

INFLUENCE OF SURFACE WAVES ON LIQUID-TO-GAS MASS TRANSFER IN MOLTEN SILICON

G. Zageris*, V. Geza, S. Pavlovs

Institute of Numerical Modelling,
University of Latvia
3 Jelgavas Str., Riga, LV-1004, LATVIA
*e-mail: girts.zageris@lu.lv

The paper focuses on the numerical analysis of the mass transfer of impurities from the wavy surface of molten silicon to the gas phase. The mathematical model is described herein, with the modelling of a wavy silicon melt surface being done with the moving mesh technique. The model employs assumptions about the mass transfer process on the surface, namely, that it can be modelled with effective diffusion across the interface. The assumption is verified against limited experimental data for a stationary melt surface, and reasonable agreement is obtained. Thereafter, numerical studies are undertaken for a wavy melt surface. The dependence of impurity removal rate on the wave amplitude, wavelength and frequency is analysed. It is shown that the waves on the surface of the liquid increase the mass transfer rate in a certain parameter range. Finally, results are analysed to find an explanation for this increase and to determine technological factors that impact it. Surface enlargement due to waves and altered flow patterns near the silicon melt are determined as potential reasons for the improved impurity removal rate. A dimensionless criterion for the minimal wave amplitude required to obtain improved impurity removal is found and discussed.

Keywords: *Computational fluid dynamics, mass transfer, silicon refinement, surface waves.*

1. INTRODUCTION

The requirement for alternative energy sources, e.g., solar, wind, hydro, etc., is growing due to the exhaustion of fossil fuel resources, with growing energy consumption and global warming. One of the most attractive sources is solar power, which is divided in two types – direct conversion to electricity (photovoltaics – PV) and solar power concentration systems. PV systems are more popular because they can be used for applications of different scales. As shown in [1], the energy cost for solar power has rapidly fallen, but it is attributed mostly to PV module efficiency improvement, manufacturing optimisation and reduction in material intensity. However, the cost of raw silicon has seen an uptick since 2021, and PV cell costs are directly related to costs for raw materials, e.g., polysilicon. Reduction of energy consumption during production of polysilicon is one of the key steps towards solar power becoming more accessible.

In 2012, it was shown that production of polysilicon constituted approx. 14 % of the total solar cell costs [2]. This number can be reduced by lowering energy consumption during solar grade silicon (SoG-Si) production. Most silicon production starts with reduction of quartzite or sand with carbon materials [3]. Such a process can achieve a purity of up to 99 %. To achieve higher purity, there are two ways – the chemical and the metallurgical route. The metallurgical route consumes about 30 kWh/kgSi (kilowatt-hours per kilogram of silicon) of energy. In comparison, the chemical route such as the Siemens process, which is the most widely used refining process nowadays, consumes 65 kWh/kgSi [4].

In the metallurgical route for silicon production, directional solidification is used

to remove metallic impurities. The most problematic elements are boron and phosphorus because their removal via the directional solidification method is limited due to their high segregation coefficients. In many investigations, phosphorus removal is found to be the most challenging task, since the purity threshold (<1 ppm) was not reached [5]. Although oxidation and slag refinement is a simple process for removing phosphorus from silicon, it is insufficient to reach the high purity threshold. The most popular approach for phosphorus removal is evacuation. In [6], it was shown that the rate for phosphorus evaporation corresponded to a first order reaction and that under medium vacuum conditions the evaporation rate was determined by chemical evaporation at the surface and gas phase mass transfer.

For boron removal, a well-known approach is blowing oxidizing gas on the free surface of the melt [7]. The highest boron refining rates can be achieved with plasma refining, but it has a high energy demand. In reactive gas refining, the concentration of boron changes according to a first order rate law:

$$\ln \left(\frac{C_{B,0}}{C_{B,t}} \right) = k_B \frac{St}{V}, \quad (1)$$

where C_B is the boron concentration with indices after comma indicating time, S is the area of interfacial surface between oxidizing gas and silicon melt, V is the volume of silicon melt, t is time, k_B is the boron mass transfer coefficient at the surface, measured in $\mu\text{m/s}$ (note that k_B does not denote Boltzmann's constant within this paper). In fact, the reaction occurring at the interface is of second order; however, the concentration of the reacting gas is kept constant by continuously supplying gas to

the surface. Thus, the law describing reaction rate becomes first order effectively. k_B is determined experimentally and is dependent on the oxidizing gas supply rate, the type of oxidizing gas, and melt temperature. Typical k_B values found in literature are 6–40 $\mu\text{m/s}$ [7]–[9], and the value for k_P is 2–5 $\mu\text{m/s}$ for phosphorus [6]. The typical melt temperature is $\approx 1425^\circ\text{C}$.

The creation of surface waves would, in principle, increase the S/V ratio, thus speeding up boron removal. Though under normal operating conditions no waves are generated

during the purification process, it has been shown that waves on liquid metal surfaces can be generated, for example, by contactless electromagnetic interaction in mercury both experimentally [10] and theoretically [11]. Estimating the surface enlargement from [10] according to Eq. (16) (see Section 3.3.) with crucible radius $R_0 = 0.09\text{ m}$, wave amplitude $A = 0.001\text{ m}$ and wave-number $n = 10$, the potential increase in the free surface is approximately 10 %. Therefore, it would potentially be of interest to create waves during purification to increase process efficiency.

2. MODEL DESIGN AND BOUNDARY CONDITIONS

2.1. Problem Description

The physical system considered in this study is that of a cylindrical tank, which contains molten silicon. The oxidizing gas is introduced via a centrally located cylindrical pipe directly above the melt. The impurities located inside the melt can then evacuate from it via the melt-gas interface and escape the tank together with the gas flow. Then surface waves are introduced on the silicon melt to study the impact of these waves on the overall purification efficiency.

In cases where this study focuses on the diffusion of the impurities on a larger time scale, the entire system (melt + gas) is modelled with a stationary interface. However, when the effects of a wavy surface are studied, only the gas domain is modelled. In this case, the silicon melt is only taken into account in the form of a boundary with a certain harmonic profile and a constant impurity concentration.

To reduce the need for substantial computational resources, the problems are modelled with 2D axi-symmetric geometries.

In this study, the gas blowing above the

melt is assumed to have the same viscosity as dry air $\nu = 1.51110^{-5}\text{ m}^2/\text{s}$ [12].

In the simulation where only the bulk gas is considered, calculations are done for a 2D axisymmetric geometry. In Fig. 1, the geometry and a representative picture of the computational mesh are given. In Fig. 1a the sketch of the geometry is shown. The mesh grid used for calculations is illustrated in Fig. 1b and 1c. As can be seen, the grid is more refined where deformations of the mesh take place, both to better absorb the mesh deformations and to resolve the diffusion boundary layer.

The computational mesh was created using an open-source program SALOME. The number of elements in the mesh is 15000. To arrive at this number, a mesh independence study was performed. An initial coarse mesh was progressively made finer and finer until no significant difference in the simulation results could be observed. The results obtained with the mesh used in this study differed no more than 1% from the previous calculation, which was

deemed precise enough in the scope of this research. A mesh twice as fine (i.e., face size of each element is two times smaller) gave

no appreciable improvement to the results as compared to the mesh used in the study (deviations were less than 1 %).

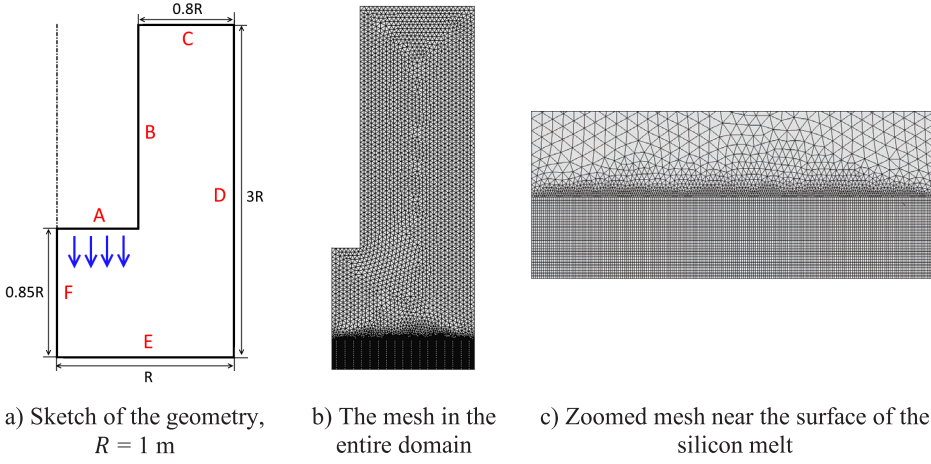


Fig. 1. Problem geometry and computational mesh.

2.2. Model Equations

To describe this problem, one needs to define the fluids in motion. The motion of an incompressible fluid is governed by the Navier-Stokes equations (Eq. (2)). The additional information necessary to describe fluid flow is the conservation of mass (Eq. (3)), expressed by the equation of continuity:

$$\frac{\partial \mathbf{u}^*}{\partial t^*} + (\mathbf{u}^* \cdot \nabla) \mathbf{u}^* = -\nabla p^* + \frac{1}{Re} \nabla^2 \mathbf{u}^*, \quad (2)$$

$$\nabla \cdot \mathbf{u}^* = 0, \quad (3)$$

$$Re = \frac{UL}{\nu}. \quad (4)$$

The species transfer equation is written in the form of

$$\frac{\partial C}{\partial t^*} + \mathbf{u}^* \cdot \nabla C = \tilde{D} \nabla^2 C, \quad (5)$$

$$\tilde{D} = \frac{1}{UL} \left(D + \frac{\mu_t}{Sc_t} \right). \quad (6)$$

Turbulence and turbulent viscosity are modelled with the standard k - ϵ model.

These equations implicitly take into account the following assumptions:

- The fluid is incompressible;
- The fluids in consideration are Newtonian;
- The molecular diffusion coefficient of the impurities D is independent of spatial coordinates;
- The effective diffusion coefficient $\tilde{D}$ is composed of molecular diffusion D and turbulent diffusion terms.

Notably, heat transfer has been omitted from the model equations, effectively solving the flow in isothermal conditions. This is a reasonable simplification because the technological process demands that the flow must be dominated by forced convection from the gas blowing, thus allowing for buoyancy to be neglected.

To numerically investigate the role of surface waves on impurity removal from silicon, the open-source toolbox *OpenFOAM* is used. The main algorithm for calculating the flow and impurity transport is *pimple*-

DyMScalarFoam, which is derived from the default *OpenFOAM* algorithm *pimpleDyMFoam*, which calculates fluid flow for a dynamic mesh by deploying the PIMPLE algorithm. However, *pimpleDyMFoam* does not contain any other scalar diffusive transport equations, so a concentration diffusion term has been added to the algorithm, renaming it to *pimpleDyMScalarFoam* (the name contains *Scalar*, but it can simulate both thermal and diffusion processes due to the equations being identical).

pimpleDyMScalarFoam solves fluid flow and concentration diffusion separately – first, it recalculates fluid velocity relatively to the moving mesh, then it solves a full PIMPLE cycle (ignoring concentration diffusion), and, finally, calculates one step for diffusion with the newly obtained fluid variables. Therefore, the fluid impacts how concentration diffusion happens but not vice versa. It is thus implicitly stated that the gas above the molten silicon is dilute with respect to the concentration of silicon impurities. The algorithm repeats additional iterations until a residual of 10^{-6} is obtained. In this study, the PIMPLE algorithm runs with two outer corrector loops, one inner corrector loop and one non-orthogonal corrector loop. The time domain is discretized with the Euler scheme, divergence terms are discretized with the Gauss upwind scheme and the Laplacian terms are approximated with Gauss linear corrected schemes.

Boundary conditions must also be set for the problem. The boundary conditions are summarised in Table 1. It is important to note that the chosen boundary condition for the value of impurity concentration on the surface of the molten silicon being constant $c=1$ is a simplification that neglects the role of transient chemical reactions and impurity transport within the molten silicon itself. However, within the scope of this research it is an acceptable simplification (see Subsec-

tion 2.3). Inlet values for k and ε were chosen to keep turbulence low at the inlet in order to allow for the system geometry, wave interaction and impurity diffusion at the interface to dominate the effects on all physical processes.

In most cases, *OpenFOAM* has keywords for standard boundary conditions. However, in this case, a custom boundary condition was necessary for the deformation of the boundary corresponding to the surface of molten silicon. To do this, a new boundary condition *SineVelocity* was defined, which moves the boundary points according to the law $u_y = A \sin\left(\frac{2\pi x}{\lambda}\right) \sin\left(\frac{2\pi t}{T}\right)$. The free parameters here are amplitude A , wavelength λ and period T . The value of L , which corresponds to the length of the moving boundary, is determined automatically. Despite the parameters λ and T being free to choose from an implementation standpoint, the dispersion relation for gravity waves is nevertheless used as an approximation for the relation between variables λ and T . Generally, the dispersion relation for gravity waves is:

$$\omega^2 = gk_\lambda + \frac{\sigma k_\lambda^3}{\rho}. \quad (7)$$

However, with the characteristic values of $g=10 \text{ m/s}^2$, $\lambda=5 \text{ mm}$, $\sigma=0.7 \text{ N/m}$ [13] and $\rho=2550 \text{ kg/m}^3$ [14] for molten silicon, the ratio between the first term and second term in Eq. (7) is approximately 140, thus allowing one to use only the first term in the dispersion relation. This permits rewriting the dispersion relation for variables λ and T :

$$\frac{\lambda}{T} = \sqrt{\frac{g\lambda}{2\pi}}. \quad (8)$$

Once calculations are complete, the concentration flow field is integrated on the outflow boundary at every time step to obtain the total amount of impurity concentration that has left the domain:

$$\Phi_C = \int C v_n dS. \quad (10)$$

The value of Φ_C serves as the main comparative quantity between different calculations if inlet velocity remains fixed.

Note also that for turbulence parameters and wall functions are used despite

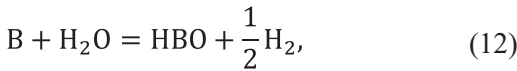
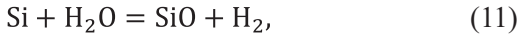
the fact that mesh resolution strongly varies in different places in the mesh. This is not an issue because *OpenFOAM* automatically implements the correct approach (linear vs. log) in a stepwise manner according to the mesh resolution at a certain point near the wall.

Table 1. Summary of Boundary Conditions in the Simulation. WF – Wall Function, SYMM – Symmetry

Boundary	Inlet	Inner wall	Outlet	Outer wall	Si surface	Axis
Label (Fig 1)	A	B	C	D	E	F
Quantity						
$\mathbf{u}^*$	$\mathbf{u}_n^* = 0.7 \text{ m/s}$	$\mathbf{u}^* = 0$	$\frac{\partial \mathbf{u}^*}{\partial \mathbf{n}} = 0$	$\mathbf{u}^* = 0$	$\mathbf{u}^* = 0$	SYMM
p	$\frac{\partial p}{\partial \mathbf{n}} = 0$	$\frac{\partial p}{\partial \mathbf{n}} = 0$	$p = 0$	$\frac{\partial p}{\partial \mathbf{n}} = 0$	$\frac{\partial p}{\partial \mathbf{n}} = 0$	SYMM
c	$c = 0$	$\frac{\partial c}{\partial \mathbf{n}} = 0$	$\frac{\partial c}{\partial \mathbf{n}} = 0$	$\frac{\partial c}{\partial \mathbf{n}} = 0$	$c = 1$	SYMM
ε	$\varepsilon = 10^{-6} \text{ m}^2/\text{s}^3$	WF	$\frac{\partial \varepsilon}{\partial \mathbf{n}} = 0$	WF	WF	SYMM
k	$k = 10^{-5} \text{ m}^2/\text{s}^2$	WF	$\frac{\partial k}{\partial \mathbf{n}} = 0$	WF	WF	SYMM
Motion	$\mathbf{v} = 0$	$\mathbf{v} = 0$	$\mathbf{v} = 0$	$\frac{\partial \mathbf{v}}{\partial \boldsymbol{\tau}} = 0$	<i>SineVelocity</i>	$\frac{\partial \mathbf{v}}{\partial \boldsymbol{\tau}} = 0$

2.3. Neglecting Chemical Reactions

The reaction scheme for partial boron oxidation with the oxidizing gas is described in [7]:



For this research, reactions at the interface were neglected. Instead, constant concentration of HBO was assumed at the silicon surface. This was done for several reasons. First, Sortland [7] argues that resistance for HBO transport stemming particularly from the reactions at the interface is very small and their influence on boron

removal rate is negligible.

Second, the supply of H_2O to the surface depends on the concentration of H_2O in the gas and the resistance of diffusion layer:

$$J_{\text{H}_2\text{O}} = k_{\text{diff}}^{\text{H}_2\text{O}} \left(C_{\text{H}_2\text{O}}^{\text{gas}} - C_{\text{H}_2\text{O}}^{\text{int}} \right), \quad (14)$$

where $k_{\text{diff}}^{\text{H}_2\text{O}}$ is the mass transfer coefficient of the H_2O from the gas to the interface, $C_{\text{H}_2\text{O}}^{\text{int}}$, $C_{\text{H}_2\text{O}}^{\text{gas}}$ – concentration of H_2O in the gas and at the interface respectively. Here only $k_{\text{diff}}^{\text{H}_2\text{O}}$ can vary spatially due to a different thickness of the diffusion layer along the silicon-gas interface.

The same principle can be applied to the diffusion of from the interface to the gas. Assuming good mixing in the silicon and slowly changing concentrations of B (char-

acteristic time is several hours), C_B can be assumed to be constant along the surface; hence, $C_{\text{HBO}}^{\text{int}}$ is also constant.

$$J_{\text{HBO}} = k_{\text{diff}}^{\text{HBO}} (C_{\text{HBO}}^{\text{int}} - C_{\text{HBO}}^{\text{gas}}). \quad (15)$$

Taking into account those consider-

ations, it is possible to simplify the model to a purely diffusion dominated impurity flux from the silicon to the gas in the boundary layer. The boron removal rate depends also on the amount of water vapor in the reactive gas, but this is not taken into account here.

2.4. Submodel for Stationary Melt Surface

A variant of the model described above that also includes the molten silicon in the crucible was implemented in ANSYS *Fluent* to, first, verify the assumption that mass transfer of impurities from the melt could be approximated by effective diffusion, and, second, to study whether impurity removal rate could be improved solely by manipulating the gas flow above the melt. The model and its results are described more in detail in [15], but key elements are outlined here as well. Afterwards, the main model in *OpenFOAM* was verified against the submodel implemented in *Fluent* to obtain at least some verification of the main model.

In this separate study, a 2D axi-symmetrical crucible of radius $R_0 = 0.0031$ and centrally located inlet radius $r_0 = 0.0031$ was considered. The height of the crucible was $H = 0.186$ m and was filled up to half height with molten silicon. The top half of the crucible is filled with (initially clean) argon gas. Additionally, there is an inductor

placed around the molten silicon that facilitates melt mixing. The current in the inductor was $I = 10$ kA with frequency $f = 50$ Hz, the inductor had 10 turns and a total height $h = 0.082$ m. The material constants were silicon density $\rho_{\text{Si}} = 2550$ kg/m³ [14], silicon viscosity $\mu_{\text{Si}} = 9.78 \cdot 10^{-4}$ Pa·s [16], argon density $\rho_{\text{Ar}} = 1.511$ kg/m³, argon viscosity $\mu_{\text{Ar}} = 7.44 \cdot 10^{-5}$ Pa·s [17]. The argon gas introduced through the top inlet was flowing in at a velocity of $v_0 = 2.21$ m/s. The temperature of the crucible was $T = 1500$ °C. Other boundary conditions are consistent with Table 1, except that in this model the interface between the melt and gas is no longer a geometric boundary. Instead, the silicon melt has an initial impurity concentration $c = 1$, which can diffuse to the gas phase according to Fick's law with a uniform diffusion constant $D_0 = 3.4 \cdot 10^{-4}$ m²/s. This corresponds to the diffusion coefficient for HBO gas [18]. A schematic representation of the model can be seen in Fig. 2a.

3. RESULTS AND DISCUSSION

3.1. Verification of Effective Diffusion Assumption

The submodel described in Section 2.4. was run in ANSYS *Fluent*. An exponential decay was obtained for the average concentration in the silicon melt with a characteristic time of $\tau = 1.36$ (see Fig. 2b). This allows for the estimation of the coefficient according to Eq. (1), which gives the value $k_B = 1.9 \cdot 10^{-5}$ m/s. This value is both in agree-

ment with the range described in Section 1 and with literature where experimental data are available for similar cases with silicon melt stirring [7], [19]. This agreement with other works appears to justify the assumptions made previously in this paper.

However, later on, a moving silicon melt surface will be considered, and this will be

modelled with the algorithm *pimpleDyMScalarFoam* outlined in Section 2.2. To verify this algorithm, identical cases were studied with the *pimpleDyMScalarFoam* algorithm in *OpenFOAM 4.1* and in *ANSYS Fluent 18*. The case was set up according to Table 1 with a stationary melt surface and the same computational mesh was deployed in both programs. Upon comparing the results, the flow velocity fields and concentration fields matched, with differences of no greater than 3 % across the domain for all physical quan-

tities and for the concentration flux at the outflow. Because the mesh independence study showed a dependence on the mesh no greater than 1 %, then the error of all results for concentration outflow is assumed to be 3 % of the flux value. This is how error bars are calculated later in the paper. This slight disagreement between *ANSYS Fluent* and *pimpleDyMScalarFoam* is most likely due to slightly different implementations of wall functions and numerical schemes.

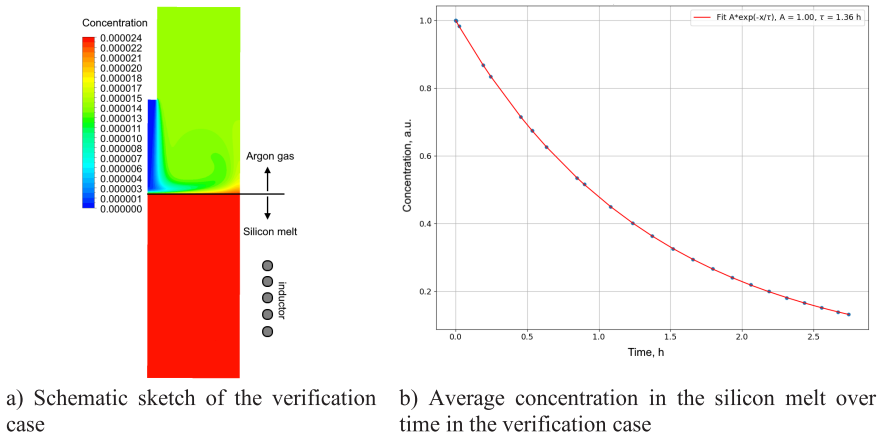


Fig. 2. Verification case setup and data of impurity concentration over time.

3.2. Simulations for Steady Surface with the Fluent Submodel

Because it was not clear whether the gas velocity and thus also the turbulence and the thickness of the boundary layer are the main parameters responsible for the removal of boron, an assumption was made that it was the uniform distribution of the incoming (clean) oxidizing gas across the surface which could enhance the purification rate. For this reason, simulations with a steady (flat) free surface were done for a different number of lances of the incoming gas jet (see [15]). More jets may lead to a more uniform distribution of the incoming gas and the normal gradient of concentration would be equal across the free surface.

Quasi-stationary gas and silicon flow patterns and boron concentration distribution are shown in Fig. 3. Similar distributions are also obtained with a 3D model (see [15]). The time scale in plots is scaled according to $t^* = D/d^2t$, where D – diffusion coefficient of HBO in gas, d – crucible diameter. Thus, time scale $t^* = 1$ corresponds to the diffusion time scale.

The computed integral boron concentration in silicon during long-time refinement process is shown in Fig. 4 – dotted and solid lines for 2D and axi-symmetrical 3D models with a single lance ($n = 1$), accordingly. The estimated dimensionless boron mass

transfer coefficient value $k_B^* = k_b \cdot \frac{d}{D}$ based on simulation of refinement is $k_B^* = 36.27$ for 2D model; for the axi-symmetrical 3D model the estimated value is by 10 % greater – $k_B^* = 39.94$ (see Fig. 4).

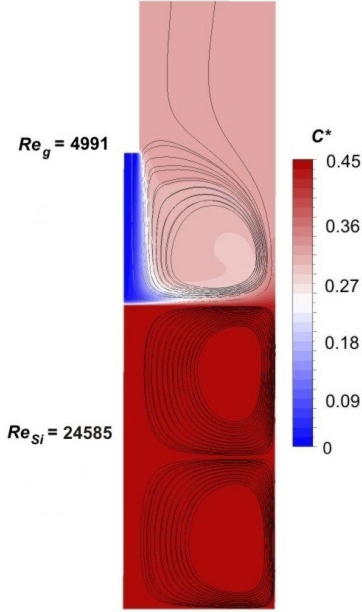


Fig. 3. 2D scheme of boron removal from silicon with gas jet: Re_{si} and Re_g – silicon and gas Reynolds numbers and C^* – boron concentration contours, where $C^* = \frac{C_{B,t}}{C_{B,0}}$ and $C_{B,0} = 10^{-5}$, obtained with 2D model for flow time $t^* = 0.022$.

The computations are performed for different numbers of lances $n = 1, 2, 3, 4, 5, 13$. The total flow rate of all gas jets is constant and equal to the flow rate of the gas jet for the model with a single lance. The coefficient k_B^* as a function of the number of lances n is shown in Fig. 5 (blue scale and triangles). The obtained results show that the largest value of k_B^* corresponds to a single lance system. A possible explanation is connected with the analysis of gas flow patterns in the vicinity of gas–silicon interface:

- The gas flow rate in each single jet for a multiple lance system is lower; hence, the turbulence is lower;

- Gas jets decelerate each other;
- The inertia of the incoming jet is lower and, thus, less gas reaches the surface, and the diffusion boundary layer is larger in case of multiple jets.

A very important issue here is the size of the diffusion boundary layer. This is essential in a real process where chemical reactions take place. As already noted, this is modelled instead via effective diffusion. A simple way of viewing the influence of the boundary layer is following the path of a single oxygen molecule. Oxygen with a water molecule diffuses through the boundary layer with a mass transfer coefficient $k_{diff}^{H_2O}$, then water reacts with boron (reaction Eq. (12)), and HBO is removed from the system, first through boundary layer with k_{diff}^{HBO} , and then with gas in bulk flow. For boron removal, two diffusion processes must follow each other.

Figure 5 also shows the dependence of the mass transfer coefficient on the height of the lance (distance from the silicon surface). It is visible that there is a slight enhancement of mass transfer if the lance is moved closer to the surface – an increase of h^* by moving the lance from the distance $h^* = h/d = 0.75$ to $h^* = 0.05$.

Simulations with slanted lances were also performed; however, the coefficient k_B^* decreased by 30 % when the angle of the slope α_{lance} increased by 45° as measured from the vertical line.

This suggests that it is not possible to improve the purification rate by manipulating only the gas flow – different numbers of lances and/or diameters of lances and/or sloping angles of the lances do not give any improvement when the total mass flow rate of the gas is kept constant and the lance height is kept constant as well.

Therefore, to obtain any improvement, an investigation on the wavy melt surface is required.

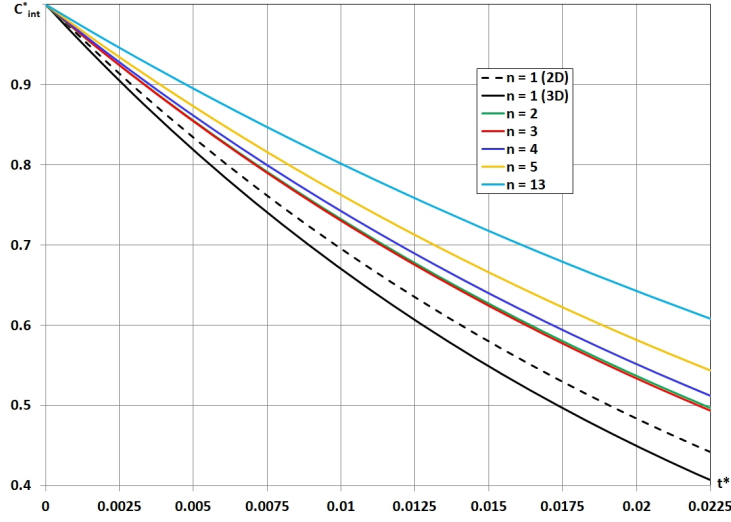


Fig. 4. Boron integral concentration C_{int}^* (where $C_{int}^* = \frac{C_{B,t}^{int}}{C_{B,0}^{int}}$) in silicon melt as a function of silicon refining process time t^* for different numbers (n) of vertical ($\alpha_{lance} = 0^\circ$) gas lances.

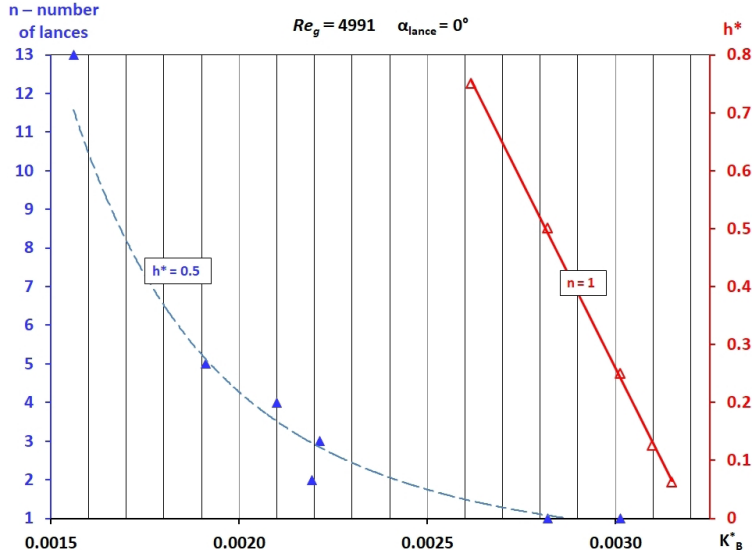


Fig. 5. Boron mass transfer coefficient k_B^* at the gas-silicon interface for vertical ($\alpha_{lance} = 0^\circ$) gas lances: (red scale and triangles) k_B^* as a function of gas lance height lance-to-melt with a linear trend line (solid) (blue scale and triangles) k_B^* as a function of the number of lances n for $h^* = 0.5$ with power trend line (dotted).

3.3. Wave Parameter Impact on HBO Diffusion

From here on out, the wavy silicon surface is considered. To study the impact of molten silicon surface waves on impurity

diffusion away from the silicon, numerical calculations were performed with the main model in *OpenFOAM*. The criterion

for the quality of impurity diffusion is the concentration flow which flows out of the computational domain Φ_C . Surface wave amplitude, frequency and wavelength are chosen as independent parameters to study the impact on impurity removal. The role of the impurity diffusion coefficient D on the factors determining impurity evacuation rate will be discussed later in Section 3.5.

In our calculations, no case went above a dimensionless wave amplitude of $A/\lambda > 0.2$. This is because waves larger than that approach the limit at which they would be expected to deform and crash. Furthermore, the obtained data were also normalized by the enlargement of the surface area due to waves to determine whether

the improvement in impurity removal was solely due to the surface area enlargement. Since the surface waves are assumed to be harmonic in the scope of this research, one can analytically calculate the surface area of the wavy surface with basic calculus. To obtain the surface area enlargement, one must then divide the enlarged surface by the original surface of the stationary melt. Thus, the average surface area enlargement q over time can be calculated numerically by using:

$$q = \frac{1}{R_0} \int_0^{R_0} \sqrt{1 + \frac{1}{2} \left(\frac{\pi n A}{R_0} \cos \frac{\pi n x}{R_0} \right)^2} dx, \quad (16)$$

where l is the crucible radius and n is the wavenumber of the surface waves.

3.3.1. Effect of Frequency

First of all, the effect of wave oscillation frequency on impurity diffusion was studied. It is important to note that in this part of the study, frequency was considered independent of wavelength (that is, only the wave oscillation was changed while the wavelength was kept constant $\lambda = 0.25$ m). Later in the study, the dispersion relation was taken in account to model the relationship between frequency and wavelength. As can be seen in Fig. 6, no change was observed – the mean value of the total impurity concentration flow away from the com-

putational domain was unchanged. Changes could be observed only in small time scale oscillations (at the same order of magnitude as the wave oscillations themselves) which did not affect long-term processes (such as the overall purification of the molten silicon). The frequencies studied were around the base frequency f_0 for the chosen base wavelength $\lambda = 0.25$ m. According to Eq. (8), $f_0 = 2.52$ Hz. The error bars for Fig. 6 (and further figures from here on out) are calculated as described in Section 3.1.

3.3.2. Effect of Amplitude

A series of calculations with fixed wavelength and variable wave amplitudes was computed. In Fig. 7, a clear upward trend with increasing wave amplitude above the

error threshold for the impurity concentration outflow can be observed. Furthermore, the normalized data almost agree with the stationary surface effective diffusion rate.

3.3.3. Effect of Wavelength

Next, a series of calculations with fixed amplitude and variable wavelengths was computed. In Fig. 8, an upward trend beyond

the error threshold is also observable. The data were once again normalized to surface area enlargement. In this case, despite hav-

ing approximately the same dimensionless flow values differ significantly. amplitudes, the observed concentration out-

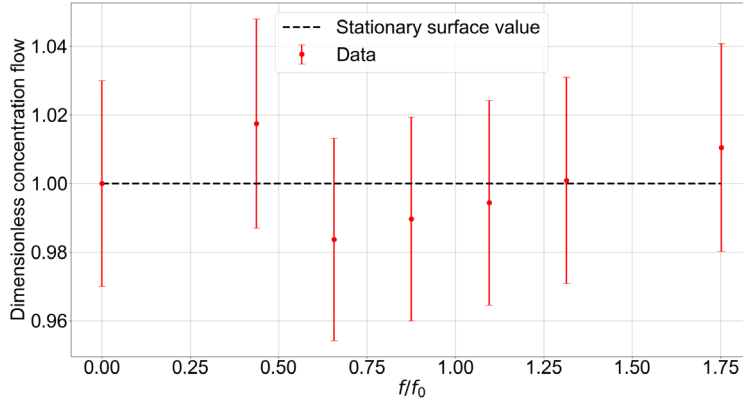


Fig. 6. HBO concentration outflow as a function frequency, $f_0 = 2.52$ Hz.

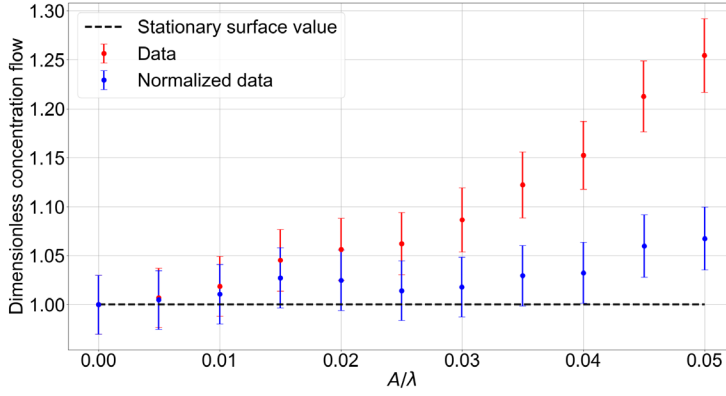


Fig. 7. HBO concentration outflow as a function of dimensionless wave amplitude for variable amplitudes. Amplitude is normalized to $\lambda = 0.25$ m.

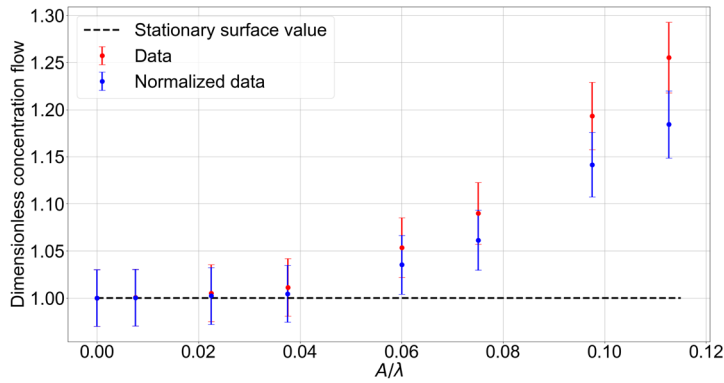


Fig. 8. HBO concentration outflow as a function of dimensionless wave amplitude for variable wavelength. The amplitude is constant $A = 0.015$ m.

3.4. Factor Analysis

In both cases of variable amplitude and variable wavelength, an improvement for integral concentration outflow is observed. There are multiple factors that could contribute to this.

To begin, there is the surface area enlargement due to waves. As impurity diffusion occurs via the surface, a larger surface area would also mean increased diffusion. In the variable amplitude case, this would almost suffice as an explanation – as can be seen in Fig. 7, the normalized data agree with the original stationary surface diffusion rate within a margin of error (except for the final two points). However, this does not explain the data obtained with variable wavelength. Here, the normalized data do not agree with the stationary diffusion rate. Therefore, some other mechanism must be in play.

As [20] has shown, thermal diffusion for inclined plates (with respect to the incoming flow direction) increases with an angle of attack. The flow above the surface waves is practically horizontal (consider Fig. 10), so the flow regime is not unlike the one studied by [20]. Therefore, the angle of the surface wave crests with respect to the incoming flow plays a role in the improvement of the diffusion rate. As the value of A/λ increases, so does the maximum angle of the wave, thus improving diffusion. This, for example, could contribute to the disparity for the final two points for the normalized data in Fig. 7.

Furthermore, it can also be shown that waves with a larger dimensionless wave amplitude generate greater turbulence in the vicinity of those waves. To support this, additional supportive calculations were performed in ANSYS Fluent, in which the flow close to the waves was studied. In Fig. 9, eddy viscosity μ_T near the waves

is larger for the case when the amplitude is also greater. This has a direct impact for impurity diffusion as well – turbulent diffusion is far greater than molecular diffusion ($D_T/D_0 \gg 1$); thus, eddy viscosity is a deciding factor for the rate of diffusion at a certain point in the flow. For larger wave amplitudes, turbulence near waves is also greater, facilitating better impurity removal from the area immediately next to the waves. This is in accord with a similar study done in [21], where an analogous problem is studied for heat diffusion in wavy channels.

Finally, the flow characteristics above surface waves must also be considered. All of the factors considered thus far affect diffusion uniformly across the whole surface. However, the flow above the waves introduce a certain asymmetry. In Fig. 10, the flow velocity vectors show that the flow both near the axis of the geometry (leftmost side) and next to the wall (rightmost side) is stagnant. In these stagnant points, particularly near the wall, a stable concentration gradient can form, as opposed to the waves in the middle, where no stable gradient can form. Because of this, diffusion is more intense where the flow is closer to the waves, and less intense in the stagnant points. Therefore, all the previously discussed effects also have a more pronounced effect for waves in the middle and less so for the waves near the edges of the geometry.

This effect allows for illustration of the tendency seen in Fig. 8. Even though values for A/λ were the same for both the cases of variable amplitude and variable wavelength, the integral concentration outflow differs significantly. This means that changing amplitude at a fixed wavelength and changing wavelength at a fixed amplitude

is not the same in terms of effect produced, even if it is in terms of dimensionless amplitude. This may be explained by the effect just discussed – when the wavelength is shortened, more waves appear in the active

diffusion zone, allowing for all the previous mechanisms to have a more pronounced effect, leading to an increase in concentration outflow.

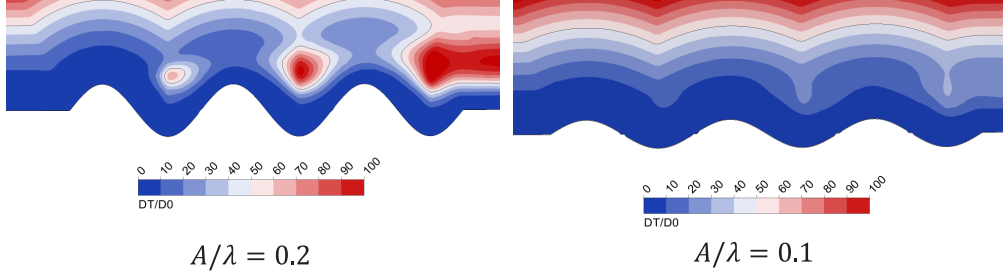


Fig. 9. Eddy viscosity near waves for different wave heights.

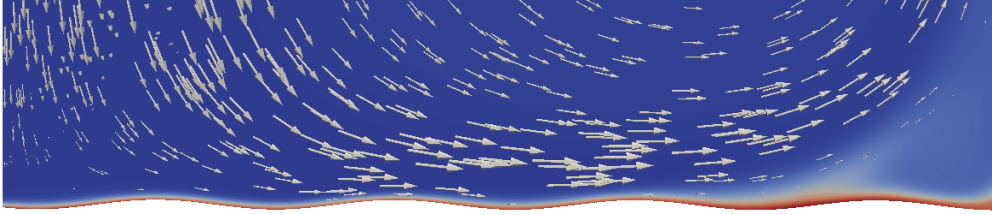


Fig. 10. Flow regime directly above the surface waves. Vectors denote velocity, background coloring denotes concentration of HBO.

3.4.1. Role of Molecular Diffusion

Up to this point, the role of molecular diffusion of HBO has not been analysed. Namely, the Peclet number in all cases considered up to this point was nearly the same. A separate study has been done to determine how the Peclet number impacts the results so far discussed. In this study, five otherwise identical cases were simulated with different values of Pe . To calculate Pe , one must choose a characteristic length and velocity. Because the silicon-gas interface is of interest, the characteristic length is chosen equal to wave amplitude and the characteristic velocity is chosen as the gas velocity directly above the interface. To better understand the factors impacting

impurity removal, this study also considers the impact of different Pe numbers near the melt-gas interface.

To determine this, simulations exactly like described in Subsection 3.3.3 were run again, but with modified molecular diffusion coefficients for the impurities in order to obtain different Pe numbers. It was found that for certain values of Pe , the surface waves had no impact whatsoever on the concentration outflow – it remained the same for all combinations of dimensionless amplitudes and never showed a value larger than for the stationary surface without waves. However, for larger Pe , the characteristic impact discussed previously reap-

peared (see Fig. 12).

The different values of Pe dictate the extent to which impurities can diffuse into the gas phase at a given time. It was empirically determined that if the molecular diffusion length was large with respect to the amplitude of the waves, the waves could

no longer impact the diffusion of HBO (see Fig. 12). Clearly, if the impurities quickly diffuse into the gas, then wave phenomena below this characteristic diffusion length have a diminishing impact. A side-by-side comparison of two cases with different values of Pe can be seen in Fig. 11.

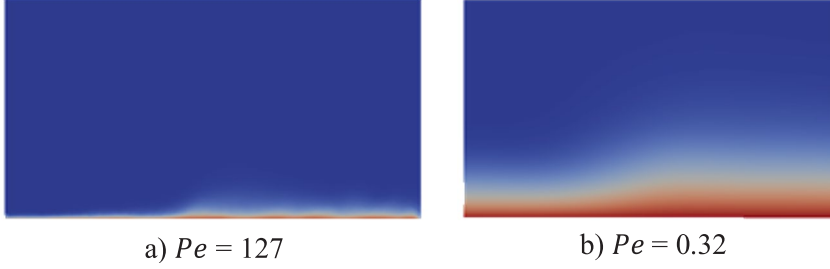


Fig. 11. Diffusion length at time t when the gas hits the melt surface for (a) a large value of Pe (b) a small value of Pe .

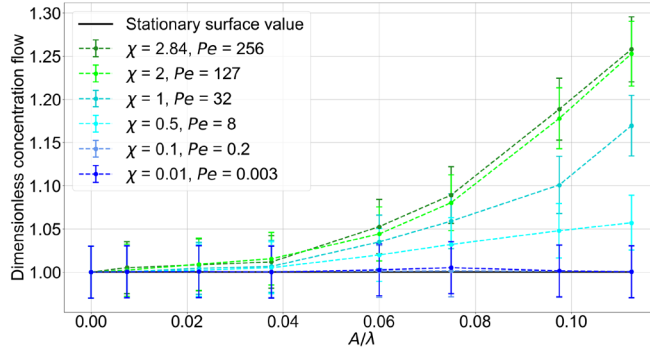


Fig. 12. HBO concentration outflow as a function of dimensionless wave amplitude for a variable amplitude at different values of χ , $A = 0.015$ m.

It is hypothesized that a dimensionless parameter that relates the molecular diffusion length to the amplitude of the waves is important for forecasting whether surface waves will have any impact on the overall diffusion of HBO impurities to the gaseous phase. It is defined in the following way:

$$\chi = \frac{A}{2\sqrt{(D_0 T)}}, \quad (17)$$

where A is the surface wave amplitude and T is the period of oscillation for these waves.

It has been observed that χ should be at least larger than unity for surface waves to have an effect on the impurity diffusion at the surface (see Fig. 12). This dimensionless number relates the wave amplitude with the characteristic diffusion length over one oscillation period. The reasoning behind choosing such a definition for this number is that the “period” of diffusion is also the wave period – that is to say that the global gas flow removes diffused impurities from the interface once per wave oscillation.

In Fig. 12, one can note that for values of $\chi \ll 1$ the existence of waves does not impact the outflow of HBO at all (at least within the amplitudes considered within the study). The behaviour considered previously in this paper, however, is described by the points corresponding to $\chi = 2.84$. One can note that, as χ approaches 1, the surface waves begin to affect the HBO removal process, but not quite to the extent as previously determined. When $\chi = 2$, practically the same behaviour is retained as when $\chi = 2.84$. This is in accord with our hypothesis that there is a requirement for $\chi > 1$ for surface waves to have an impact on the impurity removal phenomenon.

This may be counter-intuitive – greater diffusion of impurities to the gas phase leads to *less* effect from the wavy surface. However, this does not mean that the concentration outflow is less. In Fig. 12, the value on the vertical axis is the normalized concentration flow, meaning that the absolute concentration flow rates can be different for each case. In fact, total concentration outflow grows with an increasing diffusion coefficient – which is because more impurities can diffuse into the gas phase. However, as diffusion increases, the diffusion length also becomes greater, meaning that

the wavy surface has less impact on the process efficiency because it is below the characteristic length of diffusion. For example, in Fig. 11 (a) the value of $\chi = 2$, and in Fig. 11 (b) the value of $\chi = 0.1$. The first case showed a pronounced effect of surface waves on impurity diffusion, the second displayed none.

In real-life applications, it is impossible to impact the molecular diffusion coefficient of some particular substance. However, in practical terms, this allows for the calculation of the minimum wave amplitude required to observe any improvement in effective diffusion (also in terms of wave frequency f if one assumes that must be larger than unity:

$$A \geq 2\sqrt{D_0 T} = 2\sqrt{\frac{D_0}{f}}. \quad (18)$$

Thus, for a given system, one must generate waves of at least such an amplitude to expect any meaningful improvement for the molten silicon purification process. Estimating this value from [10], using $f = 5$ Hz and D_0 for HBO gas, the minimum wave amplitude $A_{\min} \approx 0.017$ m. For a small crucible it is an unfeasible limitation, but for larger crucibles wave amplitudes of a few centimeters should be attainable.

4. CONCLUSIONS

In the analysed surface-to-gas diffusion problem, it was shown that the increased number of jets directed at the surface could not ensure better mass transfer from the surface at the fixed gas flow rate. For this reason, the wavy surface was analysed and it was found that it increased the effective diffusion rate of impurities from the surface by means of several phenomena:

- waves increased the surface area and thus also the effective diffusion rate;

- they altered the flow patterns near the surface, generating more turbulence near the surface and leading to better turbulent diffusion;
- a decreased diffusion boundary length due to an angle between the main flow and the surface also improved the impurity removal rate.

However, a limitation for the effective diffusion from the surface at large molecu-

lar diffusion coefficients was found. This limitation is linked to the ratio between the characteristic molecular diffusion length

and the wave amplitude, making this approach unsuitable for small systems.

ACKNOWLEDGEMENTS

The research has been funded by the European Regional Development Fund under contract “Refinement of Metallurgi-

cal Grade Silicon Using Smart Refinement Technologies” (No. 1.1.1.1/16/A/097).

REFERENCES

1. International Renewable Energy Agency. (2022). *Renewable Power Generation Costs in 2022* (report). ISBN: 978-92-9260-544-5
2. Kavlak, G., McNerney, J., & Trancik, J.E. (2018). Evaluating the Causes of Cost Reduction in Photovoltaic Modules. *Energy Policy*, 123, 700–710. <https://doi.org/10.1016/j.enpol.2018.08.015>.
3. Delannoy, Y. (2012). Purification of Silicon for Photovoltaic Applications. *Journal of Crystal Growth*, 360, 61–67.
4. Fu, R., James, L. T., & Woodhouse, M. (2015). Measurements of Polysilicon for the Photovoltaic Industry: Market Competition and Manufacturing Competitiveness. *IEEE Journal of Photovoltaics*, 5 (2), 515–524.
5. Khattak, C., Joyce, D., & Schmid, F. (2002). A Simple Process to Remove Boron from Metallurgical Grade Silicon. *Solar Energy Materials and Solar Cells*, 74 (1), 77–89.
6. Safarian, J., & Tangstad, M. (2012). Kinetics and Mechanism of Phosphorus Removal from Silicon in Vacuum Induction Refining. *High Temperature Materials and Processes*, 31. 10.1515/htmp.2011.143.
7. Sortland, Ø., & Tangstad, M. (2014). Boron Removal from Silicon Melts by H₂O/H₂ Gas Blowing: Mass Transfer in Gas and Melt. *Metallurgical and Materials Transactions E*, 1 (3), 211–225.
8. Safarian, J., Thang, K., Hildal, K., & Tranell, G. (2014). Boron Removal from Silicon by Humidified Gases. *Metallurgical and Materials Transactions E*, 1, 41–47.
9. Nordstrand, E. F., & Tangstad, M. (2012). Removal of Boron by Moist Hydrogen Gas. *Metallurgical Material Transactions B*, 43, 814–822.
10. Galpin, J., & Fautrelle, Y. (1992) Liquid-Metal Flows Induced by Low-frequency Alternating Magnetic Fields. *Journal of Fluid Mechanics*, 239, 383–408. doi:10.1017/S0022112092004452
11. Fautrelle, Y., & Sneyd, A.D. (2005). Surface Waves Created by Low-Frequency Magnetic Fields. *European Journal of Mechanics – B/Fluids*, 24 (1), 91–112. <https://doi.org/10.1016/j.euromechflu.2004.05.005>
12. Kestin, J., & Whitelaw, J.H. (1964). The Viscosity of Dry and Humid Air. *International Journal of Heat and Mass Transfer*, 7 (11), 1245–1255. [https://doi.org/10.1016/0017-9310\(64\)90066-3](https://doi.org/10.1016/0017-9310(64)90066-3)
13. Yuan, Z., Mukai, K., & Huang, W. (2002). Surface Tension and Its Temperature Coefficient of Molten Silicon at Different Oxygen Potential. *Langmuir*, 18, 6, 2054–2062. <https://doi.org/10.1021/la0112920>
14. Sato, Y., Nishizuka, T., Hara, K., Yamamura, T., & Waseda Y. (2000). Density Measurement of Molten Silicon by a Pycnometric Method. *International Journal of Thermophysics*, 21, 1463. <https://doi.org/10.1023/A:1006661511770>
15. Geža, V., & Pavlovs, S. (2020). Numerical Modelling of Boron Removal from Silicon by Oxidizing Gas Jet. *Magnetohydrodynamics*, 56, 81–91. doi:10.22364/mhd.56.1.8

16. Rhim, W.K., & Ohsaka, K. (2000). Thermophysical Properties Measurement of Molten Silicon by High-Temperature Electrostatic Levitator: Density, Volume Expansion, Specific Heat Capacity, Emissivity, Surface Tension and Viscosity. *Journal of Crystal Growth*, 208 (1–4), 313–321. [https://doi.org/10.1016/S0022-0248\(99\)00437-6](https://doi.org/10.1016/S0022-0248(99)00437-6)
17. Guevara, F. A., McInteer, B. B., & Wageman, W. E. (1969). High-Temperature Viscosity Ratios for Hydrogen, Helium, Argon, and Nitrogen. *The Physics of Fluids*, 12 (12), 2493–2505.
18. Marrero, T.R., & Mason, E.A. (1973). Correlation and Prediction of Gaseous Diffusion Coefficients. *AIChE J.*, 19, 498–503. doi:10.1002/aic.690190312
19. Sortland, O.S. (2015). Boron Removal from Silicon by Steam and Hydrogen. PhD Thesis. Trondheim: Norwegian University of Science and Technology.
20. Khanjian, A., Habchi, C., Russeil, S., Bougeard, D., & Lemenand, T. (2018). Effect of the Angle of Attack of a Rectangular Wing on the Heat Transfer Enhancement in Channel Flow at Low Reynolds Number. *Heat Mass Transfer*, 54, 1441. <https://doi.org/10.1007/s00231-017-2244-8>
21. Dellil, A.Z., Azzi, A., & Jubran, B.A. (2004). Turbulent Flow and Convective Heat Transfer in a Wavy Wall Channel. *Heat Mass Transfer*, 40, 793. <https://doi.org/10.1007/s00231-003-0474-4>