Solar Grade Silicon from Agricultural By-products

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Executive Summary

In this project, Mayaterials developed a low cost, low energy and low temperature method of purifying rice hull ash to high purity (5-6Ns) and converting it by carbothermal reduction to solar grade quality silicon (Si_{pv}) using a self-designed and built electric arc furnace (EAF). Outside evaluation of our process by an independent engineering firm confirms that our technology greatly lowers estimated operating expenses (OPEX) to $\approx \$5/\text{kg}$ and capital expenses (CAPEX) to $\approx \$24/\text{kg}$ for Si_{pv} production, which is well below best-in-class plants using a Siemens process approach to a similar quality product (OPEX of $\approx \$14/\text{kg}$ and CAPEX of $\approx \$87/\text{kg}$, respectively).

The primary limiting factor in the widespread use of photovoltaic (PV) cells is the high cost of manufacturing, compared to more traditional sources. This is mostly due to their high materials costs. It is estimated that 45% of the cost of a traditional solar panel comes from the silicon used. In terms of cost, the best wafering technologies offer the potential to reach $\approx 6 \text{ g Si}_{\text{pv}}/\text{watt}$ (with averages closer to 8^+ g/watt). These Si_{pv} requirements may drop to $< 1 \text{ g/watt}$ if kerfless technologies prove successful and financeable.

In 2008, the spot price of Si_{pv} rose to $\$450/\text{kg}$. While prices have since dropped to a more reasonable $\$25/\text{kg}$; this low price level is not sustainable, meaning the longer-term price will likely return to prestressed levels, estimated by several analysts to be $\approx \$35/\text{kg}$. The 6-8 g Si/watt reported for various wafering technologies implies that the Si_{pv} used in a module will cost $\$0.21\text{--}0.28/\text{watt}$ for the best producers, a major improvement from the cost/wafer driven by the $\$50/\text{kg}$ Si costs of early 2011, but still a major hindrance in fulfilling DOE goal of lowering the cost of solar energy below $\$1/\text{watt}$.

While certain manufacturers have decreased the amount of Si_{pv} they use in their cells (Suntech, Sunpower, Evergreen Solar) manufacturers are still susceptible to fluctuations in the Si_{pv} market. Because the solar cell industry has grown by 40% yearly for the past eight years and is estimated to grow even faster in the future, the demand for Si_{pv} is expected to follow suit. As such, future solar silicon price spikes are expected in the next few years. Although industry has invested billions of dollars to meet this ever-increasing demand, the technology to produce Si_{pv} remains largely unchanged requiring the energy intensive, and chlorine dependent Siemens process or variations thereof. Another detrimental aspect of current Si_{pv} production is the amount of energy required to purify the silicon using the Siemens process or more energy friendly industrial processes (such as fluidized bed technology). While huge improvements have been made, current state-of-the-art industrial plant still use 65 kWh/kg of silicon purified.

Although many technologies are under development to reduce the $\text{Si}_{\text{pv}}/\text{watt}$ cost, our technology offers a key distinction as it starts one step upstream from all other Si_{pv} production efforts. Our process starts by producing high purity SiO_2/C feedstocks from which Si_{pv} can be produced in a single, chlorine free, final EAF step. This distinction is also important as it allows rapid deployment our technology at industrial scales. Specifically, our unique technology, and the resultant SiO_2/C product can serve as high purity feedstocks to *existing* metallurgical silicon (Si_{met}) producers, allowing them to generate Si_{pv} with *existing* US manufacturing infrastructure, reducing the overall capital and commissioning schedule.

Our low energy, low CAPEX and OPEX process purifies the silica and carbon present in rice hull ash (RHA) at low temperatures ($< 200^\circ\text{C}$) to produce high purity (5-6 Ns) feedstock for production of Si_{pv} using furnaces similar to those used to produce Si_{met} . During the course of this project we partnered with Wadham Energy LP (Wadham), who burns 220k ton of rice hulls (RH)/yr generating 200 GWh of electricity/yr and $>30\text{k ton/yr}$ RHA. The power generation step produces much more energy (42 kWh/kg of final silicon produced) than required to purify the RHA (5 kWh/kg of Si_{pv} , compared to 65 kWh/kg noted above).

Furthermore, our process is clearly carbon negative because the emissions from electricity generated equal the rice plant's original carbon uptake while the generation displaces conventionally fueled generation as well as the methane produced by the natural decomposition of RH. Converting the economics of ash handling from a cost to a value could expand biomass power generation in the US, expanding the displacement of fossil fueled generation. Biogenic silica offers three very important foundations for producing high purity silicon. First, wastes from silica accumulating plants, such as rice, corn, many grasses, algae and grains, contain very reactive, amorphous silica from which impurities (mostly alkali and alka-

line earths) are easily removed. Second, plants take up only a limited set of, and minimal quantities of the heavy metals present in nature, meaning fewer minerals must be removed. Third, biomass combustion generates a product with intrinsic residual carbon, mixed at nanometer length scales with the SiO_2 . RHA is 80-90 wt% high surface area ($20 \text{ m}^2/\text{g}$), amorphous SiO_2 with some simple mineral content mixed intimately with 5-15 wt% carbon. The mineral content is easily removed by low cost, acid washes using Materials IP, leading to purified rice hull ash ($\text{RHA}_{\text{clean}}$) at up to 6N purity.

This highly reactive silica is partially extracted from $\text{RHA}_{\text{clean}}$ at $\leq 200^\circ\text{C}$ in an environmentally benign process to adjust $\text{SiO}_2:\text{C}$ ratios to those needed in EAF processing to Si_{pv} . EAF processing with silica depleted rice hull ash (RHA_{SD}), with nanometer scale carbon/silica mixing, reacts up to 10x faster than in traditional EAF processing because the physical distances over which the reactions occur are measured in nm's vs cm's.

This drives another very critical component of the process described above, a simpler path to commercialization and financing. We have focused on demonstrating the efficiency in existing furnace technologies, meaning our success offers the potential to convert some portion of existing US furnace infrastructure (for Si_{met}) to high purity silicon production. The key would be merely switching from quartz and purchased carbon feedstocks to $\text{RHA}_{\text{clean}}$ or RHA_{SD} .

The linkage of our process to the existing infrastructure of the U.S. silicon manufacturing industry, already a world leader, is unique compared to all other initiatives trying to produce Si_{pv} . Purifying the silica/carbon mixture before EAF conversion to Si_{pv} greatly reduces CAPEX and OPEX costs, reducing the final solar energy cost by \$0.18-0.24/watt.

As part of this project, the following was achieved: (1) RHA purification was optimized (to $> 5\text{Ns}$ purity) and scaled to 20 kg batches. (2) The conversion kinetics whereby $\text{RHA}_{\text{clean}}$ is transformed into silicon were thoroughly investigated allowing production of 6Ns pure Si per Table 1 which compares $\text{RHA}_{\text{clean}}$ with EAF derived Si and the SEMI target for Si_{pv} .

Table 1. Comparison of purities of $\text{RHA}_{\text{clean}}$, EAF derived Si and SEMI III standard purities.

ppm (w)	$\text{RHA}_{\text{clean}}$	Si_{EAF}	SEMI III
Al	0.1	0.1	0.3
B	0.2	0.1	0.1
P	0.02	0.02	0.05
As	0	0	0.1
Sb	0	0	0.2
Ti	0	0	0.7
Cr	0	0	0.2
Fe	0.08	0.1	0.2
Ni	0	0	0.2
Cu	0	0	0.2
Zn	0	0	0.2
Mo	0	0	0.3
Na	1	0.1	0.1
K	4	0.1	0.1
Ca	1	0.1	0.1
N's	5	6	5

To undertake the kinetic studies, we had to design and build our own 50 kW EAF furnace as there are no examples of such small EAF furnaces used for silicon smelting in the open literature. This provided us with needed experience for further scaling. At the end of these studies we are able to produce as much as $>400 \text{ g}$ of silicon/batch. (3) Alternate conversion technologies were also investigated, namely plasma conversion of biogenic silica into silanes and microwave carbothermal reduction. But neither technology was scalable and efficient. (4) Economic models of this process were developed jointly with Wadham, who has partnered with us to develop this project to a full production facility.

1.0 Introduction.

The impetus for the work conducted here derives from a 1980 Exxon/Mobil Patent and several publications thereafter by Amick et al targeting the use of rice hulls (RHs) as a starting point for the direct production of photovoltaic grade polysilicon, Si_{pv} , via reaction (1) below.¹⁻⁷ The motivation for using RH and in our work, rice hull ash (RHA), comes from the fact that all plants (to some extent) extract SiO_2 from the soil. In particular, grasses including rice, wheat, oats and barley have high concentrations of SiO_2 in their hulls, husks or stalks.⁸⁻¹¹ For example rice hulls, removed at centralized rice milling plants, contain 15-20 wt% amorphous SiO_2 . In the U.S., rice production runs to multi-million ton/yr quantities. The hulls are frequently burned as a biomass fuel or simply to reduce their volume for disposal. The resulting RHA contains 65-95% amorphous, high surface area SiO_2 with the remainder being amorphous, high surface area carbon and some minerals. The plant pre-purifies the SiO_2 through selective uptake greatly reducing the various contaminants typically found in SiO_2 sources. Consequently, RHs and RHA are much purer than feedstock C and SiO_2 sources used to make metallurgical grade silicon, Si_{met} .² The traditional reactions involved in the production of Si_{pv} or electronics grade Si_{eg} are:²

The work of Amick et al strongly suggests the potential to escape the chlorosilane processing steps (Siemens Process) and rely solely on reaction (1) because one can pretreat the RH (RHA) to reduce impurity contents to those acceptable for Si_{pv} . If proven correct, the cost savings in terms of capital equipment, fewer processing steps, energy consumption and the need to implement strict environmental containment for chlorosilane intermediates would be enormous.

Mayaterials choice of RHA rather than RH is motivated by eight key factors:

1. Mayaterials has long experience extracting SiO_2 from RHA as OA, the starting material for our core silica cage business, Scheme 1.¹²⁻¹⁴ We have developed detailed methods of extracting most of the SiO_2 out of RHA at low temperatures ($\approx 100^\circ\text{C}$) with short processing times, 5-7 h at 0.5-1 kg quantities.
2. Mayaterials also developed routes to high surface area ($> 400 \text{ m}^2/\text{g}$), precipitated (ppt) SiO_2 for reaction (1), coincident with recycling all chemical extraction intermediates.
3. The impurities in RHA are mostly alkali and alkaline earth salts that are easily removed using Mayaterials acid washing IP, allowing easy purification.
4. RHA can be compacted to densities $\geq 0.5 \text{ g/cc}$ whereas RHs offer compact densities $\leq 0.2 \text{ g/cc}$ requiring much higher throughput volumes leading to lower production rates, greater energy losses, and larger furnaces for equivalent production rates.
5. The Amick process employs a second high temperature (900°C) oxidation to reduce the RH carbon content to the desired $\text{SiO}_2:\text{C}$ ratio of $\approx 1:2$. In contrast, Mayaterials RHA process steps actually extracts SiO_2 to adjust ratios but at $\approx 100^\circ\text{C}$ and only the last step, reaction (1), is high temperature.
6. The production of RHA produces more energy than the purification of silica and its conversion to Si requires, making the process energy and carbon negative, as noted above.
7. The isolation and purification of the intermediate OA in large quantities also provides other potential products for Mayaterials ranging from high purity ppt silicas, to colloidal silica for nanocomposite applications, to mesoporous and mesoscopic silicas, etc.
8. The byproduct, high surface area C also offers new markets for filtration/purification media, catalyst supports and also for novel insulation products (cores for vacuum insulation panels).

faces. Water washes after milling remove re-adsorbed species, often comparable to the amount initially removed by milling. A single cycle of acid milling and water wash, removes >90% of the impurities. Also any phosphorous present in the RHA is completely removed at this point (below detectable limits). One or two additional cycles of acid milling/water washes allows purification to 4Ns purity.

Further purification (in particular removal of iron impurities) is done by heating RHA in boiling acid (3.7-37 wt % HCl for 0.25-24 h). As described above, because the RHA re-adsorbs ions, a longer washing duration does not increase the amounts of impurities removed. Thus, a boiling water wash is required to make acid treatment effective and shorter (0.5-2 h) times are more efficient.

From this cleaned RHA ($\text{RHA}_{\text{clean}}$), we have developed several precursors/path to silicon: (1) The $\text{RHA}_{\text{clean}}$ can simply be carbothermally reduced in an EAF by mixing it with either relatively inexpensive carbon black or graphite. (2) The silica can be extracted from the RHA in the form of octaanion, re-precipitated and then combined with carbon black/graphite or recombined with residual carbon from the silica extraction reaction, before carbothermal reduction to silicon. (3) A controlled amount of silica can be extracted from $\text{RHA}_{\text{clean}}$ using the previous approach. This RHA with lower silica content (SD or RHA_{SD}) can then be used as the sole precursor to silicon during the carbothermal reduction.

For Paths 2 and 3, the amorphous silica in the purified RHA is then extracted by reaction with a tetralkyl ammonium hydroxide in boiling alcohol to adjust the C:SiO₂ ratio. The amount of silica extracted is temperature/time dependant, allowing us to adjust the silica contents remaining in the RHA (up to 82 wt % remaining SiO₂ in the RHA after extraction in ethanol, down to 10% remaining SiO₂ after extraction in butanol). It should be noted that silica extracted RHA is very porous with high specific surface areas (SSAs) $\geq 200 \text{ m}^2/\text{g}$. The silica, extracted as the octaanion, $[(\text{OSiO}_{1.5})_8]$, **OA** can be further purified by recrystallization to 99.9996% purity.¹⁵

RHA_{SD} production has now been scaled to 20⁺kg/40 h using 2 in-house built 100 L reactors, Figure 2.

Figure 1. Pre-pilot scale processing and recovery of RHA_{SD} . (EAF discussed below)

The OA is then reacted with dilute acid to generate silica nanopowders with SSAs= 150-700 m^2/g with pore volumes of 0.8-1.3 cc/g and average pore sizes of 8-30 nm. Note that the precipitated silica produced from RHA is in itself a valuable product explained in detail in the economic model below.

Note that another proprietary extraction process has been developed that greatly reduces the cost of this step and especially the recycle costs. This information is available via non-disclosure agreements. Similar properties are observed for the as produced ppt SiO₂.

The feedstocks to either of the three paths are then pelletized and placed in the EAF for carbothermal reduction. Initial studies used a tabletop EAF, with 20-50 g loads of the RHA_{SD} pellets. We gradually increased the size of the EAF to better understand the kinetics involved and currently use an in-house built 50 kW EAF to batch process 10 kg pellet loads (See Figure 2).

Larger quantities have been assessed by adding secondary amounts of pelletized RHA_{SD}. Our EAF design is based on the single top electrode, DC EAF designed by DOW chemicals for industrial scale.^{2,16,17} At this scale we have been able to produce 5Ns purity Si (see Table 1 above), in batches of 200-400 g. Note that by varying the process parameters we are also able to produce large quantities of sub-micron particle, high purity (4Ns), green SiC instead of silicon if desired.

2. Feedstock purification and processing

Scheme 2. Initial concept process flow sheet for production of Si_{pv} from RHA.

Several different RHA sources were assessed including:

1. Thailand with either 6.2 wt% or 2.5% carbon content.
2. Arkansas (Riceland Inc.) made via two processes (one conventionally, the second one used to generate steam) with C contents of 18.6 and 34.4 wt% respectively.
3. Mississippi (from Uncle Ben's)
4. California (from Wadham Energy)

They are designated RHA-T, RHA-HS, RHA-C, RHA-Ar, RHA-U, RHA-W in this report.

2.1 RHA purification.

Research has shown that rice hulls can contain many impurities whose individual concentrations depend on the rice species and the soil it grows in.^{8,21,23,26,27} RH combustion conditions also change the concentrations of various impurities as seen in Table 2a (comparing RHA made in lab glassware to RHA made in an industrial furnace). As the purity of the RHA will determine the purity of the feedstock and Si_{pv} it is essential to lower the amount of impurities which lower the efficiency of solar cells (Table 2b).

Table 2 a. Rice hulls and RHA made under different conditions.⁴⁻⁷

(in ppm)	Hulls *	RHA made under lab conditions**	Commercial RHA***
Al	10	50	1300
B	2**	10	Non-reported
Ca	1000	>1000	4500
Fe	20	200	1000
K	3800**	>1000	27000
Na	25**	10	Non-reported

*Processed by Amick et al.

** Hull impurity levels reported by Amick et al contradict recent analyses of rice plants. In particular B (higher in japonica than in indica hulls with up to 1500 ppm reported in certain japonica cultivar), K (> 10000 ppm reported), Na (> 2000 ppm reported).^{18,19}

***Example of RHA processed by Wadham energy

Table 2b. Effects of impurities on solar cell performance.¹

	(Unit : mass ppm)						
	B	P	Fe	Al	Ti	C	O
Industrial metallic Si	5-10	25-30	1000-1500	600-800	150-200	150-200	—
Remelting Si for solar cells	0.1-0.3	<0.1	<0.1	<0.1	<0.1	<5	<6
Substrate Si for solar cells	0.1-0.3	<0.1	<0.007	<0.06	<4×10 ⁻⁵	<3	<4

2.1.1 Milling

Initially to homogenize particle size, RHA was milled with zirconia milling media in up to 20 kg batches. Figure 2 shows SEMs done of selected samples showing the difference in particle size: even with low energy milling, particle size can be decreased below 1 micron. Milling extracts significant amounts of impurities per Table 3 and Figure 3.

Figure 2. SEMs of RHA-C after milling a. after 1 d, b. after 3 d.

Table 3. Impurities removed from RHA-Ar vs milling conditions.¹⁵

in ppm	1 D, water	3 D, acid
Cu	0.076	0.22
B	0.152	1.868
Fe	0.056	49
Cr	0.088	0.188
Mg	57	207
Ti	0.064	0.38
Al	0.26	23
Na	47	75
K	1790	3671

As milling is required for all paths to RHA feedstocks, it was the first step to be scaled per Figure 4.

Standard laboratory filtration techniques cannot be used to process large quantities of slurries. Thus, a pilot scale filter press was designed and built to order per Figure 5. This press allows filtration of 15 kg of RHA in less than 30 min.

Figure 3. Selected impurities removed via 5 milling methods leading to an optimized process.¹⁵

Figure 4. Low speed mill with initial milling jar (right) vs current 25 L jar (left).

Figure 5. Adjustable volume filter press.

2.1.2 Acid leaching¹⁵

Our initial idea for purifying RHA consisted of secondary acid leaching steps. Figure 6 shows efforts to optimize impurity removal via leaching.

Figure 6. Impurities (ppm) extracted in RHA-W assessing various methods, by analysis of leachates. Maxima show how much could be removed in theory (based on analysis of the RHA).

2.2. Silica extraction

Extraction of silica from RHA in the form of OA is part of Mayaterials' core business, allowing the synthesis of a wide range of specialty chemicals, Scheme 1. In this work, we refined our proprietary process to produce RHA_{SD} adjusting SiO₂:C contents and precipitated silica. In addition to serving as feedstock for two of our three approaches to Si_pv and SiC production, these highly pure feedstocks offer commercial utility by themselves; for example, high purity, high surface area ppt silica could be used for silicon wafers polishing. It is also perfect as food grade silica among other uses mentioned above.

2.2.1 Silica extraction.

For Paths 2 and 3, silica is extracted from RHA, either to adjust the RHA to the desired $\text{SiO}_2\text{:C}$ ratio for carbothermal reduction (Path 3) or to separate the SiO_2 from the C coincident with further purification and thereafter recombining them in desired ratios. These studies were run using our proprietary SiO_2 extraction technique (for Path 2).

RHA_{SD} is quite porous as shown in Figure 7 as confirmed by BET analysis showing a specific surface area of $220 \text{ m}^2/\text{g}$. Table 4 provides an example of intermediate purities before silica extraction. Following silica extraction, typical purities are those shown in Table 5.

Figure 6. SEM of RHA-C after silica extraction.

Table 4. Impurities present in RHA after milling.¹⁵

RHA	milled	B	Fe	Ti	Cu	K	Na	Other	Purity
T	1 d, water	10.8	23	3.3	0.3	120	100	38.6	99.970%
C	1 d, water	9.0	37	6.0	4.3	78.4	149	40.0	99.967%
C	3 d, water	3.2	25	3.2	0.4	5.1	9.2	28.8	99.992%

Table 5. Impurities in final wash solution.

Elements	Al	B	Ca	Cu	Fe	K	Mg	Na
Ppm in solution	0	1.26	21.2	0	0	37.5	3.43	2.17

Optimization of the production of RHA_{SD} required that we design, construct and optimize operation this process and was an essential part of our work for Q2-Q4 2011. Figure 1, shows that we have scaled to 20-30 kg/48 h for this process using two 100 l reactors. The next step will be to scale to a single stirred reactor capable of producing 50-75 kg of RHA_{SD} in approximately the same time period.

2.2.2 OA purification and SiO_2 synthesis

The main advantage to using OA as a silica precursor is that a recrystallization process we developed during this project permits easy purification of OA. Table 6 provides a few examples.

Table 6. Examples of OA produced from RHA compared to our commercial OA made from high purity silica source. Commercial OA is made from $\text{Si}(\text{OEt})_4$.

Samples	B	Fe	Ti	Cu	K	Other*	Purity
Commercial OA	0.4	0.5	<0.002	<0.003	<0.002	1.0	99.9998%
Ar	0.2	0.08	<0.002	<0.003	2	1.8	99.9996%
T	0.1	0.2	0.8	0.4	5	1.0	99.9992%
T-self-ppt	0.7	3.4	<0.002	<0.003	75	2.8	99.9918%
T-2	0.3	7.7	<0.002	<0.003	1.2	1.8	99.9989%
C-2	0.4	11	<0.002	<0.003	2.9	0.96	99.9985%
W	0.2	<0.1	<0.002	<0.003	0.05	9.0	99.9990%

*Other impurities detected include Al, Ca, Cr and Mg.

Acidification of OA solution forms silica nanoparticles and regenerates the organic base intermediate used during extraction (recycled with NaOH). The resulting silica offers quite high surface areas (500-700 m²/g) per Figure 7; although these can be manipulated by controlling the precipitation rates and aging conditions.

Figure 7. SEM of precipitated silica nanoparticles obtained from RHA.

2.3 Assessment of RHA sources and purification process

The first subtask originally planned for purification of RHA involved assessing various sources of RHA and determine final impurity level as a function of the RHA sources. The second subtask consisted of studying the elimination of these impurities as a function of the purification process. During these studies we assessed the impurity contents and reactions for individual steps in the purification process as a function of rice cultivar, origin and combustion conditions, see example in Table 7.

Table 7. Impurities removed by milling vs RHA source (milling solution after 3 d).

(ppm)	RHA-Ar	RHA-T	RHA-W
Al	23.7	143	38.9
Ca	21.2	21.2	200
Fe	49.3	64.5	27.5
K	3671	2004	1349
Mg	208	123	88.5
Na	75.3	56.0	48.9

3. Production of Si and SiC

As discussed above, three Paths to Si_{pv} were explored: (1) RHA_{clean} was carbothermally reduced in an EAF by mixing with either inexpensive carbon black or graphite; (2) Silica extracted from RHA_{clean}, was reconstituted as a fine silica precipitate and combined with carbon black/graphite or recombined with residual carbon from the silica extraction process and then EAF processed; (3) RHA_{SD} produced as discussed above serves as the sole precursor.

All approaches further differ from actual industrial silicon production because we use particles several orders of magnitude smaller than the industrial processes. This was expected to greatly reduce reaction times and therefore throughput as confirmed with Paths 1 and 3. It is also expected to significantly reduce the energy required to produce silicon. The rates of the solid-state reactions are dictated by solid-state diffusion rates and distances. The time to complete reaction is controlled solely by the distance species in the largest particles must travel (diffuse) to reach the reaction zone (typically at the particle surface). Hence the larger the biggest particles are, the longer time it takes to get complete reaction. The following empirical formula can be used as a guide to predict reaction times for solid-state reactions.¹⁶

$$[1 + (z-1)x]^{\frac{2}{3}} + (z-1)(1-x)^{\frac{2}{3}} = z + 2(1-z)\frac{Kt}{r_A^2}$$

It describes the time required for reactant A particles of radius r_A and mole fraction x , to react given a global rate constant K_t for reaction, where z is the unit volume of product formed from a unit volume of A. The latter accounts for changes in density. This formula is a relatively crude method of predicting solid-state reaction times because it does not consider phase changes, or impurities in primary particles, or aggregates. However, it predicts that reaction times in our two approaches will be shorter than industrial processes *due to the orders of magnitude* differences in particle sizes.

On an industrial scale, two different EAF processes can be used to produce Si_{mg} : either a triple electrodes or dual electrode process. In the more common triple electrode process, three graphite rods are lowered into the chamber and an arc is produced between these three electrodes by a triple-phase electric current. In the dual electrode process (DOW process) a single graphite rod is lowered into the chamber whose bottom constitutes the second electrode. An arc is generated between the rod and the chamber by either a single-phase current or a direct current.

The approach we currently use adapts the DOW process to our small scale. We have scaled this process several times from our initial batches using 7 g of feedstock to up to 10 kg/batch. In this process, our current EAF consists of a graphite chamber (25 cm ID x 25 cm high) enclosed in refractory bricks. These are illustrated in Figures 8 and 9.

While using the larger diameter chambers, one problem encountered was that refractory bricks no longer provide sufficient insulation. As a result heat loss is too great (lowering the potential temperature achieved) and the bricks themselves deteriorate easily. At larger scale, 1 cm x 1 cm alumina cylinders packed with zirconia powder provides almost air-tight insulation. The chamber itself is one of the electrodes with a moving graphite rod serving as the second electrode. See Figure 9. Original experiments were done using a 5600 W arc generator, which was later replaced with a 9000 W (15 kW input) generator, then a 50 kW generator.

The last two generators allowed electronic regulation of the voltage and amperage of the arc, allowing the arc current to be relatively constant. This provided the basis for optimization of the EAF process.

Figure 8. Base of the EAF.

It is important to note that there are very few recent publications dealing with EAF processing and the keys to optimization had to be developed in-house as our feedstock materials do not fit any previous studies including those of Amick et al.

For example, the main difficulty noted in the literature was a change in reaction paths in the carbothermal reduction at lab scales compared to industrial scales. Theoretical work by Claveau, Bourrie, and others,²⁴⁻²⁶ indicates that direct formation of silicon from silica and carbon has a very low yield and requires much higher temperatures than observed in the industrial process.

Figure 9. Inside of the graphite crucible.

A minimum temperature of 2045°C is required for any Si to be produced, with optimal temperatures being 2200°C. Even at this temperature the yield (6%) is much lower than that observed on industrial scale (70 %). On an industrial scale, SiO_g condenses on the cold top of the reactor and falls back into the furnace to eventually form Si. The reaction of SiO_g forming Si requires only 1900°C to be optimal on an industrial scale.

On a small scale, insufficient time and the absence of a temperature difference inside the reactor prevents condensation of the SiO_g formed and it escapes the reactor leading to the much lower yields. Studies by Bourrie confirm the differences at very small scales: while direct reaction between silica and carbon did not produce Si, reaction between SiO and SiC could produce Si (even at temperatures as low as 1700°C). Therefore to increase the amount of Si produced, Two paths are possible. The first option we tried is to condense and collect the SiO produced and produce Si from it. The advantage of this option is practicality and scalability: while the design is ancient, it works with good yields from mg scale to ton quantities. The second option we tried is to scale by several orders of magnitude, similar to the silicon arc-reactor used by the National Energy Technology Laboratory (NETL), which can produce kg quantities of Si. Conversation with NETL indicated that while their silicon arc-reactor does produce kg of Si, even when using fine powders as silica and carbon source, the reactions take ≈ 72 h to go to completion and 24 h for a significant amount of Si to form. Both options were tried as described below.

3.1 EAF processing studies-SiC.

EAF process studies began with an examination of several types of feed. First, loose or slightly compacted powders were charged into the graphite chamber. These initial experiments showed difficulties unique to the unusually small particle sizes we use.

First, the pressure generated by the electric arc was too great. Lightly compacted powders did not allow sufficient movement of the gases created by the EAF process. Furthermore, the compacted RHA acts as a thermal insulator reducing heat transport. From these experiments we also learned that arc intensity was essential in determining the yield from carbothermal reduction. SiO_g is an essential intermediate formed during the reduction, too high an arc generates SiO_g at too great a rate causing it to exit the system before it can be further reduced to Si or SiC. The SiO_g ends up depositing as a white solid above the zone of the arc. Too low an arc intensity results in the whole chamber being too cold and the system not generating enough SiO_g , and so no Si/SiC is generated. Contrary to the reactions producing Si described above, SiC is easily produced at our laboratory scale. The required temperature is also much lower (1530°C). We found that current in the 60-95 Amps were required for the reactions to proceed, with 75-85Amps being optimal when using a 12.7 mm diameter graphite electrode.

The SiC produced consists of very fine, 1 μm average particle sizes, shown in Figure 10. X-ray powder diffraction analysis, XRD of these powders shows that they are pure SiC with traces of cristobalite, Figure 11. Purity depends on the type of RHA used as might be expected.

Figure 10. SEM of SiC powder from RHA powder.

Figure 11. XRD analysis showing SiC with a trace of cristobalite ($21^\circ 2\theta$).

Our estimated processing costs for these fine SiC powders at 4-5 Ns purity should also be in the \$5-7/kg range. We anticipate accessing several markets where these materials could be used as high-end abrasives (polishing agents) for pressure blasting, lapping, grinding, polishing high purity ceramics or for sintering high end SiC parts.^{2,20} They may also serve as a source material for photovoltaics.²⁰⁻²³

3.2 EAF processing studies-Si.

While the production of SiC using our setup was relatively easy to optimize at a small laboratory scale, production of Si was complicated due to the slower reaction kinetics of Si formation and the complex mechanism by which Si forms in an arc furnace.

The silicon obtained in earlier experiments was 4Ns pure (Table 9), which is encouraging as these experiments were done without high purity RHA. Later experiments with purified RHA resulted in 5Ns purity silicon. The primary impurities in these materials were Fe, Ca and Al.

Table 8. Comparison of impurities (in ppm) in Si metal formed with non-purified RHA or with purified RHA.

(ppm)	Al	B	Ca	Cu	Fe	K	Mg	Na	Ti	Purity
Not cleaned RHA	1	7.2	15	<0.3	0.4	<2	<1	<0.3	<1	99.997%
RHA _{clean}	1.2	0.09	1.4	0	1.84	0.7	0.1	0.04	<0.1	99.9994%
Goal for feedstock	<0.1	<0.3			<0.1				<0.1	

The National Energy Technology Laboratory (NETL) has a pilot plant EAF that is large enough so that carbothermal reduction occurs in a two zone system, as described above. After multiple iterations and after discussions with NETL personnel, we decided to build a DOW EAF with dimensions small enough to operate in our laboratory, as seen in Figure 10. While this version was anticipated to be too small to obtain silicon recovery rates seen on industrial scale (80+%), this would allow us to obtain a significant amount of silicon.

Figure 12. EAFv5.2 in operation.

The NETL system as noted above, needs to be operated for an extended period to obtain silicon; 24 h was the targeted duration for our system. For practical reasons, there are several differences: the main one being that the NETL model is designed to be tilted to pour the molten silicon in another crucible. With our installation (and contrary to what we will do at even bigger scale) we considered it safer to let the molten silicon cool down in the initial graphite crucible and break it out of the crucible when cold. In the near future we expect to make sufficient quantities to supply to a refiner for the production of ingots and/or boules.

At this point, we can process up to 10 kg in a single batch and much to our surprise, rather than having to operate it at 24 h or even 72 h as is done in the NETL furnace, 5-10 kg batches are completely consumed in 6 h because of the much finer scale of mixing. Furthermore, we are able to get 200-400 g of silicon in 6 h, which typically represents a 30 % yield as opposed the 6% expected based on the above discussions and the literature.²⁴⁻²⁶ In operation the EAF looks as seen in Figure 10. Table 1 is reproduced below to indicate the current state of purity of our materials.

Table 1. Metal purity of silicon made using EAFv5.6

Ppm (w)	RHA _{clean}	Si _{EAF}	SEMI III ²⁷
Al	0.1	0.1	0.3
B	0.2	0.1	0.1
P	0.02	0.02	0.05
As	0	0	0.1
Sb	0	0	0.2
Ti	0	0	0.7
Cr	0	0	0.2
Fe	0.08	0.1	0.2
Ni	0	0	0.2
Cu	0	0	0.2
Zn	0	0	0.2
Mo	0	0	0.3
Na	1	0.1	0.1
K	4	0.1	0.1
Ca	1	0.1	0.1
N's	5	6	5

4. Economic Assessment

As noted above, we have now teamed with Wadham Energy to help develop our project to an industrial scale. Wadham has engaged an outside process engineering firm to assess design considerations for scale up and to work with Wadham to develop initial estimates of OPEX and CAPEX costs for a commercial facility based on this technology. Figure 13 provides an estimate of the OPEX for our process compared to a best-in-class Siemens trichlorosilane process. Likewise, Figure 14 compares the CAPEX for our process versus the top five conventional processes in operation today.

* Best in class plant (6,500MT) , developed country; Source: GTM Research, "Polysilicon 2012-2016: Supply, Demand & Implications for the PV Industry," Jan. 2012

Figure 13. Comparison of OPEX/Variable Cost Comparison for a Siemen's based process vs. a Mayate-rials based process.

Figure 14. Comparison of CAPEX per current Si_{pv} production processes vs. a Mayaterials based process.

As shown here, the Mayaterials-based Si_{pv} process appears to offer the potential to greatly reduce the overall costs for production of Si_{pv} when scaled to a commercial facility. In addition, the production of Si_{pv} with this process presents clear life cycle advantages from a renewable, carbon-negative source. Finally, there are also side products, e.g. low-cost, high purity precipitated silica, which could provide additional economic benefits to the commercialization of this process.

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