Solar Silicon Processes
Technologies, Challenges, and Opportunities
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Conventional and Advanced Purification Processes of MG Silicon

Publication details
Yves Delannoy, Matthias Heuer, Eivind Øvrelid, Sergio Pizzini
Published online on: 05 Oct 2016

How to cite :- Yves Delannoy, Matthias Heuer, Eivind Øvrelid, Sergio Pizzini. 05 Oct 2016, Conventional and Advanced Purification Processes of MG Silicon from: Solar Silicon Processes, Technologies, Challenges, and Opportunities CRC Press
Accessed on: 26 Aug 2020

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## Conventional and Advanced Purification Processes of MG Silicon

Yves Delannoy, Matthias Heuer, Eivind Øvrelid, and Sergio Pizzini

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3.1 INTRODUCTION

Studies and developments of processes which could be used to convert metallurgical grade (MG)-silicon or any kind of impure silicon in a solar grade (SoG) feedstock started early in the 1980s in the United States, Europe, and Japan with almost common objectives and strategies [1].

The main aim was to demonstrate that physical, chemical, and metallurgical treatments of MG-Si in the molten or solid state, would bring it to a SoG quality, and then to photovoltaic (PV) applications. These processes would avoid its full conversion in a gaseous compound (trichlorosilane or silane), as is the case of the Siemens or of the fluidized-bed processes, which were at that time too expensive to retard PV development dramatically.

In spite of the revolutionary improvement of gas phase processes and the consequent decrease of the cost of electronic grade (EG) silicon, which occurred in the last two decades, R&D in the field of MG-Si upgrading continued and still continues, with the aim to develop a SoG process capable to compete in terms of cost and environmental friendship with the gas phase processes [2–11].

Most of these studies were very successful in terms of basic results, few in terms of industrial applications, with the unique exception* of the Elkem process (see Chapter 4).

The main result was the identification and the preliminary development of a sequence of basic steps addressed at the selective removal of impurities [6].

This sequence consists of

- A stage based on vacuum sublimation, carried out mostly to remove phosphorous
- A stage based on the use of reactive gases (oxygen and chlorine) bubbled in a molten Si bath to remove volatile impurities such as chlorides and oxides
- An intermediate stage based on the use of liquid/liquid impurity extraction processes using molten salts or metals as extracting media
- A hydrometallurgical process on silicon powders, obtained by crashing the material upgraded in the first three steps, addressed at the solubilization of metallic impurities with acid solutions, mostly based on HCl
- And a final purification stage based on the directional solidification (DS) of a molten silicon bath to get an oriented polycrystalline ingot of SoG quality

The benefits of the first two steps, which could be carried out either in a vacuum chamber (the first one) or in a furnace with appropriate gas manifolds, are associated to the high vapor pressure of P and to the volatility of many metallic chlorides (FeCl3 and AlCl3) and of some oxides, as boron oxide (BO), at the melting temperature of silicon. The volatility of BO could be increased using wet gases, which favor the formation of boron hydroxides.

The intermediate step is a true pyrometallurgical process used for the liquid/liquid extraction of metallic and nonmetallic impurities which present favorable

* Silicor and Ferroatlantica are recent additional exceptions, but not yet at an industrial stage, see later in this chapter.
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segregation coefficients in suitable slags. Silicates, carbonates, and fluorides are the most common extracting media for silicon.

At the end of the slagging process, liquid silicon could be mechanically separated from the reacted slag if the respective densities are different, or the mixture is cooled down at room temperature and the silicate matrix is dissolved in an acid solution, after grinding, in the due of a hydrometallurgical process.

The success of the hydrometallurgical process depends on the size of the Si powders used, as the HCl-based acid solutions interact only with impurities segregated at the surface of the grains and the yield of the process of repartition of impurities between the bulk and the surface depends on the surface area.

The yield and the safety of this process is limited by the pyrophoricity of the silicon powders in air and in aqueous media, while it is favored by the use of suitable alloys of silicon, as is the case of Ca–Si alloys, which will be discussed in Section 3.2.4.

As an alternative to the use of slags as extracting media, metals might also be used, with Al as the most favorable candidate. In this case, purified silicon is separated mechanically from the reaction mixture and then submitted to a further purification using DS to grow a silicon ingot. We will show that this process is now carried out at industrial level by Silicor (see Section 3.3.2).

Eventually, a DS growth provides the last purification process, arising from the repartition of the impurities between the liquid and solid phase, favored by the very low segregation coefficients of most metallic impurities in silicon. The limit of this process, with respect to PV applications, is a practically negligible B and P segregation efficiency as we have seen in Chapters 1 and 2.

Each process step presents a number of challenges, most, but not all, of them have been practically overcome in the course of more than four decades of research and industrial development, within the limits dictated either by chemistry or physics.

Silicon compatibility with crucible materials adds additional limits in terms of process temperatures and contamination [12]. Typical, but not exhaustive, is the case of P-removal by vacuum evaporation (see Section 3.2.1), where the use of graphite containers is needed to operate the process at temperatures well above the maximum temperature of quartz crucibles utilization, with the drawback of heavy carbon contamination.

Due to massive R&D investments carried out in the last 10 years to optimize the traditional polysilicon routes, which lead to very large cost reductions, it could be now questioned whether advanced purification of MG-Si could compete in terms of cost (and PV conversion efficiency) with advanced gas phase processes.

To arrive at a conclusion, we intend to discuss first the basic chemical and physical backgrounds of the processes envisaged for this aim and then to report on some relevant processes which are close to a full industrial stage. A full chapter (Chapter 4) will be, however, devoted to the process developed by Elkem, in view of its already being in the market.

---

* Silicon is insoluble in HCl solutions.
† As individual impurities or as separate phases in the case of supersaturation conditions.
‡ Siemens and fluidized bed reactor (FBR).
3.2 CHEMISTRY AND PHYSICS OF MG-Si PURIFICATION

3.2.1 VACUUM SUBLIMATION

As already shown in Chapter 2, some of the impurities present in MG-Si (P, Mg, Al, and Ca) exhibit relatively high vapor pressures at the melting temperature of silicon (see Figure 3.1) [13].

Their actual vapor pressures depend, of course, on their concentration according to the equation

\[ p_i = p_i^\circ f(x_i) \]  (3.1)

which holds for single impurity melts.

In the ideal solution approximation, holding for very dilute solutions, the \( f(x_i) \) term is close to one and the values reported in Figure 3.1 should be lowered by a factor \( 10^3 \text{–} 10^6 \), depending on the specific impurity concentration \( x_i \), to get the final theoretical pressure.

If strong interaction among a dissolved impurity and the silicon solvent occurs, the thermodynamics of the vapor/liquid equilibrium depends on the details of the

![Graph of vapor pressures vs. temperature](image-url)

**FIGURE 3.1** Vapor pressures of the elements as a function of the temperature. (After J. Safarian and M. Tangstad, 2012. Vacuum refining of molten silicon, Metall. Mater. Trans. B, 43 1427–1445. Open access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.)
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interaction process, which could be described by several models, starting from the
regular solutions one [12, pp. 29–33]. The kinetics of impurities evaporation is, how-
ever, the main factor for the practical feasibility of the process, which implies at
least a diffusive transfer of the impurity from the bulk of the sample to the impurity-
depleted surface and a fast evaporation process from the melt surface.

Vacuum sublimation might be, therefore, enhanced either by mechanical stirring
or by local heating of a thin surface layer of molten silicon, where surface renewal
might be very fast, using plasma or e-beam heating.

Among the different impurities contaminating MG-Si, which has been dealt with
in Chapter 1, Figure 3.1 shows that P (but also Al, Ca, and Mg) does present the most
favorable conditions to be removed by vacuum evaporation from a molten MG-Si
bath, with a limited loss of silicon. This was the main reason why vacuum evapora-
tion was considered, since the end of the 1980s, a promising route for volatile impuri-
ties removal from MG-Si.

As an example, the removal of P, Ca, and Al impurities from molten silicon by
vacuum evaporation has been originally studied by Suzuki et al. [14] starting with
a MG-Si sample containing a total amount of about 1000 ppm of heavy elements
and 10 ppmw of B and P.

They showed that the rate of removal depends on the nature of the chemical spe-
cies, increases with the melt temperature and decreases with time (see Figure 3.2),
and that Ca is together with P the impurity easier to be removed.

![Figure 3.2](image_url)
They also show that the evaporation rate follows approximately a first-order kinetics

$$\frac{dC}{dt} = k_m \frac{(A/V)}{(C - C_i)}$$  \hspace{1cm} (3.2)

$$\ln \frac{C_i - C_f}{C - C_i} = k_m (A/V)t$$  \hspace{1cm} (3.3)

(see Figure 3.2b), where $C_i$ is the impurity concentration, $C_f$ is its equilibrium concentration, $k_m$ is the mass transfer coefficient, and $A$ and $V$ are the surface area and volume of the melt, respectively.

They eventually demonstrated that the rate determining step of the evaporation process of these impurities is their diffusion in the bulk toward the melt surface, once the initial impurity content has been removed.

The issue has been recently revisited by S. Zheng et al. [15], who were able to show (see Figure 3.3) that at relatively low temperatures ($T < 2173$ K), the mass transfer coefficient of the process $K_p$ fits with that of the surface evaporation $K_c$, while at higher temperatures, the rate determining step is the mass diffusion in the melt, with a rate constant $K_m$.

![FIGURE 3.3 Calculated temperature dependence of the mass transfer coefficients: $K_p$ is the effective mass transfer coefficient while $K_c$ accounts for surface evaporation, $K_g$ for the mass transfer in the gas phase, and $K_m$ for the mass transfer in the melt. (With kind permission from Springer Science+Business Media: Metall. Mater. Trans. A, Numerical simulations of phosphorous removal from silicon by induction vacuum refining, 42a, 2011, 2214–2225, S. Zheng, T. A. Engh, M. Tangstad, and X. I. Luo.)](image-url)
A. Souto et al. [16] applied the vacuum refining process to an already purified MG-Si material, with an initial Ca and P concentration of 1.4 and 3.3 ppmw. The process was carried out in an electrically heated furnace, held at 0.1 Pa during the evaporation process, using a graphite container for a charge of silicon of 500 kg.

Working in the temperature range 1550–1650°C, variable concentrations of Ca and P could be evaporated from the charge, with amounts significantly increasing with the increase of temperature and process time (see Figure 3.4).

**FIGURE 3.4** Temperature dependence of a vacuum evaporation process on the P and Ca content of molten charges of 500 kg of silicon. The sequence of isothermal concentration in the diagrams corresponds to increasing process times in the range of 180 and 510 min. (Data after A. Souto et al., 2014. Industrial scale vacuum applications in the FerroSolar project, in *Silicon for the Chemical and Solar Industry XII*, Trondheim, Norway, pp. 67–76, June 23–26.)
While it is demonstrated that the process works well in the case of P, some spread of data at intermediate temperatures is observed in the case of Ca, whose origin could have the same nature (previous oxidation treatments) as for the case of crystal system experiments carried out within a Department of Energy (DOE) project in the United States [17].

They conducted sequential vacuum evaporation tests at temperatures around 1500°C, starting from a purified commercial MG-Si. Figure 3.5 displays the results of a representative experiment carried out at 1500°C, starting from a sample containing 8 ppm of Al, 15 ppm of P, and 30 ppm of Ca. The mass of the samples amounted to 17 kg. It could be seen that the rate of the evaporation process depends on the nature of the impurity, only P showing a systematic decrease with the increase of the total process time, while the concentration of Ca and Al remains unaffected in the first runs, followed by a rapid decrease at the end of the experiment.†

In the course of the same experiment, it was also observed that the half time of the process increases with the decrease of the impurity content and was of the order of 15 h in the last run, enabling a final P-concentration of 0.3 ppmw to be reached.

The kinetics of P volatilization might be understood considering that the rate of the process is melt-diffusion controlled and that the composition of the melt affects the yield of the process, due to impurity interaction events, with a consequent decrease of the isolated impurities concentration in solution and of their vapor

![Figure 3.5](image_url)


* Compatible with the use of quartz crucibles.
† No explanation is given by the authors for the anomalous behavior of Ca and Al.
pressure and diffusivity. This conclusion is in good agreement with the results of Safarian and Tangstad [18], who showed that P removal is faster from cleaner melts.

Also, the anomalous behavior of Ca and Al in Figure 3.5 might be understood as due to impurity interaction processes.

In fact, if the MG-Si sample used in the experiments would come from a feedstock originally submitted to an oxidizing treatment (see next section), Ca and Mg would be present in the form of oxide (micro-)precipitates* which remain distributed in the solid matrix after cooling.

Ca and Al present in a MG-Si feedstock in the form of oxides cannot be removed by a vacuum treatment, but could, instead, segregate at the sample surface during a long thermal anneal, simulating the effect of a vacuum evaporation.

Among the number of vacuum evaporation attempts, P removal by local e-beam heating of a layer of molten MG-Si continuously fed into a water-cooled copper mold has been successfully proven by N. Yuge et al. [2] in the frame of a Japanese New Energy and Industrial Technology Development Organization (NEDO) project involving the company Kawasaki Steel.†

It was demonstrated that P content could be decreased to 0.1 ppmw, depending, however, on the silicon supply rate (see Figure 3.6), but no information is given about the contemporary loss of silicon.

---

* Whose presence could not be revealed by scanning ion mass spectrometry (SIMS) or other analytical techniques.

† In this process, the P concentration is initially reduced under vacuum, followed by a first directional solidification (DS) step to reduce the concentration of Al and Fe impurities. Boron is then removed from the surface by reaction with Ar plasma and water vapor, and finally a second DS growth leads to a good SoG silicon. Laboratory results were encouraging, but the overall cost of the process was presumably too high, also due to the use of two DS growths.
An unavoidable drawback of vacuum evaporation processes is the condensation of impurity vapors on the cold zones of the vacuum system* and to impurity contamination (e.g., carbon or oxygen) arising from the melt-container walls interaction. The latter could be, however, minimized (but never suppressed) by a suitable choice of container materials.

For all these reasons, vacuum sublimation of P from MG-Si melts is still considered a promising technological step for the production of SoG-Si [7], yet some concerns remain for its full industrial utilization.

### 3.2.2 Gas Phase Purification (Dry Gases)

Gas (O\(_2\) and Cl\(_2\)) blowing in a ladle filled with molten silicon has been, and still is, an industrial practice in the MG-Si industry, used to reduce the concentration of impurities which could be selectively oxidized or chlorinated. Impurity removal by blowing dry and wet oxygen has also been a widely studied process used to upgrade MG-Si to solar silicon [6,19–21]. The theoretical yield of these processes depends on the thermodynamic equilibrium relationships between dissolved impurities and the corresponding oxygenated

\[
\text{mMe} + n\text{O}_2 \rightleftharpoons \text{Me}_m\text{O}_{2n} \quad (3.4)
\]

or chlorinated species

\[
\text{mMe} + n\text{Cl}_2 \rightleftharpoons \text{Me}_m\text{Cl}_{2n} \quad (3.5)
\]

or hydrated species, in the case of use of wet gases (see next section).

Chlorination processes are particularly appropriate for Al and Fe removal, due the volatility of the corresponding chlorides, but hard environmental and materials degradation phenomena occur† at temperatures above the melting temperature of silicon using chlorine gas, discouraging their use in SoG-Si production processes.

Milder conditions could be, however, applied using silicon tetrachloride (SiCl\(_4\)) instead of chlorine as the chlorinating gas, to remove Al as volatile AlCl\(_3\) from molten MG-Si [22]. Working at 1450°C on a molten silicon bath with an initial Al concentration of 1527 ppm, a residual concentration of 128 ppm has been measured after 60 min of treatment. The calculated effect of a multiple step procedure shows that after four subsequent steps the final Al content would reach a value close to 0.5 ppmw.

The results are encouraging, and of potential use‡ as the final purification of a silicon feedstock purified with the Al-smelting process (see Section 3.2.6).

Oxidation processes present, instead, the best practical conditions for a preliminary purification process of a MG-Si meltstock from Ca, Mg, Al, and Ti impurities,

---

* With the formation of crusts that could fall back in the silicon melts.
† But also the volatilization of silicon in the form of silicon chlorides.
‡ This is the opinion of one (S.P.) of the chapter’s author, not of the company.
as could be observed in the Ellingham diagram reported in Figure 3.7 [23]. It does allow, in fact, the identification of these impurities as those that present the thermodynamic conditions to be preferentially oxidized and which, therefore, would allow favorable process paths.

From Figure 3.7, one could see, in fact, that the oxidation of Ti, Al, Mg, and Ca is thermodynamically favored with respect of that of silicon. These impurities are, therefore, the possible targets of a preferential oxidation process and their residual (theoretical) concentration might be calculated for the equilibrium between a dissolved impurity Me, a divalent oxide, and silica in a silicon melt (with silicon, MeO, and SiO$_2$ at unit activity) by writing the following equation:

$$2\text{Me}(a_{\text{Me}}) + \text{SiO}_2 \rightleftharpoons 2\text{MeO} + \text{Si} \quad (3.6)$$

where $a_{\text{Me}}$ is the residual Me activity in equilibrium conditions, with SiO$_2$, MeO, and Si at unitary activity.

In turn
\[ a_{Me} = \exp \left( -\frac{2\Delta G^{\text{MeO}}_{\text{MeO}} - \Delta G^{\text{SiO}_2}_{\text{SiO}_2}}{2RT} \right) \] (3.7)

where \( \Delta G^{\text{MeO}}_{\text{MeO}} \) is the standard Gibbs free energy of MeO formation, \( \Delta G^{\text{SiO}_2}_{\text{SiO}_2} \) is the corresponding value for silica at the melting temperature of silicon, and the activity \( a_{Me} = y_{Me}^{x_{Me}} \) would be equivalent to the impurity concentration \( x_{Me} \) in the range of dilute solutions, for which the activity coefficient \( y_{Me} \) is unitary.

The calculated, residual absolute activities of Ca, Mg, Ti, and Al at 1763 K amount, respectively, to \( 10^{-4}, 10^{-2}, 10^{-0.5}, \) and \( 10^{-3} \), showing that dry oxidation is particularly effective for Ca and Al. These figures are in good agreement with those reported by Tuset [24], who quotes a concentration of \( 8.06 \times 10^{-2} \) (Al w%) and \( 9.94 \times 10^{-3} \) (Ca w%) at 1550°C.

The oxidation with oxygen or with mixtures of oxygen in an inert gas is a practical tool, but suffers from unavoidable, silicon oxidation losses, which, however, favor the formation of a supernatant silicate slag as the stable final oxidation product in which impurities are collected.

As the equilibrium oxygen pressure in Si that arises when silicon is in equilibrium with its oxide is that needed to oxidize Ca, Mg, Ti, and Al, the oxidation of these impurities could be carried out by equilibrating a MG-Si melt with SiO\(_2\) [25]. An alternative to SiO\(_2\), SiO\(^+\) could also be used as oxidant. The amorphous SiO phase is stable, but it easily disproportionates to Si and SiO\(_2\) (see Figure 3.8)

\[ 2\text{SiO} \rightleftharpoons \text{SiO}_2 + \text{Si} \] (3.8)

as the Gibbs free energy of reaction (3.8) is slightly more negative than that of SiO formation [26].

Both processes present the advantage to suppress the loss of silicon by side oxidation but have the drawback of kinetic hindrances. The use of silica powder implies, in fact, the oxidation of the impurities at the silica/silicon melt interface, a process that involves their slow diffusion at the reaction interface. The use of SiO vapors implies the direct interaction of SiO\(^+\) with the impurities dissolved in the liquid silicon phase, a potentially slow process, which might be, however, enhanced by blowing SiO in the silicon mass associated to a vigorous stirring of the liquid bath. Details on the process kinetics are not reported in literature, but the best results should be obtained with the use of an induction furnace that would enable electromagnetic stirring.

Also carbon, present in MG-Si as dissolved carbon or segregated as SiC, when the melt is carbon saturated, is another impurity that could be removed by oxygen.

One can see in Figure 3.7, in fact, that oxidation of carbon (at unit activity) to CO is thermodynamically favored with respect to Si oxidation at temperatures slightly higher than 1500°C.

---

* Not nitrogen, as nitrogen will nitridate silicon.
† SiO is a commercial product obtained by condensing SiO vapors.
‡ And the loss of crucible material.
§ And SiO\(_2\) as its decomposition product.
Decarburization of silicon melts is particularly important for solar silicon melts produced by reaction of high purity silica with high purity carbon (see Chapter 2), as these melts are carbon saturated and DS is only a partial solution [27]. The oxidative decarburization of MG-Si has been experimentally studied, among others, by Sakaguchi and Maeda [28].

They used as the oxygen source either the quartz crucible in which a molten silicon sample* was kept under reduced pressure (10⁻³ atm) or silica powder added to the melt. The results obtained with the first method are reported in Figure 3.9 that shows that by simply melting a silicon sample contaminated with 1200 ppmw of C in a quartz crucible, decarburization occurs up to 100 ppmw. C contents lower than 1 ppmw were obtained by adding silica powder. Removal of CO under low vacuum is necessary to avoid reaction reversion.

More recently, Søiland [29] carried out a careful reexamination of the theoretical background of the carbon oxidation process, putting in evidence that the difficulty of CO exhaustion could be the reason of modest results obtained with large furnaces, as also in the case of plasma treatments.

Decarburization of MG-Si was also carried out using SiO as the oxidant [30] immediately after the tapping process.

* The experiments were carried out with small samples to facilitate the reaction.
The results are particularly interesting, as could be seen in Table 3.1, that shows that a relatively short test (48 min) carried out at 1700°C allows bringing the final C content at 5 ppmw in a MG-Si sample with an initial content of 1120 ppmw.

### 3.2.3 Boron Removal by Wet Gas or Plasma

A purely oxidative refining has little or no effect on B-concentration, due to the unfavorable thermodynamics of the process, in spite of the volatility of BO, that shifts to the right (Equation 3.4).

The process of B-removal could be, instead, carried out using wet gases (mixtures of hydrogen or inert gases with water vapor) [20,31–35] that favor the volatilization of B as boron hydride or oxyhydride species.

It is, however, known [36,37] that the reaction does not occur at a reasonable rate unless the partial pressure of oxygen is maintained lower than that leading to the formation of a surface layer of SiO₂, that would block the interface reaction.

B removal might be better carried out in the presence of steam or/and hydrogen, or operating the process under plasma conditions, which favor the dissociation of water vapor

\[
H₂O ⇌ H₂ + \frac{1}{2}O₂
\]  

(3.9)
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with the formation of ionized and radicalic species that are kinetically very active, as shown by early research using inductive plasma in France [37,38] and arc plasma in Japan [36,39,40].

The NEDO process (see Chapter 6) and the Photosil process (see Section 3.3.1.2) are examples of processes developed on the industrial scale in Japan and in France, respectively,* but the need remains to improve the boron removal yield and rate for a full accomplishment with PV requests.

Understanding the kinetic aspects and increasing the rate of the B-purification processes by wet and plasma processes are, therefore, still hot research subjects not only in France [41,42], but also in Norway [43,44], China [19], Korea [45], and the United States [46].

Wet and plasma processes might differ by

- The type of injection: Bubbling into the liquid (see Figure 3.10) or blowing at the surface (Figure 3.11)
- The mixture of injected: Plasma or “cold” gas
- The nature of reactive gases: O₂ and H₂, or H₂O and eventually H₂

However, both have in common an interface between the liquid silicon and a gaseous phase, where the boron removal takes place. In a plasma process, the reactive species can be provided as H and O atoms, or OH⁻ radicals, but the stable reacting species at the temperature of liquid silicon is always H₂O. The thermodynamics of the process can thus be discussed considering H₂O as an oxidant, keeping in mind that the actual kinetic behavior could differ, depending on the process route (wet or plasma).

Boron is removed in such processes in the form of gaseous products that were thought to be boron oxides (BO, B₂O₃) in early studies. However, a drastic increase of the purification rate is observed when hydrogen is present in the gases together with oxygen (eventually in the form of water vapor). In all cases with hydrogen, boron is removed as a hydroxide, the best candidate being HBO, as shown by Alemany et al. [37].

* With the latter still in development to reduce its cost.
Thus, the boron removal reaction can be written*

\[
\text{B}_2\text{H}_6 + \text{H}_2\text{O} \rightleftharpoons \text{HBO}^+ + \frac{1}{2}\text{H}_2
\]  

(3.10)

This reaction is in competition with the oxidation of silicon, which should be suitably addressed at the production of SiO vapors and not of SiO$_2$, in order to avoid the formation of a slag that would block the reaction occurring at the surface between liquid silicon and the gas phase.

This condition would limit the oxidant contents in the gas phase [36,37] (and the oxidation rate), but this limit can be pushed back by increasing the temperature.

---

* As in earlier chapters, a chemical symbol in a reaction equation could bring a superscript indicating the thermodynamic state and a subscript indicating the nature of the phase in which it is dissolved.
Silicon oxidation models such as that of Ratto et al. [47] or its extension with hydrogen [48] are needed to understand and predict this limit.

### 3.2.3.1 Chemistry of Oxidative B Removal

In active oxidation conditions (direct gas–liquid contact), the analysis of the overall process in equilibrium conditions might be discussed by assuming, first, that the silicon oxidation reaction at the surface occurs with the formation of a volatile SiO species

\[
Si^{1+} + H_2O \rightleftharpoons SiO + H_2
\]  

(3.11)

The competition between boron removal and silicon oxidation processes (reactions 3.10 and 3.11) might be controlled by chemical kinetics (depending on the active reaction path) or by some low transport processes of chemical species from the bulk to the surface or across the interface (see details in next section).

In the case of absence of reaction kinetics hindrances, the system is at its chemical equilibrium and the balance between the B removal and silicon oxidation is given by the equilibrium constant of the reaction

\[
SiO^r + B_{Si} + \frac{1}{2} H_2 \rightleftharpoons Si + HBO
\]  

(3.12)

\[
K = \frac{P_{HBO}}{P_{SiO}a_{B(Si)}} \cdot P_{H_2}^{-1/2}
\]  

(3.13)

where \( a_{B(Si)} \) is the activity of B in liquid silicon relative to the equilibrium conditions of reaction 3.12.

For given conditions at the interface (partial pressure of SiO and \( H_2 \) pressure), the HBO pressure in the gas phase at equilibrium is thus proportional to the boron concentration in the liquid.
For a transport limited process with the interface at equilibrium, the boron removal rate is proportional to this equilibrium HBO partial pressure and thus to the boron concentration in the liquid, which gives a pseudo first-order reaction

$$r(\text{mol/sec}) = -\frac{d[B]}{dt} = k[B]$$

(3.14)

Such a first-order process was found experimentally in plasma [36,37] and in wet gas processes [44].

Furthermore, both the experimental values of the “enrichment factor,” defined (and measured) in Reference 41 as the ratio of the boron concentration in the gas phase to the boron concentration in the liquid phase for a plasma process and of the rate constant \(k\) measured in Reference 44 for wet gas process, were found to satisfy conditions of thermodynamic equilibrium, showing that rate of the overall process is actually, not limited by reaction kinetics hindrances [48].

The thermodynamic equilibrium of reaction (3.12) depends on \(K_p/\gamma_B\) and then on the formation enthalpy and entropy of HBO and SiO, and on the activity coefficient of boron in silicon [41]. Although only a limited amount of thermodynamic data is available for SiO [49], for HBO [43], and for the activity coefficient \(\gamma_B\) of B in Si (at 1723 K \(\gamma = 0, 24\)) [50], within the uncertainty of the known data, the calculated values relative to the equilibrium conditions of reaction 3.12 well correspond to the experimental values found for both a plasma [41] and for a gas blowing process [44].

For both process conditions, thermodynamics predicts, also, that the boron to silicon ratio should decrease when the temperature increases (see Figure 3.12), and that the purification rate increases as \(p_{H_2}^{1/2}\) when the partial pressure of hydrogen increases in the blown gases (see Figure 3.13).

Therefore, to increase the amount of B removal, the partial pressure of hydrogen in the blown gas should be increased (ideally, by suppressing the presence of argon or any neutral carrier gas), and the temperature should remain sufficiently low. However, lowering the temperature also lowers the maximum amount of oxygenated species that can be injected before encapsulating the liquid silicon with a layer of silica, as discussed earlier. Therefore, a compromise concerning temperature conditions has to be found for each process.

According to Tang et al. [43], a heterogeneous process occurring at the interface of silicon/gas, not reaction kinetics, controls the rate of the B-removal process.

The rate-limiting step has to be either the transport mechanisms of reactants to surface, or that of products from the surface to the reactor exhaust, according to the following paths:

- Boron transport in the liquid to the surface
- SiO or HBO transport from the surface to the bulk gas
- Oxidant transport from the bulk gas to the surface
- Overall flow of oxygen entering the reactor

Liquid phase transport has been studied numerically by Reference 51 and was found very fast, when compared to the purification rate in a laboratory plasma reactor, used with electromagnetic stirring of the bath.
FIGURE 3.12 Variations of the B/Si ratio in liquid silicon and of the calculated enrichment factor with the temperature in a plasma process.

On the base of their experimental results, Sortland and Tangstad [44,52] also found that liquid phase transfer is not rate limiting.

Other experiments with gas blowing inside the liquid [34], that promote a “vigorous stirring” of the melt, bring diffusion outcomes in the liquid phase to be negligible. Also in large size, industrial furnaces blowing inside the liquid will often promote some turbulent convection in the melt that can be enhanced with electromagnetic stirring. Thus, liquid phase transport is normally not rate limiting.

The transport of gaseous species across the gas-side boundary layer at the interface can be, instead, rate limiting, especially for blowing systems operating with a small relative velocity of the gas at the interface.

The mass transfer coefficient will be determined by the thickness of the dynamic boundary layer for surface blowing or by the size of bubbles for internal blowing, and will have roughly the same value for HBO, for the oxidizing species (H2O or O), and for SiO because of their comparable diffusion coefficients in the bulk gas. This transport phenomenon is thought to be the rate-limiting step in a number of situations. Moreover, the transport of H2O and silicon oxides becomes complicated if SiO is re-oxidized into SiO2 (solid particles) at some place in the boundary layer, which is certainly the case in most conventional process situations (except plasma processes because of their high gas temperature).

Also, the quantity of oxygen that is fed into the reactor provides a rate limitation: even for rapid transport in the melt and across the gas-side boundary layer, the total amount of SiO molecules produced is limited by the total amount of O atoms provided, or to half this amount if SiO is transformed into SiO2 above the surface. With a system remaining in equilibrium conditions (Equation 3.13), the rate of boron removal can be deduced for a given boron concentration in the melt using Equation 3.14 and the appropriate rate constant. This gives a maximum value for the boron removal rate at a given oxygen (or water vapor) flow. Increasing it is only possible by increasing the enrichment factor by the total oxygen flow, which is limited by the formation of a silica layer at the surface.

3.2.4 Acid Leaching
Cast MG-Si consists of a heterogeneous mixture of impurity-contaminated Si and of silicide (or carbide) phases of impurities present in supersaturated conditions. It is well known that silicon is insoluble in HCl mixtures, while at least silicides are soluble in it and might, therefore, be leached out.

HCl leaching can be used, therefore, in a purification process addressed at the removal of HCl-soluble impurities or compounds, but of the several leaching processes that have been tested, only that developed by Elkem [53] went to full success, as will be described in full detail in Chapter 4.

The main reason for this is that, even when MG-Si is finely ground, only the separate impurity phases, which are distributed randomly at the grain boundaries, might be dissolved by the acid mixture, while the silicon itself remains undissolved with the impurities at, or below, their equilibrium solubility.

* In these experiments, gas blowing at the surface was carried out using an induction heated graphite crucible.
In the Elkem process [54], a liquid Ca–Si alloy is preliminarily prepared by adding a few percentages of Ca to MG-Si, which is subsequently cast in a suitable mold. Different from the solidification of MG-Si, which occurs very close to the melting point of pure silicon, for the case of Ca–Si alloys (see phase diagram in Figure 3.14), the solidification initially proceeds with the segregation of silicon until the eutectic temperature is reached.

In this temperature range, the solidification occurs with the repartition of the impurities between the liquid and solid phase in pseudo-isothermal conditions, and the distribution ratio is given by the distribution coefficient

\[ k = \frac{C_s}{C_l} \]  

(3.15)

where \( C_s \) is the concentration of the impurity in the solid and \( C_l \) is that in the liquid.

Table 3.2 reports literature data for the \( k \) values of most common impurities of MG-Si, from which one observes that for most metallic impurities \( k \ll 1 \), while it is 1 or close to 1 for C, O, B, and P.

In equilibrium conditions*, the solidification process follows the classical Scheil’s equation

\[ C_s = kC_0(1 - f)^{k-1} \]  

(3.16)

where \( C_0 \) is the initial impurity concentration and \( f \) is the fraction of liquid solidified.

* That is certainly not the practical case of the casting process of Ca-rich MG-Si.
As $k \ll 1$ for most of the metallic impurities the Scheil’s equation, actually, simplifies to

$$\frac{C_s}{C_i} = k/(1 - f_s) \quad (3.17)$$

This means that in the early stage of the casting process, which implies the nucleation and growth of silicon crystallites, each single grain will present a concentration profile, with an increase of impurity concentration (for $k$ values $<1$) from a pure core toward an impurity enriched surface.

At the eutectic temperature,* the process occurs isothermally, until the entire mass is solidified, with the simultaneous segregation of Si and a CaSi$_2$ phase, in the case

* Or peritectic temperature, depending on the multinarity of the impurity system.
of a binary Ca–Si alloy, or of ternary Ca$_{2-x}$Me$_x$Si$_2$ or of multinary silicide phases in the case where silicon is contaminated by multiple impurities.

The microstructure of this heterogeneous solid is shown in Figure 3.15, where large islands of the CaSi$_2$ phase are distributed between the almost pure silicon grains. Several inclusions of different phases are, however, also present, which may present solubility problems.

It has been empirically demonstrated that the optimization of the composition of the Ca–Si alloy is essential to maximize the amount of metallic impurities segregated as mixed silicides in the calcium silicide phase.

When the alloy is reacted with a mixture of HCl and FeCl$_3$, the silicide phases are easily dissolved, leaving a rather pure silicon phase, where the concentration of a specific impurity should closely depend on the initial impurity concentration in the liquid and on their segregation coefficients.

Results of the effect of Ca alloying and leaching tests for selected impurities are reported in Table 3.3 that shows the potential of the calcium silicide route, well developed industrially by Elkem with the Silgrain process (see Chapter 4).

Different from other impurities, B and P could not be leached out with the use of Ca–Si alloys, due to the thermodynamic instability of boron silicide at temperatures above 1370°C and to the decomposition of phosphorous silicide at 1172°C due to the thermodynamic instability of boron silicide at temperatures above 1370°C and to the decomposition of phosphorous silicide at 1172°C.

### 3.2.5 Slagging Processes

It has been already shown that B is an impurity that is very difficult to remove from a MG-Si feedstock using a liquid to solid extraction process. Molten salt mixtures,
Solar Silicon Processes

Consisting generally of silicates, or mixed silicates and fluorides, are instead shown to behave as effective media for the extraction of B from liquid silicon, where it is present at parts per million (ppm).

3.2.5.1 Thermodynamic Aspects*

The basic chemistry of the process, in the case of use of an oxidic slag, is the oxidation of the impurity at the liquid/liquid interface, with the formation of an oxide

\[
\text{Me}_\text{Si} + \text{O}_{\text{slag}} \rightleftharpoons \text{MeO}_{\text{slag}} \quad (3.18)
\]

which then dissolves in the liquid slag.

The thermodynamics of a slagging process are ruled by the activity of oxygen at the reaction interface. In turn, it depends on the activity of SiO\(_2\) [55], according to the following equation:

\[
\text{O}_{\text{slag}} + \frac{1}{2} \text{Si}_{\text{Si}} \rightleftharpoons \frac{1}{2} (\text{SiO}_2)_{\text{slag}} \quad (3.19)
\]

and then on the slag composition (see Figure 3.16 for a binary SiO\(_2\)–CaO system).

In equilibrium conditions, the removal of B from Si at the reaction interface (int) is given by the following equation:

\[
\text{B}_{\text{Si}} + \frac{3}{4} (\text{SiO}_2)_{\text{int}} \rightleftharpoons \frac{3}{4} \text{Si}_{\text{Si}} + (\text{BO}_{1.5})_{\text{int}} \quad (3.20)
\]

and by the corresponding equilibrium constant

\[
K_{\text{int}} = \frac{a_{\text{Si}}^{3/4} a_{\text{BO}_{1.5}}}{a_{\text{Si}}^{3/4} a_{\text{SiO}_2}} \quad (3.21)
\]

It should be noted that reaction (3.20) would be strongly shifted to the left when pure silica would be used as the oxidant, considering that \(\Delta G_{\text{SiO}_2} \ll \Delta G_{\text{BO}_{1.5}}\). Therefore, basic fluxes are used to reduce the activity of SiO\(_2\).

* The thermodynamic aspects of slagging processes are discussed in full detail also in Chapter 6.

**TABLE 3.3**

<table>
<thead>
<tr>
<th></th>
<th>Fe (ppmw)</th>
<th>Al (ppmw)</th>
<th>Ca (ppmw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaching alloy</td>
<td>3600</td>
<td>3700</td>
<td>29,000</td>
</tr>
<tr>
<td>Leached product</td>
<td>17</td>
<td>150</td>
<td>200</td>
</tr>
<tr>
<td>Calculated values</td>
<td>0.1</td>
<td>19</td>
<td></td>
</tr>
</tbody>
</table>

For practical applications, it would be convenient to introduce mass concentrations in Equation 3.21, using $[\% B]_{\text{Si}}$ for the concentration by mass of B in the metal and $[\% B]_{\text{slag}}$ for the concentration of B by mass in the slag.

\[
K_{\text{int}} = \frac{a_{\text{Si}}^{3/4} d_{\text{BO}_1.5}}{a_{\text{SiO}_2} a_{\text{B}_{\text{Si}}}} = k^* \left( \frac{[\% B]_{\text{slag}}}{[\% B]_{\text{Si}}} f_{\text{B}_{\text{Si}}} \right) \left( \frac{a_{\text{Si}}}{a_{\text{SiO}_2}} \right)^{3/4}
\]  

(3.22)

where $\gamma_{\text{BO}_2}$ and $f_B$ are, respectively, the activity coefficients of $\text{BO}_{1.5}$ and B in the slag and metal phases. $k^*$ is the coefficient for conversion from molar fraction to the mass concentration.

From the equilibrium constant of Equation 3.22, one could get the distribution coefficient $L_B$ of B as the ratio between the B content in the slag and that in the metal

\[
L_E = \frac{[\% B]_{\text{slag}}}{[\% B]_{\text{Si}}} = \frac{K_f B}{\gamma_{\text{BO}_1.5} k^*} \left( \frac{a_{\text{B}_{\text{O}_2}}}{a_{\text{Si}}} \right)^{3/4}
\]  

(3.23)

This distribution coefficient is a measure of the possibility for removal of B from Si.
Suzuki et al. [56] tested a number of different slag systems, which included the addition of CaF₂, for the removal of B under varying temperatures and in different atmospheres. They found that the distribution coefficient depends on the slag composition (see Figure 3.17) and that optimal distribution coefficients ($L_B$) exist for various fluxes (see Table 3.4) with a maximum value of 1.7 at 1500°C. They operated with an initial B content of 30–90 mass ppm and the experimental time varied between 1.8 and 10.8 ks. The experiments were conducted under a CO atmosphere at 1500°C. Similar experiments were performed by Tanahashi et al. [57] with comparable results (see Table 3.3).

The equilibrium distribution coefficients of B between the SiO₂–CaO–Al₂O₃ or SiO₂–CaO–Na₂O slags and liquid Si melt at 1823 K were also calculated using the new assessed thermochemical databank together with the FACT oxide thermodynamic database.*

* FactSage thermochemical software and databases, Calphad, 26, 189–228.


**TABLE 3.4**

<table>
<thead>
<tr>
<th>System</th>
<th>CaO/SiO₂</th>
<th>$L_B$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO–10%MgO–SiO₂(–CaF₂)</td>
<td>~0.9</td>
<td>1.7</td>
<td>Suzuki et al. [56]</td>
</tr>
<tr>
<td>Ca–10%BaO–SiO₂(–CaF₂)</td>
<td>~1</td>
<td>1.7</td>
<td>Suzuki et al. [56]</td>
</tr>
<tr>
<td>CaO–30%CaF₂–SiO₂</td>
<td>~2.2</td>
<td>1.7</td>
<td>Suzuki et al. [56]</td>
</tr>
<tr>
<td>6%NaO₀.₅–22%CaO72%SiO₂</td>
<td>~3.3</td>
<td>3.5</td>
<td>Tanahashi et al. [57]</td>
</tr>
</tbody>
</table>
The SiO$_2$–CaO–Al$_2$O$_3$ slag seems to work better than the SiO$_2$–CaO–Na$_2$O slag. However, the calculated $L_B$ values are approximately two times higher than the experimental values [4], showing that reaction kinetic barriers may play an important role in the refining processes, as will be discussed in the following section.

As an example, if we assume for $L_B$ a value of 1.7, absence of B in the slag and 8 ppm B in the metal, the mass balance shows that 1.4 t of slag are required to reduce the B level from 8 to 1 ppm in 1 t of Si.

It is, in every case, apparent that the slag refining using silicate fluxes does not lead to a significant reduction of B content in MG-Si feedstock with a single run. Multiple runs are, therefore, needed on demand. Better results could be, however, obtained, using slags that favor the formation of an insoluble compound of B, as suggested by L. Pelosini et al. [58].

### 3.2.5.2 Kinetic Aspects

When a dissolved element is subjected to a slag treatment aimed at its removal, as illustrated in the former section, it goes through the following five steps [59] (see also Figure 3.18):

1. The impurity element X must be transferred from the bulk metallic phase to the metal boundary layer, $[X]_b \rightarrow [X]_\delta$
2. The impurity element must diffuse through the metal boundary layer, $[X]_\delta \rightarrow [X]_i$
3. The metal is oxidized at the interphase between metal and slag, $[X]_i \rightarrow (X)_i$
4. The impurity element diffuses through the slag boundary layer, $(X)_i \rightarrow (X)_\delta$
5. The impurity element is transferred from the slag boundary layer to slag bulk phase, $(X)_\delta \rightarrow (X)_b$

The rate of steps 1 and 5 depends on the proper stirring and mixing in the metal and slag phases. Although there is a serious difficulty of mixing the impurity species in the slag phase that is often very viscous, it is currently assumed the slag phase is “completely mixed.”

![FIGURE 3.18](image-url)  
**FIGURE 3.18** Concentration profile of B in the silicon and the slag, where boron is transferred from silicon to the slag.
Stirring is often carried out by gas bubbling or using mechanical devices to increase the mass transfer in the bulk phases. Hence, the thermophysical properties of the slag, such as its density and viscosity, are important to be well known to optimize the process. A high viscosity would be responsible for a low mass transfer of the impurity element.

Steps 2 and 4 depend on the mass transfer coefficient in the metal, \( k \), and in the slag, \( k_s \), respectively. With the assumptions that steps 1, 5, and 3 are much faster than steps 2 and 4, the final concentration depends only on the transfer coefficients of the impurity across the boundary layers.

The solution of the problem may be obtained by considering, first, that the accumulation rate of the impurity in the slag corresponds to its removal rate through the melt boundary layer

\[
-\frac{d\left[\%X\right]_e}{dt} = k_s A \left(\left[\%X\right]_s - \left[\%X\right]_e\right)
\]

(3.24)

where \( k_s \) is the rate constant, \( \rho \) is a resistance factor to the mass transfer, and \( \left[\%X\right]_e \) is the hypothetical concentration of X in the metal in equilibrium with the actual concentration in the slag \( \left[\%X\right]_s \) so that \( \left(\left[\%X\right]_s - \left[\%X\right]_e\right) \) is the driving force, and

\[
\left[\%X\right]_e = \frac{\gamma_x \left[\%X\right]_s}{K f_x}
\]

(3.25)

To integrate Equation 3.24 over time to get the final concentration of X in the silicon melt, \( \left[\%X\right]_e \) must be replaced by a function of \( \left[\%X\right]_s \). \( \left[\%X\right]_e \) may be obtained in terms of \( \left[\%X\right]_s \) if we note that whatever leaves the melt enters the slag

\[
M_e \left(\left[\%X\right]_e^0 - \left[\%X\right]_s\right) = M_s \left[\%X\right]_s
\]

(3.26)

where \( M_e \) is the mass of silicon, \( \left[\%X\right]_e^0 \) is the initial concentration of X in silicon, and \( M_s \) is the mass of the slag. Here, we assume that the slag originally did not contain any component X. Thus, the above equation together with Equation 3.25 gives

\[
\left[\%X\right]_e = \frac{\gamma_x M_e}{f_x K M_s} \left(\left[\%X\right]_e^0 - \left[\%X\right]_s\right)
\]

(3.27)

The driving force from Equation 3.27 becomes

\[
\left[\%X\right]_s - \left[\%X\right]_e = \left[\%X\right]_s \left(1 + \frac{\gamma_x M_e}{K f_x M_s} - \frac{\gamma_x M_e}{K f_x M_s} \left[\%X\right]_e^0\right)
\]

(3.28)
The lowest value of $[\%X]_e$ attainable, that is, the lowest content of the impurity X in liquid silicon is when the driving force given by Equation 3.28 becomes zero. Then

$$[\%X]_e = [\%X]_e^\infty \frac{\gamma_x M_s}{(K_f M_s + M_e)} [\%X]_e^0$$

(3.29)

where $[\%X]_e^\infty$ is the value of $[\%X]_e$ when equilibrium between slag and melt is finally reached (at time $t \to \infty$).

This gives, on integration of Equation 3.24 the results schematically reported in Figure 3.20, assuming that $k_r$, $y_x$, and $f_x$ are independent of time. In Figure 3.19, we see that $[\%X]$ drops exponentially down to the value $[\%X]_\infty$, corresponding to equilibrium conditions of X in the melt and in the slag.

Here, we have assumed that resistance is in the melt boundary layer. The same procedure could be repeated for the case of a resistance in the slag boundary layer with similar results.

### 3.2.6 Impurity Transfer by Liquid–Solid Segregation: Aluminum Smelting

Al is a formidable solvent of silicon (see Figure 3.20a), while being, instead, almost insoluble in solid silicon (see Figure 3.20b), with a solubility maximum of 0.02% around 1180°C ($2.9 \times 10^{19}$ at cm$^{-3}$ at 1450 K), above which a retrograde solubility behavior does occur [60].

The most interesting feature of this system is its potential to allow an efficient repartition of metallic impurities between Al–Si melts and solid silicon [61–64], due to the very small values of their segregation coefficients (see Table 3.5) that makes Al–Si melts a convenient medium for low temperature MG-Si purification [1, pp. 21–78].

![FIGURE 3.19](image-url) Removal of an impurity X from metal to slag.
FIGURE 3.20  (a) Phase diagram of the Al–Si system, (b) the solubility of Al in solid silicon. (With kind permission from Springer Science+Business Media: Bull. Alloy Phase Diagr., The Al–Si (aluminum–silicon) system, 5(1), 1984, 74–84, J. L. Murray and A. J. McAlister, Springer Copyright licence nr. 3720130976003.)
It is, eventually, interesting to observe (see Figure 3.21) that B and P segregation works better in Al–Si melts than in liquid silicon, and increases while decreasing the temperature, also making possible reasonable B and P removal, otherwise impracticable.

The main challenge of the Al-smelting process is, however, to bring the residual concentration of Al in the purified silicon feedstock below to about 0.2 ppm.

### TABLE 3.5
Temperature Dependence of the Segregation Coefficients of Metallic Impurities in Al–Si Alloys

<table>
<thead>
<tr>
<th>Element</th>
<th>1073 K</th>
<th>1273</th>
<th>1473</th>
<th>m.p. of Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>$1.7 \times 10^{-11}$</td>
<td>$5.9 \times 10^{-9}$</td>
<td>$3.0 \times 10^{-7}$</td>
<td>$6.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>Ti</td>
<td>$3.8 \times 10^{-9}$</td>
<td>$1.6 \times 10^{-7}$</td>
<td>$9.6 \times 10^{-7}$</td>
<td>$2.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>Cr</td>
<td>$4.9 \times 10^{-10}$</td>
<td>$2.5 \times 10^{-8}$</td>
<td>$2.5 \times 10^{-7}$</td>
<td>$1.1 \times 10^{-5}$</td>
</tr>
<tr>
<td>Ni</td>
<td>$1.3 \times 10^{-9}$</td>
<td>$1.6 \times 10^{-7}$</td>
<td>$4.5 \times 10^{-6}$</td>
<td>$1.3 \times 10^{-4}$</td>
</tr>
<tr>
<td>Cu</td>
<td>$9.2 \times 10^{-8}$</td>
<td>$1.2 \times 10^{-7}$</td>
<td>$2.1 \times 10^{-6}$</td>
<td>$1.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>B</td>
<td>$7.6 \times 10^{-2}$</td>
<td>$2.2 \times 10^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>$4.0 \times 10^{-2}$</td>
<td>$8.5 \times 10^{-2}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


![Segregation coefficient between solid/liquid silicon](image)

**FIGURE 3.21** Segregation coefficients of B and P in a Al–Si melt. (Reprinted from *J. Cryst. Growth*, 311, T. Yoshikawa and K. Morita, Refining of silicon during its solidification from a Si–Al melt, 776–779, Copyright 2009, with permission from Elsevier.)
fact, Al is a dopant, but also a recombining impurity [65], that behaves as a minority carrier killer at concentrations above $10^{16}$ at cm$^{-3}$ [1, pp. 53–54] [66]. On the other side, a process of Al purification using DS suffers an inappropriately high segregation coefficient of Al at the melting point of Si ($3 \times 10^{-2}$) [67, pp. 79–125]. Therefore, Al removal should be carried out using an ad hoc designed crystallization process, that involves the simultaneous occurring of a slagging step at the top surface of the silicon melt charge [68], capable to segregate Al efficiently in the slag.

A practical way to use Al smelting for the production of purified silicon is to work with MG-Si–Al melts, solidified at temperatures lower than that corresponding to the solubility maximum, typically 1273 K or lower [62] to keep the Al concentration in the segregated Si as low as possible and to favor the B and P removal. In these conditions, the excess silicon segregates as a separate phase of platelet (flakes) Si crystals, uniformly distributed into the solidified structure [62]. A purified silicon sponge could then be recovered by acid etching at room temperature of the entire solidified mass,* or the silicon flakes could be separated by agglomeration on the bottom of the furnace when the alloy is solidified in an induction field [62]. Depending on the initial sample composition, the experimental Fe content ranges between 13 and 47 ppmw, that of Ti between 2.7 and 7.7, of B between 0.81 and 0.99, of P between 0.77 and 1.2, and that of Al between 453 and 599 ppmw.

A different practice that brings much better results, is followed by Silicor [68] in its production process brought recently to the preindustrial stage. Here, in a first step, Si is crystallized from a hypereutectic Al–Si melt by slow cooling, that is interrupted just before the eutectic point is reached. The excess silicon crystallizes with a residual content of metallic and dopant impurities ruled by the segregation equilibrium

$$\mu_{Al,l}^{Me} = \mu_{Si,s}^{Me},$$

where $\mu$ is the chemical potential of the metallic impurity Me. The remaining melt after this step has around 83 wt% Al, 16 wt% Si, and 1 wt% of other impurities and is poured away leaving behind a silicon sponge which is carefully acid leached to remove the residual Al–Si eutectic covering the silicon surface.

The final process is a single crystallization growth to reconduct the feedstock to SoG purity.$^\dagger$

According to M. Heuer et al. [69], the material obtained after a solidification growth presents an Al content around 0.1 ppmw, and could be used with success as a solar silicon feedstock (see details in Section 3.3.2).

### 3.2.7 Impurity Transfer by Liquid–Solid Segregation (DS Growth and Czochralski Pulling)

The final purification of a solar feedstock arising from MG-Si is currently carried out by DS, although in the early projects Czochralski (CZ) growth was used, as DS

---

$^*$ A very expensive process.

$^\dagger$ Section 3.3.2 reports details of the preindustrial and industrial processes developed so far using Al smelting.
furnaces addressed at the growth of multicrystalline (mc) silicon ingots were not yet available.

Among the advantages of DS growth for purification purposes, the large ingot weight (up to 500 kg) and the overall process costs are the main issues, together with a larger tolerance in the initial total impurity content.

In both the DS and CZ case, the process is based on the repartition of impurities between the liquid and solid phase. In equilibrium conditions, the distribution is ruled by distribution (or segregation coefficients) \( k \), which, as already shown in Section 3.2.4, is given by the ratio

\[
k = \frac{C_s}{C_l}
\]  

(3.31)

with \( C_s \) as the concentration of the impurity in the solid phase and \( C_l \) as the concentration of the impurity in the liquid phase.

It is easy to demonstrate [67] that the effective values of the segregation coefficients \( k_{\text{eff}} \) depend on the type of growth process used, and are a function of the growth rate \( \nu \) and of the thickness \( \delta \) of the diffusion layer which sets up at the interface between the liquid and the solid phase

\[
k_{\text{eff}} = \frac{1}{1 + ((1/k_{\text{eq}}) - 1) \exp(- (\nu \delta/D))}
\]  

(3.32)

as well as of the diffusion coefficient \( D \) of the specific impurity involved in the segregation process.

Since for the majority of metallic impurities \( k \ll 1 \) (see Table 3.2), the impurities segregate mostly in the liquid phase, and liquid–solid segregation is thus an effective, and systematically applied, purification process [1,67].

For the majority of metallic elements, assuming complete mixing in the liquid phase and no practical diffusion in the solid phase, the solidification follows the Scheil’s equation

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

(3.33)

where \( C_0 \) is the initial concentration in the liquid and \( f_s \) is the fraction of liquid solidified.

It is, therefore, apparent that an impurity profile along the ingot is expected, with an increase of the impurity concentration for \( k_{\text{eff}} < 1 \) and a decrease of the impurity concentration for \( k_{\text{eff}} > 1 \).

As the equilibrium and effective segregation coefficients for B and P are close to 1, and that of oxygen is equal to 1, for these impurities the solidification process is not a purification tool.

* The reader interested in major details concerning the DS and CZ growth of semiconductor silicon may refer to Reference 12.
3.2.8 Electrochemical Purification

3.2.8.1 Electrochemical Background

At least theoretically, electrochemistry should provide a straightforward mean to get pure silicon by electrolysis of a melt in which high purity quartz has been dissolved or by anodic dissolution of MG-Si and Si electrodeposition.

This approach, however, suffers from a number of challenges, which, at the time of writing this chapter, are still unresolved. As an example, the direct use of solid MG-Si anodes is generally precluded, due to the onset of electrode passivation phenomena associated with silicon oxidation\(^*\) [70]. Moreover, electrodeposition of liquid silicon is a high temperature operation in fluoride melts,\(^\dagger\) associated to serious construction material problems. Eventually, solid silicon electrodeposition occurs under severe overvoltages, unless working at very low current densities, which leads to microcrystalline deposits that easily detach from the electrode, independently of its nature, during the electrolytic process.

Last, but not least, the electrochemical properties of elements in fluoride melts are only partially known,\(^\ddagger\) although a series of electrochemical potentials of elements in LiF–NaF melts at 1173 K (see Table 3.6) has been proposed by S. Fabre et al. [72] as an integration of the data reported by Olsen and Rolseth [73], see Table 3.7.

From these data, one could remark that Ca, Mg, and Al are more electronegative than silicon and should preferentially dissolve from a Si alloy containing these elements, leading to a potential purification process, while the B purification would be precluded, as its deposition potential

\[
E = E^\circ - \frac{RT}{3F} \ln[B^{3+}] 
\]

at its normal concentration in MG-Si (≥50 ppm w), turns out to be very close to that of silicon (see Table 3.7).

It should be also noted that a partial dissolution of the more electronegative elements present in a Si-alloy would occur also without the application of current, with

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
 & Na & Cr & Fe & Ni & Mo & W & Ag & Au \\
\hline
E/Pt (V) & -1.40 & -0.22 & +0.04 & +0.46 & +0.65 & +0.90 & +1.10 & +2.15 \\
\hline
\end{tabular}
\caption{Electrochemical Potentials of Metals versus a Pt Pseudo-Reference Electrode in LiF–NaF Melts at 1173 K}
\end{table}


\(^*\) In mixed halide–oxide melts, the anodic dissolution of silicon could be associated to oxygen evolution.

\(^\dagger\) Which are good solvents for silica.

\(^\ddagger\) Electrochemical measurements in fluoride melts using oxygen and hydrogen reference electrodes were carried out by one of the authors of this chapter [71].
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an electroless process driven by the difference of the electrochemical potentials of silicon and metallic impurities. This system behaves, in fact, in the presence of silicon ions $\text{Si}^{4+}$ in the electrolyte, like a galvanic cell in short circuit, with Si working as the cathode and the metallic impurities at the surface of the sample as the anode.

The overall rate of this currentless process would, obviously, depend on the rate of the slow partial process, here the cathodic processes, ruled by the reduction of silicon ions $\text{Si}^{4+}$ in the fused electrolyte*

$$\text{Si}^{4+} + 4e \rightleftharpoons \text{Si} \quad (3.35)$$

taking the oxidation of Ca (as well as Mg and Al) impurities in the alloy as the fast anodic process

$$2\text{Ca} \rightleftharpoons 2\text{Ca}^{2+} + 4e \quad (3.36)$$

The electroless process would play, however, only a minor role, unless reducible substances would deliberately be added to the melt, as would be the case of melts with hexafluoride $[\text{SiF}_6]^{2-}$ ions.

In the case of MG-Si–Cu alloys, which will be discussed later in this section, electroless conditions could work even better, as Cu works as the cathode and impure Si will work as the anode and would spontaneously dissolve together with its impurities, provided reducible ions are available in the electrolyte.

### 3.2.8.2 Electrochemical Processes

The first attempt to prepare Si using an electrochemical process was by Ullik who electrodeposited silicon from a molten bath of $\text{K}_2\text{SiF}_6$–KF in the temperature range 600–900°C [74]. Later authors suggested that cryolite ($\text{Na}_3\text{AlF}_6$) melts containing silica could be suitable media for the electrodeposition of silicon and of Al–Si alloys, with a process that could bring to the production of silicon and of its alloys in a single carbon-free step, resembling the Hall–Heroult process of Al production.

---

* We will show in the next section that the reduction of $\text{Si}^{4+}$ to silicon occurs with low overvoltages, but we assume here that the anodic process would be in any case faster.

---

**TABLE 3.7**

<table>
<thead>
<tr>
<th>Element</th>
<th>P/PF$_5$</th>
<th>Fe/FeF$_2$</th>
<th>Fe/FeF$_3$</th>
<th>P/PF$_3$</th>
<th>B/BF$_3$</th>
<th>Si/SiF$_4$</th>
<th>Al/AlF$_3$</th>
<th>Mg/MgF$_2$</th>
<th>Ca/CaF$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E°(V)</td>
<td>2.363</td>
<td>2.529</td>
<td>2.621</td>
<td>2.704</td>
<td>3.538</td>
<td>3.551</td>
<td>3.698</td>
<td>4.176</td>
<td>4.899</td>
</tr>
</tbody>
</table>

*We will show in the next section that the reduction of $\text{Si}^{4+}$ to silicon occurs with low overvoltages, but we assume here that the anodic process would be in any case faster.


Note: The reference is a fluorine electrode.
The solubility of silica in pure cryolite melts is, however, low (<5% at 1010°C), but it could be increased in Na₃AlF₆–Al₂O₃ mixtures. The physicochemical properties of Na₃AlF₆–Al₂O₃–SiO₂ mixtures were investigated, among others, by F. Grjotheim et al. [74], who determined also the experimental value for the decomposition voltage of SiO₂ in a cryolite melt added with 5% of silica (1.10 ± 0.1 V on a graphite electrode at 1273 K). This value is much lower than the calculated standard potential (1.675 V at 1300 K), on the hypothesis that the anodic reaction at a graphite electrode is the carbon oxidation to CO₂.

A pilot plant addressed at the electrolytic production of silicon from a SiO₂-cryolite melt was operated in the 1960s by R. Monnier [75]. A schematic drawing of the furnace used is reported in Figure 3.22, where one can remark that the crucible walls are covered by a solid layer of the electrolyte, which makes corrosion damages negligible, while heating was provided by the electrolytic current across carbon electrodes. Current densities up to 0.8 A/cm² were applied, comparable to that used in the conventional Al process, but the effective current density under which Si deposition occurs is much less.

Under these conditions, the product consisted of small silicon crystals, few millimeters in size, which only partially adhered at the carbon electrodes.

The project failed to reach industrialization, probably as a consequence of the low deposition rates, typical of solid silicon deposition (see later for details) [76] and the difficulty in collecting the silicon powder, that once melted and zone refined, was, however, of semiconductor grade according to the authors.

Since in Na₃AlF₆–Al₂O₃–SiO₂ mixtures, Al is co-deposited with Si [74], the feasibility of a pure silicon deposition using cryolite melts is excluded, and then this process is used for SoG production.*

* The role of Al as a recombining impurity is discussed in Section 3.2.6.

![Figure 3.22](image-url)
A better, Al-free electrolyte, which could be potentially used for the electrolytic purification of Si, is a mixture of $\text{K}_2\text{SiF}_6$ in a fluoride melt, because $[\text{SiF}_6]^{2-}$ is a soluble complex of Si that dissociates in fluoride (or mixed chloride–fluoride melts)

$$[\text{SiF}_6]^{2-} \rightleftharpoons \text{Si}^{4+} + 6\text{F}^- \quad (3.37)$$

leading to silicon ions that could be electroreduced [77] without significant overvoltage, provided the current density could be kept quite low. In this and in the following case, $\text{K}_2\text{SiF}_6$ is actually the silicon feedstock, and the overall process would imply its preparation from a quartz supply.

As shown earlier by Cohen and Huggins [78], the key point is, however, that working at small current densities to bring the overvoltage small, leads to very small practical deposition rates. They used a KF–LiF melt, added with 5% molar $\text{K}_2\text{SiF}_6$ at 750°C, with electrodes consisting of single crystal Si. The deposition rate was found of the order of 1 μm/h, too low to be interesting for industrial applications, in agreement with the DeMattei and Feigelson results [79] that show that the critical current for solid silicon electrodeposition is around 40 mA/cm², while current densities of 1 A/cm² are routinely employed in the case of liquid Al.

Additional details on the silicon electrodeposition in fluoride melts were given by G. M. Rao et al. [80], who carried out the electrodeposition of silicon on a silver electrode from a ternary LiF–NaF–KF eutectic at 750°C, with $\text{K}_2\text{SiF}_6$ additions in the range 0.5–6 mol%.

At the highest $\text{K}_2\text{SiF}_6$ additions, which are essential to get successful Si deposition, relatively thick (3 mm) and inclusions-free deposits were obtained, with a current efficiency ranging from 35% to 70%, with a projected power to silicon mass value of 16 kWh/kg at 750°C. The fact that the deposits were dense and coherent was used by the authors as the proof that the silicon deposition does not occur with the primary formation of alkali metal, which then would react with $\text{Si}^{4+}$ ions

$$4\text{K} + \text{Si}^{4+} \rightleftharpoons \text{Si} + 4\text{K}^+ \quad (3.38)$$

to give just Si as the final product, but is associated to the direct reduction of the complex species $[\text{SiF}_6]^{2-}$. In the best experimental conditions, the total impurity concentration was 10 ppmw, with B at 2 ppmw. The same authors carried out electrodeposition experiments on graphite electrodes [81] using the LiF–NaF–KF eutectic mixed with 8%–14% molar $\text{K}_2\text{SiF}_6$. Dense, coherent deposits were obtained, with a total content of metallic impurities (Cu, Fe, and Ni) around 50 ppmw.

Apparently, none of these attempts seems to be appropriate for the industrial development of a silicon refining process, being limited by inherent difficulties in managing the electrodeposition of solid silicon with proper purity and at sufficiently high rates.

The same practical limits were observed when using quartz electrodes and alkali- or alkali-earth halide melt as the electrolytes, which are also good solvent for silica

---

* Using an impure silicon anode.
† The same originally used by Ullik.
and for $\text{K}_2\text{SiF}_6$. $\text{CaCl}_2$ and fluoride melts offer this opportunity, with the advantage of fluoride melts to dissolve larger amounts of $\text{K}_2\text{SiF}_6$.

The few efforts carried out very recently with the direct use of quartz electrodes (see Figure 3.23) and a CaCl$_2$ electrolyte [82–84], although of some basic interest, remain of difficult practical application. The direct electroreduction of silica, in fact, does occur using pure silicon electrodes in contact with the quartz sample at a test temperature of 1123 K, operating the system in dry argon and using a quartz crucible as the melt container. The electroreduction products are columnar microcrystals of pure silicon.

Instead, in fluoride, chloride, mixed fluoride/chloride, or mixed halide/oxide melts silica should be used as the feedstock and directly reacted as such, in the presence of $\text{K}_2\text{SiF}_6$, which, as shown before, ensures the presence of reducible $\text{Si}^{4+}$ ions and promotes as well the solubility of the silica, via an intermediate oxyfluoride complex.

Depending on the melt composition, the electrolysis could be carried out at a temperature above or below the melting temperature of silicon.

**FIGURE 3.23** The 5 mm wide, quartz electrode used in the experiments carried out by Yasuda et al. (Reprinted from *Electrochimica Acta*, 53, K. Yasuda et al., Direct electrolytic reduction of solid SiO$_2$ in molten CaCl$_2$ for the production of solar grade silicon, 106–110, Copyright 2007, with permission of Elsevier.)
The high temperature route was followed by Rao et al., with a BaO–BaF₂–SiO₂ melt as the electrolyte [81], at temperatures slightly below (1393°C) and above 1465°C, the melting point of silicon, using graphite electrodes.

As the density of silicon is close to that of the melt, in both cases the electrodeposited silicon remains adherent at the electrodes. The low Faradaic yield (40% in the best case) was explained as due to loss of SiO by sublimation and to the partial electronic conductivity of the melt, due the presence of a suspension of carbon particles detached from the electrode.

Chloride melts added with CaO are claimed to be suitable solvents for SiO₂ [70], but when tested for B and P purification, the success was modest [85].

Eventually, also carbonate melts are better solvents for oxides than chlorides, but their decomposition potentials are lower than that of silica, thus limiting the range of applicability of carbonates to the carbides electrosynthesis [86] or, by a suitable modification of the melt composition, to the electrodeposition of transition metallic borides, -carbides, and -silicides in halide melts [87,88].

Low Faradaic yield, powder form of the silicon produced, and modest quality of the electrodeposited silicon are, therefore, serious obstacles to the development of industrial processes based on conventional electrochemical processes using solid anodes and cathodes.

3.2.8.3 Electrorefining and Electrowinning Processes

Two different processes might be foreseen to produce pure silicon with an electrochemical process.

The first would be the preferential anodic dissolution of the more electronegative impurities from a MG-Si anode, which could then be melted and directionally solidified to remove the remaining metallic impurities. The preferential anodic dissolution is typically an electrowinning process.

The second would be the direct production of a pure silicon material by the anodic dissolution of a MG-Si source in a suitable electrolyte and the simultaneous deposition of silicon on an appropriate cathodic material.

It is clear that if the anodic dissolution of MG-Si occurs together with the contaminating impurities, the cathodic deposition would occur from an impurity-contaminated melt. One should, therefore, expect that the electrodeposited silicon should also be impurity contaminated.

Having this challenge in mind, several efforts were carried out to minimize or even suppress the electrolyte contamination, by using suitable anodic alloys or proper cell configurations.

The most interesting advances in this field were obtained, with

- Electrorefining processes using liquid anodes and cathodes* [89]
- Electrowinning processes using anodes solidified from a hypereutectic solution of copper and MG-Si, which behaves as a two-phase mixture of silicon embedded in a Cu₃Si matrix [90] or

* As a late realization of the suggestions of Monnier [75].
• Using additional electrocatalytic procedures, capable of inactivating impurities otherwise impossible to remove [73,91], with the application of the three-layer electrochemical refining

As said before, electrowinning processes are based on the preferential anodic dissolution of the less noble components of an alloy working as an anode in a proper electrolyte. In the case of silicon, metallic impurities more electronegative than silicon will preferentially dissolve.

After electrowinning, the purified silicon could be subjected to a DS process to remove the noble impurities dissolved in it. Electrowinning processes could be, however, associated to a silicon electrodeposition process from the same electrolyte.

The electrowinning process has been successfully applied for the preparation of 6N aluminum, but the attempts carried out at the Norwegian School of Science and Technology (NTU) and SINTEF in Norway [92–94] for the purification of MG-Si in KF–LiF–K2SiF6 melts resulted only in moderate success.

Cathodic silicon deposits are, in fact, heavily contaminated with C, O, and F, and a subsequent treatment in a CaF₂ melt was needed to get a Si powder still heavily contaminated with Fe (>1000 ppmw). The current efficiency is greater than 49%, with an energy consumption of 17 kW h/kg.

The process developed by Olson and Carleton [90] using anodes solidified from a hypereutectic solution of copper and MG-Si, which behaves as a two-phase mixture of silicon embedded in a Cu₃Si matrix, presents, instead, a considerable interest. In fact, the process works with a high Faradaic efficiency (up to 99%) at 750°C and yields a 99.999% pure electrodeposited Si, with the almost total removal of B and P (see Table 3.8).

The key issue of this process is that not only the more electropositive impurities that remain at the anode, as theoretically expected, but also the more electronegative impurities (Ca, Al, Cr, Ti, V), blocked by a diffusional trapping process, due to the

### TABLE 3.8

<table>
<thead>
<tr>
<th>Metal Impurity</th>
<th>Impurity Content in MG-Si (ppma)</th>
<th>Impurity Content in Electrodeposited Si (ppma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>3400</td>
<td>1.0</td>
</tr>
<tr>
<td>B</td>
<td>17</td>
<td>0.7</td>
</tr>
<tr>
<td>Ca</td>
<td>290</td>
<td>&lt;0.07</td>
</tr>
<tr>
<td>Mg</td>
<td>85</td>
<td>0.9</td>
</tr>
<tr>
<td>Cr</td>
<td>40</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Fe</td>
<td>&gt;2500</td>
<td>0.1</td>
</tr>
<tr>
<td>Ti</td>
<td>290</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>V</td>
<td>250</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>P</td>
<td>7</td>
<td>&lt;0.03</td>
</tr>
</tbody>
</table>

Conventional and Advanced Purification Processes of MG Silicon

presence of the Cu₃Si matrix which works as a diffusion filter. Therefore, impurities
do not accumulate in the electrolyte and the simultaneous Si-electrodeposition at a
suitable cathode occurs from an almost uncontaminated electrolyte.

The process developed by Olsen [73,91] is based on the use of a three-layer cell
with a liquid Cu–Si (17% Cu) alloy as the anode, a (liquid) silicon as the cathode and
a fluoride electrolyte consisting of a mixture of CaF₂ and BaF₂ with the addition of
SiF₆²⁻ as an Si-carrying complex ion. The electrolyte composition is selected to get a
density intermediate between the Cu–Si alloy, working as the anode and pure liquid
Si, working as the cathode. At temperatures above the melting temperature of Si,
therefore, the Cu–Si alloy stays on the bottom and the liquid Si just on top.

As already mentioned before, all impurities less noble than Si (Ca, Ba, Mg, Al)
contaminating a Si electrode in equilibrium with a fluoride electrolyte should dis-
solve while the more noble remain in the anode. B has an electrochemical potential†
that is very close to that of Si (E°₅₅ = −3.551 V, E°₇₃ = −3.538 V) but the dissolu-
tion voltage is slightly more negative, depending on its concentration. Some results
reported in Table 3.9 show that a preferential Al and Ca dissolution occurs, which is
instead negligible for iron and limited for boron.

The impurity content of Si deposited at the cathode, from an electrolyte strongly
contaminated with Ca and Al, ranges for Cu around 200 ppmw,‡ for Al around
3000 ppmw, for B between 3 and 10 ppmw, for P between 1 and 2 ppmw, for Fe
<10 ppmw, and for Ti between 10 and 50 ppmw. The overall impurity contamination
is, therefore, far from a SoG material.

In a further work, Olsen et al. [91] showed that it is possible to inactivate, at least
partially, B during the anodic process with the electrocatalyzed formation of a tita-
nium boride, which is insoluble in the Cu–Si alloy. It was shown, in fact, that at low
polarizations, the formation of intermetallic borides occurs at the electrolyte/Cu–Si
alloy interface.

---

**TABLE 3.9**

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Initial MG-Si Concentration (ppmw)</th>
<th>Concentration at the Anode (ppmw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1200–4000</td>
<td>30</td>
</tr>
<tr>
<td>Ca</td>
<td>590</td>
<td>47</td>
</tr>
<tr>
<td>B</td>
<td>20–45</td>
<td>12</td>
</tr>
<tr>
<td>P</td>
<td>27–30</td>
<td>31</td>
</tr>
<tr>
<td>Fe</td>
<td>1600–3000</td>
<td>1300</td>
</tr>
</tbody>
</table>


---

* A graphite crucible lined with sintered Si₃N₄ was used as the container.
† With reference to a fluorine electrode.
‡ The heavy Cu contamination is felt to be due to Cu vapors sublimating from the bottom electrode and
diffusing toward the anode.
It is, however, apparent that electrowinning of MG-Si presents a number of challenges, mostly due to the contamination of the electrolyte arising by impurities anodically dissolved, unless an impurity diffusion barrier is used at the anode. In general, the materials so far obtained are far away from SoG properties and would neither be a suitable feedstock for a subsequent DS process.

3.3 PROCESSES

3.3.1 Ferroatlantica: Efforts in the Ferroatlantica Group (FerroSolar and Photosil)

Ferroatlantica is the world’s largest silicon metal producer, and one of the largest ferroalloy producers, with factories in Brazil, China, France, Venezuela, Canada, South Africa, and Spain. The Ferroatlantica’s group I + D Company is its R&D Company, with several fields of interest, including solar silicon development as one of the main targets. The activities in this field are carried out within the FerroSolar and Photosil projects, the last carried out in France with the cooperation of FerroPem, Apollon Solar, CNRS, and CEA (Commissariat a l’Energie Atomique).

3.3.1.1 FerroSolar Silicon Project

Since 2000, the Ferroatlantica group has been working on a project upgrading MG-Si to SoG-Si using metallurgical methods. From the beginning, the FerroSolar project was integrated in the silicon metal (MG-Si) production facility of Ferroatlantica S.A. in Sabón, Spain, with the aim of using the technologies and knowledge developed not only to purify silicon to SoG but also to improve the production and the quality of the silicon metal.

Different from projects discussed in Chapter 2, aimed at the production of a high quality MG-Si from pure raw materials,* the FerroSolar project intends to integrate a conventional, but optimized, MG-Si production with a sequence of conventional purification steps.

A pilot plant started with standard induction furnaces in a size to process 4 t of steel which corresponds to approximately 1 t of silicon [94] and meanwhile was equipped with advanced furnaces to carry out vacuum treatments and directional solidification (DS) processes [16,95]. The total capacity of this facility is 400 t of SoG-Si per year and in 2014, about 150 t had been processed.†

The purification process starts with MG-Si of a better than standard quality, that is produced in special production campaigns. This special MG-Si is refined by a slagging process in induction furnaces. The slagging process is repeated as many times as necessary to obtain the target dopant concentrations for this step. In the first generation CS Silicon™ (GEN1) purification process, the silicon proceeds directly to the DS process after slagging. This step can be also carried out in an electromagnetic casting furnace which allows a continuous casting process and removes residual

* That was the main reason for a lack of success.
† J. Bullon, private communication, 2014.
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carbon (SiC particles) as well as residual slags. Then, the resulting ingot is cut into bricks which undergo a final inspection and cleaning treatment [96].

In the second generation purification process (GEN2), an additional vacuum purification step has been introduced between slagging and solidification to reduce the P concentration [16]. The target range of dopant concentrations B and P for the feedstock qualities GEN1 and GEN2 is given in Table 3.10.

The results of vacuum purification, carried out in the 1545–1650°C range, using an industrial resistance furnace and 500 kg charges are particularly interesting. They show, in fact, significantly low silicon losses (see Table 3.11) and a very low final P and B content (see Table 3.12) that fits closely with the specifications of high quality silicon feedstocks for the P and B concentration (see Figure 3.24 [97]) and with the target values (see Table 3.10).

### TABLE 3.10
Target Range of Dopant Concentrations with Purification Process GEN1 and GEN2, and Examples of the Measured Dopant Concentrations in the Feedstock

<table>
<thead>
<tr>
<th>CS Silicon™</th>
<th>GEN1</th>
<th>GEN2</th>
<th>GEN1</th>
<th>GEN2 (a)</th>
<th>GEN2 (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B (ppmw)</td>
<td>0.15–0.4</td>
<td>0.1–0.2</td>
<td>0.19</td>
<td>0.16</td>
<td>0.11</td>
</tr>
<tr>
<td>P (ppmw)</td>
<td>0.8–1.1</td>
<td>0.1–0.6</td>
<td>0.88</td>
<td>0.45</td>
<td>0.1</td>
</tr>
</tbody>
</table>


### TABLE 3.11
Silicon Losses in Vacuum Purification Experiments (500 kg Samples)

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Pressure (Pa)</th>
<th>Silicon Losses (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1545</td>
<td>240</td>
<td>0.1–0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>2</td>
<td>1545</td>
<td>300</td>
<td>0.1–0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>3</td>
<td>1545</td>
<td>510</td>
<td>0.1–0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>4</td>
<td>1580</td>
<td>180</td>
<td>0.1–0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>1580</td>
<td>240</td>
<td>0.1–0.3</td>
<td>0.7</td>
</tr>
<tr>
<td>6</td>
<td>1580</td>
<td>510</td>
<td>0.1–0.3</td>
<td>2.2</td>
</tr>
<tr>
<td>7</td>
<td>1600</td>
<td>180</td>
<td>0.1–0.3</td>
<td>0.7</td>
</tr>
<tr>
<td>8</td>
<td>1600</td>
<td>240</td>
<td>0.1–0.3</td>
<td>0.7</td>
</tr>
<tr>
<td>9</td>
<td>1600</td>
<td>330</td>
<td>0.1–0.3</td>
<td>1.3</td>
</tr>
<tr>
<td>10</td>
<td>1600</td>
<td>510</td>
<td>0.1–0.3</td>
<td>2.1</td>
</tr>
<tr>
<td>11</td>
<td>1650</td>
<td>180</td>
<td>0.1–0.3</td>
<td>1.2</td>
</tr>
<tr>
<td>12</td>
<td>1650</td>
<td>240</td>
<td>0.1–0.3</td>
<td>1.6</td>
</tr>
<tr>
<td>13</td>
<td>1650</td>
<td>300</td>
<td>0.1–0.3</td>
<td>1.4</td>
</tr>
<tr>
<td>14</td>
<td>1650</td>
<td>510</td>
<td>0.1–0.3</td>
<td>2.5</td>
</tr>
</tbody>
</table>
### TABLE 3.12
Residual Impurity Content in Vacuum Purification Experiments (500 kg Samples)

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>P</th>
<th>B</th>
<th>K</th>
<th>Na</th>
</tr>
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<tbody>
<tr>
<td>Starting silicon</td>
<td>1.4</td>
<td>3.3</td>
<td>0.2</td>
<td>1.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Run number</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.4</td>
<td>1.4</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>1.2</td>
<td>1.4</td>
<td>0.1</td>
<td>1.0</td>
<td>0.3</td>
</tr>
<tr>
<td>3</td>
<td>0.8</td>
<td>1.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>4</td>
<td>1.3</td>
<td>1.0</td>
<td>0.2</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>5</td>
<td>0.4</td>
<td>0.6</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>6</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>7</td>
<td>0.8</td>
<td>0.8</td>
<td>0.1</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>8</td>
<td>0.2</td>
<td>0.7</td>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>9</td>
<td>3.6</td>
<td>0.4</td>
<td>0.3</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>10</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>11</td>
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<td>0.3</td>
<td>0.1</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>12</td>
<td>0.6</td>
<td>0.4</td>
<td>0.1</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>13</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>14</td>
<td>0.7</td>
<td>0.1</td>
<td>0.2</td>
<td>0.6</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The low doping and compensation levels of the GEN2 material can be correlated with high minority carrier mobility and high solar cell efficiencies [96].

The results of many different industrial tests with current CS silicon at different stages of the PV chain showed, in fact, efficiencies of 17.3%, 0.1% below the reference cells [16].

In a comparative study between typical mc-Si and CS-Si-based modules, evaluated in real outdoor conditions during a full-year period, no difference was found between both material types [98].

The FerroSolar process is easily applicable to industrial scale, its results are reproducible, and it is cheaper and more environmentally friendly than the Siemens process.

### 3.3.1.2 The Photosil Project

The Photosil process was developed by FerroPem (part of the Ferroatlantica group) in 2004, in its Photosil site located in Chambery [99]. It aimed at producing SoG-Si, able to replace directly (without blending) the chunk material from chlorosilane processes. The Photosil silicon can be used without additional dopants, in standard solar cell production factories.

The process (see flowsheet in Figure 3.25) begins by a careful selection of the raw materials (silica, carbon-rich reducers) used to produce MG-Si in classic reduction furnaces. Then, two segregation steps are used to remove metallic impurities and a part of phosphorus, giving upgraded metallurgical silicon (UMG-Si) which is treated with plasma to remove boron and undergoes a final segregation to remove carbon and the remaining metals and phosphorus.

The innovative part of the Photosil process is the plasma purification step, developed in the frame of a research-industry consortium with Apollon Solar, CEA, and

![FIGURE 3.25 Flowsheet of the Photosil refining process.](image-url)
at the SIMaP laboratory of CNRS in Grenoble [37], where 10 kg of silicon were already successfully processed.

The Photosil process started by reducing the boron concentration of 75 kg batches down to 3.5 ppmw in 2005 [100] and was up-scaled to 250 kg batches purified at 0.3 ppmw of boron in 2012 [99]. This evolution was mainly cost driven, with a second-generation plasma facility announced in 2011 [101], and running since 2013, with an objective cost below $15/kg for the whole production chain of SoG-Si, vertically integrated from the carboreduction of silica up to Si blocks ready for crystallization.

Other parts of the process include segregation steps (before and after the plasma), and upstream optimization of the metallurgical silicon. These steps were optimized in parallel with the plasma process, to reach the SEMI specifications for SoG-Si (including a phosphorus concentration below 0.6 ppmw), together with quality criteria defined from the consortium’s experience, such as a resistivity between 0.6 and 3 Ω cm [99]. A dedicated study of the post plasma segregation is reported in Reference 102.

Photosil material has been used since 2006 to produce mc-Si ingots and since 2012 to produce single crystal boules by the CZ technique.

Table 3.13 [99–101,103–107] reports details about the evolution of the Photosil quality and its use along the development period. The feedstock used was simply a plasma purified material in early studies, then the standard silicon (Std) produced by the Photosil process, eventually trimmed to get n-type silicon (n-Std). Eventually, an optimized material (Opt or n-Opt), better purified, was used for studies on high performance cells. The impurity contents of Std and Opt feedstocks evolved during the development, showing that the process can be adjusted to meet various purity requirements.

<table>
<thead>
<tr>
<th>Year and Material</th>
<th>Impurity Contents (ppmw)</th>
<th>Crystallization</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
<td>P</td>
<td>Al</td>
</tr>
<tr>
<td>2006 UMGP</td>
<td>3.5</td>
<td>2.5</td>
<td>5</td>
</tr>
<tr>
<td>2008 UMGP</td>
<td>1.5</td>
<td>2</td>
<td>0.2</td>
</tr>
<tr>
<td>2010 Std</td>
<td>1.5</td>
<td>4</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Opt</td>
<td>0.3</td>
<td>1</td>
<td>&lt;2</td>
</tr>
<tr>
<td>2011 Std</td>
<td>0.5</td>
<td>1.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Std</td>
<td>0.3</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Std-n</td>
<td>0.3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>2013 Std</td>
<td>0.3</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Opt</td>
<td>0.12</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Opt-n</td>
<td>0.12</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Std</td>
<td>&lt;0.3</td>
<td>&lt;0.6</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>
Conventional and Advanced Purification Processes of MG Silicon

The crystallization experiments on Photosil material (see again Table 3.13) were carried out at the laboratory scale, except in 2011 and 2013 when half-ton-sized ingots were grown to be delivered to solar cell manufacturers. The material grown in 2011 was used for the production of 225 W-modules for a 100 kW solar farm, where 80 Photosil modules were monitored together with standard modules made out of EG-Si [99]. The power output of Photosil and standard modules was shown to be very close.

The material grown later was delivered to different solar cell manufacturers to test the efficiency and the light-induced degradation (LID) effects. The results of these tests are reported in Table 3.14.

The cells made with Photosil material reached comparable efficiency (not reported in Table 3.14) of cells manufactured from EG-Si for each kind of cell manufacturing process, including high performance monocrystalline cells, for which an efficiency up to 19% was measured.

The LID has been reduced below 2% of the initial efficiency, and other criteria needed for industrial cell production (high ingot yield, low percentage of broken wafers, or off-spec cells) have been reached as well.

The material is now available for further industrial evaluation.

### 3.3.2 Silicor Materials Process for Silicon Purification

Silicor Materials was founded as an R&D company in 2006 under the name Calisolar, with the goal of manufacturing low-cost PV solar cells from upgraded MG-Si. After merging with the Canadian company 6N Silicon, it had its own internal silicon
purification process which was optimized for the requirements of a solar cell production. Today, the company is fully focused on the metallurgical route of silicon purification and intends to first build a large plant of up to 19,000 t annual capacity in Grundartang in Iceland.

The Silicor Materials process can be described as a liquid to solid refining process comprising a number of refining steps, whereby, MG-Si with a purity level of at least 99.5% Si is refined up to the levels needed for solar application. The four principal refining steps, as also shown in Figure 3.26 are:

- **Solvent growth refining.** A molten aluminum–silicon alloy is allowed to cool, leading to silicon refining in the form of aluminum-coated silicon crystals.
- **Wet-chemical aluminum removal.** The aluminum coating on the silicon crystals is dissolved in hydrochloric acid forming polyaluminum chloride (PAC).
- **DS.** Clean silicon crystals are re-melted and directionally solidified resulting in fully refined silicon ingots.
- **Final preparation.** Purified silicon ingots are cleaned, cut, chunked, and blended to eliminate chemical variation.

In addition to the primary output of SoG-Si, the process route has two by-products of high commercial value, that is, an Al–Si master alloy for use in the aluminum casting industry and PAC, used for waste-water treatment applications.

![Figure 3.26 Map of process flow for the silicor process.](image-url)
3.3.2.1 Solvent Growth Refining

A molten aluminum–silicon mix, containing approximately 40% silicon by weight (Al–40 Si wt%) is the starting point for the Silicor Materials process. This is accomplished by combining, during the solvent growth refining step, MG-Si (99.57% Si) with aluminum or a frozen eutectic coming from the process and containing a high amount of Al.

The full phase diagram for the Al–Si system is given in Figure 3.27, which also shows a visual representation of the typical solidification pathway for a slowly cooled melt. With any hypereutectic Al–Si melt where the weight percent of Si is greater than 12.6%, slow cooling from the liquid state will form silicon crystals of high purity to solidify first and will cause an enhanced segregation effect due to the low temperatures of this crystallization. As more silicon crystals solidify, the remaining melt will experience an increase in the concentration of aluminum and other elements, compared to the composition of the original melt.

In such a melt that exhibits a nondirectional temperature gradient, the silicon will grow from the mold walls and in the form of platelets or agglomerates of platelets called “flakes,” resulting in a three-dimensional network of silicon flakes with the remaining melt in its cavities.

Figure 3.28 shows a scheme of the solvent refining step. Here, a counter-current system is used to achieve purification over a number of passes, which involve the melting and solidification of the Al–Si alloy at ever increasing purity. In effect, the incoming pure aluminum acts as a diluent of the impurity levels and the solidification at each pass acts to segregate these impurities so that they end up in the master aluminum alloy.

In such a process the clean silicon, which already has seen several passes of purification, can only get in contact with the purest aluminum making sure there is no cross contamination between different levels of the purification steps. The number of passes can be varied according to the quality of the incoming material and the target specification of the process [110].
After a sequence of passes, when the flake purity meets the process specification, the grown flakes are separated from the remaining eutectic. In every pass, this has to be done at a temperature above the eutectic point (577°C) to be able to drain the remaining melt from the Si network. Usually at this stage, the network is stable enough to stay intact during draining but also has enough porosity to let the melt go. Afterward silicon flakes with only a bit of aluminum coating can be harvested. The master alloy coming out of this process is poured into molds to be sold to the aluminum casting industry.

3.3.2.2 Wet-Chemical Aluminum Removal
The next principal process step is an acid wash step, which removes the aluminum present on the surface of the silicon crystals. Screening (sifting) takes place after the acid wash to remove nonstandard Si-flakes. In addition to creating clean flakes for the DS process, the acid washing process also creates PAC from the dissolution of aluminum in the hydrochloric acid. This by-product can be used as a flocculant during waste-water treatment applications.

The hydrogen evolution during the etching reaction is kept below the lowest explosion limit by air circulation. With constant process control in the etching section, using a proper HCl addition, a peak hydrogen formation is prevented.

It is targeted that the aluminum content of the etched flakes will be limited to 2500 ppmw. This value is higher than the maximum solubility of Al in Si (412 ppmw) \[111\] since some of the aluminum present in the flakes is locked in the silicon flake structures and cannot be digested by the hydrochloric acid.

The etched and rinsed flakes are then dried to be ready to be melted in a DS furnace.

3.3.2.3 DS and Final Preparation
The DS process consists of melting the flakes by using an induction furnace followed by casting and DS in molds. This step is primarily responsible for the final removal
of Al from the silicon flakes that arrive from the acid washing process. There is reduction of other impurities, but these have already been significantly reduced in the solvent growth refining step. During DS, metals segregate readily to the top of the ingot where they can physically be removed once the ingot is solid. This top material is then recycled back to the solvent refining step. Since the Al–Si purification process has multiple levels of purity over each step, it also is well suited to recycle silicon of any grade. Depending on the purity of the recycled material, it can go the shortest possible loop through the purification without wasting energy. This makes the process also potentially interesting for future tasks in the solar industry when more material, for example, from old solar cells and other processes, needs to be recycled.

Figure 3.29 shows the principal elements of the DS mold, where a top heater and air flow at the bottom of the mold ensure that the temperature gradient runs from top to bottom of the mold geometry.

The removal of Al during this process stage is further assisted by the use of a pre-fused flux both in the furnace and applied in a thin layer on the surface of the melt during DS. This flux is mentioned as the “cover flux” in Reference 68 and is a mixture of three components, SiO₂, Na₂CO₃, and CaO. The oxidation potential of this mixture is such to favor the preferential oxidation of Al and results in aluminum oxide (see Section 3.2.2), which will be dissolved by the liquid glass covering the melt.
Using a pure sodium silicate glass, which is highly efficient for the Al oxidation, the feedstock obtained after a solidification refining presents an Al content around 0.1 ppmw, and could be used with success as a solar silicon feedstock [69,112].

The final processing involves the cleaning and cutting of the ingots, a thermal cracking process (chunking), and finally mixing of batches to reduce chemical variation if necessary, followed by packing and labeling.

3.4 CONCLUSIONS

The main result of R&D activities concerning MG-Si purification is that a physical limit to its full up-grading to SoG quality exists, since even the most advanced processes are unable to bring the concentration of dopant impurities (B and P) down to that of EG-Si. The removal of other impurities is, instead, physically and experimentally feasible. The product of MG-Si purification is, therefore, a compensated material, which nevertheless is demonstrated to be of possible use for solar cell production, with limited losses of efficiency in comparison with cells manufactured with EG-Si.

As the high B and P contamination of MG-Si depends only on the B content of quartz used as the silicon source and of the P content of the reductants, which are used to feed the carbo-reduction furnace (see Chapter 2), the only solution possible to get a pure, undoped silicon would be the use of high-grade quartz and P-free reductants.

Cost problems concerning B-loan quartz and difficult furnace operation with nonconventional reductants already suggested to Elkem (see Chapter 4) to neglect the high purity option, which remains, however, open for further progress in terms of operational capability of the carbothermic furnace, possibly with pure, synthetic SiO₂.

It should be noted that the impressive progress in non-dopant impurity refining processes is eminently due to the intelligent application of thermodynamic principles and of material science schemes, which also open up hope for further progress in this respect, as seem to be shown by the Solsile and the Silicor projects, which translate these schemes to industrial applications.

The problem, however, remains that a long sequence of different chemical and physical steps is necessary to obtain the required purity.

Electrochemistry could offer viable options for single-step purification processes, although it is a matter still insufficiently studied. Here, the challenge is either to optimize the electrowinning processes or those based on the use of liquid silicon alloys at the cathode. The efficiency of the electrowinning process depends on the diffusivity of the impurities and could envisage a preliminary electroless step for the removal of most electronegative impurities.

The use of liquid alloys as the cathode helps to suppress the large overvoltage effects arising at solid silicon cathodes and to work at temperatures lower than the melting point of silicon, with the advantage to reduce or even suppress the compatibility problems with fluoride melts. Eventually, silicon alloys with a volatile or an acid-soluble second component should be considered with attention, taking into account the already existing experimental knowledge of sublimation and leaching processes of silicon alloys.
REFERENCES


Solar Silicon Processes


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