THE INFLUENCE OF ALKALIS ON THE BOUDOUARD REACTION

T. Lindstad[1,2], M. Syvertsen[1], R.J. Ishak[2,3], H.B. Arntzen[2,4] and P.O. Grøntvedt[1]

[1]SINTEF Materials Technology, N-7465 Trondheim Norway
[2]Norwegian University of Science and Technology, Dept of Materials Technology, N-7465 Trondheim Norway
[3]At present Eramet Norway AS
[4]At present Elkem ASA, Bremanger Smelteverk

ABSTRACT

Better utilisation of electric power and coke is vital in reducing production costs and CO_2-emissions in production of ferromanganese. All FeMn smelting operations consume 10 to 30 % more carbon than the carbon needed to reduce MnO and FeO to metal and the carbon contained in the alloy. Potassium which re-circulates and builds up in the furnace has been shown to be the main culprit causing both excessive carbon consumption, by catalysing the Boudouard reaction, and increased electric power consumption.

The reaction between CO_2 and ordinary metallurgical coke or coke impregnated with potassium has been studied at temperatures from 800 to 1100°C in a thermobalance apparatus. Ordinary coke did not react to any great extent at temperatures up to 1000°C, whereas the addition of potassium (2-10 %) resulted in a huge increase in reaction rates.

The ultimate goal is to fit the results into a reaction rate model containing the equilibrium constant for the solid-gas heterogeneous reaction between CO_2 and a free active site on the carbon reactant producing CO and adsorbed oxygen (an occupied site). The model includes the partial pressures of CO and CO_2, a reaction rate constant that is a function of both the total number of reaction sites of carbon, and the potassium content. The potassium dependency is taken care of by introducing activity coefficients for the carbon sites. As the first step towards such a model, a regression line for the Boudouard reaction rate has been established.

1. INTRODUCTION

In the production of carbon ferromanganese from manganese ore, the reactions in the smelting reduction zone are the reduction of MnO, the reduction of FeO, the reduction of SiO_2 and the dissolution of carbon. The minimum carbon consumption is then the carbon needed to reduce these oxides plus the carbon in the product. Swamy et. al [1] have calculated a typical minimum carbon consumption to be 275 kg/t HCFeMn for an alloy with 79 wt.% Mn, 14 wt.% Fe and 7 wt.% C. The amount of CO produced in the smelting reduction zone is in theory sufficient to reduce an ore burden consisting of MnO_2 and Fe_2O_3 to MnO and FeO.

The theoretical minimum CO_2-emission then can be calculated to be:
0.751 kg CO_2/kg ferromanganese for HCFeMn (7 wt% C) and 1.004 kg CO_2/kg ferromanganese for LCFeMn ($\leq$0.1 % C).

Both values are considerably below both the BAT[1]-values, which range from 1.1 to 1.8, IPPC-BREF[2] [16], and 1.3 kg CO_2/kg ferromanganese typically obtained in Norwegian ferromanganese production.

---

[1] Best Available Technology
[2] EU Commission, Integrated Pollution Prevention and Control, Reference Document on BAT

In the pre-reduction zone the CO produced in the hot smelting zone meets the solids flowing downwards in the shaft, reducing the higher oxides of manganese and iron to MnO and FeO. We may visualise the processes going on by dividing the pre-reduction zone in three zones, although there are no sharp borders between these zones, and the temperature ranges given below are just indicative.

Zone 1: 100-400ºC. Drying and calcination zone; Water evaporates and MnO_2 decomposes to Mn_2O_3 and O_2, which reacts with CO to CO_2, or MnO_2 reacts directly with CO.

Zone 2: 400-700ºC. Gas/solid reduction zone where Mn_2O_3 is reduced to Mn_3O_4 and partly to MnO.

Zone 3: 700-1200ºC. Mixed gas/solid reaction zone where Mn_3O_4 is reduced to MnO simultaneously with the Boudouard reaction running ($C + CO_2 = 2\ CO$).

Besides these main reactions several other gas-solid reactions take place:
- Higher iron oxides of the ore are reduced to FeO and possibly to iron metal.
- Carbonates in the ore and fluxes decompose into their oxides and carbon dioxide.
- Potassium re-circulation by K (*g*) and K_2CO_3 (*l,s*). The potassium re-circulation enhances carbon consumption, and is indistinguishable from the Boudouard reaction.

Because of the Boudouard reaction and re-circulation of potassium the carbon consumption in industrial HCFeMn production is between 305-380 kg per ton of alloy, according to Swamy [1]. Compared to the minimum amount, it is clear that it is very important to restrain the Boudouard reaction as much as possible to have a good operating economy as well as keep emissions of greenhouse gases down.

2. THE BOUDOUARD REACTION

The Boudouard reaction has the stoichiometric equation:

$$CO_2(g) + C(s) = 2CO(g) \tag{1}$$

The equilibrium diagram, calculated with Fact Sage [3], shown in Figure 1. At the prevailing temperatures in pre-reduction zone 3, most of the CO_2 produced in the reduction of oxides should be converted back to CO by the Boudouard reaction if equilibrium were obtained.

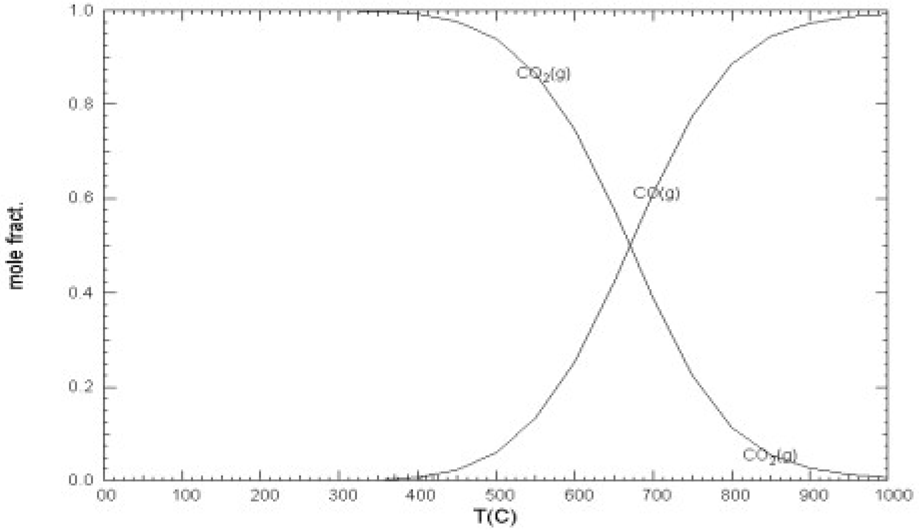

Figure 1. Equilibrium diagram for the Boudouard reaction with carbon in excess.

Ishak [4] has recently carried out a literature survey:

Ergun [5] investigated the kinetics of the reaction under various experimental conditions at a temperature range of 700-1400°C. Three types of carbons of different origin were used. His work from 1956 forms the basis for most of the studies later. A mechanism of the reaction was postulated in which certain reaction sites, carbon atoms, are able to detach an oxygen atom from a gaseous CO_2 molecule, thus reducing CO_2 to CO and forming an occupied site, as expressed in Eq. (2). The reverse reaction may also take place. These reactions are known as the "oxygen-exchange reactions". Then the transfer of carbon from solid phase to gas phase originates from the occupied sites and is expressed in Eq. (3). This latter reaction was found to be the slowest step of the reactions, and it is assumed to determine the overall rate of the Boudouard reaction.

$$\mathrm{CO}_2 + C_f \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{CO} + C_o \tag{2}$$

$$C_o \xrightarrow{k_3} \mathrm{CO} + nC_f \tag{3}$$

In these equations C_t is the total concentration of active sites, which is equivalent to the sum of occupied sites (C_o) possessing an oxygen atom and the free sites (C_f) capable of reaction. n is an integer having a value of 0, 1 or 2, when occupied sites are considered individually [5]. For a macroscopic sample the statistical expectation value is 1. The reaction rate for Eq. (3) is proportional to the total concentration of active sites, and CO retards the reaction as it reduces the concentration of occupied sites. Ergun stated that the rate constants k_1, k_{-1}, and k_3 are functions of temperature only, and common to all carbons having trigonal (coplanar) bonds. The differences in reaction rates of carbons are due to the specific number of reaction sites. From this mechanism Ergun and Mentser [6] deduced the reaction rate Eq. (4)

$$R_c = \frac{K_1 k_3 (C_t)}{K_1 + p_{\mathrm{CO}} / p_{\mathrm{CO}_2}} \tag{4}$$

where K_1 is the equilibrium coefficient for Eq. 2.

Aderbigbe and Szekely [7] made use of the same mechanism deduced by Ergun in interpreting their experimental results. Experiments were conducted on the reaction of metallurgical coke with CO- CO_2 mixtures at temperatures between 850-1000°C using a thermobalance apparatus. By employing Langmuir-Hinshelwood rate theory the reaction rate, R_C, was expressed in the following manner:

$$R_c = \frac{K_1 P_{\mathrm{CO}_2}}{1 + K_2 P_{\mathrm{CO}} + K_3 P_{\mathrm{CO}_2}} \tag{5}$$

in which $K_1 \equiv k_1 \Sigma c$, $K_2 \equiv \frac{k_{-1}}{k_3}$, $K_3 \equiv \frac{k_1}{k_3}$ and Σc = the total available active reaction sites. By transformation of Eq. (4) it is possible to obtain an equation, which except for the 1 in the denominator is identical with Eq. (5).

The rate constants were believed to be specific of the particular type of coke investigated, in contrast to the conclusions made by Ergun.

In order to take into account the catalytic effect of potassium on the Boudouard-reaction, one may introduce an activity coefficient such that the activities of free and occupied carbon sites are

$$a_f = f_f \cdot \frac{C_f}{C_t} \tag{6}$$

and

$$a_o = f_o \cdot \frac{C_o}{C_t} \tag{7}$$

respectively. f_i then takes into account the other elements or compounds that affect the activity. The activity coefficient, f_i, is then defined as

$$\lg f_i = \sum_{j=2}^{n} \left(e_j^i [\%j] + r_j^i [\%j]^2 + \mathrm{K} \right) \tag{8}$$

where e_j^i and r_j^i are the first and second order interaction coefficients, and the sum is over all abundant elements except carbon. Thus, the equilibrium constant for the Boudouard-reaction becomes

$$K_1^{'} = K_1'(\%K) = \frac{f_o}{f_i} K_1 \tag{9}$$

The equilibrium constant is then a function dependent on the potassium content [%K].

3. PREVIOUS STUDIES ON THE EFFECT OF ALKALI

Ishak [4] has also made a literature survey of the influence of alkalis, especially potassium, on the Boudouard reaction. It is not possible to separate carbon consumed by potassium re-circulation from carbon consumed by Boudouard reaction, catalysed by potassium, in a ferromanganese furnace. However, it is possible to perform laboratory experiments to study the catalytic effect.

Alkalis are present in the ferromanganese furnace, entering as components of the manganese ore and to a smaller extent also as components of the coke. The main alkali component of the ore is potassium. Alkali accumulates in the furnace by re-circulation. The re-circulation takes place by the reduction of potassium oxide in the raw materials, to metal vapour in the smelting zone, reaction (10). This potassium vapour follows the gas flow upwards in the furnace and is reoxidised in the colder regions to form potassium carbonate, reaction (11), Tangstad and Olsen [8]. This potassium carbonate condenses on the charge materials which flow downwards in the furnace shaft, and is reduced again in the melting zone by reverse of reaction (11).

$$K_2O + C = 2\ K\ (g) + CO\ (g) \tag{10}$$

$$2\ K\ (g) + 3\ CO\ (g) = K_2CO_3\ (l) + 2\ C \tag{11}$$

Calculations by Tangstad and Olsen showed that the alkali content of the burden might be as high as 15 % K_2O. Evidence of potassium accumulation is commonly observed by furnace operators during digouts and relining. In full-scale experiments Tangstad [2] observed very low potassium contents in the slag from taps during start up, thus indicating a build up of potassium in the furnace. Swamy [1] calculated a re-circulating potassium load of 8.5 times the input of potassium. Since reaction (11) is reversed, only reaction (10) should cause carbon consumption, and an amount equivalent to the potassium content in the charge materials. But the carbon produced by reaction (11) in the upper parts of the shaft, thoroughly mixed with potassium carbonate, is quite possibly more reactive with CO_2 than the coke charge.

The re-circulation of potassium may also consume coke directly:

$$K_2O + C = 2\ K\ (g) + CO\ (g) \tag{10}$$

$$2\ K\ (g) + CO_2\ (g) = K_2O + CO\ (g) \tag{12}$$

Li [9] calculated a carbon consumption of 46 kg C/t HCFeMn and an increased power consumption of 183 kWh/t HCFeMn caused by re-circulation of potassium.

Several studies of the influence of potassium on the Boudouard reaction have been reported; Aderbigbe and Szekely [7], Beyer and Peters [10], Davies et al [11], Alam and Debroy [12], Rao et al [13] and Van Niekerk et al [14]. Their results are summarised by Ishak [4]. Common to all these studies is that the impregnation of coke with potassium was done using aqueous solutions of potassium compounds (KCN, KOH, or K_2CO_3). After impregnation, the samples were dried, leaving the solid potassium compound in and on the coke particles. All these experiments show a many-fold increase in Boudouard reaction rate for the investigated temperature range (800-1200ºC).

3.1 Objectives for present experimental studies.

In the ferromanganese process, the potassium compound will condense from vapour phase on the carbon as well as on the manganese ore. We believe this will cause a distribution of alkalis in the coke different from the distribution obtained by soaking coke in aqueous solutions. This led to the decision to prepare impregnated coke by vapour phase deposition of potassium compound, thus making a better representation of the conditions in a ferromanganese furnace. A research group working on carbon materials for aluminium electrolysis at NTNU had developed an apparatus for impregnating carbon with alkalis, Kvam et al [15], and this proved to be useful for the present task.

An introductory investigation, using this procedure for impregnating was carried out by Arntzen in his M.Sc. work in 2002 [19]. He found that the reaction rate was fairly constant in the 500 to 1000 second interval after start of gas supply (25% CO_2 –75% CO). Experiments were carried out with a starting concentration of potassium ranging from 0 to 10,5% and at temperature 800ºC, 900ºC, 1000ºC, and 1100ºC, using a similar experimental procedure as in our experiments. Results are shown in Figure 2. It should be emphasised that the potassium contents given are at the start of the experiments. It was found in two of the experiments at 800ºC and 1100ºC, that the potassium content had fallen from 5,8% to respectively 4,8% and 4,0% during the experiment.

The experience gained by Arntzen was valuable in planning and conducting our further research.

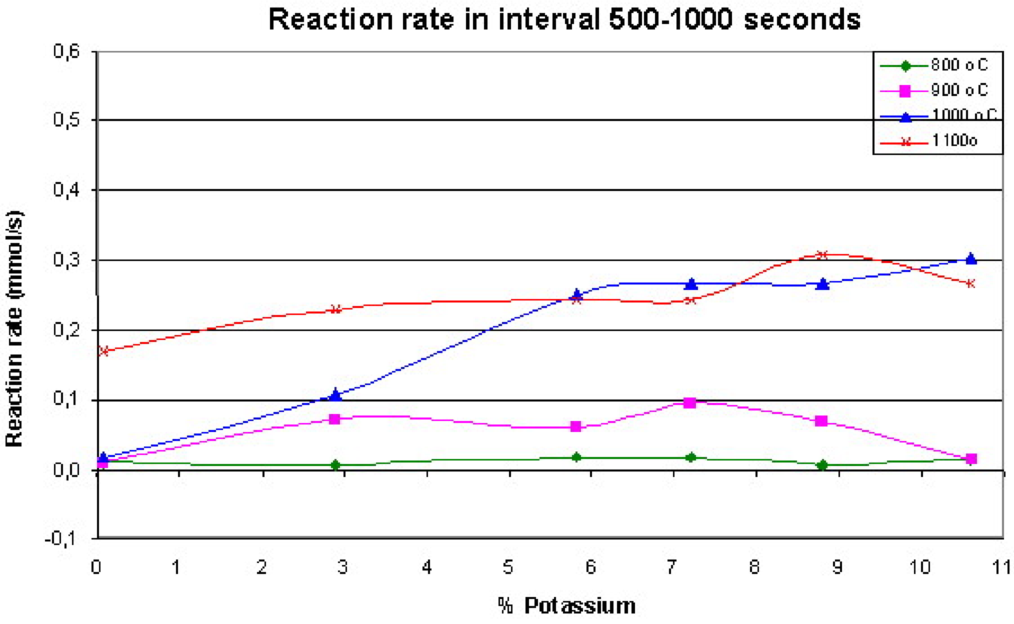

Figure 2. Reaction rate (mmol CO_2/s) for Boudouard reaction using vapour phase potassium impregnated coke, Arntzen [19].

4. EXPERIMENTAL SETUP

4.1 Apparatus

The experiments were done in a thermobalance with controlled temperature, inlet gas composition and flow rate. The charge weight and temperature, and off gas composition were continuously measured and logged on a computer. The total gas pressure was 1 atm.

The charge was placed on a grid in a crucible inside the furnace. The crucible was suspended from the balance. The gas inlet tube ran through the whole crucible through the grid and had holes in the bottom. The gas flowed through the grid and charge before it left the crucible. The gas flow was sufficient to keep about the same gas composition through the charge.

4.2 Materials

Metallurgical coke used by the manganese alloy producer Eramet Norway was employed. A chemical analysis of the coke is given in Table 1.

Table 1. Chemical analysis of coke.

Component:	WT %
Fixed Carbon	88.01
Volatiles	0.56
Ash content	11.43

The coke was received in the form of lumps of mainly 10-30 mm in size. These were crushed in a jaw crusher to less then 10 mm, and the pieces of coke were then sieved. The size range of 4.0 – 6.35 mm was used in the experiments.

Some coke was impregnated with potassium. The referred method for exposing carbon samples to potassium gas, Kvam et al [15], was used. In short, K (g) was formed by reaction of potassium carbonate with active carbon at about 1000°C in a bed below the coke:

$$K_2CO_3 + 2\ C = 2\ K + 3\ CO \tag{13}$$

The rising gas met colder coke where the reverse reaction occurred. The resulting potassium content of the coke was 6.22 wt%.

The experiments were performed at 900ºC, 1000ºC, and 1100°C. This is the temperature range in which we expect that the Boudouard reaction will be active when catalysts are present. The coke mass in a charge was 20 g, and the gas flow rate was 4.0 Nl/min (either a mixture of 25% CO_2 and 75% CO, or 50% of each). The charge used was simply coke, either regular non-prepared or impregnated with potassium

The procedure for the experiments was as follows:

- 20 g of coke was placed in the crucible.
- The crucible was hooked up in the balance and thermocouple and hoses were connected.
- The data logger was started, furnace hoisted, and set to heating while the crucible was flushed with argon gas.
- When the predefined temperature was reached, the argon gas was replaced with the appropriate CO/CO_2 mixture so that the Boudouard reaction started.
- The reaction was allowed to proceed for about 1 hour for non-impregnated and 20 – 30 min for impregnated coke.
- The CO/CO_2 mixture was then replaced with argon, and the furnace lowered, so the crucible cooled down.
- When the crucible temperature was below 50°C, the logging was stopped, argon flow was closed, and the remaining coke weighed.

In order to determine the most significant experimental parameters, factorial designed experiments were planned. Table 2 shows the values of the parameters thought to affect the Boudouard reaction.

Table 2. Reaction parameters and identification labels for the factorial designed Boudouard reaction experiments.

ID	T (°C)	p_{CO_2} (atm)	p_{CO} (atm)	wt% K
F1	1000	0.25	0.75	0
F2	1000	0.50	0.50	0
F3	1100	0.25	0.75	0
F4	1100	0.50	0.50	0
F5	1000	0.25	0.75	6.2
F6	1000	0.50	0.50	6.2
F7	1100	0.25	0.75	6.2
F8	1100	0.50	0.50	6.2

In addition to the factorial designed experiments, some supplementary experiments were done. In order to determine the decomposition and evaporation of potassium carbonate and potassium respectively, an experiment with impregnated coke was done at 1000°C in argon atmosphere.

5. EXPERIMENTAL RESULTS AND DISCUSSION

5.1 Evaporation of potassium

During the experiments using the impregnated coke, it was observed that the outlet of the crucible became clogged before the CO/CO_2 gas was introduced. This was most likely due to evaporation of potassium. Some of the reacted coke was also analysed for potassium. The result from these analyses was 5.88% K out of 12.60 g and 5.63% K out of 13.36 g. If most of the potassium evaporates before the Boudouard-reaction started (during heating), the potassium content in the coke would be 3.8 %. This was also partly confirmed by the experiment with impregnated coke done in argon. During this experiment, the temperature profile was kept as in the Boudouard-reaction experiments, but flushing with argon only during a complete test cycle. The total weight loss was 2.0 g from a charge of 20 g. If this mass loss was due to decomposition of potassium carbonate given in Eq. (11), then the potassium content in the coke would be reduced from 6.22 wt% to 3.9 wt%.

5.2 Thermobalance measurements

Results from a typical experiment are shown in Figure 3. Measured weight change and temperature are displayed. At time = 0, the temperature is stable at about 1110°C, and the argon is replaced with the CO/CO_2 mixture. It is seen from the figure that when the CO/CO_2 mixture is introduced, the temperature falls rapidly to 1090°C. This is due to start of the endothermic Boudouard reaction, $\Delta H^0 = 170.7$ kJ/mol, T Rosenqvist [17]. After the temperature has dropped it starts rising slowly due to increased heat transport into the crucible from the furnace. The magnitude of the temperature drop was dependent on the reaction rate and not known prior to the experiments. Thus, it was not possible to achieve the same pre-set temperature for the four 1000°C, and the four 1100°C, experiments.

The initial weight loss around time = 0 is not taken into account when the reaction rate (i.e. slope) is calculated.

The time scale of an experiment is strongly dependent on the potassium content. When non-impregnated coke was tested, a measurement lasted about 60 min, whereas when impregnated coke was used, less than 30 min was common. The reason for the rapid weight loss in the beginning of the measurements, is mainly due to different gas density and momentum.

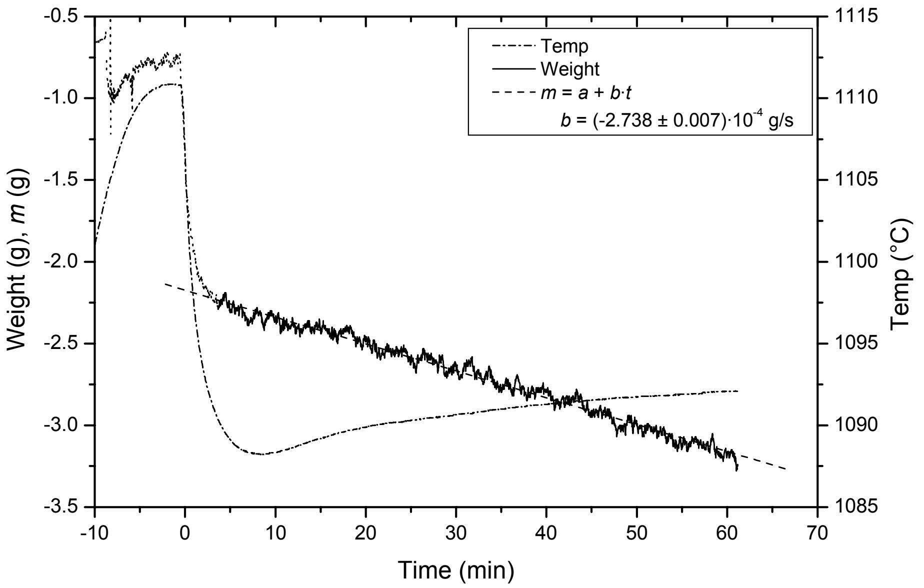

Figure 3. Boudouard reaction measurement (F3). Charge 20 g, 25% CO2 + 75% CO, 0% K. The regression line is fitted to the measured weight curve in where the slope of this is stable. The parameter *a* is an arbitrary constant, only dependent on the thermobalance zero-point. The slope *b* is proportional by a fixed constant to the reaction rate as given in Equation (4).

The results of the experiments listed in Table 2 are given in Table 3. It is clear from the table that increased temperature, partial pressure of CO_2, and amount of potassium increase the reaction rate.

Table 3. Actual temperature and reaction rate for the factorial designed Boudouard reaction experiments.

ID	T (°C)	p_{CO_2} (atm)	wt% K	$-b/10^{-3}$ (g/s)
F1	995.9 ± 0.4	0.25	0	0.0838 ± 0.0009
F2	994.4 ± 0.2	0.50	0	0.1037 ± 0.0005
F3	1091 ± 1	0.25	0	0.2738 ± 0.0007
F4	1095 ± 0.2	0.50	0	0.5971 ± 0.0005
F5	974 ± 1	0.25	3.9	3.053 ± 0.005
F6	969 ± 1	0.50	3.9	4.564 ± 0.005
F7	1090 ± 2	0.25	3.9	5.724 ± 0.005
F8	1076 ± 4	0.50	3.9	6.96 ± 0.01

5.3 Factorial analysis

When performing the factorial analysis, it is necessary to calculate an average temperature for the high and low temperature. The low temperature (should be 1000°C) is 983 ± 14°C, and the high temperature (1100°C) is 1088 ± 8°C. The coding for the factorial designed experiment is given in Table 5.

Table 4. Codes for the factorial analysis.

T (°C)	code	p_{CO_2} (atm)	code	wt% K	code
983 ± 14	-1	0.25	-1	0	-1
1088 ± 8	+1	0.50	+1	3.9	+1

As explained by Esbensen et al [18], a regression line for the Boudouard-reaction rate between the limits of the parameters becomes

$$b = b_0 + b_1 T^* + b_2 p^* + b_3 c_K^* + b_4\left[T^* p^*\right] + b_5\left[T^* c_K^*\right] + b_6\left[p^* c_K^*\right] + b_7\left[T^* p^* c_K^*\right] \tag{14}$$

where the non-dimensional variables T^*, p^*, and c_K^* are defined as

$$\begin{aligned} T^* &= \frac{T - 1036}{53} \\ p^* &= \frac{p_{CO_2} - 0.375}{0.125} \\ c_K^* &= \frac{[\%K] - 2}{2} \end{aligned} \tag{15}$$

By standard methods [18] of calculating the eight b_i parameters, they become

$$\begin{aligned} b_0 &= -2.67 \cdot 10^{-3} \\ b_1 &= -1.44 \cdot 10^{-3} \\ b_2 &= -0.77 \cdot 10^{-3} \\ b_3 &= -4.81 \cdot 10^{-3} \\ b_4 &= -0.0071 \cdot 10^{-3} \\ b_5 &= -1.1 \cdot 10^{-3} \\ b_6 &= -0.601 \cdot 10^{-3} \\ b_7 &= -0.145 \cdot 10^{-3} \end{aligned} \tag{16}$$

This means that, within the investigated parameter regions, the most significant variable for the Boudouard reaction is the potassium content (the absolute value of b_3 is more than three times larger than b_1). The cross interactions between the temperature and partial pressure, ($T^* \times p^*$), and between all three, ($T^* \times p^* \times c_K^*$), on the other hand contribute less than 4% to the reaction rate. The parameters and interactions, except for these two must then be studied further.

5.4 Supplementary experiments

In addition to the eight factorial designed experiments, some experiments were run at 900°C. These experiments consisted of two non-impregnated and two impregnated experiments (0.25 and 0.50 atm CO_2). The results from these experiments are given in Table 7.

Table 5. Supplementing Boudouard reaction experiments.

ID	T (°C)	p_{CO_2} (atm)	wt% K	$-b/10^{-3}$ (g/s)
S1	904 ± 4	0.25	0	0.0335 ± 0.0005
S2	907.3 ± 0.4	0.50	0	0.0095 ± 0.0006
S3	906.1 ± 0.1	0.25	3.9	0.459 ± 0.002
S4	900.7 ± 0.1	0.50	3.9	0.483 ± 0.002

It is seen from the supplementary experiments that the rate of the Boudouard reaction at 1000°C is about ten times higher than at 900°C.

It seems that the reaction rate for S1 is higher than for S2. This is not expected since the partial pressure of CO_2 is highest during the S2-experiment. One reason for this effect could be traces of potassium still present in the crucible (even though the crucible was cleaned out), since the S1 experiment was done after the impregnated coke experiments. Another reason could be oxidation of the steel crucible.

6. CONCLUSIONS

- By condensation and deposition of potassium compounds from vapour phase coke similar to coke in a SiMn- or FeMn-furnace is prepared.
- The potassium content does not decrease, during the Boudouard reaction. Results rather indicate an increase in concentration, due to consumption of carbon. Thus experimental results represent situation in an industrial furnace producing manganese alloys.
- Factorial designed experiments show that the potassium content is the most significant variable, in determining the reaction rate, followed by temperature and partial pressure of CO_2 (conclusions valid within the experimental variation of variables). Significant cross interactions of potassium content and temperature and of potassium content and partial pressure of CO_2 are shown.

7. ACKNOWLEDGEMENTS

The authors want to thank the Norwegian Research Council and The Norwegian Ferroalloy Producers Research Association for the financial support to this project.

8. REFERENCES

[1] K. N. Swamy, D. G. C. Robertson, P. Calvert, D. Kozak, “Factors Affecting Carbon Consumption in the Production of High Carbon Ferromanganese”, INFACON 9, pp 293-301 (2001).

[2] M. Tangstad, “ The High Carbon Ferromanganese Process – Coke Bed Relations”, PhD-thesis, The Norwegian University of Science and Technology (NTNU), 1996.

[3] Fact Sage 5.1, Center for Research in Computational Thermochemistry, École Polytechnique, Montreal, Quebec, 2002.

[4] R. J. Ishak, ”Reaction Kinetics for Reduction of Manganese Ore with Carbon Monoxide in the Presence of Carbon”, PhD-Thesis, The Norwegian University of Science and Technology (NTNU), No. 2002:135, 2002.

[5] S. Ergun, “ Kinetics of the reaction of carbon dioxide with carbon”, J. Phys. Chem., Vol. 60, pp 480-485 (1956).

[6] S. Ergun, M. Mentser, in P. L. Walker (ed), “Chemistry and Physics of Carbon”, p 203, 1965.

[7] D. A. Aderbigbe, J. Szekely, “Studies in coke reactivity: Part 1. Reaction of conventionally produced coke with CO-CO_2 mixtures over temperature range 850-1000 ºC, Iron making and Steel making, No. 1, pp 11-19 (1981)

[8] M. Tangstad, S. E. Olsen, “The ferromanganese process – Material and energy balance”, INFACON 7, pp 621-630 , 1995.

[9] H. Li et al, “Effect of moisture, combined water and volatile elements on fixed carbon requirement in a ferromanganese smelting furnace, 54th Electric Furnace Conference Proceedings, ISS, pp 269-279, 1997.

[10] H. D. Beyer, W. Peters, ”Einfluss von alkalien auf die reaktionsgeschwindigkeit von Hüttenkoks in CO_2-CO-N_2-gemischen”, Arch. Eisenhüttenwes.,Vol 50, Nr. 2, pp47-52 (1979).

[11] J. Davies, J. T. Moon, F. B. Traice, ”Alkalies in the blast furnace”, Iron making and Steelmaking, No. 4, pp 151-161 (1978).

[12] 12 M. Alam, T. DebRoy, ”A comparative study of the roles of KCN and NaCN as catalytic precursors in the Boudouard reaction”, Metal. Trans. B., Vol. 15B, No. 2, pp 400-403 (1984).

[13] Y. K. Rao, A. Adjorlolo, J. H. Haberman, ”On the mechanism of catalysis of the Boudouard reaction by alakli-metal compounds”, Carbon, Vol. 20, No. 3, pp207-212 (1982)

[14] W. H. van Niekerk, R. J. Dippenaar, D. A. Kotze, ”The influence of potassium on the reactivity and strength of coke, with special reference to the role of coke ash”, J. South Afr. Inst. Min.Metall., Vol. 86, No. 1, pp 25-29 (1986)

[15] K. R. Kvam, B. Larsen, H. A. Øye, ”Potassium resistance testing of carbon electrode materials”, Deutsche Keramische Gesellschaft, pp 433-434 (2000).

[16] EU Commission, Integrated Pollution Prevention and Control (IPPC), Reference Document on Best Available Techniques in the Non Ferrous Metals Industries, December 2001.

[17] T. Rosenqvist: “Principles of Extractive Metallurgy”, 2nd ed. McGraw-Hill, New York 1983

[18] K. Esbensen et al: “Multivariate Analysis – in practice”, CAMO, Trondheim, Norway 1994.

[19] H. B. Arntzen: “Alkali and the Boudouard Reaction in the FerroManganese Process”, M.Sc Thesis (In Norwegian), The Norwegian University of Science and Technology (NTNU), 2002.