

Methods of trichlorosilane synthesis for polycrystalline silicon production.

Part 1: Direct synthesis

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Abstract

Novel technical solutions and ideas for increasing the yield of solar and semiconductor grade polycrystalline silicon processes have been analyzed. The predominant polycrystalline silicon technology is currently still the Siemens process including the conversion of technical grade silicon (synthesized by carbon-thermal reduction of quartzites) to trichlorosilane followed by rectification and hydrogen reduction. The cost of product silicon can be cut down by reducing the trichlorosilane synthesis costs through process and equipment improvement. Advantages, drawbacks and production cost reduction methods have been considered with respect to four common trichlorosilane synthesis processes: hydrogen chloride exposure of technical grade silicon (direct chlorination, DC), homogeneous hydration of tetrachlorosilane (conversion), tetrachlorosilane and hydrogen exposure of silicon (hydro chlorination silicon, HC), and catalyzed tetrachlorosilane and dichlorosilane reaction (redistribution of anti-disproportioning reaction). These processes remain in use and are permanently improved. Catalytic processes play an important role on silicon surface, and understanding their mechanisms can help find novel applications and obtain new results. It has been noted that indispensable components of various equipment and process designs are recycling steps and combined processes including active distillation. They provide for the most complete utilization of raw trichlorosilane, increase the process yield and cut down silicon cost.

Keywords

trichlorosilane synthesis, polycrystalline silicon.

1. Introduction

1.1. General

The world's total electric power consumption reached ~229 bn. kWh in 2020 and is predicted to show a further 1.4 times growth by 2050 [1]. Along with conventional energy sources (oil, coal, gas and nuclear fission), so-

lar energy conversion is in growing demand. Analysts predict [2] that solar energy consumption will be able to compete with gas generation power consumption by 2025, whereas solar energy consumption growth rate is already ahead of that of the nuclear power. The world's total installed power of solar power plants was 42.3% of total renewable energy sources in 2019 and is predicted to grow to 60.1% by 2050, occupying the leading position among renewable energy sources [1, 3]. The world's total

GNP can resume increasing, showing a \$100 trln. growth, and this will create millions of additional jobs by 2050 if emphasis in economic recovery after COVID-19 is put on renewable energy sources. Solar energy has now become a leading segment of the world's electric power industry by total annual investments (~\$150 bn./year) and by the total power of newly built plants (>100 GW/year) [4].

1.2. Production of photovoltaic converters

The basic photovoltaic converter technologies have undergone important changes over the last 20 years of rapid photovoltaic engineering development. While in the second half of the 2000s the material having the largest market share for photovoltaic module fabrication was polycrystalline (multicrystalline) silicon, today we obviously observe the transition to more efficient single crystal solar cells which will dominate in the world's markets in the nearest future (Fig. 1).

In 2018 the market share of single crystal silicon photovoltaic cells was 46% but in 2020 the highly efficient single crystal silicon photovoltaic converters increased their market share to 79%. Silicon cost is 25–30 % of total solar cell cost.

1.3. Polycrystalline silicon market situation

The world's greatest share of polycrystalline silicon production in 2020 was concentrated at 15 companies 11 of which were Chinese. The production capacities of polycrystalline silicon companies grow permanently, by 8–12 % annually on the average, and are currently estimated at 660–675 ths. t [5, 6]. The world's polycrystalline silicon production leader is China. By the end of 2018 its polycrystalline silicon production capacity was 388 ths. t whereas the total polycrystalline silicon production volume in the rest of the world was 210 ths. t [7]. It is predicted [8] that by the end of 2020 Chinese companies will produce 450 ths. t of polycrystalline silicon. In 2020 approximately 81% of the world's total silicon production was provided by the so-called Big Six. The polycrystalline silicon production capacities of the Big Six are summarized in Table 1 [9].

The current production potential of the Big Six has already exceeded the world's total silicon production of 2016. These companies do not provide their exact polycrystalline silicon production volumes only showing their sales amounts or equipment utilization rates which are typically 0.86–0.90.

Whereas polycrystalline silicon production for photovoltaic converters varies depending on demand by solar cell companies and exhibits a growth trend until 2025 [4–7], the production of high purity polycrystalline silicon for microelectronics and high power semiconductor devices has been almost constant over the last 5–7 years, at ~ 35,000 tpy. After the 2008 price peak (up to 500 \$/kg) caused by rapid solar energy industry growth and backward raw materials production facilities the polycrystalline silicon cost in the world's markets has dropped by several times and is currently less than 12 \$/kg [5–7, 9]. One of the polycrystalline silicon production leaders, the Dago New Energy Co., cut down its production costs in the second quarter of 2020 to 5.86 \$/kg [10]. The influence of price damping and the trade barriers created by China for foreign suppliers has caused some companies that used to be among the leading polycrystalline silicon producers, e.g. Hemlock (US), REC (Norway), OCI-Poly (South Korea) and Sun Edison (US), to shrink or completely halt their production and cut down jobs. State investments, subsidies and preferential electric power prices for domestic companies combined with high polycrystalline silicon importation duties are the key strategy components of China which tends to become completely independent of foreign supplies [11].

Table 1. Production capacities of the Big Six [9]

#	Polycrystalline silicon company	Production capacity, tpy
1	Tongwei Co. Ltd	96,000
2	GCL Poly	90,000
3	Wacker	84,000
4	Dago New Energy	80,000
5	Xinte Energy	80,000
6	East Hope	80,000

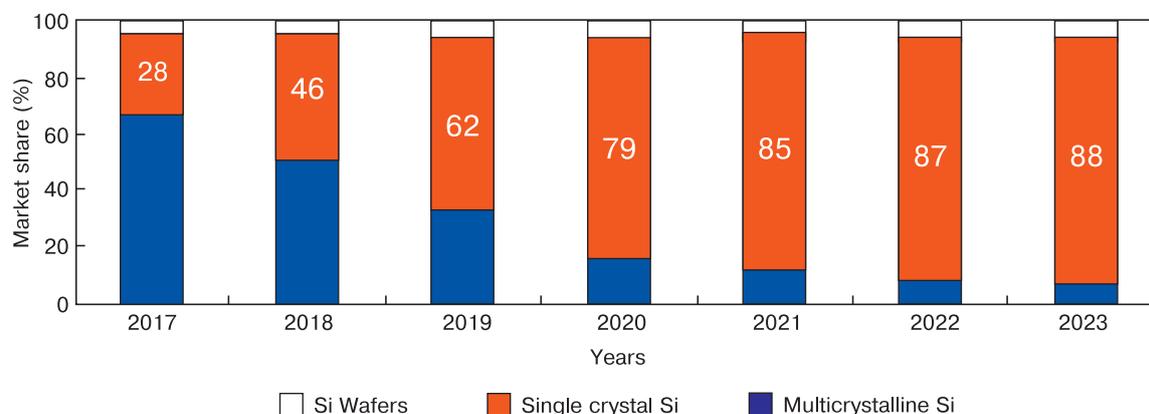


Figure 1. Use of different crystalline silicon types in photovoltaic converter technologies [4].

Establishment of private production companies “in line with the market strategy” in the former Soviet Union States has led to no success. The State has not either been eager to assume much of risks related to production premises design and construction, high quality production facilitation and product sales. Investments have not been aimed at global support of silicon industries. One should however bear in mind that export oriented production makes semiconductor industry vulnerable to sanctions especially when it comes to double purpose products. Fabrication of semiconductor devices and ICs from unknown quality silicon and purchases of electronics components in circumvention of authorized supply chains may lead to severe counterfeit problems. This policy is especially dangerous for the production of high power electronics and microelectronics components and the development of space and defense projects where special custom designed components are required. Joint use of electronics components from European and Asian suppliers will require establishing cooperation with new suppliers resulting in production stoppage and time loss.

It is therefore of utmost importance today to change the development model of domestic semiconductor grade silicon industry: we should change to producing provable high quality components while keeping costs low and ensuring environmental safety.

Cutting down polycrystalline silicon production costs can be achieved through the following steps:

- expanding the production (scalability factor): polycrystalline silicon production volumes of above 5000 tpy provide for silicon production cost cut down;
- power consumption reduction: many companies combine technical refurbishment of facilities and use of power saving equipment with building of their own power plants [9];
- reduction of main raw materials consumption for polycrystalline silicon production.

The key raw material for polycrystalline silicon production in the Siemens process and in the monosilane process is trichlorosilane. The trichlorosilane share in polycrystalline silicon cost is 12–18 % depending on technology used. The trichlorosilane market is mainly driven by the polycrystalline silicon market and grows on the average by 6.4% annually. It will reach \$10 bn. by 2025 [12].

Many publications [13–16] pointed out the similarity of the main process steps in various options (layouts) of the Siemens process and silane process:

- a) production (synthesis) of volatile silicon compounds;
- b) purification of volatile silicon compounds;
- c) decomposition of volatile silicon compounds to elemental silicon;
- d) disposal and recycling of by-products.

Large capital expenses combined with low polycrystalline silicon prices restrict potential capital investments into fundamentally new production premises and thus prevent innovations [17]. For this reason polycrystalline

silicon companies currently prefer to improve their existing main processes and concentrate their efforts on proven technologies. The urgent need to cut down polycrystalline silicon cost stimulates the search for and choice of the most efficient trichlorosilane synthesis methods regardless of whether it comes from a third-party supplier or is synthesized in-house.

The aim of this work is to analyze existing methods and approaches to trichlorosilane synthesis for the production of solar and semiconductor grade polycrystalline silicon.

2. Trichlorosilane synthesis

2.1. General

Trichlorosilane is the key raw material for silicon production both in the Siemens process and in the silane process. It is currently synthesized by hydrogen chloride exposure of technical grade silicon, homogeneous hydration of trichlorosilane, tetrachlorosilane and hydrogen exposure of silicon, sometimes with hydrogen chloride addition, and catalyzed tetrachlorosilane and dichlorosilane reaction.

The former of the above methods is the best known and most widely used one and is referred to in scientific and patent literature as direct synthesis or silicon hydrochlorination, most recently it has been suggested to use the term “direct chlorination” [18, 19].

The second method is known as tetrachlorosilane hydration (tetrachlorosilane conversion). It is used to convert tetrachlorosilane forming as a result of silicon deposition to trichlorosilane.

The third method formerly known as tetrachlorosilane hydration is currently referred to as silicon hydrochlorination.

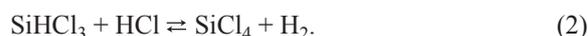
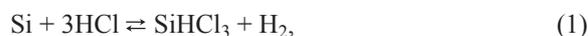
Chinese research teams use the term “cold hydration” or “cold conversion”. This definition is used to describe the processes occurring during tetrachlorosilane conversion to trichlorosilane at lower temperatures (~535 °C) as compared with homogeneous hydration (conversion) which is carried out at ~1200 °C.

The fourth method developed more recently is referred to as redistribution or anti-disproportioning. For this method trichlorosilane is synthesized by catalyzed tetrachlorosilane and dichlorosilane reaction.

We will hereinafter use the newer terms.

2.2. Trichlorosilane synthesis by direct chlorination or direct synthesis

The process includes the following main reactions:



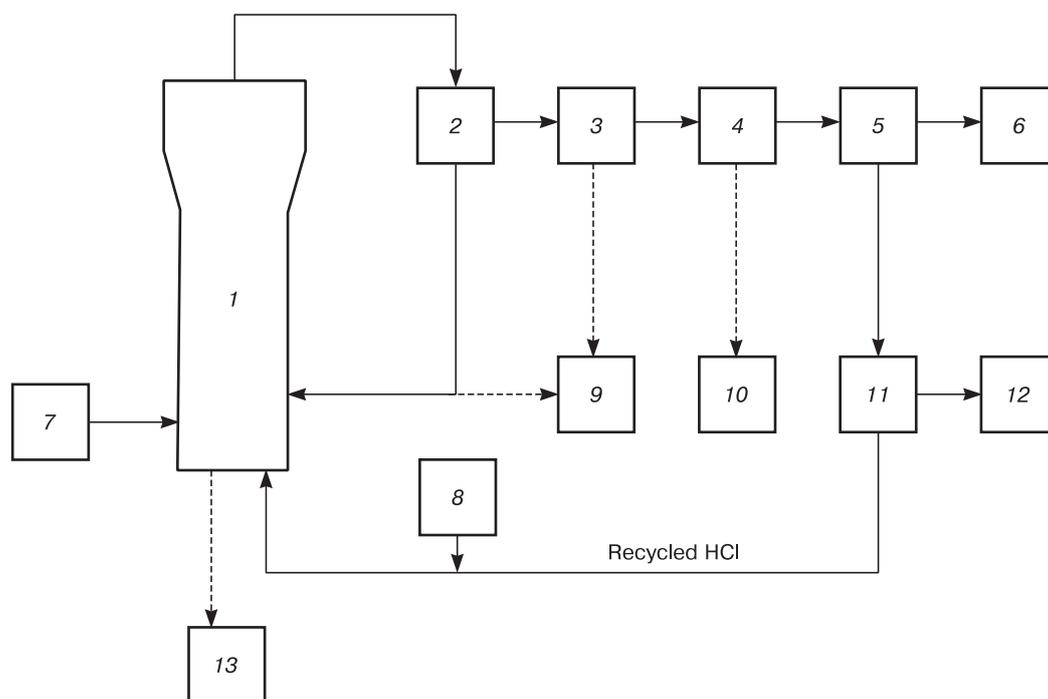


Figure 2. Diagram of trichlorosilane synthesis by direct chlorination adopted at Wacker [22, 29]: 1 is fluidized bed reactor, 2 is cyclone separator, 3 is filtering system, 4 is AlCl_3 separator, 5 is condenser, 6 is chlorosilane mixture container, 7 raw metallurgical grade silicon particle, 8 is fresh HCl feed, 9 is silicon dust container, 10 is AlCl_3 container, 11 is effluent gas separator, 12 is recycled hydrogen, 13 is silicon waste.

Along with the target product, i.e., trichlorosilane, the process also leads to the formation of tetrachlorosilane, dichlorosilane as well as high boiling point and low boiling point products with Si–Si or Si–O–Si compounds. Industrial synthesis requires process conditions providing for the highest trichlorosilane selectivity, pre-set tetrachlorosilane content and high hydrogen chloride conversion rate. The mechanisms of reactions (1) and (2) were studied under laboratory conditions by many researchers [19–25]. The standpoints suggested regarding tetrachlorosilane formation [20–24] were later confirmed experimentally [25]. Tetrachlorosilane was shown to form as a result of consecutive reaction (2) and is in

fact a trichlorosilane by-product. The reactions during trichlorosilane synthesis by direct chlorination or direct synthesis are affected by metal impurities in the raw technical grade silicon. This effect of impurities will be considered in greater detail later.

Different aspects of industrial trichlorosilane synthesis were described elsewhere [22, 26–29]. The basic diagram of trichlorosilane synthesis by direct chlorination adopted at Wacker Chemi AG (Germany) is shown in Fig. 2.

The main factors affecting direct organic silane synthesis were identified earlier [30, 31]. They are also valid for trichlorosilane synthesis by direct chlorination and will be considered below.

Table 2. Typical compositions of different silicon grades [32]

Element	Metallurgical grade silicon (ppm)	Solar grade silicon (ppm)	Electronic grade silicon (ppm)
Si	98–99%	99.9999% (6N)	99.9999999% (9N)
Fe	2000–3000	< 0.3	< 0.01
Al	1500–4000	< 0.1	< 0.0008
Ca	500–600	< 0.1	< 0.003
B	40–80	< 0.3	< 0.0002
P	20–50	< 0.1	< 0.0008
C	600	< 3	< 0.5
O	3000	< 10	—
Ti	100–200	< 0.01	< 0.003
Cr	50–200	< 0.1	—

Effect of silicon impurity composition

Typical compositions of metallurgical grade silicon, solar grade silicon and electronic grade silicon are summarized in Table 2 [32].

Intentional doping of high purity silicon with respective impurities and subsequent direct trichlorosilane synthesis from the samples [25] revealed the effect of iron group elements on the trichlorosilane selectivity, the sequence being as follows: Ni > Co > Fe. It was shown later [33] that Fe and Al in silicon reduce the onset temperature of reaction (1). The iron-rich Al–Fe–Si phases cause the formation of FeCl₂ which is accumulated in the reactor. Silicon silicide FeSi₂ is inert to HCl atmosphere. The iron-rich Al–Fe–Si phases interact actively with hydrogen chloride and transfer to the gaseous phase. The solid Al₂CaSi phase affects the surface of parent silicon and increases the process onset temperature. The selectivity of trichlorosilane synthesized under laboratory conditions is always higher than for industrial reactors [23, 33]. The reactions during the synthesis change due to the changing types of impurities and do not correlate with mass silicon analysis. Studying the so-called inductive phase during the direct synthesis process [34] the authors concluded that hydrogen chloride adsorption on the silicon surface is accompanied by chlorine diffusion into the bulk phase. Therefore along with the chemical composition of metallurgical grade silicon one should take into account the distribution of intermetallic phases in silicon, the presence of slag inclusions and pores and the distribution of crystalline grains [35]. The interaction of silicon with hydrogen chloride is inhibited by the oxide film on the silicon surface. Silicon surface can be passivated as a result of other processes, e.g. the formation of surface compounds or layers restricting the inflow of hydrogen chloride to the reaction surface [36]. These passivating layers can be broken (destroyed) by increasing the process temperature or through special pretreatment of silicon for direct chlorination.

Effect of silicon pretreatment on its reactivity

Different methods of silicon pretreatment for direct chlorination have been reported, e.g. crushed silicon exposure to fluoric or sulfuric acids [30]. Metallurgical grade silicon crushing in a vibratory mill with simultaneous supply of hydrogen chloride to the bulk was reported [37]. According to a patent disclosure, bulk silicon is first molten and then solidified using a direct crystallization process [38]. The contaminated portion of the ingot is discarded and the cleaner one is destroyed with an underwater electric discharge. Then the material with a 100–1000 μm grain size is acid etched. In accordance with another technical solution [39] which is counterpart of the one described above [38], metallurgical grade silicon is initially crushed with an underwater electric discharge following which the powder is chemically etched, dried, vacuum melted and solidified using a direct crystallization process. A simpler technique suitable for direct trichlorosila-

ne synthesis is water granulation of silicon [40, 41]. Water granulated silicon exhibits higher reactivity as compared with conventional bulk silicon [22].

Powder trapped in the effluent gases and settled down in the filters and cyclone separators downstream the reactor can be magnetically separated in an inert gas atmosphere by applying a magnetic field with a 1–1.7 Tl induction [42]. The low-impurity silicon-rich nonmagnetic fraction is directed to the reactor while the magnetic fraction is further processed or disposed of. Thus silicon pretreatment for synthesis helps improving the reactivity of silicon surface by removing crystal defects, passivating layers and inhibiting factors. One should also bear in mind that silicon from different suppliers (and even different batches from the same supplier) may have different reactivity. If the reactivity of silicon is insufficient the hydrogen chloride content in the reactor effluent gases increases and hence the load on the regeneration system grows. High reactivity of silicon leads to the formation of overheated zones in the fluidized bed. This results in a higher tetrachlorosilane content and hence lower trichlorosilane selectivity [22].

Effect of temperature and pressure on the reactivity of silicon

Since the silicon reaction with hydrochloride is rapid and is accompanied by large heat release, it is important to maintain the process temperature within the preset limits. At 260 °C the trichlorosilane concentration in the reaction products is 95 wt.%, at 400 °C it is ~ 70 wt.%, at 600 °C it is ~40 wt.% and at 800 °C it is ~ 20 wt.% [43]. To maintain the required process temperature one can install recirculation cooling water or oil piping in the reactor [43]. Also possible is to use multiple small diameter pipes¹.

Delivery of ~80 μm silicon particles to the fluidized bed reactor increases the trichlorosilane selectivity and reduces production costs [45]. Addition of these particles forming at the bulk silicon production stage (dusty wastes) stabilizes the fluidized bed temperature.

Maintaining constant fluidized bed temperature and increasing trichlorosilane yield are also possible through recycling of low boiling point by-product compounds or introduction of high boiling point compounds from synthesis products or from silicon deposition stage during chlorosilane hydrogen reduction [47]. In accordance with earlier technical solution [48] polycrystalline silicon production wastes containing high boiling point polysilanes mixed with hydrogen chloride are supplied to the furnace for decomposition at 450–700 °C. The decomposition product is delivered to the reactor. The synthesis process can be controlled through reactor cooling as well as high-precision control of the metallurgical grade silicon supply rate to the fluidized bed and the reaction zone temperature profile (± 1 °C) [49]. However due to the necessity of using multiple temperature gages for this me-

¹ Pat. CN 101279735; Pat. CN 101125654.

thod, optimum trichlorosilane selectivity and hydrogen chloride conversion are hardly achievable. A technical solution was therefore suggested [50] that includes initial separation of aluminum chloride from the effluent gases and further control of its composition by chromatography or spectral analysis. The required temperature profile in the fluidized bed is maintained using an empirical formula that takes into account reactor height.

High pressure process (0.18–0.5 MPa) allows increasing trichlorosilane content in the synthesized vapor/gas mixture. This result was attributed [49, 51] to an improvement of the fluidized bed structure and removal of stagnation zones in which overheating and surplus silicon tetrachloride formation are possible. The optimum trichlorosilane synthesis process pressure is 0.4 MPa as determined under laboratory conditions [51].

Effect of gas atmosphere composition delivered to reactor

Thermodynamic calculations of direct chlorination showed that hydrogen supply to the reactor increases trichlorosilane yield and makes the system more stable against misbalance [52].

In accordance with earlier patent [53] chlorosilanes are first separated from the effluent gases, the remainder hydrogen-rich mixture being recycled to the reactor after mixing with hydrogen chloride. The HCl : H₂ partial pressure ratio in the mixture is maintained at 1 : 1 – 1 : 50. At HCl : H₂ = 1 : 4 the chlorosilane mixture will contain more dichlorosilane [54]. It should be noted that supply of hydrogen (and sometimes nitrogen [55]) may lead to a negative result. The fluidized bed starts bubbling, with the bubbles locally mixing and forming “fountains”. This results in trichlorosilane and hydrogen chloride emission from the layer, higher load on downstream effluent gas trapping chain, and complicated rectification and chlorosilane separation.

Effect of catalysts

Catalyzed direct trichlorosilane synthesis processes in which the catalysts improve trichlorosilane selectivity have been mainly described in patent literature (Table 3).

However patent research data that are property of relevant companies can hardly be reproduced under industrial conditions, e.g. the catalytic properties of chromium have not been confirmed [25]. The effect of copper on trichlorosilane synthesis has been studied in quite a detail [26]. The suggested reaction diagram was described earlier [56].

Effect of reactor design

Trichlorosilane is synthesized by direct chlorination mainly with the use of fluidized bed reactors. Some designs of these reactors are presented in Fig. 3.

Many fluidized bed parameters, i.e., temperature, height, silicon particle size and fraction, have a critical effect on the entrainment processes during synthesis and eventually on the process efficiency. Fluidized bed parameters for trichlorosilane synthesis have been discussed in detail [26, 57]. Many improvements affecting flow thermodynamics in the reactor have also been reported². New generation reactors by Wacker, Germany [22] provide for an almost 100% hydrogen chloride conversion rate. The hydrogen chloride content in the effluent gases decreases and the gas separation efficiency in the trapping system increases.

The new generation reactors improve the trichlorosilane selectivity of the process and allow maintaining the required SiHCl₃:SiCl₄ ratio in the synthesized products. They significantly reduce dust removal from the layer thus reducing waste. Furthermore they allow a more detailed control of the reaction mass composition. Search for the optimum reactor design is still underway, reactor designs being developed and improved taking into account reactor operation experience at respective companies. Results of this work are not in public domain.

Reactor design improvement is combined with search of materials for reactors and other plant components (cyclone separator, heat exchanger, piping etc.). Carbon steels that are stable against dry hydrogen chloride undergo intense corrosion under trichlorosilane synthesis

² Pat. US 20179758384, 2017; Pat. WO 2012048494, 2012; Pat. US 200910123359, 2009.

Table 3. Catalysts used for direct trichlorosilane synthesis

Catalyst	Patent	Authors	Company	Date published
Cr	US 7462341	Hoel J.-O. Rong H.M. Roc T.	Elkem AS (NO)	09.12.2008
Ti, P	EP 3013745	Sobota M. Alber A.	Wacker Chemie (D)	04.05.2016
Fe, Cu, Al, V, Sb	US 20090060818	Bill Jr., John Merkh C.	Dynamic Engineering (USA)	05.02.2009
Ba, Cu	WO 2012021064	Hoel J.-O. Kjenli H. et.al.	Elkem AS (NO)	16.02.2012
Al	DE 102012103755	Mockel M. Keck Chr.	Centrotherm Si Tec GmbH (D)	31.10.2013
Cu	US 2943918	Panlis G.	Pechiney SA (Fr)	05.07.1960
	WO 2011075836	Dold P. et.al.	Arise Tech Corp (USA)	30.06.2011

conditions due to the presence of trace moisture especially for cyclic production. Silicon particles involved in the process are very hard and have an abrasive effect on the protective silicide layer. Pit and crevice corrosion occurs. Carbon steels undergo embrittlement under high and very high pressures. The middle section of the reactor requires repair approx. every 36 weeks of service and replacement every four or five reactor campaigns. Corrosion tests [28, 59] showed high corrosion resistance of the Hastelloy B-2 Ni–Mo alloy and high nickel and chromium stainless steel (Inkolloy 800H), the corrosion

rates being 0.7–1.2 mm/year. Reactors can be made from alloys containing at least 40% Ni [60]. At more than 95% Ni content the alloy should contain 0.5–4.0 wt.% titanium. The same alloy³ is used for inner reactor walls for operation at $T > 190$ °C. Study of corrosion mechanisms during trichlorosilane synthesis showed that the effect of silicon particles and reactor pressure on the wear resistance of the steels and alloys used in reactor design should be taken into account [61]. High nickel and chromium

³ Pat. DE 3739578, 1988.

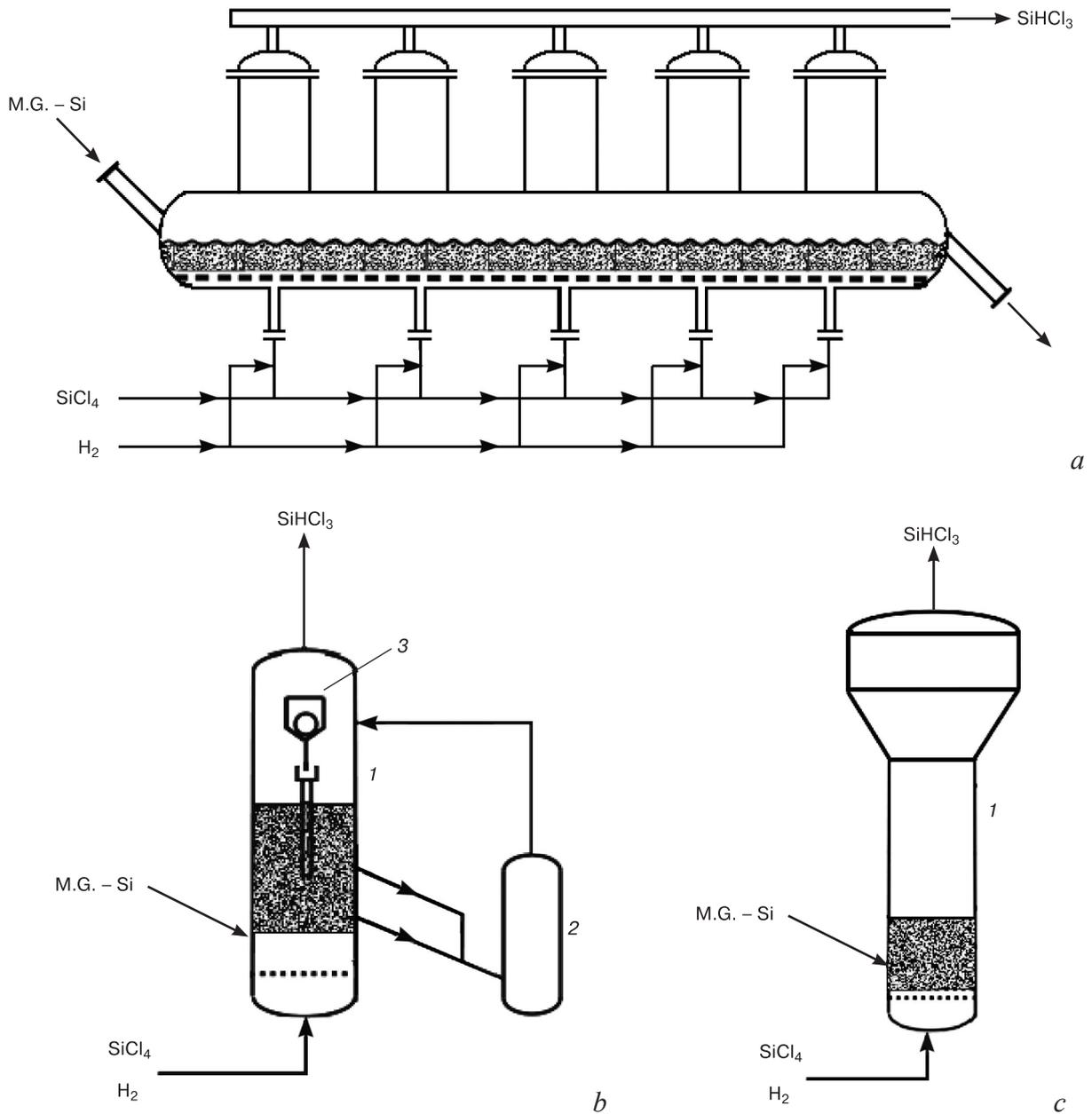


Figure 3. Some designs of direct trichlorosilane synthesis reactors: (a) multistage trichlorosilane synthesis reactor: silicon particles are fluidized in several interconnected zones that may have different composition ratios of reaction gas and supplied raw material (Pat. US 8778292, 2014); (b) two reactors (1 and 2) work in parallel: silicon particles can be directed from the first reactor to the second one; reactor 1 has selective separator 3 for Si particles (Pat. DE 102009037155, 2010); (c) reactor 1 has water cooled piping and operates at 0.5 MPa pressure; the fluidized bed temperature is maintained accurate to 1 °C; silicon supply rate to the fluidized bed is maintained accurate to 5% (Pat. US 20110297884, 2011).

steels showed high corrosion resistance. Alloy 625 has a corrosion resistance of 0.45 mm/year, Alloy 617 has that of 0.59 mm/year, and that of austenitic steel is 1.3 mm/year. For comparison, Steel Grade 12Kh18N10T in a trichlorosilane synthesis reactor (330 °C) exhibits a corrosion rate of 3 mm/year while Steel 10Kh17N13M2T in a hydrochlorination reactor (600 °C) corrodes at a 1 mm/year rate [62]. This corrosion rate for weld joints increases to 2.4 mm/year.

Known are reactor wall corrosion protection methods with carbon [37] or tungsten carbide coatings⁴.

However the use of nickel based high-alloy steels and alloys for reactors significantly increases trichlorosilane production costs while failing to completely solve reactor corrosion and wear problems. Coating large area surfaces with tungsten carbide or silicon carbide is a complex technical task. Currently there are studies of the corrosion resistance under trichlorosilane synthesis conditions for a

cheaper steel AISI316L containing 10.0–13.0% Ni; 2.0–2.5% Mo; 16.5–18.5% Cr; 2.0 % Mn; 0.045% P; 1.0% Si; 0.030 % C [63].

Another solution of reactor wall corrosion and wear problems was suggested [64]. A grid made of drawn perforated steel sheet is welded onto the reactor wall. The grid is coated with suspension from a cementing solution with silicon carbide, boron nitride silicon nitride zirconium dioxide or aluminum nitride particles. The cement also contains additions (fillers) selected from groups of oxides: SiO₂, Al₂O₃, TiO₂, CrO, Fe₂O₃. The thickness of the coating solution layer may be 5–50 mm. The cementing layer is dried at room temperature for 10–30 days, following which the reactor is put into operation. After 65 weeks of service the cementing coating should be removed and a new coating layer should be applied. The reactor can be operated at 300–600 °C and 10–30 MPa, the guaranteed service life being up to 12 years.

⁴ Pat. WO 2008/088465, 2008.

Continued see issue 7(2)

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