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A mathematical model for silicon chlorination

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Abstract

A mathematical model was developed to complement an experimental investigation on the kinetics of chlorination of a fixed bed of −4 to +14 mesh silicon particles. By comparing the experimental data with the results obtained from the model a good agreement was found. The model evaluated the mass transfer coefficient (k_g) and the rate constant (k_r) as a function of temperature, bed porosity, and bed height. It was observed that the difference between k_g and k_r was higher for the lower temperature range characterizing the greater sensitivity of k_r at more elevated temperatures. It was also evidenced that bed compacting exercised greater influence than bed height on mass transfer. Therefore, the effect of compacting on the behavior of the chlorination system was more significant due to the increased role of the diffusion component on the mechanism of mass transport.

Keywords: Silicon; Kinetics; Mathematical model; Chlorination; Mass transfer

1. Introduction

Metal chlorides are raw materials of fundamental economic and strategic importance for electronics, telecommunications, metallurgical industries, and in areas related to advanced ceramics, chemicals and automobiles. Among the metallic chlorides, silicon tetrachloride ($SiCl_4$) is prominent as an intermediate material for obtaining high purity compounds such as silicon nitrite (Si_3N_4), silicon dioxide (SiO_2), and electronic as well as solar grade metallic silicon (Si-GE/GS) [1–3].

These compounds find innumerable applications in the fabrication of:

1. Cutting tools, internal combustion engine components, high velocity roller bearings, mechanical seals, etc., in the area of advanced ceramics;
2. Optical fibers in the telecommunications industry;
3. Photovoltaic cells for generation of electricity;
4. Integrated circuits, transistors, thyristors, detectors, and rectifiers in the electrical-electronic industries.

Amid the various routes that have been used to obtain silicon tetrachloride, the chlorination of silicon with chlorine gas and HCl stands out, since the product obtained has characteristics that permit more efficient removal of metallic impurities [4–7]. However, most of these works are related to a practical analysis of the experimental data without a more detailed conceptual discussion and its mathematical interpretation.

Therefore, the main purpose of this work is to provide a relevant contribution in terms of a mathematical model developed to encompass the chemical and physical aspects of the chlorination of silicon particles with chlorine gas. In this sense, the model equations allow a comparison between the rate constant and the mass transfer coefficient under different conditions of temperature, bed porosity and bed height. A prediction of the silicon conversion along the reaction time is also obtained and compared with the experimental results.

2. Experimental method

Metallurgical grade silicon with particle size between −4 and +14 Tyler mesh, supplied by the Institute for Technological Research, São Paulo, Brazil, was used in the chlorination runs. Its chemical composition is shown in Table 1. Its density as determined by helium picnometry was 2.29 g/cm^3. This value was found to be quite close to the theoretical one (2.32±0.02 g/cm^3) [8]. The average particle size as obtained by sieve analysis was 2.1 mm [9].

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Table 1
Chemical composition of metallurgical grade silicon (−4 to +14 Tyler mesh)

Element	Quantity (ppm)
Mg	200
Al	275
P	50
Ti	1880
Mn	94
Fe	1892
Co	10
Ni	10
Cu	<10
B	120
Ca	700
Ag	15
C	80
S	6
Cr	5
Sc	0.2

The experimental procedure consisted of initially weighing the metallurgical grade silicon (Si-GM, −4 to +14 Tyler mesh) to obtain a specific bed height. The Si-GM specimen was introduced into the reactor together with an inert gas (argon). Upon reaching the run temperature, argon was replaced by chlorine gas, with a predetermined flow rate (1.80 l/min), pressure (1 atm) and for a fixed length of time (5–30 min). At the end of the run, the flow of chlorine was stopped, and argon was once again injected to cool the specimen and to purge the chlorination line for 10–15 min. Finally, the bed was removed from the furnace, stored in a dessicator for cooling, weighed and quantitatively analyzed.

Table 2
Experimental conditions

Parameters	Conditions
Temperature (°C)	500, 550, 600, 650, 700
Bed porosity	0.2914, 0.2709, 0.2100, 0.2118
Bed height (mm)	5, 10

Table 2 presents the experimental conditions that were used. The results have been interpreted in terms of the fraction of converted silicon (χ), as a function of time, according to Eq. (2.1), and compared with the silicon conversion curves, obtained from the mathematical model

$$\chi = \frac{m_{\text{Si}}^0 - m_{\text{Si}}}{m_{\text{Si}}^0} \tag{2.1}$$

where m_{Si}^0 is the initial mass of silicon (g) and m_{Si} the instantaneous mass of silicon (g). The experimental setup used in the chlorination runs is shown schematically in Fig. 1.

3. Mathematical model

The mathematical model that describes the progress of the reaction between chlorine gas and silicon is based on the kinetic equations for ‘one’ and ‘*N*’ particles.

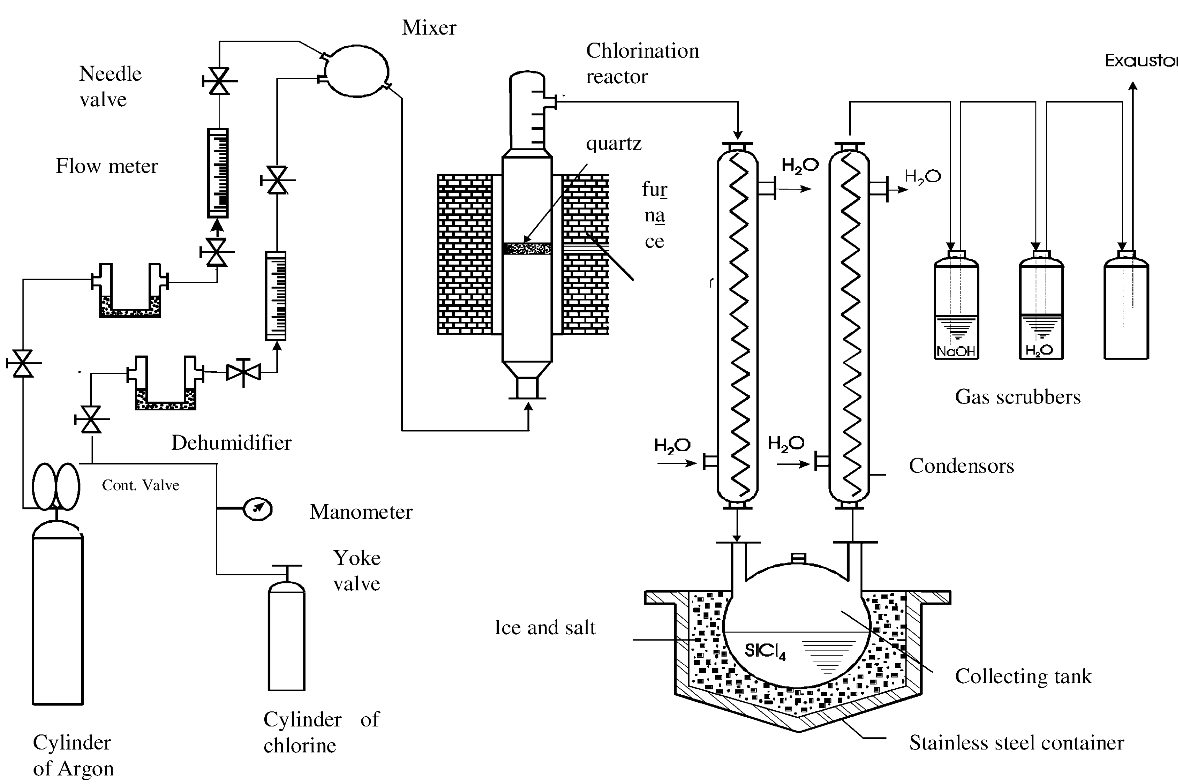

Fig. 1. Schematic representation of the experimental setup.

To express the kinetics of the reaction between chlorine and one silicon particle, the following assumptions were made:

(a) The chlorination reaction, $Cl_2\,(g) + (1/2)Si\,(s) \rightarrow (1/2)SiCl_4\,(g)$, is irreversible and first-order with respect to chlorine;
(b) The gases are ideal;
(c) The kinetics of the chlorination reaction is described by the unreacted core model [10–13] for particles decreasing in size with time and no ash layer formation;
(d) The silicon particle is considered to be spherical.

According to the unreacted core model, when a dense solid reacts with a gas, there is a sharp reaction and the two phenomena that control the rate, mass transfer and chemical reaction, occur in series. The equation that describes these two steps is

$$-\frac{dn_{Cl_2}}{dt} = \frac{4\pi r^2}{(1/k_g) + (1/k_r)}\bar{C}_{Cl_2} \quad (3.1)$$

where r is the particle radius (cm); $\bar{C}_{Cl_2}$ the average chlorine concentration in the gas stream (mol/cm^3); k_g the mass transfer coefficient of chlorine (cm/s) and k_r the rate constant, $k_r = k_0\,e^{-E_a/RT}$ (cm/s).

Under the above assumptions, the total rate constant, k (cm/s), is given by the expression:

$$k = \frac{1}{(1/k_g) + (1/k_r)} \quad (3.2)$$

Similarly, the molar balance for the solid reactant can be expressed by the equation

$$-\frac{dn_{Si}}{dt} = -4\pi\sigma_{Si}r^2\frac{dr}{dt} \quad (3.3)$$

where σ_{Si} is the molar density of Si (mol/cm^3), $n_{Si} = \sigma_{Si}V_{Si} = \sigma_{Si}(4/3)\pi r^3$ (mol). Hence

$$-\frac{dn_{Si}}{dt} = \frac{1}{2}\left(-\frac{dn_{Cl_2}}{dt}\right) = \frac{1}{2}4\pi r^2 k\bar{C}_{Cl_2}$$

With k expressed by Eq. (3.2) and after some manipulation,

$$\frac{dr}{dt} = \frac{1}{2}\left(\frac{1}{(1/k_g) + (1/k_r)}\right)\frac{\bar{C}_{Cl_2}}{\sigma_{Si}} \quad (3.4)$$

Since k_g is a function of r,

$$-\int_{r_0}^{r}\frac{dr}{k_g} + \frac{r_0 - r}{k_r} = \frac{1}{2}\frac{\bar{C}_{Cl_2}}{\sigma_{Si}}t \quad (3.5)$$

Table 3
Values of rate constant (k_r), average mass transfer coefficient ($k_{g\,ave}$), mass transfer resistance (RDF), chemical reaction resistance (RRQ) and RRQ/RDF ratio for non-compacted beds[a]

Temperature (°C)	Initial mass (g)	Initial fit	Final fit
500	12.37	$k_r = 0.34$ cm/s	$k_{r\,ave} = 0.34$ cm/s
		$k_{g\,ave} = 2.21$ cm/s	$k_{g\,ave} = 2.20$ cm/s
		RDF = 0.45 s/cm	RDF = 0.45 s/cm
		RRQ = 2.96 s/cm	RRQ = 2.93 s/cm
		RRQ/RDF = 6.53	RRQ/RDF = 6.45
550	12.59	$k_r = 0.38$ cm/s	$k_{r\,ave} = 0.37$ cm/s
		$k_{g\,ave} = 2.34$ cm/s	$k_{g\,ave} = 2.35$ cm/s
		RDF = 0.43 s/cm	RDF = 0.43 s/cm
		RRQ = 2.63 s/cm	RRQ = 2.68 s/cm
		RRQ/RDF = 6.15	RRQ/RDF = 6.30
600	12.46	$k_r = 0.43$ cm/s	$k_{r\,ave} = 0.41$ cm/s
		$k_{g\,ave} = 2.47$ cm/s	$k_{g\,ave} = 2.48$ cm/s
		RDF = 0.41 s/cm	RDF = 0.40 s/cm
		RRQ = 2.35 s/cm	RRQ = 2.46 s/cm
		RRQ/RDF = 5.80	RRQ/RDF = 6.10
650	12.67	$k_r = 0.53$ cm/s	$k_{r\,ave} = 0.52$ cm/s
		$k_{g\,ave} = 2.54$ cm/s	$k_{g\,ave} = 2.55$ cm/s
		RDF = 0.39 s/cm	RDF = 0.39 s/cm
		RRQ = 1.87 s/cm	RRQ = 1.94 s/cm
		RRQ/RDF = 4.75	RRQ/RDF = 4.96
700	12.61	$k_r = 0.72$ cm/s	$k_{r\,ave} = 0.75$ cm/s
		$k_{g\,ave} = 2.54$ cm/s	$k_{g\,ave} = 2.50$ cm/s
		RDF = 0.39 s/cm	RDF = 0.40 s/cm
		RRQ = 1.40 s/cm	RRQ = 1.33 s/cm
		RRQ/RDF = 3.55	RRQ/RDF = 3.33

[a] Conditions: $Q = 1.80$ l/min, $P = 1$ atm, $L = 5$ mm, $d_p = 0.21$ cm and $t = 30$ min.

Table 4
Values of rate constant (k_r), average mass transfer coefficient ($k_{g\,ave}$), mass transfer resistance (RDF), chemical reaction resistance (RRQ) and RRQ/RDF ratio for non-compacted beds[a]

Temperature (°C)	Initial mass (g)	Initial fit	Final fit
500	24.48	$k_r = 0.35$ cm/s	$k_{r\,ave} = 0.34$ cm/s
		$k_{g\,ave} = 1.52$ cm/s	$k_{g\,ave} = 1.52$ cm/s
		RDF = 0.66 s/cm	RDF = 0.66 s/cm
		RRQ = 2.90 s/cm	RRQ = 2.93 s/cm
		RRQ/RDF = 4.40	RRQ/RDF = 4.45
550	24.50	$k_r = 0.37$ cm/s	$k_{r\,ave} = 0.37$ cm/s
		$k_{g\,ave} = 1.62$ cm/s	$k_{g\,ave} = 1.62$ cm/s
		RDF = 0.62 s/cm	RDF = 0.62 s/cm
		RRQ = 2.74 s/cm	RRQ = 2.68 s/cm
		RRQ/RDF = 4.45	RRQ/RDF = 4.35
600	24.45	$k_r = 0.39$ cm/s	$k_{r\,ave} = 0.41$ cm/s
		$k_{g\,ave} = 1.73$ cm/s	$k_{g\,ave} = 1.72$ cm/s
		RDF = 0.58 s/cm	RDF = 0.58 s/cm
		RRQ = 2.57 s/cm	RRQ = 2.46 s/cm
		RRQ/RDF = 4.44	RRQ/RDF = 4.22
650	24.32	$k_r = 0.50$ cm/s	$k_{r\,ave} = 0.52$ cm/s
		$k_{g\,ave} = 1.79$ cm/s	$k_{g\,ave} = 1.78$ cm/s
		RDF = 0.56 s/cm	RDF = 0.56 s/cm
		RRQ = 2.02 s/cm	RRQ = 1.94 s/cm
		RRQ/RDF = 3.60	RRQ/RDF = 3.45
700	24.61	$k_r = 0.79$ cm/s	$k_{r\,ave} = 0.75$ cm/s
		$k_{g\,ave} = 1.75$ cm/s	$k_{g\,ave} = 1.77$ cm/s
		RDF = 0.57 s/cm	RDF = 0.56 s/cm
		RRQ = 1.27 s/cm	RRQ = 1.33 s/cm
		RRQ/RDF = 2.22	RRQ/RDF = 2.35

[a] Conditions: $Q = 1.80$ l/min, $P = 1$ atm, $L = 10$ mm, $d_p = 0.21$ cm and $t = 30$ min.

Using the correlation proposed by Kato et al. [14], for gas–solid mass transfer in fixed beds operated at low Reynolds numbers,

$$\frac{k_g d_p}{D_{Cl_2}} = 0.72\, Sc^{1/3}\left[Re\left(\frac{d_p}{L}\right)^{0.6}\right]^{0.95}$$

for $R = Re\left(\frac{d_p}{L}\right)^{0.6}$ where $0.1 \le R \le 5.0$

where Re is the Reynolds number, $Re = ud_p\rho_{Cl_2}/\mu_{Cl_2}$; Sc the Schmidt number, $Sc = \mu_{Cl_2}/\rho_{Cl_2}D_{Cl_2}$; u the chlorine velocity (cm/s); d_p the average particle diameter (cm); ρ_{Cl_2} the chlorine density (g/cm^3); μ_{Cl_2} the chlorine viscosity (g/s cm); D_{Cl_2} the chlorine diffusivity (cm^2/s) and L the bed height (cm).

Defining the parameter α

$$\alpha = \frac{0.72 D_{Cl_2} Sc^{1/3}}{2}\left[\frac{2u\rho_{Cl_2}}{\mu_{Cl_2}}\left(\frac{2}{L}\right)^{0.6}\right]^{0.95}$$

then $k_g = \alpha r^{0.52}$.

Table 5
Values of average mass transfer coefficient ($k_{g\,ave}$), mass transfer resistance (RDF), chemical reaction resistance (RRQ) and RRQ/RDF ratios for compacted beds

Bed height (mm)	Bed porosity	Initial mass (g)	
(a) $T = 550\,^\circ$C, $Q = 1.80$ l/min, $P = 1$ atm, $k_{r\,ave} = 0.37$ cm/s, $d_p = 0.21$ cm, $t = 25$ min			
5	0.21	13.72	$k_{g\,ave} = 0.10$ cm/s RDF = 10.20 s/cm RRQ = 2.69 s/cm RRQ/RDF = 0.26
10	0.15	29.54	$k_{g\,ave} = 0.11$ cm/s RDF = 9.52 s/cm RRQ = 2.69 s/cm RRQ/RDF = 0.28
10	0.21	27.52	$k_{g\,ave} = 0.14$ cm/s RDF = 7.71 s/cm RRQ = 2.68 s/cm RRQ/RDF = 0.35
(b) $T = 700\,^\circ$C, $Q = 1.80$ l/min, $P = 1$ atm, $k_{r\,ave} = 0.75$ cm/s, $d_p = 0.21$ cm, $t = 20$ and 25 min			
5 ($t = 25$)	0.21	13.7122	$k_{g\,ave} = 0.11$ cm/s RDF = 8.85 s/cm RRQ = 1.33 s/cm RRQ/RDF = 0.15
10 ($t = 20$)	0.15	29.66	$k_{g\,ave} = 0.18$ cm/s RDF = 5.71 s/cm RRQ = 1.33 s/cm RRQ/RDF = 0.23
10 ($t = 20$)	0.21	27.52	$k_{g\,ave} = 0.19$ cm/s RDF = 5.21 s/cm RRQ = 1.33 s/cm RRQ/RDF = 0.26

The first term of Eq. (3.5) is defined as:

$$-\int_{r_0}^{r}\frac{dr}{k_g} = -\int_{r_0}^{r}\frac{dr}{\alpha r^{0.52}} = \frac{r_0^{0.48} - r^{0.48}}{\beta}$$

where $\beta = 0.48\alpha$.

Substituting in Eq. (3.5) results in

$$\frac{r_0^{0.48} - r^{0.48}}{\beta} + \frac{r_0 - r}{k_r} = \frac{1}{2}\frac{\bar{C}_{Cl_2}}{\sigma_{Si}}t \qquad (3.6)$$

Eq. (3.6) describes the progress of the reaction of one silicon particle with chlorine. In a particle bed, the concentration of the reactant gas around a particle is affected by the presence (reaction) of other particles, which generally varies with bed height and with time. Consequently, as shown in Eq. (3.6), it is necessary to determine the average chlorine gas concentration in the bed.

Therefore, another differential equation, which describes the variation of gas concentration with bed height and with time, has been used. Thus, Eq. (3.7) expresses the mass conservation principle for a bed consisting of N silicon particles and is given by the mass balance for chlorine gas in a control volume (CV) inside the bed

$$-ALu\left(\frac{\partial C}{\partial z}\right) - 4\pi r^2 NkC = AL\varepsilon\left(\frac{\partial C}{\partial t}\right) \qquad (3.7)$$

where $-ALu(\partial C/\partial z)$ is the (entrance–exit) rate of chlorine in CV by convection (mol/s); $-4\pi r^2 NkC$ the consumption rate of chlorine in CV by chemical reaction (mol/s); $AL\varepsilon(\partial C/\partial t)$ the accumulation rate of chlorine in CV (mol/s); A the cross-sectional area of the bed (cm^2); $A = \pi D^2/4$ and $Au = Q_{Cl_2}$; Q_{Cl_2} the chlorine flow rate (cm^3/s); $C_{Cl_2} = C$ the chlorine concentration (mol/cm^3); z the position with respect to bed height (cm); N the number of particles in the bed; r_0 the initial radius of silicon particle (cm); ε the bed porosity; L the bed height (cm); t the reaction time, (s) and ρ_{Si} the silicon density, $\rho_{Si} = m_{Si}/V_S$ (g/cm^3).

Eq. (3.7) is based on the following assumptions:

1. Only the axial direction of the bed, z, is considered for convective transport of chlorine;
2. The bed is considered isothermic and at atmospheric pressure;
3. The particles do not move in the bed;
4. The reactant gas at the entrance of the bed consists of pure chlorine;

Table 6
Total rate constants obtained experimentally and from the model

Temperature (°C)	$L = 5$ mm		$L = 10$ mm	
	k_{exp} (g/min)	k_{mod} (g/min)	k_{exp} (g/min)	k_{mod} (g/min)
500	0.46	0.46	0.67	0.69
550	0.50	0.48	0.74	0.71
600	0.49	0.49	0.75	0.73
650	0.58	0.55	0.82	0.78
700	0.65	0.63	1.31	0.94

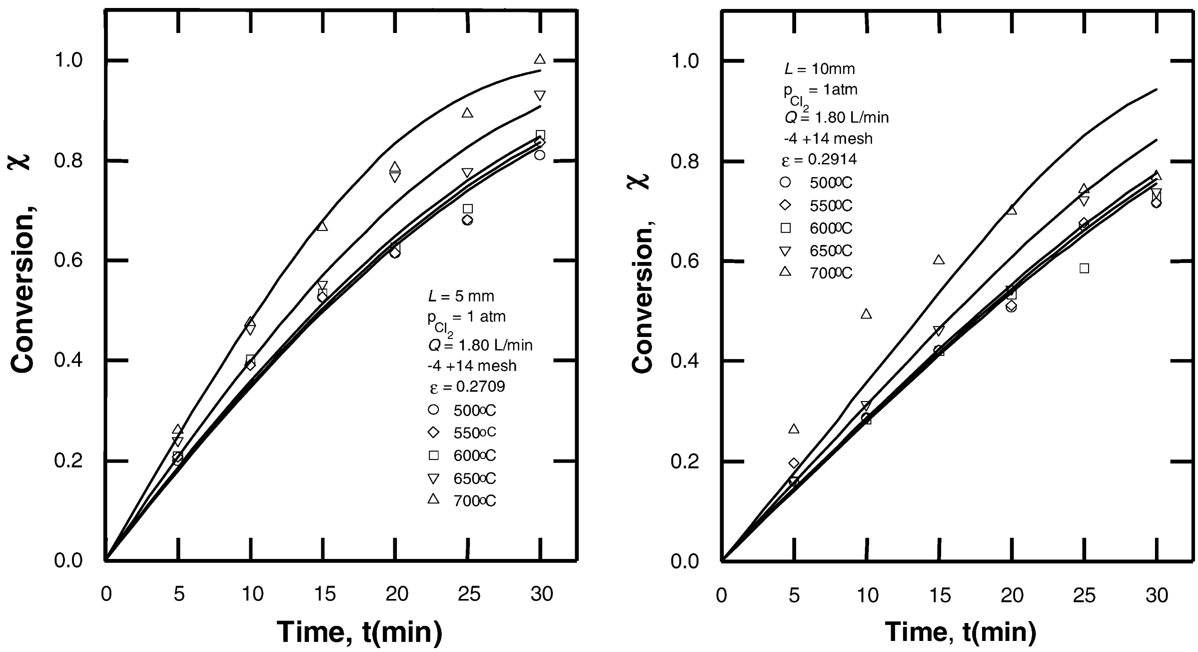

Fig. 2. Comparison of silicon conversion profiles for non-compacted beds obtained experimentally (points) and from the model (lines).

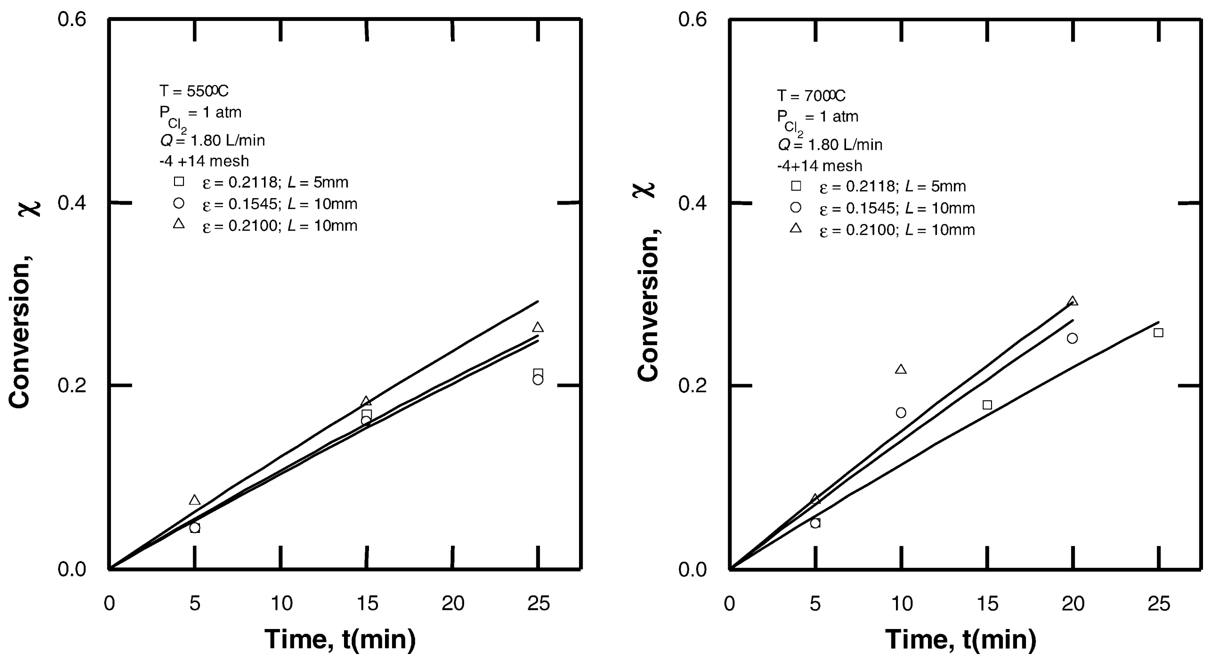

Fig. 3. Comparison of silicon conversion profiles for compacted beds obtained experimentally (points) and from the model (lines).

Table 7
Total rate constants obtained experimentally and from the model

Temperature (°C)	$L = 5\,\text{mm}$		$L = 10\,\text{mm}$			
	$\varepsilon = 0.21$		$\varepsilon = 0.21$	$\varepsilon = 0.15$	$\varepsilon = 0.21$	$\varepsilon = 0.15$
	k_{exp} (g/min)	k_{mod} (g/min)	k_{exp} (g/min)	k_{exp} (g/min)	k_{mod} (g/min)	k_{mod} (g/min)
550	0.14	0.14	0.44	0.30	0.35	0.30
700	0.18	0.16	0.83	0.47	0.74	0.42

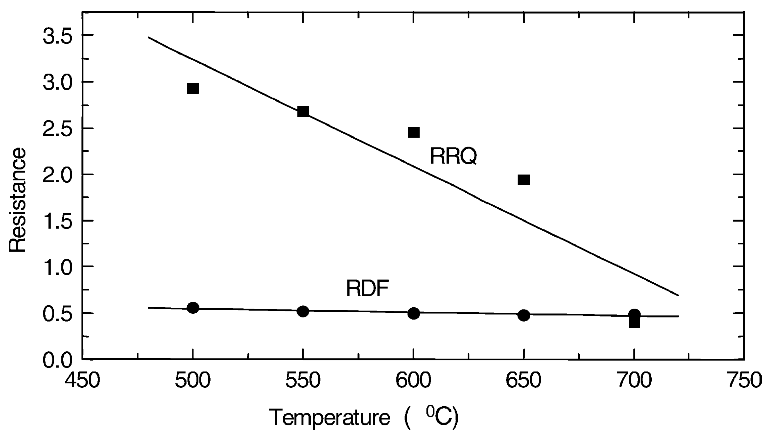

Fig. 4. Effect of the chlorination temperature on mass transfer and chemical reaction resistances.

5. The bed is shallow, thereby k does not vary with z and the whole bed is exposed to an average concentration of chlorine ($\bar{C}_{Cl_2}$);
6. Diffusive transport of gas is neglected;
7. There is no accumulation in the gas phase, that is, the gas is considered to be in a quasi-steady-state.

With the above assumptions, Eq. (3.7) can be simplified to

$$\frac{dC}{dz} = \frac{-3m_{Si}^0}{ALur_0^3\rho_{Si}} r^2 kC$$

Integrating with the boundary condition $z = 0, C = C_0$

$$\int_{C_0}^{C} \frac{dC}{C} = \frac{-3m_{Si}^0}{ALur_0^3\rho_{Si}} r^2 k \int_0^z dz$$

$$C = C_0 \exp\left(\frac{-3m_{Si}^0 r^2 kz}{ALur_0^3\rho_{Si}}\right) \quad (3.8)$$

For shallow beds, the average chlorine concentration ($\bar{C}_{Cl_2}$) used is given by the equation:

$$\bar{C}_{Cl_2} = \frac{C_0 Aur_0^3\rho_{Si}}{3m_{Si}^0 r^2 k}\left[1 - \exp\left(\frac{-3m_{Si}^0 r^2 k}{Aur_0^3\rho_{Si}}\right)\right] \quad (3.9)$$

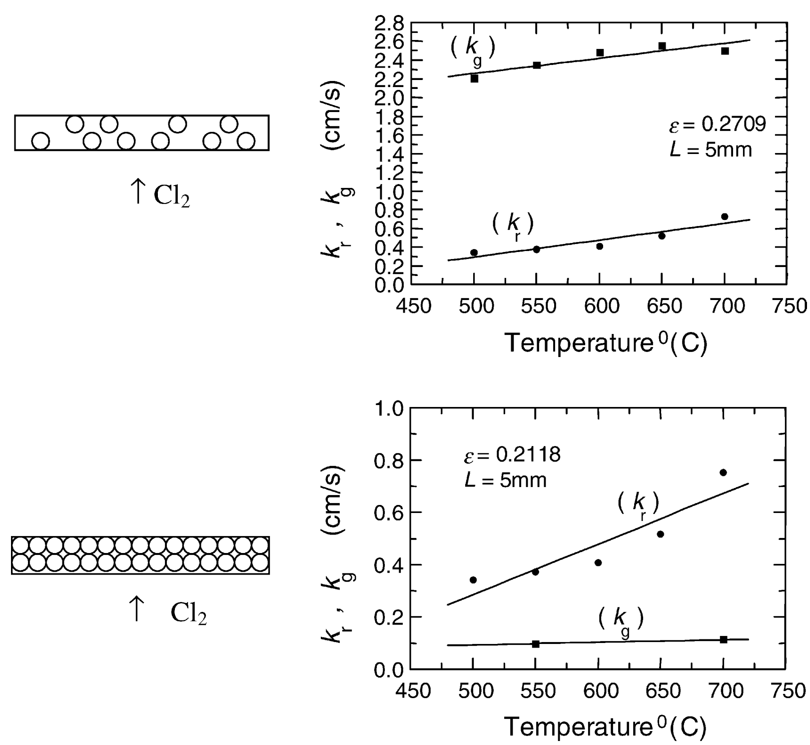

Fig. 5. Correlation between k_r and k_g for beds of different porosities and height equal to 5 mm.

Substituting (3.9) in Eq. (3.6)

$$\frac{r_0^{0.48} - r^{0.48}}{\beta} + \frac{r_0 - r}{k_r} = \frac{1}{2}\frac{C_0 A u r_0^3 M_{Si}}{3 m_{Si}^0 r^2 k}\left[1 - \exp\left(\frac{-3 m_{Si}^0 r^2 k}{A u r_0^3 \rho_{Si}}\right)\right] t \qquad (3.10)$$

Since

$$\sigma_{Si} = \frac{\rho_{Si}}{M_{Si}} \Rightarrow M_{Si} = \frac{\rho_{Si}}{\sigma_{Si}}$$

Eq. (3.10) describes the chlorination of non-compacted beds of −4 to +14 mesh particles.

Compacting of the bed, on the other hand, may increase the influence of diffusion on the transport of the gas. In this case, the model must take into consideration the diffusive mass transport.

A plausible and simpler alternative for representing the compacted bed is, after evaluating k_r, to determine k_g as a fitting parameter for each experimental condition. Starting with Eq. (3.5), the model for the compacted bed is

$$r_0 - r = \frac{1}{2}\frac{\bar{C}_{Cl_2}}{\sigma_{Si}}\left(\frac{1}{(1/k_g) + (1/k_r)}\right) t = \frac{1}{2} k \frac{\bar{C}_{Cl_2}}{\sigma_{Si}} t \qquad (3.11)$$

Substituting Eq. (3.9) in the above equation, an equation similar to Eq. (3.10) is derived

$$r_0 - r = \frac{1}{2}\frac{C_0 A u r_0^3 M_{Si}}{3 m_{Si}^0 r^2}\left[1 - \exp\left(\frac{-3 m_{Si}^0 r^2 k}{A u r_0^3 \rho_{Si}}\right)\right] t \qquad (3.12)$$

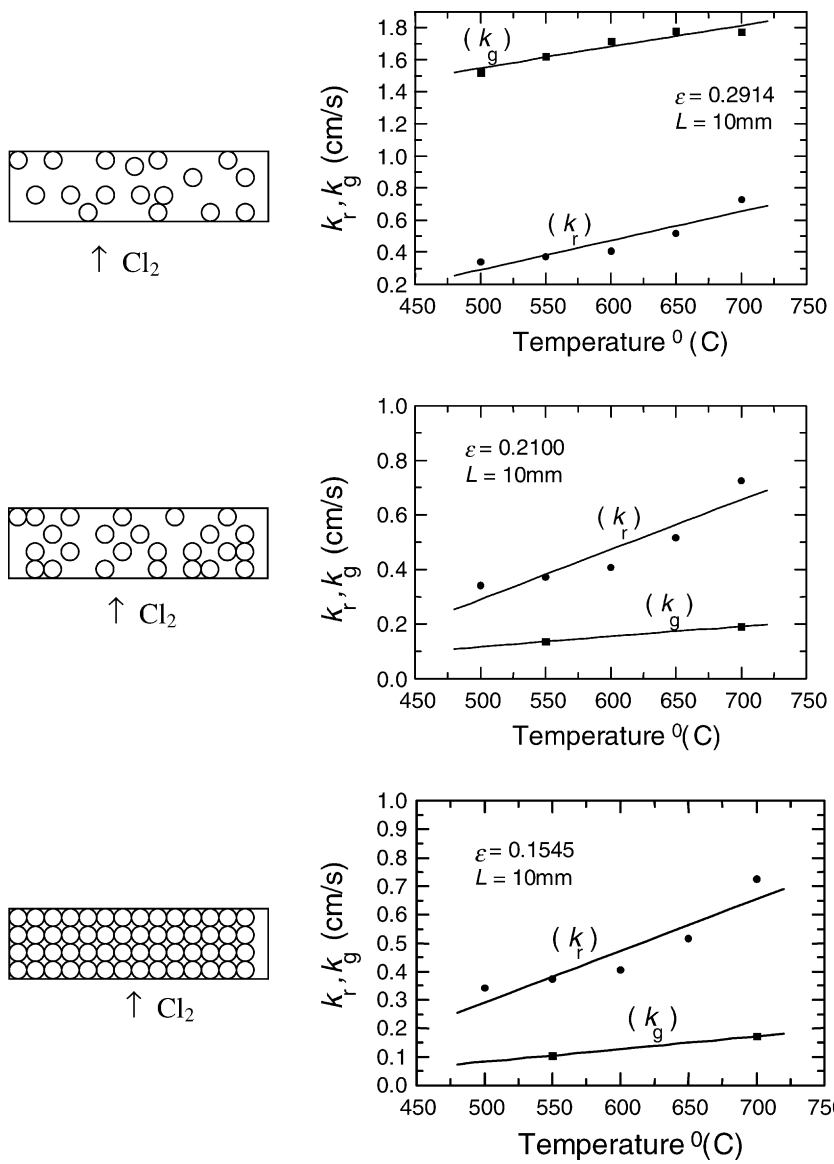

Fig. 6. Correlation between k_r and k_g for beds of different porosities and height equal to 10 mm.

Silicon conversion time profiles, $\chi(t)$, are obtained for compacted and non-compact beds of −4 to +14 mesh particles using the equation:

$$\chi(t) = 1 - \left(\frac{r}{r_0}\right)^3$$

A computer code was developed to calculate instantaneous and average mass transfer coefficients (k_g and $k_{g\,ave}$), chemical reaction and mass transfer resistances (RRQ $= 1/k_r$ and RDF $= 1/k_g$) and silicon conversions [12]. The average mass transfer coefficient ($k_{g\,ave}$) was calculated by the equation:

$$k_{g\,ave} = \frac{\alpha}{r_0 - r_f}\int_{r_f}^{r_0} r^{0.52}\,dr = \frac{\alpha(r_0^{1.52} - r_f^{1.52})}{1.52(r_0 - r_f)}$$

where r_f is the final radius of silicon particle (cm^2).

4. Results and discussion

The average mass transfer coefficient ($k_{g\,ave}$) was initially used. The rate constant values (k_r) were obtained by applying Eq. (3.10) to a set of experimental data. The results can be found in Tables 3 and 4 for bed heights of 5 and 10 mm.

Silicon conversion profiles of the chlorination runs for non-compacted beds are shown in Fig. 2. The reasonably good agreement between the profiles obtained from the model and from the data can be verified in the figure.

The application of the model for compacted beds complements the investigation of the effect of bed porosity, since the average mass transfer coefficients were obtained by adjusting the model to the experimental data [9]. The values of k_r for compacted beds are the average of the k_r values for non-compacted beds ($k_{r\,ave}$), since the rate constant should not vary with bed height, chlorine flow rate and chlorine pressure. The results are listed in Table 5.

For compacted beds the model given by Eq. (3.12) did not fit properly the experimental data as shown in Fig. 3. After fitting the model to the experimental data for compacted beds, the $k_{r\,ave}$ values used in this case were used again in the non-compacted beds model. This refit allowed the model to describe the experimental results. Tables 3 and 4 present the parameters corresponding to the final fit of the model to the experimental data for non-compacted beds. The model represented quite satisfactorily the data and a similarity can be seen between the initial and the final fit curves (Fig. 2).

The total rate constants (k_{mod}) for non-compacted and compacted beds were determined using the silicon conversion profiles obtained from the model. Tables 6 and 7 show these total rate constants and the values obtained experimentally for each condition (k_{exp}). It can be verified that the total rate constants derived from the model are quite close to those obtained from the experimental data.

The model also provided assistance to the study of the influence of temperature, bed height and bed porosity on the chlorination kinetics.

According to Fig. 4, the mass transfer resistance (RDF) remained almost constant in the temperatures investigated (500–700 °C). Conversely, the chemical reaction resistance (RRQ) decreased steadily with increasing the chlorination temperature.

Although RRQ was higher than RDF, the difference between k_r and k_g is larger for the lower temperature range, characterizing the greater sensitivity of k_r at more elevated temperatures. These results reveal that temperature variations alter more significantly the chemical reaction (k_r), than mass transfer (k_g).

Figs. 5 and 6 present k_r and k_g values for bed heights of 5 and 10 mm, respectively. It can be observed that the k_r values are the same for both non-compacted beds ($\varepsilon = 0.29$ and 0.27) and compacted beds ($\varepsilon = 0.21$ and 0.15), since the particle size is the same everywhere. In addition, the k_g values are higher than the k_r for non-compacted beds and these values decreased with increase in compacting of the bed for both heights.

Consequently, with increase in compacting, the rate constant (k) decreased with decrease in k_g, since the k_r value remained constant for both non-compacted and compacted beds at the same temperature. These results indicate clearly that the effect of compacting is significant insofar as the behavior of the reaction system, mainly as a consequence of the increased role of the diffusive component in the mass transfer mechanism. Comparing the data presented in Figs. 5 and 6 for non-compact beds ($\varepsilon = 0.27$, $L = 5$ mm) and ($\varepsilon = 0.29$, $L = 10$ mm), it can be observed that k_g increases with decreasing the bed height, although in all the cases the k_r values were lower than those of k_g (RRQ > RDF). Indeed the smaller the height of the non-compact bed, the higher is the difference between (RRQ and RDF). It can also be seen that for a compacted bed ($\varepsilon = 0.21$, $L = 10$ mm) and ($\varepsilon = 0.21$, $L = 5$ mm), compacting alone is sufficient to make $k_g < k_r$ (RDF > RRQ). In this bed, the effect of bed height is not the cause of significant changes in k_g associated with changes in silicon conversion.

5. Conclusions

The results obtained from the application of the mathematical model for the silicon chlorination reaction granted the following conclusions:

1. The mathematical model established the relationship between the mass transfer coefficient (k_g) and the rate constant (k_r) as a function of temperature, bed porosity and bed height for size −4 to 14 mesh (Tyler) silicon particles.
2. The silicon conversion time profiles obtained from the model represented adequately the experimental data for non-compacted beds.

3. The total rate constants obtained experimentally and from the model are quite close for both compacted and non-compacted beds.
4. The sensitivity of k_r to temperature changes was higher than that of k_g, that is, the difference between k_r and k_g was higher in the low temperature range which characterizes the greater sensitivity of k_r at more elevated temperatures.
5. k_r values are temperature dependent and vary from 0.34 cm/s (500 °C) to 0.75 cm/s (700 °C). k_g values are also dependent on porosity (compacting) and bed height, and vary between 0.1 and 4.0 cm/s depending on the experimental conditions.
6. With respect to mass transfer, compacting has a greater influence than variation in bed height. Indeed, at 600 °C and bed height of 5 mm, k_g decreases from 2.5 to 0.1 cm/s with compacting and to 1.7 cm/s with increase in bed height to 10 mm.
7. For non-compacted beds, increasing the temperature from 500 to 700 °C and bed height from 5 to 10 mm rendered a decrease in the chemical reaction to mass transfer resistances ratio and therefore altered more significantly the rate constant (k_r) than the mass transfer coefficient (k_g).

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