

The carbothermic process of silicon

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This chapter starts with a brief history of the development of the electric furnace for high-silicon alloys. It then gives a detailed description of observations on the furnace and ends with an interpretation of these observations, in terms of the chemical reactions and material flows in the furnace.

3.1 The origin of the silicon furnace

Ferrosilicon alloys with up to about 20 per cent weight can be produced in a blast furnace by reduction of silica with carbon. Higher silicon contents were not possible in industrial furnaces before electric heating became available.

Edward Acheson did his first experiments with silicon carbide in 1891 (Acheson, 1911). He passed a strong current through a mixture of clay and coke by means of a rod of carbon. He obtained small amounts of a material that was so hard that it could cut glass, and found that it was the carbide of silicon. According to Acheson, the temperature of formation of silicon carbide was vastly higher than that required to fuse the walls of the furnace, but the walls were protected by the furnace charge. When the silicon carbide was overheated, the silicon evaporated and left pure graphite. Acheson developed these findings into a commercial production of silicon carbide and graphite. For silicon carbide the ideal overall reaction was



The furnace was essentially heated by resistance in a core of conducting carbon and carbide. Occasionally the core became displaced, and hot spots appeared. In excavations after such runs, an apparently metallic product of bluish silver lustre was found. The product was identified as elemental crystalline silicon and called metallic silicon. Frank Tone (Tone, 1931) found that it probably was a product of the reactions



or



He decided to study the new product further and ran the first experiments to produce silicon in 1898, using a resistance furnace of the silicon carbide type. Both reactions gave silicon, but it was easier to operate with a charge of silica and silicon carbide. However, further experiments showed that an arc furnace gave better efficiency, and this furnace was finally adopted. It had just become available through the work of the French chemist Henry Moissan.

Moissan built his arc furnace in 1892, and temperatures of more than 2000°C became readily available for investigation. He treated several materials in it, including silica. Soon he could report that silica evaporated readily in a carbon-lined furnace run with 1000 ampere at 50 volts, and that it condensed to a very light product that remained stable in air for a long time (Moissan, 1895). Seen in the microscope, it consisted of small spheres of silica that were often bound together as fibres. The remains in the furnace contained crystals of silicon. When he treated a mixture of quartz and carbon, Moissan obtained silicon carbide crystals in a matrix of crystalline silicon.

This experience was soon developed into industrial production in a furnace where the electrodes were submerged in the charge. A few years later, a dissertation on ferrosilicon, with background in ‘several years of practical experience in the electrometallurgical industry’, could describe relatively large activity with several production plants and a wide patent literature (Pick, 1906).

Since this pioneering period, the process in the submerged arc furnace has undergone huge development in operational efficiency, size, electrodes, mechanical handling of raw materials, environmental protection, process control and quality management. Still, the fundamental principles – that is, the thermodynamics and the kinetics of the reactions – are very much the same.

3.2 Observation of the submerged arc furnace

Furnaces for silicon and high-silicon ferrosilicon behave similarly, and both will be described here.

The furnace system

Silicon and high-silicon ferrosilicon are produced in submerged arc furnaces. The most common type uses three-phase alternating current. A rough sketch is given in Figure 3.1. The electrodes in the corners of an equilateral triangle dip into a mixture of the charge materials. The inner structure of the furnace will be discussed later. The load can vary from less than 10 MW for small, old furnaces to more than 40 MW, and the geometrical dimensions vary roughly with the cubic root of the load. A typical small silicon metal furnace may be 20 MW, pot diameter 7 m, pot depth 2.7 m, electrode diameter 1.25 m and distance between the electrode centres 2.6 m. Many furnaces have pots that can rotate or oscillate at a speed corresponding to several days per rotation. This movement is believed to improve the tapping of the product and delay the formation of deposits at the bottom of the furnace. FeSi can also be produced in rectangular furnaces, with more than 3 electrodes, but that is not so common.

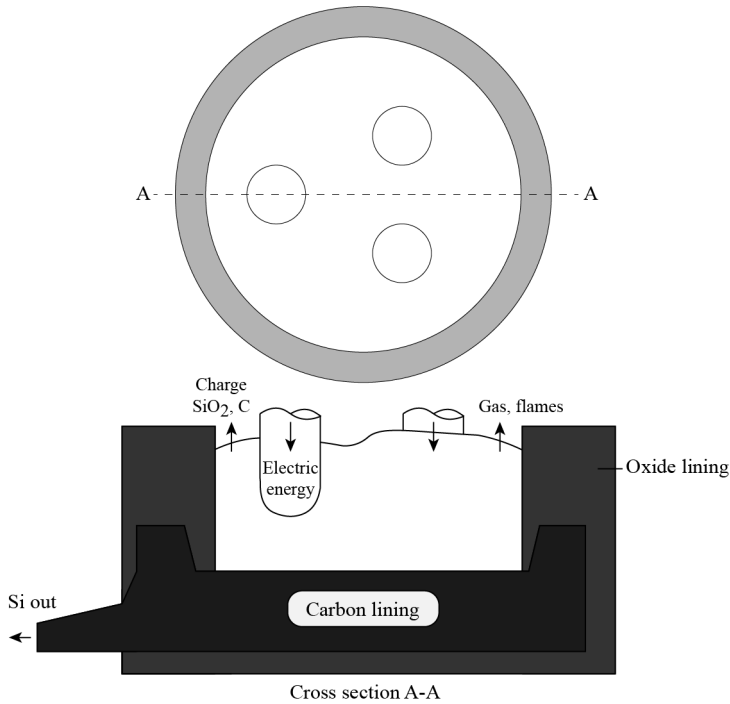
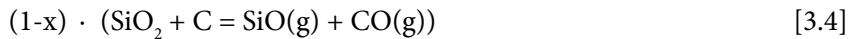


Figure 3.1 *The three phase submerged arc furnace for silicon.*

As shown in Chapter 2 (Chemistry of the Si–O–C system), the reaction between SiO₂ and C has SiO(g) and SiC(s) as intermediates. Some of the SiO leaves the furnace with the CO, and the overall chemical reaction in the furnace can be written as the following two equations, which produce silicon and SiO gas.



where x is the silicon recovery, or the silicon yield. The SiO and CO gases combust above the furnace, and SiO is oxidized to finely dispersed SiO₂, which forms the by-product ‘silica fume’. Before gas cleaning plants were installed, this was seen as the well-known white smoke from silicon plants. Reactions [3.2] and [3.4] are strongly heat-consuming, and energy is taken from the

electric grid. The current passes between the electrodes (the path will be discussed later in Chapter 6 Electric operation), and heat is produced by the electric resistance of the furnace. The electric system has restrictions on load and current. Normally, the producer wants to run the furnace at maximum load, since it gives maximum production, and the operator must select the voltage and current that give the right heat production. The resistance is determined by the resistivity of the charge, the arc, and the electrode position. As the resistance of the furnace content is not stable, it is necessary to adjust the electric system by moving the electrode or changing the voltage when the current moves away from the chosen value. The control has two aims. The first is to avoid damage to the electric system by using too high a current and, if necessary, to break the current. This control is very rapid. The second aim is to adjust the resistance to give the furnace the chosen heat production at the right location in the furnace.

Observation of the working furnace

The inner operation of the working furnace is difficult to observe. The combination of high temperature and aggressive chemical surroundings allows very few materials for probes, and few measurements can be carried out inside the furnace. Therefore, understanding of the inner operation of the furnace is built primarily on indirect qualitative observations, industrial- and pilot-scale excavations, and general knowledge of the chemistry of the system.

The operator experience

The description of the behavior of the furnace can start with a description of what a furnace operator observes and does. The operational procedure changes from place to place, but a typical operation is a cyclic sequence:

- The furnace is stoked.
- The furnace is filled with charge according to the instructions. The charging can be continuous or discontinuous.
- The furnace is run until new stoking/charging is necessary.
- The operator decides the time for stoking according to the instructions and based upon observations, either personal or from camera or IR

camera systems: hot gas with white smoke from the furnace, smoke and temperature registration in the chimney, collapse of the charge cover on the furnace.

- The furnace is stoked.

The duration of a cycle depends upon the type of the charge, and it may vary from about 30 to about 75 minutes. For operation with the traditional batch charging, a typical sequence is that the furnace is filled during charging, and the top of the charge does not sink much during the period to the next stoking. Just after the charging, the flames are bluish-yellow, and the top layer is relatively cold. The top changes gradually during the cycle period. The charge becomes hotter until white-hot particles can be seen just below the top layer, and the flames change from yellow bluish to white, with a high white smoke content. The hottest areas appear in fairly regular rings around the electrodes. Sometimes part of the top collapses, and the resulting hole then looks like the opening of an intensely hot, large cavity. As a rule, it is necessary to stoke the furnace to get enough space around the electrode for the new charge, but the stoking may be light. First, a thin crust on the top of the cavity is broken, and a continuous deep depression some 30–50 cm wide is formed around the electrode. Remaining old charge is pushed towards the electrode and distributed evenly. The new charge is then placed on the top of the old one to a predetermined level. The amount of materials for a new filling depends on the density of the raw materials and the length of the cycle. With the more continuous charging systems, that is now becoming more common, smaller amounts of charge are fed each time and spread over a larger area of the charge top. There will then be less temperature variation at the charge top, and the phenomena seen during batch charging as described above will be less pronounced. A lighter and less frequent stoking can then be sufficient.

The product is tapped through a pre-prepared hole in the lining. The hole is opened by a graphite tapping electrode, or by burning with an oxygen lance or wood rods. With discontinuous tapping, the taphole is plugged with a special clay mixture when the flow of melt has stopped. Originally, the tapping was always discontinuous. The idea was that the silicon formed a pool at the bottom of the furnace, and by tapping this pool it should be emptied completely through a hole near the bottom of the furnace. According to this idea, the silicon should flow to the taphole until the bath was empty, and

then a jet of gas flames should erupt from the interior of the furnace through the open hole. At some plants, the tappers were instructed not to plug the taphole before the flame jet appeared. The aim was to secure that the production zone was kept close to the bottom, and to detect a build-up of a deposit early. However, often the jet flame did not appear even after burning of the taphole with the graphite electrode. The flow of silicon was less intense than in a newly opened hole, but the overall production was normal. In some plants, this taphole operation developed into continuous tapping, where the taphole was only plugged when it was necessary for repair or when rotation of the furnace made access to the tap hole difficult. In continuous tapping, the tap hole opening was refreshed by the graphite tapping electrode, or by blowing with an oxygen lance, when the flow became poor.

Probes in the furnace

The first thorough study of the inner structure of the furnace was published by Zherdev *et al.* who used simple mechanical and electrical probes to show that the electrodes were surrounded by large gas-filled cavities during operation (Zherdev *et al.*, 1968a; 1968b; 1965; 1962a; 1962b; 1960). A set of the results of the measurements is shown in Table 3.1. The size of the cavity increased with increasing content of silicon. It also depended on the rotation of the furnace (Zherdev *et al.*, 1968b). The cavity was largest on the side that moved towards the electrode. This was not an effect of the rotation of the field of the alternating current, since it changed when the rotation of the furnace changed. The cavity became smaller when the rate of rotation increased. A later study of the importance of furnace rotation showed that there was a critical rate of rotation (Zherdev *et al.*, 1968b). Slow rotation (135 h/rotation) had almost no influence, and the influence increased with increasing rate until the critical value of around 70 h/rotation. At a lower rotation rate, the cavity was largest on the side that moved towards the electrode, as in the earlier runs, but above the critical rate it was largest on the other side. Above the critical rate, the electrodes were forced out of the vertical position. It can, however, be noticed that furnaces with similar rotation speed showed very different size of cavity, ranging from almost non-existence to 2 m high during excavation; however, this will be discussed later in this chapter (Ksiazek *et al.*, 2016; Tangstad *et al.*, 2014; Tranell *et al.*, 2010).

Table 3.1 *Measured size of the cavity in a 9 MW ferrosilicon furnace (Zherdev et al., 1965).*

Alloy	Maximum distance electrode to crater wall	Distance electrode tip to bottom deposit	Maximum height of the cavity	Height of charge layer in contact with the electrode
FeSi45	0.50 m	0.20 m	1.20 m	0.50 m
FeSi75	0.60 m	0.30 m	1.40 m	0.32 m
FeSi90	1.20 m	0.16 m	1.70 m	0.06 m

The qualitative content of the work of Zherdev *et al.* had probably been recognized by many metallurgists before these publications. Tone indicated a cavity in a sketch of the process (Tone, 1909). However, the accepted theory around 1960 was that such cavities only appeared when the voltage was too low. Operators who knew from experience that they had a cavity chose to remain silent, to avoid criticism for erroneous operation. The observations of Zherdev *et al.* are now rather old, and furnace operation has improved a lot since they were published. The size of the cavity in present, well-run, large furnaces may be quite variable.

Otani *et al.* continued the work on the inner structure of the furnace (Otani *et al.*, 1968). They placed a visual probe into the cavity of furnaces sized 0.5 and 5 MW, and were able to see the surroundings of the electrode tip directly. This technique yielded several interesting observations. They confirmed that the electrode was surrounded by a cavity. The electrode tip usually stood 5 to 15 cm above a bottom deposit that consisted of a spongy aggregation of silicon carbide crystals, with molten silicon metal between the crystals. In discontinuously tapped furnaces, the molten silicon sometimes covered the silicon carbide completely. A viscous mass, which must have been molten quartz or molten quartz with carbon materials, frequently fell down close to the electrode tip, where it disappeared gradually. Formation of bubbles indicated reaction in this mass. When the furnace was tapped, a porous structure was left after the melt.

The temperature was read with an optical pyrometer. The electrode showed 2000–2400°C; the crater walls showed 100–200°C less (with some doubt about the accuracy); and the metal bath showed 1900–2100°C. Sometimes, light from a very hot source outside the field of view was apparent, and temperatures up to 3500°C were read. The lower part of the electrode was hottest, and Otani *et al.* concluded that the high temperature and high SiO content of the gas made SiC

unstable there. Therefore, the electrode was consumed from the sides and became tapered at the lower end. An electric arc was burning between the electrode and the bottom deposit. The end of the electrode was cut horizontally, which was thought to be caused by reaction with SiO_2 splattered onto the electrode. Otani *et al.* compared electrode consumption in the furnace with consumption in an arc chamber in an inert atmosphere, and concluded that chemical consumption of electrode was large compared with evaporation in the arc spots.

Otani *et al.* supplemented their observations with equilibrium calculations and summed up their understanding of the process in Figure 3.2. The materials in the roof of the cavity are glued together by condensate from the gas produced in the cavity, and the roof is consumed gradually from the bottom. When the inside of the roof is exposed to heat from the arc and energy-rich gas, the silica becomes fluid and sinks down with the carbon materials.

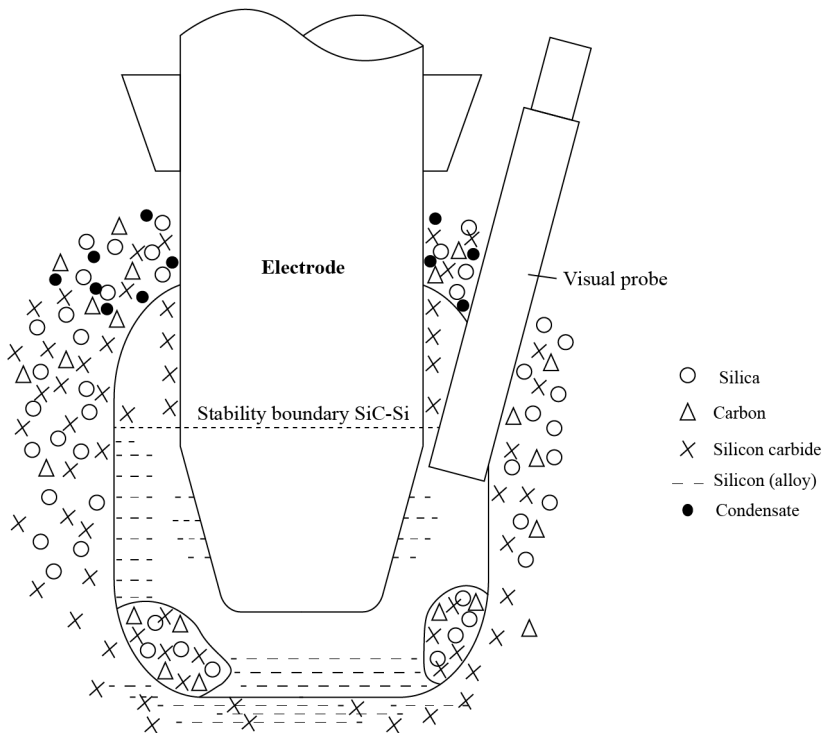


Figure 3.2 The inner structure of a silicon furnace (after Otani *et al.*, 1968). The visual probe is purged with inert gas during the observation to avoid deposits that can block the view.

Otani's visual probe had a rather narrow field of view, and only a very small fraction of the cavity could be seen. At Elkem Research in Kristiansand (Norway), a probe was built into the side of a 50 kW furnace, and the results were later confirmed in a 500 kW furnace (Schei and Larsen, 1979; Schei and Larsen, 1982). In this arrangement, the field of view was much larger than in the furnace of Otani *et al.*

Normally, the view was fairly clear, but occasionally dark smoke covered some of the details, often simultaneously with smoke production from the top of the furnace. During stoking, materials from the upper layer were forced down into the space around the electrode tip. These materials collapsed within a few minutes, while large drops of silicon appeared on the surface. The silicon pool increased significantly during the collapse, in the first minutes after the stoking. The materials blocked the view at the beginning, but when they collapsed, the view into the cavity was normally very good until the next stoking.

An electric arc burned between the electrode and a pool of molten silicon. It moved around, but could stay in the same place for many seconds. Observation through a chopping disc showed that the arc was well developed, with a bright spot on the electrode when the electrode was the cathode, but rather unstable and difficult to see when the electrode was the anode. The arc moved around on the electrode. Often, it burnt from the horizontal end of the electrode, but sometimes it burnt from the sides. A thin, irregular layer of a liquid material flowed downwards on the surface of the electrode and left scars. Sometimes, this liquid apparently ignited and gave short-duration luminous spots.

Occasionally, a viscous melt came in at the top of the field of view and slid slowly towards the bottom. This material must be silica, and some solid particles in it probably consisted of silicon carbide and carbon. Clumps of the viscous melt floated around for a while on the silicon pool, and silicon drops appeared on its surface while it was gradually consumed. When melt particles came close to the SiC walls of the cavity, intense bubbling indicated reaction by mass transport through the melt. When the carbon content of the charge was kept too high for several hours, the bottom rose gradually and blocked the probe. However, when the carbon content was decreased, the deposit disappeared slowly. In later furnace excavations, accumulation of SiC is usually found as α -SiC walls around the electrode, and it may be this that blocked the view of the probe during the high carbon additions.

When a cold steel rod was set into the cavity of the furnace, it was immediately covered with a brown, dense substance that, in the microprobe, was found to consist of droplets of silicon in a matrix of silica, a typical Si and SiO₂ condensate. In one experiment, the intention was to take out a relatively large sample of the silica dust produced when the cavity gas burns. A graphite tube with an inner plug of the same length was placed with the tip well inside the cavity during stoking, and charge materials were filled in around it. The top of the tube protruded some ten centimetres above the charge. The furnace was operated until the cavity was well established and the charge with the graphite tube became quite hot. Then the plug was removed. A strong jet of gas from the tube burnt with intense white light, giving a dense white smoke, and the outside of the graphite tube became white-hot within a short time. However, the flames soon became weaker, and the gas flow through the hole disappeared in a few minutes. The inner wall of the tube had a several-millimetre-thick, dense layer of the brown substance, and inside was a brownish, woolly material. The experiment indicates that the condensation reaction of SiO to [SiO₂ + Si] is very rapid when cooled.

The temperature in the cavity in the small furnace was measured by two methods. The first was to place a graphite tube with a closed bottom into the cavity and read the temperature at the bottom of the tube using an optical pyrometer. When the tube was open at the top end, some species containing Si diffused through the graphite walls, filled the lower part of the tube with pure silicon, and blocked the sight. The tube could be kept open when the top was sealed and some inert gas was blown in. Most readings gave $2000 \pm 100^\circ\text{C}$, but some readings were much higher. After such readings, the probe had scars indicating that an arc had burnt from the electrode to the pyrometer tube. In the second method, the crater content was photographed through the visual probe while the current through the furnace was shut off for a few seconds. The blacking density of the film was then measured and compared with a scale that was made by photography of objects of known temperature in a similar arrangement. These measurements also gave a result around 2000°C . Both methods give, in principle, the temperature of the condensed material where the reading was done, not the temperature of the gas.

Temperatures in the charge will vary both in horizontal and vertical directions. An average temperature in the charge, as a function of distance from charge-top, was calculated to increase almost linearly from 500°C to

1500°C in about 0.7 m. From 0.7 m and down to the cavity at 2.5 m, it further increased to 2000°C (Ringdalen *et al.*, 2020). This is not in accordance with industrial measurements in both FeSi and Si furnaces, where the temperature in the top layer of the charge is 1000–1200°C due to the exothermic combustion of CO and SiO as the gas meets the abundant air. Further down in the charge, between 0.5 and 1 m into the charge, the temperature was as low as 400–600°C (Ksiazek *et al.*, 2021). This was, however, between the electrodes and is dramatically lower than the calculated values. The temperature in the charge will vary with both the distance from the electrode and the charge-top, as well as with operational conditions.

Excavation of furnaces

Pilot- and industrial excavation has been done by Zherdev and Otani *et al.*, as discussed above, as well as pilot excavations (Müller, 1972; Schei, 1967; Schei and Sandberg, 1966). After 2010, a new period of pilot-scale excavations (Hoover *et al.*, 2022; Kamfjord, 2012; Myrhaug, 2003) and industrial excavations were carried out (Folstad, 2023; Jusnes, 2020; Ksiazek *et al.*, 2018, 2016; Tangstad *et al.*, 2014; Tranell *et al.*, 2010). Large-scale lab apparatus have also been used to simulate the industrial furnace, where a temperature gradient may be present from around 2000°C in the lower part of the crucible and 1200–1400°C on the charge top, and where up to 500 grams of silicon was produced in the lower part (Ksiazek *et al.*, 2015; Ringdalen and Tangstad, 2012; Saadieh *et al.*, 2018; Tangstad *et al.*, 2010). One can discuss if the shut-down furnace represents the conditions in the furnace during operation; however, when the furnace is shut down without melting it down and changing the electrodes, the zones and the materials found are believed to be close to the conditions during operation. Previously, the melt down of the furnace was believed to save time during the dig-out, however, the charge materials are typically very easy to dig-out, and there is a discussion if melting it down actually increases the amount of tough materials in the furnace like slag, metal and SiC crusts (Ksiazek *et al.*, 2018). If a furnace becomes available for careful excavation, it should be run normally until it is shut off in the middle of a stoking period. An experienced research metallurgist should be present all the time during the excavation and make a careful record of the observations, with description of the position and

surroundings of the samples taken out for further investigation. Samples gathered without a proper description of the furnace situation are almost worthless.

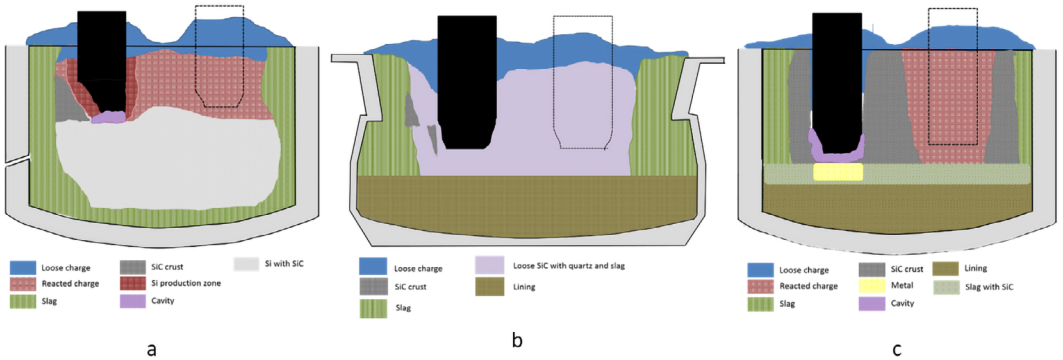


Figure 3.3 Examples of industrial excavations of silicon furnaces: a) represents a small furnace, b) represents a large furnace with loose charge, and c) represents a large Si furnace with a high amount of SiC crust (Ksiazek et al., 2016) [Used with permission from M. Ksiazek].

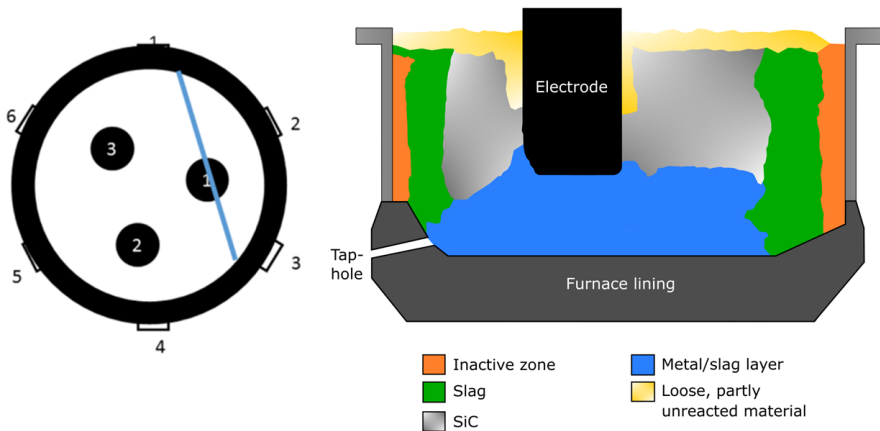


Figure 3.4 Example of a FeSi75 furnace (Jusnes, 2020) [With permission from K. Jusnes].

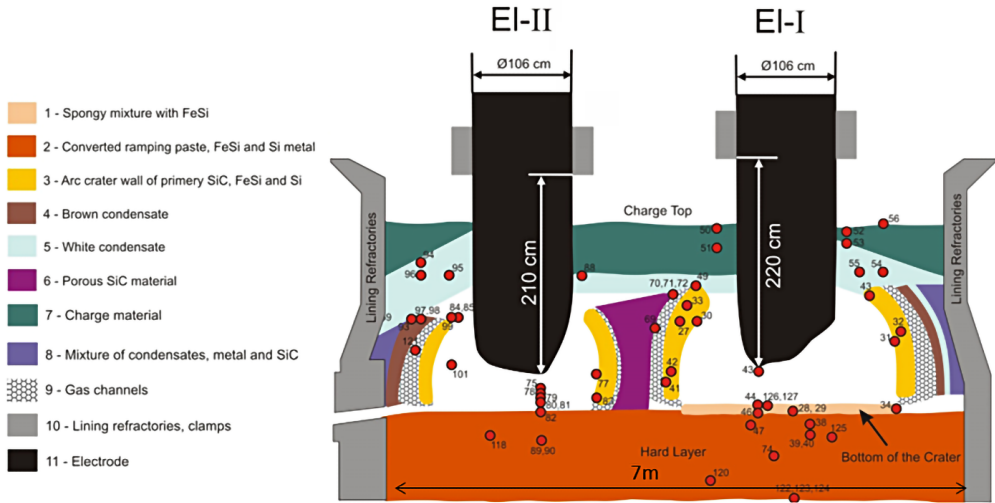


Figure 3.5 Example of a FeSi75 furnace (same furnace, but different time, as in Figure 3.4) (Tranell et al., 2010).

The zones found during excavations are illustrated in some examples in Figure 3.3 to Figure 3.5, where both silicon and FeSi furnaces are excavated. The zones present can differ considerably, despite the use of the same raw materials, the same product and similar furnaces. It is therefore believed that most of the zones present – and their extent and position – are due to operation over time, the raw materials, the carbon coverage, the energy density in the furnace, as well as furnace design and operational strategies. Differences between the furnaces include the position and extent of the cavity, the SiC crust and the slag present. The SiC crust and the slag will also be discussed in Chapter 8: Operational problems.

3.3 The inner structure of the reacting furnace

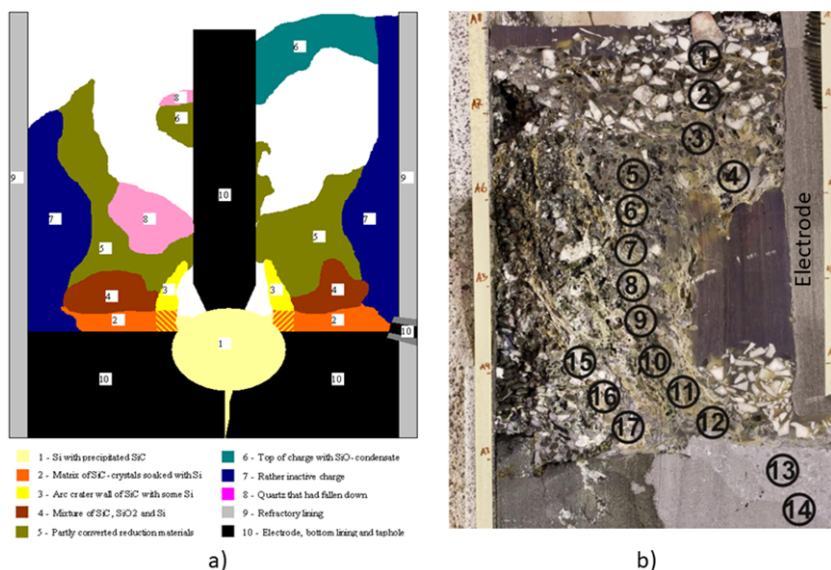


Figure 3.6 Excavation of 150 kW pilot scale furnaces producing silicon a) (Myrhaug, 2003) b) (Vangskåsen, 2011) [With permission L. V. Myrhaug and J. Vangskåsen].

The cavities in the furnaces can be found in two areas: around the electrode tip (also called the crater), and in the upper part of the charge, as seen in Figure 3.6a. These cavities can also be joined as one, as seen in Figure 3.6b. The top cavity has not been seen during industrial excavations, only in pilot-scale operation. As long as the industrial furnace is stoked regularly, it is believed that the higher cavities will be removed. The cavity around the electrode tip ranges from close to non-existent (Figure 3.3 and Figure 3.4) to relatively large (Figure 3.5). During excavation, materials in the lower part of the furnaces may be harder to spot and hence, a small cavity may be overlooked. Even in excavations where it was verified that no cavity was present, the materials could have descended after shutdown, or there could be no cavity during

operation (Ksiazek *et al.*, 2016). FeSi and silicon furnaces have a higher part of over-harmonics compared to coke bed processes like Mn-ferroalloy production (Barker *et al.*, 2007; Steenkamp *et al.*, 2017). This makes it probable that heating in Si/FeSi furnaces occurs with one or several arcs and hence, a cavity or cavities must be present. The point here is that the crater size can be large or very small. Another point is that the arc cannot be longer than around 10 cm with the voltages that are used in Si/FeSi furnaces. If the electrode is more than 10 cm from the silicon/FeSi layer, this means that the arcs will strike the sides of the electrode (Sævarsdottir and Bakken, 2010). As the electrode holders typically move more than 10 cm in a day, this shows that a significant part of the arcs strike horizontally from the electrode leg, as discussed in Chapter 6: Electrical operation. The cavity is formed because the charge does not descend, either due to condensates gluing the charge or due to the formation of a SiC crust.

The amount of SiC crust (α -SiC) varies. It may be totally absent (Figure 3.6b) or fill up a large part of the furnace volume (Figure 3.3c), but in most cases it will be somewhere in between. When the SiC crust is found, it is typically filled with silicon/ferrosilicon. If the arcs strike the SiC crust, which has a high electrical conductivity, the quartz meeting the SiC will be heated and react to liquid silicon. The silicon will then flow through the SiC crust and into the metal bath below the electrodes. When large SiC crusts are present, as in Figure 3.3c and Figure 3.5, gas channels are present in the crust; these may come from the $\text{SiO} + \text{SiC}$ reaction to liquid silicon.

Slag is typically found in the inactive zones in the furnace towards the lining; however, it may also accumulate in the bottom of the furnace, forcing the electrodes up. The most reactive area is, however, around the electrodes, and the slag layers will not be discussed further here. More information about the slag in the furnace can, however, be found in Chapter 4: Additional elements in the silicon process and in Chapter 8: Operational problems.

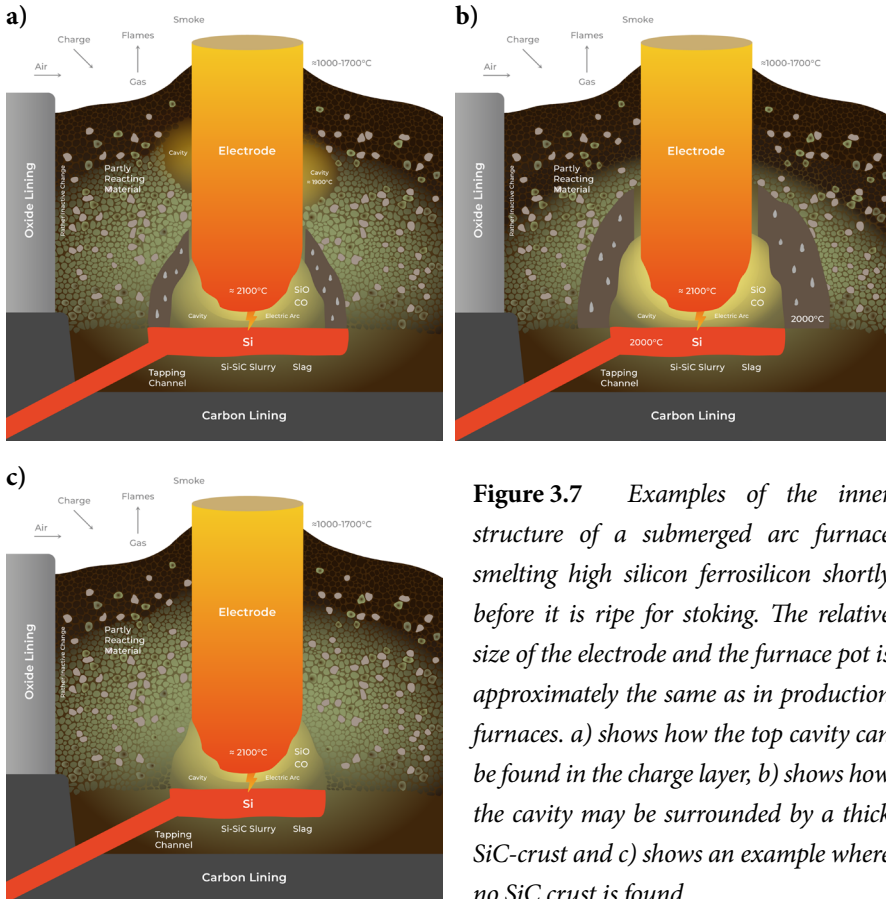


Figure 3.7 Examples of the inner structure of a submerged arc furnace smelting high silicon ferrosilicon shortly before it is ripe for stoking. The relative size of the electrode and the furnace pot is approximately the same as in production furnaces. a) shows how the top cavity can be found in the charge layer, b) shows how the cavity may be surrounded by a thick SiC-crust and c) shows an example where no SiC crust is found.

The experience and the observations described above provide examples of the overall picture of a working silicon furnace, as illustrated in Figure 3.7. It shows the furnace a short time before stoking. The electrode is surrounded by a gas-filled cavity. The cavity may however vary from very small to large, or it may form two separate cavities, as illustrated in Figure 3.7a. The cavities of the three electrodes are separated by charge materials in various states of conversion. The bottom of the cavity consists of a slurry of silicon and silicon carbide, possibly with an upper layer of relatively pure silicon. Higher up in the furnace, there are partly transformed charge materials: carbon particles partly converted to silicon carbide, softened or molten silica, and condensate.

The materials close to the inner area are heated enough to react, but the materials further away are rather inactive. The molten silica is highly viscous, and it may slowly flow down along the partly transformed charge (Dalaker, 2025).

The particles in the roof of the cavity are glued together so firmly that they do not descend. When the upper charge has lost the power to capture SiO from the gas, the operator breaks it down, fills in loose charge from the sides, and puts the necessary refill of new charge on the top. The transformed charge consists mainly of SiO₂ and SiC, with some Si from the condensate. These species react and produce SiO, which flows up through the new charge. The condensation reactions then heat the charge. The condensate glues the particles together to form a new thick deposit, which is consumed from below as the quartz melts and sinks down with other materials. It has been estimated that about 10% of the silicon produced may come from the condensate, as discussed in Chapter 2.

In operation with excess C in the charge, the carbon surplus will be deposited as SiC around the electrode. When the charge is corrected, the SiC can be consumed in the electrode path. At a distance away from the electrode, the SiC will be left as a wall, leaving a depression around the electrode. When the furnace is rotated, the depressions of the three electrodes will merge and result in a circular trench with walls of SiC, as seen in Figure 3.3c.

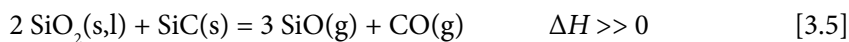
The temperature in the furnaces decreases towards the sides and below the high-temperature cavity. The tapped silicon is measured to be above 1900°C, though it loses temperature in the runner and in the ladle down to 1500–1600°C. The molten silicon is tapped through a tubular hole that reaches into the molten silicon slurry or slag from the outside. The tapping of the product can be carried out either continuously or discontinuously. Continuous tapping can go on for a long time with an even flow of silicon, without any gas jet out of the taphole. This observation shows that the taphole is not just an opening into a silicon bath, since a bath would soon be emptied down to the taphole, and then the crater pressure would send out a jet of gas. The tapping mechanism is probably that the molten silicon drains slowly through the slurry and/or the slag layer.

3.4 Reactions in the furnace

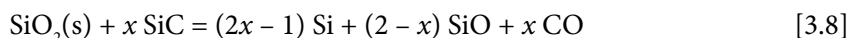
Qualitative description

This section will discuss the reactions in the furnace based on the information given above. This information is incomplete, and the reaction scheme must be treated with an open mind when more experimental material becomes available. Figure 3.7 shows the various zones of the furnace. In the hottest inner zone, the temperature of the condensed materials is around 2000°C, except for much hotter small volumes connected with the arc. The condensed species present are SiO₂, Si and SiC, with potentially some remaining free C. It is, however, rare that unreacted carbon is found in the high-temperature area at excavations. Any free C is unstable, and it will gradually change to SiC by reaction with SiO or Si.

The reaction between SiO₂ and SiC occurs in the hottest zone of the furnace, at the bottom and in the lower part of the crater. The reaction can formally be written as a combination of three reactions between condensed reactants, where Si and SiO-gas are produced:



The combined reaction can be written as



The slowest part of this set of reactions is most likely the strongly endothermic production of SiO by Reactions [3.5] and [3.6]. If the reactions are too slow to consume all the heat added from the arc, the temperature will rise, and the reaction rate will rise until a balance is obtained. The silicon-producing Reaction [3.7] requires, as can be seen from Figure 2.9, a high SiO content in the gas to give silicon. The SiO needed for the reaction can be produced in the same area as the Si-producing reaction, or lower in the furnace.

The gas leaves the furnace mainly through the charge, and Si units in the gas should preferably be recovered by reactions in the charge, otherwise,

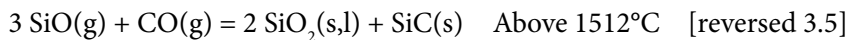
the Si units will leave the furnace. The conceivable recovering reactions are shown in Figure 2.9. When free carbon is available, the SiO can be bound by the reaction



which will give a resulting SiO content in the gas of less than 1 per cent at equilibrium. As the SiO loss of industrial furnaces is typically between 5–20%, the SiO pressure will be higher than 1% due to slow condensation reactions. These reactions are slow at temperatures below approximately 1500°C. When the gas passes through the cooler charge, the gas temperature drops, and the SiO becomes unstable. Observations show that the reaction



is preferred, even if the equilibrium graphs in Figure 2.9 show that the reactions



and



are thermodynamically more favorable. All the Reactions [3.10], [reversed 3.4] and [reversed 3.5] are strongly heat-producing. The product of Reaction [3.10] is found in relatively thick layers of a brown condensate in places where it is easy to get rid of the heat of reaction.

Reaction [3.10] heats the fresh charge until the temperature is high enough for Reaction [3.9]. If the amount of free carbon is not sufficient to bind all the SiO, the remainder will condense according to Reaction [3.10] until the charge is heated to the condensation temperature. The remaining SiO will pass the charge and burn above it, giving the white smoke that is so characteristic of open silicon/ferrosilicon furnaces. The white smoke consists mainly of silica particles less than 0.1 μm . Though the condensation product $\text{SiO}_2 + \text{Si}$ [3.10] is easier to find, the condensation product $\text{SiO}_2 + \text{SiC}$ [reversed 3.5] is also found during excavations and during lab-scale experiments.

When the brown condensate of finely dispersed Si in SiO_2 is heated, the Si droplets unite into large drops that can fall from the SiO_2 in the roof above the cavity. A fraction of the condensation according to Reaction [3.3] occurs at temperatures where the silica is molten. At these temperatures, the unmixing may be almost instantaneous, and the condensation will consist of deposition of SiO_2 at the site of condensation, while the Si falls into the cavity at once. This reaction is expected to leave a deposit of silica with a minor amount of silicon.

An alternative interpretation of the role of the condensation is that the $\text{SiO}_2 + \text{Si}$ brown mass evaporates as SiO when it flows back into the inner zone. This would give a sufficiently high content of SiO in the gas to allow production of Si. The two schemes, unmixing or evaporation, have the same overall effect on the furnace operation. However, as described in Chapter 2, it seems that most of the Si will unmix and not react with SiO_2 .

The SiO-forming reactions, with consumption of Si, SiO_2 and SiC, take place mainly in the lower part of the cavity, or at the SiC crust crater walls, where the temperature is highest. The cavity increases at the top, where the materials react partially, then fall and react further closer to the bottom. Some silica can also flow along the wall of the cavity. With excess carbon, the reaction at the bottom will give an excess of silicon carbide, which over time will produce SiC crusts. With carbon deficiency, the reaction may result in complete vaporisation of all the silica.

Stoichiometric analysis of the reactions in the furnace

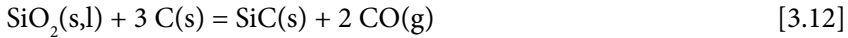
The qualitative description splits the furnace into two parts: an inner main reaction zone, where SiO_2 reacts with SiC and gives Si, SiO and CO, and an outer zone with low-temperature reactions. An overall understanding of the process can be obtained from a very simple model based on equilibria and mass balance restrictions on the flows into and out of the two zones. For simplicity, the energy needed to heat or cool the materials is neglected initially.

If we assume equilibrium between the phases SiO_2 , SiC and Si at 1 bar in the inner zone of the furnace, we have, according to Figure 2.7 or 2.8, a ratio $p_{\text{SiO}}/p_{\text{CO}} \approx 2$. The overall reaction in the inner reaction zone is then:



The inner reaction zone corresponds to the cavity and the inner layers of the charge in Figure 3.7.

First, we assume equilibrium also in the outer reaction zone, which corresponds to the low-temperature zone in Figure 3.7. The overall equilibrium reaction is:



We will balance a furnace process under these assumptions and give the result schematically in Figure 3.8. We need 3 SiO_2 and 2 SiC for the reaction in the inner zone. Addition of 2 SiO_2 + 6 C to the outer zone produces the 2 SiC . To consume the 2 SiC in the inner zone, we need 3 SiO_2 , which can be added through the outer zone. The gas from the inner zone will normally pass through the outer zone, but since it could react with C , it is assumed to bypass the outer zone in the schematic representation. The process gives, as a product, 1 Si from 5 SiO_2 , which means that the silicon recovery is only 20%.

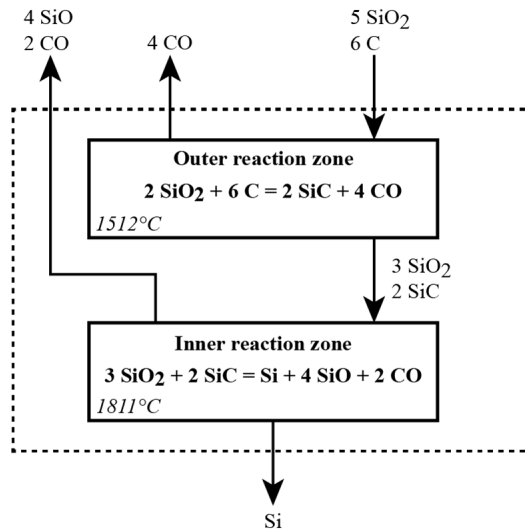


Figure 3.8 Schematic presentation of the furnace reactions for full equilibrium in the inner and outer zones. The necessary heating or cooling of the mass flowing between the zones is ignored.

Silicon recovery can be improved if SiO from the inner zone is captured by reaction with C in the upper part of the charge. This option is illustrated in Figure 3.9. In the scheme, SiO₂ is added directly to the inner zone to avoid the direct reaction between SiO₂ and C. In a real furnace, the low rate of the reaction between SiO₂ and C effectively blocks this reaction, as indicated in Chapter 2. As above, the inner zone needs 3 SiO₂ and 2 SiC. The 2 SiC are formed when SiO in the gas from the inner zone passes through the outer zone and consumes 4 C. Excess SiO is lost in the gas from the furnace. The process gives 1 Si from 3 SiO₂, that is, the silicon recovery has increased to 33 per cent.

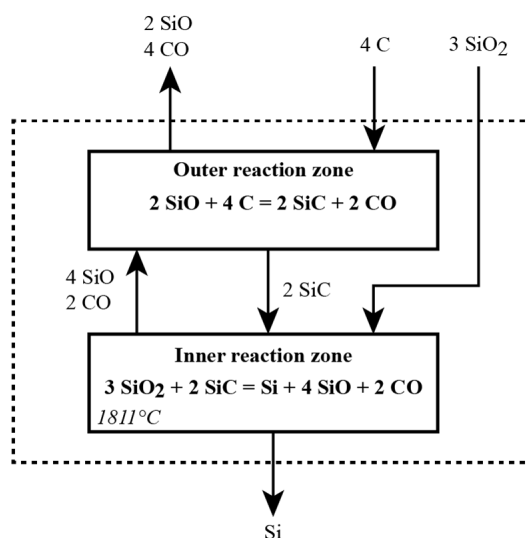


Figure 3.9 Schematic presentation of the furnace reactions for equilibrium in the inner reaction zone while the reaction between SiO₂ and C is blocked in the outer zone. The temperature in the outer zone is assumed to be high enough to prevent any condensation of SiO in the gas. The necessary heating or cooling of the mass flowing between the zones is ignored.

This silicon recovery is the highest that can be obtained if the reaction is carried out at equilibrium. In practical operation, 80–90 per cent silicon recovery is common, and close to 100 per cent can be obtained with favorable raw materials. The reason for this difference between experience and calculated results can be:

- Inaccurate thermochemical data
- The process is not running at equilibrium.

As discussed in Chapter 2, direct thermobalance measurements of the vapour pressure of the system $\text{SiO}_2 + \text{SiC} + \text{Si}$ indicate that the calculated total pressure is fairly accurate. Therefore, the most probable reason for the difference is a deviation from equilibrium. Two non-equilibrium processes are likely to be important:

- A low reaction rate in the inner zone gives a favorable reaction temperature.
- The cavity gas is cooled as it passes through the outer reaction zone, and Si-containing species condense.

Heat is added to the furnace, and, if the combined rate of the strongly endothermic Reactions [3.6] and [3.7] is too low to consume the heat, the temperature will rise. As can be seen from the equilibrium diagram in Figure 2.8, the production of free silicon requires a lower SiO content in the gas the higher the temperature. This effect will be expressed by a parameter s , defined as

$$s = \frac{p_{\text{SiO}}}{p_{\text{SiO}} + p_{\text{CO}}} \quad [3.13]$$

where the gas pressures apply to the inner reaction zone. The parameter s is assumed to be constant for given operating conditions. The value of s can be estimated from Figure 2.8, where, as an approximation, s can be set equal to the equilibrium gas ratio [3.11] for the Si-producing Reaction [3.5]. For complete equilibrium at 1811°C, it is 0.67. For $s = 0.5$, the temperature must be about 1980°C, and the inner-zone reaction becomes



For $s = 0.5$, the free C available in the charge is sufficient to bind all the SiO from the inner reaction zone, and a hundred per cent recovery is possible, as shown in Figure 3.10.

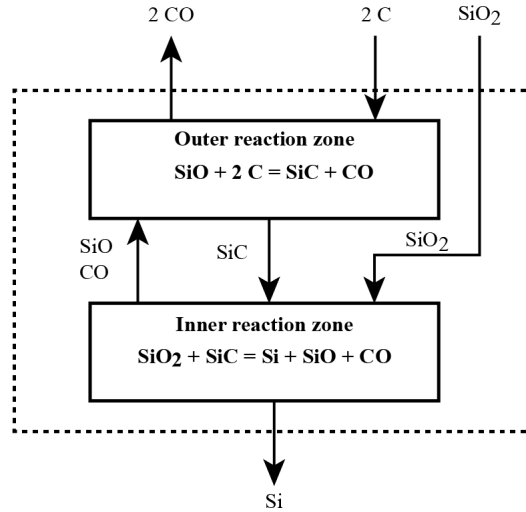


Figure 3.10 Schematic presentation of the furnace for $s = 0.50$. This is the highest value of s that allows 100 per cent silicon recovery. The temperature in the outer zone is assumed to be high enough to prevent any condensation of SiO in the gas.

In Figure 3.10 it was assumed that all the free C was converted to SiC by reaction with SiO in the outer reaction zone. However, it is known that this reaction often is incomplete. Lumps of carbon material react with the SiO in the gas and become covered with a layer of SiC. As this layer becomes thicker, the reaction slows down, and the lumps often retain a core of free carbon when they move into the inner zone. This transport of carbon into the inner reaction zone will influence the reaction. It can be characterized by a parameter r . We consider a quantity of charge with totally c moles of carbon, where c_r moles of carbon react with SiO according to Reaction [3.9].

$$r = \frac{C_r}{C} \quad [3.15]$$

The parameter r can be considered a measure of the reactivity of the carbon material. The effect of low r is shown in Figure 3.11. Here the ratio s is 0.5, as in Figure 3.10 in the inner zone, but only two thirds of the free C react with SiO in the outer zone. Then $r = 0.67$, and the silicon recovery drops from 100 per cent in Figure 3.10 to 50 per cent in Figure 3.11. This example shows

that the recovery drops strongly if the reaction with C is incomplete in the outer reaction zone.

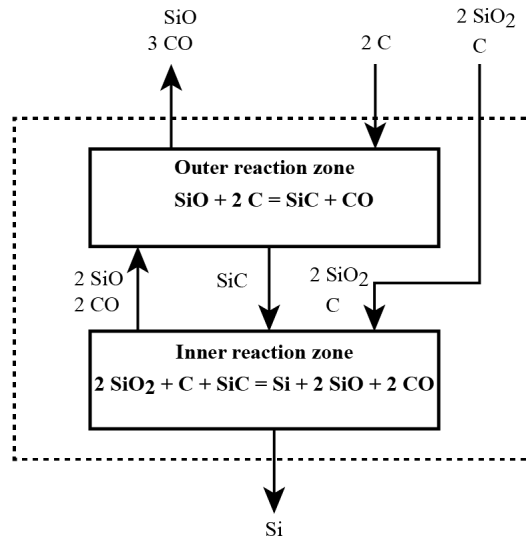


Figure 3.11 Schematic presentation of the furnace reactions with $s = 0.50$ and $r = 0.67$. The temperature in the outer zone is assumed to be high enough to prevent any condensation of SiO in the gas.

So far, the temperatures in the reaction zones have been assumed to be suitable for the expected reactions. In the furnace, however, heat is added mainly to the inner zone. In a furnace corresponding to the scheme of Figure 3.11, the raw materials are added cold to the outer reaction zone, where they are heated by the hot gas and by reactions. The heat capacity of the charge can absorb the heat of reaction for the SiO -catching condensation Reaction [reversed 3.6]. An estimation for a simplified situation, listed in Table 3.2, will indicate the order of magnitude of this effect. Here, the SiO_2 is added in the outer reaction zone, but the direct reaction between SiO_2 and C can be ignored, since the rate is low. It is seen that the energy in the SiO and CO gas from the high temperature zone, plus the exothermic reactions, is enough to heat the solid materials to close to 1700°C .

Table 3.2 *An example of estimation of the extent of condensation in a simplified version of the silicon process with data from HSC 9.0.*

Input species into the condensation zone				
	Temperature	Amount	Heat content	Total H
	°C	kmol	kJ	kJ
SiO(g)	1980	1.16	81	−39
CO(g)	1980	1	66	−45
SiO ₂	25	1	0	−911
C	25	2	0	0
				−994
Output species out of the condensation zone				
	Temperature	Amount	Heat content	Total H
	°C	kmol	kJ	kJ
SiO ₂	1700	1.08	127	−856
SiC	1700	1	78	6
CO(g)	1000	2	62	−159
Si	1700	0.08	8	8
				−1002

The estimate in Table 3.2 gives only an indication of the extent of condensation because the completeness of the reactions in the outer zone is uncertain. Heat loss during the operation is not included in the calculation. We include the calculated condensation in the overall reaction of Figure 3.11, which has the largest s value that can give 100 per cent silicon recovery without condensation. The results in Figure 3.12 show that s can be increased to about 0.54 while the silicon recovery is still 100 per cent when the condensation is included.

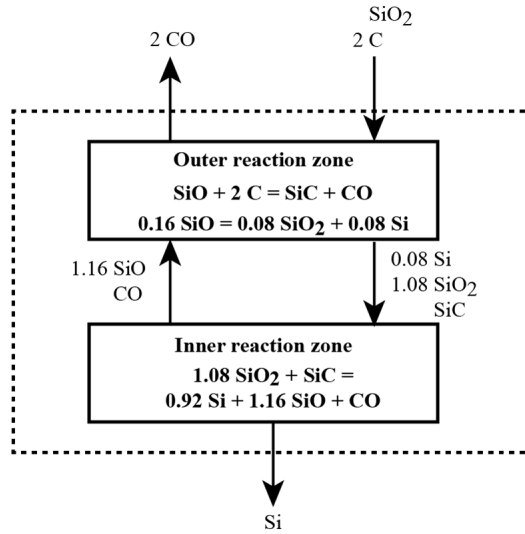


Figure 3.12 Schematic presentation of the furnace reactions with $s = 0.537$ and $r = 1.00$. Condensation according to $2\text{SiO} = \text{SiO}_2 + \text{Si}$ runs to the extent estimated in Table 3.2.

The condensation reaction



has been assumed in the discussion above. However, both condensation reactions [the reversed reactions 3.5 and 3.6] will occur in the furnaces as described in Chapter 2, and they will have the same effect in capturing SiO gas.



3.5 Critical reactions in the carbothermic process of silicon

The furnace observations and the discussion of the reaction models lead to the following conclusions:

- SiO_2 and SiC react in the inner hottest zone of the furnace and produce Si only if the SiO content of the gas is sufficiently high.
- CO from the inner zone must leave the furnace, and it necessarily carries a high content of SiO . This SiO must be recovered in the outer zone if the silicon recovery is to be high.
- The reaction between free C and SiO can capture the SiO in the outer zone and bring it back to the inner zone with the charge.
- The amount of SiO to capture depends on the content s of SiO in the inner zone.
- At equilibrium, the value of s in the inner zone is so high that the available free C is not enough to capture all the SiO .
- If s is decreased, for example by raising the temperature, the silicon recovery in the process increases.
- The silicon recovery decreases with an increasing C fraction that does not react in the outer zone.
- Condensation of SiO as $[\text{SiO}_2 + \text{Si}]$ in the outer reaction zone can increase the silicon recovery.
- The amount of SiO that can be captured by condensation is limited, because the heat of condensation can raise the temperature of the outer zone to the temperature of condensation.

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