

Additional elements in the silicon process

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Besides Si, O and C, which were already considered in Chapter 2, additional elements in small quantities will always enter the process as impurities originating from the raw materials and electrodes, as seen in Table 4.1. The main impurity elements by mass are Ti, Ca, Al, Mg, K and S. From an emission point of view, nitrogen in the atmosphere produces NO_x , however, this will be discussed in more detail in Chapter 12. Some elements may also be added deliberately to the charge mixture to make silicon-rich alloys of a desired composition. Of special importance is, of course, iron, added as scrap, mill scale and/or ore to produce ferrosilicon. This chapter focuses on the behavior of minor elements and their effect on the chemistry of the Si–O–C system. In this context, important properties include the relative stability of oxides and carbides of the elements involved, the volatility of these elements and their compounds, and their dissolution in the phases present.

4.1 Liquid silicon as solvent for impurities and alloying metals

Phase diagrams and activities

In its crystalline state, silicon has practically no solubility for metals. However, it forms stable silicides with most metals, except for its neighbours in the periodic table where Al, Ga and Ge are the most apparent examples. In its liquid state, by contrast, silicon forms continuous solutions with most metals.

The occurrence of stable silicides in the solid state indicates strong attractions between solute and solvent atoms in the liquid state as well. Thus, an exothermic heat of mixing and a strong negative deviation from ideal behavior are expected for solutions of silicon and silicide-forming metals. Figure 4.1 shows the activity relations in the iron-silicon system and provides a typical example.

Table 4.1 *Elements in raw materials and electrode after Myrhaug (2003). Both % and ppm are given by weight.*

Parameter	Unit	Quartz	Coal	Coke	Charcoal	Wood chips	Petrol-coke	Electrode
Fixed carbon	%	—	39–62	81–95	75–85	20–26	88–93	85–99
Volatiles	%	—	34–58	2–5	10–25	70–75	7–12	1–10
Ash	%	—	1–5	1–10	0.5–10	1–10	0.05–1	0.1–5
Si	%	46.1–46.6	0.3–2	0.6–4	0.05–9	0.2–1	— ¹	— ¹
C	%	~0	71–81	84–96	81–91	45–50	94–97	91–97
O	%	53.1–53.6	10–16	1–7	2–15	40–45	2–3	2–8
H	%	~0	5–8	0.5–4	1–8	5–6	1–1.5	0.2–1.3
N	%	~0	1.5–2.5	0.1–0.2	0.3–1.0	0.1	0.2–0.5	0.05–0.5
Hg	ppbw	< 5–10	< 5–60	< 5–20	< 5	< 5	< 5	< 5–40
Ti	ppmw	20–200	50–600	60–4000	10–300	≈1	< 0.5–50	~100
Al	ppmw	300–3200	800–5700	1000–10000	100–6200	< 50–100	70–110	< 50–4000
As	ppmw	< 1–3	< 1–3	< 1–14	< 1	< 1–5	< 1–10	< 1–10
B	ppmw	< 10–45	< 10–110	< 10–100	< 10–16	< 10–23	< 10	< 10
Ba	ppmw	0.5–25	4–130	15–220	10–30	2–70	1–9	6–90
Be	ppmw	< 0.5–0.6	< 0.5–4	< 0.5–3	< 0.5	< 0.5	< 0.5	< 0.5
Bi	ppmw	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5–2
Ca	ppmw	< 75–160	150–2400	600–3400	1000–4000	600–1000	< 75	200–1500
Cd	ppmw	< 0.1–1.5	< 0.1–1.1	< 0.1–1.1	< 0.1	< 0.1–0.3	< 0.1	0.6–1.2
Co	ppmw	< 1–200	1–16	6–120	< 1	< 1	< 1–13	< 1–13
Cr	ppmw	3–25	< 1–12	15–40	5–15	< 1–13	1.5–12	< 1–24
Cu	ppmw	1–3	1.5–22	4–40	2–7	1.8–4.3	< 1–6	< 1–20
Fe	ppmw	100–1500	700–5200	1400–9000	100–1700	< 100–1400	< 100–600	100–3500
K	ppmw	< 75–1700	< 75–1800	300–1800	100–1800	250–900	< 75	< 75–210
Mg	ppmw	20–140	80–1100	300–1400	200–1100	75–200	< 15–100	< 15–500
Mn	ppmw	3–600	4–110	< 1–270	80–120	10–50	1–6	50–3500

Para-metr	Unit	Quartz	Coal	Coke	Charcoal	Wood chips	Petrol-coke	Electrode
Mo	ppmw	< 2–8	< 2–4	< 2–7	< 2	< 2	< 2–12	< 2
Na	ppmw	50–170	< 320	230–2100	170–230	< 50–130	< 50–110	< 50–300
Ni	ppmw	< 1–9	2–33	3–240	~30	< 1–7	60–360	< 1–50
P	ppmw	< 5–50	< 5–143	16–160	80–300	20–110	< 5–13	< 5–170
Pb	ppmw	< 0.1–9	0.3–13	1–106	< 0.1–2.3	< 0.1–0.2	< 0.1–3.5	< 0.1–1.6
S	ppmw	< 5–1400	1200–8300	3300–11000	200–1500	100–1300	20000–50000	55–3400
Sb	ppmw	< 0.1–0.9	< 0.1–0.7	0.3–3.9	< 0.1	< 0.1	< 0.1	< 0.1–1.4
Se	ppmw	< 2–5.2	< 2–6.6	< 2–3.3	< 2	< 2	< 2	< 2
Sn	ppmw	< 0.5–2.2	< 0.5–2.7	< 0.5–3	< 0.5	< 0.5–4.5	1.1–2.4	< 0.5–2.4
Sr	ppmw	< 0.5–12	3–90	11–80	14–80	1.6–9	< 0.5–6.6	1.4–20
V	ppmw	< 1–4	2–60	4–30	< 1	< 1	400–1200	< 1–92
W	ppmw	< 0.5–640	< 0.5–3	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5–0.8
Zn	ppmw	< 1–3	3–40	4–80	2–40	6–16	3–10	1–100
Zr	ppmw	< 0.5–3.3	0.8–3.3	< 0.5–1.5	< 0.5	< 0.5–1	< 0.5	< 0.5–1.7

The activity of element i , a_i , is expressed as a function of the mole fraction of i , X_i , in the liquid phase:

$$a_i = \gamma_i \cdot X_i \quad [4.1]$$

An ideal solution is a solution in which the activities of the constituents are equal to their mole fractions:

$$a_i = X_i \text{ (Raoult's law)}$$

Real solutions deviate from ideal behavior. As expressed above, this deviation is described by introducing the activity coefficient, γ_i , which is a function of composition and temperature.

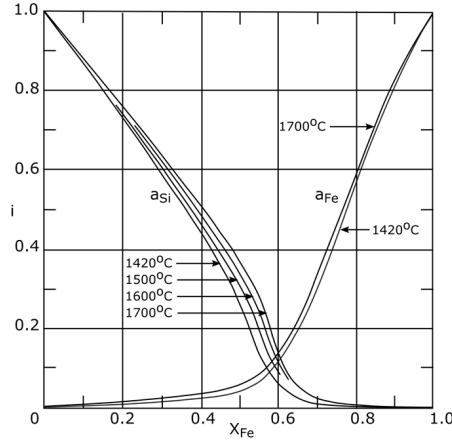


Figure 4.1 Activities in the Fe–Si system after Elliot (Elliot et al., 1963; Saadieh, 2024).

Negative deviation from ideal behavior as is the case for iron in silicon, implies that $\gamma_{Fe} < 1$. As seen from Figure 4.1, γ_{Fe} decreases with X_{Fe} and approaches a finite and non-zero value which takes a value equal to the slope of the activity curve at $X_{Fe} = 0$. Experiments have shown that this applies to metallic solutions in general and can be expressed as follows:

$$\gamma_{Me}^0 = (\gamma_{Me})_{X_{Me}=0} = \left(\frac{a_{Me}}{X_{Me}} \right)_{X_{Me}=0} = \left(\frac{da_{Me}}{dx_{Me}} \right)_{X_{Me}=0} \neq 0 \quad [4.2]$$

The activity coefficient at infinite dilution is thus a property of the system. It varies with temperature, as determined by the relative partial heat of mixing for component Me at infinite dilution, by the relation:

$$\left(\frac{\partial \ln \gamma_{Me}^0}{\partial \left(\frac{1}{T} \right)} \right)_P = \frac{\Delta \bar{H}_{Me}^0}{R} \quad [4.3]$$

As $\ln \gamma_{Me}^0$ and $\Delta \bar{H}_{Me}^0$ are both negative for exothermic solutions, the γ_{Me}^0 -value increases with rising temperature, which means that the system approaches ideality at high temperatures.

It follows from the definition of that the activity of a solute at infinite dilution can be expressed by

$$a_{Me} = \gamma_{Me}^0 X_{Me} \quad [4.4]$$

It follows from the Gibbs-Duhem equation that, if Henry's law applies for the solute, Raoult's law applies for the solvent. It can further be shown that Raoult's law is obeyed more closely for the solvent than Henry's law is for the solute. This strengthens the statement already made: the presence of impurities has no significant effect on the activity of the solvent, irrespective of whether this happens to be silicon metal or a silicon-rich alloy.

The impurities in the silicon appear as members of a multicomponent system, where they interact not only with silicon but also with themselves and with each other. At low concentrations, however, the latter two effects are often neglected. Thus, the γ_{Me}^0 remains as the main property to use in calculations based on the following equation

$$\ln \gamma_i = \ln \gamma_i^0 + \sum_{j=2}^k \varepsilon_i^j x_j \quad [4.5]$$

This property is provided for several elements in a compilation of thermochemical data on liquid silicon alloys by Engh *et al.* (2021). Thermochemical data for a smaller group of elements are shown in Table 4.2. γ_i^0 is the activity coefficient (at infinite dilution) if there is no interaction between the solute components. To determine how, for example, Al affects the activity of Ca in liquid silicon, one would need the interaction coefficient of Al on Ca, i.e. ε_{Ca}^{Al} . The interaction coefficients in liquid silicon for some elements are shown in Table 4.3 and Table 4.4. It can also be noted that $\varepsilon_j^i = \varepsilon_i^j$.

Often, it is more convenient to use the mass per cent, [%i], instead of the mole fraction, X_i , and the activity of an element can then be expressed as:

$$a_i = f_i \cdot [\%i] \quad [4.6]$$

In this case, the interaction coefficient ε_i^j is defined by the equation:

$$\log_{10} f_i = \sum_{j=2}^n \varepsilon_i^j [\%j] \quad [4.7]$$

Note that in equation [4.5] and [4.7], component number 1 is the solvent.

Table 4.2 *Thermodynamics of binary silicon-based alloys.*

Solution Reaction	γ_i° (1700 K)	ΔG° for X (J/mole)	ε_i^j	ΔG° for wt. % (J/mole)	e_i^j	Data Source (Ref.)
Al (l) = <u>Al</u>	0.32	$-9790 - 3.740T$	2.3	$-9790 - 41.694T$	0.010	a (note 2)
B (s) = <u>B</u>	3.9	$2400 + 9.894T$	--	$2400 - 20.456T$	--	c, d, e
C (s) = <u>C</u>	99.4	$63.785 + 0.715T$	--	$63.785 - 30.510T$	--	f, g, h, i
Ca (l) = <u>Ca</u>	1.7×10^{-4}	$-118.900 - 2.078T$	9.9	$-118.900 - 43.322T$	0.045	d, j
Cr (l) = <u>Cr</u>	6.1×10^{-3}	-72.000	-3.2	$-72.000 - 43.408T$	-0.010	f
Cr (s) = <u>Cr</u>	8.2×10^{-3}	$-51.500 - 9.623T$	-3.2	$-51.500 - 53.031T$	-0.010	f
Fe (l) = <u>Fe</u>	0.024	$-107.530 + 32.175T$	-13.9	$-107.530 - 11.827T$	-0.056	f
Fe (s) = <u>Fe</u>	0.025	$-92.340 + 23.765T$	-13.9	$-92.340 - 20.237T$	-0.056	f
$1/2\text{H}_2(\text{v}) = \underline{\text{H}}$	--	$102.080 + 9.764T$	--	$102.080 - 0.86T$	--	f
Mg (l) = <u>Mg</u>	0.272	$-73.850 + 32.612T$	2.6	$-73.850 - 4.473T$	0.011	a, k-l (note 2)
Mg (v) = <u>Mg</u>	2.3	$-202.350 + 125.99T$	2.6	$-202.350 + 88.908T$	0.011	a, k-l (note 2)
Mn (l) = <u>Mn</u>	0.022	$-78.000 + 13.968T$	8.1	$-78.000 - 29.898T$	0.039	f, g
$1/2 \text{N}_2(\text{v}) = \underline{\text{N}}$	--	$-17.570 + 60.766T$	--	$-17.570 + 28.23T$	--	m, n
$1/2 \text{O}_2 = \underline{\text{O}}$	--	$-290.700 + 75.287T$	--	$-290.700 + 41.678T$	--	f, o, p
$1/2\text{P}_2(\text{v}) = \underline{\text{P}}$	--	$-99.500 + 68.561T$	3.0	$-99.500 + 29.46T$	0.013	d, q, r
Zn(l) = <u>Zn</u>	1.44	$29.200 - 14.13T$	--	$29.200 - 59.442T$	--	a

Notes: T is in degrees Kelvin.

1. The liquid phase is metastable for the elements Cr, Fe, Mg at a temperature of 1700K. For example, iron is solid at this temperature.
2. Heat of solution and interaction coefficients were calculated from eq. [9] of a).

Data source: a) (Safarian *et al.*, 2012) b) (Robinson and Tarby, 1971) c) (Mostafa and Medraj, 2017) d) (Sigworth, 2020) e) (Zaitsev and Kodentsov, 2001) f) (Bakke and Klevan, 1995) g) (Yoshikawa *et al.*, 2010) h) (Dalaker and Tangstad, 2009a) i) (Nozaki *et al.*, 1970) j) (Miki, 1999) k) (Eldridge *et al.*, 1967) l) (Rao and Belton, 1981) m) (Dalaker and Tangstad, 2009b) n) (Stull and Prophet, 1971) o) (O'Mara, 1990) p) (Carlberg, 1986) q) (Liang and Schmid-Fetzer, 2014) r) (A. I. Zaitsev *et al.*, 2001) s) (Miki *et al.*, 1997)

Table 4.3 *Interaction coefficients in liquid silicon.*

Mole ratio	Weight percent	Temperature (K)	Source
$\varepsilon_{Pb}^{Al} = 2.34$	$e_{Pb}^{Al} = 0.011$	1723	a
$\varepsilon_{Pb}^{Ca} = -9.0$	$e_{Pb}^{Ca} = -0.026$	1723	a
$\varepsilon_{Pb}^{Mg} = 10.2$	$e_{Pb}^{Mg} = 0.051$	1723	a
$\varepsilon_{Ca}^{Al} = 6.46$	$e_{Ca}^{Al} = 0.030$	1723	a
$\varepsilon_{Ti}^{Ca} = 25.3$	$e_{Ti}^{Ca} = 0.078$	1723	a
$\varepsilon_{Fe}^{Ca} = 2.25$	$e_{Fe}^{Ca} = 0.008$	1723	a
$\varepsilon_{Fe}^{Mn} = (99)$	$e_{Fe}^{Mn} = (0.22)$	1700	b
$\varepsilon_{Mn}^{Fe} = (99)$	$e_{Mn}^{Fe} = (0.22)$	1700	b
$\varepsilon_p^{Fe} = 7.43$	$e_p^{Fe} = 0.018$	1723	c
$\varepsilon_p^{Mn} = 12.0$	$e_p^{Mn} = 0.029$	1723	c

Data source: a) (Miki, 1999) b) (Bakke and Klevan, 1995) c) (Wagner, 1952)

Table 4.4 *Interaction coefficients in liquid Si-C- i^{43} , Si-O- i^{22} and Si-H- i^{22} alloys.*

At temperatures near the melting point of silicon						
element, i	ε_C^i	e_C^i	ε_O^i	e_O^i	ε_H^i	e_H^i
Al	-0.72	-0.004	-118	-0.56	--	--
B	-4.02	-0.052	-2.04	-0.03	--	--
C	--	--	0	-0.006	--	--
Ca	5.46	0.018	< 0	< 0.0013	--	--
Co	--	--	--	--	4.5	0.012
Cr	10.72	0.027	--	--	--	--
Fe	3.50	0.010	-6	-0.011	3.5	0.010
H	--	--	--	--	--	--
Mn	-1.58	-0.001	--	--	1.4	0.005
N	0.55	0.000	--	--	--	--
Ni	2.28	0.007	--	--	--	--
O	18.5	0.138	--	--	--	--
P	-5.67	-0.022	-45	-0.177	--	--
Zn	-3.39	-0.004	--	--	--	--

Phase diagrams, which are important for the solidification process, will be shown in Chapter 11.

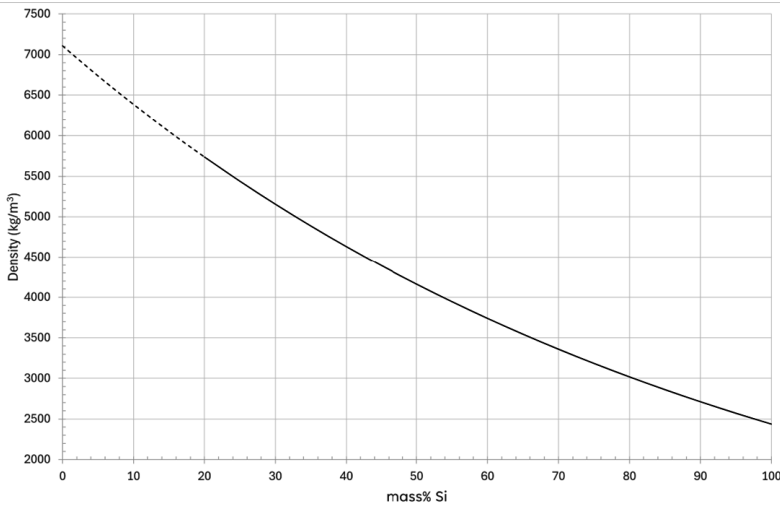


Figure 4.2 Density of liquid Fe-Si-alloys at 1450°C, reproduced from Klevan (Dumay and Cramb, 1995; Klevan, 1997; Yaws *et al.*, 1981), showing the correlation $\rho(\text{FeS}, 1450^\circ\text{C}) = 7106 \cdot \exp(-0.0107 \cdot \text{mass\% Si})$ valid for mass% Si > 16.3%.

Density

Density data were evaluated by Klevan (1997), who presented the diagram in Figure 4.2. This diagram is based on the work of Dumay and Cramb (1995) on Fe-Si alloys and Yaws *et al.* (1981) on liquid Si. The temperature dependence of the density of liquid silicon, as derived by Klevan, can be expressed by:

$$\rho(\text{Si})_{liq} = 2533 - 0.45(T - T_m) \left[\text{kg/m}^3 \right] \quad [4.8]$$

Which gives

$$\rho(\text{Si})_{liq} = 2510 \text{ kg/m}^3 \text{ at } 1450^\circ\text{C} \text{ and } 2470 \text{ kg/m}^3 \text{ at } 1550^\circ\text{C}$$

The corresponding values for liquid FeSi75, calculated from Figure 4.2 and assuming the same temperature dependency as for silicon, are:

$$\rho(\text{FeSi75})_{\text{liq}} = 3190 \text{ kg/m}^3 \text{ at } 1450^\circ\text{C} \text{ and } 3140 \text{ kg/m}^3 \text{ at } 1550^\circ\text{C}$$

An interesting property to consider is the density of α -SiC. Klevan (1997) gives the following relation for this compound:

$$\rho(\alpha - \text{SiC}) = 3211 - 0.056 T \text{ } ^\circ\text{C} \left[\text{kg/m}^3 \right] \quad [4.9]$$

Which gives

$$\rho(\alpha - \text{SiC}) = 3125 \text{ kg/m}^3 \text{ at } 1550^\circ\text{C}$$

It was previously believed that α -SiC was found in the refining slag, however, later investigations showed that this is β -SiC.

4.2 Silica as solvent for impurity oxides

The oxide phase is one of the main phases in silicon and ferrosilicon production because it is the main raw material. It is therefore important for process operation and will be present in all parts of the furnace. Although the carbothermic process for producing silicon and ferrosilicon is theoretically defined as a slag-free process, slag is still formed and regularly tapped along with the metal. During the excavation of industrial furnaces, slag has also been found accumulated in large amounts in the furnace. The amount of slag tapped depends on the total input of aluminium and calcium, their relative distribution in the feed, and the operational conditions of the furnace.

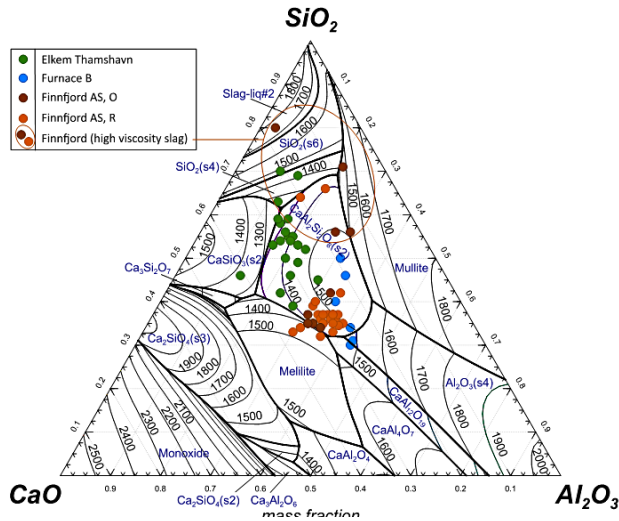


Figure 4.3 Slag composition from 4 furnaces at 3 plants. Furnace R and O produce FeSi 75 and furnace B and Elkem Thamshavn produce silicon (Folstad and Tangstad, 2021; Jusnes *et al.*, 2021b).

Examples of tapped slags are given in Figure 4.3. The main part of the tapped slag composition varies from 30–60% SiO_2 , with a $\text{CaO}/\text{Al}_2\text{O}_3$ ratio from 0.55 to 1.9, depending on the raw materials used (Folstad and Tangstad, 2021; Jusnes *et al.*, 2021b). The slag with the highest SiO_2 content was reported by the tappers to have a high viscosity, causing challenging tapping conditions. The normal samples from furnace O and R have a viscosity of around 7–30 poise at 1600°C, whereas the two challenging slags have a viscosity of 180 and 900 Poise at the same temperature. The slag will also contain small SiC particles, as shown in Figure 4.4 and hence, the viscosity will be even higher than the numbers represented by the pure slag composition. During excavations, as described in Chapter 3, slag layers are found inside the furnaces, typically surrounding the tapping channel (Folstad and Tangstad, 2021). The slag found inside the furnaces has a slag composition close to the tapped slag.

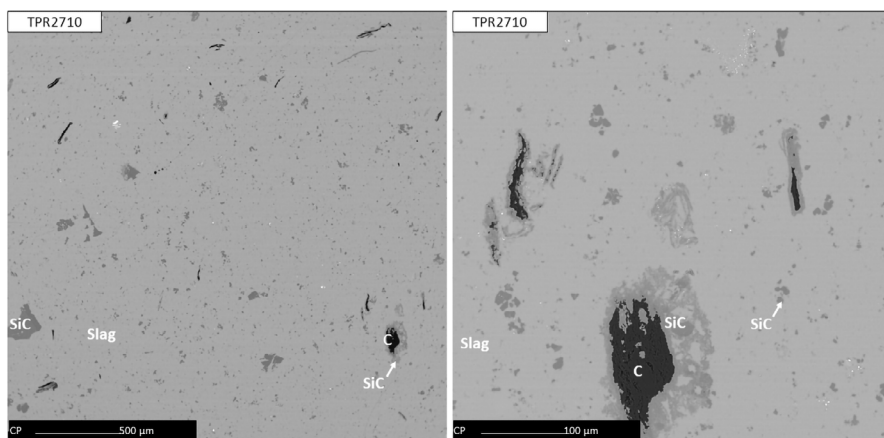


Figure 4.4 Tapped slag with small SiC particles embedded in the slag matrix containing 25% SiO_2 , 35% CaO and 39% Al_2O_3 at two magnifications (Jusnes et al., 2021a).

Aluminium is present in coal as clay minerals, most commonly mica, which introduces some alkali metals $[(\text{OH},\text{F})_2(\text{K}, \text{Na})\text{Al}_2(\text{Si}_3\text{AlO}_{10})]$, and kaolinite $[(\text{Al}_4(\text{OH})_8(\text{Si}_4\text{O}_{10}))]$. Calcium quite often appears as calcite $[\text{CaCO}_3]$. Mica may also appear as an impurity in some quartzites, together with members of the feldspar group, anorthite $[\text{Ca}(\text{Al}_2\text{Si}_2)\text{O}_8]$ is one such example. The clay minerals release their hydroxyl groups quite rapidly on heating, leaving the metal oxides behind in a concentrated form. These oxides are then exposed to carbon up to temperatures around 1600°C , and to silicon carbide at temperatures above this. Most of the alkali metal oxides will be reduced to metal vapours by carbon before silicon carbide is formed. Aluminosilicate and CaO are left behind in separated grains, where the silicate, on further heating, becomes selectively reduced to SiC or SiO, leaving the Al_2O_3 behind. Temperatures above 1800°C are needed for CaO and Al_2O_3 to be reduced to carbides, even with free carbon as a reductant. However, Al- and Ca-carbides have not been seen during industrial excavations. It is expected that most Ca and Al end up dissolved in the silicon and silica, rather than as individual phases, but some will also go to the gas phase, as seen later in this chapter.

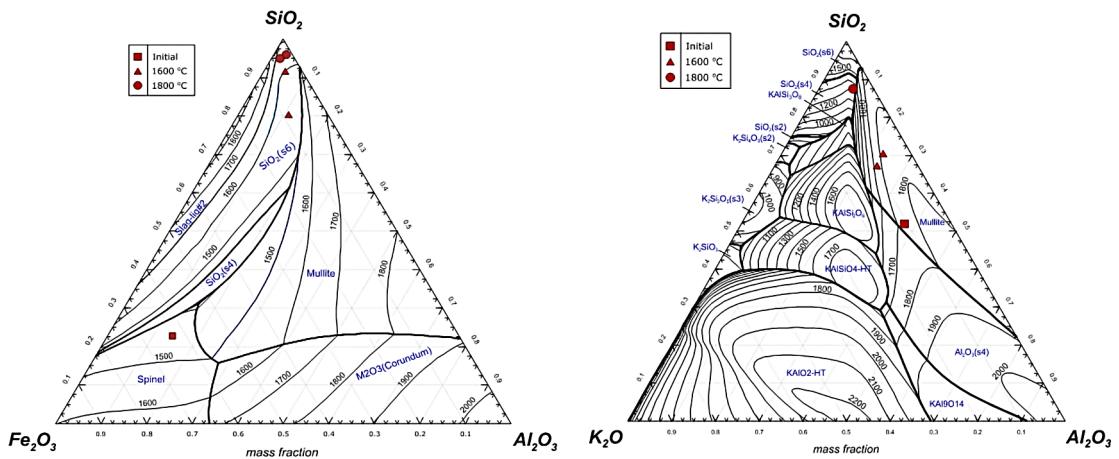


Figure 4.5 The development of impurities in quartz with heating, showing how it will dissolve more SiO_2 at higher temperatures. Squares – initial composition of impurities, triangles – composition of impurities at 1600°C and circles – composition of impurities at 1800°C (Folstad, 2023). [Used with permission from M.B. Folstad].

The impurities embedded in the quartzites are not accessible for reduction before the quartzite lumps decrepitate or melt. In the latter case, they dissolve into a phase that becomes increasingly enriched in SiO_2 , as experimentally demonstrated in Figure 4.5. When the quartz meets SiC or carbon during heating, the SiO_2 will also react to form SiO gas. As a result, the stable oxides in the impurities will continuously increase in the oxide phase. Eventually, the consumption of silica slows down and stops, leaving some silica behind, tied up in a very viscous slag that is highly enriched in alumina. The slag tends to accumulate in the furnace unless it has the opportunity to dissolve CaO, which lowers the viscosity. This makes the slag sufficiently fluid to be tapped together with the metal. For this to occur in ferrosilicon smelting, Oterkjær (1976) suggests that the slag shall have a specific mass ratio between the CaO and Al_2O_3 :

$$\frac{\%CaO}{\%Al_2O_3} > 0.6$$

Besides the three dominating oxides already highlighted, tapped slags from a ferrosilicon furnace also contain minor amounts of MgO ($\sim 1\%$), K_2O ($\sim 0.2\%$) and Na_2O ($\sim 0.05\%$). Transition metal oxides like FeO and TiO_2 are not found at detectable levels. Thus, if iron is analysed in ferrosilicon slags, it should be counted as a metal impurity.

Phase diagrams and activities

Most oxides are, in general, insoluble in solid crystalline silica. Most oxides are also insoluble in molten silica and produce two immiscible liquids in the high-silica end, as shown in Figure 4.6 a). Liquidus curves for the silica-rich part of the alkali and alkaline earth metal oxide-silica systems, and two divalent transition metal oxide-silica systems, are shown in Figure 4.7. The diagram shows that, except for BaO, small additions (beyond $\sim 2\%$) of a divalent metal oxide lead to the separation of a second liquid phase. The alkaline metal oxides behave differently: they can give off their oxygen ions completely to the three-dimensional network of Si–O-bonds, which dominates the structure of molten silica, and place themselves interstitially within the network. In this way, a gradual breakdown of the silicate network takes place, giving the characteristics of glass melts. Examples of the two immiscible liquid phases are given in the SiO_2 –CaO phase diagram shown in Figure 4.6 a). By contrast, examples of the SiO_2 – K_2O phase diagram, where this is not the case, are shown in Figure 4.6 b). Figure 4.7 summarises the liquidus lines in the high SiO_2 area for several alkali and alkaline earth metals, and two transition metal oxides. It can be mentioned that the Cr_2O_3 – SiO_2 , Fe_2O_3 – SiO_2 and TiO_2 – SiO_2 phase diagrams also have the two-immiscible liquids area that the divalent Mn- and Fe-oxides show in Figure 4.7.

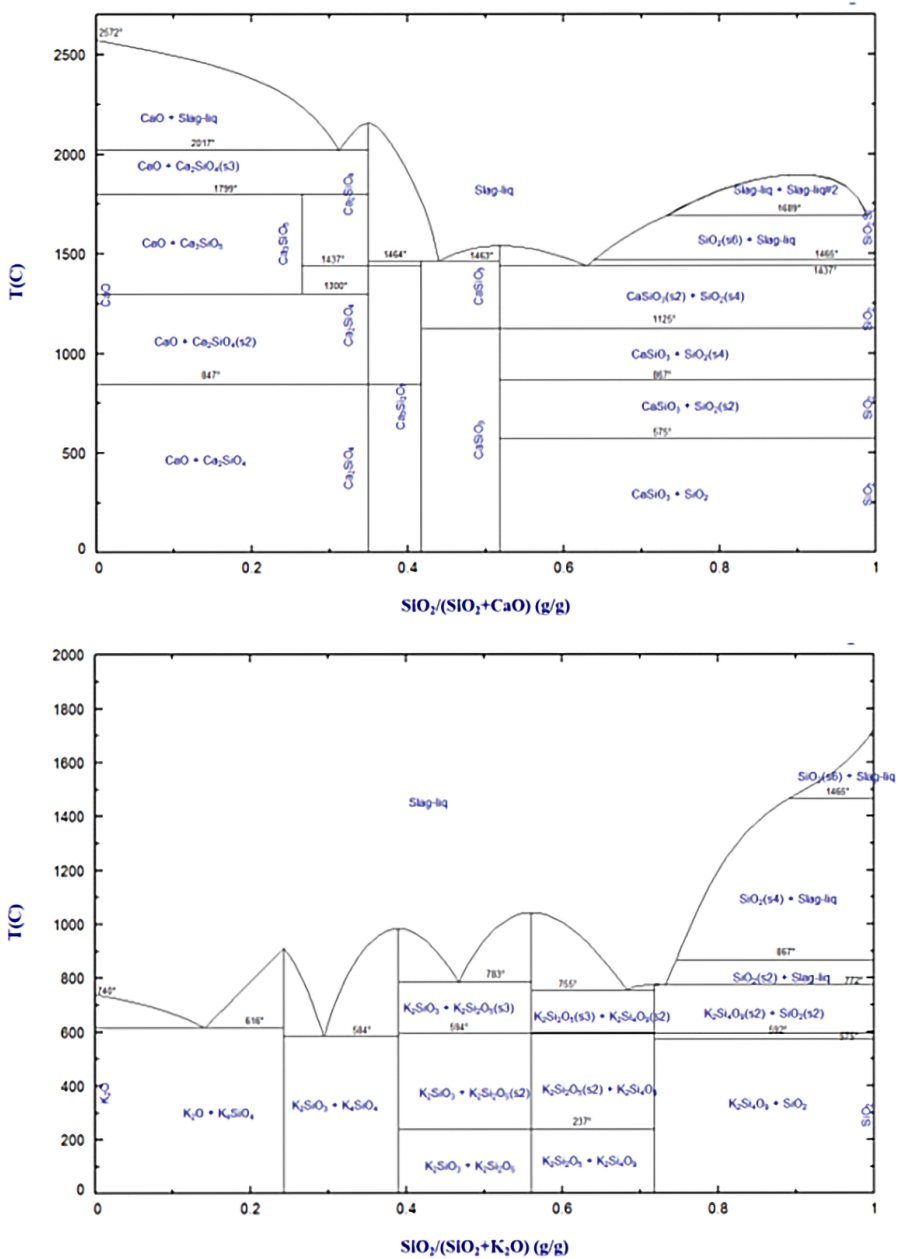


Figure 4.6 Binary phase diagrams of the a) CaO-SiO₂ system and b) K₂O-SiO₂ system calculated by commercial FToxid database of FactSage software package.

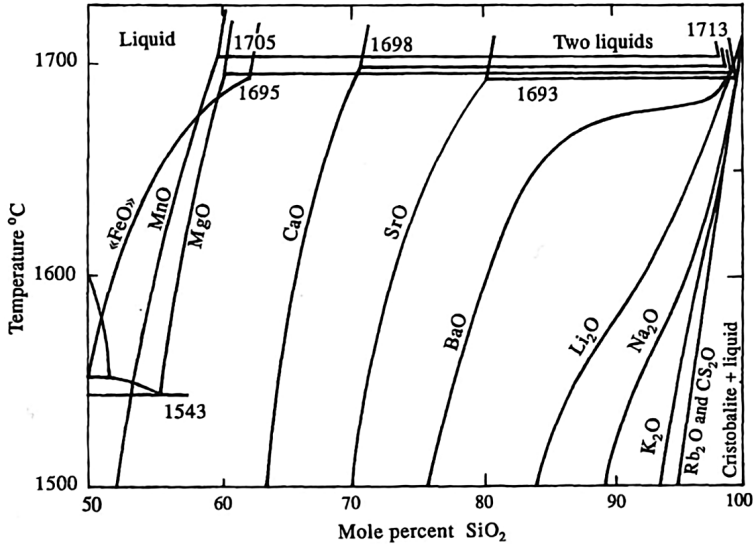


Figure 4.7 Summary of high SiO₂ part of binary phase diagrams with alkaline-, earth-alkaline-, and transition metal-oxides where it is seen that most oxides have immiscible liquid area where two liquids coexist, while the alkali-oxides together with the heavy earth-alkali oxide like BaO will not have this immiscible liquid area.

At the other end of the periodic system are B and Al, whose oxides are significant components in solar grade (SG) silicon production and in metallurgical grade (MG) silicon, respectively. These do not have a two-immiscible-liquids area, as exemplified by the Al₂O₃-SiO₂ phase diagram shown in Figure 4.8.

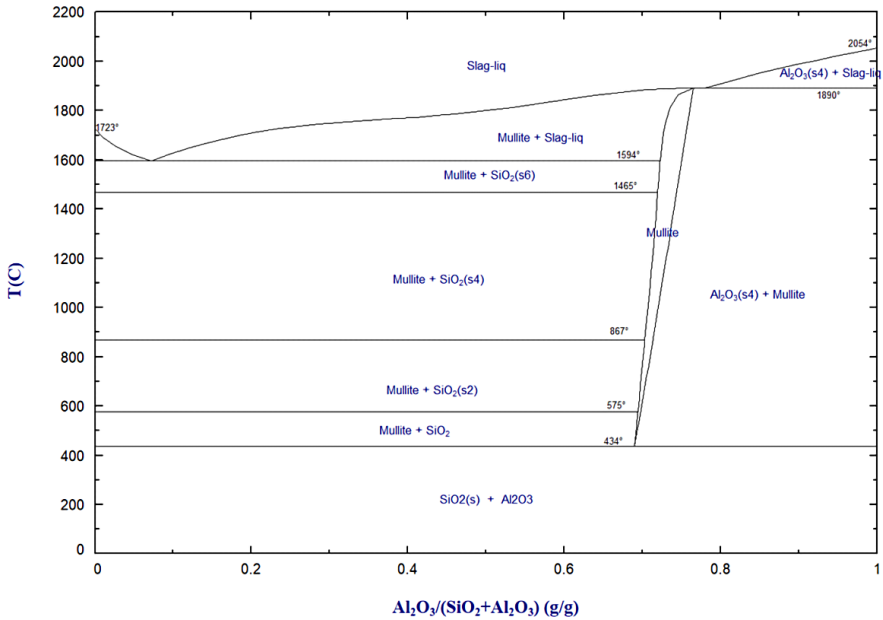


Figure 4.8 The Al_2O_3 - SiO_2 phase diagram calculated by commercial FToxid database in FactSage.

The slags that form consist mainly of CaO , Al_2O_3 and SiO_2 inside the furnace, as well as during the refining step. It is therefore relevant to focus on the CaO - Al_2O_3 - SiO_2 -system, as described by the phase diagram in Figure 4.9. This diagram shows a projection of the liquidus surface: the boundaries between coexisting phases are shown by solid curves, and liquidus isotherms by lighter curves. The diagram also shows that a homogeneous liquid slag can form over a wide compositional range at temperatures above 1550°C. However, this area can shrink if the temperature is lowered to 1500°C owing to the precipitation of pseudowollastonite (CS), anorthite (CAS) and gehlenite (C_2AS).

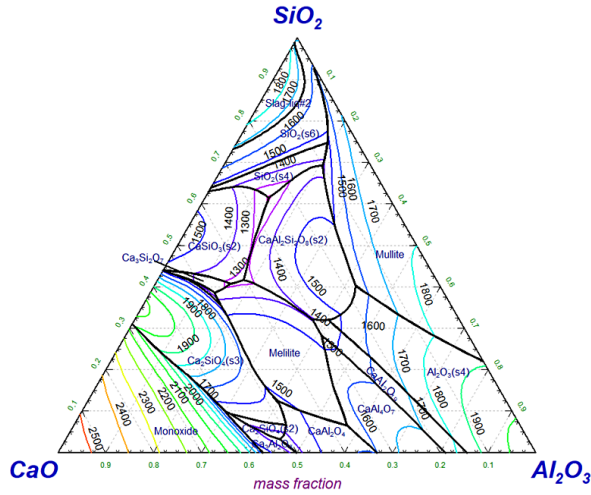


Figure 4.9 Phase diagram of the Al_2O_3 - CaO - SiO_2 ternary system calculated by commercial FToxid database in FactSage.

By adding small amounts of MgO to the SiO_2 - CaO - Al_2O_3 system, the liquid region in the silica-rich part of the system expands in both temperature and composition. However, the four-component system can be described by a compositional tetrahedron at any particular MgO level. Figure 4.10 shows an example of such a diagram at 5wt% MgO .

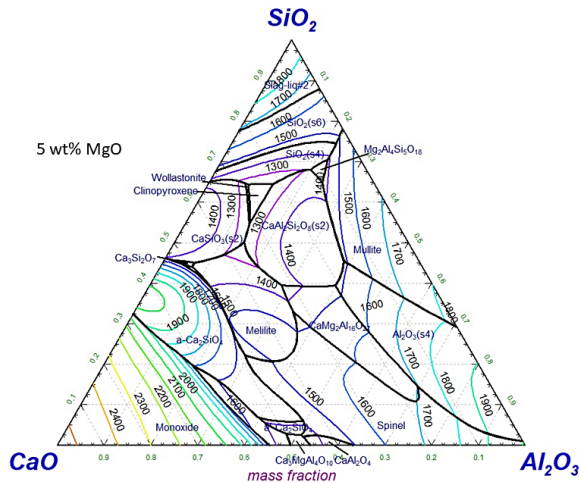


Figure 4.10 Liquidus surface in the CaO - Al_2O_3 - SiO_2 - MgO -system with 5wt% MgO , Calculated by commercial FToxid database of FactSage software package.

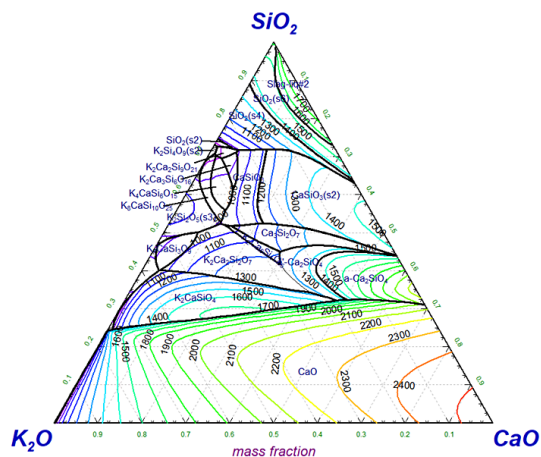


Figure 4.11 The silica liquidus lines in alkali oxide–alkaline earth oxide–silica systems, calculated using the commercial FToxid database of the FactSage software package.

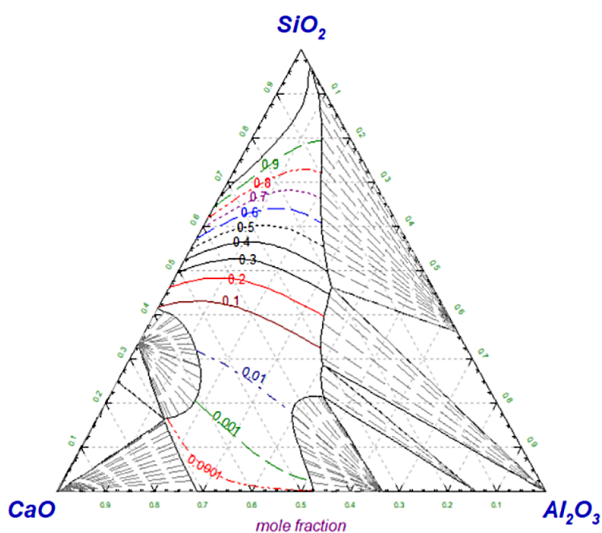


Figure 4.12 SiO_2 activities in a $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ slag at 1600°C by FactSage commercial software. Concentrations are given in mole fractions. Activity is referred to the pure solid oxide.

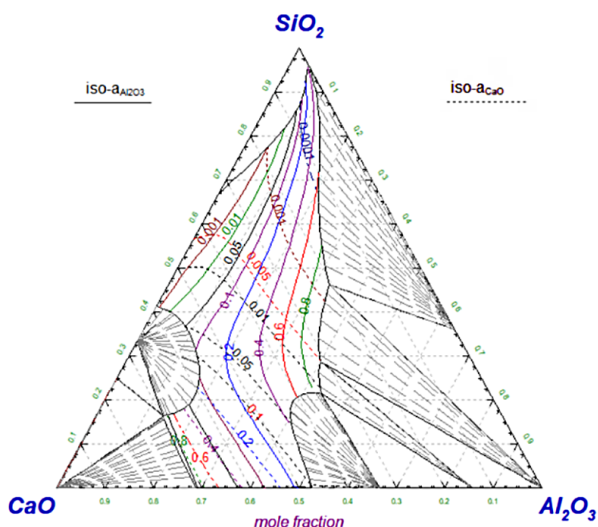


Figure 4.13 Iso-activity lines of CaO and Al_2O_3 in the SiO_2 -CaO- Al_2O_3 slag at 1600°C calculated by commercial software FactSage. Concentrations are given in mole fractions. Activity is referred to the pure solid oxide.

Figure 4.12 and Figure 4.13 illustrate the isothermal Al_2O_3 -CaO- SiO_2 diagram at 1600°C and depict the activities of SiO_2 , CaO, and Al_2O_3 in the liquid region. In the two-phase areas, tie-lines indicate the composition of the liquid phase coexisting with a solid phase. In these areas, the activity is determined by the activity of the solid phase.

In the two-liquid immiscibility region near the SiO_2 corner, the SiO_2 activity approaches that of liquid SiO_2 . This value is close to the solid SiO_2 activity and is approximately equal to one. Notably, the ratio of liquid SiO_2 activity to solid SiO_2 activity ranges from 0.94 to 1.02 between 1500 and 1800°C . Consequently, in both the two-liquid regions and the liquid + solid SiO_2 area, the SiO_2 activity remains close to 1. As observed in Figure 4.12, the SiO_2 activity decreases when moving downward in the liquid region. CaO is a basic oxide, Al_2O_3 is an amphoteric oxide, and SiO_2 is an acidic oxide. This means that, at constant SiO_2 content, the SiO_2 activity peaks at both the high CaO and high Al_2O_3 sides, but is slightly lower between these extremes.

Viscosity

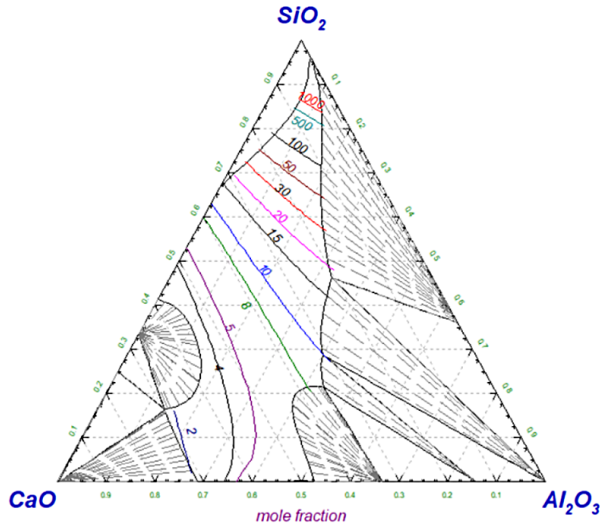


Figure 4.14 Iso-viscosity (Pa·s) contours of $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ melts at 1600°C (Tang *et al.*, 2022) [Used with permission from K. Tang].

Figure 4.14 shows the variation in viscosity within the liquid range of the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ at 1600°C . From this diagram, it is worth noting that the iso-viscosity contours run nearly parallel to lines of constant $\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3)$ ratios, and that the rate of viscosity increase escalates dramatically at ratios < 0.20 .

The presence of fluoride ions, added in the form of CaF_2 , lowers the viscosity of aluminosilicate melts. This effect is quite considerable at low temperatures (1300°C), where a 60% decrease in viscosity has been recorded, but the lowering effect decreases with increasing temperature (Turkdogan, 1983). Replacement of CaO by an equal mass of MgO , on the other hand, seems to have a neutral, or even a slightly opposite, effect.

The viscosity decreases with increasing temperature. For liquid metals and simple ionic melts, the temperature dependency can be represented by an exponential equation of the Arrhenius type:

$$\eta = \eta_0 \exp\left(\frac{E_\eta}{RT}\right) \quad [4.10]$$

This relation is usually not obeyed for polymeric melts because the degree of de-polymerization increases with rising temperature, resulting in a decrease in the activation energy for viscous flow. This effect is most apparent for acidic slags, which have the largest E_η -values. For the SiO_2 – CaO – Al_2O_3 slag system, an increase in temperature from 1500 to 1600°C gives a drop in viscosity of about 50% in the CaO-rich region and 40% in the acidic region.

One should also be aware that the effective viscosity of a slag is strongly affected by the presence of solid particles in the melt. For the estimation of the effective viscosity η_e of a solid-melt suspension, Roscoe (1953) has given the following relation:

$$\eta_e = \eta(1 - 1.35\phi)^{-5/2} \quad [4.11]$$

Where η is the viscosity of the liquid fraction of the suspension and ϕ is the volume fraction of solid particles, assumed to be of uniform size and spherical shape. The types of solids that may occur in furnace slags are SiC particles and primary precipitates of mineral phases below liquidus temperature.

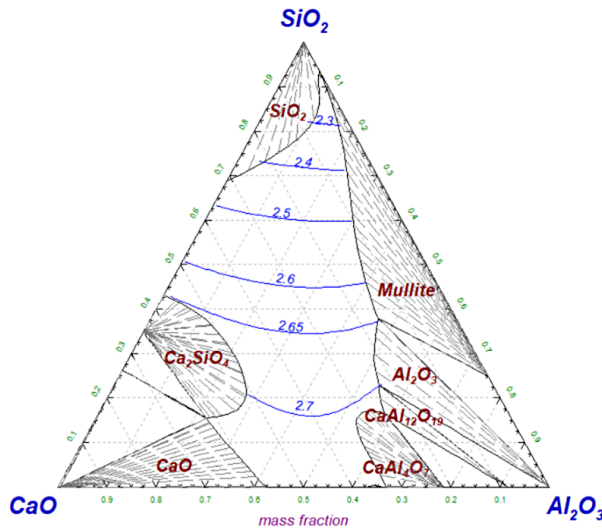


Figure 4.15 Calculated liquid SiO_2 – Al_2O_3 – CaO density at 1600°C based on 652 experimental molar volume data available in the literature (Tang et al., 2022) [Used with permission from K. Tang].

Density

Figure 4.15 shows the variation of density for $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ melts at 1550°C . To see the implication of the data in Figure 4.15 in the furnace, as well as in refining, a comparison should be made with densities for the metal phase described previously in this chapter. It follows from the Figure that $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ melts, in general, will have a lower density compared to liquid FeSi75. For liquid silicon, on the other hand, slags with a bulk density $\geq 2500 \text{ kg/m}^3$ (2.5 g/cm^3) have a higher density than the liquid silicon. The composition at which this occurs can be read from the diagram of Figure 4.15 for a pure ternary slag, but the presence of SiC may shift this limit towards higher contents of SiO_2 and Al_2O_3 . Worth mentioning is that partial substitution of CaO by MgO has no noticeable effect on this limit.

Interfacial properties

The production of high-purity silicon requires the effective removal of metallic impurities like calcium and aluminium, as well as non-metallic inclusions such as SiO_2 , Al_2O_3 , and SiC. The efficiency of these removal processes is largely determined by the interfacial energies of the system. A fundamental understanding of these properties is therefore essential for process optimisation, leading to improved product quality and operational efficiency.

Interfacial properties are fundamentally thermodynamic in nature and play a crucial role in reaction kinetics, nucleation, and the formation of suspensions of solid particles or liquid droplets in molten slags. These properties are referred to as surface tension when the second phase is a gas and, unless otherwise specified, are measured under equilibrium conditions (Eustathopoulos *et al.*, 1999).

Surface energy is defined as the work required to increase the area of a surface by one unit. Since systems at constant temperature and pressure always tend towards minimizing free energy to reach equilibrium, the surface behaves as if it were in a state of tension. By definition, the surface tension, σ , expressed in mNm^{-1} is numerically equivalent to the surface energy in mJm^{-2} (Lu and Jiang, 2005).

In general, the surface tension of liquids decreases with increasing temperature, and the variation often follows a linear relation over a limited temperature range, i.e.:

$$\sigma = \sigma_0 + \left(\frac{d\sigma}{dT} \right) T \quad [4.12]$$

Silicate melts which are rich in SiO_2 are highly polymerized and are exceptional, as they exhibit positive values for $(d\sigma/dT)$. This is associated with structural changes in the melt caused by dissociation and formation of smaller anionic groups at higher temperatures. As the extent to which this happens varies with composition, a clear effect of temperature on the surface tension is not easily seen from the reported data for the SiO_2 – CaO – Al_2O_3 melts. Figure 4.16 shows the surface tension of the liquid Al_2O_3 – CaO – SiO_2 slag at 1600°C (Tang *et al.*, 2009). As seen, there is a decrease in surface tension with increasing SiO_2 concentrations. The surface tension increases slightly if CaO is substituted by MgO in these melts.

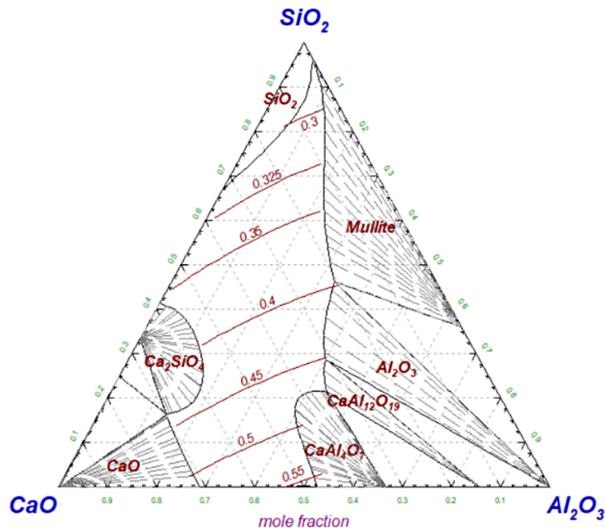


Figure 4.16 Modelled iso-surface tension curves in SiO_2 – Al_2O_3 – CaO slag at 1600°C (Tang *et al.*, 2013) [Used with permission from K. Tang].

The surface tension of pure molten silicon has been the subject of extensive research, with reported values typically in the range 700–900 mN/m at its melting point (1414°C). Hardy derived the surface tension of liquid silicon from sessile drop measurements and arrived at the following expression, which is valid for the temperature range 1415 – 1600°C (Hardy, 1984):

$$\sigma = 885 - 0.28(T - T_m) \quad [4.13]$$

With an uncertainty in the gradient of $\pm 0.004 \text{ mNK}^{-1}$, Hardy carried out his measurements with liquid silicon placed in a BN cup in a flowing argon atmosphere. He found that oxygen contamination lowered the surface tension of silicon. The surface tension increases when silicon is alloyed with iron. This is seen in Figure 4.17, where calculated and experimental data for the Fe–Si system at 1600°C are shown (Utigard, 1994). The diagram has been reproduced from the work of Klevan (1997), who included the results of Tang *et al.* (2009) and Hardy (1984) for pure silicon.

The presence of surface-active elements, particularly oxygen, can significantly alter the surface tension. Even minute amounts of oxygen can lower the surface tension of silicon, which has been a source of discrepancy in historical measurements (Mukai *et al.*, 2000). Modern experimental techniques, such as electromagnetic levitation, have allowed more accurate measurements under controlled atmospheres, leading to a better understanding of the intrinsic properties of molten silicon.

The interfacial tensions between Fe–Si alloys and $\text{CaO–Al}_2\text{O}_3\text{–SiO}_2$ slags are shown in Figure 4.18. This figure is reproduced from the work of Dumay and Cramb (1995), who employed the X-ray sessile drop method at 1450°C on two types of slag, composed as listed in Table 4.5. This method requires a certain density difference between the metal and the slag, and it loses accuracy at high silicon levels, as is also reflected in the results.

Table 4.5 Slag compositions referred to in Figure 4.18. (Dumay and Cramb, 1995).

Slag	wt% CaO	wt% Al_2O_3	wt% SiO_2
1	46	18	36
2	42	16	42

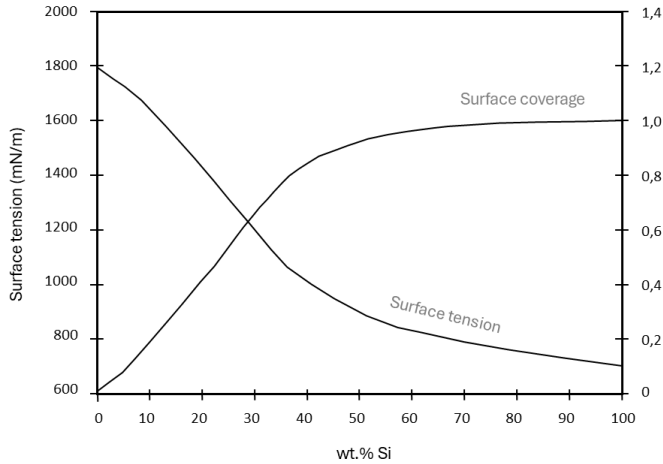


Figure 4.17 Experimental and calculated surface tension and surface coverage of Fe-Si-alloys at 1600°C after Klevan (1997).

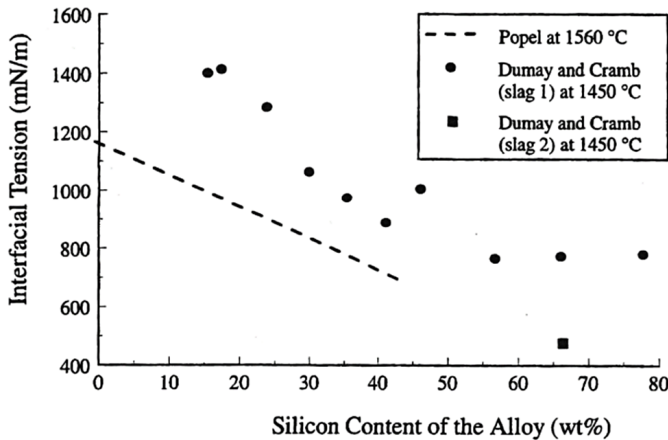


Figure 4.18 Interfacial tension between Fe-Si-alloys and slags at 1450°C (Dumay and Cramb, 1995).

The data from Dumay and Cramb reflect a situation in which the two phases are in chemical equilibrium. Experiments have shown that the transfer of reactants across the interface, due to chemical reactions between the two phases, lowers the interfacial tension. At high transfer rates, the interfacial tension

may drop to zero and even negative values have even been recorded. This creates interfacial turbulence and instabilities at the interface, and spontaneous emulsification may even occur as a result (Turkdogan, 1983).

By combining the surface properties quoted for the slag/metal system in question, we can derive an expression for the so-called spreading coefficient S , which measures the tendency for the slag to spread across the metal surface. For a situation as illustrated in Figure 4.19a, which shows a droplet of slag (s) in a gaseous environment resting at equilibrium on the surface of liquid metal (m), the spreading coefficient $S_{s/m}$ is defined as:

$$S_{s/m} = \sigma_{g/m} - (\sigma_{g/s} + \sigma_{s/m}) \quad [4.14]$$

In this expression, g/m and g/s indicate the surface energies of the gas/metal and gas/slag surfaces, respectively, and s/m indicates the slag/metal interfacial energy. The angle between the tension vectors represented by the two terms in the parentheses in Equation 4.14 defines the contact angle θ , which becomes $< 90^\circ$ for positive values of S and $> 90^\circ$ for negative values. A more familiar definition of this angle, usually referred to as the wetting angle, is the one given in Figure 4.19b. This figure shows a sessile drop of liquid (l) at rest on a flat, horizontal solid surface (ss) in a gaseous environment (g). The contact angle can now be observed directly and is here defined by the respective tension forces by:

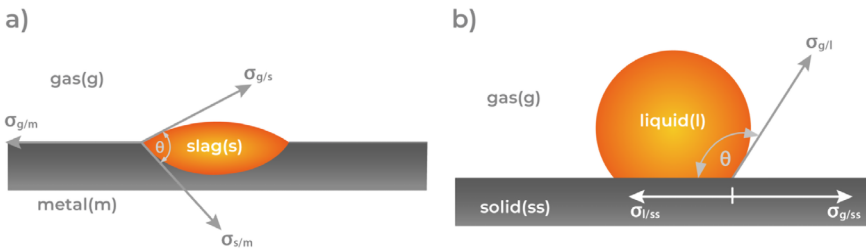


Figure 4.19 Relations between the respective surface and interfacial tensions and the contact angle at equilibrium for (a) Slag on liquid metal for $S > 0$ (b) Liquid on solid for non-wetting conditions.

$$\cos \theta = \frac{\sigma_{g/ss} - \sigma_{l/ss}}{\sigma_{g/l}} \quad [4.15]$$

If we insert the approximate values into Equation 4.14, we may read from Figure 4.17 and Figure 4.18 that, for a metal with 70% Si, and neglecting a possible temperature dependency of the interfacial energy, we obtain the following for a slag with a surface energy of 500 mJm^{-2} :

$$S_{s/m} = 800 - (500 + 400) = -100 \text{ mJm}^{-2}$$

The negative value for S indicates favorable conditions for slag/metal separation. However, the spreading coefficient may easily become positive, and the conditions for phase separation less favorable, if exchange reactions between slag and metal across the interface are still running.

Tang *et al.* (2009) proposed the constricted Gibbs energy minimization algorithm to calculate the surface tensions of the liquid Si–Al–Ca metal and SiO_2 – Al_2O_3 –CaO slag phases. The basic assumption is that the monolayer-thick surface layer is in equilibrium with the bulk phase. Thermochemical properties of the molten slag and the surface properties of pure components are the only required input for the calculations. Interfacial tensions between metal and slag phases were then modelled by applying the modified Girifalco–Good equation. The proportional factor is expressed as a function of SiO_2 concentration. The spreading coefficient for liquid ferrosilicon alloy and molten SiO_2 –CaO– Al_2O_3 slags can be expressed as:

$$S_{s/m} = (6.13 - 1.29X_{\text{SiO}_2})\sqrt{\sigma_s\sigma_m} - 2\sigma_s$$

Tang *et al.* (2013) further developed the constricted Gibbs energy minimization algorithm to calculate the interfacial tensions between the liquid Si–Al–Ca metal and SiO_2 – Al_2O_3 –CaO slag. Figure 4.20 shows the model calculations with experimental data.

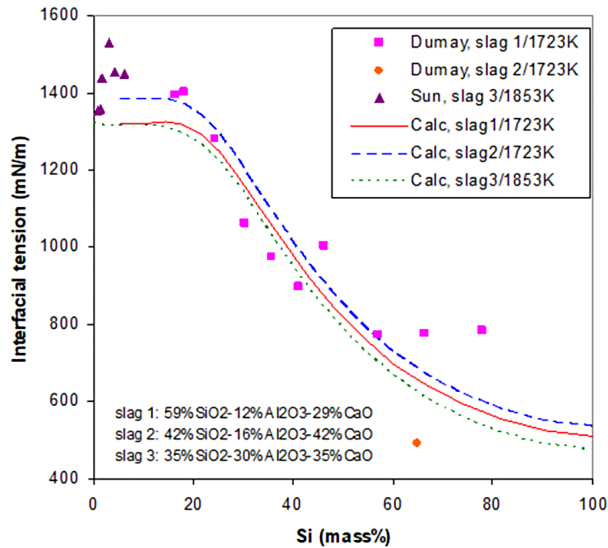


Figure 4.20 Effect of Si content of Si-Fe alloys on the interfacial tension of ferrosilicon alloy and molten SiO₂-CaO-Al₂O₃ slags (Tang et al., 2013) [Used with permission from K. Tang].

Silicon carbide will be present in all parts of the furnace, and it also enters the refining process as crystalline particles suspended in the metal phase. According to the literature surveyed by Klevan (1997), liquid silicon and Fe-Si alloys with > 33% Si wet SiC fairly well, almost independently of the crystalline form of SiC and the morphology of the specimens. Except for the work of Nogi and Ogino (1994), who claimed that silicon at 1550°C wets SiC completely, other investigators have recorded wetting angles that vary between -33–42° at temperatures ranging between 1430–1480°C, for both silicon and ferrosilicon.

The wetting behavior of silicate glasses on SiC was investigated by Yurkov and Polyak (1995). They found good or almost perfect wetting, with contact angles $\theta < 30^\circ$, at 1400°C for glass containing 12–25% Al₂O₃, 5–17% CaO and 25–70% SiO₂ (Yurkov and Polyak, 1995). From these data, we are tempted to conclude that SiC is wetted better by silicate melts than by the metal phase. The system will therefore decrease its surface energy if the SiC particles migrate across the interface into the silicate melt. The surface energy decreases most if the SiC particles are small.

Our understanding of interfacial properties in high-temperature systems has been greatly advanced by the development of sophisticated experimental and computational methods. High-temperature X-ray radiography allows direct observation and measurement of contact angles and interfacial tension in sessile drop experiments. Electromagnetic and electrostatic levitation techniques enable the measurement of thermophysical properties of highly reactive melts, like silicon, without contamination from a crucible (Nogi and Ogino, 1994). In parallel, computational modelling has become an indispensable tool. Molecular dynamics (MD) and density functional theory (DFT) simulations provide insights into the atomic-scale structure and interactions at interfaces. Validated by experimental data, these models allow efficient exploration of the effects of composition and temperature on interfacial properties, guiding the design of new alloys and refining slags.

4.3 Distribution of elements

The elements added to the silicon furnaces will be distributed among various phases, such as gas, oxide, or metal, in varying amounts depending on the element content and temperature. Assuming thermodynamic equilibrium, every element will be present in all phases, and its amount in each phase is given by the chemical potential, which will be the same in all phases. If the same reference state is used, the activity of each element must be the same in all phases. For example, if three phases are present for Ca – liquid silicon, a slag, and a gas – then $a_{\text{Ca(silicon)}} = a_{\text{Ca(slag)}} = p_{\text{Ca}} = (\text{gas})$, though one often uses $a(\text{CaO})$ instead of $a(\text{Ca})$ in slag. Another way to look at this is to state that the system will go to the phases and phase compositions that give the lowest Gibbs free energy.

Myrhaug and Kamfjord have both measured the element distribution in and out of the furnace, as seen in Figure 4.21 and Figure 4.22 (Kamfjord, 2012; Myrhaug, 2003). It must, however, be said that the accuracy of the chemical analyses of the material may vary, especially at very low element concentrations. The theory is that the distribution will be decided mainly by the boiling point of the element. Elements that have a boiling point above the temperature of the crater zone, that is 2000°C, will mainly go into the liquid silicon or ferrosilicon. Elements that have a lower boiling point will

condense in the silica fume above the charge, while the ones with the lowest boiling point will go in the off-gas. There are, of course, several exemptions from the rule:

- For some elements, the oxides have lower boiling points than the elements, like SO_3 , SeO_2 , As_2O_3 , MoO_3 and WO_2 , and may go to the gas phase in an oxidic form.
- It has been theorized that Pb will follow the gas to the charge top, where it can react with S and form PbS , which has a lower boiling point.
- In FeSi production, P may form the stable compound FeP , which is very stable, and this may explain why most of the P will go to the metal in FeSi production.

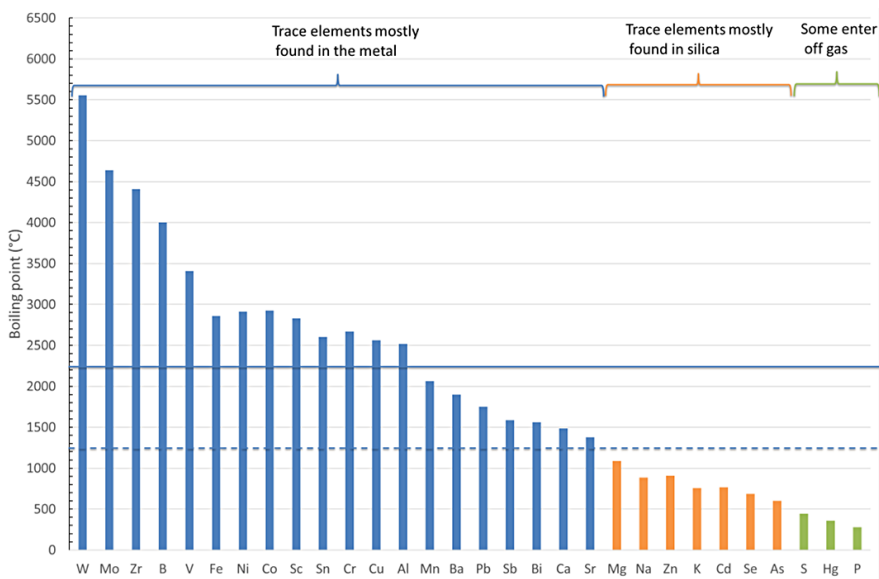


Figure 4.21 Illustration of the boiling point model describing the element distribution in the output flows of a silicon furnace. Dotted line indicates the temperature in the hot zone and dotted line the temperature in the off gas (after Myrhaug, 2003). [Used with permission from L.V. Myrhaug].

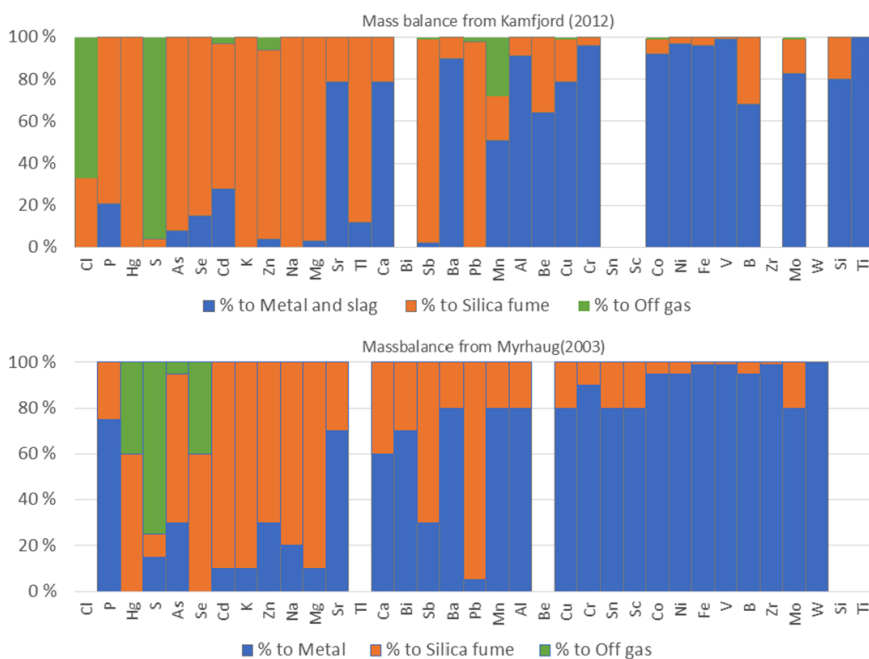


Figure 4.22 The distribution of elements in the output flows of a Si furnace measured over 2 days from Kamfjord (2012) and from ferrosilicon production Myrhaug (2003). The elements are shown with increasing boiling point. [Used with permission from N.E. Kamfjord and L.V. Myrhaug].

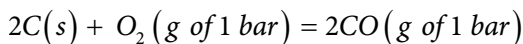
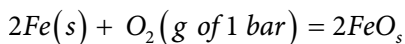
General thermodynamic overview

Most elements introduced into the furnace are in oxide form, with carbon being the notable exception. Silicon dioxide (SiO_2), added as quartz, is the primary oxide. Both quartz and carbon materials contain trace elements predominantly as oxides, such as CaO , Al_2O_3 , FeOx , and TiO_2 . In high-silicon ferrosilicon (FeSi) production, iron may be introduced as oxides (Fe_2O_3 , Fe_3O_4 , or FeO) or scrap metal. During the slag refining process, the oxide phase also plays a crucial role in determining the final metal composition.

This discussion will focus on the stability of oxides and their transition to elemental states, exemplified by the stability of SiO_2 and its conversion to elemental Si. Figure 4.23 presents an Ellingham diagram, which illustrates the standard Gibbs energies of oxide formation per mole of oxygen reacted. This

diagram provides a visual representation of the relative stability of selected metal oxides compared to those of silicon and carbon.

The diagram shows that the oxides of transition metals like Ni, Co and Fe are all less stable than SiO_2 . This means that the oxides of transition metals are liable to be reduced to their pure metal state at a lower temperature than the reduction of SiO_2 to Si. It is also clearly seen that they become unstable in the presence of graphite and 1 bar CO pressure at low temperatures. For the lowest oxide of Fe, FeO, this happens at temperatures above the intersection point between the lines representing the reactions:



Subtracting the first from the second reaction gives the reaction



for which the change in standard Gibbs energy is zero at the temperature of intersection 720°C and is < 0 at higher temperatures. What is not seen so easily in the diagram is that the reduction of FeO to Fe may occur in CO/ CO_2 mixtures, as CO is an effective reducing agent for FeO at temperatures below 1200°C .

If they appear as pure oxides in a charge mixture of SiO_2 and C, oxides like manganese should be completely reduced before the reduction of SiO_2 . As the temperature needed for the manganese reduction to be completed is at a level where liquid slag formation may take place, a liquid MnO– SiO_2 slag will be formed.

The alkali metal oxides, which are represented by the compound K_2O and Na_2O in Figure 4.23, are also relatively stable at room temperature, but their stability decreases rather rapidly with increasing temperature due to the low melting and boiling points of the alkali metals. As shown, if present in their pure state, Na_2O and K_2O are reduced to metal vapour by reaction with carbon at around 1020°C and 830°C respectively.

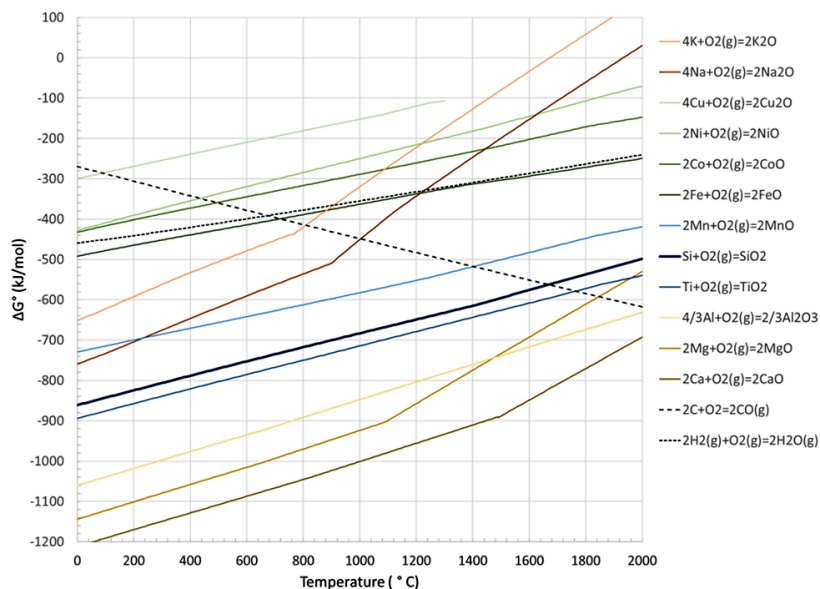
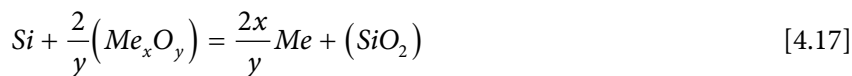


Figure 4.23 The Ellingham diagram for the oxides of some relevant additional elements in silicon smelting (calculated by HSC v.9).

The third group of metal oxides to consider are those that require a lower oxygen potential than SiO_2 to react and form metal in its standard state. This group comprises the alkaline earth metal oxides and alumina, which are among the most abundant of the impurities entering the furnace charge. Note that TiO_2 , which is the least stable of the titanium oxides, also belongs to this group, as it is more stable than SiO_2 throughout the temperature range of interest.

The high stability of these refractory oxides, and the fact that they enter as impurities tied up in silicate minerals with oxide activities less than unity, make it reasonable to assume that they will survive as oxides up to the melting point of silica at around 1700°C , where they dissolve in a slag. As the temperature increases and liquid silicon starts to form around 1800°C , their destiny is then determined by partial distribution equilibria of the following type:



The equilibrium constant of the reaction¹:

$$K_{4.17} = \frac{(a_{Me})^{\frac{2x}{y}} \cdot a_{SiO_2}}{(a_{Me_xO_y})^{\frac{2}{y}}} \cdot a_{Si} \ll 1 \text{ if the } Me_xO_y \text{ is a refractory oxide} \quad [4.18]$$

The same distribution reaction also applies at the final stage to the transition metals, as well as to the fraction of the alkali metals that may remain in the hot zone of the furnace at this stage. However, according to the examples, the K-values for these reactions are $\gg 1$ as shown in Figure 4.24.

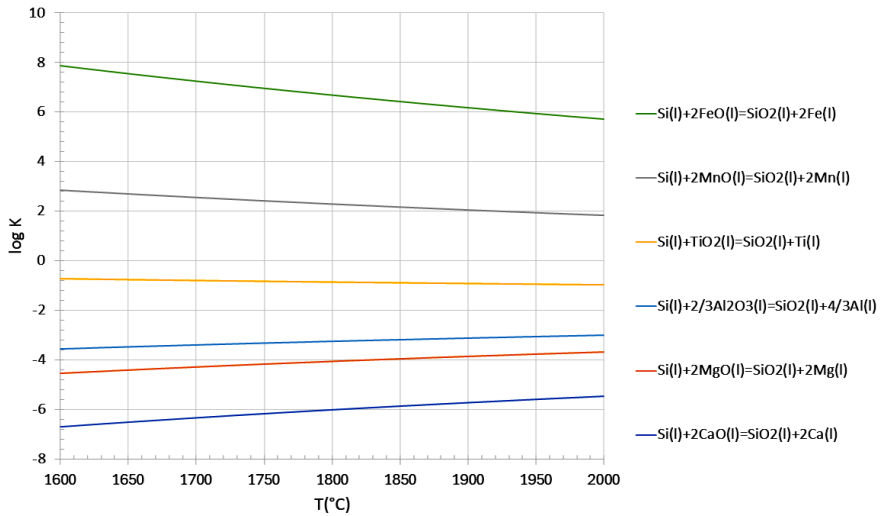


Figure 4.24 Equilibrium constant based on HSC v.9 for various types of metal oxides participating in Reaction [4.18] with liquid slag and metal.

- Note that the reference state for the activities appearing in this generalised expression is defined by the data chosen to calculate the Gibbs energy change of the reaction. According to the formalism used above, the metal activities should be replaced by partial pressures for the volatile metals above their boiling point, i.e. at 897, 1093 and 1483°C, respectively, for Na, Mg and Ca.

The equilibrium constant is a function of temperature, as expressed in the van't Hoff equation:

$$\frac{d \ln K}{d \left(\frac{1}{T} \right)} = - \frac{\Delta H^\circ}{R} \quad [4.19]$$

It follows from this that, for the endothermic reactions with the refractory oxides, the equilibrium constant increases with temperature. This makes their reduction more favorable at high temperatures. For the reactions with the transition metal oxides, which are exothermic, the situation is the opposite.

In silicon smelting, as well as in the production of Si-rich alloys, liquid silica and silicon can both act as solvents for impurities, as previously discussed. Their activities in the expression for the equilibrium constant in Equation [4.18] are therefore expected to be close to unity if the metal phase contains > 98 wt%Si and the oxide phase is saturated in silica. This simplification gives the following for the activities of a dissolved element:

$$a_{Me} = \left(K_{[4.17]} \right)^{\frac{y}{2x}} \left(a_{Me_xO_y} \right)^{\frac{1}{x}} \quad [4.20]$$

or for the partial pressure of a volatile element:

$$p_{Me} = \left(K_{[4.17]} \right)^{\frac{y}{2x}} \left(a_{Me_xO_y} \right)^{\frac{1}{x}} \quad [4.21]$$

Expressing the activity in Equation [4.6] by an activity coefficient γ_{Me} :

$$a_{Me} = \gamma_{Me} \cdot X_{Me}$$

and transforming from mole fractions to weight% by inserting for, which applies for diluted solutions, we get the following for the concentration of an impurity element:

$$[\%Me] = \left(K_{[4.17]} \right)^{\frac{y}{2x}} \cdot \frac{100 M_{Me}}{28.1} \cdot \frac{\left(a_{Me_xO_y} \right)^{\frac{1}{x}}}{\gamma_{Me}} \quad [4.22]$$

or

$$[\%Me] = k_{eff} \frac{(a_{Me_xO_y})^{\frac{1}{x}}}{\gamma_{Me}} \quad [4.23]$$

There are, however, several cases where the activity of silicon and silica is not close to unity; that is, when % Si < 90 wt% and % SiO₂ < 90 wt%. The most obvious examples are FeSi alloys produced with, e.g., 52 wt% Si or 75wt% Si. The oxide phase in the lower part of the furnace, as well as the tapped slag, will also contain about equal amounts of SiO₂, Al₂O₃ and CaO. The amount of Me in the silicon phase will then be expressed by a_{Me} , as given by equation [4.18].

Ca and Al distribution

Over a period of 2 months, Oterkjær studied the operation of a ferrosilicon furnace producing standard Fe75Si and found that 60–70% of the total aluminium and 90–95% of the total calcium entered the furnace with the reduction materials. He also found that, on average, 70% of the total aluminium and 50% of the total calcium were recovered in the metal (Oterkjær, 1976). As slag weights were not recorded, his calculations of the losses are somewhat uncertain. However, he found that as much as 60% of the unrecovered aluminium and 30% of the unrecovered calcium were lost as fume in the off-gas, which is in agreement with Hauge's data (Hauge, 2022). The rest of the Al and Ca was tapped as a constituent of the slag, with an average composition of 31.5% SiO₂, 38.7% Al₂O₃, and 26.0% CaO, containing 3.8% SiC.

The concentrations of aluminium and calcium in the metal, which averaged around 1.5% and 0.4%, respectively, fluctuated from one day to the next, with the largest amplitudes for aluminium. These fluctuations are somewhat smoothed out in the plot in Figure 4.25, which shows the calculated recoveries in the metal phase on a weekly basis.

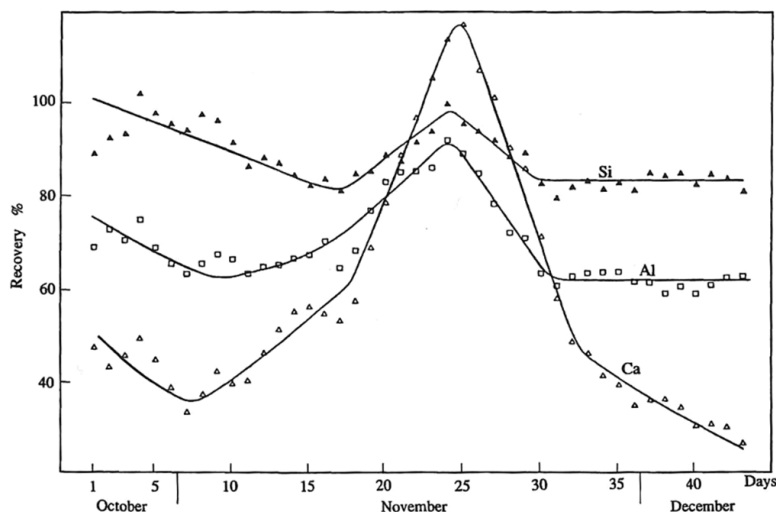
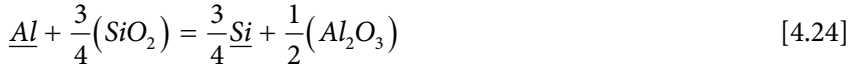


Figure 4.25 Calculated recoveries of Ca, Al and Si in tapped metal for a period of ferrosilicon smelting after Oterkjær (1976).

The peaks in the recoveries after 25 days are associated with a period of over-coking. The smaller fluctuations in the impurity recoveries were also found to be related to changes in the amount of carbon added. A decrease in furnace resistance was also found to increase the transfer of aluminium and calcium to the metal phase.

Comparing the work of Oterkjær (1976) with the industrial mass balance presented above from Myrhaug (2003) and Kamfjord (2012), 80–90% of the Al and 60–80% of the Ca entering the furnace will be distributed between the slag and the metal. As most of it will go to the metal, it goes without saying that the distribution of Al and Ca between the slag and metal phases will also be important in the refining process. In the furnace, the Al_2O_3 and CaO will be reduced, while in the refining step the Al and Ca will be oxidized. As the thermodynamics only discusses the end state, which governs both the reduction and the oxidation, this chapter will discuss the end-state distribution.

The equilibrium between the Al and Ca in the metal phase and the Al_2O_3 and CaO in the slag phase will be given by reaction [4.24] and [4.25]:



It follows from these equations that the reduction of a dissolved impurity is coupled with the distribution of silicon between the oxide and metal phases of silicon. Hence, it is also evident that the reduction of various dissolved elements is mutually coupled through similar reactions; i.e., as follows for the two elements considered:



However, at low impurity levels, the transport of the impurity elements from the bulk of the slag to the slag-metal interface may very well take over as a rate-controlling step. The recorded bulk distribution will then deviate from the equilibrium values.

Typically, it is important to calculate the amount of Al and Ca in the metal. Based on reaction [4.24] and [4.25], the equilibrium constant can be described by the following reactions:

$$K_{\text{Ca}} = \frac{a_{\text{CaO}} \cdot a_{\text{Si}}^{1/2}}{a_{\text{Ca}} \cdot a_{\text{SiO}_2}^{1/2}} \quad [4.27]$$

$$K_{\text{Al}} = \frac{a_{\text{Al}_2\text{O}_3}^{1/2} a_{\text{Si}}^{3/4}}{a_{\text{Al}} a_{\text{SiO}_2}^{3/4}} \quad [4.28]$$

Reaction [4.27] and [4.28] can be rearranged to the following reaction, where the activities in the metal phase will be the focus:

$$a_{\text{Ca}} = \frac{a_{\text{CaO}} \cdot a_{\text{Si}}^{1/2}}{K_{\text{Ca}} \cdot a_{\text{SiO}_2}^{1/2}}$$

$$a_{\text{Al}} = \frac{a_{\text{Al}_2\text{O}_3}^{1/2} a_{\text{Si}}^{3/4}}{K_{\text{Al}} a_{\text{SiO}_2}^{3/4}}$$

With the activity of Ca and Al in the metal, the molar mass can be calculated as:

$$a_{Ca} = \gamma_{Ca} X_{Ca}$$

$$a_{Al} = \gamma_{Al} X_{Al}$$

The molar fraction will hence be given by the following equations:

$$X_{Ca} = \frac{a_{Si}^{1/2}}{\gamma_{Ca}} \cdot \frac{1}{K} \cdot \frac{a_{CaO}}{a_{SiO_2}^{1/2}} \quad [4.29]$$

$$X_{Al} = \frac{a_{Si}^{3/4}}{\gamma_{Al}} \cdot \frac{1}{K_{Al}} \cdot \frac{a_{Al_2O_3}^{1/2}}{a_{SiO_2}^{1/2}} \quad [4.30]$$

The amount of Ca in the metal is given by the metal composition, by a_{Si} and γ_{Ca} , the equilibrium constant K_{Ca} , and the slag composition, given by the activities of CaO and SiO₂. These numbers are all found previously in this chapter.

To calculate this in wt.%, the activity based on wt.%, $a_{Ca} = f_{Ca} \cdot [\text{wt.\% Ca}]$, can be used, or it can be calculated from the molar fraction. Assuming that the Ca level is less than 2%, the simplified equation 4.31 can be used:

$$[\text{wt.\% Ca}] = \frac{X_{Ca} \cdot M_{Ca}}{X_{Ca} \cdot M_{Ca} + X_{Si} \cdot M_{Si}} \cdot 100 \quad [4.31]$$

where M_{Ca} is the molar weight of Ca and M_{Si} is the molar weight of the solvent. For FeSi75, it would be the molar weight of FeSi75. By using this equation below 2% Ca, the inaccuracy would be less than 1%.

Programs like e.g. FactSage, using Gibbs free energy minimization algorithms, can calculate this directly. In Figure 4.26 to Figure 4.33 one can see the resulting wt.%Al and wt. % Ca in silicon, FeSi75 and FeSi50 in coexistence with an Al₂O₃, CaO, SiO₂ slag at 1550 and 1600°C.

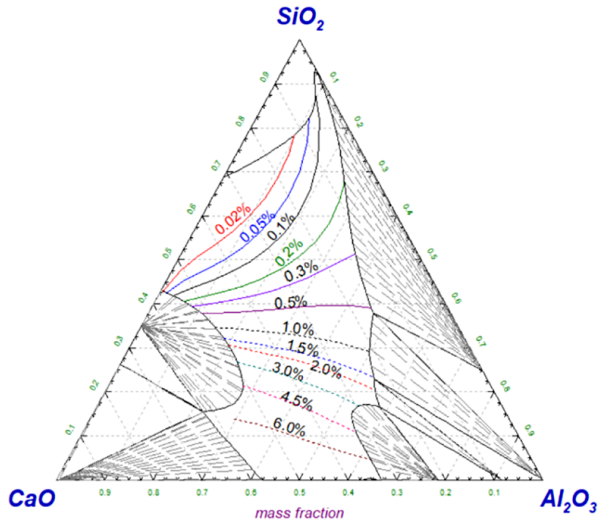


Figure 4.26 Calculated iso-content contours for Al of metal/slag equilibria at 1600°C. The FactSage commercial software and its FToixd and FTLite databases have been used.

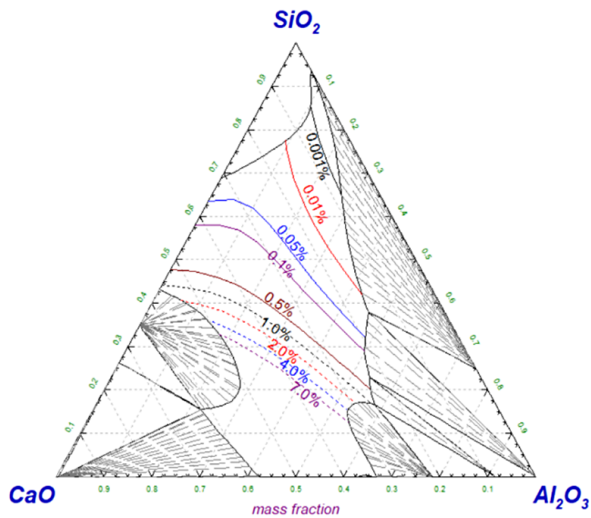


Figure 4.27 Calculated iso-content contours for Ca of metal/slag equilibria at 1600°C. The FactSage commercial software and its FToixd and FTLite databases have been used together with the updated activity coefficient from (Jakobsson and Tangstad, 2015).

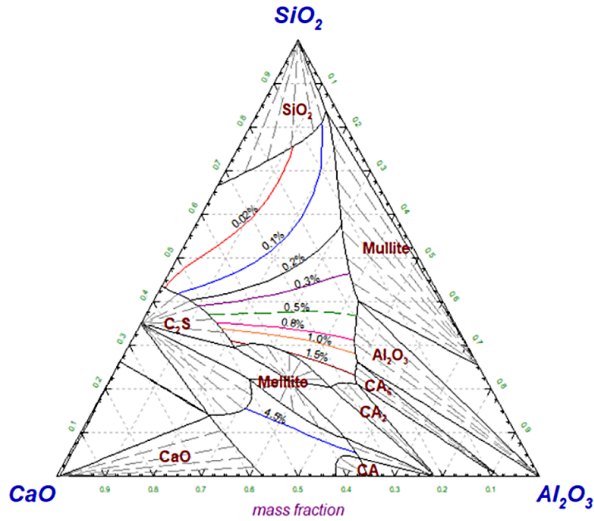


Figure 4.28 Calculated iso-content contours for Al of metal/slag equilibria at 1550°C. The FactSage commercial software and its FToixd and FTLite databases have been used.

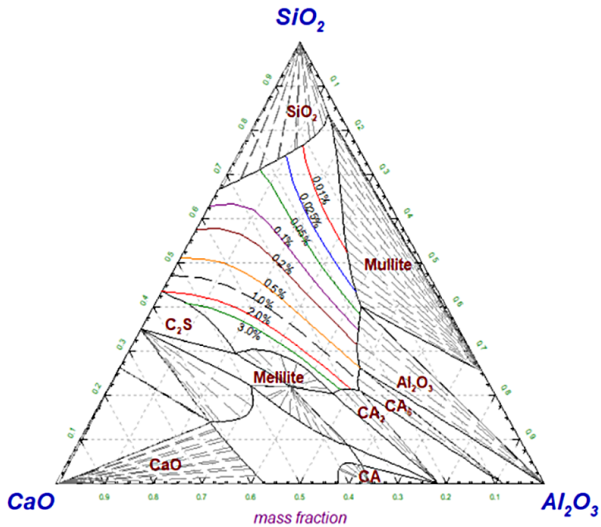


Figure 4.29 Calculated iso-content contours for Ca of metal/slag equilibria at 1550°C. The FactSage commercial software and its FToixd and FTLite databases have been used together with the updated activity coefficient from Jacobsson and Tangstad (2015).

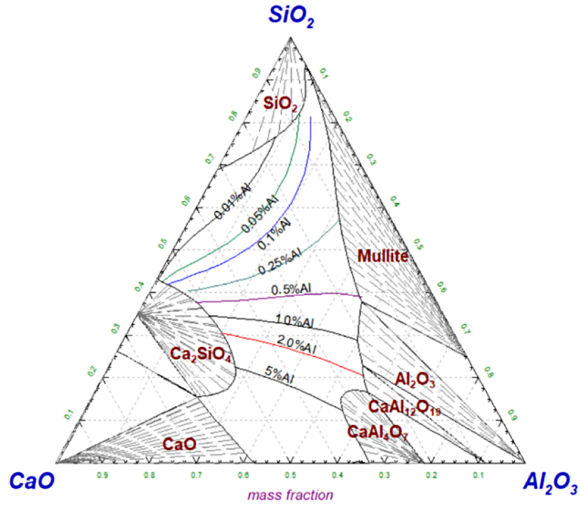


Figure 4.30 Calculated iso-content contours for Al of FeSi75/slag equilibria at 1600°C. The FactSage commercial software and its FToixd and FTLite databases have been used.

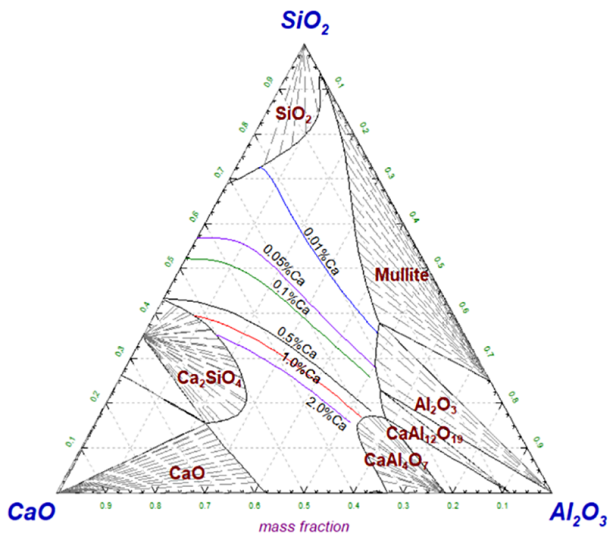


Figure 4.31 Calculated iso-content contours for Ca of FeSi75/slag equilibria at 1600°C. The FactSage commercial software and its FToixd and FTLite databases have been used together with the updated activity coefficient from Jacobsson and Tangstad (2015).

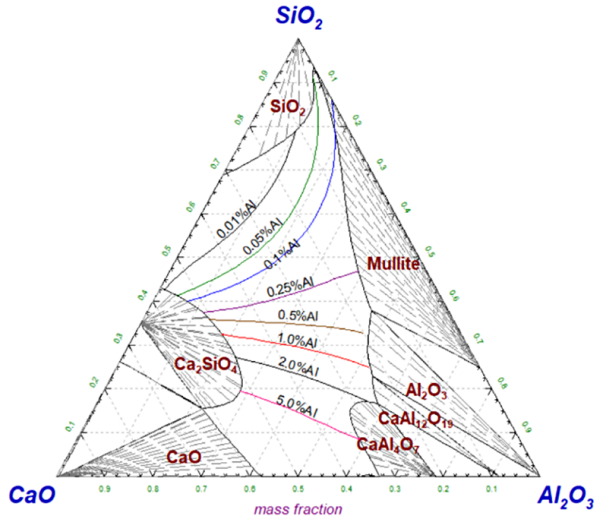


Figure 4.32 Calculated iso-content contours for Al of FeSi50/slag equilibria at 1600°C. The FactSage commercial software and its FToixd and FTLite databases have been used.

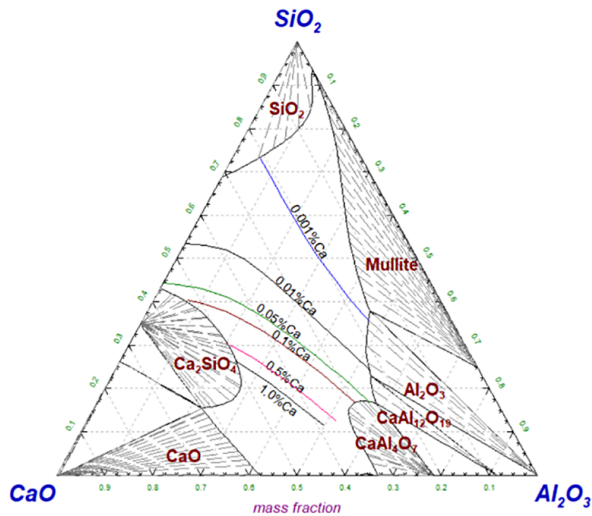


Figure 4.33 Calculated iso-content contours for Ca of FeSi50/slag equilibria at 1600°C. The FactSage commercial software and its FToixd and FTLite databases have been used together with the updated activity coefficient from Jacobsson and Tangstad (2015).

Volatile impurities

Moisture and chemically bound H_2O in the feed materials, together with volatile matter from coke, coal, char, and woodchips, are transported upwards through the charge by CO and SiO gases generated in the deeper, hotter regions of the furnace. During the initial heating stages, these volatiles are typically released as H_2O , H_2 , CO, CO_2 , and various hydrocarbons (C_xH_y).

Nitrogen enters as an organic constituent of the reductants. In the presence of alkali metal vapours at temperatures above 400°C , it forms alkali metal cyanides (KCN or NaCN). At temperatures above 1300°C , it forms HCN gas if hydrogen is also present at this stage. In the absence of these elements, the nitrogen is expelled as gaseous CN and C_2N at elevated temperatures (Jalkanen *et al.*, 1995). Possible cyanide emissions may cause an environmental problem in a closed furnace operation, but they will be effectively eliminated by combustion in an open or semi-closed furnace. Thermal NO_x is generated by direct oxidation of N_2 at temperatures above 1400°C , and reduced local temperatures on the charge top are therefore beneficial for reducing the NO_x emissions (Andersen, 2023; Kamfjord, 2012).

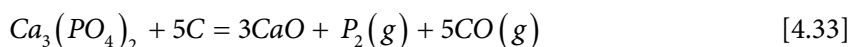
Sulfur, like nitrogen, is an inherent impurity in the reductant, but it is also present in sulfide minerals, e.g. pyrite. The fraction associated with the organic material is expected to be driven off as H_2S or COS at an early stage, together with sulfur liberated by the decomposition of pyrite. This decomposition takes place at about 700°C through the reaction:



The remaining sulfur, present as lower metal sulfides, is likely to survive up to the metal forming temperature, where an unknown fraction may be transferred to the gaseous state in the form of SiS(g).

From the mass balance and sulphur analyses for the various reduction materials used in ferrosilicon smelting given in we can calculate the weight-ratio between sulphur charged and silicon recovered as metal to be. This is about two orders of magnitude larger than recorded sulfur contents of tapped metal indicating that 98–99% of the charged sulfur leaves the process with the off-gases. This is in accordance with Kamfjord (2012) for a Si furnace, but higher than the reported values for a FeSi-furnace (Myrhaug, 2003).

Phosphorus, which is a critical impurity when metal quality is concerned, is also an inherent element in organic materials, but is in addition found as mineral particles, mainly in the form of apatite ($\text{Ca}_3(\text{PO}_4)_2$). Under oxidizing conditions, oxides of phosphorus volatilize at around 300°C as $\text{P}_5\text{O}_{10}(\text{g})$, but in the presence of C/CO they form gaseous P_4O_6 at even lower temperatures, provided that the carbon reacts at such a low temperature. This component can survive in the presence of C/CO up to around 1250°C, where $\text{P}_2(\text{g})$ becomes the dominating species. $\text{P}_2(\text{g})$ is also the dominating species formed when elemental phosphorus evaporates at 907°C. The phosphorus tied up in the mineral apatite needs to be liberated by the reaction:



This reaction proceeds to the right at $t > 1430^\circ\text{C}$ at a total pressure of 1 bar, but if the product gases are transported by flowing CO, it will proceed at reduced speed, also at lower temperatures.

The information above leads to the conclusion that phosphorus entering the process with the reductants should be efficiently transferred to the gas phase and flushed away. This may be true for a silicon process in which phosphorus is the only impurity, but it is not the case in a process where strong phosphide-forming metal impurities, like iron, manganese, magnesium and calcium, are present, as shown in the mass balances from Myrhaug (2003) and Kamfjord (2012) as shown previously in this chapter.

Iron, in particular, is expected to be in a metallized state, ready to react with gaseous P_2 , at least in the area where the apatite decomposes, and thus contribute to the transport of phosphorus into the metal phase. From the thermodynamics of liquid steel, it is known that the presence of silicon in iron increases the activity coefficient of phosphorus. This implies that the efficiency of iron as a carrier for phosphorus decreases as the iron picks up silicon on its way towards the furnace hearth.

The amount of phosphorus that enters the pool of liquid metal is expected to remain there and appear in the tapped metal with typical concentrations of 25–50 ppmw and 130–300 ppmw P for Si-metal and Fe75Si, respectively. The argument behind this statement is based on data from the experimental work of Miki and Zaitsev, showing that the equilibrium pressure of mono- and diatomic phosphorus vapour over silicon with 50 ppmw P at 1600°C is

of the order of 10^{-8} bar (Miki *et al.*, 1996; A.I. Zaitsev *et al.*, 2001). Thus, the expected evaporation rate of phosphorus at an ambient pressure of one bar is extremely slow.

Potassium will be easily reduced from the oxide phase and produce potassium gas, which will leave the furnace and oxidize on the silica fume. According to Kamfjord (2012) and Myrhaug (2003), 90–100% of the potassium will leave the furnace, and 0–10% will enter the slag according to Figure 4.22. Usually, potassium is not found in the slag inside the furnace during excavations; however, exceptions are found with ~ 5% of K in the slag (Folstad, 2023; Hoover *et al.*, 2022). Potassium will be more stable in a slag than in K_2O or K_2CO_3 . This can be illustrated by the temperature at which the partial pressure of potassium gas is about 1% i. e. 700°C in equilibrium with K_2O , 1050°C in equilibrium with K_2CO_3 and about 1500°C in equilibrium with the silicate ($K_2O \cdot SiO_2$).

4.4 Alloying elements

Various grades of ferrosilicon, with 45, 66, and 75% Si being the most common; silicomanganese with ~20 and 30% Si; silico-chromium; and calcium silicides containing up to 40 and 60% Si are all examples of commercial alloys with a high content of silicon.

These products are formed from multicomponent systems, as is also the case for silicon metal if impurities are included as part of the system. We recall from Chapter 2 that three condensed phases are needed to define our system of three components at a given temperature. As stated by Gibbs phase rule, the number of degrees of freedom increases by one for each new element added. If these additional elements are in fixed proportions to the main element, however, as is the case for a given charge mixture, an equal number of compositional restrictions is imposed on the system. Thus, the multicomponent system is still defined by the coexistence of three condensed phases at a given temperature.

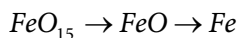
The addition of the foreign oxides needed to produce the above-mentioned alloys, as well as the accompanying oxides present as constituents of ore minerals and those added deliberately as fluxing agents, may affect the silica reduction in various ways. A common characteristic is the effect caused by a lowering of the silicon activity in the metal phase, as already discussed in this

chapter. Another is slag formation, which is inevitable in processes for making silicomanganese, silico-chromium and calcium silicides, but not to the same extent in ferrosilicon and silicon smelting. Extensive slag formation changes the inner structure of the furnace and, thus, also the conditions for heat and mass transfer in the process, but it does not change the phase relations and the equilibrium that define the conditions for silica to be reduced. Thus, slag formation alone affects the thermodynamics of the system only by the effect it may have on the silica activity. The situation becomes different, however, if new phases appear in the high-temperature region of the system. This is the case in processes for making silico-chromium and calcium silicides, where phases like $\text{Cr}_5\text{Si}_3\text{C}_x$ and CaC_2 , respectively, may form in the presence of the metal phase under given conditions. Phase constitutions that are different from those given in Chapter 2 will then determine the equilibrium conditions in the system. Consequently, these types of alloys are excluded from further discussion in this volume.

Ferrosilicon

Iron as an alloying element is added either in the form of scrap iron, mill scales, or iron ore, as lumpy material or as pellets. Independent of how it is added, however, iron is expected to enter the high-temperature region of the process ($T > 1500^\circ\text{C}$) in a metallic state, as has been discussed previously in this chapter. An interesting question to discuss in this connection is how the reduction of the iron oxides proceeds, and how it may affect the fixed C balance of the process.

Let the symbol n_{Fe} (mol Fe per mol Si) define the amount of iron needed to produce a specific grade of ferrosilicon. If this iron enters as hematite pellets, which are reduced by CO in their solid state, it will occur in two consecutive steps:



As they are descending in a counter-current flow of gas produced from the idealized gross reaction:

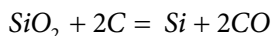


Table 4.6 shows the accumulated change in the gas composition for the completion of each reduction step for various grades of ferrosilicon, starting from 100% CO which enters from below.

Table 4.6 *Accumulated change in gas composition (%CO/(CO + CO₂)) caused by the stepwise reduction of hematite by CO during the production of various grades of ferrosilicon.*

Reduction steps (accumulated effect)	Direction of gas flow	FeSi75 $n_{\text{Fe}} = 0.168$	FeSi66 $n_{\text{Fe}} = 0.259$	FeSi45 $n_{\text{Fe}} = 0.615$
FeO _{1.5} to FeO		87.4% CO	80.6% CO	53.9% CO
FeO to Fe		91.6% CO	87.0% CO	69.3% CO
Reducing gas	2 CO per Si	100% CO	100% CO	100% CO

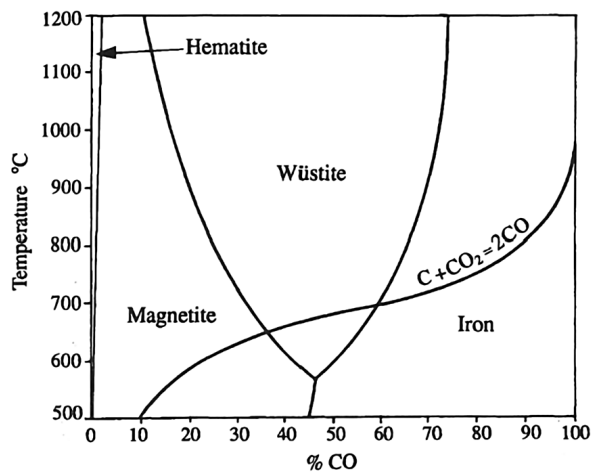
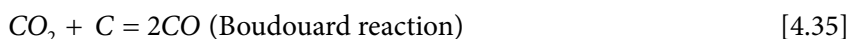


Figure 4.34 *Stability of iron oxides and solid C in CO–CO₂ mixtures of atmospheric pressure as function of temperature.*

If the values in Table 4.6 are compared with the stability of iron oxides in CO–CO₂ mixtures, as shown in Figure 4.34, it becomes evident that the quantity of CO produced by silica reduction in the heart of the smelting furnace can reduce the amount of hematite needed for the production of FeSi75 and FeSi66 at any temperature shown in the diagram. However, the amount of CO gas produced is not enough for complete FeOx reduction in the production of FeSi45 if

temperatures above 650–900°C are required. Figure 4.34 also shows that the product gas formed by the reduction of the iron oxides becomes unstable in the presence of solid C at temperatures above 700–830°C. Thus, if the last step of iron oxide reduction takes place at higher temperatures, thermodynamics of the system predict a net consumption of fixed C. The extent to which this happens, however, depends on the relative rates of the two reactions:



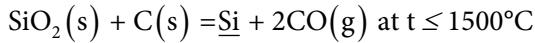
In this connection, the reactivities of the iron ore pellets and the reductants used become key properties, along with residence time in the appropriate temperature range. Since the Boudouard reaction rate is the more temperature sensitive of the two, and is believed to initiate at around 900°C when reactive reductants are used, a slow increase in temperature up to this level is favorable. A simple heat balance indicates that, in smelting of FeSi75, this is achievable through an exchange of heat with the gas phase. Another factor that prevents fixed C from being consumed is that the char, produced in situ from coal and representing a reactive fraction of the reductants, is still giving off hydrocarbons; these are the first to react with CO_2 . When charcoal is used, which is more reactive than coal, the extent of the Boudouard reaction will increase.

Although this may tempt us to conclude that, in the smelting of FeSi75, there is no need for extra additions of fixed C due to the use of iron ore pellets as the source for iron, these corrections are needed in the production of FeSi45 and probably also when smelting FeSi66. This statement is, however, disputed by experienced metallurgists, who have found it necessary to compensate for the reduction of FeO by the addition of fixed C also when smelting FeSi75. Their argument for this is the measured high temperatures of the gases leaving the furnace charge, which make the CO_2 unstable in the presence of C or volatiles.

When entering the high temperature region of the process, metallic iron dissolves carbon, and droplets of carbon-saturated iron may form at as low a temperature as 1153°C. If exposed to gas that contains SiO, these droplets can react and take silicon into solution, i.e. by the reaction:



The capacity of the iron to take silicon into solution under the prevailing conditions is determined by the equilibria:



as well as the silicon activity relations in C-saturated Fe–Si–C alloys. Results of equilibrium calculations on the iron-based system at $P_{\text{tot}} = 1$ bar, using data of (Rein, 1965), are shown by the dash-dotted curve in Figure 4.8, where the equivalent curve for the manganese-based system also is shown (Ding, 1993).

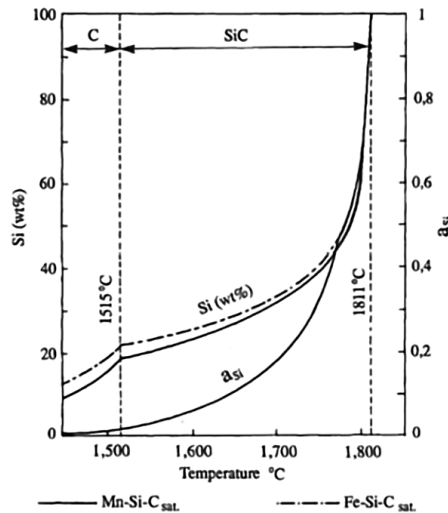


Figure 4.35 Activity and concentration of Si as function of temperature for Fe–Si–C_{sat} and Mn–Si–C_{sat} alloys in equilibrium with SiO₂ at $P_{\text{tot}} = p_{\text{CO}} + p_{\text{SiO}} + p_{\text{Mn}} = 1$ bar (Ding, 1993).

The solubility of carbon in these systems varies with the concentration of silicon. In the iron-based system, at e.g. 1600°C, the carbon content drops from 5.4% C in the silicon-free alloy to 0.4% C at 22.4% Si, where the metal coexists with both graphite and SiC; it then decreases further to a minimum at around 50% Si within the stability range of SiC, as shown in Figure 4.36.

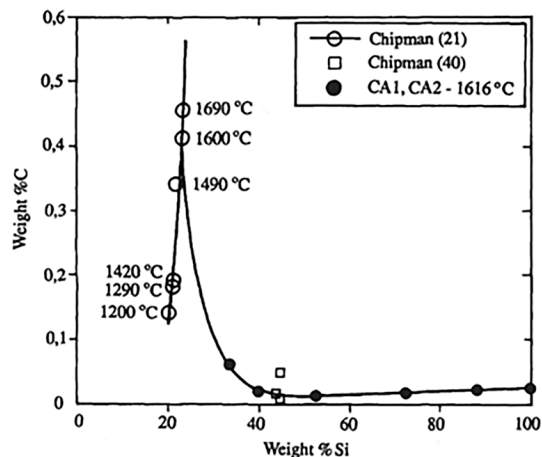


Figure 4.36 Carbon in Fe-Si alloys in equilibrium with SiC at 1616°C and the graphite/SiC boundary for various temperatures (Ottem, 1993).

The net heat effect of adding scrap iron to silicon is slightly exothermic. This results from the sum of two effects:

1. The heat required to raise the temperature of iron from room temperature to 1600°C
2. The exothermic heat of mixing of liquid iron and silicon at 1600°C.

The latter property can be taken from the integral relative enthalpy of mixing in the binary Fe-Si system at 1600°C. It is safe to say that these data also apply to carbon-saturated alloys, especially at high silicon concentrations, where the carbon solubility is extremely low, as Figure 4.36 shows.

Calculated heat effects for 1 mole of FeSi₇₅ with $X_{\text{Si}} = 0.86$ are given in the first column of Table 4.7. The contributions from two alternative models for iron oxide reduction are also included in the next columns.

As shown, the specific energy consumption decreases slightly when the iron is added in oxidic form if the reduction proceeds indirectly with CO throughout. However, the energy requirement increases by about 200 kWh per tonne Si if the final step of the reduction leads to consumption of fixed C or volatile hydrocarbons. Independent of the net effect, the process benefits

from the fact that the endothermic terms of the heat balance in Table 4.7 are all located in a temperature region where the capacity of the charge to absorb heat is a critical factor.

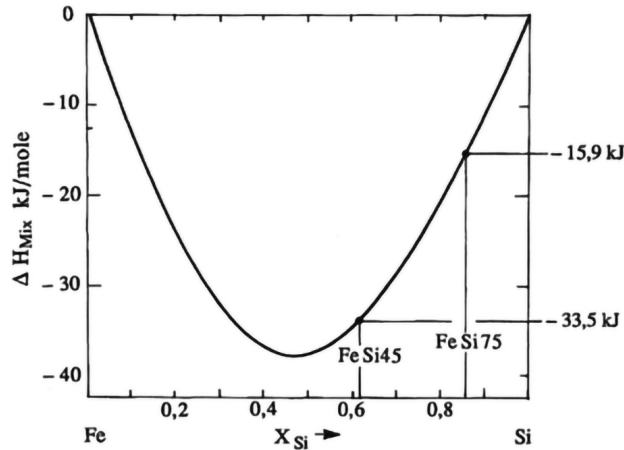


Figure 4.37 Integral relative enthalpy of mixing in the Fe–Si system at 1600°C based on data from Kubaschewski (Kubaschewski et al., 1993).

Table 4.7 Calculated heat effects caused by alternative ways of adding and reducing the iron in the smelting of FeSi75 ($X_{Si} = 0.86$).

Contribution to the enthalpy balance for $n_{Fe} = 0.14$	Addition as scrap iron	Addition as iron ore pellets and reduction of	
		$FeO_{1.5} \rightarrow FeO$ by CO $FeO \rightarrow Fe$ by CO	$FeO_{1.5} \rightarrow FeO$ by CO $FeO \rightarrow Fe$ by C
1.	-	$0.14 \times 5 = 0.7$	0.7
2.	-	$0.14 \times (-19) = -2.7$	$0.14 \times 153.5 = 21.5$
	$0.14 \times 77 = 10.8$	10.8	10.8
	$1 \times (-15.9) = -15.9$	-15.9	-15.9
Net heat effect (kJ)	-5.1	-7.1	17.1
Net energy (kWh/tonne Si)	-5.8	-82	197

In summary, adding Fe into the system will bring the following process changes:

1. For processes running at the same silicon yield, the addition of metallic iron slightly lowers ($< 0.7\%$) the consumption of electric energy per unit of silicon produced. The specific energy consumption also decreases by $\sim 1\%$ if the iron is fed as oxide pellets, provided they are completely reduced indirectly by CO. However, it increases by 2–3% if the reduction proceeds directly by formation of CO. A slight increase in the specific consumption of fixed C may be associated with the latter mode of reduction.
2. The presence of iron improves the silicon yield of the process and, thereby, also the specific energy consumption. Effects contributing to this are:
 - i. a lowering of the silicon activity, which makes the silica reduction possible at lower s -values. As a result, less SiO must be recovered in the upper shaft.
 - ii. an increase in the capacity of the charge to adsorb heat released by condensation of SiO and to react chemically with SiO.
3. Iron increases the density of the metal phase. This increase in metal density improves the conditions for separating slag and metal in the furnace hearth, as well as in the tapping ladle.

References

- Andersen, V. (2023) *Flue gas recirculation for the silicon process*. Doctoral thesis 2023:135. Norwegian University of Science and Technology (NTNU), Trondheim, Norway. Available at: <https://hdl.handle.net/11250/3069034>
- Bakke, P. and Klevan, O.S. (1995) 'Thermodynamics of liquid silicon based alloys', in *14th PTD Conference Proceedings*. Presented at the 14th PTD Conference, Orlando, FL, USA, pp. 155–165.
- Carlberg, T. (1986) 'Calculated solubilities of oxygen in liquid and solid silicon', *J. Electrochem. Soc.*, 133, p. 1940. Available at: <https://doi.org/10.1149/1.2109053>
- Dalaker, H. and Tangstad, M. (2009a) 'Time and temperature dependence of the solubility of carbon in liquid silicon equilibrated with silicon carbide and its dependence on boron levels', *Materials Transactions*, 50, pp. 1152–1156. Available at: <https://doi.org/10.2320/matertrans.M2009034>
- Dalaker, H. and Tangstad, M. (2009b) 'Temperature dependence of the solubility of nitrogen in liquid silicon equilibrated with silicon nitride', *Mater. Trans.*, 50, pp. 2541–2544. Available at: <https://doi.org/10.2320/matertrans.M2009164>
- Ding, W. (1993) *Equilibrium relations in the production of manganese alloys*. Doctoral thesis. Norges Tekniske Høgskole (NTH), now Norwegian University of Science and Technology (NTNU), Trondheim, Norway.
- Dumay, C. and Cramb, A.W. (1995) 'Density and interfacial tension of liquid Fe–Si alloys', *Metallurgical and Material Transactions B*, 26B, pp. 173–176.
- Eldridge, J.M., Miller, E. and Komarek, K.L. (1967) 'Thermodynamic properties of liquid magnesium-silicon alloys; discussion of the Mg-group IVB systems', *Trans. Met. Soc. AIMFE*, 239, pp. 775–781.
- Elliot, J.F., Gleiser, M. and Ramakrishna, V. (1963) *Thermochemistry for steelmaking*. Addition-Wesley, Pergamon Press.
- Engl, T.A., Kvithyld, A. and Sigworth, G. (2021) *Principles of metal refining and recycling*. Oxford University Press.
- Eustathopoulos, N., Nicholas, M.G. and Drevet, B. (1999) *Wettability at high temperatures*. Elsevier.
- Folstad, M. and Tangstad, M. (2021) 'SiO₂–CaO–Al₂O₃ slags in Si/FeSi furnaces', in *Proceedings of INFACON XVI*. Trondheim, Norway. Available at: <https://doi.org/10.2139/ssrn.3922187>
- Folstad, M.B. (2023) *Slag and its effect on Si and FeSi production*. Doctoral thesis 2023:317. Norwegian University of Science and Technology (NTNU), Trondheim, Norway. Available at: <https://hdl.handle.net/11250/3096091>
- Hardy, S.C. (1984) 'The surface tension of liquid silicon', *Journal of Crystal Growth*, 69, pp. 456–460. Available at: [https://doi.org/10.1016/0022-0248\(84\)90355-5](https://doi.org/10.1016/0022-0248(84)90355-5)
- Hauge, E.G.R. (2022) *Scaling in the Si off-gas systems – the effect of alkali content*. MSc thesis. Norwegian University of Science and Technology (NTNU), Trondheim, Norway. Available at: <https://hdl.handle.net/11250/3023783>
- Hoover, H., Andersen, V., Saevarsdottir, G. and Tangstad, M. (2022) 'Excavation of 160 kW pilot scale Si furnace', *AMMS*, 9. Available at: <https://doi.org/10.31031/AMMS.2022.09.000707>

- Jakobsson, L.K. and Tangstad, M. (2015) 'Thermodynamic activities and distributions of calcium and magnesium between silicon and CaO–MgO–SiO₂ slags at 1873 K (1600°C)', *Metallurgical and Materials Transactions B*, 46, pp. 595–605. Available at: <https://doi.org/10.1007/s11663-014-0268-8>
- Jalkanen, H., Kojo, M., Krogerus, H., Niemelä, P. and Oikarinen, P. (1995) 'Cyanides in FeCr submerged arc furnace production. Theoretical and practical considerations', in *Proceedings of INFACON VII*. Trondheim, Norway, pp. 179–190. Available at: <https://www.pyrometallurgy.co.za/InfaconVII/179-Jalkanen.pdf>
- Jusnes, K.F., Hjelmseth, R., Folstad, M.B., Ditlefsen, N.S. and Tangstad, M. (2021a) 'Investigation of slag compositions and possible relation to furnace operation of a FeSi75 furnace', in *Proceedings of INFACON XVI*. Trondheim, Norway. Available at: <https://doi.org/10.2139/ssrn.3930046>
- Jusnes, K.F., Ringdalen, E. and Tangstad, M. (2021b) 'The effects of cristobalite formation on disintegration of quartz', *Materials at High Temperature*.
- Kamfjord, N.E. (2012) *Mass and energy balances of the silicon process. Doctoral thesis 2012:162*. Norwegian University of Science and Technology (NTNU), Trondheim, Norway. Available at: <https://hdl.handle.net/11250/249043>
- Klevan, O.S. (1997) *Removal of C and SiC from Si and FeSi during ladle refining and solidification. Doctoral thesis 1997:11*. Norwegian University of Science and Technology (NTNU), Trondheim, Norway. Available at: <https://hdl.handle.net/11250/248844>
- Kubaschewski, O., Alcock, C.B. and Spencer, P.J. (1993) *Materials thermochemistry*. 6th edn. Pergamon Press.
- Liang, S.-M. and Schmid-Fetzer, R. (2014) 'Modeling of thermodynamic properties and phase equilibria of the Si–P system', *J. Phase Equilib. Diffus.*, 35, pp. 24–35. Available at: <https://doi.org/10.1007/s11669-013-0269-3>
- Lu, H.M. and Jiang, Q. (2005) 'Surface tension and its temperature coefficient for liquid metals', *J. Phys. Chem. B*, 109, pp. 15463–15468. Available at: <https://doi.org/10.1021/jp0516341>
- Miki, T. (1999) 'Thermodynamic properties of Si–Al, –Ca, –Mg binary and Si–Ca–Al, –Ti, –Fe ternary alloys', *JIM*, 40, pp. 1108–1116.
- Miki, T., Morita, K. and Sano, N. (1997) 'Thermodynamic properties of titanium and iron in molten silicon', *Metall Mater Trans B*, 28, pp. 861–867. Available at: <https://doi.org/10.1007/s11663-997-0014-6>
- Miki, T., Morita, K. and Sano, N. (1996) 'Thermodynamics of phosphorus in molten silicon', *Metall Mater Trans B*, 27, pp. 937–941. Available at: <https://doi.org/10.1007/s11663-996-0007-x>
- Mostafa, A. and Medraj, M. (2017) 'Binary phase diagrams and thermodynamic properties of silicon and essential doping elements (Al, As, B, Bi, Ga, In, N, P, Sb and Ti)', *Materials*, 10, p. 676. Available at: <https://doi.org/10.3390/ma10060676>
- Mukai, K., Yuan, Z., Nogi, K. and Hibiya, T. (2000) 'Effect of the oxygen partial pressure on the surface tension of molten silicon and its temperature coefficient', *ISIJ International*, 40, pp. S148–S152. Available at: https://doi.org/10.2355/isijinternational.40.Suppl_S148
- Myrhaug, E.H. (2003) *Non-fossil reduction materials in the silicon process – properties and behaviour. Doctoral thesis 2003:67*. Norwegian University of Science and Technology (NTNU), Trondheim, Norway.

- Nogi, K. and Ogino, K. (1994) 'The effect of oxygen on the surface tension of molten silicon', *Journal of the Japan Institute of Metals*, 58, pp. 437–442.
- Nozaki, T., Yatsurugi, Y. and Akiyama, N. (1970) 'Concentration and behavior of carbon in semiconductor silicon', *J. Electrochem. Soc.*, 117, p. 1566. Available at: <https://doi.org/10.1149/1.2407385>
- O'Mara, W.C. (1990) 'Oxygen, carbon and nitrogen in silicon', in *Handbook of Semiconductor Silicon Technology*. Elsevier S&T, pp. 451–549.
- Oterkjær, H. (1976) *A study of the Al- and Ca-balance of industrial production of FeSi75. Doctoral thesis*. Norges Tekniske Høgskole (NTH), now Norwegian University of Science and Technology (NTNU), Trondheim, Norway.
- Ottem, L. (1993) Solubility and thermochemical data of oxygen and carbon in liquid alloys of silicon and ferrosilicon. SINTEF Report No. STF34 F93027. Trondheim, Norway.
- Rao, Y.K. and Belton, G.R. (1981) 'Thermodynamic properties of Mg–Si system', in *Chemical Metallurgy – A Tribute to Carl Wagner*. Presented at the Carl Wagner commemorative symposium on metallurgical thermodynamics and electrochemistry, TMS-AIME, pp. 75–96.
- Rein, R. (1965) 'Activities in the liquid solution SiO_2 – CaO – MgO – Al_2O_3 at 1600°C', *Transactions of the Metallurgical Society of AIME*, 223, pp. 415–425.
- Robinson, V.S. and Tarby, S.K. (1971) 'The thermodynamic properties of liquid Ag–Si alloys', *Metall Trans*, 2, pp. 1347–1352. Available at: <https://doi.org/10.1007/BF02913358>
- Roscoe, R. (1953) 'The viscosity of suspensions of rigid spheres', *Brit. J. Appl. Phys.*, 3, pp. 267–269. Available at: <https://doi.org/10.1088/0508-3443/3/8/306>
- Saadieh, R. (2024) *Process phenomena in furnaces producing ferrosilicon alloys*. Doctoral thesis 2024:199. Norwegian University of Science and Technology (NTNU), Trondheim, Norway. Available at: <https://hdl.handle.net/11250/3132796>
- Safarian, J., Kolbeinsen, L. and Tangstad, M. (2012) 'Thermodynamic activities in silicon binary melts', *Journal of Materials Science*, 47, pp. 5561–5580. Available at: <https://doi.org/10.1007/s10853-012-6449-4>
- Sigworth, G.K. (2020) 'Thermodynamics of dilute liquid silicon alloys', *Canadian Metallurgical Quarterly*, 59, pp. 251–261. Available at: <https://doi.org/10.1080/00084433.2020.1771012>
- Stull, D.R. and Prophet, H. (1971) JANAF thermochemical tables. 2nd edn. NIST.
- Tang, K., Chou, K.-C. and Lu, X. (2013) 'Modeling the interfacial tension of Fe–O–Si/ SiO_2 – CaO – Al_2O_3 –FeO system using the modified Gibbs energy minimization technique', *Journal of Metals and Metallurgy*.
- Tang, K., Olsen, J., Johansen, S. and Kolbeinsen, L. (2009) 'Modeling of the surface/interfacial tension for the ladle refining of silicon metal process', in *Proceedings of the VIII International Conference on Molten Slags, Fluxes and Salts*. Santiago, Chile.
- Tang, K., van der Eijk, C., Gouttebroze, S., Du, Q., Safarian, J. and Tranell, G. (2022) 'Rheological properties of Al_2O_3 – CaO – SiO_2 slags', *Calphad*, 77, 102421. Available at: <https://doi.org/10.1016/j.calphad.2022.102421>
- Turkdogan, E.T. (1983) *Physiochemical properties of of slags and glasses*. London: The Metal Society.

- Utigard, T. (1994) 'Surface and interfacial tensions of iron based systems', *ISIJ International*, 34, pp. 951–959.
- Wagner, C. (1952) *Thermodynamics of alloys*. Cambridge, MA: Addison-Wesley Press.
- Yaws, C.L., Li, K.-Y., Hopper, J.R., Fang, C.S. and Hansen, K.C. (1981) *Process feasibility study in support of silicon material Task 1. Final report to Jet Propulsion Laboratory*. Californian Institute of Technology under NSA contract NA7100 for the U.S. Dept. of Energy, Division for Solar Energy.
- Yoshikawa, T., Morita, K., Kawanishi, S. and Tanaka, T. (2010) 'Thermodynamics of impurity elements in solid silicon', *Journal of Alloys and Compounds*, 490, pp. 31–41. Available at: <https://doi.org/10.1016/j.jallcom.2009.09.190>
- Yurkov, A.L. and Polyak, B.J. (1995) 'Contact phenomena in interactions in the system SiC–SiO₂–R_xO_y in condensed matter', *J. Mat. Sci.*, 30, pp. 4469–4478.
- Zaitsev, A.I. and Kodentsov, A.A. (2001) 'Thermodynamic properties and phase equilibria in the Si–B system', *JPE*, 22, pp. 126–135. Available at: <https://doi.org/10.1361/105497101770338987>
- Zaitsev, A.I., Litvina, A.D. and Shelkova, N.E. (2001) 'Thermodynamic properties of Si–P melts', *High Temperature*, 39, pp. 227–232. Available at: <https://doi.org/10.1023/A:1017570715796>

