

Winning the Global Race for Solar Silicon: The Sequel

David Lynch

Chief Technical Officer, Solar Technology
Research Corporation, Tucson, AZ

&

Professor of both Mining Engineering &
Materials Science & Engineering,
University of Arizona

dclynch@email.arizona.edu



PV Market History

- Prior to 1996 market driven by demand
- 1996/97 market limited by supply, price of off-spec Siemens Si triples to **\$75 per kg**.
- 1998 to 2004 market driven by demand
- 2004 to 2009 market limited by supply, price of Siemens Si rises to **\$450 per kg** during summer of 2008.
- 2006 more Siemens Si used to produce PVs than electronic devices
- 2009 to 2013 market projected to be driven by demand
- Beyond 2013 market expected to be limited by supply, eventually transitioning to being resource limited

Material	Element	Reserve Base (ktonnes)	TWY
Poly-crystalline Silicon	Ag contact	570	2.3
CdTe	Te	48	0.02
CIGS	In	16	0.04

Feltrin and Freundlich stated “that many existing technologies, albeit playing an important [role] in the present sub-GW energy production levels, are affected by severe material shortages, preventing their scale-up to the terawatt range” Renewable Energy, 33 (2), 2008, pp. 180-185.



Why Silicon?

Projected Shortfall in Electrical Energy for the World

2030 1.4 TWY

2050 4.0 TWY

Hubbert Plots – World’s oil production expected to peak between 2010-2016

Linkage

- Resource Availability: Primary & Secondary
- Competition/Substitution
- Distribution/Geo-political
- Environmental
- Life Expectancy
- Disposal/Recycle

Three Routes to Producing a Low Cost Solar Silicon

- Siemens Like Processes (REC)
- Upgrading of Metallurgical Silicon (Elkem Solar, Dow Corning, Timminco, Solar Value, Nippon Steel, JFE, & STRC, ...)
- Direct route to Solar Silicon (FESIL & STRC)

Experiments done by major PV cell manufacturers have revealed shortcomings in the quality of ugm-Si from some vendors. **Solar cells made with ugm-Si have in some cases experienced efficiency losses up to 30% within the first year after installation**

Source: Lars Podlowski, CTO, SOLON, Private Communication, September 15, 2009



What PV Producers Want

P-type s-Si

Molar ratio of

B : P > 3

Mass ratio of

B : P > 1.05

acceptable

Desired B and P Content in p-Type s-Si			
Resistivity (ohm-cm)	Number Density (#/cm ³)	Boron (ppmw)	Maximum Phosphorus (ppmw)
0.1	2.48E+17	1.909	1.821
0.3	5.42E+16	0.418	0.398
1	1.32E+16	0.102	0.097
3	4.12E+15	0.032	0.030
10	1.21E+15	0.009	0.009

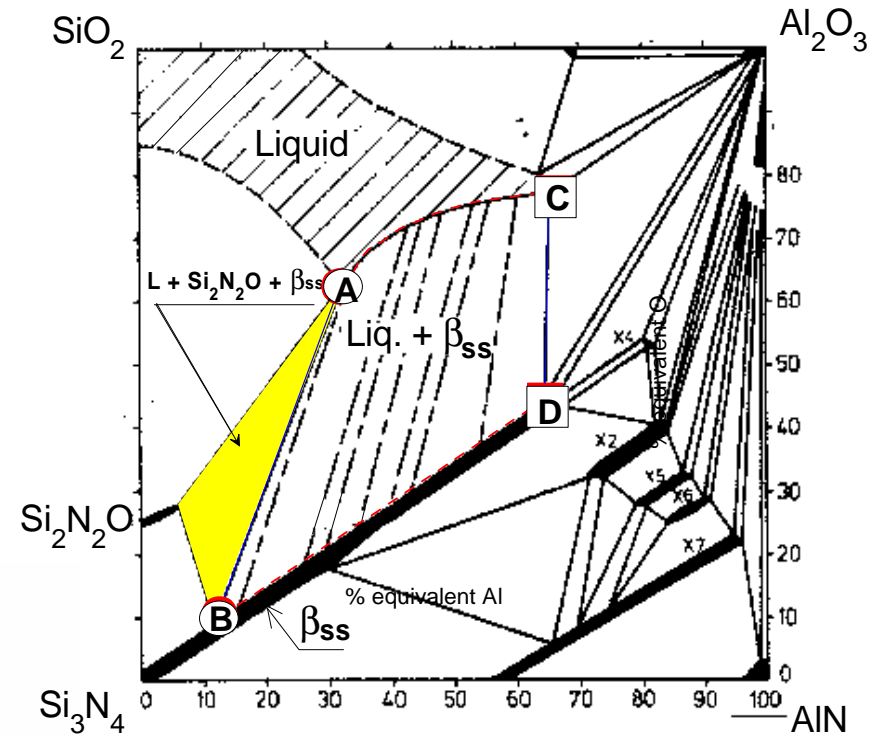
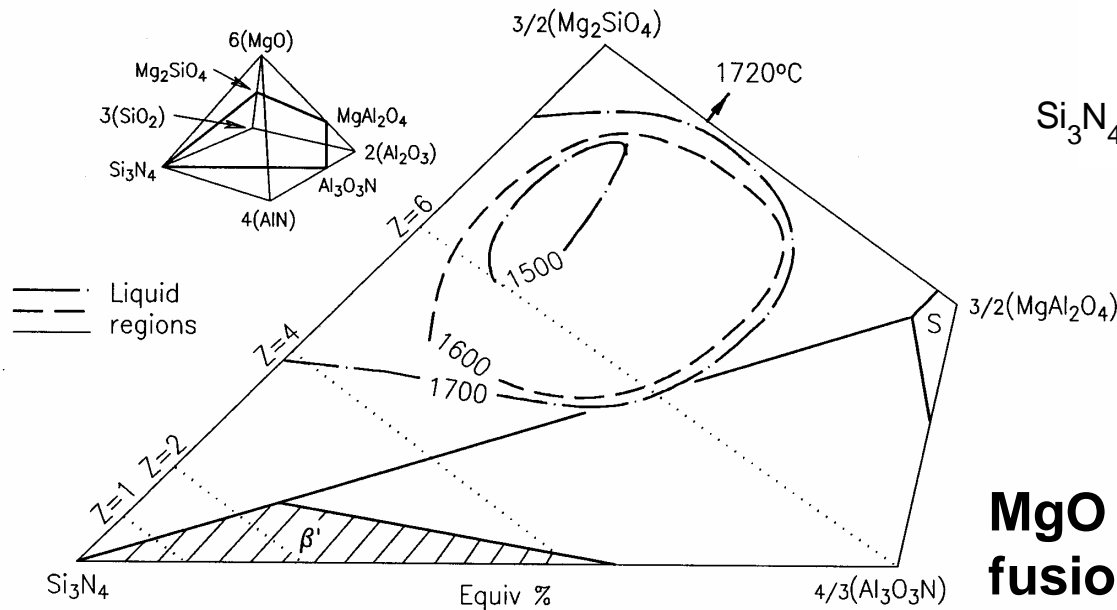
- **Guaranteed, uninterrupted supply**
- **Consistent quality of s-Si requiring little or no manufacturing deviations,**
- **Low price**



STRC Technology: Slagging Chemistry

Based on

- phase diagrams
- thermodynamic calculations
- ionic structure of slag



The Si-Al-N-O phase diagram at 1750 °C.

MgO significantly lowers fusion temperature of the liquid phase.

STRC's Technical Approach

- **Focus changed from B to P based on competitors' problems.**
- **With success in removing P from silicon, company now seeks to improve ability to remove both B and P.**
- **Looking to incorporate slagging chemistry with direct process, or confine refining to STRC's Modified Silgrain Process after reduction of silica.**

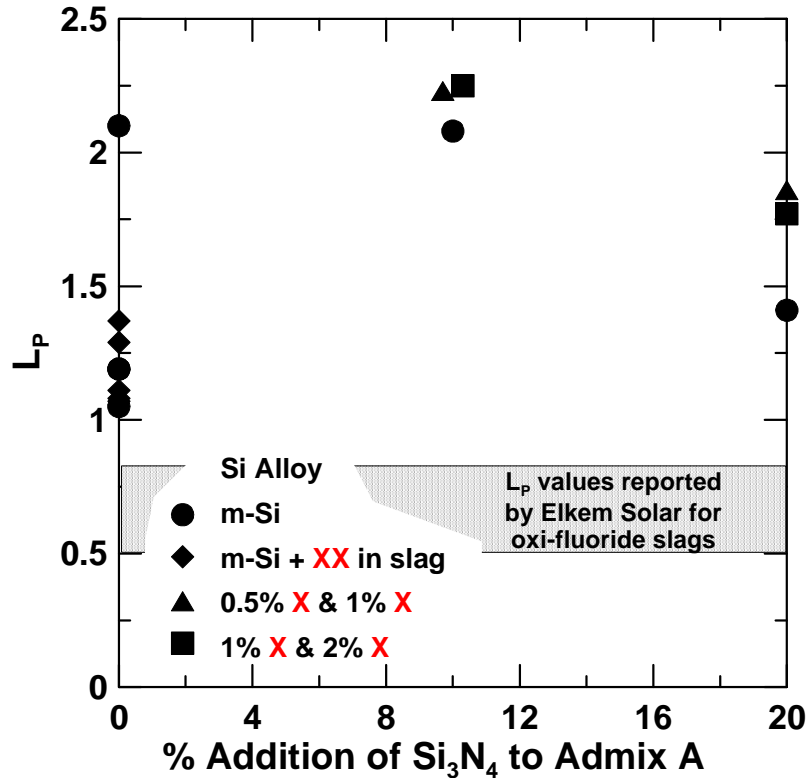


STRC's Technical Progress

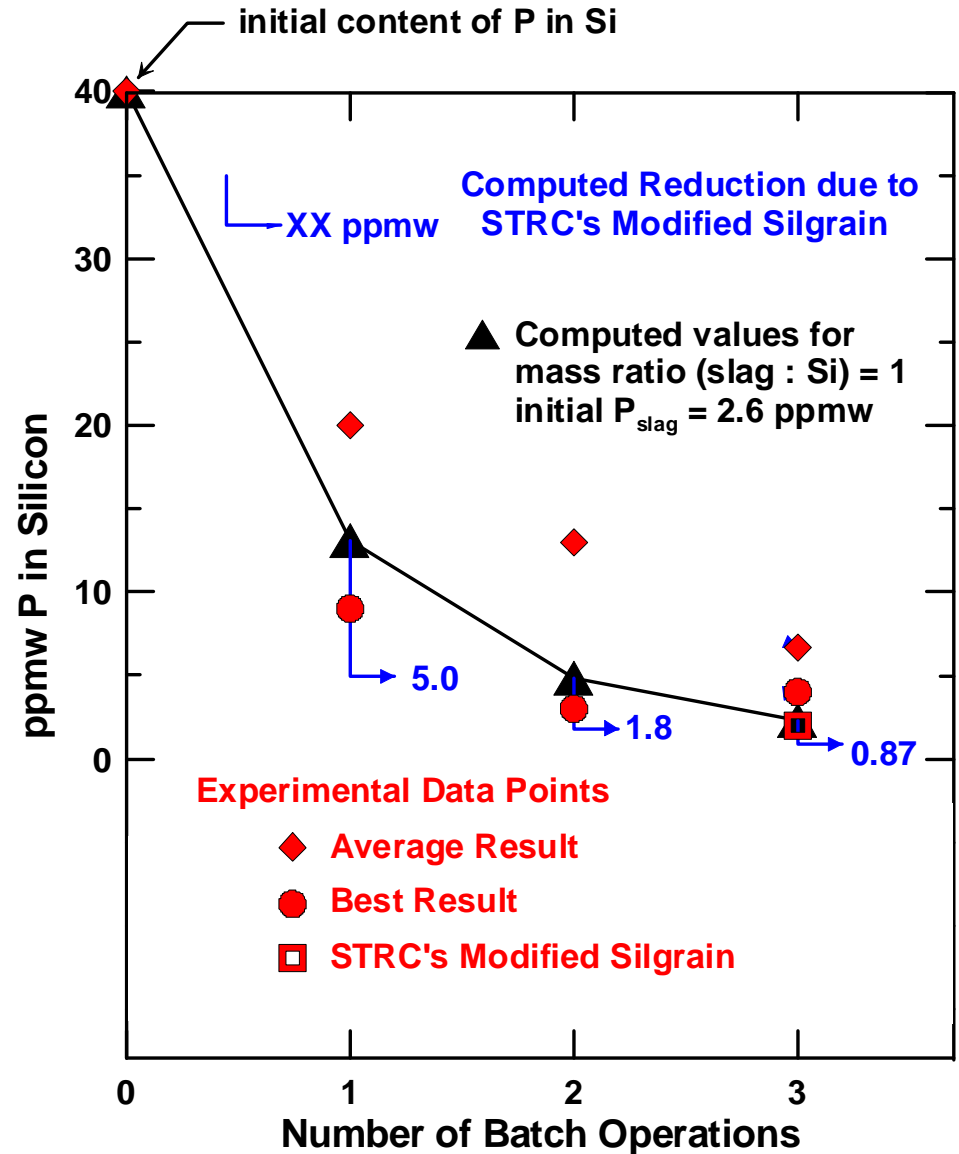
- **created superior slag for removal of P from molten silicon**
- **produced fluid refining slag at the fusion temperature of Si (impacts thermodynamics, refining time, and energy cost)**
- **developed low temperature & low cost route to form nitrides**
- **developed STRC's Modified Silgrain Process for removal of P from silicon**
- **located deposits of silica with very low B and P content**



Slagging Chemistry: Phosphorus

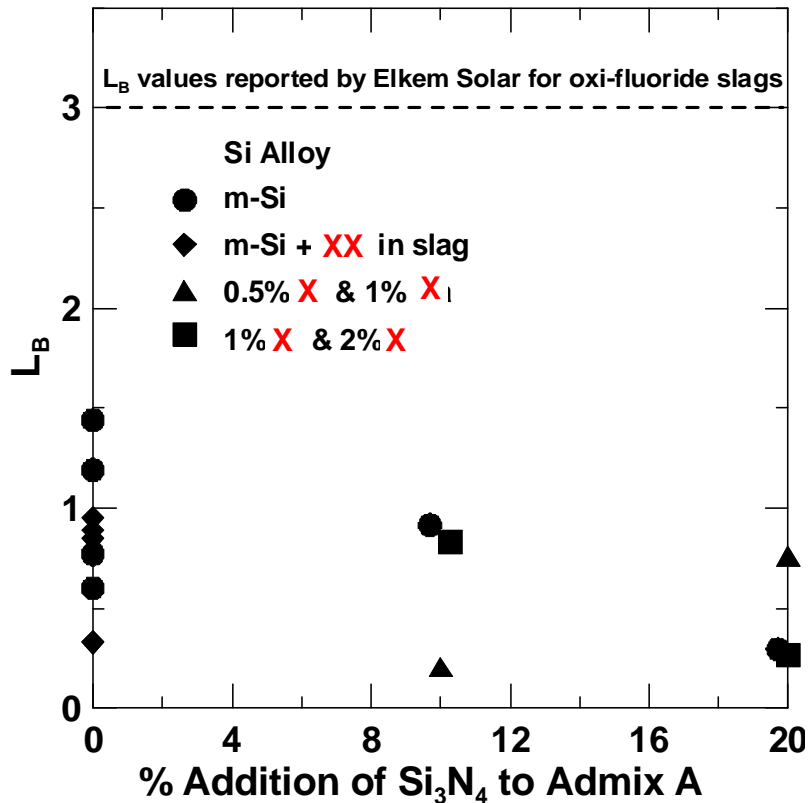


$$L_p = \frac{\text{ppmw P in slag}}{\text{ppmw P in Si}}$$

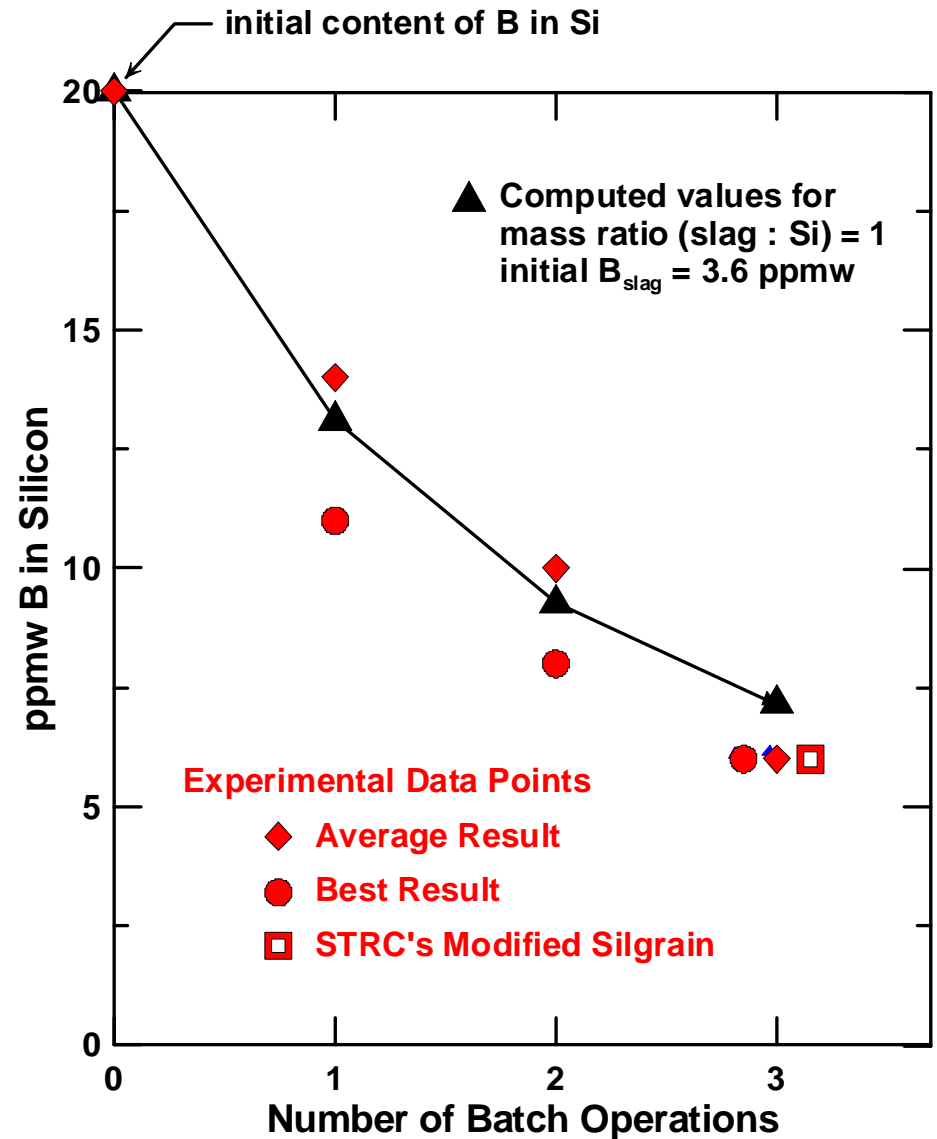


95% Reduction in P Content

Slagging Chemistry: Boron



$$L_B = \frac{\text{ppmw B in slag}}{\text{ppmw B in Si}}$$



70% Reduction in B

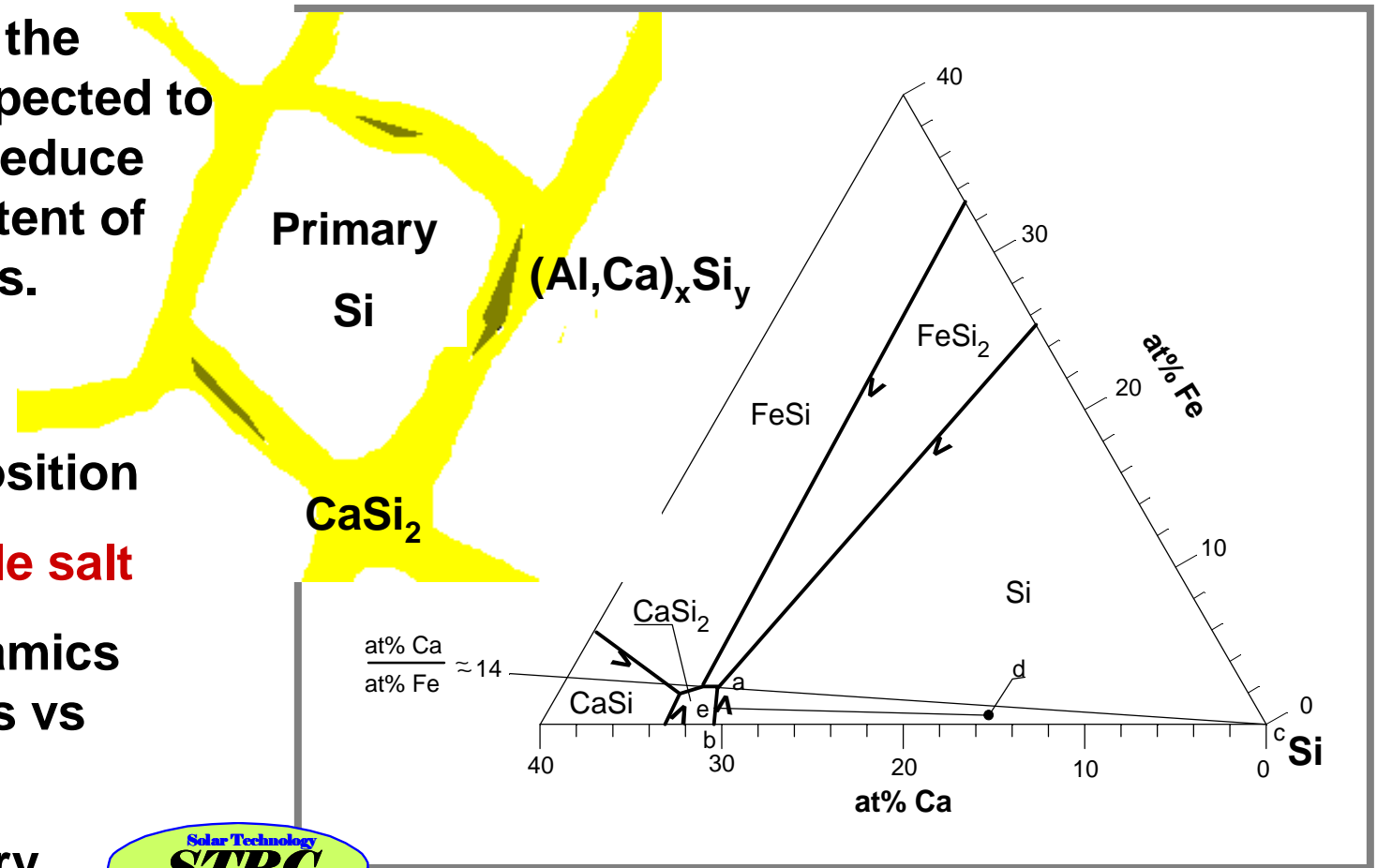
Silgrain

In STRC's Silgrain experiments **90% reduction** in P was achieved. Further refinement of the process is expected to significantly reduce the overall extent of alloy additions.

Key Points

- Alloy composition
- **Water soluble salt**
- Thermodynamics of phosphides vs silicides
- Stoichiometry

“Simultaneously there was obtained a reduction of the phosphorus content of up to 90%.” G. Halvorsen, “Method for Production of Pure Silicon,” US patent 4,539,194 (3 Sept. 1985).



The Value of Quartz Sand after Processing

Product	Value Density of Quartz Sand [*] (\$/m ³)
Silica Sand	42
Metallurgical Silicon	1,455 ^{**}
Solar Silicon	20,400 to 34,000 [^]



* Bulk density of sand 1,820 kg/m³

** 95% recovery of Si, valued at \$1.80 per kg.

[^] 80% recovery of Si, valued at \$30 to \$50 per kg.

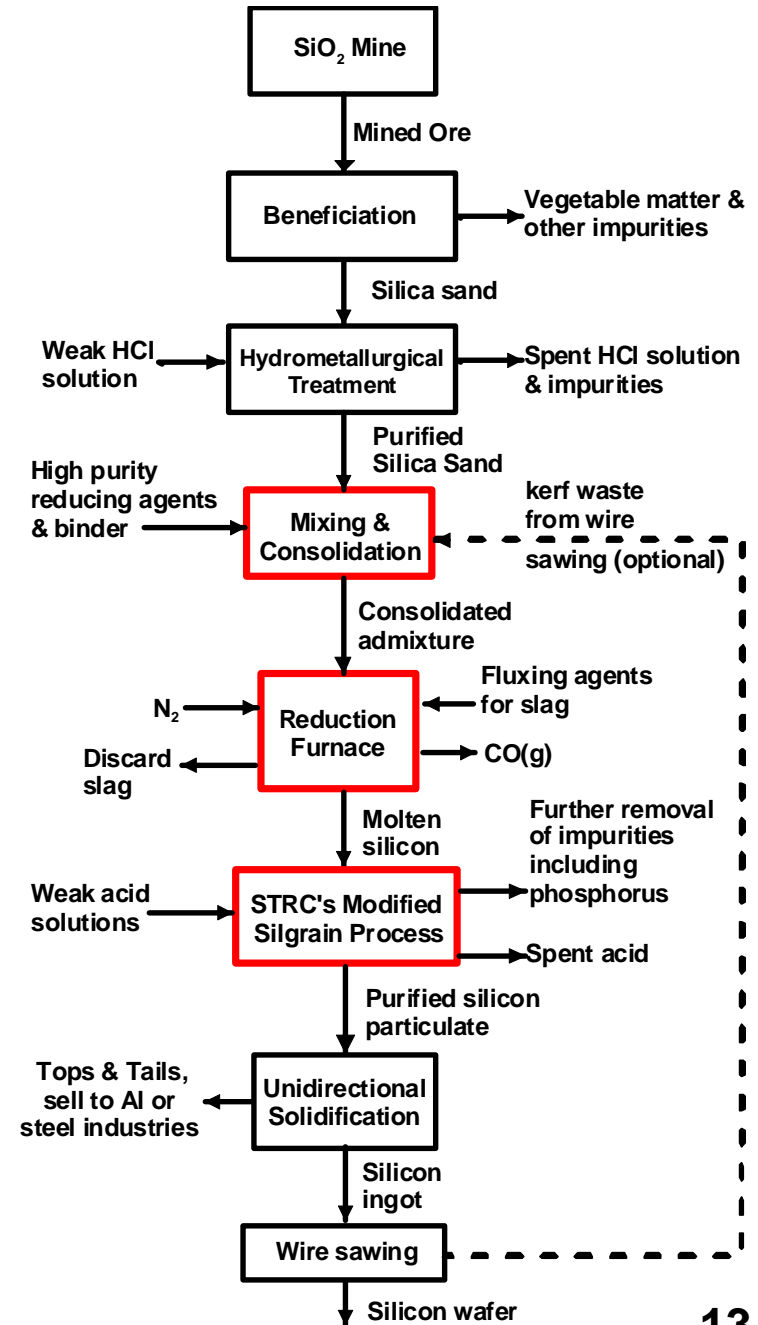
STRC Looks to Integrate Upstream

STRC has found that the highest purity silica has acceptable B content, but 2 to 10 times too much P.

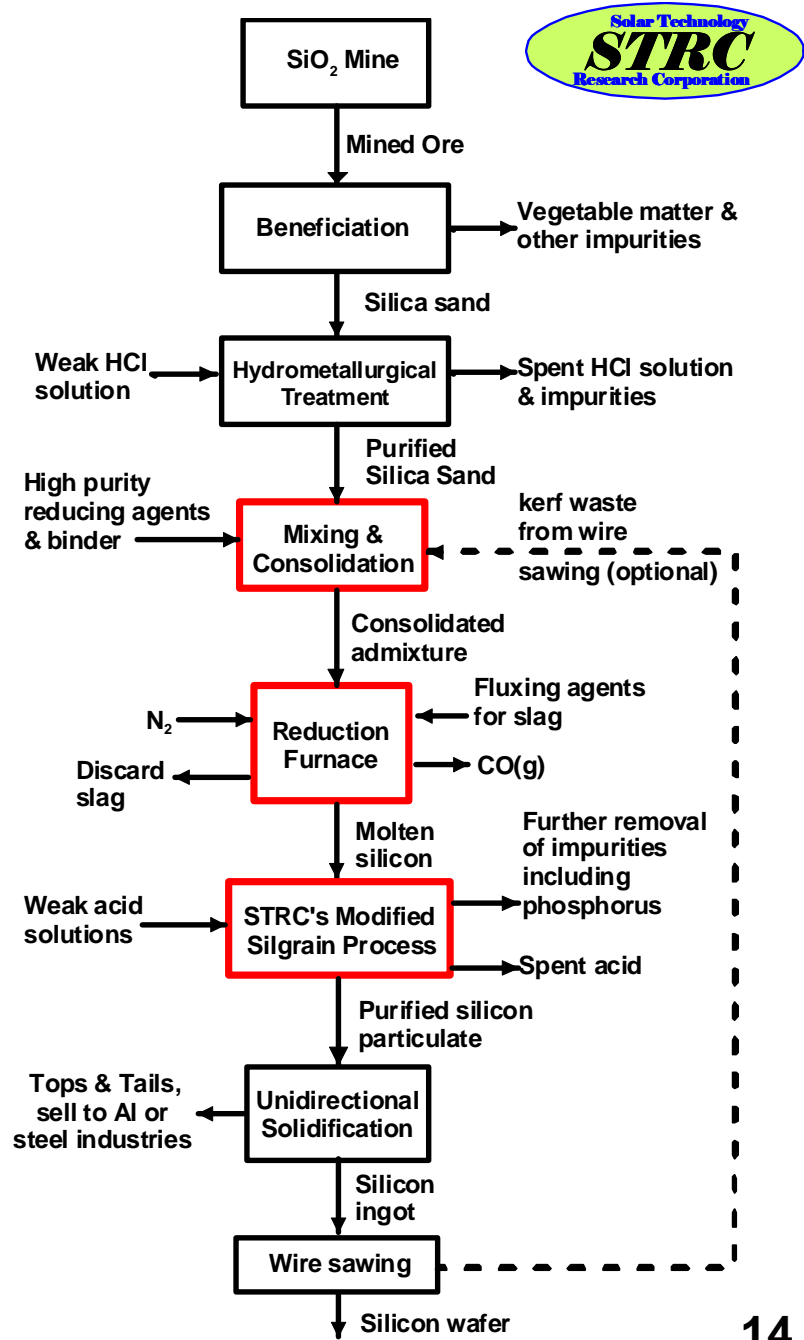


Table II - Concentration of B and P in silica from select suppliers and locations.

Source	B (ppmw)	P (ppmw)
Commercial Suppliers		
Alfa Aesar	247	29
Sigma (sand)	77	29
U.S. Silica	22	228
IO	1	16
Ore Deposits		
A1 (rock)	0.8	0.9
A2 (rock)	0.4	0.3
B1 (sand)	<0.05	<0.5
C1 (sand)	<0.05	26
D1 (sand)	<0.05	<0.5
E1 (sand)	0.8	1.6
F1 (sand)	0.5	0.9
F2 (sand)	0.3	21.3



Process	Unit Cost (\$ per kg Si)			
	Reduction in Silicon Submerged Arc Furnace		Mixing & Consolidation Includes Kerf Waste Reduction in Arc Furnace	
	A Slagging and STRC's Silgrain	B STRC's Silgrain Only	C Slagging and STRC's Silgrain	D STRC's Silgrain Only
STRC Production Cost / kg Si	\$13.59	\$9.21	\$12.60	\$8.22
UDS	6	6	6	6
s-Si Total	\$19.59	\$15.21	\$18.60	\$14.22
\$ per kg Si				
Siemens Production	\$35			
UDS	6			
e-Si Total	\$41			



Starting Data for Mass Balances that Follows

1. Initial B and P content in silica: B <0.05 to 0.5 ppmw, P <0.5 to 0.8 ppmw
2. B & P content of silica after Hydromet. Treatment: B <0.05 to 0.5 ppmw, P <0.5 to 0.7 ppmw
3. B & P content in silicon through reduction of silica with high purity reducing agents: B <0.1 to 1 ppmw, P <1 to 1.4 ppmw
4. Single batch slagging with initial concentration of 0.44 ppmw B and 1.4 ppmw P in the slag
5. STRC's Modified Silgrain Process reduces P content by 90%

Processing Approaches for s-Si (see Table IV for additional processing details for A through D)	B Content in Si (ppmw), max target 0.42 ppmw	P Content in Si prior to UDS (ppmw)	Concentration of P at 1% & 80% Solidification after Single UDS (ppmw), max allowable P 0.40 ppmw	
			1%	80%
A - Slagging and STRC's Silgrain	<0.28 to 0.76	<0.075 to 0.087	<0.026 0.030	<0.064 0.074
B - STRC's Silgrain Only	<0.10 to 1.0	<0.10 to 0.14	<0.035 0.049	<0.085 0.12
C - Slagging and STRC's Silgrain	<0.33 to 0.70	<0.067 to 0.074	<0.023 0.026	<0.057 0.063
D - STRC's Silgrain Only	<0.10 to 1.0	<0.08 to 0.11	<0.028 0.038	<0.068 0.094

STRC's Direct Process: 10 Year Financial Projections

Annual production of s-Si ramps to 11,400 tonnes over 8 years.
 10 year non-production cost, \$162,195,000 (84% in plant construction)
 10 year production cost, \$698,020,000 @ \$13.60 per kg

Sales Price (comments)	\$20/kg	\$30/kg (undercuts production cost of Siemens-Si)	\$40/kg (inferior 5N Si sold during shortage)	\$50/kg (current sale price for 6N Si)
Production (tonnes)	51,325	51,325	51,325	51,325
Sales Value \$(000)	1,026,500	1,539,750	2,053,000	2,566,250
EBITA \$(000)	166,285	679,535	1,192,785	1,706,035

Conclusions

STRC believes that by integrating up stream to include reduction of high purity silica it can satisfy the 3 main requirements PV producers want in solar silicon, namely;

- **Guaranteed, uninterrupted supply**
- **Consistent quality of s-Si requiring little or no manufacturing deviations,**
- **Low price**

The latter can best be achieved by including SiC from kerf waste (from wire sawing of silicon ingots) in processing high purity silica.