



Emerging Technologies for Decarbonizing Silicon Production

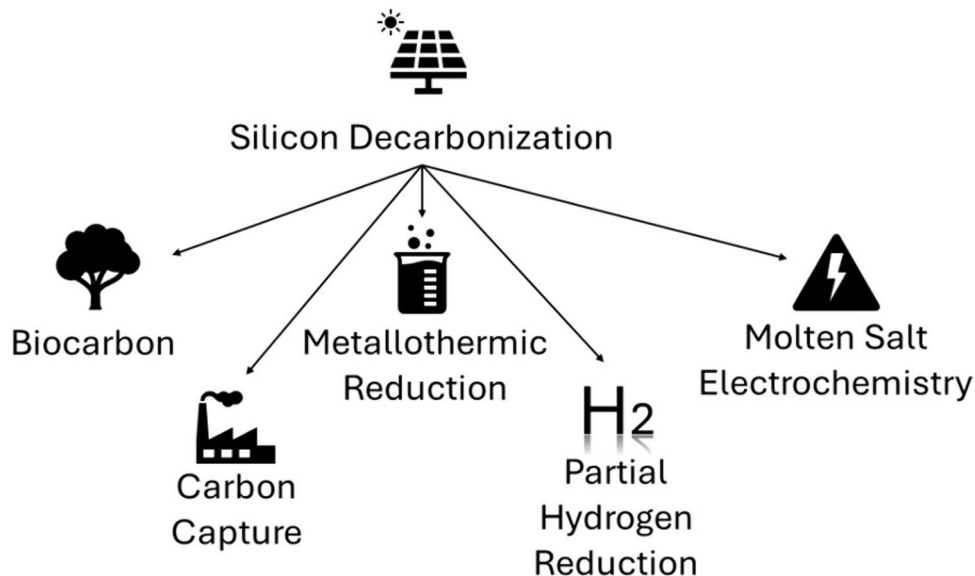
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Abstract

Silicon (Si) is an important material for alloying, solar photovoltaics, and electronics. However, current methods of producing silicon require energy consumption of around 11–13 kWh/kg_{Si} and direct carbon emissions are 4.7–5 tons CO₂ per ton Si which conflicts with global efforts to limit climate change. In this work, we discuss several promising methods for reducing or eliminating carbon emissions from the silicon production process. Such methods include using biocarbon, integrating the current process with carbon capture and utilization/storage (CCU/CCS), metallothermic reduction, hydrogen reduction, and molten salt electrolysis. We present the positive aspects and challenges of each approach. Biocarbon coupled with CCU/CCS is the most industrially mature technology and can be carbon-neutral or -negative but is not carbon-free. Hydrogen directly reducing silicon dioxide is not thermodynamically favorable, but it may be viable to use hydrogen in conjunction with other processes to reduce emissions. Metallothermic and electrochemical methods of production are promising and have the potential to create high-purity silicon with no reduction-related carbon emissions but have only been demonstrated at lab scale. Economic viability will likely be the next determining factor for which technologies are more widely researched and implemented.

Graphical Abstract



Keywords Silicon · Decarbonization · Metallurgy · Hydrogen · Electrochemistry

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Extended author information available on the last page of the article

Introduction

Silicon (Si) production is a large industry and will continue to grow as current technological trends continue and the world moves to combat climate change. This is because silicon has a wide range of uses, including alloying, electronics, silicones, and solar cells (Fig. 1). Worldwide production of silicon in 2021 amounted to 8,500,000 metric tons [1]. The largest producers were China, Brazil, and Norway [1]. According to the International Energy Agency, demand for silicon for use in solar photovoltaics was 390,000 tons in 2020 and is set to grow to between 452,000 and 810,000 tons by 2030 [2].

In the initial stage of production, quartz (SiO_2) is reduced to metallurgical grade silicon (MG-Si) with a purity of > 98%. This step produces roughly 5 tons of carbon dioxide (CO_2) per ton MG-Si [3]. Production of metallurgical grade silicon is, depending on application, either a final or intermediate step in Si production. Metallurgical grade silicon can either be used for alloying or be sent for further refining for solar and electronic uses, which require higher purity levels. To achieve these purity levels, the Siemens process is often used, producing additional emissions.

While Siemens process emissions are very high due to an energy consumption of up to 100kWh/ kg Si [5], only a relatively small fraction of all silicon goes through this process, as illustrated in Fig. 1. Thus, the total carbon emissions from MG-Si production are significant even when compared to the Siemens process, which is more energy intensive on a per-kg basis.

Current industrial production of metallurgical silicon predominately uses submerged arc furnaces (SAFs), which

require carbon as a reducing agent in addition to large amounts of electricity [6]. Given global trends in the price of both electricity and carbon-based reductants, there is interest in decarbonizing the silicon industry beyond reducing the impact of climate change. However, this poses a challenge, given the inherent stability of SiO_2 , as well as the efficacy of carbon as a reductant. Various innovations have been introduced in recent years to minimize carbon emissions from the traditional SAF. Process optimization developments have led to very high efficiency in the furnace to minimize energy and carbon consumption. Efforts are also being made to address inputs and outputs from SAFs, including increased substitution of biocarbon for fossil-carbon (with potential for reduction in net emissions, depending on biocarbon source) and carbon capture and utilization/storage (CCU/CCS) of emissions. However, existing SAF-based technologies fail to fully eliminate carbon emissions intrinsic to reactor chemistries. Other SiO_2 reduction technologies exist in various states of readiness from research and development to pilot scale, but all face their own technological hurdles before they can compete with SAF [7].

This review seeks to explore promising methods of reducing or eliminating carbon emissions from MG-Si production. We discuss five methods, representing some of the most widely researched and/or promising methods to date. The methods are: (1) use of biocarbon; (2) CCU/CCS; (3) metallothermic reduction; (4) use of hydrogen as a reductant coupled with other methods; and (5) electrolysis. The first three methods are relatively mature, and use of biocarbon has already been implemented at the industrial scale. In contrast, hydrogen and electrolysis-based reduction routes are promising, but still in early experimental stages [7].

We note that these decarbonization approaches will require affordable and reliable low-carbon sources of electricity. We acknowledge that this is not given, as decarbonization of the electric grid and deployment of clean electricity technologies poses a significant challenge, but this is beyond the scope of this review. We also note that, in addition to producing MG-Si, many silicon producers also produce ferrosilicon. Therefore, they can in some sources be discussed interchangeably. However, ferrosilicon is primarily used for alloying and will not be refined to high-purity silicon. The production processes for both silicon and ferrosilicon are mainly the same. The exception is the addition of iron scrap to the raw material mix. This work deals mainly with silicon, not ferrosilicon; however, a ferrosilicon plant is mentioned in the context of biocarbon use.

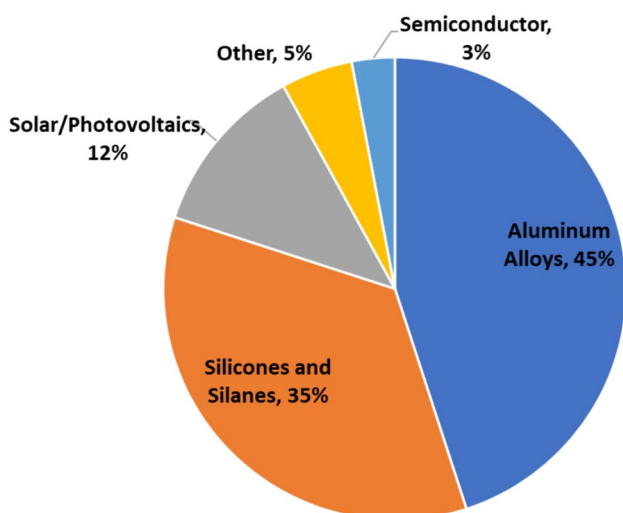


Fig. 1 Silicon use by application, according to the CRU Market Data, 2017, adapted from [4]

Background

SAFs

Carbothermic reduction of quartz to silicon is a key operating principle of SAFs. Consumable carbon electrodes supply

energy to the system by striking an arc with the molten slag/silicon pool at the furnace bottom. The SAF is typically divided into two zones based on temperature [8], as illustrated in Fig. 2. In the high-temperature zone, which is deeper in the furnace, temperatures are up to 2000 °C. Silicon monoxide (SiO) gas is produced in this region (Reactions 5 and reverse of Reaction 3). Silicon is also produced in this region via Reaction 4 from SiO gas and solid silicon carbide (SiC). As SiO and carbon monoxide (CO) gas rise, they reach the low-temperature zone in the furnace. In this zone, SiO gas reacts with solid carbon or CO gas to produce the SiC (Reactions 1 and 2) needed for the silicon-producing reaction. Additionally, SiO can disproportionate/reform into Si and SiO₂ (Reaction 3). Any gases not captured when they reach the top of the furnace will oxidize in air to produce microsilica and CO₂. Microsilica, or silica fume, is a valuable byproduct used primarily for cement and concrete manufacturing [9]. As shown, SiO₂ is not directly reduced by the carbon, but rather requires two important intermediates, SiO and SiC. These two components allow for the reaction that produces most of the silicon.

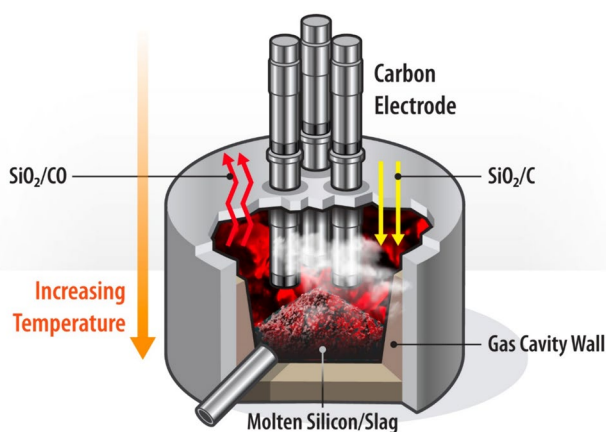
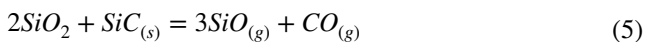
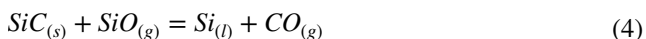
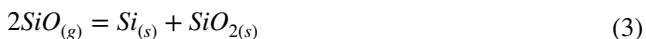
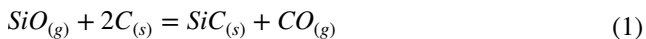


Fig. 2 Illustration of the area around a single electrode in the SAF. Gas diffuses upwards in the furnace through the arc cavity, with fresh raw materials flowing downward toward the hotter areas of the furnace. Molten silicon and slag are tapped from the bottom. Illustration by Alfred Hicks, NREL

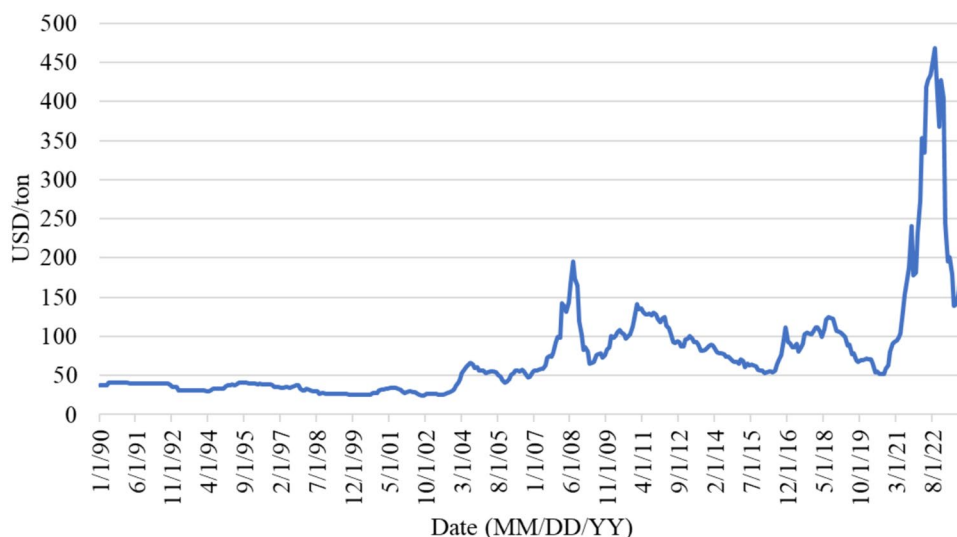
SAFs used in silicon production are considered very efficient in terms of silicon yield. This is due to the heat dissipated from the arc and the successful recapture of microsilica in the off-gas. Some furnaces report operating at up to 90% silicon yield [6]. However, even with such a high yield, energy consumption is usually 11–13 kWh/kg_{Si} and direct carbon emissions are 4.7–5 tons CO₂ per ton Si [3]. In some ways, in this SiC-mediated route, the high energy usage and emissions are unavoidable, as both the heat to drive the reactions and carbon-forming SiC are key points in the process. Energy recovery systems have been used to reduce energy consumption, but this is outside the scope of our analysis, which assumes clean energy and focuses on the reduction process.

The raw materials used in the SAF are quartz and some combination of carbon materials, including coal, coke, charcoal, and woodchips. Quartz, one of the most common and most mined materials in the earth's crust [10], is not considered scarce. It is usually relatively pure, though impurities in the quartz can be important for both the production process and the quality of the final silicon product [11]. However, coal and coke are considered commodities and thus are vulnerable to price swings based on the global landscape. Figure 3 shows the global price of coal from Australia from the International Monetary Fund, which shows the large spike in early 2022 [12]. Coal and coke are also nonrenewable, fossil-based reductants. Charcoal and woodchips, which are renewable and biobased, are used in relatively small amounts (around 10–20% of the total carbon in the charge) to increase permeability of the charge [13].

Siemens Process

Some applications of silicon, such as photovoltaics and semiconductor industries, require a much higher purity than is achievable with conventional MG-Si production. The Siemens process, and related purifications, are the main way in which high-purity silicon is produced [14]. The process is depicted in Fig. 4 and involves converting MG-Si to Si-rich gases followed by distillation purification and subsequent vapor deposition of solid Si. In the Siemens process, the MG-Si is typically converted to SiCl₃H, trichlorosilane (TCS), though related silane or SiCl_xH_{4-x} chemistries are targeted in some purification processes. The production, purification, and reaction of these chlorosilanes to and from solid Si is much more energy-intensive than the generation of MG-Si. Some of the technologies that will be discussed propose a modified Siemens process, wherein MG-Si is replaced as the raw material, but a similar process is implemented to produce pure silicon [15]. However, as seen in Fig. 1, the majority of MG-Si is used for alloying, and therefore any modified Siemens process would only replace applications in which high-purity Si is needed.

Fig. 3 Global price of Australian coal, 1990–2022, in U.S. dollar (USD)/ton, adapted from [12]



The Siemens process and related techniques use hydrogen (H_2) as part of the reduction of the Si-containing gases into high-purity Si and hydrogen-halide gases. It is worth noting that, at the time of writing, the vast majority of global H_2 production is via reforming of natural gas and has large associated CO_2 emissions. As water electrolysis and renewable energy technologies are more widely adopted, the emissions associated with this H_2 feedstock will decrease. For the purposes of this article, we do not focus on emission reductions associated with the H_2 feedstock of the Siemens process; instead, we focus on reducing net emissions of Si reduction and purification steps.

Discussion

Overview of Low-Carbon Technologies

Table 1 summarizes the five main technologies we examined, including their raw materials, main process method, emissions, and relative readiness level. The use of biocarbon is at the highest readiness level, given that it is already being used to varying degrees of substitution for fossil-carbon in processes across the world. No CCU/CCS for silicon production is in use as of this publication due to the relatively low amount of CO_2 in the off gas, making it economically unviable. However, CCU/CCS technology is in use across other sectors today and could be implemented onto existing SAFs [16].

Use of Biocarbon

Using biocarbon is a relatively straightforward method to reduce net CO_2 emissions from silicon production. This process uses the SAF in the same way as conventional

MG-Si production but replaces coal and coke with biocarbon such as charcoal and recycled woodchips. While this does not eliminate carbon emissions, the process approaches carbon neutrality, depending on the emissions associated with growing, harvesting, processing, and transporting the plant matter and offset by the CO_2 absorbed by the plant during its lifetime.

Figure 5 illustrates the climate change impact of six different carbon materials [17]. Total impacts include contributions from uptake, production, transport, and direct emissions. For woodchips, transport accounts for the small total impact. Processing biomass into charcoal (energy and emissions) must also be considered and could be offset differently if the volatile organics evolved during pyrolysis are combusted to heat charcoal production or are captured for further use. The life cycle emissions for biomass use in SAFs are a complex convergence of factors that are impacted by several biomass growth and processing parameters; Fig. 5 provides a representative snapshot of current trends. Finally, coal and coke have the highest impact from their direct emissions because they are fossil-based.

Studies have shown that biocarbon performs similarly to fossil-based reductants in the silicon furnace; therefore, silicon yield would in theory not need to be sacrificed to make the switch [18]. However, this substitution still poses challenges, as the full supply chain for biocarbon is still emerging. According to J.D. Supra, the demand for biochar is expected to triple by 2030 [19]. Silicon producers would need to be aware of the sustainability of their sources of biomass and adjust accordingly if necessary. There are efforts to assess the potential supply of biocarbon feedstocks—for example, the U.S. Department of Energy’s *2023 Billion-Ton Report* [20]. This report sought to assess the availability of renewable biomass to replace fossil fuel resources in the

SIEMENS PROCESS

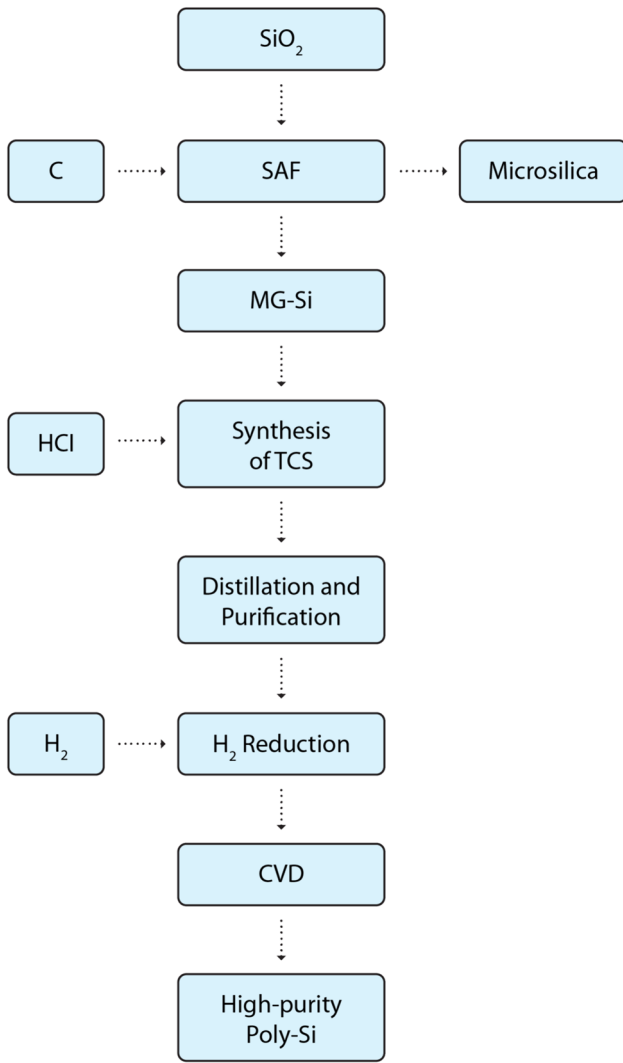


Fig. 4 Schematic of basic Siemens process, starting with SiO₂ and the production of MG-Si. HCl is hydrochloric acid, TCS is trichlorosilane, CVD is chemical vapor deposition. Graphic by Dominique Barnes, NREL

United States without affecting demand for industries such as agriculture and exports.

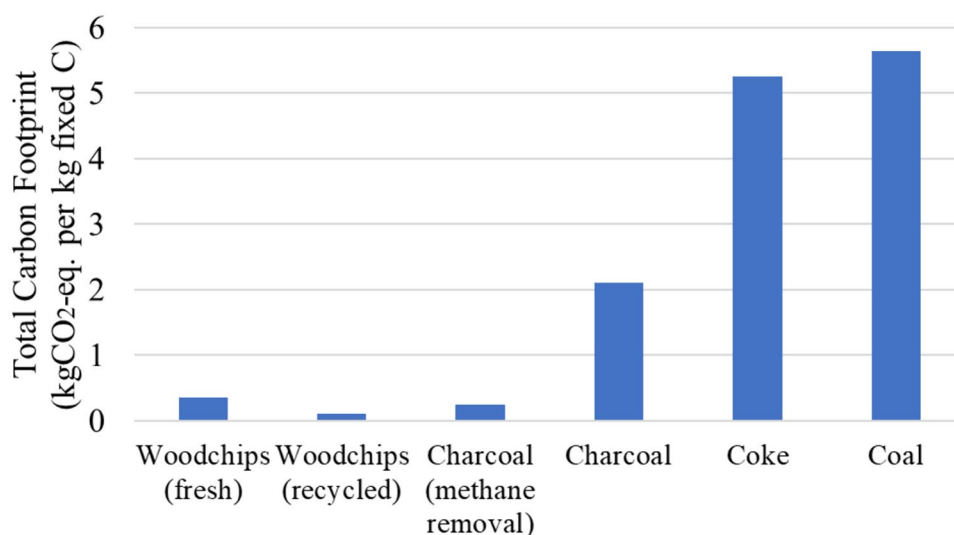
Use of 100% biocarbon still poses some challenges for the operation within the SAF. Charcoal, for example, has a weak mechanical strength and is prone to producing fines, which are small dust and particulate matter, which in large quantities could block the proper flow of gas through the furnace unless additional design changes are implemented. Studies have sought to address this challenge through densification and heat treatment of charcoal feedstocks [21]. Additionally, the carbon electrode remains a source of carbon emissions because it is consumed during the process. Carbon electrodes are historically produced via processing

Table 1 Summary of technological possibilities of reducing or eliminating carbon emissions for silicon production

Technology/Method	Raw Materials*	Main Method of Utilization	Source of Emissions**	Readiness Level
1. Use of Biocarbon	Charcoal or other manufactured biocarbon	SAF	Raw materials, carbon electrode (unless similarly replaced with renewably generated graphite) can be coupled with carbon capture	Industry-ready
2. CCU/CCS	Same as SAF (e.g., fossil carbon or in combination with biocarbon substitution)	SAF with carbon capture and/or flue gas recirculation	None, if 100% captured and later used	Industry-ready
3. Metallothermal Reduction	Less noble metal, aluminum or magnesium	Metallothermal reduction	No direct emissions, but associated emissions from production of metal reductant	Lab scale
4. Hydrogen Reduction of SiO ₂ , Followed by a Modified Siemens Process or a Modified SiC Pathway Using Natural Gas	Green hydrogen	Various possible technologies	Depends on technology, combination of H ₂ O, and if relying on SiC-involved pathway, then CH ₄ , CO, and CO ₂ . Can be coupled with carbon capture	Lab scale
5. Electrochemistry	Molten salts, cathode/anode	Electrolytic cell/reactor	None if noncarbon electrode is used, and 1.6–3.1 tonCO ₂ /tonSi if a carbon electrode is used and consumed to form CO ₂ or CO	Lab scale

*Excluding SiO₂. **Assuming CO₂-free electricity

Fig. 5 The total carbon footprint in kg CO₂eq per kg of fixed C for carbon materials used in silicon production, adapted from [17]. Total includes contributions from uptake, production, transport, and direct emissions



geological/fossil carbon. Carbon electrodes require a much more graphitized carbon than is produced by conventional biomass processing. Although, in theory, biocarbon could be used to make carbon electrodes, economic production of more-engineered carbons, such as electrodes, is much less mature than the production of biocarbon used to substitute for coal or coke.

Elkem's Limpio plant in Paraguay [22, 23], which opened in March 2018, is an interesting case study in utilizing local resources to create a mostly carbon-neutral production process of ferrosilicon. The plant has one 11.5-MW SAF, which has an annual capacity of 11,000 metric tons of ferrosilicon. The process uses 100% charcoal in their raw material mix. Eucalyptus trees are grown on-site for harvesting so local forests are not affected. Electrical power is supplied to the plant using 100% hydroelectric power from the region. They further claim that quartz is locally mined, and the produced ferrosilicon is supplied for alloying needs in the region. However, emissions associated with electrode consumption are not addressed. While this plant is a great example for the circular economy, it is not necessarily scalable.

CCU/CCS

CCU/CCS is gaining popularity across many sectors looking to decarbonize. The basic concept is to capture the CO₂ produced before it is released to atmosphere, and either repurpose or permanently store it to prevent it from entering the atmosphere. This technology on its own is not specific to the MG-Si industry and can be applied to a variety of processes. However, given its prevalence in decarbonization discussions, it is worth discussing the advantages and challenges that are specific to the MG-Si process. Within the MG-Si sector, it is seen as a favorable solution because it involves little disruption to existing operation. Carbon capture

apparatuses can be retrofitted and incorporated into existing plants. Furthermore, if coupled with the use of biocarbon, the process becomes carbon-negative. A challenge for silicon producers to implement CCU/CCS is the concentration of CO₂ in the off-gas. Only about 3%–4% of the off-gas from the furnace is CO₂, with the remaining being a combination of nitrogen, oxygen, water, nitrogen oxide, SO_x, and some heavy metals [24]. This makes it expensive and difficult to justify capturing. Work has been done regarding the possibility of recirculating exhaust gas to increase the concentration of CO₂ for CCS capability [13]. In this method, exhaust gas is recirculated back into the furnace after it has been filtered for particulate matter and slightly cooled, replacing a part of what would normally be fresh air coming into the furnace. A pilot-scale Si furnace tested this theory and found they successfully increased the CO₂ concentration to above 20 vol%. This recirculation also happened to reduce specific nitrogen oxide emissions, which is another important pollutant gas. However, while this study showed the increased CO₂ concentration and reduced cost of carbon capture on a pilot-scale furnace, additional work is needed in this area to determine viability on an industrial scale [13]. One techno-economic study of a ferrosilicon plant suggests that it is viable to combine the gas recirculation of the SAF with carbon capture in molten salts, wherein the CO₂ is looped through a calcium oxide-rich salt, converted to calcium carbonate, and then run through a desorber [24].

There is also the question of what to do with the captured carbon. Geological storage of CO₂, by far the most mature use of captured CO₂, is restricted to certain geological formations [25]. Elkem is heading a project that seeks to reduce their carbon emissions through carbon looping—in other words, utilization rather than storage [26]. This involves capturing the CO₂ in the off-gas and converting it to solid carbon that can be reused in the furnace. Elkem believes

perfecting this process will be an important achievement for decarbonizing MG-Si if it can be made cost-competitive. In addition to cost, they likely face the challenge of managing the properties of the produced carbon to be favorable in the furnace. For example, porosity, electrical resistivity, and SiO reactivity are important properties to evaluate the carbon’s suitability for use in the furnace.

Metallothermic Reduction

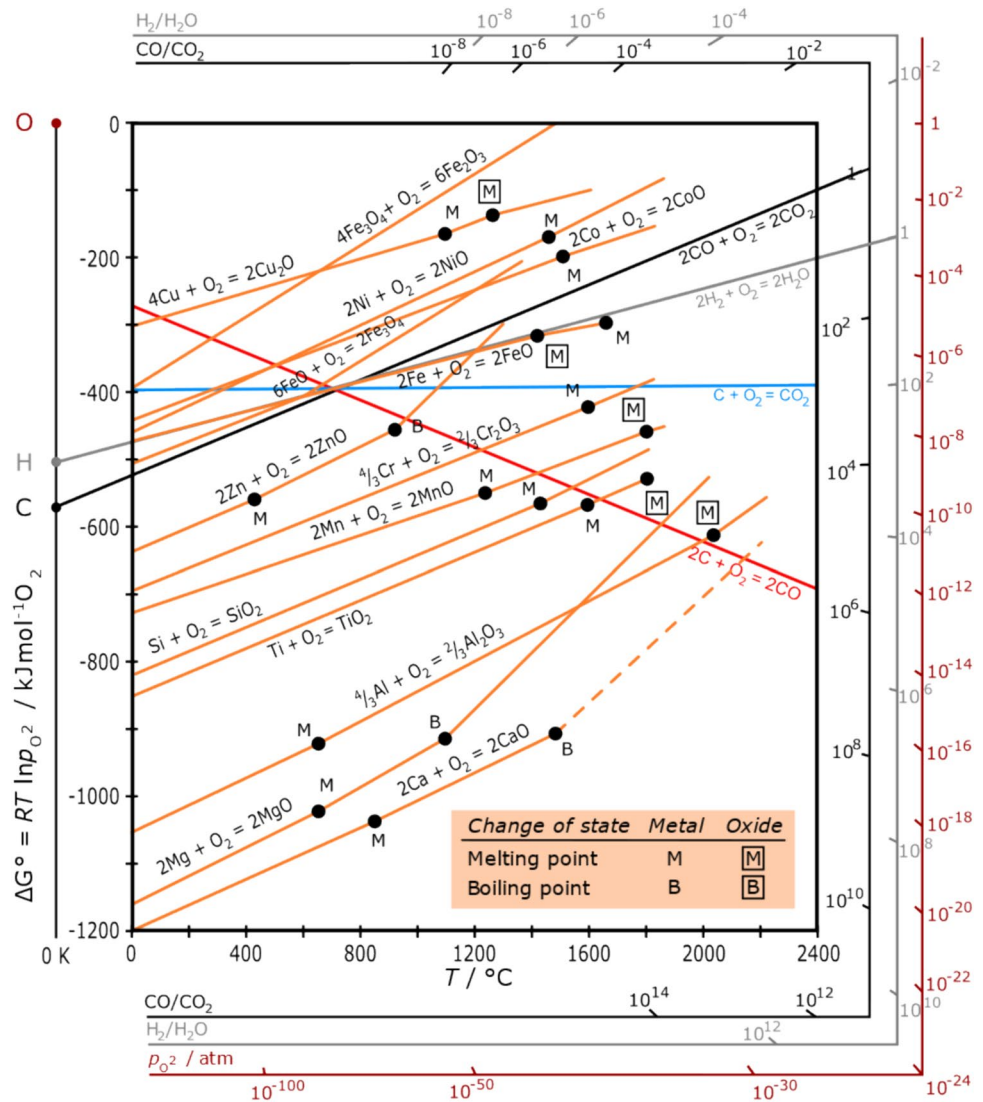
Metallothermic reduction is based on the principle that a metal can be used as a reductant for the oxide of a more noble metal. This has been explored as a means of silicon production. Based on the thermodynamics, shown by the Ellingham diagram in Fig. 6, calcium (Ca), aluminum (Al), magnesium (Mg), and titanium (Ti) (not an exhaustive list) are all less noble than Si and thus could be used for metallothermic reduction of SiO₂ [7]. Of these candidates, Al

and Mg have been most explored. However, metallothermic reduction consumes a metal that otherwise has substantially more value than typical carbon reductants. The resulting product could either be a mixture of Si and a different metal oxide, or an alloy of Si with the metal reductant in a mixture with a metal oxide. Markets for some of these alloys include the use of silicon-aluminum alloys in the automobile industry. While these methods may be chemically efficient, a critical look at the practicality will be needed if the technology is to be developed further.

Metallothermic Reduction Using Aluminum

An investigation of using aluminum to reduce silica was performed in the European Union’s SisAl project [28]. In this process, quartz and flux, normally calcium oxide, are melted together to form a silicate slag. Aluminum is then added, either as dross or pure metal, which reduces the silicon in

Fig. 6 Ellingham diagram, reprinted from Wikimedia Commons [27]



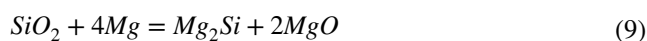
the slag to form a silicon alloy of some purity via Reaction 7. The choice of aluminum reductant influences the purity of the silicon, as pure aluminum has fewer impurities than dross. However, dross is a mixed Al-Al₂O₃ byproduct of the aluminum process, making it a much less expensive and potentially lower net emissions reductant, with potential mutual benefits for both the aluminum and silicon industries. The use of dross further addresses the possible circularity of using one metal to produce another, because dross is a byproduct of aluminum production.

Reduction of Si has been proven on the lab scale using both aluminum and dross as raw materials at 1650 °C [29]. The potential for further circularity exists if the byproducts of the process are recycled. The remaining reduced aluminosilicate slag can be recovered, the calcium oxide can be recycled back into the process, and the alumina (Al₂O₃, product from Reaction 7), which should be of relatively high purity compared to many primary aluminum feedstocks, can be used as raw material for primary aluminum production or further refined to high-purity alumina [30].



Metallothermic Reduction Using Magnesium

Another possibility is magnesiothermic reduction of quartz. In this process, Mg reduces SiO₂ and produces MgO and either Si or magnesium silicide (Mg₂Si), depending on the molar ratios of Mg to SiO₂, temperature, time, and particle sizes. This process produces either high-purity Si, or Mg₂Si (Reactions 8 and 9), which acts as a substitute for MG-Si in a modified Siemens process. Challenges of this method include the formation of byproducts, the high reactivity of Mg, and incomplete reactions [31]. On the lab scale, the publication showed that about 75% of the silicon was reduced (either as Mg₂Si or Si) after 240 min at 1173 K [32]. At higher temperature, the reaction was faster, with all the SiO₂ reduced after 20 min at 1,273 K [31].

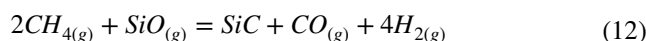


Hydrogen

Replacement of carbon reductants with H₂ is becoming a popular solution for decarbonization, as this substitution produces steam (H₂O) instead of CO₂. However, thermodynamically, SiO₂ will not be reduced directly by 1 atm of hydrogen until temperatures exceed 2400 °C, as evident in Fig. 7. To understand the challenges, it is helpful to consider

how SiO₂ goes through a series of intermediates with carbon before it reduces to Si. Similarly, based on the thermodynamics of the Si–O–H system, H₂ can reduce SiO₂ to SiO, which is the first half of the main silicon production process (Reaction 8). Only a fraction of H₂ would participate in Reaction 8, requiring an excess of H₂ (such as could be achieved by higher total gas pressures). However, SiO must then be reduced to Si. More issues arise for the second step, as H₂ reducing SiO to Si is not thermodynamically favorable (Reaction 9) [33].

Two possible paths have been explored to achieve this second step of reduction of SiO to Si with H₂. The first is to introduce methane gas to form SiC (Reaction 10), which can then in theory form Si in the same reaction used in the SAF (Reaction 11) [34–36]. While still relying on carbon, this route would use substantially less carbon than current methods and could be paired with CCU systems to obtain carbon neutrality. However, temperature, the stability of the SiO, methane, and water vapor, all pose significant challenges that would need to be overcome for any large-scale production to occur [34]. Preliminary work was conducted using selective condensation of SiO gas to form Si and SiO₂ (Reaction 3). However, extraction of the produced silicon proved difficult [37].

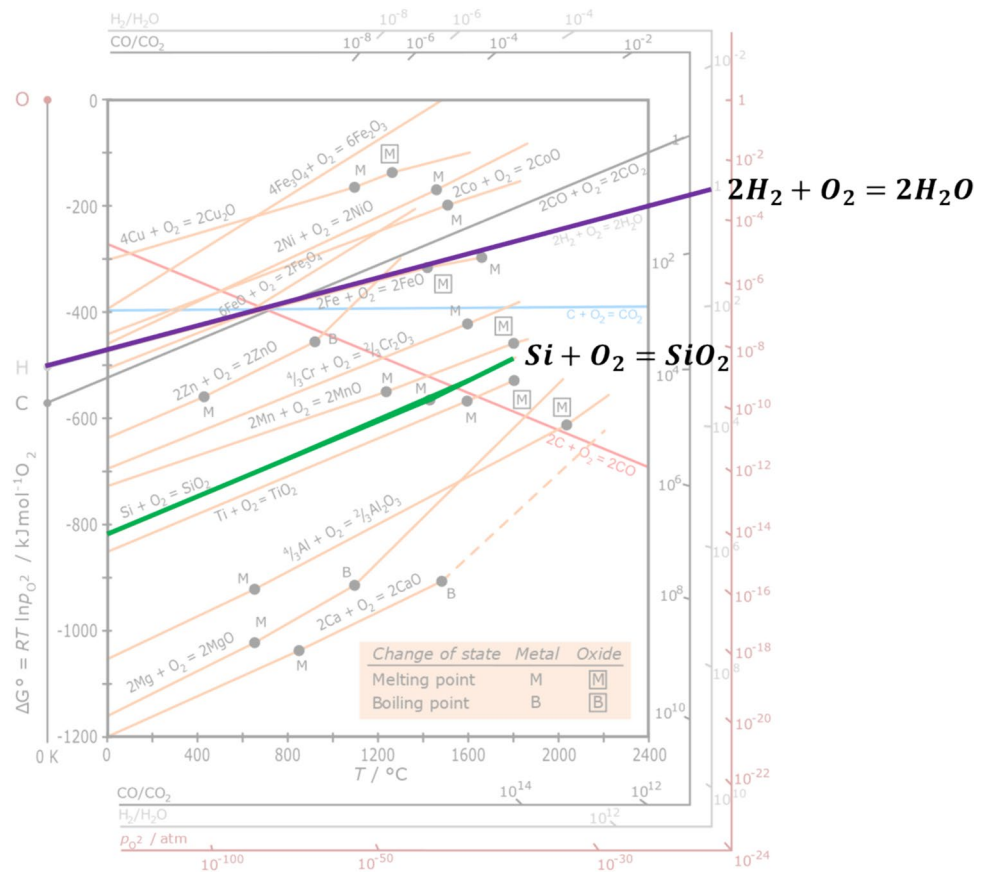


The second option for reducing SiO to Si is specific to high-purity Si products. In this path, hydrogen-produced SiO could be used directly as a feedstock for a modified Siemens process (Fig. 8). This utilizes Reaction 8 to form the SiO gas. The SiO gas can then be chlorinated, which will lead into the Siemens process at the silane step. However, an essential aspect would be separation of H₂/H₂O from the SiO produced in the initial reduction step (Reaction 8), prior to the chlorination step [33]. Both solutions to utilize hydrogen-produced SiO gas still require high temperatures to be reasonable, as well as large-scale hydrogen and gas separation infrastructure. Therefore, significant challenges must be overcome before this path can be scaled.

Electrochemical Reduction with Molten Salt Electrolytes

There is interest in using electrochemistry and molten salt electrolytes to facilitate silicon production without the use

Fig. 7 Ellingham diagram, same as Fig. 6, reprinted from [27], with silicon (lower bold green line) and hydrogen (upper bold purple line) highlighted for clarity



of SAFs. The working principle is so called “electro-deoxidation,” in which electrons are directly used as the reducing agent. Molten salt electrochemistry has been successfully applied to reducing multiple metals with larger free energies of reduction than Si, such as most Al_2O_3 reduction occurring using molten fluoride electrochemistry [25] and the FFC Cambridge process [38], in which titanium is produced from titanium oxide in molten calcium chloride ($CaCl_2$) at 900 °C, (not to be confused with the Kroll process, which uses a titanium tetrachloride gas phase).

Similar principles have been applied to silica to produce silicon [39]. In these molten salt electrochemical processes, a metal oxide located at the cathode is reduced by electrons (Reaction 12), generating oxide ions (O^{2-}) that are transported as-is, or as an ionic complex, to the anode, leaving metal deposited at the cathode. If the anode is carbon, then the oxide ion reacts at the anode to form either CO (Reaction 13) or CO_2 . Lower-emission anodic reactions are theoretically possible, such as Reactions 14 and 15.



where M is an arbitrary metal



However, challenges must be addressed for the technology to become fully viable. The first is the choice of electrolyte. $CaCl_2$ is a popular choice due to its physical and electrical properties, as well as its easy availability and environmental friendliness. Fluoride salts, similar to those used for Al_2O_3 reduction, are another possibility that has been studied, though the potential for hydrofluoric acid formation and purity and diffusivity problems remain an issue [39]. However, fluoride salt electrochemistry is used for Al_2O_3 reduction at a large scale, so solutions to many of the concerns with fluorides may be translatable from the Al industry. Eutectic metallic melts, rather than salts, of lithium (Li), potassium (K), etc., have also been studied, but tend to have slow diffusivity. Spherical silicon powder was also produced in $LiCl-Li_2O$ melts on a lab scale at low temperature [40].

The second challenge is the choice of anode. Carbon is the typical anode material used in literature to successfully reduce silica to silicon. This creates CO/CO_2 emissions, in addition to consumption of the anode, which erodes and must be replaced. However, if the goal is a carbon-free

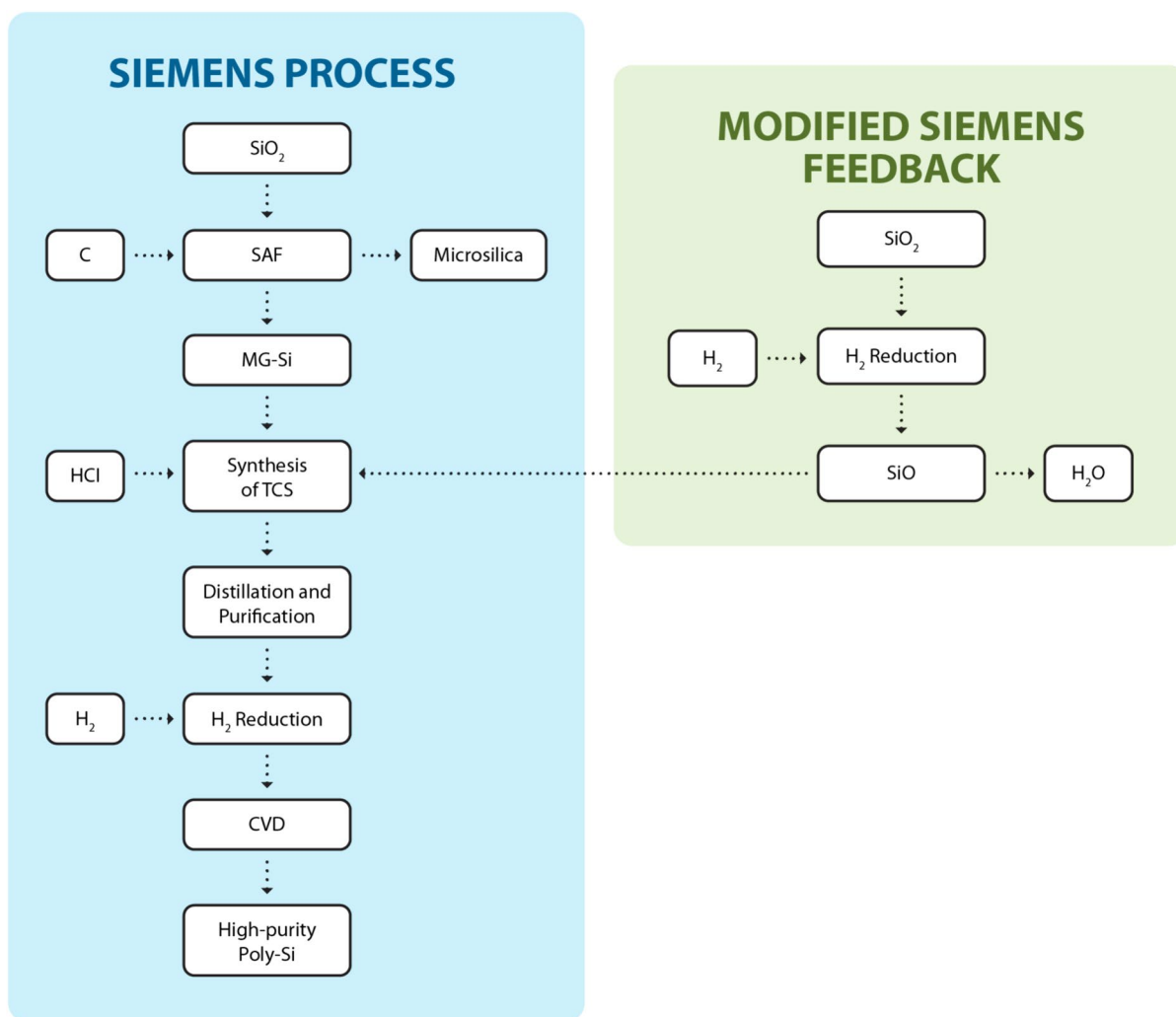


Fig. 8 Schematic of potential modified Siemens process with SiO_2 as feedstock instead of MG-Si. HCl is hydrochloric acid, TCS is trichlorosilane, CVD is chemical vapor deposition. Graphic by Dominique Barnes, NREL

process, then alternatives must be found with the same effectiveness. Various alternatives have been proposed; however, one of the most promising is a solid solution of CaTiO_3 and CaRuO_3 (sometimes abbreviated Ti-Ru) to evolve oxygen (Reaction 15) [39]. However, the cost of Ru remains a concern for any large-scale adoption. Another study experimented with Ti_4O_7 as an anode in molten CaCl_2 at 850°C , and successfully produced silicon wires, films, and particles [41]. They further suggested that H_2 reduction could be used to extend the lifetime of the anode.

Relative to SAF production, molten salt electrochemical pathways have potential advantages in emissions, operating temperature, energy efficiency, and product purity, but do have lower kinetics. While use of a carbon anode would generate CO_2 emissions, these are potentially still lower than SAF emissions, and use of alternative anodes with an O_2 - or H_2O -forming reaction completely removes intrinsic

CO_2 emissions. The peak operating temperature of proposed molten salt electrochemical pathways for SiO_2 reduction tend to be $500\text{--}900^\circ\text{C}$, as opposed to SAF's 2000°C silicon-producing reaction. The lower temperature of the electrochemical approach could enable lower reactor costs and may be more readily integrated with electrifying heating than SAF. The energy consumption of electrochemical SiO_2 reduction depends on the reactor design, including choice of electrolyte and anode, with claims of 13 kWh/kg Si using calcium chloride salt and graphite anodes [39] and $7\text{--}9\text{ kWh/kg Si}$ using molten CaCl_2 with a Ti_4O_7 anode (notably not forming CO or CO_2 at a carbon anode) [41]. In comparison, MG-Si production in SAFs use between 11 and 13 kWh/kg Si [8].

Many of these electrochemical processes are slow compared to the SAF, in part due to the 2D nature of the reactive interface between metal oxide and electrolyte. Also, the

500–900 °C range of electrochemical approaches does sacrifice kinetics to SAF reactions above the melting point of Si.

The purity of the electrochemically reduced Si would be limited primarily by the source SiO₂ and any reactions with the reactor components. Claims have been made that purities could reach 99.999% using electrochemistry [39], which approaches requirements for photovoltaic and electronic applications. Thus, an additional possible advantage of this route is that it could replace not just MG-Si production, but also the Siemens process, resulting in even greater emissions reductions.

Conclusions

Of the technologies discussed, two were deemed at or approaching industry readiness: the use of biocarbon coupled with CCU/CCS. The potential for adoption of both technologies is largely tied to how they are compatible with existing SAF reactors, with either (mostly) drop-in replacement of carbon feedstock or alteration on exhaust handling. While simple substitution of H₂ for carbon reductants is not thermodynamically viable, renewably generated H₂ may play a role in electrochemical Si reduction and in modified Siemens processes. Metallothermic and electrochemical methods have been proven on the lab scale as promising alternatives and have the potential to use readily available raw materials, lower operating temperatures, and the ability to form high-purity products. If a carbon-free method is truly the end goal, these technologies should be a primary focus for researchers, as further development is needed to move to the pilot-scale stage. Finally, we note that economic viability will play a vital role in which technologies are investigated and implemented further, and, as such, techno-economic analyses of these methods are needed to push development forward.

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Declarations

Conflicts of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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