The Silicor Process: Environmentally Friendly Solar Silicon

Silicon is the primary building block for the solar photovoltaic (PV) industry. To enable its use in PV cells and modules, metallurgical grade silicon (MG-Si) must be purified to remove boron, phosphorous, oxygen, carbon and other metals. Unfortunately, traditional approaches to removing these impurities, such as the Siemens process or fluidized bed reactors (FBR), require huge amounts of energy, employ toxic chemicals and often create hazardous by-products.

In contrast, Silicor Materials has developed a disruptive process for purifying silicon that reduces energy needs by as much as two-thirds and requires no hazardous chemicals to either enter or leave its facilities.

Below is an overview of each process, focusing on energy requirements and environmental footprints.

Environmental Concerns: The Siemens Process and Fluidized Bed Reactors

Since the 1960s, the Siemens process has served as the dominant method of purification. During the Siemens process, MG-Si is milled to a fine powder and reacted with hydrogen chloride (HCl), an extremely reactive and toxic gas (note: the ratio of chlorine to silicon produced throughout this process is approximately 4:1). This chemical reaction results in the production of several gases including trichlorosilane ($HSiCl_3$), which combusts on contact with air and must be distilled in order to remove the contaminating compounds. Once purified, this gas is decomposed in a reaction chamber to yield pure silicon. Unfortunately, the reaction pathway to yield silicon is but one of several, the result of which is an inefficient conversion of the $HSiCl_3$ to silicon.

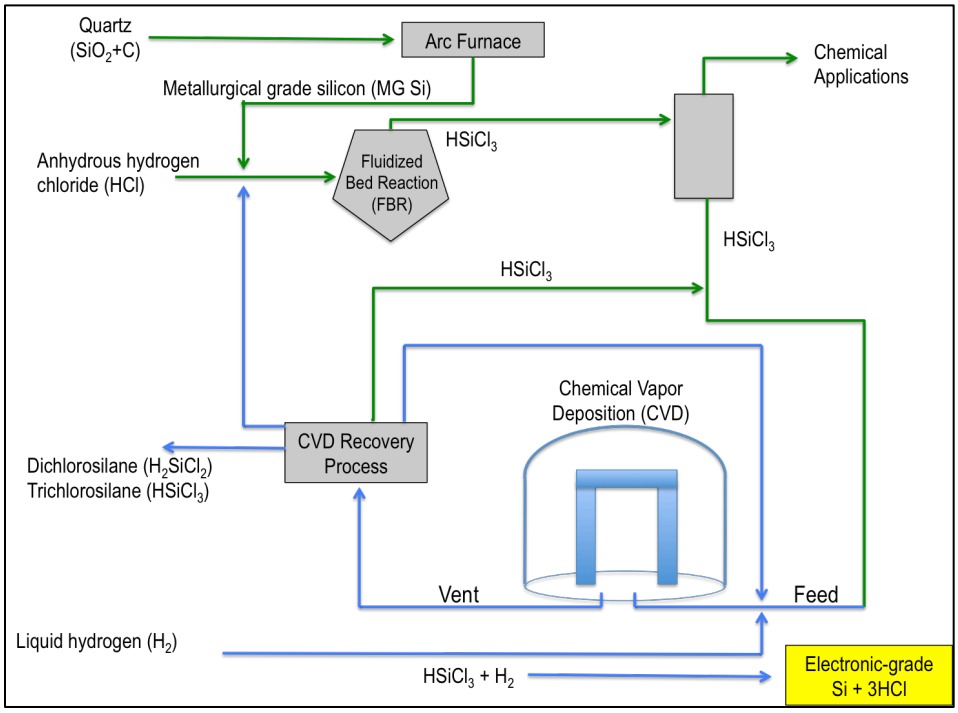

Figure 1. The Siemens Process

One of the primary by-products products of the Siemens process is silicon tetrachloride (STC), which must also be handled with care, as it is both toxic and reactive. STC is further reacted with hydrogen and then recycled, sold as a by-product or disposed.

To reduce energy requirements for silicon purification, the chemical vapor deposition (CVD) reactor of the Siemens process can be replaced with a fluidized bed reactor (FBR). In an FBR, $HSiCl_3$ is thermally decomposed in a counterflow with small silicon particles (dust). Silicon deposits onto the already existing particles, causing the granules to grow until they reach the appropriate size, at which time they fall out of the reactor.

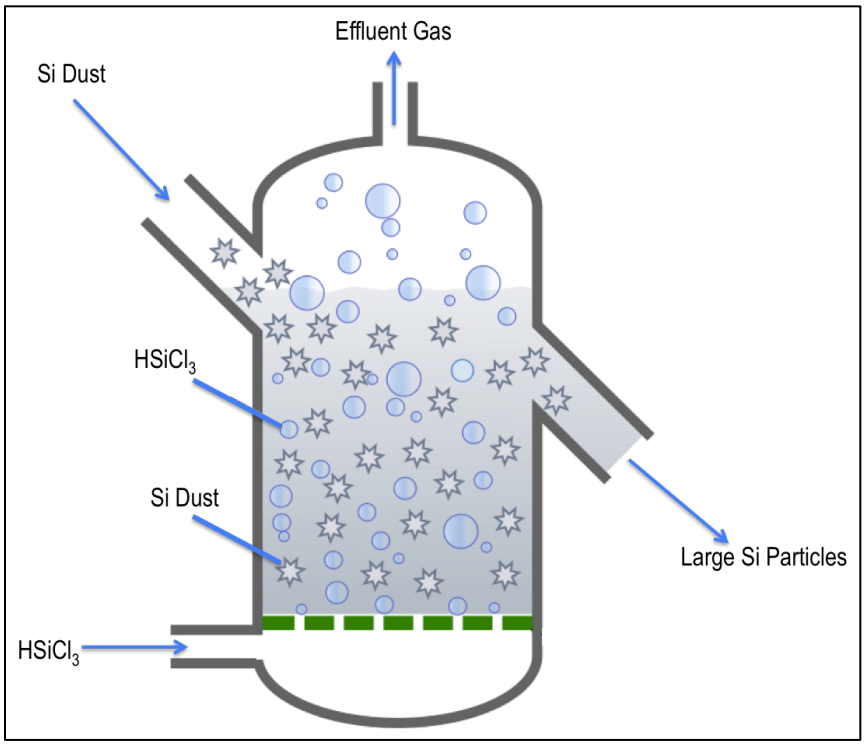

Figure 2. Fluidized Bed Reactor

While the use of FBR technology reduces the amount of energy needed for purification, it also adds considerable complications. FBR requires the use of toxic and explosive gases, which must be carefully handled at all times. The process also yields significant amounts of hazardous by-products, including silicon tetrachloride (SiCl4) and hydrogen (H_2), which require costly transportation and disposal procedures.

The Silicor Process

Silicor's revolutionary purification technique leverages a metallurgical process, rather than the chemical process utilized by the competition. The company uses molten aluminum as a solvent to remove boron, phosphorus and other impurities from MG-Si. The impurities have an affinity to stay in the melt, from which silicon can be grown in form of pure flake-like crystals. This combination of aluminum and silicon also reduces the melting point of the alloy, enabling lower-temperature operations.

Silicor's patented purification process is summarized below:

Step 1: Aluminum Solvent Refining – The first purification process step and the underpinning of Silicor's purification process is the use of "solvent refining," whereby MG-Si is dissolved at relatively low temperatures (less than 1,000°C) in a molten aluminum metal smelt. The material is and then solidified by lowering the solution temperature.

Step 2: Solar Silicon Flake Harvesting – The next step is to remove solar silicon flakes and the remaining aluminum-silicon alloy (master alloy) from the molds used for the melt. The master alloy — which now contains the original aluminum, along with the impurities of the silicon and approximately 18% of the original silicon from the melt — is sold back to aluminum suppliers as a by-product for use in a number of industries, including the automotive, aerospace and building materials sectors.

Step 3: Acid Wash – This step dissolves away the aluminum present on the surface of the solar silicon flakes using hydrochloric acid. This acid wash process also creates polyaluminum chloride (PAC) from the dissolution of aluminum in the hydrochloric acid. PAC is sold as a by-product for water treatment applications at the municipal and industrial scales.

Step 4: Directional Solidification – The final step involves melting the solar silicon flakes in a furnace, followed by casting and directional solidification (DS) in molds. The solar silicon is then allowed to solidify into an ingot. The higher purity portions of the ingot are sold as solar silicon, while the lower purity portions are recycled back into the purification process at the first step.

Overall, Silicor's process slashes the energy required to produce solar silicon by as much as two-thirds, and eliminates the need for harmful chemicals. The result is a critical PV industry feedstock produced in an environmentally friendly fashion – and at ~50% of the traditional manufacturing cost.