10,000 MTA Polysilicon Plant Commercialization Comparison

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ABSTRACT

A 'hybrid' TCS-Siemens process to save operation cost caused by energy consumption and equipment investment cost from processes for TCS (Trichlorosilane) synthesis and converting of STC (Silicon Tetra Chloride) into TCS in a TCS-Siemens process for polysilicon plants size over 10,000 MT/YR is provided. The hybrid TCS-Siemens of current introduction is equipped with a direct chlorination FBR (Fluidized Bed Reactor), which is disclosed in the U.S. Patent Application Publication No. 20100264362 of the applicants of current invention.

Three different TCS-Siemens processes of;

1) a traditional TCS- Siemens Process that uses 'thermal converter' for STC to TCS conversion,
2) a 'Closed Loop Hydro Chlorination TCS-Siemens Process' using a FBR, which is REC type FBR that is designed to produce Silane gas, but that claims to convert STC to TCS at 550 ℃, 25 bar, and
3) a hybrid TCS-Siemens process are compared based on mass balance calculation.

For the processes 1) and 3), mass balances of two different direct chlorination FBRs, traditional direct chlorination FBR that uses internal cooler to remove the exothermal heat from the reaction of HCl with MGSi only, and 'turbo charger' direct chlorination FBR wherein no internal cooler is used instead the 'turbo charger' transfers the exothermal heat to the outer cooling jacket by convectional heat transfer, are compared.

The hybrid TCS-Siemens process equipped with 'turbo charger' direct chlorination FBR saves at least 78,000,000Kwhr per year from TCS generation only in a 10,000 MTA polysilicon plant compared to the same capacity polyilicon plant built by 'Closed Loop TCS-Siemens Process.' Compared with traditional TCS-Siemens Process, the 'Hybrid TCS-Siemens Process' saves 220,000,000Kwhr per year from 10,000 MT/YR polysilicon plant.

Introduction

Since the severe shortage of polysilicon material in 2007, construction of poly-silicon plants has boomed in China. About 48 polysilicon plants were built and after seven years, only GCL (Golden Concord Holdings Limited) produces polysilicon with purity of 9 N.[1)]

On the other hand, situation was much better in South Korea. After 10 years of preparation, OCI (Oriental Chemical Industry) has successfully produced 9N grade polysilicon since 2008. Just after that some other Korean companies built 3,000 MTA scale polysilicon plants. HKS (HANKOOK SILICON) built their plant partly based on PPP (Poly Plant Project, Inc.)'s technology of direct chlorination TCS-Siemens process and equipments. HKS completed their 1st goal of producing 3,000 MTA polysilicon with 9N purity within 2 years and started expand their capacity via "Closed Loop Hydro Chlorination TCS Sienmens Process" to meet customers' request to supply more of their products [2].

Encouraged by the success of their neighbors, some of Korean major chemical companies, such as HANWHA and SMP(50:50 joint venture between SAMSUNG Fine Chemical and MEMC (Monsanto Electronic Materials Company), which later changed to Sun Edison), started build large scale polysilicon plants, which has capacity over 10,000 MTA, to overcome the demerit of late starter and become world class major player. But, recently SAMSUNG Fine Chemical sold part (35%/50%) of their stock share back to Sun Edison.

However, due to decrease of Solar Cell demand from EU (European Union) and over supply from numerous small plants newly built, polysilicon price dropped almost down to 15 $/kg at the 4th quarter of 2013. At this price no polysilicon producer can make profit at all even the largest plant built by "Closed Loop Hydro-chlorination Siemens" process technology.

So, almost every small polysilicon plants in China and some Korean 3rd tier plants had to shut down their plants and even OCI needed to lower their production rate.

The news release from the GCL [3] clearly show that adding 30,000 MT/Yr capacity with "Closed Loop Hydro-Chlorination-TCS Siemens" process could not lower production cost down below 18$/kg polysilicon.

At last GCL announced that they will use FBR (Fluidized Bed Reactor) for producing granular polysilicon to lower the production cost down to 9$/Kg.[4]

Why did they suddenly changed their process from Hydro-chlorination-Siemens CVD, in other words TCS-Siemens CVD process, to Hydro-chlorination-FBR, Silane-FBR process?

To find the answer, we have to fully understand the basic principle of the "Closed Loop Hydro-chlorination" process. That terminology was introduced first time in a series of JPL (Jet Propolusion Laboratory) research report, which is known by another name of 'Sistersville's report.' Later UCC (Union Carbide Corporation) awarded U.S. Patents regarding a process producing granular polysilicon in FBR(s) combined with "hydro-chlorination" FBR. The patents expired on 2004. In that process all TCS (Trichlorosilane) is converted into Silane by 're-distribution' reaction.

Here, let me review how the polysilicon producing processes are progressed.[1] Pre 1985, virtually all polysilicon was produced via 'Direct Chlorination', TCS CVD reactors and 'Thermal Conversion' of STC back to TCS. From 1985 forward two additional technologies were utilized to produce polysilicon. UCC developed to Silane process in confirmation with Silane CVD to produce high purity EG(Electronic Grade) polysilicon. Ethyl Corporation, utilizing alternate Silane production technology, commercialized a Silane to polysilicon FBR process. This process, although with potentially lower OpEx, produced a lower quality polysilicon.

UCC initiated R&D for Silane to polysilicon FBR technology which was further developed by ASiMi (Advanced Silicon Materials Inc.) when Komatsu purchased the UCC polysilicon operation. Final commercialization occurred after REC (Renewable Energy Corporation) purchased the ASiMi polysilicon operation.

In 2009, "Closed Loop Hydro-chlorination TCS-Siemens" process is introduced to the polysilicon plant market. Actually it is changed from the original concept. At the beginning Union Carbide's target is to produce Silane from the "Hydro-chlorination" FBR and feed them to CVD and later, from 2004, to FBR. But, in 2009 version the target chemical is changed from Silane to TCS and FBR is deleted. The process technology package sold on the market was this changed process. Even though this process uses less energy to convert STC to TCS, as they claim, than the 'Thermal Converter', which is used in traditional "Siemens" process, there are many other demerits not well known to outside of this industry.

Due to the inherent nature of the "Hydro-chlorination" FBR reaction system, about 3 times of STC is produced more than the TCS produced. Because of this extra volume of STC, this new "Closed Loop Hydro-chlorination TCS-Siemens Process" technology have some limits to build a single FBR to produce TCS enough for a polysilicon plant that has production capacity over 10,000 MTA.

OCI handled this excess STC by developing "Enervac®" business. Meanwhile, GCL, who acquired "Closed Loop Hydro-chlorination Process" to make TCS and utilize TCS CVDs, recently introduced the ability to make Silane and tried Silane to polysilicon FBR. GCL believes that it will lower the production cost of polysilicon down to 9 $/kg.[4]

PPP is providing proven solutions to the industry and improve the proven technologies for more economical way without sacrificing the quality of the product, polysilicon, from the process.

Hybrid TCS-Siemens Process; a combination of two commercialized processes of 'traditional TCS-Siemens process'and 'Hydro-chlorination TCS- Siemens Process', is proposed and compared with 'Closed Loop Hydro-chlorination TCS- Siemens Process' to find more economical method of constructing a ploysilicon plants of production capacity over 10,000 MTA. Following results are calculated from in-house data of PPP from operating or operated plants of each process.

1. TCS production by direct chlorination and Siemens Process

1-1-1. Traditional Direct Chlorination and FBR (Fluidized Bed Reactor)

Industrial production technologies to produce TCS are developed since middle of 20th century. Table 1 summarized the technologies developed by many different companies.

All of the patents in the Table 1 commonly described that TCS is generated according to the following equation (1) , which is a vigorous exothermal reaction around 300 ℃ and as the temperature goes up a side reaction of the equation (2) dominants and STC is produced more than TCS [5] .

$$2Si + 6\,HCl \rightarrow 2\,SiHCl_3 + 2\,H_2 \qquad (1)$$

$$Si + 4\,HCl \rightarrow SiCl_4 + 2H_2 \qquad (2)$$

Many companies tried to produce TCS commercially from FBR because FBR is known as the best reactor to control vigorous exothermal reactions. However, shortage of proper understanding for the FBR dynamics inside of the fluidized bed results in mistake of inserting cooling coil inside of the fluidizing bed to disturb smooth circulation, convection, of fluidizing bed materials, etc.

Once the fluidization, in other words circulation or mixing, of the bed material is restricted, the heat of the reaction is accumulated inside of the bed and specific portion of the bed temperature raise steeply and forms 'hot spot'.

And if the heat of the reaction (1) continuously accumulated the temperature, in isolated areas of inside the MGSi, which is called the 'hot spot', easily reaches above 600 ℃ and the downside of this elevated temperature, in addition to possible structural damage, is the excess production of STC.

In addition to this, high molecular weight silicon complexes, by-products, are formed at higher temperature. Since these by-products have higher boiling point and viscosity, they usually stay around the bottom of the FBR and plug the nozzles of gas distributor to disturb continuous operation of the FBR.

Due to the above mentioned limitations, all of the commercially known as traditional FBR for TCS production, by direct chlorination, have production capacity limitation and have to shut down every 2~3 months to check the structural damage and to remove the agglomerated MGSi that has sintered to form large particles that cannot fluidize.

1-1-2 'Turbo Charger' Direct Chlorination FBR

PPP has designed and provided a FBR for producing high purity crude TCS to a client on 2008 and the client commercially using the new FBR to produce TCS since Autumn of 2010 for their 3,000 MTA polysilicon plant [2].

Fig. 1 shows the representative feature of the new FBR for producing high purity crude TCS. [6] Two different curves of mean average temperature deviations, from six different locations, inside of fluidizing bed of the new FBR along the reaction time laps are recorded.

The blue line shows the temperature deviation when MGSi and HCl react according to traditional method and the red line shows the temperature deviation when MGSi reacts with HCl in the presence of the 'Turbo Charger'.

The mean average temperature deviation was calculated by averaging the deviations of temperature at each location, six locations, inside of the fluidizing bed from average temperature of the six locations.

Figure 1 illustrates that the mean average temperature in traditional direct chlorination shows deviation over ± 5 ℃ and the deviation fluctuated unstablly during the reaction. Meanwhile, in 'Turbo Charger' method the deviation is stable less than ±1 ℃ even the average

Table1. Granted U.S.Patents disclosing various direct chlorination technologies.

U.S.Patent (year)	Company (Country)	Contents, TCS selectivity
2,943,918 (1960)	Electrometalurgiques (Fr)	Lab. scale, hot spot at the bottom.
3,148,035 (1964)	WackerChemie (German)	Bench scale, cool the bottom.
3,704,104 (1972)	Texas Instrument (USA)	Recycle DCS and STC to cool hot spot
4,044,109 (1977)	Dynamit Nobel (German)	Co-feed iron chloride with MGSI, 85%
4,213,937 (1980)	Texas Instrument (USA)	Commercial, Internal cooling coil, 85%
4,428,198 (1984)	Nippon Aerosol (Japan)	Internal Mixer, GE type FBR, 90~ 95%
4,585,643 (1986)	Union Carbide (USA)	Lab. scale.Oxygen to boost up, 98%

temperature of the fluidizing bed material is 350 ℃.

Such phenomenon is strongly supported by the following Figures of 2 and 3, which shows the temperature profile in each location in the FBR.

Fig. 2 illustrates temperature profile inside of a FBR when direct chlorination is under going according to traditional method. Lines TE-26 A to TE-26D indicate the temperature readings at the four corners of gas distribution plate, which placed at the bottom of the FBR. From TE-7 to TE-12, the number means

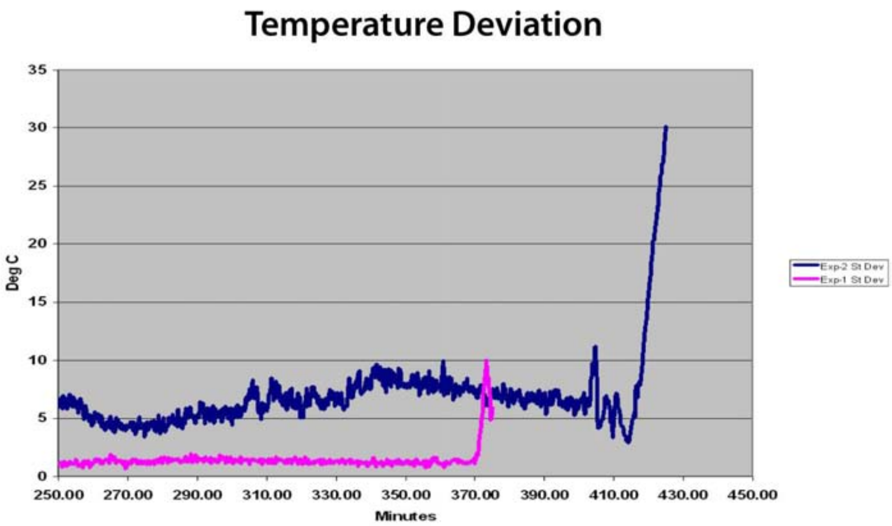

Fig 1. Mean average temperature deviations along the reaction time for two different direct chlorination methods. Blue (Traditional), Red (Turbo Charger)

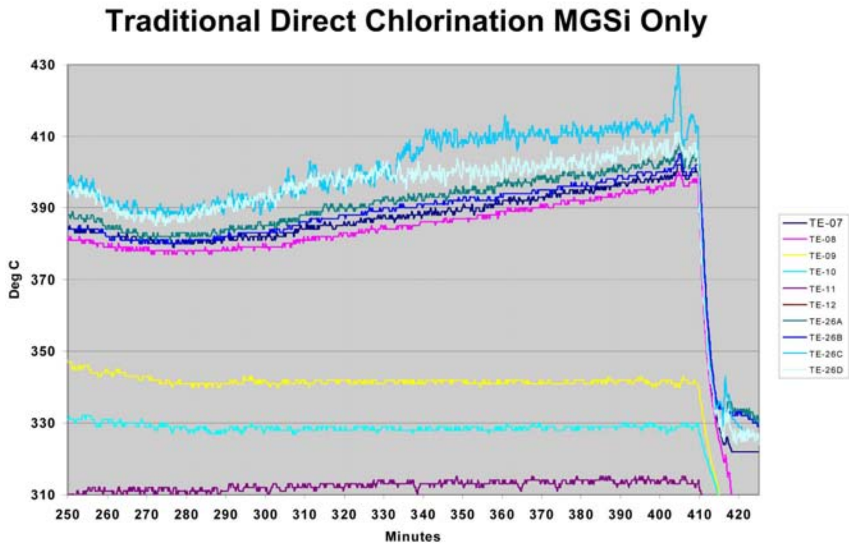

Fig 2. Temperature profile inside of a FBR when MGSi directly reacts with HCl according to traditional direct chlorination method.

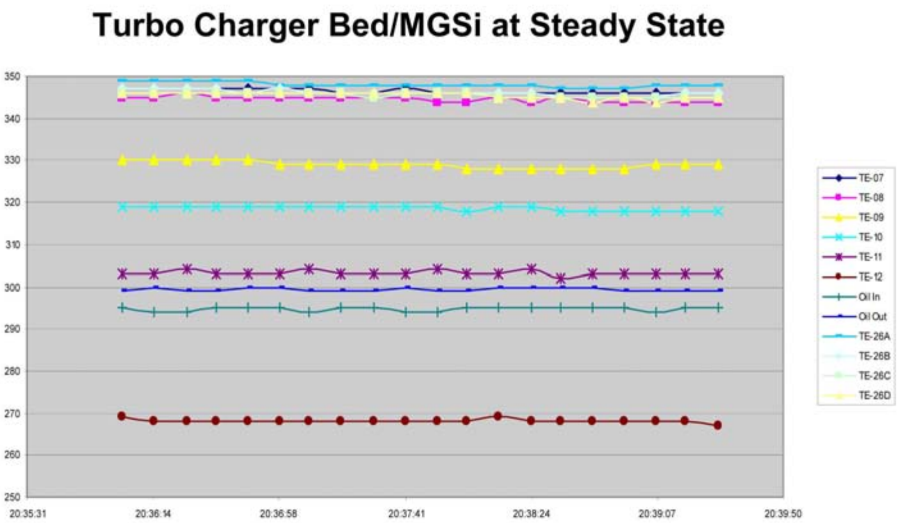

Fig. 3. Temperature profile along the reaction time in a FBR operated with 'Turbo Charger' direct chlorination method at steady state.

temperature readings away from the bottom of the FBR at intervals equivalent to the inner diameter of the fluidizing bed.

Fig. 2 clearly shows that temperature profiles in traditional direct chlorination method are very irregular and unstable. Most of all, the temperature inside of the fluidizing bed steadily increased. Because of such steady temperature increase the FBR running with traditional direct chlorination should be shut down every 2 to 3 months. Therefore, at least two FBRs are recommended to be installed for continuous TCS production.

Meanwhile, in the 'Turbo Charger' direct chlorination method, as shown in Fig.3, the temperature of 4 points on the gas distribution plate and two points inside of the fluidizing bed are almost same temperature and do not change along the reaction time.

Due to such advantages of the 'Turbo Charger' direct chlorination method, stable production of high purity crude TCS is possible. PPP's client commercially produces 95% purity crude TCS at much lower pressure and temperature compared to other methods.

1-2 Siemens Reactor

The 'Siemens Reactor' is named after the German company Siemens, which developed a chemical vapor deposition (CVD) reactor that deposits silicon molecules on silicon filament by thermal decomposition of TCS and other chlorosilane gases therein [7].

Lots of improvements were made since then and this reactor is proven as most reliable method of producing high purity polysilicon in commercial scale.

Chemical reaction inside the reactor is known as the following equations (3-1) and (3-2).

$$SiHCl_3 + H_2 \rightarrow Si + 3\,HCl \qquad (3\text{-}1)$$

$$4SiHCl_3 \rightarrow 3SiCl_4 + Si + 2H_2 \qquad (3\text{-}2)$$

1-3 TCS- Siemens Process

Early polysilicon manufacturers, Hemlock, for example, purchased TCS from out side like Dow Corning to avoid the difficulty of controlling exothermal heat of the direct chlorination. This is the start of TCS-Siemens Process.

Actually Hemlock was a joint venture between Dow Corning, Shin Etsu Handotai Co., Ltd. and Mitsubishi Materials Corporation and has their facilities over the fence of Dow Corning in Michigan. Dow Corning needs a lot of chlorosilane chemicals and has processes for separation and purification of the chlorosilanes to produce various kinds of silicone chemicals. Dow Corning uses chlorosilane from Hemlock's Siemens Reactor and separates TCS and send back to Hemlock. So, Hemlock does not need to take care of Off Gas from their Siemens reactors, which contains lot of STC.

However, other new polysilicon plants using TCS-Siemens process must invest for recycling STC. Because, TCS and other chlorosilane gases are introduced to Siemens reactor at high speed in turbulent flow and only part of the introduced TCS deposited as polysilicon. Most of them come out of the reactors as un-reacted or changed to STC by reacting with HCl generated according to the above equation (3-1) and (3-2).

The amount of the off gas from the Siemens reactors is huge and the off gas contains lots of un-reacted TCS, STC, HCl, and hydrogen that must be recovered. This recovering process is called as OGR (Off Gas Recovery) and plays key role in economical operation of a polysilicon plant. So, an independent TCS-Siemens process includes OGR.

1-4. STC handling in TCS-Siemens Process

TCS, HCl and Hydrogen can be separated from the off gas and re-used in the process after additional purification. But, STC causes trouble. According to Chinese report [8], over 15 metric tons of STC are generated per one metric ton of polysilicon produced. That amount is next to the un-reacted TCS from Siemens reactor.

PPP, like many other technology providers, supplies 'Thermal Converters' that converts STC to TCS by hydrogenation of STC. 'Thermal Converters' has been commercially used for decades and regarded as most reliable STC to TCS converter because it converts all the STC into TCS. Standard TCS-Siemens process includes the 'Thermal Converter'.

But, it consumes large amount of electricity to maintain the reaction temperature around 1,200 ℃. In addition to this if low purity graphite material is used for electrodes inside of the converter, the electrodes are easily damaged or consumed.

Fig. 4-1 is block diagram of the traditional TCS-Siemens process for 10,000 MTA polysilicon plant built with "turbo charger" direct chlorination FBR. The numbers between each unit block represents mass balance of TCS and STC.

Even for standard TCS-Siemens process, PPP's 'turbo charger' direct chlorination FBR, Fig 4-1, has advantage (5% STC, (3/57), contents in the crude product) over traditional direct chlorination FBR in terms of STC (15 ~40 %(29/73) in the crude product) generated as shown in the Fig. 4-2.

Because of the low selectivity of TCS from the traditional direct chlorination FBR, the amount of STC that should be removed from the process is maximum ten times of the amount of STC from the 'turbo charger' direct chlorination FBR when STC contents in the crude product is 40 %.

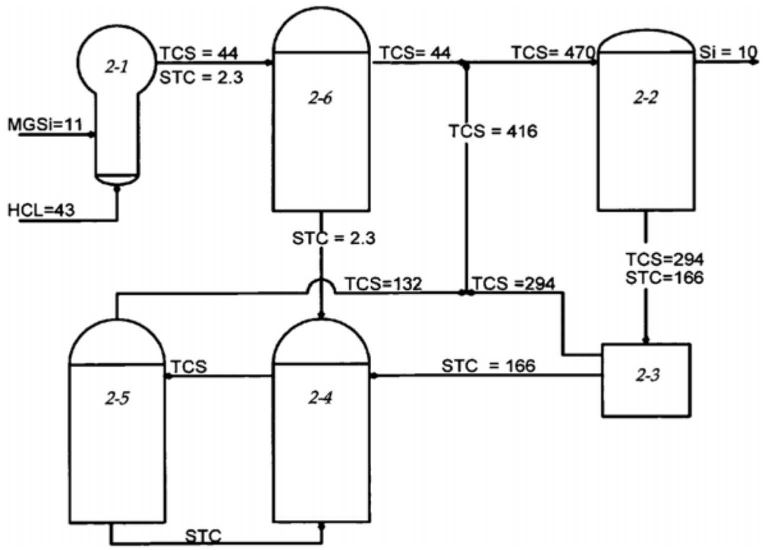

Fig. 4-1. Process block diagram of TCS-Siemens Process with thermal converter and 'turbo charger' direct chlorination FBR.

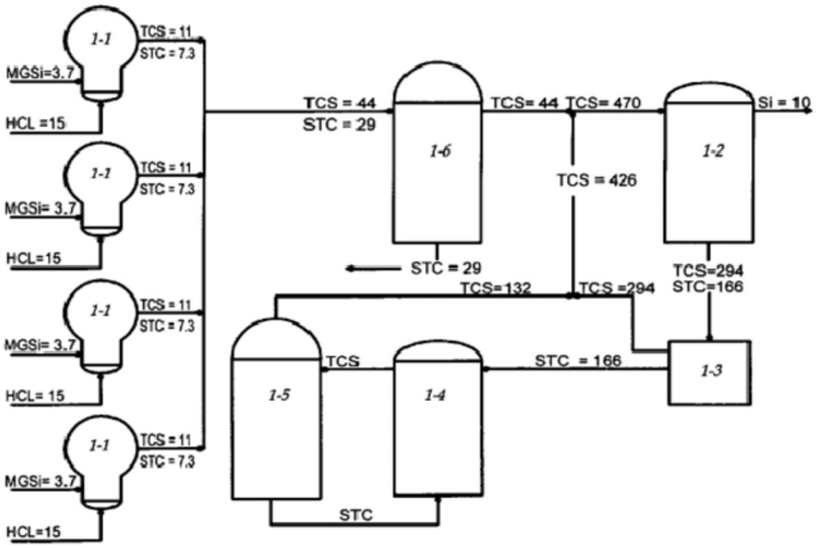

Fig. 4-2. Process block diagram of TCS-Siemens Process with thermal converter and traditional direct chlorination FBR.

2. TCS production by Hydro-chlorination and Siemens Process

General Electric disclosed a technology of converting STC to TCS at 400 ℃ in the presence of Aluminum catalyst and hydrogen in 1940's [9]. Soon, Libbey-Owens-Ford Glass Company, disclosed similar STC to TCS converting technology in the presence of silicon [10].

After that G.H.Wagner studied the hydrogenation of

STC in more detail in Linde Air Product [11] and Union Carbide [12]. In Union Carbide, he investigated the reaction with fluidized bed reactor at various temperatures and pressures. According to his patent, silicon, STC, and hydrogen react according to an apparent reaction described as the following equation (4).

$$Si + 2\,H_2 + 3\,STC \rightarrow 4\,TCS \qquad (4)$$

All of the above four researches commonly found that theoretical maximum selectivity of TCS in the product of hydrogenation of STC is 31%. But, here it is assumed as 25%. When a FBR is used for the reaction, the selectivity of TCS in the product increases with reaction pressure and retention time of the gas phase reactants, hydrogen and STC.

In later 1970's, Union Carbide made a contract with the Department of Energy/ NASA for a pilot plant scale research [13] including fluidized bed reactor for TCS synthesis and Si deposition titled as "Low cost silicon solar array project; Feasibility of low cost, high volume production of silane and pyrolysis of silane to semiconductor grade silicon" and disclosed later by U.S.patent [14].

In these studies [13, 14], all the chlorosilanes produced from a FBR were converted to silane to deposite them into granular polysilicon to overcome the low conversion of STC to TCS by the hydrogenation in the presence of silicon granule in a FBR. So, that was not a research for TCS-Siemens Process.

They re-confirmed that STC to TCS conversion rate is lower than 25% and the conversion rate increased with retention time. To increase the retention time of the gaseous reactants, they had to lower the SGV (Specific Gas Velocity) of gases. Then the production rate of TCS per volume of the FBR, volumetric production rate, decreases and the process becomes less economical. By increasing the reaction pressure up to 25 ~30 bars, they compensated for the production loss. This is maintained even after the department was sold to ASiMI and later to REC.

Later, Motorola disclosed an idea of increasing TCS production by adding direct chlorination reactor section on the top of hydro-chlorination reactor [15].

In 1992, Professor Akio and his team in Waseda University of Japan [16] studied the same reaction with fixed bed reactor. They found that the real reaction of the hydrogenation is not a simple reaction like that presented by the above equation (4) but a series and parallel reactions presented as follows.

$$SiCl_4 + H_2 \rightarrow SiHCl_3 + HCl \qquad (5\text{-}1)$$

$$Si + 3HCl \rightarrow SiHCl_3 + H_2 \qquad (5\text{-}2)$$

The equation (5-2) is same as suggested by Wacker Chemie [17]. And according to their results STC is generated much more than TCS at a temperature of 500 ℃.

After that people of this industry changed the name of the reactor from Hydrogenation Reactor to Hydro-chlorination Reactor.

However, REC still produce chlorosilane complexes from the same high pressure, high temperature process and converts them into Silane to use in a kind of Siemens reactor to produce polysilicon rods. Current REC process is not TCS-Siemens. It is Silane －Siemens process. A benefit of this process is simple and small Off Gas Recovery (OGR) process because STC is not generated from the CVD. Many companies try the same method with their Siemens Reactors available from the open market but failed.

As a conclusion, the REC reactor type Hydro-chlorination Reactor was not developed to produce TCS for TCS-Siemens process nor developed as a STC converter to consume it.

2-1. TCS production by Hydrochlorination and Modified TCS-Siemens Process; Closed Loop Process

Fig. 5 is a block diagram of the 'Closed Loop Hydro Chlorination TCS-Siemens Process' for 10,000 MTA polysilicon plant. The number between each blocks represent TCS and STC mass balance.

However, some company start to sell the same old REC's technology just changing the named as 'Closed Loop TCS-Siemens Process' just after the Chinese polysilicon industry announced the STC problems in their plants.

In the 'Closed Loop TCS-Siemens Process' all the STC from Off Gas of the Siemens Reactors are recycled to one huge Hydro chlorination Reactor filled with MGSi to react with hydrogen to generate TCS for Siemens Reactors.

3. TCS-Siemens Process vs. Closed Loop Process

3-1. Overall Process

The mass balances in each process are calculated based on the following assumptions.

In the block diagrams of Fig, 4-1, 4-2 and 5, the Siemens Reactors are the same. The amount and purity of TCS for Siemens reactors are the same in both processes. Therefore, the amount and composition of Off Gas from the Siemens reactors to OGR process are the same for both of the processes. In both processes, TCS is returned to Siemens Reactors after separation.

3-2 STC Flow

In a traditional TCS-Siemens Process STC recycled to Siemens Reactors after converted to TCS in a proper converter. In a 'Closed Loop Hydro-chlorination TCS-Siemens Process' STC is returned to a huge hydro-chlorination reactor and is converted into TCS and injected to Siemens reactors. As seen from the two processes, all STC is recycled in both processes. Therefore, both processes are 'Closed Loop Process' in terms of recycling the whole STC.

In the past, all the traditional Direct Chlorination FBR technologies had problems in controlling the exothermal heat of the reaction. So, the FBR had to be opened every 2 to 3 months disabling continuous 'Closed Loop Operation'.

However, PPP's newly designed direct chlorination FBR combined with 'Turbo Charger' operation technology resolved the problems to realize commercial 'Closed Loop Operation' in traditional TCS-Siemens Process.

3-3 Quantity of STC Mass Flow in Closed Loop Hydro-Chlorination Siemens Process

As disclosed in the many previous articles, the REC type hydro-chlorination reactor should be built with especially expensive material, Inconel® 800 H, because of the high reaction temperature, over 500 ℃, and reaction pressure, over 25 bars. In spite of using expensive material and extreme operation condition, contents of TCS from the FBR are less than 30% and most of the rest is STC.

Siemens Reactors need TCS to produce polysilicon chunk, not STC. Therefore, REC type hydro-chlorination FBR must produces unnecessary by product, STC, 3 times amount of TCS needed as shown in the block diagrams of Fig. 5.

In a 10,000 MTA Polysilicon plant, the amount of STC recycling between the hydrochlorination FBR and purification process forever is 800,000 MTA. For a

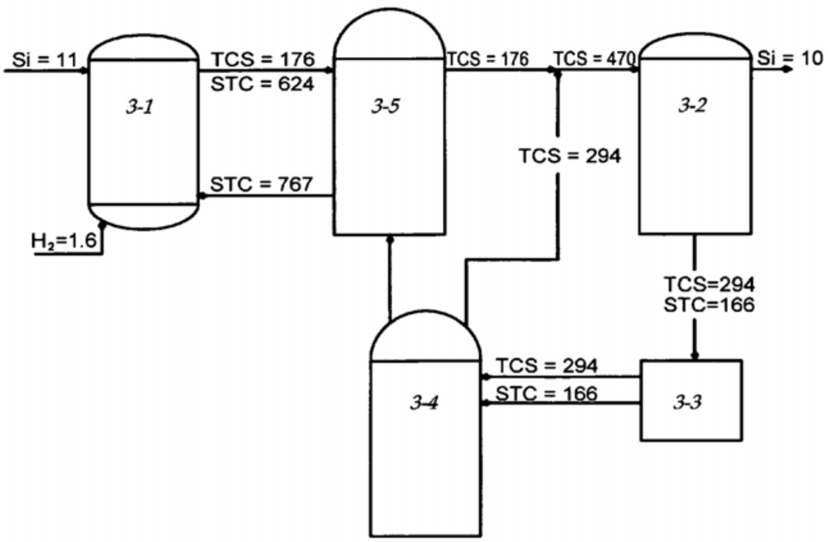

Fig. 5 Block diagram of a 10,000 MTA polysilicon plant by 'Closed Loop Hydro-Chlorination TCS-Siemens Process'

20,000 MTA plant the amount is one million and six hundred thousand metric tones. This is equivalent to 100 metric tons to 200 metric tons per hour.

3-4 Quantity of STC Mass Flow in TCS-Siemens Process

Meanwhile, in a TCS-Siemens Process small amount of STC is converted in a thermal converter. The amount is 166,000 MTA for 10,000 MTA polysilicon plant. This is equivalent to 20.75 tons/hr(Fig. 4-1).

3-5 Quantity of STC Mass Flow in Hybrid TCS-Siemens Process

To reduce the enormous amount of electricity consumption by thermal converters, hydrochlorination FBR is suggested for converting STC to TCS. The process is named as 'Hybrid TCS-Siemens Process.' The process block diagram of the 'Hybrid TCS-Siemens Process' is illustrated in Fig. 6-1 and 6-2.

Here, some technical modification is needed to resolve inherent problems of the hydro-chlorination. If all the STC from OGR is put into the hydrochlorination FBR, it generates more moles of TCS than STC according to the equation (4). Then we have excess TCS that breaks the steady state mass balance of the entire process.

To avoid such undesirable situation, part of STC is removed from the process to meet the TCS overall balance. The amount of STC removed is 38% of STC from OGR. The removed STC is reacted with pure water to recycle HCl and make SiO_2 for sales or use in the process.

Or, the total STC is converted to TCS and the extra TCS is reserved for emergency or sell at other chemical industry after purification.

If the hybrid process is equipped with traditional direct chlorination FBR the STC mass flow is hard to control in overall balance due to excess STC generation from the FBRs. Fig. 6-2 shows the STC balance in a Hybrid TCS-Siemens Process equipped with traditional direct chlorination FBRs.

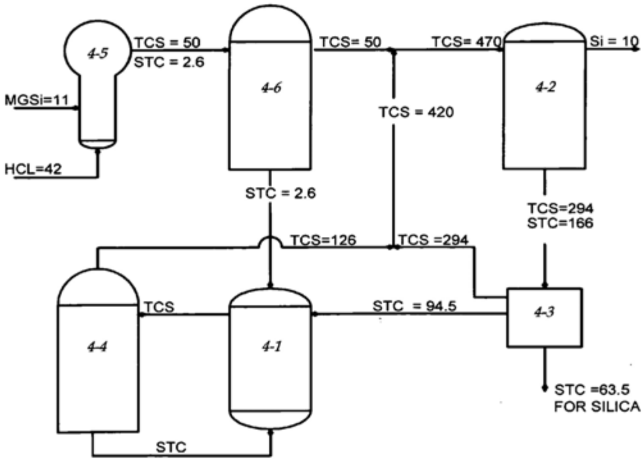

Fig. 6-1. Block diagram of a Hybrid TCS-Siemens Process of 10,000 MTA equipped with 'turbo charger' direct chlorination FBR.

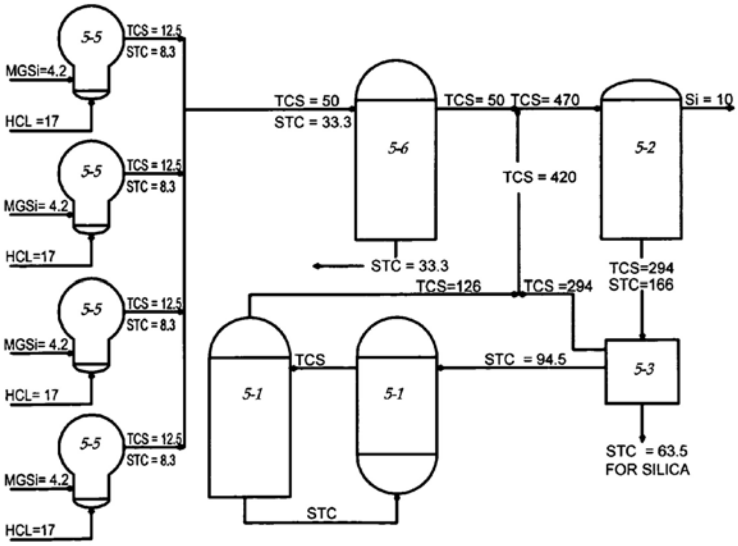

Fig. 6-2. Block diagram of a Hybrid TCS-Siemens Process of 10,000 MTA equipped with traditional direct chlorination FBR.

3-6 Total Energy Consumption for TCS production in Each Process

Total energy consumption related with TCS generation and STC conversion for "Closed Loop Hydro-chlorination TCS- Siemens Process", "TCS-Siemens Process", and "Hybrid TCS-Siemens Process" are listed in Table 2 for comparison. The total energy consumption related with TCS generation and STC conversions are calculated by adding the energy needed to heat the recycled STC to the STC to TCS convert.

For 'TCS-Siemens Process' and 'Hybrid TCS-Siemens Process' energy consumption to generate TCS by direct chlorination is added.

Table 2 clearly shows that traditional 'TCS-Siemens

Table 2. Energy consumption related with STC conversion and TCS generation in three different Siemens Processes for 10,000 MTA Polysilicon Plant *

	Mass to Converter MT/YR	Converter Energy		1,000 Kwhr
		Kwhr/kg Si**	Toatal (Kwhr)	
(A); Closed Loop Hydro Chlorination TCS-Siemens	800,000	10 (HydroChlorination)	10 × 10,000,000= 100,000,000	100,000
TCS-Siemens	166,000	20 for TC 4 for DC (traditional)	24 × 10,000,000=240,000,000	240,000
(B); Hybrid TCS-Siemens	94,500	1.18 † for HC 1 for DC (turbo charger)	2.18 × 10,000,000 = 21,800,000	21,800
(A) − (B)	705,500	7.818		78,200

* Energy consumption in Distillation, Siemens Reactor, and Off Gas Recycle steps are not considered because they are common steps for all the three processes.
** Energy consumption from commercial plants. Includes heater, cooler and compressor power consumption.
† 10 x (94,500/800,000); Reduction of H.C. reactor size reduces energy consumption.

Process' using 'Thermal Converter' consumes energy most. The "Closed Loop Hydro-Chlorination TCS Siemens Process" consumes about 40% of energy compared to the traditional process. The 'Hybrid TCS-Siemens Process' consumes about 10% of energy compared to the traditional 'TCS-Siemens Process.' Here, the FBR used for direct chlorination is the new 'Turbo Charger' FBR.

4. Reactor Sizes and Initial Capital Investment

In addition to lower energy consumption in STC conversion and TCS generation, the 'Hybrid TCS-Siemens Process' has another advantage over the 'Closed Loop Hydro-Chlorination TCS-Siemens process' in terms of reactor sizes due to its inherent disadvantage of the hydro chlorination.

The 'Turbo Charger' FBR, adopted in direct chlorination process of the 'Hybrid TCS-Siemens Process, is operated at a controlled temperature between 300 ~ 350 ℃ and at a pressure range about 5bar. The FBR can be manufactured with various construction materials such as carbon steel, stain less steel, and Inconel®.

Since hydro chlorination FBR reactor of U.S. Patent 4,676,967 operates at high temperature of 550 ℃, and high pressure above 25 bar, that FBR must be constructed with the expensive Incoloy 800 H® or equivalent material for safety reason. In addition to this, due to complex internal structure, difficult level control, and excess side product, it is almost impossible to build a single large hydro chlorination FBR, which has a capacity to produce TCS for 10,000 MT/YR polysilicon plant. The maximum size of the hydro chlorination FBR provided to GCL is equivalent to produce TCS for 7,500 MT/YR polysilicon plant.

On the other hand, the 'Turbo Charger' FBR for direct chlorination, developed by the PPP's genuine in-house technology, is totally different from the old FBR for direct chlorination and from the FBR for hydro chlorination disclosed in the U.S. Patent 4,676,967.

One key feature of the 'turbo charger' direct chlorination FBR is to control the reaction in stoichiometrically equivalent, which is impossible for the other two FBRs. The other key feature is operating the fluidizing bed in 'Bubbling Bed Mode' that maximise mixing of the bed material.

Meanwhile, the other two type FBRs are just large scale reactor of a laboratory state reactor. They just pile up unnecessarily excess amount of MGSi in a FBR without considering movement of the bed material. Therefore, the fluidizing bed, where the reaction occurs is in an 'extended fixed bed' mode (hydro-chlorination FBR) or 'slugging bed' mode (traditional direct chlorination FBR). So the fluidizing bed is unstable and the reactant gas feeding rate is limited. Due to the limitation, the heat of the reaction is controlled by only 'conductional heat transfer' and as a result temperature profile in the reaction zone is unstable and not uniform in case of hydro-chlorination FBR. For the case of old direct chlorination FBR, over all heat transfer to the reactor wall in the fluidized bed is lower than the 'bubbling bed mode' because of the slugging that happens when the ratio of the bed height/ bed diameter is greater than 4. This is first time found by PPP.

The new FBR for direct chlorination utilize an inert medium named as 'turbo charger' inside of the fluidizing bed to dilute heat generated per volume of the bed and at the same time transfer the heat generated to the reactor wall by 'Convectional Heat transfer' due to the 'Bubbling Bed Mode' movement of the bed material. Features of the 'turbo charger' FBR for direct chlorination are listed in Table 3 and compared with other two FBRs.

The result of such effective heat transfer control is shown in the Fig.1 and Fig. 3 as the uniform temperature profile inside of the fluidizing bed, the reaction zone.

Since this new 'Turbo Charger' FBR has no internal structure, it is easy to scale-up. For example, Union Carbide commercialized similar 'Bubbling Bed Mode' FBR, Uniopl ® Reactor, for Polyolefin production. Since the commercial operation in 1980, as of 2013 about 100 reactor of 100,000 MTA are commercially in operation without any single accident. Maximum size of the reactor is 500,000 MTA from single reactor [18].

GTAT(Gupta and Talbot Advanced Technology), a U.S. company, announced a feasibility study report [19] comparing "Traditional direct chlorination TCS-Siemens Process" and their "Closed Loop Hydro chlorination Process" working at high temperature, high pressure. In the article, the maximum size of single FBR which can be built by their technology is for a polysilicon plant of 7,000 MTA. But, even that number is from simulation, not a designed capacity.

4-1. Initil Capital Investment

Due to the limitations of the previous TCS-Siemens processes discussed above a new process is needed to build a large scale polysilicon plant over 10,000 MT/YR to save Opex and CaPex.

Size and number of FBRs for TCS production for 10,000 MT/YR and 20,000 MT/YR polysilicon plant according to three different processes are summarized in Table 4. Specific cost is not estimated because material cost and fabrication cost are different for each plant site. Sizes of each reactor are based on commercial reactors.

As shown in the Table 4, at least 4 to 8 FBRs are needed to comprise a 'Hybrid TCS-Siemens Process' using traditional direct chlorination TCS FBR. In this case, due to frequent shut-down of the FBR, additional maintenance man power is needed and the possibility of malfunction of the FBR is very high.

Meanwhile, with PPP's new 'turbo charger' FBR automatically produces enough TCS through a whole year without shut-down of the FBR. Therefore, initial capital investment for TCS production is reduced.

On the other hand, 'Closed Loop Hydro-Chlorination TCS-Siemens Process' does not need separate FBR for TCS production only. TCS is generated from single hydro chlorination FBR with un-necessarily huge amount of STC at the same time. Therefore, the size and number of hydro chlorination FBR increases.

To build one polysilicon plant of 10,000 MTA or 20,000 MTA by 'Hybrid TCS-Siemens Process' using 'Turbo Charger' FBR, one small 'Turbo Charger' FBR for TCS production and one small REC type hydro chlorination FBR for STC converter is enough.

Meanwhile, at least 2 or 4 large hydro chlorination reactors, which has twice larger diameter than the Hybrid process case, are needed to build a 10,000 MTA or 20,000 MTA polysilicon plant by 'Closed Loop Hydrochlorination TCS-Siemens Process'.

In addition to this, the FBR for this process should be built with the expensive Inconel® 800H to secure the operation conditions of high temperature and high pressure. And at the same time size of super heater and settler, which are mandatory supplementary equipment to the FBR, should also be increased. As we know well, Inconl® 800 H is very expensive and hard to fabricate. And the wall thickness of a pressure vessel increases with square of the diameter ratio of the vessels. Therefore, the price of FBR also increases with square of diameter ratio.

As a conclusion, initial capital investment for TCS production for 'Hybrid TCS-Siemens Process is much smaller than 'Closed Loop Hydro-Chlorination TCS-Siemens Process.'

Depending on the compositions and components from the "turbo charger" direct chlorination FBR and the "Hydro-chlorination FBR" the purification train might be separated, one for DC and one for HC, however if there are no big difference between the two 'out gases' from the two FBRs, there may be way to share some equipments.

'Hybrid TCS-Siemens Process' equipped with applicants' 'Turbo Charger' direct chlorination FBR saves at least 78,000,000Kwhr per year from TCS generation only in a 10,000 M/YR polysilicon plant compared with a same capacity polyilicon plant built by 'Closed Loop Hydro-Chlorination TCS-Siemens Process.' For 20,000 MT/YR plant the amount is 156,000,000 Kwhr.

Compared with traditional TCS-Siemens Process, the 'Hybrid TCS-Siemens Process' saves 220,000,000 Kwhr per year from 10,000 MT/YR plant.

In addition to this, 'Hybrid TCS-Siemens Process' equipped with applicants' 'Turbo Charger' direct chlorination FBR saves huge amount of initial capital investment from TCS generation related equipment.

As a conclusion, 'Hybrid TCS-Siemens Process' equipped with applicants' 'Turbo Charger' direct chlorination FBR is the most economical process for a polysilicon process over 10,000 MT/YR capacities.

As shown in the Table 4, at least 4 to 8 FBRs are needed to comprise a 'Hybrid TCS-Siemens Process' using old direct chlorination TCS FBR. In this case, due to frequent shut-down of the FBR, additional maintenance man power is needed and the possibility of malfunction of the FBR is very high.

Meanwhile, with PPP's new 'Turbo Charger' FBR automatically produces enough TCS through a whole year without shut-down of the FBR. Therefore, initial capital investment for TCS production is reduced down to 1/4 to 1/8 level.

On the other hand, 'Closed Loop Hydro-Chlorination TCS-Siemens Process' does not need separate FBR for

Table 3. Features of different FBRs for TCS Production

	Traditional Direct Chlorination FBR	Turbo Charger Direct Chlorination FBR	Hydrochlorination FBR
Temperature (℃)	300~ 400	300 ~350	520 ~550
Pressure (bar)	4~5	5	25~30
Δ T across bed	> ± 10 ℃	< ± 1 ℃	> ± 10 ℃
Bed Mode	Extended ~Slugging	Bubbling*	Extended Fixed Bed
Reaction	Non-Stoichiometric	Stoichiometric	Non-Stoichiometric
Cooler	Internal Cooling Coil	External Cooling Jacket	External Heater
Inside Bed Cooling Medium	STC,N_2, H_2 and O_2 gases	Turbo Charger	STC, H_2
Thermal Conductivity	0.1 ~0.2 W/(mK)	1~2 W/ (mK)	0.1 ~0.2 W/(mK)
Internals	Cooling Coil, Bubble Breaker	None	Bubble Breaker, Internal Cyclone
Bed Level Control	Semi-Auto	Auto	Semi-Auto
Specific Gas Velocity	< 20 cm/sec	20~60 cm/sec **	6 ~10 cm/sec
Crude TCS Selectivity	60 ~90 %	> 95 %	< 30%
Up-Time	~40 %	>90%, 11 months	>90%, 11 months
Scale-up limit, MT/YR TCS	15,000	500,000	96,000***
Reason of limit	Hot Spot, Poor heat transfer	Mechanical Structure	Mechanical Structure
Construction Material	Carbon steel, SUS, Incoloy	Carbon steel, SUS, Incoloy	Incoloy

* Bed Mode; bubbling bed mode shows maximum mixing
** High SGV enables the bed material convects. So, convectional heat transfer is possible.
*** For 96,000 MTA TCS at least 288,000 MTA STC is generated from the same FBR

TCS production only. Instead, TCS is generated from one hydro-chlorination FBR with unnecessarily huge amount of STC at the same time. Therefore, the size and number of hydrochlorination FBR increases.

To build one polysilicon plant of 10,000 MTA or 20,000 MTA by 'Hybrid TCS-Siemens Process' using 'Turbo Charger' FBR, one small 'Turbo Charger' FBR for TCS production and one small REC type hydro chlorination FBR for STC converter is enough if some portion of STC is being removed from the cycle loop.

New application of those extra STC is also under develop in PPP.

Meanwhile, at least 2 or 4 large REC type hydro-chlorination reactors, which has twice larger diameter than the Hybrid process case, are needed to build a 10,000 MTA or 20,000 MTA polysilicon plant by 'Closed Loop Hydro-chlorination TCS-Siemens Process'.

5. Conclusion

'Hybrid TCS-Siemens Process' equipped with PPP's 'Turbo Charger' direct chlorination FBR saves at least 78,000,000Kwhr per year from TCS generation only in a 10,000 MTA polysilicon plant compared with a same capacity polyilicon plant built by 'Closed Loop Hydro-

Table 4. Size and number of FBRs for TCS production for 10,000 MTA and 20,000 MTA Polysilicon plant according to three different processes.

	TCS FBR: MT/YR	No. of FBR	Dimension	H.C. FBR MT/YR STC Only	No. of H.C. FBR	Dimension
Hybrid w. traditional D.C. FBR	83,000 (166,000)	4 8	ø 1.5 m, H 25m ø 1.5 m, H 25m	95,000 190,000	1 1	ø 1.4 m, H 25m ø 2.1 m, H 25m
Hybrid w. 'Turbo' D.C. FBR	53,000 (106,000)	1 1	ø 1.5 m, H 25m ø 2.2 m, H25m	95,000 190,000	1 1	ø 1.4 m,H25m ø 2.1 m, H25m
H.C. Closed Loop FBR	0	0		STC & TCS	No. of FBR 400,000 MT/YR	
				800,000 1,600,000	2 4	ø 3.0 m, H 25m ø 3.0 m, H 25m

Chlorination TCS-Siemens Process.'

Compared with traditional TCS-Siemens Process, the 'Hybrid TCS-Siemens Process' saves 220,000,000Kwhr per year from 10,000 MTA plant.

In addition to this, 'Hybrid TCS-Siemens Process' equipped with PPP's 'Turbo Charger' direct chlorination FBR saves huge amount of initial capital investment from TCS generation related equipment.

Finally, 'Hybrid TCS-Siemens Process' equipped with PPP's 'Turbo Charger' direct chlorination FBR is the most economical process for a polysilicon process over 10,000 MTA capacity.

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