

Silicon alloy refining

Gabriella Tranell

Si and FeSi alloys are typically refined in their liquid state, where the furnace alloy is processed into an alloy that satisfies product specification. Generally, this occurs during/after the alloy is tapped from the SAF into a ladle. Of the several impurity elements present in Si and FeSi alloys, Ca and Al are considered especially important by the industry, due to their abundance in the raw materials, ease of refining, and impact on customer use. Two routes are available for refining these:

- Those based on oxidation and slagging of impurities
- Those based on chlorination and removal of impurities as volatile chlorides

Oxidation and slagging of impurities is the method used in the industry today, with the chlorination process seeing minor industrial interest, owing to the environmental, handling, and waste problems associated with the use of chlorine and the formation of corrosive metal chlorides.

To produce high purity silicon, e.g., with the intention to use as solar- or electronic-grade silicon, supplemental refining processes are required. Typically, solar grade silicon (SOG–Si > 99.9999% purity) is produced by HCl gas chlorination of MG–Si (> 96% Si) to trichlorosilane (SiHCl_3), which is purified by distillation and thermally decomposed in H_2 to pure silicon in a Siemens reactor. This chemical refining process has been extensively described in literature, for example by Hesse and Pätzold (2006) and Yang (2019).

With the exponential growth in the silicon-based solar cell industry since the turn of the century, research into cost-effective and environmentally advantageous methods of producing solar grade silicon entered a new era in the early 2000s. Since then, the research and development of metallurgical processes designed for the removal of harmful impurities like carbon, boron, phosphorus and metals (Fe, Al, Cr, Ti etc.) has resulted in a large body of publications.

In this chapter, Section 10.1 covers the fundamental and industrial aspects of oxidation and slagging of impurities, with a special focus on Ca and Al, while Section 10.2 provides a short summary of Si refining by chlorination. Finally, Section 10.3 gives an overview of relevant pyro- and hydrometallurgical refining techniques to further purify MG-Si into high purity silicon, such as slag-, solvent-, gas/plasma-, vacuum-, crystallization and acid-treatments.

10.1 Oxidation and slagging of impurities

Impurity elements with greater oxygen affinity than Si can be refined from the liquid alloy by oxidation and associated formation of an immiscible slag phase. Oxygen can be introduced by:

- A gas, either as pure oxygen gas or part of a gas mixture, like synthetic air (oxygen/nitrogen mixture) or atmospheric air. Oxygen may also be introduced passively, as the alloy is exposed to air, which is the case during most post-furnace liquid handling processes.
- Addition of solid oxidizing agents, such as Fe_2O_3 , SiO_2 , and oxides containing alloying elements.
- Addition of a suitable slag from a different process.

Development of the ‘Inject plug’ in the early 1980s revolutionized Si and FeSi refining, allowing ladles to tolerate high specific flowrates from a bottom mounted plug (Skei, 1991). The bubble column formed by purging gas through such a configuration creates a high contact area between the alloy, gas and produced slag, while also providing a high degree of mixing and intermixing, to ensure refining occurs throughout the whole vessel. This development made bottom mounted gas purging the most common refining

practice employed by industry today (Holta, 1995), even though top mounted lances are also available.

Typically, gas purging occurs in the ladle, either throughout the SAF tapping cycle and continuing for some time after, if necessary, or at a designated refining station, depending on the desired composition and other practical considerations, like equipment availability and logistics. Alloy temperatures are typically around 2000°C when tapped from the SAF, however, when the alloy reaches the ladle, it typically ranges between 1500 and 1700°C . The tapping process and ladle are illustrated in Figure 10.1.

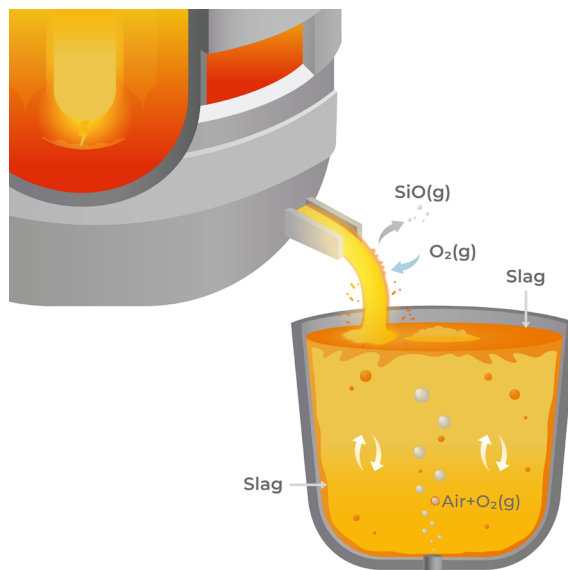


Figure 10.1 *Schematic of furnace tapping and oxidative bottom blowing in a refining ladle.*

Gas purging may be combined with the addition of slag-forming compounds such as limestone/burnt lime (CaCO_3/CaO) and silica sand. These may also act as oxidizing agents, and will be further discussed in Section 10.1.2. This addition is usually carried out by injection when a top mounted lance is used for gas purging, or by direct charging if a bottom mounted porous plug is used. The way the 'oxygen' is introduced affects the heat balance and the kinetics

of the refining process, as discussed in Sections 10.1.2 and 10.1.3. The oxidation reactions are exothermic, providing a way to increase/maintain the alloy temperature without the need for external heating of the ladle. However, to control the alloy temperature and maintain SiO_2 formation preferentially over SiO fuming (see reactions [10.1] to [10.3]), the alloy can be cooled by adding cooling metal. This cooling metal may consist of alloy fines, lower value alloys, etc., and allows the plant to recycle or upgrade production side streams.

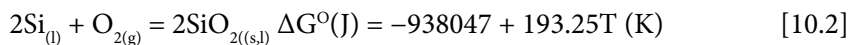
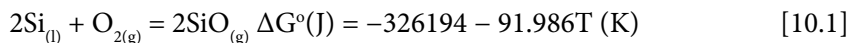
The slag needs to be separated from the alloy during/before casting to avoid slag contamination of the alloy product. Density and viscosity differences between the two phases are therefore critical, as these determine the slag flowability and whether it sinks or floats on the alloy. In Chapter 4, it was shown that $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ melts in general will float on liquid FeSi75 , while for liquid Si, this varies for different slag compositions (Figure 4.15).

Fundamental reactions and element distribution equilibria

With the introduction of an oxidizing gas, typically oxygen-enriched air, Ca, Al and other impurities less noble than silicon are predominantly transferred to a slag phase created through reactions between the gas and melt. A small fraction of Ca and Al in the metal, along with other elements with high vapor pressures, such as Mg, K and Na, also report to the tapping/refining gas as oxide particulate matter (Næss *et al.*, 2013).

Bjørnstad described the initial nucleation and growth of slag droplets on gas bubbles from a bottom mounted plug (Bjørnstad and Tranell, 2021). Initially, as the gas bubbles ascend, the most abundant element, Si in the alloy, reacts with oxygen in the gas phase to form SiO_2 (liquid or solid) nuclei on the gas/metal interface, and SiO gas in the gas bubble, through equilibrium reactions 10.1 and 10.2. These nuclei serve as a starting point for further slag formation, thereby defining the oxygen potential at the slag/alloy interface. This allows the driving force for nucleation to be expressed as a local oversaturation of dissolved oxygen in the alloy. As the SiO_2 nuclei grow, Ca and Al will react, shifting the slag composition towards equilibrium with the alloy. Bjørnstad and Tranell (2021) also showed that the interfacial tension for a liquid slag on a gas substrate surrounded by a liquid Si alloy gives rise to individual slag nuclei, instead of a film, as illustrated in Figure 10.2.

The Gibbs energy functions for the reactions between the Si-alloy and gas [10.1–10.3] are valid from 1773 to 2273K (FACTSage 8.3):



The formation of SiO_2 as a precursor to slag formation is sensitive to melt temperature and the oxygen partial pressure of the refining gas. Above a certain temperature, T_{crit} , the SiO_2 product becomes unstable, and the only oxidized product becomes SiO gas (reaction 10.3). This does not facilitate refining, it only causes loss of silicon product to gas. Hence, cooling metal is used to control the metal temperature. T_{crit} is dependent on, and increases with, the oxygen content of the gas, as illustrated by Figure 10.3.

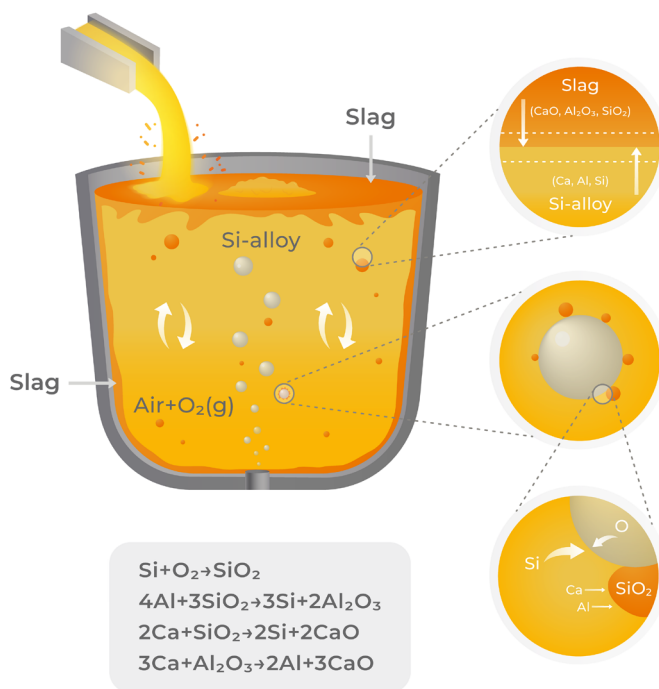
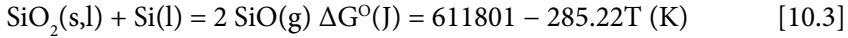


Figure 10.2 Schematic representation of the metal/slag/gas interface.



The critical temperature, in degrees Celsius, can be expressed as a function of oxygen mole fraction in the gas mixture per mole of silicon, x , as shown below:

$$T_{\text{crit}} = \frac{71229}{33.2531 + 2\ln(1+x) - 2\ln(2x)} \quad [10.4]$$

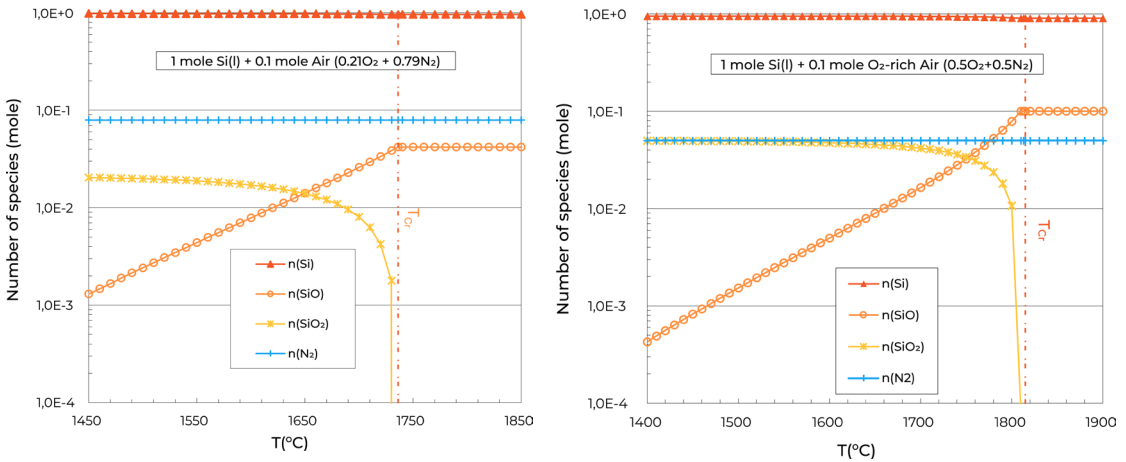


Figure 10.3 The moles of SiO_2 and SiO respectively formed at different temperatures, calculated from reaction 10.4 for two examples of different gas compositions, assuming the activities of Si and SiO_2 are close to unity at the gas/metal interface.

As the SiO_2 nucleus grows, it reacts with dissolved Ca, Al, and other impurities less noble than Si, according to reactions 10.5–10.7. This results in a SiO_2 –CaO– Al_2O_3 slag droplet on the metal/gas interface. SiO_2 will continue to determine the slag's surface properties until the concentration of CaO and Al_2O_3 reaches a critical limit, because SiO_2 has greater surface activity than CaO and Al_2O_3 . After reaching this critical limit, the slag droplet's surface properties become highly dependent on composition and determine whether it detaches or stays on the bubble surface.

$$\underline{Al} + \frac{3}{4}(\text{SiO}_2) = \frac{3}{4}\underline{Si} + \frac{1}{2}(\text{Al}_2\text{O}_3) \quad \Delta G^{\circ}(J) = -81204 - 7.1097T(K) \quad [10.5]$$

$$\underline{Ca} + \frac{1}{2}(\text{SiO}_2) = \frac{1}{2}\underline{Si} + (\text{CaO}) \quad \Delta G^{\circ}(J) = -95595 - 12.262T(K) \quad [10.6]$$

$$\underline{El} + \frac{y}{2x}(\text{SiO}_2) = \frac{y}{2x}\underline{Si} + \frac{1}{x}(\text{El}_x\text{O}_y) \quad [10.7]$$

For global slag-alloy equilibrium, the oxidation of various dissolved elements is mutually coupled through exchange reactions such as [10.8] for Ca and Al:

$$\underline{Al} + \frac{3}{2}(\text{CaO}) = \frac{3}{2}\underline{Ca} + \frac{1}{2}(\text{Al}_2\text{O}_3) \quad \Delta G^{\circ}(J) = 62189 + 11.283T(K) \quad [10.8]$$

Based on thermodynamic data, the calculated iso-concentration contours for calcium and aluminium in liquid Si and FeSi, in equilibrium with SiO_2 – CaO – Al_2O_3 slags at 1550°C and 1600°C respectively, are illustrated in Figures 4.26–4.33. Deviations from the expected equilibrium may occur, in some cases resulting from slow reaction kinetics between solid inclusions and high viscosity slags, as discussed in Section 10.1.2. At low impurity levels, transport of impurity elements from the bulk alloy to the slag/alloy interface may be a rate-limiting step.

Equilibrium reaction paths

Earlier in this chapter we discussed the primary reactions taking place during refining processes, where impurities are oxidized and removed as part of a separate slag phase. This section expands on that discussion by considering how the liquid alloy composition changes to equilibrate with a slag, and how an equilibrium can be modified to reach a target composition. Figure 10.4 illustrates the isothermal map of the SiO_2 – CaO – Al_2O_3 slag system. From this map, it becomes evident that relatively small changes in the ladle temperature may quickly affect the liquid slag composition through precipitation of solids, thereby also affecting the equilibrium alloy composition.

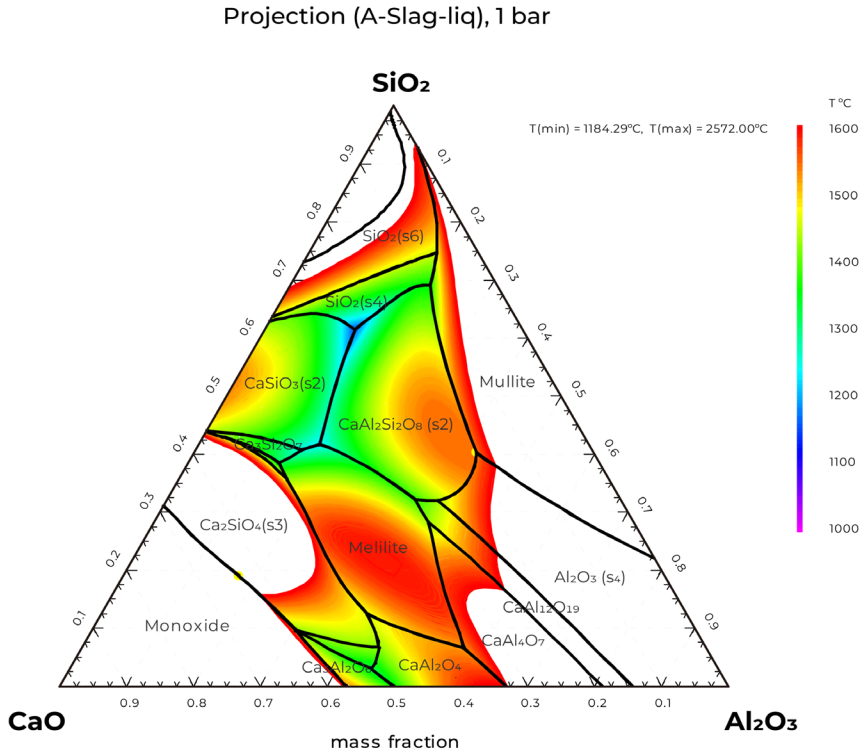


Figure 10.4 $\text{SiO}_2\text{--CaO--Al}_2\text{O}_3$ slag liquidus projection drawn with *FACTSage* 8.3.

Based on step-wise isothermal equilibrium calculations (Figure 10.5) and laboratory experiments by Bjørnstad *et al.*, we can first discuss what happens when a FeSi75 or MG–Si alloy is blown (isothermally) with an oxygen-bearing gas, without any initial tapped slag present or slag additives (CaO or SiO_2) (Bjørnstad *et al.*, 2022).

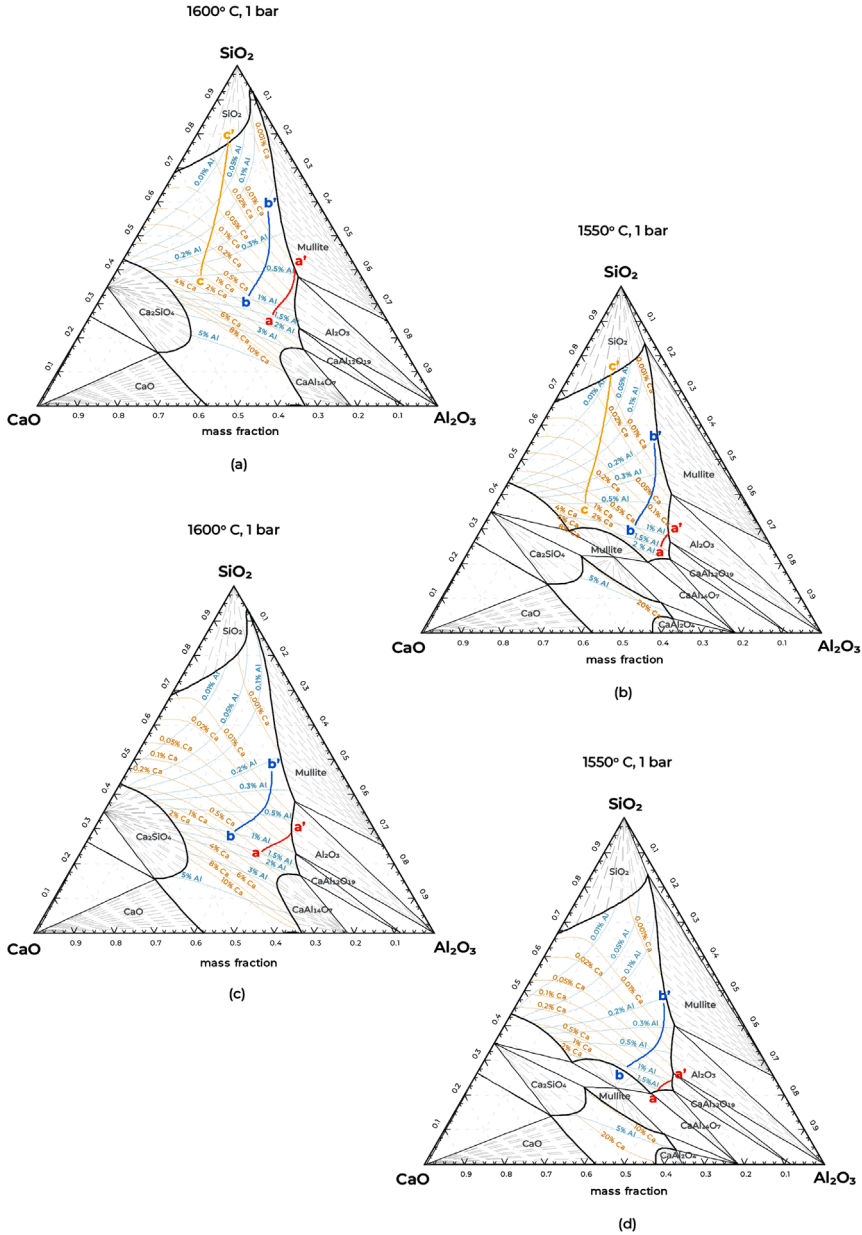


Figure 10.5 Theoretically calculated alloy compositional paths (a-a', b-b', c-c') for a) MG-Si alloy with different initial Ca and Al compositions at 1600°C, b) MG-Si alloy with different initial Ca and Al compositions at 1550°C, c) FeSi75 alloy with different initial Ca and Al compositions at 1600°C, d) FeSi alloy with different initial Ca and Al compositions at 1550°C.

In Figure 10.5, iso-Al and iso-Ca contours were calculated using the FactSage software, with the commercial database FTOxid for the liquid slag phase and a private database for liquid Si-Al-Ca-Fe alloys, taking into account more accurate Ca-activity data at 1600°C and 1550°C respectively (Jakobsson and Tangstad, 2015). The figure illustrates oxidative refining of MG-Si, initially containing 1.5wt% Al and 0.5wt% Ca at point *a*, 1wt% Al and 0.5wt% Ca at point *b*, and 0.5wt% Al and 1wt% Ca at point *c*, for both 1600°C and 1550°C. By introducing oxygen into the refining vessel, the compositions change along the curves *a-a'*, *b-b'*, and *c-c'* respectively. For the FeSi75 case, the refining paths for the two starting compositions, 1.5wt% Al and 0.5wt% Ca at point *a*, and 1wt% Al and 0.5wt% Ca at point *b*, are marked.

Due to the higher oxygen affinity/oxidation rate of Ca compared to Al, alloys with high initial Al:Ca ratios produce slag that becomes saturated with Al_2O_3 or mullite. This forms viscous alumina-rich slag and/or solid alumina-rich inclusions. Without additional quartz and lime in the refining vessel, this represents the practical refining limit¹. This occurs more rapidly at lower temperatures, because the liquid slag region is smaller. Thus, if the initial calcium content is low and no fluxes are added, two different types of slag may form: a free-flowing, sinking type (due to its higher density) in the initial stage of the process, which tends to accumulate at the bottom of the reaction vessel, and a highly viscous and partly solidified type at the end, floating on top of the metal. The results align well with the laboratory measurement results by Bjørnstad *et al.* and illustrate that, regardless of the tapped alloy composition and temperature, the oxidation initially results in a CaO-rich slag and an increasingly Ca-depleted alloy (Bjørnstad *et al.*, 2022). For Ca:Al ratios ≥ 1 , subsequent gas bubbles entering the bath form slags richer in SiO_2 , with decreasing calcium-to-aluminium ratios. From the point where the alloy reaches a composition corresponding to the formation of solid slag/oxide, refining slows down, and the refining path transitions from refining by slag formation to refining by global slag equilibrium. This transition is critical for industrial production, because further gas purging alone to lower the aluminium concentration will result in product losses (i.e., excess oxidation

1 Thermodynamic calculations indicate further refining following the Al_2O_3 /mullite-liquid phase boundary. While this is theoretically viable, the physico-chemical properties of the slag will not make this path practically possible.

of the Si-alloy). The problem is that the more slag is present in the ladle, the more slag must be generated to change its composition. Producing this slag and changing the refining path requires silica, resulting in an exponentially cumulative loss of silicon to silica formation if extra silica is not added to the ladle. This also agrees with observations made during unpublished industrial trials (described by Tuset, 1992).

Industrially, there are methods to modify the equilibrium and reaction route to alter the final alloy composition:

- making new/more slag or solid precipitates,
- changing global slag or alloy composition,
- changing the temperature.

Making new/more slag or solid precipitates

- If slag is physically removed, a new slag will form. With a lower availability of slag-forming impurities, the alloy will move towards a different equilibrium composition.
- Adding a slag will influence the equilibrium pull from the start, which, depending on alloy/slag composition, may differ from the equilibrium attained during initial oxidation of the alloy alone. This may unintentionally be the case when slag from the SAF is tapped together with the alloy into the ladle, as described by Folstad *et al.* (2023).

Figure 10.6 illustrates two simulated cases in which an Si alloy with the composition 1wt% Al and 0.5wt% Ca, or 0.5wt% Al and 1wt% Ca, is refined by air, or in which an initial amount of furnace slag is tapped together with the alloy. In the latter case, this initial slag is either 5wt% of the alloy weight (with composition 60wt% SiO₂, 25wt% CaO and 15wt% Al₂O₃) or 5wt% of the alloy weight (with composition 30wt% SiO₂, 35wt% CaO, 35wt% Al₂O₃). As illustrated by the graph, for the alloy tapped with a higher Al content, the tapped slag in both cases contributes to a refining path that reaches a more aluminium-lean alloy composition. In a case with a more calcium-rich tapped alloy, the tapped slag composition plays a more important role in determining the refining path.

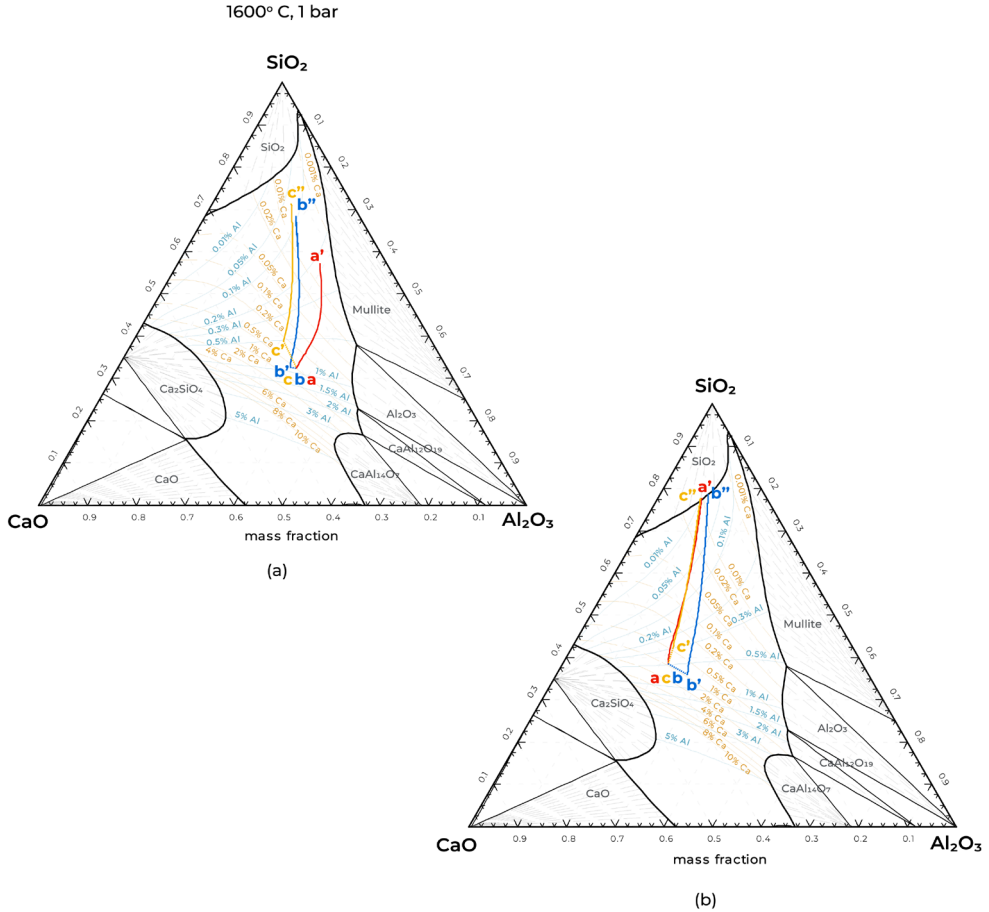


Figure 10.6 (a) Simulated refining paths for a tapped Si alloy containing 1wt% Al and 0.5wt% Ca without furnace slag (a-a'), 5wt% furnace slag of initial alloy weight with composition 30wt% SiO₂, 35wt% CaO, 35wt% Al₂O₃ (b-b'-b''), or 5wt% furnace slag (c-c'-c'') of initial alloy weight with composition 60wt% SiO₂, 25wt% CaO, 15wt% Al₂O₃. (b) Simulated refining paths for a tapped Si alloy containing 0.5wt% Al and 1wt% Ca without furnace slag (a-a'), 5wt% furnace slag of initial alloy weight with composition 30wt% SiO₂, 35wt% CaO, 35wt% Al₂O₃ (b-b'-b''), or 5wt% furnace slag (c-c'-c'') of initial alloy weight with composition 60wt% SiO₂, 25wt% CaO, 15wt% Al₂O₃.

Changing global slag or alloy composition

By strategically changing the availability of specific species at given times, one may shift to a more desirable reaction path or force a target equilibrium. One strategy for maintaining refining without excessive losses of silicon product is therefore to add both slag formers, such as limestone or burned lime, and silica in some form, to adjust the global slag composition. Recycled glass, containing around 70–75wt% SiO_2 , 10–11wt% CaO and 13–14wt% Na_2O , has also been proposed as a low-cost material, but it brings some sodium into the metal (60–80 ppmw Na) and, if the glass contains lead oxide, may contaminate the metal with traces of lead (Haaland *et al.*, 1994). An example of an intended change in the alloy refining path is illustrated in Figure 10.7, which describes the difference between isothermal (1550°C) air-blowing and air-blowing + slag additives to FeSi75. The *a-a'* refining path is defined by air-purging (identical to Figure 10.4). The final metal phase consists of 0.9wt% Al and 0.1wt% Ca, whereas the slag consists of 24.5wt% SiO_2 , 49.5wt% Al_2O_3 and 26wt% CaO . To further remove Al from the metal phase, slag additives (SiO_2 and CaO) are added. Assuming the final Al wt % to be 0.02wt% and Ca wt % to be 0.005wt%, addition of SiO_2 and CaO is required at the *b''* point of the above figure. The refining path is now represented by the *b-b'-b''*. The final contents of metal are 0.02wt% Al and 0.005wt% Ca, and the slag consists of 66wt% SiO_2 –16wt % Al_2O_3 –18wt % CaO .

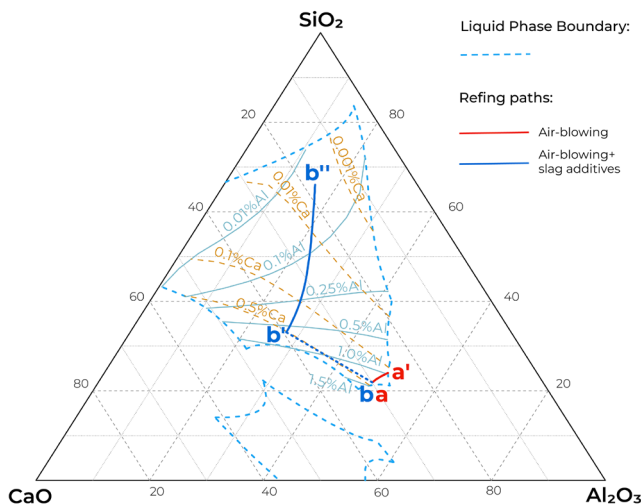


Figure 10.7 Refining path for FeSi75 at 1550°C with air-blowing, with and without slag additives.

While the global slag composition affects the final alloy composition, the interaction between slag and alloy may also be inhibited. This can affect the reaction path and kinetics by limiting the slag's equilibrium pull. This may be due to both limited slag/alloy contact area and other mass transport barriers, such as high viscosity or solid slag phases.

Changing the temperature

The alloy temperature will decrease if left alone, but insulation, external heating, and exothermic/endothermic reactions/phase changes will all affect the temperature in their own way. Temperature affects reaction kinetics, the phase of reaction constituents, reaction priority, and much more. Some aspects of the total heat balance will be further described in Section 10.1.3.

Mass and heat balance

We now look at the mass and energy balance for the FeSi case described in Section 10.1.2, following the refining line b–b'–b". Assuming the final Al% to be 0.02wt% at the b" point of the above figure, addition of SiO₂ and CaO is required, as outlined in the prior section. The refining path is now represented by the b–b'–b". The final contents of metal are 0.02wt% Al and 0.0005wt% Ca, and the slag consists of 66wt% SiO₂–16wt% Al₂O₃–18wt% CaO. A mass and energy balance model, using HSC Chemistry (illustrated in Figure 10.8), can be used to explain details about the refining process.

For the aluminium to be lowered from 1.5wt% to 0.02wt%, i.e. by $\Delta[\% \text{Al}] = 1.48$

A quantity of 14.8 kg Al per tonne of alloy corresponding to:

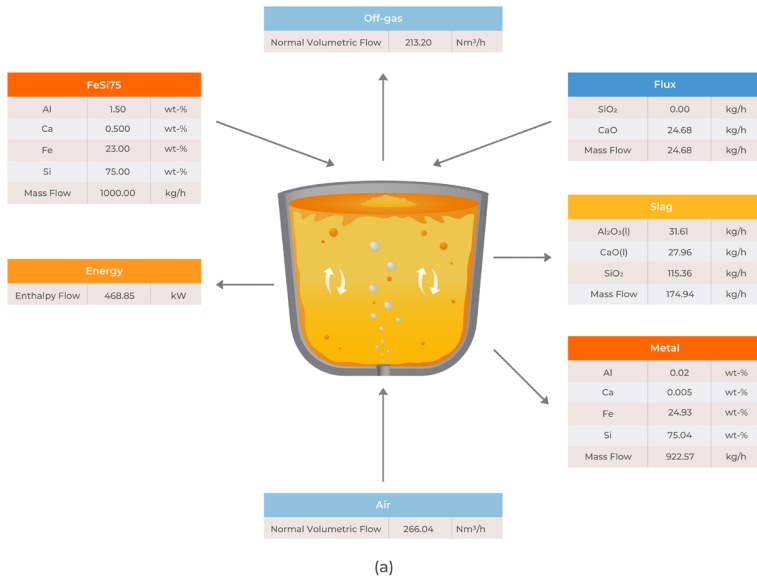
$$14.8 \cdot \frac{M_{\text{Al}_2\text{O}_3}}{2M_{\text{Al}}} = 14.8 \cdot 1.89 = 28 \text{ kg Al}_2\text{O}_3 \quad [10.9]$$

has to be transferred to a slag with $\leq 16\text{wt}\% \text{ Al}_2\text{O}_3$.

This defines the minimum quantity of refining slag (Wr) required:

$$\frac{\Delta[\% \text{Al}] \cdot 1.89}{(\% \text{Al}_2\text{O}_3)_R} \cdot 1000 = 175 \frac{\text{kg}}{\text{tonne}} \text{ alloy} \quad [10.10]$$

FeSi75 Oxidative Refining Process



FeSi75 Oxidative Refining Process

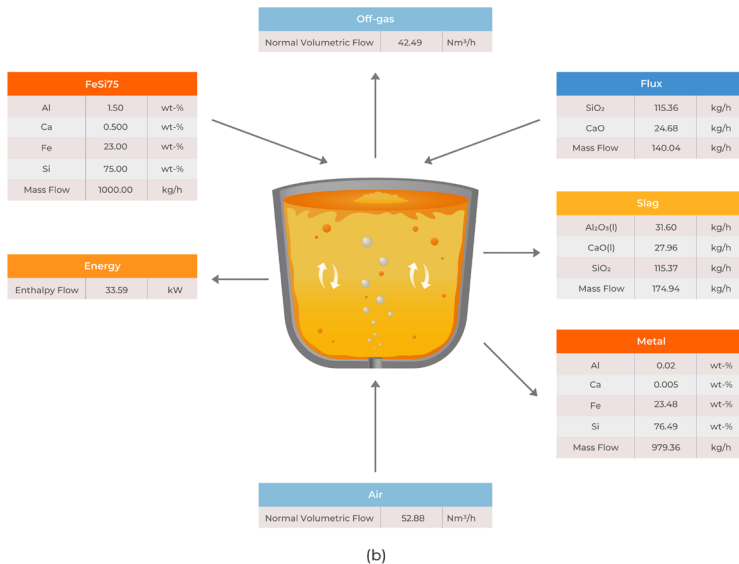


Figure 10.8 HSC model parameters for FeSi refining model: (a) silica required for the formation of the final slag is produced 100% by oxidation of silicon; (b) silica required for the formation of the final slag is added totally as SiO₂ in the form of silica sand. The input T for the FeSi75 is 1550°C and the air and flux 25°C.

If W_F kg of furnace slag with an alumina content of $(\text{wt}\% \text{Al}_2\text{O}_3)_F$ enters the refining vessel, the total slag quantity needed increases by:

$$W_t = W_r + W_F \cdot \frac{(\% \text{Al}_2\text{O}_3)_F}{(\% \text{Al}_2\text{O}_3)_R} \quad [10.11]$$

For $W_5 = 0$, the material balance for our case will then be as given in Table 10.1.

Table 10.1 *Material balance for refining of FeSi75 as described in the text and given in kg/tonne alloy.*

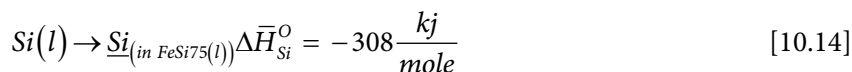
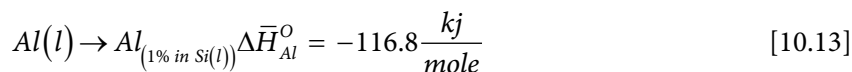
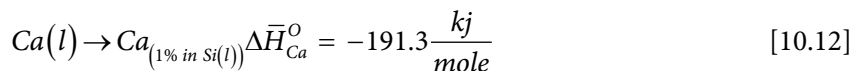
Zero addition of silica (oxidation of Si, Al and Ca)											
Initial metal		Flux		Air		Final metal		Final slag		Off-gas	
Al	15	CaO	24.68	O ₂	78.72	Al	0.20	Al ₂ O ₃	27.96	N ₂	259.24
Ca	5					Ca	0.05	CaO	31.61		
Fe	230			N ₂	259.24	Fe	230	SiO ₂	115.36	SiO	5.89
Si	750					Si	692.33				
Sum	1000		24.68		337.95		922.57		174.94		265.12
All the SiO ₂ in slag added as silica (no oxidation of Si, only oxidation of Al and Ca)											
Initial metal		Flux		Air		Final metal		Final slag		Off-gas	
Al	15	CaO	24.68	O ₂	15.65	Al	0.20	Al ₂ O ₃	27.96	N ₂	51.53
Ca	5					Ca	0.05	CaO	31.60		
Fe	230	SiO ₂	115.36	N ₂	51.53	Fe	230	SiO ₂	115.37	SiO	1.39
Si	750					Si	749.11				
Sum	1000		140.04		67.17		979.36		174.94		52.92

As indicated in the table, the silica required for the formation of the final slag in Table 10.1 can be produced 100% by oxidation of silicon, or it can be added totally or partly as SiO₂ in the form of silica sand. The calculated heat effects associated with the two most extreme ways of supplying the silica are given in Table 10.2.

Table 10.2 *Energy balance for refining of FeSi75 as described in the text and given in kWh per tonne alloy.*

Species	Zero addition of silica		All the SiO ₂ in slag added as silica	
	Input total enthalpy	Output total enthalpy	Input total enthalpy	Output total enthalpy
Al	8.82	0.12	8.82	0.12
Ca	2.12	0.02	2.12	0.02
Fe	83.60	83.60	83.60	83.60
Si	669.05	617.60	669.05	668.26
CaO	-77.62	-80.06	-77.60	-80.05
SiO ₂		-424.58	-485.80	-424.59
O ₂	0		0	
N ₂	0	128.02	0	25.45
Al ₂ O ₃		-105.78		-105.78
SiO		-1.83		-0.43
Surplus heat	468.85		33.59	

The calculations show that the oxidation of dissolved calcium and aluminium generates sufficient heat to keep the temperature theoretically constant at 1550°C, even if all the silica is added as SiO₂. In this case, however, there is almost no surplus heat available to cover the heat losses. There will also be a heat deficit if air is used instead of oxygen for blowing. This is seen from Figure 10.9, which shows the effect of a mixed supply of silica and SiO₂ produced by oxidation of Si, using oxygen or air.



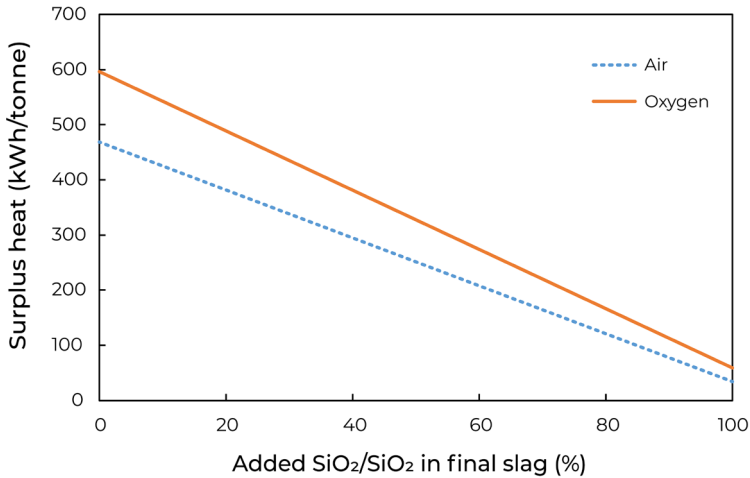


Figure 10.9 Calculated heat effect vs the relative amount of SiO₂ in the final slag added as silica during ferrosilicon refining at 1550°C.

Table 10.3 summarizes the heat losses related to oxidative ladle refining of silicon and ferrosilicon.

Table 10.3 Summary of data on heat losses related to oxidative ladle refining at 1550°C from a ladle lined with ordinary fireclay bricks according to Christensen (1988).

Heat loss source	kW/m ²
Ladle walls and bottom (275°C)	7
Ladle cover (230°C)	4.5
Radiation losses from a partly slag-covered ferrosilicon surface during tapping	115–180
Radiation losses from empty ladle after pouring	130

Oxygen and carbon in refined metal

Oxygen and carbon in refined liquid metal are present both as dissolved elements and as suspended phases: slag droplets, crusty aluminium silicates, or silica films in the case of oxygen, and silicon carbide particles in the case of

carbon. As the solubility of oxygen and carbon decreases to a few ppm when the metal solidifies, these elements appear in solidified metal almost entirely as oxide and carbide inclusions, respectively, as discussed in Chapter 4. Thus, the lowest concentrations that can be reached for oxygen and carbon in bulk metal refining are determined by their solubility in the liquid metal at the casting temperature.

Studies show that the actual oxygen and carbon content in refined metal is much higher than their reported solubilities. This is particularly true for oxygen in silicon, where the conditions for phase separation are extremely unfavorable. Laroze investigated representative samples of silicon that had been refined and cast in various ways and found that the oxygen content varied between 0.04 and 0.70 wt% O (Laroze, 1994). The same absolute level and variation in oxygen has also been reported by others (Forwald *et al.*, 1994). This is an issue when producing alloys for methyl-chlorosilane production, as the reactivity and selectivity of the feed is highly dependent on the type and distribution of intermetallic phases. These phases form during the solidification process and rely on a given balance between metallic constituents such as Ca, Al and Fe. If oxygen is present in the metal, unknown fractions of Ca and Al are tied up in oxide inclusions that behave as inert constituents in the direct process (Forwald *et al.*, 1994). Analytical methods such as atomic absorption or x-ray fluorescence spectroscopy do not distinguish between elements that are present as oxides and those present as intermetallics, with Eie *et al.* suggesting that the amount of active intermetallics in silicon can be derived on the basis of results from leaching tests (Eie *et al.*, 1998).

In order to minimize the oxygen content, the refining process should be carried out in a way that prevents crusty silica- or alumina-rich films from forming initially by:

- Maintaining a reservoir of calcium in the system by the addition of CaO or CaO-containing silicates
- Activating the fluid bottom layer of slag throughout the entire purging process
- Avoiding 'over-oxidation' at the termination of the refining process
- Preventing gas bubbles from collapsing by adding an inert component to the oxygen, i.e., by using air especially at the end of the blow.

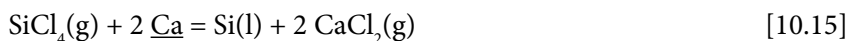
Specifications of carbon in refined products have up to now been stricter for producers of ferrosilicon than for metallurgical grade silicon, due to requirements from demanding customers within certain sectors of the steel industry, e.g., producers of silicon-alloyed steel sheets for electrotechnical applications, and some stainless steel producers which specify <200 ppmw C in FeSi75. Thus, the carbon problem has been more actively addressed by producers of ferrosilicon than by those of silicon. The extensive studies of Klevan are a reflection of this (Klevan, 1997). According to Klevan's work, when the metal is tapped from the furnace it contains 700–1100 ppmw C, which corresponds closely to the solubility at the metal forming temperature in the hearth of the furnace. When this metal is delivered as standard lumpy FeSi75 after casting, crushing and screening, a statistical treatment of the analyses of 779 shipments from one plant over a three-year period shows that the carbon content has dropped to an average of 300 ppmw C (Klevan, 1997). The average figures for ferrosilicon delivered as water granulated or refined qualities during the same period were 210 and 120 ppmw C, respectively. This implies that the carbon, which precipitates as SiC particles as the temperature drops during tapping and handling, is physically removed as particles to a fairly large extent. While there is a large variation between reported solubilities of carbon in silicon, the work by Dalaker and Tangstad determined the carbon content as a function of temperature as: $C_c = 839.4 \cdot \exp(-19856/T)$, giving a solubility of 65 ppmw at the silicon melting point of 1414°C (Dalaker and Tangstad, 2009).

10.2 Refining by Chlorination

The use of various types of halides for purification of metallurgical grade silicon in its liquid state has been studied because of their potential use in solar grade silicon production (Hunt *et al.*, 1976). This text focuses on the use of chlorine only, as this is the only type of halide that is used commercially and is, in addition, the one that has been found most effective on elements like calcium and aluminium. For other impurities that are present, the average percentage removal obtained from 20 experiments has been summarized by Hunt *et al.* (1976) as follows:

0%	for Fe, Ni, Ti, and V
20–50%	for Cr, Cu, and Mn
10%	for P
40%	for B (not reproduced in more recent experiments)

When Cl_2 is introduced as bubbles rising through pure liquid Si, it reacts to form gaseous silicon chlorides. SiCl_4 , SiCl_3 and SiCl_2 are the main components formed at a total pressure of 1 bar. SiCl forms in minor amounts and, together with Cl_2 , can be neglected as a constituent of the gas phase. If calcium is present at low concentrations, gaseous CaCl_2 and negligible amounts of CaCl(g) are formed, as seen from a reaction of the following type:



Here, $\text{SiCl}_4(\text{g})$ enters with the partial pressure as given by the equilibria between Si(l) and Cl_2 at $P_{\text{total}} = 1$ bar. CaCl_2 melts at 771.85°C , boils at 1934.77°C , and has a vapour pressure of 0.018 bar at 1423°C . The partial pressure of CaCl_2 , as calculated for reaction [10.15], will reach this value for $a_{\text{Ca}} = 1.14 \cdot 10^{-10}$ at 1423°C . The concentration of calcium corresponding to this activity is 2 ppmw Ca if $\gamma_{\text{Ca}} = 1 \cdot 10^{-4}$ is used as an appropriate activity coefficient for calcium in silicon at 1423°C . The same calculations carried out for 1523°C give 10 ppmw Ca as the equilibrium concentration of calcium in the presence of liquid CaCl_2 .

The Al removal by chlorinating reactions is shown in Figure 10.10. The chlorination refining process is more efficient than the oxidation refining process for Al and Ca removal, and for the recovery rate of the metal (Figure 10.11).

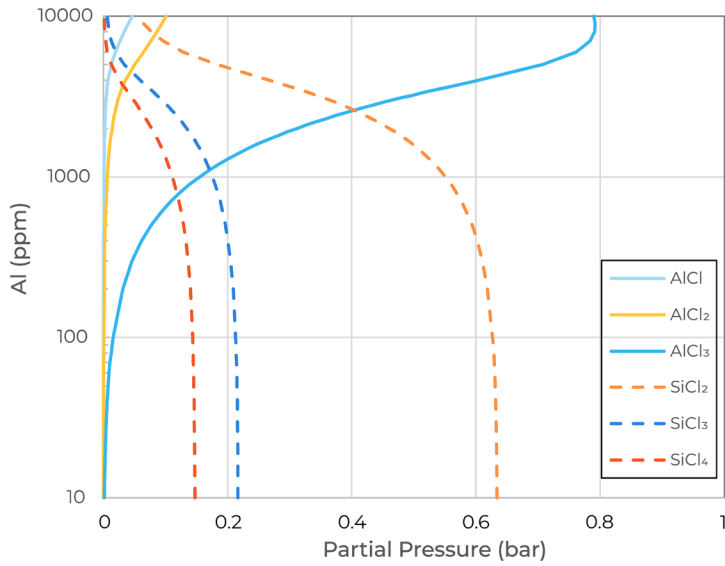


Figure 10.10 Calculated equilibrium gas compositions over liquid silicon containing various concentrations of Al in the presence of Cl_2 at 1423°C and $P_{\text{Total}} \approx \Sigma p_{\text{MeCl}_2} = 1 \text{ bar}$.

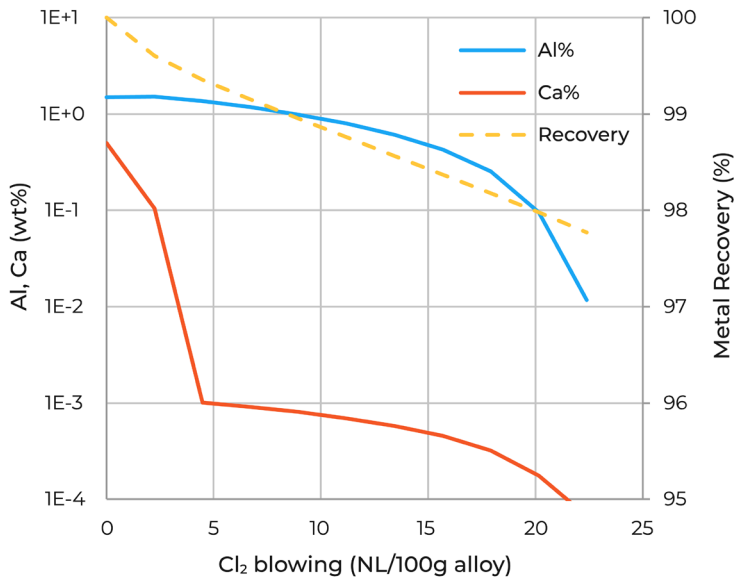


Figure 10.11 Calculated metal recovery and resulting Al and Ca concentrations in a Cl_2 refined Si at 1423°C .

Aluminium forms a variety of chlorides, all of which are in the gaseous state above 180°C. Of these, AlCl_3 and AlCl_2 appear to be the most stable at temperatures around 1400°C. Both components are more stable than the chlorides of silicon. Thus, when liquid Si containing Al is treated with Cl_2 , the chlorine is converted almost selectively into gaseous AlCl_3 and AlCl_2 at high concentrations of Al. At low contents of Al, the chlorides of Si become the dominating gas components. This is also seen from Figure 10.10, which shows how the calculated equilibrium composition of the gas phase varies with the Al concentration at 1423°C and a total pressure of 1 bar. In these calculations $\gamma_{\text{Al}}^{\text{O}} = 0.1$ has been used. Liquid silicon will be refined for Al as long as the Al/Si ratio in the gas phase is greater than the Al/Si ratio of the metal phase. According to the data used in these calculations, these two ratios become equal at 2.3 ppmw Al. This concentration represents the theoretical purification limit if the chlorination is conducted at 1423°C and $P_{\text{total}} = 1$ bar, provided that pure Cl_2 is used as the chlorinating agent.

If a mixture of Cl_2 and Ar is used, the purification limit will be even lower, and the calculations will predict a lower limit if a larger and more realistic $\gamma_{\text{Al}}^{\text{O}}$ value is used. In the initial stage, when silicon containing both calcium and aluminium is treated with Cl_2 , nearly all supplied Cl_2 will be consumed by Ca to form liquid CaCl_2 . As the Ca concentration decreases, a gas phase of atmospheric pressure forms, and Al starts to react together with some silicon. The composition of the gas phase will then change with the decreasing Al concentration, as indicated in Figure 10.11. In addition to the components given, the gas will also be saturated by $\text{CaCl}_2(\text{g})$ as long as $\text{CaCl}_2(\text{l})$ is present. In this period, the Ca concentration in the metal levels off at the limits given, but it will continue to decrease as soon as the liquid chloride phase disappears due to evaporation. The advantage of using an Ar/ Cl_2 mixture with a low content of chlorine during the evaporation stage is hence clear.

10.3 Refining towards Solar Grade Material

While MG-Si specifications vary according to its application, the purity demand on solar grade silicon (SoG-Si) is substantially stricter and is generally obtained through chemical purification. Table 10.4, adopted from the review paper of Hosseinpour and Tafaghodi Khajavi, summarizes literature

data of elemental specifications for different silicon grades (Hosseinpour and Tafaghodi Khajavi, 2018a). With the development towards high-efficiency cells based on single-crystal silicon materials, purity is often even more stringent than those described below.

Table 10.4 *Impurity specifications for different silicon grades. (Adapted from Hosseinpour and Tafaghodi Khajavi, 2018a).*

Impurity content (ppm)			
Impurity	Solar grade silicon (Baba <i>et al.</i> , 2000; Dietl and Wohlschlager, 1981; Hunt, 1984; Parisi <i>et al.</i> , 1980)	Metallurgical grade silicon (98–99%) (Bathey and Cretella, 1982; Chu <i>et al.</i> , 1978; Dietl, 1983)	99.5% (Baba <i>et al.</i> , 2000; Hunt, 1984; Kapur and Choudary, 1983)
Al	< 0.1	1000–4000	50–600
Fe	< 0.1	1500–6000	100–1200
Ca	< 1	250–2200	100–300
Mg	< 1	100–400	50–70
Mn	<< 1	100–400	50–100
Cr	<< 1	30–300	20–50
Ti	<< 1	30–300	10–50
V	<< 1	50–250	< 10
Zr	<< 1	20–40	< 10
Cu	< 1	20–40	< 10
B	0.1–1.5	10–50	10–15
P	0.1–1	20–40	10–20
C	0.5–5	1000–3000	50–100

With the rapidly growing Si-based photovoltaic market, great efforts have been made – particularly during the past two decades – to establish alternative metallurgical methods to the Siemens-based chemical route for removing critical elements to these low levels (Chigondo, 2018; Safarian *et al.*, 2012). While effective removal of metallic impurities, and to some extent carbon/nitrogen as solid SiC/Si₃N₄ particles, may be obtained via, for example, directional solidification, the solid–liquid segregation of neither boron nor phosphorus makes this a viable direct method for removing such impurities.

In the following sections, metallurgical techniques for the removal of carbon, metallic impurities, boron and phosphorus are described.

Removal of carbon

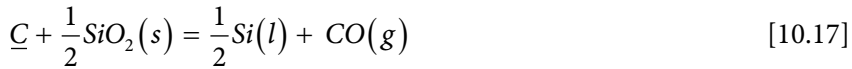
Several investigators have contributed to carbon removal, and the methods employed have been: settling combined with directional crystallization (Aulich *et al.*, 1986; Mühlbauer *et al.*, 1991), filtration combined with oxidation (Sakaguchi and Maeda, 1992), decarburization by inert gas purging or under vacuum (Klevan, 1997; Sakaguchi and Maeda, 1992) and the use of plasma (Thomas *et al.*, 1992) or electron beam melting techniques (Ikeda and Maeda, 1992). In contrast to ferrosilicon, the removal of suspended SiC particles in silicon by settling is found to be effective. The settling rate in a quiet bath of silicon is given by Stokes's equation:

$$v = \frac{d^2 g}{18\eta} (\rho_1 - \rho_2) \quad [10.16]$$

where g is the acceleration of gravity; d is the diameter of a SiC particle; η is the viscosity of silicon ($0.8 \cdot 10^{-3}$ Ns/m² at 1450°C); and ρ_1 and ρ_2 are the densities of SiC (3200) and Si (2517 kg/m³ at 1450°C), respectively. This can be exemplified by calculating that SiC particles larger than 10 μ m in diameter will settle to the bottom of a 10 cm deep layer of silicon in 30 minutes. This has been utilized in the purification methods employed by Aulich *et al.* on silicon produced by carbothermic reduction from high purity raw materials (Aulich *et al.*, 1986). The metal was tapped at 1750°C into high purity molds and allowed to cool slowly to 1450°C, where it was kept for a certain period of time before the mold was cooled from the bottom in order to achieve unidirectional solidification. The remaining SiC particles were then pushed ahead of the solidification front and became concentrated in the top layer of the ingot. After cutting away the top and bottom layers, the metal was found to contain 5 ppmw C.

An alternative treatment of high purity silicon produced by carbothermic reduction was presented by Ciftja (2009) and Sakaguchi and Maeda (1992). They claim that suspended SiC particles are effectively removed by filtration through a packed bed of spherical particles of silica. A further decrease in

carbon is achieved in a subsequent treatment, where the metal is decarburized by flushing and stirring with argon in the presence of silica. Under optimal conditions, the decarburization rate will then be controlled by the reaction pressure of CO, as defined by the equilibrium:



With

$$K_{10.17} = \left(\frac{a_{\text{Si}}}{a_{\text{SiO}_2}} \right)^{\frac{1}{2}} \frac{P_{\text{CO}}}{a_{\text{C}}^1} = \exp \left(-\frac{36558}{T} + 19.5 \right) \quad [10.18]$$

where the activities of Si and SiO₂ can both be assumed as unity, and the activity of C, which refers to a 1% solution as the standard state, can be replaced by [% C]. Inserting T = 1773 K (1500°C) and [% C] = 0.005 (50 ppmw C) in the expression for K, we arrive at: P_{CO} = 0.32 · 0.005 = 1.5 mbar as a maximum value for the reaction pressure of CO. The decarburization process is therefore expected to be slow, and dependent on the specific flow rate of argon, as also experienced by (Sakaguchi and Maeda, 1992). In their experiments, they used between 4–6 hours to reach 10 ppmw C from the initial 50 ppmw. Klevan developed a mathematical model that describes the kinetics of the decarburization process in detail when using inert gas purging (Klevan, 1997). When this model was tested on experimental data in which metallurgical-grade silicon was purged with a mixture of argon and oxygen, it became clear that the overall decarburization rate was controlled by the mass transfer coefficient of carbon at the metal/gas interface. The obvious reason for this was the formation of a dense silica/slag layer at the interface, which slows down the diffusion rate of CO.

Removal of (metal) impurities by directional solidification

The crystal structure of silicon means that the solid solubility of most elements is very limited compared to their liquid solubility in silicon. Table 10.5 lists the solid solubility of selected elements in Si.

Table 10.5 *Solid solubilities of selected elements in silicon, reproduced from (Møll, 2014).*

Atom	Maximum Solid Solubility (at/cm ⁻³)	Reference	Atom	Maximum Solid Solubility (at/cm ⁻³)	Reference
Al	$2.0 \cdot 10^{19}$	(Trumbore, 1960)	N	$4.5 \cdot 10^{15}$	(Hull, 1999)
B	$6.0 \cdot 10^{20}$	(Trumbore, 1960)	Ni	$8.0 \cdot 10^{17}$	(Hull, 1999)
C	$3.0 \cdot 10^{17}$	(Hull, 1999)	O	$3.0 \cdot 10^{18}$	(Hull, 1999)
Cu	$1.5 \cdot 10^{18}$	(Trumbore, 1960)	P	$1.3 \cdot 10^{21}$	(Hull, 1999)
Fe	$3.0 \cdot 10^{16}$	(Trumbore, 1960)	Sn	$5.0 \cdot 10^{19}$	(Trumbore, 1960)
Mn	$3.0 \cdot 10^{16}$	(Trumbore, 1960)	Zn	$6.0 \cdot 10^{16}$	(Trumbore, 1960)

Hence, as liquid silicon containing impurities starts to solidify, an almost pure silicon phase will form first, enriching the liquid in impurities. This mechanism is purposefully used to refine silicon in controlled crystallization processes such as Bridgman directional solidification, illustrated in Figure 10.12. In such a process, heat is slowly extracted from molten silicon from the bottom of the crucible, maintaining an equilibrium surface between the solidified and molten solvent (Si). Assuming that the bulk concentration of the solute in the liquid is homogeneous and that there is no back-diffusion from the solid to the liquid, the distribution of the solute between solid and liquid Si can be expressed by the equilibrium distribution coefficient k , defined as:

$$k = \frac{C_s}{C_L} \quad [10.19]$$

where C_s and C_L are the solid and liquid concentrations of the solute at the solid–liquid interface. k values for selected elements are listed in Table 10.6. As seen from the table, the segregation coefficient for most metals is very low, while those for B and P are relatively high.

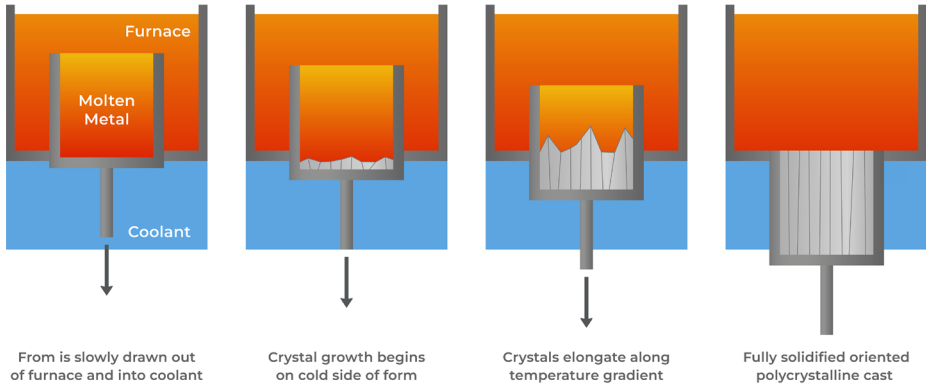


Figure 10.12 *Illustration of the directional solidification process.*

Table 10.6 *Equilibrium solid–liquid distribution coefficients for selected solutes in silicon.*

Impurity	Segregation coefficient	Impurity	Segregation coefficient
B	0.80	Fe	$6.4 \cdot 10^{-6}$
P	0.35	Ti	$2.0 \cdot 10^{-6}$
C	$5.0 \cdot 10^{-2}$	Cu	$8.0 \cdot 10^{-4}$
Al	$2.8 \cdot 10^{-3}$	Mg	$3.2 \cdot 10^{-6}$
Li	$1.0 \cdot 10^{-2}$	S	$1.0 \cdot 10^{-5}$
Ag	$1.0 \cdot 10^{-6}$	As	$3.0 \cdot 10^{-1}$
Au	$2.5 \cdot 10^{-5}$	Sb	$2.3 \cdot 10^{-2}$
Ni	$1.0 \cdot 10^{-4}$	Zn	$1.0 \cdot 10^{-5}$
Ca	$8.0 \cdot 10^{-3}$	Bi	$7.0 \cdot 10^{-4}$
Mn	$4.5 \cdot 10^{-3}$	Cr	$1.1 \cdot 10^{-5}$

For a starting concentration C_0 of the solute, the mass balance of the system can be expressed as:

$$C_s f_s + C_l f_l = C_0 \quad [10.20]$$

Where f_s and f_l are the fractions solid and liquid, respectively.

By rearranging equations 10.19 and 10.20 into the so-called Gulliver-Scheil equation, we can describe the concentration of solute in a given fraction of solid material:

$$C_s = kC_0(1 - f_s)^{k-1} \quad [10.21]$$

Because of the exponential increase in solute concentration in the last solidifying part of the material, this part (typically around 10% of the weight) can be removed from the solidified ingot if this technique is used for refining purposes.

While the assumption of negligible back-diffusion from the solid to the liquid during solidification is valid for most elements, there are exceptions, such as Fe and Cu. Several authors have experimentally documented significant (back) diffusion of iron from intrinsic and extrinsic (e.g. from the crucible) sources during solidification of both multicrystalline and single-crystal silicon (Kvande *et al.*, 2008; Wen *et al.*, 2024). The degree of iron diffusion during different cooling rates has been modelled by Boulfrad (2012), as shown in Figure 10.13.

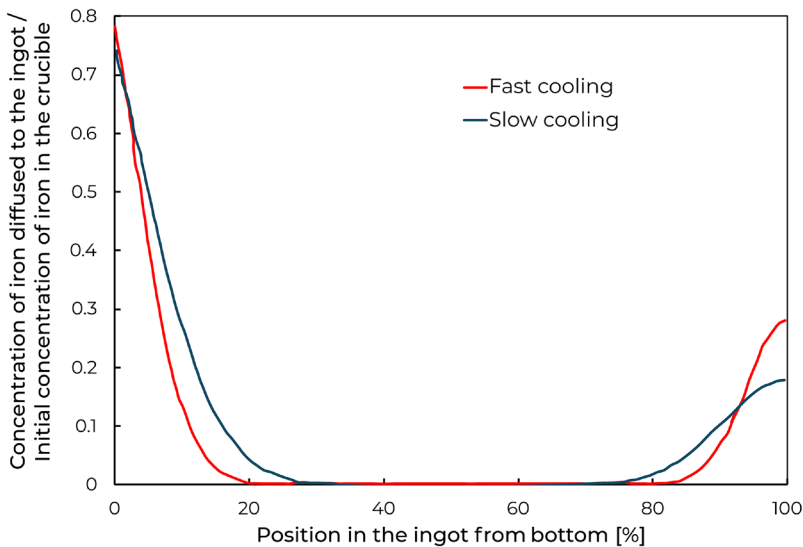


Figure 10.13 Modelled content/diffusion of iron contained in feedstock and crucible as a function of ingot height during directional solidification. (Updated from figure in (Boulfrad, 2012)).

Removal of boron

Boron has nearly the same affinity towards oxygen as silicon and forms gaseous suboxides such as BO, an analogue to SiO. Its condensed stable oxide (B_2O_3) behaves, like SiO_2 , as an acid in the presence of alkali and alkaline earth metal oxides at slag-forming temperatures. From this starting point, oxidative refining of boron may seem challenging. However, considerable industrial and scientific efforts have been placed on developing methods to remove boron, either as a constituent of a slag or in the form of a gaseous suboxide at elevated temperatures.

Slag refining

The transfer of boron to the slag phase can be described as a two-step reaction: oxidation at the metal-slag interface, followed by dissolution of the oxide into the ionic slag liquid, according to:



The overall boron equilibria / transfer can hence be expressed by:



However, because the distribution between boron in metal and slag is coupled to the Si/ SiO_2 equilibrium, the generic reaction is often expressed as:



The equilibrium constant K for [10.25] will hence be described by:

$$K = \frac{(a_{Si}^{Si \text{ alloy}})^{3/4} \cdot a_{BO_{1.5}}^{slag}}{a_B^{Si \text{ alloy}} \cdot (a_{SiO_2}^{slag})^{3/4}} = \frac{(a_{Si}^{Si \text{ alloy}})^{3/4} \cdot (x_{BO_{1.5}}^{slag})}{(a_{SiO_2}^{slag})^{3/4} \cdot x_B^{Si \text{ alloy}}} \cdot \frac{\gamma_{BO_{1.5}}^{slag}}{\gamma_B^{Si \text{ alloy}}} \quad [10.26]$$

Data for the Henrian activity coefficient for boron in pure silicon are illustrated as a function of temperature in Figure 10.14.

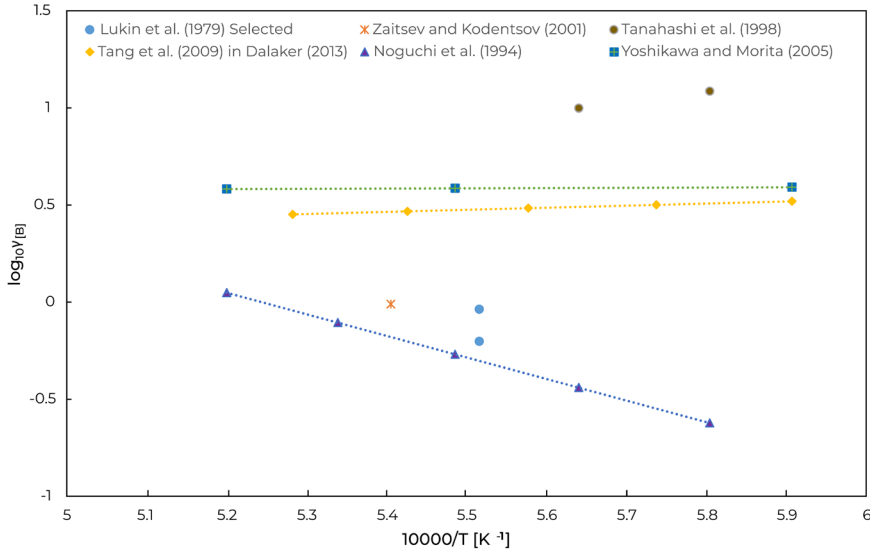


Figure 10.14 The Henrian activity coefficient of dissolved boron in silicon (Dalaker, 2013; Lukin et al., 1979; Morita, 2005; Noguchi, 1994; Tanahashi et al., 1998; Tang et al., 2009; Zaitsev and Kodentsov, 2001).

While the positive deviation from ideality, found by most researchers, works in favor of slag refining of B, more complex thermodynamic data are often sparse. Hence, an experimentally determined metal slag distribution coefficient, L_B , as expressed by [10.27], is often used to evaluate the refining efficiency of the system:

$$L_B = \frac{(\text{wt}\%B) \text{ in slag}}{[\text{wt}\%B] \text{ in silicon}} \quad [10.27]$$

A large number of researchers, as summarized in Table C-1 in Appendix C, have investigated the boron distribution between slag and silicon for a number of slag systems. Selected experimental data are illustrated in Figure 10.15.

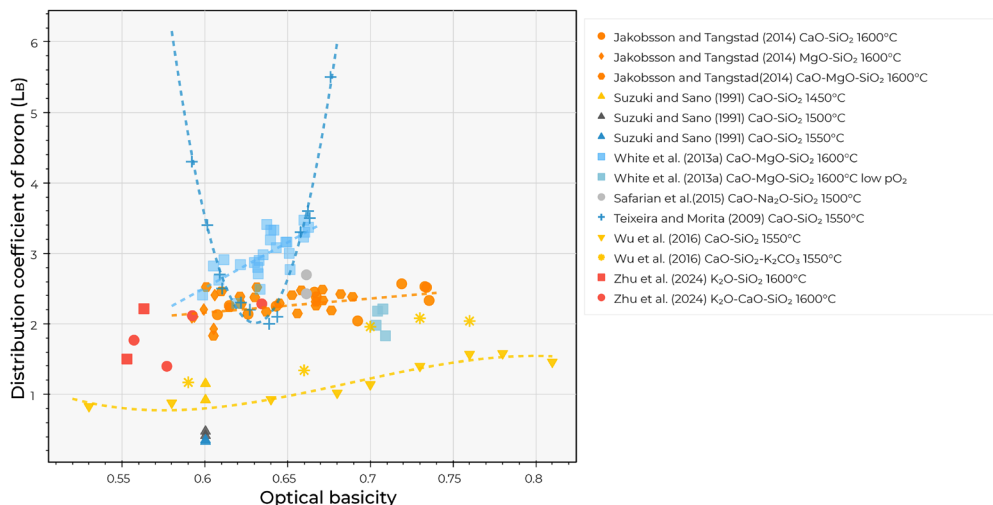


Figure 10.15 L_B values for selected slag systems in equilibrium with silicon (Jakobsson and Tangstad, 2014; Safarian et al., 2015; Suzuki and Sano, 1991; Teixeira and Morita, 2009; White et al., 2013a; Wu et al., 2016; Zhu et al., 2024).

As seen by the figure, typical L_B values are concentrated around 2 for CaO-SiO₂-based slag systems. As such, the reported distribution coefficients render slag refining rather weak for boron unless very large volumes of slag are used in a batch process, or it is implemented in a process where metal and slag are equilibrated in a stepwise counter-current flow pattern. Nevertheless, slag refining was successfully implemented industrially by Elkem Solar, resulting in silicon with boron concentrations as low as 0.23 ppmw (Søiland et al., 2014). In systems where one of the slag compounds is volatile, such as Na₂O in the Na₂O-CaO-SiO₂ system, additional boron removal via volatilization may also be involved. Such systems are, however, not very practical for industrial implementation.

Solvent refining and combinatory slag/solvent refining

Similarly to the acid leaching method described in Section 10.3.5, the basic principle of solvent refining is to adjust the impurity segregation behavior during Si solidification via alloying. The solvent element is cho-

sen to retain impurities to a higher degree than silicon and to create a low temperature melting point system with silicon. During cooling, primary Si is first precipitated, and the impurities continuously enrich the remaining liquid phase until it is fully solid. The Si crystals may subsequently be purified by acid washing, and the remaining binary alloy can be used for other applications.

The Si–Al melt is the most studied solvent refining system, first reported by Obinata and Komatsu, 1957. The segregation behavior of both P and B in the Si–Al melt was later investigated by Yoshikawa and Morita, 2003, 2005. It was found that both segregation coefficients decrease with decreasing temperature, as illustrated for B in Figure 10.16. With Ti addition into the Si–Al melt, B can be effectively removed due to the formation of TiB_2 precipitates. In addition to the Si–Al system, a number of other solvent refining systems have been developed with good purification performance, such as Si–Sn (Hu *et al.*, 2013), Si–Fe (Hosseinpour and Tafaghodi Khajavi, 2018, 2019) and Si–Cu (Huang *et al.*, 2016).

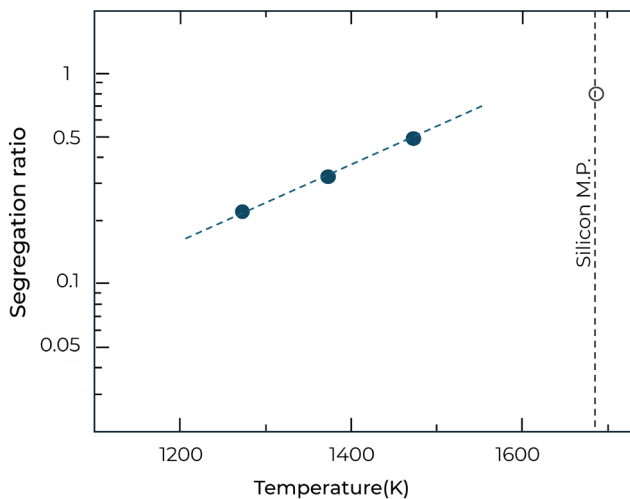


Figure 10.16 Temperature dependence of segregation ratios of boron between solid silicon and Si–Al solvent. Data from Yoshikawa and Morita, 2012.

A combined slag/solvent refining approach to increase the refining efficiency is to alloy the silicon melt (e.g., with Sn, Cu etc.) and combine it with a suitable slag system, thereby increasing the L_B value. This is summarized in Figure 10.17, adapted from (Thomas *et al.*, 2021), where D_B values, which are normalized L_B values by oxygen partial pressure, are presented as a function of slag optical basicity for various Si-alloy systems.

$$D_B = \frac{L_B}{(p_{O_2})^{\frac{3}{4}}} \quad [10.28]$$

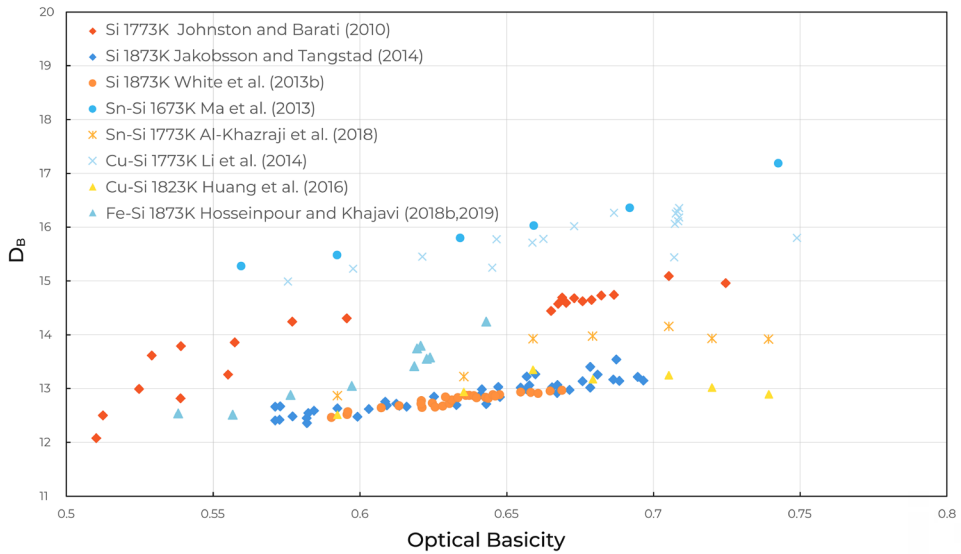


Figure 10.17 Calculated DB values from slag refining of different silicon alloys (adapted from (Thomas *et al.*, 2021)) (Al-khazraji *et al.*, 2018; Hosseinpour and Tafaghodi Khajavi, 2019, 2018b; Huang *et al.*, 2016; Jakobsson and Tangstad, 2014; Johnston and Barati, 2010; Li *et al.*, 2014; Ma *et al.*, 2013; White *et al.*, 2013b) [Reproduced with permission from SNCSC].

The relationship between L_B value in alloyed Si system (L_B^*) and in unalloyed Si melt system (L_B^0), with the same slag composition, can be estimated using the following equation (Zhu *et al.*, 2021):

$$\frac{L_B^*}{L_B^0} = \left(\gamma_{Si}^{*Si-Me \text{ melt}} \right)^{\frac{1}{4}} \left(\frac{1}{1 - x_A^{*Si-Me \text{ melt}}} \right)^{\frac{3}{4}} \exp \left(\varepsilon_{Me}^B x_{Me}^{*Si-Me \text{ melt}} \right) \cdot \left(1 + \frac{M_{Me} - M_{Si}}{M_{Si}} x_{Me}^{*Si-Me \text{ melt}} \right) \quad [10.29]$$

where $x_{Me}^{*Si-Me \text{ melt}}$ represents the concentration of the alloying element Me in the Si-Me melt, $\gamma_{Si}^{*Si-Me \text{ melt}}$ denotes the activity coefficient of silicon in the Si-Me melt, ε_{Me}^B indicates the interaction coefficient between the alloying element and the boron impurity, and M_{Me} is the molar mass of the alloying element.

Given these variables, to improve the L_B value it is preferable to choose an alloying element with a positive interaction coefficient ε_{Me}^B and a high alloying element concentration $x_{Me}^{*Si-Me \text{ melt}}$, as these significantly affect the exponential term and power term in the formula. Moreover, an alloying system with a positive activity coefficient of silicon $\gamma_{Si}^{*Si-Me \text{ melt}}$ also promotes boron removal. In addition, if the alloying metal has a higher molar mass, i.e. $M_{Me} > M_{Si}$, the alloying process can magnify the L_B value by physically diluting the boron mass fraction in the metal phase.

Gas refining

Since the early plasma work of Theuerer, the potential of purifying silicon from boron as volatile B species has been known (Theuerer, 1956). More intense efforts in the area started in the late 1980's (Amouroux *et al.*, 1987) and early 1990's (Suzuki *et al.*, 1992, 1990), when this method of removing boron was demonstrated using a plasma torch with Ar-H₂O as the plasma gas.

Plasma-enhanced refining of P was also used by Khattak to refine silicon using combinations of reactive gas, slag and vacuum (Khattak *et al.*, 2002). Nordstrand and Tangstad (followed by Safarian *et al.*, Sortland, Altenberend *et al.* and Vadon *et al.*) first introduced the use of a gas lance delivering H₂-H₂O-containing gases with no active heating, demonstrating that such refining is also possible without the aid of plasma (Altenberend *et al.*, 2017; Nordstrand and Tangstad, 2012; Safarian *et al.*, 2014; Sortland, 2015; Vadon

et al., 2018). Using plasma leads to ionization of the reactive gases (O_2 , H_2O , H_2 , etc.), forming O , H , OH , $O +$, $OH +$ species in the plasma flame and hence enhancing their chemical reactivity. These gas species react with the silicon melt containing B , forming, for example, HBO , HBO_2 , BO , B_2O , BO_2 species. Thermodynamic data for the system have been assessed by (Tang *et al.*, 2012). The oxidation/volatilization of boron takes place simultaneously with oxidation of Si , also leading to formation of SiO and associated Si losses. While the exact boron volatilization reaction may vary depending on the type of gas/conditions used, a simplified description of the reactions between dissolved boron and water vapour, forming HBO in equilibrium with its silicon counterpart SiO^2 , may be written:



The equilibrium partial pressure, p_{HBO} , for a given boron concentration in the melt can hence be calculated using the expression:

$$\frac{p_{HBO}}{x_B} = \gamma_B \cdot \frac{K_{Eq.10.32}}{p_{O_2}^{1/2}} \cdot p_{SiO} \cdot p_{H_2}^{1/2} \quad [10.33]$$

The purification rate/efficiency is, however, affected by the gas type, flow rate and refining temperature, as illustrated by Figure 10.18.

Table C-2 in Appendix C summarizes research in the area to date.

2 Silicon may, however, also form $Si-O-H$ species. (Jacobson *et al.*, 2005; Opila *et al.*, 1997).

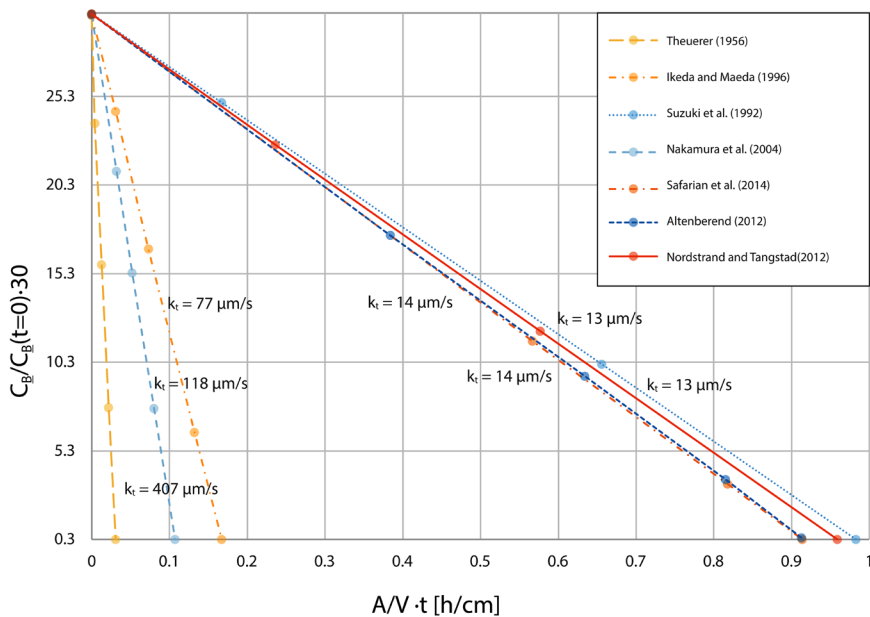


Figure 10.18 The rate of boron refining by gas blowing with the aid of plasma (Ikeda and Maeda, 1996; Suzuki et al., 1992; Theuerer, 1956), or without the aid of plasma (Altenberend, 2012; Nakamura et al., 2004; Nordstrand and Tangstad, 2012; Safarian et al., 2014) (after Sortland, 2015). [Used with permission from Ø.S. Sortland].

Removal of phosphorus

Two main metallurgical methods are interesting for removal of phosphorus from silicon: vacuum refining and alloying-aided acid leaching.

Vacuum refining

Unlike boron, phosphorus displays a high standard vapour pressure at elevated temperatures and is hence potentially a candidate for refining via vacuum evaporation treatment, as illustrated by Figure 10.19. This is summarized by Safarian and Tangstad from available thermodynamic data (Safarian and Tangstad, 2012a).

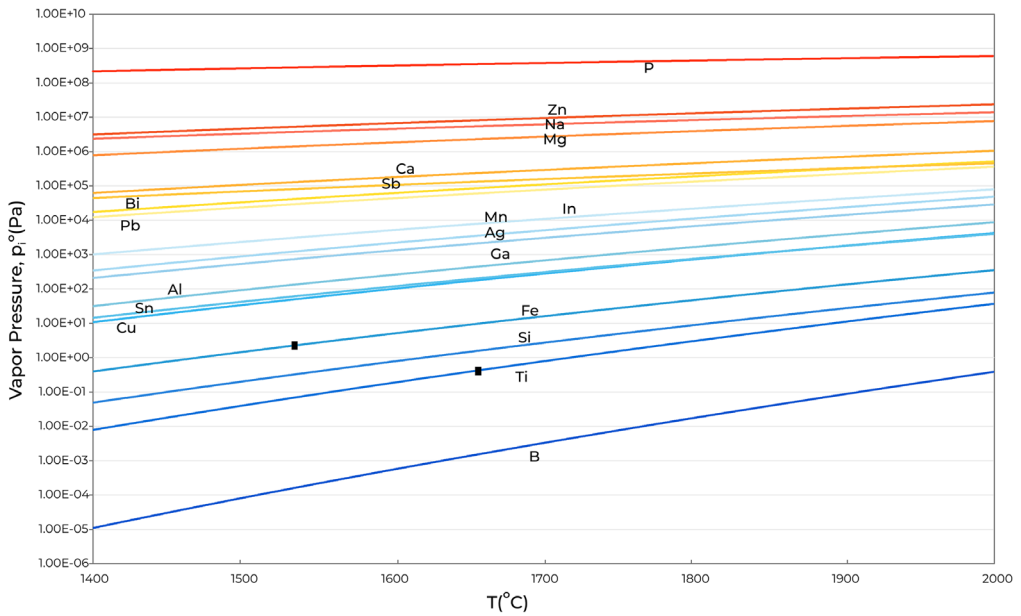


Figure 10.19 The changes in standard vapour pressure over pure substances with temperature (Safarian and Tangstad, 2012a). Creative Commons CC BY license.

The viability of P-refining of silicon via evaporation/vacuum treatment is, however, dependent on both thermodynamic and kinetic factors. Miki *et al.*, Zaitsev *et al.*, Schlesinger, Safarian and Tangstad, Liang and Schmid-Fetzer, Hoseinpur and Safarian, and Hoseinpur *et al.* have all contributed to the thermodynamic understanding of the behavior of phosphorus in liquid silicon at different temperatures and pressures through measurements and modelling (Hoseinpur *et al.*, 2022; Hoseinpur *et al.*, 2021; Hoseinpur and Safarian, 2021; Liang and Schmid-Fetzer, 2014; Miki *et al.*, 1996; Safarian and Tangstad, 2011; Schlesinger, 2002; Zaitsev and Kodentsov, 2001). While early work took into account only the desorption/evaporation of monoatomic (P) and, primarily, diatomic (P_2) gas species, Hoseinpur showed that phosphorus may occur concurrently as several different gaseous species (P , P_2 , P_3 , P_4 , SiP , Si_2P , Si_3P and SiP_2) over Si, where their relative prevalence depends on temperature and the concentration of P in the liquid. He introduced three main groups

of reactions leading to phosphorus evaporation from the melt surface, as depicted in Figure 10.20:

1. Molecular evaporation: formation and desorption of phosphorus species (P , P_2 , and P_4) at the melt surface.
2. Decomposition of transient silicon phosphides: in this mechanism, the transient silicon phosphides are decomposed to phosphorus species (P , P_2 , and P_4) and other lower phosphides (Si_xP_y).
3. Evaporation of lower silicon phosphides (formed in mechanism 2) formed at the melt surface: in this mechanism, the transient silicon phosphides could directly desorb at the melt surface.

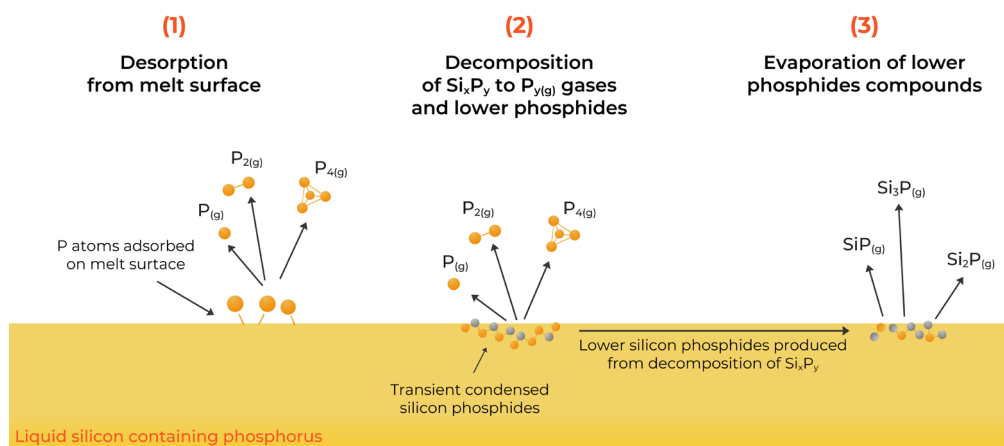


Figure 10.20 Schematic of different mechanisms for P evaporation from liquid Si (Hoseinpur *et al.*, 2022). Creative Commons Attribution 4.0 International License.

The partial pressures of different gas species as a function of melt composition were measured by Hoseinpur *et al.* through a Knudsen effusion cell at 1442°C, and are summarized in Figure 10.21 (Hoseinpur *et al.*, 2022). As seen from the figure, at a temperature close to the Si melting point the gas is dominated by the monoatomic P and P_2 species at higher P concentrations, while the phosphide species are more prevalent than P_2 at low-P concentrations.

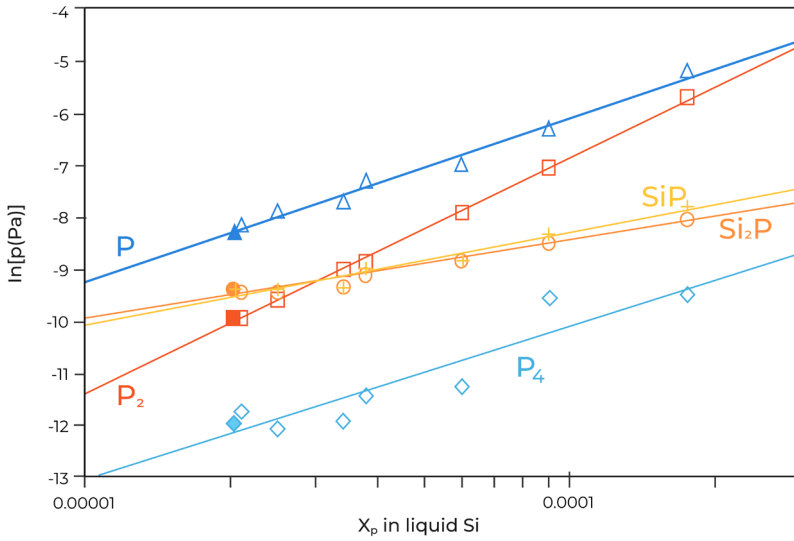


Figure 10.21 Partial pressures of different gaseous P species as a function of P concentrations at 1442°C from (Hoseinpur et al., 2022). Creative Commons Attribution 4.0 International License.

The relative partial pressures of species are also temperature dependent, and experimental evidence suggests that at ultra-high temperatures (> 1750°C) the P_4 species is a major contributor to the gas composition. The thermodynamic feasibility of removing phosphorous from silicon, i.e. whether the evaporation rate of phosphorous dominates over that of Si, may be evaluated through the ‘volatility coefficient’ for phosphorous, a , expressed through:

$$\alpha = \left[\frac{\gamma_p \cdot p_p^\circ \cdot \sqrt{M_{Si}}}{\gamma_{Si} \cdot p_{Si}^\circ \cdot \sqrt{M_p}} \right] \quad [10.34]$$

where γ_{Si} and γ_p denote the activity coefficients of Si and P respectively, p_{Si}° and p_p° the saturated vapour pressures of Si and P, and M_{Si} and M_p the molar masses of Si and P. For selective evaporation, a has to be > 1. The Henrian activity coefficient for P in dilute solution of Si (γ_p°) as a function of T can be calculated according to reaction [10.36], using the Gibbs energy change for

the diatomic evaporation of phosphorous [10.35] determined by Zaitsev *et al.* with pure phosphorous as reference state (Zaitsev *et al.*, 2001):

$$\frac{1}{2}P_2(g) = P(l) \quad \Delta G^0 = -99500 + 29.46T \text{ J/mol} \quad [10.35]$$

$$\ln(\gamma_p^o) = 2.08 - \frac{4766}{T} \quad [10.36]$$

Safarian and Tangstad calculated α values for a number of elements in dilute solution with Si, including P, using data from Figure 10.19 together with known activity coefficients. They found the volatility coefficient for P to be in the range 22–15 in the temperature range 1400–2000°C (Safarian and Tangstad, 2012b).

The rate of P evaporation at different temperatures and vacuum conditions has been investigated since the first reported studies by Suzuki *et al.* (Suzuki *et al.*, 1990). Subsequent studies were carried out by Yuge *et al.*, Hanazawa *et al.*, Zheng *et al.*, Safarian and Tangstad, Hoseinpur and Safarian, and Hoseinpur *et al.* (Hanazawa *et al.*, 2004; Hoseinpur *et al.*, 2022; Hoseinpur and Safarian, 2021; Safarian and Tangstad, 2012b, 2011; Yuge *et al.*, 2001, 1997; Zheng *et al.*, 2011, 2010). Most published data show that the rate fits a first order kinetic model according to:

$$\ln\left(\frac{[P\%]_0}{[P\%]_t}\right) = k_p \left(\frac{A}{V}\right)t \quad [10.37]$$

where $[P\%]_0$ and $[P\%]_t$ denote the initial and instant concentrations of phosphorus in the melt, respectively. The A/V ratio describes the geometry of the melt, where A and V are the surface area and volume of the melt, and k_p the total mass transfer coefficient. From experimental data on the P reduction rate at different temperatures, the relationship between k_p and T was obtained. Figure 10.22, adapted from Hoseinpur and Safarian, summarizes the data from various studies (Hoseinpur and Safarian, 2021). It is clearly seen that the evaporation mass transfer is significantly increased at high temperatures ($> 1800^\circ\text{C}$).

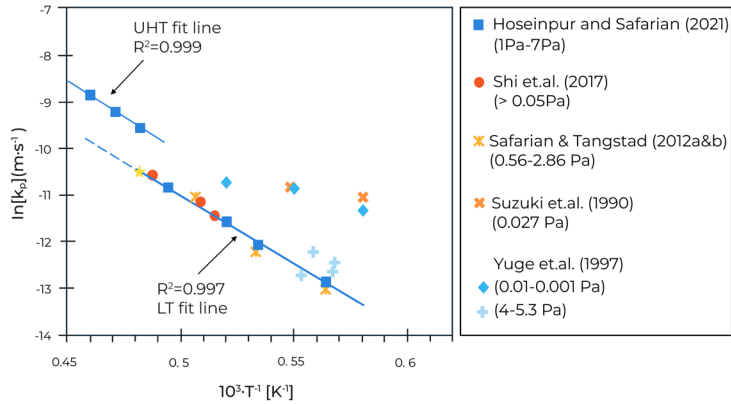


Figure 10.22 *P* evaporation mass transfer coefficient as a function of temperature (Adapted from (Hoseinpur and Safarian, 2021)). (Hoseinpur and Safarian, 2021; Safarian and Tangstad, 2012a, 2012b; Shi et al., 2017; Suzuki et al., 1990; Yuge et al., 1997) Creative Commons CC-BY-NC-ND license.

Acid leaching

Due to the low solid solubility of most elements in silicon, as discussed above, metal impurities largely segregate during solidification and precipitate as silicides at the silicon grain boundaries, as illustrated in Figure 10.23, taken from the PhD work of Zhu (Zhu, 2021).

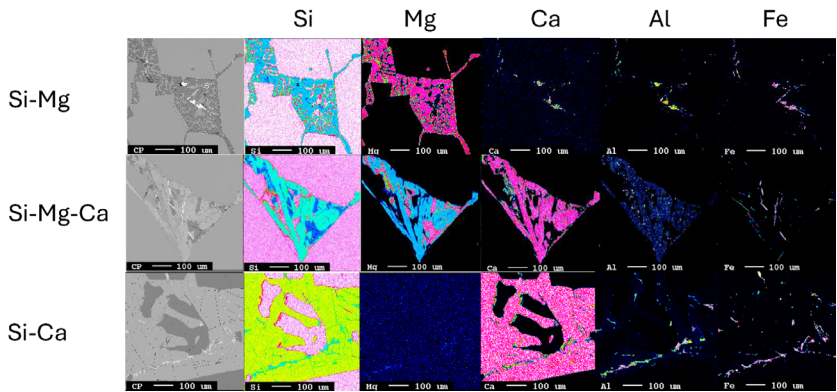


Figure 10.23 Segregation of impurities to complex silicides in a primary silicon matrix in solidified Si-4.7 wt% Mg, Si-2.5 wt% Mg-2.1 wt% Ca, and Si-3.6 wt% Ca alloy system (Zhu, 2021). Printed with permission from M. Zhu.

As was illustrated by Table 10.6, P has a high segregation coefficient compared to most metals. This makes it challenging to separate directly via segregation in Si alone, and difficult to remove via subsequent acid leaching. However, by adding certain alloying elements with a high affinity for P, such as Ca and Mg, the segregation of P can be significantly enhanced. In a binary alloying system (Si–Me), the P segregation coefficient can be estimated by the following equation:

$$k_p^{Si-Me} = k_p^{Si} \exp\left(\frac{\varepsilon_{Me}^P x_{Me}}{1 - f_s}\right) \quad [10.38]$$

where k_p^{Si} is the P segregation coefficient in pure silicon, which is 0.35, and x_{Me} denotes the concentration of alloying elements Me in alloy liquid. ε_{Me}^P represents the interaction coefficient between Me and P, and f_s represents the solid fraction of primary Si. It is seen that a negative ε_{Me}^P and high alloying concentration x_{Me} promote the P segregation.

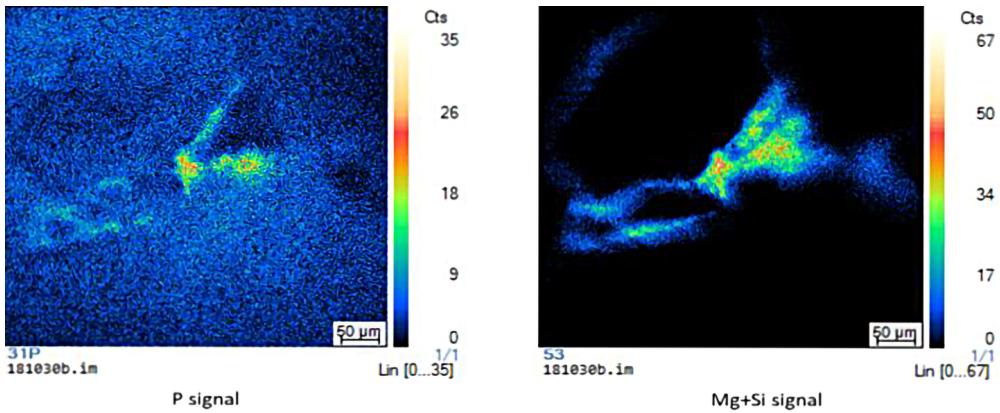


Figure 10.24 P segregation in Mg-doped Si alloy observed by SIMS elemental mapping (Zhu et al., 2020a). Open access article under the CC BY license.

As shown in Figure 10.24, P impurity can segregate together with the alloying elements and remain in the dissolvable silicide phase. This allows its removal, along with other metallic impurities, through acid treatment that preferentially attacks the silicides at the grain boundaries rather than the primary silicon grains.

Considerable research, as summarized in Table C-3 in Appendix C, has been performed to study impurity extraction from Si by acid leaching. It has been found that most metallic impurities can be effectively extracted by optimizing two perspectives: improving segregation through the selection of alloying elements, concentration, and cooling rate; and enhancing leaching separation efficiency by adjusting acid type, pH, leaching temperature, time, and particle size of the leaching materials. A typical acid leaching procedure and important factors are illustrated in Figure 10.25.

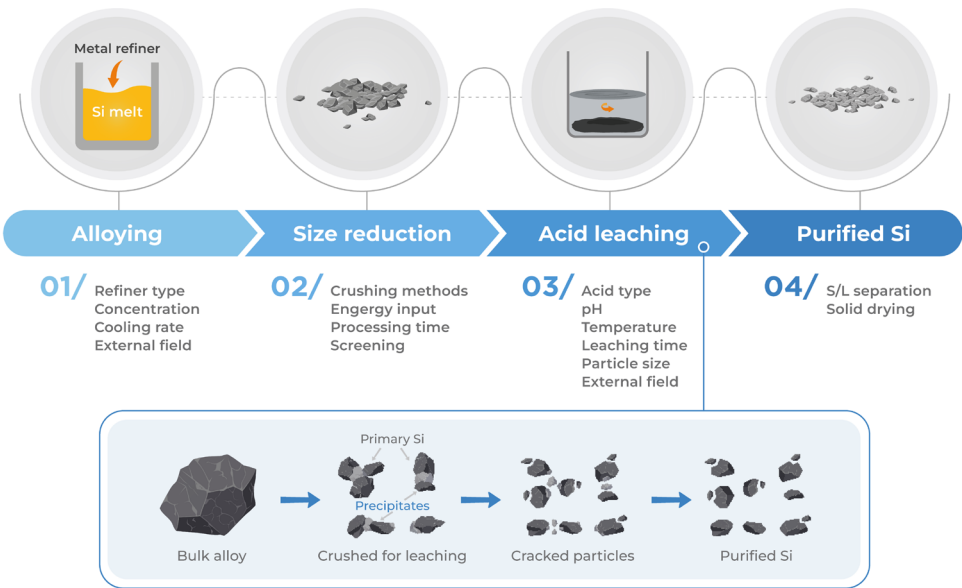


Figure 10.25 A typical acid leaching procedure with the main factors governing purification performance, including an illustration of particle size evolution and the removal of dissolvable precipitates enriched with impurities.

Figure 10.26 illustrates the concentration/degree of removal of Ca, Al, P, and other impurities as a function of leaching time in 10% HCl solution at a temperature of 60°C, for a starting Si–Ca–Al alloy that primarily consists of 75.18wt% Si, 14.94wt% Ca, and 9.07wt% Al. The alloy has a P content of 12.4 ppmw and other minor metallic impurities such as Mg, Fe, Mn, Ti, V, and Ga. It is evident that P segregated into the leachable precipitate phase is removed along with these phases.

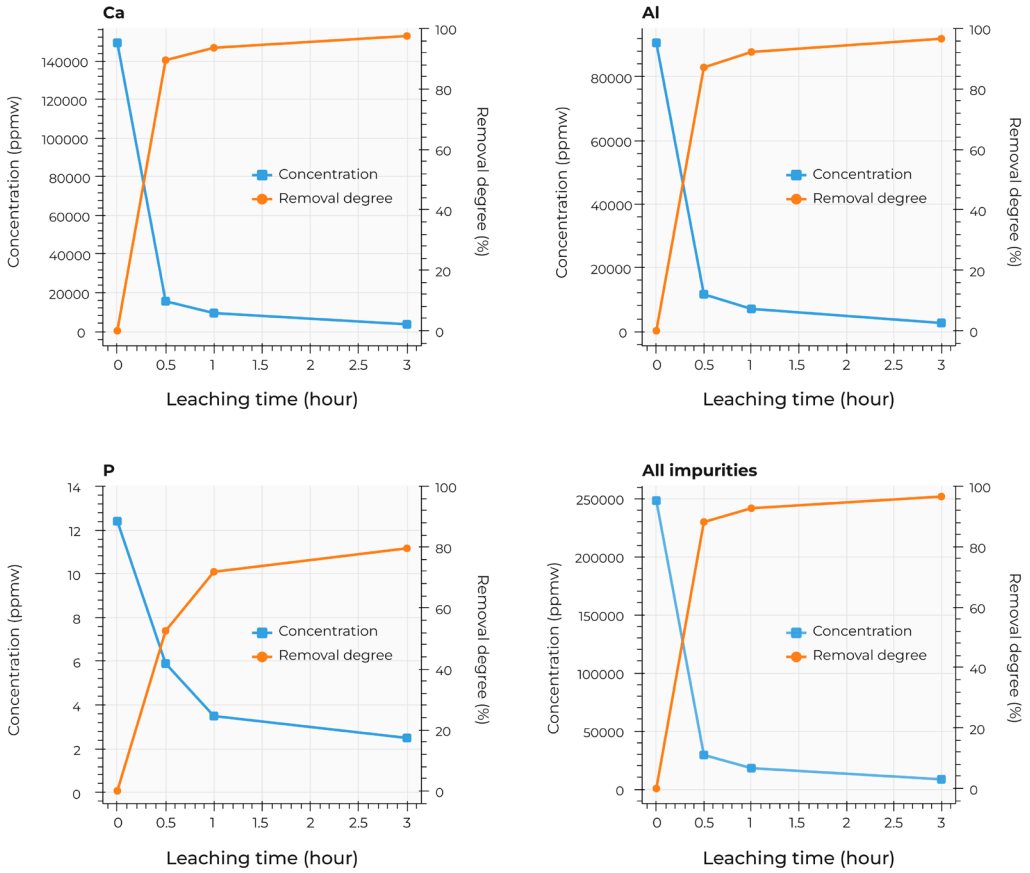


Figure 10.26 The effect of leaching time on the removal of Ca, Al, P and other impurities from a Si-14.94 wt% Ca-9.07 wt% Al alloy containing 12.4 ppmw P, leached in 10% HCl at 60°C (Zhu et al., 2022) Printed with permission from M. Zhu.

Using the Scheil equation to describe P segregation behavior in a Si-Me binary alloy system, and assuming that all precipitates formed during the eutectic transformation are removed, the following formula can be derived to describe the P removal degree (η) after acid leaching (Zhu *et al.*, 2020a):

$$\eta = \left\{ 1 - \frac{\exp\left(k_p^{Si} E_i\left(\frac{\varepsilon_{Me}^P X_{Me \text{ in Si}(l)}^{initial}}{1 - f_s^{Eu}}\right)\right)}{\exp\left(k_p^{Si} E_i\left(\varepsilon_{Me}^P X_{Me \text{ in Si}(l)}^{initial}\right)\right)} \right\} \times 100\% \quad [10.39]$$

where the $E_i(x)$ function is defined as the integral $E_i(x) = \int_{-\infty}^x \frac{e^t}{t} dt$, $X_{Me \text{ in Si}(l)}^{initial}$

represents the initial doping concentration of alloying element Me in Si melt, and f_s^{Eu} denotes the primary Si solid fraction at the eutectic point.

The selection criteria for the alloying system include high affinity for impurities, limited solubility in Si, and formation of a dissolvable phase; it should also be cost-effective, ensuring high Si recovery and an environmentally friendly leaching process. While Mg has been proven to be an effective getter for P, reaching high Si recovery, Ca additions are more efficient. They require a lower concentration in the solidifying metal for the same P removal effect and offer faster leaching kinetics. Mixing Ca and Mg is considered to capture the advantages of both elements. A comparison of the impurity removal degree of P, Al, Fe and Ti in the Mg-Si, Ca-Si and Ca-Mg-Si alloying systems after 3 h acid leaching by 10% HCl at 60°C under magnetic stirring is illustrated in Figure 10.27.

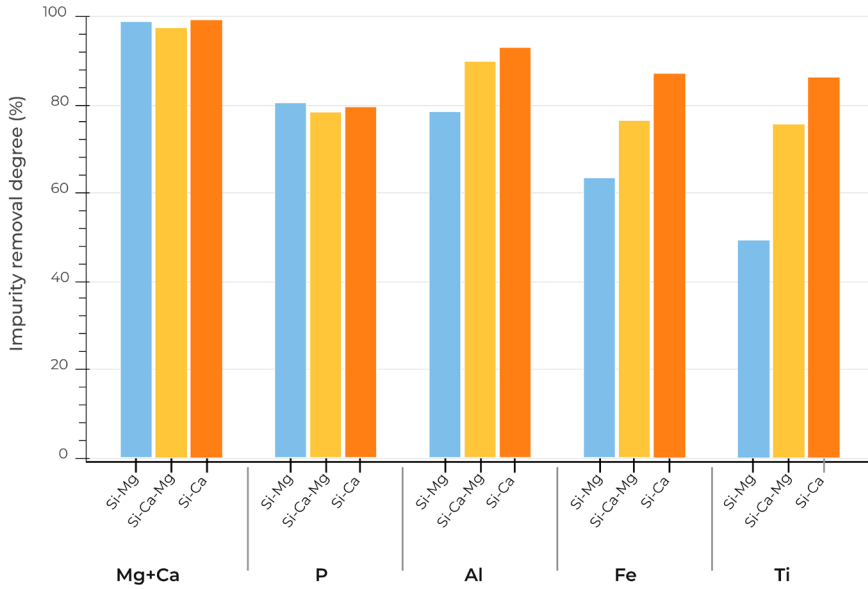


Figure 10.27 Comparison of impurity removal degree of P, Al, Fe and Ti in Si-4.7wt% Mg, Si-2.5wt% Mg-2.1wt% Ca, and Si-3.6wt% Ca alloy systems after 3 h acid leaching in 10% HCl at 60°C (Zhu et al., 2020b). Open access licensed under CC-BY.

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