CHARCOAL FOR MANGANESE ALLOY PRODUCTION

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ABSTRACT

Charcoal is an interesting reducing agent because it is produced from growing wood which is renewable and does not contribute to global warming, provided that there is a balance between the felling of timber and growth of trees. In the biocarbon project the possibilities for using charcoal is investigated as well as other biological based and renewable reductants for ferroalloy production. The background for the project is that the Norwegian ferroalloy producers wish to contribute to reduction of CO_2- emissions.

This paper focuses on the use of charcoal instead of coke for the production of manganese alloys, and the consequences of doing so. Results from practical SiMn smelting experiments on a pilot scale have previously been reported, where only 12-14 % Si in the metal was obtained when charcoal was used. Recently we have attained satisfactory 18 %Si also for charcoal, but good results are indeed dependant on good furnace performance.

There is no tradition for using charcoal for manganese production in Norway. A change from using mainly coke to the use of some charcoal will demand new routines for furnace operation, raw material and off-gas handling. Hence, characteristic properties of charcoal, which may cause change of furnace operation, have been measured and are compared to coke. The following results are presented:

- *Thermal abrasion strength together with CO_2- reactivity; important parameters for the performance of the upper part of the furnace.*
- *Coke-bed resistance; it will increase with the use of charcoal (a review of new results).*
- *Slag reactivity; a relevant method for testing slag reactivity of industrial reductants is of interest. The suggested method can serve for comparing slag reactivities towards graphite.*

1. INTRODUCTION

The Norwegian production of ferroalloys is well above one million tonnes per year and includes FeMn, SiMn, silicon (Si) and ferrosilicon (FeSi). The established Norwegian producers are ERAMET Norway, Tinfos Jernverk A/S, Elkem AS, Fesil ASA, and Finnfjord AS. In 2003 CVRD also started production of manganese alloys at Mo (RDMN).

The production of ferroalloys and silicon metal in Norway are modern, energy intensive activities where efficient large electric submerged –arc furnaces give high yields and facilitate low energy consumptions. While the production of the slag-bearing processes FeMn and SiMn is carried out in closed covered furnaces, the production of FeSi and Si is carried out in semi-covered furnaces. Some of the smelting plants have installed electrical energy recovery from the off-gas while others utilize some of the excess heat in the off-gas for other purposes. The electric power supply is based on hydropower, which has very low CO_2 emissions.

The Norwegian ferroalloy industry has joined forces in the Norwegian Ferroalloy Producers Research Organization (FFF). Since its foundation in 1989, FFF has funded R&D projects worth ~ 130 MNOK (including contribution from The Research Council of Norway). In 1997 FFF launched a 5- year long biocarbon research project, succeeded by two 3-year long biocarbon projects, the last for the period 2005-7. Central participants in the biocarbon project are SINTEF and NTNU together with the industry representatives. The main objective is to reduce CO_2 emissions by substituting a part of the fossil reductant with biocarbon. Important sub-goals are to identify consequences of and reduce costs connected to increased use of charcoal, and optimize or develop charcoal processes with high carbon yield and/or high purity. Biocarbon is biological based renewable materials, and examples are wood chips and charcoal. Since charcoal is produced from growing wood it does not contribute to global warming, provided that there is a balance between the felling of timber and growth of trees. The reason is well known, growing plants utilize CO_2 in the photosynthesis during daytime and convert CO_2, sun energy and water into polysaccharide while oxygen is released.

At present the Norwegian ferroalloy industry is responsible for about 3 million tonnes of CO_2-emissions [1] which come from fossil carbon, mainly coal and coke used as reductant in the smelting processes. The SiMn industry in Norway uses mainly coke as reductant and has no tradition for the use of charcoal. At the moment we do not believe that there are process benefits by using charcoal. However, in the production of Si and FeSi charcoal and wood chips are used to a small extent because of possibilities for process improvements [2][3]. South America and Asia have been the main charcoal suppliers as charcoal is not produced in Norway

2.   PROPERTIES OF REDUCTANTS FOR SIMN AND FEMN PRODUCTION

Typical chemical analyses and selected properties of reducing agents for SiMn/FeMn production are compared in Table 1. The selected properties are of special importance for manganese alloy production and have of this reason been measured at SINTEF/NTNU, using appropriate equipment designed/built during the last 5 years. Detailed descriptions of these measurements are presented in the following sub- chapters. There are major differences between charcoal and the most common metallurgical type of cokes used today. Usually charcoal has a lower fixed carbon content and much higher content of volatile matters, while ash is rather low with composition strongly dependant on soil and use of fertilisers. Charcoal volume weight is low. Compared to coke industrial charcoal has higher CO_2- reactivity, lower thermal abrasive strength and higher electrical resistivity, which is decreasing with increasing temperature. Other possible reductants have been included in Table 1 for comparison, where some relevant properties have been measured.

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

	Industrial charcoal	Metallurgical Coke	Charcoal from preserved pine	Petrol coke
Fixed carbon (%)	65 – 85 (94)	86-88	93.8	84-90
Volatile matter (%)	15-35 (4)	=1	3.8	9-16
Ashes (%)	0.4-4	10-12	2.4	<1
Ash composition (% of ash):				
SiO_2	5-25	25-55	23	
Fe_2O_3	1-13	5-45	5	
Al_2O_3	2-12	13-30	5	
P_2O_5	4-12	0.4-0.8	-	
CaO	20-60	3-6	11	

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

	Industrial charcoal	Metallurgical Coke	Charcoal from preserved pine	Petrol coke
MgO	5-12	1-5	-	
K_2O	7-35	1-4	-	
Volume weight on dry basis (kg/m^3)	180 -350	500-550		450-800
CO_2-reactivity at 1060ºC (%C/s)	$(2.1 - 2.3) \cdot 10^{-2}$	$(0.2 - 0.50) \cdot 10^{-2}$	$(2.8 - 3.2) \cdot 10^{-2}$	-
Thermal cohesion strength: C.I (%)	74 - 84	93 – 97	93 - 95	-
Thermal abrasion strength: T.I.3 (%)	78 – 82	82 - 89	84	-
Electrical resistance (Ùm) at 1000ºC at 1400ºC	5-35 mm 0.014 - 0.023 0.009 – 0.018	10-20 mm 0.003 – 0.008 0.003 – 0.009	- - -	10-20 mm 0.012 - 0.035 0.007 - 0.021

2.1 CO_2- reactivity

NTNU/SINTEF has developed a special CO_2-reactivity test relevant for manganese alloy production in close cooperation with Eramet and Tinfos. This CO_2-reactivity test can be combined with other measurements after the test, i.e. cohesion strength (C.I.) and thermal abrasive strength (T.I.3), described in the following section.

A highly reactive material will have a high reactivity number, reflecting a high rate of the Boudouard reaction (1).

$$CO_2 + C = 2CO \tag{1}$$

A high rate of this endothermic reaction is undesirable in manganese alloy production according to energy consideration [4], because it will increase both coke and power consumption in the upper part of the furnace. An existing standard ASTM test measures carbon reacting with 100 % CO_2 at 1100°C [5]. Other versions of the NTNU/SINTEF CO_2-reactivity test are carried out in an atmosphere of 75% CO and 25% CO_2 or 50% CO and 50% CO_2, at 1000 ºC or 1100 ºC, described and discussed elsewhere [6][7][8][9].

In the industrial manganese processes the CO_2 concentration range from 0 – 50%, and the temperature increases quickly from the top of the charge towards the metal at the bottom. The CO_2-reactivity test should be carried out in an atmosphere relevant to furnace atmosphere in the upper part of the furnace. We have chosen a composition of 50% CO_2 and 50% CO and a temperature close to 1100 ºC for the present CO_2-reactivity test. The sample amount (60-100 g) is large enough to be sufficient for further tests afterwards. The chosen amounts take up the crucible room. The crucible is made of stainless steel. For the further tests, it is of utmost importance to stop the reaction after a certain amount of solid carbon has reacted, because the abrasion strength decreases with the extent of reaction, and a weight loss corresponding to 20% of the fixed carbon was chosen. The required weight loss is calculated from proximate analysis (volatiles, ash and fixed carbon). The reaction is stopped by purging with inert gas and withdrawal of the sample crucible from the furnace. The thermo-weight and experimental set-up are shown in Figure 1.

From the slope of the curve for the recorded weight measurements during oxidation with CO_2, the fraction of reacted fixed carbon per time is calculated, and an example is shown in Figure 2:. The slope is defined as the CO_2-reactivity. It can be seen that the temperature drops once the endothermic Boudouard reaction starts, starting temperature is close to 1175ºC while stop temperature is close to 1050 ºC. The test temperature is calculated as the average temperature during the period where the slope of the weight measurements is constant.

Figure 3: shows a comparison of different carbon materials at 1060 ºC. An adjusted CO_2-reactivity has been calculated based on a theoretical reaction mechanism [6] in order to determine the reactivity at 1060 ºC. It is seen that the CO_2-reactivity for the Brazilian charcoal made from eucalyptus (BE-1, BE-2, BE-3: 3 parallels) is 4-12 times higher than the 3 different metallurgical cokes, while the CO_2-reactivity of charcoal made from preserved wood is somewhat higher than for the industrial charcoal. There is also a span in reactivity for the cokes, Corus coke being less reactive.

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. Al-

Figure 1: Thermoweight for measurement of CO_2-reactivity

kalis are known to accumulate and re-circulate in the furnace, and may condense on the coke in the upper parts. Potassium speeds up the Boudouard reaction several times [6][7][8][9] and remove some of the differences between CO_2-reactivities for charcoal and coke.
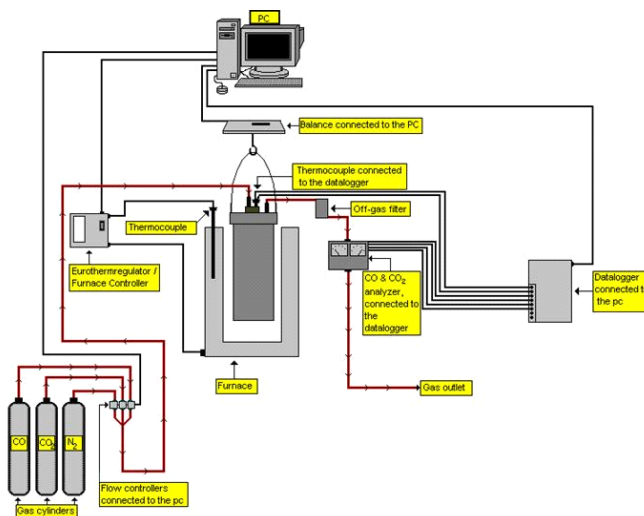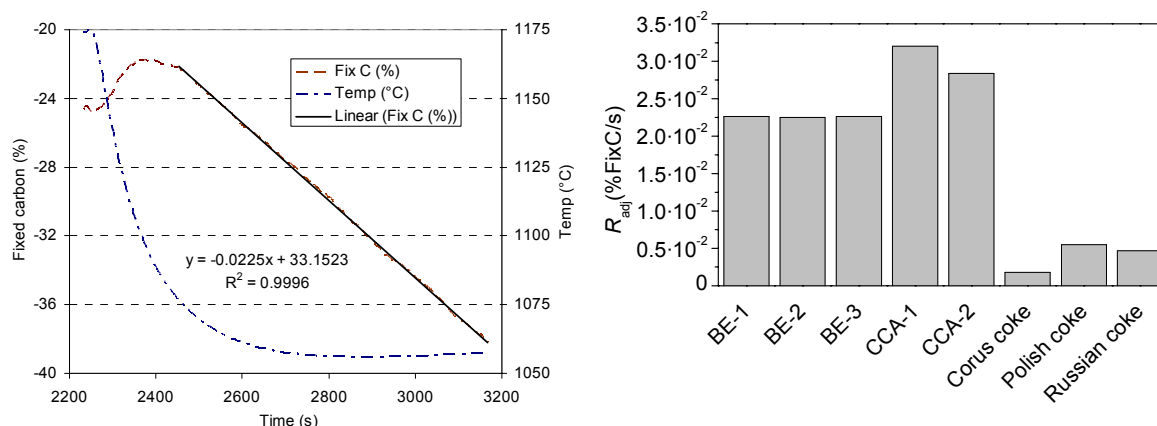

Figure 2: CO_2-reactivity at 1060 ℃ of Brazilian charcoal

Figure 3: CO2-reactivity at 1060 ℃ of industrial charcoals, charcoal from preserved wood and metallurgical cokes

2.2 Thermal abrasion strength

The abrasion strength is tested on partly reacted materials which have been oxidized according to the Boudouard reaction at about 1100°C and with an atmosphere consisting of 50% CO and 50% CO_2, as described in the previous section. The strength is measured independently of the CO_2 reactivity, since around 20% of the fixed carbon is reacted for all samples.

The abrasion test is done on partly reacted material by analyzing the size distribution of the carbon materials before and after tumbling for 30 minutes in a Hannover drum at 40 rpm. The drum diameter is 200 mm, the depth is100 mm, and there are 4 baffles with height 16 mm and thickness 6 mm. The cohesion index (C.I) tells about the ability of the material to maintain its strength (cohesion) after reaction with the furnace gas, and its ability to withstand generation of fines.The thermal stability index (T.I.3) is measured after tumbling

and tells something about the material ability to resist abrasion toward other particles under charge pressure. A high number is preferred for both indices.

C.I. =   Cohesion Index; the fraction larger than 4.75 mm before tumbling

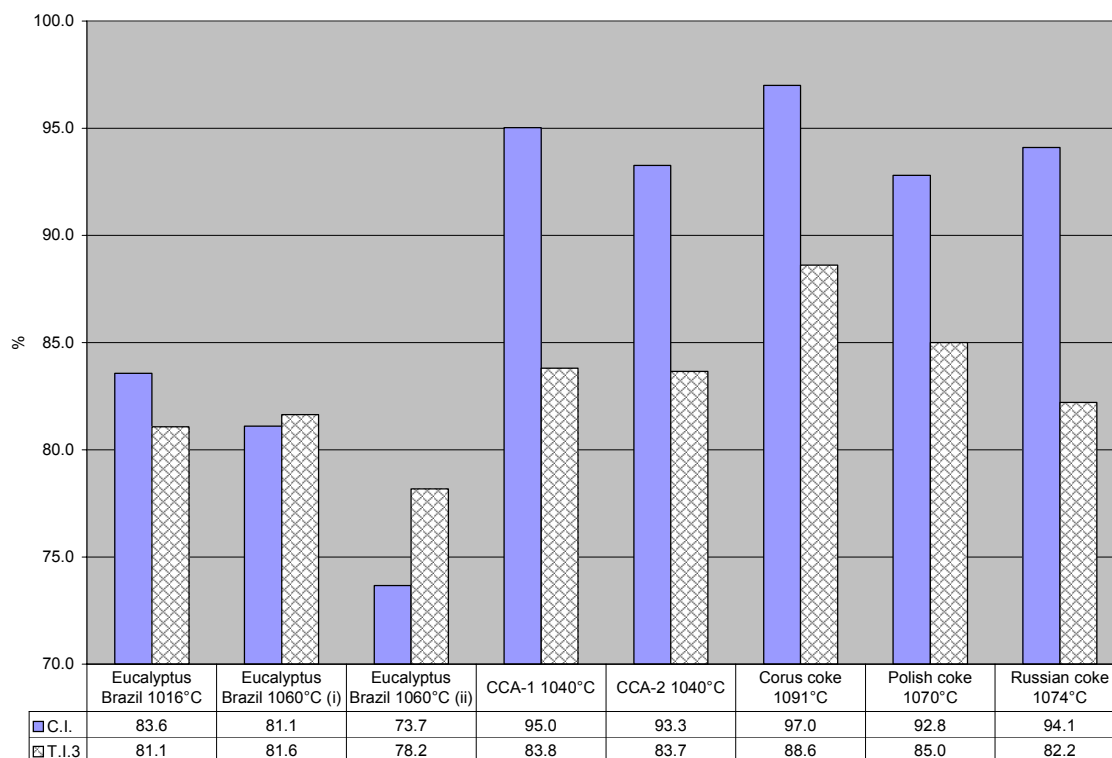T.I.3 = Thermal stability index; the fraction larger than 3.33 mm after tumbling.

	Eucalyptus Brazil 1016°C	Eucalyptus Brazil 1060°C (i)	Eucalyptus Brazil 1060°C (ii)	CCA-1 1040°C	CCA-2 1040°C	Corus coke 1091°C	Polish coke 1070°C	Russian coke 1074°C
C.I.	83.6	81.1	73.7	95.0	93.3	97.0	92.8	94.1
T.I.3	81.1	81.6	78.2	83.8	83.7	88.6	85.0	82.2

Figure 4: Abrasion strength (C.I. and T.I.3) for Brazilian charcoal and charcoal from preserved wood compared to different metallurgical cokes. C.I = fraction larger than 4.75 mm before tumbling, T.I.3 = fraction larger than 3.33 mm after tumbling

From Figure 4: it can be seen that the cohesion index of the industrial charcoals from Brazil are in the range 74-84%, which is lower than the cohesion index for the metallurgical cokes, being in the range 93-97%. The charcoal made from preserved wood have as high cohesion strength as the cokes.

However, regarding the thermal stability based on T.I.3 there are only minor differences between charcoal and coke.

2.3 Electrical resistivity

The electrical resistivity of the coke bed is of utmost importance for the operation of the submerged arc furnace in the production of manganese alloys. Typical position of this coke bed is below and around the electrode tip, as for example shown in Figure 18:. In addition to the carbonaceous particles, the coke bed contains slag and metal droplets, and furnace gas is flowing up through it. However, the present work focuses on measurements of electrical resistivity of dry coke beds.

A reliably method has been developed which is suitable for measuring industrial sized reductants at elevated temperatures, up to 1600 ºC and at current densities present in an industrial coke bed [10][11][12]. A sketch of the apparatus is shown in Figure 5:, consisting of a high-alumina refractory cylinder built around a 30 cm

standard graphite electrode. The layer of Kao-Wool reduces heat losses and minimizes temperature gradients inside the coke bed. Water-cooled copper bus bars connect the power supply to the top and bottom graphite electrodes. To ensure optimal contact, weights were placed at the top to increase the load. The temperature was measured by thermocouples entering through the top electrode at the positions indicated. The 4-electrode-principle was used, and the voltage drop was measured by molybdenum wires. The current was delivered by two series couples AC arc welding transformers and the current density was kept in the range 7.4-14.1 kA/m^2. Particle sizes were kept below 10% of the diameter of the alumina tube to reduce wall effects. The coke bed was heated until one of the thermocouples showed 1600ºC. This temperature is the limit due to furnace lining.
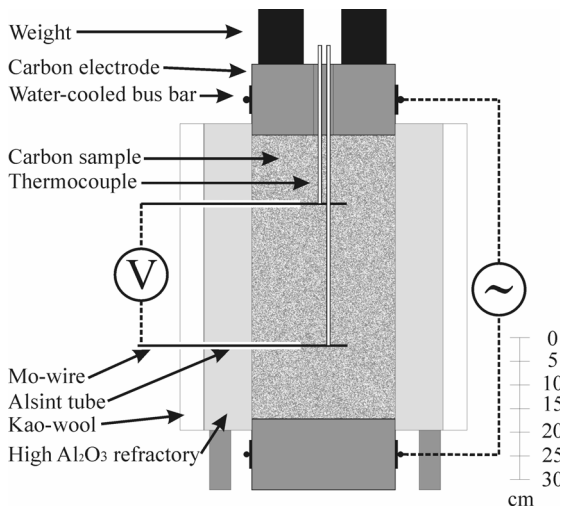

Figure 5: Apparatus for measurement of bulk electrical resistivity [10]

Figure 6: Electrical resistivity of charcoal (different grain sizes) at high temperature [10]

The resistivity is calculated from the simplified equation shown in equation (2) where ρ is the resistivity (Ωm), U is the cell voltage (V), I is the current (A), A is the area of the cross section (m^2) where measurements were made, and h is the height (m) between the measuring points.

$$\rho = (U \cdot A)/(I \cdot h) \qquad (2)$$

The charcoal was heat treated prior to the measurements at 850ºC for one hour in a tight container without oxygen access. Due to the high content of volatiles in charcoal the untreated materials has a high resistivity, too high to carry current through the packed bed at room temperature.

Figure 6: shows that the electrical resistivity decreases with increasing temperature and increasing particle size for the industrial charcoals from Brazil and Indonesia. This is also the general trend for all carbonaceous materials measured.

Figure 7: Comparison of electrical resistivity of different carbon materials

The results for charcoal are compared to metallurgical coke and petrol coke on a general basis in Figure 7: The petrol cokes had also to be heat treated prior to the measurements, and have the highest electrical resistivity at all temperatures. The resistivity of charcoals is 2-8 times higher than that of metallurgical coke in
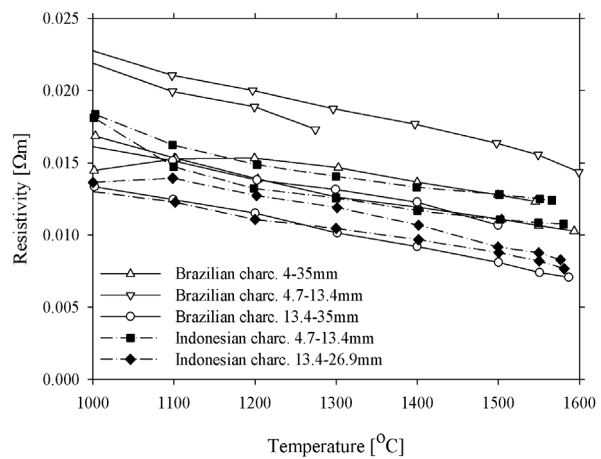
the temperature range 1000-1300 ºC, while at higher temperatures the electrical resistivities can be similar or up to 2-3 times as high.

3.   SLAG-REACTIVITY

The reactivity of different slags towards different reductants is of industrial interest if a simple test could give reliable and quick answers. In the thermo-gravimetrical method at 1600°C (CO atmosphere) used by I. Solheim[7][13] the crucible was made of selected large pieces of the reductant to be tested. A synthetic slag was made and filled to the rim into the crucibles. The results showed that charcoal and coke slag reactivity was equally good and thermodynamic equilibrium was achieved within 1 hour with 20% Si in the metal produced in all experiments. The rate of reaction was equal too, if the reductants had been calcined at 1600 °C prior to the experiments. However, this method is not suitable for testing industrial reductants, because of the difficulties with getting large enough pieces of the reductants for making crucibles. Besides, there is the question of representative samples regarding the huge differences in particle size for the crucible and the size fraction to be tested.

In order to develop a simple test method for different reductants and slags with relevance for the production of FeMn and SiMn, the reduction of MnO and SiO_2 was investigated in a graphite crucible in an induction furnace. The two most important slag-reactions are shown in formulas (3, 4).

$$(SiO_2)_{slag} + 2C = Si_{metal} + 2CO_{(g)} \qquad (3)$$

$$(MnO)_{slag} + C = Mn_{metal} + CO_{(g)} \qquad (4)$$

The experimental set-up is shown in Figure 8:. The crucible cover reduces heat losses and let evolved gas escape through holes, but is also designed to keep the reductant below the slag surface and prevent it to float at the top. Both synthetic slag (S) and industrial HC slag (I) have been tested in different experimental series, and reductants have been charcoal, metallurgical coke, anthracite, and petrol coke. Reference experiments without the use of reductant were also carried out. The experimental procedure is described in detail by Figure 9:. The figure shows the temperature during an experiment for I3 which is the third of six experiments in the series with industrial HC slag, using the same crucible and cover each time. The first and last experiments in this series are reference experiments with no reductant added, while 160 g fixed carbon from reductants are added in the raw material mixture in the experiments I2 – I 5. As for the rest, the raw material mixture in each of these experiments consisted of:

- HC slag (1400 g) containing 34.2% MnO and 23.1% SiO_2

- Quartz (400 g) in order to increase the SiO_2 content to 41.7% (before the reduction begins)

- Iron (43 g) in order to produce SiMn metal with around 10% Fe.

The results from the experimental series with industrial HC slag are presented in Table 2: and Figure 10:. The reduction rate is nearly identical for the reference experiments and the other experiments with reductants. The graphite consumption from the crucible and cover is in the range (300-440) gram in each experiment. The calculated amount of fixed carbon necessary to perform the reduction is only 160 g. Although some of the graphite consumption is due to combustion with air on the outside, it is rather obvious that part of this high loss is due to the reduction with slag. The method may be used for testing different slags towards graphite, but not for testing the performance of different reductants.
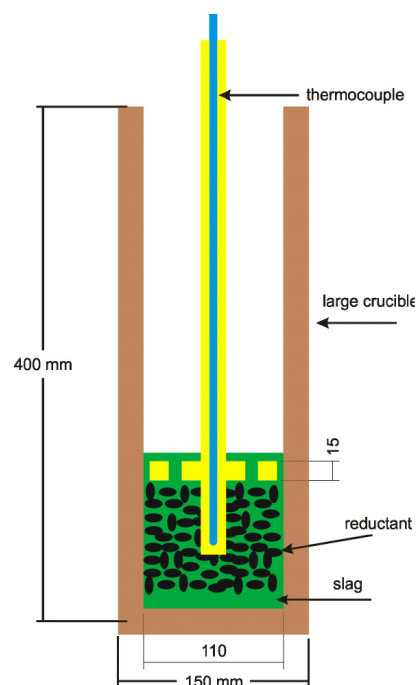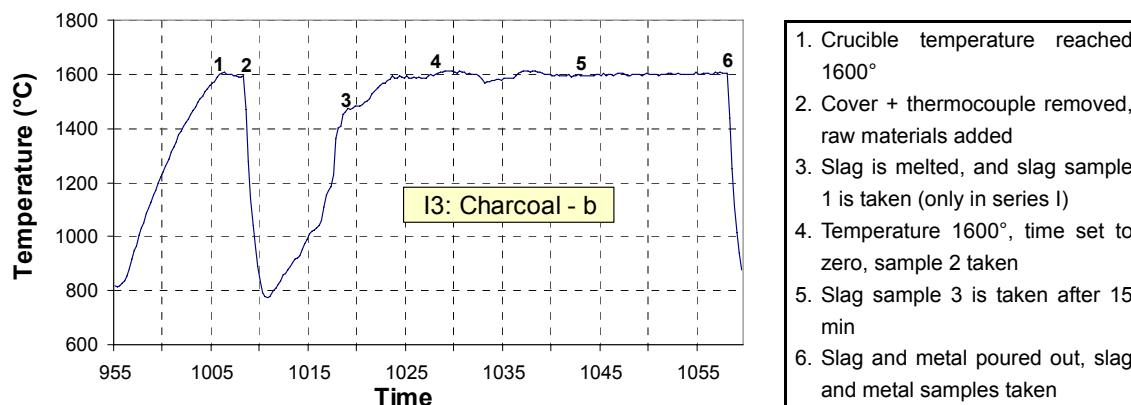

Figure 8: Sketch of experimental set-up

Figure 9: Temperature recorded during an experiment using HC slag (I3), including experimental explanations

Table 2: Analysis of slag and metal in the experimental series with industrial HC slag (I)

Reductant	Time (min)	Slag analysis (%)							R	Final metal			
		MnO	FeO	Al2O3	SiO2	CaO	MgO	Sum		%Si	%Fe	%Mn	%C
I-1 Reference 1	-14	31,8	1,0	10,3	36,8	13,7	3,6	97,1	1,69				
	0	18,2											
	15	12,9	0,2	13,7	46,9	18,1	4,9	96,6	1,67				
	30	10,3	0,1	15,0	45,9	19,8	5,2	96,2	1,67	13,8	12,3	70,4	2,9
I-2 Charcoal- a	-14	28,8	0,4	10,8	38,8	14,4	3,7	96,9	1,68				
	0	17,6	0,2	12,2	46,2	16,2	4,2	96,6	1,67				
	15	10,8	0,2	14,0	48,1	18,5	4,9	96,4	1,67				
	30	10,7	0,1	15,0	46,1	19,9	5,2	97,1	1,67	14,1	10,9	71,6	2,8
I-3 Charcoal- b	-9	23,9	0,2	11,5	42,0	15,4	4,0	97,0	1,69				
	0	17,5	0,2	12,5	45,8	16,6	4,3	96,8	1,67				
	15	11,5	0,2	14,1	47,2	18,6	4,9	96,4	1,67				
	30	11,2	0,2	14,9	46,1	19,6	5,1	97,1	1,67	13,3	11,5	71,5	3,0
I-4 Petrol coke	-9	23,7	0,2	11,2	42,5	15,1	3,9	96,6	1,70				
	0	15,9	0,2	12,6	46,6	16,5	4,3	96,1	1,66				
	15	10,8	0,2	14,1	47,6	18,8	4,9	96,4	1,68				
	30	9,9	0,1	15,1	45,5	20,1	5,3	96,0	1,68	14,0	11,3	71,2	2,8
I-5 Anthracite	-11												
	0	18,9	0,2	12,3	44,4	16,6	4,3	96,6	1,70				
	15	11,0	0,2	14,4	47,0	19,0	5,0	96,5	1,67				
	30	9,6	0,1	15,4	45,8	20,3	5,3	96,5	1,65	14,1	11,4	71,0	2,8
I-6 Reference 2	-8	28,3	0,7	11,0	38,7	14,6	3,8	97,0	1,68				
	0	18,5	0,2	12,3	45,5	16,5	4,3	97,2	1,68				
	15	12,3	0,1	14,0	46,5	18,8	4,9	96,6	1,69				
	30	10,5	0,1	15,0	45,9	19,9	5,2	96,6	1,68	13,3	11,9	71,2	2,9

The results from the experimental series with synthetic slag are presented in Table 3: and Figure 10:. The synthetic made slag composition is also shown, being high in MnO (39.2%) and SiO_2 (36.2%), containing 0.44% sulphur. The reactivity of synthetic made slag is similar to industrial slag of approximately the same composition, provided that sulphur is added.

A comparison of test values is shown in Figure 11: for the experiments with industrial slag (I, R=1.7) and synthetic slag (S, R=1.5-1.7) to chemical equilibrium between SiO_2 in the slag and silicon in metal for R=1 and R=2.

$$R=(MgO+CaO)/Al_2O_3 \tag{5}$$

Table 3: Analysis of slag and metal in the experimental series with synthetic slag (S). The slag did also contain 0.44% S, and the slag mixture contained metal droplets (3.6% Fe)

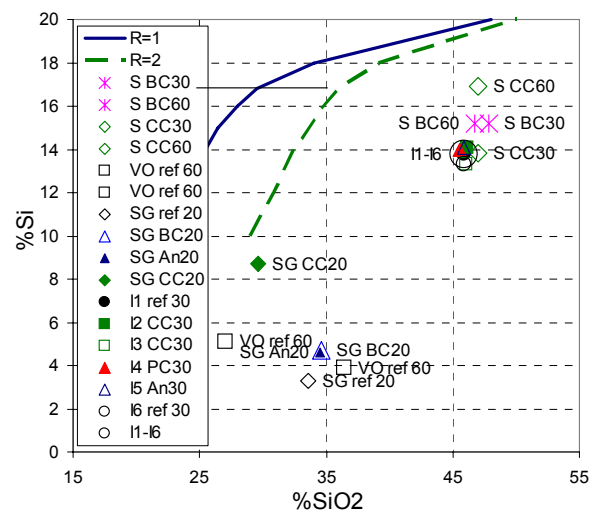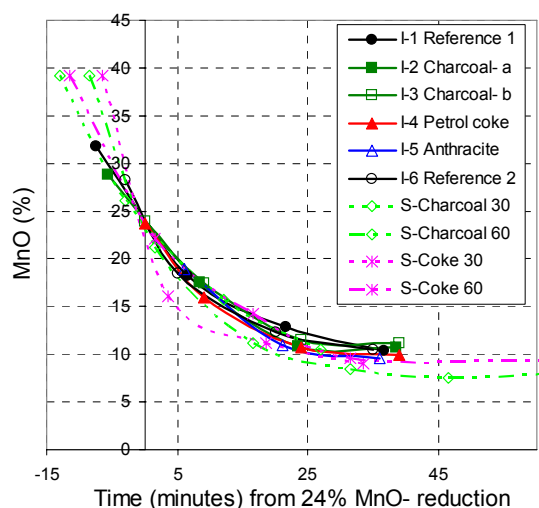| Reductant	1600 °C Time (min)	Slag analysis (%)							R	Final metal		
		MnO	FeO	Al2O3	SiO2	CaO	MgO	Sum		%Si	%Fe	%Mn
S-Charcoal 30	-10	39,2		8,4	36,2	10,5	5,3	99,5	1,87			
	0	26,1	0,8	10,2	45,1	11,3	6,0	99,5	1,69			
	15	15,7	0,5	12,7	49,5	13,8	7,5	99,7	1,68			
	30	10,5	0,4	14,5	50,2	15,5	8,4	99,5	1,65	13,7	11,3	72,5
S-Charcoal 60	-10	39,2										
	0	21,2	1,1	11,6	46,5	12,6	6,7	99,7	1,66			
	15	11,2	0,5	14,5	49,7	15,5	8,5	99,8	1,65			
	30	8,4	0,5	15,3	50,1	16,4	8,9	99,5	1,65			
	45	7,5	0,5	16,0	49,4	17,0	9,3	99,6	1,65			
	60	7,9	1,3	17,1	47,0	16,6	9,9	99,7	1,55	16,9	9,7	71,2
S-Coke 30	-10	39,2										
	0	16,1	1,1	12,9	48,3	13,8	7,5	99,6	1,65			
	15	11,2	0,5	14,1	50,5	15,0	8,2	99,5	1,65			
	30	9,0	0,5	15,0	50,4	15,9	8,7	99,6	1,64	15,2	9,4	73,4
S-Coke 60	-13	39,2										
	0	22,2	0,4	11,0	47,0	12,4	6,6	99,5	1,72			
	15	14,2	0,6	13,6	48,8	14,6	7,9	99,8	1,65			
	30	9,6	0,3	14,6	50,6	15,9	8,7	99,5	1,68			
	60	9,4	0,5	16,5	46,7	17,2	9,5	99,7	1,62	15,3	13,9	68,7

Figure 10: Reactivity of industrial HC slag (I1-I6) and synthetic slag (S) towards carbon materials at 1600°C

Figure 11: Comparison of test values to chemical equilibrium between SiO_2 in the slag and silicon in metal for R=1 and R=2

The test values from the series with industrial HC slag (I1-I6) are all extremely close to each other and rather high in silicon (14%) which is achieved after 30 minutes at 1600ºC. These values are also rather close to test values with synthetic slag, and reasonable close to chemical equilibrium, compared to previous results by S. Gaal (SG [14], R=1..8) and V. Olsø (VO, R=2.5). Abbreviations: charcoal (CC), blast furnace coke/metallurgical coke (BC), petrol coke (PC), anthracite (An), reference (ref), reduction time in minutes (20, 30 or 60).

It is not recommended to test slag reactivity towards different reduction materials in a graphite crucible in an induction furnace. The actual reactions are highly endothermic and by continuously supplying the graphite crucible with the required inductive energy, the temperature of the crucible will be higher than of the coke particles. The observed reduction is most probably due to reduction by the graphite crucible and only to a minor extent by the added reductants.

4.   EXPERIENCE FROM USING CHARCOAL IN A PILOT FURNACE

Silicomanganese has been produced in six pilot scale experiments with three different reductants with a large variation in CO_2 reactivity. The results from the first 5 were reported at INFACON X [7], and detailed description of procedures, raw material analyses and results for the first 5 can be found there. The reductants have been metallurgical coke, reactive coke and charcoal, with increasing CO_2 reactivity. 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. Metal with 18% silicon was produced using metallurgical and reactive coke, but not for the experiments with charcoal, neither with charcoal as the sole reductant (run 3 and 4) nor with charcoal/coke in a 50%-50% mixture on fixed carbon basis (run 5).

   The aim of the last experiment (run 6) is to see if a colder charge top will improve the previous results of run 5, and this paper puts weight on describing differences between these two experiments. In run 6 the ore and coke were moistened to 10% and 8%, respectively. The charged composition is shown in Table 4:. The amount of HC FeMn slag (15 kg), quartz and ore on a dry basis (35kg) was the same. The experiments started with 3-5 kg coke-bed, and the amount of coke in the charge is calculated to give an off gas composition of $CO/(CO+CO_2)$ close to 1. 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.

Table 4: Charge composition (kg, wet), based on 35kg dry ore and 15kg HC slag in each charge

Run no	Starting coke-bed (kg)	Charged materials	Moisture (%)	Charge 1 (kg)	Charge 2 (kg)	Charge 3 (kg)	Charge 4-11 (kg)
5	3	Charcoal	7	5.5	6	6.3	6.6
		Industrial coke	0	4.8	5.2	5.5	5.7
		Quartz	0	0	6.5	11	13.3
		Ore	0	35	35	35	35
6	5	Charcoal	7	5.5	6	6.3	6.7
		Industrial coke	8	5.1	5.6	6.0	6.3
		Quartz	0	0	6.5	11	13.3
		Ore	10	38.8	38.8	38.8	38.8

   The 150 kW single electrode furnace at SINTEF/NTNU is shown in Figure 12: (max 80 V, max 6 kA). During excavation the outer lining of silica sand can be easily removed. 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 144-155 kW was obtained in the 6 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 position was fixed with a tip position of 15 cm above the bottom lining in run 5 and 6. Power consumption was the same in these two runs, 3.6 kWh/kg metal produced, even though the silicon levels in the metal produced were different. The iron content was around 5-7% in all the last taps. Selected experimental results are presented in Table 4
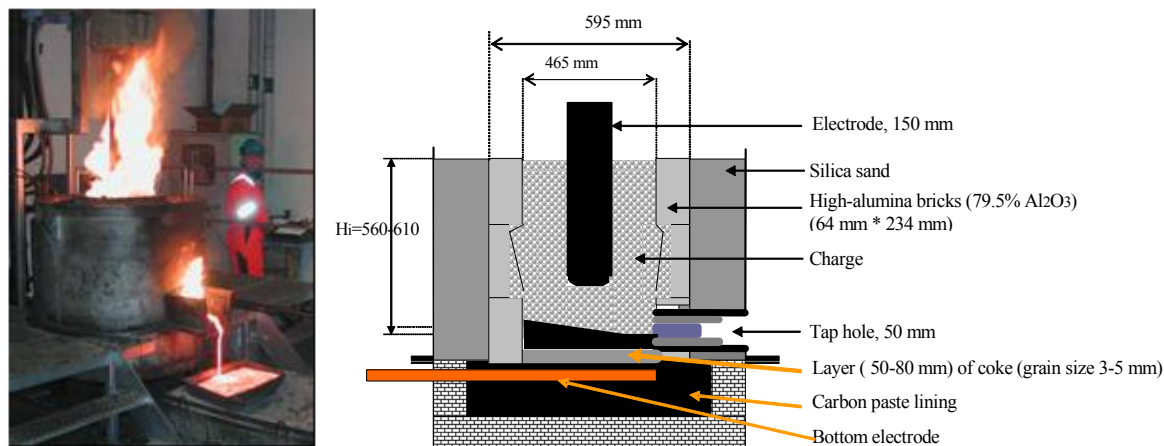
Figure 12: Sketch of pilot furnace and picture taken during tapping

Table 5: Furnace operation during stable production (average numbers for tap 4-8). Mean slag and metal analyses for the taps 4-8 are shown

Run no.	Current (kA)	Voltage (V)	Load (kW)	Resistance (m·ohm)	Produced metal (kg)	Produced slag (kg)	% MnO in slag	% SiO₂ in slag	%Si in metal
5	2.1	71	148	35	180	223	19.0	39.2	12.9
6	3.4	48	155	15	151	182	29.1	37.5	16.6

The metal and slag analyses are shown in Figure 13: and Figure 14:. Run 6 (and the coke experiments, run 1-2) deviates from run 5 (and run 3-4 with charcoal) with a higher %Si in the metal. The manganese reduction is lower, which leads to a lower 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 total reduction of both MnO and SiO_2 is of course important.
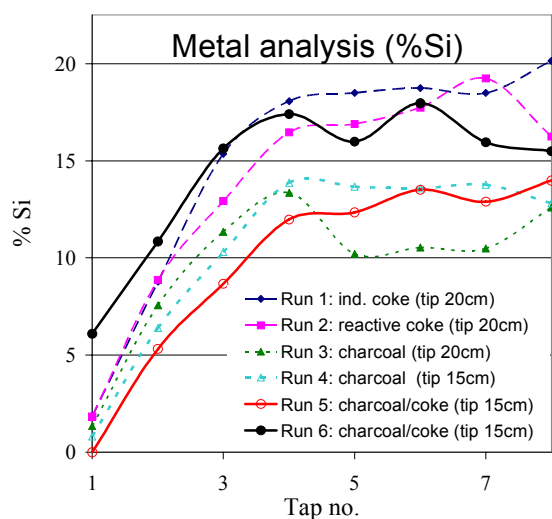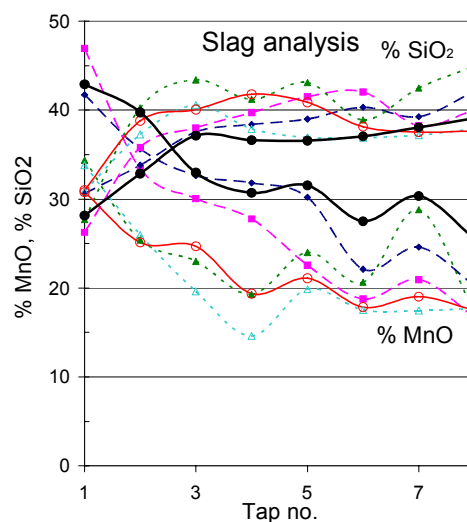

Figure 13: %Si tapped metal
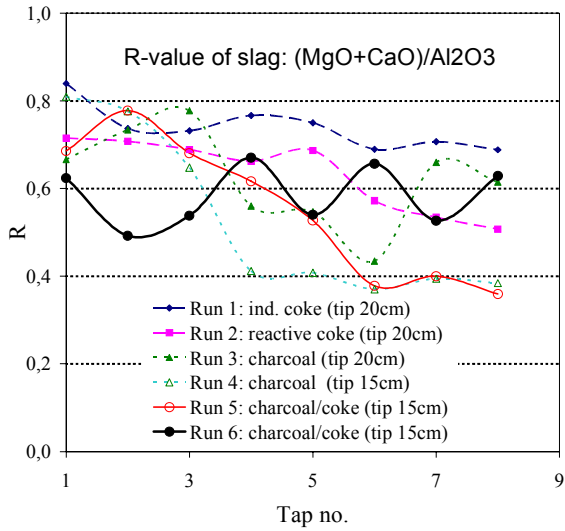
Figure 14: %MnO and %SiO₂ in tapped slag

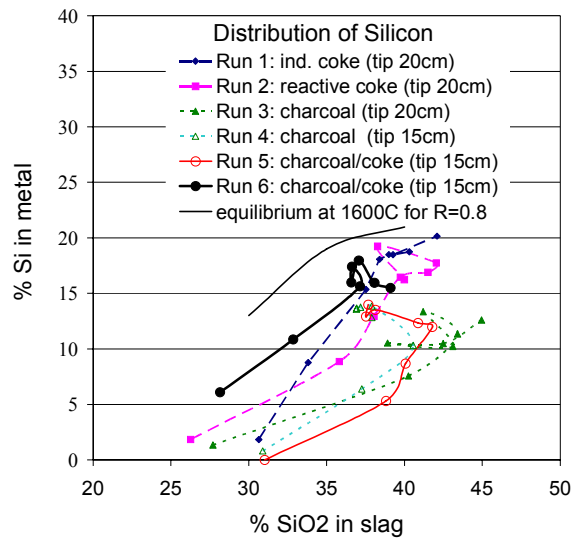*Figue 15: R value of tapped slag*

Figure 16: Si-distribution between slag and metal

   The R-value 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. As shown in Figure 15:, the R value varies in the range 0.5-07 in run 6. In run 5 the R-value is 0.7 at start but is reduced to 0.4 in the last taps, due to dissolution of the alumina lining in the slag [7]. A more resistant lining was used in the last run. In Figure 16: we see how silicon is distributed between the metal and the slag, compared to equilibrium at 1600 °C. At an equally high content of SiO_2 in the slag, run 6 has a much higher %Si in the metal than run 5, it is even higher than for the cokes. For an equal electrode tip position of 15 cm, run 6 has probably a higher temperature in the reduction zone than run 5 (even though water was added with the ore and coke in run 6). The coke-bed temperature in run 6 seems to be higher than for the cokes in run 1 and 2 with a higher electrode position (20 cm), especially at the beginning of the experiment.
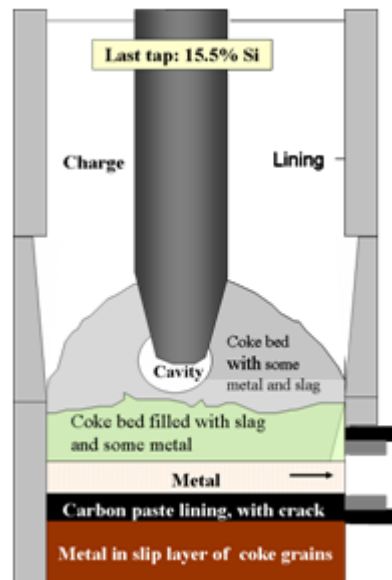

Figure 17: Excavation plate from run 6

Figure 18: Furnace in run 6
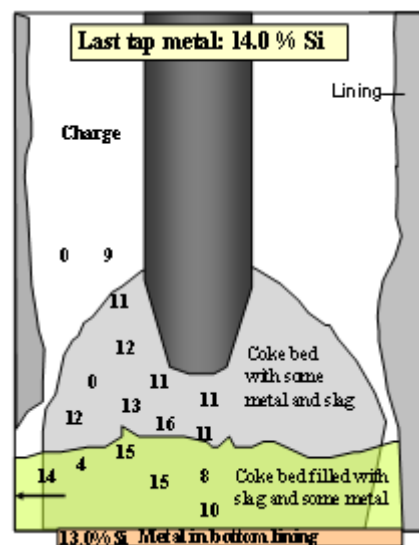
Figure 19: Excavation plate from run 5 (charcoal)

Figure 20: Degree of Si-reduction in run 5

A photo of the excavation plate from run 5 and 6 is shown in Figure 17:and Figure 19:. Figure 18: and Figure 20:show the different zones which this plate can be divided into, together with the silicon microprobe analyses of the 18 samples cored out from the plate from run 5.

Metal is found at the bottom (and slag and metal are observed in the bottom lining of run 6). Above is a "coke"-bed filled with green slag and some metal. Reaching up around the electrode tip is the coke-bed with some metal and slag droplet. The excavation plates from run 5 and 6 look similar. However, there is a big difference in the resistance in the two experiments that shows that the current paths have been somewhat different. For both 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 seems to be rather equal. However, the size of the coke bed in run 6 may be somewhat bigger (wider). A larger coke-bed should give a somewhat higher amount of energy development in the coke-bed when no quartz is present. By measuring the electrode length before and after the runs we find that 2 and 2.7 cm of the electrode were consumed in run 5 and 6. Some bottom lining was also consumed, the most in run 5. The electrode tip position, which was set to 15 cm above the bottom lining at start, has increased towards the end of both runs.

5. CONCLUSIONS

Selected reductant properties of special importance for manganese alloy production have been measured at SINTEF/NTNU, using appropriate equipment designed/built during the last 5 years. There are many differences between charcoals and common metallurgical cokes used today. Industrial charcoal has higher CO_2-reactivity, lower thermal abrasive strength and higher electrical resistivity, which is decreasing with increasing temperature.

It is not recommended to test slag reactivity towards different reduction materials in a graphite crucible in an induction furnace. The observed reduction is most probably due to reduction by the graphite crucible and only to a minor extent by the added reductants. The method may be used for testing different slags towards graphite, but not for testing the performance of different reductants.

A pilot experiment (no. 6 in a series) shows that SiMn with 18% Si can be produced when charcoal is substituting 50% of the coke on a fixed carbon basis. The main difference from a previous similar run is that the

ore and coke were moistened to 8-10% moisture in order to keep the charge top colder, avoid carbon burn-off at the top and improve temperature distribution in the furnace.

6.   ACKNOWLEDGEMENTS

REFERENCES

[1]   Nestaas, I., Lehmann, M. and Lindstad, T., "Hvitbok om klimagassutslipp fra norsk landbasert pros-essindustri" ["White-book dealing with greenhouse gas emissions from Norwegian on-shore process industry"], SINTEF & Det Norske Veritas, 2003, pp. 18 and 62.

[2]   Eikeland, I.J., Monsen, B., and Modahl, I.S.: "Reducing CO_2 emissions in Norwegian ferroalloy production", COM 2001 (Greenhouse gases in the metallurgical industries: policies, abatement and treatment), Toronto 2001.

[3]   Monsen, B., Grønli, M., Nygaard, L. and Tveit, H., "The use of biocarbon in Norwegian ferroalloy production", INFACON 9, 2001, pp 268-276

[4]   Ostrovski, O., Olsen, S.E., Tangstad, M., Yastreboff, M., "Kinetic modelling of MnO reduction from manganese ore", INFACON 9, 2001, pp 302-312.

[5]   ASTM D 5341 – 99: "Standard Test for Measuring Coke Reactivity Index (CRI) and Coke Strength After Reaction (CSR).

[6]   Lindstad, T. et al, "The influence of alkalis on the Boudouard reaction", INFACON X, Cape Town South Africa, 2004, pp 261 – 271.

[7]   Monsen, B., Tangstad, M. and Midtgaard, H., "Use of charcoal in silicomanganese production", INFACON X, Cape Town South Africa, 2004, pp 392 – 404.

[8]   Ishak, R.J., "Reaction kinetics for reduction of manganese ore with carbon monoxide in the presence of carbon", PhD thesis at NTNU, Norway 2002.

[9]   Arntzen, H.B.,"Alkalier og Boudouard-reaksjonen i ferromanganeprosessen. [Alkalies and the Boudouard reaction in the ferromanganese process]", Diploma Thesis at NTNU, Norway, 2002.

[10]   Eidem, P.A., Tangstad, M. and Bakken, J.A.,"Determination of Electrical Resistivity of Dry Coke Beds", to be published in Met. Trans. 2007.

[11]   Eidem, P.A., "Determination of Specific Resistance of Coke", Diploma Thesis at NTNU, Norway 2003.

[12]   Eidem, P.A., "Electrical resistance measurements of charcoal compared to coke", SINTEF- report STF80 F04012, Norway 2004.

[13]   Solheim, I., "Reactivity of coke and charcoal towards SiMn slag", SINTEF report STF24 F03522, Norway 2003

[14]   Gaal, S. et al: "An investigation into aspects of liquid phase reduction of manganese and silica containing slag", Molten Slags, Fluxes & Salts, South Africa 2004, pp 651-657.