Energy Market

The photovoltaic (PV) solar industry is growing rapidly since it is a non-polluting renewable energy source. Polycrystalline silicon (PCS) is a key component of solar panel construction: it is the cell membrane material that allows the conversion of sunlight into electricity. The production of PCS is presently booming in Asia, Europe and North America as a result of the ramp up of production of solar cells or panels.

The base material for making PCS is the silicon in sand (SiO\textsubscript{2}). This raw material is heated with reducing agents (such as carbon) in an arc furnace to produce liquid silicon, which is then cooled and transformed into metallurgical grade silicon of 98% purity. Most metallurgical-grade silicon is used in the steel and aluminum industries for making alloys. A smaller, but increasing, proportion is used for making PCS and electronics-grade silicon. Every one of the PCS plants (that use the TCS or trichlorosilane conversion process) requires the use of anhydrous hydrogen chloride (AHCL) in the TCS reactor.

This is a major market potential for Mersen products, including engineered systems that generate or recover AHCl and speciality graphite components that are used in the processing of PCS.

This paper focuses on the application of Mersen systems that generate or purify HCl gas that can be used in this process.
TCS or Trichlorosilanes process

Trichlorosilane (TCS or SiHCl₃) is generated as follows within a high temperature, pressurized reactor:

\[
\begin{align*}
\text{Si} + 3 \text{HCl} & \rightarrow \text{SiHCl}₃ + \text{H₂} \\
\text{Si} + 3 \text{SiCl₄ +2H₂} & \rightarrow 4 \text{SiHCl}₃
\end{align*}
\]

The TCS is then sent to the CVD (Chemical Vapor Deposition) reactor. In the Siemens process, high-purity silicon "starter" rods or hairpins are exposed to trichlorosilane at 1150 °C in the CVD reactor. The trichlorosilane gas decomposes and deposits additional pure silicon onto the rods in the CVD reactor, enlarging them according to chemical reactions like:

\[
2 \text{SiHCl}_₃ + \text{H₂} \rightarrow \text{Si} + \text{SiCl₄} + 2 \text{HCl} \quad \text{(at 1100 °C / 6 barg)}
\]

Silicon produced in this reaction is called polycrystalline silicon (PCS).

The SiCl₄ + HCl is then "recycled" and returned to the TCS plant via SiCl₄ conversion (in the converter):

\[
\text{SiCl₄ +H₂ + catalyst} \rightarrow \text{HCl + SiHCl₃}
\]

In all of the above reactions, we note the use or generation of HCl and H₂.

Make-up anhydrous HCl gas is needed in the TCS reactor due to the incomplete conversion and recycling of the SiCl₄ and TCS in the recycling step, meaning that some of the chlorine is generated as a waste product in the overall process and sent elsewhere. The AHCl needs to be dry and of high purity but it can contain H₂, which is also a recycled bi-product.

The make up "pure" AHCl can thus be produced by a number of ways including:

1. **A dry HCl synthesis unit** (Cl₂ + H₂ to generate HCl with ~5% excess H₂)
2. **An HCl desorber (stripper)**; nominal 33% aqueous HCl converted to AHCl plus ~19% HCl bi-product (Note: the feed aqueous 33% acid can also be generated by a classic wet synthesis unit which can then be close loop coupled to a HCl desorber - this means Cl₂ + H₂ generates AHCl without a bi-product)
3. **An HCl azeotrope breaker** 15% to 35% aqueous HCl acid which generates AHCl + waste water
4. **An HCl gas purification/recovery system**; these systems generally take an impure HCl waste gas stream (containing organics or other impurities from another process) and then purify it; generally the waste gas is absorbed to make ~35% aqueous HCl with impurities, then purified through an "organics stripper" to make pure aqueous acid and then desorbed to make AHCL with the 19%bi-product sent to the absorber to "close loop" the water

The AHCl gas generated must also be relatively dry. In general, a dryness level of less than 20 ppm V% H₂O to meet requirements in the TCS reactor or possibly less if a compressor is used to further compress the AHCl gas. For this reason, additional drying steps may also be required.

Depending on the required quality of the final PCS product, the make-up HCl gas purity varies. Generally, generation of HCl gas by any of the above means will provide AHCl of sufficient quality for PCS destined for use in the solar industry (PV grade). Further purification steps may be required to make electronics grade PCS.

Mersen Systems

Mersen can provide the four following systems to produce AHCl:

1. **Dry HCl synthesis unit**

A "dry" synthesis unit can be used to generate dry HCl vs. a "wet" synthesis unit that makes aqueous HCl by adding water. The end user would provide clean and dry (or wet) Chlorine and hydrogen as the primary feed streams. If the feed gas contains impurities, they will be present in the "outlet gas". Excess hydrogen is required to ensure conversion to HCl (from H₂ & Cl₂) and this means that the produced AHCl will have ~3% to 5% H₂ excess in it.

The generated AHCl gas should be limited to a maximum pressure of ~2 barg.

Mersen Equipment

- Skid mount Graphilor® synthesis unit package
- Optional HCl drying package - skid mount
- Optional HCl absorber (scrubber package) integrated into skid
**HCl desorber (stripper)**

33% to 35% feed HCl acid is sent to a desorber system where it generates pure AHCl gas at pressures up to 5 barg and a bi-product aqueous acid of ~19% HCl acid. The AHCL generated is pure if the feed acid is pure.

The 19% bi-product acid can be eliminated by close looping this system via an HCl absorber or wet synthesis unit. The 33% to 35% feed acid could be generated by a "wet" synthesis unit. In other words, one could make wet 33% to 35% aqueous HCl from primary feed streams of clean and dry (or wet) chlorine and hydrogen and de-ionized (or demineralized) water.

Excess hydrogen is required to ensure conversion to HCl (from H2 & Cl2) but the excess H2 and other inert gases are safely vented out of the synthesis unit system through the synthesis unit's scrubber.

The 33% to 35% HCl product acid from the synthesis unit is generally sent to a buffer tank and then sent to the HCl desorber where the desorber converts the aqueous HCl into AHCl typically with less than 100 ppm H2O and produces bi-product ~19% acid which in turn is sent and held in a buffer tank. The 19% HCl acid is then used as the absorption solution for the HCl synthesis package. The desorber with a 33% HCl acid feed uses approximately 1.4 kg of steam per kg of HCl stripped.

If there are impurities in the feed Cl2 and H2 stream, most if not all of them will be removed in the wet synthesis unit system (via the vent of the synthesis unit's scrubber). If there are other impurities such as organics that end up in the 33% to 35% HCl acid, these can be stripped by an organics stripper. This system can thus inherently produce much purer AHCL than the dry synthesis unit. It can also generate AHCI at gas pressures up to 4 barg with a conventional TFE lined steel stripper columns and can even generate AHCl up to 5 barg using a CL-Clad (Ta) or Tantalum lined stripping columns.

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**Mersen Equipment**

- Stripper columns in Graphilor ®3, Armylor® (PTFE) or tantalum CL-Clad ®
- Reboiler, condenser, interchanger, cooler in Graphilor ®3, Armylor ® piping
- Complete skid mount Stripping system
- Complete skid mount "wet" synthesis unit integrated to the stripper system

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**HCl azeotrope breaker**

AHCI can be generated from commercially available industrial or food grade HCl at anywhere from 15% to 35% concentration by using an HCl azeotrope breaker. AHCI is generated along with a wastewater stream.

Two types of HCl azeotrope breakers are available. The CaCl2 azeotrope breaker using CaCl2 to break the azeotrope of HCl. The other method is called a "pressure-swing" or a Pressure-Vacuum azeotrope breaker.

The azeotrope breaker using a 33% feed will use approximately 6 kg of steam per kg of AHCI stripped. The CaCl2 breaker generates AHCL gas up to ~2 barg pressure while a Pressure-Vacuum azeotrope breaker can generate up to 5 barg AHCl.

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**HCl gas purification / recovery system**

This is really just an offshoot process of the desorber and/or wet synthesis unit/desorber process mentioned in the paragraph "HCl desorber"

Some PCS plants may be located in close proximity to other industrial complexes that may generate "dirty" or off spec HCl gas ; for example a VCM or TDI plant that may generate HCl gas with small amounts of organic or other inert impurities. This off spec HCl gas can be absorbed, then purified and then desorbed similar to what was discussed in 2 above.

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**Optional Drying systems**

As was mentioned above, further drying of the product AHCI gas is generally required to meet dryness specifications for the AHCl. Carbone Lorraine can offer two distinct types of "final" drying packages to accomplish this task, either a sulfuric acid drying system or a molecular sieve drying system.
Sulfuric acid drying system
The AHCL generated is sent through packed towers that recirculate sulfuric acid. The concentrated sulfuric acid has a very high affinity to absorb H2O from the AHCL gas stream. Either one or two stages are used depending on the size of the system and depending on the dryness level and amount of “spent” acid generated. Make-up acid of nominal 98% H2SO4 is required. Spent acid at either 96% (for a single stage dryer) or ~92% for a two stage dryer package is rejected from the system. The make-up acid required and the spent acid generated is relatively small. A special candle filter demister is used at the tail end of the process to minimize any H2SO4 droplet carry-over.

Molecular Sieve drying system
A molecular sieve drying system is an adsorption type process whereby H2O from the AHCL gas passes through the mole sieve media in columns and is adsorbed on the surface of the adsorption media (tiny balls). This process uses a flip flop batch process of two streams where one stream is always adsorbing and the other stream is either purging or regenerating (media ridding itself of H2O). Either N2 or H2 can be used as the regeneration gas.

For each of the above systems, Mersen can supply either the single main equipment or the fully integrated system that is skid assembled in our workshops.

Technical information for quotation
In general, the following information is required to allow us to make a quotation for an AHCL system

End customer and location
- Required AHCL pressure and temperature
- Required purity (water content), etc.
- Specific details of the primary feed streams whether this be Chlorine and Hydrogen, aqueous HCl acid or contaminated HCl gas.

For each feed stream, we require
- Temperature & pressure
- Detailed composition of each feed stream with impurity levels (down to the ppm range)

Utility requirements
- Advise cooling water design inlet & outlet temperature
- Advise steam pressure available (typically up to 10 barg is required)
- Chilled brine or glycol (at -18°C) is typically required
- Nitrogen ; advise temperature and pressure available
- Instrument air : advise temperature and pressure available
- Motor electrics - voltage, phase and frequency (Hz).

Mersen Chemical Equipment References

Based on our systems experience, our know-how of corrosive applications, our materials portfolio and our major manufacturing and service facilities in the USA, Europe, India and China, Mersen’s Chemical Equipment is the preferred choice for these type of systems.

We have or are providing all of these types of systems to make AHCL and are currently very busy processing requests for these types of systems in North America, Europe and Asia...

Our reference lists are available upon request.