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# Simulation of a Silicon CVD Spouted Fluidized Bed Reactor: Semi-Batch Operations

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# SIMULATION OF A SILICON CVD SPOUTED FLUDIZED BED REACTOR: SEMI-BATCH OPERATIONS

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## ABSTRACT

A comprehensive multiphase gas-solid mathematical model that successfully describes the batch growth of silicon particles in a chemical vapor deposition (CVD) submerged spouted bed reactor is extended to simulate semi-batch operations with periodic seeds additions and product extractions. This model takes into account the fluidized bed reactor as well as a population balance equation representing particle growth and agglomeration. Experimental data obtained from semi-batch operation in a pilot scale reactor at REC Silicon Inc. are used to evaluate the proposed mathematical model.

## INTRODUCTION

At the present, the great demand of solar cells as modules to convert solar energy into electric power has exceeded the capacity of production of solar grade (SG) silicon by approximately 50 % (1). CVD fluidized bed (FB) technology constitutes an attractive alternative to produce granular SG silicon from silane pyrolysis, replacing the energy- and labor-intensive Siemens process. In this CVD-FB reactor, silane ($SiH_4$) is thermally decomposed into silicon and hydrogen via two major pathways: a heterogeneous step where silicon deposits directly on existing silicon seed particles by CVD and a homogeneous step that leads to fines formation (2). FBs envisioned for this application contain a gas distribution grid. A specialized submerged spouted bed (SSB) design substitutes the distribution grid with a submerged spout injector, which allows maintaining particles in a spouted circulation zone while keeping the upper zone, where particles are fluidized, in a bubbling regime (3).

The accurate modeling of the silicon CVD-FB process constitutes one of the critical developments required for the reliable and successful scale-up from batch operations in pilot reactors to continuous commercial units. Several mathematical descriptions, which take into account the FB hydrodynamics, heterogeneous and homogeneous decomposition, CVD growth of seeds and scavenging of fines by large particles, were reported in the technical literature to study the silane pyrolysis in FBs (4–7). However, most of the reported models are limited to monodispersed seeds that grow at the same rate up to an average final particle diameter (7). To evaluate the evolution of the particle size distribution (PSD), the CVD-FB fundamental balance equations (which provide the growth rate) have to be solved simultaneously with the population balance equation (PBE); a statement of continuity that describes the changes of PSDs due to particle growth, eventual agglomeration, seeds inflows and/or particles outflows (8). Consistent with this approach a gas-solid semi-dynamic model that describes the batch growth of silicon particles in a CVD-SSB reactor has been reported in a previous paper by Piña et al. (11). As it has been shown (11), the proposed mathematical model successfully simulates experimental data obtained from batch operation in a pilot scale reactor at REC Silicon Inc.

In this work, the developed CVD multiphase reactor model is extended to the semi-batch operation of SSB, with the long-term objective of predicting the continuous growth of silicon particles in commercial units.

## MATHEMATICAL MODEL

The SSB reactor for silicon production by CVD is illustrated in Figure 1a (3).

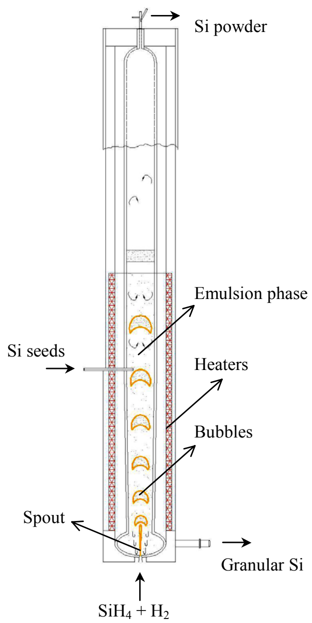


**Figure 1a.** Lateral section view of the SSB unit.

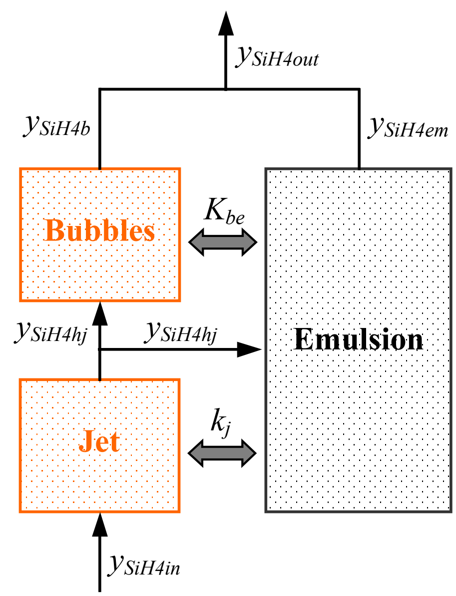


**Figure 1b.** Schematic representation of the adopted model for the SSB.

The preheated silane and hydrogen gas mixture that fluidizes the silicon particles is introduced through the spout injector located at the bottom of the reactor. In addition, the bed is heated to the reaction temperature by wall heaters. Silane thermally decomposes to hydrogen and solid silicon. Most of the solid silicon is deposited on the particles. The hydrogen and some entrained silicon fines leave the reactor at the top. In a continuously operated reactor, seed particles will be fed permanently into the unit and the silicon product will be discharged from it. During semi-batch production, seed particles are added periodically into the reactor while granular silicon is withdrawn (also periodically) to keep the bed mass almost invariable.

**Submerged Spouted Bed Reactor Module**

The multizone SSB reactor model used to describe the silicon production by CVD from silane pyrolysis is schematized in Figure 1b (11). Two regions in series are taken into account, an inlet spout zone followed by a developed fluid bed region. Details about the reactor mathematical model, the adopted kinetics expressions and the estimation of the fluid dynamic, mass transfer and kinetic parameters can be found elsewhere (11).

**Population Balance Equation Module**

To describe the dynamic behavior of the PSD, the population balance for a particulate system undergoing simultaneous particle growth and aggregation is included. By using the concept of MOC combined with the Kumar and Ramkrishna discretization technique (9), which has been effectively applied in a variety of batch processes (10), the PBE can be expressed as the following ODE system:

$$\frac{dN_i}{dt} = \sum_{\substack{j,k \\ L_{i-1} \le L \le L_{i+1}}}^{i \ge j \ge k} \left(1 - \frac{1}{2}\delta_{kj}\right)\eta\, \beta_{kj} N_j N_k - N_i \sum_{k=1}^{M} \beta_{ik} N_k \tag{1}$$

$$\frac{dd_{pi}}{dt} = \frac{2}{\pi d_{pi}^2} G \frac{S_{pi}}{S_{pt}} = \frac{2}{\pi \sum_{i=1}^{M} d_{pi}^2} G \qquad \text{BC: } t = 0,\ d_{pi} = d_{pi,0} \tag{2}$$

The factor $\eta$ proposed by Kumar and Ramkrishna (9) to preserve both the total particle number and mass when a new particle is formed by agglomeration, is given by equation (3) where $L_j$ and $L_k$ denote the volume of the capturing and captured particles in binary collisions, respectively.

$$\eta = \begin{cases} \dfrac{L_{i+1} - L}{L_{i+1} - L_{\mathrm{i}}} & L_i \le L \le L_{i+1} \\ \dfrac{L - L_{i-1}}{L_i - L_{i-1}} & L_{i\text{-}1} \le L \le L_i \end{cases} \qquad L = L_j + L_k \tag{3}$$

As it is described in the upcoming equation (4), the particle growth is attributed to two simultaneous contributions: heterogeneous CVD in both spout and emulsion and scavenging of fines generated by homogeneous reaction in each of the three gas-phase regions. The scavenging of fines is assumed to be proportional to the total amount of powder produced.

$$G = \frac{M_{Si}}{\rho_p}\left[\left(r_{hetj} S_{pj} + r_{hetem} S_{pem}\right) + \alpha\left(r_{\mathrm{hom}\, j}\, \varepsilon_j A_{rj} h_j + r_{\mathrm{hom}\, b}\, N_b V_b + r_{\mathrm{hom}\, em} V_{gem}\right)\right] \tag{4}$$

For batch operations where the silane molar fraction changes over time, the scavenging factor $\alpha$ was found to be dependent on $y_{SiH_4}$ as follows (11):

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$$\alpha = \alpha_0 \frac{y_{SiH_4}}{y_{SiH_4,0}} \tag{5}$$

where $\alpha_0$ and $y_{SiH_4,0}$ are the scavenging factor and silane molar fraction at the beginning of the experiment, respectively.

As postulated by Piña et al. (11), the agglomeration factors $\beta_{ik}$ are considered zero for particle diameters larger than 500 μm (critical diameter for this mechanism, based on experimental data) and size- and time-independent for smaller particles (i.e., $\beta_{ik} = \beta$).

### Numerical Solution

To deal with the dynamic particle growth that takes place during semi-batch operations in the silicon CVD-SSB reactor, the gas- and solid-phase modules are combined according to the calculation scheme presented in Figure 2. Except for the seeds addition (represented by the dashed arrow), the calculation procedure is fully analogous to the one described for batch scenarios (11).

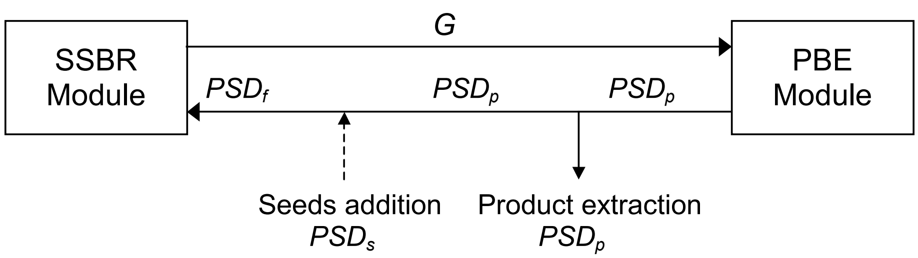


**Figure 2**. Scheme of the calculation procedure. Semi-batch operations. CVD-SSB reactor.

The solution of the SSBR module provides the growth rate $G$ used by the PBE to compute the product particle size distribution ($PSD_p$). As it can be seen in equation (2), MOC involves the shift of the particle size coordinate over time (the population is tracked with a velocity equal to the growth rate; i.e., moving grid technique). The addition of seeds at discrete time intervals poses a numerical difficulty when a moving grid is employed in the calculations. In fact, the seeds appear as a new population in the smaller sizes of the initial grid ($PSD_s$) at times-on-stream for which the particles, and hence the grid points, have already grown ($PSD_p$). A simple solution to this problem would be to insert new points to the moving grid whenever an addition of seeds is performed. However, the use of an extended grid becomes computationally intensive. To avoid an excessive increase in the number of grid points, the incorporation of seeds with particle sizes between the points of the moving grid (at the corresponding time-on-stream) is accomplished by using the $\eta$ factor (9) to assign the added particles to the adjacent sizes. The addition of those seeds smaller than the smallest particle size represented in the moving grid is achieved by including new grid points. The resulting distribution is called $PSD_f$ . This numerical approach reduces the number of grid points for processes with relatively low growth rates, as for the silicon case.

## RESULTS AND DISCUSSION



In the present work, the results of the predictions of the CVD SSB-PBE model are compared with experimental data obtained from semi-batch operation in a pilot unit at REC Silicon Inc., with operating conditions within the following ranges: $T_{in}$ = 473-673 K, $T_{FB}$ = 873-1073 K, $P_{in}$ = 100-200 kPa, $y_{SiH_4 in}$ = 0-50 %, $t_f$ = 12-24 h, $U/U_{mf}$ = 3-6, $dp_{mean,0}$ = 750 $\mu$m.

The effects of decreased residence time and silane concentration were tested simultaneously as shown in Figure 3. The hydrogen flowrate is increased after each product withdrawal (a natural step length) while the silane flowrate remains invariable. Consequently, the silane concentration decreases continuously during the production period.

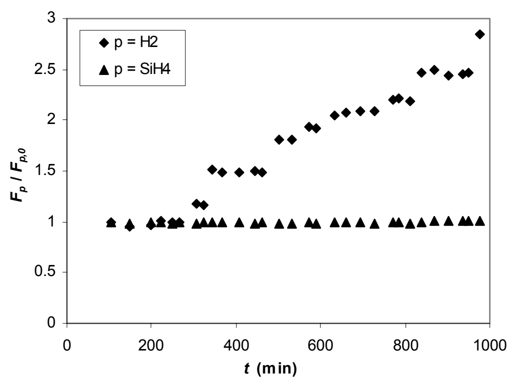


**Figure 3:** Experimental $H_2$ and $SiH_4$ flowrates as a function of time.

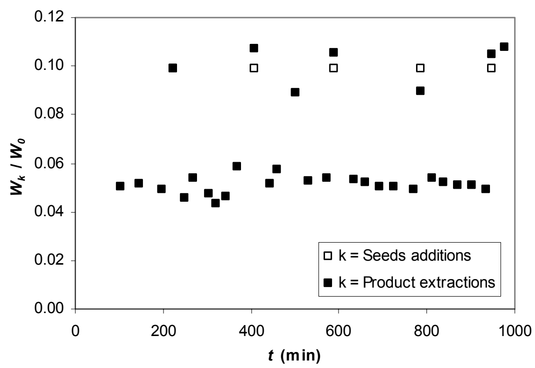


**Figure 4:** Experimental seeds additions and product extractions as a function of time.

As it can be seen in Figure 4, throughout operation granular product samples of around 5% of the initial bed mass are frequently extracted to keep the bed mass approximately constant (Figure 6). In addition, product masses of about 10% of the initial bed mass are replaced at regular time intervals by an equivalent mass of seeds with the purpose of maintaining the mean particle diameter under control (i.e., avoiding an excessive growth).

For the studied experiment, Figure 5 presents the initial PSD and the composition of the seeds that are added to the system periodically. The seeds added periodically to the reactor were obtained by sieving a complete distribution produced in a previous batch process. Only the fractions within 500-850 $\mu$m range were selected and reserved as seeds.

The $\alpha_0$ value of equation (5) was established from the correlation reported by Piña et al. (11), derived from short-term batch operations, and the initial silane molar fraction of the selected experiment. Figure 6 shows, for the studied case, the experimental and predicted dimensionless bed masses. As it can be noticed in this figure, the CVD SSB-PBE model tracks well the experimental data for the complete run duration.

The calculated scavenging efficiency indicates that at the beginning of the experiment the particles capture a majority of the silicon fines homogeneously produced. As the experiment proceeds, due to the higher hydrogen flowrates and thus the lower gas residence times (11), the generated fines contributing to the granules growth are significantly reduced.

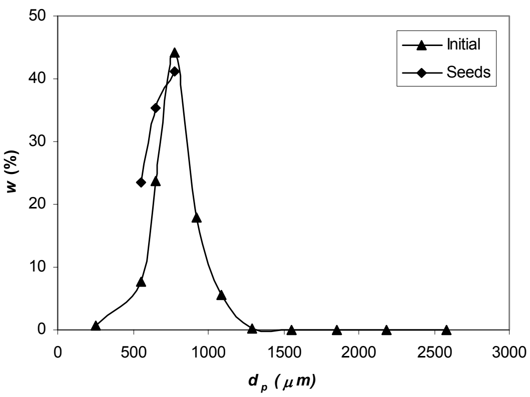


**Figure 5:** Experimental initial and seeds particle size distributions.

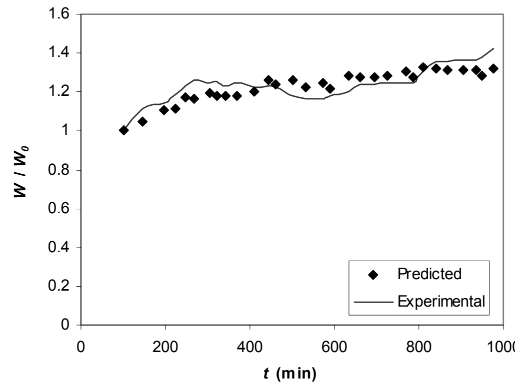


**Figure 6:** Experimental and predicted bed masses as function of time.

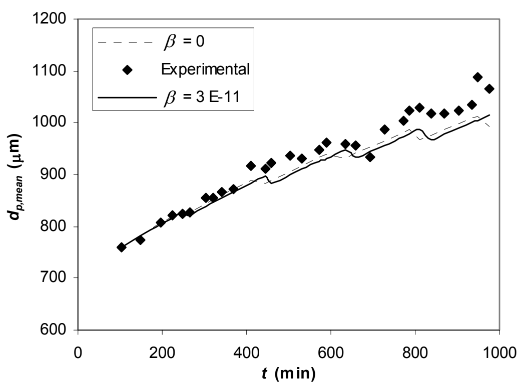


**Figure 7:** Experimental and predicted mean particle diameter as function of time.

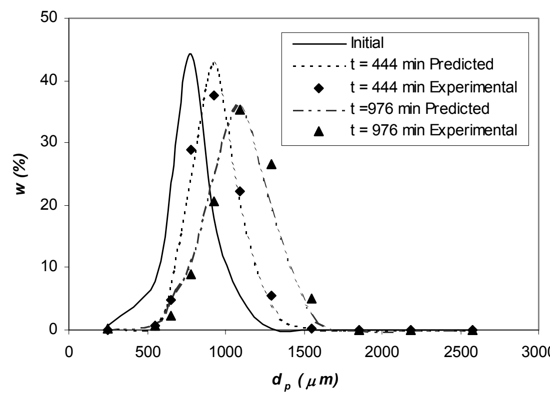


**Figure 8:** Experimental and predicted PSDs at different times-on-stream.

Regarding aggregation, the $\beta$ factor was adjusted to match the mean particle diameter ($d_{pmean}$) along the duration of the experiment. Figure 7 presents the mean particle diameter as a function of time with and without agglomeration. The difference between the two theoretical curves suggests that the effect of the aggregation phenomenon is not significant. In fact, the very low fitted $\beta$ parameter (an order of magnitude less than those obtained for batch operations, 11) as well as $\beta$ =0, allowed following satisfactorily the trend exhibited by the experimental $d_{pmean}$. Since only the particles with diameters smaller than 500 $\mu$m are subjected to agglomeration and the added seeds are larger than this critical diameter (Figure 5), the number of particles that can undergo aggregation (and hence the probability of collision between them) diminishes constantly over time. This is the reason why agglomeration does not play an important role in the studied experiment.

The calculated and experimental PSDs, for the studied experiment at different times-on-stream, are reported in Figure 8. The particles growth is evidenced by the shift of the PSDs to higher diameters as the process progresses. Figure 8 also displays the initial PSD. At the beginning, the mass fraction of the smaller particles (diameters lower than 500 μm) decreases due to the simultaneous growth and agglomeration phenomena.

According to the results presented in Figure 8; the developed SSB-PBE model, which employs the dynamic scavenging factor concept (equation 5) and just one adjustable parameter ($\beta$), predicts well the evolution of the particle size distributions for experiments with multiple seeds additions and product extractions. Moreover, these outcomes indicate that the proposed calculation procedure allows handling efficiently semi-batch operations of 12-24 hours. In fact, immediately after all the seeds additions, the PSDs are successfully reproduced.

## CONCLUSIONS

The comprehensive multiphase gas-solid mathematical model developed to describe the batch growth of silicon particles in a CVD submerged spouted bed reactor, has been satisfactorily extended to 12-24 hours semi-batch operations. The simulation of these scenarios has been implemented via a relatively simple and effective modification of the numerical procedure that solves for batch processes the submerged spouted bed reactor and the population balance equation compartments sequentially.

The proposed CVD SSB-PBE model, which involves a dynamic correlation of the scavenging factor and only one adjustable parameter (agglomeration efficiency), has been successfully tested under an ample range of operating conditions from the pilot scale reactor at REC Silicon Inc., including multiple particle additions and extractions. Furthermore for the studied semi-batch experiments, where agglomeration does not play an important role (the added seeds are larger than the critical diameter for aggregation), the model results fully predictable (i.e., without any adjustable parameter).

This study provides a useful tool for predicting the performance of the CVD SBB reactor (i.e. silane conversion rate, granule/powder product ratio, particle growth rate and the particle size distributions as a function of time-on-stream) under semi-batch operations that can also contribute to the design of the continuous process.

## ACKNOWLEDGEMENTS

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## NOTATION

| | | | |
|---|---|---|---|
| $A_{rj}$ | Spout cross-sectional area, $m_j^2$. | $V_b$ | Volume per bubble, $m_b^3/\#_b$. |
| $d_p$ | Particle diameter, $m_p$. | $V_{gem}$ | Gas volume at the emulsion, $m_g^3$. |
| $F$ | Gas molar flow rate, kmol/s. | $y_{SiH4}$ | Silane molar fraction. |
| $h_j$ | Spout penetration, $m_j$. | $w$ | Particle mass fraction. |
| $K_{be}$ | Bubble-emulsion mass transfer | $W$ | Particle mass, kg. |

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| | |
|---|---|
| | coefficient, $m_g^3/m_b^3s$ (Figure 1). |
| $k_j$ | Spout-emulsion mass transfer coefficient, $kg/m_j^2s$ (Figure 1). |
| $M$ | Number of classes on the size grid. |
| $M_{Si}$ | Silicon molar weight, kg/kmol. |
| $N_b$ | Total number of bubbles, $\#_b$. |
| $N$ | Number of particles, $\#_p$. |
| $P$ | Pressure, kPa. |
| $r_{het}$ | Heterogeneous reaction rate, $kmol/m_p^2s$. |
| $r_{hom}$ | Homogeneous reaction rate, $kmol/m_g^3s$. |
| $S_p$ | External surface of the particles, $m_p^2$. |
| $t$ | Operating time, s. |
| $T$ | Gas temperature, K. |
| $U$ | Superficial gas velocity, $m_g^3/m_r^2s$. |

***Subscripts***

| | |
|---|---|
| *0* | Initial. |
| *b* | Bubble. |
| *em* | Emulsion. |
| *f* | Final. |
| *i* | At the $i^{th}$ size range. |
| *in* | Inlet. |
| *j* | Spout or $j^{th}$ size range. |
| *mf* | At minimum fluidization conditions. |
| *out* | Outlet. |

***Greek Letters***

| | |
|---|---|
| $\delta_{ij}$ | Dirac-delta function. |
| $\varepsilon_j$ | Void fraction in the spout, $m_g^3/m_j^3$. |
| $\rho_p$ | Particle density, $kg/m_p^3$. |

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