Background informal technical document on the analysis of the impact of decarbonisation on emissions of air pollutants in selected industrial sectors
(first draft)

TFTEI informal background technical document

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Prepared by KIT DFIU - TFTEI Technical Secretariat

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List of Abbreviations / Acronyms

BAT	Best Available Technique
BREF	Best Available Technique Reference Document
CHP	Combined Heat and Power
GHG	Greenhouse Gas
IPCC	Intergovernmental Panel on Climate Change
LRTAP	Long-range Transboundary Air Pollution
LCA	Life Cycle Assessment
OECD	Organisation for Economic Co-operation and Development
PM	Particulate Matter
TFTEI	Task Force on Techno-Economic Issues
UNFCCC	United Nations Framework Convention on Climate Change

Executive Summary

This document was prepared by the TFTEI Technical Secretariat as a first overview of the effect of implementing low-carbon technologies in key industries on the emission of major air pollutants. Starting with a general description of low-carbon solutions for major industries, we systematically analyse the synergy effects on air pollutants. To this end, we compare state of the art emission levels with expected emissions in a low carbon industry. The report focuses on the most important industrial emitters of carbon dioxide which are the steel and cement industries as well as crude oil refineries. In addition to these major emitters of greenhouse gases (GHGs), we take into account energy intensive industries such as the glass industries. The analysis shows clear synergies between low-carbon technologies and the reduction of emissions of air pollutants. This is due to two major effects: the substitution of fossil fuels by renewable fuels, e.g. green hydrogen, directly reduces air pollutants from combustion. In several cases, such as in steel industries, the low carbon alternative (direct reduction of steel through hydrogen) replaces some high emission processes such as coking ovens or blast furnaces. Last but not least, removing CO_2 from exhaust gases through e.g. absorption processes (carbon capture technologies) reduces various air pollutants such as SO_x, NO_x and PM in the tail gases as well.

1 Introduction

In the quest for a more sustainable future, the industrial sector remains at the nexus of transformation, facing the intertwined challenges of air pollution and global climate change. Of the vast industrial landscape, the steel, cement, crude oil refining, and glass production sectors have been distinctly selected for this report, given their substantial contributions to global emissions and their unique operational and environmental footprints. These industries not only stand out for their significant emission outputs but also embody the diversity and complexity inherent in modern decarbonisation challenges. Within this context, technologies such as carbon capture and storage, the use of green hydrogen in steel production, the incorporation of alternative binders in cement manufacturing, and the deployment of electric furnaces in glass production emerge as potential game-changers. However, while these innovations hold promise for drastically reducing GHG emissions, their broader effects on other air pollutants, both positive and negative, warrant deep exploration. Through the lens of TFTEI's dedication to environmental stewardship, this report offers an intricate analysis of these sectors, aiming to understand the multifaceted impacts of such technologies. Our ambition is not only to highlight the pressing need for sustainable advancements but also to illuminate their broader environmental implications, thereby fostering a harmonized approach to industry innovation, environmental health, and policy formulation.

This report focuses on the most important industrial emitters of carbon dioxide which are the steel and cement industries as well as crude oil refineries. In addition to these major emitters of greenhouse gases (GHGs), we take into account energy intensive mineral processing industries such as the glass industry. Figure 1 depicts the share of industrial CO_2 emissions by industry in Germany, which is Europe's largest carbon emitter.

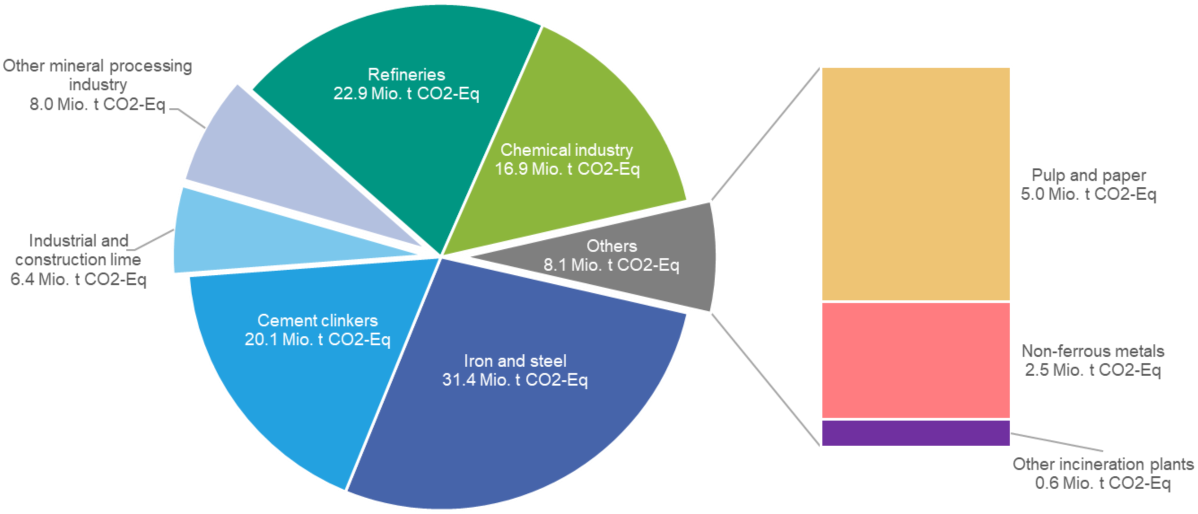


Figure 1: Share of industrial CO2 emissions by source in Germany in % (data based on UBA, 2021).

When it comes to the analysis of carbon emissions and the quantification of the carbon footprint of specific processes or products, different scopes as indicated in Figure 2 are distinguished according to international standards (ISO 14064). Scope 1 emissions refer to the direct emission caused by a production process, scope 2 emissions are those emissions associated with the external energy provision (mainly electricity) of a process and scope 3 emissions are the embodied emissions of the raw material input for a production process, hence, the upstream value chain emissions. The economy-wide decarbonization will strongly affect the energy system by replacing fossil fueled power plants and, hence, will reduce scope 2 and scope 3 emissions. However, the focus of this report is no to analyze the entire value chain of the regarded industries but to focus on specific production processes and associated air pollution. Hence, we focus on the reduction of scope 1 emissions of the most important industrial emitters and we analyse the respective effect of low carbon technologies on the reduction of further air pollutants.

Figure 2 Emissions scopes according to the GHG protocol.

To this end, in the following Chapter 2, we first describe state-of-the-art technologies of the respective industries and then compare these technologies to low-carbon technologies that are expected to replace current technologies in the course of the transition towards a low-carbon economy. In Chapter 3 we then assess how these low-carbon technologies are expected to affect further air pollutants. Subsequently we summarize the results in Chapter 4 and we provide an outlook on next steps and further research required to fill the identified knowledge gaps.

2 State of the art technology and basic approaches to reduce GHG emissions in key industries

In the following sections, state-of-the-art technologies and their green alternatives in a low-carbon economy for the regarded sectors (steel production, cement production, oil refineries and glass production) are described. In this context it is important to take a look at the general strategies that are taken in various industry sectors to reduce carbon emissions. As depicted in Figure 3, measures to reduce GHG emissions can be generally distinguished into substitution measures and end-of-pipe removal of CO_2 through so called carbon capture technologies (e.g. through absorption processes). In this case, CO_2 would be further processed (Carobon Capture and Utilization, CCU) or stored to avoid CO_2 emissions (Carbon Capture and Storage). In the case of substitution, either fossil fuels are substituted by green alternatives (e.g. green hydrogen or renewable electricity) or entire technologies are replaced such as the substitution of steel reduction with coke in blast furnaces by direct reduction technology with green hydrogen.

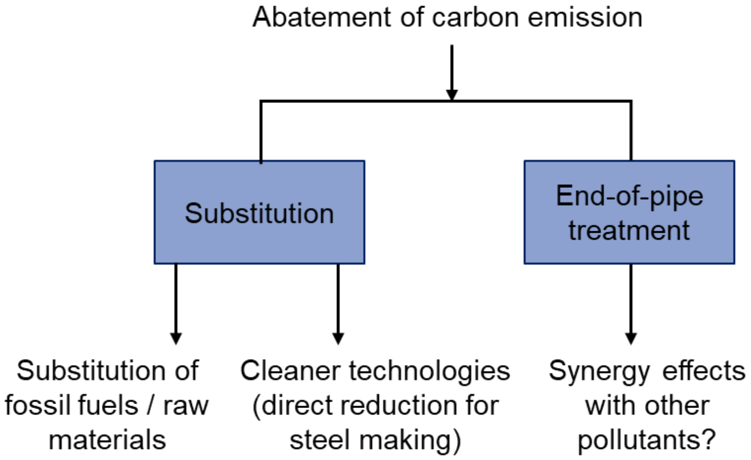


Figure 3 General strategies to reduce GHG emissions in industrial production.

2.1 Steel industries

In the following, we first describe state-of-the-art steel processing and give a brief explanation of the processing routes of the low-carbon alternative via direct reduction with green hydrogen. As indicated before, we only focus on the processing of steel and directly related processes such as coking but do not include the production of green hydrogen via electrolysis.

2.1.1 State of the art technology

The Blast Furnace-Basic Oxygen Furnace (BF-BOF) route is the dominant method of steel production globally, particularly for producing large volumes of high-quality steel. While electric arc furnaces require reduced elementary iron as input material and are mainly applied for steel scrap smelting, blast furnaces are the dominant technology for primary steel reduction with coke (see Figure 4). There are already few direct reduction plants based on natural gas that produce iron sponges from ore which are then further processed in electric arc furnaces, however, this is still a niche technology an mainly used in areas where natural gas is available at low costs.

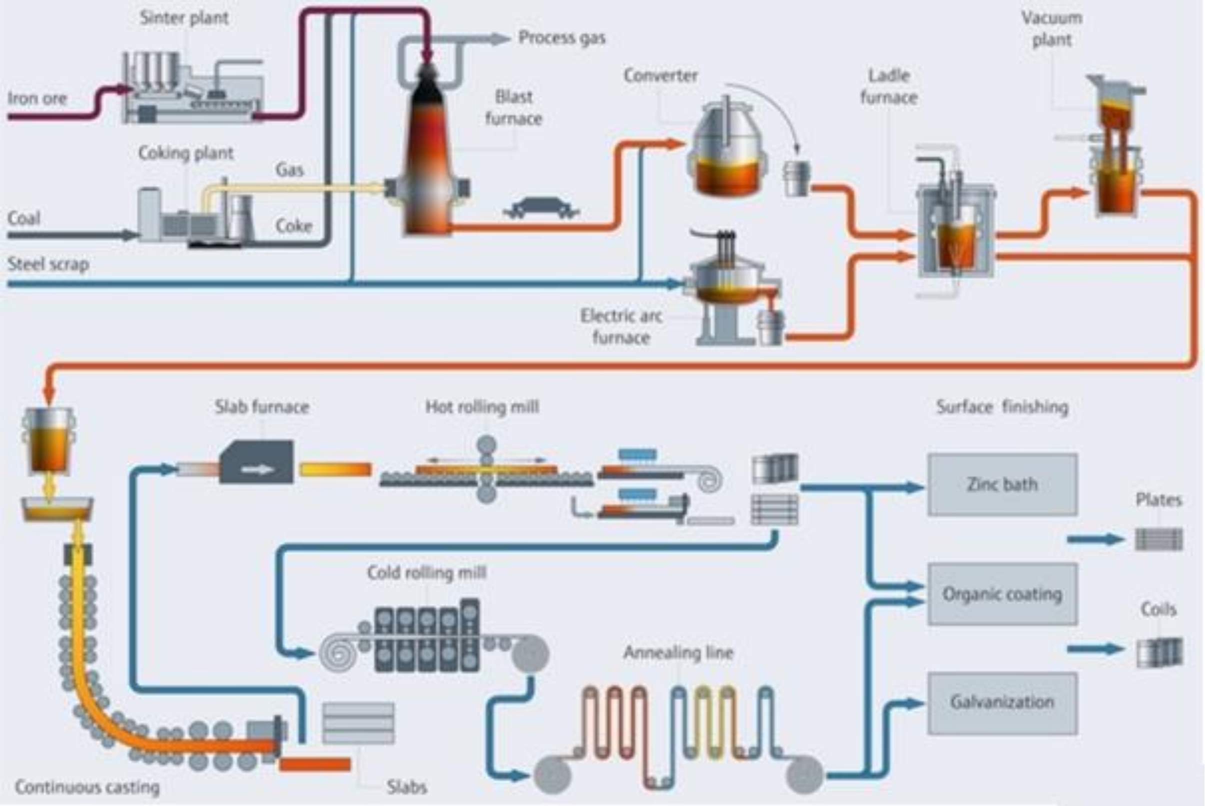


Figure 4 Classical processing routes for steel making (Endress + Hauser 2022).

As illustrated in Figure 4, the main processing steps for primary steel production are the following:

1. Raw Material Preparation:

- Iron Ore: Predominantly hematite (Fe_2O_3) or magnetite (Fe_3O_4) are selected. Prior to being introduced to the blast furnace, they undergo agglomeration processes to enhance reactivity, typically resulting in sinter or pellets.
- Coke: Derived from coking coal in dedicated ovens, volatile organic compounds are expelled under anaerobic conditions, yielding a near-pure carbon material. Coke serves not only as a carbon source but also provides necessary permeability within the furnace.
- Limestone (Calcium Carbonate): Integrated as a flux, it aids in binding with impurities to produce slag.

2. Blast Furnace Operation:

- Charging: A stratified charge of iron ore, coke, and limestone is introduced from the furnace top.
- Combustion: Injected hot air, elevated to approximately 1200°C, facilitates coke combustion at the furnace's base. The ensuing exothermic reactions yield CO and CO_2, generating the necessary heat for endothermic reduction reactions in the upper regions of the furnace.

- Reduction: As the iron ore descends, it interacts with CO, facilitating a reduction reaction yielding molten iron. The primary chemical reaction is represented as: $Fe_2O_3+3CO \rightarrow 2Fe+3CO_2Fe_2O_3+3CO \rightarrow 2Fe+3CO_2$
- Slag Formation: Calcium carbonate decomposes to form calcium oxide (CaO), which reacts with silicates and other ore-borne impurities to produce a molten slag phase, aiding in the segregation of non-metallic inclusions from the molten metal.

3. Hot Metal and Slag Extraction: Periodically, both molten iron and slag are simultaneously tapped from dedicated tapholes. The density differential ensures effective separation, directing each to distinct containment structures.

4. Basic Oxygen Furnace (BOF) Operation:

- Charging: The hot metal is introduced into the BOF, occasionally complemented with scrap steel for thermal equilibrium.
- Oxygen Blowing: Oxygen, of a purity exceeding 99%, is directed onto the molten bath. This rapidly oxidizes residual carbon, silicon, and other elements. The exothermic reactions further elevate the bath temperature. The pivotal reactions include: $C+O_2 \rightarrow CO_2C+O_2 \rightarrow CO_2$ and $C+12O_2 \rightarrow COC+21O_2 \rightarrow CO$
- End Point Determination: Advanced sensors and computational models analyze the temperature profile and off-gas composition, ensuring the attainment of the targeted carbon content.
- Post-Oxygen Blowing Adjustments: To achieve the prescribed chemical composition, precise quantities of alloying elements are integrated. Concurrently, refining procedures may be instituted to regulate trace elements and non-metallic inclusions.

5. Continuous Casting: The refined steel is ushered to continuous casting units, wherein it is solidified in molds tailored to the requisite cross-sectional geometry, yielding semi-finished products: slabs, blooms, or billets.

The BF-BOF route, while proficient in large-scale, high-quality steel production, has inherent environmental implications, primarily owing to its carbon-intensive nature. As the European Union propels toward a sustainable future, it becomes pivotal to investigate and integrate alternative, low-carbon steelmaking technologies such as the use of green hydrogen.

2.1.2 Green alternative

The contemporary urgency to curb CO_2 emissions has invigorated interest in sustainable steelmaking. An emergent, promising method capitalizes on green hydrogen, derived from water electrolysis powered by renewable energy sources. This technique primarily pivots around hydrogen-based Direct Reduction (H-DR) combined with an Electric Arc Furnace (EAF). Figure 5 depicts an exemplary processes for steel production through direct reduction with green hydrogen.

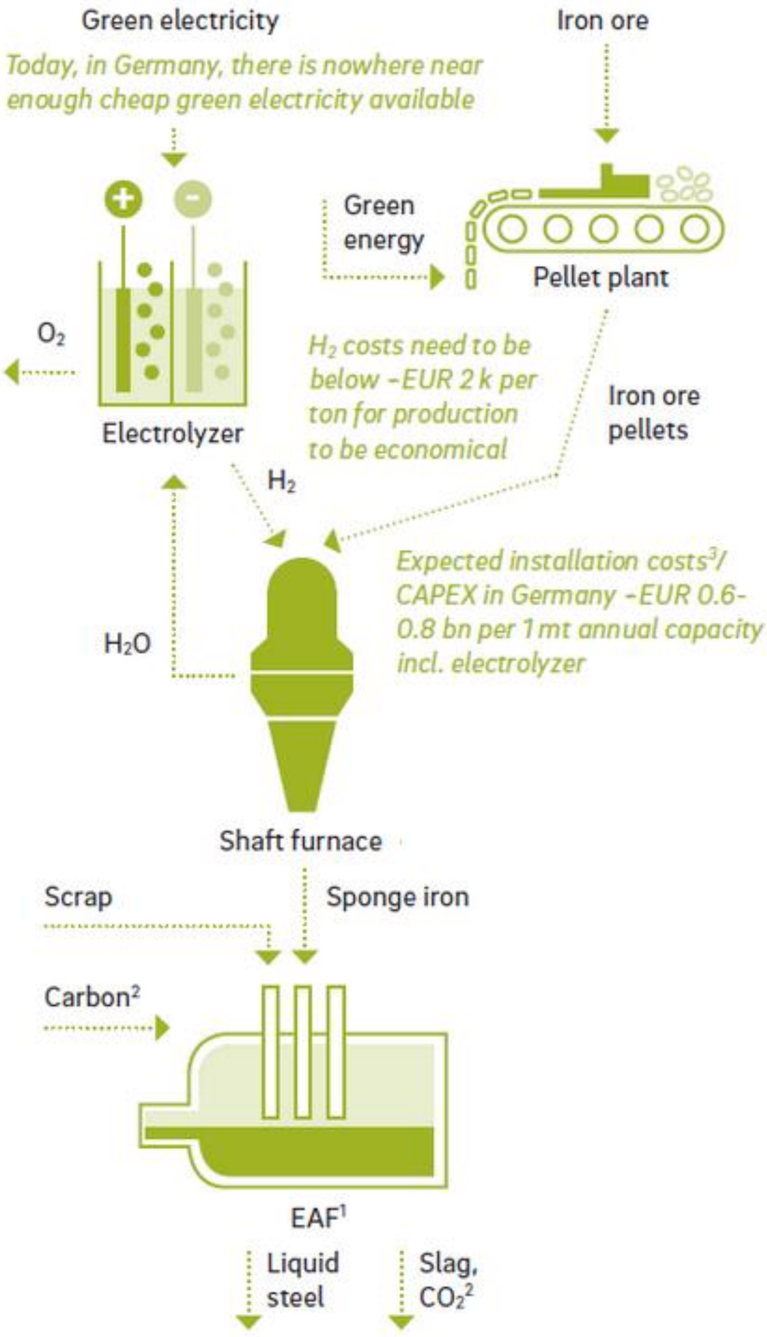


Figure 5 Production processes of steel through direct reduction with hydrogen (Roland Berger 2020).

The basic processing steps as depicted in Figure 5 are as follwos:

1. Green hydrogen production:

- Electrolysis: By subjecting water to electrolysis, facilitated by renewable energy sources (e.g., wind, solar), molecular hydrogen (H_2) and oxygen (O_2) are produced. The fundamental reaction is expressed as: $2H_2O \rightarrow 2H_2 + O_2$

The derived hydrogen, devoid of carbon contaminants, is then employed for iron ore reduction.

2. Direct Reduction (DR) process using hydrogen:

- Iron Ore Preparation: Iron ore, primarily in the form of pellets or lump ore, is introduced into a Direct Reduction (DR) reactor, usually a shaft furnace.
- Reduction with Hydrogen: Unlike traditional DR processes that use natural gas, green hydrogen is used as a reducing agent. In the reactor, hydrogen gas reduces iron ore to produce sponge iron (or direct reduced iron, DRI). The overarching chemical reaction is: $Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O$

Notably, the primary by-product is water vapor, contrasting sharply with the CO_2 evolved in carbon-based methods.

3. Melting in an Electric Arc Furnace (EAF):

- Charging: The DRI, occasionally combined with scrap steel, is charged into an EAF.
- Melting: Utilizing graphite electrodes, an electric arc is generated, rapidly melting the DRI and scrap. The process is facilitated by the high metallic iron content in DRI, ensuring efficient energy utilization.
- Refining: To achieve specific compositions and properties, precise amounts of alloying elements are introduced, and sophisticated refining techniques are applied.

4. Casting:

- Similar to conventional methods, the molten steel is transferred to continuous casting units, solidifying the steel to yield semi-finished products such as slabs, blooms, or billets.

The integration of green hydrogen in steelmaking illuminates a pathway toward significantly diminished CO_2 emissions. However, its viability hinges on the scalability and cost-effectiveness of green hydrogen production. Given the European Union's steadfast commitment to a green transition, investments in infrastructure and research in this domain are paramount to actualize a sustainable steel industry.

2.2 Cement industries

In the following, state-of-the-art technology for cement production is briefly described.

2.2.1 State of the art technology

The conventional production process of cement, specifically Portland cement, involves several stages. The primary raw materials used for this process are limestone, clay or shale, and sometimes other materials like iron ore. A step-by-step breakdown of the production process can be described as follows:

1. Raw material preparation:

- Crushing and Grinding: Limestone and clay are crushed and grinded to a fine powder. This is usually done in a multi-stage crushing process using jaw crushers, cone crushers and ball or roller mills for subsequent grinding.
- Mixing: The crushed limestone and clay are mixed in the right proportion to form the 'raw mix'.

2. Raw Material Processing:

- Blending: The raw mix is stored in blending silos for proper mixing and homogenization.
- Pre-heating: The raw mix is pre-heated using waste heat from the kiln. This process drives off the moisture content and starts the chemical reactions necessary for cement formation.

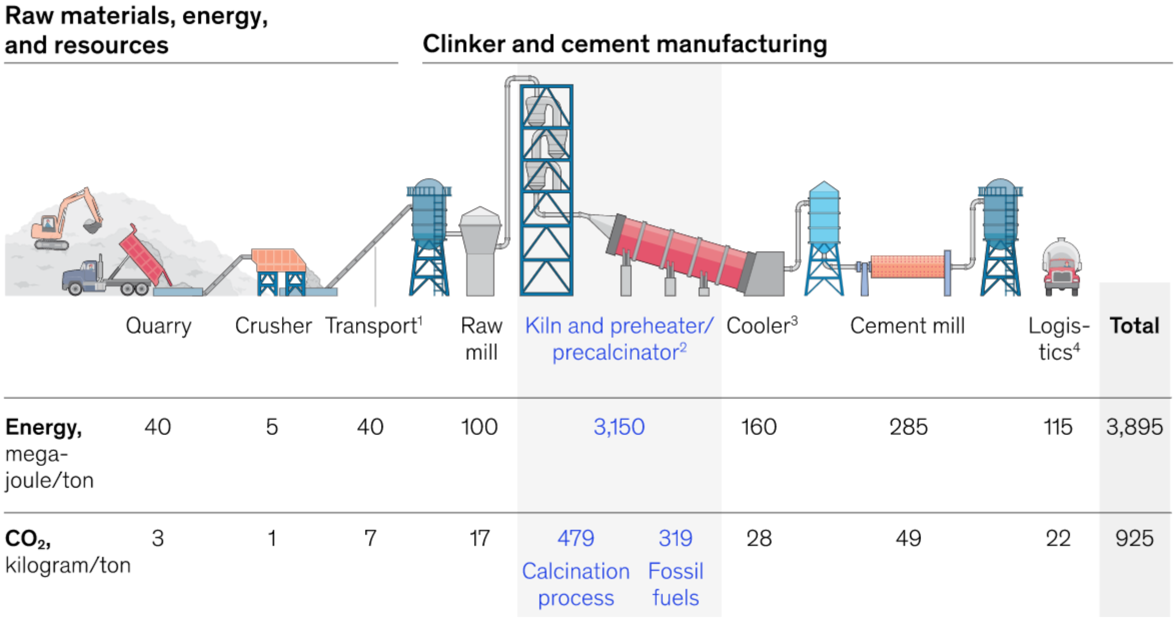
3. Pyroprocessing in the Kiln:

- Calcination: In the kiln's upper section, carbon dioxide (CO_2) is driven off from the limestone, leaving behind calcium oxide (lime).
- Clinkering: As the material moves down the kiln, it reaches temperatures of around 1400-1450°C. In this section, calcium oxide reacts with silica, alumina, and ferric oxide to form clinker compounds: C_3S (Alite), C_2S (Belite), C_3A (Aluminate), and C_4AF (Ferrite).
- Cooling: Once the clinker is formed, it is rapidly cooled to retain the reactive crystalline structure.

4. Clinker Grinding and Cement Milling:

- Grinding: The cooled clinker is mixed with gypsum (usually around 3-5%) and then finely ground to a fine powder. Gypsum is added to control the setting properties of the cement.
- Additives: Depending on the type of cement required, other materials like fly ash, slag, or pozzolana might be added during grinding.

The cement production process is energy-intensive and produces significant amounts of carbon dioxide, primarily from the calcination step and the combustion of fuels in the kiln. Figure 6 shows the energy consumption and the associated carbon emissions along the processing chain of cement production. As indicated by Figure 6, the majority of carbon emission in cement production comes from the calcination process. In this reaction, calcium carbonate is decomposed by heat to produce calcium oxide (lime) and carbon dioxide: $CaCO_3 \rightarrow CaO + CO_2$. As these carbon emissions are process based, they cannot be simply avoided by using alternative fuels. This is why the reduction of carbon emission from cement production is often linked to end-of-pipe treatment through carbon capture and storage (CCS) or carbon capture and utilization (CCU).



	Raw materials, energy, and resources			Clinker and cement manufacturing					
	Quarry	Crusher	Transport[1]	Raw mill	Kiln and preheater/ precalcinator[2]	Cooler[3]	Cement mill	Logistics[4]	Total
Energy, mega-joule/ton	40	5	40	100	3,150	160	285	115	3,895
CO_2, kilogram/ton	3	1	7	17	479 Calcination process 319 Fossil fuels	28	49	22	925

Figure 6 Basic steps in cement production including associated energy demand and CO_2 emissions (McKinsey 2020).

2.2.2 Green alternative

Due to its significance for overall industrial carbon emissions (cf. Figure 1), there are different strategies to reduce CO_2 emissions in cement production. These strategies can be divided in the two general approaches which are in line with the abatement strategies indicated in Figure 3. This includes substitution on the one side and end-of-life treatment on the other side:

1. First approaches avoid emissions beforehand by changing materials in the cement industries, mainly by replacing calcium oxide (CaO). A new type of clinker (mixed with other ingredients, such as dicalcium silicate, Ca_2SiO_4) with less bound CO_2 could reduce the emissions by about 20-30%. This new clinker type has the same strength in comparison to the standard used cement (Antunes et al. 2021).
2. The second approaches decrease emissions by applying post-combustion removal of CO_2 in the cement production process and subsequent sequestration of CO_2. The separated pure CO_2 might be stored (CCS) or further processed for chemical synthesis with green hydrogen (CCU). An example how to remove CO_2 from flue gases would be Calcium Looping Technology (CLT) using a lime-based (CaO) sorbent that absorbs the CO_2 and could afterwards be used for clinker production (Carbone et al. 2022). The overall process relies on two reversible chemical reactions: carbonation and calcination. This technology has several advantages such as a small loss of net efficiency, low CO_2 avoidance cost with high CO_2 absorption (>90%) and low environmental impact due to generally positive effect of further air pollutants (Perejón et al. 2016).

Both approaches will be analyzed regarding their effect on further air pollutants in the next chapter (see chapter 3).

The basic principle of the Calcium Looping Technology, which is not restricted to cement industries but could be applied for various processes to remove CO_2 from flue gases, is illustrated in Figure 7.

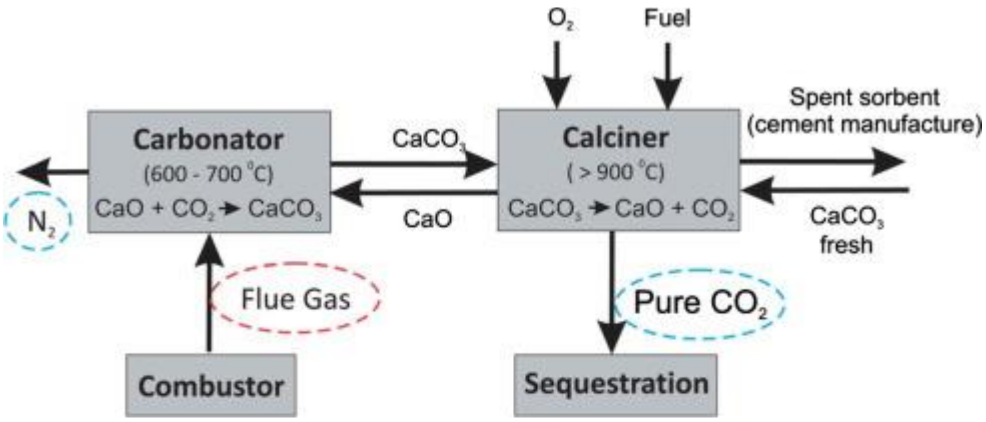


Figure 7 Basic principle of the Calcium -looping technology (CLT) with the two reversible chemical reactions of carbonation and calcination. The spent sorbent can be directly reintroduced in the cement production process leading to minimal losses (Perejón et al. 2016).

As illustrated in Figure 7, the calcium looping process is a two-stage system with 2 different reactors:

1. **Carbonator:** In the first reactor, the CO_2 from the flue gas reacts with calcium oxide (CaO) to form calcium carbonate ($CaCO_3$), capturing the CO_2 in the process:
   $CaO + CO_2 \rightarrow CaCO_3$

2. **Calciner:** In the second reactor, the calcium carbonate is regenerated back to calcium oxide by heating, releasing the captured CO_2 in a concentrated form suitable for storage or utilization:
   $CaCO_3 \rightarrow CaO + CO_2$

2.3 Crude oil refineries

A refinery serves to transform natural raw materials, predominantly crude oil, into valuable marketable products. Crude oil, a blend of naturally occurring fossil hydrocarbons, is sourced globally, leading to variations in its composition. This means elements like Sulphur, nitrogen, and oxygen, as well as trace metals like vanadium, nickel, and sodium, can differ based on the oil's provenance. To derive the array of products from crude oil, it is processed in specialized refining facilities, either in its pure form or mixed with biofuels. Collectively, these facilities, inclusive of supporting units, are termed a 'refinery.' Factors such as product demand, available crude quality, and regulatory stipulations dictate a refinery's size, design, and intricacy. Given these variable factors, each refinery possesses unique characteristics, ensuring no two are exactly alike (Pascal et al. 2015, p. 1).

2.3.1 State of the art technology

To grasp the implications of refinery emissions, it's essential to first comprehend the foundational principles of refinery operations. As illustrated in the subsequent figure, several core processes dominate the inner workings of an oil refinery.

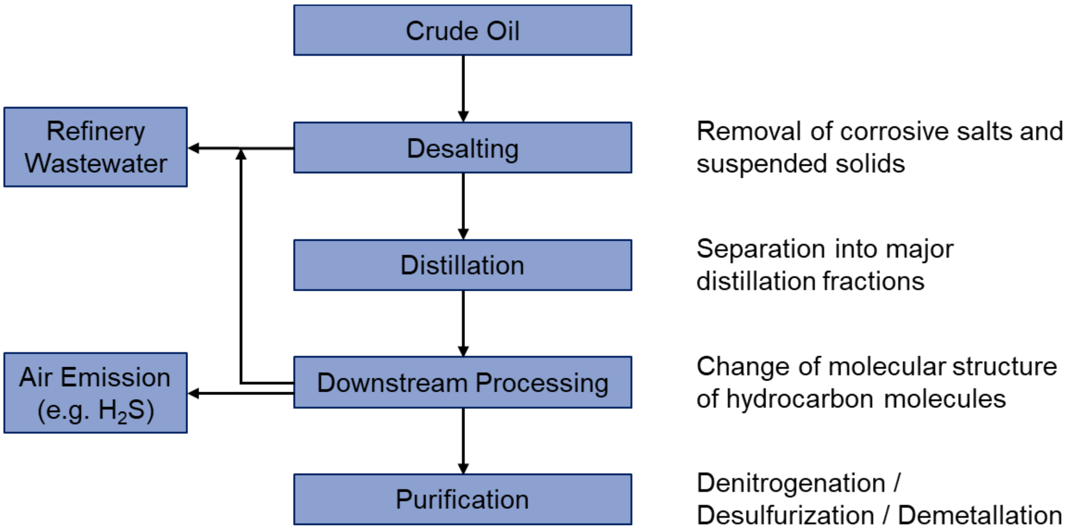


Figure 8: General process elements in an oil refinery (Bachmann et al. 2014)

In the initial phase, desalting and dewatering occur. Crude oil, when extracted from the reservoir, often contains a mixture of gases, water, and minerals. Therefore, the refining process begins with the extraction of fluids from the reservoir, followed by subsequent pretreatment operations. Removing salt, which is found in brines mixed with the recovered crude oil, is crucial to prevent corrosion during further refining stages. Desalting can be accomplished through heating under pressure, water washing, or electrostatic methods. (Speight 2000)

Crude oil is processed to segregate it into distinct components or 'fractions'. The physical and chemical properties of crude oil can exhibit significant variability across, and even within, production regions. A common method for categorizing crude oil is by labeling it as 'light' or 'heavy'. Essentially, crude oils are complex mixtures of numerous pure components (Institut français du pétrole 1995). Distillation stands as the paramount initial step in refining, facilitating the separation of the myriad hydrocarbon compounds (Speight 2000). Subsequent distillation of lighter elements yields components such as naphtha, methane, and ethane, which are pivotal for refinery fuels, LPG, or gasoline blending. Distillation techniques span atmospheric or vacuum conditions, as well as azeotropic or extractive methods (Speight 2000).

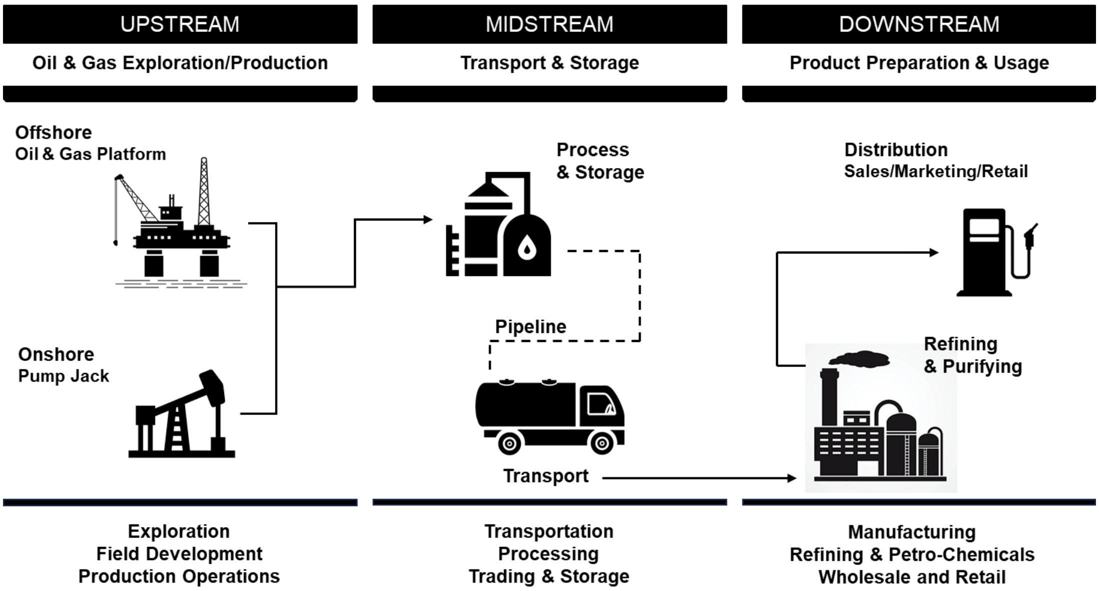


Figure 9: List of upstream, midstream and downstream processes and steps (Eland Cables 2023)

Downstream processing constitutes the final phase of oil and gas operations, as delineated in Figure 9, which illustrates the operational steps encompassing upstream, midstream, and downstream stages. While upstream activities encompass the exploration and extraction of crude oil and natural gas, downstream pertains to post-extraction processes leading up to the final delivery of products in their requisite forms (Eland Cables 2023).

Refining activities in the downstream sector can be broadly bifurcated into two categories:

1. Fractionation/separation, where no molecular alterations transpire, and
2. Upgrading/conversion, characterized by molecular transformations.

A pivotal supplementary activity is the blending of crude oils, both to adhere to refinery design constraints and to ensure that the final refinery products are aligned with stringent specifications and optimal performance benchmarks (Hsu and Robinson 2017). The specific amalgamation of these downstream processes primarily defines a refinery's type.

Modern refineries also exhibit a significant hydrogen demand. A portion of this requirement is self-fulfilled as hydrogen is concurrently produced as a byproduct during the refining process. The majority, however, is derived from steam reforming, denoted as the "net hydrogen demand." This demand fluctuates between 20% to 32% and is primarily utilized in hydrocarbon processing, particularly in the synthesis of petrol and diesel fuels (Baur 2018).

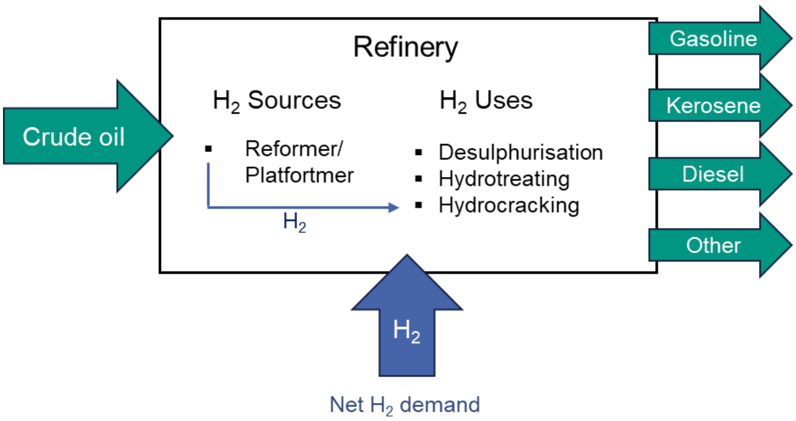


Figure 10: Downstreaming Processes (Baur 2018)

The following three technical processes can be identified in this:

1. **Desulphurization/Hydrodesulphurization:** This process involves the removal of organosulphur compounds using catalysts. Inadequate removal of sulphur can result in the emergence of harmful sulphur oxides upon fuel combustion, which are primary contributors to air pollution. Not all refinery desulphurization techniques guarantee efficient results. (Rigutto et al., p. 892)
2. **Hydrotreating and Dewatering:** These procedures target the extraction of contaminants, including heavy metals, sulphur, nitrogen, and ammonia. Concurrently, the substrate undergoes aromatic saturation. The process conditions typically span a temperature range of 205°C to 370°C and pressures between 2500kPa to 8500kPa.
3. **Hydrocracking**: Positioned subsequent to hydrotreating, hydrocracking utilizes a catalytic reactor, high pressures, and temperatures ranging from 280°C to 450°C. Its primary objective is to cleave and segregate long-chain hydrocarbons, aiming to procure low-boiling fractions suitable for diesel and gasoline production. (Pascal et al. 2015, p. 85)

Despite the reduction in emitted air pollutants, additional measures are imperative to achieve further reductions.

Emissions to the atmosphere:

Figure 11 and Figure 12 show the amount of air pollutants emitted in the year 2007 and 2009 in the European Union through the oil refining industry (Pascal et al. 2015). Despite the reduction in emitted air pollutants, additional measures are imperative to achieve further reductions.

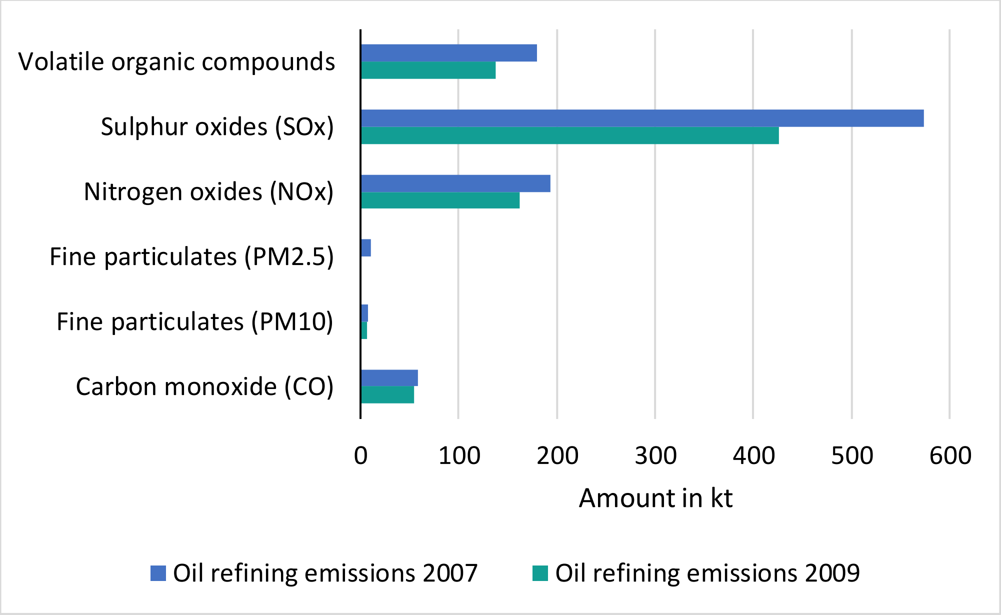


Figure 11: Contribution of oil refining to the EU-27 air emissions (2007-2009)

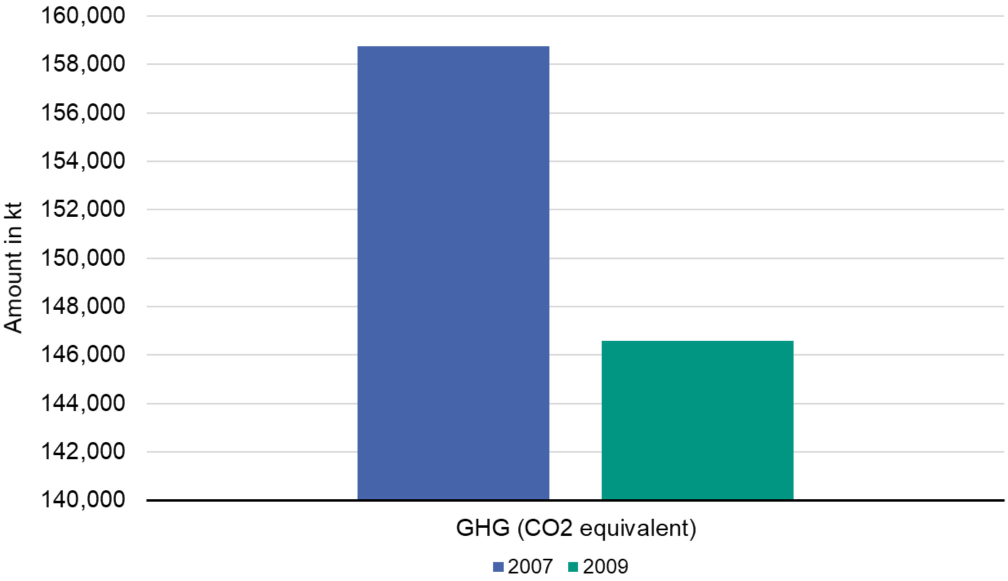


Figure 12: Greenhouse gases as CO_2-equivalent of oil refining (2007-2009)

Power plants, boilers, heaters, and catalytic cracking units are the primary emitters of carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NOx), particulates, and sulphur oxides (SOx) in the refining process. The substantial energy requirements account for approximately 60% of all refinery-related air emissions. Sulphur recovery units and flares also contribute significantly to these emissions, while particulate releases primarily arise during catalyst changeovers and coking operations. Moreover, volatile organic compounds (VOCs) find their origins in valves, seals, storage tanks, flanges, and drains. Table 1 succinctly highlights the chief pollutants discharged by a standard refinery and pinpoints their primary sources (Pascal et al. 2015).

Table 1: Main air pollutants and their main sources emitted by refineries (Pascal et al. 2015)

Main air pollutants	Main sources
Carbon dioxide	Process furnaces, boilers, gas turbines Fluidised catalytic cracking regenerators CO boilers Flare systems Incinerators LNG plant CO_2 separator
Carbon monoxide	Process furnaces and boilers Fluidised catalytic cracking regenerators CO boilers Sulphur recovery units Flare systems Incinerators
Nitrogen oxides (NO, NO_2)	Process furnaces, boilers, gas turbines Fluidised catalytic cracking regenerators CO boilers Coke calciners Incinerators Flare systems
Nitrous oxide (N_2O)	Fluidised catalytic cracking regenerators
Particulates (including metals)	Process furnaces and boilers, particularly when firing liquid refinery fuels Fluidised catalytic cracking regenerators CO boilers Coke plants Incinerators
Sulphur oxides	Process furnaces, boilers, gas turbines Fluidised catalytic cracking regenerators CO boilers Coke calciners Sulphur recovery units (SRU) Flare system Incinerators
Volatile organic compounds (VOCs)	Storage and handling facilities Gas separation units Oil/water separation systems Fugitive emissions (valves, flanges, etc. Vents Flare systems

2.3.2 Green alternative

Oil refineries stand out as some of the predominant consumers of hydrogen, given its multifaceted applications as a feedstock, reagent, or energy source. The utilization of hydrogen is concurrently one of the most substantial CO_2 emission sources within an oil refinery, rendering it a critical area of focus (International Energy Agency- IEA). Grey hydrogen production (unless derived as a by-product during refining) is primarily achieved through the steam reforming of fossil fuels, such as natural gas or coal, culminating in significant CO_2 emissions. In Germany, this method accounts for the production of over 90 % of hydrogen.

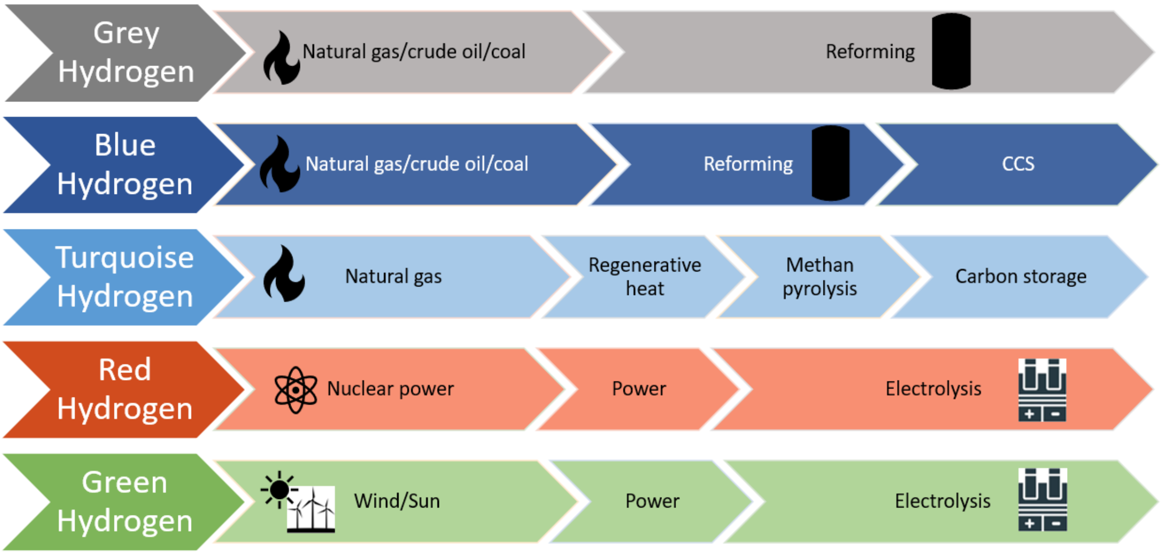


Figure 13: Summary of the five-color theory of hydrogen

Green hydrogen is produced via the electrolysis of water, a process wherein electricity—sourced from renewable energy technologies such as solar or wind—splits water into its constituent elements of hydrogen and oxygen. Because the production of electricity from these renewable sources, as well as the resulting hydrogen and oxygen, does not harm the environment, green hydrogen stands out as a CO_2-neutral and environmentally friendly solution. Its integration can significantly reduce emissions in sectors like oil refining.

Beyond green hydrogen, there are other 'colors' denoting different production methodologies:

- Blue hydrogen is derived from natural gas through steam methane reforming (SMR), coupled with carbon capture and storage (CCS) to reduce the associated carbon emissions.
- Grey hydrogen, like blue, is also produced from natural gas using SMR but lacks the carbon capture process, resulting in the release of CO_2.
- Turquoise hydrogen is produced through the pyrolysis of methane, producing solid carbon rather than CO_2 as a byproduct.
- Pink/Red hydrogen refers to hydrogen produced via electrolysis but powered by nuclear energy.

Each of these hydrogen production methods has its own advantages, challenges, and environmental impacts, necessitating a comprehensive evaluation based on application and sustainability goals.

While targeted technical enhancements or modifications to production units might offer benefits in specific instances, transitioning from grey to green hydrogen promises a transformative impact on the CO_2 footprint of every refinery.

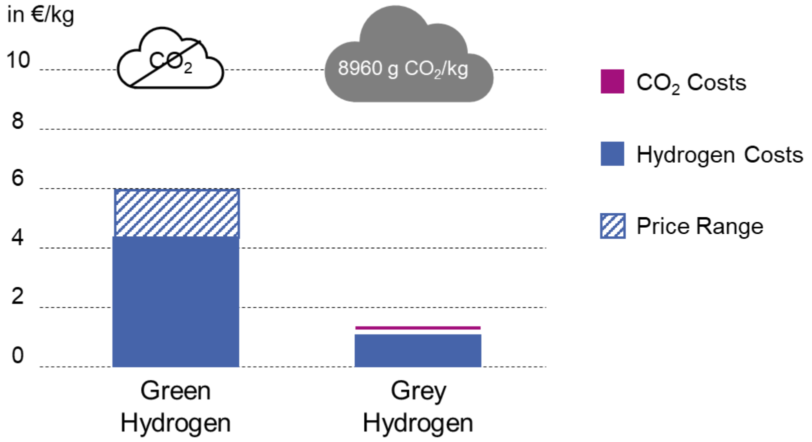


Figure 14: advantages of hydrogen (dena - Deutsche Energieagentur 2018)

In addition to transitioning from steam-reformed hydrogen, incorporating green energy sources in oil refineries presents another avenue to curb emissions. Although the direct application of renewable electricity for heat generation in refineries remains improbable, green hydrogen can serve as an alternative fuel, further influencing air pollutant profiles. Nonetheless, in a carbon-neutral future, traditional oil refineries may undergo a paradigm shift. Anticipated are integrated refineries adept at processing diverse feedstocks, such as pyrolysis oil derived from biomass and waste, as well as hydrocarbons from chemical routes like Fischer-Tropsch synthesis. Given this evolving landscape, the extent to which green hydrogen will fuel future refineries remains uncertain. Instead, refined products—potentially light fractions—could be repurposed as energy sources, aligning with existing refinery paradigms (dena - Deutsche Energieagentur 2018).

In summary:

- Heat generation: fuel switching and electrification:

At the highest temperatures, the combustion of hydrogen is a viable substitute for currently used fossil fuels because, as mentioned above, most refineries already provide hydrogen via steam reforming or as a by-product. Refineries produce most of their current fuel mix on site as a waste product called refinery fuel gas, which can be cleanly steam reformed into hydrogen instead of being burned for heat.

- Process emissions: Carbon Capture, Utilization and Storage (CCUS)

For point sources CCUS technology can be a key solution to mitigate process emissions. The captured CO_2 can be used in other products e.g., curing cement or producing synthetic aggregate for low-carbon concrete. As many refineries are located near CO_2 pipelines and underground storage formations, they are ideal CCUS hubs. Carbon dioxide can be used on-site as feedstock for a low carbon “semi-circular” refinery. But this is still a theoretical concept (Byrum et al. 2021).

2.4 Glass production

Glass manufacturing is a significant energy-intensive process, characterized by its diverse products and techniques. Products span from intricate handmade crystal artifacts to vast float glass structures for construction. Production methods vary from small electric furnaces to large high-temperature gas units. Although the raw materials for glass, such as silicon dioxide (SiO2), sodium oxide (Na2O), and calcium oxide (CaO), are abundant and economical, the industry is predominantly localized. This is due to the logistic complexities and costs associated with transporting both raw materials and finished goods (IFC Manufacturing, Agribusiness & Services 2020). The range of glass types, determined by chemical composition and additives, is vast. Notable types encompass soda-lime glass, used in containers and light bulbs; borosilicate glass for pharmaceuticals; lead glass for electronic components; barium glass for TV panels; and aluminosilicate glass for fibreglass. These glasses are typically available in green, brown, and colourless shades (Jani and Hogland 2014).

The broad spectrum of products, each with unique material properties, is intrinsically shaped by the chosen raw materials and their proportions. Notably, Table 2 depicts typical product compositions across various German glass sectors. Given the natural abundance of these raw materials, the environmental footprint linked to their procurement is relatively minimal (Zier et al. 2021, pp. 2–3).

As the majority of the raw materials occur naturally and in abundance, the environmental impact associated with their supply is relatively low (Scalet et al. 2013).

Table 2: Typical product compositions (Zier et al. 2021)

	SiO_2 /wt%	Na_2O /wt%	CaO /wt%	MgO /wt%	Al_2O_3 /wt%	K_2O /wt%
Container glass	71 - 73	12 - 14	8.5 - 12	0 - 3.5	1 - 3	0 - 1.5
Flat glass	70 - 73	13.5 - 14	8.5 - 9	0 - 5	0.3 - 1.5	0.3 - 0.7
Glas fibers	52 - 65	< 17	16 - 25	0 - 5	12 - 16	< 2

2.4.1 State of the art technology

Figure 15 illustrates Scope 1 emissions directly originating from glass manufacturing. The primary concerns are emissions of Carbon dioxide, Nitrogen oxides, and fine particulates. These pollutants primarily arise from combustion processes and the high-temperature oxidation of atmospheric nitrogen. Moreover, furnaces release dust which, contingent on the raw materials employed, can contain chlorides, fluorides, and trace metals. Additionally, emissions associated with Scope 2 and 3 activities—such as raw material extraction and product transportation—also significantly impact environmental metrics (Scalet et al. 2013).

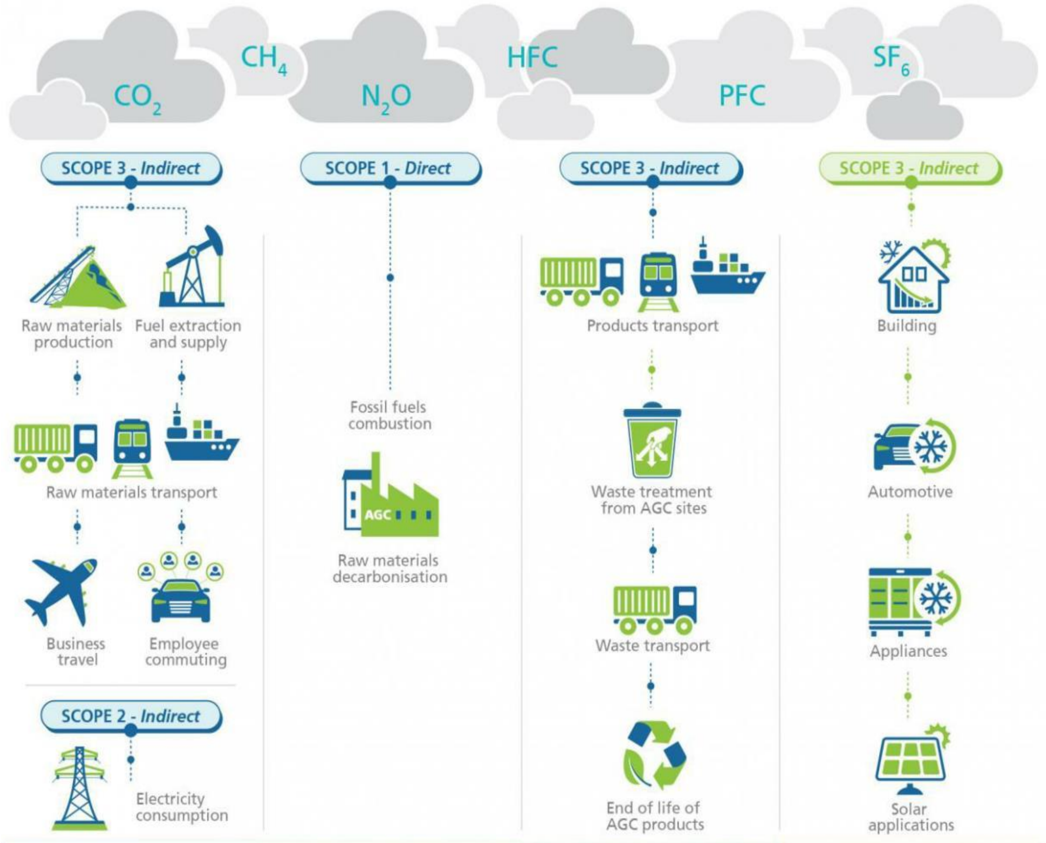
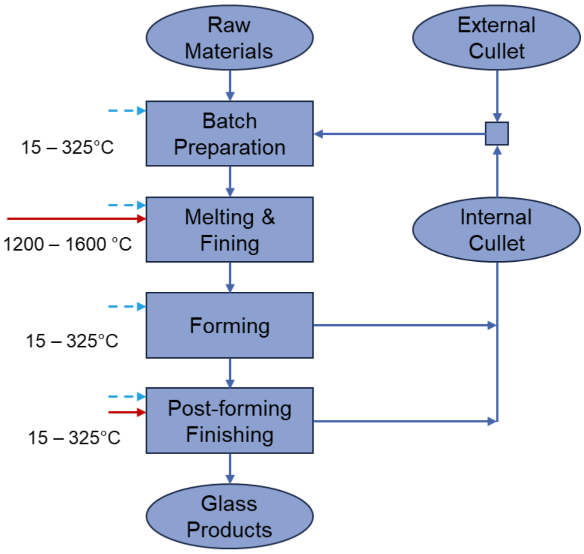


Figure 15: Carbon footprint of glass production (AGC Glass Europe 2023a)

To fully grasp the emissions and environmental ramifications associated with glass production, akin to refinery emissions, it's imperative to delve into the intricacies of the glass manufacturing process. The most elucidative method to represent this procedure is through a flow chart, as depicted below. At its core, the process can be segmented into three principal stages as shown in Figure 16.

1. Collection of raw materials
2. Melting of these raw materials and
3. Forming and finishing of the final products



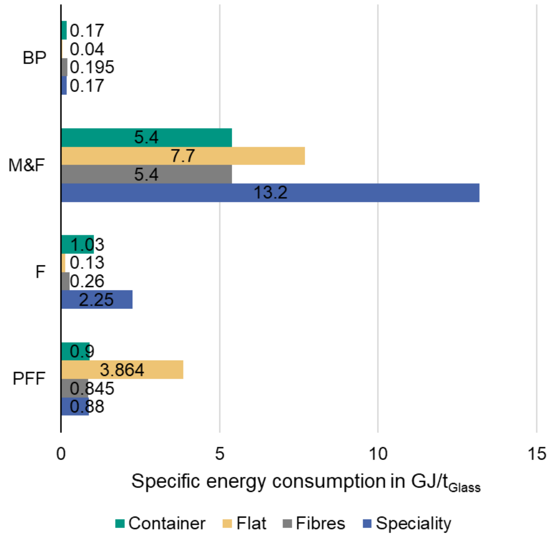


Figure 16: Specific energy consumption (Zier et al. 2021, p. 5) *Figure 17: Process steps (Zier et al. 2021, p. 5)*

Figure 16 delineates that the melting and fining phase stands out as the most energy-intensive, with energy consumption ranging from 5.4 GJ t_{Glass}^{-1} to 13.2 GJ t_{Glass}^{-1}. This significant energy demand largely contributes to it being the predominant source of pollution within the entire process. The intensive energy requirement is primarily attributed to the necessity of melting the raw materials at exceptionally high temperatures, spanning 1,200°C to 1,600°C. Predominantly, the energy source driving this is natural gas, alongside other fossil fuels. The subsequent table, referenced as Figure 18, provides a breakdown of energy consumption specific to the glass manufacturing industry. While this data primarily reflects the American sector, it offers valuable insights, as the fossil fuel proportions are strikingly comparable.

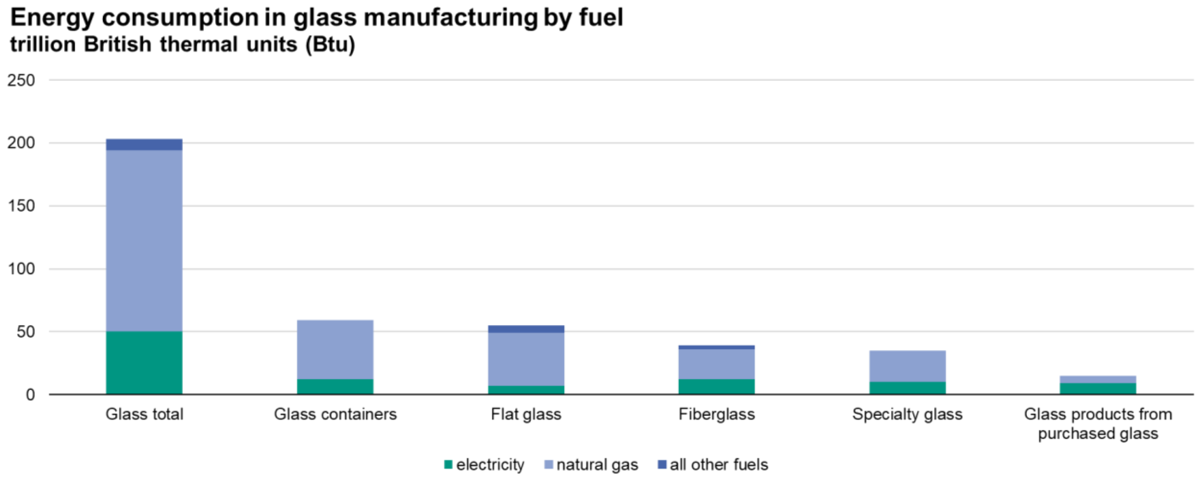


Figure 18: Manufacturing energy consumption (Glass manufacturing is an energy-intensive industry mainly fueled by natural gas 2023)

Figure 19 shows the final energy consumption in the non-metallic industries with the production of glass taking up to 250 PJ of energy and 73.8 % of which is provided by natural gas.

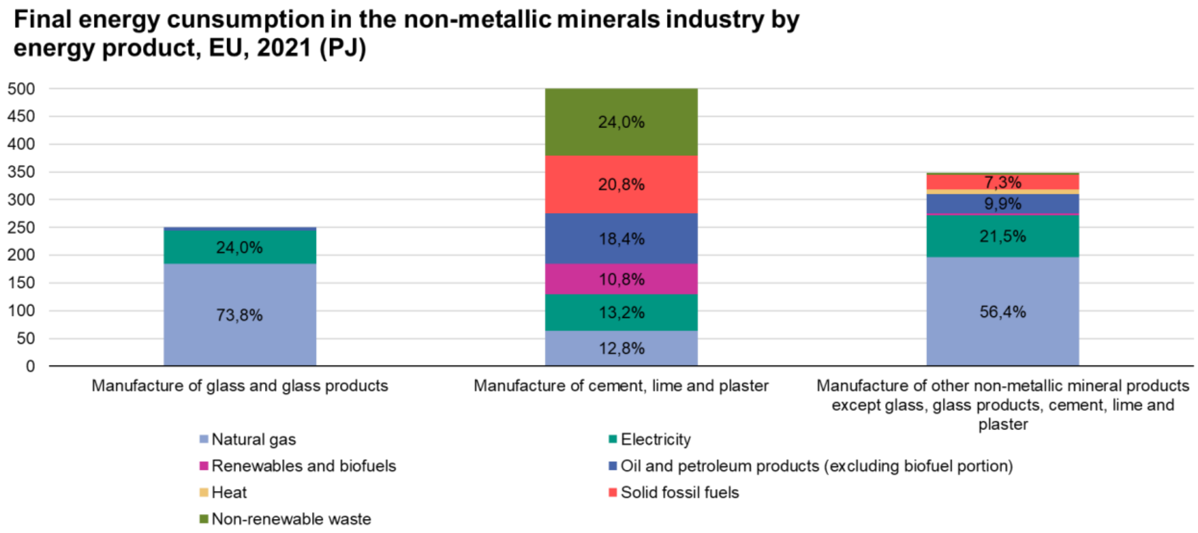


Figure 19: Manufacturing final energy consumption in the non-metallic minerals industry by energy product for the EU (Leisin 2019)

The various stages in the production of glass are integral to the industry's value chain, as illustrated in Figure 20. The entire manufacturing journey, from batch preparation to the packaging of the final glass product, unfolds within a singular glass facility. Notably, the extraction of raw materials and cullet falls outside the direct responsibilities of the glass industry. However, in a bid to augment the waste glass recycling rate, some contemporary container glass plants are beginning to incorporate waste glass processing directly into their operations (Leisin 2019).

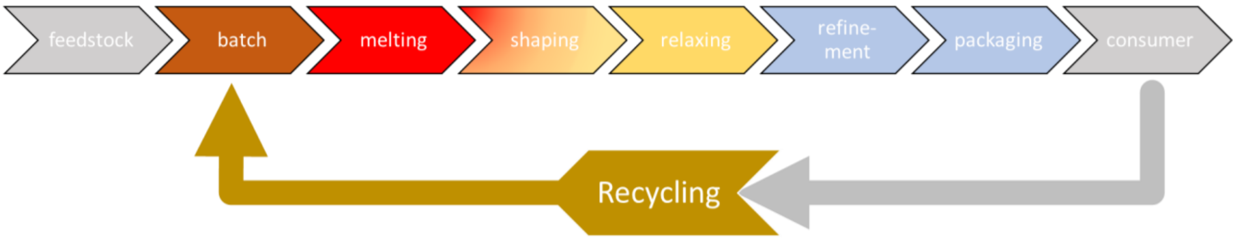


Figure 20: value chain of the glass industry

In the realm of air quality assessment, it's crucial to factor in heavy metal emissions. These emissions stand out as potential significant pollutants, contingent on the specific manufacturing processes deployed. The magnitude and potential impact of these emissions become evident when examining real-world data. A representation of these emission levels, specific to certain glass processes, can be observed in Table 3. Based on the estimated relative environmental impact, the concentration limit is regulated in emission regulations as the TA Luft 1986 (Scalet et al. 2013).

Table 3: Potential heavy metal pollutants from glass processes without abatement (Scalet et al. 2013)

Metal	**Container glass**	**Flat glass**	**Lead crystal glass**
Vanadium (when firing fuel oil)	Up to 4 mg/Nm^3	Up to 2 mg/Nm^3	
Nickel (when firing fuel oil)	Up to 0.5 mg/Nm^3	Up to 0.4 mg/Nm^3	
Chromium, total (green glass)	Up to 3 mg/Nm^3		

Selenium, total (green container glass)	Up to 0.8 mg/Nm^3		
Selenium, gaseous (flint hollow glass)	Up to 14 mg/Nm^3		
Selenium, total (flint hollow glass)	Up to 25 mg/Nm^3		
Selenium, total (float bronze glass)		Up to 80 mg/Nm^3	
Lead	Up to 4 mg/Nm^3	Up to 1 mg/Nm^3	Up to 700 mg/Nm^3
Cadmium	Up to 0.3 mg/Nm^3	Up to 0.1 mg/Nm^3	
Antimony			Up to 10 mg/Nm^3
Arsenic			Up to 20 mg/Nm^3

The production of container glass involves a sophisticated interplay of mass and energy. Figure 21 provides an overview of the mass and energy flow rates of the inputs and outputs for the production of container glass. For every ton of glass melted, there's a requirement of 1,010 kg of raw material, 1,800 kg of fresh water, 1,806 kWh of thermal energy, and 222 kWh of electrical energy. To put this in perspective, for the creation of 1,000 kg of container glass, these inputs are imperative. Breaking down the emissions, they can be categorized into emissions to air and other emissions. The primary air pollutant in this process is carbon dioxide, which is released at a rate of 0.420 t for every 1 t of glass. While other air pollutants such as NOx, SO_2, dust, HCl, HF, and heavy metals collectively contribute about 0.006 t per 1 t of glass, their environmental impact can be significant.

For instance, nitrogen oxides, when in the atmosphere, can lead to the formation of acid rain due to their reaction with water, oxygen, and other chemicals. This underlines the importance of not just monitoring these emissions but striving to minimize them. Meanwhile, other by-products like waste and waste water, although noteworthy, will not be delved into in this paper.

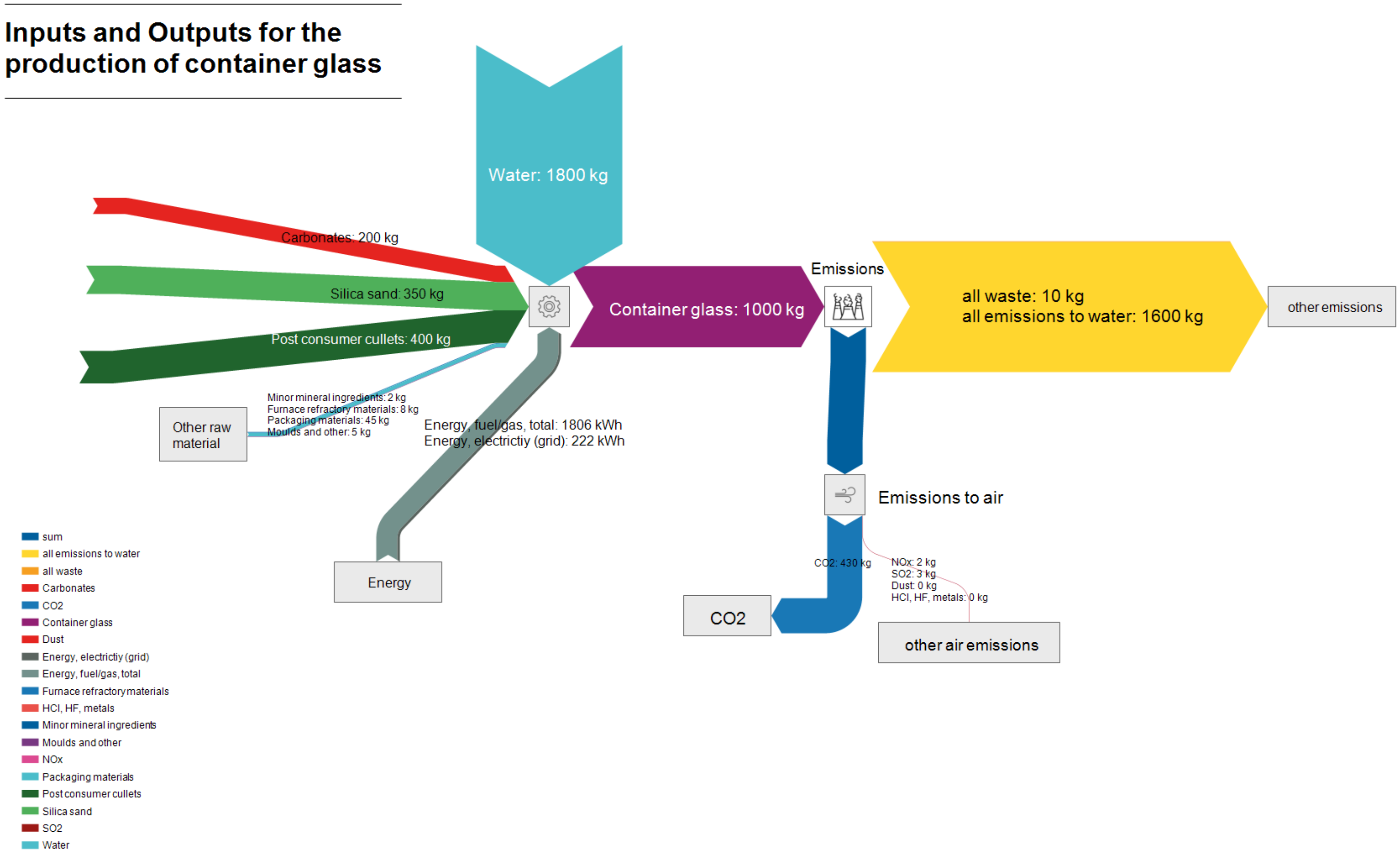


Figure 21: Inputs and Outputs for the production of container glass, given per ton of glass melted (Hischier 2007)

2.4.2 Green alternative

One of the great things about glass is that it is generally a fully recyclable material that can be reprocessed and reused in a closed loop (AGC Glass Europe 2023a). Although the materials used in glass production have little environmental impact, keeping recycling rates high is important to build a circular economy and conserve raw materials, scarce natural resources and energy. Recycled glass is available in the form of cullet, glass powder or crushed glass. One limitation to recycling forms broken and mixed colour waste glass because the recycling process becomes impractical and highly expensive. This is due to the variation in the chemical composition of the recycled glass. Impurities and contaminants that may be found in mixed-coloured used glass can affect the properties of the new glass produced. The recycling rate in the EU is estimated with 60 %. Worldwide the recycling rate of waste glass is quiet and it is mainly concentrated on the container and packaging sectors (Jani and Hogland 2014).

As 100 kg of cullet substitute about 120 kg of primary resources, recycling results in indirect energy savings and can therefore contribute to a greener glass industry.

The following figure (Figure 22) gets to the heart of the matter and summarizes the effect of several industry and not industry related options for a less polluting glass industry and therefore a greener future. The main key points are:

1. Design: Glass is designed more ecological, that means glass bottles are 30 % lighter today than 20 years ago.
2. Production: Production has increased by 39.5 % in the last 25 years, while energy has been reduced by 80 % in the last 50 years.
3. Distribution: 50 % or more of the glass bottles and jars are delivered to customers within a 300 km distance.
4. Consumption - Use and reuse: 87 % of Europeans prefer glass and it can be recycled, refilled or reused.
5. Collection: Over 70 % of all glass bottles are collected for recycling annually.
6. Recycling: Glass is 100 % recyclable in a bottle-to-bottle closed loop without a loss of quality. Recycled glass is a valuable raw material and permanently available for multiple recycling.
7. Raw materials: 1 ton of recycled glass saves 1.2 tons of virgin raw materials and avoids 60 % of CO_2. 70 % of raw materials travel less than 300 km.

Figure 22: Improved glass cycle to ensure a circular economy (AGC Glass Europe 2023b)

One alternative to create a more sustainable option is to change the energy used. Natural gas is the main fuel used in glass production, followed by oil products. Both fuels are interchangeable in the melting process. More than 75% of the energy used in the float sector comes from furnace activities, as shown in Figure 23.

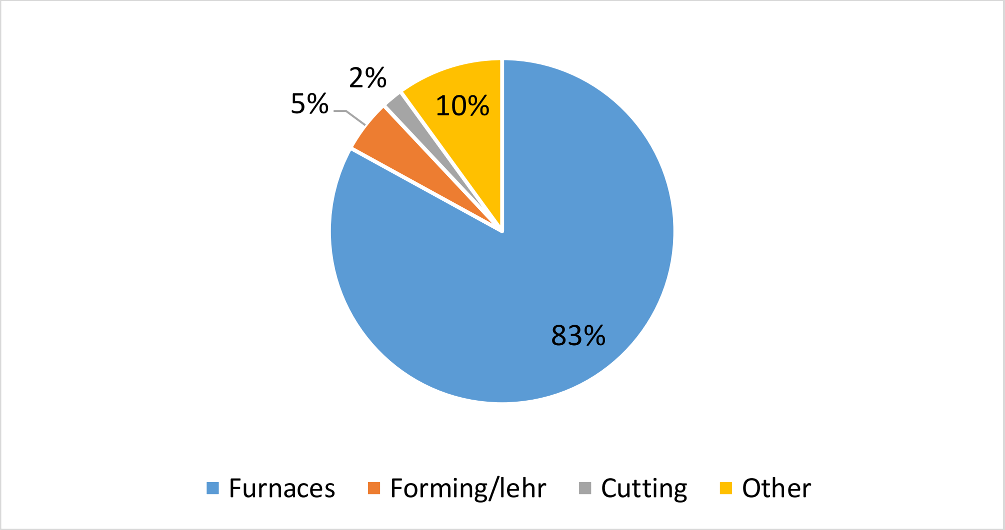


Figure 23: Energy use distribution in the float process

5% of the total energy is used for forming and annealing and 2% for cutting. The remaining energy is used for service, control systems, lighting, plant heating and other activities. As there is no technology available to run large float furnaces on electricity alone, other measures must be taken to reduce the energy requirements of the process (Schrefler et al. 2014). It has been found that a 10% increase in the use of cullet in glass raw materials reduces energy consumption by 2% to 3%. Furthermore, the use of cullet as a raw material in the production of glass requires only 40% of the energy used to make glass from sand (Jani and Hogland 2014).

Another strategy to reduce emissions is to use waste glass in the production of cement and concrete (Jani and Hogland 2014). Two problems can be combined as emissions and air pollution for cement production was discussed in chapter 2.2. The chemical composition of different colors and crushed waste glass shown in Table 4 shows that glass has a large quantity of silicon and calcium. Also, glass has the ability to be pozzolanic with its amorphous structure and can even be a cementitious material. As of now glass waste is used in landfills, which is a bad solution due to its nonbiodegradable structure. On the other hand, the cement and concrete industry can provide a more environmentally friendly waste management for the glass waste. Different studies have investigated different uses of waste glass: as an aggregate, as a cement replacement and some studies as aggregate and as a cement replacement in the same mixture (Jani and Hogland 2014).

Table 4: The chemical composition of cement and different colored glasses (Jani and Hogland 2014).

Chemical	Cement /%	Clear glass / %	Brown glass / %	Green glass / %	Crushed glass / %	Glass powder / %	Sand
SiO_2	20.2	72.42	72.21	72.38	72.61	72.20	78.6
Al_2O_3	4.7	1.44	1.37	1.49	1.38	1.54	2.55
CaO	61.9	11.50	11.57	11.26	11.70	11.42	7.11
Fe_2O_3	3.0	0.07	0.26	0.29	0.48	0.48	2.47
MgO	2.6	0.32	0.46	0.54	0.56	0.79	0.46
Na_2O	0.19	13.64	13.75	13.52	13.12	12.85	0.42
K_2O	0.82	0.35	0.20	0.27	0.38	0.43	0.64
SO_3	3.9	0.21	0.10	0.07	0.09	0.09	-
TiO_2	-	0.035	0.041	0.04	-	-	0.15
Loss on ignition	1.9	-	-	-	0.22	0.36	7.6

As shown in Table 5 waste glass and natural sand have almost the same physical properties. The comparison between the properties of the two materials shows that the absorption rate of waste glass is lower than that of sand by 14 % meaning that concrete made up with glass as an aggregate has a lower absorption rate for water. Because of this waste glass builds an interesting material to be used as an aggregate in the production of concrete. An optimum percentage of waste glass that can be used as aggregate has to be found without a loss off quality on the properties of the produced concrete. Particle size of the waste glass aggregate is e.g. playing a vital role in finding an optimal solution for this (Jani and Hogland 2014).

Table 5: Physical properties of waste glass and sand (Jani and Hogland 2014).

Physical property	Waste glass	Sand
Specific gravity	2.19	2.57
Density / kg/m^3	1672	1688
Absorption / %	0.39	2.71
Pozzolanic index / %	80	-

In summary, to decarbonize glass production processes, the following options can be considered:

- Increase the share of electrical energy for the glass melting process.
- The portion of energy that cannot be provided by electric power should be replaced by combustion of hydrogen.
- Deploy advanced process control systems to compensate for fluctuating energy prices and availability.
- Enhance the melting efficiency by preheating the recycled material, by special furnace design, or with combustion system adjustments.
- Recovery the combustion heat and use it either within the glass production process or otherwise for district heating or other industrial processes.
- Carbon capture and storage processes for emissions that cannot be prevented.

3 Effect of GHG emission reduction on major air pollutants

In the following section, the effect of the low-carbon technologies described in the previous chapter on further air pollutants are discussed and quantified as far as possible. As most low-carbon technologies are not yet implemented at industrial scale, a precise quantification of effects on air pollutants is not always possible due to a lack of respective data. However, in most cases, the substitution and replacement of specific technologies additionally leads to a reduction of associated air pollutants and can be quantified. End-of-pipe treatment of exhaust gases for carbon-capture and storage (CCS) is expected to also have positive effects on further air pollutants such as PM, SO_x or NO_x emission. These effects, however, are more difficult to quantify without real data from industrial applications.

3.1 Steel industries

As described in Section 2.1.2, the most relevant carbon-neutral alternative for steel production is the direct reduction of iron or with green hydrogen. This would lead to a replacement of blast furnaces and coke ovens (Figure 24). On the other side, after the direct reduction of iron ore, the resulting iron sponges are melted in an Electric Arc Furnace (EAF) for further processing (see Figure 5). Sintering and pelleting will change in the direct reduction route, however, this processing step will not be fully replaced. Therefore, sintering is not regarded in the direct comparison of both processing routes below.

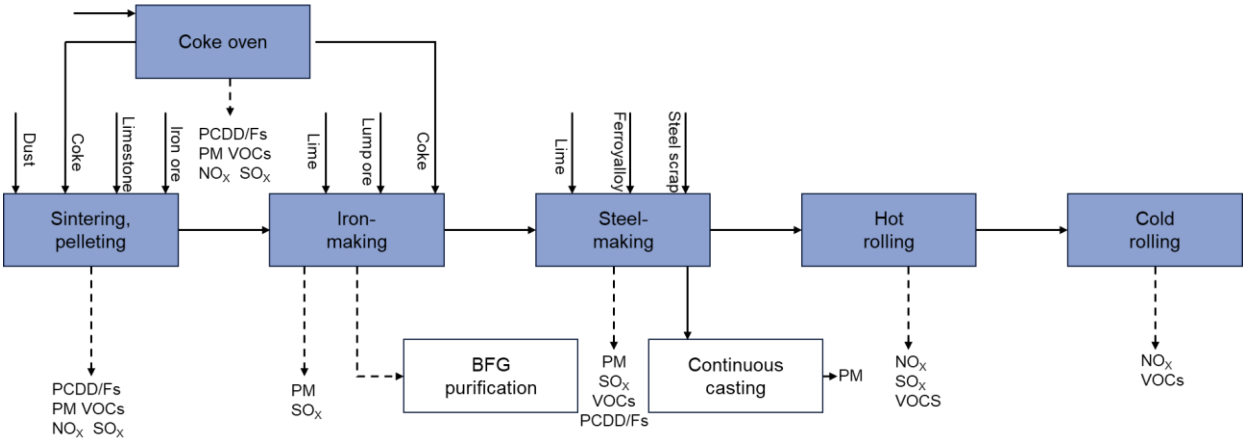


Figure 24 Elements of classical steel production in the blast furnace route through the reduction with coke and major air pollutants by processing step. The grey shaded part of the production process would become obsolete in case of direct reduction with green hydrogen (Wu et al. 2015).

Hence, in order to provide an outlook on the effect of replacing the blast furnace route of steel production on further air pollutants the replaced processing steps and associated emissions have to be compared to the additional processing steps in the direct reduction route. In the following, this is done in a qualitative and a quantitative manner. Therefore, we first list the different processing steps and associated air pollutants. In a second step, we quantify the level of pollutants and provide a direct comparison as far as data are available.

Coke ovens used in the production of coke for steel manufacturing are significant sources of air pollutants. During the coking process, volatile components of the coal are released, and they can become pollutants if not properly captured, treated, or combusted. Major air pollutants are (Remus et al. 2013; Liberti et al. 2006):

- Particulate Matter (PM): Can originate from the coke itself, as well as from combustion processes. PM from coking process may also include heavy metals.
- Sulphur Compounds: These include sulphur dioxide (SO_2) and hydrogen sulfide (H_2S). Sulphur dioxide can cause respiratory problems and contributes to the formation of acid rain. Hydrogen sulfide has a distinctive rotten egg smell and can be harmful to human health at high concentrations.
- Nitrogen Oxides (NOx): These are formed when nitrogen in the coal or air reacts with oxygen during the coking process. NOx can lead to respiratory problems, smog formation, and acid rain.
- Volatile Organic Compounds (VOCs): They can include a wide variety of individual compounds, many of which are toxic. For example, aromatic compounds such as Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) but also methane and longer chain hydrocarbons.
- Polycyclic Aromatic Hydrocarbons (PAHs): These are a class of chemicals that occur naturally in coal, crude oil, and gasoline. They are of concern because many PAHs are carcinogenic.

To reduce these emissions, modern coke ovens are equipped with pollution control equipment like electrostatic precipitators, scrubbers, and flares. The captured volatile compounds can also be recovered and used as valuable by-products, such as tar, light oil, and sulphur. Proper operation and maintenance of these systems are crucial to minimize emissions and their impacts on the environment and public health.

The subsequent steel manufacturing in blast furnaces produces a range of air pollutants, which result from the combustion of coke and coal, the reduction of iron ore, and various associated processes. The major air pollutants from blast furnace-based steel production are comparable to those of the coking process (Liberti et al. 2006; Remus et al. 2013):

- Particulate Matter (PM): This includes both fine and coarse particles that arise from the raw materials, as well as from combustion processes. This may include heavy metals like zinc, lead, and cadmium released during the reduction process and from impurities in raw materials.
- Nitrogen Oxides (NO_x): Formed during high-temperature combustion in the blast furnace.
- Sulphur Dioxide (SO_2): Emitted during the combustion of sulphur-containing coke and coal.
- Volatile Organic Compounds (VOCs): These are emitted during the coking process but also during the handling of coke and coal in the blast furnace.
- Hydrogen Chloride (HCl) and Hydrogen Fluoride (HF): These can be emitted in trace amounts from certain processes in the blast furnace, especially if the raw materials contain chlorides or fluorides.

Blast furnace steel plants are equipped with a range of pollution control technologies to capture and reduce these emissions, such as fabric filters, ESPs and scrubbers.

The air pollutants from the direct reduction of steel using green hydrogen in shaft furnaces are difficult to describe precisely, as this process does only exist at a demonstration level but not yet at industrial scale. Due to the absence of coke, the pollution levels are definitely lower as compared to the blast furnace process (Wu et al. 2015). Pollutants may include:

- Particulate Matter: Dust and particulates might be released from the handling of raw materials and from the furnace itself.
- Depending on the purity of the hydrogen and the iron ore, other gases might be produced. For example, sulfur impurities can lead to the formation of hydrogen sulfide (H_2S), and other volatile impurities in the iron ore might be released during the reduction process.
- Trace Emissions: Even if hydrogen is the primary reducing agent, there might be traces of other gases used or formed due to the presence of impurities in the feedstock or due to minor leaks and inefficiencies in the system.

Pollutants from the subsequent smelting in an Electric Arc Furnace (EAF) are expected to be identical to those of steel scrap smelting in EAFs (Remus et al. 2013; Mohiuddin et al. 2014). These include:

- Particulate Matter (PM): Particulate matter is the major pollutant emitted from EAFs and consists of dust and metal oxides and may include heavy metals depending on the purity of the iron sponges.
- Nitrogen Oxides (NOx): These are formed due to the high-temperature process conditions in the EAF, particularly from the high-energy arcs and the nitrogen in the air.
- Further classical pollutants such as SOx, VOCs, or PCBs may occur if contaminated scrap is smelted. However, in case of smelting pure iron sponges, these pollutants are not expected to occur. In case of scrap smelting, also metallic fumes, especially those of zinc and lead, can be volatilized. This is especially true if the scrap contains galvanized steel or other coated materials.

To reduce these emissions, modern EAFs are equipped with air pollution control devices, such as baghouses and fabric filter systems, electrostatic precipitators, and wet scrubbers.

A subsequent comparison of both alternatives (**Table *6***) clearly demonstrates the positive side-effects on air pollutants when regarding the substitution of coke ovens and blast furnaces with direct reduction of iron ore using green hydrogen and final smelting in EAFs. The emissions of the coke oven are calculated given that around 0.6 to 0.8 tons of coke are needed to produce 1 ton of steel in a blast furnace. As clearly quantified in **Table *6***, especially the blast furnace process based on a reduction with coke produces significant amounts of particulate matter and the processing of coke and hard coal in conventional steel making also causes emission of SO_x and VOCs which would be avoided in case of direct reduction and smelting in EAFs.

Table 6: Direct comparison of emission levels via the conventional blast furnace route and the direct reduction with hydrogen and subsequent smelting in an EAF. Data originate from own calculations and conversion to the reference of 1 ton of steel based on various literature data (Remus et al. 2013; Wu et al. 2015; Liberti et al. 2006).

Route	Processing step	Major pollutants and emission levels per ton of steel produced
Conventional	Coke oven	0.1-1.2 kg PM 0.6-3.2 kg SOx 0.1-0.4 kg NOx 0.6-3.2 kg VOCs
	Blast furnace	around 5 kg PM 0.5-2 kg SOx 0.5-5 kg NOx
Direct Reduction	Direct reduction (shaft furnace)	no data available yet
	Smelting in electric arc furnace	0.5-2.5 kg PM 0.1-0.5 kg SOx 0.2-1 kg NOx

3.2 Cement industries

The main air pollutants from cement production are dust (pm) and pollutants from fuel combustion such as NO_x or SO_x. BATs for emission abatement of dust (beside primary measures such as cyclone preheaters and enclosing of process equipment) are classical approaches such as fabric filters (bag filters) and electrostatic precipitators (ESPs). NOx emissions are influenced by different parameters such as the type of fuel, the type of combustion, the combustion air-ratio and the flame temperature. Thus, to reduce NO_x emissions, several primary measures can be implemented as a first step, while additional secondary end-of-pipe measures such as Selective Non-Catalytic Reduction (SNCR) or Selective Catalytic Reduction (SCR) are necessary to meet the emission levels summarized in the table below (Schorcht et al. 2013). The main measure to reduce SO_2 emissions is the use of sulphur free fuel or fuel with low sulphur content. In case low sulphur contents in combustion fuels cannot be guaranteed, e.g. due to the use of substitute fuels form hydrocarbon waste streams, wet scrubbing is the BAT for desulphurization. In wet scrubbing technologies, the flue gas is first dedusted and subsequently scrubbed with a solution of alkali compounds. SO_2 reacts with this absorbent to form different by-products, which can be upgraded as sulphuric acid, sulphur, gypsum or scrubbing agent. Based on these briefly described technologies, the emission values listed in **Table *7*** can be achieved according to the EU BREF document about cement and lime production (Schorcht et al. 2013).

Table 7: State-of-the-art emission levels from cement clinker production (Schorcht et al. 2013).

Pollutant	Current abatement technology (BAT)	Emission level
PM	Primary measures plus fabric bag filters or ESPs	10-20 mg/m^3 as daily average
NO_x	Selective Non-Catalytic Reduction (SNCR) or Selective Catalytic Reduction (SCR)	200 to 450 mg/m^3 as daily average (at 10% O_2)
SO_x	Wet scrubbing	50-400 mg/m^3 as daily average

In section 2.2.2, two different approaches for reducing carbon emissions from cement production were described. The substitution of calcium oxide (CaO) through the admixture of further minerals, such as dicalcium silicate (Ca_2SiO_4) with less bound CO_2 could reduce the emissions by about 20-30%. The effect of adding additional minerals for reducing the carbon footprint of clinker production is not expected to have any significant effects on the state-of-the-art pollution levels listed in **Table *7***.

The second approach was based on end-of-pipe removal of CO_2 (carbon capture technology), which is most relevant to achieve significant carbon emission reduction of up to 90%. Calcium looping technology (CLT) is an emerging carbon capture and storage (CCS) technology, especially for CO_2 capture from industrial sources like cement production. While the technology has been described in section 2.2.2, here we focus on the effect of CLT on further air pollutants. As CLT is based on absorption of CO_2 with a lime-based (CaO) liquid sorbent, it is comparable to scrubbing systems in secondary treatment of air pollutants and is therefore expected to have positive effects on the reduction of further air pollutants. Dust, especially small particles such as $PM_{2.5, that}$ might pass common abatement technologies (e.g., bag filters) are expected to be efficiently removed through the liquid sorbent of the CLT system. While the primary focus of the calcium looping process is CO_2 capture, the nature of the sorbent and the process conditions can have some effects on SO_x (Sulphur oxides) and NO_x (nitrogen oxides) emissions. Specifically, calcium can react with SO_2 to form calcium sulfate ($CaSO_4$), thereby potentially reducing SO_x emissions. As for NO_x emissions, these are largely a function of combustion conditions. The introduction of an additional combustion step (in the calciner) might change NO_x emissions, and this would depend on the specific design and operating conditions of the reactor.

In summary, while calcium looping primarily targets CO_2 emissions in cement production, its impact on other pollutants depends on the specifics of the system design, operation, and the accompanying pollution control measures. Proper design and operation can minimize the release of additional pollutants (such as NO_x), and in some cases, co-benefits in terms of reduced emissions of certain pollutants such as SO_x and PM are expected. As CLT technology has not yet been applied in large-scale industrial cement plants, it is difficult to precisely quantify these effects on further air pollutants.

3.3 Oil refineries

Based on the previous considerations, three major sources of air pollution can be defined within a crude oil refinery.

- Combustion of fossil fuels for heat generation
- Steam reforming for the use of hydrogen for down-streaming processes
- Separation and storage of (by)-products from the hydrocarbons.

As discussed before, mainly the replacement of steam reforming by electrolytic hydrogen production is expected to be realized in the step towards more carbon neutrality of oil refineries.

Therefore, emission reduction potentials are mainly based on the substitution of air emissions values from steam reforming. As an electrolyser will not directly cause any air pollution, a full reduction of emissions from steam reforming could be assumed. Nonetheless, it has to be considered that both the renewable energy provisions, e.g., through photovoltaics of wind energy, as well as the transportation of hydrogen in case of not being produced at the refinery location will cause further emission. As this is not the focus of this report, we limit our focus on the direct emissions from steam reforming.

Figure 25 summarizes all air pollutants and emission values of a steam reforming plant.

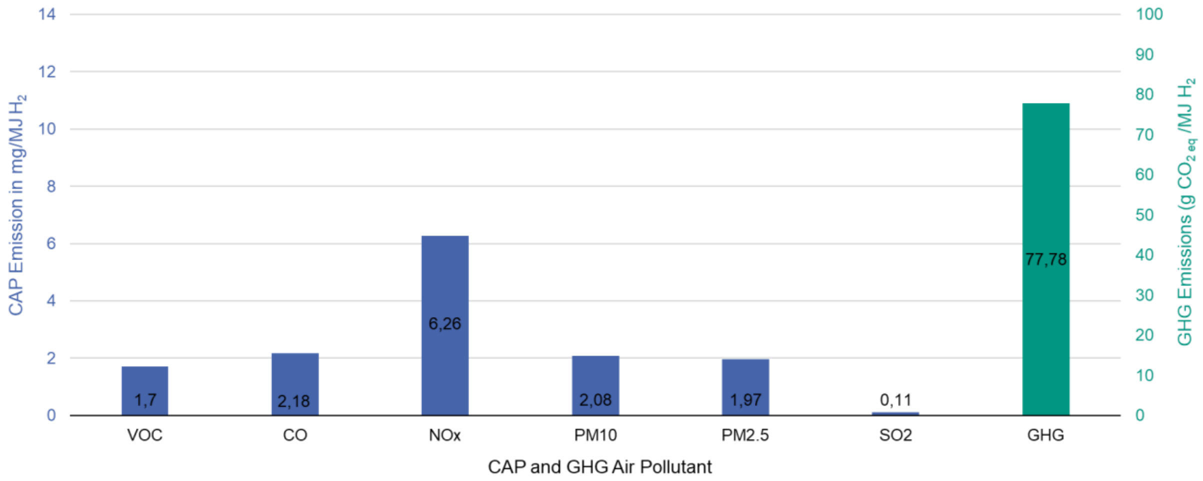


Figure 25: GHG emissions and CAP emissions associated with hydrogen production by steam reforming (Sun et al. 2019)

In summary, the impacts of decarbonisation can be addressed as follows:

- **Reduced Greenhouse Gas Emissions:** The most direct and significant consequence of decarbonization in the refinery sector is the reduction of greenhouse gas emissions, primarily carbon dioxide (CO_2) emissions. Refineries are major sources of CO_2 emissions due to the energy-intensive nature of their operations, particularly in the processing of crude oil. Decarbonization efforts can involve adopting cleaner technologies, such as renewable energy sources and carbon capture and storage (CCS) systems, to lower these emissions.
- **Energy Transition and Technological Innovation:** Decarbonization drives the adoption of cleaner and more efficient technologies in the refinery sector, leading to increased innovation. This transition can stimulate research and development in

renewable energy, battery technologies, hydrogen production, and carbon capture, fostering economic growth and job creation in these fields.

- **Supply Chain and Market Shifts:** As the demand for fossil fuels declines in favor of cleaner energy sources, there will be shifts in the supply chain and market dynamics. Refineries may need to adjust their operations to produce alternative fuels like biofuels, synthetic fuels, or hydrogen, which can have ripple effects throughout the energy sector.
- **Resilience and Risk Mitigation:** Decarbonization can enhance the resilience of the refinery sector against potential future carbon pricing mechanisms and regulatory changes aimed at reducing emissions. By diversifying their energy sources and reducing their carbon footprint, refineries can mitigate financial and regulatory risks.
- **Local Air Quality Improvement:** Traditional refining processes emit not only CO_2 but also other pollutants that can harm local air quality and human health. Decarbonization measures, such as improved emission controls and cleaner technologies, can lead to better air quality in the vicinity of refineries.

The specific impact of decarbonization on other air pollutants can be summed up as follows:

1. **Particulate Matter (PM) and Sulphur Dioxide (SO_2):** While the main focus of decarbonization is on reducing CO_2 emissions, it can also lead to reductions in particulate matter and sulphur dioxide emissions. Cleaner technologies and improved combustion processes associated with decarbonization can result in fewer emissions of these harmful pollutants, leading to improved air quality and human health around refineries.

2. **Nitrogen Oxides (NOx):** Depending on the specific technologies adopted for decarbonization, there could be mixed effects on nitrogen oxide emissions. Some advanced combustion processes and emission control technologies might reduce NOx emissions, while others could lead to increased NOx emissions. Balancing these effects will be important to ensure overall air quality benefits.

3. **Volatile Organic Compounds (VOCs):** Decarbonization may involve the use of cleaner fuels or alternative feedstocks in refineries, potentially leading to reductions in volatile organic compound emissions. VOCs can contribute to the formation of ground-level ozone and smog, so any decrease in their emissions can positively impact air quality.

4. **Air Quality Improvement:** Overall, the adoption of cleaner technologies and energy sources as part of decarbonization efforts can lead to improved local air quality around refineries, with reductions in various pollutants contributing to better health outcomes for nearby communities.

3.4 Air pollutant reduction in the glass production

Based on average CO_2 emission values for the German glass industry, the next chapter identifies CO_2 reduction potentials of some selected decarbonization techniques. Due to the high share of energy-related CO_2 emissions, that take up to 75 %, the most promising option to achieve a decarbonized glass industry is the substitution of fossil fuels for combustion. Especially electrical melting and hydrogen combustion can make a big difference here. And even though they are technical challenging, there are various heat recovery techniques that can be applied for CO_2 reduction, also.

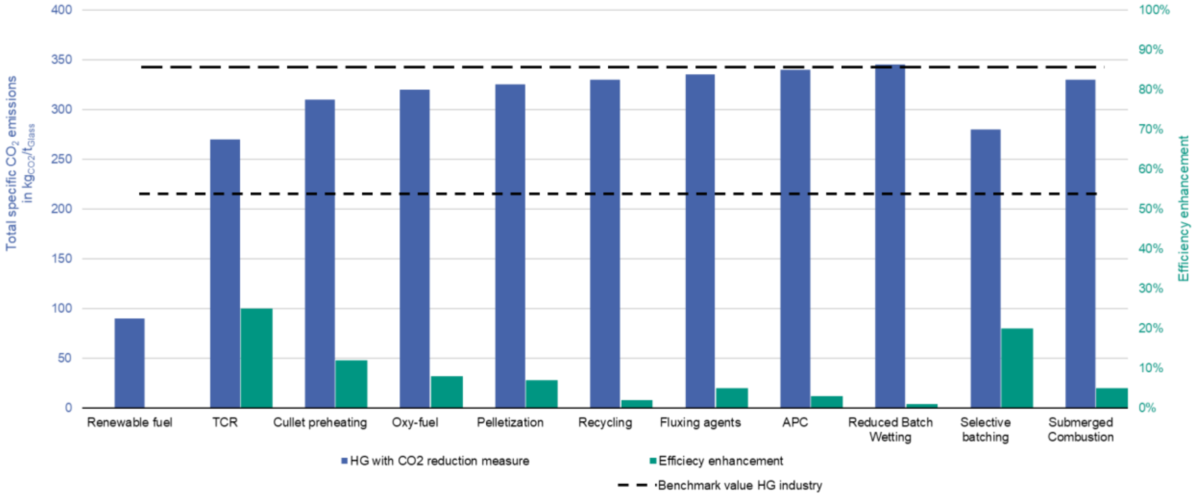


Figure 26: CO_2 efficiency enhancements (Zier et al. 2021, p. 23)

Except for cullet preheating, all enhancement assumptions shown in Figure 26 above are identical both container and flat glass production. A high cullet share is only common in the container glass industry and that's why cullet preheating cannot be applied for flat glass production correspondingly.

It becomes clear, that the defined benchmark values can be undercut significantly by using renewable energy sources instead of fossil fuels and only by that. All the other techniques alone will not achieve a sufficient reduction in CO_2 emission but can of course make a difference when used in combination. As mentioned before, TCR – techno-chemical heat recovery can be the second-best way when it comes to pollution reduction. Next to CO_2, all other emissions which occur due to the use of nonrenewable sources for heat production are going to reduce that way and have to be taken into account.

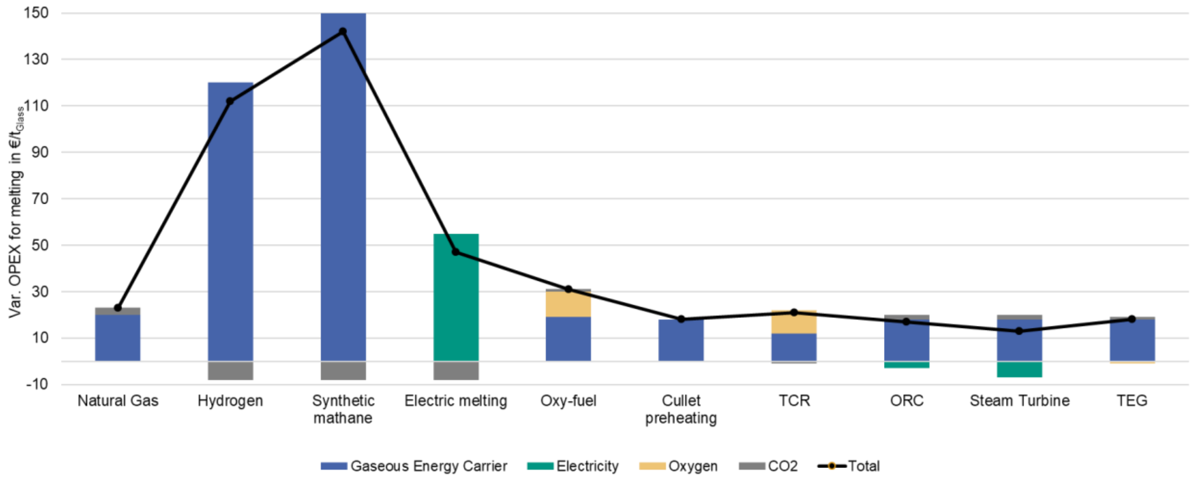


Figure 27: Variable OPEX (Zier et al. 2021, p. 23)

As part of the total costs for an ownership, variable OPEX (operational expenditures) expresses the actual costs associated with operating a machine or a technique. (Definition: OPEX 2021) As the technical and environmental progress is strongly linked to economic considerations, the variable OPEX is supposed to be an important indicator for future development. Among the previous fuel substitution options, electric melting by submerged electrodes has the greatest potential due to its efficiency. Nowadays electric melting furnaces are limited in size and is uncertain to what extent they can become increased. Therefore, hybrid melting concepts like combinations of electric melting and hydrogen combustion might be a trendsetting way of improvement. (Zier et al. 2021)

Influence on emission reduction by using waste glass in the production of cement and concrete:

In the glass manufacturing process, emissions arise primarily from the decarbonisation of carbonate-based raw materials, notably sodium carbonate (Na_2CO_3), limestone ($CaCO_3$), and dolomite ($CaMg(CO_3)_2$). These are termed as 'process emissions'. One strategic approach to curtail these emissions is to diminish the inclusion of virgin raw materials in the mix and amplify the proportion of 'cullet', or recycled glass. The utilization of cullet proves pivotal for the glass industry. Not only does it decrease the energy prerequisite for melting, but it also significantly cuts back on heat emissions. Various recycling methodologies that accentuate these benefits are discussed in more detail in chapter 2.4.2.

For a comprehensive breakdown of air emissions associated with the glass manufacturing process, refer to Table 8, with data primarily sourced from German research and European manufacturers.

Table 8: Ecoinvent data for air emissions in the glass manufacturing for white packaging glass (Hischier 2007).

Output Air emission	in kg
Carbon monoxide, fossil	7.00E-06
Carbon dioxide, fossil	3.13E-01
Nitrogen oxides	8.69E-04
Sulphur oxides	7.41E-04
Particulates, > 10µm	8.21E-06
Particulates, > 2.5 µm	5.20E-07
Particulates, < 2.5 µm	1.29E-06
Hydrogen chloride	1.69E-05
Hydrogen fluoride	5.21E-06
Ammonia	2.62E-08
Dinitrogen monoxide	4.34E-07
Methane, fossil	8.94E-08
Benzene	7.07E-08
Dioxins	7.85E-17
Formaldehyde	3.02E-07
Benzo(a)pyrene	1.01E-11
NMVOC	3.26E-06
Hydrocarbons	1.19E-05
Cadmium	1.41E-08
Arsenic	1.41E-08
Cobalt	1.41E-08
Nickel	1.41E-08
Selenium	1.54E-06
Anitmony	1.41E-08
Lead	1.62E-07
Chromium	1.41E-08
Copper	1.41E-08
Manganese	1.41E-08

In summary, the impacts of decarbonisation can be addressed as follows:

- **Lower Carbon Footprint:** Decarbonizing glass production involves reducing the energy consumption and emissions associated with the melting and forming of glass. This can lead to a significant reduction in the carbon footprint of the glass industry, as it is energy-intensive and relies heavily on fossil fuels.
- **Energy Efficiency and Conservation:** Implementing energy-efficient technologies and processes in glass production can lead to reduced energy consumption and operating costs. This can drive innovation and stimulate the adoption of advanced materials and techniques.
- **Resource Conservation:** Decarbonization efforts often encourage the efficient use of raw materials and resources. In the glass industry, this could involve the development of new recycling methods, reduced material waste, and improved resource management.
- **Product Innovation:** Decarbonization can spur the development of new types of glass products, such as energy-efficient windows, solar panels, and lightweight glass

materials for transportation, which can contribute to sustainable urban development and renewable energy adoption.

- **Regulatory Compliance and Reputation:** As environmental regulations tighten and consumer preferences shift towards sustainable products, glass producers that prioritize decarbonization can enhance their reputation, meet compliance requirements, and tap into growing markets for eco-friendly products.
- **Job Creation and Economic Growth:** The shift toward cleaner and more sustainable glass production methods can drive job creation in research, development, engineering, and manufacturing, contributing to economic growth in the sector.

The specific impact of decarbonization on other air pollutants can be summed up as follows:

1. **Particulate Matter (PM):** The adoption of energy-efficient and cleaner technologies in glass production can lead to reduced particulate matter emissions. This is particularly relevant in processes like glass melting, where the combustion of fossil fuels can release particulates into the air.

2. **Sulphur Dioxide (SO_2) and Nitrogen Oxides (NOx):** Similar to refineries, the use of cleaner energy sources and improved combustion processes in the glass production sector can result in decreased emissions of sulphur dioxide and nitrogen oxides, contributing to better air quality.

3. **Carbon Monoxide (CO):** As decarbonization efforts encourage the adoption of cleaner and more efficient combustion processes, the emission of carbon monoxide, a byproduct of incomplete combustion, can be reduced. This would contribute to improved air quality and reduced health risks.

4. **Hazardous Air Pollutants (HAPs):** Glass production processes can release hazardous air pollutants, such as heavy metals and volatile organic compounds. Decarbonization measures, including the adoption of cleaner technologies and emission controls, can lead to lower emissions of these harmful substances, thereby reducing potential risks to human health and the environment.

5. **Air Quality Benefits:** The overall impact of decarbonization in the glass production sector would likely be positive for air quality, as cleaner technologies and practices reduce the emission of multiple pollutants, leading to healthier living conditions for nearby communities.

4 Conclusions

In conclusion, decarbonization efforts of industrial sectors hold significant potential to bring about positive effects on air pollution. While the primary aim of decarbonization is to reduce greenhouse gas emissions and combat climate change, it also yields a range of consequential effects on other air pollutants. This is partly due to the substitution and replacement of emission intensive conventional processes and due to secondary measures for CO_2 removal via absorption during end-of-pipe treatment (CCS or CCU) which is expected to also reduce further pollutants such as PM and SO_x. In this study, we analyzed the most important industrial emitters of CO_2 which are the steel industry, the cement industry and oil refineries and as a representative of energy intensive mineral processing, we further took into account the glass production. The effect of decarbonization technologies and strategies on air pollutants of course strongly depends on the regarded industries and technologies which is summarized for each sector in the following paragraphs.

In the case of steel industries, the most relevant decarbonization strategy is the replacement of the reduction of iron ore with coke in blast furnaces with direct reduction of iron ore using green hydrogen and subsequent smelting in electric arc furnaces. Especially the replacement of the coking oven and the avoidance of coke and coal in the furnace process will have positive effects regarding the reduction of all major air pollutants including PM, NO_x, SO_x and VOCs. However, both the electrolysis for hydrogen production and the electric arc furnace for smelting of sponge iron from the direct reduction will require large amounts of electricity. Indirect emission through energy provision were not the scope of this study, however, it is self-explaining that the applied electricity has to originate from renewable resources with respective low emission to achieve the described effects regarding both GHG emissions and further air pollutants.

In the case of cement production, carbon capture through the calcium looping technology (CLT) is the most promising strategy to achieve significant reduction of CO_2 emissions. This absorption process using a lime-based (CaO) sorbent does not only reduce carbon emission by up to 90% but also is expected to have a positive effect on further pollutants, particularly leading to a reduction of PM and SO_x emission. The wet absorption is expected to lead to an additional removal of small sized PM and calcium can react with SO_2 to form calcium sulfate ($CaSO_4$), thereby reducing SO_x emissions.

In the case of glass production, the adoption of cleaner technologies and energy-efficient practices can result in reduced emissions of particulate matter, sulfur dioxide, nitrogen oxides, carbon monoxide, and hazardous air pollutants. These changes not only contribute to improved air quality and reduced health risks but also stimulate innovations in product development and resource conservation.

Similarly, in the refinery sector, the transition to cleaner energy sources and advanced technologies can lead to decreased emissions of particulate matter, sulfur dioxide, nitrogen oxides, volatile organic compounds, and other pollutants associated with traditional refining processes. This shift improves local air quality, enhances public health, and strengthens the sector's resilience against evolving regulatory frameworks.

In summary, the effects of decarbonization on other air pollutants in the four sectors considered are multifaceted and interconnected. Decarbonization efforts, primarily aimed at reducing greenhouse gas emissions, can inadvertently lead to a cascade of positive impacts on various air pollutants.

However, the specific outcomes on air pollutants will depend on the strategies chosen for decarbonization, technological advancements, and regional factors. As these sectors transition to more sustainable practices, the overall trajectory points toward cleaner operations, reduced pollution, and a healthier environment for communities living near these facilities. Effective management, careful planning, and comprehensive emission control measures are essential to maximize the positive impact of decarbonization on air quality and promote a sustainable future.

In conclusion, decarbonization efforts in the four considered sectors have the potential to trigger a positive chain reaction, resulting in reduced emissions of various air pollutants beyond just greenhouse gases. By embracing cleaner technologies and practices, these sectors can contribute to healthier environments, sustainable economic growth, and a more resilient and responsible industrial landscape.

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