From Sand to Silicon Wafers:
A Process Systems view of Solar Cell Production

CAPD ESI Overview, 2014

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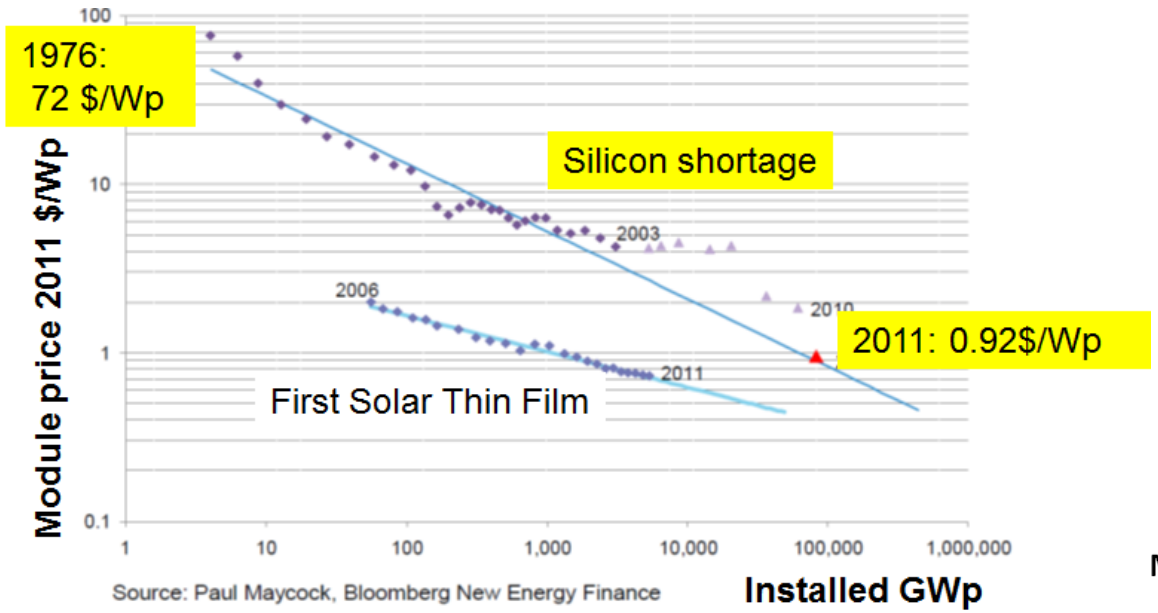
1. Market outlook
2. A Suite of projects
   a) Metallurgical Silicon MGSi
   b) (The Silgrain Process UMG)
   c) Solargrade Silicon SoG
   d) Silicon wafers
3. Conclusions

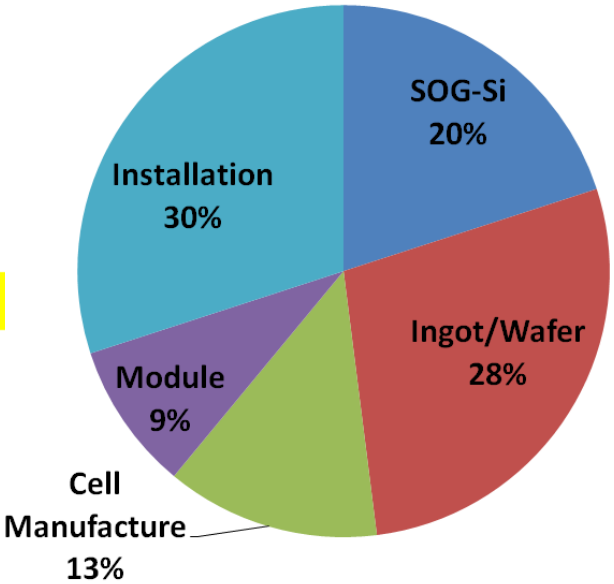
16kWp

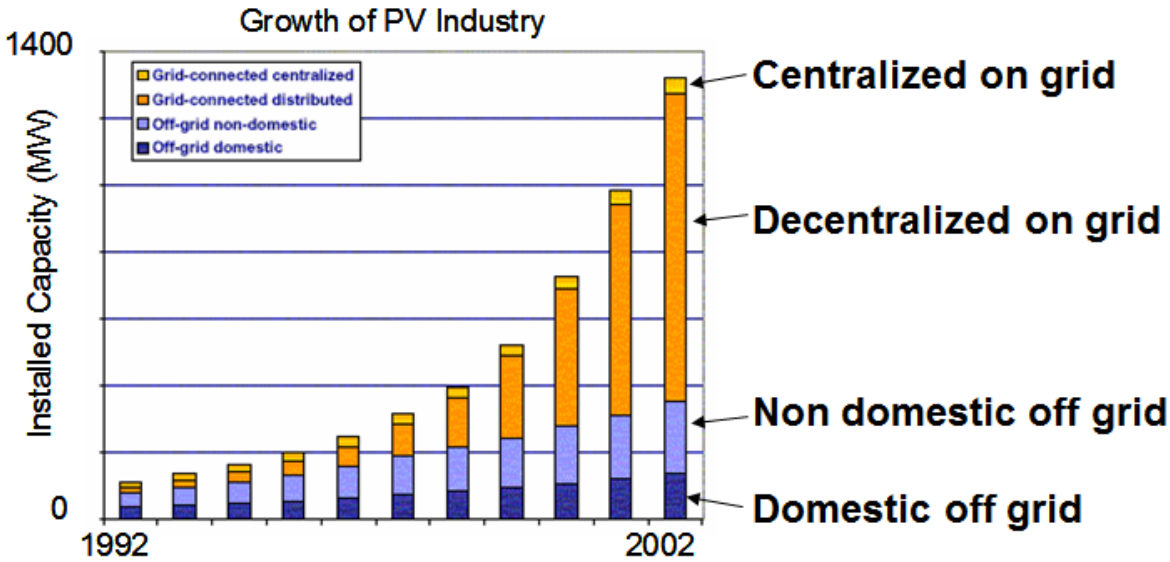
Total system cost	$ 53,894
Federal tax credit	$ 16,168
PA (SEP)	$ 7,500
PA SREC	$ 8,847
Net Cost to Rob	**$ 21,379**

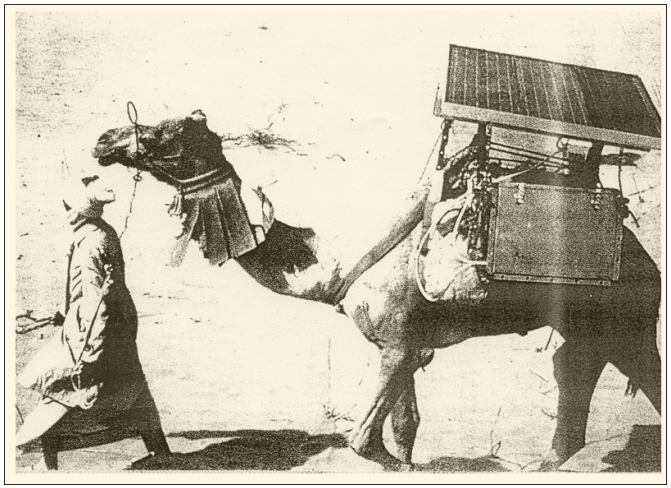
Pay back about 5 years with Pittsburgh conditions

The Market Outlook









Metallurgical Silicon Production → Poly-Crystalline Silicon Production → Silicon wafers → Solar Cells → Solar Modules

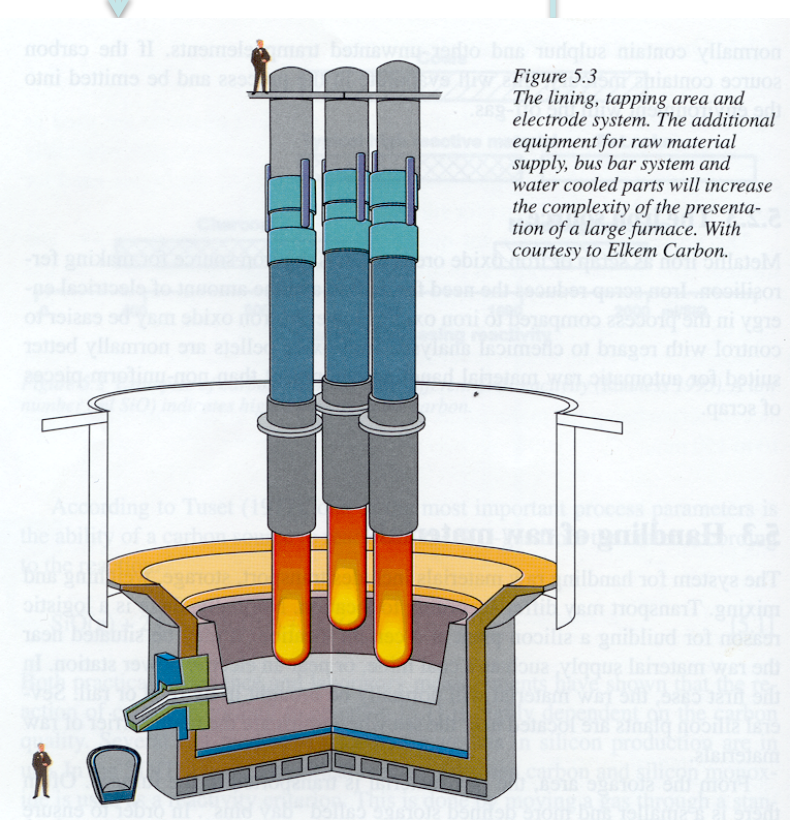
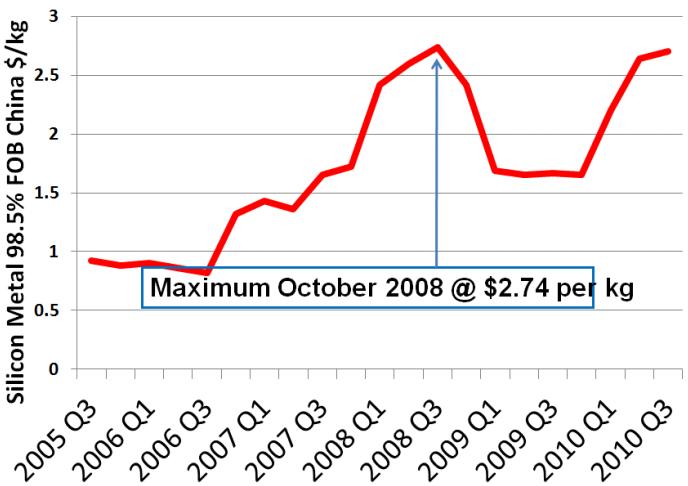


Figure 5.3
The lining, tapping area and electrode system. The additional equipment for raw material supply, bus bar system and water cooled parts will increase the complexity of the presentation of a large furnace. With courtesy to Elkem Carbon.



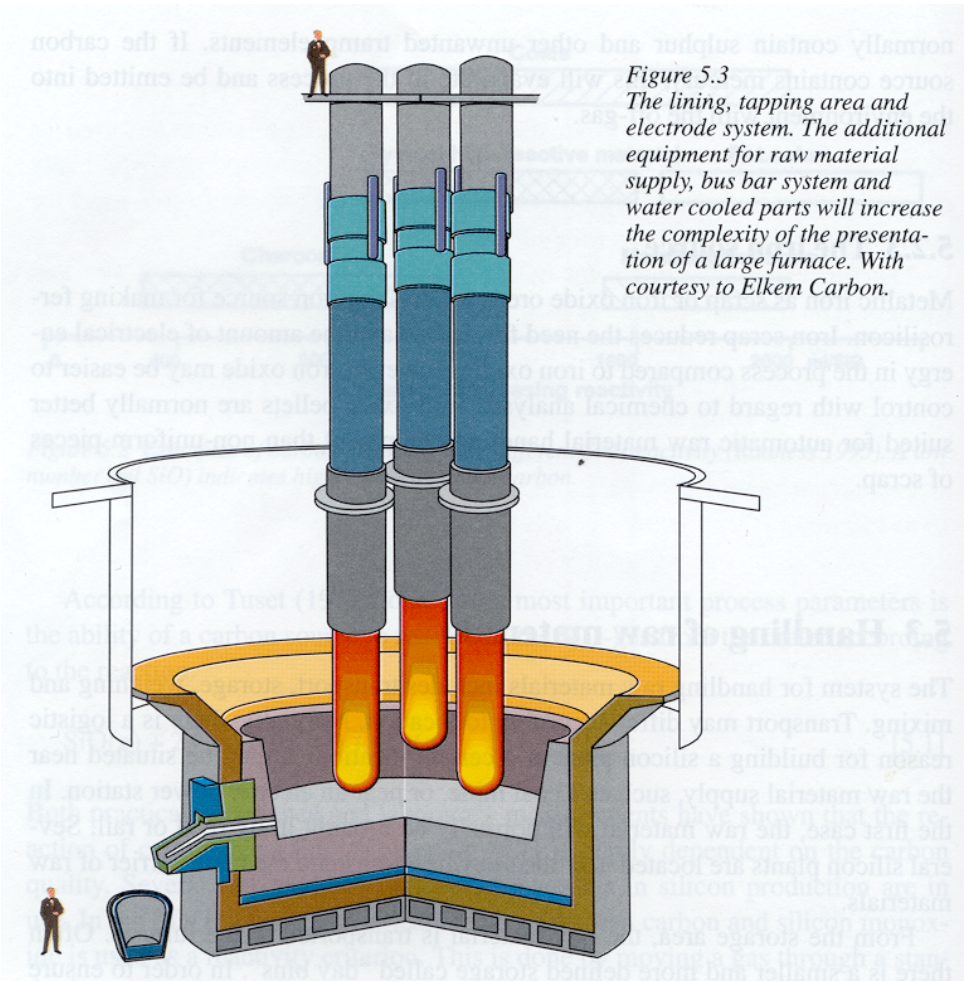
$$SiO_2 + 2\,C = Si + 2\,CO$$

energy

Micro-electronics
Photovoltaics
Aluminum
Silicones

Control and Optimization of Silicon (COPS)

M.Ruszkowski, J. H. Hill, N. Arora (L. Biegler) ELKEM.



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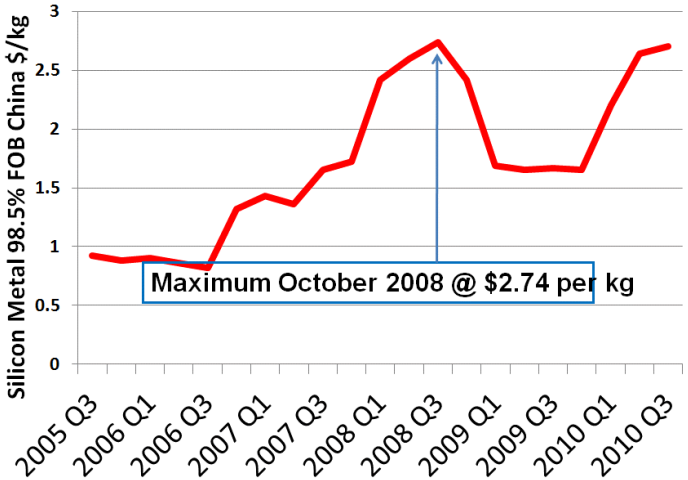

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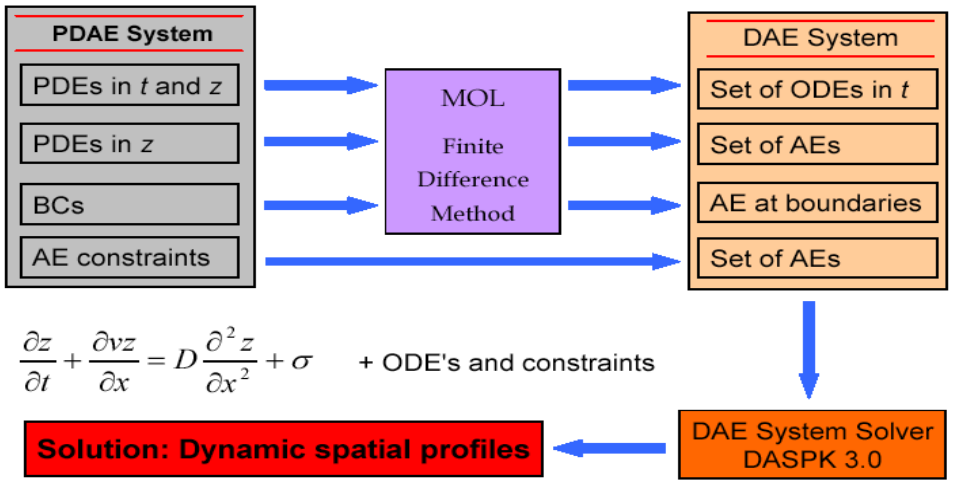
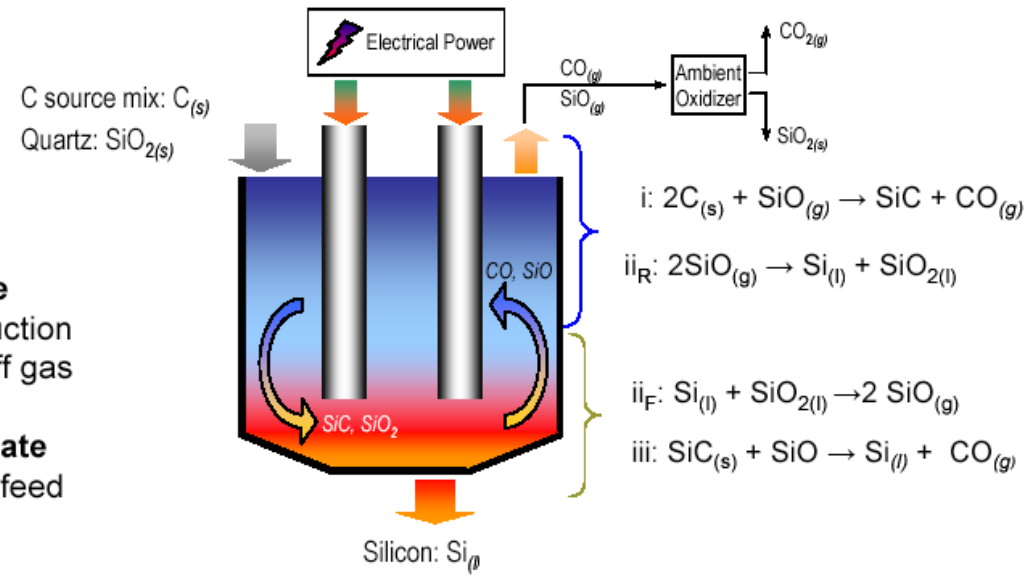


$$\frac{\partial z}{\partial t} + \frac{\partial vz}{\partial x} = D\frac{\partial^2 z}{\partial x^2} + \sigma$$

Process Modeling, parameter and State Estimation, Control, Optimization

tion SiO2+2C = Si+2CO



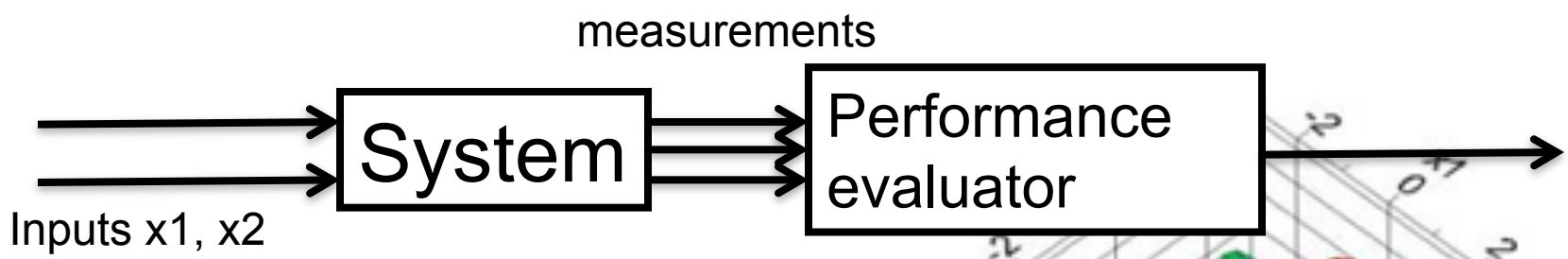
Measure
Si-Production
SiO in off gas

Manipulate
C, SiO2 feed

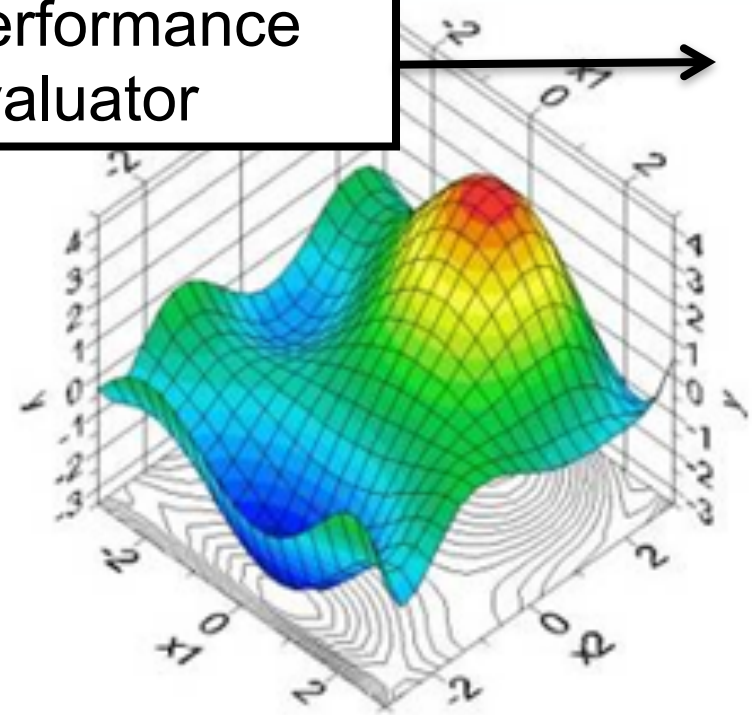
Collect data

Response Surface Methods

- RSM explores the relationships among input variables and one or more response variables.
- First proposed by Box and Wilson in 1951
- Uses designed experiments to map out a multi-dimensional surface which guides the user towards more optimal performance.
- Box and Wilson suggested that a quadric model to parameterize the response surface



1. Vary variables to explore search space
2. Map response
3. Move towards optimum



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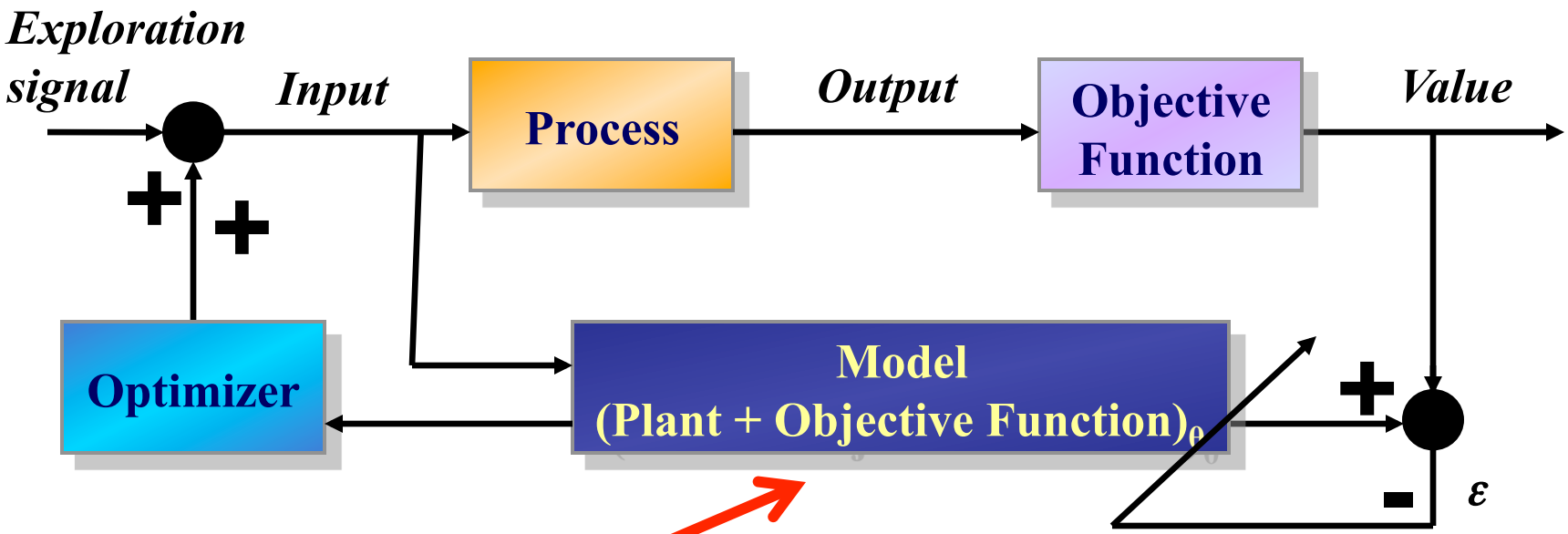
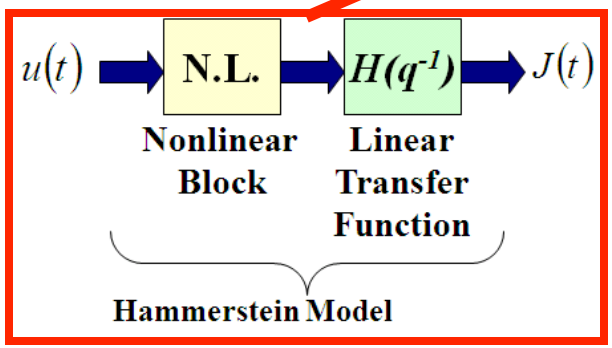
Extremum Seeking Steady State Control





Model:

$$J(t) = aJ(t-1) + g_0 + g_1 u(t-1) + g_2 u^2(t-1)$$

Adapt parameters using regression analysis

The system is $J(t) = aJ(t-1) + g_0 + g_1 u(t-1) + g_2 u^2(t-1)$

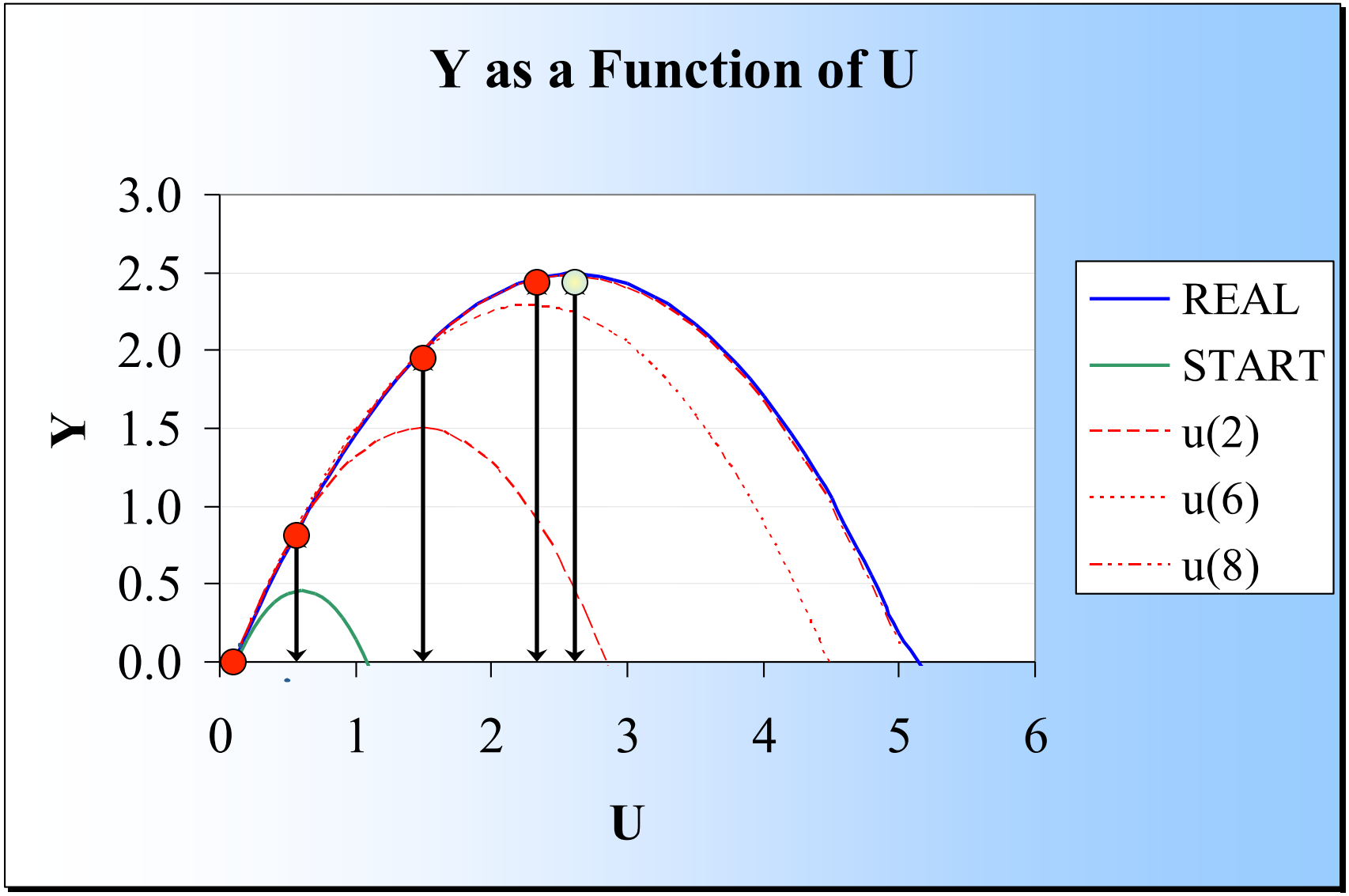
At steady state $J(t) = J(t-1) = J$

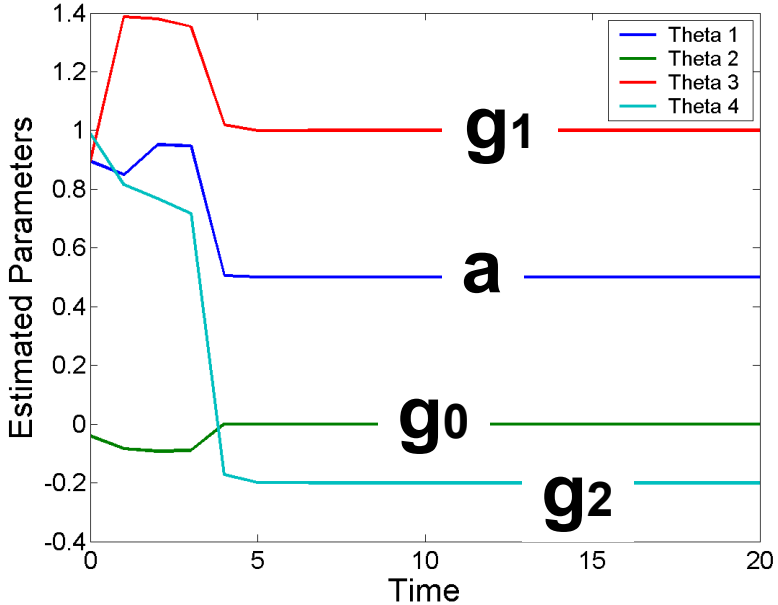
Hence:

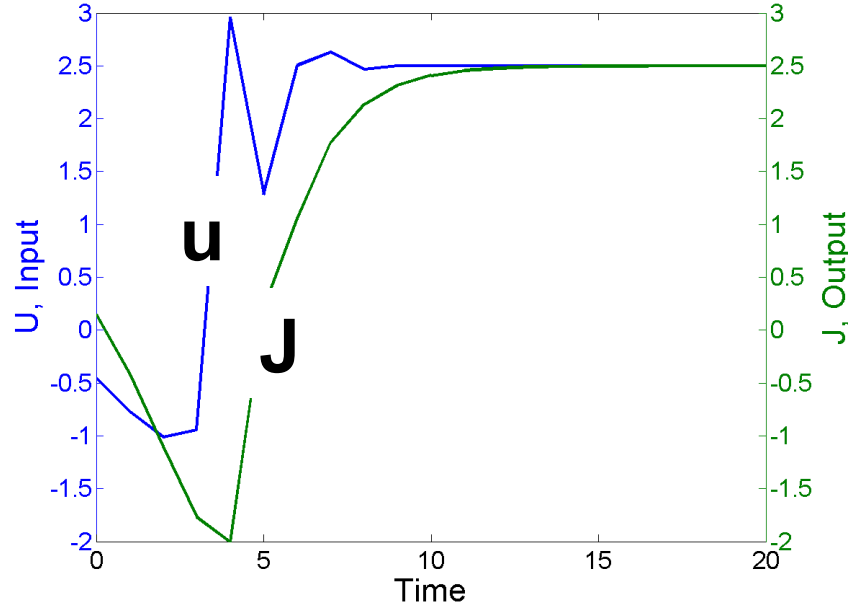
$$J = \frac{g_0}{1-a} + \frac{g_1}{1-a}u + \frac{g_2}{1-a}u^2$$

Solving $\frac{dJ}{du} = 0$ **gives optimal input**

$$u^*(t) = -\frac{g_1}{2g_2}$$


Y as a Function of U
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Y
0
1
2
3
4
5
6
U
REAL
START
u(2)
u(6)
u(8)





$$y(t) = ay(t-1) + g_0 + g_1 u(t-1) + g_2 u^2(t-1)$$

$$a = 0.5$$

$$g_0 = 0$$

$$g_1 = 1.0$$

$$g_2 = -0.2$$

$$J^* = u^* = 2.5$$

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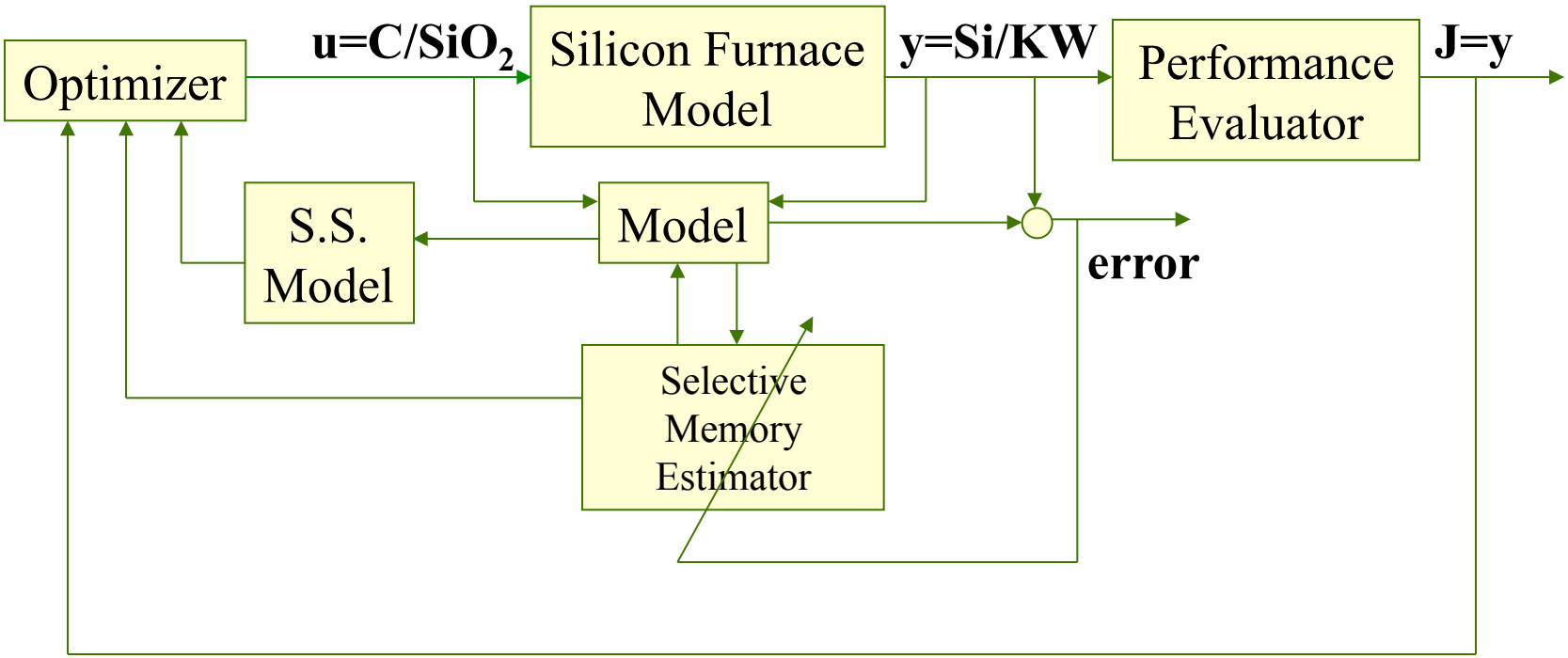
Review of Adaptive RSM for Silicon Process



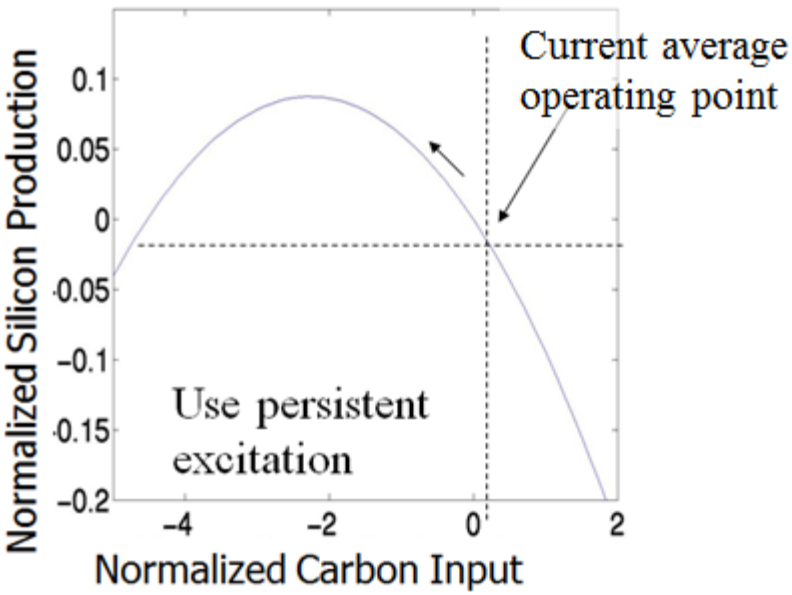
- Step 1: Calculate adaptive model parameters using Least Squares
- Step 2: Calculate u_{max}
- Step 3a: Every N steps set $u(t) = u_{max}$
- Step 3b: All other steps, excite the process by setting

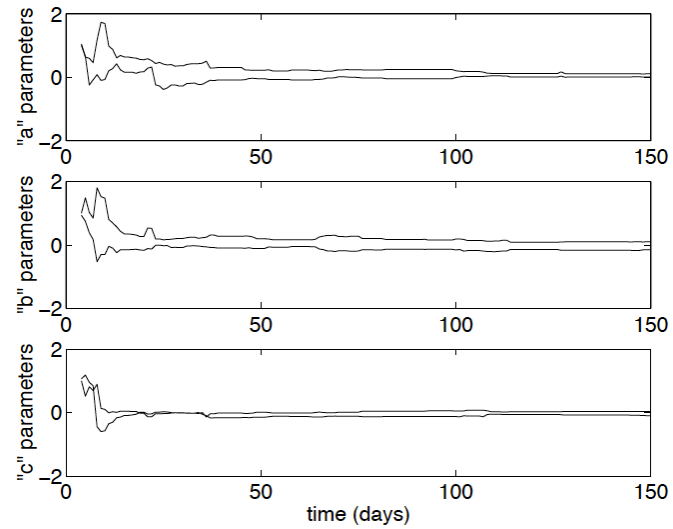
$$u(t) = u(t-1) + \Delta$$

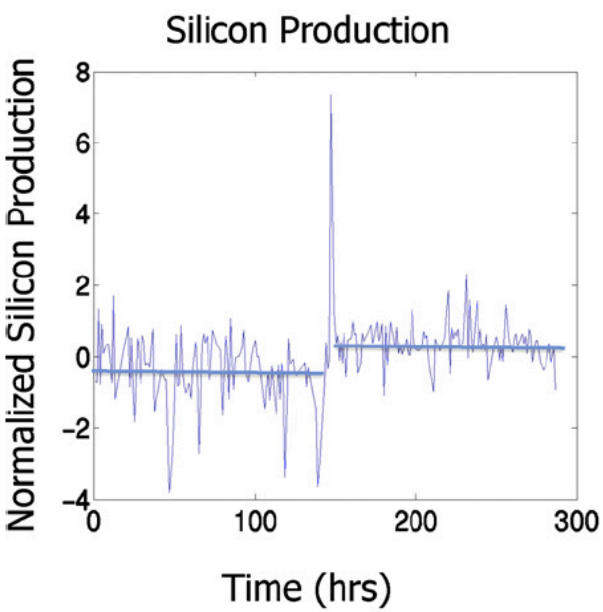
where Δ is randomly selected between three points. $\Delta = \{-d, 0, d\}$

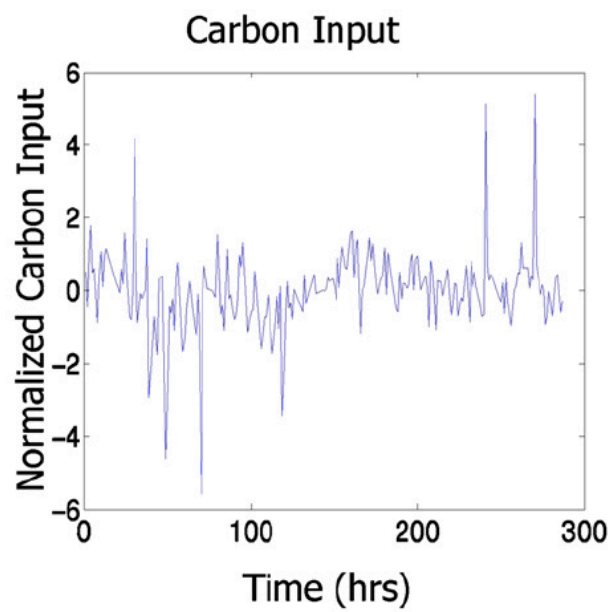
Plant Trials

$$y(t) = a_1(t-1) + a_2 y(t-1) + b_1 u(t-d) + b_2 u(t-d-1) + c_1 u(t-d)^2 + c_2 u(t-d-1)^2$$









Metallurgical Silicon Production → **Poly-Crystalline Silicon Production** → Silicon wafers → Solar Cells → Solar Modules

Process flow diagram disproportionation and pyrolysis

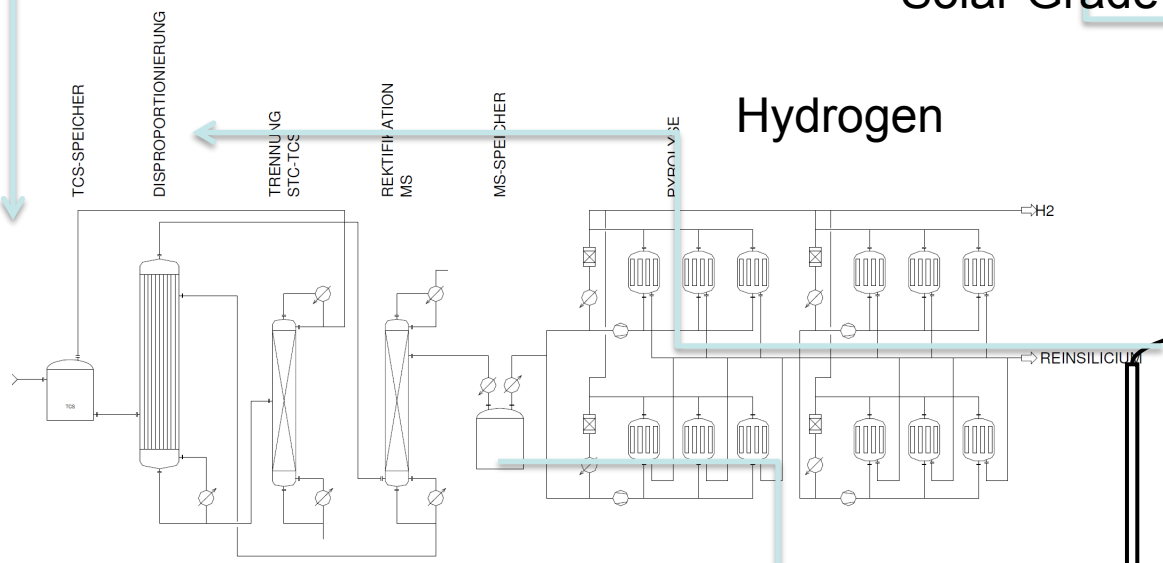
$4\ SiHCl_3 \rightarrow SiH_4 + 3\ SiCl_4$

$SiH_4 \rightarrow Si + 2\ H_2$

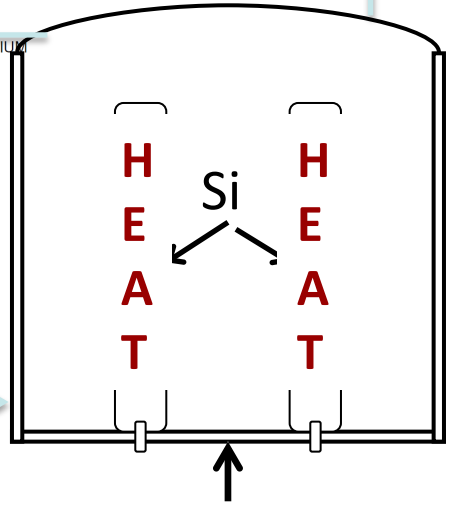
Solar Grade Silicon (SoG)

(About 385,000 tons, cost @ $ 20-30 per kg, 2012)

Hydrogen



High Purity Silane (SiH_4)



$SiHCl_3$ or SiH_4

Poly-Silicon Production – a Roller Coast Ride

Metallurgical Grade $3-5 per kg

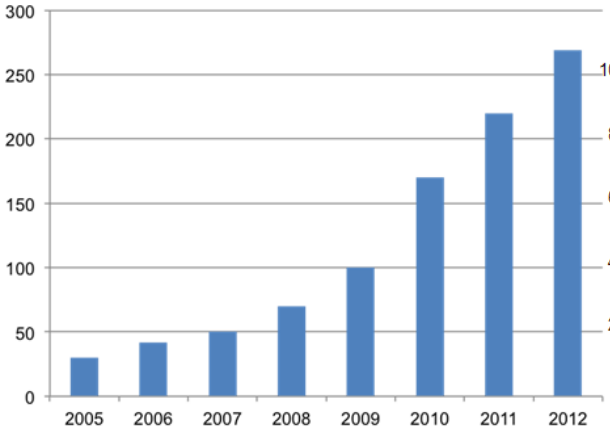
Electronic Grade $40-60 per kg

Raw Material → $SiHCl_3$ (TCS) Distillation → Decomposition → Crystallization → Wafers → ICs

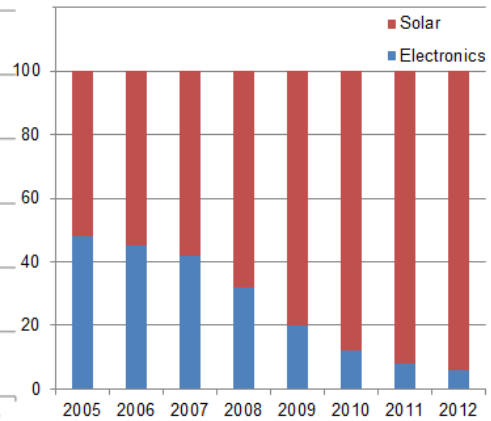
10% Waste

1998 Appx. 2000 tons per yr solar silicon $20 -25 per kg

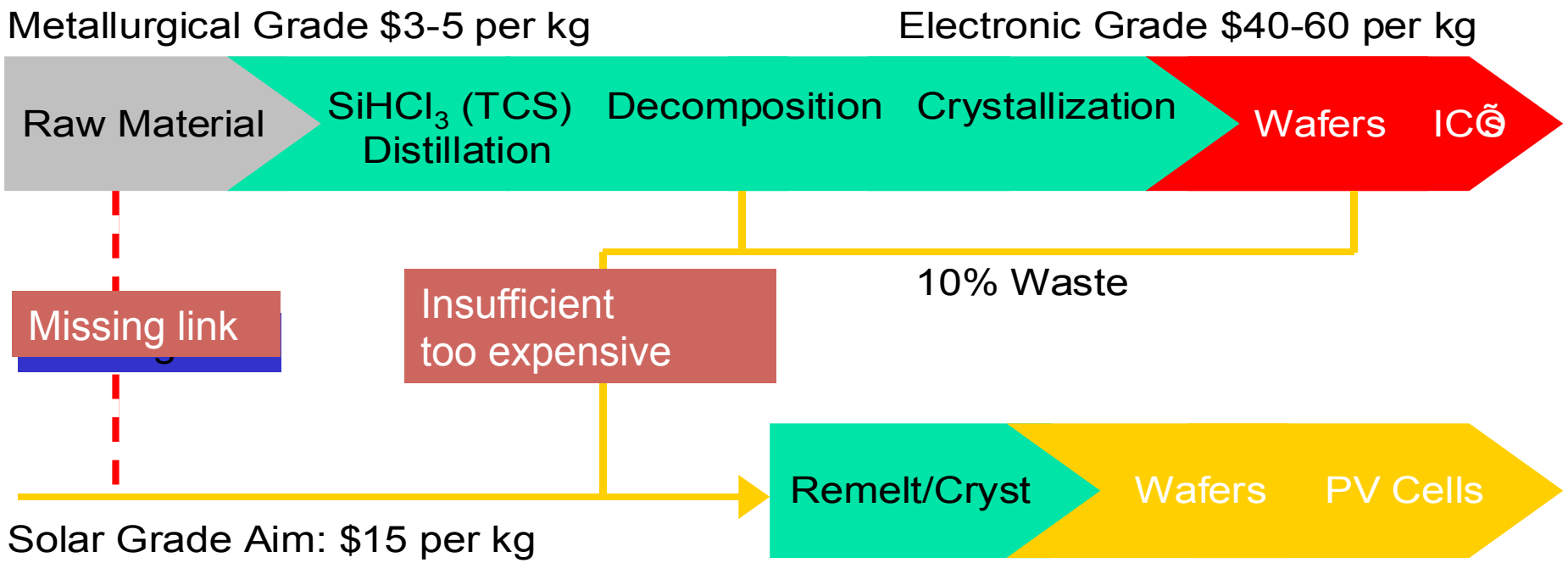
Remelt/Cryst → Wafers → PV Cells → Modules and Installation



Silicon production per year



Consumption percentage of solar and electronics



2006 Spot Price $ 200 + per kg
2013 spot price $ 17.50 per kg

Metallurgical Grade $3-5 per kg

Electronic Grade $40-60 per kg

Raw Material → $SiHCl_3$ (TCS) Distillation → Decomposition → Crystallization → Wafers → ICs

ELKEM ASA
Metallurgical Route

REC Silicon LLC
Chemical Route

New Products !!!!

Remelt/Cryst → Wafers → PV Cells

Solar Grade Aim: $15 per kg

ELKEM ASA
Purification by LLE/crystallization
Production Plant built 2009

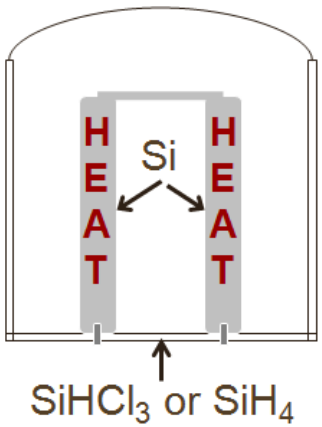
Cost @ 15 per kg

Solar Grade Silicon LLC
Silane Decomposition in FBR
Production Plant built 2009

Cost @ $ 18 per kg

Solar Silicon Grade Silicon via the FBR process

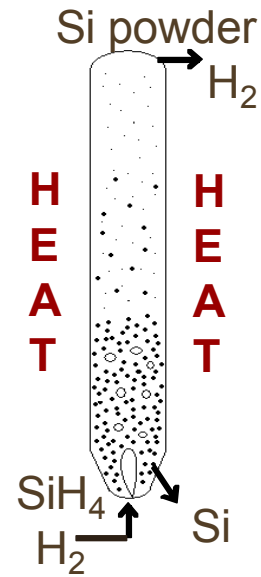
From Silane to Solar Silicon



Siemens Reactor
Batch Process
1100°C (TCS)
650 °C (Silane)

$$SiH_{4(g)} \rightarrow Si_{(s)} + 2H_{2(g)}$$

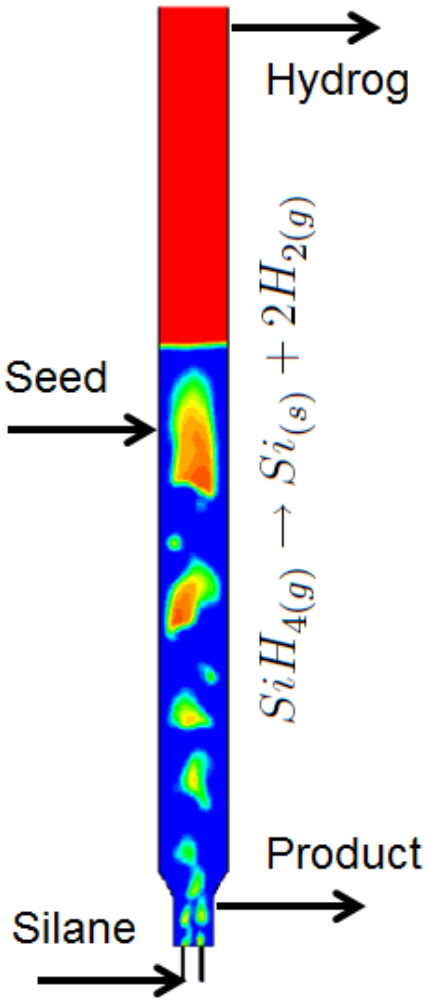
increase throughput
Reduce energy cost

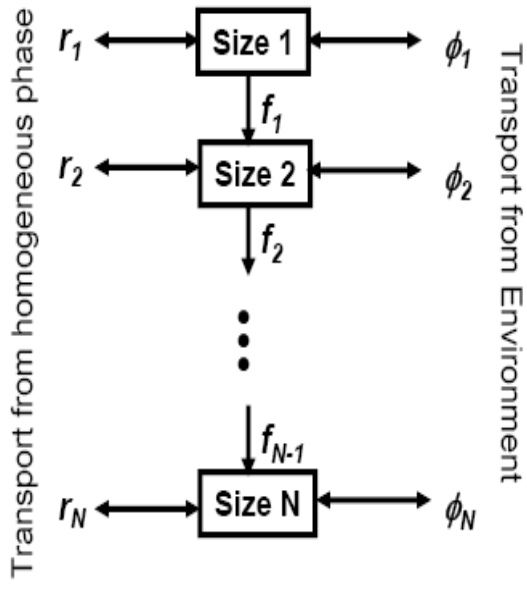


Fluid Bed Reactor
Continuous Process
Large surface area
650 C

Goal: develop scale-up and control models to optimize granular yield and control particle size.

The Population Balance





Mass balance:

$$\frac{dM_i}{dt} = f_{i-1} - f_i + r_i - \phi_i$$

Number balance:

$$\frac{dn_i}{dt} = \frac{f_{i-1}}{m_i} - \frac{f_i}{m_{i+1}} - \frac{\phi_i}{m_i}$$

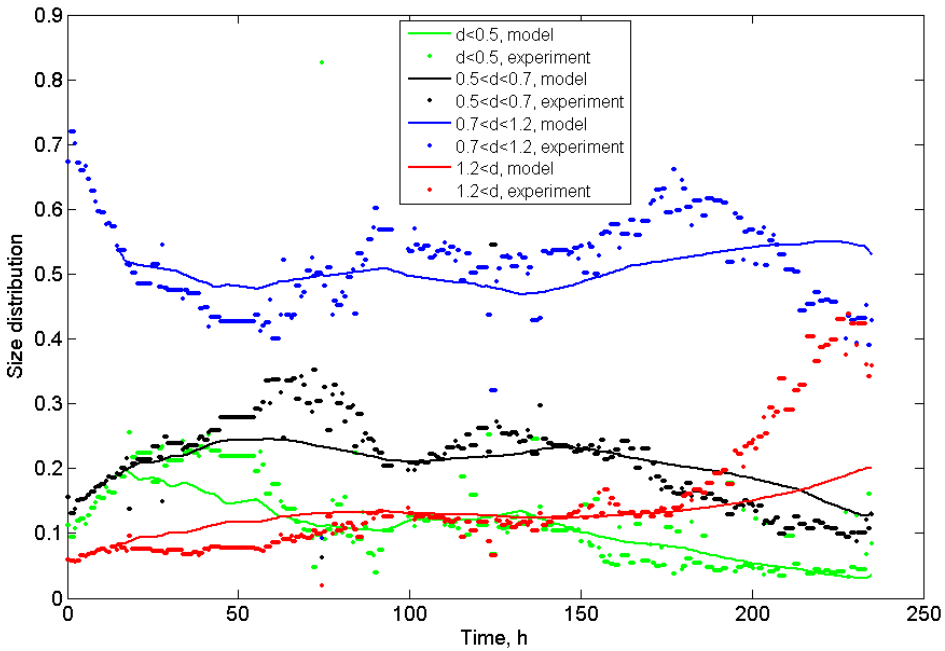
$$f_i = \frac{m_{i+1}}{m_{i+1} - m_i} r_i$$

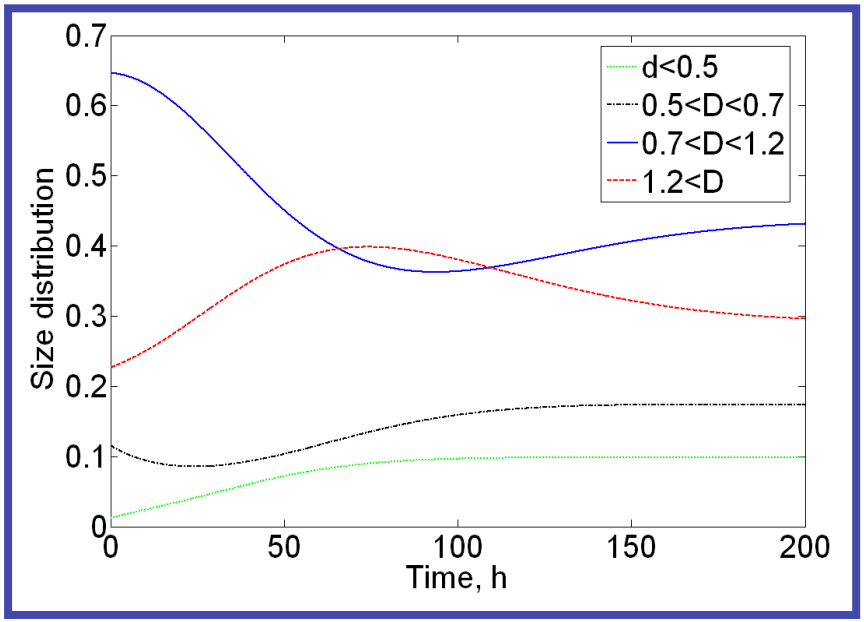
Theorem 1:

The discretized balances converge to the continuous population balance as the number of size intervals approaches to infinity.

$$\frac{\partial n}{\partial t} + \frac{\partial (Gn)}{\partial l} = B - D + \frac{F_{in}}{V} n_{in} - \frac{F}{V} n$$

Model Verification using Pilot Plant Data



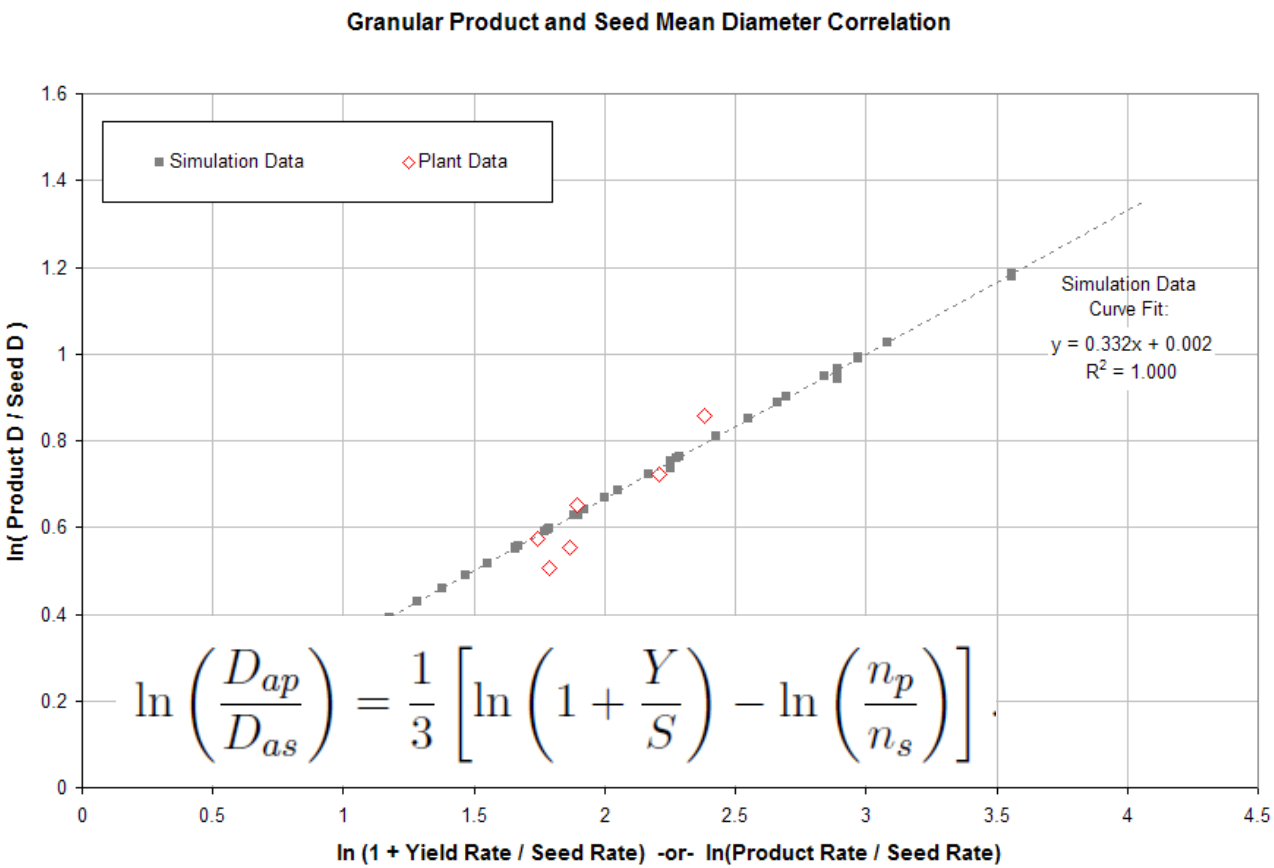


Time constant for particle size distribution about 50 hours.

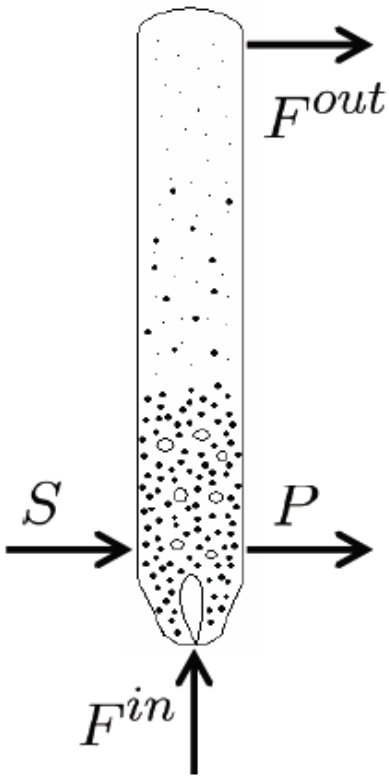
Weak control of distribution function

Difficult to control yield loss (sensitive system)

Scale-up models: from pilot to demonstration plant



$$\ln\left(\frac{D_{ap}}{D_{as}}\right) = \frac{1}{3}\left[\ln\left(1+\frac{Y}{S}\right) - \ln\left(\frac{n_p}{n_s}\right)\right].$$



Y-Yield
S-silane feedrate
D- average diameter(p - product, s-feed)
n- particle feedrate (p -product, s-feed)

Steady State Analysis

Theorem 2: The cumulative mass fraction at steady state is given by

$$\Phi_m(l) = 1 - \exp\left(-\frac{l}{G\tau}\right)\left(1 + \frac{l}{G\tau} + \frac{1}{2}\left(\frac{l}{G\tau}\right)^2 + \frac{1}{6}\left(\frac{l}{G\tau}\right)^3\right);$$

the resulting particle mass distribution is defined as

$$\phi_m(l) = \frac{d\Phi_m(l)}{dl} \quad \text{so that} \quad \phi_m(l) = \frac{1}{6}\frac{l^3}{(G\tau)^4}\exp\left(-\frac{l}{G\tau}\right).$$

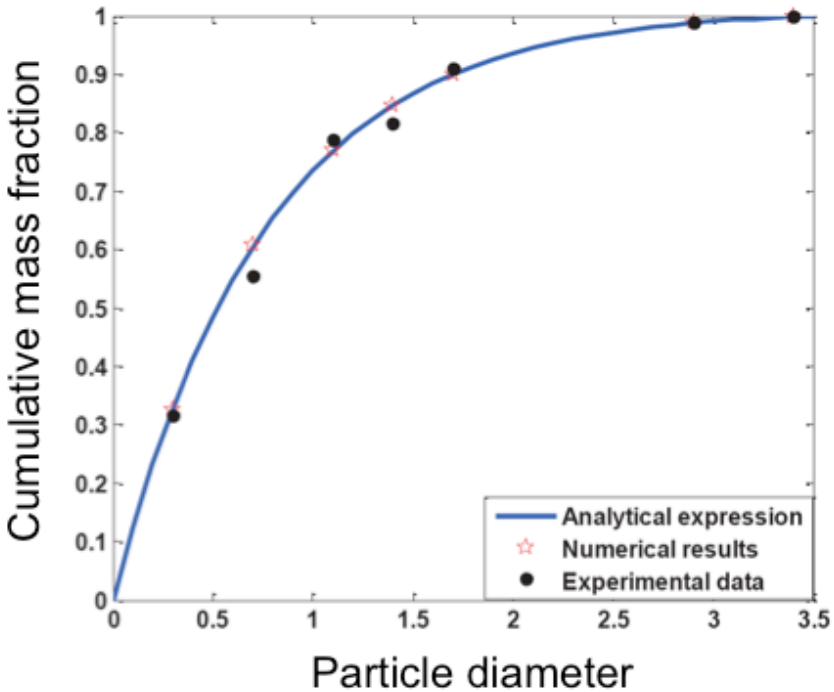
Remark: The cumulative number fraction at steady state is given by

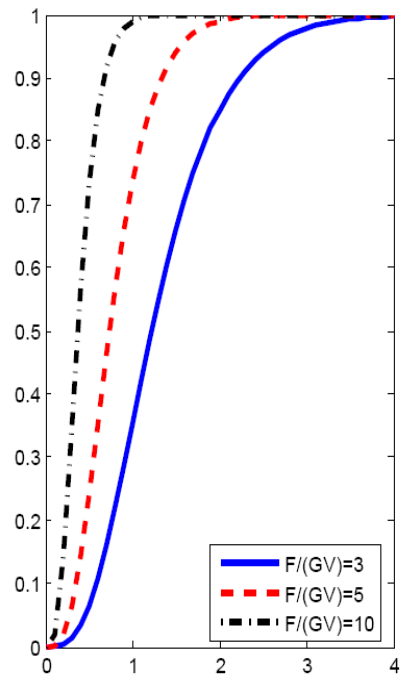
$$\Phi_n(l) = 1 - \exp\left(-\frac{l}{G\tau}\right)$$

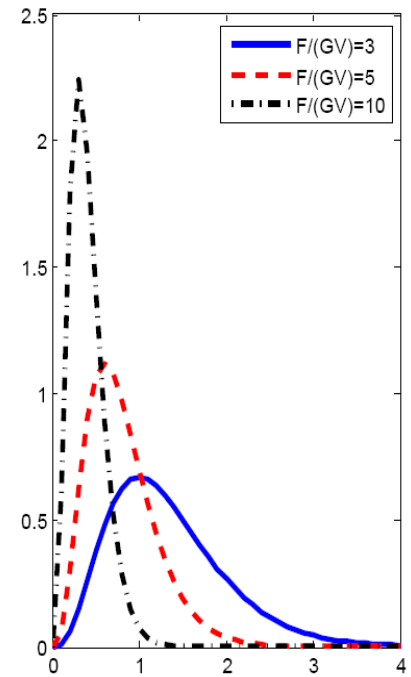
which corresponds to the residence time distribution for a continuous stirred tank reactor.

Model Validation- Distribution Fn

Cumulative mass fraction of silicon particle at steady state







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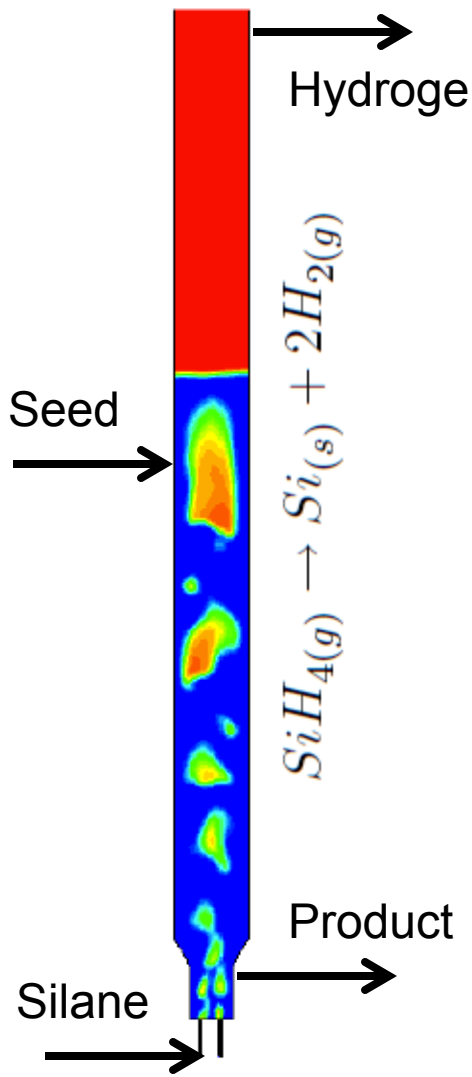
Stability of Population Balance for Silicon Production



$$\frac{\partial n}{\partial t} + \frac{\partial (Gn)}{\partial l} = B - D + \frac{F_{in}}{V} n_{in} - \frac{F}{V} n$$

Stability analysis using Lyapunov function $W = \frac{1}{2} \int_0^{\infty} \overline{m(l)}^2 dl$

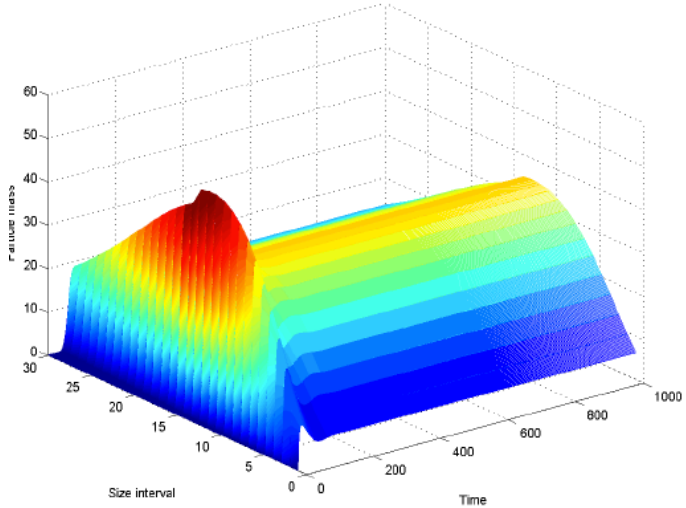
$$\frac{dW(t)}{dt} = -\frac{c_s}{\rho V \Theta} \int_{l_{min}}^{l_{max}} \left(\frac{F}{V} - \frac{\rho}{lG}\right) \bar{m}(l)^2 dl$$

Theorem 3: Population balance converges to the stable steady state provided that the powder concentration is constant and

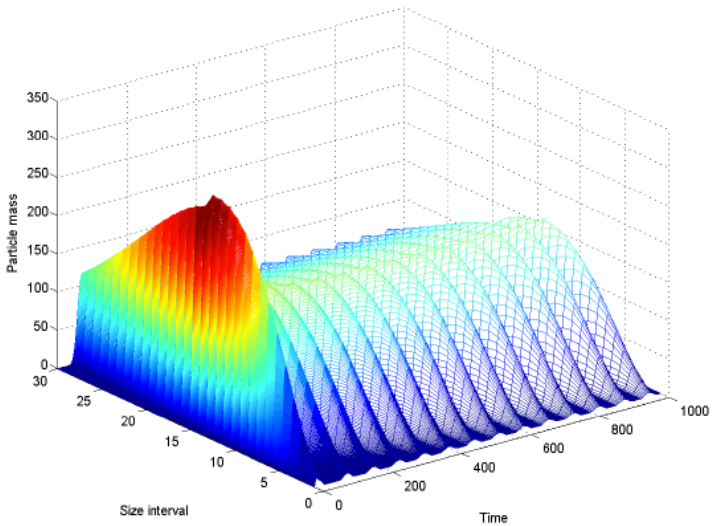
$$\frac{V}{F} < \frac{G}{\rho} l_{min}$$

- Small volume *V*
- High throughput *F*
- Large seed size l_{min}
- High growth rate G

Stability



Seed size larger than critical



Seed size smaller than critical

- Developed method for scale-up and control
- Predict particle size distribution for product
- Stability conditions

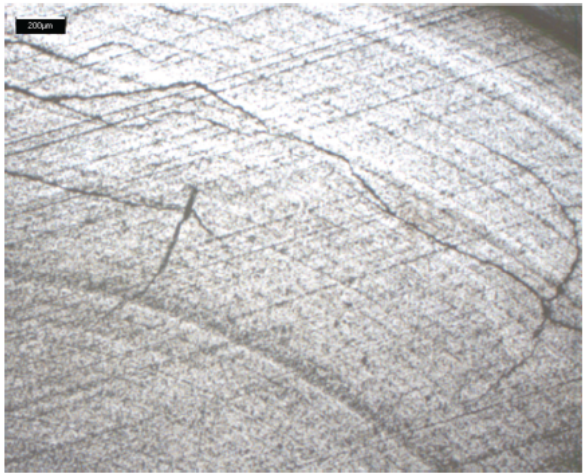


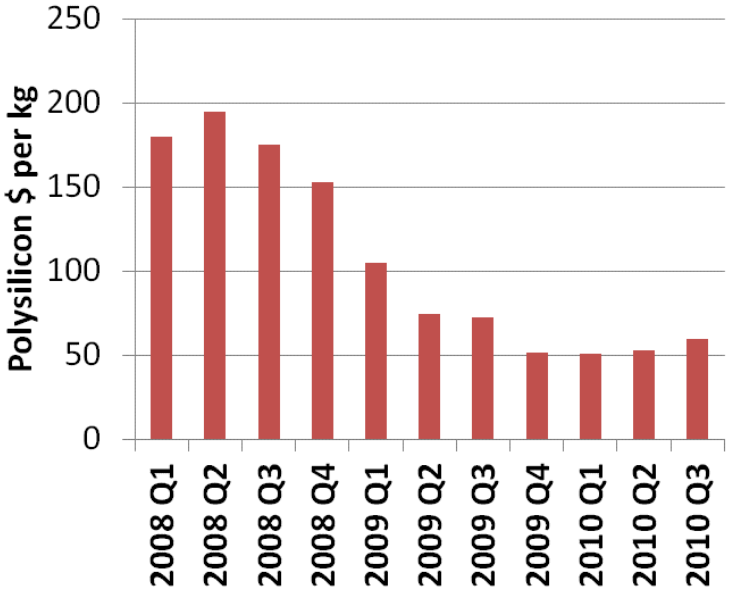
Figure 3: Radially distributed lines

- Christy starts thesis 2002
- Population and FBR modeling
- REC starts small pilot 2002
- Fluor involved in 2004
- Inventory control solves several control challenges
- Christy completes thesis 2007
- **REC Silicon $970 million expansion project** 24 fluid bed reactors to produce 6,500 metric tons of polysilicon per year

Ground Breaking August 2006

Mar. 2008

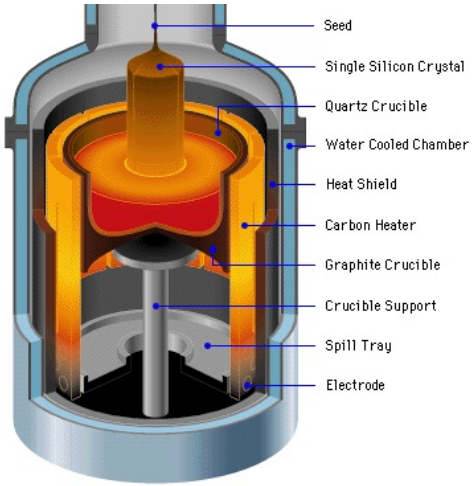
Sept. 2008



Current about <$ 20 per kg !!

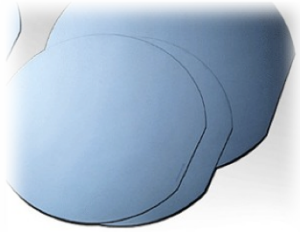
Production Nov. 2009

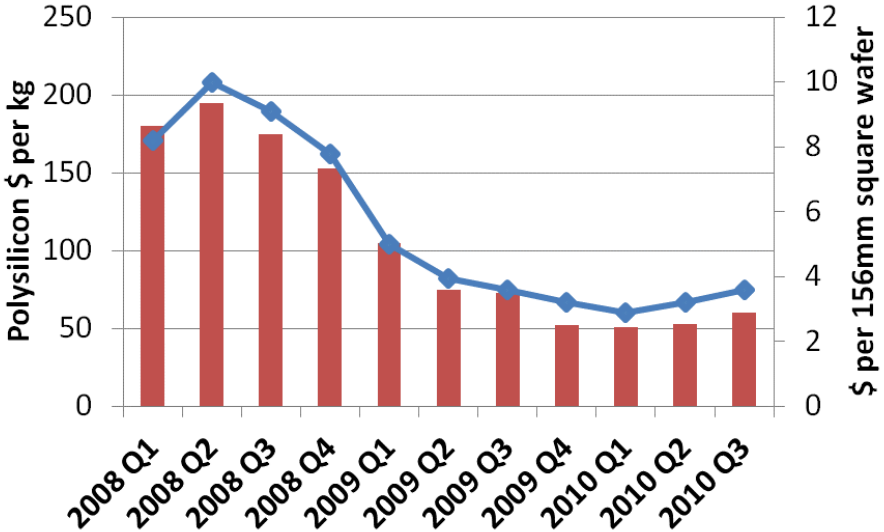
Metallurgical Silicon Production → Poly-Crystalline Silicon Production → **Silicon wafers** → Solar Cells → Solar Modules

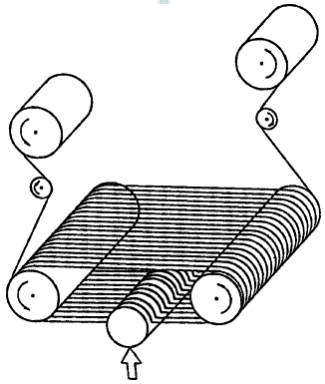


Czochralski Process →

Diamond Wire Cutting →



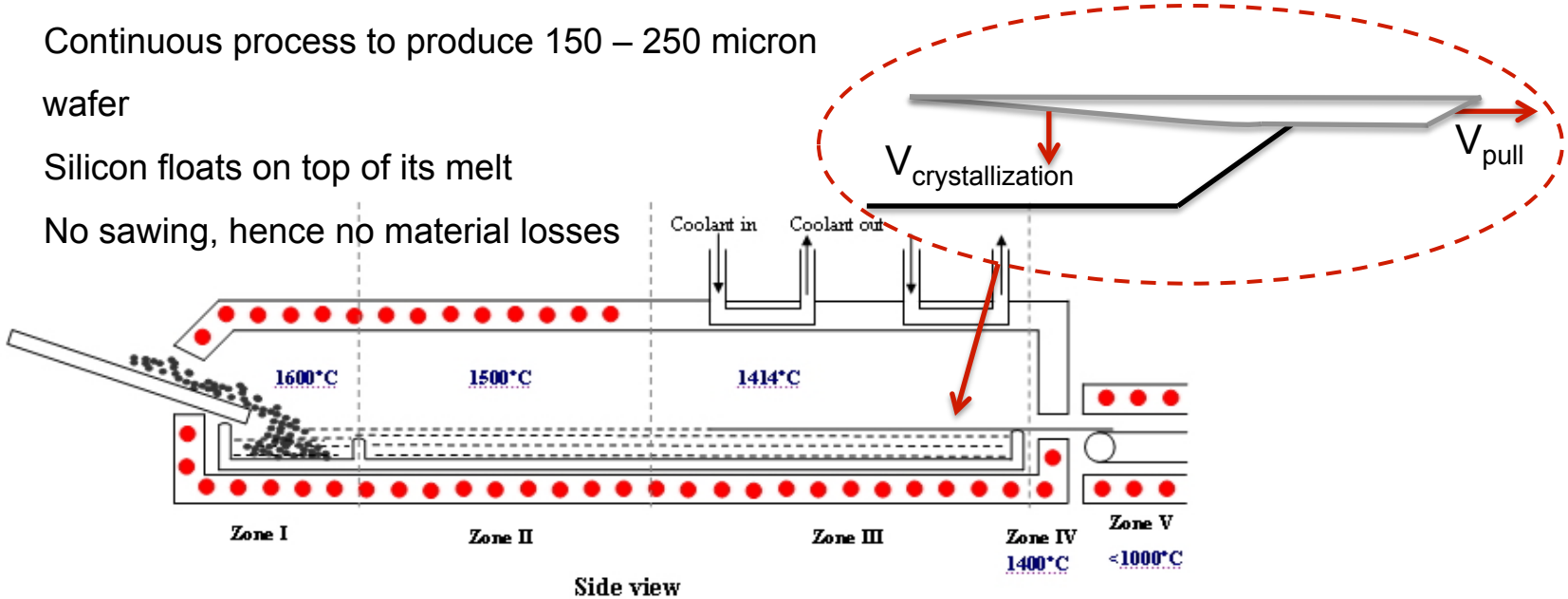




Sawing accounts for 30% of wafer fabrication costs and generates up to 50% of material losses

Horozontal ribbon growth (HRG)

- Continuous process to produce 150 – 250 micron wafer
- Silicon floats on top of its melt
- No sawing, hence no material losses

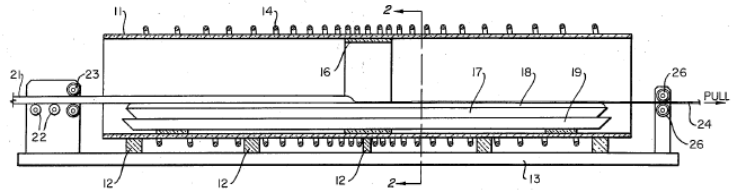


Challenges:

- Crystallization and stability (micro-scale) to achieve single crystalline Silicon film
- Complex fluid flow and heat transfer interaction
- Impurity modeling
- Lack of experimental data and proof of concept

Horizontal ribbon growth

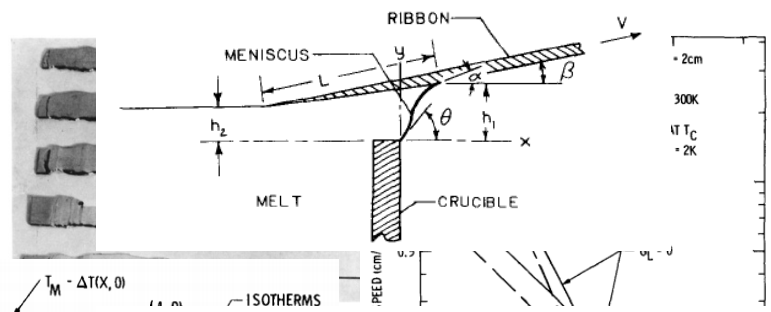
Idea



- William Shockley (1962)

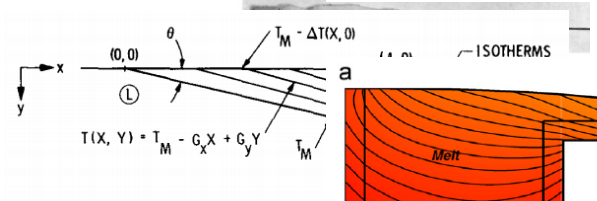
Experiments

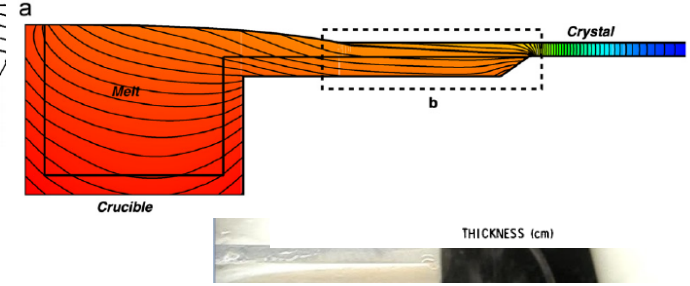
- Carl Bleil (GM, 1969)
- Bossi Kudo (Japan Silicon Co. Ltd, 1979)



Theory

- John Zoutendyk (JPL, 1978)
-



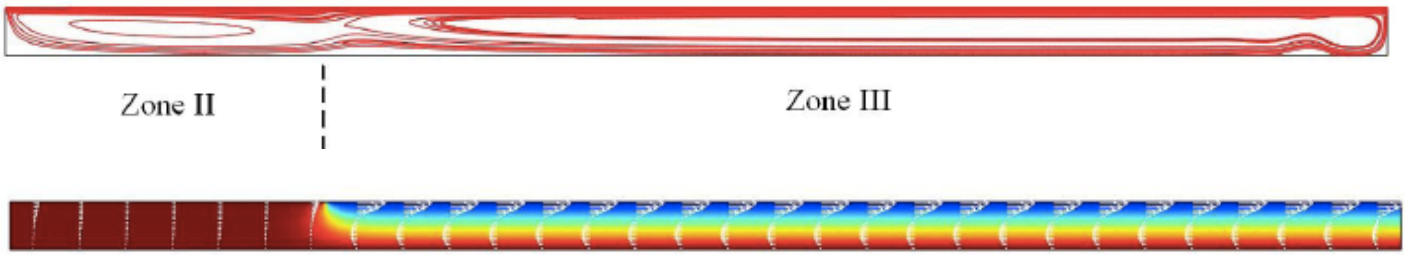


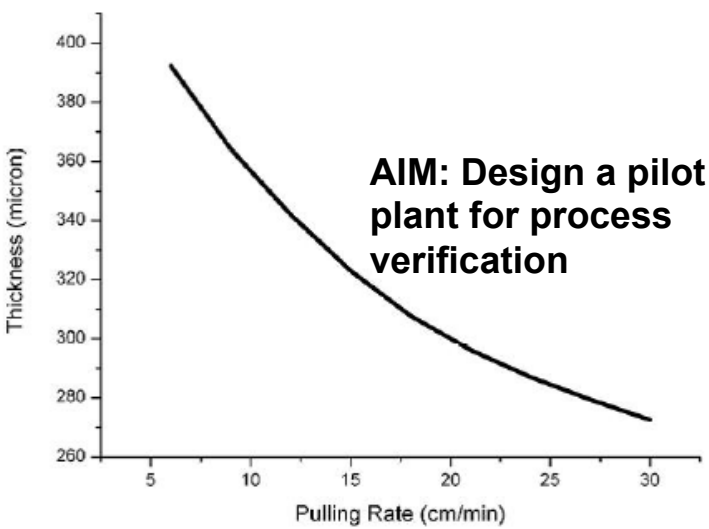
Mathematical Modeling

- Curtis Rhodes and collaborators (U. of South Carolina, 1980)
- Parthiv Daggolu, Andrew Yeckel, Carl Bleil and Jeff Derby (U. of Minnesota, 2012 & 2013)

Sensitivity study using multi-scale models

- Fluid flow and heat transfer model implemented using COMSOL (Eulerian)
- Crystallization dynamics implemented in MATLAB (Lagrangian)





AIM: Design a pilot scale plant for process verification

Scale-up models

↓

Interaction between fluid flow and heat transfer

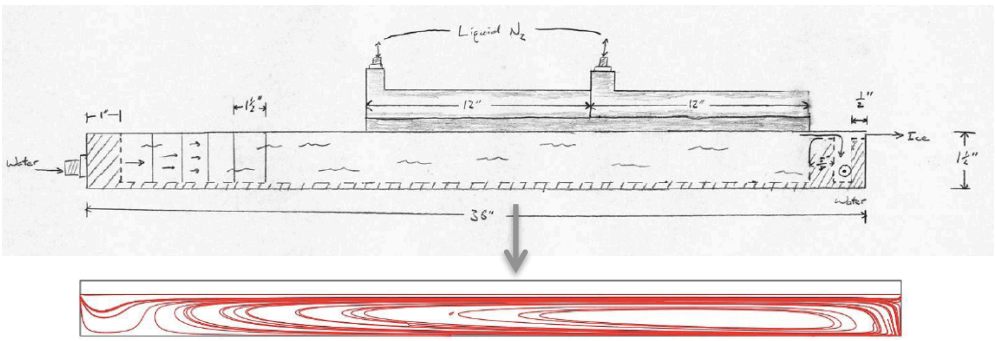
↓

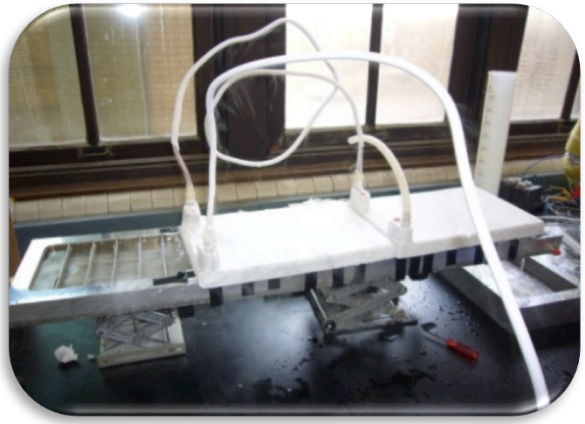
Crystallization dynamics

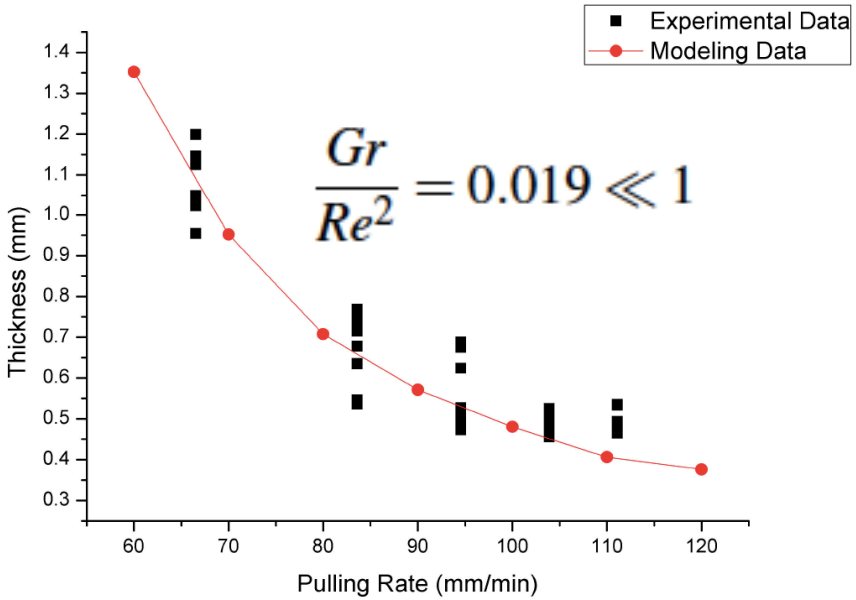
↓

Interfacial Stability

Ice Machine validation



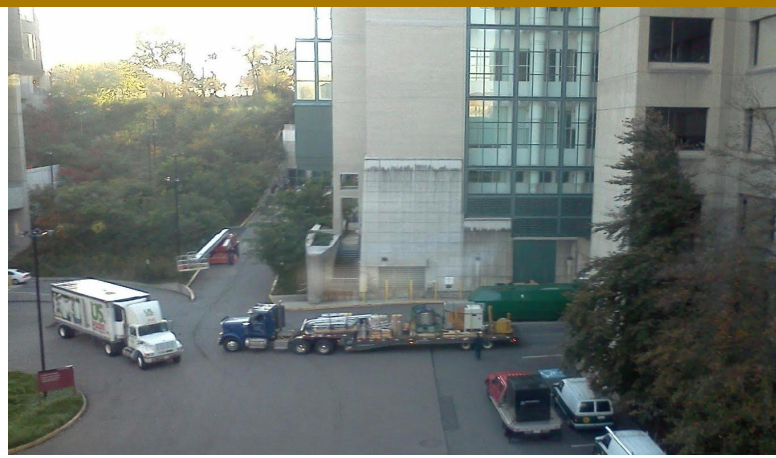


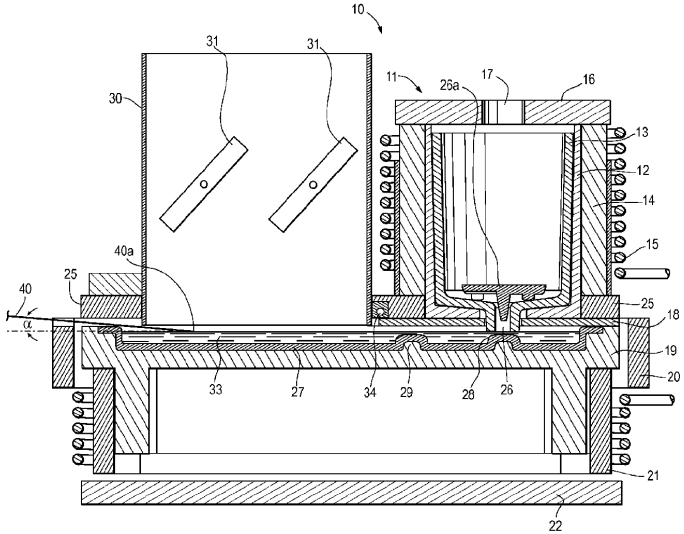


$$\frac{Gr}{Re^2} = 0.019 \ll 1$$

Property	Silicon	Water
Relative density (liq/sol)	1.11	1.09
Relative heat capacity	0.93	2.05
Kinematic viscosity x10^{-3}	0.22	1.70
Relative thermal conductivity	3.23	0.26
Latent heat of fusion	070	0.33

Installation of HRG Pilot Plant at CMU





1. ~ $1M investment capital
2. ~$1.5M R&D (modeling small scale,..)
3. 60kW induction furnace
4. 5in wide
5. 10 ft long
6. Ar controlled atmosphere
7. Allen Bradely control system

Conclusions

- Price has come down to a level where solar technology competes successfully in some markets (with subsidies)
- Technology has been developed to reduce cost further
- New challenge: Increase efficiency (Si current ~18%)
- Reduce cost by 50%
- Multi-junction cells at 40% and higher
- Process systems engineering can play an important supportive role

- Solar power may be cheaper than electricity generated by fossil fuels and nuclear reactors within three to five years (2017) because of innovations,

Mark M. Little, the global research director for General Electric Co. (GE)