Recycling of silicon from photovoltaic production sludge

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The shortage of fossil energy resources, the dependency of the European Union on energy imports, the protection of the climate and therefore the need of reducing CO_2 emissions, these are some reasons for the strong growth of the photovoltaic industry in the last 10 years. Therefore the cumulative worldwide installed PV capacity in 2008 was about 15 GW and the European Photovoltaic Industry Association (EPIA) estimates a total volume of the PV market of up to 86 GW in 2013 [1].

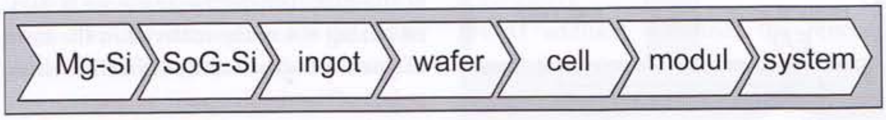


Fig. 1: Value chain of the PV-industry

The most important raw material for the manufacture of solar cells is high purity silicon (SoG-Si: solar grade silicon), which is derived from metallurgical grade silicon (MG-Si). After appropriate processing, this material is used in approx. 90 % of all solar cells, mainly in crystalline form [2]. In 2008, the demand of the photovoltaic industry for solar grade silicon was about 35,000 t [3].

The value chain of the photovoltaic industry to a complete photovoltaic system for converting sunlight into electrical energy is given in figure 1. Starting with MG-Si which is produced in an electric arc furnace, the silicon is converted to SoG-Si by thermal decomposition of $SiHCl_3$ or SiH_4. New approaches for a cheaper SoG-Si production are pursued e.g. from Elkem or 6N silicon (metallurgical route) or Joint Solar Silicon (tube reactor, reaction of SiH_4 + H_2). Afterwards the silicon is crystallized, firstly to obtain a suitable ingot for the wafer production and secondly to remove still remaining impurities with low segregation coefficients.

The process steps of ingot and wafer production generate a certain silicon saw dust, especially the wafer production with the multi wire slurry sawing (MWS). During this machining step, approx. 45 % of the starting material is lost in form of fine silicon powders (particle size < 5 µm), which accumulates in the sawing slurry. Besides the silicon, these slurries usually consist of polyethylene glycol (PEG) as a cutting fluid, fine silicon carbide particles as cutting material, as well as other metallic impurities that have been eroded from the wire during the cutting operation. State of the art is a pre-processing of the "exhausted slurries", i.e. partially separation of the coarser silicon carbide particles and PEG. This treatment is illustrated in figure 2.

At the end a by-product (sludge) of approx. 40 - 50 % Si and SiC, 5 - 20 % PEG, 1 -6 % Fe and < 0.5 % other metallic impurities remains, which contains the entire silicon saw dust.

The utilisation of the sludge can focus on the recovery of the two main fractions SiC or Si. In the first case, there are some approaches which use the sludge as a feedstock for the production of non-oxide ceramics like silicon nitride bonded SiC or silicon infiltrated SiC [5], [6]. This work investigates the second case, i.e. the recovery of silicon from the sludge. The aim is the utilisation of the sludge as a new feedstock for solar grade silicon production.

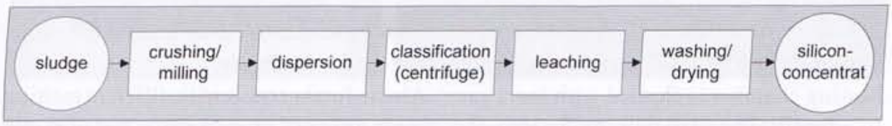


Fig. 3: Process flow for conditioning of the sludge

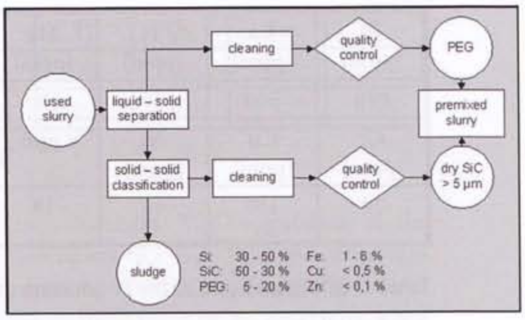


Fig. 2: Treatment of used slurries at SiC Processing AG [4]

Preparation of the sludge for metallurgical treatment

To achieve the aim of the research project, the sludge is processed by project partners to supply a PEG free and low SiC material for the subsequent metallurgical processes. Figure 3 illustrates the process flow for sludge conditioning.

Firstly the sludge is crushed and milled to a powder. Then the powder is dispersed in water to obtain a pumpable suspension. This suspension is treated with different centrifuge techniques to reduce the SiC content. Presently the SiC content can be lowered to 30 % with 70 % rate of yield (standard case). In the best case the SiC content is reduced to 10 %. In the latter case the extraction rate reaches only 10 %. Afterwards the mixture is leached in hydrochloric acid to remove metallic impurities, especially iron. Finally the suspension is filtered, washed and dried and the material is supplied as so called "silicon concentrate". Table 1 lists the remaining impurities in the obtained Si-concentrate (standard case). Leaching removes the metallic impurities effectively; nevertheless the content is in sum with 0.3 %, much too high for application in PV industry. XRD analysis shows that carbon exists in form of SiC resulting in 30 % SiC content in the Si-concentrate.

Metallurgical concept

The aim of the concept is the recovery of the fine silicon with maximum yield. Though the silicon concentrate contains up to 30 % SiC and numerous metallic impurities refinement of this material is necessary. Therefore the metallurgical concept is divided into two process steps. In the first step SiC must be removed to the greatest possible extent. For this purpose the following methods are investigated:

- Melt filtration for removal SiC in a ceramic foam filter.

Al [ppm]	Ca [ppm]	Ti [ppm]	Mg [ppm]	Mn [ppm]	B [ppm]	P [ppm]	Fe [%]
890	500	49	250	11	2,6	10	≈ 0,11
Cr [ppm]	**Cu [ppm]**	**Ni [ppm]**	**V ppm]**	**Co [ppm]**	**Zn [ppm]**	**C [%]**	
20	110	49	48	1,6	19	9,2	

Table 1: GDMS-analysis of the Si-concentrate (C-content by melt extraction)

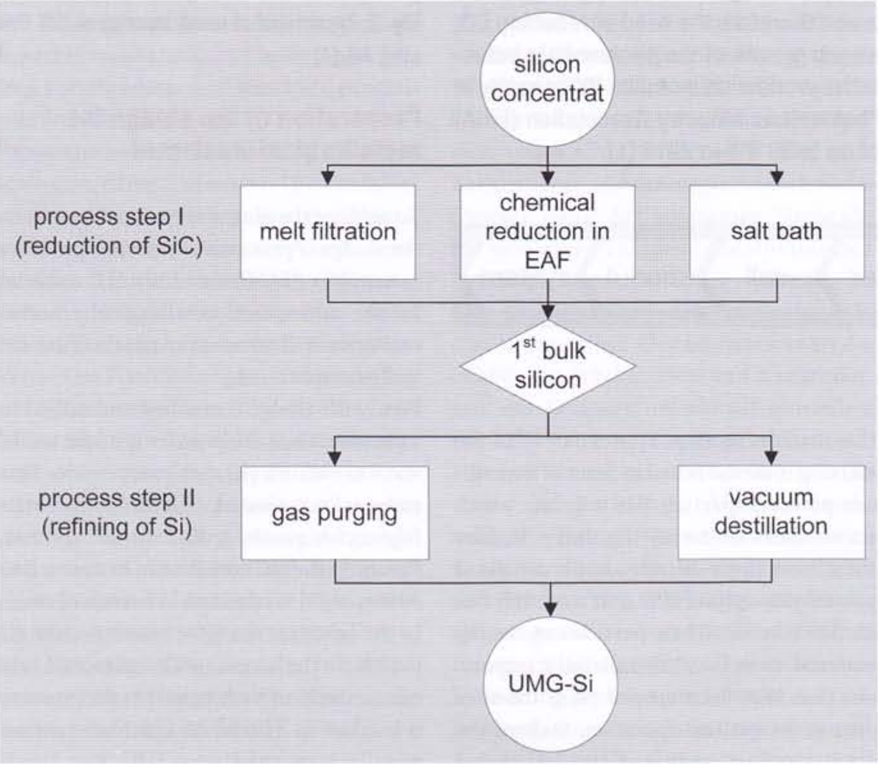


Fig. 4: Metallurgical concept of the work for processing the Si-concentrate

- Chemical reduction of SiC by addition of SiO_2 in an electric arc furnace.
- Separation of SiC from the Si-concentrate by use of a liquid salt bath.

The product of the first process step should be bulk silicon with improved purity compared to MG-Si. This material must be refined in the second process step. Therefore the methods "gas purging" and "vacuum distillation" are determined. The result of the second process step should be upgraded metallurgical silicon, which can be converted into solar grade silicon by use of crystallisation techniques.

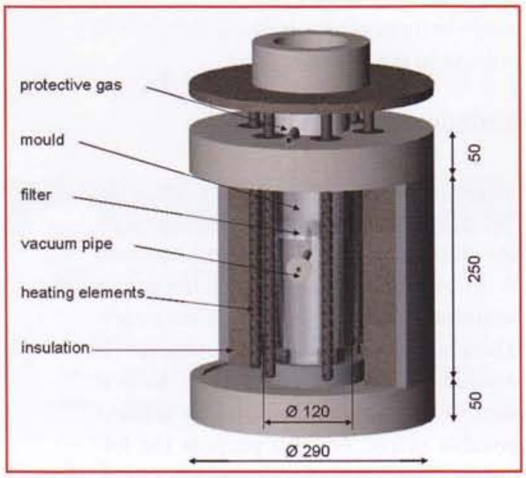


Fig. 5: Assembly of the filter box for melt filtration of silicon

Process step I - reduction of remaining SiC

Removal of SiC by melt filtration

First a filter box is designed for the filtration of silicon melts. The box is equipped with a separate heating system to avoid freezing of the melt during filtration. The mould is made of graphite and surrounded outside with different high temperature insulation materials. Furthermore, the heating chamber is flushed with inert gas to protect the graphite mould from air burn and the SiC heating elements against the reducing atmosphere. A vacuum pipe below the filter creates an additional pressure difference to support the filtration process if necessary. In preliminary tests, the box (figure 5) was successfully tested with conventional silicon melts.

Parallel to the preliminary tests of the filter box with metallurgical grade silicon, the Si-concentrate was supplied by project partners. For the melt trials 250 g of Si-concentrate was placed in pure graphite crucibles (SGL Carbon) of 60 mm inner diameter and 100 mm height. The crucible was set in an induction furnace, heated up to 1500 °C (power input 20 kW) with a dwell time of 1 hour in argon atmosphere of 800 mbar. During the treatment Si started oozing out of the material in the form of clusters, because of the different melting points of the substances.

Fig. 6: Melting behaviour of Si-concentrate: top 30 % SiC containing material, bottom 10% SiC containing material

Figure 6 depicts at the top the result of the melting tests with standard Si-concentrate. The high SiC content in the material avoids the formation of a liquid phase; instead a kind of sinter body is obtained. In contrast Si droplets are formed by using the low SiC containing concentrate, as shown at the bottom of figure 6. However a mechanical separation of the Si droplets and the sinter material is necessary.

Also in further trials with different melting agent like Na_2CO_3 or Na_2SiO_4 and different ratios of Si-concentrate to flux between 1/1

to 1/10 no liquid phase could be obtained. Consequently the melt filtration of the Si-concentrate for SiC removal is not possible as long as no liquid phase is achieved.
In the following processes (EAF, salt bath) only the melt behaviour of the standard Si-concentrate (30 % SiC) could be investigate, because of a lack in the material supply for the 10 % SiC material.

Removal of SiC by chemical reduction

The challenge of melting the Si-concentrate is the high SiC content. SiC decomposes at temperatures of approx. 2540 °C, so SiC is solid in the working temperature of silicon melts. The idea of this process is the reduction of SiC by chemical reaction with SiO2. The reaction of SiC can be described as:

$$K\ SiO_2 + SiC = (2\text{-}K)\ Si + (2K\text{-}1)\ SiO + CO \qquad (1)$$

i.e. the boundaries of the reaction are:

- $K_{min} = 0{,}5$ (no formation of SiO)
- $K_{max} = 2$ (no formation of Si)

The trials are conducted in a 70 kW laboratory scale electric arc furnace, which runs in a.c. mode. Tailor made crucibles out of pure graphite (SGL Carbon, measure: $Ø_i = 120$ mm, $Ø_o = 150$ mm, H = 200 mm) are used to avoid further impurities in the process. Prior each trial, the furnace is preheated until the outer side of the crucible is around 700 °C and then approx. 3500 g material is charged in batches of 200 g with a frequency of 5 min. Finally melt samples are taken by vacuum pipes from quartz glass (Heraeus Electronite) and analysed by ICP-OES.
In preliminary trials the following parameters are investigated:

- Material form during charging (powder vs. pellets).
- Additional Si for melt formation.
- Different slag systems (Na_2O-SiO_2, Na_2O-SiO_2-CaO, SiO_2-CaO).
- Variation of quartz factor K (0.5 / 0.75 / 1).

As a result of the preliminary trials the following statements can be made:

- Pelletizing of the material is necessary to avoid material losses in the flue dust and optimize the charging operation.
- Si addition for melt formation is not necessary.
- CaO addition stabilized the process and is currently required, although new impurities are introduced in the system.
- An influence of the quartz factor is not detected. In all trials the C-content is reduced to approx. 0.05 %.

Finally a trial without any additives is conducted in comparison to a trial with SiO2-CaO slag. Figure 7 depicts the obtained products of these trials.
The silicon is analysed via ICP-OES and table 2 lists the main impurities. By use of the additives SiO_2 and CaO the contents of Al, Ca and Fe are increased clearly. On the other hand the additives stabilized the process and results in an even and improved operation. Without additives the silicon yield is lower but silicon is produced with 99.9 % purity.

Elements in %	Al	Ca	Fe	Ti	Cu	Zn	C
with additive	0,12	0,56	0,35	0,05	0,06	0,04	0,10
without additive	0,05	< 0,01	< 0,01	< 0,01	< 0,01	-	0,04

Table 2: ICP-OES-analysis of Si obtained in EAF

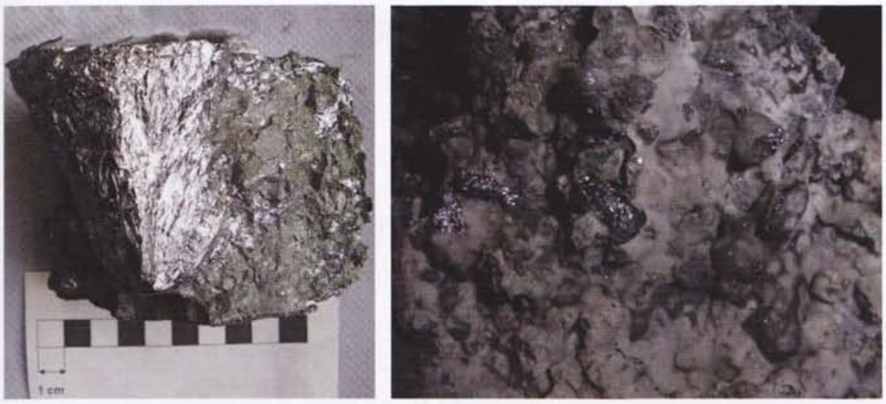


Fig. 7: Result of the melting trial with standard Si-concentrate with (left) and without (right) addition of SiO_2-CaO slag (ratio CaO/SiO_2 = ½)

Removal of SiC in a salt bath

The function of the salt is the separation of Si and SiC. By process temperatures below the melting point of Si, only a mechanical separation is possible with settling of the substances. The coagulation of the Si-droplets to a liquid phase can be supported by working at temperatures above the melting point of Si, especially when the density of the salt bath is set between the densities of Si and SiC.
For the low temperature process ($T_{salt} < T_{m,\ Si}$) at around 800 °C a mixture of 70 % NaCl and 30 % KCl is used. These trials are carried out in a resistance furnace with stirring unit. The high temperature process ($T_{salt} > T_{m,\ Si}$) with a mixture out of 80 % CaF2 and 20 % BaF_2 is conducted in an induction furnace by temperature of approx. 1500 °C. In the latter case 72 g Si-concentrate and 750 g salt mixture (ratio $V_{solid}/V_{liquid} \approx 1/10$) are heated in a graphite crucible ($Ø_i = 70$ mm, $Ø_o = 90$ mm, H = 120 mm) to process temperature and held for 30 min under stirring. Samples of the product are examined by SEM and the phases determined by EDX analysis. A separation of Si and SiC cannot be detected in this high temperature process.
In the low temperature process 330 g Si-concentrate and 1650 g of the salt mix-

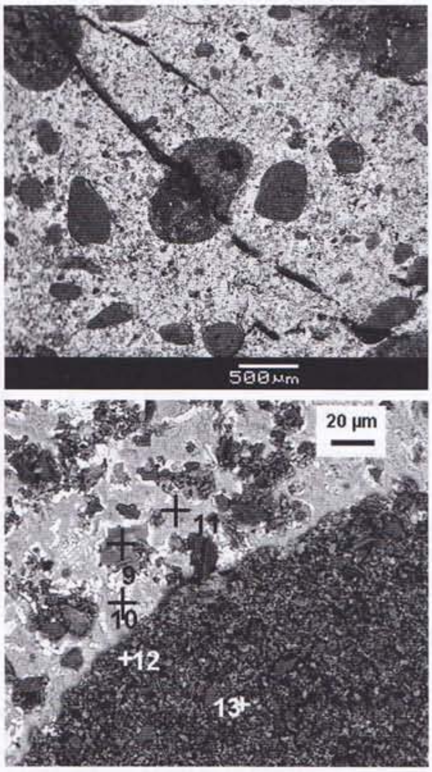


Fig. 8: SEM-micrograph of the low temperature process, magnification (top) and resolution in a cluster (bottom)

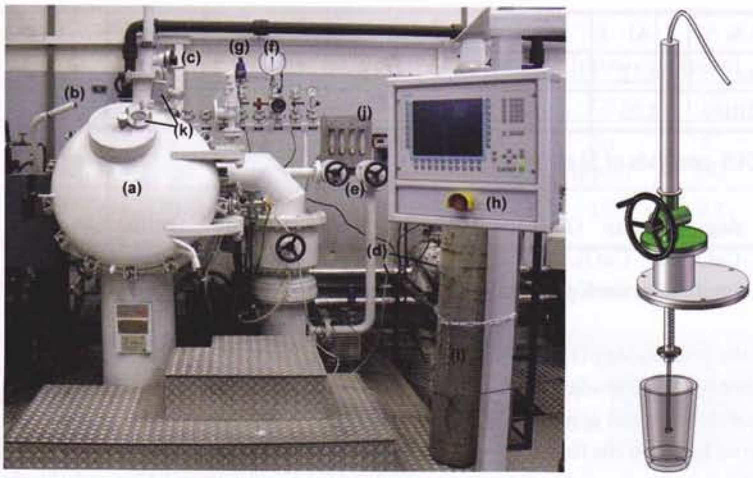


Fig. 9: Set-up for gas purging of Si and CAD sketch of the gas purging system

ture (ratio $V_{solid}/V_{liquid} \approx 1/8$) are heated in a graphite crucible ($Ø_i$ = 140 mm, $Ø_o$ = 160 mm, H = 200 mm) to 800 °C, stirred for the dispersion of Si and SiC in the salt bath, held at temperature for 1-3 h (settling phase) and cooled down slowly. A SEM-micrograph of the product is given in figure 8. The magnification shows dark rounded areas embedded in a bright matrix. The EDX analysis on the right side identifies in area (9) NaCl, Si, SiC, in (10) KCl, for (11) NaCl and in the dark area SiC (12) and Si (13). Consequently a separation of Si and SiC does not take place and so the process is not suitable for the removal of SiC from Si-concentrate.

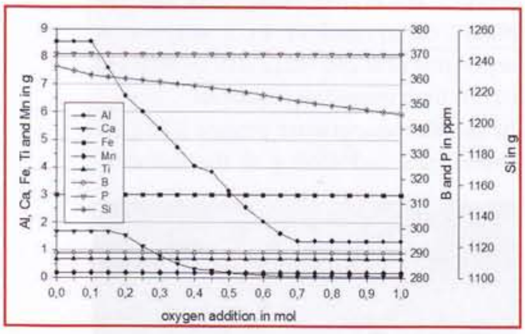


Fig. 10: Simulation of gas purging by addition of O_2, T = 1500 °C, p = 0.8 bar

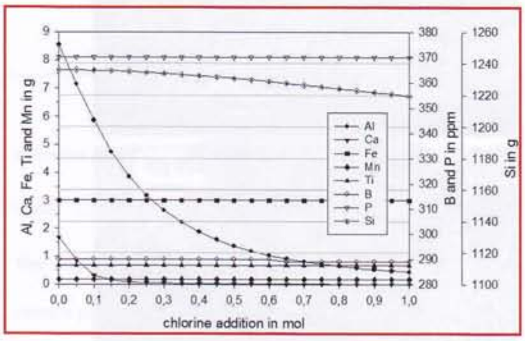


Fig. 11: Simulation of gas purging by addition of Cl_2, T = 1500 °C, p = 0.8 bar

Process step II - refining of silicon

Refinement by gas purging

The trials are conducted in an induction furnace (10 kHz, 50 kW) with quartz crucibles (Heraeus Rotosil OFM 70, $Ø_a$ = 110 mm, $Ø_i$ = 85 mm, H = 210 mm). The experimental set up is illustrated in figure 9.

Prior to the trials the refinement of Si is simulated by thermochemical calculations (FactSageTM 5.5, databases FSupsi/Fact53). The variation of the impurities in the silicon melt in the case of O_2 addition as reactive gas is shown in figure 10. By addition of H_2O, the reduction of the impurities is analogue to the O_2 addition, but lower because of less O_2. Figure 11 gives the result for the simulation with chlorine as reactive gas.

Generally, the simulation shows, that the addition of reactive gases can reduce especially Al and Ca, but no influence of the Fe, Mn, Ti and P content is visible. The removal of B as HBO is possible but marginal. This is contrary to information from literature [7] - [10].

In addition to the thermochemical simulation, the process is also simulated in a water model to determine the optimal gas flow rate. The aim is the creation of small gas bubbles. The gas is led through a lance in the melt. To obtain small gas bubbles the lance is equipped with a porous disc with pore size of 40 µm. All materials are made from quartz glass (Heraeus HSQ 300) to avoid impurities in the process. As a result of the simulation, the gas flow rate is set to 2.2 l/min.

The main impurities in the silicon are Al with 0.68 % and Ca with 0.13 % (table 3). Assuming that Al is removed as Al_2O_3 and Ca as CaO from a 1.2 kg Si charge, 0.245 mol oxygen are necessary for total removal. That means different purging times are required to provide the amount of O_2. At first, screening trials with 15 min purging time are conducted to avoid damages to the lance, especially the connection between lance and porous filter disc. Table 4 gives an overview of the trials with different gas combinations.

Figure 13 depicts the decomposition rate of the different impurities for all purging trials with 15 min treatment. In all trials Ca is removed to < 20 % of the starting concentration. Also Al is reduced in all trials by approx. 20 %. A removal of Fe, Mn and Ti is not detected. Figure 12 shows the reduction for V7 with 45 min treatment.

The thermochemical calculation reveals that reactive gases like O_2, H_2O and Cl_2 firstly reduce the impurities Al and Ca. By 100 % yield of the gases 0.245 mol O_2 are required for oxidation of Al and Ca. During 15 min purging, 0.134 mol O_2 are added to the melt; for 45 min purging it is 0.495 mol. Figure 14 depicts the removal efficiency for Al and Ca for the cases 100 %

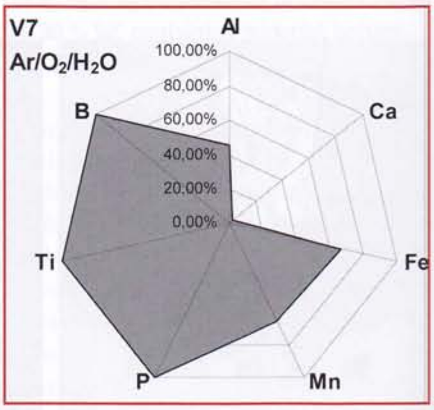


Fig. 12: Reduction of the impurities by gas purging (t = 45 min, V = 2.2 l/min, p = 0.8 bar, T = 1500 °C

	Al [%]	Ca [%]	Fe [%]	Ti [%]	Mn [%]	P [ppm]	B [ppm]
x_m	0,683	0,134	0,240	0,055	0,014	29	23
σ	0,146	0,025	0,070	0,006	0,009	17	5

Table 3: Analysis of silicon for refinement by gas purging

trial:	gas:	V [l/min]	f_m [g/m³]	m_{in} [g]	m_{out} [g]	m_{Si}, slag [%]	T_m [°C]	p_m [mbar]	s_{in} [cm]
V 1.1	Ar	2,2	0	1350	1322	2,1	1498	820	10
V 1.2	Ar	2,2	0	1342	1295	3,6	1507	877	10
V 2.1	Ar/5% H_2	2,3	0	1225	1206	1,6	1522	851	9
V 2.2	Ar/5% H_2	2,3	0	1225	1187	3,1	1492	867	10
V 3.1	Ar/20-50% O_2	var.	0	1236	1100	11,0	1519	851	9
V 3.2	Ar/O_2 pulsed	2,25	0	1336	1219	8,8	1517	864	10,5
V 4.1	Ar	2,2	17,4	1219	1164	4,6	1515	833	10,5
V 4.2	Ar	2,2	18,1	1258	1223	3,8	1527	873	11,5
V 5.1	Ar/5% H_2	2,3	18,1	1246	1204	3,4	1522	849	10
V 5.2	Ar/5% H_2	2,3	18,2	1204	1183	2,1	1518	868	10
V 6.1	Ar/2% Cl_2	2,2	0	1256	1116	11,2	1533	822	9,5
V 6.2	Ar/2% Cl_2	2,2	0	1258	852	32,3	1485	876	11
V 7	Ar/8% O_2	2,2	23,6	1225	1037	15,3	1580	820	10

Table 4: Parameter of the different trials (V1-V6: t = 15 min, V7: t = 45 min)

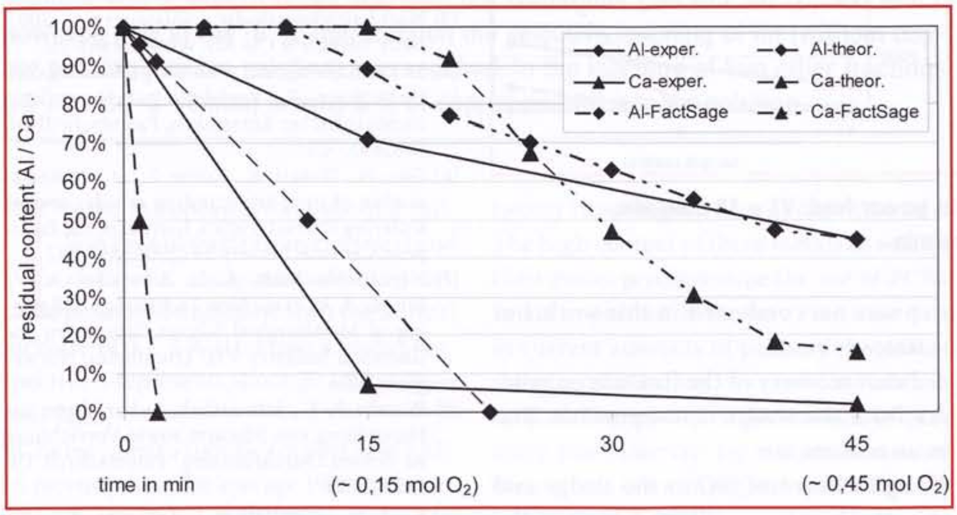
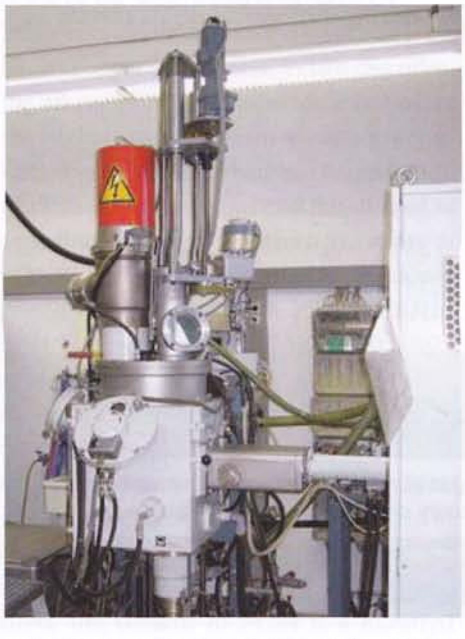


Fig. 14: Removal efficiency for Al and Ca by addition of O_2



- Leybold-Heraeus Typ ES 1/3/60
- 85 kVA connection power
- 380 V connection voltage
- 60 kW electron beam power
- 30 kV beam voltage
- *inside dimension mould (l*b*t)*
  170 mm x 90 mm x 15 mm

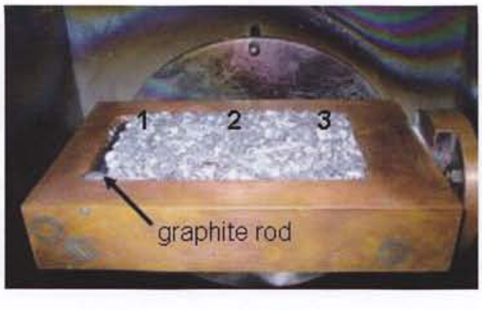


Fig. 15: Electron beam furnace with water cooled copper mould

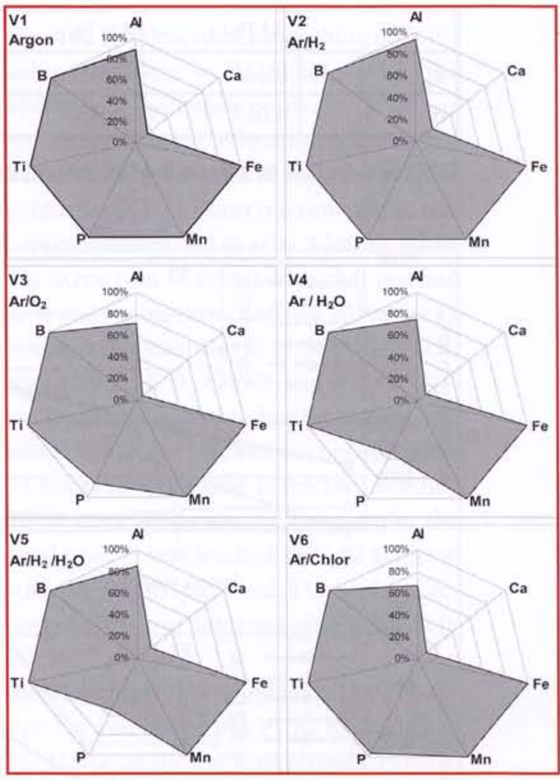


Fig. 13: Reduction of the impurities by gas purging (t = 15 min, V = 2.2 l/min, p = 0.8 bar, T = 1500 °C

theoretical yield of O_2, FactSage calculations and experimental investigation.

Refinement by vacuum distillation

The refinement of Si by selective evaporation of impurities is conducted in an electron beam furnace (figure 15). Due to the experimental set-up (the electron beam moves in y-axis over the charge, the mould moves in x-axis) beside distillation also segregation of impurities occurs.

In each trial 380 g Si (analysis in table 5) is melted with 6 kW power and a pressure of approx. 10^{-5} mbar. The power feed of the mould and so the speed of the melting zone varies between 15 to 5 mm/min. After each trial, 3 samples from the Si-plate (position 1-3) are taken and analysed by ICP-OES.

In figure 16 the distribution of the impurities in the three sampling zones of the Si-plate is illustrated. Ca is removed in all trials, independently from the power feed of the mould. Especially the impurities Fe ($k_0 = 6.4 \cdot 10^{-6}$) and Ti ($k_0 = 2.0 \cdot 10^{-6}$) with low segregation coefficients show better removal with lower power feed and enrich at the end of the Si-plate in zone 3.

The residual content of the impurities is plotted in figure 17 against the power feed of the mould. The lower the power feed is, the higher the refinement effect.

	Al [%]	Ca [%]	Fe [%]	Ti [%]	C [%]
x_m	0,440	0,023	0,315	0,042	0,046
σ	0,062	0,004	0,069	0,006	0,014

Table 5: Analysis of silicon for refinement by vacuum distillation

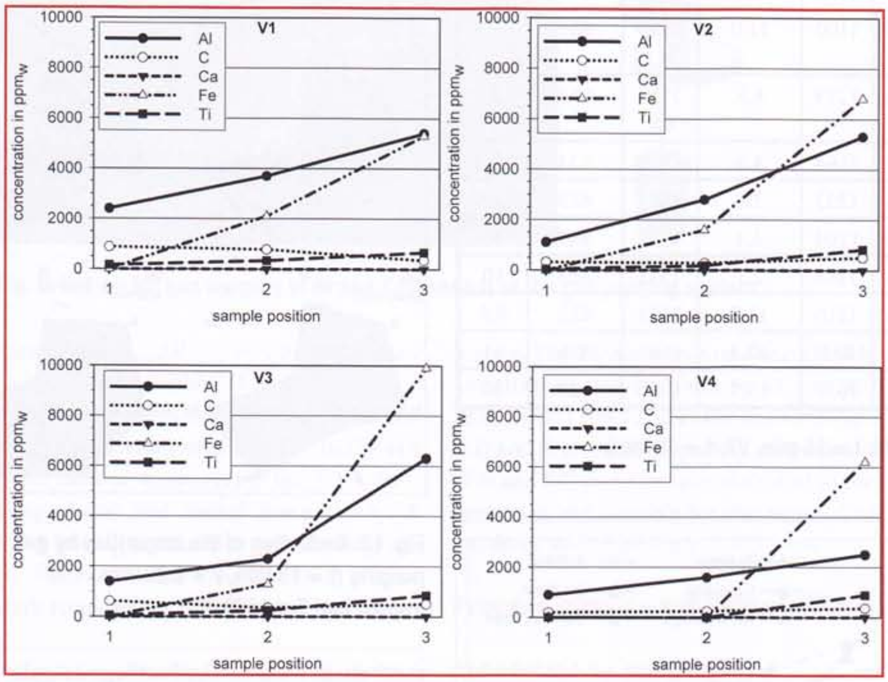


Fig. 16: Distribution of impurities in the Si-plate, power feed: V1 = 15 mm/min, V2 = 10 mm/min, V3 = 7.5 mm/min, V4 = 5 mm/min

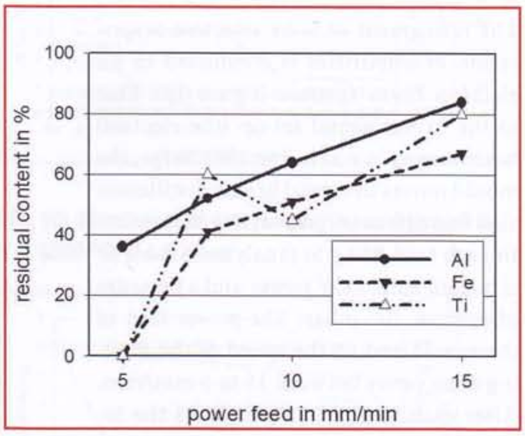


Fig. 17: Residual content of metallic impurities in dependency of the power feed

Conclusion

Figure 18 summarises the concept for processing silicon sludge from the solar wafer production. In the first step, a silicon concentrate is obtained with 70 - 90 % Si. By chemical reduction in an electric arc furnace, silicon in upgraded metallurgical quality can be produced. To achieve solar quality, this material must be refined and finally crystallised. The crystallisation step was not conducted in this work, but is state of the art.

A direct recovery of the fine silicon powder from the sludge is not possible. The main reasons are:

- High content of SiC in the sludge and in the best case still 10 % SiC in the Si-concentrate.
- Extreme low grain size of the material (Si and SiC) of < 5 µm.
- Presences of metallic impurities like Fe, Cu, and Zn form the cutting wire.

For recovery of the silicon powder in solar grade quality, an almost complete separation of all other compounds from the slurry is crucial. Before melt formation of the material, a surface leaching of the Si particles is necessary, because all impurities surrounded by the Si particles are directly solved by the liquid Si phase. A complete physical separation cannot be achieved, because a precise separation cut cannot be made between Si and SiC.

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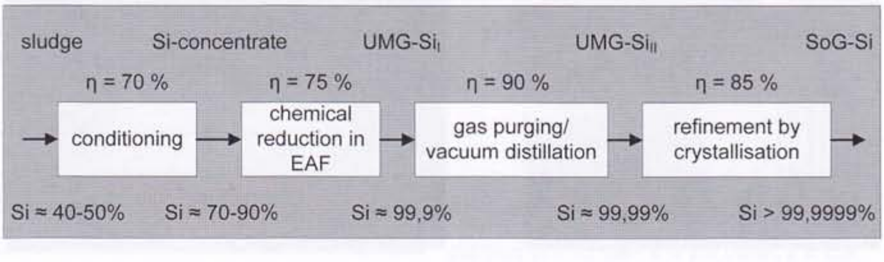

Fig. 18: Concept for processing sludge of the solar wafer production to solar grade quality