including the carbon paste and the slipping layer of coke. Hence, the electrode tip position has changed and is exceeding the initial set distance towards the end of the runs.

The size and type of zones found was very similar in run 1-3. The coke-bed is very wide, as illustrated in Figure 12, as more coke was charged in these experiments. Metal is found at the bottom, above this a coke-bed filled with slag and above this again a coke-bed with some slag and metal. The size of the coke-bed should therefore give close to the same energy development in the coke-bed when no quartz is present.

The excavation plate from the industrial coke experiment (run 1) shows that an electrode breakage has occurred. The only experiment with single quartz particles observed in the coke-bed was in run 3 with charcoal. This verifies the lower temperature and the lower %Si in the metal produced in this experiment.

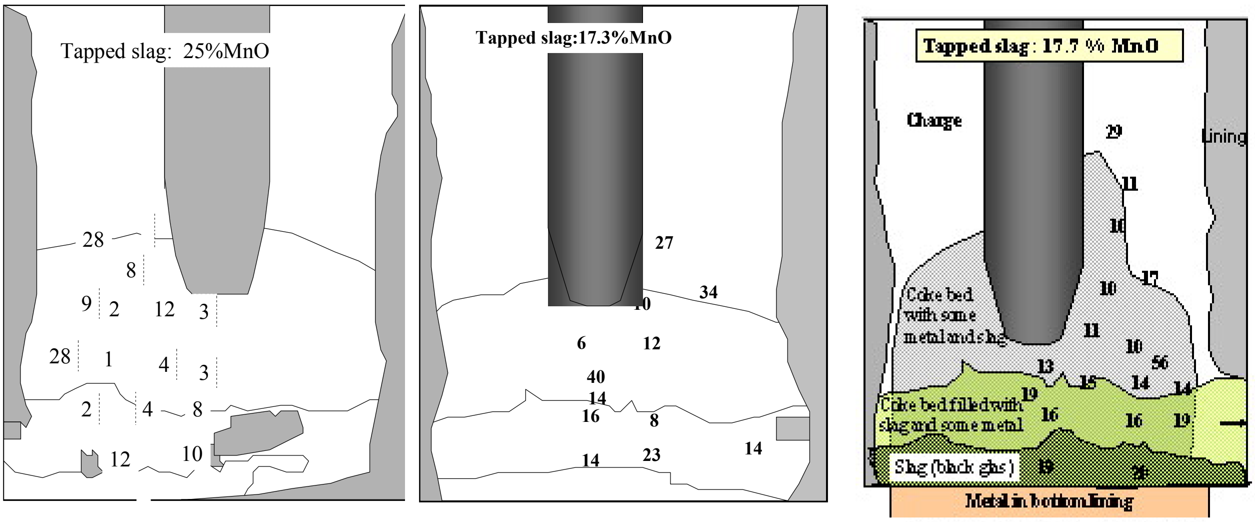


Run 1: industrial coke – tip 20 cm

Run 3: charcoal – tip 20 cm

Run 4: charcoal – tip 15 cm

Figure 12. Degree of reduction inside the furnace expressed by % silicon in metal.



Run 1: industrial coke – tip 20 cm

Run 3: charcoal – tip 20 cm

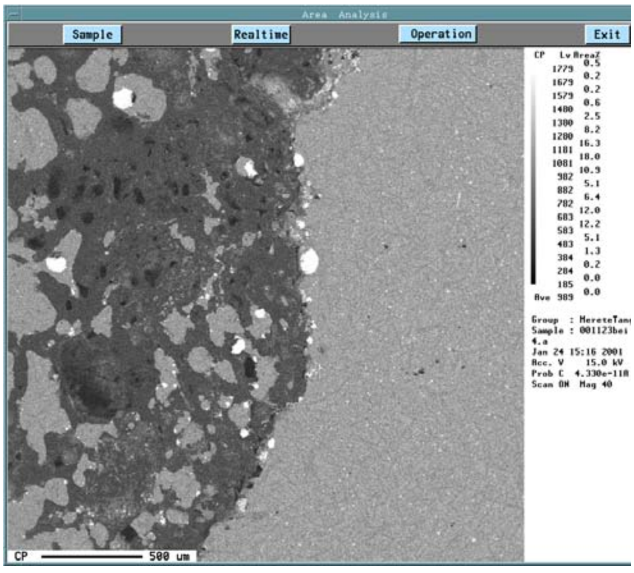
Run 4: charcoal – tip 15 cm

Figure 13. Degree of reduction inside the furnace expressed by % MnO in slag.

The excavation plate from the reactive coke experiment (run 2) showed the presence of a small quartz-bed, in between the metal layer and the coke-bed filled with slag, centred below the electrode. Below this quartz-bed some pure slag is also seen. Both the quartz-bed and the pure slag layer will increase the resistance significantly. When the quartz-bed is present it would force the current paths outward, giving a higher temperature close to the lining, and the probability for dissolving the lining increases. This could be the reason for a somewhat lower %Si in the last tap.

The degree of reduction inside the furnace, expressed by %Si in the metal and %MnO in the slag, is also shown in Figure 12 and Figure 13 for 3 selected experiments. These are microprobe analyses of the 18 samples cored out from the excavation plates. The aim is to find trends, which can tell something about the reaction mechanism.

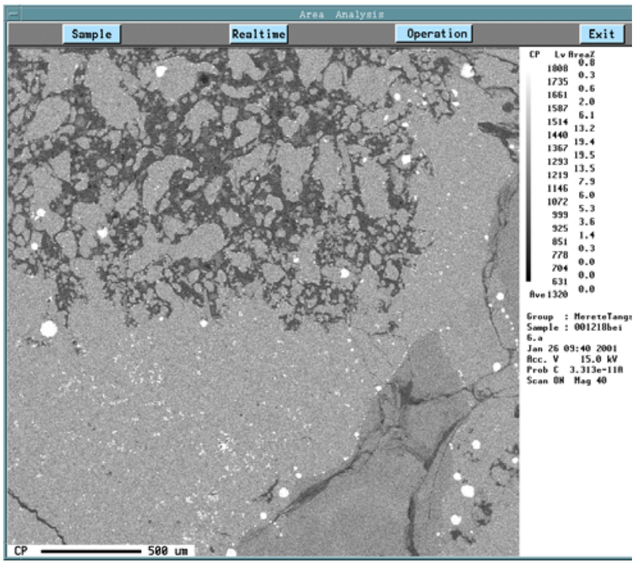
Most of the reduction occurs almost immediately as the charge melts down. Generally, there is reasonable good agreement between analyses of tapped metal and slag and the microprobe analyses from inside the furnace. The metal droplets inside the furnace contain less silicon in the charcoal experiments than in the industrial coke experiment. However, in the industrial coke experiment there is a big reduction zone (%MnO < 10), also seen in previous experiments [17][18], and the excavation plate has a higher degree of reduction compared to the tapped slag and metal.



```
CP   Lv AreaZ
          0.5
   1779   0.2
   1679   0.2
   1579   0.6
   1480   2.5
   1300   8.2
   1200  16.3
   1181  18.0
   1081  10.9
    982   5.1
    882   6.4
    782  12.0
    683  12.2
    583   5.1
    483   1.3
    384   0.2
    284   0.0
    185   0.0
Ave 989   0.0

Group  : MereteTan
Sample : 001123bei
4.a
Jan 24 15:16 2001
Acc. V     15.0 kV
Prob C  4.330e-11A
Scan ON  Mag 40
```

Figure 14. Microprobe sample, showing industrial coke, slag, and metal droplets



```
CP   Lv AreaZ
          0.8
   1808   0.3
   1735   0.6
   1661   2.0
   1587   6.1
   1514  13.2
   1440  19.4
   1367  19.5
   1293  13.5
   1219   7.9
   1146   6.0
   1072   5.3
    999   3.6
    925   1.4
    851   0.3
    778   0.0
    704   0.0
    631   0.0
Ave1320   0.0

Group  : MereteTang
Sample : 001218bei
6.a
Jan 26 09:40 2001
Acc. V     15.0 kV
Prob C  3.313e-11A
Scan ON  Mag 40
```

Figure 15. Microprobe sample, showing reactive coke, slag, and metal droplets.

Microprobe photos of the industrial coke and the reactive coke are shown in Figure 14 and Figure 15. These are typical observations showing the intimate contact between slag and coke, with slag penetrated into the pores of the coke, most pronounced for reactive coke. Metal droplets are often found on the slag/reductants interface.

Figure 16 shows a microprobe photo of sample 2 cored out from the zone “coke-bed filled with slag” on the excavation plate from run 3. The observed charcoal particle is in intimate contact with the slag, and some of the pores are also filled with slag. Slag inside charcoal pores is not often observed in these experiments, and a more typical observation is shown in Figure 17. The photo is from the analogous zone in run 4, showing no slag inside the charcoal pores.

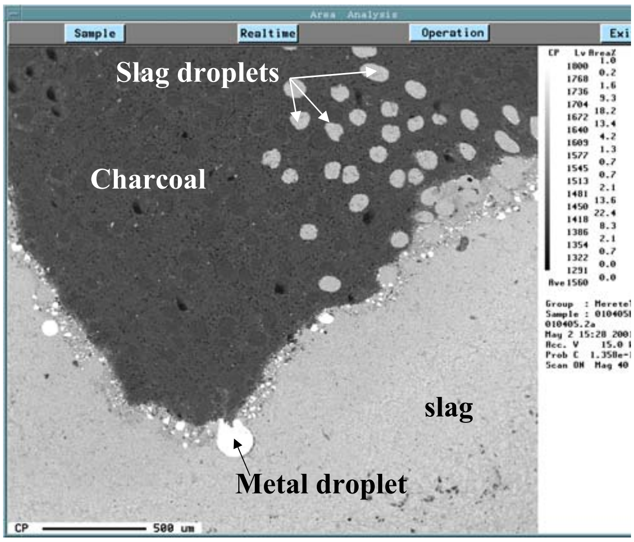


Figure 16. Microprobe sample from run 3 (s2): Charcoal particle, slag, metal droplets.

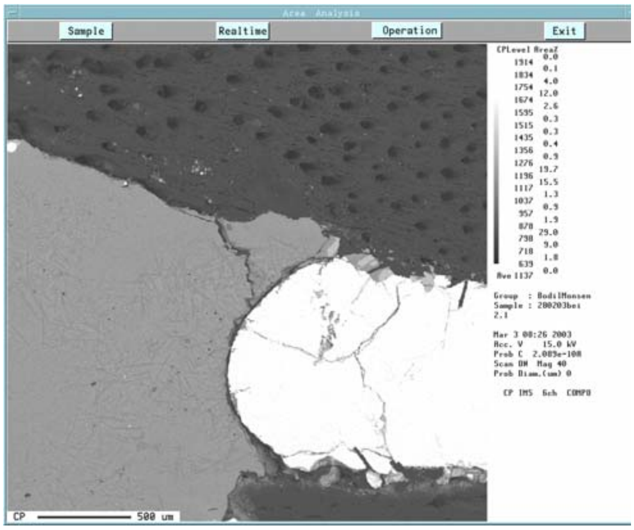


Figure 17. Microprobe sample from run 4 (s2): Charcoal particle, slag and metal.

These observations are somewhat surprising. We would expect slag intrusion in the pores of all these reductants, especial in a highly porous material as charcoal. However, charcoal may have a high degree of closed pores or micro-pores, and be less reactive to slag of this reason. But if the slag has been less fluid in the charcoal experiments due to a lower temperature, slag intrusion will be more difficult.

It must be added that the thermo-weight experiments with slag/charcoal and slag/coke at 1600 °C [10] showed that the charcoal and coke slag-reactivity are equally good at this temperature. The SiMn metal produced contained approximately 20% silicon in all experiments. The rate of reaction was equal too, if the reductants had been pre-calcinated at 1600 °C prior to the experiments. However, the rate of weight loss was faster for coke if a lower pre- calcinating temperature (1200 °C) was used, mainly due to ash reactions in the coke. Veena Sahajwalla [20] claims that the ash enhances carbon reactivity and slag wetting, and that slag wetting is dependant on the carbon material at 1500°C, but nearly independent at 1600-1700°C.

4. CONCLUSIONS

The results of the presented 5 pilot scale experiments with production of SiMn have shown that charcoal gives a higher metal production than coke, but also the lowest silicon content in the metal. With equal amounts of energy supply, the energy will mainly be used for reduction of MnO and/or SiO_2. The more manganese that is reduced, the less energy remains for reduction to silicon. The high charcoal reactivity can be the reason why more manganese has been reduced.

Reactive coke is in-between the charcoal and industrial coke both in metal production and %Si in the metal. Industrial coke will have the lowest metal production, but with the highest silicon content in the metal. The charcoal gave a significant difference, while the difference between the reactive coke and the industrial coke is small.

However, the reaction mechanism is not fully understood. Interpretation of the pilot experiments is difficult, and there might be an important parameter so far overseen. We know for a fact that Brazil has long experiences in using charcoal in the production of ferroalloys, and that charge mixes with 50-80% charcoal on a fixed carbon basis are used for SiMn production in relatively large furnaces.

The charcoal increased the total resistance in the coke-bed and gave the highest slag production. The low silicon content in the produced metal indicates a lower temperature in the reduction zone. We might expect slag intrusion in the pores of all reductants, especial in a highly porous material as charcoal. However, slag in charcoal pores is rarely seen while there is an intimate contact between slag and coke, with slag frequently penetrated into the pores.

Other experiments have shown that the charcoal - slag and coke – slag reactivity at 1600°C are equally good, and the metal produced contained around 20% silicon for both reductants.

5. ACKNOWLEDGEMENTS

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