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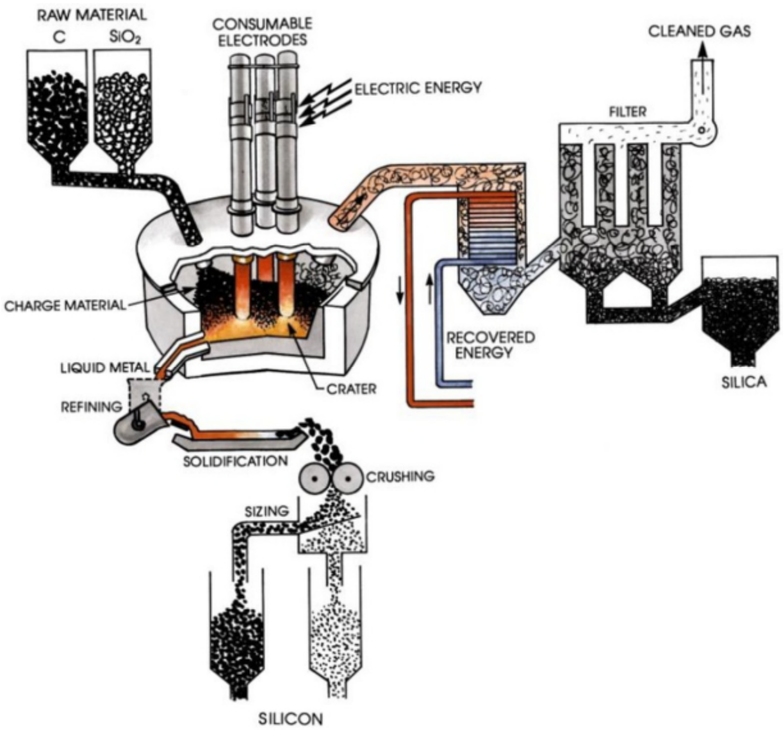

Modelling the Inner Structure in a Silicon Furnace

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1. Introduction

The Silicon Process

Silicon is found in high quantities in the earth's crust, second only to oxygen as an element. It naturally occurs in quartz and other rock, from which it must be extracted. Elkem Silicon Materials are one of several global companies which extract silicon and sell it to a range of industries. Customers use Elkem's silicon for semiconductors in solar panels and computers, polysilicone such as paint and textiles and for use in other metallic alloys.

Silicon is reduced from quartz using carbon.

To produce silicon (Si) from the raw material quartz (SiO2), carbon (C) is used in the form of woodchips or coke. The diagram on the front page, taken from Schei, Tuset and Tveit (1998), gives a schematic of the silicon process. The carbon and quartz are continually fed into a furnace and heated by electrodes. Liquid metal is tapped from the base of the furnace and undergoes further processes to produce silicon with desired purity and grain size for the customer's needs. Here we are interested in the furnace behaviour.

Crust Formation

Solid crust builds up around gas cavities, preventing the raw materials from reacting.

In the furnace, raw materials (charge mix) are poured in continuously to the top and a layer of silicon carbide (SiC) forms in the hotter regions below, as can be seen in Figure 2. Further down around the base of the electrodes a gas cavity develops, filled predominantly with SiO and CO gas. Liquid silicon drains towards the base of the furnace, where it melts and mixes with other materials before exiting through the tap hole. Ideally, raw materials would slowly fall down the furnace and be consumed at the same rate in which they are fed into the system. However, in practice, a solid crust region builds up around the gas cavities, preventing the solid and liquid materials from reaching the lower part of the furnace and being heated sufficiently to facilitate the necessary reactions. This crust gets thicker and rises, increasing the volume of the gas cavity. In order to counter the crust build up, operators ‘stoke’ the furnace, where the crust is manually broken up by a bar from a ‘stoking car’. This typically occurs on an hourly basis.

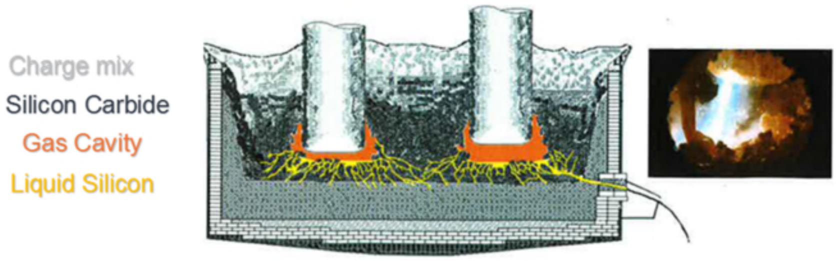

Figure 2: Schematic of a silicon furnace and a picture of crust build up around a gas cavity (both reproduced from an internal Elkem report).

Overview

We consider chemistry, heat flow and material transfer.

Our aim is to understand the formation of furnace crust. We will develop a mathematical model, taking into account the relevant chemistry, heat flow and material transfer. Particular detail is given to discussion of the complex chemical reactions. This model is applied to describe experiments carried out in the pilot furnace, with brief analysis of interesting special cases given. We then outline further areas for research and the potential impact of the work to industry.

2. Mathematical Model

We model the dynamics of the following chemical species which are found in a silicon furnace: C(s), SiC(s), SiO_2(s), SiO_2(l), CO(g) and SiO(g). We make a distinction between solid quartz, SiO_2(s), which is the raw material taken to be unreactive, and liquid, sticky quartz, SiO_2(l), which is reactive. Here the bracketed notation (s) denotes a solid, (l) a liquid, and (g) a gas. The silicon is assumed to be pure; different furnace dynamics are observed when ferro-silicon is produced. The important reactions taking place in the furnace are:

$$\begin{aligned}
\mathrm{SiO(g)} + 2\mathrm{C(s)} &\xrightarrow{R_1} \mathrm{SiC(s)} + \mathrm{CO(g)},\\
2\mathrm{SiO(g)} &\underset{R_{-2}}{\overset{R_2}{\rightleftharpoons}} \mathrm{SiO_2(l)} + \mathrm{Si(l)},\\
\mathrm{SiO_2(s)} &\xrightarrow{R_3} \mathrm{SiO_2(l)},\\
\mathrm{SiO(g)} + \mathrm{SiC(s)} &\xrightarrow{R_4} 2\mathrm{Si(l)} + \mathrm{CO(g)},\\
\mathrm{SiO_2(l)} + \mathrm{C(s)} &\xrightarrow{R_5} \mathrm{SiO(g)} + \mathrm{CO(g)}.
\end{aligned}$$

We use a 1-D model to understand the vertical structure in the furnace.

We only consider one spatial dimension, being height in the furnace, to represent a vertical section parallel to an electrode. We assume that diffusion of the chemical species can be neglected and that both gases, CO and SiO, move at a varying upwards velocity U_g, whilst solid and liquid components move at a constant downwards velocity U_S. It is assumed that the total pressure is constant and that it is comprised solely of the partial pressures of SiO and CO gases. For simplicity we assume that gas, liquid and solid have the same temperature, although in practice the gas will be much hotter. The conservation of mass equations describing the dynamics for each chemical concentration are:

$$\begin{aligned}
\frac{\partial C_{\mathrm{C}}}{\partial t} - \frac{\partial (U_s C_{\mathrm{C}})}{\partial z} &= -2R_1 - R_5,\\
\frac{\partial C_{\mathrm{SiC}}}{\partial t} - \frac{\partial (U_s C_{\mathrm{SiC}})}{\partial z} &= R_1 - R_4,\\
\frac{\partial C_{\mathrm{SiO_2(s)}}}{\partial t} - \frac{\partial (U_s C_{\mathrm{SiO_2(s)}})}{\partial z} &= -R_3,\\
\frac{\partial C_{\mathrm{SiO_2(l)}}}{\partial t} - \frac{\partial (U_s C_{\mathrm{SiO_2(l)}})}{\partial z} &= R_2 - R_{-2} + R_3 - R_5,
\end{aligned}$$

$$\frac{\partial C_{\mathrm{Si}}}{\partial t} - \frac{\partial (U_s C_{\mathrm{Si}})}{\partial z} = R_2 - R_{-2} + 2R_4,$$
$$\frac{\partial C_{\mathrm{CO}}}{\partial t} + \frac{\partial (U_g C_{\mathrm{CO}})}{\partial z} = R_1 + R_4 + R_5,$$
$$\frac{\partial C_{\mathrm{SiO}}}{\partial t} + \frac{\partial (U_g C_{\mathrm{SiO}})}{\partial z} = -R_1 - 2R_2 + 2R_{-2} - R_4 + R_5.$$

We assume that the heat flux is due to conduction through the solid material and radiation. Each reaction releases or absorbs heat energy, which changes the local temperature. The mathematical equation describing the temperature dynamics is not included here for brevity. The gas velocity U_g is determined by an overall Darcy law and this is further simplified by assuming that the permeability is large, giving an algebraic relationship between the concentrations. Hence we have nine equations for the nine unknown variables (seven chemical concentrations, temperature, and gas velocity).

Reaction Rates

Reactions are dependent upon concentrations, partial pressure, temperature, and activation energy.

We model each reaction rate using the ideas from the literature and the existing dynamic model used by Elkem, called SiMod [2]. Concentrations are used to describe the amount of the solid and liquid reactants present, while partial pressures are used to model gas reactants. Partial pressures are related to gas concentrations, and equilibrium partial pressures are given as functions of temperature. We include the activation energy of the reaction, where appropriate. Specific reaction rate are detailed below.

$$\mathrm{SiO(g)} + 2\mathrm{C(s)} \xrightarrow{R_1} \mathrm{SiC(s)} + \mathrm{CO(g)}$$

We model the reaction assuming that the rate depends on the reactivity and the concentration of carbon. We incorporate a varying reactivity of carbon, which decays exponentially in time. The SiO partial pressure difference to the equilibrium curve is included.

$$2\mathrm{SiO(g)} \underset{R_{-2}}{\overset{R_2}{\rightleftharpoons}} \mathrm{SiO_2(l)} + \mathrm{Si(l)}$$

The forward condensation reaction is modelled through a linear SiO partial pressure difference to the equilibrium curve. In the backward evaporation reaction, we include the influence of concentrations of Si and SiO_2(l), but also the SiO partial pressure difference. This is because the gas phase is limited as to the amount of new gas it can accommodate.

$$\mathrm{SiO_2(s)} \xrightarrow{R_3} \mathrm{SiO_2(l)}$$

The melting of quartz has a distinct form to the other reactions, since it is dependent on a temperature difference from the melting point of quartz (1996K).

$$\mathrm{SiO(g)} + \mathrm{SiC(s)} \xrightarrow[-]{R_4} 2\mathrm{Si(l)} + \mathrm{CO(g)}$$

This reaction is dependent on the concentration of SiC, the SiO partial pressure difference to equilibrium and the activation energy.

$$SiO_2(l) + C(s) \xrightarrow{R_5} SiO(g) + CO(g)$$

Since this reaction takes place in the crater, or at the crater wall, we assume that all carbon is reactive. We include the concentrations of SiO_2(l) and C.

Pilot Furnace

Pilot furnace experiments replicate behaviour in a vertical shaft of an industrial furnace.

Elkem have performed experiments on 'Process Simulator Pilot Furnaces', which are cylinders of inner radius 13cm and height 43cm, filled with raw material and externally heated from room temperature. They are designed to replicate behaviour in an industrial furnace and are cut open after being cooled, to analyse the remaining material. Photographs are shown in Figure 3. The solid is stationary in these experiments, and we assume that the internal pressure gradients are not large enough to move any of the liquids.

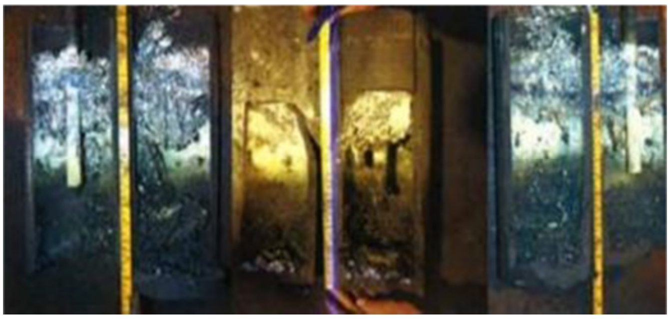

Figure 3: Photographs of three cylinders after excavation, exhibiting the formation of a gas cavity in the lower region (reproduced from an Elkem internal report).

No Gas Flow

An interesting limit to consider is where the gas does not move. Thus, we have no material transport mechanisms in the reduced model. We prescribe a linear temperature profile of 2400K at the base and 1400K at the top.

The no-gas-flow case indicates two distinct regions in the pilot furnace.

We find two distinct regions in the pilot furnace. These are where the temperature is hotter than the melting point of quartz (1996K), at the bottom of the cylinder, and where the temperature is cooler than 1996K, at the top of the cylinder. Numerical simulations for each region are shown in Figure 4. The horizontal axis shows non-dimensional time on a logarithmic scale, with $10^{-4,}$ 10^{-2}, 10^{0}, and 10^{2} corresponding to 0.00013 seconds, 0.013 seconds, 1.3 seconds, and 2.1 minutes respectively. The vertical axis shows concentration, relative to the initial concentration of carbon, also on a logarithmic scale. The concentrations of some chemicals are so small that they are not shown.

For typical parameters describing the relative importance of each reaction rate, we find a very thin boundary region between the top and bottom region, which could represent a crust formation. The thickness of this boundary region correlates with the size the non-dimensional parameter controlling the evaporation reaction R_{-2}. Decreasing this by a factor of ten corresponds to an increase in the thickness of the boundary region by a factor of ten, until all the lower region of the cylinder has liquid quartz present.

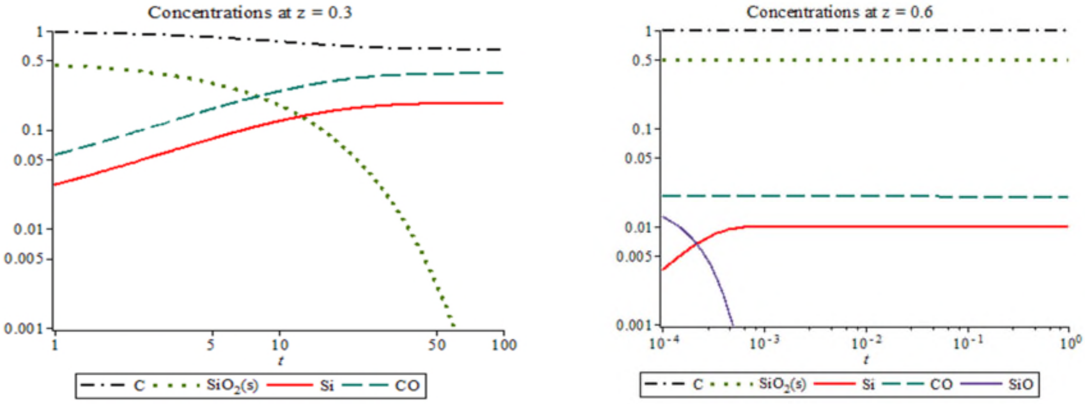

Figure 4(a): Representative behaviour for the bottom region.

Figure 4(b): Representative behaviour for the top region.

Figure 4: Numerical simulations at fractional height (a) z=0.3 and (b) z=0.6. In (a) we see carbon reacting away until it settles down to a constant concentration after around 30 seconds. The solid quartz melts until it is all used up after a similar time. In (b) SiO gas is burned off very rapidly and trace amounts of silicon are created before the dynamics quickly stabilize.

Instantaneous Gas Flow

To gain insight, we also consider the case where the gas velocity U_g is so large that we can lose the time derivatives in the equations describing the evolution of the concentrations of the gases, which we call the "instantaneous gas flow" case. Allowing temperature to vary according to heat release from the reactions, we find that it goes very rapidly to an equilibrium value throughout the pilot furnace. Silicon is produced in the top part of the furnace but not in the lower part. Neglecting all reactions except the condensation reaction R_2, we find that the instantaneous gas flow case is a good approximation to the case where the time derivatives are not neglected.

Expanding the Model

The work outlined in this report will be continued during a three year Research Project, commencing in October 2015. Directions for further work includes comparison with the existing model SiMod [2] to validate and improve our model. Further numerical simulations will be carried out to capture behaviour in the full model and further explore parameters influencing crust formation. Also we will seek to incorporate additional physical effects into our mathematical framework, including motion and heating due to electricity and fluid motion in the wider furnace.

3. Discussion and Conclusions

We have developed a mathematical model for the chemical reactions and crust formation found in a silicon furnace, taking account of chemical concentrations, material transfer and temperature. By looking at the limits of large or small gas velocity we can simplify the analysis and discover useful insights. In the no-gas-flow case we find a silicon producing region residing underneath an upper, relatively unreactive region. The thickness of the

The evaporation reaction R_{-2} has an important effect on the size of the crust.

crust-like boundary layer between these regions is controlled by importance of the evaporation of Si and $SiO_2(l)$ to $SiO(g)$.

Elkem plan to carry out further experiments using pilot furnaces, to add to the understanding of furnace behaviour. In existing experiments, material may have moved when the cylinders were cut open after cooling, so we can visualise the volume of a gas cavity, but not be confident as to the final position of each material. In the next experiments the cylinders will be lined with epoxy, allowing the material to remain in its final position when cut open. Measurements of chemical concentrations in these experiments will provide useful data to compare with our model. They will help to calibrate parameter values, providing further insight into crust formation.

4. Potential Impact

In the short term, the mathematical model in this report provides a framework to get a fresh perspective on the dynamics in a silicon furnace. Analysis of the model suggests that evaporation of Si and $SiO_2(l)$ may have a strong influence on the size of the crust region, though this may be quantified in greater detail after further experiments.

The formation of crusts in silicon furnaces is a phenomenon that is not presently understood in detail. The modelling work focusing on the crust formation, together with experimental testing, are important steps in the development of new understanding. In the long term these will potentially enable an improvement in production technology for silicon furnaces.

Espen Hvidsten Dahl, R&D Engineer in Process Development at Elkem, commented "*Ben's approach to solving the modelling problem was both elegant and efficient, and should be applicable to a range of other problems in Elkem that can be described mathematically*."

References

1. Diagram on the front cover taken from A. Schei, J.Kr. Tuset, and H. Tveit. *Production of high silicon alloys*. Tapir, Trondheim, Norway, 1998.
2. S.O. Wasbø and A. Hammervold. SiMod – a silicon furnace process model, March 2014.