

Introduction

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Silicon is the second-most abundant element in the earth's crust after oxygen. In its natural form, it is almost exclusively combined with oxygen as fairly pure silicon dioxide and silicates. Silicon dioxide, in the form of flint, was a main tool for humans in the Stone Age and, later, silicates have been essential in materials such as ceramics and glass. Silicon was recognized as an element in the early nineteenth century and was produced industrially, as silicon or in alloys, from the end of that century. Around 1950, extremely pure silicon was produced and used in semiconductors, the key unit in computers and other electronic devices. Elementary silicon has a semi-metallic, shiny look; it is hard but rather fragile and not suited to the making of structural materials. Silicon is more commonly used to improve the properties of other materials, such as aluminium. Therefore, silicon and its alloys were relatively unknown to the general public before the computer industry made it famous and Silicon Valley became a symbol of the modern world.

This chapter gives a short survey of the production and use of high-silicon alloys. Finally, the availability of raw materials and the sustainability of the production process are discussed.

1.1 Metallurgical production of high-silicon alloys

Silicon is produced industrially by reducing silicon dioxide with carbon in arc furnaces. In an idealized form, this can be written as a mass balance:



We will see later that the real process is more complex. In industry, the available raw materials are not pure, and the product will contain other elements. With pure raw materials and electrodes, it is possible to obtain silicon with less than 1–2 per cent of other elements. This product is traditionally called ‘silicon metal’ even though solid silicon is not a metal but a semiconductor. The furnace behavior during the production of silicon has several features that are markedly different from the corresponding behavior during the production of most metals. These features will be discussed in detail later; here it suffices to state a few characteristic features of the silicon process:

1. The gas in the hottest zone of the furnace has a high content of a silicon-containing gas that must be recovered in the outer charge layers to obtain a high silicon recovery.
2. The silicon-recovering reactions in the outer charge layers heat the charge to a high temperature and create a sticky charge that does not flow easily into the high-temperature zone.
3. The gas from the furnace contains significant amounts of fine particles consisting of SiO_2 , called microsilica or condensed silica fume.
4. The hot off-gas is suited for energy recovery, and microsilica and energy are important by-products in many plants.

This characteristic behavior of silicon furnaces will also be found if we add a limited amount of metals to the charge. The most common alloying element is iron. Silicon content is given by numbers. For example, FeSi75 means an iron-silicon alloy with 75 weight % silicon. In practice, there may be up to several per cent of other elements than silicon and iron. In this book,

the term high silicon alloys include all the silicon-containing alloys where the silicon dominates the behavior in the furnace. We also include alloys that can be produced by metallurgical refining of high silicon alloys from the arc furnace. Such metallurgical refining may be done by slag treatment, gas purging or crystallization. This definition includes the purest silicon that can be made by metallurgical means, but not semiconductor silicon made through distillation and decomposition of compounds containing silicon.

The production of high silicon alloys is presently based on the carbo-thermal reaction that is idealized in Reaction [1.1]. In practical operation, there is always some silicon loss in the gas. This is mainly due to a loss of SiO gas. The SiO combusts together with CO above the charge with the abundant air. This can be summarized in the following equations:



Equations [1.2] and [1.3] describe the process seen inside the furnace. Equations [1.4] and [1.5] include the reactions that take place above the charge layer. Here, x denotes the silicon yield.

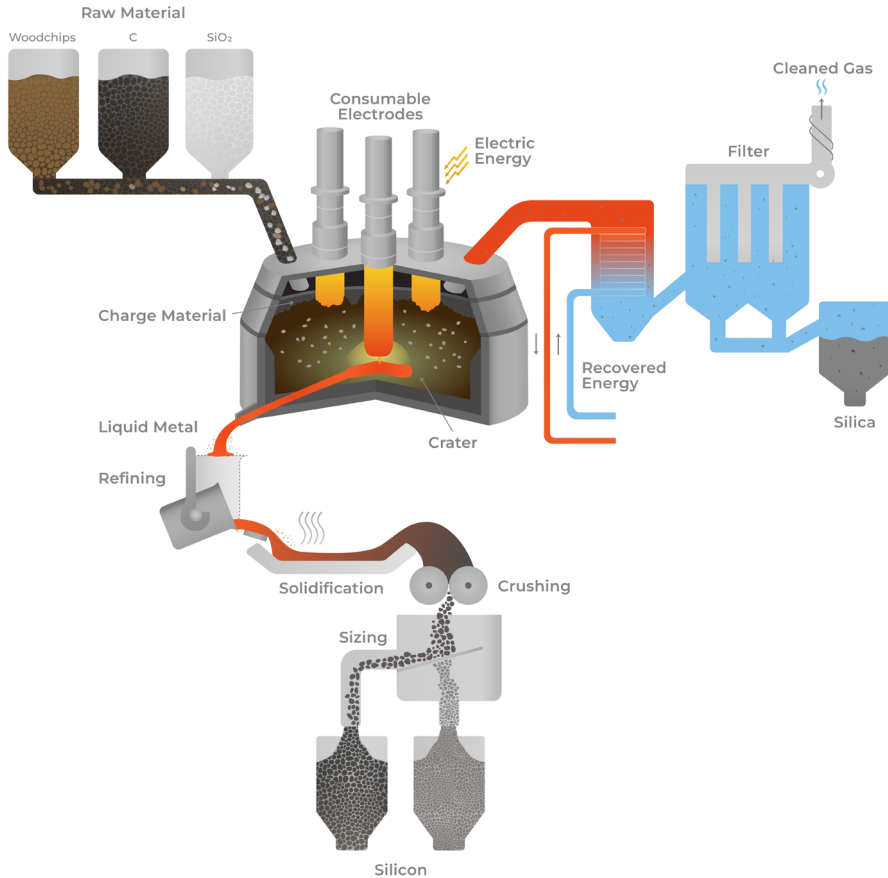


Figure 1.1 A typical plant for the production of metallurgical grade silicon (after Tangstad, 2013).

Figure 1.1 shows a typical silicon plant producing metallurgical grade silicon. The core of the plant is the arc furnace. A typical furnace has a pot with a diameter of around 10 meters, which is filled with charge materials. Three electrodes, submerged in the charge, supply a three-phase current that passes through the contents of the furnace. The current heats part of the charge to about 2000°C in the hottest region. At this high temperature, silicon dioxide is reduced to molten silicon. The silicon is tapped from the bottom of the furnace through a taphole and refined by slag treatment and/or gas purging. During refining, oxides and particles of carbide are removed, and the com-

position is adjusted to the specified value. After refining, the molten alloy is allowed to cool in a suitable mold and is then crushed to the specified size. The consumption of electric energy is 11–13 MWh per metric ton of silicon in most plants.

The gas from the furnace burns above the surface of the charge. Its heat content is of the same order of magnitude as the electric energy added to the furnace. This heat can be used in a heat recovery station for heating or to produce electricity in a power plant. About 30% of the electric energy can be recovered from the off-gas. If the energy is recovered as steam, about 60% of electric energy can be recovered. The filtered gas still has some impurities, mainly sulfur dioxide. The dust in the filter consists mainly of amorphous SiO_2 with a particle size around $0.1\ \mu\text{m}$ and is sometimes named condensed silica fume or microsilica. The silica fume has a specific surface around $20\ \text{m}^2$ per gram. It can be used as an addition or filler to concrete, ceramics, refractory, rubber etc. A furnace produces 0.1–0.4 tons of silica per ton of silicon.

The products of the process are:

1. High silicon alloy.
2. Condensed silica fume.
3. Recoverable heat energy.

The most important high silicon alloys are silicon (higher than 96 per cent silicon) and ferrosilicon with 90, 75 or 65 per cent silicon. Any composition in the Fe–Si system can be produced, and small amounts of alloys of other compositions are produced. Special compositions are most common when small amounts of additional elements, such as magnesium, calcium and rare earth metals, are added. High silicon Al–Si alloy can be produced in the arc furnace, but it has not yet found a large market.

The world production in 2019 of the main high silicon alloys is shown in Figures 1.2 and 1.3. The total production is approximately 2.8 million tons of silicon and 6 million tons of silicon contained in ferrosilicon. Compared to the numbers of 1997, when the previous silicon book was published, global production of silicon and ferrosilicon increased by 3 and 2.3 times, respectively. China, in particular, increased its production from 24% and 31% of global production to 70% and 74%, respectively.

Production of high silicon alloys

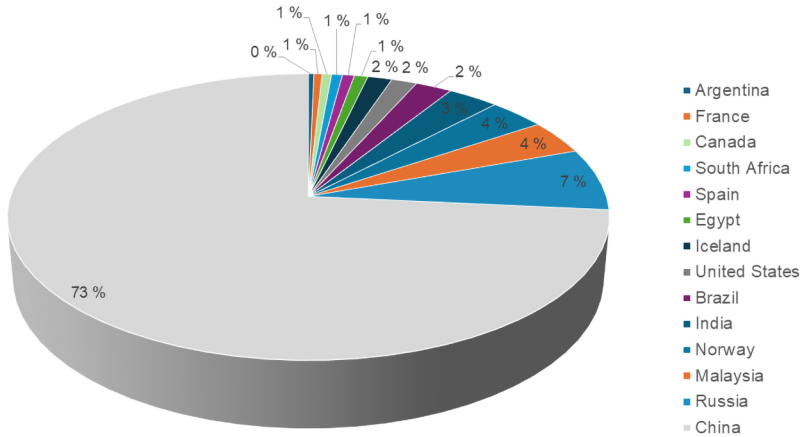


Figure 1.2 The figure shows the global production of silicon by countries in 2019 which was in total about 2 810 000 tons. (Aurelien and Ayre, 2021) [With permission from The Norwegian Ferroalloy Producers' Research Association – FFF].

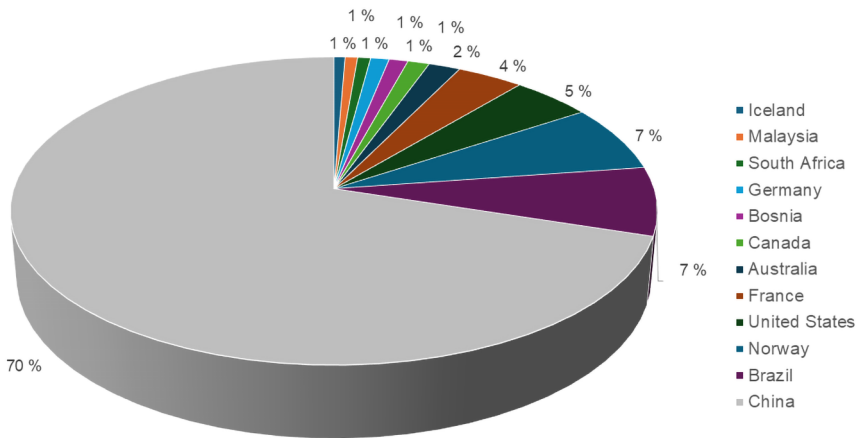


Figure 1.3 The figure shows the global production of silicon in ferrosilicon by countries in 2019 which was in total about 6 million tons. (Aurelien and Ayre, 2021) [With permission from FFF].

1.2 Silicon applications

The main applications for silicon, illustrated in Figure 1.4, are:

1. Deoxidation and alloying of steel and cast iron (mainly ferrosilicon)
2. Raw material for solar cells
3. Alloying of other metals, especially aluminium (mainly silicon)
4. Raw material in the chemical industry (mainly silicon)
5. Raw material for the semiconductor industry
6. Ceramic and refractory products

Ferrosilicon alloys

The largest application of ferrosilicon is steel and cast iron production. The deoxidation task is to bind and remove oxygen and oxides in steel. One example is stainless steel production: ferrosilicon reduces the Cr-rich slag, and consequently most of the valuable elements in the slag, such as chromium and manganese, are recovered.

As an alloying element, silicon is used to increase elasticity and tensile yield, as well as annealing resistance, for different steel qualities.

In cast iron applications, ferrosilicon is used as a base for inoculant materials. Inoculation of liquid iron is the practice of adding small quantities of alloys, which induce graphite nucleation and thereby realize the graphitization potential of the liquid. This use of silicon for the application mentioned above is not expected to grow rapidly, since the iron and steel industry grows slowly, and the consumption of silicon per ton of product decreases.

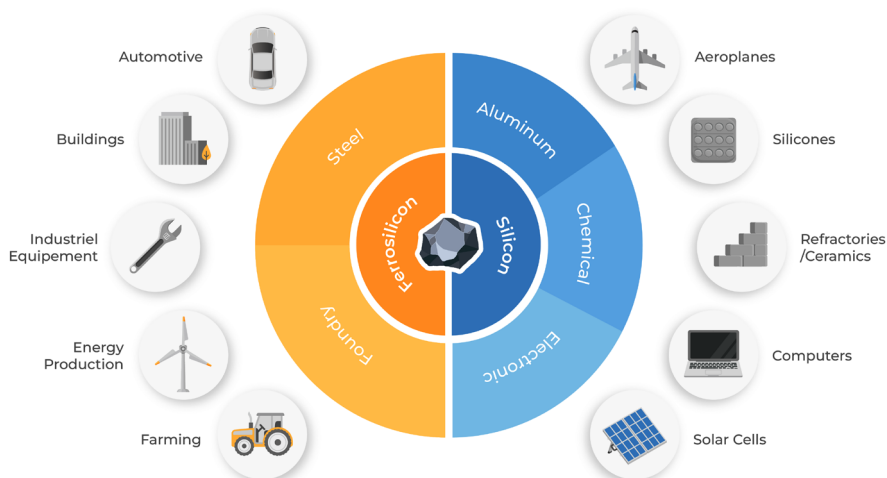


Figure 1.4 Examples of usage of silicon and ferrosilicon alloys (Graphic: Lingyi Ren).

Silicon as an alloying element

Alloying in other metals consumes about 30% of the production of silicon. The use of silicon as an alloying element for aluminium is parallel to ferrosilicon for steel. The main difference is that iron is normally a contaminant in aluminium. The need to achieve low iron content in silicon induces several process parameters, such as the choice of raw material and the use of special iron-free electrodes for silicon production.

Silicon for chemical use

The main products from the chemical industry are silicones, which are silico-organic polymers. They consist of long chains --O--Si--O-- where the two other bonding positions are taken by organic groups, usually the methyl --CH_3 groups.

The first step in the production of silicones is to react silicon with methyl chloride in the presence of a copper catalyst and promoters, for instance zinc and tin, in a fluidized bed reactor. In the second step, dimethyldichlorosilane is hydrolysed to replace the chlorine atoms with hydroxyl groups (silanol). Finally, silicone (polysiloxane) is produced by condensation polymerisation

of the silanols, forming long polysiloxane chains with alternating silicon and oxygen atoms.

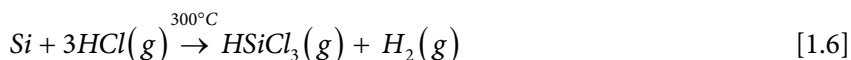
The impurities present in silicon can impact the selectivity for dimethyldichlorosilane, the reactivity between methyl chloride and silicon, and the yield in the process. It is therefore common to adjust the silicon production parameters (raw materials, refining process and casting process) to optimize performance.

The properties vary over a wide range of liquid oils, greases, rubbers and solid resins. Silicones are chemically inert, water-repellent and stable up to about 400°C. They are used as lubricants, hydraulic fluids, protective coatings, electric insulators and artificial body parts.

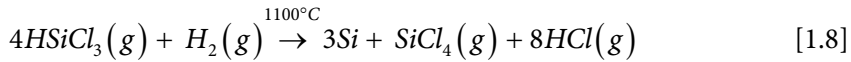
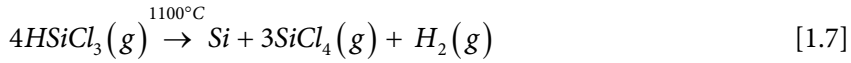
Fumed silica is used as filler in a series of products. Silicon is converted to SiCl_4 in reaction with HCl. The SiCl_4 is later burned to SiO_2 with an extremely high specific surface (fumed silica). The production process can be varied and gives a set of product types with a strong variation in price. Fumed silica can also be produced from by-products from the production of silicones (CH_3SiCl_3).

Silicon for electronic use

Another important application of silicon is its use in semiconductors in everyday electronic devices. This use is well known, even if it stands for a rather small percentage of the total silicon consumption (about 40 000 tons per year in 2025). Silicon for semiconductors must be extremely pure, with an overall content of other elements in the low ppb range (9–11N). This purity is obtained by a complex chemical purification of metallurgical grade silicon. Several processes are possible, but at present the so-called Siemens process is the most important. There, the silicon is transformed to a silicon-containing gas:



The gas is purified by distillation and reduced to silicon at high temperature (1100°C) in the presence of large amounts of hydrogen. A small amount (about 5%) of HCl is typically produced as a by-product, which can be reacted with silicon. The silicon produced in the chemical vapour deposition (CVD) process is typically called polysilicon.



The real process is more complicated than shown here, and the yield of silicon is rather low for most producers. The product is deposited on silicon rods in bell jars with cooled steel walls. Deposition is a slow process, and much energy is used both to keep the interior of the bell jar cold and to heat the reaction gases. There has been a major improvement in the design of the bell jars (CVD reactors) to lower power consumption. Power consumption is today typically less than 50 MWh per metric ton.

Silicon for photovoltaics

Photovoltaic cells convert energy in light directly to electricity. The cells can be made from many materials, but silicon is the most dominant main material, since it is available in virtually unlimited quantities, is non-poisonous, and only moderately expensive. For many years, multi-crystalline solar cells were the dominant technology, and the specification for these types of solar cells was less strict (6N) than the specification for semiconductor silicon.

Recently (2020–2023), technology has changed from multi-crystalline solar cells to mono-crystalline solar cells that require a higher purity (9N). Therefore, polysilicon has become the preferred raw material for solar cells. By-products from polysilicon production that previously could be recycled into multi-crystalline solar cell production need new recycling processes.

Due to the high amount of SiCl_4 by-product from the Siemens process described above, the production of HSiCl_3 for solar applications has changed to mainly recycle the SiCl_4 . This is done by reacting Si with SiCl_4 and H_2 at 500°C and high pressure (up to 30 bars). While the Siemens process needs about 4 kg of metallurgical silicon to produce 1 kg of polysilicon, the recycling process only needs about 1.2 kg metallurgical silicon.

Trichlorosilane (HSiCl_3) can also be converted to SiH_4 . Several companies have developed technology for the decomposition of SiH_4 to granular polysilicon in a fluidized bed reactor. This technology typically had some contamination from the reactor wall, making it very difficult to use in the production of mono-crystalline solar cells. Therefore, coating of the reactor

walls is required to obtain high enough purity of the polysilicon. The advantage of the fluidized bed decomposition process is significantly lower energy consumption (less than 10 MWh per metric ton).

1.3 Availability of raw materials

The silicon process can only be operated with lumps of quartz or quartzite (10–150 mm), and due to losses in the refining process, quartz with low Al content is preferred. The silicon process needs quartz/quartzite that are thermally stable. Some quartz qualities disintegrate when exposed to heat, and they cannot be used in silicon production. In addition, there are strict requirements for impurities in quartz, such as iron and titanium, and therefore only a few quartz deposits are suitable for silicon production. As the total production of metallurgical grade silicon is increasing, the availability of high-quality quartz for this product segment is challenged. The earth's crust is, however, estimated to contain about 28 per cent silicon bound as SiO_2 and silicates. A large fraction of this exists as relatively pure SiO_2 in huge deposits. As long as pure SiO_2 is available, it will be the favored source of silicon. SiO_2 can be upgraded from quartz-containing rock species, and even extraction from silicates is possible, but with a higher environmental impact and higher cost.

The resources of reduction materials are more limited. An important source is coal, which can be used either directly or as a char after heating. The specification of the product composition limits the number of coal types that can be used. The process also requires a certain reactivity of the carbon material, which further reduces the number of available types of coal. Petroleum coke from the oil industry is normally very pure, but it can have lower reactivity. Renewable materials, such as charcoal and other biobased carbon materials, have partly replaced fossil carbon. Though charcoal has a lower mechanical strength compared to coal and char, it has a higher reactivity and may be beneficial for the process. Though charcoal is termed a renewable raw material, it still has an environmental impact through its Global Warming Potential and other factors. It is hence important to focus on sustainable growth and production processes. It is also expected that other biomass than lumpy charcoal will be used ahead, like e.g. agglomerated pyrolysed biomass.

It is also important for society to use more recycled materials. In the silicon production process, this could, in the future, be agglomerates of SiO_2 or carbon, or composite agglomerates containing both carbon- and SiO_2 -fines, and, for the FeSi producers, iron sources.

Silicon production is dependent on electric energy. A change in global energy use or the energy price may affect silicon production. Production of silicon is mainly found in areas with availability of low-cost electric energy.

1.4 Sustainability

Environmental impacts of silicon and ferrosilicon are one of the drivers shaping the production processes, together with cost and product quality. Environmental impacts can be investigated by Life Cycle Assessments (LCA) to determine the quantitative impacts. One of the major impacts of the silicon process is the Global Warming Potential, given by the emissions of CO_2 equivalents from the process itself or from the energy used.

The major CO_2 emissions are from the fossil carbon in the production process, like coal and coke. As today's processes need lumpy, solid carbon, the only short-time mitigation is to replace the fossil carbon with bio-carbon. Most plants today already use woodchips for permeability and some lumpy charcoal as a reductant. The goal is hence to substitute more of the fossil carbon with charcoal, to decrease the total CO_2 emissions. Charcoal has better properties when it comes to permeability and reactivity; however, it typically has lower mechanical strength and will thus create more fines and dust. The reduction of the Global Warming Potential is, however, also dependent on the equivalent CO_2 emissions from the charcoal production itself. Today, some producers have significant methane (CH_4) emissions during the charcoal production process due to incomplete combustion and lack of treatment of the off-gas from the charcoal furnaces.

Though not yet used extensively industrially, it is also expected that biomass agglomerates will be an important part of the reductants in the years to come. As the need for charcoal is much higher than the production of charcoal, not all producers can expect to have access to lumpy charcoal. There is hence a drive towards using other biomass materials, like e.g. agricultural waste. Here, the trace elements will be of importance. One can also agglomerate

the biochar to design a more optimal product, with e.g. higher mechanical strength, and hence have less fines and dust formation.

For silicon plants that are relying on fossil electricity, energy produced by combustion of fossil fuels, energy production can emit more CO₂eq. than the silicon process itself (Sævarsdóttir *et al.*, 2021). For plants consuming renewable energy, this will of course be minimal. Energy is hence a vital part of the environmental impact and cost, and it is important to use less energy per ton of silicon and to recover energy from the process. The energy can be recovered both through hot water and production of energy from high-temperature off gas.

Recycling silicon will reduce environmental impacts. Today, silicon is extensively recycled together with Al in Al–Si parts. The silicone industry is developing methods to recycle silicone products, but it will not be feasible to convert silicones back to silicon. The solar industry has grown from very small volumes 30 years ago to consuming about 30% of the silicon produced today. Recycling technology has been developed for sawing fines (Kerf), and there is now also considerable research on recycling solar cells. As growing numbers of solar cells are taken out of operation, the need for recycling will increase. Raw materials that today cannot be used in the production of silicon due to size can be agglomerated and reused.

References

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