REACTION MECHANISMS OF CHARCOAL AND COKE IN THE SILICON PROCESS

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ABSTRACT

Silicon metal as a commodity material is produced by carbothermic reduction of quartz in electric submerged arc furnaces, where CO_2 forms as a by-product. Since 1997 the Norwegian Ferroalloy Producers Association have been engaged in research programmes aiming for reduced CO_2-emissions associated with fossil carbon in their processes. One important issue has been to study how charcoal and wood chips perform compared to coal and coke in the silicon process.

The ability of the carbon-rich reduction materials to react with SiO-gas is commonly assumed to be of large importance to the performance of the process. Based on laboratory experiments with different carbon materials, combined with estimation of parameters in a mathematical model of the reaction between carbon and SiO-gas, a foundation for a theoretical study of the performance of the carbon materials in a silicon furnace is established.

1. INTRODUCTION

The most economically feasible way to produce silicon metal as a commodity material of high purity (>99%) is still by carbothermic reduction in an electric submerged arc furnace, approximately 100 years after its introduction as a commercial process. Carbon from charcoal, wood chips, coal and coke is used as reduction agent in the silicon process to release the silicon from quartz. This process requires high temperatures and a lot of energy. The content of trace elements in both the quartz and the reduction materials determines the purity of the produced silicon metal (Myrhaug and Tveit [1]).

The ability of reduction materials to react with SiO-gas, an intermediate product in the silicon process, has during the last decades been a subject of attention. This ability referred to as SiO-reactivity affects the losses of energy rich SiO from the process and therefore also the silicon recovery, the specific energy consumption and the productivity of a given furnace. Several attempts have been made to develop relevant methods to measure the influence of the reduction materials on the performance of the silicon process. The probably most known and used so far is the SINTEF SiO-reactivity test, developed by Tuset and Raaness [2] . A similar method was later developed by Paull and See [3]. Work on another test has been described by Videm [4]. In addition, petrographic analysis has been carried out to understand how the microstructure of coal and coke influences the SiO-reactivity, among others by Raaness and Gray [5].

The present work, which is a part of a doctoral study by Myrhaug [6] focusing on the properties and behaviour of non-fossil reduction materials in the silicon process, has its aim to develop a new method with a mathematical model and estimation of parameters of the reaction kinetics of the reaction between carbon and SiO-gas for various reduction materials. This model can be extended to simulate the effect of the SiO-reactivity of the reduction materials in the silicon process. Some of this work has also been previously published by Myrhaug and Tuset [7].

2. THE SILICON PROCESS

The principal parts of a modern silicon plant are shown in Figure 1. The core of this plant is the electric submerged arc furnace. It consists of a furnace body with the shape of a shallow crucible, which is filled up to its rim with raw materials charged by gravity through a system of silos and tubes as shown. The energy needed for the smelting is delivered as 3-phase alternating current through three carbon electrodes positioned vertically and submerged deep into the charge mixture. 90-95% of the supplied energy is dissipated as heat in gas-filled cavities surrounding the tip of the electrodes.

The silicon forming reactions, which requires temperatures in excess of 1800ºC, take place in these inner zones of the furnace. The produced silicon metal is tapped from the furnace through tapping holes at the connection between the side and bottom of the furnace body. The gas leaving the inner zones carries mostly CO- and SiO-gas. Most of the latter is recovered in the outer (upper) and colder zones of the charge, either by reaction with C in the charged reduction materials to SiC or by condensation to a sticky mass of SiO_2 and Si(l). These materials are transported down to the cavity in the inner zones, while the last fraction of the SiO-gas is lost together with the CO-gas above the top of the charge. This gas mixture mixes with air from the surroundings and burns under formation of CO_2 and silica fumes. The latter, which is mostly amorphous SiO_2, may be recovered in off-gas filters, while the CO_2 enters the atmosphere.

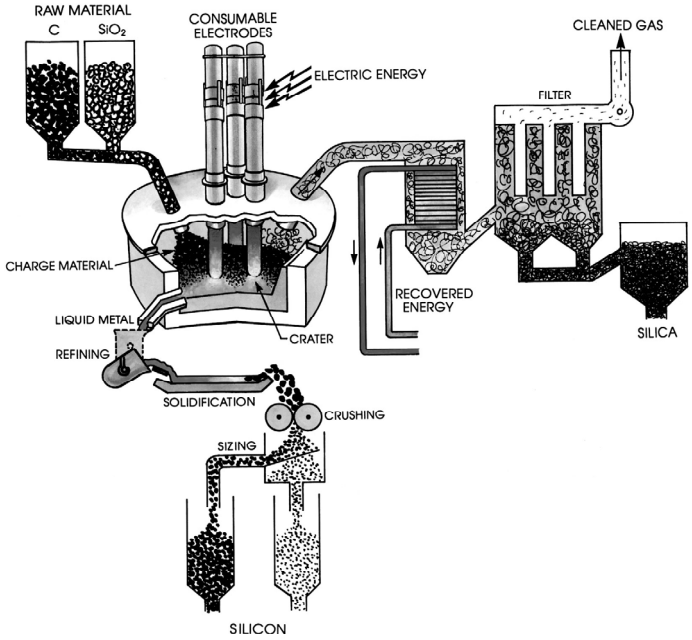


Figure 1. Principal parts of a modern silicon plant. After Schei, Tuset and Tveit.

3. REACTION BETWEEN THE REDUCTION MATERIALS AND SIO-GAS

When coals are exposed to high temperatures at the top of the silicon furnace, they are devolatilized and converted into char or coke before starting to react with the SiO-gas. The wood chips will undergo a similar conversion to charcoal. Due to this, it is assumed in the further discussions that the SiO-gas reacts with coke or charcoal.

Tuset and Raaness [2] found during their work on SiO-reactivity that this property to a large extent is related to the effective diffusivity of SiO-gas in the pores of the reduction materials. Raaness and Gray [5] have investigated the SiO-reactivity and petrography of several chars/cokes as well as the petrography of the coals from which these samples were derived. They described a relation between the microstructure and carbon forms of several chars/cokes and the SiO-reactivity. Based on some assumptions they showed that there is a good correlation between the SiO-reactivity of the chars/cokes and the rank of the coals they are derived from. In addition Raaness, Kolbeinsen and Byberg [9] established a model for prediction of coal properties in the silicon or ferrosilicon production based on multivariate analysis on SiO-reactivity of coke and petrographic properties of the coals they were derived from.

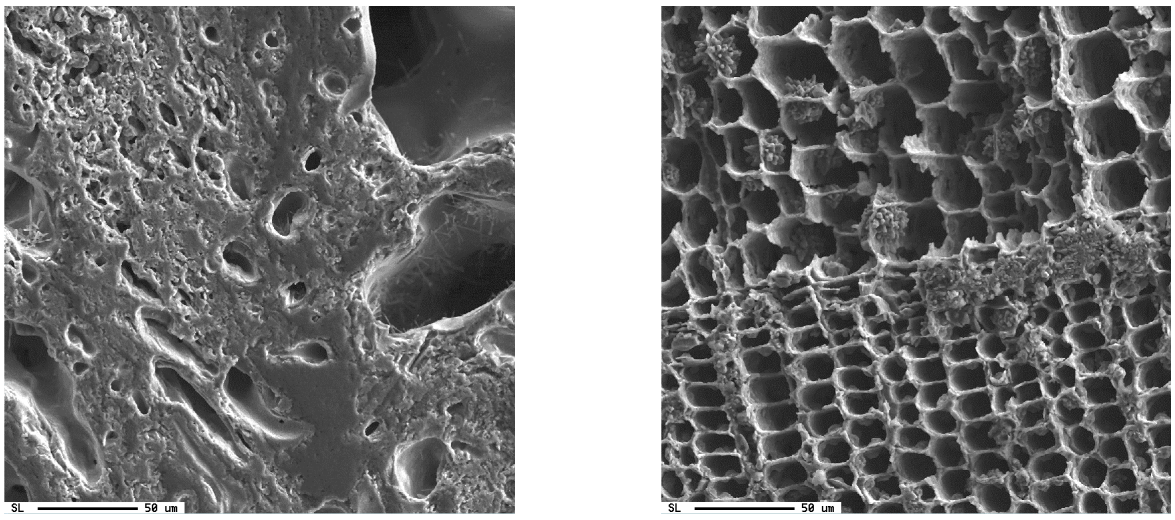
They found that such a model for predicting SiO-reactivity should include the following properties of the coals:

- Distribution and amounts of vitrinite types in the coals or amount of carbon form precursors
- Reflectance
- Amount and distribution of reactive macerals
- Amount and distribution of inert macerals

Figure 2 shows the microstructure of samples of coke and charcoal, respectively, as obtained using a microprobe of type JXA-8900 M WD/ED Combined. The pictures show clearly the porous structure of the samples. The coke displays thicker walls and more inhomogeneous structure and pore sizes than the charcoal, which has very thin walls. The walls in the charcoal can be identified as the cell walls in the wood it was derived from. In both materials the walls in the solid matrix consists of amorphous C.

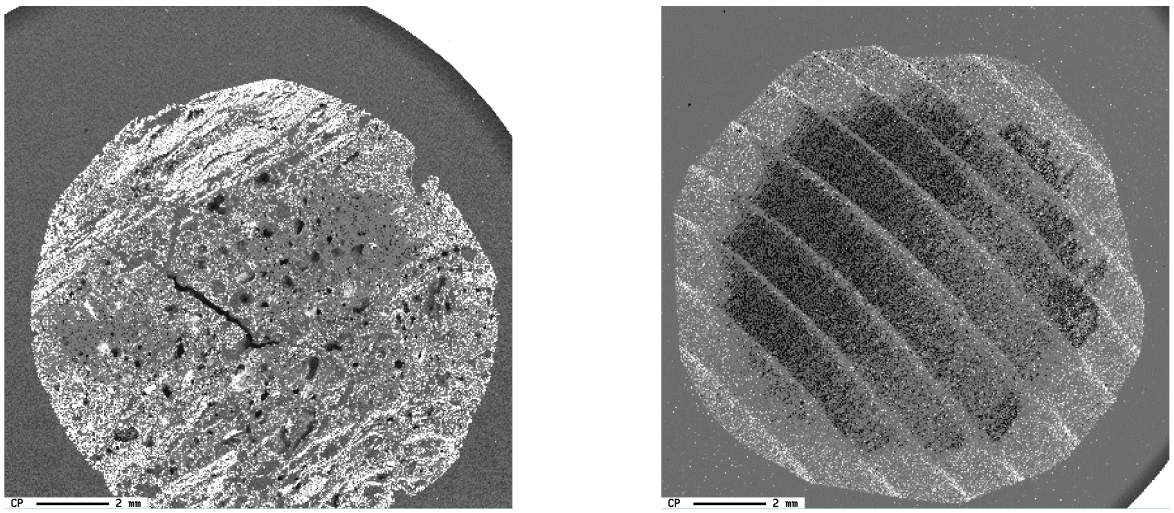
The reaction between the SiO-gas and the C in the reduction materials goes as follows:

$$SiO(g) + 2\,C(s) = SiC(s) + CO(g) \qquad (1)$$



(a) **(b)**

Figure 2. Microprobe pictures showing microstructure of samples of (a) Coke B and (b) Charcoal A (refer to Tables 1 and 2).



(a) **(b)**

Figure 3. Microprobe pictures of porous carbon spheres of (a) Coke B and (b) Charcoal A (refer to Tables 1 and 2) displaying topochemical conversion from carbon particle to SiC. Both spheres are about 50 % converted.

In the equilibrium gas composition established in a charge mixture of SiO_2/C at 1 atm. pressure, this reaction is shifted to the right at temperatures above approximately 1500 °C (Schei et.al. [8]). For a reaction of the above type the conversion is assumed to progress from the outer surface to the interior of a particle, forming a product layer around the unreacted central part. The reaction zone may have a diffuse extension in the radial direction as can be seen from the microprobe pictures displayed in Figure 3, where the cross section of two partially converted carbon spheres are shown.

4. KINETIC MODEL OF REACTION BETWEEN CARBON AND SIO-GAS

According to Sohn [10] the most important group of reactions in metallurgical and materials processing operations consists of those in which a solid reacts with a fluid to produce a coherent layer of porous products. Such reactions may in general be expressed by:

$$a\ \mathrm{A(g)} + b\ \mathrm{B(s)} = c\ \mathrm{C(g)} + d\ \mathrm{D(s)} \qquad (2)$$

4.1 Application of the shrinking core model

The earliest model of gas-solid reactions in this context is the shrinking core model. Among the earliest and most often mentioned contributors to this are Yagi and Kunii [11]. The shrinking core model is based on assumptions of an initially nonporous reactant and progress of the reaction in a topochemical manner from the outer surface of the solid towards the centre. The chemical reaction forms a product (or ash) layer around the shrinking unreacted core of the solid and takes place at a sharp boundary between the two zones. This model is illustrated for conversion of a carbonaceous particle to SiC in Figure 4 and have been extensively studied and applied to a wide range of reactions.

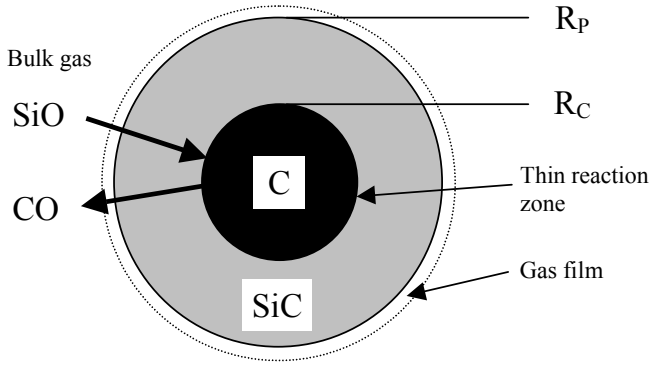


Figure 4. Shrinking core model for carbonaceous sphere.

In the doctoral study of Myrhaug [6] various models for both nonporous and porous solids were used in parameter estimation based on experimental data gathered from thermogravimetric experiments. Afterwards, the models with the found parameters were tested against results from both the thermogravimetric experiments and the SINTEF SiO-reactivity test. The results from the estimation and testing showed that the shrinking core model gave the best prediction of conversion of particles versus time for both the thermogravimetric experiments and the SINTEF SiO-reactivity test, with an overall range of particle diameters from approximately 5 up to 25 mm.

When using the shrinking core model for reacting carbonaceous particles in an atmosphere with SiO-gas some assumptions are made:

- The chemical reaction is going on in an infinitely thin layer on the unreacted core with a radius R_C in a sphere of radius R_P, as showed in Figure 4.
- Reaction (1) at the surface of the unreacted core of C is of first order.
- The concentration profiles of gases within the product layer at any instant time are assumed to be the steady-state profiles over the distance (R_P-R_C) with equimolar counterdiffusion and no accumulation of gaseous species within the particle (pseudo-steady-state approximation).
- Particle volume remains unchanged during conversion.
- There are no temperature gradients within the reacting particle or between the particle and the surrounding gas.

The overall rate of conversion of the particle is determined by both external mass transfer through the gas film at the surface of the sphere, diffusion through the pore structure in the product layer and chemical reaction rate at the surface of the shrinking unreacted core. The relation between degree of conversion and time incorporating these effects for a particle with a shrinking unreacted core is described by many authors, among others Sohn [10], Yagi and Kunii [11], Szekely et. al. [12] and Levenspiel [13]. In this work, spherical particles are assumed, and the following expression for time t versus the overall degree of conversion X is deduced from Sohn [10] and Szekely et. al. [12]:

$$t(X) = \frac{\alpha_C R_p C_C \left(\frac{1}{k_C}\left(1-(1-X)^{\frac{1}{3}}\right) + \frac{1}{D_E}\frac{R_p}{6}\left(1+\frac{1}{K_E}\right)\left(3-3(1-X)^{\frac{2}{3}}-2X\right) + \frac{1}{h_D}\frac{1}{3}\left(1+\frac{1}{K_E}\right)X \right)}{b\left(C_{SiO,B} - \frac{C_{CO,B}}{K_E}\right)} \tag{3}$$

In this equation, k_C is the chemical reaction rate constant in m/s for Reaction (1) and D_E is the effective diffusivity of the gas in the product layer of the sphere in m^2/s. These parameters are assumed to be different for different kinds of carbonaceous materials. h_D is the mass transfer coefficient from the bulk gas to the surface of particle in m^2/s, K_E is the equilibrium constant for Reaction (1), R_P is the radius of the sphere and b is the number of moles of C(s) per mole SiO(g) in Reaction (1). $C_{SiO,B}$ and $C_{CO,B}$ are concentrations of SiO(g) and CO(g) in the bulk gas around the particle. α_C and C_C are volume fraction and molar density of solid C(s) in the particle, respectively. The overall degree of conversion X of C(s) to SiC(s) in the particle ($0 \le X \le 1$) may be calculated from the radii R_P and R_C with the formula:

$$X = 1 - \frac{R_C^3}{R_P^3} \tag{4}$$

Reaction (1) results in a weight increase for the particle, and if the weight is recorded during conversion, for instance as a part of an experiment, the degree of conversion may be calculated from measurements with the formula:

$$X = \frac{(m_P - m_{P0})}{w_{FC0} m_{P0} (40.10 - 2 \cdot 12.01)/(2 \cdot 12.01)} \tag{5}$$

where m_P is the actual weight, m_{P0} is the initial weight of the particle and w_{FC0} is the mass fraction of fixed carbon. m_P, m_{P0} and w_{FC0} are all recorded or calculated without content of volatile matter in the particle. 12.01 and 40.10 are molar weights of C(s) and SiC(s), respectively. The formula depicts that the 2 moles of C(s) react to 1 mole of SiC(s). The overall rate of conversion can be derived from Equation (3):

$$\frac{dX}{dt}(X) = \frac{\frac{b}{\alpha_C C_C R_P}\left(C_{SiO,B} - \frac{C_{CO,B}}{K_E}\right)}{\frac{1}{k_C}\left(\frac{1}{3}(1-X)^{-\frac{2}{3}}\right) + \frac{1}{D_E}\frac{R_p}{6}\left(1+\frac{1}{K_E}\right)\left(2(1-X)^{-\frac{1}{3}}-2\right) + \frac{1}{h_D}\frac{1}{3}\left(1+\frac{1}{K_E}\right)} \tag{6}$$

5. THERMOGRAVIMETRIC EXPERIMENTS AND ESTIMATION

5.1 Equipment and procedures

Laboratory experiments on single spheres of carbon using a thermogravimetric method are carried out in a controlled atmosphere containing known concentrations of SiO, CO and Ar at a temperature of 1650°C, and with a chosen flow rate of the gas. By recording the weight of the sphere continuously during the experiments, and using the fact that conversion from C to SiC results in a certain increase of weight, it is possible to estimate k_C and D_E by curve fitting (linear regression). A sketch of the experimental equipment is given in Figure 5, but a more detailed description is found in the thesis by Myrhaug [6]. The diameters of the spheres used in the experiments were in the range 8-25 mm. Some precautions have been made in order to prevent unwanted chemical reactions with surrounding parts in the reaction chamber.

Typical time series for weight and temperature from one experiment are given in Figure 6. About two hours are spent in order to reach 1650°C, and at approximately 1500°C the weight starts to increase due to available SiO-gas supplied from a separate reaction chamber which is heated at nearly the same rate as the spherical sample itself. This chamber is filled with an agglomerate of SiO_2 and SiC in order to produce SiO- and CO-gas according to the reaction:

$$2SiO_2 + SiC = 3SiO(g) + CO(g) \quad (7)$$

Argon is used as carrier gas at a constant flow rate upwards through the reaction chamber. The SiO-source is kept at a slightly lower temperature than the carbon sphere in order to ensure that an increase in weight of the sphere is caused by Reaction (1) and not by condensation of SiO-gas.

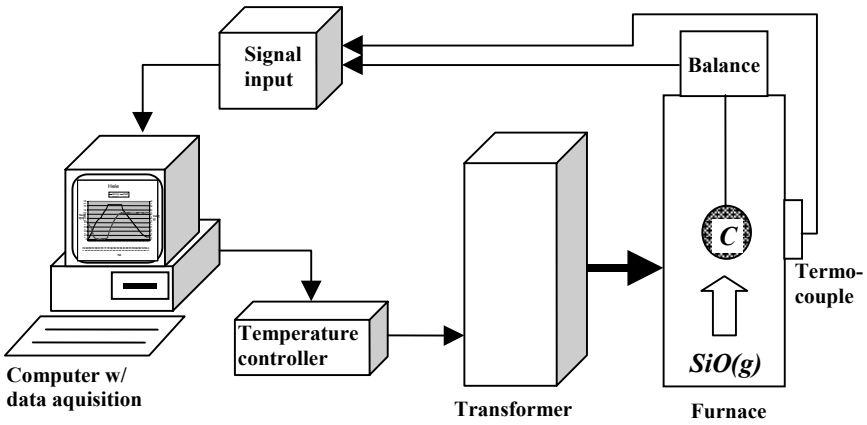


Figure 5. Main principles of equipment used during experiments.

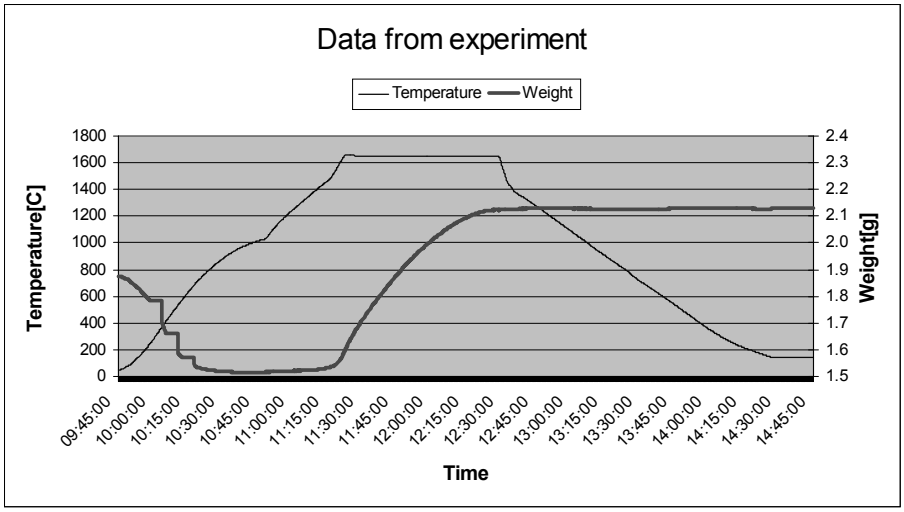


Figure 6. Data from one experiment showing the temperature and weight of a carbon sphere.

5.2 Estimation of kinetic parameters

The kinetic parameters D_E and k_C in the shrinking core model in Equation (3) are estimated from the recorded time series for weight by calculating the degree of conversion from Equation (5) and fitting the shrinking core model to the experimental data for time versus degree of conversion. The model is fitted to the data by using the method of least squares as described by among others Kreyzig [14].

Data from three or more experiments with spheres from the same material, but with different radii, are combined and used as basis for the estimation of the kinetic parameters for that particular material. The combination of data in this way is done to ensure physically realistic or valid estimates of D_E and k_C for the whole range of R_P investigated for each kind of carbonaceous material. In addition, some corrections were made to the data and the shrinking core model to improve the quality of the estimated parameters. Further details about this and the experimental techniques applied are described in the thesis of Myrhaug [6].

5.3 Results

The types of carbonaceous materials selected for testing in the laboratory experiments using a thermogravimetric method are listed in Table 1 together with their approximate analysis and results from specific surface measurements using nitrogen adsorption, pore size distribution using mercury intrusion porosimetry and absolute density using helium. The results from estimation of the kinetic parameters D_E and k_C for each investigated carbonaceous material are given in Table 2 where also the results of the SINTEF SiO-reactivity test are included. The latter test is described by Tuset and Raaness [2], who also estimated D_E and k_C from experiments in the equipment used for that. For a medium reactive coke they arrived at $D_E = 2 \cdot 10^{-5}$ m^2/s and $k_C = 8 \cdot 10^{-2}$ m/s, while for a less reactive coke they found $D_E = 6 \cdot 10^{-6}$ m^2/s and $k_C = 4 \cdot 10^{-2}$ m/s. These values correspond very well with the values listed in Table 2. Two materials have a double set of SiO-reactivity measurements, one displaying some variance. This is probably due to the fact that there were some variations between samples of the same material. Charcoal A, C, D and E are charcoals produced in laboratory scale experiments as a part of a diploma work at the Norwegian University of Science and Technology [15], while the others are samples from reduction materials used in the ferroalloy industry.

To illustrate the ability of the shrinking core model to represent the conversion of single spheres, some examples of data from selected experiments are presented in Figure 7 and compared with simulations using the shrinking core model and the estimated parameters listed in Table 2. While the time series are from individual experiments, the corresponding model calculations are based on estimated parameters D_E and k_C that are obtained from fitting of the model to data from a group of experiments with the same kind of material. The obtained parameters represent therefore some kind of average values, which evens out the differences in properties of individual spheres. This may explain some of the deviations between experimental data and the model calculations, as seen for at least two of the materials in Figure 7 (b) and (c). In addition, the carbonaceous materials used as reducing agents in the ferroalloy industry are generally inhomogeneous. Measurements using mercury intrusion porosimetry show that they have a distribution of pore sizes. Petrographic analysis shows that the fossil carbons contain a number of carbon forms, which are assumed to have different reactivities against SiO-gas. This may give an effective diffusivity and a reaction rate constant that both are depending on the degree of conversion of the particles. The shrinking core model does not incorporate these effects.

Table 1. Proximate analysis and porosity measurements of the tested reduction materials.

Material	Proximate analysis			Porosity parameters				
	Fixed carbon [%]	Volatiles [%]	Ash [%]	Porosity [%]	Spec. surface [m^2/g]	Pore volume [cm^3/g]	Abs. density [g/cm^3]	Geom. density [g/cm^3]
Charcoal A	74.6	25.0	0.4	85.4	1.5	2.82	2.05	0.30
Charcoal B	82.2	17.4	0.4	56.1	0.9	0.74	1.74	0.76
Charcoal C	77.2	21.5	1.3	76.7	1.3	1.64	2.00	0.47
Charcoal D	76.2	22.7	1.1	84.2	1.7	2.66	1.99	0.32
Charcoal E	74.7	24.9	0.4	76.7	1.5	1.85	2.00	0.42
Charcoal F	77.1	13.3	9.6	72.4	2.7	1.38	1.89	0.52
Coal A (calcined)	98.1	0.3	1.7	42.0	0.1	0.42	1.72	1.00
Coal B (calcined)	97.7	0.3	2.0	50.2	0.6	0.58	1.74	0.87
Coke A	94.6	3.6	1.8	55.9	1.3	0.74	1.68	0.74
Coke B	91.5	3.0	5.5	51.9	1.4	0.60	1.69	0.81

Table 2. Estimated effective diffusivity (D_E) and reaction rate constant (k_C) for different reduction materials, compared with results from SINTEF SiO-reactivity test.

Material	Kinetic parameters		SiO-reactivity test		
	D_E [m^2/s]	k_C [m/s]	SiO-reactivity [ml SiO]	Weight incr. [%]	Reactivity classification
Charcoal A	1.19E-04	0.0644	281	45	High
Charcoal B	5.78E-04	0.0263	975 / 974	59.1 / 72.0	Normal
Charcoal C	1.77E-04	0.0424	495	58	High
Charcoal D	2.49E-02	0.0431	160	33	High
Charcoal E	1.47E-03	0.0344	302	35	High
Charcoal F	1.14E-03	0.0382	275	45	High
Coal A (calcined)	1.81E-05	0.0712	1275	51	Normal
Coal B (calcined)	2.67E-05	0.0676	1114	71	Normal to high
Coke A	5.90E-05	0.0219	900	45	High
Coke B	5.16E-06	0.0400	1400 / 2110	50.0 / 33.4	Very low

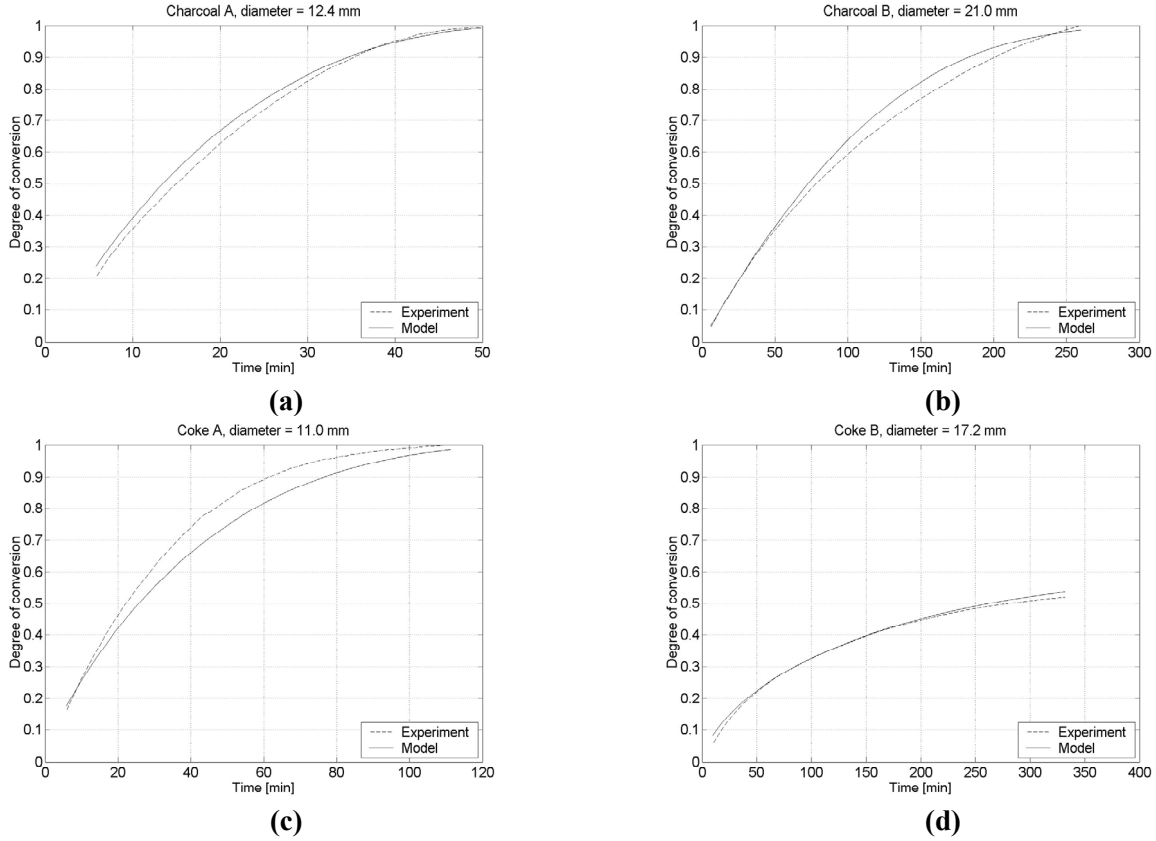


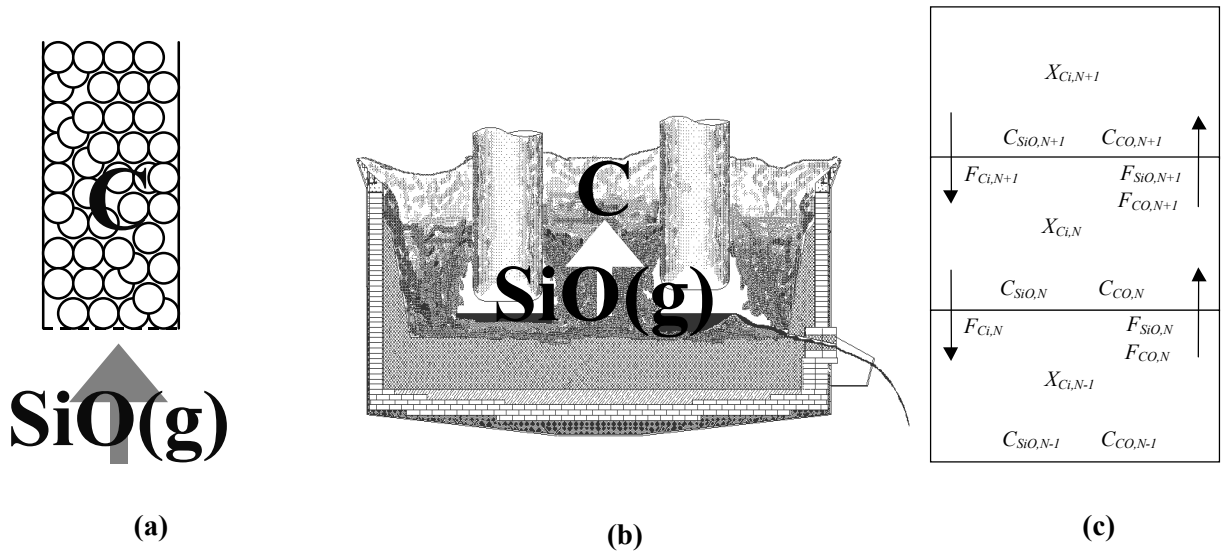
Figure 7. Example of data from individual experiments and results from simulations with shrinking core model for some carbonaceous materials with diameters as given. (a) Charcoal A, (b) Charcoal B, (c) Coke A and (d) Coke B.

6. MODEL CALCULATION OF PACKED BEDS

6.1 Model description

The kinetic parameters D_E and k_C, when known, can be used to predict how efficient a given reduction material can be in recovering the SiO-gas according to Reaction (1) in a packed bed. In the charge mixture of a silicon furnace the particles of both reduction materials and quartz form a packed bed. Formulas for gas-solid reactions in packed bed combined with the shrinking core model for individual spherical particles are described among others by Szekely et. al. [12]. The parameters found for the shrinking core model for single spheres can be used directly in these formulas. This means that the results from experiments on single spheres can be used to model the behaviour of various reduction materials with respect to their reaction with SiO-gas in the charge mixture of a silicon furnace. Also SINTEF's SiO-reactivity test, where SiO-gas flows through a bed of nearly spherical and equally sized carbonaceous particles that are converted to SiC, can be modelled in the same way. This gives a good possibility to compare results with this test. Both these cases are illustrated in Figure 8 (a) and (b).

The model of a packed bed is made up of mass balances of carbon and SiO- and CO-gas for a number of control volumes as generally described by Patankar [16]. The model includes the possibility of using two carbon types of different diameters and properties in order to investigate combinations of reduction materials, but is isothermal and at present stage restricted to 1650°C because the reaction kinetic parameters are based on data from experiments carried out at this temperature. Figure 8(c) gives a schematic overview of the control volumes and the main variables involved. In present formulation, the mass and degree of conversion of carbon is evaluated in the middle of the control volumes assuming to be an average for the whole control volume. Plug flow of both solids and gases is assumed. Upwind-difference scheme (Patankar [16]) is used to handle the flows of mass at the boundaries of the control volumes, where also the gas concentrations (alternatively pressures) are evaluated.



(a) **(b)** **(c)**

Figure 8. (a) The packed bed in the SINTEF SiO-reactivity test, (b) the packed bed in the silicon furnace, and (c) schematic overview of the model of the packed bed with control volumes and main variables.

The mass balance for the two types of carbon in one control volume is given by

$$\frac{dm_{Ci,N}}{dt} = r_{Ci,N} + F_{Ci,N+1} - F_{Ci,N} \tag{8}$$

where N is the number of the actual control volume, $m_{Ci,N}$ is the mass of unreacted carbon type i in that control volume, $r_{Ci,N}$ is the reaction rate of carbon type i and $F_{Ci,N}$ is the flow of unreacted carbon of type i out of the control volume. By defining an initial mass of unreacted carbon in all the control volumes (in case of a fixed bed as in the SINTEF SiO-reactivity test) or mass of unreacted carbon of type i added at top of the uppermost control volume (in the case of the moving bed of the silicon furnace), in both cases denoted $m_{Ci,0}$, and a mass flow of unreacted carbon $F_{Ci,0}$ at the top of the packed bed, new useful relations can be established:

$$m_{Ci,N} = m_{Ci,0}(1 - X_{Ci,N}) \tag{9}$$

$$F_{Ci,N} = F_{Ci,0}(1 - X_{Ci,N}) \tag{10}$$

where $X_{Ci,N}$ is the degree of conversion of carbon of type i in the actual control volume in the packed bed. The reaction rate of carbon may be given by

$$r_{Ci,N} = -m_{Ci,0}\frac{dX_{Pi,N}}{dt} \tag{11}$$

where $dX_{i,N}/dt$ is the rate of conversion for a single sphere made up of carbon of type i as defined by Equation (6). The mass balances of carbon can then be reformulated into balances of the degree of conversion for a whole control volume:

$$\frac{dX_{Ci,N}}{dt} = \frac{dX_{i,N}}{dt} + \frac{F_{Ci,0}}{m_{Ci,0}}\left(X_{Ci,N+1} - X_{Ci,N}\right) \tag{12}$$

The necessary parameters in Equation (6) are known from the experiments with single spheres, except the concentrations of SiO and CO in the bulk-gas, which must be computed by separate mass balances.

Pseudo-steady-state approximation is used for the gas concentrations in the packed bed, which gives

$$C_{SiO,N+1} = C_{SiO,N} - \sum_i \frac{1}{2} \frac{n_{Ci,0}}{Q_{GAS}} \frac{dX_{i,N}}{dt} \tag{13}$$

$$C_{CO,N+1} = C_{CO,N} + \sum_i \frac{1}{2} \frac{n_{Ci,0}}{Q_{GAS}} \frac{dX_{i,N}}{dt} \tag{14}$$

where $n_{Ci,0}$ is the initial amount of unreacted carbon of type i in moles in one control volume and Q_{GAS} is the volumetric flow of gases upwards in the bed. These quantities and the initial concentrations of SiO and CO at the entrance of the packed bed in the bottom, $C_{SiO,0}$ and $C_{CO,0}$ are parameters in the model. Composition of gases is presented for the user of the model as pressures, and the ideal gas law is used for conversion between pressures and concentrations of gases. The SINTEF SiO-reactivity test and a silicon furnace were simulated using the given equations and the parameters given in Table 3. The results are presented and discussed in the next subsections.

Table 3. Main parameters used in the simulations of the SINTEF SiO-reactivity test and the outer zone of the silicon furnace.

Description	**SINTEF SiO-reactivity test**	**Outer zone of silicon furnace**
Gas composition at inlet in bottom	$p_{SiO,0}$=0.135, $p_{CO,0}$=0.045, $p_{Ar,0}$=0.82	$p_{SiO,0}$=0.5, $p_{CO,0}$=0.5
Temperature	1650°C	1650°C
Packing density of bed[a]	0.65	0.65
Height of bed	6.0 cm	1.5 m
Cross-section area of bed	3.14 cm^2	5 m^2
Particle diameter	0.52 cm	1.0, 2.0, 3.0 cm
Amount of initially unreacted carbon	1.95-7.40 g[b]	1350-2940 kg[c]
Gas flow at 1650°C	46.0 cm^3/s	7.385 m^3/s
Flow of quartz and initially unreacted carbon[d]	0 kg/s (fixed bed + no quartz)	F_{SiO2}=1.41 kg/s $F_{C,0}$=0.51 kg/s

[a]Assumes dense random packing of equally sized spheres.
[b]From weighing of samples for the experiments with SINTEF SiO-reactivity test
[c]Calculated from bulk weight of quartz, packing density of bed and geometric density of carbon particles from Table 2.
[d]Assuming furnace load of 20 MW, specific energy consumption of 3950 kWh/ton quartz from energy balances carried out by Schei et. al. 9.[8] and fixed carbon coverage of charge mixture of 90 %

6.2 Simulations of the SINTEF SiO-reactivity test

Diagrams from simulations of the SINTEF SiO-reactivity test are presented in Figure 9 and Figure 10. The first of these shows calculated degree of conversion of carbon as a function of time at different levels in the packed bed and the CO-pressure at the top of the packed bed. The latter is compared with results from a SiO-reactivity test in laboratory with the same reduction material. In Figure 10 CO-pressures on top of the bed during experiments and from simulations are compared for four different reduction materials. Even though the diameters of the spheres used in the SINTEF SiO-reactivity test are about half of the smallest used in the thermogravimetric experiments for single spheres, it appears that the shrinking core model with the estimated parameters is able to predict the behaviour of the SINTEF SiO-reactivity test for a wide range of reduction materials, from low reactive to high reactive. This validates both methods in terms of providing a measure of the reaction kinetics or the ability of the carbonaceous materials to react with SiO-gas.

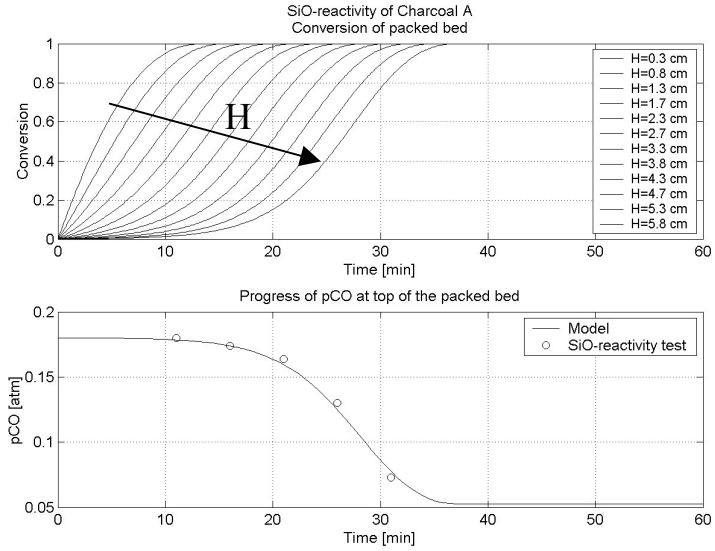


Figure 9. Simulation and comparison of results with the SINTEF SiO-reactivity test for Charcoal A.

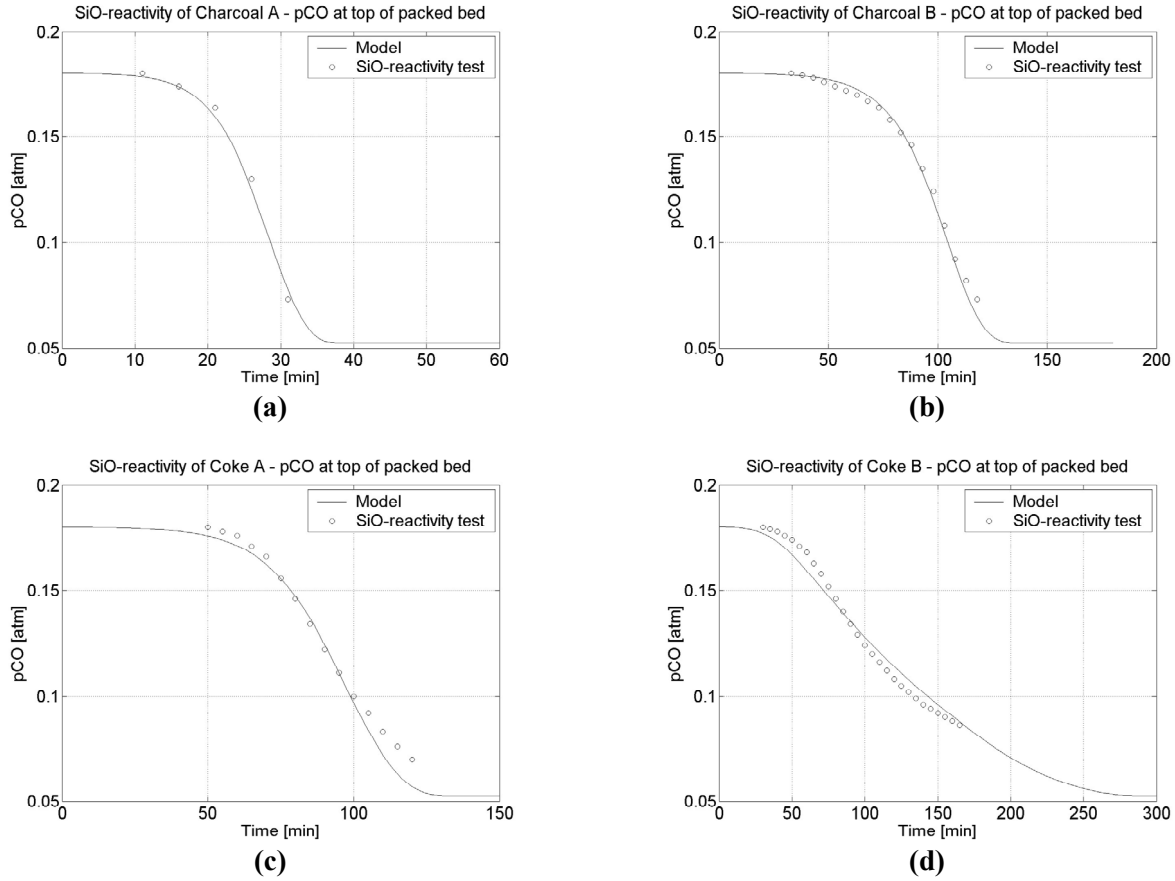


Figure 10. Simulation and comparison of results from the SINTEF SiO-reactivity test for carbonaceous materials, showing progress of p_{CO} at the top of the packed bed for (a) Charcoal A, (b) Charcoal B, (c) Coke A and (d) Coke B.

6.3 Simulations of the outer zone of a silicon furnace

Diagrams from simulations of the outer zone of a silicon furnace are presented in Figure 11. Conversion of carbonaceous particles of various kinds and diameters compared in Figure 11(a)-(c). It is evident from these diagrams that Charcoal A requires shorter time or distance to be completely converted to SiC than the cokes as would also be expected from the SiO-reactivity test. Similarly, Coke A is converted much faster than Coke B. When increasing the diameter of the Charcoal A to 20 mm, it is converted approximately as fast as Coke A with diameter 10 mm, but when the size of Charcoal A is increased to 30 mm, it is converted slower than Coke A with diameter 10 mm.

In Figure 11(d) the effect of mixing Coke A and Charcoal A with diameters 10 mm on the overall conversion of carbon in the upper zone of the furnace is demonstrated. The two reduction materials are mixed in ratio 1:1 on fixed carbon basis.

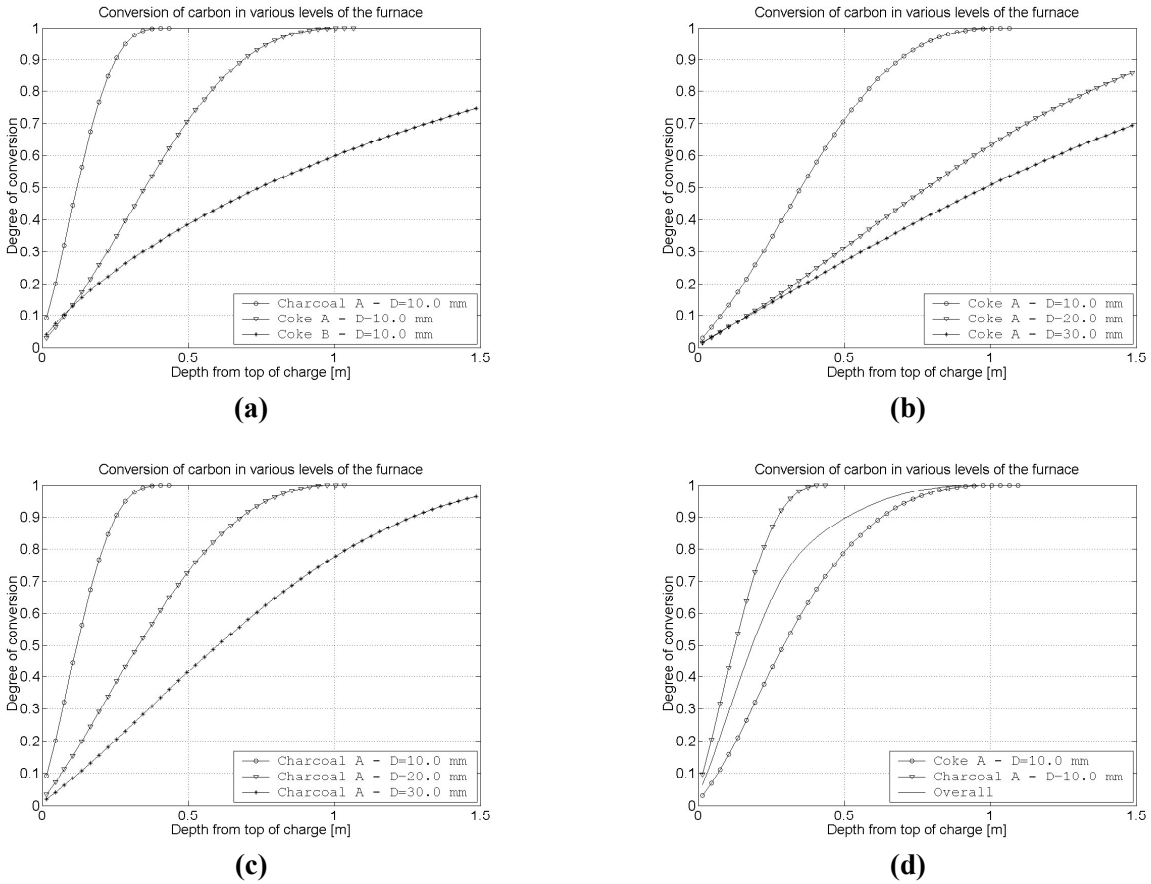


Figure 11. Conversion of carbon in various levels of the charge mixture in a silicon furnace comparing various reduction materials with various sizes. Cases depicted here are (a) Charcoal A, Coke A and Coke B of diameters 10 mm, (b) Coke A of diameters 10, 20 and 30 mm (c) Charcoal A of diameters 10, 20 and 30 mm. In (d) the effect of mixing Coke A and Charcoal A of diameter 10 mm in equal amounts on fixed carbon basis is presented.

The simulations were originally based on design data for a 20 MW silicon industrial furnace. When doing the simulations, it became evident that using the whole available cross section area and height within the furnace lining for the packed bed model resulted in complete conversion of the reduction materials in a very short distance from the top of the charge mixture. It is known that this is necessarily not the case, and some reduction materials may even pass partly unreacted to the inner zone of the furnace (Schei et. al. [8]). Therefore, both the cross section area and height of the packed bed were decreased until a more realistic behaviour was indicated. The cross-section area and the height of the reacting bed were set to 5 m^2 and 1.5 m, respectively. These restrictions resulted in higher velocities of the gases and the solids, as the total mass flows were kept at the original levels, which gave less time for contact between the reacting species. This proved to give results that clearly distinguished between the various reduction materials.

Meanwhile, it must be pointed out that the results from the simulations have not been analysed thoroughly and compared with data from industrial furnaces. Therefore, there are uncertainties about to what extent the results represent the behaviour of the reduction materials in an industrial furnace. Even so, the simulations demonstrate differences between the reduction materials that seem logical.

Some other simplifications and assumptions were also made to minimise the number of parameters that could vary and affect the interpretation of the simulated cases:

- The flows of quartz and carbon were constant, with fixed carbon coverage of the charge mixture held at 90 %.
- The gas flow and gas composition entering the bed of reduction materials from inner zones of the furnace were held constant for all cases, not taking into account the total stoichiometry of the furnace
- The temperature was held at 1650°C, as the shrinking core model and the packed bed model are isothermal and the kinetic parameters were estimated with data from experiments at this temperature.

7. CONCLUSIONS

Based on laboratory experiments where the reaction kinetics between carbonaceous spheres and SiO-gas were studied, estimation of kinetic parameters in a mathematical model, which describes the degree of conversion versus time, was carried out. The shrinking core model proved to give the best description of the overall reaction kinetics for the particles, but does not give a complete representative description of the conversion progress in the inner of the particles. Some deviations between the shrinking core model and the experimental data are observed. Most of these deviations are probably due to the inhomogeneous nature of the carbonaceous materials.

The estimated parameters were used in packed bed models with the shrinking core model for the individual particles to study theoretically how different reduction materials perform in the SINTEF SiO-reactivity test and in a silicon furnace. Results from simulations and experiments with the SINTEF SiO-reactivity test were compared and agreed very well. This validated in high degree the chosen model and the estimated parameters. In addition, the estimated parameters agreed with results from an earlier work.

Similarly, based on the mentioned models and parameters, several cases were simulated for a hypothetical silicon furnace with some selected reduction materials of various sizes and spanning a range of SiO-reactivity figures. In order to achieve reasonable differences in responses for the selected reduction materials, the cross section area and height of the bed were assumed substantial smaller than the available space within the lining of the furnace. The validity of these assumptions is somewhat uncertain, as the results have not been compared with data from industrial furnaces. However, the simulations indicate some differences between the reduction materials that appear logical.

8. ACKNOWLEDGEMENTS

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