EPSRC Centre for Doctoral Training in Industrially Focused Mathematical Modelling

Modelling Microsilica particle formation and growth

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1. Introduction

Background

The main use of microsilica is as an additive in high performance concrete

Elkem is one of the world's leading suppliers of silicon and microsilica. In the past, the silica fume or microsilica produced when making silicon was a major source of local and regional pollution, until it was captured by filters and sold as a by-product. In 1950, Elkem became one of the first companies worldwide to start research into applications of microsilica. The main use of the silica fume is as an additive in high performance concrete, since it increases its toughness, giving a higher bond strength, enhances its durability, has a very low permeability to chloride and water intrusion, and has a high electrical resistivity. Commercial sales of microsilica to the concrete industry began in 1971. Since then, multiple studies aiming to understand the mechanisms of formation and growth of these particles have been carried out, with the objective of controlling the quality and properties of microsilica.

A typical silicon furnace (as shown on the left hand side of figure 1) is fed with raw materials (called charge materials) such as quartz, carbon, and woodchips from above, and liquid silicon is tapped at the bottom. Three electrodes are submerged into the charge supplying the energy required for the reduction process of SiO_2 (quartz) into Si. Sometimes the operator is required to stoke the surface in order to maintain the raw material flow down into the furnace or to stop gas escaping from the reaction zone of the furnace. This gas is mainly composed of SiO and CO, which are created in the furnace craters due to other chemical reactions involving the raw materials.

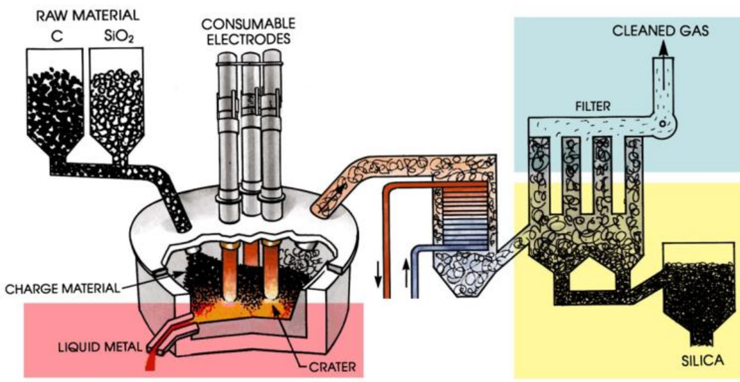

Figure 1: Schematic of the silicon production process.

Both gases flow upwards from the crater area and some will escape through the charge surface. Above this surface, both SiO, CO, and volatiles, burn due to the high temperatures and the presence of excess air coming from the surroundings. The combustion of SiO with oxygen produces bright white flames, and forms SiO_2 or microsilica. Similarly, CO reacts with oxygen to produce CO_2. Finally, the fume (mainly composed of SiO_2, CO_2, and water vapour) generated during the combustion reactions continues straight up to the exhaust system, where is cooled down before entering a bag house filter. This type of filter uses cylindrical bags where the gas enters, and removes small particles that accumulate on the bags surface until air can no longer move through it. The dust trapped on the filter bags is then collected and sold as Elkem Microsilica.

Silica fume

The silica fume mainly consists of very fine spherical particles of SiO_2, with more than 95% of them being smaller than 1µm; see Figure 2.

Microsilica consists of very fine spherical particles of SiO_2, with more than 95% of them being smaller than 1µm

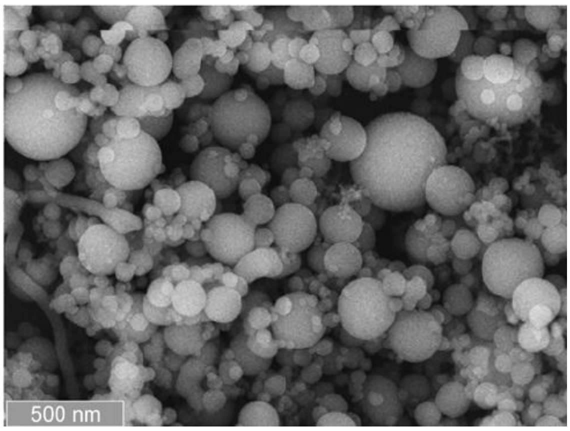

Figure 2: Microsilica particles.

Modifications in the silicon production process have affected not only the microsilica yield, but also the particle quality, size, and surface area. With respect to the quality of the silica fume, there is great concern about the impurities found and the tendency of these silica spheres to form agglomerates. These impurities and agglomerates have great impact on the performance of customer's products. Elkem are interested in understanding the operating conditions which are favourable for microsilica particle formation and growth.

Our aim is to identify the local conditions where microsilica is formed, taking account of the relevant chemistry, heat transfer, fluid flow, and mass transfer. A key challenge is that the fluid flow is turbulent which affects the species mixing process. We will also consider a microscopic model that accounts for particle formation and growth.

Glossary of terms

- Furnace hood: Region in the furnace located between the charge surface and the top of the furnace where the exhaust system is found.
- Exothermic reaction: Chemical reaction that releases energy into the environment in the form of heat.
- Turbulence flow: Type of flow characterised by chaotic changes in the velocity and pressure.
- Droplet nucleation: First step in the phase transformation from gas to liquid, involving the irreversible formation of a nucleus.
- Particle size distribution: The particle size distribution defines the relative amount of particles present according to size.
- Steady-state solutions: Solutions obtained from a system that does not change in time.
- Gas Blow: Escape of gas at high velocity from the charge surface.

2. Mathematical model

We model the microscopic dynamics of the main chemical species found inside the furnace hood: N_2(g), O_2(g), SiO(g), SiO_2(s), CO(g), and CO_2(g). Here, the notation (g) denotes a gas, and (s) denotes a solid. Other compounds, such as water, are not taken into account. We model the following dominant combustion reactions:

$$2\mathrm{SiO(g)} + \mathrm{O_2(g)} \xrightarrow{R_1} 2\mathrm{SiO_2(s)},$$

$$2\mathrm{CO(g)} + \mathrm{O_2(g)} \xrightarrow{R_2} 2\mathrm{CO_2(g)},$$

which are highly exothermic and fast. The fluid that we are considering is a combination of the five gas species and the solid microparticles. We make the modelling assumption that the flow is homogenous in the sense that the relative motion and differences in temperature between the gas and solid phases are sufficiently small that they can be neglected. To fully describe the fluid flow we assume:

- Conservation of chemical species: The rate of change in the concentration (measured in mol/m^3 of the whole mixture) of each of the six species depends on convection and diffusion mechanisms, as well as on the reaction rates, R_1 and R_2. The diffusion term in our model combines the effects of molecular diffusion and turbulence mixing. Moreover, as the reactions are not elementary, the law of mass action cannot be applied here to determine the reaction rates. Instead, experiments suggest that the reaction rates are proportional to the concentrations of the respective reactants. Additionally, as the rates are highly dependent on the temperature, we also include an exponential factor in terms of the temperature.
- Conservation of energy: The temperature is affected by convection of the fluid, heat released by the reactions, radiation from the flames and flue gases, and external heat sources. Heat transfer in the gases due to conduction is neglected. As before, an additional diffusion term accounting for turbulence effects is incorporated into this equation.
- Conservation of momentum: We assume the fluid is compressible and study its velocity field by considering pressure, viscous forces, and inertial effects. The viscosity considered is the sum of the kinetic viscosity and turbulence viscosity.

We assume unidirectional flow at the inlets and outlet, as well as atmospheric pressure, and consider the no-slip condition on the furnace walls. On the charge surface, we impose a heat flux from the crater; on all other boundaries, we consider fixed temperature values. For the species concentrations, we prescribe constant concentration values at the inlets, no flux of species through the walls, and advective flux of species through the outlet.

Turbulence model

Turbulence increases the species mixing process, enhancing the chemical reactions

The Reynolds number (Re) is defined as the ratio between inertial forces and viscous forces. Since our gas mixture has a very low viscosity, the Reynolds number ($Re \sim 10^8$) in our system is large enough to consider the flow to be turbulent. This is reasonable due to the turbulent nature of any combustion process. Since inertial forces are dominant, they tend to create eddies and other fluid instabilities. It is important to incorporate turbulent effects into our model since turbulence increases the species mixing process, which enhances the chemical reactions. We thus include a term in the conservation of momentum equation that depends on the turbulent or eddy viscosity. The eddy viscosity is defined in terms of two new variables: the turbulence kinetic energy (k) and its dissipation rate (ε). These two variables are described by two transport equations. This model is known as the k-ε model of turbulence.

3. Results

To help visualise the effect that turbulence has on the fluid flow behaviour and mixing of the species, we solve our model numerically using COMSOL. Our two dimensional geometry (see Figure 3 (left)) is based on some experiments in a pilot furnace aiming to understand the formation of NOx compounds in the furnace hood, which is correlated to the formation of microsilica. We couple the turbulent model for the fluid flow to the temperature and to the transport of concentrated species, and solve this to find the temperature, pressure, velocity field and concentration of the reacting species.

Temperature and velocity field

In Figure 3 (right), we show the steady-state solution for the temperature, represented by a heat map, and the velocity field, represented by arrows and streamlines. The air inlets are placed close to the charge surface and at both sides of the furnace hood, while the hot gases, SiO and CO, enter the system from the bottom.

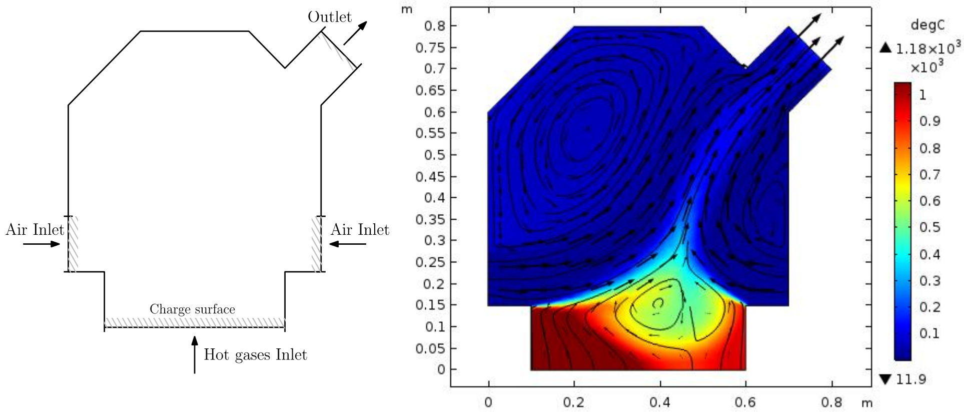

Figure 3: (Left) Schematic diagram of the furnace hood. (Right) Temperature (heat map) and velocity field (arrows surface and streamlines). The height and width are shown in metres.

The creation of eddies below the air streams may be involved in the mixing of the chemical species

We see that the temperature is much higher at the charge surface, due to the constant heat flux from inner areas in the furnace. However, the velocities of the gases in that region are smaller since we assume the system to be in equilibrium, that is, there are no gas blows. The velocity of the fluid increases along the air streams, and as it reaches the exhaust system. We also notice the formation of small eddies below the air streams, which may be involved in the mixing of the species. The air streams extend from the air inlets up to the outlet.

Species concentrations

The SiO reaction happens closer to the charge surface than the CO reaction

In Figure 4, we show the steady-state solution for the concentrations of the reacting species. By looking at the SiO and SiO_2 concentrations (top figures) we see a clear interface at which the reaction occurs, which is enhanced by the formation of eddies below the air streams. Small amounts of oxygen are dragged inside the eddies where they encounter the SiO gas. Comparing these results to the ones obtained for CO and CO_2 (bottom figures), we find that they have a similar behaviour. The first thing that we notice is that, since there is more CO reacting, and so more CO_2 is produced, the concentrations of these species are much higher in the reaction area. Secondly, the SiO reaction happens more rapidly than the CO reaction, as in reality. Since the interface at which the reaction happens in the top left figure is much closer to the hot gases inlet than the one in the bottom left figure, we expect the SiO reaction to happen closer to the charge surface than the CO reaction.

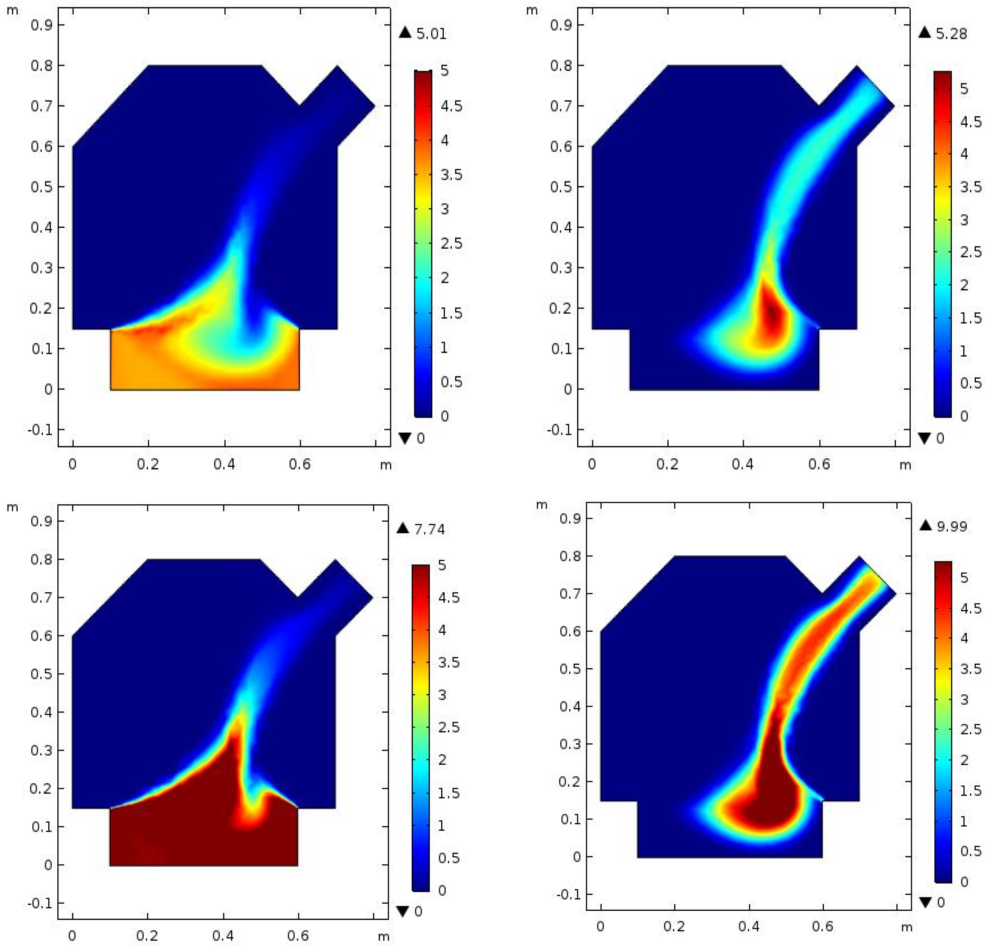

Figure 4: Steady-state chemical species concentrations throughout the furnace. Top left: SiO, top right: SiO_2, bottom left: CO, bottom right: CO_2.

4. Particle formation model

Our macroscopic model describes the fluid flow inside the upper area of the furnace. We are also interested in particle formation on the microscale, so we focus on a small region and only consider the condensation reaction between SiO and oxygen that creates the microsilica particles. We assume that the condensation rate alters the concentration of oxygen and SiO, and varies with the size of the particles. Furthermore, we assume that the ability of a particle to exchange heat with its surroundings controls the rate of particle growth.

The amount of microsilica particles created depends on nucleation and growth processes.

Our microscale domain consists of a finite width diffusion flame, in which the SiO and O_2 mix by diffusion. We assume that we have a 1-D situation that is time independent, and considers diffusion as the main transport mechanism, as well as the condensation rate. This rate represents the amount of microsilica particles being created per unit volume, and includes nucleation and growth processes. We use this model to obtain particle size distributions.

5. Discussion, Conclusions & Recommendations

We have built a detailed mathematical model that takes into account heat transfer, fluid velocities, pressure, and the main chemical reactions involved in the formation of microsilica. After analysing the sizes of the key dimensionless parameters, we found that it was essential to incorporate turbulence into the model. COMSOL simulations were considered with the purpose of giving a better insight into the turbulent mixing of the species and fluid flow pattern inside the furnace hood. These results showed where, and how fast, the chemical reactions take place, and suggest that they are enhanced by the formation of eddies due to the turbulent nature of the flow. Finally, by joining the fluid flow model and the model for particle formation, we would be able to relate the fluid flow, temperature, and concentrations to the particles size and so give a full analysis on how they affect the microsilica properties.

The simulations can be used to advise the user what would happen if changes are made in the system. This may suggest different operating strategies.

Expanding the model

Directions for further work include:

- Adding other reactions occuring in the furnace hood, such as the Boudouard reaction (2CO ↔ C+CO2) or the condensation of SiO into Si+SiO2, as well as incorporating the effects of the presence of other compounds such as volatiles and water.
- Linking the fluid flow model to the model for particle formation, in order to see the macroscale effects on the microsilica properties.
- Modelling particle surface reactions as well as particles interactions to analyse the formation of agglomerates.
- Incorporating additional heat sources, e.g. radiation.

6. Potential Impact

Our simulations can be used by Elkem to predict what would happen if changes are made in the system and the solutions may suggest different operating strategies or design of the furnace in order to obtain a higher microsilica yield.

Rolf Birkeland, Elkem Technology, commented "*Raquel has done some really good work during her mini project. The potential impact of the mini- and research-project for Elkem is large. The development of a mathematical model that explains the silica particle formation and growth and couples these phenomena with furnace design and operation has not been done before. Such a model will give Elkem a significant edge over the competition in the future.*"