

Modified and alternative processes

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9.1 General

The submerged arc process for silicon and high silicon alloys has now been in operation for about a century. During this time, efficiency has improved and the scale has, as seen in Figure 9.1, increased dramatically (Nelson, 2014). However, the fundamentals and main principles of the current process, as described in Chapters 2 and 3, are still very much the same.

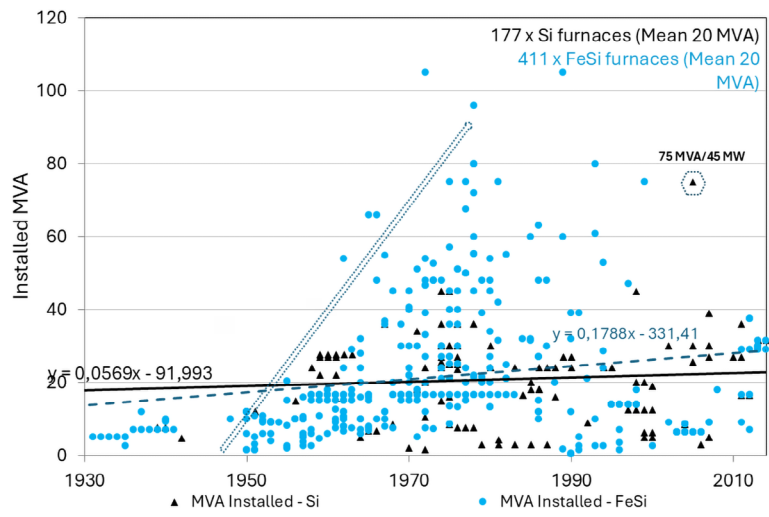


Figure 9.1 *Historical progression of installed MVA of silicon and ferroalloys furnaces (Based on Nelson, 2014).*

Silicon producers have continuously investigated methods to improve the existing carbothermic process and to develop and industrialize alternative process routes. The production of silicon metal and high silicon alloys is technically well established, and alloys with almost any specification can be produced using known technology. The initial drive behind process modification was mainly cost reduction. Subsequently, modifications and the development of new processes to improve the working environment and minimize emissions to the outer environment became increasingly important. In the wake of the climate crisis, the focus on developing new and improved carbon-lean processes has intensified. Decarbonization of the production process, including the energy supply system, is the first and most important step. Recirculation of by-products and the use of alternative raw material sources are other means of reducing the carbon footprint of the process.

With the scope of lowering or avoiding greenhouse gas emissions, some proposed modifications of the carbothermic process are described in the first part of this chapter. In the second part of the chapter, alternative process concepts are described.

The cost and risks of full-scale testing of modified and alternative processes are typically very high. As such, the path towards industrialization will often start with a combination of thorough mathematical modelling and small-scale experiments. If these are successful, they can be followed up with larger-scale and pilot experiments. The main performance indicators to consider during development of process modifications and alternative processes can be summarized as:

- Specific greenhouse gas (GHG) emissions (CO_2 , CO , CH_4 , NO_x , etc.)
- Other non-GHG emissions to outer and working environment (dust, SO_x , etc.)
- Economic feasibility
- Silicon yield
- Energy losses
- Flexibility in use of raw materials
- Operational and maintenance costs
- By-product quality and quantity (e.g. silica fume recovered from off-gas, slag)
- Process suitability for energy recovery and carbon capture
- Process adaptability for automation and control

Approaching a carbon neutral process, while continuing to rely on carbothermic reduction, can be done by using biocarbon reductants, as discussed in Chapter 5, and/or carbon capture, as described in Chapter 9.4 (Mathisen *et al.*, 2019; Surup, 2019). In a long-term perspective, there are many reasons to look for other technological solutions (Kero *et al.*, 2022). The presented methods for production of silicon without greenhouse gas emissions cover elimination of direct process emissions (Scope 1) in the reduction step, indirect emissions from electricity production (Scope 2), and transport or other activities/raw materials (Scope 3).

The diversity of silicon alloy products, both with respect to raw materials and reduction processes, must also be considered. The use of aluminothermic reduction may, for example, be a way to recirculate various industrial by-products into silicon alloys (Zhu *et al.*, 2024). There are many environmental aspects to consider beyond greenhouse gas emissions, for example, the generation of new types of wastes and emissions.

9.2 Modified carbothermic process

Closed furnace

Most silicon and ferrosilicon furnaces are open or semi-open, with an influx of air just above the charge level where the combustible gases (mainly CO and SiO) from the process oxidize. This is in contrast to most other ferroalloys produced in SAF, with only 26% of FeMn and none of FeNi production taking place in open/semi-open furnaces (Nelson, 2014).

The main advantages of closed furnaces are:

- Cooler charge top (less vapour/dust losses) and less oxidized materials will improve capture and control of emissions.
- Less dilution of the combustible gases (i.e., CO and H₂), making them suitable for later production of CO as a saleable by-product and for energy recovery and carbon capture.
- Less infiltration of air for combustion and cooling will give a smaller volume of off-gas and thus less amount of gas that needs to be cleaned. There will also be less direct energy losses through off-gas. The downstream off-gas handling systems can hence have a lower capacity.

The possibility of closing FeSi and Si furnaces has been investigated over the years by different companies, using different approaches. However, despite previous attempts at closing silicon furnaces, closed furnaces are not used for silicon production industrially today (Andersen, 2023; Monsen, 2009). Most modern and large furnaces are, however, semi-closed, with ports or doors that can be opened for inspection and stoking.

An obstacle for closing Si furnaces is the need for access to, and visual inspection of, the charge top for stoking, to obtain a sufficient downward flow of the materials and avoid clogging due to SiO condensation. Another obstacle, and the main challenge, is the handling of unburned gas with high amounts of SiO and tar, which might lead to scaling in the off-gas channels. The contamination of the valuable silica fume by-product will also be an issue.

With modern camera technologies, both standard and IR cameras, already installed at several furnaces, visual inspection is possible. The remaining obstacles – contamination of fumed silica and scaling in the off-gas handling system – need further research and development (Li *et al.*, 2024).

Closing of Si-furnaces has been investigated in pilot scale and by industrial campaigns, mainly by Dow Corning and Elkem (Monsen, 2009). It is also reported that a Japanese company operated a commercial furnace for FeSi75 successfully for a long time around 1970, with stoking carried out by 17 stoking machines that were operated through holes in the lid (Schei *et al.*, 1998). Dow Corning ran several pilot campaigns in the period 1987–1991, producing Si in closed furnaces (Dosaj *et al.*, 1991, 1994; Dosaj, 1995), which resulted in a patent (Arvidson *et al.*, 1991). The first experiments were run at 90 kW in a 0.1 MW AC furnace. Further work focused on DC technology, and pilot campaigns were run in a 2 MW DC furnace and then in a 6 MW DC furnace, operated in 12 campaigns for 3–6 weeks at up to 2.5 MW. The furnace was not rotating and was stoked by rods through holes in the lid. Charcoal (30–100%) was used as reductant to reduce the amount of volatiles and tar. The off-gas contained 70–75 vol % CO. The fume was not pure SiO₂ but contained both some Si and 2–14% SiC, with the highest levels with coal and the lowest with charcoal as reductant. There was no blockage of the pipes by silica fume when charcoal was used as reductant, but an incident occurred when a high percentage of coal was in the charge mixture. Dow considered the pilot campaigns to run well. Reported benefits included reduced oxidation of, and loss of, carbon at the charge top and fewer contaminants in the produced Si.

Material flow was one of the main challenges. The main reported challenges that stopped further upscaling and industrialization were downward material flow and energy distribution.

Elkem ran pilot and industrial campaigns from 1973 to around 1978 to produce FeSi in closed furnaces (Arnesen and Bjørdal, 1981; Lundberg, 1978; Schei *et al.*, 1998). Introductory experiments were first run in a 0.5 MW furnace and carried further in a 2 MW furnace. Then FeSi75 was produced in an 8.5 MW furnace at Elkem Bremanger in test campaigns for more than 3 years. Instead of stoking, the charge movement was controlled by the split furnace body, as described in a separate section, where a furnace ring rotated with a speed of 3–5 hours per revolution. The furnace was equipped with a complex system for feeding the raw materials. In the beginning, many practical difficulties resulted in a low operating time. In spite of this, the metallurgical operation was surprisingly easy and the silicon recovery high.

The gas from the furnace had to be cleaned because it contained silica dust, tar, and other unacceptable environmental pollutants. Wet scrubbing is an established technology for removing pollutants from the gas, but cleaning the water is expensive. Therefore, a dry gas-cleaning system was selected and after some development work, it operated satisfactorily. The dust had a volume weight of about one third of the volume weight from open furnaces, and its specific surface was slightly higher than the 20 m²/g typical for open furnaces. The primary particles were equal to or smaller than those from open furnaces, but in filters and cyclones the dust behaved as if it consisted of larger particles.

An analysis of the dust is shown in Table 9.1 and of the gas in Table 9.2. The main difference is the very high carbon content. In the small-scale experiments, the dust also contained considerable amounts of free Si from the condensation reaction:



However, the dust from the industrial furnace had a very low content of Si. This was most likely caused by oxidation by water from the raw materials:



Thus, the chemical energy of the SiO is recovered as chemical energy in the gas, rather than as heat. A few samples were analysed for critical environmental contaminants, and the results showed that the dust contained about 0.4 wt% of PAH (polyaromatic hydrocarbons), as well as small amounts of phenols and cyanides. The gas contained tar, so it was necessary to run the dry filter at a temperature above the dew point of tar to avoid clogging. Such contaminants are destroyed effectively in the flames of open furnaces.

Table 9.1 *Average composition of the filter dust from open and closed furnaces producing FeSi75 (Arnesen, 1981).*

	Analysis wt%			
	SiO ₂	Si (met)	C (tot)	Ignition loss
Open furnace	86–90	0	0.8–2.3	2–4
Closed furnace	80.3	0.25	9.3	8.3

Table 9.2 *Average composition of the gas from a closed furnace producing FeSi75 (Arnesen, 1981).*

Volume%								
CO	H ₂	CO ₂	O ₂	N ₂	CH ₄	C _m H _n	H ₂ O	H ₂ S
70	20	3	< –0.5	4	2	0.3	8	0.1

While the closed furnace at Elkem Bremanger was being developed, a market for silica fume from open furnaces was successfully established, and the value of the fume subsequently became important to the overall economy of the process. Since the silica fume from the closed furnace contains too much carbon and toxic substances to be used without expensive treatment, it is uncertain whether the purified dust has the same sales value as dust from open furnaces.

Since small industrial closed furnaces have operated for long periods with fair metallurgical results and acceptable dry cleaning of the gas, there are no indications that operating a large furnace will be impossible. However, compared with an open furnace, the silica fume from the furnace is less valuable,

and the furnace produces more environmental contaminants that must be treated. With the upcoming CCS discussions and upgrading of the off-gas, this process will again be of interest.

Direct current

Direct current does not introduce any principal changes in the mechanism of the process, but it may reduce some costs and open the way to automation of stoking and charging.

Power plants sell alternating current, which needs to be transformed on site to direct current. Rectification has a direct cost and an energy loss, but these costs can be compensated by advantages in the process. The main expected benefits of direct current are:

- Strongly decreased electrode consumption (if the electrode is the negative pole).
- Decreased induction losses to the surroundings give higher thermal efficiency and avoids the need for expensive non-magnetic construction materials in the vicinity of the current conductors.
- The possibility of using a single-electrode furnace with bottom contact can give simpler furnace operation. With alternating current, the induction will be prohibitively large. With single-electrode furnaces, the reactor will be symmetrical, and the stoking and charging operation will be simpler and can be automated. It will be necessary to develop a reliable bottom contact, but it should be possible to solve this problem since the furnaces for high-silicon alloys use conducting carbon as the bottom lining.

Experiments in small direct current furnaces have confirmed reduced electrode consumption (Müller and Magnussen, 1972), but long-term experience is necessary to quantify the gain. The behavior of the furnace is similar for direct and alternating current, and the chemical reactions are essentially the same. However, one can expect a change in the gas flow in the crater (Andresen, 1995; Larsen, 1996). The arc acts as a pump that sets up a circulation of gas in the crater, and the resulting flow may be different if the flow is continuous rather than changing direction many times per second.

The internal heating of the electrodes will be different for direct and alternating current. In a cold electrode, heat production is uniformly distributed over the cross section with direct current, whereas it is highest near the surface with alternating current. This heating raises the temperature, and the direct current electrode will be hotter in the centre, since heat flow towards the surface requires a temperature gradient. Heating of the centre is self-amplifying, since the conductivity of the electrode material increases with temperature and the centre then draws more current. The excess temperature of the centre will be higher with larger electrode diameters. This internal heating may therefore set lower limits for the allowable load of DC electrodes compared with AC, especially for large diameters. If a single-electrode direct current furnace is to have the same productivity as the present three-electrode furnaces with alternating current, the electrode load will be three times as large. The craters around the electrode tip must then treat much more material than the craters in present-day furnaces. The metallurgical effects of such large craters are not known.

In summary, there is some doubt about the behavior of large direct current furnaces. The problems will appear mainly with large electrode diameters, and they cannot be investigated with small-scale experiments. Some understanding can, however, be obtained from mathematical modelling.

Split furnace body

The purpose of the split furnace body is to make the top of the charge sink continuously. This operation is expected to give constant production conditions and savings in investment and labour. The split furnace body changes the furnace process from semi-continuous to continuous.

As described in Chapters 3 and 5, silicon furnaces have cavities around the electrode tips and further up in the charge. The cavities occur because condensate from SiO in the gas glues the charge particles together, forming a bridge in the charge. This bridge is gradually consumed from below during operation, and the cavity expands, while the upper part of the charge stays in place until the bridge becomes thin and breaks down. Normally, it breaks down irregularly, and it is necessary to stoke down remains of the bridge to achieve a uniform distribution of the new charge and avoid bridges of sintered

charge around the electrodes. Before the bridge breaks down, the available free C in the charge materials has been transformed to SiC, and condensation has heated the charge to the condensation temperature. The materials then lose their ability to capture SiO, and the SiO content of the outgoing gas increases. The operator will normally stoke down the charge layer when the SiO loss increases sharply. The stoking can be mild, since the purpose is not to stir the content of the furnace, but only to remove obstructions to an even distribution of the new materials.

This discontinuous operation requires expensive stoking machines, large space around the furnace, and much labour. It leads to periodic variations in the charge content of the furnace, and there will be periods with high silica loss before and during stoking. Compared with standard operation, continuous operation with uniform sinking of the charge is expected to give higher Si recovery and constant conditions, without strong blows on the top of the furnace. The heat strain on the furnace hood and other equipment will be lower.

For a closed furnace, it is particularly important to achieve smooth operation with even sinking of the charge, since access to the surface is difficult. Krogsrud *et al.* worked on the development of an automatic stoking system for a closed furnace, and one of their ideas was to improve the material flow in the furnace through a reconstruction of the furnace (Krogsrud *et al.*, 1978). The upper part of the furnace wall was replaced by a separate rotating part called the *ring*. This ring, which rotated once every few hours, had a lining formed as a regular polygon, preferentially a nonagon. The rotation and the inner form should transfer force to the charge and improve sinking.

Some experience with the split furnace is recorded by Arnesen and Bjørdal (1981) for FeSi75 and by Tveit and Gard (1982) for silicon metal. The ring was operated with one rotation every few hours. The rotation could be in one direction, or with controlled changes in direction. The furnace ran with good results without stoking. On the furnace top, one could see that a thin charge layer close to the lining rotated with the ring, while the inner part of the charge was motionless or lagged behind. This relative movement created shearing forces in the charge, and a shearing circle was visible on the furnace top. The gas from the reactions came up, and the charge sank down smoothly within this circle. Compared with the standard furnace, the charge sank over a much wider area. The operators had to add charge where it was needed on

the top of the charge. The split body furnace needs a better distribution of the charge than the standard furnace, since there is no horizontal movement of the charge after addition. A 30 MW split body furnace was operated for about sixteen years with FeSi75 in Norway, with good operation without stoking.

The split body furnace has been run for years without stoking for FeSi75, and for long periods with silicon metal. This can make the operation continuous, with a strongly reduced tendency to blowing.¹

Carbon Capture (CC) and Carbon capture and use (CCU)

Carbon Capture

With carbothermic Si production currently being the only commercial technology for Si/FeSi production, Carbon capture and storage (CCS) or CCU is hence a possible carbon abatement strategy for this industry, although a costly one (IPCC, 2022). For silicon production, the low CO₂ concentration in the off-gas is a challenge that both limits the technology available for CC and increases the cost of employing any available technology.

The reason for the low CO₂ content in the gas, as described in previous chapters, is that a large amount of air is introduced to the furnace hood to combust CO and SiO. This limits the temperature from the combustion and ensures strong enough under-pressure to contain the process in the hood. Operation of the baghouse filter capturing the silica fume sets limitations on the temperature of the off-gas (Fereday *et al.*, 2013). Higher furnace off-gas temperatures allow for less process gas dilution, as less ambient air is needed for temperature control, this also leads to higher CO₂ concentration in the off-gas. However, at a certain point, two other factors besides filter operation would start to limit the maximum off-gas temperature from the furnace. One is the need for under-pressure inside the hood to contain the process, which requires some suction of ambient air into the process. The other is the increased potential for scaling in the off-gas system, under the wrong hood conditions, due to the combustion of SiO gas into particulate silica fume (Hauge, 2022; Schei *et al.*, 1998). While the maximum operation temperature often is set by

1 Personal communication from Nygaard in 1998.

the filter bags, the minimum operation temperature is usually given by the acid dew point temperature, which is dependent on sulfur and moisture content in the off-gas (Belo *et al.*, 2014). Condensation of acids, specifically H_2SO_4 , causes excessive corrosion issues; the off-gas temperature must therefore be kept sufficiently high. The most common and mature CC approach considered for the silicon industry is the use of chemical solvents such as amines to separate CO_2 from the reduction gas. Amines are water-soluble organic chemicals that contain reactive nitrogen atoms and can rapidly, selectively, and reversibly react with CO_2 . For this technology, SO_2 in the flue gas causes free amine loss, which may lead to a rise in CO_2 capture energy consumption. SO_2 in the flue gas has also been shown to result in amine degradation, with heat stable salts produced (Gao *et al.*, 2015). Hence, the silicon furnace off-gas may require pre-capture SO_2 gas cleaning. An industrial pilot of amine-based CC from FeSi production in Mo i Rana, Norway, was carried out during 2022 and 2023 in a collaboration between Elkem and Aker Solutions, claiming above 95% CO_2 capture efficiency.

Carbon Capture and Use (CCU)

There are a number of well-known methods to convert CO_2 into useful industrial chemicals. Examples of these include:

- **Methanol synthesis:** CO_2 can be catalytically converted with hydrogen to produce methanol, which is a basic chemical building block for many other products.
- **Urea production:** This is a well-established process where CO_2 reacts with ammonia to produce urea, a key component in fertilizers.
- **Polymers:** CO_2 can be used in the production of polymers, plastics, and other materials, such as polycarbonates and polyurethane.
- **Synthetic fuels:** Using the Fischer-Tropsch process, captured CO_2 can be converted into synthetic fuels and other valuable products, such as building materials.
- **Other chemicals:** CO_2 can also be used to produce formic acid and synthesis gas.

While CO₂ separated from an industrial off-gas has different industrial applications, one innovative *direct* use of the FeSi furnace off-gas at the Norwegian Finnjord plant is cultivation of photoautotrophic microalgae (diatoms) by utilizing the CO₂ in the gas as a carbon source in the photosynthetic production process. Additionally, the NO_x in the gas may be used by the diatoms as an inorganic nitrogen source. The diatom species is adapted to low temperatures and irradiance levels found in northern Scandinavia. Further, the cultivated species handle low pH levels, which is necessary since addition of Si production fumes with high (7–8%) CO₂ content lowers the pH in the photobioreactors.

Flue-gas recycling (FGR) for CCS or CCU

As an alternative to a closed furnace, and with a purpose of increasing the CO₂ content of the off-gas (allowing for a more cost-effective carbon capture), Andersen and co-workers did extensive modelling and pilot studies on flue gas recirculation (FGR) for MG–Si production (Andersen *et al.*, 2023b, 2023a, 2021). The basic principle of FGR is to replace some of the ambient air added to the process with cooled and cleaned recirculated flue gas, to avoid dilution of the CO₂ in the off-gas with additional air. FGR is also a known method for NO_x reduction in combustion processes (Qian *et al.*, 2013), a potential added bonus for the Si process (Houshfar *et al.*, 2012; Sidorkin *et al.*, 2016).

Andersen *et al.* (2021) developed a mass- and energy balance, based on available literature, for a 100 MW silicon operation with a flue gas de-sulfurization (FGD) unit and a conventional chemical absorption carbon capture plant. Results illustrate the change in off-gas compositions (Figure 9.2). With five different scenarios for extent of flue gas recycling, economic modelling illustrated potentially large savings by the introduction of FGR, given other factors such as charge composition, yield etc. being constant (Figure 9.3).

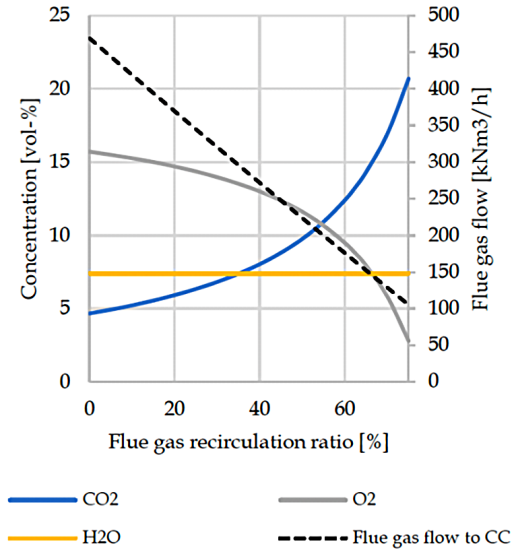


Figure 9.2 HSC chemistry simulations of off-gas composition and flow to the carbon capture unit with different degrees of FGR (Andersen et al., 2021).

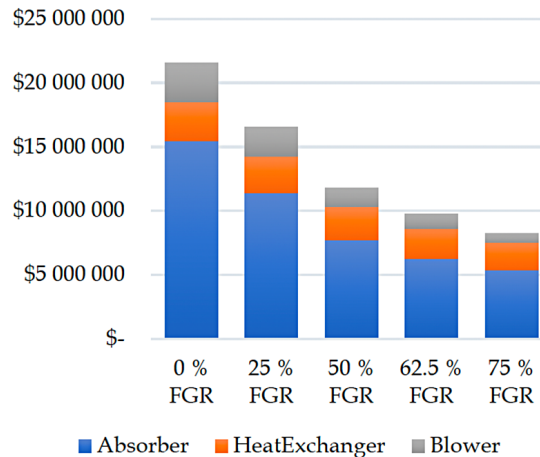


Figure 9.3 Calculated cost for implementation of carbon capture for a 100 MW Si operation with different degrees of off-gas recirculation including absorbers, heat exchangers and blowers (Andersen et al., 2021).

In their FGR piloting work, Andersen *et al.* used a rebuilt off-gas system on a 150 kW single electrode SAF, fitted with extensive measurements of gas composition of in-going and out-going gas to/from the furnace, as well as sampling of silica fume (Andersen *et al.*, 2023b). The composition of raw material used in the campaign is listed in Table 9.3.

Table 9.3 *Details of the raw material mix used for the pilot scale experiment (Andersen et al., 2023b).*

		Coal	Charcoal	Coke	Woodchips
Share of C-coverage	% of FixC	40	15	30	15
Compound					
Moisture	%	10.8	4.7	11.7	4.8
FixC	% DW	57.6	79	90.5	14.6
Volatiles	% DW	40.4	17.7	6.64	84.2
Ash	% DW	2.04	3.32	2.84	1.16
Elements					
Carbon	% DW	78	83	89.3	50.7
Nitrogen	% DW	1.58	0.39	1.78	0.2
Oxygen	% DW	12	9.6	3.83	41.4
Hydrogen	% DW	5.79	3.71	1.83	6.48
Sulfur	% DW	0.52	<0.1	0.42	0.11

Results obtained from the campaigns show that it is possible to reach above 20 vol% CO₂ in the off-gas by controlling the gas flow and the degree of gas recirculation (Figure 9.4). The measurements are well aligned with the modelled/calculated CO₂ contents. Figure 9.5 illustrates that, while the NO_x concentration in the off-gas increases with a higher degree of FGR, the total amount of NO_x generated is lower with FGR and also lower than the modelled content. While there was a concern that the quality of the silica fume product, as measured by its specific surface area (SSA), would be adversely affected by the lower oxygen content in the off-gas, it appeared that SSA was not significantly lowered through either lower gas flow or higher FGR (Andersen *et al.*, 2023).

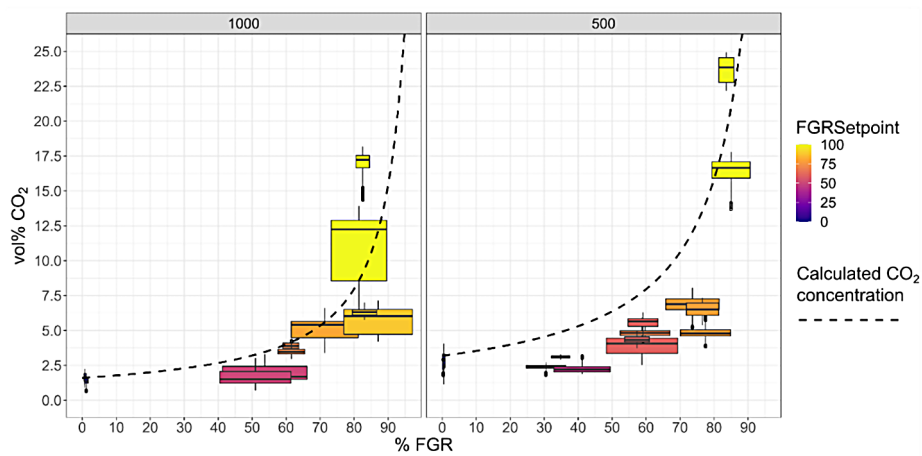


Figure 9.4 CO₂ content in the off-gas measured and modelled for different FGR settings at total gas flows of 1000 Nm³/h and 500 Nm³/h respectively (Andersen, 2023).

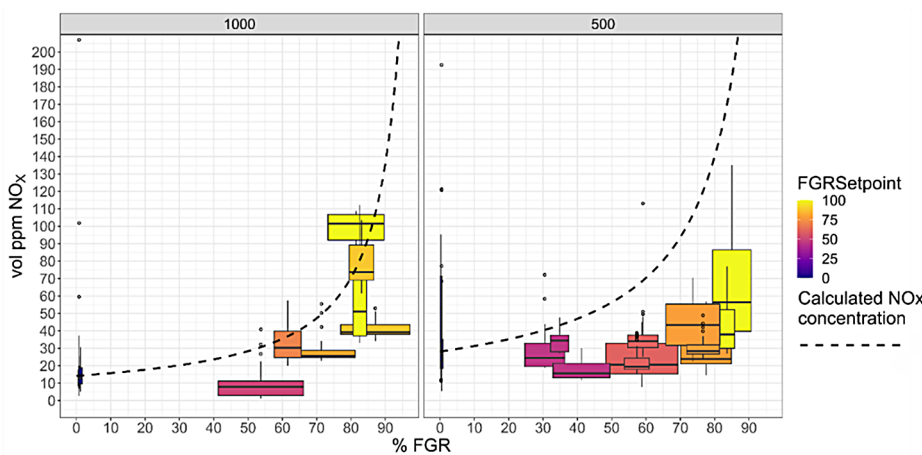


Figure 9.5 NO_x content in the off-gas measured and modelled for different FGR settings at total gas flows of 1000 Nm³/h and 500 Nm³/h respectively (Andersen, 2023).

Composite agglomerates

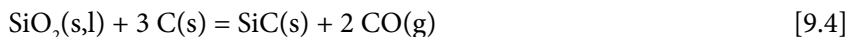
With composite agglomerates, the reaction scheme changes thoroughly, and the materials in the outer reaction zone increase their ability to recover SiO. In this section, the idea will be described first, then the available practical experience will be summarized, and the possibilities will be discussed.

The principle

In the standard process, SiO from the inner zone is recovered from the gas leaving through the outer zone, mainly by reaction with free C. When the raw materials SiO₂ and C are added as lumps, the direct reaction between them in the outer zone is so slow that it can be disregarded. If the materials are powdered and mixed, the reaction will be much faster. For use in a furnace, the mixed materials must be agglomerated to make the charge sufficiently porous to let the process gas out. Hot SiO-rich gas from the inner zone passes through the charge mix in the outer zone. Then the gas is cooled, and the strongly heat-producing condensation reaction:



will run. As explained in Chapter 2, this reaction is the main condensation reaction in a submerged arc furnace. The SiO pressure of this reaction is very low at, say, 1300°C, and the SiO content of the gas leaving the furnace may be low. However, the produced heat will raise the temperature of the charge to the condensation temperature, and then the SiO will be lost from the furnace. If the strongly heat-consuming reaction:



runs in the outer zone, it will consume the heat, and the temperature cannot rise at equilibrium above the co-existence point 1512°C for SiO₂-C-SiC. Therefore, when SiO-containing gas is conducted through a charge originally consisting of SiO₂ and C, the lowest layer will reach a temperature of 1512°C if the reactions are fast. The gas leaving this layer will contain about 4 per cent SiO, according to Figure 2.9 under equilibrium conditions. This gas will pass through the cool charge above, and SiO will condense to an extremely

low content. Stoichiometry of a reaction based on recovery of SiO by the condensation Reaction [9.3] is shown in Figure 9.6. The inner zone reaction corresponds to equilibrium between SiO₂, SiC and Si.

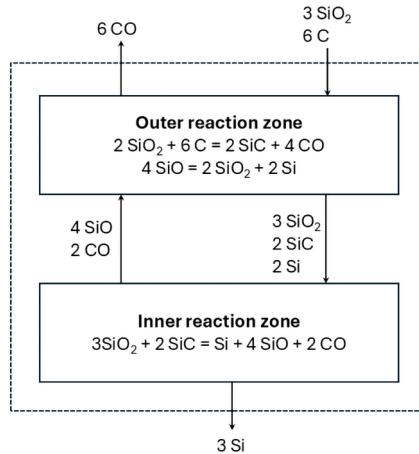


Figure 9.6 Stoichiometry of a reaction based on recovery of SiO by the condensation Reaction [9.3]. The inner zone reaction corresponds to equilibrium between SiO₂, SiC and Si.

The reaction in the inner zone is characterized in Chapter 3 by the content s of SiO in the gas leaving the zone.

$$s = \frac{p_{\text{SiO}}}{p_{\text{SiO}} + p_{\text{CO}}} \quad [9.5]$$

The value $s = 0.67$ corresponds to equilibrium in the inner reaction zone. The discussion in Chapter 3 showed that the Si recovery will be only 33 per cent when SiO is recovered by reaction with C. A 100 per cent Si recovery requires a reduction of s to 0.50, and to ≈ 0.54 if condensation is allowed to heat the charge to reaction temperature. In Figure 9.6, the process is balanced stoichiometrically with rapid reaction between SiO₂ and C in the outer zone. The crucial point is now whether the charge in the outer zone can accept all the heat that this condensation produces. The heat balance for the outer reaction zone is calculated in Table 9.4. It is assumed that the reactions run at

a temperature slightly above equilibrium, that is, at 1800 K for the SiC-forming reaction and at 2100 K for the Si-forming reaction. The result shows a small net heat consumption in the outer zone. Therefore, the furnace top will be cool and the SiO loss low if the reaction between SiO_2 and C is fast.

Table 9.4 *Heat balance for the outer reaction zone of Figure 9.6 (Chase et al., 1985).*

Reaction	Heat consumption kJ
$2 \text{ SiO}_2 + 6 \text{ C} = 2 \text{ SiC} + 4 \text{ CO}$ at 1800 K	1163.34
$4 \text{ SiO} = 2 \text{ SiO}_2 + 2 \text{ Si}$ at 1800 K	-1227.62
Heating of $[3 \text{ SiO}_2 + 6 \text{ C}]$ from 298 to 1800 K	520.44
Cooling of $[2 \text{ CO} + 4 \text{ SiO}]$ from 2100 to 298 K	-376.40
Sum	79.76

A gas containing 6 moles of CO and 4 per cent of SiO leaves the 1512°C zone at the bottom of the outer zone if the reaction between SiO_2 and C is infinitely fast. According to Figure 2.10, the equilibrium gas contains about 4 per cent of silicon. The 6 moles of CO in Figure 9.6 will contain $6 \cdot 4/96 = 0.25$ moles of SiO, which will give off about $1227.62/4 \cdot 0.25 \approx 77$ kJ when it condenses. This amount is low compared with the heat necessary to raise the temperature of the charge, and the SiO will condense in the upper layers of the outer zone. The heat is already included in the balance of Table 9.4. The charge can thus capture all the SiO given off from the equilibrium inner zone if the reactions proceed close to equilibrium. Although the accuracy of the assumptions and data behind this calculation are limited, the calculation demonstrates that the direct SiC-forming reaction is potentially more efficient than the reaction with C in capturing the SiO in the outer zone. The effect of agglomerated charge is also demonstrated in Example 4 in the Process model section in chapter 5.

However, the efficiency of the process is based on the assumption of rapid reaction. The condensation reaction is rapid if it can get rid of the heat, but the reaction between SiO_2 and C may be slow and the rate depends upon several factors, such as the reactivity and the particle size of the materials. The temperature will be higher than the value of the coexistence point for SiO_2 -C-SiC, and the reaction between SiO_2 and C may therefore be incomplete. As a result,

the gas leaving the furnace will contain more SiO than expected from complete reaction. The situation is complex, and the reaction rates are known only qualitatively. In addition, in the industrial situation the raw materials are not pure elements, but natural raw materials with impurities. The conclusion of the examination is therefore only that rapid direct reaction in the outer zone may give a very high silicon recovery if the reaction between SiO_2 and C is rapid. It has been shown that composite reactions of quartz and charcoal are very fast and should hence be an asset in the silicon furnace (Straum *et al.*, 2026).

The kinetics of the reaction between SiO_2 and C are discussed in Chapter 2. The reaction is slow between lump materials, but faster when the materials are crushed finely and mixed. A practical application of the idea will thus include crushing or milling, mixing, and agglomeration. The overall reaction will then change, depositing large amounts of condensate in the upper layers of the charge, and it is expected that stoking the furnace will be more difficult. The furnace behavior using agglomerated materials has to be tested experimentally.

Pilot and industrial testing

The composite concept has been demonstrated in a 50 kW single electrode furnace with bottom contact (unpublished Elkem work). The raw materials quartz sand, carbon black, and ground petroleum coke were pelletised with sugar as a binder and dried. Three raw material combinations were tested as indicated in Table 9.5. The furnace was operated with visual observation into the crater. A fairly stable arc burned against a silicon bath. A viscous material moved slowly downwards from the roof and floated around on the silicon bath, where it was consumed while it sweated out silicon. The operation was fairly smooth for all charge combinations, and when the runs stopped after 1 to 2 days, the furnace was in a good state for further operation. The stoking was apparently no more difficult than for lump charges. A SiC bottom deposit began to build up at the start, but it could be removed by a period with carbon deficit. It seems that it is necessary to use a lower carbon content than for lump charge during the period where steady state conditions are established in the furnace. Later in the test, the furnace recovered easily from periods with excess of carbon when the charge was corrected. An initial increase in the SiC deposit was detected early by the visual observation, and the charge composition was corrected.

Table 9.5 *Results of reduction tests with composite pellets [$\text{SiO}_2 + \approx 2 \text{ C}$] in a 50 kW single electrode submerged arc furnace (unpublished Elkem work). Each energy consumption is a mean of more than one run.*

Raw materials	Energy consumption MWh/tonne	Comments
Ground quartz sand Carbon black ¹⁾	16	Smooth operation. Very low silica loss as smoke.
Ground quartz sand Ground petroleum coke	20	Smooth operation. Some silica loss as smoke.
Quartz sand Ground petroleum coke	24	Smooth operation. Considerable silica loss as smoke.

¹⁾ Carbon black made by thermal decomposition of hydrocarbon gas, specific surface 7 m²/g.

The small furnace has a much higher heat loss than a production furnace, and the energy consumption is therefore always high. The 16 MWh/tonne consumption corresponds to a high silicon recovery, most likely more than 90 per cent (the material balance is not reliable for short tests). Petroleum coke is normally expected to give very poor operation when it is used as the only reductant. The fairly good result with this material therefore shows that the nature of the process has been changed. The results of Table 9.5 also indicate that finely ground materials are necessary to achieve sufficient Si recovery, at least on the small scale. The need to grind the quartz may be a serious difficulty because of the health hazard connected to quartz dust. It will be very difficult to avoid some dust during operation with agglomerates, especially if the agglomerates are dried.

The agglomerated charge has also been tested in industrial furnaces. An addition of a fraction of the charge as high-carbon briquettes [$\text{SiO}_2 + \approx 6 \text{ C}$] has improved the silicon recovery (Lask and Ruuth, 1989). Short-term runs with agglomerates [$\text{SiO}_2 + \approx 2 \text{ C}$] as the main raw material source have indicated that the process may run, but there are difficulties (unpublished Elkem work). The raw materials petroleum coke and silica sand were pelletized with sugar as a binder and dried. Even though the pellets became fairly strong, some were crushed during transport and weighing, and the dry materials produced dust. The pellets were charged to a furnace that operated fairly well on standard charge. They sank so easily that it was impossible to get a stable lid above the inner zone,

and the furnace was blowing almost constantly. The operators tried to stop the blowing by adding more charge, and as a result, the furnace was gradually filled with charge that had reacted incompletely. Almost no silicon was tapped. After a few hours, the operation was changed to standard charge, and the furnace recovered easily. In the next test, the pellets were mixed with some wood chips to impede the sinking. Then a stable lid formed above the reaction zone, and operation was possible. However, the inner zone of the furnace became very hot, and the reaction sometimes became violent during stoking or when the lid collapsed. The flames damaged the electric equipment under the hood and, in extreme cases, charge materials were thrown out of the furnace. Pure charcoal agglomerates were tested at one of the industrial FeSi furnaces at OFZ, and it was seen that the operation did not change dramatically compared to lumpy raw materials (Gryshan *et al.*, 2026). This has also been seen in other industrial SAF processes like FeCr₂, and hence the use of briquettes is a matter of quality.

Discussion

The production of agglomerates will have a cost that is permanently added to the raw material cost if the process is changed to composite agglomerates. Earlier, when the silicon recovery was often below 80 per cent, the potential for improved recovery could justify a change of process. Presently, however, the silicon recovery of well-run furnaces is about 90 per cent for silicon metal and higher for ferrosilicon, and the value of the recovery increase cannot pay the cost of ordinary agglomeration. Other advantages are therefore necessary to justify an agglomerated charge. Such advantages may be the availability of cheap waste material or the possibility of a smooth operation that is easy to control. In the future, the need for sufficiently pure raw materials may require an upgrading that gives powdery materials, and then agglomeration is necessary.

The experience in the 50 kW furnace indicates that the chemistry of the process works. However, the introductory tests on an industrial scale can give some challenges. Some of the problems could probably have been solved with more test work. In the runs with pellets [SiO₂ + ≈2 C] no stable roof on the inner zone was formed. The reason may be that the carbon content was too high in the starting period. The beginning reaction in the inner zone:

2 Presented by Ludvig Ännhagen from Vargön Alloys at Pyro 26–28 May 2026, South Africa.



gave a gas with a low SiO content, and the condensate formed in the upper layers was not enough to glue the pellets together and give a stable roof in the large furnace. After this, more pellets fell down, reacted, and consumed heat. Therefore, the temperature never became high enough for an extensive reaction in the next step:



With a larger excess of SiO_2 at the beginning of the pellet charging, the gas would contain more SiO, and a stable roof may have been formed with normal operation.

A main problem in the introductory large-scale tests was the violent reaction during stoking or spontaneous charge collapse. A tentative explanation for this behavior is suggested here. The temperature in the inner zone is determined by the balance between heat production and heat consumption. With low availability of silica, the energy consumption of the reaction will be low and the temperature will rise. The silica-containing agglomerate will need a higher temperature to become sufficiently fluid to sink down than would be the case with silica lumps in the standard charge. With agglomerated charge, the inner zone will have a higher temperature and more accumulated heat. When fresh materials enter the inner zone, the reaction may therefore be violent. It is hence important to have a controlled movement of the charge.

The split furnace body described earlier may be a means to obtain this control of charge movement. It induces the charge to sink smoothly, and the new agglomerates can be distributed continuously on the top of the charge. Then wet agglomerates can possibly be added without drying. The agglomeration can be put in as an operation in the transport chain to the furnace, and the weighing of the charge can be done on the powder side of the agglomeration. This set-up may reduce the cost of agglomeration significantly, and at the same time give a smooth operation.

The SiO loss will depend on the condensation temperature, as can be seen from Figure 2.10. The condensation is heat-producing, and the resulting temperature is determined by the temperature of the heat sink. The heat sink is the heat-consuming reaction:



which, according to the equilibrium in Figure 2.10, can run at temperatures above the coexistence point for SiO_2 –C–SiC at 1512°C. It is important to have a high reactivity of the materials, since high reactivity will make the reaction run at a temperature closer to the coexistence point, and therefore give a lower temperature and, consequently, a low SiO content. The results from the 50 kW furnace indicate that fine crushing of the quartz is necessary. The relation between agglomerate properties and reactivity has to be studied experimentally. Full-scale experiments will be very expensive, but the cost may be reduced by a pre-study that elucidates the situation by means of laboratory experiments, small-scale physical simulation and mathematical modelling.

In the discussion of the split charge, it was shown that the carbon charge would be hot at the top and therefore have a heat loss. This loss can be reduced by the addition of a suitable amount of compound agglomerate.

Blast furnace

While production of MG–Si in a blast furnace would be challenging, FeSi alloys have been produced industrially. One example is from the Chelyabinsk plant in west-central Russia, producing FeSi alloys containing up to 12.3% Si from limonite, siderite ores and quartzite (Lukin *et al.*, 1963). The production was carried out periodically, switching between iron and FeSi, with a coke consumption between 1.0–1.5 tonnes/tonne. The furnace was operated with a pre-heated (up towards 1000°C), oxygen-enriched air blast to increase the temperature and hence facilitate enhanced SiO_2 reduction. The periods of FeSi smelting lasted between 50–55 days, after which problems with tuyer burn-out were experienced due to clogging of the furnace hearth.

Plasma reactor

The submerged arc furnace can be characterized as a plasma furnace, since most of the heat is produced in an arc that is a plasma if we define a plasma as a gas with an ionization high enough to make it electrically conductive. However, in arc furnace technology the term plasma has commonly been reserved for arcs that are stabilized by an externally controlled gas jet.

A simple plasma furnace is obtained if a hole is drilled along the centre line of the carbon electrode and a gas is blown through the hole. The resulting gas jet tends to keep the arc in a stable position, as an elongation of the centre line of the electrode. This electrode will be consumed, like an ordinary carbon electrode. The most common plasma burners, however, have non-consumable electrodes made of temperature-resistant metals such as tungsten. A principle of a plasma burner installed in a silicon reactor is indicated in Figure 9.7. It consists of two non-consumable electrodes with a gas flow between them. Such a burner can run in two modes. In the *non-transferred arc mode*, the arc burns between the two electrodes, and the heat produced is transported away with the gas. In the *transferred arc mode*, the arc burns between the main electrode in the burner and the outside conductor. The heat is then produced in the cavity of the furnace. The silicon process has a very high consumption of electric energy, and it would need very large amounts of gas to transport all this energy as heat in a gas. Therefore, it is expected that the burner must work in the transferred arc mode in a silicon reactor.

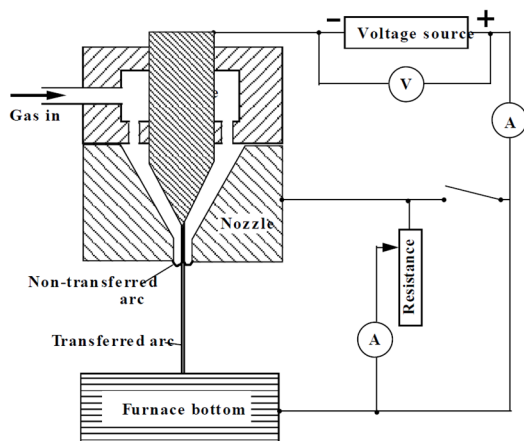


Figure 9.7 Principles of a plasma burner in a silicon reactor. The operation starts with a non-transferred arc between the cathode and the nozzle, and after a short heating period the switch is broken and the main current goes through a non-transferred arc in the crater arc. A small arc between the nozzle and the cathode may be maintained to stabilise the arc.

An alternative to the plasma burner is *inductive plasma heating*. The gas is then kept in the plasma state by induction, and the reactants can be added to the plasma.

The main expected advantages of a plasma reactor in the silicon reactor are:

1. The heat production is independent of the resistivity of the charge.
2. The electrode costs are reduced strongly.
3. The reaction volume will be smaller.
4. The process can use powder raw materials without agglomeration.
5. When Si condenses out of a very high temperature plasma, it may be separated from impurities that would stay in the product in the standard process.

The literature contains some references to plasma processes for silicon, and a few central contributions will be reviewed here. Dosaj and Rauchholz proposed a plasma reactor for the production of silicon (Dosaj and Rauchholz, 1987). They stressed that the burner should be the transferred arc type because it uses much less gas than the non-transferred arc burner. They gave few details of the reactor design, temperatures, and chemical reactions in the plasma reactor. Santén and Edström, and Eriksson and Santén, proposed a plasma furnace where the shaft was filled with carbon lumps while SiO_2 powder was blown into the reactor at the bottom (Eriksson and Santén, 1985; Santén and Edström, 1984). Some carbon powder could be mixed with the SiO_2 powder. A main advantage of the process is that it can use powdered SiO_2 .

In the applications above, it seems that the plasma burner essentially replaces the carbon electrode as a heat source in a process where the main reactions appear to run at a temperature around 2000°C , as in the submerged arc furnace. In the thermodynamic discussion of the process, it has been shown in Chapter 2 that the SiO content of the gas from the final reaction between SiO_2 and SiC is high. Therefore, the standard process has to be run as a two-step process, in which SiO from the SiO_2 -SiC reaction is captured in counter-current with the charge going in. However, if the process is run at a much higher temperature, the SiO content of the gas decreases, and a one-step process may be possible. Coldwell carried out an equilibrium calculation for the temperature range 500–6000 K (Coldwell, 1976). He considered only the

three base elements Si, C, O and the compounds SiO, SiO₂, SiC, CO, CO₂ and O₂, and concluded that Si would be formed at a temperature above a threshold value of about 2225°C. A computer simulation of the condensation as a function of the quench rate indicated that there exists a maximum in the amount of silicon produced (Coldwell, 1977). Coldwell and Roques tested the idea experimentally (Coldwell and Roques, 1977). The reactants SiO₂ and C were introduced into a radio frequency induction plasma where they reacted and vaporized. The product collected in a cooled tube was amorphous. It consisted of 25 to 250 µm globules that had to be sintered to give reproducible analyses. The yield was less than 15 per cent of the theoretical. The authors concluded that a high yield is unlikely by quenching of an Si-rich gas.

Hutchison *et al.* extended the equilibrium calculation by including all the chemical species and discussed the result when Si was allowed to condense from the gas by cooling (Chase *et al.*, 1985; Hutchison *et al.*, 1988). In the range of reactant mixture [SiO₂ + 1.1 C] to [SiO₂ + 2.35 C], the first condensed material to precipitate from the gas is Si(l), and then, at a lower temperature, SiC. With further cooling, all the Si(l) is transformed to SiC. Hutchison *et al.* assume that the molten silicon must be separated from the system at a suitable temperature. The best yield is found for a charge of composition [SiO₂ + 1.75 C], where the Si precipitation starts at 2807°C and the SiC precipitation at 2540°C. The maximum amount of silicon can be taken out just above the precipitation temperature of SiC. The amount of Si(l) is then 57 per cent of the total amount of silicon in the system. Therefore, the optimum condensation temperature is thought to be 2540°C.

According to the description of the Si–C system in Chapter 2, the Si that condenses from the C-containing gas at a high temperature will contain a lot of C in solution. At the optimum condensation temperature, the silicon is saturated with SiC, and the solubility of C can then be estimated from the phase diagram (Chapter 2) to be of the order of magnitude 20 at%. This C content corresponds to an alloy [4 Si + C], which after cooling will give 3 Si and SiC, or more than 30 per cent by weight of SiC in the silicon. The result is uncertain because the measurements behind the phase diagram scatter strongly. Hutchison *et al.* (1988) did not discuss the solubility of C in molten Si, and it is not clear how it is included in the calculation.

The advantages of plasma application have not been demonstrated. The most promising idea in the short run is to develop an inert electrode. Since the arc most likely must operate in the transferred mode and produce

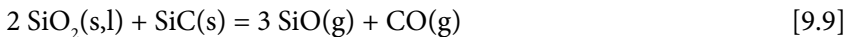
the heat in the gas of the reactor, the resistance will depend on the properties of the charge. The operation problems will therefore be similar to the problems of the submerged arc furnace. This application is more a question of furnace design than of metallurgy.

The use of plasma technology is one of the processes where one can theoretically use H_2 as a reductant and thus cut the CO_2 emissions. This is further discussed in sub-chapter about hydrogen plasma.

Non-atmospheric pressure

Normally one assumes that the furnace will run at atmospheric pressure. Operation at non-atmospheric pressures causes obvious difficulties. The charging and the tapping must occur through a lock gate system, and the electrode connection must be airtight. The stoking must be carried out by machines without any visual observation of the furnace top. However, modern blast furnaces are run at a pressure of a few bar. Therefore, the problems with feeding or tapping through a non-atmospheric pressure lock gate can be solved. The carbon electrodes are penetrable for gas, but possibly the entire electrode system can be placed within the non-atmospheric hood, with immovable conductors through the shell. We conclude that non-atmospheric operation is not impossible, and it is justified to discuss the potential even if a process is not obviously attractive. The possibility has been discussed in the literature (Downing, 1965).

The influence on the equilibrium of a lower ambient pressure can be seen from Figure 2.7. The reaction temperature becomes lower, and the ratio p_{SiO}/p_{CO} increases. Silicon production has a lower recovery the higher this ratio is. For a limiting pressure ratio of 3, the silicon recovery is zero, which corresponds to the inner zone reaction:



The temperature and pressure of this limiting reaction can be read approximately from Figure 2.7. The pressures p_{SiO} and p_{CO} are related by the stoichiometry:

$$\ln p_{CO} = \ln p_{SiO} - \ln 3 \quad [9.10]$$

A graph is drawn parallel to p_{SiO} , at a vertical distance $\ln 3$ below it. This graph crosses the p_{CO} graph at about 1740°C, with $p_{\text{CO}} \approx 0.12$ bar and $p_{\text{SiO}} \approx 0.36$ bar. At a lower pressure, it is impossible to establish equilibrium SiO_2 –SiC–Si from a reaction between SiO_2 and SiC. Therefore, production of Si is impossible in an *isothermal* reaction at a pressure below about 0.5 bar. However, SiO_2 and SiC can react in vacuum and give a SiO-containing gas that produces Si by condensing to $[\text{SiO}_2 + \text{Si}]$ at lower temperatures.

The equilibrium in Figure 2.8 shows how the equilibrium pressure of the coexistence point for SiO_2 –SiC–Si varies with temperature. With increasing temperature, the total pressure of the reaction increases, while the molar fraction of SiO decreases. According to the discussion in Chapter 3, the amount of SiO to recover becomes less when this molar fraction decreases. Figure 3.12 indicates that the reaction with C can capture all the SiO if the gas of the inner zone contains less than 50 per cent of SiO. From Figure 2.8 we can read that this gas content corresponds to a temperature of about 1980°C and a total pressure of about 6 bar. Therefore, the inner zone reaction that gave only 33 per cent Si recovery at 1 bar can give 100 per cent recovery if the pressure is increased to 6 bar.

However, this favorable result seems to be related to temperature and not to pressure. The SiO content of the inner zone gas can be calculated from the reaction:



The law of mass action gives:

$$\frac{p_{\text{CO}}}{p_{\text{SiO}}} = K_{9.11} \quad [9.12]$$

An equilibrium constant K varies with temperature and not with pressure. This means that the equilibrium SiO content of the inner zone will be determined exclusively by temperature. The real process does not run at equilibrium, and observations indicate that the inner zone temperature is about 2000°C. The equilibrium benefit for a pressure of about 6 bar is therefore already used up, and the resulting operation is determined by the kinetics. By application

of the split charge method, it is possible to reach even higher temperatures for the Si-producing step.

The flow of charge into the inner zone is important for the reaction, and this flow increases as the viscosity of the molten SiO_2 in the charge decreases. The viscosity decreases when the temperature increases, therefore, we can expect the flow to increase. The coexistence points for $\text{SiO}_2\text{--C--SiC}$ and $\text{SiO}_2\text{--SiC--Si}$ move to higher temperatures when the pressure increases. Therefore, both the minimum temperature for reaction in the inner zone and the condensation temperature will be higher. The SiO_2 in the charge will become less viscous, and the flow into the inner zone will increase. This resulting flow of SiO_2 and other materials into the inner zone may require more energy for reaction than is added, and thus give melting of the charge and not reduction. This is the behavior that metallurgists describe as ‘melting before smelting’.

Low pressure operation is a disadvantage for the submerged arc process for silicon, and silicon production is impossible by an isothermal reaction for pressures below about 0.5 bar. Low pressure can, however, be used for production of SiO that is later cooled and condensed to $[\text{SiO}_2 + \text{Si}]$.

High pressure increases the temperature of the equilibrium reduction of SiO_2 , and the increased temperature gives a more favorable equilibrium ratio $p_{\text{SiO}}/p_{\text{CO}}$. However, the same temperature obtained by other means will give the same ratio. The influence of high pressure upon the operation is not clear, but consideration of the material flow indicates that it may lead to incomplete reduction of the SiO_2 in the inner reaction zone. The situation is complex, and an overall advantage of increased pressure cannot be ruled out without experiments. The understanding of the flow processes, including the material properties, is not sufficient for reliable mathematical modelling, and experimental testing in a physical model of a submerged arc furnace is necessary.

9.3 Non-carbothermic processes and reductants

To avoid CO_2 emissions, other reductants not containing carbon must be found, or carbon must be reused in the process. Materials that have a thermodynamic potential to reduce SiO_2 to Si can be identified by an Ellingham diagram, as shown in Figure 9.8, which shows a selection of relevant reac-

tions for oxide reduction into metals. The difference in Gibbs free energy (on the y-axis) is the driving force for the reactions to go forward. From this diagram, elements like Ca, Al, Mg and Ba are strong reductants for most oxides and can be used to reduce quartz (SiO_2).

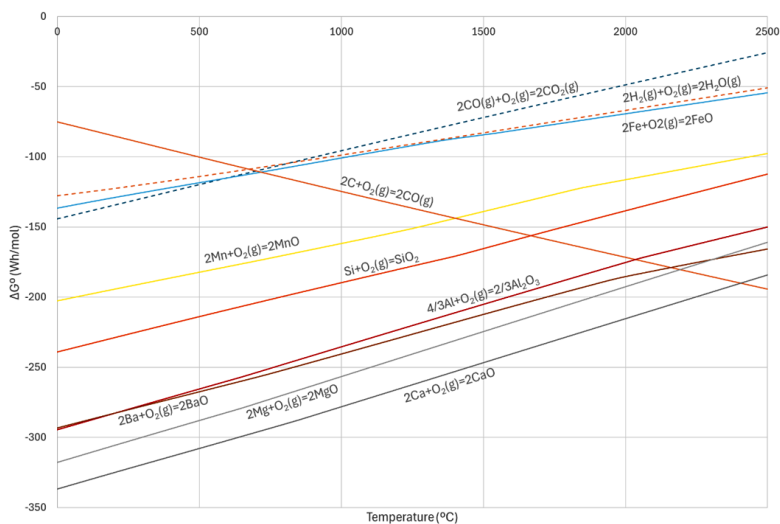


Figure 9.8 Ellingham diagram for oxides (Calculated in HSC v.9).

Reduction with gases is another alternative to reduction with solid carbon. Possible gaseous reductants include hydrogen (H_2) or methane (CH_4) and, in addition, processes involving these, such as hydrogen plasma or use of carbon from methane decomposition. Equilibrium considerations show that they have a lower thermodynamic potential than solid carbon. However, new gas-based processes may offer good alternatives to the gradually scarcer resources of suitable types of coal and give a potential for CO_2 -lean production of silicon. To contribute to decarbonization of silicon production, the gaseous reductants must be produced from renewable sources. Hydrogen produced by traditional methods from coal or natural gas is energy-demanding and CO_2 -emitting. Instead, so-called 'green' H_2 produced from water electrolysis using renewable electricity and so-called 'blue' H_2 produced from natural gas with carbon capture and storage (CCS) are alternative gas sources. Methane must be produced from biological sources, so-called bio-methane.

Hydrogen

Equilibrium discussion

We assume that we can establish equilibrium in the Si–O–H system without any speculation about how the reaction must be carried out in a process. The calculations will be based on a certain assumed reaction mechanism, but it is not necessary that this mechanism really occurs, since all consistent mechanisms for the same overall reaction will give the same result in equilibrium calculations. The mechanism used consists of several chemical reactions with equilibrium constants (Chase *et al.*, 1985).

The $\text{SiO}_2\text{--H}_2$ system has three components, and the phase rule then states:

$$Ph + F = 3 + 2 = 5 \quad [9.13]$$

The important species in the system are $\text{SiO}_2(\text{s,l})$, $\text{Si}(\text{l})$, $\text{SiO}(\text{g})$, $\text{H}_2(\text{g})$, $\text{H}_2\text{O}(\text{g})$ and $\text{H}(\text{g})$. Other species, such as $\text{O}_2(\text{g})$, $\text{O}(\text{g})$, $\text{Si}(\text{g})$ and gaseous compounds ($\text{Si--O}_x\text{--Hy}$), are disregarded. Compared with carbon reduction, there is one important difference: carbon has the solid compound SiC with silicon, while hydrogen has only gaseous compounds, and they are not present in significant amounts at the temperatures of interest. In an isothermal production process, both the raw material SiO_2 and the product Si must be present as condensed phases in the hot main reaction zone, together with a gas phase. Therefore, the system has two degrees of freedom, and we must specify two properties to determine its state completely. We choose temperature and total pressure, and this enables the composition of the gas to be calculated.

When $\text{SiO}_2(\text{s,l})$ and $\text{Si}(\text{l})$ coexist with a gas phase, there will always be some $\text{SiO}(\text{g})$ present:



Free silicon can be made by the reduction of $\text{SiO}(\text{g})$ by H_2 :



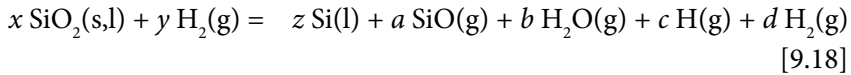
At high temperatures, the H_2 molecules may dissociate:



There are no inert gases present, and the other gas species in the system occur at such low partial pressures that they can be ignored in the calculation of the total pressure P . Therefore,

$$p_{\text{SiO}} + p_{\text{H}_2} + p_{\text{H}_2\text{O}} + p_{\text{H}} = P \quad [9.17]$$

The SiO pressure is determined by Reaction [9.14]. The relation between p_{H_2} and $p_{\text{H}_2\text{O}}$ is given by Reaction [9.15], and the relation between p_{H_2} and p_{H} by Reaction [9.16]. By combining these, the partial pressure of H_2 can be found from the total pressure and the equilibrium constants for the reactions. Once the partial pressure of H_2 is known, the partial pressures of SiO, H_2O and H can be calculated from the equilibrium constants of Reactions [9.14], [9.15] and [9.16]. The overall equilibrium reaction can be written as



We consider that the reaction produces the equilibrium mixture for a total of P moles in the gas mixture. The partial pressures can then be interpreted as the number of moles of each species in the reaction, and the coefficients a , b , c and d of Equation [9.18] are known from the equilibrium calculation. The unknowns x , y and z represent the consumption of raw materials and the production of silicon. The element balance gives:

$$\text{O:} \quad 2x = a + b$$

$$\text{H:} \quad 2y = 2b + c + d$$

$$\text{Si:} \quad x = z + a$$

The efficiency of the reaction as a silicon producer can be evaluated by two criteria: high silicon recovery and low hydrogen consumption.

$$\text{The Si recovery } s = \frac{z}{x} = \frac{\text{mol Si(l) produced}}{\text{mol SiO}_2 \text{ consumed}} \quad [9.19]$$

The remaining silicon is lost as SiO(g) , with energy and material costs. The resulting Si recovery as a function of pressure and temperature is shown in Figure 9.9. A negative Si recovery means that the Si has to be placed on the left-hand side of Reaction [9.19], and it is necessary to consume Si to establish the equilibrium. The results show that a very high pressure is necessary to produce Si with a high silicon recovery, and the hydrogen consumption is excessive. The pressures and temperatures used here require a very strong extrapolation of the thermochemical data compared with the original measurements, and the results should therefore be seen only as indications. The equilibrium relations at 1 atm, calculated by HSC and shown in Figure 9.10, show similar unfavorable thermodynamics (Ringdalen *et al.*, 2024).

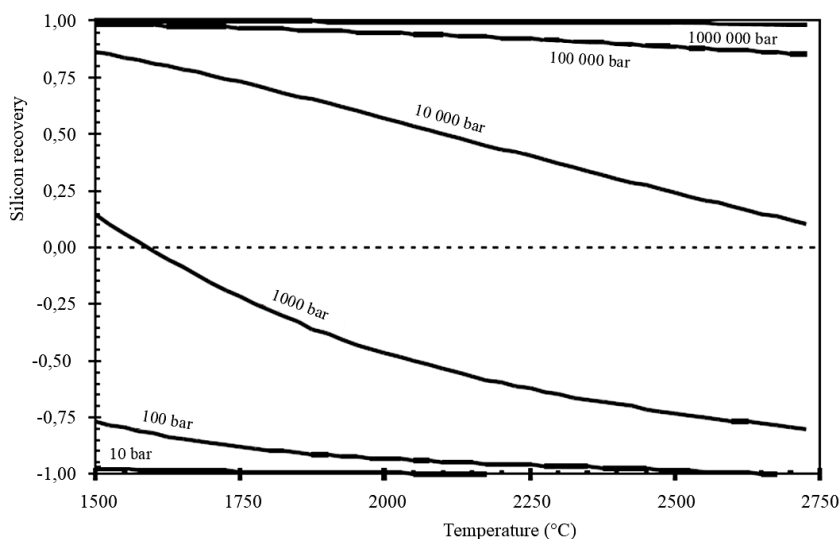


Figure 9.9 Silicon recovery as a function of temperature for various pressures. A negative value means that the equilibrium reaction between SiO_2 , Si and H_2 will consume Si and produce SiO .

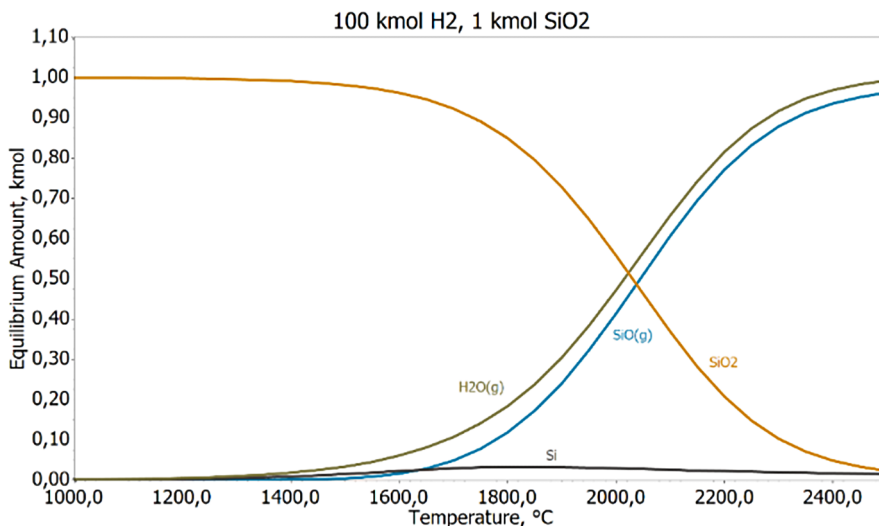


Figure 9.10 Amount of SiO_2 that can be reduced with different temperatures at 1 atm. Equilibrium conditions calculated by HSC.

The required high pressures are completely unrealistic in an industrial process. Therefore, it can be concluded that free Si cannot be produced by the reduction of SiO_2 by H_2 at equilibrium.

Development of new processes for production of Si with hydrogen will thus require alternative approaches to reduction of SiO_2 with H_2 . Since today's industrial carbothermic Si production does not take place at complete equilibrium, this also makes it a natural way forward. The intermediate product, SiO gas, contributes to the unfavorable thermodynamics for Si production with H_2 . An alternative could therefore be to produce SiO gas by other methods and then further reduce it to Si or Si-H compounds. Other alternatives include taking advantage of differences in kinetics for the involved reactions, using hydrogen plasma, or using alternative energy sources such as microwave. Examples of alternative processes based on these thoughts are presented below. They are on low TRL level, and fundamental investigations are needed to clarify whether they can be used in industrial Si-production.

SiH₂ process

In the proposed SiH₂ process, illustrated in Figure 9.11, SiO is produced from SiO₂ and Si in a separate reactor by reaction [9.20], and the produced SiO is reduced with hydrogen to Si according to reaction [9.21] in another reactor (Ringdalen *et al.*, 2024). At 1 atm, reaction 9.20 requires temperatures above around 1700°C, and reaction 9.21 temperatures below around 800°C, to give reasonable respectively SiO and Si production. Realization of a process based on this principle will thus require either conditions where Si can be produced from SiO at higher temperatures, or conditions where SiO will not react back to SiO₂ and Si when cooled down to temperatures where it can be reduced with H₂. Based on the well-known slow kinetics of SiO-dissociation, the last scenario seems most probable (Broggi, 2021).

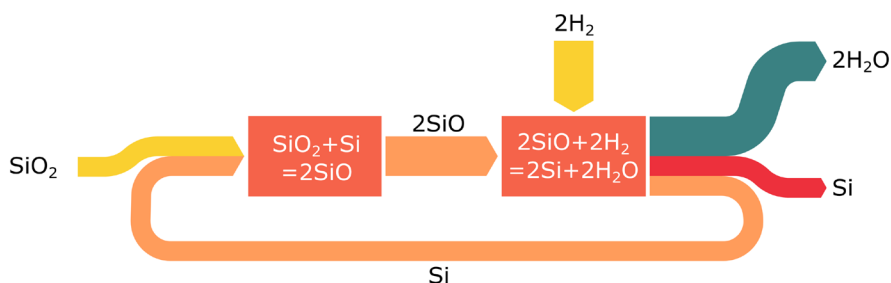


Figure 9.11 Concept for SiH₂ process.

Hydrogen plasma

Another alternative for hydrogen reduction of a stable oxide like SiO₂ is to excite the gas into a plasma. In the plasma state, hydrogen is present as ionic or radical species like H, H⁺, H²⁺, etc., which are far more reactive than the gas. The reduction could then take place according to reaction 9.22:



The reaction is thermodynamically favorable below 2589°C. However, hydrogen plasma studies on silicon dioxide reduction are limited in the literature. To date, only small-scale studies with scattered outcomes with respect to Si/SiH₄ production have been reported (Altmannshofer *et al.*, 2016; Gupta *et al.*, 2013; Sabat *et al.*, 2014; Watanabe *et al.*, 1999). In terms of industrialization of plasma production of silicon, Swedish company Green14 has announced their plans for technology exploitation, but no technical information has been published.

An alternative and even more energetic approach is to dissociate the SiO₂ itself to the plasma state: SiO₂ > Si + 2O. Silicon granules of 100–200 µm have been obtained with this technique (Grishin *et al.*, 2012).

Methane, CH₄

Methane gas (CH₄) used as a reducing agent is quite well-known. Traditionally, the methane has been provided by fossil natural gas, but it is equally possible to use biologically generated methane from biogas. Biogas is created from the biological digestion of organic material, and its main component is methane, CH₄, which can be a biological alternative to methane from fossil natural gas. CH₄ has a high reduction potential at temperatures above its equilibrium decomposition temperature (548°C), and metastable CH₄ has been shown to reduce oxides of manganese, chromium, and titanium faster than solid carbon. A major challenge is the spontaneous decomposition of the methane into hydrogen and carbon at the high temperatures necessary for SiO₂ reduction (Ostrovski and Zhang, 2006).

The carbon obtained from the cracking of the methane from biogas may, however, be used as an indirect source of biocarbon. Methane decomposition may be used to deposit carbon onto the ore itself (Li, 2017; Lindgård, 2015). Additionally, SiC can be quite readily produced by this method (Ksiazek *et al.*, 2014; Monsen *et al.*, 2013). Since SiC is an intermediate phase in a regular SAF, a part of the solid carbon might be replaced by methane.

Metallothermia

Metallothermia is thermally induced metal displacement reactions of the kind:



where A and B are metals while X most commonly is either oxygen or a halide.

Metallothermic reactions may be endo- or exothermic. Exothermic reactions continue spontaneously after ignition and are often referred to as ‘thermite’ or ‘bomb’ reactions (Habashi, 2018). Industrially, metallothermic reduction has been outcompeted for most metals except for some rare earth elements and other high-value metals (Xing *et al.*, 2018). More commonplace examples in modern industry include the Kroll process for titanium and the Pidgeon process for magnesium.

For a metallothermic reduction process to be considered climate neutral, a number of criteria must be fulfilled. Firstly, the reductant metal must be produced without greenhouse gas emissions. The thermodynamics are challenging because, for a metal to be a candidate for reducing another metal, it must have a strong affinity for the X-element in the compound to be reduced. This strong affinity makes the reductant very stable, so producing the reducing metal typically demands more energy than producing the actual product. Higher energy requirements also typically mean higher costs, which constitute an important commercial barrier.

Secondly, the reducing metal should have a high boiling point and a low vapour pressure, and it must be practically possible to handle it in safe and environmentally acceptable ways. Thirdly, if the reducing metal forms intermetallic compounds with the metal produced, this typically reduces the productivity of the process and may contaminate the product. A couple of exceptions exist, though, for example in magnesiothermia, and in those cases when the product alloy itself is valuable.

Finally, the reductant must be recyclable, cost-effective, and available in large enough quantities. Recycling would typically imply looping the reductant which, due to the inherent thermodynamic constraints, is an energy-intensive process.

Considering these criteria, most candidate metals from Figure 9.8 are disqualified. Calcium may be an interesting option because it is a fairly well-known and potent reducing agent for silicon, but the reaction can be explosive (Mishra *et al.*, 1985). Barium is less available, toxic, and highly unstable in the presence of oxygen.

Magnesiothermic reduction

While most Mg is currently produced via the carbon-intensive Pidgeon process, electrolytic production of magnesium metal (Mg) from MgCl_2 without significant CO_2 emissions is an alternative reductant in a magnesiothermic reduction of silica. Depending on the stoichiometry of the $\text{Mg}:\text{SiO}_2$ ratio in the reduction, different reaction products are formed, as described by equations 9.24–9.26. The structure of these reaction products, when Mg is reacted with natural quartz, was described by Rasouli *et al.* (2022), and illustrated in Figure 9.12.

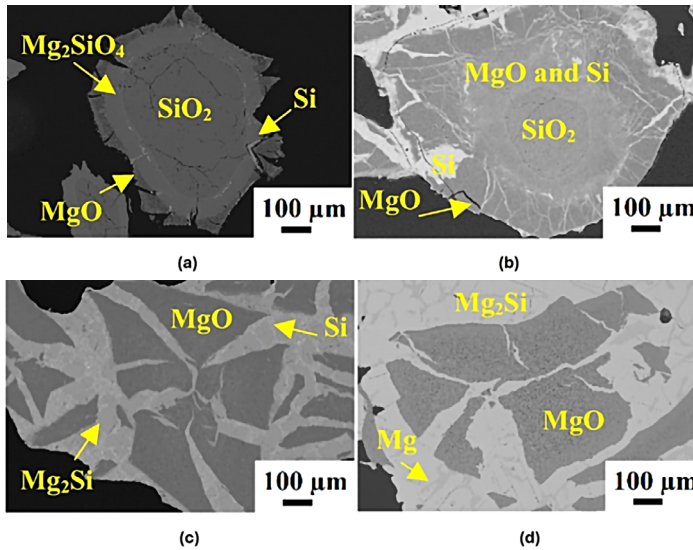
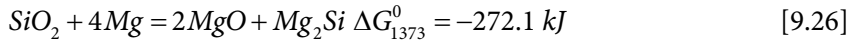
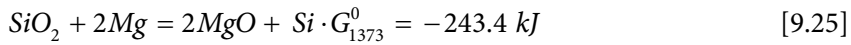
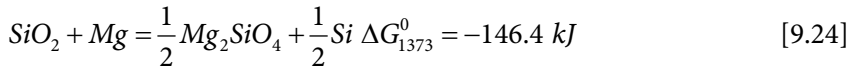


Figure 9.12 (a) Backscattered electron image of magnesiothermally reduced natural quartz sample with a $\text{Mg}:\text{SiO}_2$ mole ratio of 1 and 120 min reaction time, (b) backscattered electron image of sample with a $\text{Mg}:\text{SiO}_2$ mole ratio of 2 and 120 min reaction time, (c) backscattered electron image of sample with a $\text{Mg}:\text{SiO}_2$ mole ratio of 3 and 120 min reaction time, (d) backscattered electron image of sample with a $\text{Mg}:\text{SiO}_2$ mole ratio of 4 and 10 min reaction time. Initial quartz particle size is 704 μm for all samples. Adapted from Rasouli, 2022. [Used under Creative Commons Attribution 4.0 International License].

After reduction, acid leaching (and/or other purification steps) may be needed to remove impurities and unwanted intermetallic phases (e.g. MgO , Mg_2Si , Mg_2SiO_4) from the Si product if it is used directly.

An interesting magnesiothermic approach makes use of intermetallic phases like Mg_2Si instead of avoiding them (as is usual in metallothermic practices). The idea is to use the intermetallic as the raw material for production of silane (SiH_4) through hydrolysis in e.g. HCl , which in turn constitutes the feed material for the Siemens or fluidized bed reactor processes (Tang *et al.*, 2023). However, SiH_4 will not be the only hydrolysis reaction product and other silanes such as Si_2H_6 and Si_3H_8 are co-products of the reaction. When the $\text{Mg}_2\text{Si}/\text{MgO}$ reaction product is hydrolysed with HCl , the MgO will be converted to MgCl_2 , which may be used as input in Mg electrolysis (Rasouli *et al.*, 2022).

Aluminothermic reduction

Aluminothermic reduction is a relatively well-known method for production of silicon and silicon alloys. Inefficiencies in solid-state reduction are caused by back-reactions and the formation of intermetallic phases, most notably mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), which can be challenging to separate (Dietl *et al.*, 1982; Dietl and Holm, 1987; Sadique, 2011). These barriers are overcome in the liquid-state reduction of SiO_2 in SiO_2 – CaO slags, forming liquid Si alloy (which is simply slag refined to MG-Si) and liquid $\text{CaO-Al}_2\text{O}_3$ slag, as demonstrated by the SisAl technology (Philipson *et al.*, 2021; Safarian and Tranell, 2024; Toli *et al.*, 2021; Zhu *et al.*, 2024). The $\text{CaO-Al}_2\text{O}_3$ slag may be hydrometallurgically processed to CaO (e.g. for input to new CaO-SiO_2 slag raw material) and Al_2O_3 (for Al electrolysis), or used directly as a product. The process was piloted at large scale (100's of kg) using primary aluminium, aluminium scrap, and aluminium dross as reductants. Under the stoichiometric $\text{Al}:\text{SiO}_2$ conditions given by reaction 9.27, and using a 50/50 wt% SiO_2/CaO slag as raw material, an alloy with the approximate composition 75wt% Si 15wt% Ca 10wt% Al was formed, along with a slag containing 50–60% Al_2O_3 , 40–45% CaO and small residual amounts of SiO_2/Si (< 5 wt%). Using slags with initially higher silica content, or applying a lower $\text{Al}:\text{SiO}_2$ ratio, formed alloys with higher silicon content. The results agreed largely with thermodynamic simulations as illustrated in Figure 9.13.

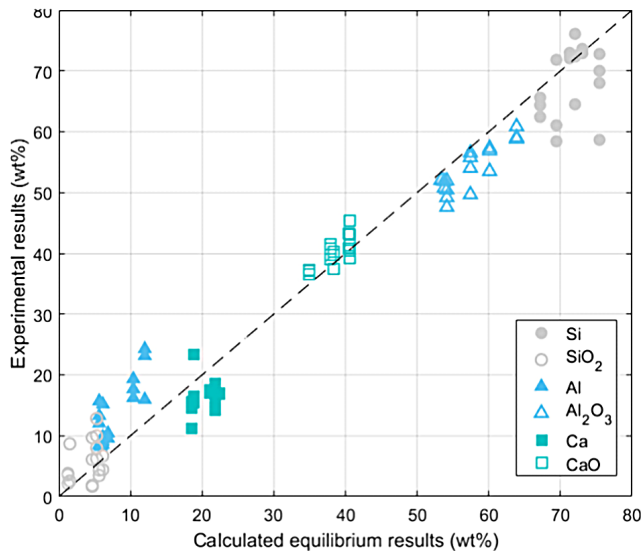


Figure 9.13 Compositions of SiCaAl alloy and slag resulting from aluminothermic reduction of CaO–SiO₂ slag (Zhu et al., 2024) [Used under licence CC-BY 4.0].

The resulting alloy, high in Ca and Al, was subsequently refined using different slags, obtaining an alloy with up to 99% Si.

A barrier to climate neutrality for aluminothermia is the production and regeneration of the Al. Today, Al is produced by electrolysis in the Hall-Heroult process. This process is not climate neutral. It emits large amounts of CO₂ through the consumption of the carbon electrode. In theory, however, Al electrolysis could be decarbonized (e.g. by the use of inert anodes or other measures). Climate neutral aluminium production could hence enable the climate neutral production of many other metals, including Si, by aluminothermic reduction.

Electrolysis

A climate neutral electrolysis process for direct production of silicon may short-cut some important process steps in the total value chain in a future scenario where the energy grids are decarbonized. The main technological

obstacle that must be overcome is to find a durable inert anode that either does not contribute to pollution of the product or gives the 'right' impurities for the product to still meet the specifications. For solar and electronic Si applications, for example, the focus is often to avoid dopants such as B and P in the product.

Utilizing electrolytes like the Hall-Heroult process (i.e. cryolite or other fluoride melts) with an inert anode might enable the production of CO_2 -free silicon by electrolysis. Si electrolysis from SiO_2 with oxygen evolving anodes has a theoretical energy consumption of 12.0 kWh/kg Si (temperature range 1000°C, calculated for 80% current efficiency with HSC v.9). For comparison, carbothermal reduction has a theoretical energy requirement of 9.6 kWh/kg Si, which is substantially lower. Then again, direct comparison may be misleading because the two product grades are quite different. Electrolytic reduction processes have been reported to produce rather pure Si (99.99–99.999%). Hence, some refining steps might be avoided downstream in the value chain, which in turn would save energy.

Silicon is less noble than most metals, as well as hydrogen, and additionally has a high melting point. These constraints make electrolytic reduction of SiO_2 very challenging. It is not possible to use aqueous electrolytes, for example, since the high voltage necessary for splitting SiO_2 is higher than the decomposition voltage of water. So, even if SiO_2 were soluble in water, H_2 gas would be produced before Si and would thus consume the aqueous electrolyte.

Silicon must therefore be electrolysed either in a molten salt or in a molten oxide. Molten salt electrolytes can be used at temperatures in the range of 700–1000°C, which means that the Si must be deposited in the solid state. This, in turn, makes the processes relatively slow. To substantially increase the rate of production, the temperature must be above the melting point of Si (> 1410°C). This means that the only electrolyte types available are molten oxides.

In the following, some of the literature on Si electrolysis in various electrolytes will be discussed. It is important to note that most processes for reduction of SiO_2 have, so far, been investigated with consumable carbon anodes, which means that they emit CO_2 . To become climate neutral, inert oxygen-evolving anodes suitable for the specific electrolytes must be developed. At the same time, replacing the carbon anode with an O_2 -evolving anode would also result in an energy increase, since the thermodynamics are less favorable without the help of carbon.

Molten salt electrolysis

The most common molten salt electrolytes used for metal production from oxide feed are chloride and fluoride melts. The Hall-Heroult process for aluminium production has been, and still is, the major industrial electrolytic method. The process takes place in liquid cryolite (Na_3AlF_6). Fluoride melts, and especially cryolite, are used because of their high metal oxide solubility. Unfortunately, these salts are also very corrosive, and suitable inert anode materials are correspondingly hard to find.

Patented EW processes to produce Si from quartz in molten fluoride salts exist. These are often multistep electrolytic and electrefining processes, claiming to produce Si of semiconductor quality after some additional refining (like zone refining, leaching and/or directional solidification). The temperatures are well below the melting point of silicon (1410°C). Hence, production occurs by solid-state deposition and is therefore slow. Si, being a poor conductor, limits the production rate even further. The low production rate is probably the main reason why no process of this type has been commercialized. Another important challenge is that fluoride salts are difficult to separate from the produced silicon (Elwell, 1982; Monnier and Barakat, 1965; Rao *et al.*, 1980).

Chloride salts do not readily dissolve oxides like quartz, but they are easier to remove from a solid Si cathode product than fluorides. The FFC Cambridge process (named after Fray, Farthing and Chen) circumvents the problem of low SiO_2 solubility by allowing a SiO_2 pellet to be directly reduced in a CaCl_2 melt. This was first suggested for reduction of titanium from TiO_2 (Chen *et al.*, 2000) but has also been proven at laboratory scale for silicon and other elements. In the FFC process, a pellet of the oxide raw material is polarized so that it constitutes the cathode of the system. The electrolyte consists mainly of liquid CaCl_2 with small amounts of CaO . As the reduction progresses, oxygen ions from the oxide are released into the melt and discharged at the anode, as CO/CO_2 if a consumable carbon anode is used, or as O_2 on an inert anode.

Other suggested processes include dissolving SiO_2 in a CaO -rich liquid electrolyte (Olsen, 2004). The temperature of this type of process would typically be $800\text{--}950^\circ\text{C}$, which is well below the melting point of Si. Consequently, the production occurs in the solid state and is slow. As for fluoride melts, the low production rate is seen as a commercial disadvantage (Nohira *et al.*, 2003; Yasuda *et al.*, 2007).

Molten oxide electrolysis (MOE)

Several electrolysis processes for producing liquid silicon by molten oxide electrolysis (MOE) have been suggested over the years. Such processes use SiO_2 as raw material and silicate electrolytes (De Mattei *et al.*, 1981). The greatest advantage of MOE is that it enables production at very high temperatures. Liquid deposition and favorable kinetics enhance the productivity rate. Metals produced in the molten state are also easier to harvest, as the separation between electrolyte and metal can be continuous. Generally, this is done by tapping (e.g. aluminium). In the case of silicon, however, the product alloy typically floats on top of the heavier electrolyte, and continuous separation would require siphoning.

Crucially, the high temperatures necessary to keep the silicon liquid imply very severe material challenges. For MOE, this is not only true for the (inert) anode but also for the cathode and container materials. Nevertheless, this type of process may offer reasonably good prospects for commercialization. Various electrolyte mixtures like $\text{BaO-BaF}_2\text{-SiO}_2$ have already been investigated, and multistep processes have been suggested to improve product purity (Elwell and Rao, 1988; Sadoway, 2001).

9.4 Alternative silicon sources for new processes

The most common raw material for bulk silicon and high-silicon alloy production is quartz. Sometimes ultrapure quartz is required, and in some cases the quartz goes through an acid washing process to remove certain impurities. Nonetheless, the overall purity of typical mineral quartz is quite high compared to many ores and other mineral raw materials used in metallurgical industries.

Silicon oxides can also be found in other materials like diatoms, rice husks, kerf, dust, and other by-products from various industries. Some non-oxidic by-products, like hydrofluorosilicic acid (H_2SiF_6), also exist. The use of by-products as silicon sources is attractive with respect to increased circularity and industrial symbiosis, but the volumes of silicon alloys required to ensure a global green transition will most likely mean that mined quartz minerals will continue to be a primary raw material for high-silicon alloy production for some time yet.

Silicon halides (i.e. chlorides, fluorides, bromides & iodides) are often less stable than the oxides and therefore easier to reduce. This makes them

attractive as feed to new reduction processes, particularly electrolytic and metallothermic ones. Among the halides, the chlorides are by far the most widely studied.

From the perspective of climate gas reduction, however, the use of halides is not necessarily a good idea. While the reduction step itself may not produce any CO₂, the quartz must always be halogenated first. This typically requires carbon and emits CO, as illustrated in the following example. First, the quartz is carbo-chlorinated:



Then, the tetrachloride can be reduced to Si, e.g. by sodium metal (Na):



But the sum net reaction is identical to the overall reaction of a submerged arc furnace:



A reduction process based on halide feed may therefore be less efficient, yet equally carbon intensive as carbothermic reduction.

If this obstacle could be overcome, though, a great many new possibilities open up. Many more metals/elements are able to reduce the halides than the oxide, including zinc, aluminium, sodium, potassium, and magnesium (Yasuda and Okabe, 2010). Using biocarbon in a carbochlorination would not require the same type of biocarbon as the SAF. Most notably, mechanical strength would not be crucial. Therefore, carbochlorination might be a cost-effective and circular way to use biocarbon fines and by-products from e.g. agri- or aquaculture to produce feed materials for new reduction routes.

Climate-friendly halide feed materials could, for example, be used in low-temperature electrolysis. If the gas evolved on the anode is a halide like chlorine, it is possible to use a carbon anode and still have a CO₂-free electro-winning process. Contrarily, if the gas evolved on the anode is fluorine, CF₄ gas may form. CF₄ is a climate gas with a global warming potential 6500 times higher than CO₂ (Maeda *et al.*, 2014; Platek *et al.*, 2017; Yasuda *et al.*, 2017).

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