ENGINEERED METALLURGICAL SILICON (EMS) - AN ALTERNATIVE TO MECHANICALLY MILLED SILICON AND A METHOD TO RECYCLE WASTES

Frank A. Weber, Louis Parous, Valdiney Domingos de Oliveira

e-mails: frank.weber@viridis-iq.de; lou.parous@viridis-iq.de; valdiney.domingos@viridis-iq.de;
Viridis.iQ GmbH – www.viridis-iq.de

ABSTRACT

The EMS-process used by viridis.iQ GmbH is an inert gas granulation process, which supplies Metallurgical Silicon in form of a tailored homogeneous powder. The process can also be used to recycle some unusable forms of silicon wastes into a uniform feedstock material for direct feeding into Trichlorosilane (TCS) synthesis or, in some cases, for direct casting into multicrystaline ingots. Not only is the macro structure a uniform quasi spherical shape with a very narrow size distribution but also on the micro scale, the beads are quite uniform in regard to structure (grain density) and composition (low segregation effects). This method furthermore open possibilities in doping and surface engineering of the particles which are not accessible with classic milled material or other methods for micro particles.

KEYWORDS: *EMS, milled silicon, catalyst, granulation, MCS and TCS process.*

1. INTRODUCTION

Milling is common process in the silicon industry as all polysilicon producers need the material in a fine grain form for charging into the TCS Fluidized Bed Reactor or Methylchlorosilane Process.

At this point the chemistry of the material is not so important so long as it meets certain internationally recognized specifications such:

- 2202 (0,2%Fe, 0,2%Al, 0,02%Ca) or;
- 3303 (0,3%Fe, 0,3%Al , 0.03%Ca) which are basically produced for chemical and photovoltaic purposes or;
- 441 (0,4%Fe, 0,4%Al, 0,1%Ca) and 553 (0,5%Fe, 0,5%Al, 0,3%Ca) grades normally for use in the alloying of aluminium.

2. MILLING

In the standard metallurgical silicon process, the liquid silicon, leaving the smelting furnace at 1550 °C, is cast into iron moulds, typically lined with highly contaminated silicon fines from milling operations [3].

To protect the mould, as well as to save money, a layer of these fines is placed inside the mould. If the production process quality oriented, the used fines are of the same quality as the molten silicon, but this is rarely the case and there is almost no quality control on the level of the silicon fines [5].

If the process is only geared toward lowest costs, all kind of material is also added, such as sweepings from the production area. But even in the best case, this material melts only partially and gives poor grain structures in the bottom of the solidified block, not to mention a high and varying amount of metals content.

During the solidification process, the growing grains push out impurities, which then end up in the impurity rich inner grain boundaries [2]. The cooling rate at the position of the considered grain has a large impact on its growth rate. Therefore depending on the location of any particular grain in the regarded volume, large variations in grain size and impurity content, as well as impurity composition are possible. The large ingot is then broken and battered with heavy iron tools to break it into smaller pieces, usually on a concrete or metal floor until the pieces are small enough to move to a mechanical, iron rich, grinding system.

In this system the friable nature of the material tends to cause fracturing along the grain boundaries first and a tendency toward the generation of small grain particles [2] and dust that are relational to the variability of the grain distribution.

These smaller grains have high surface area and generally are high in the impurity content that segregated to the grain boundary as the last liquid silicon cooled.

The result is that a large portion of the material is pulverized into highly variable dust particles that cannot be used except for certain low value applications.

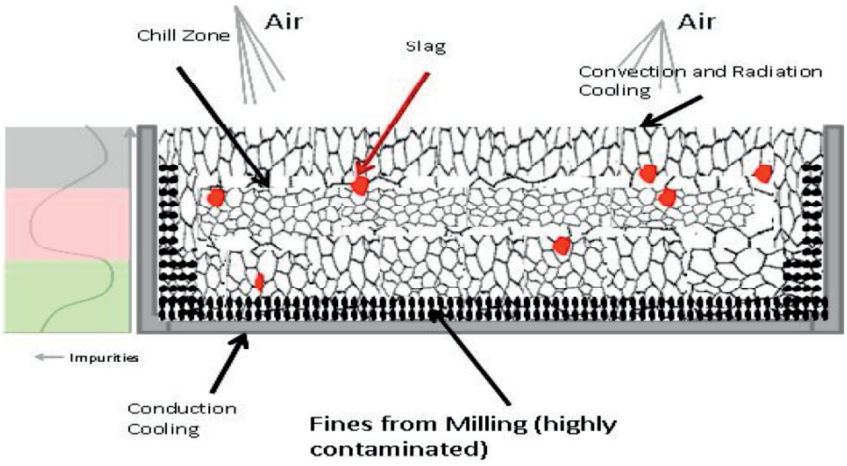

Figure 1: Schematic view of solidified mold

For the more advanced applications in chemistry or to be used as feedstock for a Poly Silicon plant delivering to the Photovoltaic or Semiconductor industry, this material is still to coarse.

This problem is compounded as the required size for the material decreases. In standard Polysilicon production, the nominal size distribution is 45 µm to 425 µm with an Average Particle Size (APS) of 250 µm. This requirement varies from customer to customer but normally falls in this range.

Material below 45 µm tend must be screened out as the end consumer cannot use the material in the TCS reactors due to the high gas flow rate and un-reactive nature of this size material.

Normal loss rates of milled silicon vary from system to system but during the total production of liquid silicon (including casting) to 45 µm to 425 µm production, the overall losses can range from 10% – 15% by weight.

It is estimated that based on today's reduced rate of Polysilicon production and the metallurgical silicon industry supply to it, a total demand of 225,000 metric tons of silicon is needed in this size range resulting in approx 22,000 to 30,000 metric tons per year of < 45 µm dust.

The milled silicon within this range of 45 µm to 425 µm is highly variable, slightly more contaminated that the original liquid silicon and extremely friable and subject to easy self milling during transport, handling and most importantly, when injected into a TCS or MCS reactor [1].

Those close to the mechnical grinding and milling industry know that the process is more complicated there than an outside person might imagine. The size distribution of the final material is not only depending on the type of the tool but although on the wear status and the raw material. The latter one is quite inhomogeneous as pointed out before. Big grains are mixed with smaller ones and different amounts of impurities are located throughout the whole volume.

As stated, usually such aggregates tend to break at impurity accumulations or a grain boundary, which then explains the high variability.

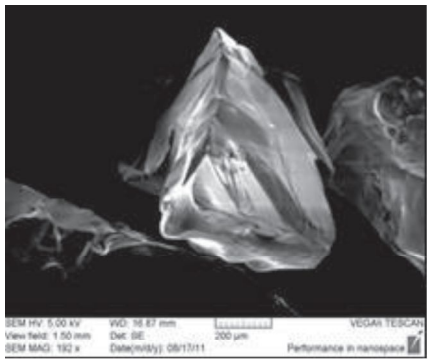

Figure 2: SEM picture of a milled silicon particle

At this point we are touching another unpleasant and sometimes painful characteristic of this milling dust. Fine dispersed in air it could be ignited and then in a dust explosion.

Looking at the average public statistics over the last 50 years every second year a mechanical milling involved with silicon wither has a fire or dust explosion, many of these occurring at well-known silicon companies operating under nitrogen gas cover. Setting aside the obvious safety hazard of such a practice the process is not optimized to reduce wastes.

3. GRANULATION PROCESS

The gas atomisation is not a new technology, although there have been significant advances in the process in the last decades.

The EMS process uses this basic process and tailors it to the need for homogeneous silicon powders for the Polysilicon, PV, Chemicals and Semiconductor areas.

The process begins with liquid silicon either from the refining unit following a traditional Submerged Arc Smelting furnace or a detached induction melting furnace and is transferred into a tundish that is integrated into an inert gas atomizer. From there it is released into a cooling chamber and collected in the bottom of the later after being dispersed with high velocity gas jets.

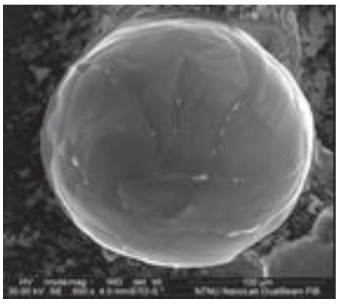

Figure 3: SEM picture of EMS particle

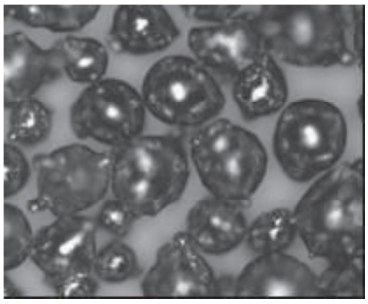

Figure 4: Optical image of EMS particles

4. PHYSICAL PROPERTIES

The formed particles are all bead shaped and very homogeneous regarding their shape. The size distribution is very tight and can be tailored depending on a combination of variables such as gas speed and temperature, nozzle design and materials, metal temperature, cooling reactor size, gas type, etc.

This process offers a variety of new possibilities, which were not available or optimized with milled silicon. The visual difference of the material is immediately noticeable and offers extremely high flow-ability. It can easily be seen that this physical characteristic can offer an improved logistics costs for the transport of large volumes of this material, as needed in some large Polysilicon or Chemical factories. Bulk handling of the material is much easier and pneumatic conveying much less costly as the material flows like water.

Vigorously shaking of the material makes obvious another difference between this and milled silicon, i.e. these is almost no self-milling and dust formation during handling thereby reducing the yield loss in the TCS reactors (direct and hydro chlorination) as well as in the Mueller-Rochow case. At the same time the explosion risk is decreased to almost zero. A completely new degree of freedom is made available to the customer by the possibility of fine tuning the size at tight distribution [5]. As all the end use consumers of this material use the fluidized bed principle, the output could be controlled by the used gas stream in conjunction with the particle size. In other words, production output can be modulated by using smaller or larger particles within some established operating parameters, allowing customers to more effectively match market demand.

5. CHEMICAL PROPERTIES

A second perspective which must be taken into account is the chemical reactivity improvements in the TCS process. First of all, all the particles have the same shape; size and composition as there are produced from the same liquid and solidified very fast [1]. This degree of homogeneity is unseen in any milled silicon. The degree of cooling and small physical shape means also that segregation of certain elements remains small and isolated to individual particles.

Differences in the reaction behaviour in the TCS process are not expected as all of beads have the same surface, grain structure, impurity level and distribution. Even more, catalysts can be added into the material, without segregating out during solidification, a common problem with adding catalysts to cast liquid silicon.

Silicon has a tendency to form an oxide layer on the surface when exposed to air. The immense total surface area of milled silicon means that this material contains approximately 70% more SiO_2 on its surface than equivalent EMS particles; even more so if the EMS particles are packaged under inert gas until used in the TCS process. This SiO_2 retards the reaction in the TCS synthesis and leads to higher than needed unit energy consumption, high ballast in the reactor and high waste stream content.

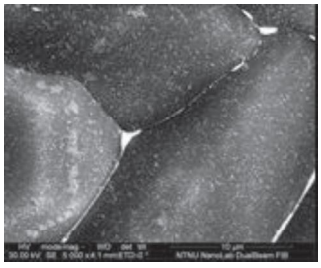

Figure 5: EMS particle grain structure forming a three dimensional catalyst network

For the Hydro chlorination process, normally a catalyst is added to faster approach the process equilibrium of the reaction and thereby increase the outputx [4]. With milled material the downside is that the material having the catalyst normally added physically on the surface of the milled silicon, leads to catalyst loss by blow out in the waste stream. The waste stream normally contains high levels of unreacted catalysts, un-reacted silicon dust and other gaseous impurities as well as crude silane. Additionally, the catalyst must be activated on the surface of the silicon usually via some defect in the silicon oxide layer. All this can be avoided by simply adding the catalyst directly to the EMS in the solid form.

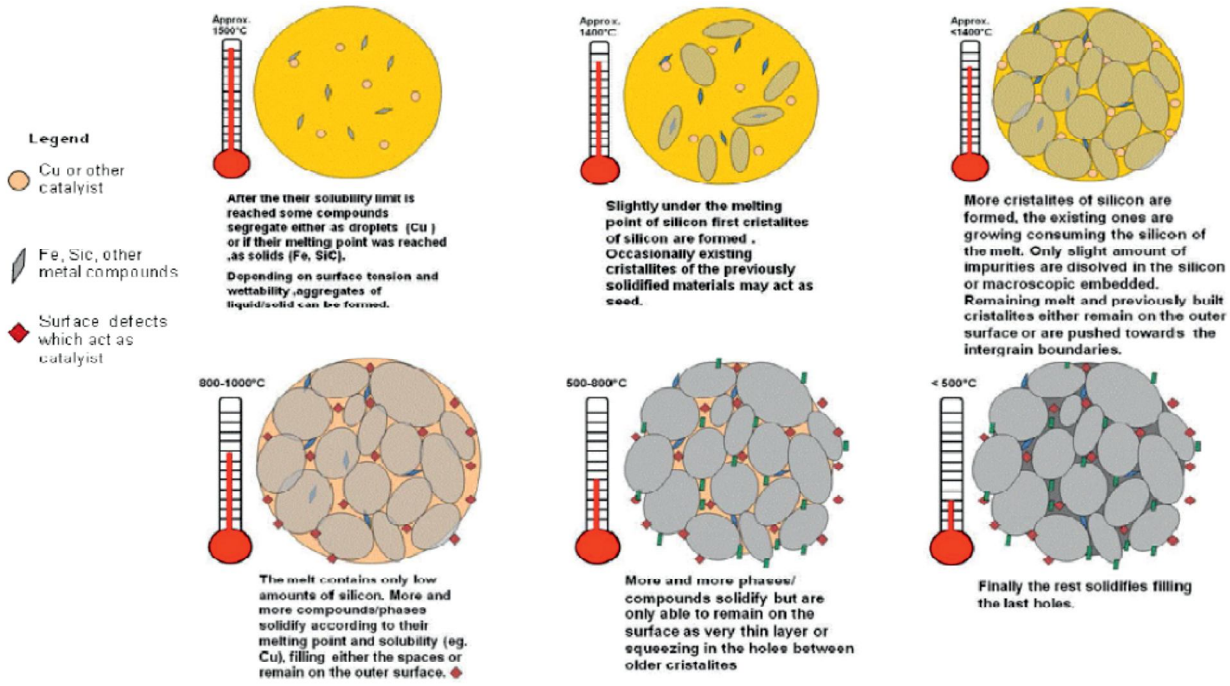

Figure 6: EMS cooling process

One interpretation of the mechanism during TCS synthesis with a CuCl catalyst is the formation of $CuSi_2$ on the surface of the silicon, which then is converted to TCS in the reactor. The detailed TCS process is not important here, but if $CuSi_2$ is the driving catalyst, the EMS particles with Cu catalysts have an advantage:

Key Concept	Role
Surface Coating	The surface of the mg Silicon is covered with the native SiO_2 layer, several microns thick, which shows the reaction with Hydrogen and Silicon Tetra Chloride (STC). The abrasion of this coating via the traditional catalyst addition is seemed as the initiation of the process
Surface Activity	The traditional catalyst is coated on the surface of the particle and rapidly diffuses into the silicon to form catalyst chlorides which are the real driving force for the reaction. Surface catalyst on the surface is not the active agent in the catalystic activity
Catalyst Role	The role of the traditional catalyst is to promote and accelerate the absorption of the Hydrogen on the surface of the particle
Morphology	The surface of milled mg Silicon is random, highly disordered and fractured which creates losses in both mg Silicon and the catalyst. The more even consumption of the particle is preferred

The Cu solid solubility in Silicon is very low, but when Cu exceeds the solubility limit upon the cooling of the EMS particles [5], the copper is pushed to the granular boundaries and forms other Copper phases, such as $CuSi_2$.

The net result is a 3 dimensional network of $CuSi_2$ throughout the EMS particle. Additionally, it is suspected that at the EMS particle surface, there may be a slight extrusion of copper rich phases.

It has to be admitted that it could be expected that the lower surface area of the EMS particle is negatively influencing the reaction velocity, but this could be already overcompensated by the oxide free surface, as the material could be handled under inert gas atmosphere at all time after formation.

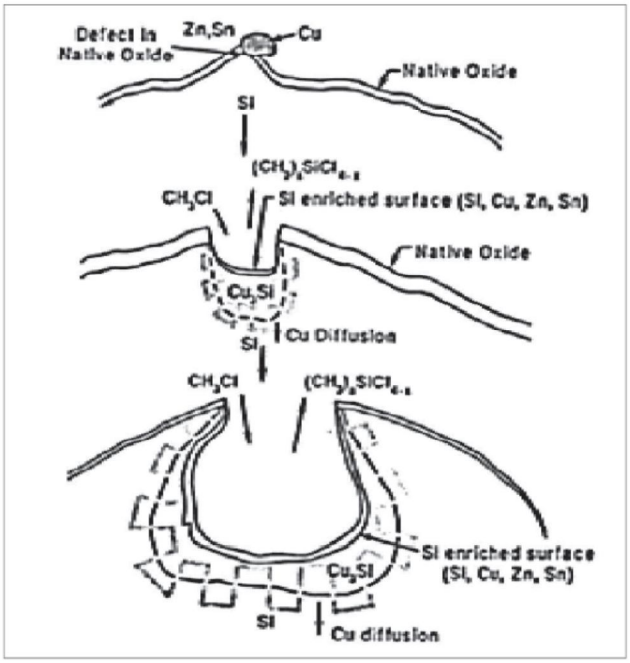

Figure 7: One interpretation of the TCS synthesis formation

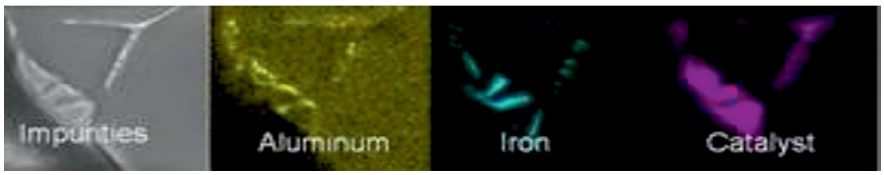

Figure 8: Grain Boundaries contain Impurities separated by melting point and catalyst which acts as reservoir for later diffusion

6. BENEFITS FOR RECYCLING

The use of EMS process is being investigated for its apparent promising use to recycle silicon materials such as

- < 45 micron silicon milling dust [5]
- TCS reactor waste dust

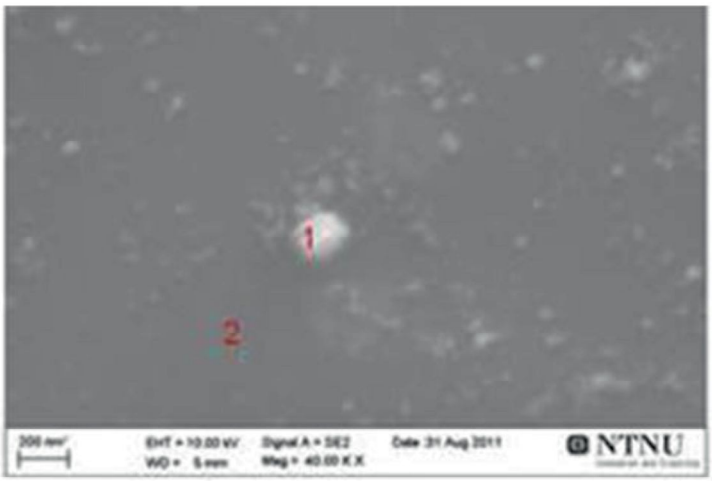

Figure 9: SEM of surface defect high in catalyst content

Location	C, at.%	O,at.%	Si, at.%	cat, at.%
1	11.8	5.6	79.3	3.4
2	11.7	0.5	87.6	0.2

- Recovered diamond wire kerf
- Polysilicon production waste
- Mono and Multi crystalline ingot waste
- Recycled micro silicon for Semi applications

The implications for this material can be immense, specifically for the Polysilicon industry. In normal operations, waste losses are accounted in the final product costs.

As Polysilicon prices are likely to remain depressed until the PV industry [4] strongly recovers the focus on process optimization and waste recovery can mean reduction in OPEX costs with very little CAPEX investment. This waste recycling can prepare the industry for a new growth period by driving optimization and cost reduction with the primary raw material.

7. SUMMARY

Numerous advantages of the EMS process can be already be identified from a theoretical standpoint, whereas the most important ones being:

- Higher tuning capabilities
- Better reactivity
- Lower abrasion of Reactors
- Homogeneous Sizing
- Lower Oxide level
- Higher safety level
- Improved handling and logistics
- Improved yield due to recycling

Table 1: OPEX mg Silicon increase x OPEX Poly Silicon decreases [5]

	Places	Item Description	Units	Standard Quantity (Unit / t mgSi)	Cost Unitary (U$S / Unit)	Cost Standard (U$S / tmgSi)	% in Standard Cost
MATERIAL	Raw Material and Feeding System	Charcoal Eucaliptus	m3	6.00	85.480	512.88	22.98%
	Raw Material and Feeding System	Wood Chips Pinus 30 *180 * 2000 mm	m3	3.00	37.820	113.46	5.08%
	Raw Material and Feeding System	Quartz	t	2.521	58.780	148.18	6.64%
	Raw Material and Feeding System	Limestone 3/4" to 2.5"	t	0.038	17.597	0.67	0.03%
	Raw Material and Feeding System	Auxiliar Energy	Kwh	54.00	0.0384	2.07	0.09%
	EAF	Electric Energy	Kwh	12,000	0.0462	554.40	24.84%
	EAF	Electrode	Kg	100.00	2.3770	237.70	10.65%
	EAF	Auxiliar Energy	Kwh	162.00	0.0462	7.48	0.34%
	Tapping	Electrode Graphite 4" * 48"	kg	2.00	3.350	6.70	0.30%
	Tapping	Trefilate Tube 17 * 9 * 4 mm with Sewing	kg	0.40	1.194	0.48	0.02%
	Tapping	Auxiliar Energy	Kwh	6.00	0.0384	0.23	0.01%
	Refining	Plug Porous	unit	0.03	20.330	0.60	0.03%
	Refining	Nitrogen liquid	m3	2.00	0.460	0.92	0.04%
	Refining	Oxygen liquid	m3	50.0	0.520	26.00	1.17%
	Refining	Auxiliar Energy	Kwh	60.0	0.0384	2.30	0.10%
	Refining	Losses				60.00	2.69%
	Casting Milling Crushing Screning	Auxiliar Energy	Kwh	300.0	0.0384	11.52	0.52%
	Casting Milling Crushing Screning	Losses				260.00	11.65%
	Other Places	Auxiliar Energy	Kwh	18.0	0.0384	0.69	0.03%
	Other Places	Losses				0.50	0.02%
	Other Places	Expenses Packaging				12.17	0.55%
	Total	Total Materials				1,059.85	72.33%
	Total	Electry Energy EAF	Kwh	12,000.0	0.0	554.4	0.2
	Total	Total Auxiliar Energy	Kwh	600.0	0.0384	24.30	1.09%
	Total	Total Losses				320.50	14.36%
	Total	Manufacturing Overhead Factory				64.61	2.90%
	Sub Total 1 - Material Cost					2,023.66	90.68%
Expenses and Labour	Raw Material and Feeding System	Direct Labour	h	1.93	3.84	7.40	0.33%
	EAF	Direct Labour	h	2.87	3.84	11.02	0.49%
	Tapping	Direct Labour	h	4.50	3.84	17.27	0.77%
	Refining	Direct Labour	h	1.29	3.84	4.93	0.22%
	Casting Milling Crushing Screning	Direct Labour	h	8.27	3.84	31.75	1.42%
	Casting Milling Crushing Screning	Milling Crushing and Screening Expenses	h	0.28	3.84	1.08	0.05%
	Other Places	Direct Labour	h	4.16	3.84	15.96	0.71%
	Total	Direct Labour	h	23.28	3.84	89.41	4.01%
	Total	Indirect Labour	h	19.83	3.84	76.16	3.41%
	Total	Direct Materials	h	1.16	3.84	4.45	0.20%
	Total	Personal Expenses	h	0.23	3.84	0.88	0.04%
	Total	Expedition Expenses	h	0.58	3.84	2.23	0.10%
	Total	Environmental Maintenance Expenses				2.33	0.10%
	Total	Administrative Expenses				32.63	1.46%
	Sub Total 2 - Expenses and Cost Labour					208.10	9.32%
Sub Total 3 - Industrial Cost						2,231.76	100.0%

Increasing approximately 2,35% on the OPEX of mgSi (in refining for example) could represents, for example a reduction of up to 162 US$ per ton of Polysilicon

The silicon recovery matrix:

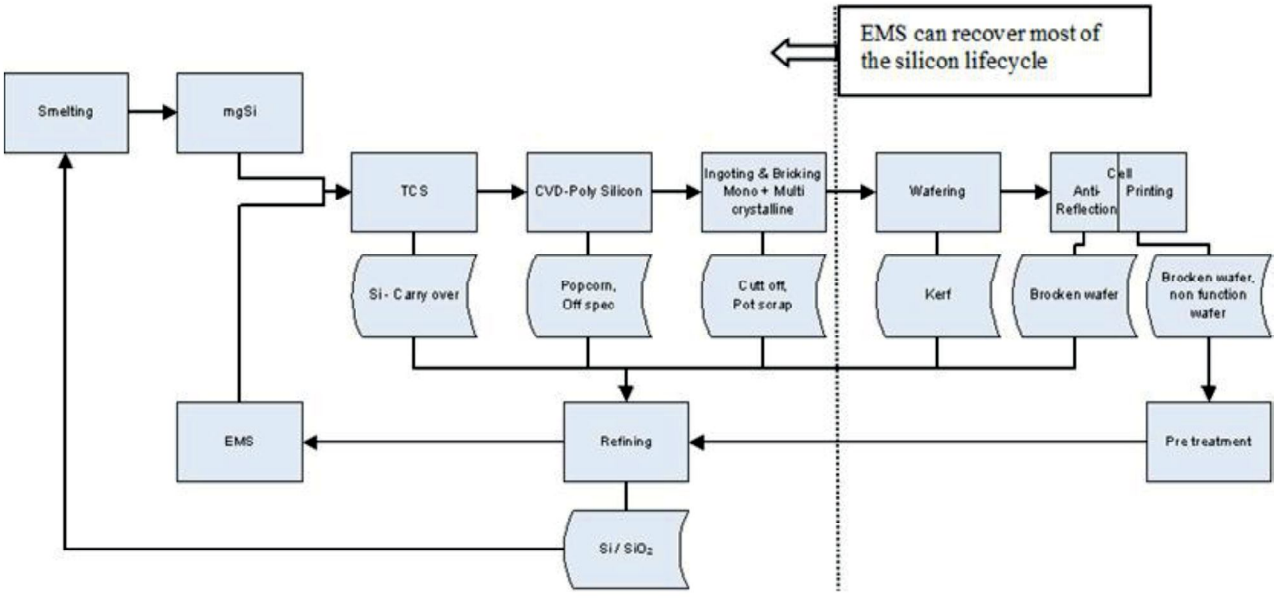

Figure 10: Silicon Recovery Matrix for the EMS Efficient Technology

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Viridis.iQ GmbH *is a newly formed German spin-off of Centrotherm Photovoltaics AG specializing in process, technology and optimization consulting for the PV and related industries, as well as materials production of advanced silicon materials.*
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