

Reducing CO₂ emissions from the ferro-alloy and silicon production

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ABSTRACT

The CO₂ footprints in the production of Mn-ferroalloys and silicon/ferrosilicon are correlated with the fossil carbon consumption. The CO₂ emissions may be reduced in the Mn-ferroalloy process by increasing the degree of prereduction and reduction of carbonate materials, while the silicon/ferrosilicon process is optimised based on silicon yield. By changing the fossil reductant into biogenic reductants, the global warming potential will be decreased even more. Even if the reductants are biogenic reductants, there will still be a global warming potential (GWP) in e.g. the electrode consumption and the CH₄ emissions in the charcoal production. To reduce the use of fossil reductants there are also more disruptive technologies like the use of H₂ that at least for the silicon production is on a very low technology readiness level (TRL). Using metallothermic processes will reduce the use of carbon but requires carbon neutral metal reductants. Electrowinning can have low CO₂ emissions, and the electrowinning of pure Mn is a technology of high TRL. Salt and oxide electrolysis is under investigation for both Mn and Si production however the research is still on a low TRL. The use of CCS/CCU is a part of obtaining carbon neutral processes. Last, the energy mix used for these energy demanding processes is discussed.

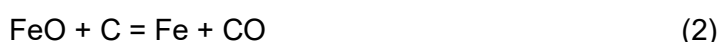
INTRODUCTION

The production of metals is a vital part of the green transition, which the production of solar cells and windmills are examples of. Thus, to reach the goals of international agreements with respect to reducing greenhouse gas emissions, one expects an increased production of metals and other materials related to green technologies. At the same time, the production processes of metals are also responsible of emitting a high amount of CO₂ and other greenhouse gases, and this industry is now racing towards the goal of carbon neutral production. Most of the industry have ambitious goals both for 2030 and 2050, of reducing their CO₂ emissions. In this paper, the reduction of CO₂ emissions from the manganese alloy and silicon/ferrosilicon alloy industries will be discussed. The mitigation tasks range from activities in adjusting today's process to researching disruptive technologies that may be potential future processes.

Mn-ferroalloy and silicon alloy production are both carbothermic reduction processes operated in Submerged Arc Furnaces (SAF). The raw materials are ore and/or quartz, some fluxes like lime, and carbon materials. The carbon materials added are the main origin of direct CO₂ emissions. As there is high gas production in the lower part of the furnace, the raw materials must be lumpy to achieve a permeable path for the gas through the charge.

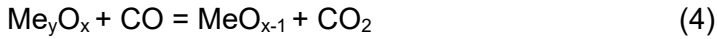
Mn ferroalloys are mainly produced in Submerged Arc Furnaces (SAF) as many other ferroalloys. The most typical geometry is the circular furnace with 3 Søderberg electrodes. In the lower part of the furnace the electrical energy is provided by the electrodes, and here the temperature is between 1400-1600 °C. At these high temperatures, the oxide materials are melted, mixed and reduced to metal, and then drained from the furnace as metal and slag. The slag/metal ratio is typically around 0.5-1.2. The raw material mix, containing Mn-sources, fluxes and carbon materials, are being fed to the charge by gravity at the top of the furnace, where the temperature is at its lowest, in the area of 200-600 °C. As slag and metal are being tapped from the furnace the rest of the material in the furnace will descend while heated by the gas coming from the high temperature zone. The high temperature zone is called the coke-bed (1400-1600 °C), due to a stagnant layer of carbon materials, while the low temperature zone (200-1400 °C) is called the pre-reduction zone.

In the high temperature zone, the following carbon consuming reactions occur in the metal producing reactions during High Carbon FeMn (HC FeMn) production:



The typical composition of HC FeMn is 76-79%Mn, 7%C and the rest is iron. As shown in Table 1, this will lead to a consumption of 273kg carbon/tonne alloy, however only 203 kg will go the gas

phase as CO, and the rest will be dissolved in the metal. There is however also some carbon consumption in the prereduction zone. The reduction of higher Mn- and Fe-oxides is reduced with CO gas to CO₂ (Rx.4) and if this reaction happens above about 800 °C, the CO₂ will subsequently react with the carbon materials according to the Boudouard reaction (Rx.5), and the sum of these two reactions (Rx.6) will consume carbon.



CO₂ from the decomposition of carbonates may also react according to the Boudouard reaction (Rx.5), and hence the total reaction will be according to Rx.7:



Based on industrial operation over 5 years and 4 different furnaces (Ishak and Tangstad, 2007) it has been seen that the CO₂ from the reduction of MnO₂, Mn₂O₃ and Fe₂O₃ with CO gas, will not react with solid carbon, and hence the total oxygen content of the charge mix will not affect the total carbon consumption. The CO₂ from Mn₃O₄ and Fe₃O₄ to MnO and FeO, as well as the CO₂ from the decomposition of lime (CaCO₃), may or may not react with carbon to CO gas. If none of this CO₂ is reacting with C, it has been defined as 100% degree of prereduction, and if all of this CO₂ reacts, it has been defined as 0% degree of prereduction. Industrially, it was seen that the typical degree of prereduction varied between 0% to 60%. The degree of prereduction is determined by type and size of Mn-sources as well as furnace operation(Ishak and Tangstad, 2007).

So far, we have discussed the carbon consumption, as this is proportional with the final CO₂ emissions (with the exemption of the carbon dissolved in the metal). This is always the case for open furnaces where all CO gas will burn on the charge top. There are however some notes that must be included on this issue. For closed furnaces the off gas will be a mixture of CO and CO₂ gas. If the gas is flared, again the carbon consumption will be proportional with the C consumption. As the off gas from Mn-alloy production may contain high amounts of CO (50-90%), this gas may be sold to other users of CO as e.g. fuel. When this gas is burned to CO₂ and emitted, the total amount of CO₂ emissions will again be proportional with the original carbon consumption. This CO₂ may however be reported as a part of the customers CO₂ emissions and not the metal producer. From an environmental point of view, the total CO₂ emission will still be proportional with the carbon consumption in the metal producing furnace, and hence this will be the focus in this article.

In Table 1 the carbon consumption needed in the HC FeMn is shown. In the high temperature zone 273kg of carbon per ton of metal is required, however 70kg of these will be dissolved in the metal and hence 203 kg C or 743kg CO₂ will be emitted from the reactions in this zone. If no prereduction is occurring the additional carbon consumption in the prereduction zone is 81 kg C, that is 341kg CO₂ will be emitted. This means that with these operating conditions, 31% of the CO₂ emitted from the furnace will come from the prereduction zone. Figure 1 shows how the total emission will vary with the degree of prereduction. On a day-to-day basis it is hence important to increase the degree of prereduction and lower the use of carbonates.

Table 1. Example of carbon consumption and subsequently CO₂ emission producing a metal with 79%Mn, a slag/metal ratio of 0.7, 40% MnO in the slag, 100kg lime/ton metal and 0% prereduction.

		kg C	kg CO ₂
790 kg Mn	MnO+C=Mn+CO	173	633
140 kg Fe	FeO+C=Fe+CO	30	110

70kg C	C dissolved in metal	70	0
C in cokebed zone		273	743
s/m=0,7, 40%MnO	$Mn_3O_4+C=3MnO+CO$	59	217
	$Fe_3O_4+C=3FeO+CO$	10	37
100kg $CaCO_3$ /tonne metal	$CaCO_3+C=CaO+2CO$	12	88
0% degree of prereduction		81	341
Total		354	1084

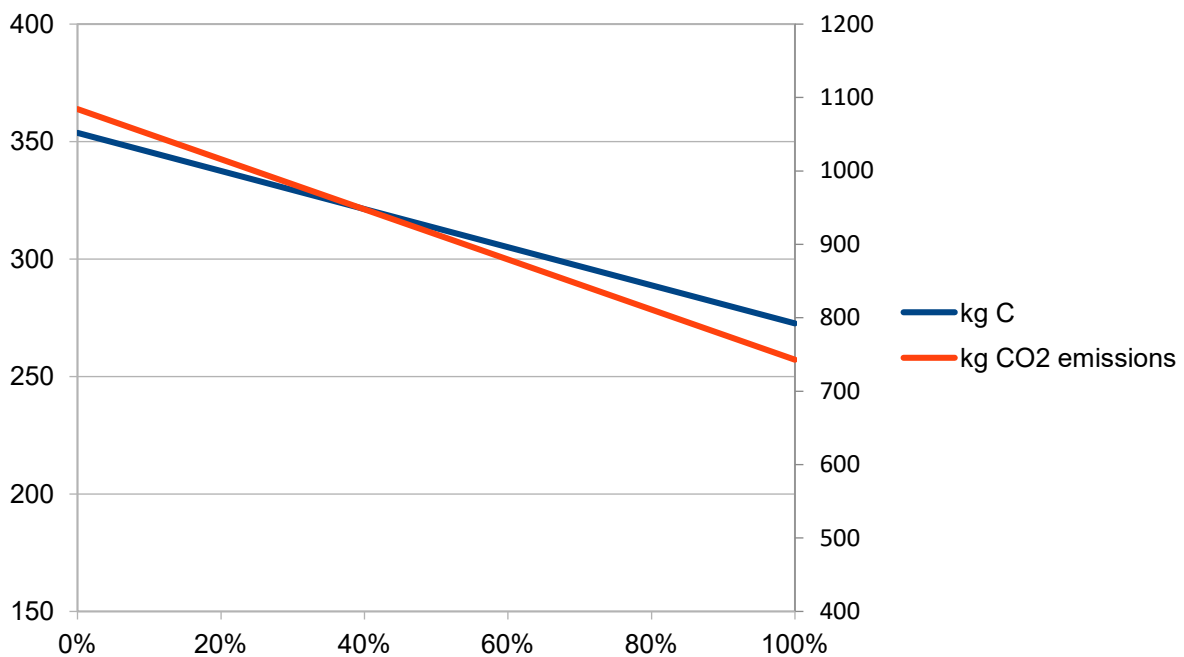


Figure 1. Consumption of Fix C and CO₂ emissions from the fix C (volatiles and electrodes not included) for a given charge (slag/metal ratio=0.7, %MnO in slag=40%, 100kg CaCO₃ per ton metal, all Mn-sources are MnO₂, Mn₂O₃ or Mn₃O₄) as a function of degree of prereduction.

“High-silicon alloys” typically denote silicon-containing alloys in which silicon dominates the behaviour in the production furnace. This normally includes metallurgical grade silicon (MG-Si) with 96–99% purity and ferrosilicon (FeSi) with a silicon content of 45–90%. MG-Si is a precursor for pure Si (electronic grade, solar grade etc) and silicone production. MG-Si is also used as an alloy for aluminium while FeSi is typically used to de-oxidise or alloy steel or cast iron. Both MG-Si and FeSi alloys are produced through carbothermic reduction of quartz (and Fe-containing raw materials in the case of FeSi) in open or semi-open Submerged Arc Furnaces (SAF).

In the Si furnace, most of the silicon is tapped from the furnace as liquid silicon, but some of the silicon escape from the charge as SiO gas. A simplified overall mass balance for the production of Si and SiO can be expressed by reaction (8) and (9):



The silicon furnaces are open or semi-closed furnaces, and hence the CO will burn with ambient air to CO₂. The Fix C consumption and the CO₂ emissions from the Fix C will hence be given by the Si-yield as seen in Figure 2.

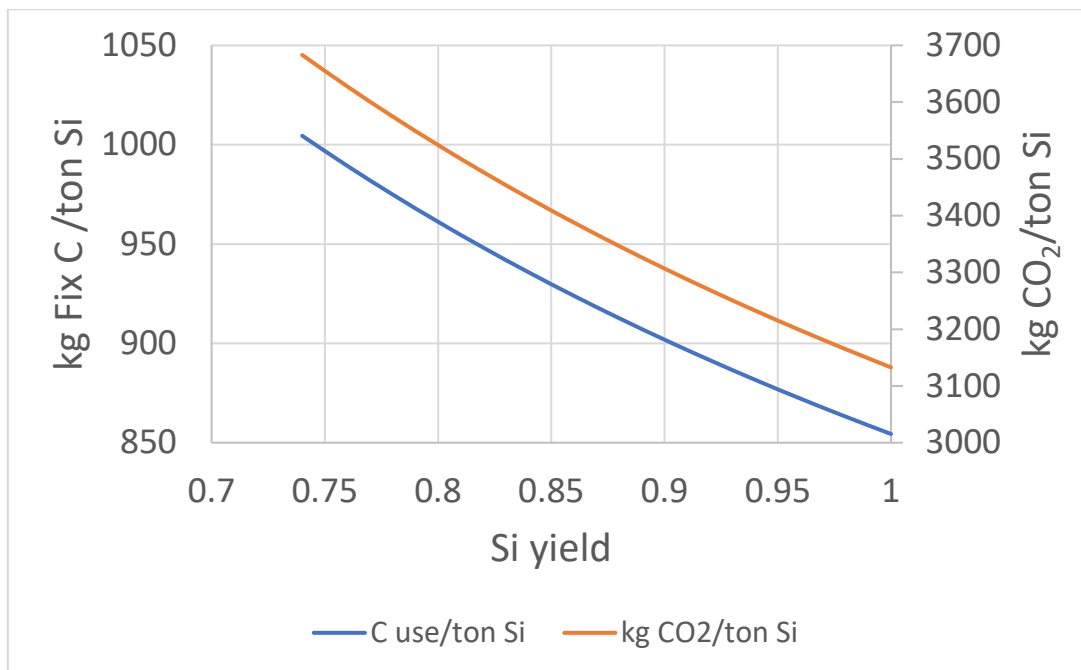


Figure 2. Theoretical energy consumption and CO₂ emissions from the furnace not including the volatiles and the electrodes.

The Si yield (typically 85-92% Si in metal alloy with respect to total input of Si), and hence the specific carbon consumption and thus the CO₂ emissions, is determined by the mode of operation and the carbon material properties. The rest of SiO₂-unit input is ending up as silica fume in the furnace off-gas, typically sold as a valuable bi-product. Typical carbon materials are coke/char, coal, charcoal and woodchips. The raw metal produced in the SAF is tapped into a ladle where dissolved Ca and Al is refined by oxidation, resulting in a Si alloy-infused (20-30% Si) Al₂O₃-CaO-SiO₂ slag by-product, typically representing a Si-loss of up to 8% Si. The CO gas produced in the furnace is combusted above the charge to CO₂ and released together with other hydrocarbons. The fixed C contributes to around 65% of the CO₂ emissions, and carbon fines in the off gas, volatiles in the carbon materials and the combustion of the electrode will be around 35%. The standard emission factors for different Si-based alloys are listed in Table 2 where all the factors affecting the Global Warming Potential (GWP) is included.

Table 2. Generic CO₂ emission factors for Si and FeSi alloys (ton CO₂/ton tapped metal) (Lindstad, 2007)

Type of alloy	Generic emission factors
Ferrosilicon 45% Si	2.5
Ferrosilicon 65% Si	3.6
Ferrosilicon 75% Si	4.0
Ferrosilicon 90% Si	4.8
MG-Si (>98% Si)	5.0

With the high electricity consumption involved in both Mn-alloy production and even more so the silicon alloy production as seen in Figure 3, the specific electricity mix clearly has a large impact on the total environmental footprint of the process (Saevarsdottir et al., 2021). An LCA study on the Si-process analysed the effect of energy mix. It was seen that with an almost 100% renewable energy

mix (like in Norway), the Global Warming Potential decreases to about 55% of an European mix, that still contains coal-based energy as seen in Figure 4. This number is of course very dependent on the amount of biogenic carbon used in the charge. Using mainly biogenic materials, this number would be down to 40% (Nøstvold, 2022).

A significant part of the energy input to the furnace is contained in the furnace off-gas. Several of the Si-alloy plants in Norway have incorporated energy recovery systems, producing both electricity and hot water for the grid and local community use. The energy consumption is decided by type of alloy, by silicon yield (as seen in Figure 3 for MG-Si) and energy losses.

CCS/CCU (Carbon Capture Storage/Utilization) is part of the strategy to produce carbon neutral metals for many companies. The Mn-ferroalloy process can be, and is often, produced in closed furnaces, which means that the off gas can eventually contain close to 100% CO₂. The silicon and high ferrosilicon are today produced in semi-open furnaces. With an exhaust gas system designed to both optimize CO and hydrocarbon combustion and produce a high-quality silica fume, this means that the CO₂ content in the off gas will be in the area of a couple of percentages. This gas can as an example be used to produce algae for fish feed (Giæver, 2024). If this gas will be used in CCS, the cost to pretreat the gas will be expensive due to the low CO₂ content. The CO₂ content can however be increased by recycling the flue gas as shown in Figure 5. Closed furnaces have also been investigated but the mechanical stoking and effect on off-gas temperature and silica product has prevented further development in this area.

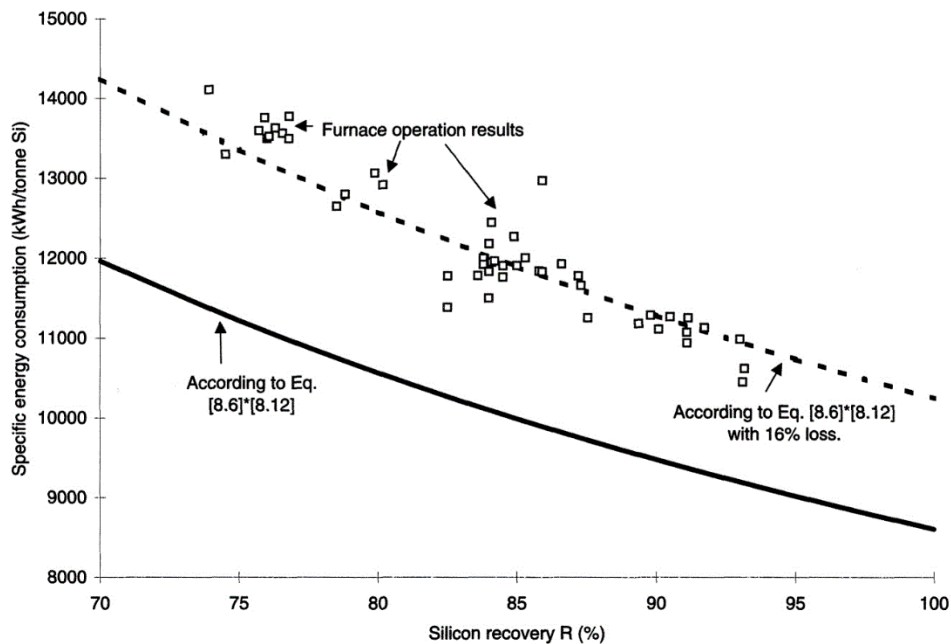


Figure 3. Measured and calculated energy consumption. Dotted line is assuming an energy efficiency of 84% (Schei et al. 1998)

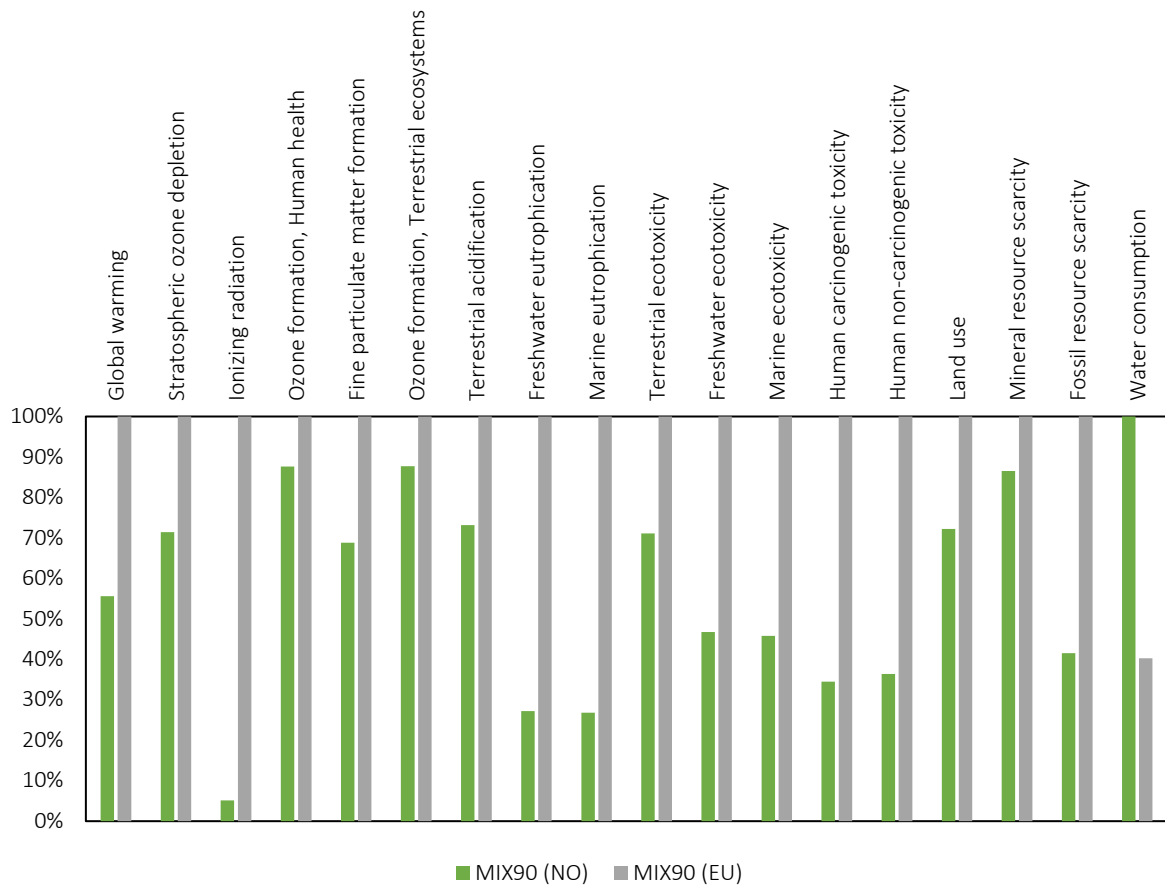


Figure 4. Environmental impacts comparing the Norwegian and European energy mix for a fossil based carbon mix and silicon yield of 90% (Nøstvold, 2022)

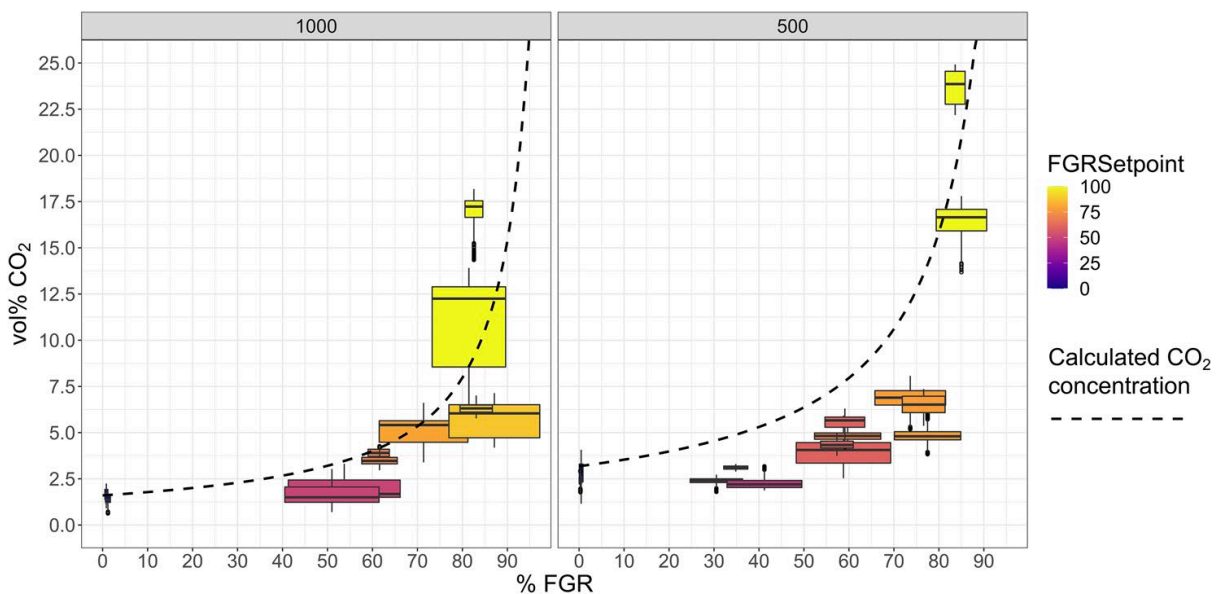


Figure 5. Increased CO₂ content in off gas by recycling. %FGR (Flue Gas Recycling) is fraction of off gas recycled.(Andersen, 2023)

BIOCARBON

Brazil has for many years used charcoal as the main reductant in Mn-ferroalloys. Using biomass, like charcoal, the CO₂ emitted will be consumed when growing new agricultural biomass and hence

the CO₂ will not be enriched in the atmosphere. In addition to the issues regarding the availability of charcoal or other biomass addressed above, there are also some technical issues regarding the use of charcoal in the Mn-ferroalloy process in the SAF. The mechanical strength may be an issue in large furnaces. In addition to the dusting outside of the furnace and the subsequent HES issues, the issues inside the furnace will be the following:

1. The electrical energy is developed by the electrical voltage over the coke bed. It is hence important that the carbon in the coke bed is lumpy material with low amount of fines, both for the positions of the electrode-tips, but also for the slag flow through the coke bed.(Tangstad et al., 2021)
2. Fines in the prereduction zone clogs the voids and hence disrupts the gas flow. This will affect the degree of prereduction, and hence the energy consumption, but may also pose as a safety threat.
3. The density is low for charcoal (about 350 kg/m³) versus coke (about 550 kg/m³)(Ramos et al., 2021). This means that the volumetric carbon/ore ratio will be higher. This may lead to less agglomeration in the charge mix. This phenomenon may also affect higher electrical current paths, however as the charcoal at low temperatures are more or less insulating (Pedersen, 2020; Surup et al., 2020), this is not believed to be a problem. The higher descending rate, in m/s, may cause a lower prereduction. The CO₂ reactivity will at the same time be higher for charcoal versus coke, and this may also increase the extent of the Boudouard reaction.

In the silicon process, many producers are partially using biogenic carbon. The goal is now to convert the fossil carbon-based reduction material charge. No fossil reductant in the charge is common in South America and Australia where there is local access to bio-carbon. While bio-based reductants are considered carbon neutral if the wood is responsibly regrown, a recent LCA study (Nøstvold, 2022)) comparing the environmental impact of different carbon charge mixes and silicon furnace yields identified areas where also bio-based charge mixes have negative environmental impacts such as land use, water consumption etc, as illustrated in Figure 6. When the CO₂ emissions is reduced from 100% fossil CO₂ to 8% fossil CO₂ and 92% biogenic CO₂, the total global warming potential will decrease with 40%.

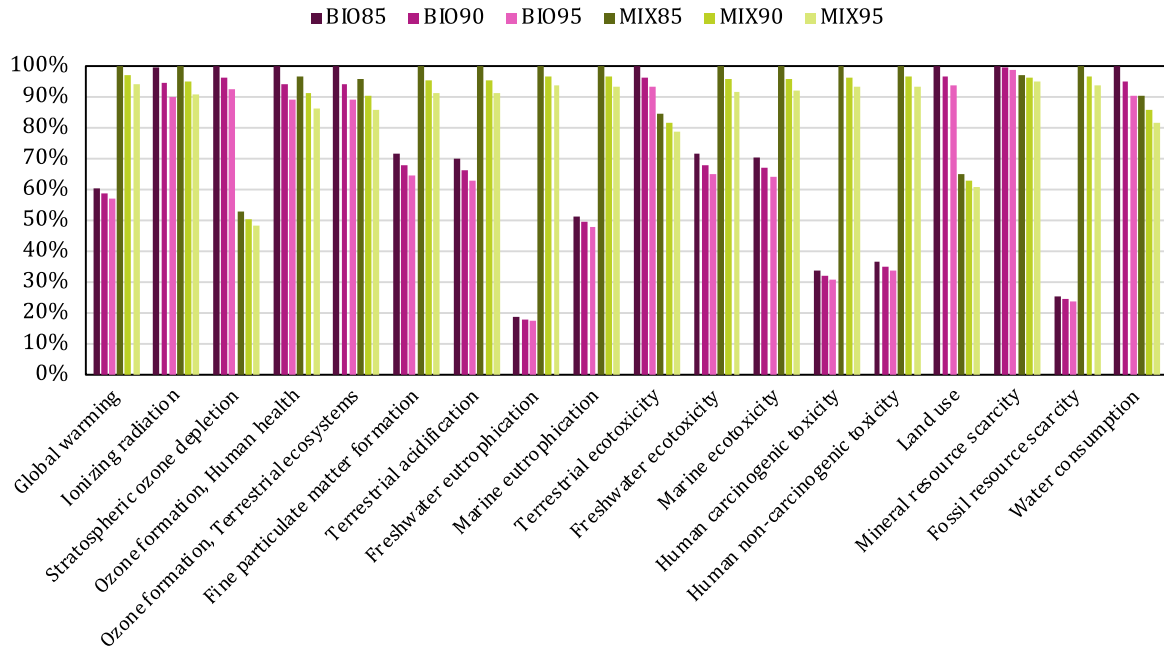


Figure 6. Environmental impact when using biocarbon versus fossil reductant for various silicon yields (Nøstvold, 2022)

HYDROGEN

One of the strategies to reduce the CO₂ emissions in today's processes is to increase the degree of prereduction in the furnace, that is to reduce the extent of the Boudouard reaction, and hence the

total carbon and energy consumption. Figure 1 shows the carbon consumption and the CO₂ emission for the same charge as shown in Table 1 as a function of degree of prereduction. As previously noted, the highest degree of prereduction seen industrially was in the area of 60% (Ishak and Tangstad, 2007), and this would reduce the CO₂ emissions to 870 kg CO₂, that is 19%. To obtain such numbers, the operation is optimal under today's conditions. The main factor for this to happen is first and foremost, optimal raw materials. If the raw materials could be developed further to obtain 100% degree of prereduction, a total reduction of 31% CO₂ emission compared to 0% prereduction could be obtained.

MnO is a stable oxide and cannot be reduced with H₂, only with C as shown in reaction 1, as seen in Figure 7. FeO and the higher manganese oxides can however be reduced with H₂ according to reaction 10 and 11 (Davies et al., 2023; Tangstad et al., 2023). According to the above discussion between 20 and 30% of the CO₂ emission could then be reduced.

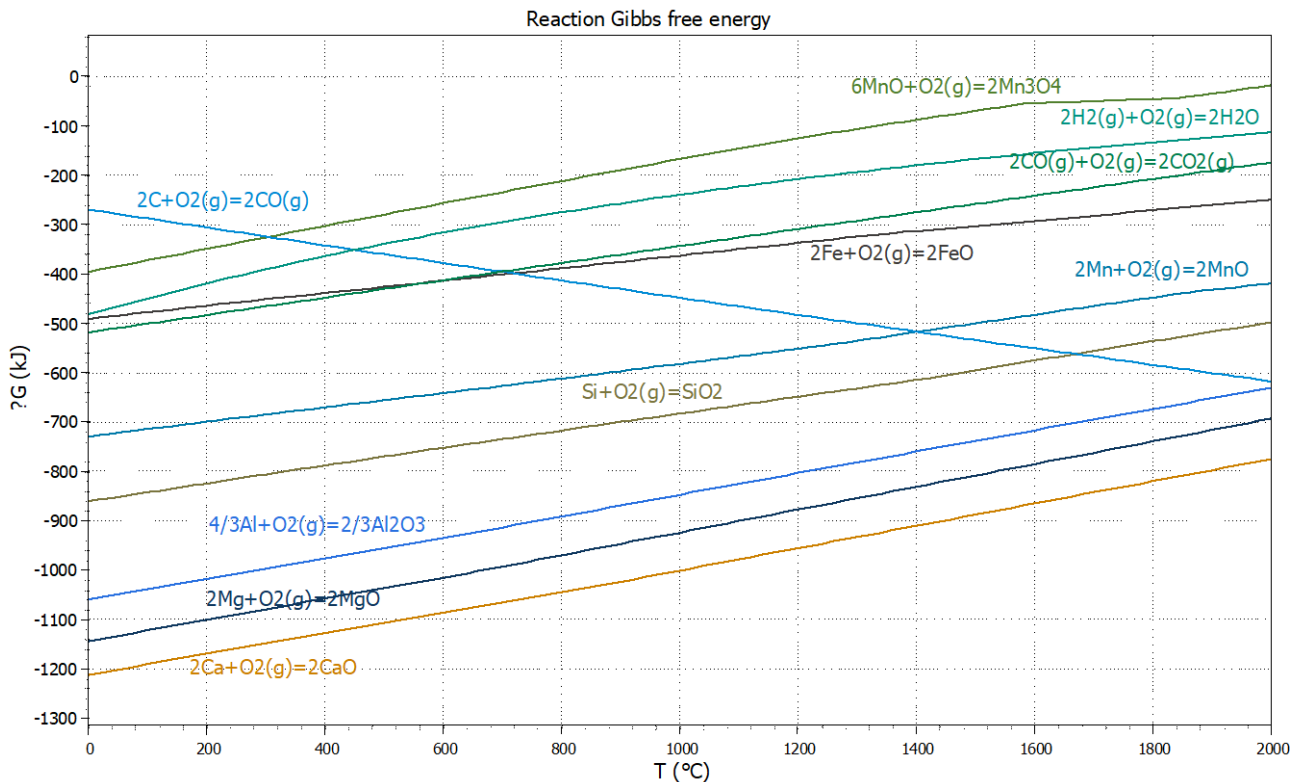


Figure 7. Gibbs free energy diagram showing the stability of various oxides versus C, CO and H₂. (HSC Chemistry v9)

In a process where the reactions of the prereduction zone could be separated from the high temperature coke bed zone, like e.g. in a prereduction unit, H₂ could be used to reduce the higher manganese oxides and the FeO without any Boudouard reaction. A more possible scenario is to operate a prereduction unit with no solid carbon, and hence both the CO from the coke bed and/or additional H₂ may be used. In both cases, the total emitted CO₂ would now be down to 633 kg CO₂ per ton of metal produced (or 743 kg CO₂ if the iron is not reduced to metallic iron). The conditions, which is required to reduce the ore down to MnO and Fe is extensively investigated to mention a few: (Davies et al., 2023; Larssen et al., 2021; Schanche, Trygve, 2022)

In the silicon process, where SiO₂ is an even more stable oxide than MnO, hydrogen cannot be used directly as indicated in Figure 7. Hydrogen gas can, however, produce the silicon sub-oxide SiO and water according to the reaction 12.



at atmospheric pressure and temperatures above 1800°C (Aarnæs, 2023; Dalaker, 2022). However, to directly convert SiO₂ with H₂ to Si and H₂O with reasonable yields require pressures > 10.000 bars and would need excessive amounts of H (typically 2500:1 H:Si at 2000°C), as shown in Figure 8.

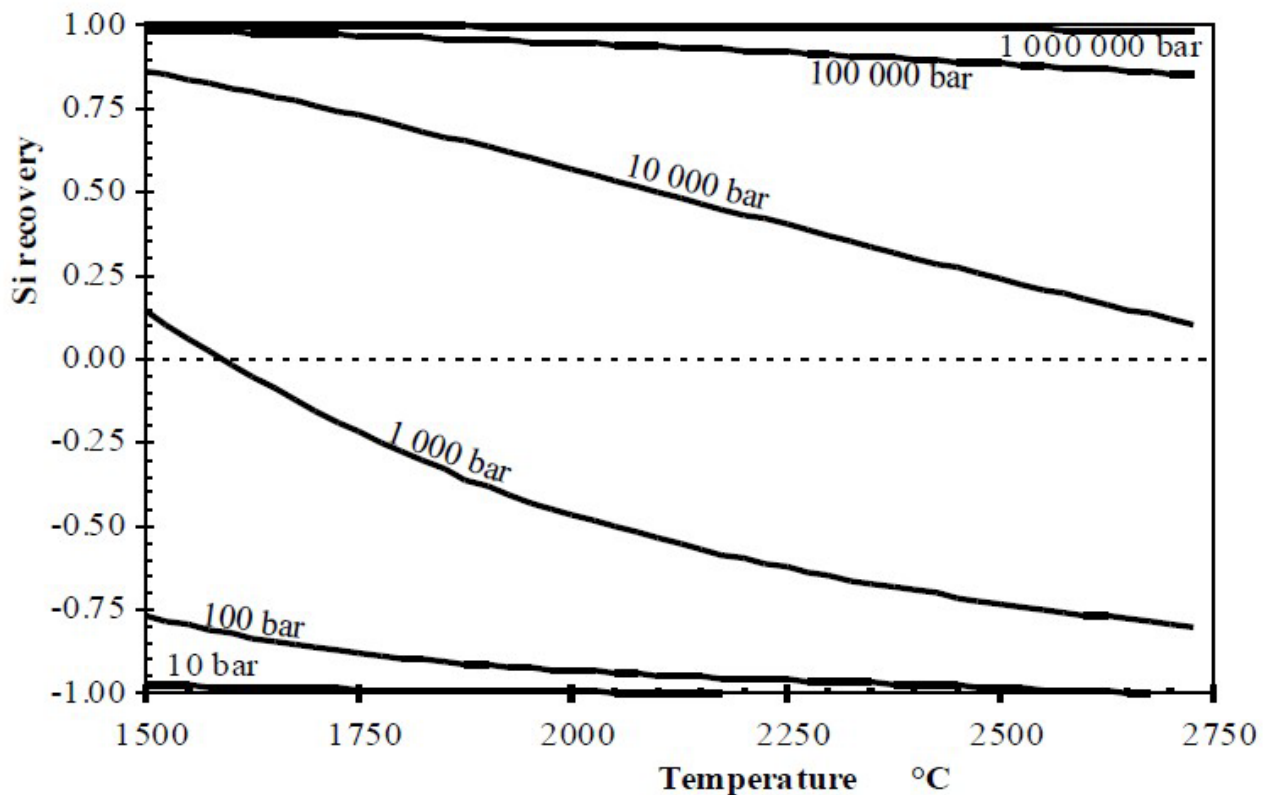


Figure 8. Silicon recovery as a function of temperature for various pressures. A negative value means that the equilibrium reaction between SiO₂, Si and H₂ will consume Si and produce SiO.*(Schei et al., 1998)*

As an alternative, in plasma, where H⁺ is stabilized (rather than H₂), direct production of SiH₄ may be viable at temperatures below 1400 °C, although back reaction with the water vapour in the gas phase may be prohibitive. The use of hydrogen as a reductant in manganese production is currently under investigation where plasma is investigated, according to reaction 13.



Dividing the silicon reduction in the two following reactions, reaction 14 and 15, is also proposed as illustrated in Figure 9 (Svenum and Ringdalen, 2022).



The overall reaction will then be the production of Si and water vapor according to reaction 16. There are several challenging parts, as e.g. both the thermodynamics and the rates of the reactions. The main challenge is that reaction 15 requires a low temperature, and one has hence to stop the SiO gas from producing Si and SiO₂.

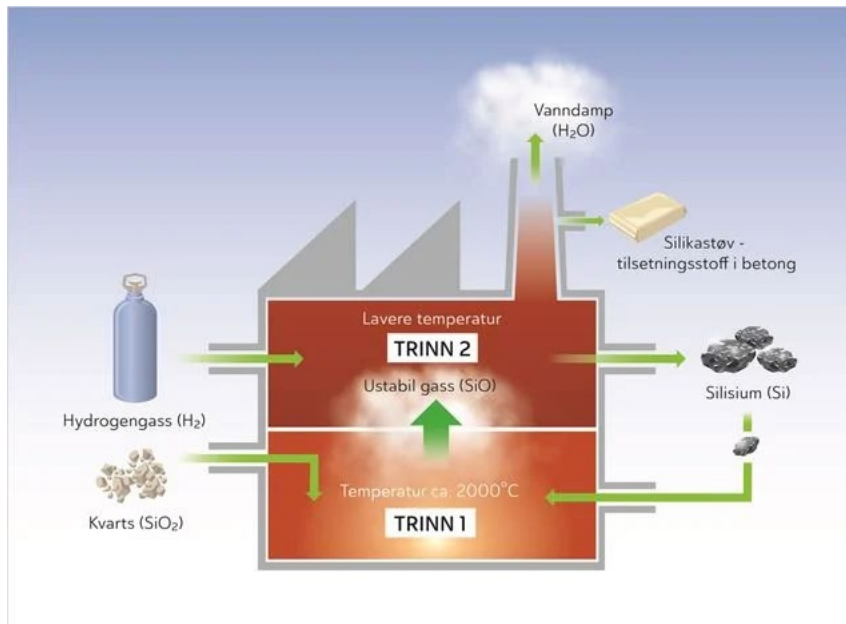


Figure 9. The concept of a hydrogen producing silicon furnace (illustration: Knut Gangåssæter / SINTEF)(Svenum and Ringdalen, 2022)

METALLOTHERIC PRODUCTION

While most of the metallic manganese is produced as manganese ferroalloys in Submerged Arc Furnaces by carbothermic reduction, manganese ferroalloys may also be produced in other processes e.g. in the blast furnaces. As the energy is here produced by combustion of carbon this may increase the carbon consumption by a factor of 6-7, and hence will typically not be a sustainable alternative for Mn-ferroalloy product. With the exception of the type of energy production, it is assumed that the chemical reactions are quite close to the reactions in the SAF as described above.

Another quite mature technology is the production of Mn-metal or Mn-ferroalloys using metallic reductants like Si or Al instead of using carbon according to reaction 17.



This process can be carbon free and hence CO₂ free. The raw materials, the Si and Al, will however be produced with the use of carbon, and hence again the metallothermic reduction will not globally reduce the CO₂ emissions, only locally. The exception may of course be either if the reductant is produced without any consumption of carbon (e.g. inert electrodes) or if waste Si or Al is used that is not being used for other purposes.

In the same way, it is possible to produce silicon by using metals with a higher affinity to oxygen than silicon as a reducing agent. The most relevant metals are aluminium, magnesium and calcium, where the most viable option from a material access perspective in Norway is aluminium. Research on Si production by aluminothermic reduction of SiO₂ has been carried out since the early 1900's (Islam et al., 2011). As aluminium is an expensive reductant compared to carbon, this has not been widely acknowledged as a viable route to production of MG-Si. However, interest in the last decades in production of pure Si for PV applications, as well as a growing interest in Si nanoparticles for Li-ion batteries has created extensive activity within metallothermic reduction of Si oxides. For this purpose, aluminothermic reduction has been applied in Cl-solvents, enabling relatively low temperature processes (Liu et al., 2012; Y Qian and et al., 2015; Ueda et al., 2005; Xie and et al., 2016). Si production through reaction between silicon tetrachloride (STC, SiCl₄) and Al has been investigated by several researchers and companies (Y. Qian and et al., 2015). Reaction products include AlCl₃, which can be electrolysed for recycling. Aluminothermic reduction of SiO₂ in cryolite (Na₃AlF₆) to produce an Al-Si alloy has also been proposed (Gorji et al., 2007). Previous work also includes aluminothermic reduction of either quartz or silicate-glasses that are heated with Al to temperatures above the melting point of Al, and in some cases above the melting point of Si (Dietl et al., n.d.; Smith, 1960; Thurmond, 1959; Wartenberg, 1956; Yusada and Okabe, 2010). Recently, an integrated process (SisAl) for production of silicon via alumino-thermic reduction of SiO₂-

containing slag using different aluminium sources, such as for example scrap and Al dross, with subsequent processing of slag, followed by recycling of Al_2O_3 and CaO , has been developed (Phillipson et al., 2022). This process, illustrated in Figure 10, has the ability of delivering different grades of silicon and Al-Si alloys, depending on the raw materials used. The process is currently developed in large scale pilot through the EU H2020 program.

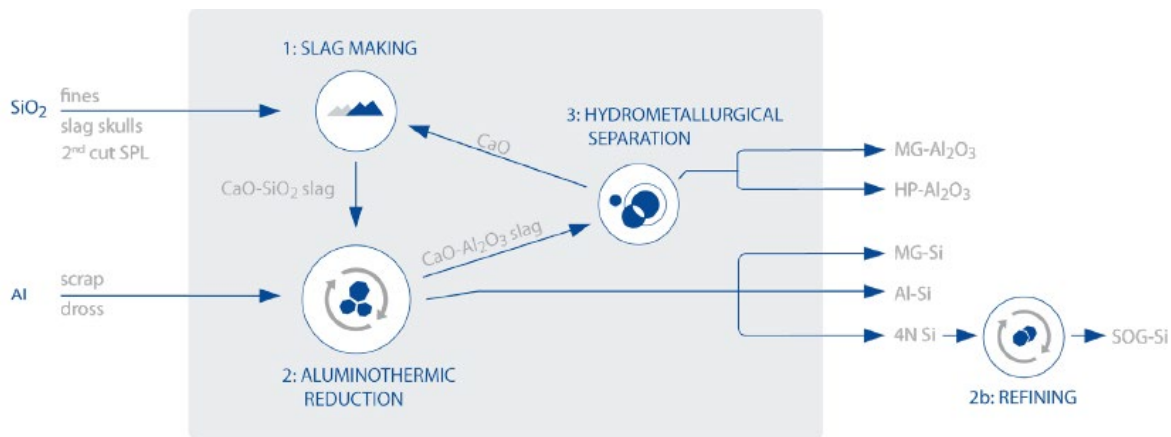


Figure 10. Overview of the SisAl project where silicon is produced industrially from waste materials, will a following refining of both the silicon and the slag produced.

ELECTROWINNING

Mn-metal, 99% pure, can also be produced by aqueous electrolyses (Kero et al., 2020). EMM (electrolytic manganese metal) is produced by hydrometallurgy, dissolving the Mn-source in acid followed by electrolyses. There are some advantages with this process, as e.g. very low CO_2 emissions. The main part of the CO_2 comes from the prereduction of the ore, but this can be done with H_2 . The disadvantages are quite large amount of waste materials and the fact that it is a costly process. New electrowinning processes can be based on salt- or molten oxide- electrolyses (Kero et al., 2020)

At the start of the century, as a result of the increased demand for high purity silicon for solar cells, research on electrochemical processes for silicon production was intensified and new processes developed at the laboratory scale. Electrolytic production of silicon can be a low-carbon alternative if an inert anode can be used. An important reason why electrolysis processes have not been industrialized is the high melting point of silicon compared to other electrolysis processes such as aluminium. Various electrolytes have been investigated.

- Fluoride / cryolite-based electrolytes,
- Oxide-based electrolytes, and
- Chloride-based (CaCl_2 , AlCl_3) electrolytes.

Chloride and fluoride electrolytes are typically very corrosive and will present significant material challenges if operated at temperatures above the melting point of silicon. While both chloride and fluoride electrolytes have comparatively low melting temperatures operating at such temperatures would mean that silicon would be deposited as a powder or in solid form at the cathode, prohibiting a continuous process. Powder-based Si products may however be interesting for the battery market, in which Si powder is currently produced by crushing and grinding of cast metallurgical silicon.

CONCLUSIONS

In the production of Mn-ferroalloys and silicon/ferrosilicon the daily production processes is optimized to minimize the CO_2 emissions. On a day-to-day basis the Mn-process is optimized based on increasing the degree of prereduction and reduction of carbonate materials, while the silicon/ferrosilicon process is optimised based on silicon yield. This may reduce the CO_2 emissions in the order 10%. By changing the fossil reductant with biogenic reductants, the reduction of the

global warming potential will be approximately 60%. It can be pointed out that the emissions of CH₄ in the charcoal production will add to the global warming potential and also that the electrodes cannot, so far, be made with biogenic materials. To reduce the use of fossil reductants there are also more disruptive technologies like the use of H₂ that at least for the silicon production is on a very low technology readiness level (TRL). Using metallothermic processes requires carbon neutral metals which will be vital for the overall CO₂ emission. Electrowinning of Mn is a technology of high TRL, however salt and oxide electrolyses is also discussed and researched for both Mn and Si production where the research is still on a low TRL. Additionally, to the discussed technologies, CCS/CCU is also a part of the industries plan, and especially for the open furnaces where the CO₂ level in the off gas is low, research is ongoing to increase the CO₂ level in the off gas to lower the resources needed for the treatment of the off gas. Finally, as all these processes are energy intensive, the energy mix will be an important part of the total CO₂ emissions, and countries with a high amount of renewable energy will hence have a lower CO₂ footprint.

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REFERENCES

- Aarnæs, T.S., 2023. The Effect of Hydrogen and Methane Containing Gases on SiC and SiO formation, PhD thesis, Norwegian University of Science and Technology, Doctoral theses at NTNU, 2023:48.
- Andersen, V., 2023. Flue Gas Recirculation for the Silicon Process, PhD thesis, Norwegian University of Science and Technology.
- Dalaker, H., 2022. Silicon Production from SiO Gas via Gas-Phase Reactions, in: Tesfaye, F., Zhang, L., Guillen, D.P., Sun, Z., Baba, A.A., Neelameggham, N.R., Zhang, M., Verhulst, D.E., Alam, S. (Eds.), *REWAS 2022: Energy Technologies and CO₂ Management (Volume II)*. Springer International Publishing, Cham, pp. 33–40.
- Davies, J., Tangstad, M., Schanche, T.L., du Preez, S.P., 2023. Pre-reduction of United Manganese of Kalahari Ore in CO/CO₂, H₂/H₂O, and H₂ Atmospheres. *Metall. Mater. Trans. B.* 54, 515–535. <https://doi.org/10.1007/s11663-022-02705-0>
- Giæver, I., 2024. Mass cultivation of diatoms at Finn fjord AS.
- Gorji, Y.M., Soltanieh, M., Hibabolahzadeh, A., 2007. Production of Al-Si Master Alloy by Aluminothermic Reduction of Silica in Molten Cryolite. *Canadian Metallurgical Quarterly* 46, 385–390. <https://doi.org/10.1179/cmqr.2007.46.4.385>
- Ishak, R., Tangstad, M., 2007. Degree of Prereduction Without Coke Consumption in Industrial Furnaces. Presented at the *INFACON XI, The Indian Ferro Alloy Producers' Association*, New Delhi, India, pp. 268–280.
- Islam, M.S., Rhamdhani, M.-A., Brooks, G.A., 2011. Solar-Grade Silicon: Current and Alternative Production Routes. *Chemeca 2011*, Sidney Australia.
- Kero, I., Dalaker, H., Osen, K.S., Ringdalen, E., 2020. Some carbon-free technologies for manganese ferroalloy production I.T. Kero, H. Dalaker, K.S. Osen and E. Ringdalen. *Infacon XVI*, Trondheim, Norway, 26.-29-September.
- Larssen, T.A., Senk, D., Tangstad, M., 2021. Reduction of Manganese Ores in CO-CO₂ Atmospheres. *Metall Mater Trans B.* 52, 363–381. <https://doi.org/10.1007/s11663-020-02018-0>
- Lindstad, T., 2007. Greenhouse gas emissions from ferroalloy production. *INFACON XI* 457–466.
- Liu, X., Giordano, C., Antonietti, M., 2012. A molten-salt route for synthesis of Si and Ge nanoparticles: chemical reduction of oxides by electrons solvated in salt melt. *J. Mater. Chem.* 22, 5454–5459.
- Nøstvold, C., 2022. Mass and Energy Balanced Life Cycle Assessment of Metallurgical Grade Silicon Production, MSc Thesis at Norwegian University of Science and Technology, Department of Material Science and Engineering.
- Pedersen, T., 2020. Electrical Resistivity in Carbon Materials Converting to SiC, MSc Thesis at Norwegian University of Science and Technology, Department of Material Science and Engineering.
- Phillipson, H., Blandhol, K., Engvoll, K., Djupvik, V., Wallin, M., Tranell, G., Haarberg, T., 2022. Preliminary Techno-Economic Considerations of the Sisal Process - Closing Materials Loops through Industrial Symbiosis. *Proceedings of the Silicon for the Chemical & Solar Industry XVI*.
- Qian, Y., et al., 2015. A low temperature molten salt process for aluminothermic reduction of silicon oxides to crystalline Si for Li-ion batteries. *Energy Environ. Sci.* 8, 3187–3191.
- Qian, Y., et al., 2015. Preparation of Nanocrystalline Silicon from SiCl₄ at 200°C in Molten Salt for High-Performance Anodes for Lithium Ion Batteries. *Angew. Chem. Int. Ed.* 54, 3822–3825.
- Ramos, D.C., Carneiro, A.C.O., Tangstad, M., Pereira, B.L.C., Saadieh, R., Oliveira, A.C., Vital, B.R., 2021. Reactivity assessment of charcoal for use in silicon production. *Eur. J. Wood Prod.* <https://doi.org/10.1007/s00107-021-01683-5>
- Saevarsdottir, G., Kvande, H., Magnusson, T., 2021. Greenhouse gas emissions from silicon production - development of carbon footprint with changing energy systems. *Proceedings of the 16th International Ferro-Alloys Congress (INFACON XVI) 2021*.

- Schanche, T., 2022. Pretreatment of manganese ores in CO/CO₂/H₂ atmospheres, PhD thesis, Norwegian University of Science and Technology.
- Schei, A., Tuset, J.K., Tveit, H., 1998. Production of High Silicon Alloys. Tapir, Trondheim.
- Surup, G.R., Pedersen, T.A., Chaldien, A., Beukes, J.P., Tangstad, M., 2020. Electrical Resistivity of Carbonaceous Bed Material at High Temperature. *Processes* 8. <https://doi.org/10.3390/pr8080933>
- Svenum, I.-H. and Ringdalen, E., 2022. Vi er storforbrukere av silisium. Nå er vi kanskje på sporet av en produksjonsmåte uten CO₂-utslipp.
- Tangstad, M., Bublik, S., Haghdani, S., Einarsrud, K.E., Tang, K., 2021. Slag Properties in the Primary Production Process of Mn-Ferroalloys. *Metall. and Mater. Trans. B* 52, 3688–3707. <https://doi.org/10.1007/s11663-021-02347-8>
- Tangstad, M., Schanche, T., de Preez, F., 2023. Use of H₂ in Mn-Ferroalloy Production, in: Fleuriault, C., Steenkamp, J.D., Gregurek, D., White, J.F., Reynolds, Q.G., Mackey, P.J., Hockaday, S.A.C. (Eds.), *Advances in Pyrometallurgy*. Springer Nature Switzerland, Cham, pp. 35–53.
- Ueda, M., Abe, Y., Ohtsuka, T., 2005. Reduction of SiO₂ to Si by aluminium metal fog in NaCl–KCl–AlCl₃ molten salt. *Materials Letters* 60, 635–638.
- Xie, X.M., et al., 2016. Aluminothermic reduction enabled synthesis of silicon hollow microspheres from commercialized silica nanoparticles for superior lithium storage. *Chem. Commun.* 52, 8401–8404.