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RECYCLING OF SILICON CARBIDE AND SILICON FROM WAFER SAWING SLURRY

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In the production of silicon wafers for the photovoltaic industry a wafer saw cutting process is employed to slice the mono- or polycrystalline ingots to wafers. For that, multi-wire sawing using SiC slurry is the main slicing technology in photovoltaic (PV) and semiconductor (SC) industry. The cutting process produces a large quantity of saw dust (kerf). Dependent on the wafer thickness and the diameter of the cutting wire, the amount of sawing chips yields up to 30 – 50% of the ingot weight. This residue contains mainly the abrasive SiC, the Si-abrasion and Fe with other metals coming from the saw wire in a suspension of polyethylen glycol (PEG). They thus constitutes valuable materials which are well suited to be recycled to the photovoltaic industry. A solution of the waste slurry problem is unfortunate, both from an economical and environmental point of view. This paper reports on different concepts and own experiences related to Si and SiC recycling.

Keywords: Si-Recycling, SiC-Recycling, Trichlorosilane, Hydrocyclone.

Introduction

Over 80 % of the global solar cell production requires the cutting of silicon blocks into wafers [1]. For that, multi-wire sawing using SiC slurry is the main slicing technology in photovoltaic (PV) and semiconductor (SC) industry. During sawing a large amount of slurry is produced, which contains polyethylene glycol (PEG) as suspending fluid, silicon carbide (SiC), iron and silicon. Much attention is paid to recycling of SiC and PEG to the sawing process. The base publication in this direction is an article by Neesse [2], where the variants of SiC recycling from wafer sawing slurries are reported.

These technologies have reached a high standard and are industrially applied.

On the other hand, Si –recycling from wafer sawing residues is much more difficult and challenging and has been subject of a large European Project [3] (Recycling of Silicon Rejects, 2006) Methods for this are actually still in the development.

After reporting on SiC recycling in this paper options and limitations of physical Si-separation processes are reported. High grade solar Si can be achieved applying combined physical and chemical treatment considering a special chemical technology were Si is reacting with chlorinated acid to trichlorosilane [4-6]. First experiences with this process are reported.

1. Recycling of SiC

The SiC- recycling technology should fulfil the following requirements:

- Production of PEG and SiC of a quality, comparable with virgin material
- User-friendly handling of the recycling products
- Consideration of environmental aspects for the separated residues

As can be seen from Fig.1, two variants are to consider: The “in-house” approach consists of equipment that the semiconductor- manufacturer purchases, sometimes offered during the original saw purchase, and runs in-line with their own slurry system. In the US these systems exist in many wire sawing plants.

The alternative is outsourcing the SiC-recycling to a specialised recycling company. The recycler can operate an on-site system using mobile equipment or requires the manufacturer to transport the slurry to a stationary recycling plant (off-site-system).

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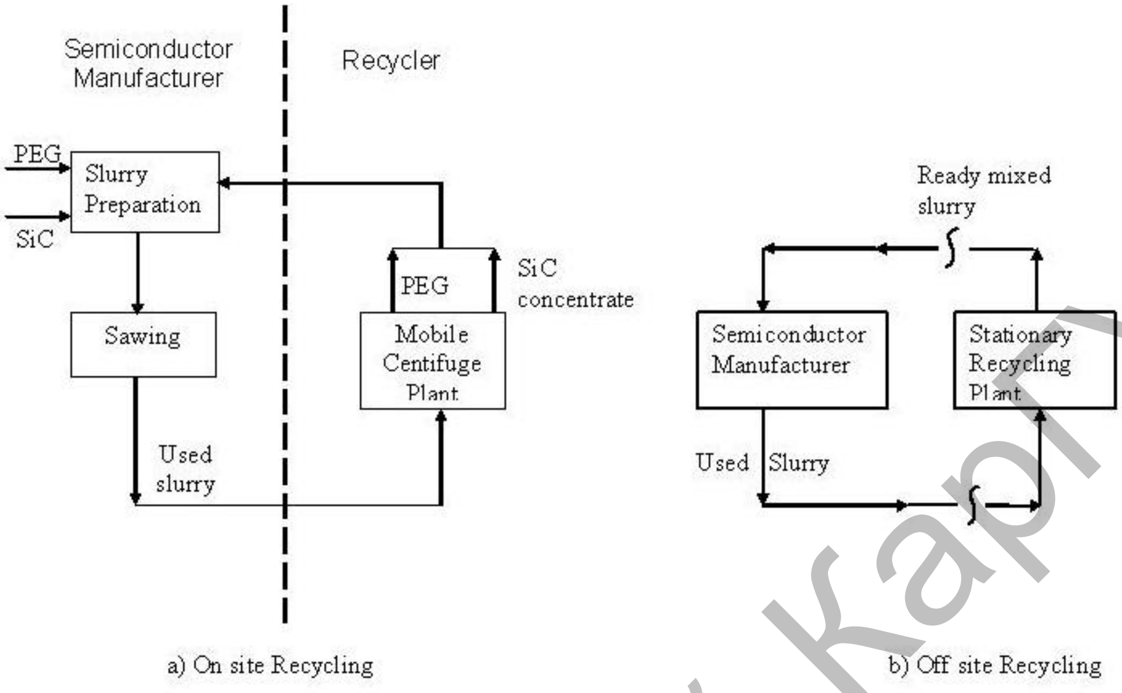

Fig.1. In house-(a) and outsourced (b) SiC recycling [2].

Necessary steps of SiC recycling are the separation of liquid medium PEG by filtration and separation of SiC as recycling products from the contaminants by hydroclassification. The contaminants are fine dispersed Si, SiC and Fe.

As classifiers in the range with cut sizes of of about 10 μm Decanter centrifuges and hydrocyclones are available. The decanter centrifuges spin at a high rotational speed and the classification is accomplished because the particles settle with different settling rates dependent on their size. Due to the fact that all particles (more or less) settle, the decanter is more a solid/liquid separator than a classifier.

A marked portion of particles < 5mμ (contaminants) is misplaced and discharged together with the coarse SiC-particles (recycling product). The remaining contaminants from even the most elaborate decanter technologies are generally ~3-4%. The enrichment of fine particles in the recycled SiC-product leads in the closed circuit to a deterioration of the suspension properties. Under these conditions only 3 – 4 passes of the slurry through the sawing process can be carried out. In this regard, the use of hydrocyclones deliver better results.

At present, the tendency seems to increase that semiconductor- manufacturers (because of overall-cost improvement) replace the “in-house” system running their entire slurry volume with an outsourced system. An enhanced outsourced system in a stationary plant prefers a multistage technology. The market leader describes a plant scheme in Fig.2 consisting of following steps [2]:

1. Separation of PEG
2. Cleaning of PEG
3. Separation of SiC
4. Cleaning of SiC
5. Drying of SiC
6. Conditioning of SiC

It is obvious that a multistage cleaning can approach the final SiC-product to zero-contamination. Therefore, the number of passes of slurry through the sawing process is not limited.

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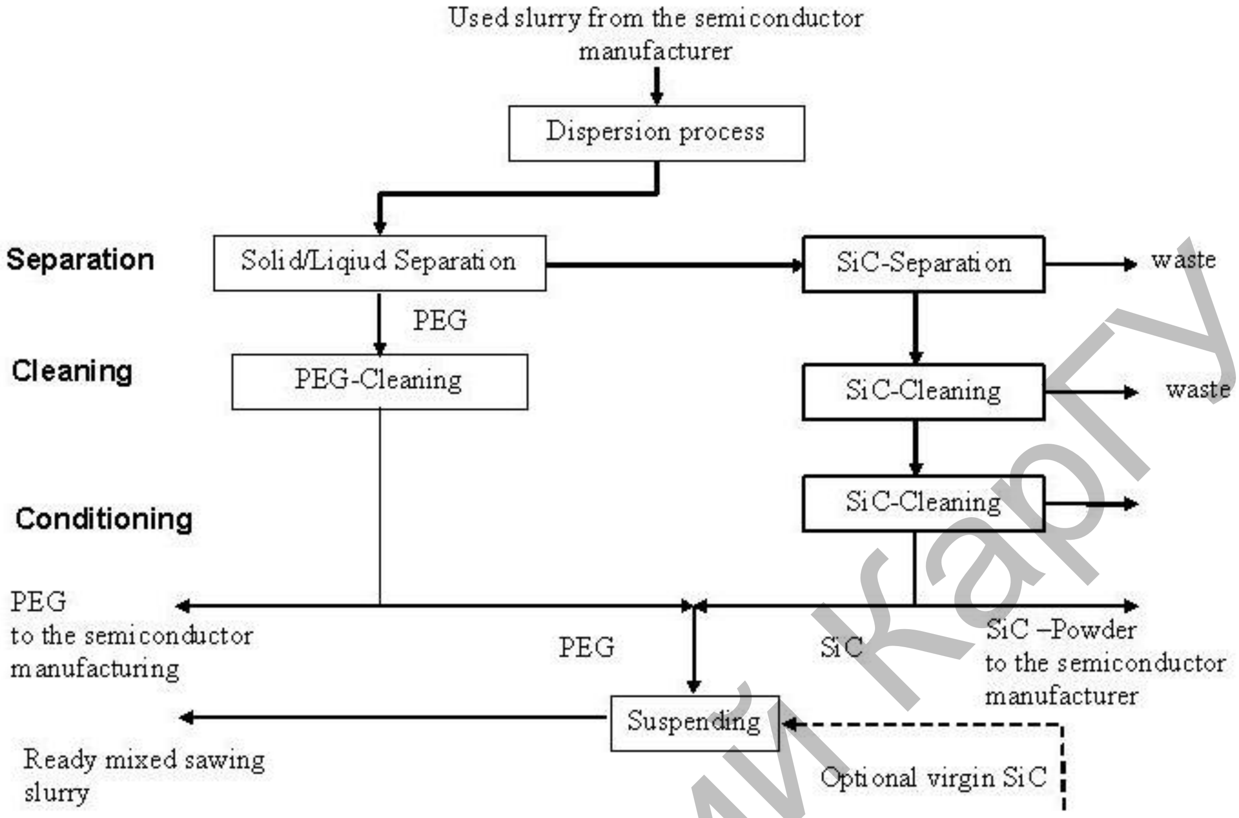

Fig.2. Multistage technology of SiC processing [2].

Further, multi-stage systems show higher cost effectivity, if a well sophisticated process sequence is found avoiding expensive centrifuges. Additionally, the specific costs per ton are reduced due to the high throughput of a stationary plant.

Outsourced systems have to answer the demands of user- friendly handling of the recycled products. Applied is the transport of wet SiC products which are discharged from hydroclassifier without further drying and cleaning. The material must be reconstituted with carrier into slurry. This means that the manufacturer is forced to install equipment to remix the slurry after the transport because the solids will settle in the containment.

More appropriate are products separated into dry SiC powder and PEG. The manufacturer has three options to receive SiC and PEG from the recycling plant:

1. Separated delivery of reclaimed SiC powder and reclaimed PEG. Slurry preparation by adding of virgin material at the manufacturer.
2. Separated delivery of reclaimed SiC powder mixed with virgin SiC powder and of reclaimed PEG mixed with fresh PEG (slurrying is performed at the manufacturer).
3. Delivery of a ready mixed slurry consisting of SiC (reclaimed and virgin) and PEG (reclaimed and virgin), In this case no slurry preparation at the manufacturer.

In the EU a tendency of increasing outsourcing the entire slurry preparation to the recycler can be observed.

2. Recycling of Si

Concerning Si there are two concepts for the recycling: Production of a low grade metallurgical Si or production of solar Si. The first variant can be achieved using only physical separation processes.

High grade solar Si can be achieved applying combined physical and chemical treatment.

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3. Physical separation of Silicon

The feed for the Si-recycling was dried filter cake with 24% moisture, as it occurs typically in the SiC (Silicon carbide) recycling from the wafer production at a separation cut at 10 microns. As further components after SiC were 9.5% iron, 31% elemental silicon and 1.8% polyethylene glycol were determined. The initial particle size distribution of material after intense dispersing can be found in Fig.3.

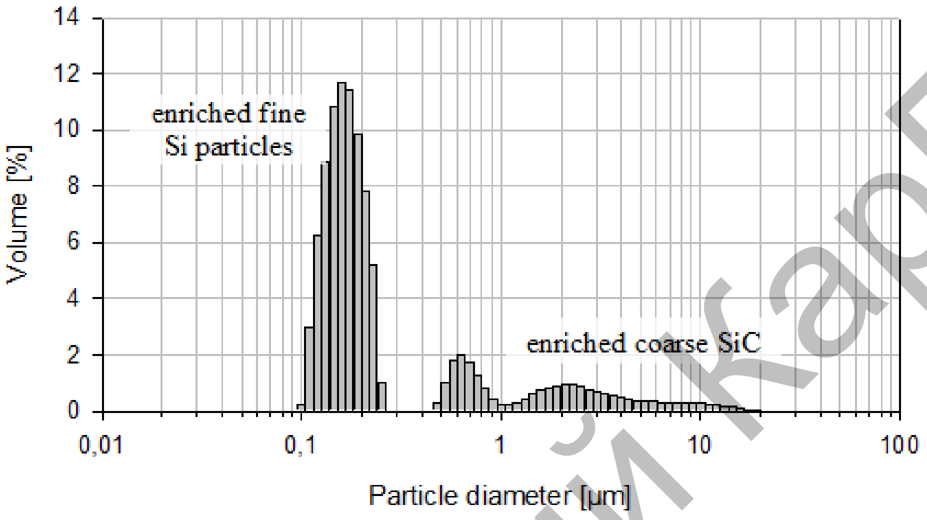

Fig.3. Volume fractions of particles in the SiC/Si suspension with enriched fine Si particles

As can be seen from Fig. 3, the material contains finest Si-abrasive in the range 0.1 – 0.3 µm and coarser silicon carbide SiC. The gap between the fine and the coarse portion delivers an advantage for the hydroclassification.

This material was used as a feed for a special 20mm-hydrocyclone, which operated in closed circuit duration 60 min [7]. Because no fluid is discharged in the underflow, the suspension can be kept indefinitely in the circuit as can be seen in Fig.4.

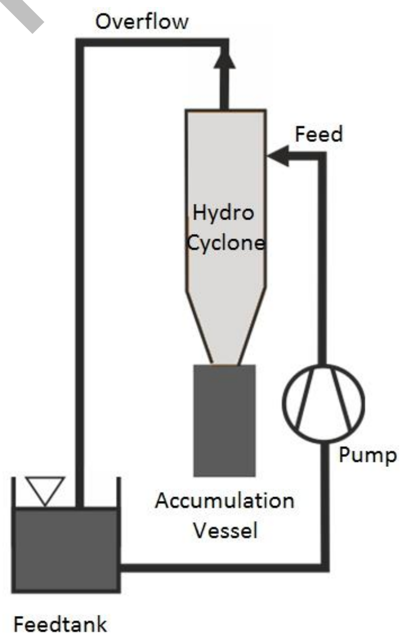

Fig.4. Scheme of the hydrocyclone test rig with closed circuit and attached accumulation box for the underflow.

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Fig. 5 and 6 show the final particle size distributions of the coarse product and of the overflow, respectively.

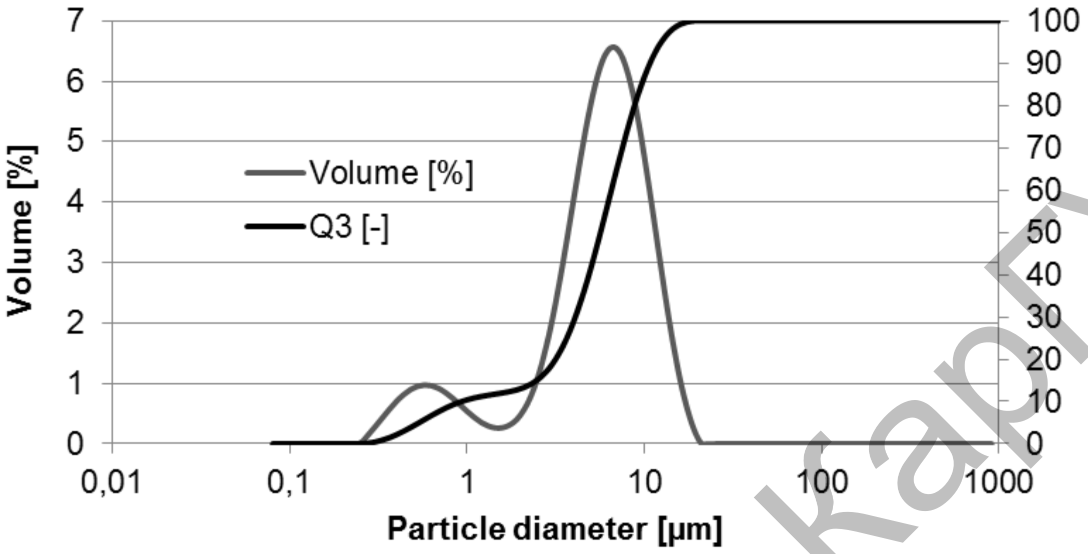

Fig.5. The final volume fractions and cumulative particle size distributions in the coarse product of the hydrocyclone.

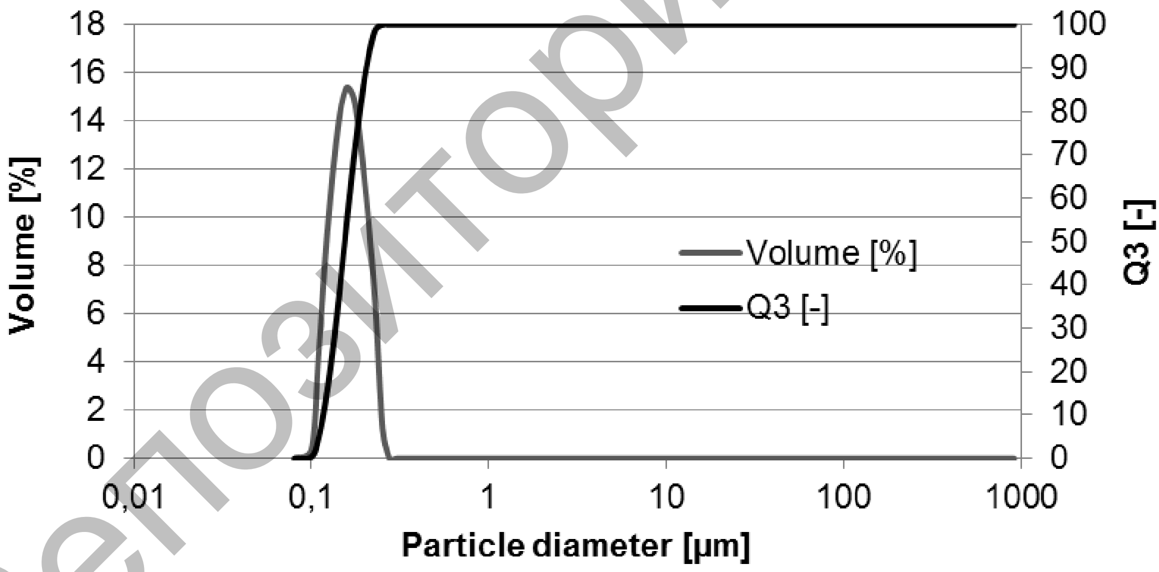

Fig.6. The final volume fractions and cumulative particle size distributions in the fine product of the hydrocyclone.

As can be seen, the overflow contains only particles < 0,3 µm. The chemical analysis of this Silicon-concentrate have shown that Si contents 90 – 95 % may be achieved. Due to the high specific surface the Si-particles are covered with silicon oxide and adsorbed metal ions of this product . This indicates the limit of the physical Si-recycling. Even acid leaching did not deliver an acceptable cleaning to produce high grade solar silicon.

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5. Thermo-chemical separation of Silicon

The goal of these tests was to successfully perform the hydrochlorination of silicon metal in waste filter cake and to recover a condensed sample of the product, trichlorosilane (TCS). By-products of this reaction include also dichlorosilane and silicon tetrachloride. The reaction summary is written below.

$3\ HCl\ (g) + Si\ (s) \rightarrow SiHCl_3\ (g) + H_2\ (g) - 218\ kJ/mol$

Details on the chemistry of this reaction can be found for example in [4-6].

This equation requires gas to solids contact. Fluid bed treatment provides excellent solids-gas contact and heat transfer. Hydrogen chloride is thereby used as the fluidizing gas stream in an indirectly-heated fluid bed reactor with integrated filter head. The process gases used included only anhydrous HCl and nitrogen. For each test, a quantity of starting solids was loaded, heated to temperature under nitrogen, and reacted with HCl gas.

The starting material for these tests was in the form of solid dispersed filter cake, containing silicon carbide (60-80%), iron (5-10%), and silicon metal (15-30%).

The process employed to accomplish the objectives of the testing involved the use of a fluid bed reactor system, using nitrogen and hydrogen chloride as fluidizing gases. The solids bed was loaded, fluidized on nitrogen, and heated to the operating temperature where the reactant gas, HCl, was introduced either at 100% concentration or as a partial atmosphere in nitrogen.

6. Lab scale

The experiments were carried out at a flow apparatus [4], shown in Fig. 7. The test rig was equipped with a glass-vibration reactor of about 35 ml volume. The reactor is equipped with a rotating vibrator, which leads to a fluidized bed of the reactive silicon-containing material. The experiments were carried out at atmospheric pressure and the specified reaction temperatures. HCl was used undiluted. All experiments were executed with a HCl standard flow rate of 1.26 l / h (room temperature). The reactor heating was an electrically operated radiant oven. The reaction products were analyzed online by gas chromatography.

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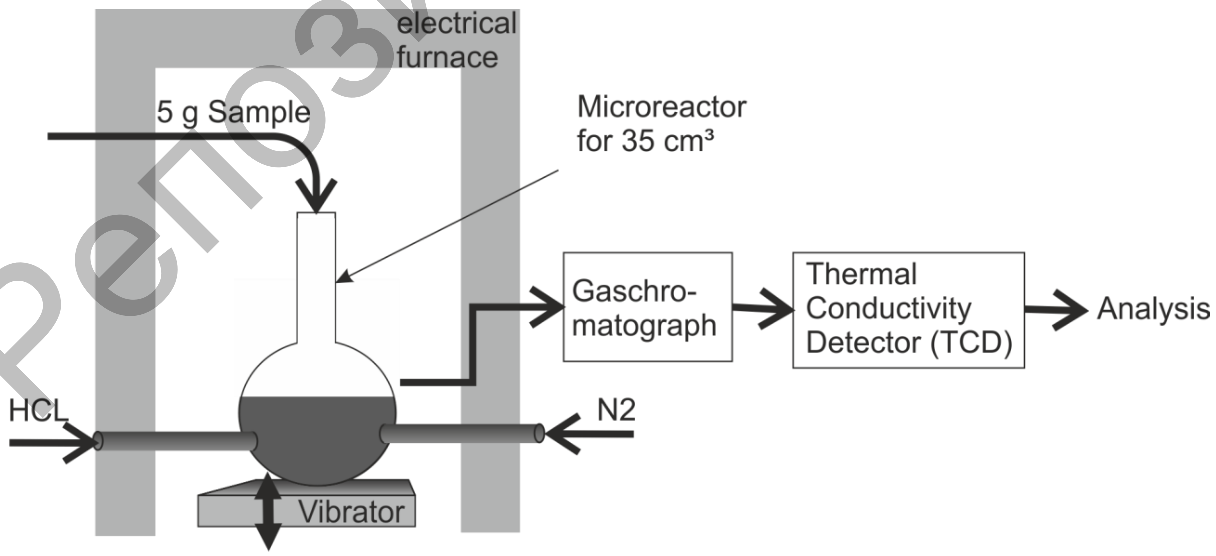

Fig 7. Test Rig for trichlorosilane (TCS)-Synthesis.

The gas chromatogram in Fig.8 indicates trichlorosilane (TCS) dichlorosilane (DCS), and silicon tetrachloride (STC) as products of the reaction.

Product selectivities are dependent on the reaction conditions, especially temperature, residence time and catalytic additions.

The use of Cu powder and CuCl as potential catalysts for accelerating the reaction and / or influencing the selectivity has been tested. These additions have a marked effect on the reaction and may even be a precondition for the technical usability of the TCS- reaction. Under appropriate conditions (variation of T and catalyst) high HCl - recoveries of about 90% TCS, and on the other hand even high selectivities of 90% can be achieved.

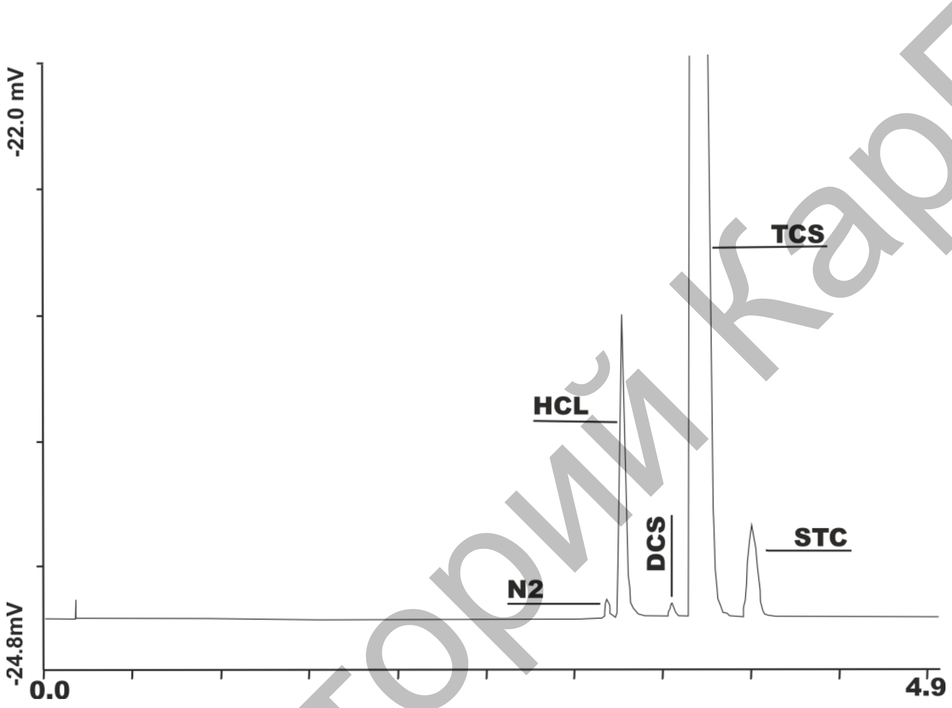

Fig. 8. Typical gas chromatogram of chlorination.

A typical run of completeness and selectivity of the reactions is shown in Fig. 9.

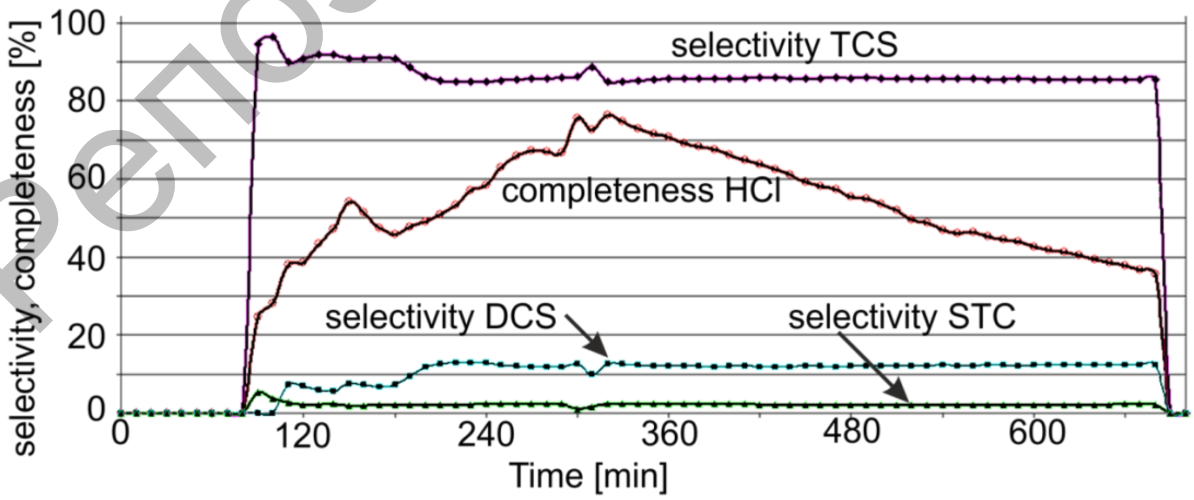

Fig 9. Typical run of completeness and selectivity of the reactions.

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Figure 9 indicates that the reaction at the beginning is inhibited and starts at the reaction temperature of > 330 ^{0} C after 80 min, than developing with increasing completeness of the reaction. The resason for the inhibition may be the blockage of the Si-surface by oxide layers [6].

7. Pilot scale

Referring to Fig. 10, a series of experiments were performed using a 6”-diameter fluid bed reactor constructed entirely of high temperature alloys, with graphite gaskets for the flange connections. The unit was equipped with a screw plate gas distributor and Fines Retention Filter System. Nitrogen was used as blowback gas to clear filters. This vessel was submerged in an electric indirectly heated fluidized Sand Bath. A custom manifold was constructed to meter both nitrogen and hydrogen chloride.

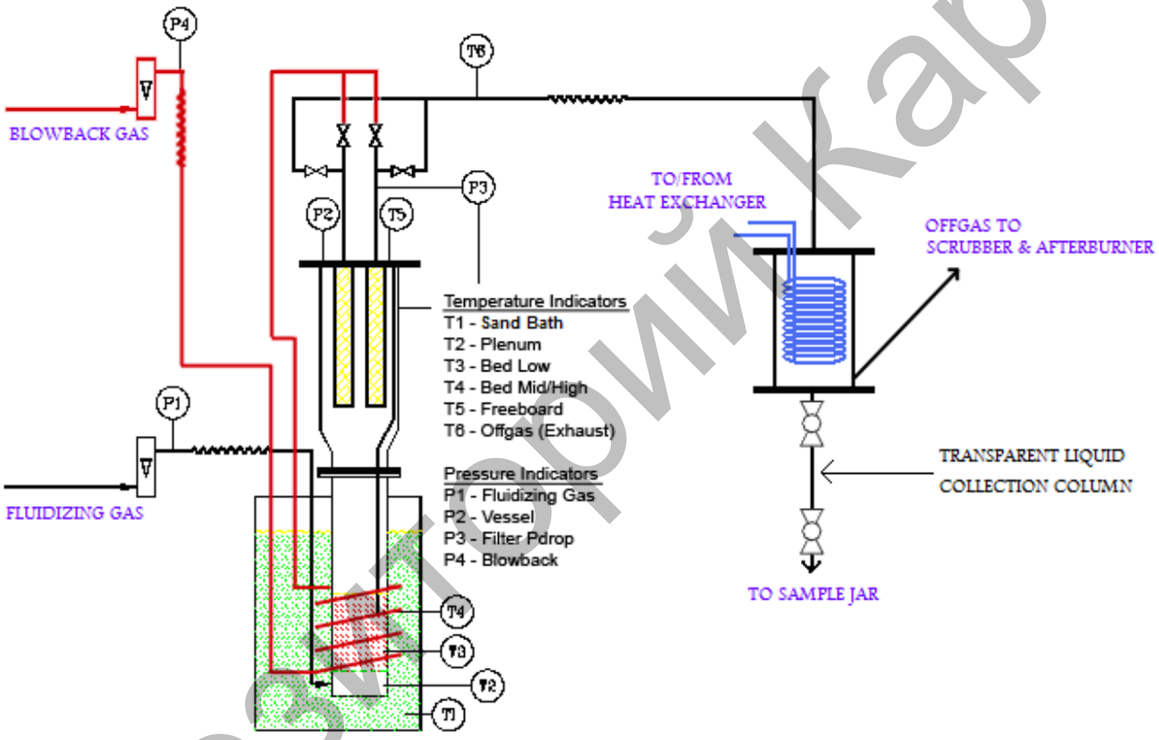

Fig. 10. Pilot scale fluid bed system [8].

The hydrochlorination reaction is exothermic, increasing the temperature of the solids bed. Total flow rate of gases were maintained to keep the solids bed fluidized. These bed temperatures were controlled by limiting HCl in the fluidizing gas.

The reaction is exothermic and the rate of the reaction, once the activation energy is sufficient, increases as the temperature is driven up according to Arrhenius equation. In perfect fluidization, this additional heat is transferred evenly within the fluidized solids bed. Fluidizing gas enters the reactor, is in contact with the solids bed, and exits the reactor through the filters. Also exiting the filters is any additional blowback gas clearing the filters. Certain exothermic activity was seen throughout the solids bed in the familiar trend seen in Fig.11. This is characterized by an increase in the upper bed temperatures followed by a delayed, higher temperature increase in Bed Low. The temperature profile indicates the strongly exothermic character of the reaction. To stabilize the reaction, at high temperature gradients the dosage of HCL was down regulated.

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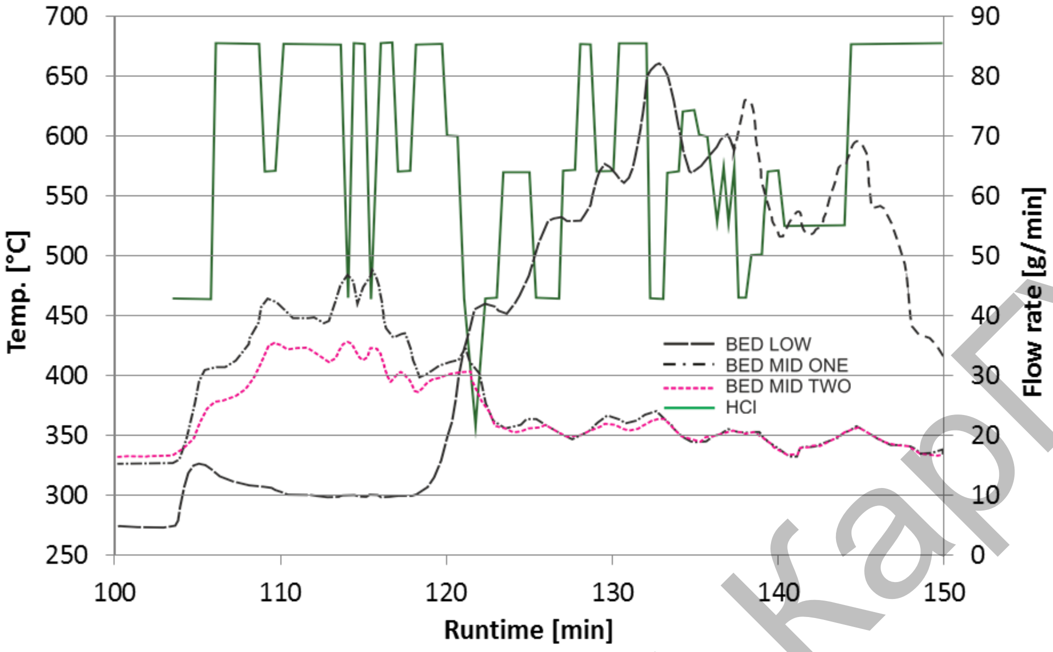

Fig.11. Temperature Profiles and HCL Mass flow Rate [8].

A condenser was built to condense liquids and solids in the reactor off-gas generated during the tests. The single stage condenser was cooled by solid carbon dioxide (dry ice) in a bath of ethylene glycol, which held the condensate/vapor stream between -10°C to -20°C. The temperature is enough to condense the compound of interest, trichlorosilane, as well as other by products of the reaction. The solids bed was loaded, fluidized on nitrogen, and heated to the operating temperature where the reactant gas, HCl, was introduced either at 100% concentration or as a partial atmosphere in nitrogen.

The batch, which was deemed the most successful of the trials, exhibited a mass loss of 37.1% the material loaded. If 10% was lost from iron hydrochlorination and 5% to volatiles, then a 22.1% is likely lost due to silicon reaction. This mass loss falls well within the determined silicon content of the feed.

Summary

In recent years the problem of recycling of SiC and PEG to the sawing process has achieved substantial progress. The recycling of SiC from wafer sawing slurry is already used industrially.

High modern technology fulfills the following requirements:
a) PEG and SiC can be produced of a quality, comparable with virgin material,
b) the recycling products can be user-friendly handled,
c) environmental aspects for the separated residues are considered.

An enhanced outsourced system in a stationary plant prefers a multistage technology. The recycling plant consists of following steps: separation of PEG, cleaning of PEG, centrifugal separation of SiC, cleaning of SiC, drying and conditioning of SiC.

However, Si –recycling from wafer sawing residues is much more difficult and challenging. Methods for this are actually still in the development. Concerning Si there are two concepts for the recycling:

a) Production of a low grade metallurgical Si or production of solar Si. This can be achieved using physical separation processes. The options and limitations of physical separation processes are reported.

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b) High grade solar Si can be produced applying combined physical and chemical treatment considering a special chemical technology were Si is reacting with chlorinated acid to trichlorosilane.

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