

# Crust Formation in a (Ferro)Silicon Furnace

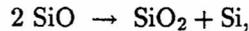
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## Abstract

Elkem Research brought two problems concerning the (ferro)silicon process in an electric furnace to the 27th ESGI.

The first problem concerned suggestions for and discussion of, improvements to an existing unidimensional model of the silicon process. The unidimensional model was developed to describe dynamic aspects of the thermo-chemical processes occurring within the furnace. A major area for improvement in the model is in providing a more accurate description of the hearth region of the furnace.

The second problem concerned the proposal of mathematical models to describe mechanisms for the formation of a hard crust at the furnace top. Crust formation appears to be dominated by SiO-condensation, due to the reaction:



which occurs near the top of the furnace for sufficiently low temperatures.

## 1 Introduction.

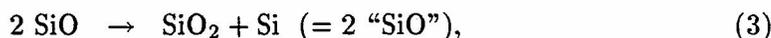
At Elkem a/s, ferrosilicon is produced in large three-phase electric furnaces. A charge consisting of quartz ( $\text{SiO}_2$ ), coal (C) and iron ore is supplied to the top of the furnace. The product, ferrosilicon, is formed at high temperatures ( $\approx 2300\text{K}$ ) and is tapped at the bottom of the furnace. The furnace can be pictured as a large vessel containing one or more vertically oriented cylindrical electrodes. The furnace is then conceptually divided into "hearth" regions under the electrodes, where it is very hot, and "shaft" regions alongside the electrodes, where it is cooler; see Fig. 1. The charge of raw materials is at approximately room temperature when supplied to the top of the furnace and is "forced" into the furnace by stoking. The stoking takes place after a certain amount of SiO and CO gases has escaped from the top of the furnace, with each stoking cycle taking approximately one hour.

In the hearth of the furnace, during each stoking cycle, a gas filled cavity is formed around the tip of each electrode. During operation the size of the cavity increases as the charge materials are consumed on the sides and at the bottom of the cavity. This continues until either the layer of charge material at the top of the cavity breaks down or the shaft material is stoked down into the hearth and new materials are added at the top, thus starting a new stoking cycle.

The overall process is strongly endothermic (hence the large electrodes) and is dominated by the silicon reactions. For this reason, one can concentrate largely on the production of pure silicon, ignoring the iron. The main components in the silicon process are: C, SiC and SiO<sub>2</sub> (solids); Si and SiO<sub>2</sub> (liquids); SiO and CO (gases). An additional component is a SiO “condensate”, denoted by “SiO”, which consists of a mixture of Si and SiO<sub>2</sub>. The melting temperatures of “SiO”, Si and SiO<sub>2</sub> are approximately 1700K and the temperatures in the furnace are in the ranges of 300 – 2200K in the shaft and 2200 – 2400K in the hearth. The two dominant reactions that take place in the hearth of the furnace are:



The first of these reactions produces Si, which can be tapped. The second reaction consumes some of this Si in producing SiO. In the shaft region two reactions dominate:



The production of SiO in the hearth and its recovery in the shaft are the essential steps in the process. The hearth of the furnace must be in a state where silicon can be produced. This gives conditions on the temperatures and a lower bound for the SiO-pressure in the hearth. The gas exiting the top of the furnace also contains CO, which has been produced in the hearth via (1). However, if the gas exiting the top of the furnace contains a high content of SiO, then this means that the rate of silicon recovery at the bottom of the furnace will be low. Reactions (3) and (4) govern the recovery of SiO. Reaction (3) involves the condensation of gaseous SiO, whilst through (4) a certain amount of SiO reacts with carbon present in the charge. A by-product of the process is silicon carbide, SiC, a hard porous solid material which is deposited both at the bottom and on the walls of the hearth, whenever there is too much SiC to be consumed in reaction (1). It is favourable to have all the carbon used in the shaft of the furnace, but conversely one does not want too much SiC to enter the hearth. This gives some bounds on the content of carbon in the charge.

Furthermore, there is the formation of a hard crust at the walls of the furnace in the upper part of the furnace. The crust consists mainly of SiO<sub>2</sub> (which can occur in different structures, i.e. crystals), but also carbon, silicon and silicon carbide are found in the crust. After some months or years of operation the hard layer of SiC in the hearth, and/or the crust, may get too thick for the furnace to function well and it then needs to be emptied, with a consequent productivity penalty.

## 2 Current process models and proposed improvements.

Elkem a/s have had an ongoing research programme into various aspects of the ferrosilicon process since the 1950’s. Initially the mathematical aspects of this programme were

confined to the development of a stoichiometric model, which has yielded much information about the basic operational requirements of the process. However, to reflect the essentially dynamic nature of the process (e.g. the variations throughout the stoking cycles), starting in 1984, Dr Halvorsen has been developing a unidimensional dynamic model of the (pure) silicon process.

The essential elements of the current model are as follows. Firstly, there is a set of sub-models giving the kinetic rate laws for each chemical reaction. The shaft region of the furnace is then modelled through a set of coupled partial differential equations, describing mass conservation for each species, together with a one-dimensional heat conservation equation. Solid phase velocity is determined by assuming that all gases, liquids and "SiO" occupy only the interstitial spaces between granules of solid charge, and then by assuming that any further voids created (e.g. by reaction and/or melting) are filled immediately by the solid flow. The liquid phase mass flux is computed backwards from an equation for the total conservation of the liquid phase, and the gas velocity is computed by including the additional assumption that the sum of the partial gas pressures is 1 atm. The shaft equations are coupled through boundary conditions to a set of ordinary differential equations describing the hearth region of the furnace. These ordinary differential equations describe species/mass conservation and heat conservation.

This unidimensional model has been solved numerically for a range of process conditions, both when the furnace is stoked continuously and in cycles. Although very useful, it has been recognised by Elkem that there are still a number of deficiencies in the model. Possible areas for improvement of the unidimensional model that have been proposed include the following.

- Shaft region:

- The electrodes also provide power to the shaft region.
- Heat losses through the furnace walls in the shaft region can be included.
- Improve the description for the flow of solids and liquids.
- The volume fraction occupied by the solids is not constant.
- The carbon electrode is, as well as an energy source, a supplier of carbon to the process.

- Hearth region:

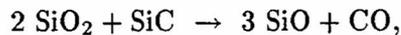
- The finite size of the hearth region should be included, perhaps by a distributed hearth region model consisting of one or more zones/computation cells of finite volume.
- The reactions taking place in the hearth and the effects that these reactions have on the hearth volume need to be reexamined.
- Include heat losses by conduction through the bottom and walls of the hearth region.
- The position of the electrodes, which is adjusted by the furnace control system, can be included in this description.

- Include continuous or limited tapping periods of the silicon.
- Slagging may occur, when viscous  $\text{SiO}_2$  and solid  $\text{SiC}$  are tapped along with the silicon.

One major aim of Elkem a/s, in bringing this problem to the study group, was to discuss ways of incorporating some of the above effects into the unidimensional model. The foremost consideration in doing this however, was that improvements suggested should be able to be incorporated reasonably simply into the current computational framework. During the week many of the above problems were discussed, with various participants at the study group making practical suggestions, mostly in keeping with the spirit of the current model. The suggestions focussed mainly on an improved description of the furnace hearth region. Below are outlined some of these suggested improvements.

1. A single zone finite volume hearth model was recommended as an initial improvement. In this model the hearth is described by variables for the volume, the floor area, the wall area and the height below the electrode tip. There were some arguments for considering a multi-zone model, with different phases and species present in each zone, but the inter-zone reaction/transfer rates then become difficult to model.
2. Currently the mass flux into the hearth region is partially determined by a boundary condition on the solid phase velocity, between the hearth and shaft regions. The influence of the finite size of the hearth region can be included by a smooth "cut-off" of the solid phase velocity when a certain critical volume of solid is exceeded in the hearth. This critical volume can be determined approximately from the maximum amount of new charge material that can be added at the top of the furnace after stoking in each stoking cycle.
3. If there is too much  $\text{SiC}$  in the hearth region, then reaction (1) cannot consume it fast enough, and the surplus becomes deposited on the sides and walls of the hearth. It was suggested that this effect be incorporated via an additional "reaction" (postulated to take place when the total mass of  $\text{SiC}$  in the hearth exceeds a certain critical mass), which converts normal "active"  $\text{SiC}$  to another species of "inactive"  $\text{SiC}$ , only present in the hearth. The reaction rate and critical mass of active  $\text{SiC}$  need to be determined/modelled.
4. Of the inactive  $\text{SiC}$  formed in the hearth, an amount proportional to the hearth wall area is deposited on the walls; the remainder is deposited on the floor of the hearth. Given a known hearth floor area, the height of the "layer" of inactive  $\text{SiC}$  deposited on the bottom of the hearth can be computed, and then this can be continuously subtracted from the hearth volume.
5. Also for given hearth floor area and mass of silicon in the hearth, the height of the pool/layer of liquid  $\text{Si}$  can be computed, including in the computation any  $\text{Si}$  that has been tapped.

6. The position of the electrode is usually adjusted to maintain a constant power input, which corresponds (approximately) to maintaining a constant distance from the electrode tip to the top of the layer of liquid Si on the base of the hearth.
7. In the current model the reaction rate for (2) is not assumed to depend upon the concentration of Si. This is because normally there is a plentiful supply of Si in the hearth, with which the SiO<sub>2</sub> can react. It was suggested that the reaction (2) would be influenced by the amount of liquid Si in the hearth region, when this amount is small, and that this effect should also be incorporated. This highlighted the problem that, if reaction (2) is “cut-off” for a low mass of Si, then there is no mechanism in the current model for the production of SiO gas, which is potentially catastrophic for the process. Thus, it would then be necessary to reintroduce into the model the reaction:

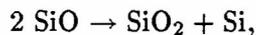


which is known to take place in the hearth, but is not dominant usually.

8. It was suggested that heat losses, by conduction, through the bottom and walls of the hearth region be included computationally by two separate, fairly coarse, one-dimensional finite-volume heat transfer models. The thickness of inactive SiC on the bottom of the hearth is usually much greater than that on the sides of the hearth. Thus, the two models should correspond to the sideways and downwards heat losses respectively. A number of different process response time scales have already been identified from the existing unidimensional model. It was suggested that a variable thickness of volume elements be used in each of these two models, and that the different element thicknesses used should correspond to the distance of propagation of a thermal transient on each of the different time scales.

### 3 Crust formation close to the furnace top.

The second problem area of interest to Elkem a/s, in coming to the study group, concerned the proposal of mathematical models to describe mechanisms for the formation of a hard crust near the top of the furnace. Reactions (3) and (4) are both exothermic and can take place at the lower temperatures that are found in the furnace shaft. Close to the top of the furnace a hard crust of porous material may be formed, consisting of SiO<sub>2</sub>, C and SiC. It is believed that the crust formation is dominated by the SiO-condensation,



which (depending on the temperature), can produce a hard glass-like solid. In extreme cases, and over a period of months or years, this crust growth can result in the furnace being shut down.

The solid charge is fed in at the top of the furnace at approximately room temperature and with a constant void fraction. Lower in the shaft, the solid temperatures increases to nearly the hearth temperature. It is postulated that crust formation results from

condensation on the (cold) wall. The main driving force for the condensation is the temperature difference between the hot gas coming from the hearth ( $\approx 2300K$ ) and the solid material. Condensation takes place if the temperature drops below a certain critical temperature ( $T < T^* \approx 2000K$ ). Since the solid material is relatively cold, it is assumed that the condensation takes place at the solid particles, i.e. the condensation is a surface reaction.

The above suggested mechanism for crust formation is supported by the evidence that the crust is observed only to form at the furnace walls and not at the electrode, where the temperature will typically be too high for significant condensation to occur. As well as the vertical temperature gradient in the shaft, there will be a temperature gradient across the shaft due to heat inflow from the electrode and outflow through the furnace walls. The condensation reaction will take place throughout the shaft, the voids in the incoming material being filled with condensate. However, nearer the electrode and in the bulk of the shaft region the condensate will be forced down into the hearth, together with the charge. Only near the furnace walls (where the lower temperatures should guarantee a higher condensation rate), is the condensate likely to stick, cool and form a hard crust.

In the following analysis the growth rate of the crust is therefore modelled as being proportional to the rate of condensation and to the surface area of the wall exposed to reaction at which the solid material may stick. The liquid and solid phases will be treated the same, so that melting of the different species need not be considered. In the furnace shaft we assume a downwards solid/liquid flux opposed by an upwards gas flux. Two models for crust formation are considered. In the first model it is proposed that the crust is formed slowly, and due to SiO-condensation alone. In the second model the exothermic reaction (4) is also taken into account and furthermore, the process is studied on the stoking time scale.

The following notation will be used:

$t$  = time,  $z$  = vertical position in shaft,  $x, y$  = horizontal position,  
 $T_s, T_g$  = local absolute temperature of solid, gas component ( $K$ ),  
 $c_s, c_g$  = local concentration of solid, gas ( $mol/m^3$ ),  
 $v_s, v_g$  = velocity of solid, gas ( $m/s$ ),  
 $R$  = reaction rate ( $mol/m^3s$ ),

and we define the following constants and coefficients:

$T^*$  = equilibrium (critical) temperature,  
 $T_e, T_w$  = temperatures of electrode and wall,  
 $\alpha, \beta, \gamma, \delta$  = (reaction) constants,  
 $D$  = diffusion coefficient gas,  
 $\kappa_i = \frac{k_i}{\rho_i c_i}$ ,  $k_i$  = thermal conductivity,  $\rho_i$  = density,  $c_i$  = specific heat,  $i = g, s$ .

### 3.1 Crust formation due to SiO-condensation on a long time scale.

A first model for the crust formation simplifies the process to a SiO-condensation:  $2 SiO \rightarrow SiO_2 + Si$  at sufficiently low temperatures. Restricting the domain of interest to the shaft

of the furnace, a given supply of SiO gas is coming from the hearth, and similarly a given supply of charge is fed to the top of the idealised reactor. See Fig. 2.

Since only one reaction is used, only the concentration  $c_g$  of the SiO gas needs to be considered. Its change is determined by the diffusion and the reaction rate:

$$\frac{\partial c_g}{\partial t} + \nabla \cdot (\underline{v}_g c_g) = \nabla \cdot (D \nabla c_g) - R. \quad (5)$$

For this condensation two gas molecules react to form solid (or liquid) if the temperature at the surface of the solid is below the critical condensation temperature. Therefore the reaction rate is modelled by:

$$R = \delta c_g^2 (T^* - T_s)_+, \quad (6)$$

with reaction constant  $\delta$ . The temperatures  $T_g$  and  $T_s$  of gas and solid are given by heat conduction equations:

$$\rho_g c_g \left( \frac{\partial T_g}{\partial t} + \nabla \cdot (\underline{v}_g T_g) \right) = \nabla \cdot (k_g \nabla T_g) + \alpha_1 R - H, \quad (7)$$

$$\rho_s c_s \left( \frac{\partial T_s}{\partial t} + \nabla \cdot (\underline{v}_s T_s) \right) = \nabla \cdot (k_s \nabla T_s) + \alpha_2 R + H. \quad (8)$$

The terms  $\alpha_i R$  give the amount of heat that is released from the exothermic reaction, going into the gas or the solid respectively. We will assume that the heat released from the reaction will go into the solid material that is formed by the condensation reaction. This means that  $\alpha_1 = 0$ .

The term  $H$  models the heat transfer from the gas to the solid, depending on the temperature difference ( $T_g - T_s$ ). This will be modelled with a linear relation:

$$H = \beta (T_g - T_s), \quad (9)$$

for a given constant  $\beta$ . If  $\beta$  is very large, then the heat transfer between solid and gas is almost immediate and the solid and gas will have approximately the same temperature at each height in the shaft. If  $\beta$  is small, the temperature of the gas that escapes at the top of the furnace will be almost the same as the temperature at the bottom.

Boundary conditions are given by:

- at the crust boundary  $h$  (heat transfer and no flux conditions):

$$\frac{\partial T_g}{\partial n} = \gamma_{wg}(T_g - T_w), \quad \frac{\partial T_s}{\partial n} = \gamma_{ws}(T_g - T_w), \quad (10)$$

$$\frac{\partial c_g}{\partial n} = 0, \quad (11)$$

- at the electrode (heat transfer and no flux conditions):

$$\frac{\partial T_g}{\partial n} = \gamma_{eg}(T_g - T_e), \quad \frac{\partial T_s}{\partial n} = \gamma_{es}(T_s - T_e), \quad (12)$$

$$\frac{\partial c_g}{\partial n} = 0, \quad (13)$$

- at the bottom and top of the shaft:

$$T_g = T_0, \quad c_g = c_0, \quad \text{at } z = 0, \quad T_s = T_L, \quad \text{at } z = L \quad (14)$$

The formation of the crust is modelled by:

$$\frac{\partial h}{\partial t} = \gamma R, \quad \text{at the crust boundary } h, \quad (15)$$

which gives the growth of the thickness of the crust layer, proportional to the reaction rate and the surface area of the wall.

To close the system we need initial conditions at  $t = 0$  and an equation for the velocities. A possible choice is describing the flow through a porous medium; however we will use constant velocities for simplicity.

An important model assumption is the time scale on which the process of the crust formation takes place. In this first model the time scale for the crust formation is assumed to be long, such that after scaling, the only time component is in the dynamical equation for the growth of the crust and all other processes are quasi-static.

### One-dimensional model for a thin crust.

We will first concentrate on the one-dimensional model, in the case of a thin crust (which does not influence the flow through the shaft). For a one-dimensional model we need similar boundaries on each side of the shaft. Both boundaries (wall or crust and electrode) are assumed to be good insulators.

A scaling is done for a thin crust and for a long time period. Non-dimensionalisation and scaling (with  $\varepsilon$  the ratio of crust thickness over shaft width,  $\varepsilon \ll 1$ ) are as follows. With at  $z = 0$  a given gas temperature  $T_0$ , gas concentration  $c_0$ , gas velocity  $v_0$ , and with  $L$  the length of shaft, define the non-dimensional variables:

$$\begin{aligned} \bar{z} &= \frac{z}{L}, & \bar{t} &= \frac{tv_0}{L}, & \bar{h} &= \frac{h}{\varepsilon L}, & \bar{v}_g &= \frac{v_g}{v_0}, & \bar{v}_s &= \frac{v_s}{v_0}, & \bar{c}_g &= \frac{c_g}{c_0}, \\ \bar{T}_g &= \frac{T_g}{T_0}, & \bar{T}_s &= \frac{T_s}{T_0}, & \bar{T}^* &= \frac{T^*}{T_0}, & \bar{R} &= \frac{RL}{v_0 c_0}, & \bar{H} &= \frac{HL}{v_0 T_0 \rho_g c_g}. \end{aligned}$$

The temperature at  $z = L$  is scaled to  $T_L/T_0$  which we will set to zero. The dimensionless parameters are:

$$\bar{\alpha} = \frac{\alpha_2 c_0}{T_0 \rho_g c_g}, \quad \bar{\beta} = \frac{\beta L}{v_0 \rho_g c_g}, \quad \bar{\gamma} = \frac{\gamma c_0}{L}, \quad \bar{\delta} = \frac{\delta c_0 T_0 L}{v_0}, \quad \bar{\kappa}_i = \frac{\kappa_i}{Lv_0}, \quad \bar{D} = \frac{D}{Lv_0}.$$

To leading order in  $\varepsilon$  and on a long time scale (such that all processes are stationary except for the crust growth), ignoring small terms related to diffusion and conduction, we find the following set of equations:

$$\frac{\partial(v_g T_g)}{\partial z} = -H, \quad (16)$$

$$\frac{\rho_s c_s}{\rho_g c_g} \frac{\partial(v_s T_s)}{\partial z} = \alpha R + H, \quad (17)$$

$$\frac{\partial(v_g c_g)}{\partial z} = -R, \quad (18)$$

$$R = \delta c_g^2 (T^* - T_s)_+, \quad (19)$$

$$H = \beta(T_g - T_s). \quad (20)$$

Boundary conditions are given by:

$$T_g = c_g = 1, \text{ at } z = 0, \text{ and } T_s = 0, \text{ at } z = 1, \quad (21)$$

and the crust growth is found from:

$$\frac{\partial h}{\partial t} = \gamma R, \quad \text{with } h = 0 \text{ at } t = 0. \quad (22)$$

For the analysis we will assume constant values of vertical velocities  $v_g$  and  $v_s$ . We define the positive constant:

$$\tilde{v} = -\frac{\rho_s c_s}{\rho_g c_g} v_s.$$

By adding the equations (16), (17) and (18) multiplied by  $\alpha$ , we find an integral for the equations, which can be used to simplify the calculations:

$$T_g - \frac{\tilde{v}}{v_g} T_s + \alpha c_g = \text{const} = A. \quad (23)$$

In dimensional form this integral is  $A^* = (\rho_g c_g T_g v_g) + (\rho_s c_s T_s v_s) + (\alpha c_g v_g)$ , which is related to energy conservation in the shaft region.

The shaft is divided into two regions, separated at  $z = z^*$ , defined as the height where  $T_s = T^*$  (i.e.  $T_s > T^*$  for  $0 < z < z^*$  and  $T_s < T^*$  for  $z^* < z < 1$ ).

For  $0 < z < z^*$  the equations are easily solved by:

$$\begin{aligned} c_g &= 1, \\ T_g &= (1 - \tilde{A}) \exp \tilde{\beta} z + \tilde{A}, \\ T_s &= \frac{v_g}{\tilde{v}} (1 - \tilde{A}) \exp \tilde{\beta} z + \tilde{A}. \end{aligned}$$

using the two boundary conditions  $c_g = T_g = 1$  at  $z = 0$ . We have defined the constants  $\tilde{\beta} = \beta(v_g - \tilde{v})/v_g \tilde{v}$  and  $\tilde{A} = v_g(A - \alpha)/(v_g - \tilde{v})$ . This gives the transition height:

$$z^* = \frac{1}{\tilde{\beta}} \ln \frac{\tilde{v}(T^* - \tilde{A})}{v_g(1 - \tilde{A})}.$$

For  $z^* < z < 1$  the equations can be reduced to:

$$c_g = \frac{1}{\alpha} \left( A - T_g + \frac{\tilde{v}}{v_g} T_s \right), \quad (24)$$

$$T_s = \frac{v_g}{\beta} \frac{\partial T_g}{\partial z} + T_g, \quad (25)$$

and the following o.d.e. for the temperature of the gas:

$$-\frac{\tilde{v}v_g}{\beta}T_g'' + (v_g - \tilde{v})T_g' = \frac{\delta}{\alpha} \left( A + \left( \frac{\tilde{v}}{v_g} - 1 \right) T_g + \frac{\tilde{v}}{\beta} T_g' \right)^2 \left( T^* - T_g - \frac{v_g}{\beta} T_g' \right). \quad (26)$$

We will look at the solution in more detail for the case of small parameter  $\delta$ , which corresponds to the physical situation that only a negligible amount of gas is taken up by the condensation (which seems to be in agreement with numerical experiments) and/or that the ratio of surface area of the solid particles over the total volume is small. Asymptotic expansion in  $\delta$  gives in leading order that no reaction takes place, although the temperature drops below the critical temperature. Expand  $z^*$ ,  $A$ , the crust thickness, gas concentration and temperatures in series of  $\delta$ . To leading order this is easily found to give:

$$\begin{aligned} c_g^0 &= 1, \\ T_g^0 &= \frac{v_g(\exp \tilde{\beta} z - \exp \tilde{\beta})}{\tilde{v} - v_g \exp \tilde{\beta}}, \\ T_s^0 &= \frac{\tilde{v} \exp \tilde{\beta} z - v_g \exp \tilde{\beta}}{\tilde{v} - v_g \exp \tilde{\beta}}. \end{aligned}$$

The integration constants are found from continuity of the temperatures at:

$$z_0^* = \frac{1}{\tilde{\beta}} \ln \left( T^* \frac{\tilde{v}}{v_g} + (1 - T^*) \exp \tilde{\beta} \right), \quad \text{with } A^0 = \alpha + \frac{(\tilde{v} - v_g) \exp \tilde{\beta}}{\tilde{v} - v_g \exp \tilde{\beta}}.$$

The growth of the crust to leading order (with  $h^0 = 0$ ) is then given by:

$$h^1(z, t) = \begin{cases} 0, & 0 \leq z \leq z^*, \\ \gamma t \left( T^* - \frac{v_g(\exp \tilde{\beta} z - \exp \tilde{\beta})}{\tilde{v} - v_g \exp \tilde{\beta}} \right), & z^* \leq z \leq 1. \end{cases} \quad (27)$$

The solution is found more accurately from the expansion to higher order in  $\delta$  and the crust growth is then found similarly for  $z > z_0^* + \delta z_1^* + O(\delta^2)$ .

### Other simplifications of the model.

When looking at the asymptotic expansion for large parameter  $\beta$ , which corresponds to a immediate heat transfer between gas and solid, it is found in leading order that the gas and solid in the lower part of the shaft will have constant temperatures  $T_g = T_s = 1$  and also the gas concentration is constant,  $c_g = 1$ . There will be a transition region given by a boundary layer around some value  $z^*$ . The inner solution in this transition layer must be matched with the outer solutions in the lower and the upper part of the shaft. It is not clear what will determine the value of  $z^*$  however and this might be interesting to investigate.

An other case that can be investigated further is the model for a thick crust, using either a boundary layer approach or lubrication theory. The (non-dimensionalised) equations and boundary conditions are given by:

- in the flow domain or boundary layer:

$$\nabla \cdot (\underline{v}_g T_g) = -H, \quad (28)$$

$$\nabla \cdot (\underline{v}_s T_s) = \alpha R + H, \quad (29)$$

$$\nabla \cdot (\underline{v}_g c_g) = -R, \quad (30)$$

$$R = \delta c_g^2 (T^* - T_s)_+, \quad (31)$$

$$H = \beta (T_g - T_s), \quad (32)$$

- in the crust ( $c_g = 0$ ):

$$\nabla \cdot (k_g \nabla T_g) = 0, \quad (33)$$

- at the wall:

$$\frac{\partial T_s}{\partial n} = 0, \quad (34)$$

- at the crust  $h(z, t)$ :

$$T_s \text{ continuous, } \frac{\partial T_g}{\partial n} = \gamma_g (T_g - T_s), \quad \frac{\partial c_g}{\partial n} = 0, \quad (35)$$

$$\frac{\partial h}{\partial z} = \frac{u_s}{v_s}, \quad \frac{\partial h}{\partial t} = \gamma R, \quad (36)$$

- at the electrode:

$$\frac{\partial T_g}{\partial n} = \gamma_g (T_g - T_e), \quad \frac{\partial T_s}{\partial n} = \gamma_s (T_s - T_e), \quad \frac{\partial c_g}{\partial n} = 0, \quad (37)$$

- at the bottom and top of the shaft:

$$T_g = 1, \quad c_g = 1, \quad \text{at } z = 0, \quad T_s = 0, \quad \text{at } z = 1. \quad (38)$$

Again an equation for the velocities is needed, for instance for a porous medium or constant velocities as before. This model will not be studied further.

In this section we have considered the condensation as the only mechanism for crust formation. However, under normal circumstances the condensation reaction is dependent on the amount of available SiO gas. In this simple model there is always sufficient gas available; in the furnace the SiO gas may be used in the other reaction,  $\text{SiO} + 2 \text{C} \rightarrow \text{SiC} + \text{CO}$ . This will be considered in the next section.

### 3.2 Crust formation due to the basic reactions in the top of the furnace during stoking cycles.

We will consider the system of equations for the two reactions that take place in the top of the shaft. The system is studied on a time scale of the stoking cycles, as the cold charge that is fed into the furnace at each cycle influences the reaction rates and therefore the growth of the crust. When simulating the normal stoking operation, the charge level (shaft top) is constant between stokings. The stoking operation is then idealised to an

instantaneous time discrete event, when the remaining shaft material is pushed down and the shaft is restored to its full height by adding the necessary amount of fresh charge mix.

We need to consider the temperature  $T_g$  of the gases SiO and CO and  $T_s$  of the solids and liquids SiO<sub>2</sub>, Si, SiC, C. The gases move upwards with velocity  $v_g$  while the solids are not pushed down during one stoking cycle ( $v_s = 0$ ). For simplicity we take  $v_g$  constant and assume that the crust is thin.

From the two reactions it follows that the model equations can be reduced to equations for the concentrations of the gas SiO and of the solid carbon C, which we will denote by  $c_g$  and  $c_s$ . (The temperatures  $T_g$  and  $T_s$  are still temperatures of the ensemble of gases and solids in the shaft.)

Again it is assumed that all the heat released from the reactions goes in first instance into the solid product, after which it can be transferred into the other material. Both reactions are exothermic. The condensation (reaction 1):  $2 \text{SiO} \rightarrow \text{Si} + \text{SiO}_2$  takes place below a critical temperature  $T^*$  ( $\approx 2000\text{K}$ ), with reaction rate:

$$R_1 = \delta_1 c_g^2 (T^* - T_s)_+ \quad (39)$$

The burning of carbon (reaction 2):  $\text{SiO} + 2 \text{C} \rightarrow \text{SiC} + \text{CO}$  takes place above a critical temperature  $T^{**}$  ( $\approx 1700\text{K}$ ), with reaction rate:

$$R_2 = \delta_2 c_g c_s (T_s - T^{**})_+ \quad (40)$$

The (non-dimensionalised) equations are now given by:

$$\frac{\partial T_g}{\partial t} + \nabla \cdot (\mathbf{v}_g T_g) = -H, \quad (41)$$

$$\frac{\partial T_s}{\partial t} = \alpha_1 R_1 + \alpha_2 R_2 + H, \quad (42)$$

$$\frac{\partial c_g}{\partial t} + \nabla \cdot (\mathbf{v}_g c) = -2R_1 - R_2, \quad (43)$$

$$\frac{\partial c_s}{\partial t} = -2R_2, \quad (44)$$

$$H = \beta (T_g - T_s), \quad (45)$$

and boundary conditions, for a thin crust, are given by:

- at the wall:

$$\frac{\partial T_g}{\partial n} = \frac{\partial T_s}{\partial n} = 0, \quad \frac{\partial c_g}{\partial n} = \frac{\partial c_s}{\partial n} = 0, \quad (46)$$

- at the electrode:

$$\frac{\partial T_g}{\partial n} = \gamma_g (T_g - T_e), \quad \frac{\partial T_s}{\partial n} = \gamma_s (T_s - T_e), \quad \frac{\partial c_g}{\partial n} = 0, \quad \frac{\partial c_s}{\partial n} = 0, \quad (47)$$

- at the bottom and top of the shaft:

$$T_g = c_g = 1, \text{ at } z = 0, \quad T_s = 0, \quad c_s = c_{s_0} \text{ at } z = 1. \quad (48)$$

Finally the crust growth will be determined by the amount of solid close to the wall that will stick:

$$\frac{\partial h}{\partial t} = \gamma R_1. \quad (49)$$

Since no crust is formed at the electrode, the crust is believed to be formed due to the condensation (which does not take place at the high temperatures near the electrode). However, also other solid particles may get “trapped” when SiO<sub>2</sub> particles stick to the wall and carbon and silicon carbide are found in the crust.

## 4 Conclusion.

During the study group week, several suggestions were given as to how to improve the unidimensional model of the silicon furnace. These suggestions have been outlined in section 2. Dr Halvorsen came to the study group with a large number of improvements already in mind and wanted to discuss as many of these as possible. Due to limited time however, the focus of these discussions was mainly on improvements to the furnace hearth description in Elkem’s current model. It is hoped that the suggestions are of some practical use.

Throughout the week there was also a lively discussion of Elkem’s second problem area, concerning possible mechanisms for crust formation in the upper part of the shaft. Some simple models have been studied and appear able to describe the phenomenon, as is shown by simple analysis of the one-dimensional case.

The crust formation is believed to occur mainly due to the condensation of SiO. If the temperature of the shaft is kept sufficiently high, this condensation cannot take place. This of course may not be practical, since the charge is fed in at a temperature far below the critical temperature for condensation. An alternative suggestion would be to heat up the furnace walls, in order to stop/reduce condensation close to the wall. Condensation will also not take place if no SiO gas is available at the top of the shaft. This could be achieved by adding more carbon to the charge, so that SiO will be used up in burning carbon, lower in the shaft. This however has the consequence that too much SiC is produced, which again affects the productivity of the process.

On a much longer time scale, if the condensation persists, other reactions may take place, changing the material state of the crust. The crust is usually made up of SiO<sub>2</sub>, C and SiC particles, but in time this changes to mainly SiC. The reactions  $\text{SiO}_2 + 3 \text{C} \rightarrow \text{SiC} + 2 \text{CO}$  and  $2 \text{Si} + \text{CO} \rightarrow \text{SiO} + \text{SiC}$  may be responsible for the formation of a hard layer of silicon carbide in the part of the crust nearest to the wall. Thus, other ways of lowering the amount of SiO in the top of the shaft would also be worth considering. More information about the permeability of the crust and the temperatures in the crust are required to model these processes.

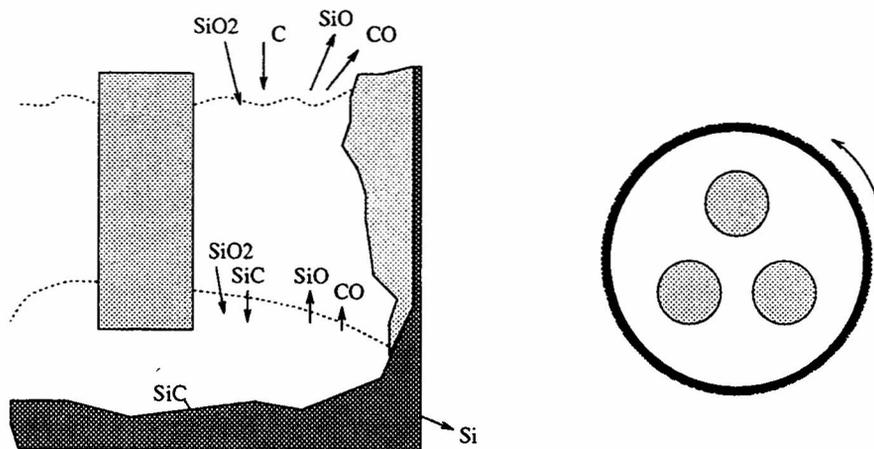


Figure 1: Detail of an operating (ferro)silicon furnace. At the bottom and the walls of the furnace a hard layer of silicon carbide SiC is formed. At the top of the furnace also a crust is formed. Right: cross-section of a furnace with three electrodes; the wall of the furnace rotates slowly, such that a rather even crust is formed at the wall.

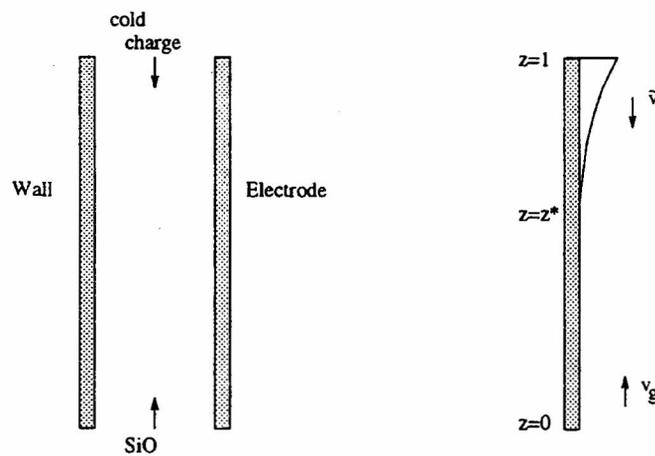


Figure 2: Simplified model for the crust formation in the shaft.