



## Declaration

I hereby declare that I completed this thesis without any improper assistance from a third party and without using any aids other than those cited. All ideas, data, and information derived directly or indirectly from other sources are appropriately acknowledged and referenced.

In the selection and use of materials and in the preparation of this manuscript, I received academic support from:

- Prof. Dr. Gero Frisch, TU Bergakademie Freiberg
- Dipl.-Ing. Julien Göthel and his team at Rouge H2 Engineering AG.

Artificial intelligence (AI) tools were used solely as supportive research and writing aids and did not replace my independent scientific judgment, analysis, process modeling, interpretation of results, or conclusions. ScienceOS was used exclusively for the initial screening and identification of relevant scientific literature during the literature review process. ChatGPT (OpenAI) was used exclusively for language editing, text review, and formatting to improve the clarity of the manuscript.

This thesis has not previously been submitted or published, in whole or in part, in the same or a substantially similar form in Germany or abroad.

Date: 13.08.2026

Gunel Rahimli

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## List of Abbreviations

|                   |                                                     |
|-------------------|-----------------------------------------------------|
| AACE              | Association for the Advancement of Cost Engineering |
| BF                | Blast Furnace                                       |
| BOF               | Basic Oxygen Furnace                                |
| BFG               | Blast Furnace Gas                                   |
| CaL               | Calcium Looping                                     |
| CAPEX             | Capital Expenditure                                 |
| CCS               | Carbon Capture and Storage                          |
| CCU               | Carbon Capture and Utilization                      |
| CCUS              | Carbon Capture, Utilization and Storage             |
| CL                | Chemical Looping                                    |
| CLC               | Chemical Looping Combustion                         |
| CLH               | Chemical Looping Hydrogen                           |
| DRI-EAF           | Direct Reduced Iron - Electric Arc Furnace          |
| EAF               | Electric Arc Furnace                                |
| EOR               | Enhanced Oil Recovery                               |
| EU ETS            | European Union Emissions Trading System             |
| FCI               | Fixed Capital Investment                            |
| GHG               | Greenhouse Gas                                      |
| GOD               | Gas Oxidation Degree                                |
| IEA               | International Energy Agency                         |
| LCOC              | Levelized Cost of CO <sub>2</sub> Capture           |
| LCOP              | Levelized Cost of Product                           |
| LHV               | Lower Heating Value                                 |
| MDEA              | Methyldiethanolamine                                |
| MEA               | Monoethanolamine                                    |
| MOF               | Metal-Organic Framework                             |
| NETL              | National Energy Technology Laboratory               |
| NPV               | Net Present Value                                   |
| OC                | Oxygen Carrier                                      |
| OPEX              | Operating Expenditure                               |
| PR-BM             | Peng-Robinson Boston-Mathias Equation of State      |
| PSA               | Pressure Swing Adsorption                           |
| QGESS             | Quality Guidelines for Energy System Studies        |
| RG-H <sub>2</sub> | Rouge H <sub>2</sub> Engineering AG                 |
| TEA               | Techno-Economic Assessment                          |
| TIC               | Total Installed Cost                                |
| TRL               | Technology Readiness Level                          |
| TSA               | Temperature Swing Adsorption                        |
| VSA               | Vacuum Swing Adsorption                             |
| WGS               | Water-Gas Shift                                     |

## Abstract

Blast furnace gas (BFG) is the largest CO<sub>2</sub> emission source in an integrated steelwork. However, its low CO<sub>2</sub> concentration makes conventional capture economically challenging. This thesis investigates an integrated CO<sub>2</sub> capture concept that first concentrates BFG through an iron-oxide chemical looping process (H2Loop) and subsequently captures CO<sub>2</sub> using two alternative separation routes, cryogenic distillation and calcium looping. A 1,000 Nm<sup>3</sup>/h BFG base case is modelled in Aspen Plus. In the chemical loop, magnetite is reduced by the CO and H<sub>2</sub> content of BFG, while steam re-oxidation produces hydrogen as a by-product and generates a CO<sub>2</sub>-enriched off-gas containing approximately 40 mol% CO<sub>2</sub>.

Due to the absence of a solid-phase thermodynamic model capable of reproducing the non-stoichiometric wüstite equilibrium, the process performance is evaluated within two limiting cases. The adopted flowsheet, using stoichiometric FeO in the reduction step and wüstite in the oxidation step, represents an optimistic upper bound, while a phase-consistent wüstite-based case provides a conservative lower bound. Both CO<sub>2</sub> separation routes are assessed using a common techno-economic framework based on factorial costing and discounted cash flow analysis.

For the upper-bound case, cryogenic distillation produces a ≥99.9 mol% liquid CO<sub>2</sub> product with a maximum single-pass recovery of 95 %. This value represents the vapour–liquid equilibrium limit of the column model; as the simulated overhead condition lies within the CO<sub>2</sub> solid-formation region, the recovery is conditional on frost-free operation being secured by an anti-sublimation or defrost section, which is not included in the present cost estimate. The resulting levelized cost of CO<sub>2</sub> (LCOP) is approximately 351 EUR/t CO<sub>2</sub> for the cryogenic route, compared with 393 EUR/t CO<sub>2</sub> for calcium looping. The higher cost of calcium looping is mainly attributed to the electrical energy demand of the calcination step. When accounting for all carbon leaving the process as unconverted CO, the overall plant-level carbon capture reaches approximately 85 % for cryogenic separation and 93 % for calcium looping. Across the bounded performance range, the main conclusions remain unchanged: the concentrated CO<sub>2</sub> feed provides a significant advantage for cryogenic separation, while electrically driven calcination remains the dominant economic penalty for calcium looping. Future work should focus on phase-consistent simulation of the iron-oxide loop, frost-safe cryogenic column design, and evaluation of varying BFG compositions.

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# 1 Introduction

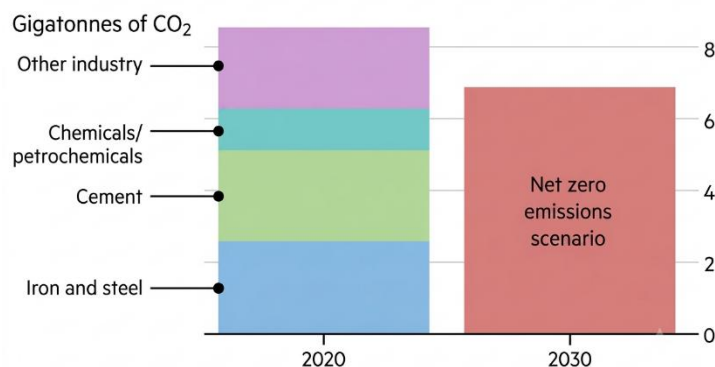
Anthropogenic greenhouse gas (GHG) emissions have driven the approximately 1.1 °C increase in global mean surface temperature since the pre-industrial period (1850-1900). Carbon dioxide (CO<sub>2</sub>) is the dominant contributor because of its long atmospheric lifetime and high efficiency in trapping outgoing long-wave radiation, creating a net energy imbalance in which more heat is retained. Global temperature is approximately linearly related (transient climate response to cumulative emissions, TCRE) to cumulative CO<sub>2</sub> emissions, which also means that stabilizing temperatures requires achieving net-zero CO<sub>2</sub> emissions. [2] This physical effect supports the temperature goals of the Paris Agreement, which emphasize that limiting warming to 1.5°C is a critical threshold for 'planetary health'. While the Paris Agreement originally noted with concern that 2030 emissions were projected at 55 gigatonnes (GtCO<sub>2</sub>e), the UNEP Emissions Gap Report 2025 reveals that global emissions reached a record 57.7 gigatonnes (GtCO<sub>2</sub>equivalent) in 2024, which represents a 2.3% year-on-year increase. [3], [4], [5]

To compare to the CO<sub>2</sub>-equivalent (CO<sub>2</sub>e) metrics, which consider total global greenhouse gas emissions, energy-related CO<sub>2</sub> emissions reached 33.904 Gt in 2020, which considers only carbon dioxide emissions from energy production and fuel combustion. [1] A sectoral breakdown of the 2020 data shows that electricity and heat were the largest emitting sector, with emissions reaching 13.514 Gt. The industry emerged as the second most dominant source of emissions at 8.478 Gt, which also represents approximately 25% of global emissions. [1]

Within the industrial sector, iron and steel production was the largest sub-sector emitter at 2.349 Gt of CO<sub>2</sub>, which is also shown in **Figure 1.1**, accounting for 27.7% of industrial emissions and 6.93% of the global total. Cement production closely followed with emissions of 2.339 Gt, positioning it as the second most emitting industrial sub-sector. By 2024, global energy-related emissions reached a record 37.8 Gt which is reflecting a total increase of 3.896 Gt since the 2020 baseline based on IEA statistics. CO<sub>2</sub> emissions from fuel combustion in the power sector grew by approximately 8.04%, equivalent to 1.086 Gt relative to 2020, reaching 14.6 Gt in 2024 due to record heatwaves and rising cooling demand. Simultaneously, the total industrial emissions grew by roughly 7.34%, reaching 9.1 Gt. While the total industrial footprint increased, the IEA (2025) highlights a structural shift as industrial process emissions declined by 2.3% (62 Mt) in 2024 alone. This decoupling is attributed to the rapid expansion of solar, wind and electric vehicles, alongside efficiency gains in heavy manufacturing which are beginning to limit the carbon intensity of global economic growth. [1], [6]

However, this transition creates a material paradox. While the shift towards a low-carbon economy aims to reduce greenhouse gas emissions, it simultaneously drives a substantial increase in steel demand due to the rapid expansion of industrial infrastructure, electric vehicles, and urbanization,

## Emissions from Hard-to-Abate Sectors

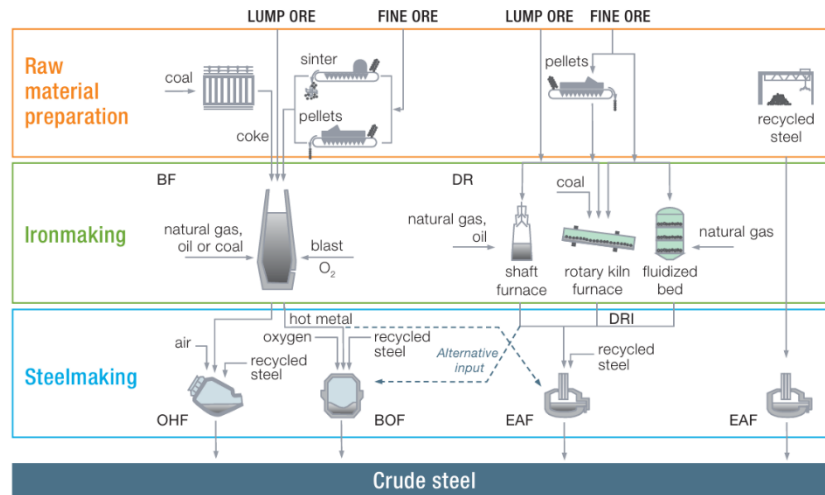


**Figure 1.1** Global hard-to-abate sector CO<sub>2</sub> emissions and net-zero pathway. [1]

with steel remaining essential for industrial machinery, reinforced concrete, transformers, wind turbine towers, and solar mounting systems. [7]

As a result, steel production rose almost tenfold from 189 million tonnes in 1950 to almost 1.885 billion tonnes in 2024 [8]. Currently, steel manufacturing is characterized by high carbon intensity due to its dependence on primary fossil-fuel-based energy and reductants. For every tonne of steel produced in 2024, approximately 2.18 tonnes of CO<sub>2</sub>e (Scopes 1, 2, and 3) were emitted into the atmosphere, which was equivalent to 2.8 Gt of direct emissions. [9]

However, the steelmaking route itself also significantly affects the carbon intensity of the process, as illustrated in **Figure 1.2**. [7]



**Figure 1.2** Overview of integrated and direct-reduction steelmaking routes. [7]

The BF-BOF route represents the conventional and most widely used primary steel production pathway, which relies on virgin iron ore and coal and accounts for roughly 70% of global steel output and nearly 90% of the sector's emissions. [8], [10] In this route, ironmaking occurs in a blast furnace (BF), where iron ore is reduced to pig iron using coke derived from coal. Coke serves both as a fuel, providing the heat required for the process, and as the source of carbon monoxide (CO), the primary reducing agent. The resulting molten pig iron, with a high carbon content of approximately 4-5 wt%, is then transferred to a basic oxygen furnace (BOF). In the BOF, high-purity oxygen is injected into the melt to oxidize excess carbon and impurities, thereby refining the material into crude steel with a significantly lower carbon concentration. The BF-BOF route is considered highly carbon-intensive because it combines unavoidable process emissions from the chemical reduction of iron oxide with substantial combustion emissions from coal and coke use. Average emissions for this route lie in the range of 2.0-2.3 t CO<sub>2</sub> per tonne of crude steel compared with approximately 1.4 CO<sub>2</sub>/t for natural-gas-based Direct Reduced Iron-Electric Arc Furnace (DRI-EAF) and only ~0.3 t CO<sub>2</sub>/t for scrap-based EAF production [11]. In addition to its high process emissions, BF-BOF steelmaking is also extremely energy-intensive, as the production of molten iron and steel requires temperatures exceeding 1 500 °C, and the average specific energy consumption is approximately 19-21 GJ per tonne of crude steel cast. [11]

The dominance of the BF-BOF route is also reflected in the structure of the global ironmaking fleet. According to the World Steel Association, total iron production was 1,437.6 Mt, of which 1,293.5 Mt (90%) was BF pig iron and 144.1 Mt was direct reduced iron. [8]. This output is geographically highly concentrated, with the five largest producers together accounting for more than 80% of global blast-furnace ironmaking, as summarized in the Appendix. [8], [12] Overall, China alone produced 851.7 Mt of pig iron in 2024, followed by India (144.9 Mt), Japan (61.0 Mt), Russia (59.0 Mt) and South Korea (44.1 Mt). In detail, China's post-2000 capacity expansion produced a relatively young global blast furnace fleet with an average age of approximately 13

years in 2019, less than one-third of the typical 40-year operating lifetime of such plants. [11], [12] This creates a major carbon lock-in risk since if these furnaces are operated to the end of their design life under current conditions, the already-installed steel fleet alone could consume up to 21 Gt CO<sub>2</sub>-eq of the remaining carbon budget [13]. Furthermore, the coexistence of state-of-the-art steelmaking facilities, such as those in South Korea, alongside blast furnaces that have operated with little change since the 1950s–1970s highlights the heterogeneity that any decarbonization strategy, including carbon capture from blast furnace gas, should address. [8], [12]

While Chemical Looping (CL) has been researched for decades, its integration into iron and steelmaking has started to gain significant attention by the industry as a strategic and promising pathway for deep decarbonization. [14], [15] The primary target stream for such integration is the Blast Furnace Top Gas (BFTG), which is a complex, nitrogen-diluted mixture typically composed of CO (22–28%), CO<sub>2</sub> (18–25%), H<sub>2</sub> (1–5%), H<sub>2</sub>O, N<sub>2</sub> (45–55%), and other impurities. [15] In conventional combustion-based heat recovery or post-combustion capture systems, the high nitrogen content significantly dilutes the flue gas, which increases the energy demand for CO<sub>2</sub> separation. This dilution effect makes conventional carbon capture technologies, such as amine scrubbing and cryogenic separation, energetically and economically challenging. [16], [17]

CL offers a fundamentally different approach by eliminating direct contact between reduction and oxidation gases. Instead of combusting the gas with air, CL employs a solid oxygen carrier (OC), typically metal oxides (Me<sub>x</sub>O<sub>y</sub>), such as ilmenite (FeTiO<sub>3</sub>), hematite (Fe<sub>2</sub>O<sub>3</sub>), or copper oxide (CuO). In the reduction reactor, the oxygen carrier provides lattice oxygen to oxidize the combustible species (CO and H<sub>2</sub>) present in the blast furnace gas according to the reactions (1.1 and 1.2): [14]



Because oxidation occurs without direct contact with atmospheric nitrogen, the outlet stream from the reduction reactor consists mainly of a highly concentrated CO<sub>2</sub> stream. This CO<sub>2</sub> is significantly more concentrated than that produced in conventional processes, reducing the need for additional downstream separation units. As a result, the inherent separation mechanism greatly reduces the energy penalty typically associated with CO<sub>2</sub> capture.

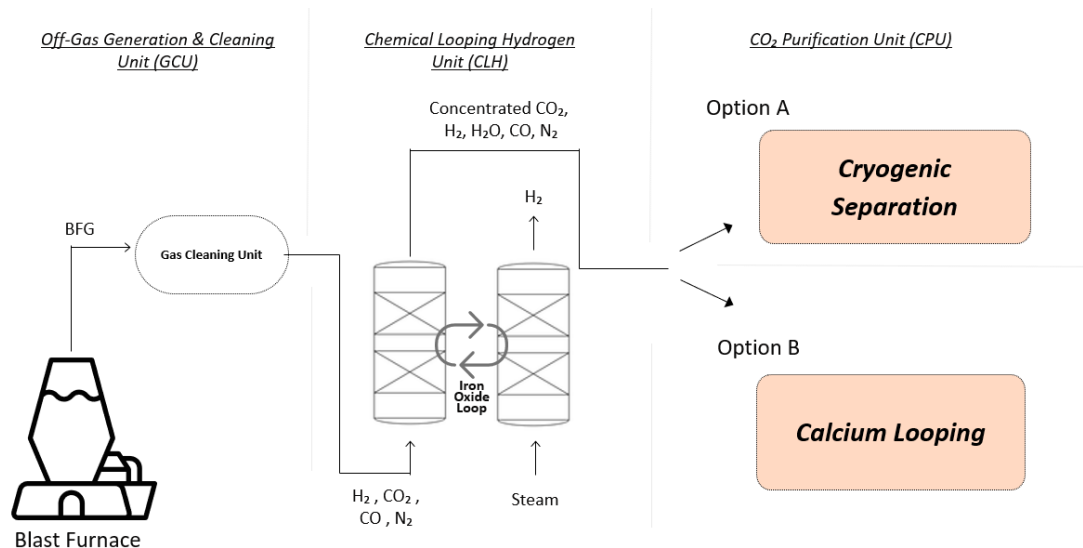
The reduced oxygen carrier is subsequently transferred to the oxidation reactor, where it is re-oxidized by steam according to equation (1.3). This reaction regenerates the oxygen carrier while simultaneously producing hydrogen:



The H2Loop process developed by Rouge H<sub>2</sub> Engineering AG applies this concept specifically to integrated steelworks. Using a thermochemically stabilized iron-oxide oxygen carrier in cyclic fixed-bed reactors, the process converts blast-furnace gas into two valuable products, namely, a concentrated CO<sub>2</sub> stream and hydrogen. Although the chemical-looping front end concentrates the CO<sub>2</sub> in the stream, the resulting concentrated stream must still undergo purification and conditioning into a saleable or storable product, and the choice of that downstream separation technology has not yet been systematically evaluated on a techno-economic basis for the H2Loop context.

The published literature examines the individual components of the process chain in isolation, including amine and hybrid cryogenic-adsorption capture from dilute blast-furnace top gas, the chemical-looping front end itself, and generic techno-economic assessments of cryogenic separation and calcium looping, typically at plant scales that differ substantially from a steelworks slipstream. As a result, the relative technical and economic merits of the principal CO<sub>2</sub> separation

technologies remain uncertain when applied to the concentrated  $\text{CO}_2$  stream generated by chemical looping. This thesis addresses that gap by developing a common modeling framework and performing a harmonized techno-economic comparison of the leading separation technologies. To achieve this, two downstream separation technologies, namely cryogenic distillation and calcium looping, are developed, modeled, and evaluated using a common process design basis. Their technical and economic performance is benchmarked against monoethanolamine (MEA) absorption as an industrial reference technology for post-combustion  $\text{CO}_2$  capture.



**Figure 1.3** Overview of the H2Loop process and evaluated  $\text{CO}_2$  capture routes.

The scope of this work is limited to the process simulation and techno-economic assessment of cryogenic distillation and calcium looping integrated downstream of an iron-based chemical-looping process (**Figure 1.3**). Both technologies are evaluated under an identical design basis corresponding to the treatment of  $1,000 \text{ Nm}^3/\text{h}$  of blast-furnace gas, ensuring that differences in performance arise from the separation technologies rather than from modeling assumptions. The economic assessment includes capital and operating cost estimation, calculation of the levelized cost of  $\text{CO}_2$  (LCOC), sensitivity analysis, plant-scale evaluation, and consideration of potential  $\text{CO}_2$  utilization and hydrogen valorization pathways. Cost estimates are developed using the AACE Class 4 methodology (-30%/+50%) based on a factorial approach and equipment quotations provided by the industrial partner.

The following objectives guide the research:

1. Establish a consistent process design basis, including feed composition, flow rate, operating conditions, and product specifications.
2. Develop steady-state Aspen Plus models of the H2Loop process integrated with cryogenic distillation and calcium looping, and verify them against element and energy balance closure, independent hand calculations and published literature benchmarks. Because no single available solid-phase representation reproduces the non-stoichiometric wüstite equilibrium exactly, process results are reported as upper and lower bounds reflecting the oxygen-carrier phase representation.
3. Evaluate the technical performance of each separation technology in terms of  $\text{CO}_2$  purity, capture efficiency, specific energy consumption and heat-integration potential.
4. Perform a comparative techno-economic assessment, including capital expenditure (CAPEX), operating expenditure (OPEX) and the levelized cost of  $\text{CO}_2$  (LCOC), and benchmark the results against MEA absorption and published literature.

5. Identify the principal technical and economic drivers through sensitivity and plant-scale analyses to determine the most promising technology for industrial implementation.

The remainder of this thesis is organized as follows. Chapter 2 reviews steel industry decarbonization, the fundamentals of iron-based chemical looping, and the current state of CO<sub>2</sub> capture and utilization technologies. Chapter 3 surveys the available CO<sub>2</sub> capture and separation technologies and selects the two candidates evaluated in this study. Chapter 4 presents the methodology, including feed characterization, process modeling in Aspen Plus, model verification and literature benchmarking, and the techno-economic assessment framework. Chapter 5 presents and discusses the results for both processes, covering their technical performance and economic performance through detailed techno-economic analysis, sensitivity studies, plant-scale evaluation, and benchmarking against MEA absorption and published literature. Chapter 6 summarizes the main findings and presents the conclusions. Finally, Chapter 7 identifies opportunities for process optimization and directions for future work.

## 2 Literature review

### 2.1 Blast Furnace Top Gas Emissions

The gas exiting the top of the blast furnace, known as blast furnace gas (BFG) or blast furnace top gas, is the cumulative product of all the chemical reactions that occur as the reducing gas ascends through the burden. Its composition reflects the extent to which the ascending CO has been utilized for iron oxide reduction. In a well-operated blast furnace, approximately 40-50% of the CO entering the burden is converted to CO<sub>2</sub>, while the remainder exits as unreacted CO alongside the large volume of nitrogen introduced with the hot air blast. [18], [19] In detail, BFG is typically produced at a rate of 2.5 - 3.5 tonnes per tonne of liquid steel, corresponding to approximately 1 200 - 2 200 Nm<sup>3</sup> per tonne of hot metal. [20] For a modern large blast furnace producing 6 000 - 12 000 tonnes of hot metal per day, this translates to a continuous gas flow of approximately 300 000 - 1 000 000 Nm<sup>3</sup>/h. [21] This enormous volumetric flow rate makes BFG by far the largest single gas stream at an integrated steelworks, exceeding coke oven gas (COG), typically 50 000 - 80 000 Nm<sup>3</sup>/h and basic oxygen furnace gas (BOFG), approximately 50-100 Nm<sup>3</sup> per tonne of steel produced intermittently by a wide margin. [20], [22]

As iron ores are natural materials, BFG also carries a broad spectrum of trace elements such as zinc and lead, which are problematic because they concentrate in recycled dust streams and can poison downstream catalysts. The typical composition consists of CO, CO<sub>2</sub>, H<sub>2</sub>, and N<sub>2</sub>, along with minor amounts of water vapor, H<sub>2</sub>S, and dust, which are removed in the gas cleaning system. The high nitrogen content is an inherent consequence of using air as the blast oxidant and can only be avoided by switching to oxygen-enriched operation, which fundamentally alters furnace design and operation. [18], [22]

With a CO content of 20-25 vol% and a representative flow of 300,000 Nm<sup>3</sup>/h, BFG contains approximately 60,000-75,000 Nm<sup>3</sup>/h of combustible CO. At a lower heating value of 12.63 MJ/Nm<sup>3</sup>, this corresponds to a continuous thermal power of roughly 210-265 MWth. The relatively low heating value of BFG (3.0-4.0 MJ/Nm<sup>3</sup>), compared with coke oven gas (16.4-18.0 MJ/Nm<sup>3</sup>) and natural gas (~35.8 MJ/Nm<sup>3</sup>), arises from its high nitrogen dilution and the fact that a significant fraction of the coke's chemical energy has already been consumed during iron ore reduction. [23], [22], [24]

Despite its low calorific value, blast furnace gas is too voluminous and energy-rich to be simply vented or flared. [22] At a modern integrated steelworks, BFG is currently utilized in three principal applications; preheating the blast air in the regenerative cowper stoves (consuming approximately 30-40% of the total BFG produced), firing power plant boilers or gas turbines for on-site electricity generation (consuming 40-50%), and supplementary heating in various process furnaces such as coke ovens, reheating furnaces and sinter plants (consuming the remaining 10-20%) as demonstrated in **Figure 2.1**. [24], [25]

Hot blast (Cowper) stoves are the largest single consumer of BFG. They act as regenerative heat exchangers that preheat the air supplied to the blast furnace. In the heating phase, BFG is combusted with air to raise the temperature of refractory checkerwork to approximately 1300-1400°C. In the subsequent blasting phase, cold air passes through this hot structure and is heated to 1100-1350°C before entering the furnace. Stove consumption typically ranges from 30-40% in modern plants but can exceed 50% in older facilities. In practice, BFG is often blended with COG to ensure sufficient heating value. [26], [27]

In terms of electricity generation, blast furnace gas exhibits a broad efficiency spectrum depending on the technology used. At the lowest extreme, open flaring provides no energy recovery, representing a complete loss of the gas stream's chemical energy potential. [28] In modern steelworks, however, BFG is primarily used for power generation via boilers, gas engines or gas turbines. Older subcritical steam systems achieve 18-22% electrical efficiency while

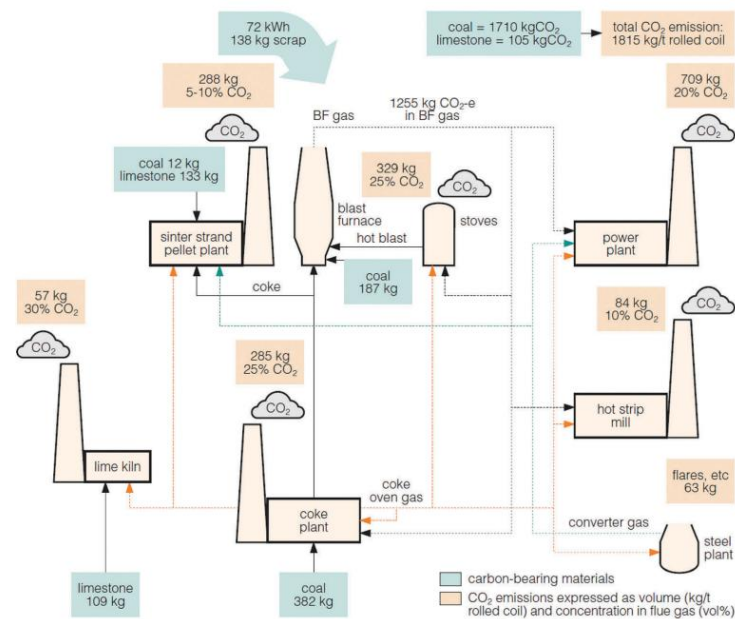
modern steam cycles reach 28-32%. Gas engines can deliver 35-40% efficiency but require enrichment with higher-calorific gases. [21] Simple-cycle gas turbines achieve 25-35%, while combined-cycle systems reach 40-45%. Additional energy recovery is possible using top-pressure recovery turbines (TRT), which generate power from gas expansion without combustion. Advanced integrated systems combining CO<sub>2</sub> cycles and carbon capture can exceed 50% efficiency with high capture rates. The remaining BFG is used for process heating in units such as coke ovens, reheating furnaces, and sinter plants. Due to its low heating value, it is typically blended with richer fuels and must be cleaned to low dust levels (~0.023 g/m<sup>3</sup>) before use. [21], [29], [30] In all applications, the combustible components of BFG, primarily CO and H<sub>2</sub>, are oxidized to release energy. Consequently, CO<sub>2</sub> is emitted in two stages: first during the reduction of iron ore in the blast furnace and subsequently during the combustion of blast furnace gas. The resulting flue gas typically contains 25-30% CO<sub>2</sub>, and under conventional utilization pathways, none of this carbon is permanently captured. [18], [24]

The Materials Processing Institute's Blast Furnace 2030 study identifies four key innovation pillars to transform blast furnace operation into a more sustainable process, targeting CO<sub>2</sub> emissions of <10% of the current European average (from ~1.3 t CO<sub>2</sub>/t steel to ~0.2 t CO<sub>2</sub>/t steel). [31] These pillars include: (1) carbon capture and utilization (up to 60% reduction), (2) coke substitution with biomass and alternative carbon sources (up to 30% reduction), (3) development of improved ferrous raw materials to reduce cost and emissions, and (4) cross-cutting measures such as waste heat recovery, by-product minimization, and life-cycle carbon optimization. [31] Building on this framework, **Table 2.1** summarizes an expanded set of innovation strategies for future blast furnace development.

**Table 2.1** Overview of carbon capture and decarbonization technologies applicable to blast furnace ironmaking.

| Technology                                      | Description                                                                                                                                                                             | CO <sub>2</sub> Performance                     |
|-------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|
| <b>Carbon capture and utilization (CCU)</b>     | Captures CO <sub>2</sub> from BFG and uses it as feedstock for chemicals and synthetic fuels (such as methanol, Carbon2Chem-type integration)                                           | Up to ~60% utilization [31], [32]               |
| <b>Top-gas recycling blast furnace (TGR-BF)</b> | CO <sub>2</sub> removed from top gas, CO converted to H <sub>2</sub> via water-gas shift, H <sub>2</sub> -rich gas recycled and CO <sub>2</sub> separated for storage/use               | 24-50% CO <sub>2</sub> reduction [31], [33]     |
| <b>Post-combustion CCUS (BFG streams)</b>       | CO <sub>2</sub> capture from flue gases of stoves, boilers and sinter plants using amine, calcium looping or cryogenic systems                                                          | 50-70% site-wide capture [17], [31],            |
| <b>Oxy-fuel / oxygen enrichment</b>             | Air blast replaced with O <sub>2</sub> , eliminating N <sub>2</sub> dilution and concentrating CO/CO <sub>2</sub> in top gas and improving capture efficiency.                          | Enables ~80% CO <sub>2</sub> capture [31], [34] |
| <b>Hydrogen injection</b>                       | H <sub>2</sub> injected via tuyeres partially replaces carbon-based reductants, producing H <sub>2</sub> O instead of CO <sub>2</sub> and lowering the top-gas carbon load              | 10-30% CO <sub>2</sub> reduction [31], [35]     |
| <b>Biomass/biochar substitution</b>             | Fossil coke or PCI replaced with biogenic carbon, making CO <sub>2</sub> emissions carbon-neutral on a life-cycle basis.                                                                | Up to ~30% substitution [31]                    |
| <b>Chemical looping (CLC/CLH)</b>               | Metal-oxide oxygen carriers enable inherent CO <sub>2</sub> separation; CLH mode additionally produces high-purity H <sub>2</sub> via steam oxidation without external separation units | >90% of BFG carbon captured [36], [37]          |

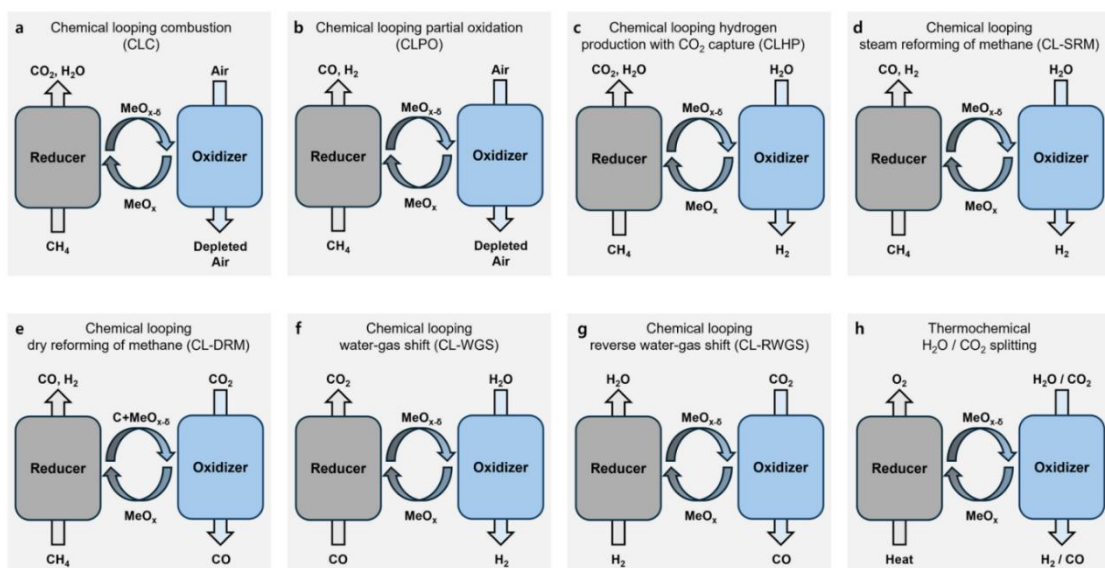
Overall, these technologies demonstrate that deep decarbonization of the blast furnace is achievable, with effective CO<sub>2</sub> capture playing a central role in reducing emissions.



**Figure 2.1** Typical blast furnace gas utilization pathways in an integrated steelwork [24]

## 2.2 Chemical Looping: Principles and Fundamentals

Chemical looping technology is a process that avoids the direct contact of fuel and an oxidant, typically air, by the common principle of using a solid oxygen carrier to transfer the oxygen. [38] This inherent separation yields distinct product streams such as concentrated  $\text{CO}_2$  from the fuel side and nitrogen-free products from the oxidant side without requiring energy-intensive downstream gas separation. However, the specific objectives of the process, the choice of oxygen carrier material, and the reactor configuration vary considerably across the different chemical looping variants. [39] The chemical looping concept can be classified into several variations depending on the desired product, including chemical looping combustion (CLC) for heat and power, chemical looping reforming (CLR) or gasification (CLG) for syngas production, and

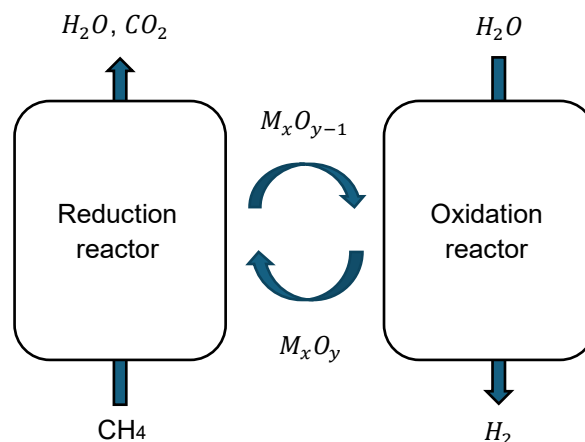


**Figure 2.2** Overview of major chemical looping process configurations. [41]

chemical looping hydrogen production (CLH) or water splitting (CLWS) for high-purity hydrogen. [40] This can be seen in **Figure 2.2** as well:

Starting with chemical looping combustion (CLC), it is the simplest and most technologically mature chemical-looping configuration. It consists of two interconnected reactors: a fuel reactor, where an oxygen carrier transfers lattice oxygen to the fuel, and an air reactor, where the reduced oxygen carrier is regenerated by atmospheric oxygen. Because fuel oxidation occurs without direct contact between fuel and air, the combustion products remain undiluted by nitrogen, enabling inherent  $\text{CO}_2$  separation after water condensation without the need for conventional gas-separation processes. [14], [41] CLC is typically operated at temperatures of 800-1200 °C to ensure rapid reaction kinetics while maintaining oxygen-carrier stability. Although most systems operate near atmospheric pressure, pressurized operation has also been proposed for process intensification. Process performance depends on the properties of the oxygen carrier, which govern oxygen transfer capacity, reaction kinetics, and thermal behavior. [38], [42]

The reduction reaction in the fuel reactor depends on both the fuel and the oxygen carrier and may be either endothermic or exothermic, whereas oxidation in the air reactor is inherently exothermic. Heat released in the air reactor is transported to the fuel reactor through the circulating oxygen carrier, maintaining the process energy balance. CLC is compatible with gaseous, liquid, and solid fuels. However, solid fuels generally exhibit slower conversion because they must first undergo gasification before reacting with the oxygen carrier. [43], [44], [14], [45] To overcome the slow conversion of solid fuels in conventional CLC, Chemical Looping with Oxygen Uncoupling (CLOU) was developed. In CLOU, selected oxygen carriers release gaseous oxygen directly in the fuel reactor, accelerating solid-fuel combustion while retaining the inherent  $\text{CO}_2$  separation characteristic of chemical looping. [46], [47], [48], [49]

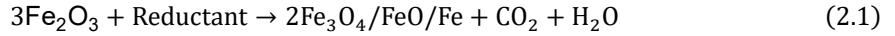


**Figure 2.3** Schematic of the chemical looping hydrogen production (CLHP) process. [42]

Chemical Looping Reforming (CLR) is a variant of chemical looping that produces synthesis gas (syngas), consisting primarily of  $\text{H}_2$  and  $\text{CO}$ , instead of fully oxidizing the fuel to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . This is achieved by supplying a sub-stoichiometric amount of lattice oxygen from the oxygen carrier, resulting in partial oxidation of the fuel, typically methane or other light hydrocarbons. By controlling the oxygen carrier circulation, CLR can operate under near-thermoneutral conditions while producing syngas with an  $\text{H}_2/\text{CO}$  ratio suitable for downstream processes such as Fischer-Tropsch and methanol synthesis. CLR is typically operated at 800-950 °C using Ni-based oxygen carriers because of their high catalytic activity, although research increasingly focuses on alternative materials to mitigate coking, toxicity, and cost. [39], [44], [38], [50], [51], [52] The next configuration is chemical looping hydrogen (CLH) production, which appears in the literature under several names, including CLHP, chemical looping water splitting (CLWS), and the steam-iron cycle, and constitutes the most relevant class of configurations for direct hydrogen

generation with integrated carbon capture as shown in **Figure 2.3**. The recognized three-reactor architecture exploits the multivalent redox chemistry of the  $\text{Fe}_2\text{O}_3$  /  $\text{Fe}_3\text{O}_4$  /  $\text{FeO}$  /  $\text{Fe}$  system, cycling the oxygen carrier between three distinct oxidation states in three dedicated reactors [53].

In the fuel reactor (FR), the fully oxidized carrier (hematite ( $\text{Fe}_2\text{O}_3$ )) is reduced by a fuel, which can be natural gas, syngas, or blast furnace gas, to a lower oxidation state, such as wüstite ( $\text{FeO}$ ) or metallic iron ( $\text{Fe}$ ), producing a stream of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , as shown in Equation 2.1: [53], [54]



Secondly, the reduced iron-based carrier is then transferred to the steam reactor (SR), where it reacts with steam ( $\text{H}_2\text{O}$ ) to produce a high-purity stream of hydrogen ( $\text{H}_2$ ). In this step, the carrier is re-oxidized to an intermediate state, typically magnetite ( $\text{Fe}_3\text{O}_4$ ) (Equ. 2.2 and 2.3). [53]



Finally, the magnetite is sent to the air reactor, where it is fully re-oxidized back to hematite by air, releasing heat and completing the cycle (Equ. 2.4). [53]



The process generates two valuable, inherently separated product streams, namely a concentrated  $\text{CO}_2$  stream from the FR and a near-pure  $\text{H}_2$  stream from the SR, thereby eliminating the need for complex downstream gas separation. Additionally, the AR is considered essential to re-oxidize  $\text{Fe}$  to  $\text{Fe}_2\text{O}_3$  fully, as its inclusion provides the thermodynamic driving force for the next reduction and restores full oxygen transport capacity. [54]

Thermodynamically, the fuel reactor may be endothermic, thermoneutral, or mildly exothermic depending on the fuel composition. The steam reactor is mildly exothermic, whereas the air reactor is strongly exothermic and provides most of the heat required to sustain the process. The thermodynamic necessity of the air reactor lies in the Baur-Glässner equilibrium for the iron-steam system, where steam can only partially re-oxidize metallic iron, with the equilibrium steam-to-hydrogen conversion for the  $\text{Fe} \rightleftharpoons \text{Fe}_3\text{O}_4$  couple constrained to approximately 60-75% at 750-850 °C, which will be discussed in the upcoming section in detail. By inserting the air reactor, the carrier is theoretically restored to its fully oxidized hematite state, providing a stronger thermodynamic driving force in the subsequent reduction, which raises the per-cycle oxygen transport capacity to approximately 30 wt% and combusts any carbon deposits or sulphuric species if present and accumulated during reduction. [54]

A simplified two-reactor variant of the same chemistry omits the air reactor and cycles the iron carrier between  $\text{FeO}$  and  $\text{Fe}_3\text{O}_4$  in alternating reduction and steam-oxidation steps, which is the classical steam-iron process. In contrast, the three-reactor configuration includes an air reactor that fully regenerates the oxygen carrier to hematite ( $\text{Fe}_2\text{O}_3$ ), restoring its oxygen transport capacity and supplying the heat required for sustained cyclic operation. As a result, the three-reactor system generally achieves higher fuel conversion, greater hydrogen productivity and improved oxygen carrier stability, as the air reactor also removes deposits formed from fuel impurities. However, these advantages are accompanied by increased reactor volume, greater process complexity and higher capital cost. Conversely, the two-reactor configuration offers a simpler and less expensive design but typically exhibits lower fuel conversion, reduced hydrogen production and more stringent feedstock purity requirements. Nevertheless, the benefit of the extra stage must be evaluated carefully, because a greater number of reactors does not necessarily correspond to a deeper thermodynamic reduction of the iron oxide. In many cases,

the first stage already places the material within the same wüstite-dominated region, so the added stage mainly improves process configuration rather than the fundamental reduction endpoint. [55]

Both architectures can be implemented either as interconnected circulating fluidized-bed reactors, in which the oxygen carrier is continuously transported between physically separate reactors, or as fixed-bed reactors, in which the oxygen carrier remains stationary while the gas atmosphere is switched sequentially using valves. [56] In the fixed-bed configuration, the spatial separation achieved by solids circulation is replaced by temporal separation between phases of operation within a single reactor. The bed is first exposed to the reducing fuel gas, then to steam to produce hydrogen, and finally to air to regenerate the oxygen carrier in the three-stage configuration. Although the mode of operation differs, the underlying redox chemistry and reaction stoichiometry remain unchanged. [57] Depending on whether an air oxidation step is included, fixed-bed CLH operates using either a two-stage or a three-stage cycle, directly corresponding to the two-reactor and three-reactor configurations described above. In the two-stage cycle, the bed alternates between reduction and steam oxidation, cycling between  $\text{FeO}$  and  $\text{Fe}_3\text{O}_4$ . In the three-stage cycle, an additional air oxidation step is introduced after steam oxidation to regenerate the oxygen carrier to  $\text{Fe}_2\text{O}_3$ , thereby restoring its maximum oxygen transport capacity and removing accumulated carbon and sulfur deposits. For feedstocks with low carbon and sulfur contents, two-stage operation can be sustained for many cycles before regeneration becomes necessary. For cleaned blast furnace gas, two-stage operation can be preferred due to its process simplicity. [58]

The fixed-bed configuration has been adopted in several steam-iron processes, including the H2Loop technology developed by Rouge H<sub>2</sub> Engineering. In this approach, the spatial separation achieved by particle transport in circulating systems is replaced by temporal separation of the reduction and steam oxidation stages within a single reactor vessel. This concept has been extensively investigated by Bock and co-workers at TU Graz under the Reformer Steam–Iron Cycle (RESC) designation. [56], [59] Compared with circulating fluidized-bed systems, this operating principle offers several practical advantages while also introducing unique engineering challenges.

Several features make the fixed-bed architecture particularly suitable for decentralized small-to-medium-scale hydrogen production. The absence of solids transport eliminates mechanical attrition and removes the need for cyclones, loop seals, and carbon strippers, thereby reducing both capital cost and mechanical complexity. Additionally, gas-tight separation between reactive atmospheres is achieved by valve switching rather than aerodynamic isolation. [57] Furthermore, the stationary oxygen carrier provides a more uniform reaction environment than circulating fluidized-bed systems, allowing the material to cycle more effectively over the  $\text{Fe}_2\text{O}_3$  -  $\text{Fe}$  redox range and operate closer to its thermodynamic limits. To maintain this efficiency, operating temperatures are controlled between 700 °C and 850 °C, as this range is narrow enough to suppress Boudouard carbon deposition at the lower bound while preventing carrier sintering and thermodynamic losses at the upper bound. [56], [58]

However, the principal disadvantages are the inherent transient nature of single-reactor productivity, which requires parallel-reactor operation for continuous output. This configuration introduces steep axial and radial temperature gradients caused by the alternating cycle of strongly exothermic oxidation and endothermic reduction. Furthermore, the need to minimize pressure drops across the bed requires larger carrier pellets, which unfortunately introduce intra-particle diffusion limitations. Ultimately, these thermal and mechanical stresses place a burden on the system's hardware. [54], [57], [59]

As mentioned, continuous hydrogen output is achieved by operating multiple reactors in parallel. In this operational sequence, one reactor undergoes reduction while the others simultaneously perform steam oxidation and air oxidation; heat removal can also be added, depending on the configuration. However, the phase durations are inherently unequal, which leads to significant timing challenges for continuous hydrogen production. While the steam oxidation phase is highly

productive and determines the hydrogen output rate, the reduction phase is typically slower, and the intermediate purging steps further complicate the cycle timing, which is an active area of research. [60] To address these operational complexities and validate the system's performance at a larger scale, Bock and Hacker have demonstrated a 10 kW<sub>th</sub> fixed-bed chemical looping system coupled to a biogas digester, which achieved hydrogen purities of 99.998% and hydrogen production efficiencies of 73%. [56] Regardless of the reactor configuration employed, oxygen carrier materials remain a key consideration in the design and operation of CLH systems.

### 2.2.1 Oxygen Carrier Materials

The performance of any chemical looping process is fundamentally determined by the oxygen carrier material. It is selected based on reactivity, oxygen-transport capacity ( $R_0$ ), cost, toxicity, and cyclic durability. Through the literature review, five principal transition metal oxide systems have been investigated extensively, namely iron ( $\text{Fe}_2\text{O}_3$ ), nickel ( $\text{NiO}$ ), copper ( $\text{CuO}$ ), manganese ( $\text{Mn}_3\text{O}_4$ ), and cobalt ( $\text{Co}_3\text{O}_4$ ), each of which has its distinct advantages and limitations. Cho et al. (2004) conducted the first systematic comparison of iron-, nickel-, copper-, and manganese-based oxygen carriers for chemical looping combustion, and their data have served as a baseline for material selection for more than two decades. [61] A comprehensive operational review by Lyngfelt (2020) reports that across 46 chemical looping combustion units worldwide, totaling over 11,000 hours of operation, manufactured  $\text{NiO}$ -based carriers account for 29% of operational time,  $\text{Fe}_2\text{O}_3$ -based carriers account for 16%,  $\text{CuO}$ -based carriers account for 13%, combined oxides account for 11%,  $\text{Mn}_3\text{O}_4$  accounts for 1%, and  $\text{CoO}$  accounts for 2%. The remaining 28% of operational time was dominated by "natural ores" and waste materials, such as Ilmenite (13%), which are preferred for solid fuel combustion because they are cheap enough to be discarded once contaminated by coal ash. [36], [62]

**Table 2.2** Oxygen-carriers and stabilization materials for the chemical looping hydrogen process.

| Function                                                                                                                                                                      | Material                                                                            | $R_0$ / Key property                  | Key Advantages and Limitations                                                                                                                                                             |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|---------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Active Redox Phase</b>                                                                                                                                                     | <b>NiO</b>                                                                          | 0.21                                  | Highest reactivity for $\text{CH}_4$ /syngas, preferred for reforming  carcinogenic, sulphur-poisoned, $\approx 250\times \text{Fe}_2\text{O}_3$ cost. [63], [64]                          |
|                                                                                                                                                                               | <b>CuO</b>                                                                          | 0.20                                  | $\text{O}_2$ uncoupling (CLOU) above $\sim 900^\circ\text{C}$   low Cu melting point ( $1085^\circ\text{C}$ ) limits temperature and causes agglomeration. [61]                            |
|                                                                                                                                                                               | <b><math>\text{Mn}_3\text{O}_4</math></b>                                           | $\sim 0.07$                           | Low-cost and non-toxic  low capacity and forms unreactive phases with $\text{SiO}_2$ , $\text{Al}_2\text{O}_3$ and $\text{TiO}_2$ . [64]                                                   |
|                                                                                                                                                                               | <b><math>\text{Co}_3\text{O}_4</math></b>                                           | $\sim 0.07$                           | Fast kinetics and low sintering tendency, less prone to coking than NiO   toxic and costly (battery-sector competition). [65]                                                              |
|                                                                                                                                                                               | <b><math>\text{Fe}_2\text{O}_3/\text{Fe} \checkmark</math></b>                      | 0.30                                  | Enables steam-iron $\text{H}_2$ , abundant, non-toxic, sulfur-tolerant, lowest cost. [38], [62], [66]                                                                                      |
| <b>Structural Stabilization</b>                                                                                                                                               | <b><math>\text{Al}_2\text{O}_3</math></b>                                           | Tammann $\approx 885^\circ\text{C}$   | Low-cost and mechanically robust; promotes near-complete $\text{CO}/\text{H}_2$ conversion  forms inactive $\text{Fe Al}_2\text{O}_4$ (hercynite), reducing $\text{H}_2$ yield. [66], [67] |
|                                                                                                                                                                               | <b><math>\text{ZrO}_2</math></b>                                                    | chemically inert                      | Inert, forms no secondary phases, 90% of stoichiometric $\text{H}_2$ over 20 cycles at $850^\circ\text{C}$   higher carbon deposition than $\text{CeO}_2$ . [61], [68], [69]               |
|                                                                                                                                                                               | <b><math>\text{CeO}_2</math></b>                                                    | $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox | Redox-active promoter that suppresses sintering and coking  expensive rare-earth material. [66], [69]                                                                                      |
|                                                                                                                                                                               | <b><math>\text{Al}_2\text{O}_3/\text{ZrO}_2</math> dual <math>\checkmark</math></b> | strength + inertness                  | $\text{Al}_2\text{O}_3$ mechanical strength + $\text{ZrO}_2$ chemical inertness, no unreactive ferrites, ternary system validated. [70]                                                    |
| <b>Assumption for Ceramic-Stabilized Pellet: 90 wt% <math>\text{Fe}_2\text{O}_3</math> + 10 wt% <math>\text{Al}_2\text{O}_3</math> /<math>\text{ZrO}_2</math> binder [71]</b> |                                                                                     |                                       |                                                                                                                                                                                            |

Among these oxygen carriers, as shown in **Table 2.2**, iron oxide is uniquely suited for direct hydrogen production through the steam-iron reaction, in which reduced iron reacts with steam to produce high-purity  $H_2$ . The other oxygen carriers do not share this capability at 700-1000 °C, as nickel cannot be re-oxidized by steam, copper melts at these temperatures, and manganese and cobalt do not provide sufficiently favorable thermodynamics. On full reduction ( $Fe_2O_3 \rightarrow Fe$ ), iron attains an oxygen transport capacity of  $R_0 = 0.30$ , one of the highest among common oxygen carriers, compared with 0.21 for  $NiO/Ni$  and 0.20 for  $CuO/Cu$ , and far above the 0.03 achieved in the partial  $Fe_2O_3/Fe_3O_4$  redox cycle used in conventional chemical looping combustion. [66] It is additionally abundant, low-cost, non-toxic, and tolerant of sulfur-containing impurities (trace  $H_2S$  and  $COS$ ), making it particularly suitable for chemical looping applications. [45], [61], [72]

However, unsupported  $Fe_2O_3$  exhibits a rapid decline in hydrogen production during repeated redox cycling because sintering reduces the reduction rate, thereby limiting subsequent re-oxidation. [69] In general, high Tammann temperature oxides, principally  $Al_2O_3$ ,  $ZrO_2$ ,  $SiO_2$ ,  $TiO_2$ ,  $CeO_2$  and  $MgAl_2O_4$  are therefore added to preserve porosity against the atomic diffusion that drives particle fusion. [66], [73] [69] [78] [74]

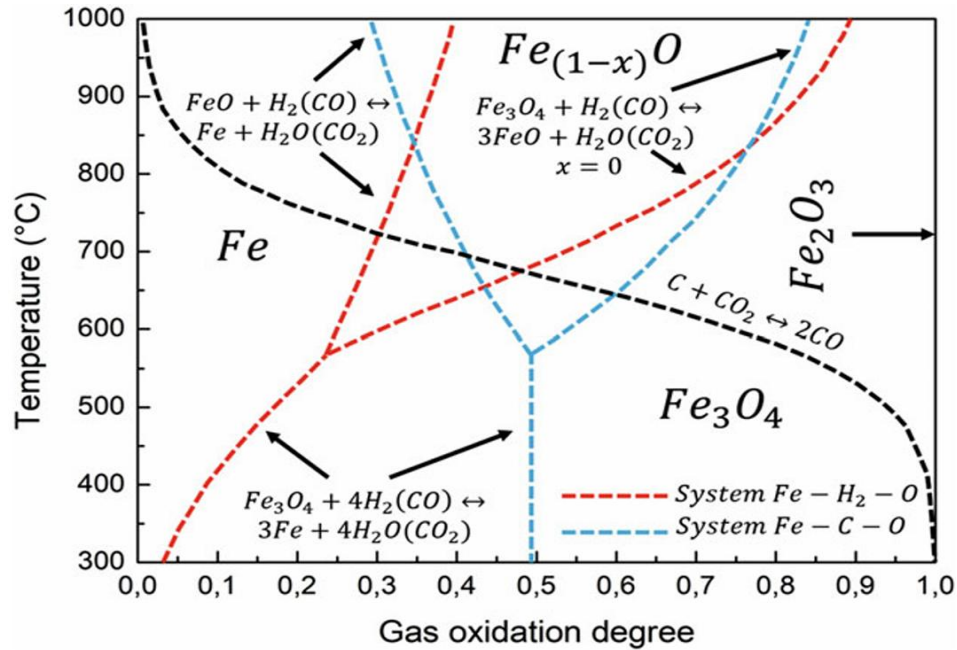
Alumina (Tammann temperature  $\approx 885$  °C) is the cheapest and most robust support and promotes near-complete  $CO/H_2$  conversion in the fuel reactor. However, it forms hercynite ( $FeAl_2O_4$ ), which is largely inactive for water splitting and gradually reduces  $H_2$  yield. [66] [69] [67] Recent studies, including the systematic investigation by Liu et al. (2024), indicate that these adverse effects can be mitigated through careful selection of  $Al_2O_3$  precursors. [67] Furthermore, zirconia ( $ZrO_2$ ) is chemically inert and forms no secondary phases. A coprecipitated 30 mol%  $ZrO_2$  - 70 mol%  $Fe_2O_3$  carrier sustained 90 mol% of the theoretical  $H_2$  yield over 20 cycles at 850 °C, although it promotes greater carbon deposition than  $CeO_2$ . [61], [74], [68] Ceria acts as a redox-active promoter, ( $Ce^{4+}/Ce^{3+}$ ) that counteracts both sintering and coking but is comparatively heavy and expensive. [74]

In terms of the combination of both  $Al_2O_3$  (mechanical strength and sintering resistance) with  $ZrO_2$  (chemical inertness and no ferrite formation) as a dual support, the two materials complement one another by overcoming their individual limitations. Kao et al. (2021) demonstrated the feasibility of this ternary  $Fe_2O_3 - Al_2O_3 - ZrO_2$  system for chemical looping applications. [70] A pellet composition containing 90 wt%  $Fe_2O_3$  and 10 wt%  $Al_2O_3 - ZrO_2$ -based cement was subsequently validated in thermogravimetric analyzer (TGA) experiments between 600 and 800 °C, confirming stable redox performance while providing sufficient mechanical strength and resistance to sintering. [71] Göthel et al. (2025) assumed a representative composition of 95 wt% active iron oxide and 5 wt% ceramic binder to evaluate the redox cycle potential of ceramic-stabilized pellets, highlighting their high cycling capability and oxygen exchange capacity. Ultimately, these findings emphasize that such optimized ceramic-stabilized pellets are essential for ensuring the long-term durability and efficiency required for industrial-scale hydrogen production and energy storage within the iron-steam process. [75]

## 2.2.2 Thermodynamics and Kinetics of Iron Oxide Reduction

Understanding the thermodynamic boundaries of the Fe-O-H-C system is fundamental to the design and optimization of the chemical looping process. A comprehensive review by Spreitzer and Schenk provides the principal thermodynamic framework describing the reduction of iron oxides and has become one of the most widely cited references in this field. [76] The thermodynamic behaviour of iron oxide reduction is commonly represented using the Baur-Glässner diagram, which illustrates the stability regions of hematite ( $Fe_2O_3$ ), magnetite ( $Fe_3O_4$ ), wüstite ( $Fe_{1-x}O$ ) and metallic iron (Fe) as a function of temperature and gas oxidation degree

(GOD), as described in **Figure 2.4**. The diagram plots the GOD, defined as the ratio of the oxidized gas species to the total reactive gas species, and for the Fe-O-C system gas oxidation degree is defined with the equation: [23], [76]



**Figure 2.4** Baur-Glässner equilibrium diagram.

$$\text{GOD} = \frac{p\text{CO}_2}{p\text{CO} + p\text{CO}_2} \quad (2.5)$$

whereas for hydrogen-containing systems, equation:

$$\text{GOD} = \frac{p\text{H}_2\text{O}}{p\text{H}_2 + p\text{H}_2\text{O}} \quad (2.6)$$

The equilibrium boundaries separating the different iron oxide phases are derived from Gibbs free energy minimization and can be calculated using thermochemical software such as HSC Chemistry or FactSage. [77], [78] A key feature of the diagram is the eutectoid temperature at approximately 570°C, below which wüstite is thermodynamically unstable. Consequently, reduction below this temperature proceeds directly from magnetite to metallic iron without the formation of a stable wüstite phase. [76], [79] Furthermore, the Baur-Glässner diagram further shows that CO is the preferred reducing agent at lower temperatures, whereas H<sub>2</sub> becomes thermodynamically more favorable above approximately 800-820°C owing to the different enthalpic characteristics of the respective reduction reactions. At 850 °C, the Fe<sub>3</sub>O<sub>4</sub>/wüstite equilibrium boundary in **Figure 2.4** occurs at a gas oxidation degree of approximately 0.78-0.80 (≈0.74 based on standard Gibbs free-energy calculations). This boundary represents the thermodynamic constraint on the maximum reduction extent achievable under equilibrium conditions and is adopted as the reference for the bounding analysis in Chapter 5. [78], [80]

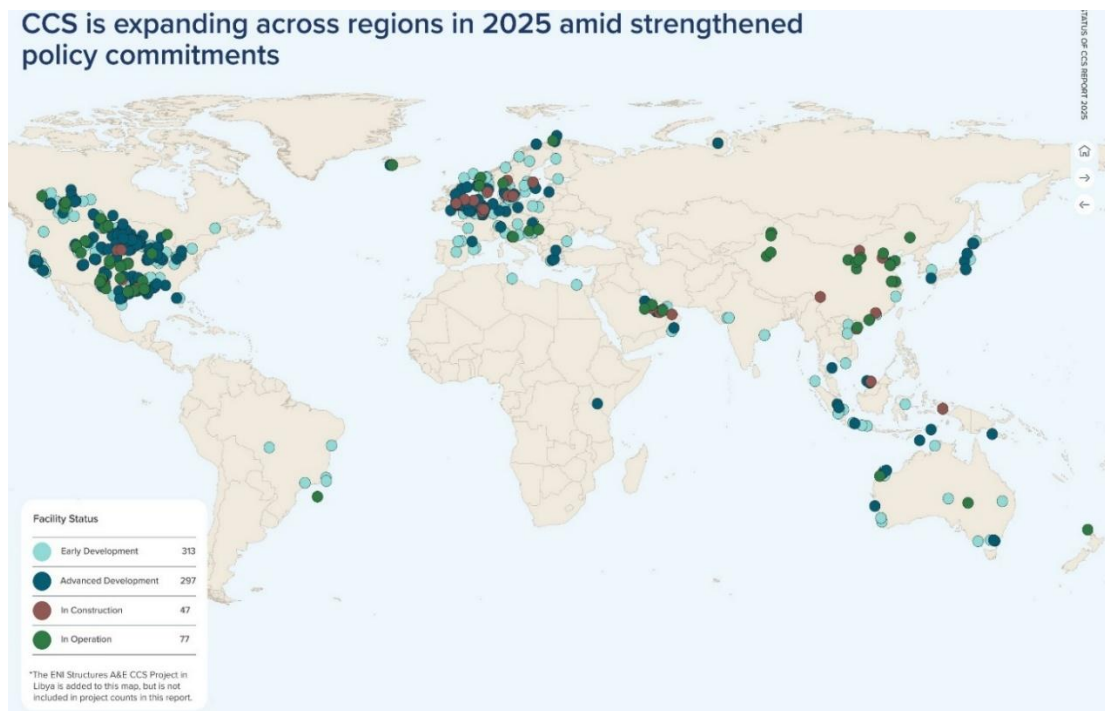
For practical chemical looping applications involving carbonaceous gases, the Baur-Glässner diagram is commonly supplemented by the Boudouard equilibrium, the disproportionation of carbon monoxide into solid carbon and carbon dioxide, which defines the conditions under which carbon deposition becomes thermodynamically favorable. Above the equilibrium boundary, typically at temperatures between 800 and 1100 °C, carbon deposition is thermodynamically suppressed even under CO-rich atmospheres, whereas lower temperatures (below 700 °C) increase the likelihood of coke formation. [46], [76], [81] Consequently, the Boudouard equilibrium provides an important criterion for selecting reactor operating temperatures in iron-based chemical looping systems processing blast furnace gas. [82]

The composition of the blast furnace top gas (BFTG) is plotted on the Baur-Glässner diagram as an operating point. [23], [76], [80] Experimental studies using simulated BFTG at 700-900°C have demonstrated that the reduction of iron oxide compacts reaches only 30-34% under these conditions, with the material converting primarily to wüstite and only traces of metallic iron appearing at 900°C [23]. For chemical looping combustion of BFTG, however, this limited reducing power is actually advantageous as the objective is to oxidize the residual CO and H<sub>2</sub> to CO<sub>2</sub> and H<sub>2</sub>O while reducing the oxygen carrier from Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>. This enables the carbon to be captured as a concentrated CO<sub>2</sub> stream, which improves overall carbon capture efficiency. [46], [67] These thermodynamic considerations form the basis for selecting the operating conditions employed in H2Loop, where sufficiently high temperatures are required to achieve deep iron oxide reduction while simultaneously avoiding carbon deposition.

## 2.3 State of the Art: CO<sub>2</sub> Capture Technologies

The scale of CCS and CCU deployment has expanded dramatically over the past decade, although a persistent gap remains between ambition and operational reality. As of mid-2024, the global CCS project pipeline comprised 628 projects across all stages of development, representing an increase of 236 projects compared with the previous year and a cumulative CO<sub>2</sub> capture capacity of 416 million tonnes per annum (Mtpa) (**Figure 2.5**). This growth represents a seven-year compound annual growth rate (CAGR) of 32%. Currently operational facilities account for 51 Mtpa of CO<sub>2</sub> capture and storage capacity, with this figure expected to more than double to over 100 Mtpa once facilities under construction commence operation. [83], [84]

Within the European Union, CCUS deployment is being driven primarily by policy. The EU's Industrial Carbon Management (ICM) strategy establishes a staged trajectory under which the Union aims to develop the capacity to capture approximately 280 Mt CO<sub>2</sub> per annum (Mtpa) by 2040, increasing to around 450 Mtpa by 2050. Achieving these targets depends on the parallel development of shared CO<sub>2</sub> transport, storage and utilization infrastructure, which the strategy identifies as the key enabling factor for scaling industrial carbon management. [85]

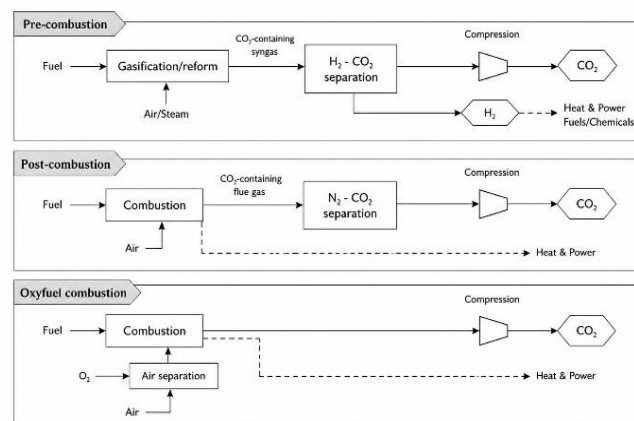


**Figure 2.5** Global distribution and development status of carbon capture and storage (CCS) facilities in 2025. Adapted from [83], [84]

Despite this global momentum, deployment within the iron and steel sector remains noticeably limited. In the steel industry specifically, steelmaking accounts for just 2% of operational CCUS projects and only 1% of projects under development globally, which indicates that the sector barely features in global plans for CCUS implementation. The Al Reyadah facility in the United Arab Emirates, which was commissioned in 2016 with a nominal capacity of 0.8 Mtpa, still remains the sole operational commercial-scale CCUS installation linked to steelmaking. However, its real-world overall impact is constrained as it is capturing only approximately 19.3-19.9% of total plant emissions, with the captured CO<sub>2</sub> primarily utilized for enhanced oil recovery (EOR) rather than permanent storage. Furthermore, there are no commercial-scale CCUS facilities currently operating on coal-based blast furnace systems, which dominate global steel production, indicating a significant technological and economic gap. [86]

Furthermore, despite the EU Emissions Trading System providing strong carbon price signals, CCUS deployment in the European steel sector has achieved limited commercial progress. Existing initiatives, such as ArcelorMittal's Steelanol CCU project in Ghent, illustrate the current limitations of CCU-based approaches. The project captures approximately 0.125 Mt of CO<sub>2</sub> annually, equivalent to less than 2% of the plant's total emissions. In contrast, the planned transition to a direct reduced iron–electric arc furnace (DRI-EAF) configuration at the same site is expected to achieve substantially higher emission reductions, amounting to several million tonnes of CO<sub>2</sub> per year. Although Steelanol contributes approximately 4% of the emission reductions expected from the DRI-EAF transition, it represents around 18% of the associated investment cost, highlighting the comparatively limited cost-effectiveness of current CCU pathways. Consequently, the limited commercial viability of CCUS, even under strong carbon pricing mechanisms, has accelerated the industry's shift towards DRI-based routes compatible with low-carbon hydrogen, which offer deeper and more economically efficient emission reductions. [86] Despite the long-term transition to hydrogen-based steelmaking, improving CO<sub>2</sub> capture for existing blast furnace routes remains essential for near-term decarbonization. [87]

These developments highlight the need to critically evaluate the underlying capture technologies that determine the performance and feasibility of CCUS in industrial applications. The three primary point-source capture routes, namely pre-combustion, post-combustion and oxy-fuel



**Figure 2.6** Schematic overview of the main CO<sub>2</sub> capture technologies. [91]

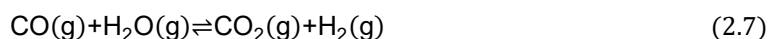
combustion, differ fundamentally in where and how CO<sub>2</sub> is separated from the process stream. Each has distinct thermodynamic characteristics, feedstock requirements, maturity levels and cost structures which can be seen from **Figure 2.6**. [88]

Starting with the Post-Combustion Capture (PCC), it is currently the most mature and widely used CO<sub>2</sub> capture technology, with over 20 large-scale post-combustion capture projects operating worldwide. [89]

In PCC, the fuel is combusted conventionally in air, producing a dilute flue gas stream typically containing only 4-20% CO<sub>2</sub> by volume, depending on the fuel type. Natural gas combustion generally results in lower CO<sub>2</sub> concentrations, whereas coal combustion produces higher concentrations. Consequently, CO<sub>2</sub> must be selectively separated from a large volume of flue gas dominated by nitrogen. The dominant industrial approach for this separation is chemical absorption using amine-based solvents, most commonly monoethanolamine (MEA). The flue gas is contacted with the amine solvent in an absorber column, where CO<sub>2</sub> reacts reversibly with the amine to form carbamate and/or bicarbonate species. The CO<sub>2</sub>-rich solvent is subsequently transferred to a stripper or regenerator operating at elevated temperatures (~120 °C), where heat supplied through steam reverses the reaction, releasing a concentrated CO<sub>2</sub> stream and regenerating the lean solvent for recycle. [90], [91] However, the largest drawback of the process is its high regeneration energy requirement. In power plant applications, particularly coal-fired power generation, post-combustion CCS can reduce overall plant efficiency by approximately 25-30% due to the steam demand of the stripper reboiler. This reduction, commonly referred to as the energy penalty, translates directly into increased fuel consumption, higher operating costs, and additional indirect emissions associated with the extra fuel required, which must be considered when evaluating the net capture efficiency. [92]

Beyond chemical absorption, post-combustion separation can also be achieved via physical adsorption onto solid sorbents (zeolites, activated carbons, metal-organic frameworks/MOFs), membrane permeation (polymer or inorganic membranes that preferentially permeate CO<sub>2</sub>), or cryogenic fractionation. These technologies differ in their separation mechanisms, energy requirements, and cost profiles and are elaborated in Chapter 3. Overall, post-combustion capture costs for power generation typically range from USD 50-100/tCO<sub>2</sub> avoided depending on the flue gas CO<sub>2</sub> concentration, plant size and heat integration. [92], [93]

Secondly, pre-combustion capture removes CO<sub>2</sub> before fuel combustion by converting the primary fuel into synthesis gas (syngas) through steam methane reforming or gasification, followed by the water-gas shift (WGS) reaction to convert CO into CO<sub>2</sub> and additional H<sub>2</sub>, (Equ. 2.7). [94]



The resulting high-pressure syngas typically contains 35-40 vol% CO<sub>2</sub>, enabling more energy-efficient separation than post-combustion capture using physical solvents such as Selexol and Rectisol or pressure swing adsorption (PSA). Pre-combustion capture is primarily applied in Integrated Gasification Combined Cycle (IGCC) power plants and hydrogen or ammonia production, where CO<sub>2</sub> removal is an integral part of the process. However, despite its thermodynamic advantages, it is less mature than post-combustion capture. It remains economically challenging owing to the high capital cost and process complexity associated with gasification and syngas production. Under the evaluated conditions, it has also been reported to exhibit a higher carbon emission intensity (0.05 tCO<sub>2</sub>/MWh) and cost of CO<sub>2</sub> avoidance (USD 150.33/tCO<sub>2</sub>) than post-combustion capture. [95], [96]

Finally, oxy-fuel combustion replaces air with high-purity oxygen (95-99.5%), which produces a flue gas composed primarily of CO<sub>2</sub> and water vapor. After water condensation, a highly concentrated CO<sub>2</sub> stream is obtained that requires only compression and purification, eliminating the need for chemical solvent regeneration. This process is enabled by an air separation unit (ASU), which supplies the oxygen required for combustion. Compared with post-combustion capture, oxy-fuel combustion benefits from higher CO<sub>2</sub> concentrations and lower energy demand in the capture stage, while also reducing NO<sub>x</sub> emissions. [97] However, its commercial deployment remains limited by the high energy consumption of the ASU, which typically reduces overall plant efficiency by 15-20%. [92] Furthermore, oxy-fuel combustion has the highest total investment cost (TIC) of \$8,258,483.99 and annual production cost (APC) of \$9,234,870 among the three primary capture technologies, which has limited its commercial deployment despite its

thermodynamic advantages. Large-scale demonstration projects include the Schwarze Pumpe pilot plant in Germany (Vattenfall, 30 MW) and the Callide Oxyfuel Project in Australia (30 MW). [95]

In the present research, the focus is placed on post-combustion CO<sub>2</sub> capture, as the process under investigation involves treating the blast furnace top gas stream after chemical looping hydrogen production (CLHP). Standard post-combustion flue gases from power plants typically contain only 4-20 vol% CO<sub>2</sub>, while blast furnace gas from conventional integrated steelmaking contains 20-25 vol% CO<sub>2</sub>. The CLH process, by virtue of its chemical looping mechanism, inherently pre-concentrates the carbon species, producing a CO<sub>2</sub>-rich stream whose elevated partial pressure fundamentally shifts the techno-economic landscape of downstream separation. This is consequential because the energy penalty and capital cost of CO<sub>2</sub> separation are strongly inversely correlated with CO<sub>2</sub> partial pressure in the feed gas, which is a well-established thermodynamic relationship that drives the entire cost hierarchy of carbon capture across industries. [17], [94]

The IEA reports that CO<sub>2</sub> capture costs vary substantially depending on the CO<sub>2</sub> concentration of the source. Industrial processes producing highly concentrated CO<sub>2</sub> streams, such as ethanol production and natural gas processing, have capture costs of only USD 15-25 per tonne of CO<sub>2</sub>, whereas processes with dilute gas streams, such as cement production and power generation, face capture costs of USD 40-120 per tonne of CO<sub>2</sub>. [98] At the far extreme of dilution, direct air capture operates on ambient air containing only about 420 ppm CO<sub>2</sub>, roughly 100 times more dilute than even a typical power-plant flue gas. It is currently incurring commercial operational costs of USD 300-600 per tonne of CO<sub>2</sub>, and this figure reflects both the thermodynamic work penalty of extracting CO<sub>2</sub> from so dilute a medium, and the very large volumes of air that must be contacted with the capture medium per tonne of CO<sub>2</sub> recovered. [17], [98] This three-tier cost structure, namely, concentrated industrial streams at USD 15-25/t, dilute industrial flue gases at USD 40-120/t, and ambient air at USD 300-600/t, establishes a clear and practically significant hierarchy in which the CO<sub>2</sub> concentration of the feed stream is the single most consequential variable determining the economics of capture. By pre-concentrating CO<sub>2</sub> through the chemical looping mechanism before the dedicated separation step, the CLHP process shifts the downstream capture operation from the mid-range dilute-stream tier toward the concentrated-stream tier.

## 2.4 CO<sub>2</sub> Utilization Pathways

Unlike carbon capture and storage (CCS), which aims to permanently sequester CO<sub>2</sub> in geological formations, carbon capture and utilization (CCU) converts captured CO<sub>2</sub> into value-added products that can generate additional revenue streams. Hong (2022) provides authoritative baseline indicating that approximately 230 Mt CO<sub>2</sub>/year are utilized globally, of which 57% goes to the fertilizer industry for urea production (132 Mt CO<sub>2</sub>/year), 34% to the oil sector for enhanced oil recovery (EOR, 25 Mt CO<sub>2</sub>/year in dedicated CCU), 3% each for food and beverage production and metal fabrication and 4% for other commercial applications such as cooling, fire suppression, and crop cultivation in greenhouses. [94] The global market breakdown across all CO<sub>2</sub> utilization pathways establishes the TRL, market size, CO<sub>2</sub> utilized, and storage duration for each pathway. A critical caution established is that CO<sub>2</sub> utilization may not reduce CO<sub>2</sub> emissions and may not deliver a net climate benefit, because the amount of CO<sub>2</sub> utilized by a pathway is likely to differ from the amount of CO<sub>2</sub> captured or stored. The same authors estimated that the contribution of CCU to the global CO<sub>2</sub> mitigation challenge would be negligible at 0.2 Gt CO<sub>2</sub>/year in 2050; it could not compete with geological CCS, which has an estimated potential of 7.8 Gt CO<sub>2</sub>/year in 2050. Therefore, CO<sub>2</sub> utilization should be considered as a complement, not an alternative to geological storage for large-scale climate mitigation. [94]

Among current CCU applications, two mature technologies (TRL 9) dominate global CO<sub>2</sub> utilization. Urea synthesis, which reacts CO<sub>2</sub> with ammonia, consumes approximately 0.74 t CO<sub>2</sub> per tonne of product and represents the largest utilization route by volume. However, it provides no permanent carbon storage because the CO<sub>2</sub> is re-released when urea decomposes in soil. CO<sub>2</sub>-enhanced oil recovery (CO<sub>2</sub>-EOR) is another major application, in which CO<sub>2</sub> is injected into depleted oil reservoirs to improve hydrocarbon recovery. Around 80% of the injected CO<sub>2</sub> remains stored, and the process is often revenue-positive for operators. Nevertheless, its overall climate benefit remains debated because the additional recovered oil is ultimately combusted. [17], [94] Together, these examples demonstrate that large market size and commercial maturity do not necessarily correspond to permanent carbon mitigation.

The purity requirements of commercial CO<sub>2</sub> utilization pathways vary considerably, with greenhouse horticulture and the food and beverage industry representing two important markets for high-purity CO<sub>2</sub>. Greenhouse horticulture is a commercially established application (TRL 9), where enrichment of greenhouse atmospheres to approximately 1,000 ppm CO<sub>2</sub> can increase crop yields by up to 30%. The OCAP network in the Netherlands demonstrates the commercial feasibility of supplying captured industrial CO<sub>2</sub> directly to greenhouse operators, displacing fossil-derived CO<sub>2</sub>. [99] Similarly, the food and beverage industry is a major consumer of high-purity CO<sub>2</sub>, requiring approximately 8.2 Mt/year for food packaging and 2.9 Mt/year for beverage carbonation, where stringent food-grade specifications are required to ensure product quality and consumer safety. Although these applications provide only temporary carbon storage, they create established commercial markets for captured CO<sub>2</sub> with stringent purity requirements. [94]

Beyond these mature applications, several emerging CCU pathways remain under development, including methanol and methane synthesis, CO<sub>2</sub>-derived chemicals and polymers, microalgal cultivation and carbonate mineralization. Their deployment is generally constrained by high energy consumption, renewable hydrogen demand, production costs, or limited market size. In contrast, carbonate mineralization and concrete curing (TRL 7-8) provide long-term carbon storage by permanently incorporating CO<sub>2</sub> into stable solid products, although wider commercial development remains limited by market acceptance.

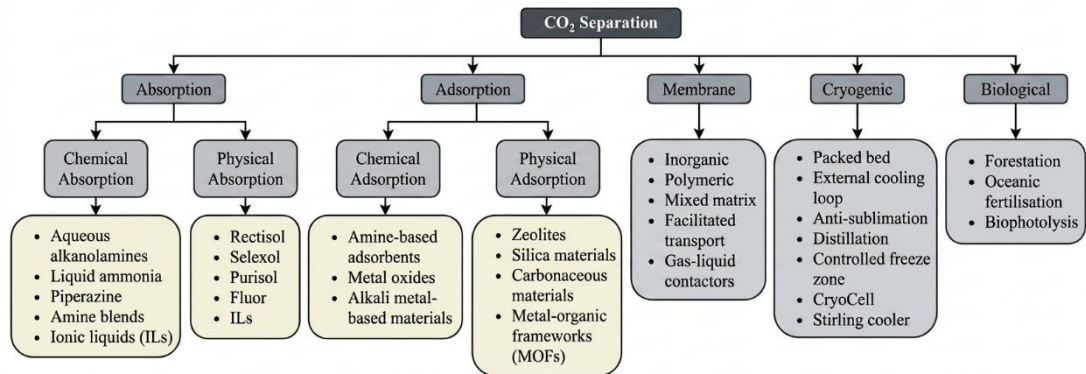
Across all utilization pathways, the commercial value of captured CO<sub>2</sub> depends strongly on its purity and intended end use. ISO 27913:2024 specifies a minimum CO<sub>2</sub> purity of 95 mol% with total impurities below 5 mol%, while each additional mol% of non-condensable gases increases compression energy by approximately 1%. [100], [101], [102] Consequently, capture technologies producing high-purity CO<sub>2</sub> require less downstream conditioning and can access a broader range of higher-value utilization pathways. CO<sub>2</sub> purity therefore influences not only downstream processing requirements but also the range and value of commercially accessible utilization pathways. [103], [104], [105], [106]

### 3 CO<sub>2</sub> Capture Technology Selection

The recent survey of European industrial post-combustion capture deployment is provided by Marques et al., who reviewed 49 industrial facilities across the continent. Their analysis reveals that chemical absorption remains the dominant technology, employed in 39% of installations, followed by adsorption-desorption systems (24%), cryogenic techniques (12%), and membrane separation (10%). [107] This distribution reflects both the commercial maturity of amine scrubbing (TRL 9) and the gradual emergence of alternative technologies at lower TRL levels. Lu et al. provide a progress review concluding that post-combustion capture is unlikely to be displaced by pre-combustion or oxy-fuel approaches in the near future as it offers the critical advantage of retrofittability to existing combustion infrastructure without requiring fundamental process modifications. [108]

Furthermore, Santos and Hanak offer a comparative review of the techno-economic feasibility of solid looping cycles across energy-intensive industries, finding that conventional amine scrubbing was the least feasible option for iron and steel applications, with avoided CO<sub>2</sub> costs reaching €104.6 per tonne. [109] In contrast, solid looping cycles, which include both calcium looping and chemical looping, demonstrated significantly lower costs, particularly when process integration synergies were exploited. Thiedemann and Wark estimated calcium looping costs at USD 29-50 per tonne of CO<sub>2</sub>, which is approximately 50% cheaper than amine-based capture. These cost differentials are especially pronounced for concentrated CO<sub>2</sub> streams, where the thermodynamic and kinetic advantages of alternative technologies over chemical absorption become most apparent. [110]

Furthermore, an overview of the existing CO<sub>2</sub> capture pathways and CO<sub>2</sub> separation technologies is presented in **Figure 3.1**.



**Figure 3.1** Classification of CO<sub>2</sub> separation technologies. [100]

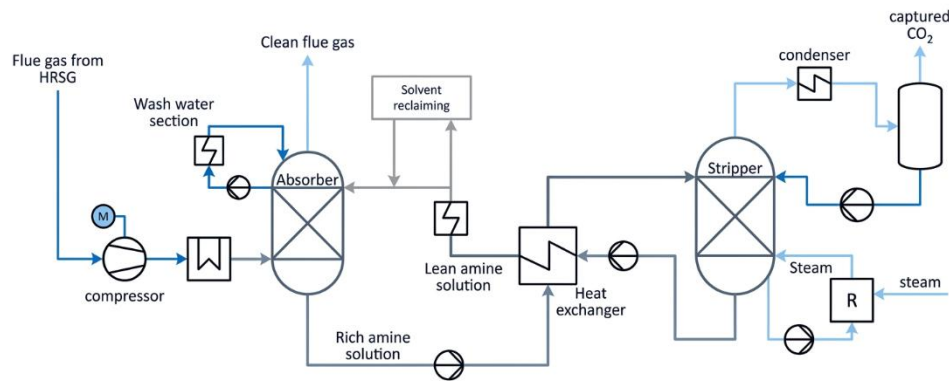
#### 3.1 Chemical Absorption (Amine Scrubbing)

Chemical absorption using aqueous amine solutions remains the most commercially mature CO<sub>2</sub> capture technology with a technology readiness level (TRL) of 9 for post-combustion applications. In this process, the CO<sub>2</sub>-containing gas is contacted counter-currently with a lean amine solvent in an absorption column where CO<sub>2</sub> is chemically bound to the amine through exothermic reactions (**Figure 3.2**). The CO<sub>2</sub> rich solvent is then regenerated in a stripper column by heating which breaks the amine CO<sub>2</sub> bond and releases a concentrated CO<sub>2</sub> stream suitable for compression and storage. [111], [112] Currently, monoethanolamine (MEA) at 20-30 wt% aqueous

solution is considered as an industrial benchmark for post-combustion carbon capture. It is a primary amine (HOCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) that reacts as in the equation and with CO<sub>2</sub> via two pathways. (Equ. 3.1) [113]



Industrial monoethanolamine (MEA) scrubbing typically delivers a CO<sub>2</sub> product purity of ≥99 mol% with a CO<sub>2</sub> capture rate of 85-95%, with 90% capture commonly adopted as the design basis in techno-economic studies. [111] Standard MEA processes require 3.5-4.0 GJ/t CO<sub>2</sub> for solvent regeneration when capturing CO<sub>2</sub> from coal-fired flue gas, resulting in a 25-30% reduction in net power plant output. [92], [113] At this performance level, the benchmark CO<sub>2</sub> avoidance cost for MEA-based post-combustion capture at commercial scale is USD 55-77/t CO<sub>2</sub>. [112] The dominant cost driver is the reboiler steam demand for solvent regeneration, which accounts for 70-80% of the total operating cost of an amine capture plant. [113]



**Figure 3.2** Process flow diagram of an amine-based post-combustion CO<sub>2</sub> capture system. [91]

To reduce this energy penalty, advanced amine solvents are being developed commercially. Methyldiethanolamine (MDEA), a tertiary amine, operates through the slower base-catalyzed hydration pathway with a heat of reaction of -60 kJ/mol versus -85 kJ/mol for MEA, reducing regeneration energy to 2.0-2.5 GJ/t CO<sub>2</sub>, which is a 30-40% reduction. [114] Blended amine systems combining the kinetic advantage of MEA or piperazine with the thermodynamic efficiency of MDEA achieve the best of both properties, as the piperazine-activated MDEA systems demonstrate regeneration duties of 2.2-2.8 GJ/t CO<sub>2</sub>. [113] Jiang et al. 2024 further identify homogeneous Brønsted acid catalysts and enzyme mimetics as a frontier for reducing the activation energy of CO<sub>2</sub> hydration and potentially enabling stripping temperatures to be reduced by 10-20°C, which would reduce steam demand by a further 10-15% and bring capture costs closer to USD 28-38/t CO<sub>2</sub>. [113] The sustainability profile of chemical absorption is, however, substantially compromised by the thermal and oxidative degradation of MEA, which generates nitrosamines, aldehydes and heat-stable salts that impose environmental management costs and regulatory constraints. [115]

### 3.2 Physical Absorption

Physical absorption exploits Henry's law CO<sub>2</sub> solubility in organic solvents, with regeneration by pressure reduction rather than thermal stripping. Applied to pre-combustion syngas, where the CO<sub>2</sub> partial pressure is 10-12 bar at a concentration around 40 mol% [116], the energy advantage over chemical solvents is decisive. Aspen Plus comparison of four solvents on an identical IGCC syngas gives a specific heating consumption of 0.333 MJ/kg CO<sub>2</sub> for Selexol and 0.350 MJ/kg CO<sub>2</sub> for Rectisol, against 3.702 MJ/kg CO<sub>2</sub> for MDEA, an eleven-fold reduction at capture rates of 90-91% for all solvents tested. [116] Selexol showed the lowest power, heating, and cooling

duty of the four and was identified as the most energy-efficient option. [116] Detailed simulation of a dual-stage Selexol unit confirms a CO<sub>2</sub> product purity of 97.2 mol% at 90 % carbon capture, rising to 97.6 mol% at 95 % capture, with 99 % H<sub>2</sub> recovery and under 20 ppmv H<sub>2</sub>S in the CO<sub>2</sub> product; however, raising capture from 90 % to 95 % increases total auxiliary power consumption by 65 %. [117] Rectisol achieves comparable capture at -40 to -60 °C, offering deeper H<sub>2</sub>S removal and lower hydrogen loss but incurring higher energy demand, higher solvent loss, and greater process complexity from the sub-zero refrigeration duty [116], [118]. In a lignite-fired IGCC techno-economic comparison, a Rectisol-based process at 89 % CO<sub>2</sub> capture required 0.30 MJe per kg of CO<sub>2</sub> captured and conditioned, giving a CO<sub>2</sub> avoidance cost of 46.7 €/t and an LCOE of 96 €/MWh. [118]

Two constraints exclude physical absorption from this study. First, feed partial pressure, as physical solvents require CO<sub>2</sub> partial pressures of 10-20 bar, [116], [117] whereas the reduction-reactor off-gas in this work carries approximately 40 mol% CO<sub>2</sub> at 2 bar, giving pCO<sub>2</sub> below 1 bar. Second, hydrogen loss: Selexol has the highest H<sub>2</sub> solubility among commercial physical solvents, and recovering 99 % of the hydrogen requires a dedicated flash drum operating at 18.5-19.5 bar solely to strip H<sub>2</sub> from the CO<sub>2</sub>-rich solvent before regeneration. [117] Both constraints arise from the same feature that makes physical absorption attractive on shifted syngas, and neither is present in the H2Loop configuration.

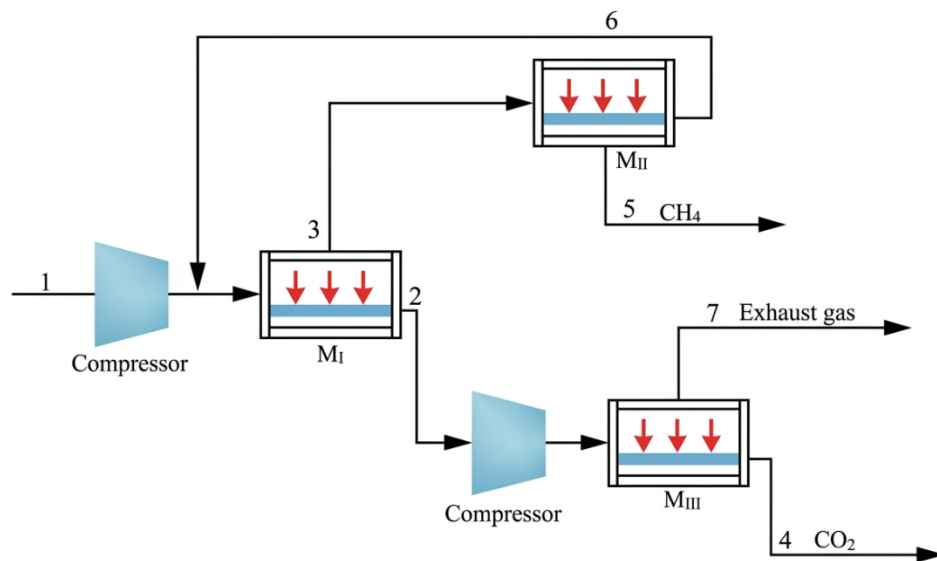
### 3.3 Adsorption-based CO<sub>2</sub> Separation

Adsorption systems operate by preferential binding of CO<sub>2</sub> to solid porous surfaces, followed by regeneration via pressure reduction (PSA), temperature increase (TSA), or combined approaches. The CO<sub>2</sub> product purity achievable from adsorption systems is substantially more dependent on process configuration than for absorption systems, because purity and recovery are in direct tension through the adsorption isotherm. Operating closer to sorbent saturation increases throughput but lowers product purity, while deeper regeneration improves purity but reduces working capacity and increases energy consumption. Single-stage PSA with zeolite 13X from post-combustion flue gas typically delivers CO<sub>2</sub> product purities of 85-95% at CO<sub>2</sub> recoveries of 70-90%, which is below the ≥95% threshold required for geological storage, necessitating multi-stage VSA or vacuum-pressure swing configurations to reach pipeline specification. [119], [120] The additional cost of multi-stage processing to achieve >95% CO<sub>2</sub> purity in adsorption systems is estimated at USD 8-18/t CO<sub>2</sub>, which is partially negating the capital cost advantages of solid-sorbent systems over liquid absorption. [121]

Advanced adsorbent materials, particularly MOFs, offer a pathway to simultaneously high purity and high recovery in fewer stages. A landmark computational screening study evaluated 55,818 experimentally characterized MOFs via grand canonical Monte Carlo simulations and machine learning process optimization. It identified thousands capable of achieving within 4% of the practical energy limit for P/VSA capture from both dry and humid flue gas streams while meeting the simultaneous targets of ≥95% CO<sub>2</sub> purity and ≥90% recovery targets that are difficult to achieve simultaneously with conventional zeolite or carbon PSA in a single stage. [122] MIL-160(Al) is synthesizable at kilogram scale under green aqueous conditions at an estimated cost of USD 8-15/kg which demonstrates low CO<sub>2</sub> heat of adsorption, fast mass transfer, water stability and SO<sub>2</sub> resistance that collectively position it as the most commercially realistic near-term MOF candidate for post-combustion capture with projected total capture costs of USD 35-55/t CO<sub>2</sub> at the purity targets above 95% purity and 90% recovery. [123] For direct air capture (DAC) applications, amine-functionalized solid sorbents regenerated in TVSA cycles achieve CO<sub>2</sub> product purities of ≥99%. It is sufficient for most utilization applications at energy consumptions of 1,500-2,500 kWh/t CO<sub>2</sub> and current commercial costs of USD 300-1,000/t CO<sub>2</sub>, which is the highest in the portfolio due to the thermodynamic cost of concentrating CO<sub>2</sub> from 420 ppm in ambient air. [112]

### 3.4 Membrane Separation

Membrane separation is based on the selective permeation of gas species through a thin polymeric or composite barrier driven by a transmembrane partial pressure gradient. Both polymeric materials such as polysulfone and polyimide, and inorganic or hybrid membranes such as zeolitic, carbon molecular sieve, and mixed-matrix systems are applied for CO<sub>2</sub>-selective transport, with current technologies reaching TRL of approximately 6-7. CO<sub>2</sub> preferentially permeates over N<sub>2</sub> in polymer membranes due to its higher condensability (critical temperature 31 °C versus -147 °C), which enhances dissolution in the polymer matrix despite only a modest difference in kinetic diameter. [124] Unlike competing technologies, membrane systems operate as continuous steady-state processes without phase changes, cyclic pressure or temperature swings, or solvent requirements, resulting in significantly reduced operational complexity and maintenance demands. Pilot systems have demonstrated capture rates above 90%, and the U.S. Department of Energy membrane program targets capture costs of approximately USD 40/t CO<sub>2</sub>. [125]



**Figure 3.3** Multi-stage membrane separation process for CO<sub>2</sub> capture. [126]

Membrane-based CO<sub>2</sub> separation is subject to a key limitation described by the Robeson upper bound, an empirical relationship showing that CO<sub>2</sub>/N<sub>2</sub> selectivity and CO<sub>2</sub> permeability in polymer membranes are inherently inversely correlated. The second is the recovery-purity trade-off inherent to single-stage operation. [124] For a feed containing 15 vol% CO<sub>2</sub> at 10 bar, a CO<sub>2</sub> recovery of 60% produces a permeate containing approximately 61 vol% CO<sub>2</sub>; increasing the recovery to 80% and 90% reduces the permeate purity to 52% and 45%, respectively, while the additional membrane area required to raise recovery from 80% to 90% is nearly equal to that required for the initial 60% recovery. [126] Such purities are critically below the ≥95% requirement for geological storage and pipeline transport, rendering single-stage membrane systems unsuitable as standalone capture technologies for these applications. From an economic perspective, gas compression rather than the membrane itself dominates the process cost, typically accounting for at least 50% of the capital expenditure and 60-80% of the operating expenditure. [126]

Reaching pipeline specification from dilute streams therefore requires multi-stage configurations (typically two to three stages), (**Figure 3.3**). For blast furnace gas specifically, Ramírez-Santos et al. optimized multistage membrane configurations for a feed containing 23.2 mol% CO<sub>2</sub>, 22.6 mol% CO, 50.3 mol% N<sub>2</sub> and 3.9 mol% H<sub>2</sub> using Polaris membrane permeances. They reported

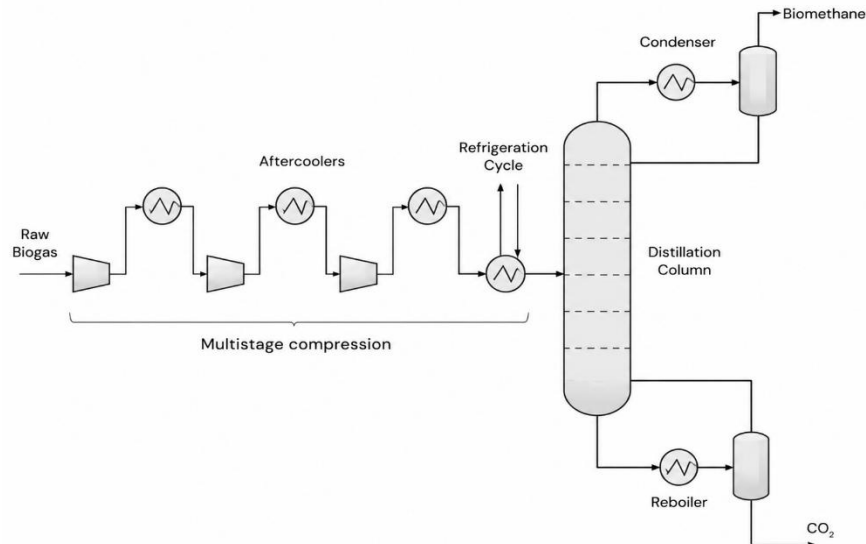
CO<sub>2</sub> separation costs of 29.0-75.7 EUR/t CO<sub>2</sub> for two-stage systems and 28.9-45.1 EUR/t CO<sub>2</sub> for three-stage systems, corresponding to CO<sub>2</sub> recoveries of 90–99% and product purities of 96.1-99.5 mol%, at an assumed electricity price of 0.044 EUR/kWh. Adding a fourth membrane stage reduced the separation cost by less than 1 EUR/t CO<sub>2</sub>, indicating diminishing economic returns. [127] These results demonstrate that pipeline-grade purity is achievable from BFG-like streams, but at costs that depend strongly on the recovery target. Membrane systems are consequently also deployed as a pre-concentration or bulk-separation step in hybrid configurations, upgrading dilute flue gas to intermediate concentrations before a second-stage process (absorption, adsorption or cryogenic) completes the purification, which can be more economical than either technology alone. [124]

Recent advances in membrane materials have begun to systematically overcome the permeability-selectivity trade-off imposed by the Robeson upper bound. Polymers of intrinsic microporosity (PIMs) breach this bound through ultra-high CO<sub>2</sub> permeability of 2,300-4,000 Barrer, though their CO<sub>2</sub>/N<sub>2</sub> selectivity remains moderate at 10-20. [128] Mixed-matrix membranes address the selectivity deficit by embedding MOF or zeolite fillers within a polymer host, combining substantially higher selectivity with high permeability. [129] Where polymer membranes remain constrained by the bound, ceramic molten-carbonate membranes operating at high temperature bypass it entirely through an ionic CO<sub>2</sub> transport mechanism, conferring near-complete selectivity. However, high module costs currently limit deployment. [130] Furthermore, Karatas et al. (2023) demonstrated that refurbished ceramic modules retain 98% removal efficiency at 40-60% lower cost. [131] Looking across material classes, Ochiai et al. used machine learning to screen 3,219 polymer candidates and identified approximately 500 that simultaneously exceed the Robeson bound while exhibiting predicted biodegradability, suggesting that the next generation of membranes may resolve the selectivity, cost, and end-of-life challenges within a single material framework. [132] Despite these promising performances, membrane separation was not selected for detailed evaluation in this work. The scope agreed with the industrial partner comprises one low-temperature physical separation process and one high-temperature solid-looping process, both governed by phase and reaction equilibria and therefore suitable for modelling in Aspen Plus using a common thermodynamic framework. In contrast, membrane performance is determined by material permeance, module geometry, and stage-cut optimisation. The multistage configurations required to achieve the target product specification [127], would therefore require experimental permeation data for the specific membrane material and gas mixture, which cannot be reliably assessed using an equilibrium-based flowsheet model alone. Nevertheless, membranes remain a promising option for the enriched off-gas considered in this study and are recommended for future dedicated experimental and techno-economic investigations.

### 3.5 Cryogenic Separation

Cryogenic separation exploits differences in phase-change temperature between CO<sub>2</sub> and the co-components of the gas stream, principally N<sub>2</sub> (boiling point –196 °C), to achieve separation by controlled cooling (**Figure 3.4**). [133] CO<sub>2</sub> has an unusually high triple-point pressure of 518 kPa; below that pressure no liquid phase exists, and CO<sub>2</sub> desublimates directly to a solid, at temperatures between 130 and 180 K depending on its concentration in the gas. [134] Based on these thermodynamic principles, cryogenic CO<sub>2</sub> separation can be broadly classified into two process families according to the governing phase equilibrium. Desublimation, governed by solid-vapor equilibrium, operates at near-atmospheric pressure and is suited to dilute post-combustion flue gases containing 5-15 mol% CO<sub>2</sub>. Cryogenic distillation and condensation, governed by liquid-vapor equilibrium, require elevated pressure and have been applied to streams of higher CO<sub>2</sub> content in the range of 20-70 mol%, such as natural gas, shifted syngas and biogas. [134] The reduction-reactor off-gas considered in this work, at approximately 40 mol% CO<sub>2</sub>, falls within

the latter range, and the process developed in Chapter 4 is accordingly configured for pressurized distillation rather than a desublimation process.



**Figure 3.4** Cryogenic distillation process for CO<sub>2</sub> separation. [134]

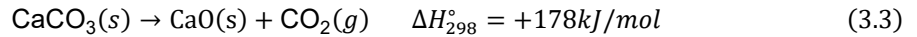
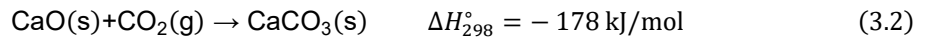
Cryogenic CO<sub>2</sub> separation is capable of producing very high product purity, with CO<sub>2</sub> purities exceeding 99.9% and recoveries of 90-99% reported simultaneously. [133], [134] Since the captured CO<sub>2</sub> is recovered directly in the liquid phase, additional downstream compression is largely avoided. The separation is driven solely by temperature differences and therefore requires no solvents, sorbents, or membranes, resulting in high selectivity, low water consumption, and simultaneous removal of impurities such as SO<sub>x</sub> and NO<sub>x</sub>. [133], [134]

Cryogenic separation also exhibits high thermodynamic efficiency. The theoretical minimum work required to recover 90% of CO<sub>2</sub> from a gas stream containing 15 mol% CO<sub>2</sub> is 140 kJ<sub>e</sub>/kg CO<sub>2</sub> for the separation duty alone. When liquefaction and compression to 50 bar are included, this minimum increases to approximately 400 kJ<sub>e</sub>/kg CO<sub>2</sub>. These values represent thermodynamic limits determined by the specified feed composition, recovery level, and final product state, and are independent of the separation technology applied. For cryogenic processes with internal cold-energy recovery, an overall energy consumption of approximately 450 kJ<sub>e</sub>/kg CO<sub>2</sub> at 90% recovery has been reported, which is close to the minimum work requirement for the same system boundary. In comparison, amine-based absorption requires approximately 4-6 MJ/kg CO<sub>2</sub> when solvent regeneration, compression, and transport are included, corresponding to an energy demand roughly one order of magnitude higher than the same thermodynamic limit. [133] A system-level assessment of cryogenic CCC deployment across Denmark's energy system found that CCC can reduce wind power capacity requirements by approximately 47% and annual system costs by nearly 45% relative to amine-based alternatives, owing to its superior thermodynamic efficiency and its demand-flexibility capability in renewable-dominated electricity systems. The study further quantified that integrating CCC with energy storage cuts variable costs by an additional 2.5% [135]. The integration of cryogenic separation with LNG regasification, which provides a low-cost cold energy source from the LNG cold reservoir, offers a pathway to reduce refrigeration operating costs by an estimated 25-40% in coastal and port industrial contexts, potentially reducing total capture costs to USD 50-70/t CO<sub>2</sub> in these favorable

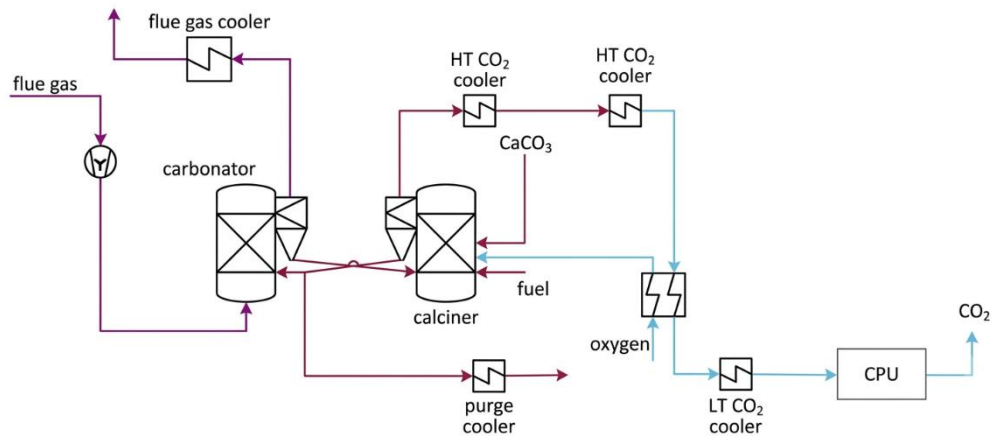
configurations. [136] The TRL of cryogenic CO<sub>2</sub> capture subvariants ranges from 4-5 for novel sublimation processes to 6-7 for cryogenic distillation applied to concentrated CO<sub>2</sub> streams.

### 3.6 Calcium Looping

Calcium looping (CaL) exploits the reversible thermochemical cycle, which cycles between a carbonator at 600-700°C and a calciner at 880-950°C in interconnected circulating fluidized bed (CFB) reactors, (Equ. 3.2 and Equ. 3.3), (**Figure 3.5**).



The economics of CaL are underpinned by the extraordinary cheapness of the CaO sorbent derived from natural limestone, at €10-25/t contrasting sharply with high unit cost and degradation losses of amine solvents and by the potential for high-grade heat recovery from the exothermic



**Figure 3.5** Process flow diagram of the calcium looping CO<sub>2</sub> separation process. [94]

carbonation reaction at 600-700°C, which can generate electricity in a steam cycle and partially offset the calciner energy demand. Techno-economic assessments of large-scale power plants report CO<sub>2</sub> avoidance costs of USD 105/t CO<sub>2</sub> for a first-of-a-kind CaL retrofit, with a markedly lower energy penalty than MEA absorption (36% against 28% net plant efficiency) but a higher capital cost and levelized cost of electricity under comparable boundary conditions, the difference being driven by capital intensity rather than by sorbent cost. [137] Pilot plant operations at TRL 7 by Arias et al. have confirmed CO<sub>2</sub> capture efficiencies approaching 99%, although the calciner outlet reaches only around 93 vol% CO<sub>2</sub> and requires a downstream purification unit to meet pipeline specification, demonstrating technical feasibility at meaningful scale and materially advancing the technology toward commercial deployment. [137], [138]

An innovative solar-integrated calcium looping (CaL) configuration, in which concentrated solar power (CSP) provides the heat required for calcination, eliminates the need for oxyfuel combustion and the associated energy demand and capital cost of the air separation unit (ASU). Process simulations demonstrated a carbonator CO<sub>2</sub> capture efficiency of 90% and a 93% reduction in annual CO<sub>2</sub> emissions, while requiring a specific primary energy consumption for CO<sub>2</sub> avoided of only 0.24 MJ/kg CO<sub>2</sub>. The system achieved a net plant efficiency of 40.95%, only slightly lower than the 41.82% of the unabated reference plant. Although the heliostat field accounted for 63-67% of the capture plant's capital cost, the levelized cost of electricity was estimated at approximately 111 \$/MWh, compared with 76 \$/MWh for the reference plant. [139] A techno-economic assessment of CaL retrofit to a German waste-to-energy (WtE) plant treating 200 kt of waste per year employing Aspen Plus process modeling also identified a novel integrated

concept in which pretreated waste fires the calciner, achieving a CO<sub>2</sub> avoidance cost of 27 €/t CO<sub>2</sub> inclusive of compression, reported as the lowest capture cost from waste incineration documented in the peer-reviewed literature. [140] This cost level is competitive with current EU ETS carbon prices (70-90 €/t CO<sub>2</sub>), which represents an important milestone for the economic viability of CaL in the near term. [141]

However, the primary technical barrier is sorbent sintering, as the progressive thermal densification of CaO during repeated high-temperature cycling reduces capture capacity by up to 50% over repeated cycles from a nominal 0.78 g CO<sub>2</sub>/g CaO toward a residual conversion of only a few percent after extended cycling. This necessitates continuous limestone make-up addition at a rate of approximately 0.12-0.18 kg limestone/kg CO<sub>2</sub> captured at commercial scale, which adds EUR 2-3/t CO<sub>2</sub> to the operating cost. Wang et al. reviewed 1,042 reported CaO-based sorbent materials, which identify structural support incorporation such as Al<sub>2</sub>O<sub>3</sub>, MgO, CeO<sub>2</sub>, and Y<sub>2</sub>O<sub>3</sub>, together with sol-gel, template, and combustion synthesis routes, as the most effective mitigation strategies, with bi-dopant systems such as Fe/Mn, Mn/Zr, and Al/Ce/Zr showing the lowest decay rates over 10-20 cycles. [142] From a sustainability perspective, the spent sorbent (CaO/CaCO<sub>3</sub>) is directly compatible with cement kiln feed, which creates a circular economy integration that both reduces CaL waste disposal costs and offsets cement production CO<sub>2</sub>. Crediting the spent sorbent at 50 €/t CaO reduces the reported WtE avoidance cost from 27 to 17.5 €/t CO<sub>2</sub>. [140]

The synergy between calcium looping and the iron-oxide-based H2Loop chemical looping process is particularly noteworthy. Both processes operate at similar temperature ranges (600-1000°C), use inexpensive mineral-based materials, and follow cyclic batch-mode operation. A combined iron-calcium looping system could simultaneously produce hydrogen via the iron oxide cycle, capture CO<sub>2</sub> via the calcium carbonate cycle, and manage the thermal balance of the system, where the exothermic carbonation reaction can supply part of the heat required for feed preheating and steam raising within the system. Furthermore, pilot-scale calcium looping facilities (TRL 6-7) have been operated at the 1-2 MWth scale, namely, the La Pereda plant in Spain (1.7 MWth) and the Darmstadt Technical University facility (1 MWth). [140], [143]

### 3.7 Overall Assessment

The evidence assembled in this chapter reveals a technology landscape in which cost, TRL, energy penalty and sustainability profile vary dramatically across the six families and in which the optimal choice is irreducibly context-dependent. For large-scale post-combustion capture from dilute (4-15% CO<sub>2</sub>) atmospheric-pressure flue gas, chemical absorption with amine solvents at USD 55-77/t CO<sub>2</sub> and TRL 9 remains the deployed benchmark with blended amine formulations capable of reducing costs to the lower end of this range. [113] Physical absorption at 46.7 €/t CO<sub>2</sub> in a lignite IGCC application dominates high-pressure pre-combustion and natural gas sweetening applications where its low regeneration energy and TRL 9 status provide decisive advantages. Calcium looping at 27-143 €/t CO<sub>2</sub> depending on the degree of process integration is strategically positioned to challenge amine scrubbing in cement and steel decarbonization, where its circular economy integration with cement production, [144] and pilot-demonstrated 99% capture efficiency represent compelling near-term commercialization arguments. [138] The innovative waste-to-energy integrated configuration at 27 €/t CO<sub>2</sub> is the most cost-competitive emerging-technology result in the peer-reviewed literature. [140] Membrane technology with DOE-targeted costs of ~USD 40/t [125], three-stage configurations achieving 28.9-45.1 €/t CO<sub>2</sub> on blast furnace gas, [127] no hazardous chemicals and intrinsic modularity represent perhaps the strongest near-term commercialization candidate among emerging technologies, with the ML-driven biodegradable membrane frontier Ochiai et al., 2025 addressing long-term sustainability concerns. [132] It should be noted that these figures originate from studies at industrial scale, typically 10<sup>5</sup>-10<sup>6</sup> Nm<sup>3</sup>/h, and are therefore not directly comparable with the small-scale case

evaluated in Chapters 4 and 5. They are presented here to rank the technology families, not to predict the costs of the present configuration.

The overarching conclusion of this assessment is that no single CO<sub>2</sub> separation technology can be considered universally optimal; rather, an effective decarbonization portfolio requires the systematic matching of each technology to the operating conditions under which it exhibits maximum performance and efficiency. Accordingly, amine absorption remains the preferred technology for large post-combustion emission sources, and physical absorption is most effective for high-pressure gas streams. At the same time, membrane systems provide a promising alternative for modular and medium-scale CO<sub>2</sub> capture applications. In the specific context of the H2Loop process, however, the assessment narrows the field considerably because H2Loop already produces a concentrated, high-temperature CO<sub>2</sub> stream; the two technologies that most naturally exploit these conditions emerge as the strongest candidates. Calcium looping, which operates at compatible temperatures of 600-950°C and directly leverages the concentrated CO<sub>2</sub> stream for high-efficiency carbonation, and cryogenic separation, which becomes increasingly energy-efficient and cost-effective as CO<sub>2</sub> concentration rises above 40 vol%, both offer a pathway to a high-purity CO<sub>2</sub> product stream with lower specific energy penalties than would be required for the same separation applied to a dilute flue gas. These two technologies therefore represent the most technically and economically rational downstream capture options for the H2Loop system.

## 4 Methodology

The primary objective of this study is the simulation-based evaluation of the technical and economic performance of two downstream CO<sub>2</sub> separation technologies, namely cryogenic distillation and calcium looping, applied to the concentrated CO<sub>2</sub> off-gas produced by the H2Loop chemical looping reduction reactor operating on blast furnace gas. This chapter presents the methodology adopted to develop and evaluate these technologies. Section 4.1 outlines the overall modeling approach and common design basis, while Section 4.2 describes the feed stream characterization. Section 4.3 presents the H2Loop process model, which generates the common CO<sub>2</sub>-rich stream supplied to both separation routes. Sections 4.4 and 4.5 describe the cryogenic distillation and calcium looping models, respectively. Finally, Section 4.6 presents the techno-economic assessment (TEA) methodology used to compare the economic performance of the two CO<sub>2</sub> separation technologies. Both technologies are additionally benchmarked against conventional monoethanolamine (MEA) absorption using published literature data, which represents the current industrial reference for post-combustion CO<sub>2</sub> capture. [145], [146]

### 4.1 Modeling Approach: Aspen Plus Process Simulation

To ensure a consistent and fair comparison, both separation technologies were evaluated using the same CO<sub>2</sub>-rich feed stream generated by the common upstream H2Loop simulation. Therefore, differences in capture performance and capture cost reflect the intrinsic characteristics of each separation technology rather than variations in feed composition or operating conditions. Differences in revenue, however, additionally arise from the distinct product specifications delivered by each technology and the corresponding market assumptions applied for these products (Section 4.6.1).

The process models were developed using an integrated process modeling approach in Aspen Plus® V14 (AspenTech, 2023), which is officially licensed by Rouge H2 Engineering AG. Aspen Plus was selected because it provides validated thermodynamic property methods, an extensive library of unit operation models, and established capabilities for modeling both high-temperature gas–solid reaction systems and cryogenic separation processes. The software includes rigorous equilibrium reactor models, multistage distillation columns (RadFrac), flash separators, heat exchangers, and compressor models required to represent the H2Loop, cryogenic distillation, and calcium looping process configurations investigated in this work. [147], [148], [149], [150]

The overall modeling methodology adopted in this study is illustrated in **Figure 4.1**. First, the overall process configurations, system boundaries, and design basis were established from published literature and industrial process information supplied by RG-H<sub>2</sub>. Subsequently, an appropriate thermodynamic framework was selected and applied consistently throughout all simulations. The H2Loop process was then modeled to generate the concentrated CO<sub>2</sub> rich process stream required for downstream separation. Using this identical feed stream, independent steady-state models of the cryogenic distillation and calcium looping processes were developed, simulated, and verified before proceeding to the techno-economic assessment. This sequential modeling strategy simplified model convergence, facilitated independent validation of each subsystem, and ensured consistent comparison between the two capture technologies.

The BFG feed to the H2Loop reduction reactor was defined on a dry volumetric basis using the representative industrial composition presented in Section 4.2. The base-case plant processes 1,000 Nm<sup>3</sup>/h of BFG at 2 bar and 25 °C, with an annual operating time of 8,059.2 h/year (92% availability). This capacity was selected as the reference case to enable direct comparison of energy consumption, capital investment, and CO<sub>2</sub> capture performance independent of plant scale. The functional unit for the techno-economic assessment is one tonne of CO<sub>2</sub> captured. To evaluate scale effects, two larger cases of 68,500 and 274,000 Nm<sup>3</sup>/h were also investigated,

representing a single industrial off-gas stream and a full integrated steelwork, respectively. The BFG composition and principal stream quantities are summarized in **Table 4.1**.

**Table 4.1** Base-case blast-furnace-gas feed definition (Case 1, 1,000 Nm<sup>3</sup>/h)

| Quantity                             | Value                                                                            | Unit               | Basis                                   |
|--------------------------------------|----------------------------------------------------------------------------------|--------------------|-----------------------------------------|
| <b>BFG molar composition</b>         | CO 22.29 / H <sub>2</sub> 3.57 /<br>CO <sub>2</sub> 21.65 / N <sub>2</sub> 52.49 | mol %              | Aspen feed specification                |
| <b>BFG mass flow</b>                 | 1,362.9                                                                          | kg/h               | = 1,000 Nm <sup>3</sup> /h × 30.5 g/mol |
| <b>BFG annual throughput</b>         | 10,983.9                                                                         | t/y                | hourly × 8,059.2 h                      |
| <b>Lower heating value (derived)</b> | 3.20                                                                             | MJ/Nm <sup>3</sup> | composition-weighted                    |
| <b>Operating hours</b>               | 8,059.2                                                                          | h/y                | 92 % × 8,760 h                          |

The selection of an appropriate thermodynamic property method is essential for reliable phase-equilibrium and energy calculations in process simulation. Therefore, the Peng-Robinson equation of state was selected as the global property method because it provides reliable thermodynamic predictions for CO, H<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O-rich gas mixtures over the operating range of 25-900 °C and up to 43 bar, and it has been widely applied in gas-processing and high-temperature calcium-looping studies. [151], [152]

As equations of state do not adequately represent crystalline solids, the oxygen carriers (Fe, FeO, Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>), support materials (Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>), and calcium-looping sorbents (CaO and CaCO<sub>3</sub>) were modeled as conventional solids using thermodynamic data from the Aspen SOLIDS, INORGANIC and PURE databanks. [153] Fluid and solid species were assigned to the MIXED and CISOLID sub streams, respectively, while particle-size effects were neglected because the equilibrium model does not consider particle-scale transport phenomena.

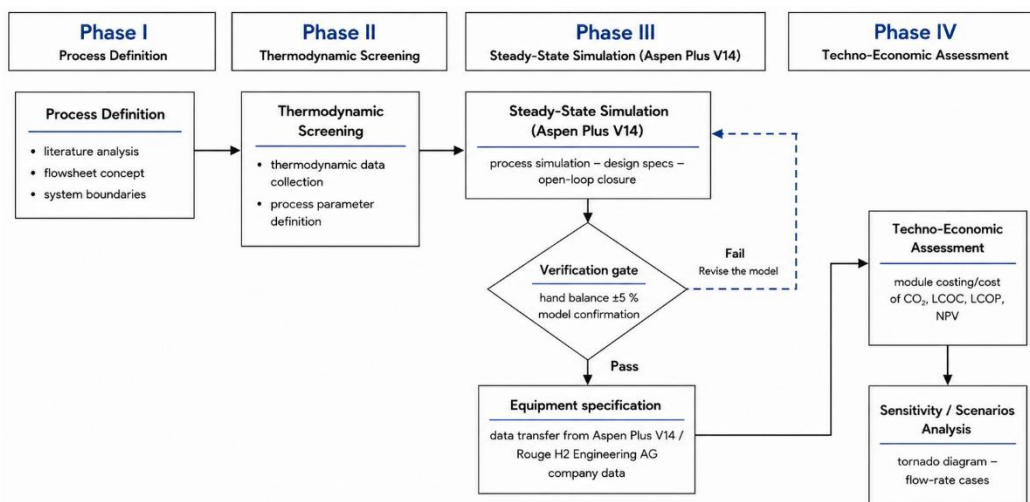
The technical performance of each process was evaluated using a common set of performance indicators, comprising:

- CO<sub>2</sub> capture efficiency (%): molar fraction of inlet CO<sub>2</sub> recovered in the product stream, defined on a CO<sub>2</sub> basis at the separation-section battery limits.
- CO<sub>2</sub> product purity (vol%): concentration of CO<sub>2</sub> in the final captured product stream
- Specific energy consumption (MJ/kg CO<sub>2</sub> captured): total thermal and electrical energy demand per unit mass of CO<sub>2</sub> captured

Each capture route was designed according to the CO<sub>2</sub> purity specification required for its intended end use rather than a common purity target:

- The cryogenic distillation route, in which the CO<sub>2</sub>-rich gas is compressed, dried over a molecular-sieve adsorber (MS-101) and separated in a low-temperature distillation column (DC-01) to yield a food-/merchant-grade product (≥ 99.9 mol %) delivered at 43 bar.
- The calcium-looping route, in which CO<sub>2</sub> is chemically separated by carbonation of a CaO sorbent at 650 °C and released in an electrically heated calciner at 900 °C which is yielding a ≥ 95 mol % product delivered at 21 bar to a greenhouse-supply pipeline.

Following process development, all simulations were performed under steady-state conditions. Although the H2Loop process employs parallel fixed-bed reactors operating in cyclic mode, transient behavior was neglected, as the objective was to evaluate overall process performance and compare the two CO<sub>2</sub> separation technologies. A fixed-bed reactor configuration was adopted because it avoids particle circulation, pellet attrition, and the associated solids-handling equipment required in moving- and fluidized-bed reactors.



**Figure 4.1** Methodological framework used for process modelling, verification, and techno-economic assessment.

Additionally, a particular modeling challenge in the calcium- and iron-based looping systems concerns the representation of solid circulation between reactors. To address this, an open-loop (matched-stream) approach was adopted instead of implementing explicit recycle loops. The inlet solids to each reactor were specified to match the temperature, composition, and mass flow rate of the corresponding outlet stream from the paired reactor, thereby maintaining the iron and calcium inventories. This approach was adopted because recycle loops involving CISOLID streams often exhibit poor convergence in Aspen Plus, particularly in flowsheets containing multiple heterogeneous equilibrium reactors. It also reflects the H2Loop concept, in which switching fixed-bed reactors approximate cyclic operation without continuous solids transport. Consequently, the matched-stream approach provides a robust representation of cyclic steady-state operation.

Model predictions were verified through mass and energy balance closure, hand calculations, comparison with published literature, and internal process information supplied by RG-H<sub>2</sub>. Verification was completed before any economic calculations were undertaken to ensure that the process models accurately represented the intended system behavior. Only after satisfactory verification were the simulation results transferred to the techno-economic assessment, where equipment, capital costs, operating costs, and overall economic performance were evaluated. To ensure transparency and reproducibility, all modeling data, assumptions, and supporting information are documented in Appendix.

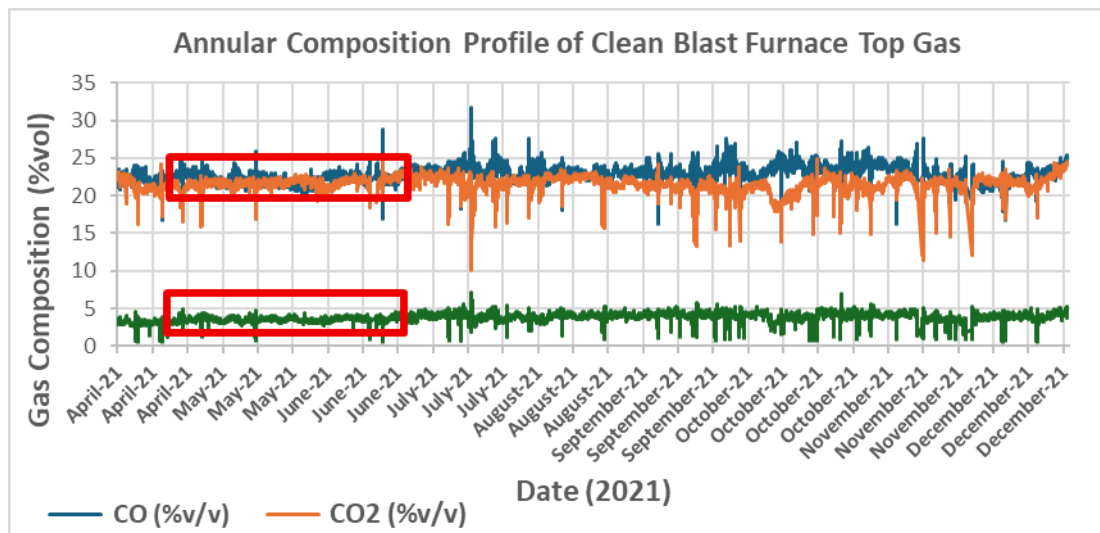
## 4.2 Stream Characterization

The blast furnace gas composition data used in this study were obtained directly from an industrial project partner of Rouge H2 Engineering and correspond to operational measurements recorded throughout the year 2021 because this period was specifically identified as representing more stable blast furnace operation relative to subsequent years such as 2023. The annual time-series profile is presented in **Figure 4.2**, which illustrates the measured dry-basis volumetric

concentrations of CO, CO<sub>2</sub> and H<sub>2</sub> across the full year. The nitrogen balance was calculated as the remainder to 100 vol% as it was not directly measured by the installed analyzer. The mean gas composition was determined from a period of continuous normal operation, excluding intervals affected by maintenance shutdowns and process upsets, which are not representative of the intended design case. This period extends from 22 April 2021 to 1 July 2021 and is highlighted in red in the graph to indicate its selection as the reference operating window.

The resulting average composition is 22.29 vol% CO, 21.65 vol% CO<sub>2</sub>, 3.57 vol% H<sub>2</sub>, and 52.49 vol% N<sub>2</sub> (**Figure 4.2**), which is consistent with the typical composition ranges reported in the literature for conventional air-blown blast furnaces. The adopted composition therefore represents normal operation rather than an annual average including outages; the influence of feed-composition variability and of trace components not included in the model is identified as future work in Chapter 7, where low, central and high feed cases are recommended. To ensure sufficient driving force through the downstream process, the blast furnace gas is compressed to 2 bar using an air blower to overcome the pressure losses across the subsequent process units. [23], [154]

Analysis of the time-series data in **Figure 4.2** indicates that anomalous excursions arise from short-term maintenance stoppages of the blast furnace, during which gas composition deviates



**Figure 4.2** Composition profile of clean blast furnace top gas in 2021, with the selected representative operating period highlighted.

from steady-state conditions. Periods containing undefined values are attributed to instrumentation unavailability rather than actual process changes and were therefore excluded from the representative dataset used for model inputs. Outside of these disturbances, the concentrations of CO and CO<sub>2</sub> fluctuate within a relatively narrow range of approximately 18-26 vol%, which reflects inherent but controlled variability associated with burden descent behavior, tuyere operating conditions, and fluctuations in raw material quality. In contrast, the H<sub>2</sub> concentration, although lower in absolute terms (approximately 2-6 vol%), exhibits comparatively larger relative variability. This behavior is primarily driven by variations in the moisture content of the injected pulverized coal and the coke charge.

**Table 4.2** Composition of the representative clean blast furnace gas (BFG) feed (vol.%)

| CO%    | CO <sub>2</sub> % | H <sub>2</sub> % | N <sub>2</sub> % |
|--------|-------------------|------------------|------------------|
| 22.287 | 21.653            | 3.574            | 52.486           |

The gas composition was measured by an extractive analyzer installed downstream of the gas cleaning system, which is at the point of injection into the plant gas network and therefore reflects

the cleaned gas quality rather than the raw top gas exiting the furnace throat. Within the analyzer, CO and CO<sub>2</sub> concentrations are determined by infrared detection while H<sub>2</sub> is quantified via a thermal conductivity detector. Crucially, the analyzer incorporates an integrated gas cooler to remove moisture prior to measurement, and consequently, the Aspen Plus H2Loop feed stream is defined on a dry basis consistent with this. Furthermore, prior to any downstream utilization in the H2Loop process, blast furnace gas must undergo a multi-stage cleaning sequence to meet the compositional and purity requirements of the gas grid and downstream reactors. As the top gas exits the blast furnace, it carries significant quantities of dust, zinc oxide, carbon particles, cyanides (HCN), ammonia (NH<sub>3</sub>) and sulfur compounds. [154] This cleaning step is essential not only to protect downstream equipment but also to prevent trace contaminants from poisoning or deactivating the iron oxide oxygen carrier during cyclic redox operation.

The variability observed in the BFG composition has direct consequences for CO<sub>2</sub> capture efficiency in the H2Loop reduction reactor. Thermodynamically, producing H<sub>2</sub> requires deep reduction of the oxygen carrier into the FeO/Fe regime, as only reduced iron can split steam to produce H<sub>2</sub>. However, reduction beyond the Fe<sub>3</sub>O<sub>4</sub> stability field increases the equilibrium CO/CO<sub>2</sub> ratio, resulting in incomplete CO oxidation and CO slip that dilutes the captured CO<sub>2</sub> stream. [76], [155] At elevated CO/CO<sub>2</sub> ratios and moderate temperatures, the gas may also enter the carbon-forming region of the Boudouard equilibrium on the Baur-Glässner diagram, promoting carbon deposition on the oxygen carrier and reducing its oxygen transfer capacity. [156]. Consequently, stable BFG composition is essential to maintain the balance between H<sub>2</sub> production, CO<sub>2</sub> purity, and overall capture efficiency.

### 4.3 H2Looping Modeling

The common front end converts blast furnace gas (BFG) into a hydrogen-rich product stream and a concentrated CO<sub>2</sub> stream for downstream separation. It is based on a twin fixed-bed reactor configuration comprising a reduction reactor (R-101) and a steam-oxidation reactor (R-102) as shown in **Figure 4.3**. During operation, one reactor undergoes reduction by BFG while the second is regenerated by steam oxidation. The gas flow is switched every 30 min, resulting in alternating reduction and oxidation cycles. In the steady-state Aspen Plus model, this cyclic operation is represented by two continuously operating reactor blocks corresponding to the time-averaged behavior of the switching reactor pair. The iron-based oxygen carrier is assumed to sustain 3,000 redox cycles, in line with the long-term cyclic stability demonstrated by Chung et al. (2017). [157] This durability allows the carrier to be treated almost as a one-time charge rather than a consumable, with 100 % retention assumed thereafter. Rather than being replaced, the carrier is periodically re-dispersed and regenerated at 20 % of the fresh-pellet price, which is consistent with catalyst-regeneration practice. [157]

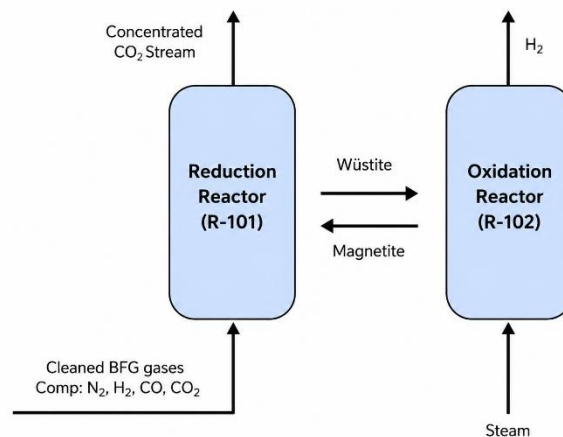
The cleaned BFG enters the process at 25 °C and 2 bar, after which it is heated to 850 °C before entering the reduction reactor. In the reduction step, the oxygen carrier is reduced by the CO and H<sub>2</sub> present in the BFG according to Equ. 4.1 and Equ. 4.2:



The reduced carrier is subsequently regenerated in the steam-oxidation reactor operating at 700 °C, where hydrogen is produced through Equ. 4.3:



For reactor sizing and material balance calculations, the theoretical oxygen-carrying material inventory and steam requirement were determined from the reaction stoichiometry assuming 100% conversion of the oxygen carrier during both the reduction and oxidation steps. These values provide the upper-bound material requirements for the base-case process and were used as the basis for the Aspen Plus model. Based on the reaction stoichiometry, complete conversion of the reducing gas would require 11.54 kmol/h of  $\text{Fe}_3\text{O}_4$ . The oxygen carrier is a supported material in which  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  act as inert stabilisers, and the carrier stream was specified at a total molar flow of 11.54 kmol/h, so that with 10 wt% inert support, as described below, the active magnetite feed is 9.38 kmol/h within a total solid flow of 2,412 kg/h. In the stoichiometric-FeO representation this active fraction is completely consumed, so that the reductant conversion reported at the beginning of Chapter 5 is limited by the active carrier supply rather than by the gas-solid equilibrium, whereas in the wüstite representation 4.19 kmol/h of  $\text{Fe}_3\text{O}_4$  remain unreacted and the conversion is equilibrium-limited. The steam feed to the oxidation reactor was set to 9.38 kmol/h, corresponding to the stoichiometric requirement for complete regeneration of the equilibrium amount of FeO produced in the reduction reactor. Although this feed is stoichiometric for complete regeneration, its conversion is limited by equilibrium to 46.1%, so that only 4.32 kmol O/h are restored to the carrier compared with the 9.38 kmol O/h withdrawn during the stoichiometric-FeO reduction step. The remaining steam is condensed and recycled. The consequences of the different representations are discussed at the beginning of Chapter 5. Additionally, the oxidation stage was also modelled using the iron-deficient wüstite phase ( $\text{Fe}_{0.947}\text{O}$ ). Its Gibbs-energy data place the  $\text{Fe}_3\text{O}_4/\text{Fe}_{0.947}\text{O}$  equilibrium at a lower gas oxidation degree, so that the reduction reaches equilibrium earlier and transfers less lattice oxygen, resulting in lower CO conversion and a lower equilibrium  $\text{CO}_2$  concentration.



**Figure 4.3** Front-end process configuration.

Both configurations use identical iron-looping reactors and differ only in feed heat integration. In the cryogenic route, blast-furnace gas is preheated to 639 °C in HX-101 (258 kW) and heated to 850 °C by HE-101 (98 kW). In the calcium-looping route, four heat exchangers (HX01-HX04) preheat the gas to 849 °C, reducing the electric trim (HE01) to 0.4 kW. In both configurations, oxidation steam is preheated from 200 °C using the R-102 effluent before entering the oxidizer. The complete configurations are shown in the process flow diagrams (**Figure 4.9** and **Figure 4.12**). The iron oxide oxygen carrier is defined in the Aspen Plus component list as a CISOLID feed stream consisting of 90 wt% iron (II, III) oxide ( $\text{Fe}_3\text{O}_4$ , magnetite) and 10 wt% inert filler materials (which is 5%  $\text{Al}_2\text{O}_3$  and 5 wt%  $\text{ZrO}_2$ ), the latter representing the ceramic binder and support structure used in the H2Loop fixed-bed pellets to provide mechanical stability and prevent sintering during repeated redox cycling.

Using blast furnace gas, equilibrium at 850 °C remains within the wüstite (FeO) stability region, providing reversible oxygen transfer while avoiding reduction to metallic iron and its associated

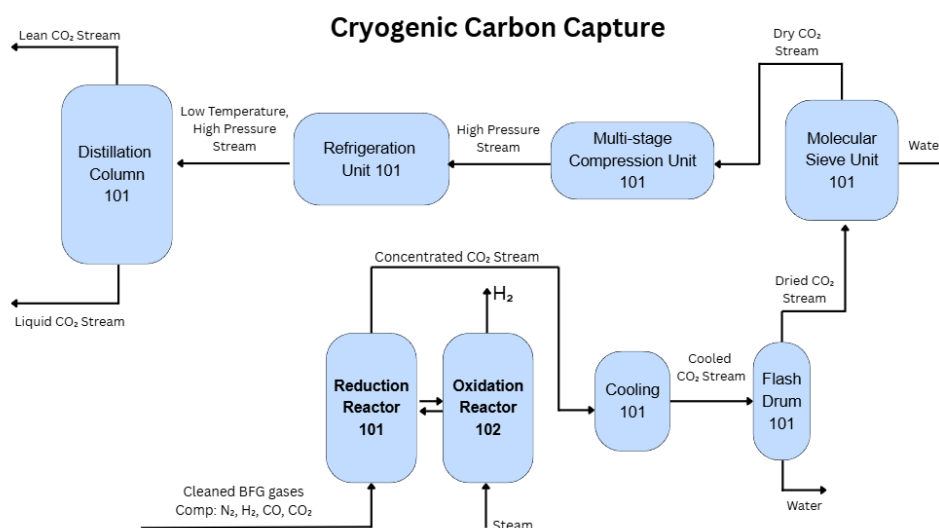
sintering.[64] In addition, temperatures above the Boudouard-favored range ( $\approx 400\text{--}700\text{ }^{\circ}\text{C}$ ) suppress carbon deposition, whereas temperatures above  $900\text{ }^{\circ}\text{C}$  increase heat demand and oxygen-carrier degradation. Therefore,  $850\text{ }^{\circ}\text{C}$  represents a practical compromise between oxygen-transfer performance, carbon suppression, and material stability. The oxidation temperature was fixed at  $700\text{ }^{\circ}\text{C}$  to balance thermodynamic and kinetic constraints. Lower temperatures favor hydrogen production by increasing the equilibrium steam conversion of the exothermic steam oxidation reaction. Still, they also slow the reaction kinetics and, below approximately  $570\text{ }^{\circ}\text{C}$ , wüstite becomes thermodynamically unstable and disproportionates into Fe and  $\text{Fe}_3\text{O}_4$ . Therefore,  $700\text{ }^{\circ}\text{C}$  provides high equilibrium hydrogen production while maintaining adequate reaction kinetics and oxygen-carrier stability. [64]

The reduction reactor was modeled as an isothermal RGibbs block in Aspen Plus, which determines the equilibrium product distribution by minimizing the total Gibbs free energy of the reacting system at a specified temperature and pressure, without requiring the user to specify individual reaction stoichiometries or kinetic parameters. This approach is appropriate because the H2Loop process operates under conditions where iron oxide reduction approaches thermodynamic equilibrium, while Gibbs minimization rigorously captures the coupled gas–solid equilibrium. The RGibbs model is widely adopted for Aspen Plus simulations of iron-based chemical looping systems. [147], [149]

#### 4.4 Cryogenic Separation

The cryogenic route separates  $\text{CO}_2$  from the nitrogen-rich off-gas of the reduction reactor by liquefying the  $\text{CO}_2$  under pressure and distilling it from the non-condensable nitrogen. The feed to this section is the gas leaving the reduction reactor R-101, in which the carbon monoxide and hydrogen have been oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  over the iron carrier. On a dry basis, this stream is approximately 45.6 mol%  $\text{CO}_2$  and 54.4 mol%  $\text{N}_2$ , which is a manual calculation from the BFG composition with complete CO conversion; meanwhile, the converged value is approximately 40 %  $\text{CO}_2$  from the Aspen run with traces of unconverted CO and  $\text{H}_2$ . This feed, at  $\sim 40\text{ mol}\%$ , has a  $\text{CO}_2$  partial pressure high enough that liquefaction and distillation become thermodynamically and economically credible, which is the basis on which the cryogenic route was selected in Section 3.

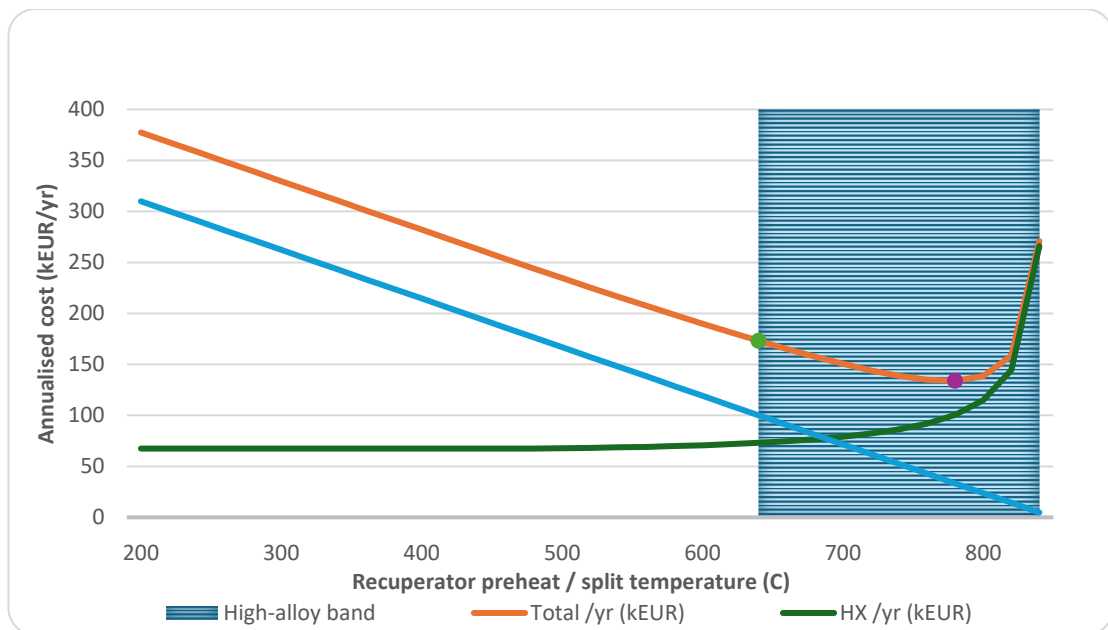
In process order, the separation train comprises recuperative cooling, an air cooler, a knock-out (flash) drum, a molecular-sieve dehydrator, a multistage intercooled compressor, a refrigerated cold box and the distillation column (DC-01) producing liquid  $\text{CO}_2$ , (Figure 4.4).



**Figure 4.4** Overall process configuration of the integrated H2Loop–cryogenic carbon capture system.

#### 4.4.1 Recuperative cooling, air cooler and condensate knock-out

The hot reduction off-gas first passes through the recuperative exchanger (HX-101), where it preheats the incoming cold BFG feed, recovering its sensible heat and simultaneously performing the first stage of cooling. This heat integration is deliberate, as it reduces both the external cooling duty on the off-gas and the heating duty on the feed, which improves the overall energy balance of the front end. Then, the division of the feed-preheat duty between the feed/effluent exchanger (HX-101) and the electric trim heater HE-101 was fixed from the capital-operating-cost trade-off shown in **Figure 4.5**. Recovering a larger fraction of the duty in HX-101 lowers the electric-trim electricity cost. Still, it raises the exchanger area and capital, steeply so as the temperature approaches the 850 °C reduction off-gas narrows. Although the unconstrained cost optimum lies near 780 °C, that region requires nickel-based superalloy construction and a rapidly escalating surface area. The preheat was therefore capped at 639 °C, the highest outlet at which a conventional high-temperature alloy-steel exchanger remains adequate, recovering  $\approx 258$  kW (about three-quarters of the preheat duty) and leaving a  $\approx 98$  kW electric trim to bring the feed to the 850 °C reactor inlet. This selection is consistent with the preliminary engineering assessment provided by RG-H<sub>2</sub> which recommended fixing the recuperator outlet at  $\approx 639$  °C to keep the unit within a standard high-alloy design envelope. The modest cost penalty relative to the theoretical optimum is accepted in return for the lower metallurgical risk and more robust operation of the conventional-alloy design.



**Figure 4.5** Effect of recuperator preheat on annualized cost.

The partially cooled off-gas is then brought down to 50 °C in the air cooler AC-101, modeled as a heater block. Air cooling is used for this duty because  $\approx 50$  °C is the practical lower limit of an air-cooled exchanger set by the approach to the ambient design temperature and achieves the bulk of the sensible cooling without cooling water or refrigeration. The final stage of cooling and dehydration is carried out by the product-gas cooler HX-102 and the knock-out drum FV-101. The HX-102 trims the gas from 50 °C to  $\approx 38$  °C with a small duty ( $\approx 7$  kW), met by recovering cold from the returning CO<sub>2</sub>-lean overhead stream rather than from an external utility. The gas leaves the air cooler still fully vapor at 50 °C, so this further cooling takes it below its water dew point ( $\approx 40$  °C) and condenses part of the water vapor. The cooled, partially condensed stream then passes to FV-101, a vertical gas-liquid knock-out drum operating at  $\approx 35$  °C, in which the condensed water is drained from the base while the gas, water-saturated at 35 °C, is taken overhead. This

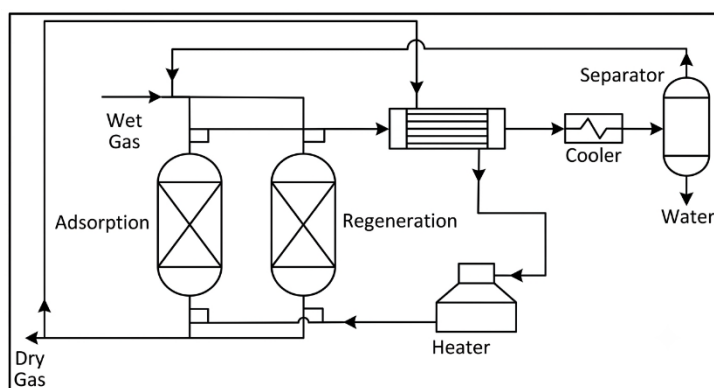
removes the free liquid water, but the residual water vapor still carried at 35 °C is then reduced to the low-ppm level required by the cryogenic section in the molecular-sieve dryer (MS-101) that follows. Removing the bulk water protects the dryer from liquid loading, prevents ice and hydrate formation downstream, and reduces the duty of the dryer and of the CO<sub>2</sub> compression train by lowering both moisture and volumetric flow.

#### 4.4.2 Molecular-sieve dehydration

The gas leaving the knockout drum FV-101 is water-saturated at 35 °C, carrying  $\approx 24,000$  ppmv (2.4 mol%,  $\approx 19$  kg/h) of water vapor and must be dried before it is cooled further. At cryogenic temperatures, any residual moisture freezes to ice or forms gas hydrates that plug exchangers, valves, and column internals. Therefore, the dehydration target is  $\leq 1$  ppmv water, which is the specification conventionally adopted to guarantee against ice and hydrate formation in low-temperature CO<sub>2</sub> service, representing a reduction of more than four orders of magnitude from the content leaving the drum.

To achieve this specification, a conventional twin-bed temperature-swing adsorption (TSA) molecular sieve dryer was selected. In this study, the 3A molecular sieve is used because its  $\approx 3$  Å pore admits water (kinetic diameter 2.65 Å) but size-excludes CO<sub>2</sub> (3.3 Å) and the permanent gases. [158], so it dries this CO<sub>2</sub>-rich feed ( $\sim 40$  mol% CO<sub>2</sub>) without co-adsorbing CO<sub>2</sub>. It prevents the loss of product CO<sub>2</sub> to the regeneration purge and preserves the full water capacity of the bed. In TSA operation, two beds run in parallel, one adsorbing while the other is regenerated by a hot purge gas ( $\approx 200$ -300 °C) and cooled back into service, giving continuous dry output. Based on the 19 kg/h water load and the working adsorption capacity, the unit requires approximately 2.7 t of molecular sieve for an 8 h half-cycle and a four-year replacement interval. These design parameters were taken from the dehydration-design literature. [159]

In the simulation, the dryer is idealized as a component-separation (Sep) block that removes water to the specified outlet level ( $\leq 1$  ppmv, taken as essentially complete removal), rather than modeled as a rigorous, dynamic adsorption bed. This is the standard and defensible modeling assumption for a steady-state cold-box balance since Aspen Plus doesn't contain a standard Molecular Sieve unit. Accordingly, the dryer is assumed to deliver an essentially water-free feed to the cryogenic section. However, the actual unit (**Figure 4.6**) is a conventional twin-bed TSA molecular sieve dryer with a regeneration circuit. [160]



**Figure 4.6** Simplified process flow diagram of a twin-bed temperature swing adsorption (TSA) system for gas dehydration. [161]

#### 4.4.3 Multistage intercooled compression

The dried process gas leaving the molecular-sieve dryer, a nitrogen-rich mixture containing approximately 41 mol% CO<sub>2</sub>, 54 mol% N<sub>2</sub>, and 5 mol% CO, is compressed from 2 bar to 43 bar, the operating pressure of the downstream cryogenic distillation column, via the multistage compressor M-S-COMP (Aspen Plus *MComp* block). The compressor consists of four isentropic stages with inter-stage cooling to 35 °C. The thermodynamic basis of the compressor design is described by the isentropic compression work equation, including the compressibility factor (*Z*) to account for real-gas behavior, Equ. 4.4:

$$W_s = \frac{\gamma}{\gamma - 1} ZRT_1 \left[ \left( \frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} - 1 \right] \quad (4.4)$$

The actual compression work is given by Equ. 4.5:

$$W = \frac{W_s}{\eta_{is}} \quad (4.5)$$

where  $\gamma$  is the heat-capacity ratio,  $T_1$  is the stage inlet temperature,  $P_2/P_1$  is the stage pressure ratio, and  $\eta_{is}$  is the isentropic efficiency. Although Aspen Plus calculates compressor performance using a rigorous real-gas model, it is based on the same isentropic compression principles represented by these equations, which also justify the selected multistage, intercooled design. [161]

Because compressor work is proportional to the inlet temperature, cooling the gas to 35 °C before each stage reduces the overall power requirement and approaches the minimum-work isothermal limit. For a fixed number of stages, the work is minimized when each stage operates at the same pressure ratio, Equ. 4.6:

$$r = \left( \frac{P_{out}}{P_{in}} \right)^{1/N} \quad (4.6)$$

For the present case,

$$r = \left( \frac{43}{2} \right)^{1/4} = 2.153$$

which lies within the practical range of 2-4 for centrifugal compressors. [161]

The stage pressure ratio also determines the discharge temperature, Equ. 4.7:

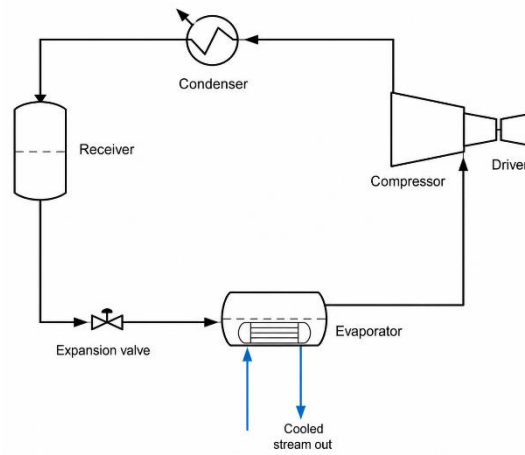
$$T_2 = T_1 \left( \frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} \quad (4.7)$$

For the present gas mixture ( $\gamma \approx 1.35$ ), single-stage compression from 2 to 43 bar would produce an isentropic discharge temperature of approximately 685 K ( $\approx 410$  °C), with the actual temperature being even higher due to compressor inefficiency. Dividing the duty into four intercooled stages limits the discharge temperature to approximately 376 K ( $\approx 103$  °C) per stage, maintaining practical operating temperatures while reducing power consumption. Additionally, the compressor was modeled as an integrally geared centrifugal compressor with an isentropic efficiency of 0.78, representative of continuous CO<sub>2</sub> compression service. [161]

#### 4.4.4 Refrigeration cycle

After the compression stage, initial cooling is achieved in the cold-box heat exchanger (HX-103), where the compressed feed is cooled from approximately 35 °C to - 20 °C by recovering refrigeration from the cold nitrogen-rich vent gas exiting the distillation column. The stream is

subsequently cooled to -35 °C in the refrigeration unit (REF-UNIT), which is represented in Aspen Plus by a Heater block with an equivalent cooling duty of approximately 15 kW. The external refrigeration system required for both this precooling duty and the colder overhead condenser is not modeled explicitly. A rigorous simulation would require a multistage refrigeration cascade with multiple refrigerant circuits, compressors, intercoolers, expansion devices and dedicated property packages. However, incorporating these units would substantially increase the model complexity and computational effort while providing limited additional benefit for a feasibility-level techno-economic assessment. Therefore, the refrigeration system is represented indirectly, with each cooling duty modeled by its corresponding heat load. Subsequently, the associated capital and operating costs are estimated using the temperature-dependent refrigeration cost correlations developed by Luyben (2017). The corresponding conceptual refrigeration configuration is illustrated schematically in **Figure 4.7**. [162]



**Figure 4.7** Schematic of a single-stage vapor-compression refrigeration cycle. Adapted from [163]

The theoretical minimum energy required for refrigeration is governed by the coefficient of performance (COP). For a reversible Carnot refrigeration cycle operating between a cold temperature,  $T_C$ , and a heat rejection temperature, ( $T_H$ ), Equ. 4.8:

$$\text{COP}_{\text{Carnot}} = \frac{T_C}{T_H - T_C} \quad (4.8)$$

with the corresponding minimum compressor work given by Equ. 4.9.

$$W_{\min} = Q_C \frac{T_H - T_C}{T_C} \quad (4.9)$$

where  $Q_C$  is the refrigeration duty. For cooling from 35 °C (308 K) to -35 °C (238 K), the ideal COP is approximately 3.4, corresponding to a minimum work requirement of about 0.29 times the refrigeration duty. In practice, second-law efficiencies of 30-50% increase the actual power requirement to approximately 0.6-1.0 times the refrigeration duty. As the refrigeration temperature decreases, the COP declines rapidly; at -150 °C (123 K), it falls to approximately 0.66, increasing the theoretical minimum work by about a factor of five. Consequently, refrigeration costs rise sharply as lower operating temperatures are required.

To account for this behavior, Luyben (2017) developed temperature-dependent refrigeration cost correlations based on representative industrial refrigeration cascades. [163] These correlations incorporate both compressor power consumption and the additional capital associated with increasingly complex refrigeration systems. In the present process, refrigeration is required at two temperature levels. The refrigeration unit (REF-UNIT) provides precooling to -35 °C, which can be supplied by a relatively simple single- or two-stage refrigeration system. The dominant

refrigeration duty, however, is associated with the overhead condenser of the cryogenic distillation column, which is operating at approximately -95 °C to minimize CO<sub>2</sub> losses in the nitrogen-rich vent gas.

#### 4.4.5 Pressure and temperature selection for CO<sub>2</sub> liquefaction

The operating temperature and pressure of the cryogenic distillation section are among the principal design variables, as it governs the vapor–liquid equilibrium, refrigeration requirement, compression duty, and ultimately the achievable CO<sub>2</sub> purity and recovery. The feasible operating window is constrained by the phase behavior of carbon dioxide (**Figure 4.8**). Pure CO<sub>2</sub> exhibits a triple point at -56.6 °C and 5.18 bar and a critical point at 31.0 °C and 73.8 bar. [164], which define the lower and upper thermodynamic limits for conventional distillation. Below the triple-point pressure, liquid CO<sub>2</sub> cannot exist, and the fluid desublimates directly to solid CO<sub>2</sub>, creating a risk of dry-ice formation and equipment blockage. Conversely, operation above the critical pressure eliminates the vapor–liquid equilibrium required for distillation. Although the solidification boundary is displaced in CO<sub>2</sub>-N<sub>2</sub> mixtures, operation must nevertheless remain sufficiently above the freeze-out limit to avoid CO<sub>2</sub> deposition.

Within the thermodynamic constraints imposed by the CO<sub>2</sub> phase diagram, an operating pressure of 43 bar was selected. This pressure represents a compromise between refrigeration demand, compression duty, and product purity. Increasing the operating pressure raises the CO<sub>2</sub> condensation temperature, thereby reducing the refrigeration requirement, but simultaneously increases compression work and nitrogen dissolution in the liquid CO<sub>2</sub> product. Conversely, decreasing the pressure improves product purity but requires lower refrigeration temperatures and moves operation closer to the CO<sub>2</sub> freeze-out limit. In the Aspen Plus model, nitrogen solubility and consequently the purity-recovery trade-off is calculated directly using the Peng–Robinson equation of state through its CO<sub>2</sub>-N<sub>2</sub> binary interaction parameters.

The operating pressure can be rationalized using Dalton's law, which relates the partial pressure of each component to its mole fraction in the gas mixture, Equ. 4.10:

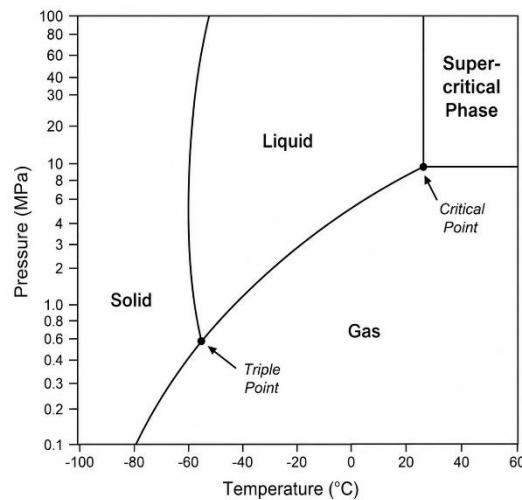
$$p_i = y_i * P \quad (4.10)$$

For the dried column feed containing approximately 41 mol% CO<sub>2</sub> and 54 mol% N<sub>2</sub>,

$$p_{\text{CO}_2} = y_{\text{CO}_2} * P = 0.41 * 43 = 17.6 \text{ bar}$$

$$p_{\text{N}_2} = y_{\text{N}_2} * P = 0.54 * 43 = 23.2 \text{ bar}$$

Condensation begins when the partial pressure of CO<sub>2</sub> equals its saturation pressure. According to the Span-Wagner vapor-pressure correlation, a saturation pressure of approximately 17.6 bar corresponds to a temperature of approximately -24 °C, representing the dew point of the feed mixture. [164]



**Figure 4.8** Phase diagram of carbon dioxide.

The compressed feed is cooled to -35 °C, approximately 11 °C below its calculated dew point, such that it enters Stage 8 as a partially condensed vapor-liquid mixture. This temperature was selected for two reasons. First, partial condensation generates liquid before the feed enters the column, thereby reducing the internal separation duty and the refrigeration load on the overhead condenser. Second, -35 °C lies within the practical operating range of a conventional single-stage refrigeration system, where the coefficient of performance is substantially higher than that of the deep-cryogenic refrigeration required at the column overhead. Consequently, most of the sensible and latent cooling duty is removed at the higher-efficiency refrigeration level, while only the final overhead condensation is supplied by the cryogenic refrigeration cascade. Further precooling was not adopted because it would require deep-cryogenic refrigeration while providing only marginal additional separation benefit.

#### 4.4.6 Distillation column (DC-01): design and specifications

The final separation of the compressed and dehydrated gas into a high-purity CO<sub>2</sub> product and a nitrogen-rich vent stream is performed in a single cryogenic distillation column (DC-01). The column is modeled in Aspen Plus using the rigorous RadFrac equilibrium-stage model, which simultaneously solves the MESH (material, equilibrium, summation, and enthalpy) equations for each stage. Vapor-liquid equilibrium and thermodynamic properties are calculated using the Peng-Robinson equation of state [165], which is well suited for high-pressure cryogenic CO<sub>2</sub>-N<sub>2</sub> systems. As the column operates far below ambient temperature, the block is solved with the Cryogenic initialization option to promote robust convergence of the low-temperature profile.

DC-01 is configured with 10 equilibrium stages which numbered from the top according to the Aspen Plus convention, where Stage 1 corresponds to the condenser and Stage 10 to the reboiler. The compressed feed enters on Stage 8, where the partially condensed feed is well matched to the internal vapor-liquid traffic of the lower section of the column. The column operates at 43 bar, which maintains the CO<sub>2</sub>-rich bottoms as a liquid at approximately 7 °C while remaining safely

above the CO<sub>2</sub> triple point (5.18 bar, -56.6 °C), thereby minimizing the risk of dry-ice formation within the column. [164])

The overhead product is withdrawn as a vapor through a partial condenser (Aspen Plus condenser type: Partial-Vapor). This configuration is appropriate because the overhead stream is predominantly nitrogen (88.5 mol% N<sub>2</sub>), making complete condensation impractical at the selected operating conditions. Only the condensed fraction is returned to the column as reflux, while the remaining nitrogen-rich gas, containing primarily N<sub>2</sub> and CO with residual CO<sub>2</sub>, exits as the overhead vent stream.

Once the number of stages, the feed location, and the pressure profile are fixed, the column retains two operating degrees of freedom. Hence, the reboil ratio was fixed at 1 as it provided sufficient vapor generation to maintain the required separation without excessive reboiler duty, while the reflux ratio was determined automatically using the Aspen Plus Design Spec/Vary tool. The Design Spec adjusted the reflux ratio within a range of 1-5 until the CO<sub>2</sub> purity in the bottoms product reached 99.9 mol%, using a convergence tolerance of 0.005. Consequently, CO<sub>2</sub> purity was specified, whereas the CO<sub>2</sub> recovery was predicted by the simulation rather than imposed as a design constraint.

The resulting configuration is summarized in **Table 4.3**.

**Table 4.3** Configuration of the DC-01 distillation column as implemented in Aspen Plus

| Parameter                   | Value in the Aspen Plus model                                                 |
|-----------------------------|-------------------------------------------------------------------------------|
| Block / model               | DC-01, RadFrac (rigorous equilibrium-stage)                                   |
| Property method             | Peng-Robinson equation of state                                               |
| Initialization              | Cryogenic                                                                     |
| Number of stages            | 10 (stage 1 = partial condenser, stage 10 = reboiler)                         |
| Feed stage                  | 8                                                                             |
| Feed (stream 18)            | -35 °C, 43 bar; 40.8% CO <sub>2</sub> / 54.2% N <sub>2</sub> / 4.6% CO (mol)  |
| Top pressure                | 42 bar                                                                        |
| Condenser type              | Partial-vapor (vapor distillate)                                              |
| Overhead vent (stream 20)   | -95.3 °C, 42 bar; 88.5% N <sub>2</sub> / 7.6% CO / 3.3% CO <sub>2</sub> (mol) |
| Bottoms product (stream 19) | +6.9 °C; 99.9% CO <sub>2</sub> (mol)                                          |
| Fixed operating spec        | Mole boil-up (reboil) ratio = 1                                               |
| Design specification        | CO <sub>2</sub> mole purity = 0.999 (tol. 0.005)                              |
| Manipulated variable        | Mole reflux ratio, searched 0.5-5 (step 0.5)                                  |

Carbon dioxide and nitrogen form a relatively easy-to-separate system owing to their high relative volatility ( $\alpha \approx 7.4$ ), calculated from the Peng-Robinson vapor-liquid equilibrium at the column operating conditions. Consequently, the adequacy of the selected 10 equilibrium stages can be evaluated using the Fenske equation, which estimates the minimum number of stages at total reflux, Equ. 4.11. [166]

$$N_{\min} = \frac{\ln \left( \frac{x_{LK,D}}{x_{HK,D}} \cdot \frac{x_{HK,B}}{x_{LK,B}} \right)}{\ln \alpha} \quad (4.11)$$

Taking nitrogen as the light key (LK) and carbon dioxide as the heavy key (HK), with the distillate composition (N<sub>2</sub> = 0.885, CO<sub>2</sub> = 0.033) and the bottoms composition (CO<sub>2</sub> = 0.99895, N<sub>2</sub> = 0.00097):

$$N_{\min} = \frac{\ln\left(\frac{0.885}{0.033} \cdot \frac{0.99895}{0.00097}\right)}{\ln 7.4} \approx 5.1$$

The ten installed stages thus provide roughly 2 times the theoretical minimum. [167] This confirms that the selected 10 stages provide an adequate design margin and that the separation is governed primarily by the reflux ratio and overhead refrigeration rather than by the number of stages.

The overhead vapor leaves the partial condenser at approximately -95 °C (-95.3 °C, 42 bar). This condenser provides the principal refrigeration duty of the cryogenic separation by condensing a fraction of the nitrogen-rich overhead stream to generate the reflux required for separation, while the remaining vapor exits as the nitrogen-rich vent. At this temperature, refrigeration is substantially more energy-intensive than the -35 °C precooling stage, with an ideal Carnot COP of approximately 1.4 compared with 3.4 for precooling. Accordingly, the refrigeration duty is represented in Aspen Plus as a heat load, while the associated capital and operating costs are estimated using the temperature-dependent refrigeration cost correlations of Luyben (2017a). [163]

One limitation must be stated explicitly, as the RadFrac model resolves only vapour–liquid equilibrium and does not predict the formation of a solid phase. At the simulated overhead condition of -95.3 °C, the CO<sub>2</sub> partial pressure of approximately 1.4 bar exceeds the CO<sub>2</sub> sublimation pressure of approximately 0.22 bar, so that the operating point lies inside the CO<sub>2</sub> solid-formation region rather than merely approaching it. The reported 95.0 % single-pass recovery is therefore conditional on the vapour-liquid-equilibrium assumption. Frost-safe operation would require the overhead to be held at or above the solidification boundary, either by raising the overhead temperature or by reducing the residual CO<sub>2</sub> content of the overhead through additional reflux and refrigeration; both alter the recovery and the associated duties, and the resulting values cannot be established without re-simulation. Retaining the present recovery at a frost-safe condition would instead require an anti-sublimation section, for example a switching, periodically defrosted overhead condenser in which deposited CO<sub>2</sub> is intermittently re-melted and returned to the column while a parallel unit maintains reflux, an approach drawn from established low-temperature CO<sub>2</sub> practice. [168] The reported recovery and the derived techno-economic results are accordingly conditional on this limitation, and the design and costing of a frost-safe column are identified as future work in Chapter 7.

At the base of the column, the CO<sub>2</sub>-rich bottoms boil at only about +7 °C at 42- 43 bar. The reboiler duty is set by the fixed molar boil-up ratio of 1 and, because of this mild temperature, can be supplied by a low-grade heating medium such as tempered water or low-grade process heat rather than steam. As the reboiler operates at only around +7 °C, the energy demand and operating cost of the cryogenic distillation process are dominated by the -95 °C overhead condenser.



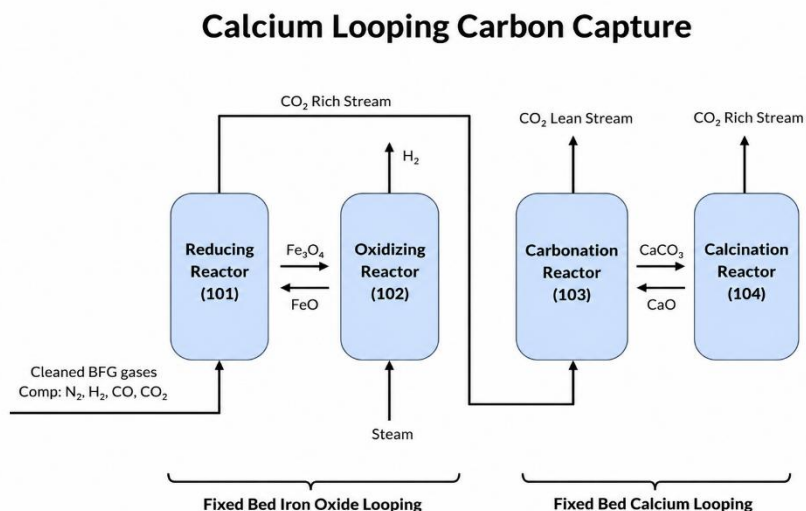
**Figure 4.9** Process flow diagram of the cryogenic process developed using draw.io

## 4.5 Calcium Looping

The calcium-looping route separates  $\text{CO}_2$  from the nitrogen-rich off-gas of the reduction reactor through the reversible gas-solid reaction of calcium oxide. In this process,  $\text{CO}_2$  is chemically captured as  $\text{CaCO}_3$  in a carbonator and subsequently released as a concentrated stream when the  $\text{CaO}$  sorbent is regenerated in a calciner. The feed to this section is the same off-gas that leaves the reduction reactor (R-101), and its converged Aspen composition is approximately 40 mol%  $\text{CO}_2$  with traces of unconverted  $\text{CO}$  and  $\text{H}_2$ .

Unlike the cryogenic route, which exploits this relatively high  $\text{CO}_2$  concentration at elevated pressure and low temperature, calcium looping operates at near-atmospheric pressure and high temperature. Accordingly, the reduction-reactor off-gas is first cooled to 650 °C in a heat exchanger before entering the carbonator (R-103), where  $\text{CO}_2$  is captured by  $\text{CaO}$ . The carbonated sorbent is then regenerated in the calciner (R-104), producing a concentrated  $\text{CO}_2$  stream for downstream compression and conditioning as shown in **Figure 4.10**.

In Aspen Plus, the  $\text{CaO}/\text{CaCO}_3$  sorbent is represented using an open-loop matched-stream approach rather than a closed solids recycle. The regenerated  $\text{CaO}$  entering the carbonator is specified to match the calciner outlet in flow rate, composition, and temperature, while the carbonated sorbent entering the calciner is matched to the carbonator outlet. This representation reflects the switching fixed-bed configuration adopted in this study. Throughout the simulation, the gas phase is modeled using the Peng-Robinson equation of state, while the calcium-based sorbents are represented as conventional solids (SOLIDS), consistent with established Aspen Plus practice for high-temperature calcium-looping systems. [152]



**Figure 4.10** Overall process configuration of the integrated H2Loop-calcium looping carbon capture system.

#### 4.5.1 Carbonation reactor (R-103)

In the carbonator, CO<sub>2</sub> is removed from the process gas by reaction with calcium oxide to form calcium carbonate through the reversible carbonation reaction shown in Eq. (3.2). The reaction is strongly exothermic in the carbonation direction. [169]. The direction of the reaction is governed by the CO<sub>2</sub> partial pressure relative to the equilibrium decomposition pressure of CaCO<sub>3</sub>, which is expressed as Equ. 4.12:

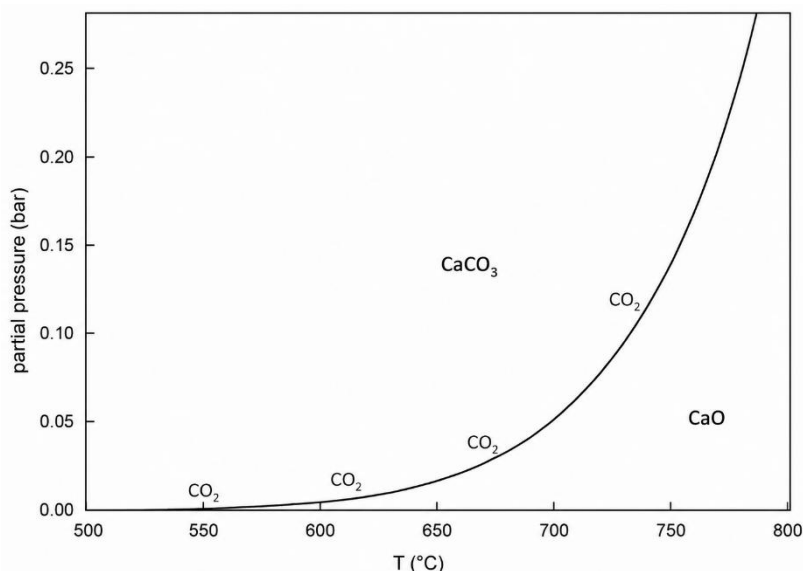
$$P_{eq} [\text{atm}] = 4.137 \times 10^7 \exp\left(-\frac{20474}{T[\text{K}]}\right) \quad (4.12)$$

where  $P_{eq} [\text{atm}]$  is the equilibrium decomposition pressure of CaCO<sub>3</sub> and T is the absolute temperature in Kelvin. Carbonation proceeds whenever the feed CO<sub>2</sub> partial pressure exceeds  $P_{eq} [\text{atm}]$  whereas calcination occurs when it falls below this value.

At the selected carbonator operating temperature of 650 °C, Eq. (4.12) gives  $P_{eq} \approx 0.0097 \sim \text{atm}$ , while the carbonator, which in calcium-looping systems is conventionally operated at near-atmospheric pressure, receives the reduction-reactor off-gas leaving R-101 at 2 bar and was modelled at approximately 1.5 bar, the pressure remaining after the losses across the intermediate heat exchangers. At this pressure the feed gas has a CO<sub>2</sub> partial pressure of approximately 0.59 bar, so that the thermodynamic driving force is about sixty-fold, strongly favoring carbonation; at the conventional atmospheric operating pressure the corresponding values would be 0.40 bar and a forty-fold driving force, so that the carbonation equilibrium is not sensitive to this difference. Under equilibrium conditions, the reaction can reduce the gas-phase CO<sub>2</sub> concentration to approximately 0.01 atm, corresponding to a theoretical CO<sub>2</sub> capture exceeding 97%. In practice, however, the achievable capture is limited by the available sorbent inventory and its cyclic conversion.

The selected operating temperature of 650 °C represents an optimum compromise between thermodynamics and kinetics. As temperature increases,  $P_{eq} (\text{atm})$  rises rapidly from 0.030 atm at 700 °C to 0.21 atm at 800 °C and approximately 0.50 atm at 850 °C. Above about 850 °C, the equilibrium pressure approaches the feed CO<sub>2</sub> partial pressure, substantially reducing the thermodynamic driving force for carbonation. Conversely, carbonation kinetics become progressively slower at lower temperatures. Consequently, the range of approximately 600-700 °C provides both rapid reaction kinetics and a strong thermodynamic driving force, and 650 °C has therefore been widely adopted in calcium-looping studies (**Figure 4.11**).

In Aspen Plus, the carbonator is represented by block R-103 as an isothermal RGibbs reactor operating at 650 °C and 1.5 bar. The reactor determines the equilibrium composition by minimizing the total Gibbs free energy of the declared species (CaO, CaCO<sub>3</sub>, CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O), eliminating the need to specify reaction stoichiometry or kinetic parameters. The reactor receives two inlet streams: the process gas cooled to 650 °C, and the regenerated CaO supplied from the calciner through the open-loop matched stream. The outlet stream contains the carbonated solids together with the CO<sub>2</sub>-depleted gas, which is subsequently routed to the calciner. [170]



**Figure 4.11** Equilibrium CO<sub>2</sub> partial pressure as a function of temperature. [170]

#### 4.5.2 Calcination reactor (R-104)

The calciner reverses the carbonation reaction, regenerating the sorbent and releasing a concentrated CO<sub>2</sub> stream (eq. 3.3). This highly endothermic decomposition requires high-grade heat. Complete calcination occurs only when the equilibrium CO<sub>2</sub> pressure ( $P_{eq}$ ) exceeds the CO<sub>2</sub> partial pressure in the calciner. As the product gas is essentially pure CO<sub>2</sub>, its partial pressure is approximately 1 atm, requiring temperatures above about 894 °C. Accordingly, the calciner is operated at atmospheric pressure. As the sorbent remains in a fixed bed and the two phases are alternated by valve switching rather than by solids transport, the bed is carbonated at approximately 1.5 bar and depressurized to 1 bar for regeneration at 900 °C. At this condition, Eq. (4.12) gives an equilibrium decomposition pressure of approximately 1.09 atm, which exceeds the CO<sub>2</sub> partial pressure in the calciner and therefore confirms that calcination is thermodynamically favoured at the selected temperature. As the calcination conversion was specified rather than resolved from equilibrium, the reported calcium-looping performance nevertheless constitutes an upper bound, and alternative operating strategies are discussed in Chapter 7. Operating at 950 °C would increase  $P_{eq}$  to approximately 2.2 atm but would also increase the heat requirement without providing a significant modeling advantage. Furthermore, as the objective of the process is to produce a concentrated CO<sub>2</sub> stream for capture, conventional natural-gas or coal firing was avoided because combustion would either dilute the product gas with additional CO<sub>2</sub> or require oxy-firing with an air-separation unit, substantially increasing capital cost. Therefore, the calciner was assumed to be electrically heated following recommendations from RG-H<sub>2</sub>. Electrified calcination eliminates the need for an air-separation unit while maintaining a high-purity CO<sub>2</sub> product, although at the expense of increased electricity demand. This trade-off is consistent with recent studies on electrified calcium looping, and the regeneration duty represents the dominant operating cost considered in the economic analysis presented in Chapter 5.

In Aspen Plus, the calciner is modeled as block R-104, a stoichiometric (RStoic) reactor operating isothermally at 900 °C and 1 bar, with the endothermic heat of calcination appearing as the block

duty. The single reaction is specified in the block with the conversion fixed at 1.0 (100%), so the block regenerates the sorbent completely and releases the captured  $\text{CO}_2$ , the calcium species being carried on the conventional-solids (CISOLID) sub stream. It receives the carbonated solid from the carbonator and returns the regenerated CaO and the released  $\text{CO}_2$ . Unlike the equilibrium reactors used elsewhere in the process, this fixed-conversion approach provides explicit control over sorbent regeneration and follows the techno-economic methodology of Dai (2017). The assumption of complete regeneration is also supported by pilot-scale calcium-looping studies, which have demonstrated near-complete calcination at temperatures around 900 °C. [171], [143] Unlike carbonation, which becomes diffusion-limited by the formation of a dense  $\text{CaCO}_3$  product layer, calcination proceeds without this limitation because  $\text{CO}_2$  is released directly as a gas. Combined with the favorable thermodynamic driving force at 900 °C, this justifies assuming complete sorbent regeneration in the Aspen Plus model. [171]

#### 4.5.3 Sorbent Design Assumptions and Fixed-Bed Swing Operation

The design basis adopts an engineered, high-performance synthetic CaO sorbent, each pellet modeled as a co-precipitated structure of 85 wt% active CaO within a 15 wt% inert matrix of mayenite,  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ . The calcium-aluminate/mayenite matrix stabilizes CaO against sintering. Li et al. (2005) synthesized  $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  sorbents retaining a carrying capacity of order 0.4-0.5 after cycling, and Manovic and Anthony (2009) showed that CaO pellets bound with calcium-aluminate cement form an in-situ mayenite framework that markedly improves cyclic stability. [172] [173] The 85:15 split is a formulation choice within this well-supported family, and this synthetic basis is what makes the conversion target adopted here defensible across several cycles, the central assumption on which the remainder of the design basis depends.

The capture achievable per pass is set by the sorbent conversion  $X$  (mol  $\text{CO}_2$  captured per mol CaO). For natural limestone,  $X$  decays with cycle number as the sorbent sinters, following the semi-empirical law of Grasa and Abanades (2006), Equ. 4.13. [174]

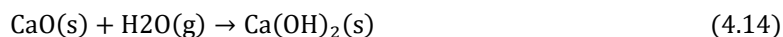
$$X_N = 1/[1/(1 - X_r) + kN] + X_r \quad (4.13)$$

which falls from  $X_1 \approx 0.70$  to a residual  $X_r \approx 0.075$ -0.08 within tens of cycles. The mayenite-stabilized pellet instead retains a much higher residual capacity ( $\approx 0.4$ -0.5), so the design adopts an operational conversion held near  $X \approx 0.80$ -0.82, with an initial conversion  $X_1 \approx 0.95$  decaying to the 0.80 floor over approximately 50 cycles before scheduled steam reactivation restores it.

This design value must be distinguished from what the equilibrium reactor itself returns. In the model, the carbonator is an RGibbs (Gibbs free-energy minimization) block, used to resolve the equilibrium stream behavior rather than to impose a conversion. Because the equilibrium at 650 °C is strongly displaced towards  $\text{CaCO}_3$ , the RGibbs carbonator carbonates almost all of the circulated CaO, at the near-stoichiometric calcium-to-carbon ratio used. It returns a conversion of  $X \approx 0.94$  and a  $\text{CO}_2$  capture of  $\approx 98\%$ . This equilibrium value is therefore a thermodynamic upper bound and does not represent the sintering- and kinetics-limited behavior of a real sorbent. The operational conversion  $X \approx 0.80$ -0.82, together with its cyclic decay from  $X_1 \approx 0.95$ , is accordingly adopted as the sorbent-limited design value carried into the techno-economic assessment. The sorbent is declared as an engineered-material design choice rather than a property of natural limestone.

Furthermore, Fernández et al. investigated a packed-bed carbonator operating at atmospheric pressure and 650-750 °C and reported approximately 97%  $\text{CO}_2$  capture throughout the pre-

breakthrough period, with breakthrough occurring after approximately 15-18 min under adequately preheated conditions. [175], [176] Extending carbonation beyond breakthrough shifts the reaction into the product-layer diffusion regime, where CO<sub>2</sub> uptake decreases while productivity declines. Accordingly, a carbonation time of 15 min was adopted, representing the beginning of the reported breakthrough window and providing a conservative balance between productivity and sorbent utilization. As the experimental study did not report sorbent conversion at exactly 15 min, the carbonation conversion used in the Aspen Plus model was treated as an engineering assumption. The process operates with asymmetric half-cycles consisting of 15 min carbonation followed by 10 min of calcination and purge, giving a total cycle time of 25 min (57.6 cycles/day per vessel). Consequently, each reactor spends 60% of its operating time in carbonation. Continuous CO<sub>2</sub> capture therefore requires multiple fixed beds operating in parallel with staggered switching. Therefore, a five-vessel configuration staggered at 5 min intervals was adopted because it maintains three beds in carbonation and two in regeneration at all times. This arrangement provides uninterrupted CO<sub>2</sub> capture while defining the sorbent inventory used in the techno-economic assessment. The steady-state model represents the fixed-bed configuration by a single carbonator and a single calciner sized to process the total gas flow and reproduce the cycle-averaged behaviour of the five-vessel system. The operating cost assessment, however, is based on the five-vessel configuration because sorbent inventory, bed switching, and reactivation depend on the actual operating strategy rather than on the simplified reactor representation. The reactor capital cost is estimated for two equivalent reactors providing the required total bed volume, while the additional equipment associated with the multi-vessel arrangement is included separately as the switching valve manifold. This simplification therefore affects neither the predicted process performance nor the reported techno-economic results. Even with a mayenite support, repeated carbonation-calcination cycles promote CaO sintering, progressively reducing the CO<sub>2</sub> carrying capacity according to Eq. (4.13). A reactivation interval of 50 operating cycles was therefore adopted, corresponding to approximately 21 h of continuous operation. This value is conservative relative to the approximately 60-cycle service life reported for calcium-aluminate-supported sorbents. [173] Therefore, at the end of each operating interval, the bed is isolated and reactivated by injecting superheated steam at 250-300 °C for approximately 20 min, promoting the hydration reaction, Equ. 4.14:



Steam hydration causes a substantial increase in solid volume, fracturing the sintered product layer and restoring pore structure. Upon subsequent heating, Ca(OH)<sub>2</sub> decomposes back to porous CaO, recovering sorbent reactivity. The adopted sorbent performance, with a conversion of approximately 0.80–0.82, more than 98% recovery after each reactivation, 15 reactivations, and a service life of 750 cycles, lies at the optimistic end of the range reported in the cited literature and is therefore treated as an upper-bound assumption. This assumption directly affects the annual sorbent make-up requirement and, consequently, the operating cost of the calcium-looping process. The make-up rate scales inversely with the assumed sorbent lifetime, meaning that a shorter service life would increase the reported operating expenditure. A sensitivity analysis examining the effects of sorbent conversion and lifetime is included as part of the future work presented in Chapter 7. [177] Experimental studies have shown that steam reactivation can restore more than 98% of the initial carbonation capacity, provided the treatment temperature remains below the decomposition temperature of Ca(OH)<sub>2</sub>. [178] The repeated hydration and dehydration gradually weaken the sorbent through micro-cracking and attrition. A maximum of 15 steam reactivation treatments was therefore assumed before sorbent replacement, giving an overall lifetime of 750 operating cycles (50 cycles × 15 reactivations), equivalent to approximately 13 days of continuous operation at 57.6 cycles/ day. At the end of its

service life, the spent sorbent, consisting predominantly of CaO with a calcium-aluminate support and proposed as a potential clinker substitute, provides a circular end-of-life utilization route while avoiding landfill disposal. Overall, the assumptions are demonstrated in Table 4.4.

**Table 4.4** Consolidated process modeling parameters for the fixed-bed calcium-looping system.

| Design parameter                      | Baseline value                             | Engineering rationale / source                                      |
|---------------------------------------|--------------------------------------------|---------------------------------------------------------------------|
| Sorbent formulation                   | 85 wt% CaO / 15 wt% $Ca_{12}Al_{14}O_{33}$ | Mayenite-stabilized pellet family [172], [173]                      |
| Operational conversion, X             | ( $X_1 \approx 0.95$ )                     | Design target held above the floor by steam reactivation            |
| Carbonation time, ( $t_{carb}$ )      | 15 min                                     | Design choice [175], [176]                                          |
| Calcination + purge, ( $t_{calc}$ )   | 10 min                                     | Endothermic decomposition at 900 °C with steam swing, design choice |
| Total loop time, ( $t_{total}$ )      | 25 min                                     | $t_{carb} + t_{calc}$                                               |
| Daily cycling                         | 57.6 cycles/day                            | 1440/25                                                             |
| Reactivation interval                 | every 50 cycles                            | Decay-informed[174]                                                 |
| Steam flush                           | 250-300 °C, ~20 min                        | Below $Ca(OH)_2$ decomposition onset (~445 °C) [178]                |
| Max. reactivations, ( $R_{max}$ )     | 15 per batch                               | Assumed mechanical limit [178]                                      |
| Ultimate pellet life, ( $N_{total}$ ) | 750 cycles $\approx$ 13.02 days            | $50 \times 15$ , 750/57.6                                           |
| Annual sorbent turnover               | $\approx$ 28 batches/year                  | 365/13.02 (exact)                                                   |
| Vessel matrix                         | 5 (3 carbonating / 2 regenerating)         | Duty-balanced from 3:2 ratio                                        |

#### 4.5.4 Heat integration

The heat-integration scheme of Calcium looping matches the loop's hot streams (to be cooled) against its cold streams (to be heated), recovering heat internally wherever the temperature levels allow, as indicated (**Table 4.5**).

**Table 4.5** Process stream characteristics and intended heat exchange for the calcium-looping heat recovery network.

| Stream                                     | Stream Type       | Temperature (°C) | Intended Heat Exchange                                                                                |
|--------------------------------------------|-------------------|------------------|-------------------------------------------------------------------------------------------------------|
| Regenerated CaO (calciner → carbonator)    | Hot (cooled)      | 900 → 650        | Transfers sensible heat to the returning carbonated sorbent through solid–solid recuperation.         |
| Carbonated sorbent (carbonator → calciner) | Cold (heated)     | 650 → 900        | Preheated by the regenerated CaO before entering the calciner.                                        |
| Calciner CO <sub>2</sub> product           | Hot (cooled)      | 900 → 40         | Heat recovered to preheat incoming process streams before cooling for compression.                    |
| Reduction-reactor off-gas                  | Hot (cooled)      | ~850 → 650       | Cooled to the carbonator operating temperature while recovering heat for process preheating.          |
| Carbonation reaction                       | Hot (heat source) | 650              | Exothermic reaction heat exported as steam; insufficient temperature to supply the calciner directly. |
| Calcination reaction                       | Cold (heat sink)  | 900              | Endothermic heat supplied externally by electrical heating.                                           |

#### 4.5.5 CO<sub>2</sub> product conditioning

The CO<sub>2</sub> released from the calciner (R-104) is considered essentially pure as it has no other contamination in an idealized case. It is subsequently compressed to 21 bar in a three-stage intercooled compressor (M-COM-01) with an isentropic efficiency of 0.78 per stage, consistent with the compressor design adopted for the cryogenic separation route. The discharge pressure was selected to match the operating conditions of the OCAP (Organic CO<sub>2</sub> for Assimilation by Plants) network, which has supplied industrial CO<sub>2</sub> from the Rotterdam region to Westland greenhouses since 2005. Compression to 21 bar therefore defines the battery-limit product specification for the calcium-looping process.

Unlike food-grade applications, which require extensive trace-contaminant certification, horticultural CO<sub>2</sub> is primarily limited by phytotoxic species such as ethylene, NO<sub>x</sub> and SO<sub>2</sub> together with occupational CO limits. Because the calciner is electrically heated, no such combustion-derived contaminants are introduced, and the Aspen Plus model predicts an essentially pure CO<sub>2</sub> stream (≈100 mol% after steam removal). The suitability of this stream for OCAP delivery is therefore adopted as a design assumption.

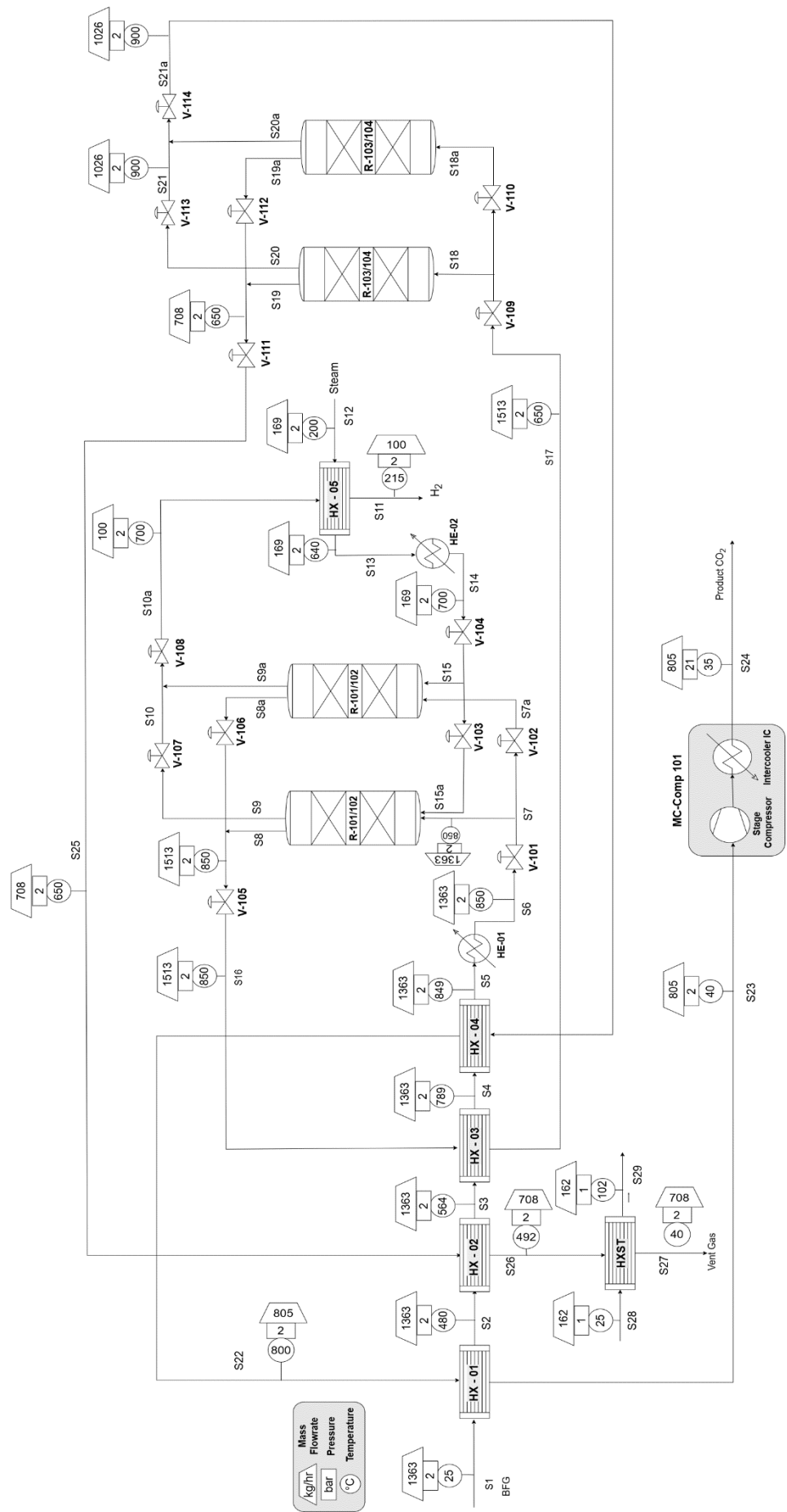


Figure 4.12 Process flow diagram of the calcium looping process created using draw.io

## 4.6 Techno-Economic Assessment

### 4.6.1 Scope, accounting perspective and functional unit

The techno-economic analysis (TEA) evaluates the economic performance of the cryogenic separation and calcium-looping processes using the verified mass and energy balances developed in Aspen Plus. Capital expenditure (CAPEX), operating expenditure (OPEX), and levelized cost indicators are determined using the structured TEA methodology of Zimmermann et al. (2020), while economic viability is assessed through a discounted cash flow (DCF) analysis. [179] The evaluation is conducted from a process engineering perspective. The system boundary extends from the blast-furnace-gas (BFG) inlet to the delivery of conditioned CO<sub>2</sub> and hydrogen products, including all reaction, separation, dehydration, compression and product-conditioning units. Utility requirements are assumed to be supplied entirely by purchased grid electricity, representing an all-electric base case.

Both routes are evaluated at 1,000 Nm<sup>3</sup>/h BFG with 92 % availability (8,059 operating hours per year) and share the same iron chemical-looping front end but differ only in the downstream separation sections. For the cryogenic route, product corresponds to high-purity liquid CO<sub>2</sub> at 43 bar, whereas the calcium-looping route delivers a concentrated CO<sub>2</sub> stream at 21 bar for integration with the OCAP horticultural network. The product specifications are intentionally technology-specific, reflecting the natural process output and intended end use of each route, rather than imposing additional conditioning steps that are not intrinsic to the separation technology. After condensing out the water, the recovered hydrogen is returned to the integrated steelwork for on-site use in galvanizing, annealing, and other reducing-atmosphere processes, and is valued at 4,000 EUR/t (4 EUR/kg) in the economic assessment. Consequently, differences in economic performance isolate the effect of the downstream CO<sub>2</sub> capture and conditioning processes under realistic operating scenarios. Performance is evaluated using the levelized cost of CO<sub>2</sub> product (LCOP), the levelized cost of CO<sub>2</sub> capture (LCOC), net present value (NPV), and payback period.

The study is a feasibility-level estimate corresponding to Class 4 of the AACE International (Association for the Advancement of Cost Engineering) classification (study/feasibility), with an expected accuracy of about -30 % to +50 %. This class is appropriate for screening competing technologies and identifying the dominant cost drivers for the comparison; however, it is not a basis for a final investment decision; hence, results are therefore reported with explicit sensitivity ranges. [180]

### 4.6.2 Common economic and financial basis

A common set of financial assumptions is applied to both process routes, as summarized in **Table 4.6**. The base-case analysis assumes a discount rate of 5% and an economic project life of 10 years, which corresponds to a capital recovery factor (CRF) of 0.1295, which is calculated with the equation 4.15:

$$CRF = i(1 + i)^n / [(1 + i)^n - 1] = 0.05 \times 1.6289 / 0.6289 = 0.1295 \quad (4.15)$$

The reciprocal of the capital recovery factor, the annuity factor, is  $AF = 1/CRF = 7.7217$ , representing the present value of a €1 annual payment over 10 years at a 5% discount rate.

Capital expenditure is distributed over a three-year construction period (2026-2028) using a 20/40/40 expenditure profile, with commercial operation commencing in 2029. The remaining financial

assumptions and cost factors are adopted from established industrial, governmental, and company sources. The corporate tax rate of 29.9% corresponds to the combined German corporate tax rate, while the 2% annual price escalation reflects the European Central Bank's long-term inflation target. [181] [182] Straight-line depreciation over 10 years follows the German depreciation tables.[183] Process and project contingency allowances, engineering, procurement and construction (EPC) costs, commissioning, land acquisition and working-capital factors are based on company recommendations and AACE Practice. [180], [184] Overall, **Table 4.6** summarizes the financial basis.

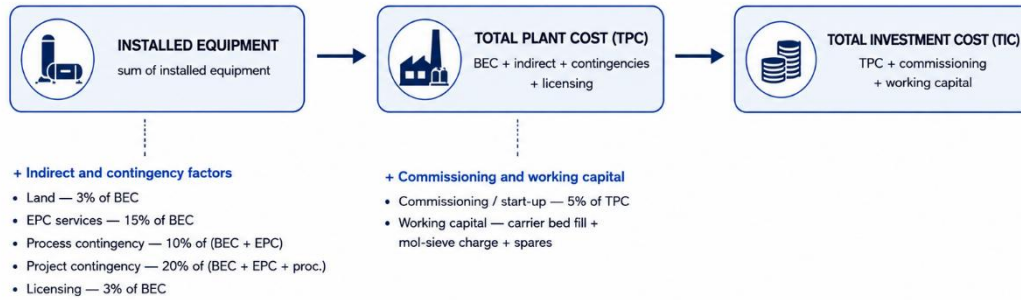
**Table 4.6** Consolidated economic and financial basis (both routes).

| Parameter                     | Value                                | Note                    |
|-------------------------------|--------------------------------------|-------------------------|
| Plant availability            | 92 % (8,059 h/y)                     | design basis            |
| Discount rate / life          | 5 % / 10 y                           | CRF = 0.1295            |
| Construction / operation      | 2026-28 (20/40/40) / 2029            | phased CAPEX            |
| Escalation                    | 2 %/y                                | ECB target              |
| Depreciation / loan           | straight-line 10 y / 10 y            | financed annex          |
| Corporate tax                 | 29.9 %                               | on profit               |
| Land / EPC / licensing        | 3 % / 15 % / 3 % of BEC              | factorial               |
| Process / project contingency | 10 % / 20 %                          | Class-4 allowance       |
| Commissioning                 | 5 % of TPC                           | start-up                |
| Maintenance                   | 5 % of FCI/y                         | fixed OPEX              |
| Insurance & taxes             | 1.15 % of FCI/y                      | fixed OPEX              |
| Operating labour              | 3 operators × 85,000 EUR/y = 255,000 | fixed OPEX              |
| Supervision                   | 15 % of labor = 38,250               | fixed OPEX              |
| Laboratory / QC               | allowance = 15,000                   | fixed OPEX              |
| Plant overheads               | 30 % of labor = 76,500               | fixed OPEX              |
| Electricity                   | 0.14 EUR/kWh (140 EUR/MWh)           | grid tariff             |
| EU-ETS price                  | 95 EUR/t CO <sub>2</sub>             | on CO <sub>2</sub> slip |

#### 4.6.3 Capital cost estimation (CAPEX)

Equipment such as heat exchangers, compressors and other process units are sized directly from the Aspen Plus modeled data. Installed equipment costs are obtained primarily from the internal cost database of RG-H<sub>2</sub> and supplemented by standard costing correlations where required. For example, the cryogenic distillation system is costed as the combined cost of the column, condenser and reboiler. The two RGibbs reactors have no physical volume within Aspen Plus and are therefore sized externally based on the oxygen-carrier inventory and reactor cycle time. They are subsequently costed as refractory-lined carbon-steel pressure vessels, which is consistent with company practice.

The installed equipment costs are then combined to determine the bare erected cost (BEC), and then the overall capital investment is estimated using the factorial method, which is shown in **Figure 4.13**. The bare erected cost (BEC) is increased by allowances for land (3%), engineering, procurement and construction (EPC, 15%), process contingency (10%), project contingency (20%), and licensing (3%) to obtain the total plant cost (TPC). Commissioning (5% of TPC) and working capital are then added to determine the total investment cost (TIC) (**Figure 4.13**). Then, the fixed capital investment (FCI), which excludes the cost of land but includes commissioning costs, is used as the basis for estimating annual maintenance and insurance costs. The installed equipment costs for the cryogenic route and calcium looping, estimated using the methodology described above, are summarized in Appendices.



**Figure 4.13** Methodology for estimating total investment cost (TIC).

#### 4.6.4 Operating cost estimation (OPEX)

Annual operating costs are divided into fixed and variable components. Variable operating costs are calculated by multiplying the annual consumption of each utility or material by its corresponding unit price. Annual material consumption is determined from the simulated mass flow rates and operating hours, while electricity costs are calculated from the equipment power demand and annual operating hours. The route-specific variable cost items are summarized in the Appendix.

The blast furnace gas (BFG) feedstock is assigned an opportunity cost rather than being treated as a free raw material. In the base case, the BFG is valued according to its energy content (Eq. 4.16):

$$P_{\text{BFG}} = \text{LHV} \times p_{\text{energy}} = 0.652 \text{ MWh/t} \times 35 \text{ EUR/MWh} = 22.83 \text{ EUR/t} \quad (4.16)$$

where the lower heating value (LHV) of 0.652 MWh/t is calculated from the BFG composition, and the energy price of 35 EUR/MWh is adopted from RG-H<sub>2</sub>. This value is included as a feedstock cost in the economic analysis.

The system boundary assumes that the nitrogen-rich off-gas leaving the CO<sub>2</sub> separation step, which contains the unconverted CO and H<sub>2</sub>, is returned to the steelworks fuel-gas network and combusted outside the battery limits of this study. Its CO<sub>2</sub> emissions and the associated EU-ETS liability are therefore attributed to the receiving installation, and no fuel-value credit is assigned to the exported gas. This is a conservative assumption because the residual heating value of approximately 168 kW would improve the economics of both capture routes. Consequently, the EU-ETS charge within the battery limits applies only to the CO<sub>2</sub> slip.

On the other hand, fixed operating costs comprise operating labor, supervision, laboratory and quality control (QC), plant overheads, maintenance, insurance, taxes and permits. Operating labor is based on three operators at an annual cost of 85,000 EUR per operator. Supervision, laboratory/QC and plant overheads are estimated according to the factors listed in **Table 4.6**, while maintenance and insurance are calculated as percentages of the fixed capital investment (FCI). Unit prices for utilities and consumables, including electricity, steam, water, sorbent, oxygen carrier and other process consumables, are obtained from the internal cost database of RG-H<sub>2</sub> and supplemented by current market references where required.

Annual revenue was calculated from the annual production of CO<sub>2</sub> and H<sub>2</sub> multiplied by their respective market prices (Eq. 4.17). The cryogenic route assumes food-grade CO<sub>2</sub> (€260/t), while the calcium-looping route assumes greenhouse-grade CO<sub>2</sub> (€80/t). Hydrogen was valued at €4/kg.

$$\text{Revenue} = \dot{m}_{\text{CO}_2} p_{\text{CO}_2} + \dot{m}_{\text{H}_2} p_{\text{H}_2} \quad (4.17)$$

#### 4.6.5 Performance indicators

Project profitability is evaluated using a DCF model, in which annual cash flows comprising revenues, operating costs, taxes, and the depreciation tax shield are discounted over the project lifetime. Accordingly, each investment cost is discounted back to the base year.

The principal economic performance indicator is the levelized cost of CO<sub>2</sub> capture (LCOC), which annualizes the total investment using the capital recovery factor (CRF) and combines it with the annual operating cost, Equ. 4.18:

$$\text{LCOC} = \frac{\text{CRF} \cdot \text{TIC} + \text{OPEX} - \text{Revenue}_{\text{non-CO}_2}}{\dot{m}_{\text{CO}_2, \text{captured}}} \quad (4.18)$$

The levelized cost of product (LCOP) is also determined as the CO<sub>2</sub> selling price that results in a net present value (NPV) of zero. The equation is used where  $\phi$  is the present-value factor accounting for the phased capital expenditure, and  $\psi$  is the discounted annuity factor, Equ. 4.19 and Equ. 4.20.

$$\text{LCOP} = \frac{((\text{TIC} \times \phi)/\psi) + \text{OPEX}_{\text{gross}} - \text{Revenue}_{\text{non-CO}_2}}{\dot{m}_{\text{CO}_2, \text{captured}}} \quad (4.19)$$

$$\text{NPV} = \sum_{t=0}^n \frac{CF_t}{(1+i)^t} \quad (4.20)$$

Both indicators are evaluated on an annualized, pre-financing and pre-tax basis to enable a consistent comparison of the two process routes. To complement the screening analysis, a financed cash-flow model is also developed. This model incorporates debt financing, straight-line depreciation over 10 years, corporate taxation, and annual price escalation, providing a more representative assessment of the project's commercial performance.

#### 4.6.6 Sensitivity analysis

A single-parameter sensitivity analysis is also performed around the base-case conditions to assess the robustness of the economic results. The parameters considered include plant scale, evaluated at 1,000, 68,500, and 274,000 Nm<sup>3</sup> h<sup>-1</sup> of BFG (1%, 25%, and 100% of the available stream), electricity price, and the EU ETS carbon price, which affects both the emissions cost associated with the residual CO<sub>2</sub> slip and the economic value of CO<sub>2</sub> capture.

Capital does not scale linearly with plant size; therefore, each equipment cost is scaled by a power-law scaling relationship, Equ. 4.21:

$$C = C_{\text{ref}} \left( \frac{S}{S_{\text{ref}}} \right)^{0.65} \quad (4.21)$$

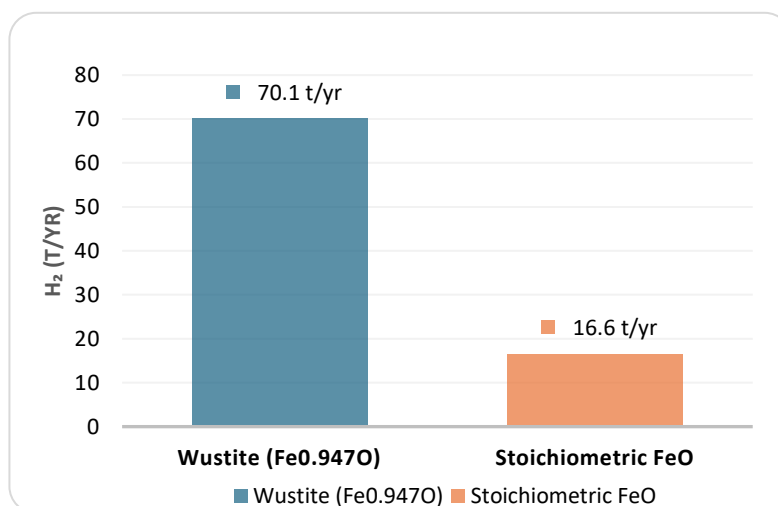
Where  $C$  - scaled equipment cost,  $C_{\text{ref}}$  - reference equipment cost,  $S$  - equipment size or capacity, and  $S_{\text{ref}}$  - reference equipment size or capacity, and the scaling exponent of 0.65 is applied consistently throughout the economic model. Variable operating costs, CO<sub>2</sub> captured, and hydrogen revenue were assumed to scale linearly with plant throughput, while operating labor increased in discrete steps (three, six, and ten operators). The levelized cost at each scale was then calculated by annualizing the scaled capital cost, adding the scaled operating cost, subtracting the hydrogen revenue, and dividing by the annual CO<sub>2</sub> captured. As plant capacity increases, the levelized cost decreases because capital costs increase less rapidly than CO<sub>2</sub> production. Consequently, considering different plant capacities enables the effect of plant scale on the economic performance to be evaluated.

## 5 Results and Discussion

This chapter presents and discusses the technical and economic performance of the proposed process configurations. The technical and economic outcomes are analyzed to compare the performance of the calcium-looping and cryogenic separation routes. Detailed Aspen Plus simulation outputs, including stream tables and unit operation results, are provided in Appendix. Both technologies comprise a common front-end iron-oxide loop which is examined first, as its performance fixes the composition and flow of the  $\text{CO}_2$ -rich stream that both capture routes should subsequently treat. The blast-furnace gas is fed to the reduction reactor R-101, which has a total flow of 1,362.9 kg/h (44.62 kmol/h), where the reducing species in the gas ( $\text{CO}$  and  $\text{H}_2$ ) strip lattice oxygen from the carrier and are themselves oxidized. Throughout this chapter the adopted flowsheet is referred to as the upper-bound (adopted) case and the phase-consistent wüstite case as the lower bound; the basis for this bounding is established below, and the scale-up results of Section 5.4.3 are to be read as a conditional screening on this basis.

The reduced iron phase in this temperature range is non-stoichiometric wüstite,  $\text{Fe}_{1-x}\text{O}$ , whose composition varies continuously with temperature and oxygen potential, and no single fixed-composition component available in Aspen Plus reproduces this behaviour. Two complete and internally phase-consistent simulations were therefore carried out, one representing the reduced phase as stoichiometric  $\text{FeO}$  ( $x = 0$ ) in both reactors and one as the databank phase  $\text{Fe}_{0.947}\text{O}$  ( $x = 0.053$ ) in both reactors. The two compositions bracket that of the real phase, and their equilibria bracket the measured  $\text{Fe}_3\text{O}_4$ /wüstite boundary of **Figure 2.4**, the  $\text{FeO}$  representation predicting an off-gas oxidation degree of 0.897 and the wüstite representation 0.66, against a measured value of approximately 0.78 at 850 °C.

In the reduction reactor (R-101), the  $\text{FeO}$  representation predicts the more complete oxidation of  $\text{CO}$ , and the equilibrium  $\text{CO}_2$  mole fraction in the reduced gas is 0.394, compared with approximately 0.29 when the reduced phase is represented as wüstite. This difference arises from the equilibrium position determined by the Gibbs-energy data of the two solid phases rather than from their oxygen-carrying capacity. The Gibbs-energy data for wüstite place the  $\text{Fe}_3\text{O}_4/\text{Fe}_{0.947}\text{O}$  equilibrium boundary at a lower gas oxidation degree, causing the reaction to reach thermodynamic equilibrium earlier and resulting in the conversion of fewer moles of  $\text{CO}$ . This is consistent with the Baur-Glässner diagram, which



**Figure 5.1** Comparison of  $\text{H}_2$  yield for wüstite and stoichiometric  $\text{FeO}$ .

identifies non-stoichiometric wüstite as the thermodynamically stable reduced iron oxide under the operating temperatures and oxygen potentials considered in this study. [76] Consequently, the equilibrium predicted using the Aspen wüstite component is more conservative, resulting in lower CO conversion and reduced CO<sub>2</sub> production. However, in the oxidation reactor, the opposite trend is observed. Gibbs free-energy minimization using the wüstite representation predicts a higher steam-to-hydrogen conversion and therefore a higher H<sub>2</sub> yield than the FeO representation, which returns a yield of only about 1.02 kmol/h H<sub>2</sub> under the same steam feed (**Figure 5.1**). These opposing effects are summarized in **Table 5.1**.

The two simulations differ correspondingly in the oxygen transferred per pass. At the simulated active carrier feed of 9.38 kmol/h Fe<sub>3</sub>O<sub>4</sub>, the wüstite case is equilibrium-limited. 4.32 kmol O/h are transferred to the gas, 4.19 kmol/h of Fe<sub>3</sub>O<sub>4</sub> remain unreacted, and the same 4.32 kmol O/h are restored in the oxidation step, so that the carrier returns to its initial composition and the solid loop closes. The FeO case is instead limited by the carrier supply, the whole feed being converted and 9.38 kmol O/h transferred, of which only 1.02 kmol O/h are restored under the same steam feed. The CO conversion of 79.8% reported for that case is therefore set by the carrier feed rate rather than by the gas-solid equilibrium.

The values reported for the adopted case combine the CO conversion and off-gas composition of the FeO simulation with the hydrogen yield of the wüstite simulation. This combination does not correspond to a single simulation and is therefore reported as an optimistic upper bound, with the phase-consistent wüstite case (**Table 5.1**, 32.6% CO conversion, off-gas CO<sub>2</sub> fraction 0.289) as the lower bound.

These findings demonstrate that the oxygen-carrying characteristics of the iron-oxide material play a crucial role in determining CO<sub>2</sub> conversion and H<sub>2</sub> production, and that engineering the oxygen carrier to maximize reversible oxygen transfer while maintaining structural stability is essential for improving the performance of chemical looping systems. Future work should therefore re-simulate both reactors with a single, consistent non-stoichiometric wüstite composition, repeat this at several compositions across the Fe<sub>1-x</sub>O field, and carry each case through to the techno-economic assessment in order to confirm whether the levelized costs and the ranking of the two capture routes remain unchanged.

**Table 5.1** Results of the two phase-consistent simulations and the values combined in the upper-bound (adopted) case.

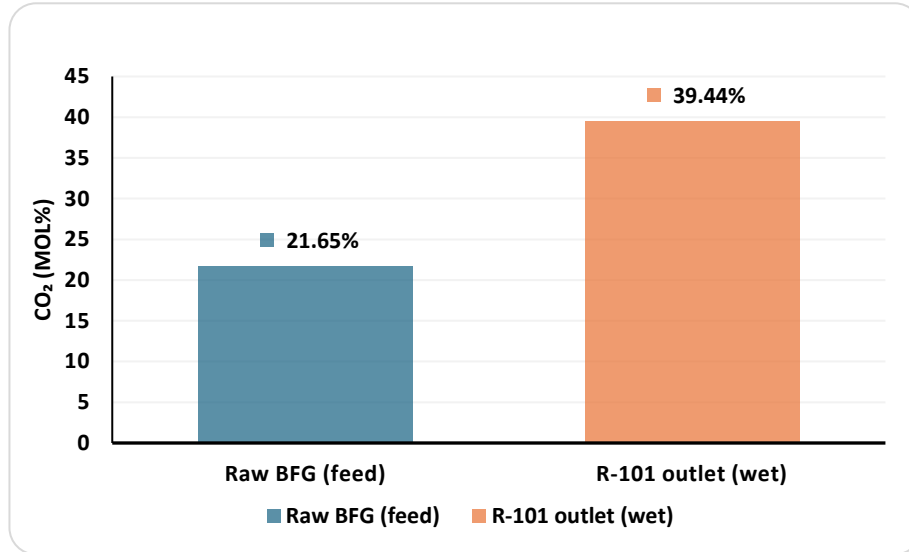
| Quantity                                      | FeO model | Wüstite model | Upper bound (adopted) |
|-----------------------------------------------|-----------|---------------|-----------------------|
| R-101 CO conversion (%)                       | 79.8      | 32.6          | FeO                   |
| R-101 CO <sub>2</sub> mole fraction (off-gas) | 0.394     | 0.289         | FeO                   |
| R-102 H <sub>2</sub> yield (t/y)              | 16.6      | 70.1          | Wüstite               |
| R-102 Steam-to-H <sub>2</sub> conversion (%)  | 10.9      | 46.1          | Wüstite               |

The upper bound (adopted) case simulation converts 79.8 % of the inlet CO (from 9.945 to 2.009 kmol/h) and 90.4 % of the inlet H<sub>2</sub> (from 1.593 to 0.152 kmol/h). Because each mole of CO or H<sub>2</sub> that reacts abstracts one oxygen atom from the carrier, 7.94 kmol/h of CO is oxidized to CO<sub>2</sub> and 1.44 kmol/h of H<sub>2</sub> to steam. The reactor therefore generates 1.44 kmol/h (26.0 kg/h) of water that is absent from the feed and raises the CO<sub>2</sub> flow from 9.66 to 17.59 kmol/h. The reduced gas leaves R-101 strongly enriched in CO<sub>2</sub> (CO<sub>2</sub> mole fraction 0.394) (**Figure 5.2**) and depleted in the combustible species, with the full outlet composition summarized in **Table 5.2**. The 9.38 kmol/h of lattice oxygen

transferred to the gas reduces the 9.38 kmol/h of  $\text{Fe}_3\text{O}_4$  entering the reactor to 28.13 kmol/h of iron (II) oxide, which is then oxidized in the R-102 oxidation step.

**Table 5.2** Inlet and outlet molar flows of the reduction reactor R-101 (850 °C, 2 bar).

| Species          | Feed in (kmol/h)                    | R-101 (kmol/h) | out | Out mole frac. | Change / note                          |
|------------------|-------------------------------------|----------------|-----|----------------|----------------------------------------|
| CO               | 9.945                               | 2.009          |     | 0.045          | 79.8 % converted                       |
| H <sub>2</sub>   | 1.593                               | 0.152          |     | 0.003          | 90.4 % converted                       |
| CO <sub>2</sub>  | 9.659                               | 17.59          |     | 0.394          | +7.93 (formed)                         |
| H <sub>2</sub> O | 0                                   | 1.441          |     | 0.032          | +1.44 (formed)                         |
| N <sub>2</sub>   | 23.42                               | 23.42          |     | 0.525          | inert                                  |
| Gas total        | 44.62                               | 44.61          |     | 1.000          | –                                      |
| Carrier (solid)  | Fe <sub>3</sub> O <sub>4</sub> 9.38 | FeO 28.13      |     | –              | Fe <sub>3</sub> O <sub>4</sub> → 3 FeO |



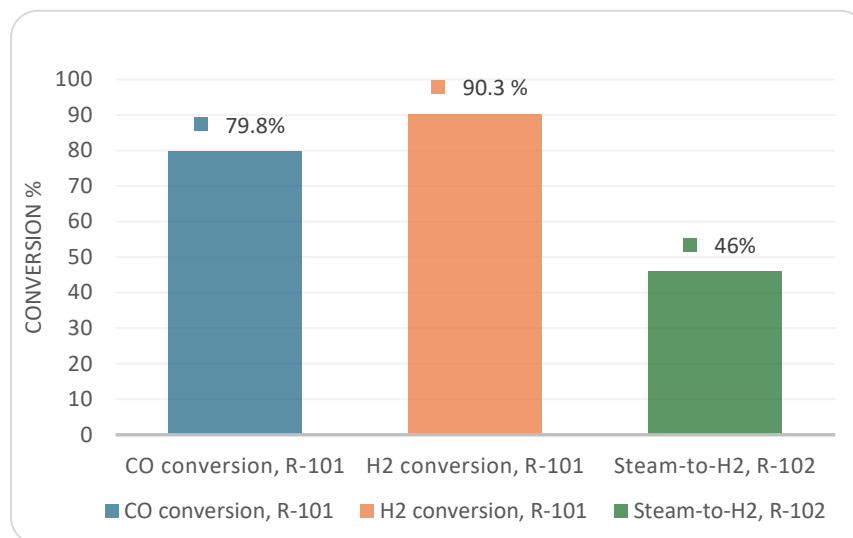
**Figure 5.2** CO<sub>2</sub> concentration before and after the H2Loop front-end process.

The outlet gas of R-101 corresponds to a gas oxidation degree of  $\text{GOD} = 17.59 / (17.59 + 2.009) = 0.897$ , which exceeds the measured  $\text{Fe}_3\text{O}_4$ /wüstite boundary of approximately 0.78 at 850 °C. This reflects the idealized stoichiometric-FeO representation, whose Gibbs-energy data place the equilibrium at a higher oxidation degree, and the adopted reduction step is therefore an optimistic upper bound, as discussed above.

In the steam-iron reactor (R-102) operating at 700 °C, the reactor feed is supplied with 169 kg/h of steam (9.38 kmol/h) and produces 8.7 kg/h of hydrogen (4.32 kmol/h), which is equivalent to 70.1 t/yr. This corresponds to a steam-to-hydrogen conversion of 46.1% with approximately 78 kg/h of steam consumed and the remaining 91 kg/h leaving unreacted to be condensed and recycled. This conversion is set by thermodynamic equilibrium and by the quantity of reduced carrier available, rather than by reaction kinetics. At 700 °C, the  $\text{Fe}_3\text{O}_4/\text{Fe}_{1-x}\text{O}$  equilibrium establishes the maximum attainable  $\text{H}_2/\text{H}_2\text{O}$  ratio, beyond which no further hydrogen can be produced regardless of residence time. The steam feed of 9.38 kmol/h is stoichiometric with respect to the oxygen withdrawn in the stoichiometric-FeO representation of the reduction step. In the phase-consistent wüstite case, in which 4.32 kmol O/h are withdrawn, the same feed represents a molar excess of about 2.2, and the 4.32 kmol/h of hydrogen produced restore exactly the oxygen removed, so that the carrier leaving the oxidation reactor is returned to its initial composition of 9.38 kmol/h  $\text{Fe}_3\text{O}_4$  and the solid loop closes.

The conversion of 46.1 % accordingly refers to the utilization of the supplied steam and not to incomplete regeneration of the carrier; the unreacted fraction is condensed and recycled. The operating cost assessment nevertheless charges the full steam flow of 169 kg/h, with no credit taken for condensate recovery, and is therefore conservative in this respect. Furthermore, operating the oxidation reactor at a lower temperature than the reduction reactor (700 °C versus 850 °C) favors hydrogen production, as the exothermic steam oxidation reaction shifts towards higher hydrogen yields at lower temperatures (**Figure 5.3**).

Furthermore, the selected operating temperatures also resulted in the absence of carbon deposition in both reactors. No solid carbon phase was predicted in either the reduction reactor (850 °C) or the



**Figure 5.3** Reactant conversions in the H2Loop front-end process.

oxidation reactor (700 °C) at equilibrium, which confirms that the chosen operating conditions remain outside the thermodynamically favorable region for carbon formation. This is consistent with the temperature selection discussed in the methodology and supports stable cyclic operation of the oxygen carrier.

Aspen Plus reports the net heat duty required to maintain the specified operating temperature for each RGibbs reactor. The reduction reactor (R-101) is endothermic, requiring approximately 517 kW at 850 °C, whereas the steam oxidation reactor (R-102) is exothermic, releasing approximately 158 kW at 700 °C. Because the loop is implemented as valve-switched fixed beds in which the same bed alternates between the two half-cycles, the heat released during oxidation is deposited as sensible heat in the bed and reduces the external heat required in the subsequent reduction step, giving a net thermal demand of 359 kW; this is a consequence of the cyclic fixed-bed configuration and not of heat exchange between the two reactors, which would not be permissible from a 700 °C source to an 850 °C demand. Applying the 95 % electrical conversion efficiency used throughout the cost assessment gives the 377.9 kW charged. Supplying the reduction duty entirely by electricity without any credit for the oxidation exotherm would add approximately 166 kW of electrical demand to both routes and would not alter the ranking of the two routes. These duties exclude the separate sensible heat required to preheat the incoming blast-furnace gas from 25 °C to 850 °C, which contributes a further 356 kW.

The magnitude and sign of the reactor duties reflect the thermodynamics of the redox cycle resolved by the RGibbs model. In the reduction reactor, heat must be supplied to maintain the operating temperature while lattice oxygen is transferred from magnetite to the reducing gases, thereby reducing the oxygen carrier to a lower oxidation state. Although the oxidation of CO and H<sub>2</sub> is individually exothermic, the overall equilibrium at 850 °C requires a net heat input to sustain the reduction of the oxygen carrier under the specified operating conditions. In contrast, the oxidation reactor reverses this process. Steam re-oxidizes the reduced iron oxide, thereby restoring lattice oxygen to the oxygen carrier while hydrogen is produced. As this oxidation step is overall exothermic, heat is released rather than consumed, which results in the negative reactor duty predicted by Aspen Plus.

## 5.1 Cryogenic Separation

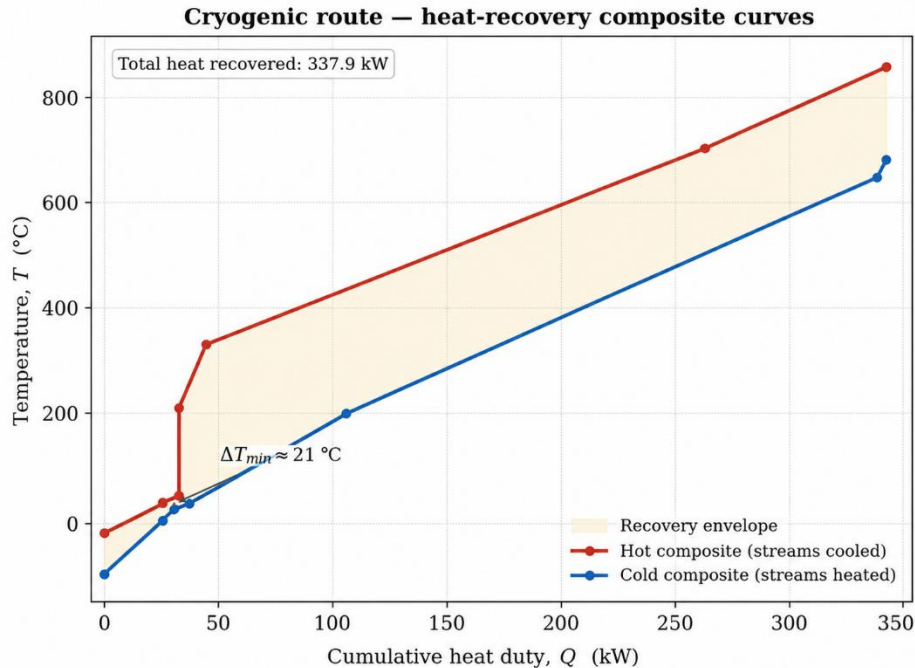
Using the 10-stage RadFrac distillation column operating at 43 bar and -35 °C produced a high-purity liquid CO<sub>2</sub> product containing 99.9 mol% CO<sub>2</sub>, which slightly exceeds the required product specification. Of the 774.4 kg/h of CO<sub>2</sub> entering the column, 735.7 kg/h was recovered in the liquid bottoms product while only 38.7 kg/h was lost with the nitrogen-rich overhead vapor, corresponding to a single-pass CO<sub>2</sub> recovery of 95.0%. Maintaining this separation required a condenser duty of approximately 88.8 kW at -95.3 °C and a reboiler duty of approximately 44.0 kW at 6.9 °C. The corresponding reflux ratio and boil-up ratio obtained from the Aspen Plus design specification were 0.62 and 1.00, respectively.

The high purity and recovery achieved are a direct consequence of the favorable vapor-liquid equilibrium of the CO<sub>2</sub>-N<sub>2</sub> system under the selected operating conditions. At 43 bar and a cryogenic temperature of -35 °C, CO<sub>2</sub> readily condenses while nitrogen remains predominantly in the vapor phase owing to its substantially higher volatility. Consequently, only a small amount of CO<sub>2</sub> is lost with the overhead stream while the liquid bottoms product reaches the required purity. The simulation predicts that the liquid CO<sub>2</sub> product still contains approximately 0.1 mol% N<sub>2</sub>, which indicates that complete nitrogen removal is thermodynamically unattainable under the selected operating conditions because of the finite vapor-liquid equilibrium solubility of nitrogen in liquid CO<sub>2</sub>. As a result, the product purity approaches 100 mol% CO<sub>2</sub> but does not reach it.

The simulated operating conditions are also thermodynamically consistent with the CO<sub>2</sub> phase behavior. The condenser operates at -95.3 °C, providing the refrigeration required to condense CO<sub>2</sub> selectively, whereas the reboiler operates at only 6.9 °C, which reflects that the elevated operating pressure of 43 bar substantially increases the saturation temperature of CO<sub>2</sub>. The relatively low reflux ratio of 0.62 represents the converged value determined by the Aspen Plus Design Specification to satisfy the desired CO<sub>2</sub> purity. As the reflux ratio governs the internal liquid and vapor traffic within the column, it directly determines the condenser and reboiler duties required to achieve the specified separation. This value indicates that the desired product purity can be achieved without excessive internal recirculation, which confirms the favorable separation characteristics of the CO<sub>2</sub>-N<sub>2</sub> system under the selected operating conditions. Overall, these results demonstrate that the selected operating conditions provide an effective balance between CO<sub>2</sub> purity, recovery, and energy consumption, which confirms the suitability of cryogenic distillation for producing high-purity liquid CO<sub>2</sub> from the iron-oxide looping process.

Prior to cryogenic separation, the CO<sub>2</sub>-rich gas is compressed to the column operating pressure of 43 bar using a four-stage intercooled compressor, for which the simulation predicts a total shaft power requirement of 127 kW. The compressor is sized and costed on a design basis of 138.5 kW, which includes a margin of approximately 9 % over the calculated duty, and the operating cost assessment charges 145.8 kW<sub>e</sub>, obtained by dividing this design rating by the 95 % drive efficiency applied throughout the cost model. Charging electricity on the margined rating rather than on the calculated shaft power is conservative by approximately 12 kW, or about 2 EUR per tonne of CO<sub>2</sub>. The compressed gas is subsequently pre-cooled from 35 °C to -35 °C, requiring 40.9 kW of cooling, before entering the distillation column. Within the column, a further 88.8 kW of refrigeration is required in the condenser operating at approximately -95.3 °C, whereas the reboiler requires only 44.0 kW at approximately 6.9 °C. The combined feed precooling and condenser duties therefore amount to approximately 130 kW of refrigeration. The refrigeration duty is therefore comparable to the compressor power requirement (127 kW); however, it represents the defining energy requirement of the cryogenic route because it must be supplied at cryogenic temperature levels.

The composite curves for the cryogenic route (**Figure 5.4**) span a much broader temperature range than those of the calcium-looping process, extending from approximately -95 to 850 °C. The proposed heat-exchanger network recovers 337.9 kW of heat internally through four process-to-process heat exchangers, operating with a minimum temperature approach of approximately 21 °C. Two distinct heat-recovery regions are evident. Above ambient temperatures, the hot reactor effluents preheat the blast-furnace-gas feed and reactor steam, with HX-101 and HX-104 recovering 257.9 kW and 47.3 kW, respectively, similar to the heat-recovery arrangement of the calcium-looping process. Below ambient temperatures, the cold nitrogen-rich overhead stream leaving the distillation column (as cold as -95 °C) is used in HX-102 and HX-103 to pre-cool the compressed CO<sub>2</sub>-rich feed before it enters the refrigeration system, recovering an additional 32.7 kW of refrigeration. The near-vertical step in



**Figure 5.4** Composite curves of the cryogenic heat-recovery network, showing 337.9 kW of recovered heat, sub-ambient integration to -95 °C, and a minimum temperature approach of approximately 21 °C.

the hot composite curve at approximately 35-50 °C marks the transition between these high- and low-temperature recovery regions, while the minimum temperature approach of about 21 °C occurs within the cryogenic section. This low-temperature heat recovery directly reduces the external refrigeration duty required before cryogenic distillation.

Comparison of the composite curves with the proposed heat-exchanger network (**Table 5.3**) indicates that, although 337.9 kW of heat is already recovered internally, additional heat integration remains theoretically possible. However, even under ideal heat-integration conditions, the process still requires a minimum external cold utility of approximately 180 kW. Because much of this remaining duty occurs at cryogenic temperatures, it cannot be supplied by conventional process heat exchange and instead requires mechanical refrigeration. This irreducible refrigeration demand is the physical basis for the electricity consumption attributed to the cryogenic route in the techno-economic assessment.

**Table 5.3** Process-to-process heat exchangers in the cryogenic model (duties computed from stream enthalpies).

| Unit   | Hot stream (cooled)                        | Hot T (°C)    | Cold stream (heated)                       | Cold T (°C)   | Duty (kW) | Function                         |
|--------|--------------------------------------------|---------------|--------------------------------------------|---------------|-----------|----------------------------------|
| HX-101 | 4 – reduced gas (CO <sub>2</sub> -rich)    | 850.0 → 330.0 | 1 – BFG feed                               | 25.0 → 638.7  | 257.9     | Feed / reactor-effluent recovery |
| HX-104 | 5 – H <sub>2</sub> + steam (R-102 product) | 700.0 → 210.2 | 7 – steam                                  | 200.0 → 680.0 | 47.3      | Steam pre-heat                   |
| HX-103 | 16 – compressed CO <sub>2</sub> gas        | 35.0 → -20.0  | 20 – N <sub>2</sub> -rich vent (column OH) | -95.3 → 5.3   | 25.6      | Cold recovery (pre-cooling)      |
| HX-102 | 10 – CO <sub>2</sub> -rich gas             | 50.0 → 38.0   | 21 – N <sub>2</sub> -rich vent             | 5.3 → 35.7    | 7.1       | Cold recovery                    |

## 5.2 Calcium looping

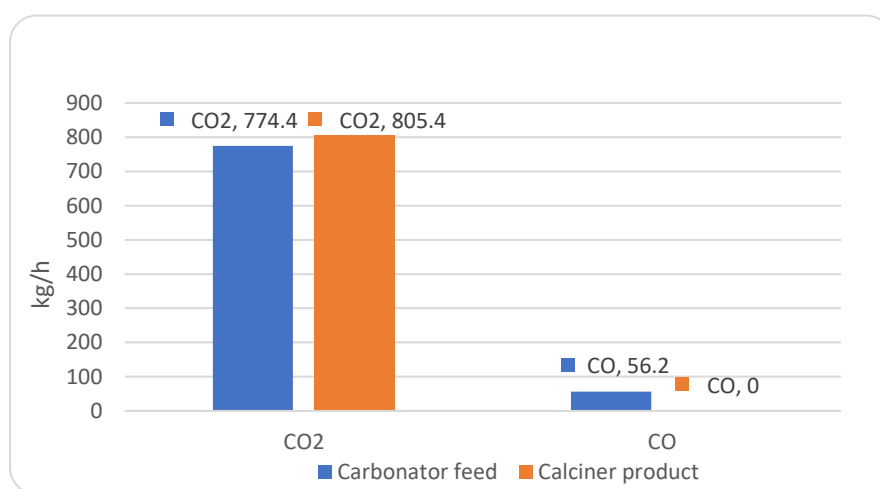
In terms of the calcium-looping route, following the front-end iron-oxide looping process, the CO<sub>2</sub>-rich gas enters the carbonator where gaseous CO<sub>2</sub> is chemically absorbed by CaO to form CaCO<sub>3</sub>. The carbonator operating at 650 °C achieved a single-pass CO<sub>2</sub> capture efficiency of 97.6%, reducing the gaseous CO<sub>2</sub> flow from 774.35 kg/h at the reactor inlet to only 18.91 kg/h in the outlet stream. Consequently, approximately 755.4 kg/h of gaseous CO<sub>2</sub> is transferred from the gas phase to the solid sorbent as CaCO<sub>3</sub>, leaving only a small residual CO<sub>2</sub> concentration in the outlet gas. The very low CO<sub>2</sub> slip demonstrates that the carbonation reaction proceeds close to thermodynamic equilibrium under the selected operating conditions.

This high capture performance is primarily a consequence of the favorable thermodynamics of the CaO-CaCO<sub>3</sub> system at 650 °C. At this temperature, the equilibrium CO<sub>2</sub> partial pressure over CaO is approximately 0.01 atm, whereas the CO<sub>2</sub> partial pressure in the inlet gas at 1.5 bar is approximately 0.59 bar. The resulting driving force is therefore around sixty times greater than the equilibrium value, which strongly favors carbonation. Under these conditions, CO<sub>2</sub> continuously reacts with CaO to form calcium carbonate and progressively decreases the gas-phase CO<sub>2</sub> concentration until only a small equilibrium residual remains. The selection of 650 °C therefore represents an effective compromise between thermodynamic equilibrium and reaction kinetics. At higher temperatures, the equilibrium

CO<sub>2</sub> pressure increases rapidly, which reduces the carbonation driving force, whereas lower temperatures improve equilibrium but significantly decrease the reaction rate.

In the calciner operating at 900 °C, the captured calcium carbonate was completely decomposed, regenerating CaO for recycling to the carbonator while releasing a concentrated CO<sub>2</sub> product stream of 805.38 kg/ h (6,491 t/yr). Thereby, the simulated CO<sub>2</sub> stream exceeded the required product specification of ≥95 mol% CO<sub>2</sub> for the end use. Unlike the cryogenic route where CO<sub>2</sub> must be separated from a multicomponent gas mixture, the calciner generates CO<sub>2</sub> directly through the thermal decomposition of CaCO<sub>3</sub>. As a result, nitrogen remains in the process gas, while the electrically heated calciner avoids dilution by combustion flue gases, producing a highly concentrated CO<sub>2</sub> stream. Furthermore, the calcination temperature of 900 °C ensures that the equilibrium CO<sub>2</sub> pressure exceeds the CO<sub>2</sub> partial pressure within the reactor, thereby driving CaCO<sub>3</sub> decomposition towards completion and enabling efficient regeneration of the CaO sorbent for subsequent carbonation cycles. The calciner was modeled as an RStoic reactor assuming complete decomposition of CaCO<sub>3</sub>, consistent with common modeling practice reported in the literature. [171] Under this assumption, the simulated product stream consists almost entirely of CO<sub>2</sub> released during calcination. In practice, however, the product purity is expected to be marginally lower due to the presence of trace impurities, such as residual water vapor left from the carbonation step. Nevertheless, these impurities are expected to have only a negligible effect on product quality, and the CO<sub>2</sub> purity would remain well above the required specification of ≥95 mol%, even if the product is not perfectly pure under industrial operating conditions.

Furthermore, an initial inspection of the converged Aspen Plus results revealed an apparent mass-balance inconsistency within the calcium-looping subsystem. The concentrated CO<sub>2</sub> product stream leaving the calciner contained 805.38 kg/h of CO<sub>2</sub>, exceeding the 774.35 kg/h entering the carbonator. At first glance, this suggests that the system produces 31.03 kg/ h more CO<sub>2</sub> than it receives, apparently violating mass conservation. However, a species-level analysis demonstrates that the overall carbon balance is rigorously satisfied (**Table 5.4**). The apparent discrepancy arises because the carbonator, modeled as an RGibbs reactor, is not restricted to the carbonation reaction alone but allows all thermodynamically favorable equilibrium reactions to occur simultaneously.



**Figure 5.5** CO<sub>2</sub> and CO flow rates across the full-scale carbonator.

Consequently, residual carbon monoxide reacts with steam via the water-gas shift (WGS) reaction (Eq 2.7), generating additional  $\text{CO}_2$  and  $\text{H}_2$  within the carbonator.

The simultaneous occurrence of carbonation continuously removes the newly formed  $\text{CO}_2$  from the gas phase through  $\text{CaCO}_3$  formation, reducing its partial pressure and shifting the WGS equilibrium further towards the products according to Le Châtelier's principle. This coupling between the two equilibrium reactions promotes additional CO conversion while increasing the amount of carbon fixed within the circulating sorbent.

The simulated stream compositions clearly demonstrate this behavior. The CO flow decreased from 56.27 to 24.49 kg/h, corresponding to the conversion of 31.78 kg/h of CO through the WGS reaction. This generated approximately 50.0 kg/h of additional  $\text{CO}_2$  together with an increase in  $\text{H}_2$  production from 0.31 to 2.57 kg/h. Consequently, the total  $\text{CO}_2$  available for carbonation increased from 774.35 to approximately 824.35 kg/h before being captured by CaO. As a result, the calciner ultimately released 805.38 kg/h of concentrated  $\text{CO}_2$ , exceeding the  $\text{CO}_2$  entering the carbonator because part of the carbon initially present as CO had been converted into  $\text{CO}_2$  and subsequently transported through the  $\text{CaCO}_3/\text{CaO}$  looping cycle as shown in **Figure 5.5**.

To confirm that this behavior does not violate mass conservation, an elemental carbon balance was performed across the integrated carbonation-calcination subsystem. As summarized in **Table 5.4**, the balance closes within 0.004%, with 235.31 kg/h entering and 235.30 kg/h leaving the system, which is well within the numerical convergence tolerance of Aspen Plus. The synergistic interaction between carbonation and the water-gas shift reaction increases single-pass  $\text{CO}_2$  capture by converting residual CO into additional recoverable  $\text{CO}_2$  while simultaneously enhancing  $\text{H}_2$  production. Beyond improving carbon utilization, this behavior also provides a favorable contribution to the overall process economics by increasing the quantity of valuable products obtained from the same blast furnace gas feed.

**Table 5.4** Carbon balance verification for the calcium-looping process.

| Stream                | Species                 | Mass flow (kg/h) | Carbon calculation    | Carbon flow (kg C/h) |
|-----------------------|-------------------------|------------------|-----------------------|----------------------|
| Carbonator inlet      | CO                      | 56.27            | $56.27 \times 12/28$  | <b>24.12</b>         |
|                       | $\text{CO}_2$           | 774.35           | $774.35 \times 12/44$ | <b>211.19</b>        |
|                       | <b>Total carbon in</b>  | —                | —                     | <b>235.31</b>        |
| Carbonator outlet     | CO                      | 24.49            | $24.49 \times 12/28$  | <b>10.49</b>         |
|                       | $\text{CO}_2$           | 18.91            | $18.91 \times 12/44$  | <b>5.16</b>          |
| Calciner product (M2) | $\text{CO}_2$           | 805.38           | $805.38 \times 12/44$ | <b>219.65</b>        |
|                       | <b>Total carbon out</b> | —                | —                     | <b>235.30</b>        |

In terms of thermal performance, the Aspen Plus energy balance shows that the calcium-looping process is dominated by the large reaction enthalpies associated with carbonation and calcination. The RGibbs reactors directly report the heat duties specified at operating temperatures, which provides insight into the thermal behavior of the calcium-looping process. The carbonator (R-103), operating at 650 °C, is strongly exothermic which is releasing 897.8 kW as  $\text{CO}_2$  reacts with CaO to form  $\text{CaCO}_3$ . In contrast, the calciner (R-104), operating at 900 °C, is highly endothermic and requires 1,024.4 kW to decompose  $\text{CaCO}_3$  and regenerate the CaO sorbent. The integrated H2Loop front end contributes an additional 517.4 kW reduction duty in reactor R-101, partially offset by the 158 kW released during oxidation in R-102, resulting in a net front-end thermal demand of 359 kW,

corresponding to an electrical input of 377.9 kW, as shown in **Figure 5.7**. Consequently, the calciner represents the largest thermal duty in the process.

Although the carbonator releases almost 900 kW of heat, this energy cannot directly supply the calciner because the two reactors operate at significantly different temperature levels. The carbonator operates at 650 °C, whereas the calciner requires 900 °C, creating a temperature difference of approximately 250 °C. According to the second law of thermodynamics, heat cannot be transferred spontaneously from a lower-temperature source to satisfy a higher-temperature demand. Consequently, despite the substantial heat released during carbonation, external energy is required to drive the endothermic calcination reaction. In the present study, this heat is supplied electrically. The 1,024.4 kW calcination duty therefore corresponds to an electrical input of 1,078.3 kW, assuming an electric heater efficiency of 95%. Together with the net front-end reactor heating (377.9 kW), the CO<sub>2</sub> compression power (52.7 kW), and the two small trim heaters (7 kW), the total electrical demand of the calcium-looping process reaches approximately 1.52 MW (**Table 5.5**). Although several units contribute to the overall electricity consumption, the electric calciner alone accounts for approximately 71% of the total plant demand, making it the dominant consumer of electrical energy. This high-temperature regeneration step is therefore the principal contributor to the process-specific electricity consumption of 1.88 MWh/t CO<sub>2</sub> captured and, as discussed in the techno-economic assessment, is the primary factor limiting the economic competitiveness of the electrically heated calcium-looping route.

**Table 5.5** Electrical demand of the calcium-looping process at 1,000 Nm<sup>3</sup>/h BFG feed.

| Electrical load                               | kW           | Share        |
|-----------------------------------------------|--------------|--------------|
| Electric calciner (CAL-101)                   | 1,078        | 71.1 %       |
| Front-end reactor heating (R-101/R-102)       | 378          | 24.9 %       |
| CO <sub>2</sub> compressor (M-COM01 → 21 bar) | 53           | 3.5 %        |
| Feed-preheat and steam-superheat trims        | 7            | 0.5 %        |
| <b>Total electricity demand</b>               | <b>1,516</b> | <b>100 %</b> |

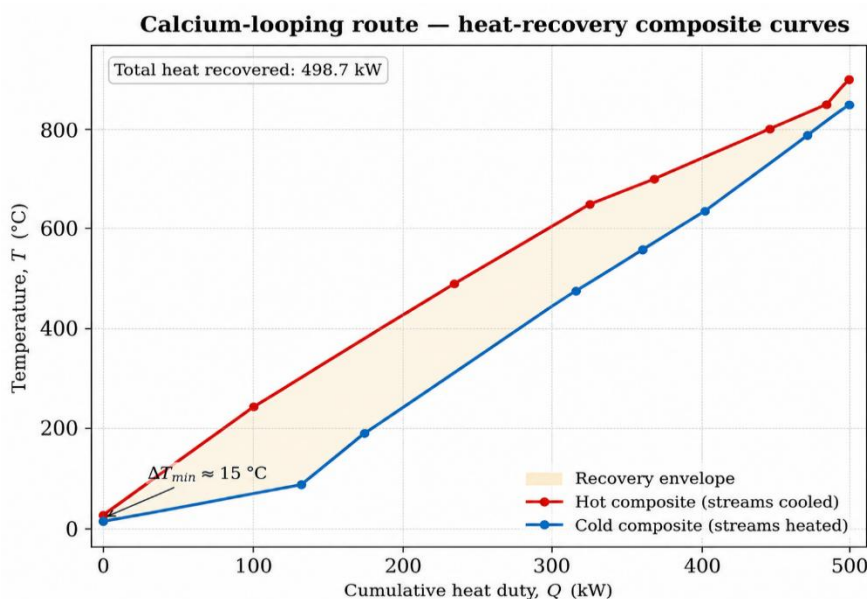
Furthermore, the composite curves for the calcium-looping process (**Figure 5.6**) demonstrate that the process is highly integrated and capable of recovering substantial quantities of sensible heat internally. Heat exchange occurs entirely within the high-temperature range of 25-900 °C where the hot and cold composite curves remain closely matched, corresponding to 498.7 kW of process-to-process heat recovery. The hot composite is primarily formed by the calciner CO<sub>2</sub> product stream, the reduced gas leaving the reduction reactor, and the decarbonized nitrogen-rich off-gas, whereas the cold composite is dominated by preheating the blast furnace gas feed together with steam generation for the oxidation reactor.

The closest approach between the composite curves occurs at heat exchanger (HX01), where a minimum temperature difference of approximately 15 °C defines the process pinch. The nearly parallel shape of the composite curves over most of the temperature range indicates an effective thermal match between the available hot and cold streams, allowing the majority of the recoverable sensible heat to be recycled internally. As a result, the blast furnace gas feed can be heated from ambient temperature to almost its reactor inlet temperature with only minimal external utility input.

The benefits of this integration are further reflected in the exchanger network summarized in **Table 5.6**. Six process-to-process heat exchangers recover a combined 498.7 kW, with HX01 providing the largest individual duty (187.3 kW) by recovering heat from the calciner CO<sub>2</sub> product stream to preheat the incoming blast furnace gas. The remaining exchangers recover heat from the reduction products,

the decarbonized off-gas, and the hydrogen-rich oxidation products, thereby distributing thermal energy efficiently throughout the process. Consequently, only two small trim heaters are required to raise the reactor feeds to their final operating temperatures, supplying 0.43 kW (HE01) and 6.4 kW (HE02), respectively. Of this total, 398.9 kW is process-to-process integration that offsets the sensible heating requirement of the process streams, while the remaining 99.8 kW recovered in HXST is low-grade heat raised as hot water at 101.5 °C from the nitrogen-rich vent. This stream does not displace an internal duty and is therefore not part of the internal integration; it is credited instead as exported waste heat in the operating cost assessment.

Despite this high degree of heat integration, the composite curves also demonstrate an important limitation of the process. The 498.7 kW recovered through process-to-process heat exchange offsets only the sensible heating requirements of the process streams and does not reduce the intrinsic



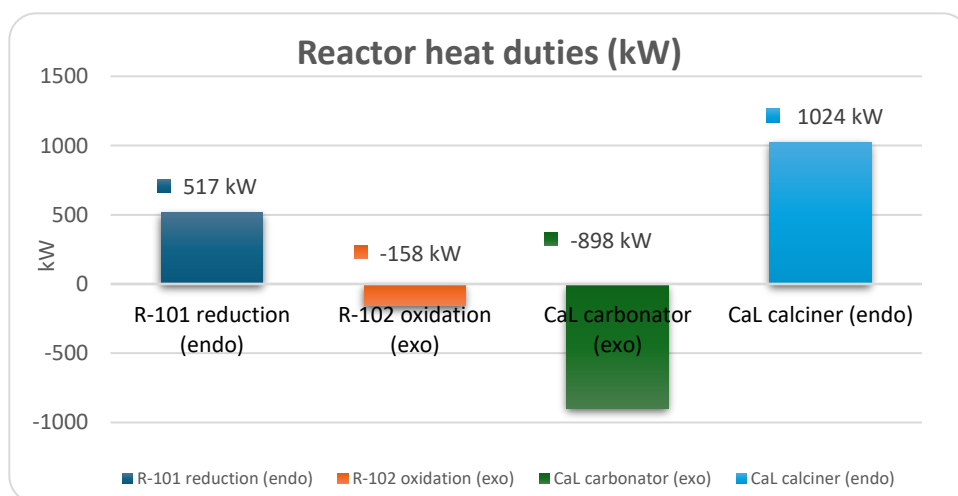
**Figure 5.6** Composite curves of the calcium-looping heat-recovery network. The network recovers 498.7 kW of heat with a minimum temperature approach of approximately 15 °C.

reaction enthalpy associated with carbonation and, in particular, calcination. Consequently, the 1.02 MW endothermic calcination duty remains an external energy requirement because it represents the energy required to decompose  $\text{CaCO}_3$  rather than to heat the material. This demonstrates that, although the process is well integrated from a sensible-heat perspective, substantial external energy input is still required.

**Table 5.6** Process-to-process heat exchangers in the calcium-looping model

| Unit | Hot stream (cooled)                             | Hot T (°C)          | Cold stream (heated) | Cold T (°C)         | Duty (kW) | $\Delta T(\text{min})$ (°C) | LMTD (°C) | UA (cal/s·K) | Area (m <sup>2</sup> ) |
|------|-------------------------------------------------|---------------------|----------------------|---------------------|-----------|-----------------------------|-----------|--------------|------------------------|
| HX01 | S16-CO <sub>2</sub> product                     | 800.5<br>→<br>40.0  | S1 – BFG feed        | 25.0<br>→<br>480.2  | 187.3     | 15                          | 99.7      | 449          | 2.21                   |
| HX02 | S12-decarbonised off-gas (N <sub>2</sub> -rich) | 650.0<br>→<br>491.8 | S2 – BFG             | 480.2<br>→<br>564.0 | 37.1      | 10                          | 37.1      | 239          | 1.18                   |
| HX03 | S7- reduced gas (CO <sub>2</sub> -rich)         | 850.0<br>→<br>650.0 | S3 – BFG             | 564.0<br>→<br>789.2 | 103.2     | 10                          | 72.6      | 339          | 1.67                   |
| HX04 | S15-CO <sub>2</sub> product (calciner)          | 900.0<br>→<br>800.5 | S4 – BFG             | 789.2<br>→<br>849.0 | 28.1      | 10                          | 26.3      | 256          | 1.26                   |
| HX05 | S8-H <sub>2</sub> +steam (R-102 product)        | 700.0<br>→<br>255.9 | S9 – steam           | 200.0<br>→<br>640.0 | 43.2      | 10                          | 57.9      | 178          | 0.88                   |
| HXST | S13 – N <sub>2</sub> -rich vent                 | 491.8<br>→<br>40.0  | S1w – water/steam    | 25.0<br>→<br>101.5  | 99.8      | 10                          | 50.2      | 475          | 2.34                   |

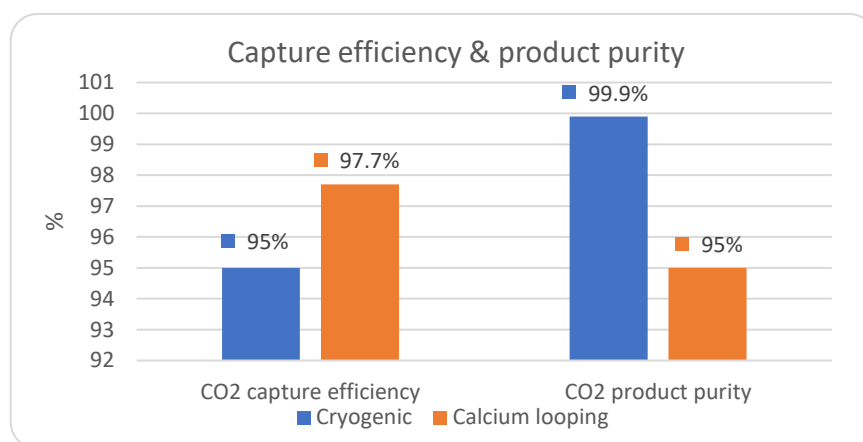
The overall picture emerging from the thermal analysis is therefore twofold. On one hand, the heat-exchanger network performs efficiently, recovering almost 500 kW of high-grade sensible heat while requiring only minor trim heating. On the other hand, the large endothermic duty associated with sorbent regeneration fundamentally limits the energy performance of the process. This distinction between recoverable sensible heat and unavoidable reaction enthalpy is central to understanding the energy consumption of calcium looping and explains why the electrically heated calciner dominates both the plant electricity demand and the operating cost of the process.

**Figure 5.7** Heat duties of the H2Loop and calcium-looping reactors.

### 5.3 Comparative Technical Performance of the CO<sub>2</sub> Capture Routes

Overall, the Aspen Plus simulations demonstrate that both the calcium-looping and cryogenic routes are feasible for producing a high-purity CO<sub>2</sub> product suitable for transport, storage and utilization. However, despite treating the same CO<sub>2</sub>-rich stream generated by the common H2Loop front-end, the two technologies employ fundamentally different separation mechanisms and consequently exhibit distinct energy requirements, heat-integration characteristics and operating behavior.

Both process configurations successfully exceeded the target product specification of more than 95 mol% CO<sub>2</sub>, although by different mechanisms. The cryogenic route achieved a liquid CO<sub>2</sub> product containing 99.9 mol% CO<sub>2</sub> with a single-pass recovery of 95.0%, while the calcium-looping process chemically captured 97.6% of the incoming CO<sub>2</sub> within the carbonator before regenerating almost 100% CO<sub>2</sub> product during calcination (**Figure 5.8**). Although the cryogenic route achieved a slightly higher product purity, both technologies produced CO<sub>2</sub> streams well above the purity required for most CCUS applications. Consequently, product quality alone is unlikely to determine technology selection.



**Figure 5.8** CO<sub>2</sub> capture efficiency and product purity.

As separation mechanisms, cryogenic distillation relies on the difference in volatility between CO<sub>2</sub> and nitrogen under elevated pressure and cryogenic temperature, whereas calcium looping removes CO<sub>2</sub> through reversible chemical absorption by CaO followed by thermal regeneration of the sorbent. As a result, the calcium-looping process is additionally able to convert residual CO into recoverable CO<sub>2</sub> through the simultaneous water-gas shift reaction within the carbonator, thereby increasing the overall carbon utilization of the blast furnace gas. This synergistic behavior is absent in the cryogenic process, where separation occurs purely by phase equilibrium without further chemical conversion.

In terms of energy performance, the cryogenic process is characterized primarily by mechanical energy consumption. Compression of the CO<sub>2</sub>-rich gas to approximately 43 bar, followed by refrigeration to approximately -95 °C, represents the principal energy requirement. Consequently, the process requires relatively modest above-ambient heating duties but significant electrical input for gas compression and refrigeration. Conversely, the calcium-looping process is dominated by high-temperature reaction enthalpy. The endothermic decomposition of CaCO<sub>3</sub> in the calciner requires approximately 1.02 MW of thermal energy, substantially exceeding the corresponding duties within the cryogenic process. Although the carbonator releases approximately 898 kW through the

exothermic carbonation reaction, this heat is available at 650 °C, whereas calcination requires 900 °C. Consequently, the released heat cannot directly satisfy the calciner duty, and substantial external energy input remains necessary. When electrically heated, the calciner alone accounts for approximately 71% of the total plant electricity demand, making sorbent regeneration the dominant contributor to the operating energy consumption.

These results indicate that the two technologies impose fundamentally different energy penalties. Cryogenic separation is mechanically intensive whereas calcium looping is thermally intensive. Therefore, the preferred technology depends not only on the amount of energy required but also on the form in which that energy is available and economically feasible.

The pinch analysis further highlights the contrasting thermal characteristics of the two routes. The calcium-looping process recovered 498.7 kW through process-to-process heat exchange, whereas the cryogenic process recovered 337.9 kW. The larger heat recovery achieved by calcium looping reflects the abundance of high-temperature process streams generated by carbonation, calcination, and the H2Loop reactors, allowing extensive recovery of sensible heat for feed preheating. Despite recovering considerably more heat internally, the calcium-looping process still exhibits the larger external energy requirement, which is apparent contradiction arises because the recovered heat offsets only the sensible heating requirements of the process streams and cannot eliminate the endothermic reaction enthalpy required for  $\text{CaCO}_3$  decomposition. Consequently, the dominant utility demand remains the calcination duty rather than the sensible heating load.

In terms of the cryogenic process, it exhibits the opposite behavior. Although its above-ambient heat recovery is lower, the overall heating requirement is also substantially smaller because no high-temperature sorbent regeneration is required. Instead, the principal energy penalty shifts towards refrigeration and gas compression. These utilities are largely absent from conventional temperature-enthalpy composite curves because they involve mechanical work and low-temperature refrigeration rather than direct process heat exchange. Internal cold recovery within the cryogenic heat exchanger network therefore becomes particularly important, as every kilowatt of refrigeration recovered directly reduces the external refrigeration duty required by the condenser.

Overall, both technologies successfully achieve high-purity  $\text{CO}_2$  suitable for CCUS applications, but they impose fundamentally different energy demands. Calcium looping benefits from chemical  $\text{CO}_2$  capture, additional CO conversion via the water-gas shift reaction, and greater sensible heat recovery, although these advantages are offset by the substantial thermal energy required for sorbent regeneration. In contrast, cryogenic separation avoids high-temperature regeneration but relies on energy-intensive gas compression and refrigeration. These fundamental differences directly influence the capital investment, utility consumption, and operating costs, which are evaluated quantitatively in the following techno-economic assessment.

## 5.4 Techno-Economic Results and Discussion

The techno-economic assessment translates the mass and energy balances obtained from the Aspen Plus simulations into economic performance indicators for the two CO<sub>2</sub> capture routes. All results correspond to the treatment of 1,000 Nm<sup>3</sup>/h of blast furnace gas (BFG) with a plant availability of 92 %, equivalent to 8,059.2 operating hours per year. Since both process configurations employ the same H2Loop front-end, the economic differences presented in this chapter arise exclusively from the downstream CO<sub>2</sub> separation technology. The following sections compare the capital investment, operating costs, and overall economic performance of the two capture routes to identify the key cost drivers and assess their techno-economic viability.

**Table 5.7** presents the calculated factorial capital cost breakdown for both process configurations from the bare erected cost (BEC) to the total investment cost (TIC). The BEC amounts to 1.50 M EUR for the cryogenic process and 1.24 M EUR for the calcium-looping process, representing an initial capital difference of approximately 0.27 M EUR. Because engineering, procurement and construction (EPC), contingencies, licensing and commissioning are estimated as fixed percentages of the installed equipment cost, this difference propagates throughout the factorial cost estimation, increasing the total investment cost (TIC) difference to approximately 0.44 M EUR. The indirect costs therefore amplify the capital cost difference between the two technologies rather than create it.

The higher capital investment required for the cryogenic route is primarily associated with the equipment necessary for gas compression, dehydration and low-temperature CO<sub>2</sub> separation, as shown in **Figure 5.9**. Multi-stage CO<sub>2</sub> compression, the cryogenic distillation column and cold-box assembly, the mechanical refrigeration package and the molecular-sieve drying unit together contribute approximately 0.93 M EUR, corresponding to around 62 % of the total bare erected cost. These units are unique to the cryogenic process and are essential for achieving CO<sub>2</sub> liquefaction and purification under high-pressure cryogenic operating conditions. In particular, the four-stage CO<sub>2</sub> compressor (350,000 EUR) and the cryogenic distillation package (350,000 EUR) represent the largest individual capital items within the entire process.

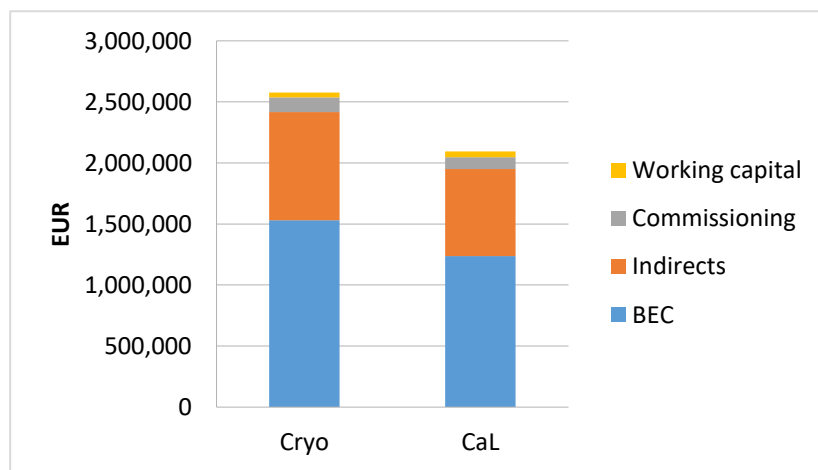
By comparison, the capital investment of the calcium-looping route is concentrated in the additional high-temperature process units required for chemical CO<sub>2</sub> capture, namely the carbonator and calciner, together with a smaller three-stage CO<sub>2</sub> compressor. Although these units operate at elevated temperatures, they avoid the mechanically complex refrigeration and cryogenic separation equipment required by the cryogenic process. Consequently, the installed equipment cost remains lower, resulting in a lower total investment despite the additional reactor required for chemical CO<sub>2</sub> capture. Furthermore, the calcium-looping product compressor operates at a lower discharge pressure of around 21 bar compared with 43 bar for the cryogenic process, which results in lower power requirements and a correspondingly lower equipment cost.

**Table 5.7** Factorial capital build-up (cryogenic route; calcium-looping route shown for comparison).

All values in EUR

| Step                   | Factor                       | Cryogenic | Calcium looping |
|------------------------|------------------------------|-----------|-----------------|
| Bare erected cost, BEC | $\Sigma$ installed equipment | 1,531,625 | 1,236,000       |
| Land                   | 3 % of BEC                   | 45,949    | 37,080          |
| EPC services           | 15 % of BEC                  | 229,744   | 185,400         |
| Process contingency    | 10 % of (BEC+EPC)            | 176,137   | 142,140         |
| Project contingency    | 20 % of (BEC+EPC+proc.)      | 387,501   | 312,708         |
| Licensing              | 3 % of BEC                   | 45,949    | 37,080          |
| Total plant cost, TPC  | sum                          | 2,416,904 | 1,950,408       |
| Commissioning          | 5 % of TPC                   | 120,845   | 97,520          |
| Working capital        | inventory lump               | 40,000    | 45,000          |
| Total investment, TIC  | TPC+comm.+WC                 | 2,577,749 | 2,092,928       |
| Fixed capital, FCI     | TPC+comm.–land               | 2,491,801 | 2,010,848       |

Overall, the higher capital investment of the cryogenic process originates from its reliance on mechanically intensive separation equipment, including gas compression, refrigeration and cryogenic distillation, rather than high-temperature chemical conversion. Since identical factorial cost factors

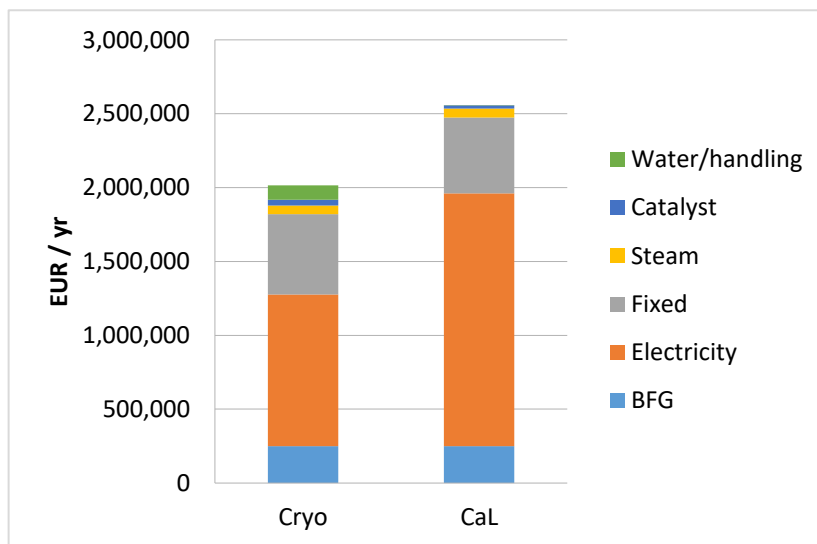
**Figure 5.9** Breakdown of the total investment cost (TIC).

were applied to both process configurations, the observed 17 % difference in total investment reflects genuine differences in process equipment rather than differences in the costing methodology. Although the cryogenic process exhibits the higher capital requirement, the relatively modest difference in total investment suggests that the overall economic comparison will be influenced at least as strongly by operating costs as by the initial capital expenditure.

In terms of operating cost, **Table 5.8** summarizes the annual operating costs of both processes. Variable operating costs dominate the total expenditure of both configurations, although their distribution differs considerably because of the contrasting energy requirements of the two CO<sub>2</sub> capture technologies. The electrically heated calciner of the calcium-looping route is the single largest variable cost. Based on an electrical demand of 1,078.3 kW, it consumes approximately 8.69 GWh/y and, at the assumed electricity price of 0.14 EUR/kWh, incurs an annual operating cost of approximately 1.22 M EUR.

**Table 5.8** Annual operating-cost breakdown (EUR/y) at the base scale.

| OPEX component                                  | Cryogenic | Calcium looping |
|-------------------------------------------------|-----------|-----------------|
| BFG feedstock (opportunity cost)                | 250,762   | 250,762         |
| Electricity                                     | 1,026,629 | 1,710,541       |
| Electric calciner only                          | —         | 1,216,633       |
| Steam                                           | 57,885    | 60,351          |
| Process / cooling water                         | 96,710    | 873             |
| Carrier, sorbent and ETS on slip                | 40,132    | 22,654          |
| Fixed costs (labor, maint., insurance, permits) | 542,996   | 513,417         |
| Gross OPEX                                      | 2,015,113 | 2,558,598       |



**Figure 5.10** Operating expenditure (OPEX) breakdown for the cryogenic and calcium-looping processes.

In contrast to the capital investment, the operating cost comparison favors the cryogenic process as shown in **Figure 5.10**. Although calcium looping is the cheaper plant to build, it is considerably more expensive to operate, with a total annual operating cost of 2.56 M EUR compared with 2.02 M EUR for the cryogenic route. Electricity is the highest operating cost in both configurations, but its contribution is substantially greater for calcium looping, accounting for 67% of the total operating cost compared with 51% for the cryogenic process. Within the calcium-looping electricity demand, the

electrically heated calciner alone represents approximately 48% of the total operating cost, corresponding to 1.22 M EUR/yr. This is because the calcination of  $\text{CaCO}_3$  is a highly endothermic process and, in the present configuration, the required heat is supplied entirely by grid electricity rather than by fuel combustion or recovered process heat. Consequently, the electric calciner is the principal contributor to the higher operating cost of the calcium-looping configuration and is the primary factor reducing its economic competitiveness. The pinch analysis presented in the previous chapter independently confirms that the calciner duty lies above the process pinch and therefore cannot be supplied through internal heat recovery. Additionally, the fixed operating costs of the two process configurations are similar, amounting to 0.51 M EUR/yr for calcium looping and 0.54 M EUR/yr for the cryogenic process. At the relatively small plant capacity considered in this study, labor-related expenses constitute a significant proportion of the fixed-cost component, making fixed costs a comparatively large fraction of the total annual operating expenditure.

Furthermore, revenue is generated from the sale of the captured  $\text{CO}_2$  and the hydrogen co-produced during the steam-iron oxidation step. In the calcium-looping configuration, additional minor revenue is obtained from spent-sorbent reuse and waste-heat export. The captured  $\text{CO}_2$  commands markedly different market values because the two processes deliver products with different specifications. The cryogenic process produces a high-purity ( $\geq 99.9$  mol%) liquid  $\text{CO}_2$  stream at 43 bar, valued at 260 EUR/t, whereas the calcium-looping process delivers a  $\geq 95$  mol%  $\text{CO}_2$  stream at 21 bar for horticultural applications, valued at 80 EUR/t.

Although the calcium-looping route captures slightly more  $\text{CO}_2$  (6,491 t/y compared with 5,929 t/yr), the substantially lower selling price results in a much lower annual  $\text{CO}_2$  revenue; consequently, the total annual revenue of the calcium-looping process is only 0.81 M EUR, compared with 1.82 M EUR for the cryogenic route. The hydrogen credit (0.28 M EUR/yr) is identical for both configurations and therefore does not influence the comparison. Nevertheless, it remains economically significant, representing approximately 15% of the total revenue for the cryogenic process and 35% for the calcium-looping process. The assumption that 70.1 t/yr of hydrogen can be sold at 4,000 EUR/t is considered a by-product credit in the economic assessment. The revenue gap between the routes is thus driven almost entirely by the threefold difference in  $\text{CO}_2$  product price, which in turn reflects the difference in product purity and delivery pressure that the two separation technologies can achieve.

On a screening basis (excluding taxes, financing effects, and inflation), both processes yield negative annual net cash flows of -193,073 EUR for the cryogenic process and -1,750,049 EUR for the calcium-looping process. Consequently, neither configuration covers its operating costs at the base scale prior to accounting for capital expenditure, although the deficit is significantly smaller for the cryogenic process.

Following the methodology described in Chapter 5, the capital investment is distributed over a three-year construction period (2026-2028) according to an expenditure profile of 20%/40%/40%, followed by a ten-year operating period from 2029 to 2038. Discounting all project cash flows to the 2026 base year at a discount rate of 5% gives an NPV of -3,785,037 EUR for the cryogenic process and -14,232,281 EUR for the calcium-looping process. In both cases, the cumulative discounted cash flow remains negative throughout the project lifetime, indicating that the discounted payback period exceeds the ten-year operating horizon. The abbreviated cash-flow statement for the cryogenic process is presented in **Table 5.9**, while the calcium-looping cash flow follows the same trend but deteriorates further because of its persistent annual operating losses.

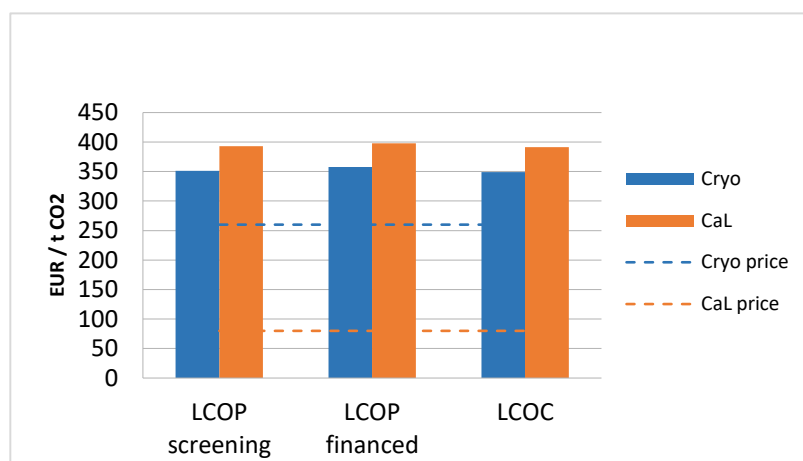
Under these conditions, the internal rate of return (IRR) does not provide any insight because neither process generates sufficient discounted returns over the project lifetime. The cryogenic process does

not achieve the required 5 % rate of return, while both configurations yield negative annual cash flows throughout the operating period, preventing the calculation of a meaningful IRR. Applying the levelized-cost analysis to the discounted cash flows gives an LCOP of 351.1 EUR/t and an LCOC of 348.9 EUR/t for the cryogenic process, compared with 393.1 EUR/t and 391.4 EUR/t, respectively, for the calcium-looping process as shown in **Figure 5.11**.

As the captured CO<sub>2</sub> tonnage follows from the single-pass recovery of the cryogenic column, the levelized costs reported here are conditional on the vapour–liquid-equilibrium assumption discussed in Section 4.4.6. For the cryogenic process, the difference between the LCOC and LCOP is only 0.7%, arising because the LCOP explicitly accounts for the phased capital expenditure during construction, whereas the LCOC employs an equivalent annualized capital charge. This close agreement confirms the internal consistency of the economic model. A similarly small difference between the two metrics is observed for the calcium-looping process, demonstrating that both approaches produce consistent economic estimates despite the different treatment of capital expenditure. More importantly, the approximately 43 EUR/t lower LCOC of the cryogenic process demonstrates that its higher capital investment is more than offset by its lower operating costs, in particular the absence of the electrically heated calciner. The higher market value of the high-purity liquid CO<sub>2</sub> product benefits the revenue-side indicators such as net present value and payback period, but does not enter the LCOC, which by definition (Eq. 4.18) subtracts only non-CO<sub>2</sub> revenue. In contrast, the calcium-looping process is penalized by the electricity demand of the electrically heated calciner, which dominates the operating expenditure and outweighs the benefit of its lower capital cost. Consequently, although calcium looping captures slightly more CO<sub>2</sub>, the cryogenic process achieves the more favorable overall cost of CO<sub>2</sub> capture under the base-case assumptions.

**Table 5.9** Discounted cash flow analysis for the cryogenic carbon capture process.

| Year          | CAPEX     | Net cash   | Cumulative | PV of net cash |
|---------------|-----------|------------|------------|----------------|
| 2026          | 515,550   | -515,550   | -515,550   | -515,550       |
| 2027          | 1,031,100 | -1,031,100 | -1,546,650 | -982,000       |
| 2028          | 1,031,100 | -1,031,100 | -2,577,749 | -935,238       |
| 2029 (op. 1)  | -         | -193,073   | -2,770,882 | -166,781       |
| 2033 (op. 5)  | -         | -193,073   | -3,543,112 | -137,213       |
| 2038 (op. 10) | -         | -193,073   | -4,508,475 | -107,510       |
| NPV           |           |            |            | -3,785,037     |



**Figure 5.11** Comparison of LCOP/LCOC and CO<sub>2</sub> sale prices.

#### 5.4.1 Base-case comparison and the dominant cost drivers

Based on the economic indicators summarized in **Table 5.10**, the cryogenic route performs more favorably than the calcium-looping route. This difference is primarily driven by operating performance rather than capital investment. Mainly, two factors combine to produce this outcome. First, under the assumed market conditions, the high-purity liquid CO<sub>2</sub> produced by the cryogenic route commands a selling price of 260 EUR/t compared with 80 EUR/t for the gaseous CO<sub>2</sub> product from the calcium-looping route, a factor of 3.25. Consequently, although the cryogenic route captures approximately 9% less CO<sub>2</sub> (5,929 compared with 6,491 t/yr), it nevertheless generates 1.82 M EUR/yr in total revenue compared with 0.81 M EUR/yr for the calcium-looping route, corresponding to more than twice the annual revenue. Second, the calcium-looping route incurs a substantially higher electricity cost of 1.71 M EUR/yr compared with 1.03 M EUR/yr for the cryogenic route, representing 67% and 51% of the total operating costs, respectively. This difference arises almost entirely from the electrically heated calciner, which alone contributes 1.22 M EUR/yr, equivalent to approximately 48% of the total operating cost of the calcium-looping process. These two effects combine to determine the operating balance. Against annual operating costs of 2.02 M EUR for the cryogenic route and 2.56 M EUR for the calcium-looping route, both processes generate negative annual operating cash flows of - 0.19 M EUR and -1.75 M EUR, respectively, indicating that neither process recovers its operating costs before capital expenditure is considered.

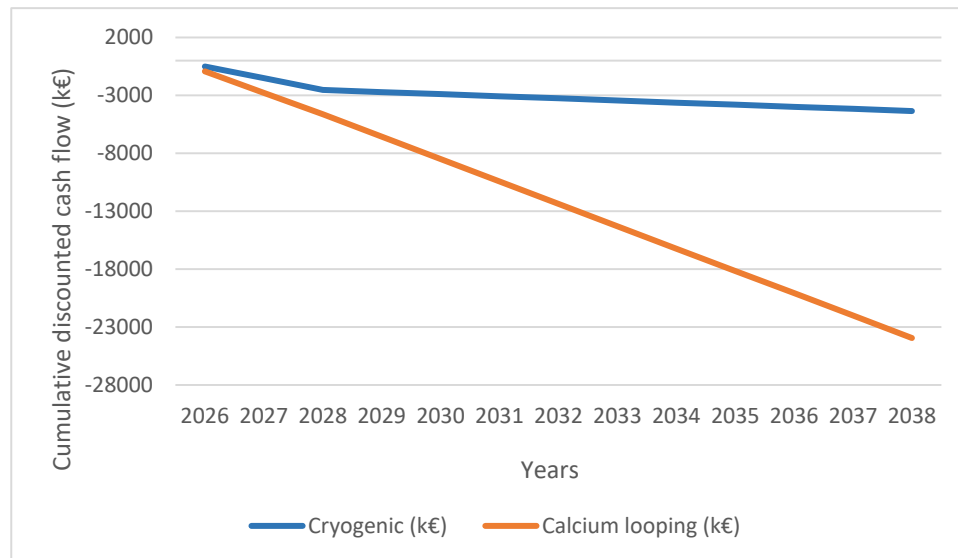
**Table 5.10** Base-case techno-economic indicators (1,000 Nm<sup>3</sup>/h; 5 %, 10 y; CRF 0.1295).

| Indicator                          | Cryogenic | Calcium looping |
|------------------------------------|-----------|-----------------|
| Total investment cost, TIC (M EUR) | 2.58      | 2.09            |
| Gross OPEX (M EUR/yr)              | 2.02      | 2.56            |
| Revenue (M EUR/yr)                 | 1.82      | 0.81            |
| Net annual cash (M EUR/yr)         | - 0.193   | -1.750          |
| CO <sub>2</sub> captured (t/yr)    | 5,929     | 6,491           |
| LCOC (EUR/t)                       | 348.9     | 391.4           |
| LCOP - screening (EUR/t)           | 351.1     | 393.1           |

|                         |        |        |
|-------------------------|--------|--------|
| LCOP - financed (EUR/t) | 357.6  | 397.9  |
| NPV - screening (M EUR) | - 3.79 | -14.23 |
| Payback (yr)            | > 10   | > 10   |

Comparing the levelized costs with the assumed CO<sub>2</sub> selling prices further illustrates the economic gap between the two technologies. The cryogenic route requires a break-even CO<sub>2</sub> price (LCOP) of 351 EUR/t while achieving an assumed selling price of 260 EUR/t, corresponding to a shortfall of approximately 91 EUR/t. In contrast, the calcium-looping route requires 393 EUR/t but achieves only 80 EUR/t, resulting in a shortfall of approximately 313 EUR/t, more than three times larger and almost four times the assumed selling price of its CO<sub>2</sub> product. The same disparity is reflected in the screening net present values, with the cryogenic route yielding an NPV of -3.79 M EUR compared with -14.23 M EUR for the calcium-looping route. Although neither process is economically viable under the base-case assumptions, the cryogenic route is substantially closer to economic viability than the calcium-looping route. In both configurations, electricity remains the dominant operating cost driver through compression and refrigeration in the cryogenic route (1.24 MWh per tonne of CO<sub>2</sub> captured) and through electric calcination in the calcium-looping route (1.88 MWh/t, of which approximately 71% is consumed by the calciner). The influence of electricity costs is quantified in the sensitivity analysis presented in Section 5.4.2, while the thermodynamic origin of these energy requirements is explained by the pinch analysis discussed earlier in this chapter.

Additionally, the screening indicators presented above exclude the effects of financing, taxation, and inflation. To assess their influence, an additional financed case was evaluated using the assumptions described in TEA methodology. Each plant was capitalized with 100% debt over a ten-year term at an annual interest rate of 5% with linearly declining interest, depreciated using the straight-line method over ten years, subjected to the German combined corporate income-tax rate of 29.9% on positive taxable profit only, and analyzed assuming an annual inflation rate of 2%. Under the financed case, the calcium-looping route accumulates a far larger cumulative deficit than the cryogenic route over the ten-year horizon (**Figure 5.12**).



**Figure 5.12** Cumulative financed cash flows of the cryogenic and calcium-looping routes.

The most notable outcome is that neither process pays corporate income tax during the operating period. For the loss-making calcium-looping process, this is expected. The cryogenic process exhibits the same behavior. An annual operating loss of -193,073 EUR, combined with annual depreciation of 257,775 EUR (assuming straight-line depreciation over 10 years on a 2.58 M EUR investment) and a first-year interest expense of 128,887 EUR, results in a first-year taxable loss of -579,735 EUR. Consequently, no corporate income tax (29.9%) is payable, and the depreciation tax shield cannot be utilized because there is no positive taxable income against which it can be offset. Financing therefore affects the economic performance only through debt servicing costs.

The financing structure itself contributes negligibly to the project cost, with the change in net present value arising primarily from cost escalation rather than financing costs. Total interest over the loan term amounts to approximately 0.71 M EUR for the cryogenic process (based on 2.58 M EUR of debt) and 0.58 M EUR for the calcium-looping process (based on 2.09 M EUR of debt), repaid on a declining schedule from 128,887 EUR and 104,646 EUR in the first year to one-tenth of these values in the final year. Incorporating debt service together with 2 % annual escalation decreases the net present value from -3.79 M EUR to -3.81 M EUR for the cryogenic process, a change of 0.02 M EUR, and from -14.23 M EUR to -15.21 M EUR for the calcium-looping process, a change of 0.98 M EUR. These differ by a factor of forty-five even though the cryogenic route carries the larger loan and pays the greater interest, which shows that the difference is not a financing effect. The negligible impact of financing is explained by the assumed financing structure. The loan interest rate is equal to the discount rate and no interest is accrued during the construction period, making debt financing effectively NPV-neutral and resulting in only a marginal present-value benefit (+0.09 M EUR for the cryogenic route and +0.08 M EUR for calcium looping). The financed case differs from the screening case primarily through the inclusion of 2 % annual cost escalation. Because both routes operate at a net annual loss, this escalation increases the deficit over time, with the present-value impact proportional to the magnitude of the annual shortfall: -0.12 M EUR for the cryogenic route (annual deficit of 0.19 M EUR) and -1.06 M EUR for calcium looping (annual deficit of 1.75 M EUR). Consequently, the small financing benefit almost completely offsets the escalation penalty for the cryogenic route, whereas the much larger operating deficit of the calcium-looping route results in a substantial net deterioration in project value.

Expressed as a levelized cost, the required break-even CO<sub>2</sub> price (LCOP) increases from 351.1 EUR/t to 357.6 EUR/t for the cryogenic process and from 393.1 EUR/t to 397.9 EUR/t for the calcium-looping process, which corresponds to increases of only 6.4 EUR/t (approximately 1.8%) and 4.8 EUR/t (approximately 1.2%), respectively. Financing captures the cost of debt servicing but does not alter the relative economic performance of the two process routes. The cryogenic process retains its economic advantage over the calcium-looping process, the gap in levelized cost being 41.9 EUR/t before financing and 40.3 EUR/t after it. This confirms that the ranking is an intrinsic characteristic of the process configurations rather than a consequence of the financing assumptions. Over the project lifetime, the cryogenic process remains close to operating break-even, allowing the declining interest expense to more than offset the gradual increase in operating costs. As a result, its annual net cash flow improves from - 0.58 M EUR in 2029 to - 0.50 M EUR in 2038. In contrast, the calcium-looping process remains substantially loss-making, with the 2% annual escalation applied to its considerably larger operating cost base exceeding the reduction in interest expense, causing the annual deficit to increase from - 2.06 M EUR to - 2.31 M EUR. Inflation therefore marginally strengthens the economic position of the cryogenic process without affecting the overall ranking of the two technologies.

### 5.4.2 Sensitivity analysis

The base-case levelized costs are single-point estimates conditioned on a set of fixed assumptions, and their credibility rests on knowing how strongly each assumption influences the outcome. A one-factor-at-a-time sensitivity analysis was therefore performed on the levelized cost of product (LCOP) defined as the CO<sub>2</sub> selling price at which the discounted net present value equals zero by varying each economically significant input across a realistic range while holding all other parameters at their base-case values. The corresponding base-case LCOPs are 351.1 EUR/t for the cryogenic route and 393.1 EUR/t for calcium looping.

Two deliberate boundaries define the analysis. First, all quantities determined by the Aspen Plus process simulation, including the capture efficiency, hydrogen yield, stream flow rates, and reactor conversions, are fixed and are not treated as uncertain variables. The sensitivity analysis is therefore confined to market and financial parameters that are subject to genuine uncertainty and cannot be controlled through process design. Second, the levelized-cost formulation enables the influence of each variable to be interpreted directly which allows the relative importance of the different economic drivers to be assessed transparently. The analysis considers five key parameters namely, the electricity price, the aggregate operating cost, the capital estimate, the plant life and discount rate and the EU ETS carbon price before comparing their relative influence on the economics of the two process routes.

Firstly, electricity is a variable operating cost, and its effect on the LCOP is directly proportional to the specific electricity consumption of each process (**Table 5.11**). The cryogenic route consumes 1,237 kWh/t CO<sub>2</sub> (1.24 MWh/t), whereas calcium looping requires 1,882 kWh/t CO<sub>2</sub> (1.88 MWh/t). Consequently, every 10 EUR/MWh change in electricity price alters the LCOP by 12.4 EUR/t for the cryogenic route and 18.8 EUR/t for calcium looping. The ratio of these sensitivities (1.52) reflects the corresponding ratio of the processes' electricity intensities, demonstrating that calcium looping is inherently almost 1.5 times as sensitive to electricity price as the cryogenic route.

**Table 5.11** Sensitivity of LCOP to electricity price for the cryogenic and calcium-looping processes.

| <b>Electricity price (EUR/MWh)</b>  | 50    | 90    | 140 (base) | 180   |
|-------------------------------------|-------|-------|------------|-------|
| <b>Cryogenic LCOP (EUR/t)</b>       | 239.8 | 289.3 | 351.1      | 400.6 |
| <b>Calcium-looping LCOP (EUR/t)</b> | 223.7 | 299.0 | 393.1      | 468.4 |

The key economic indicator is the electricity price at which the LCOP equals the achievable product value. For the cryogenic route, equating the LCOP to the assumed CO<sub>2</sub> product value of 260 EUR/t yields a break-even electricity price of approximately 66 EUR/MWh. Below this threshold, the process becomes profitable even at the base plant scale, with the LCOP decreasing to 239.8 EUR/t at an electricity price of 50 EUR/MWh. In contrast, the calcium-looping process does not approach its assumed product value of 80 EUR/t over the investigated range. Even under the hypothetical assumption of zero-cost electricity, the extrapolated LCOP remains approximately 130 EUR/t, around 50 EUR/t above the break-even value, indicating that reducing electricity prices alone is insufficient to overcome the high energy demand of the electrically heated calciner.

This contrast highlights fundamentally different economic regimes for the two technologies. The cryogenic process is primarily constrained by electricity price and could become commercially viable under favorable power-market conditions. However, calcium looping exhibits a structural economic deficit that cannot be resolved through electricity-price reductions alone. This behaviour reflects the underlying process design which is electricity supplies the principal separation duty in both systems

such as compression and refrigeration in the cryogenic process and electrical calcination in calcium looping. It is making power consumption the dominant determinant of their operating economics.

In terms of assessing the effect of uncertainty in the overall operating-cost estimate rather than individual cost components, the total gross operating cost was varied proportionally by  $\pm 30\%$  as shown in **Table 5.12**. Since operating costs contribute directly to the LCOP, their sensitivity is determined by the specific operating cost per tonne of CO<sub>2</sub> captured. This corresponds to 3.40 EUR/t per 1 % change for the cryogenic route (2.02 M EUR/y over 5,929 t/y) and 3.94 EUR/t per 1 % for calcium looping (2.56 M EUR/y over 6,491 t/y).

**Table 5.12** Sensitivity of LCOP to variations in gross operating expenditure (OPEX).

| Gross OPEX relative to base         | -30 % | -20 % | -10 % | Base  | +10 % | +20 % | +30 % |
|-------------------------------------|-------|-------|-------|-------|-------|-------|-------|
| <b>Cryogenic LCOP (EUR/t)</b>       | 249.2 | 283.2 | 317.2 | 351.1 | 385.1 | 419.1 | 453.1 |
| <b>Calcium-looping LCOP (EUR/t)</b> | 274.8 | 314.3 | 353.7 | 393.1 | 432.5 | 471.9 | 511.4 |

Aggregate operating cost represents the largest economic sensitivity for both routes because it encompasses all operating expenditures, including electricity, which is the dominant individual cost component. It should therefore be interpreted as an overall measure of operating-cost uncertainty rather than as an independent variable separate from the electricity-price sensitivity discussed.

The analysis also highlights the fundamentally different economic positions of the two technologies. For the cryogenic route, the 91 EUR/t gap between the base-case LCOP and the product selling price corresponds to approximately a 27 % reduction in operating cost, which is a target that could potentially be achieved through lower electricity prices, improved heat integration, or economies of scale. In contrast, calcium looping would require an operating-cost reduction of approximately 79 % to reach break-even, indicating that its economic deficit is structural rather than a consequence of cost-estimation uncertainty. The comparison further demonstrates that operating costs dominate overall project economics. For the cryogenic process, a  $\pm 20\%$  variation in operating cost changes the LCOP by approximately  $\pm 68.0$  EUR/t, around six times the impact of an equivalent  $\pm 20\%$  variation in capital cost ( $\pm 11.7$  EUR/t).

Additionally, the installed capital cost was varied across the AACE Class 4 accuracy range of  $-30\%$  to  $+50\%$ . The adjusted investment was annualized using the same phased capital expenditure profile and financial assumptions as the base case before being divided by the annual CO<sub>2</sub> captured. This corresponds to a capital contribution of approximately 58.6 EUR/t for the cryogenic route and 43 EUR/t for calcium looping. The cryogenic LCOP changes from 351.1 EUR/t to 333.6 EUR/t ( $-30\%$ ) and 380.4 EUR/t ( $+50\%$ ), while the calcium-looping LCOP varies from 393.1 EUR/t to 380.1 EUR/t and 414.8 EUR/t, corresponding to changes of  $-17.6/+29.3$  EUR/t and  $-13.0/+21.7$  EUR/t, respectively.

Capital expenditure is therefore an important but secondary economic driver. Even a 30 % reduction in capital cost lowers the cryogenic LCOP only to 334 EUR/t, which remains approximately 74 EUR/t above its product selling price. Similarly, the relative ranking of the two technologies is unchanged throughout the entire capital uncertainty range. These results demonstrate that the overall conclusions are insensitive to reasonable uncertainties in capital estimation and are instead governed primarily by operating costs.

The base-case economic evaluation assumes a 10-year operating life and a 5 % discount rate. To assess the influence of financing assumptions, an alternative scenario with a 20-year plant life and an 8 % discount rate was evaluated. This affects only the annualized capital charge, increasing the

annuity factor from 7.72 to 9.82, while operating costs remain unchanged. Although the discount rate is higher, the longer amortization period reduces the annual capital burden, decreasing the LCOP from 351.1 to 339.7 EUR/t for the cryogenic route (-11.4 EUR/t) and from 393.1 to 384.6 EUR/t for calcium looping (-8.5 EUR/t). Therefore, the modest reduction also confirms that financing assumptions have only a limited influence on project economics because capital represents a relatively small proportion of the total levelized cost. Consequently, adopting financing conditions more representative of commercial utility projects slightly improves the economics of both routes without altering their relative ranking or the overall conclusions of the techno-economic assessment.

Furthermore, the EU ETS carbon price was varied between 60 and 120 EUR/t, with 95 EUR/t as the base-case value. Since the ETS charge applies only to uncaptured CO<sub>2</sub> emissions, its effect depends solely on the residual CO<sub>2</sub> slip rather than the total carbon processed. The uncaptured emissions amount to 311.9 t/y (5.0 % of feed carbon) for the cryogenic route and 152.4 t/y (2.3 %) for calcium looping. Consequently, the LCOP sensitivity is very small, corresponding to 0.053 EUR/t per EUR/t carbon price for the cryogenic route and 0.024 EUR/t for calcium looping.

These capture efficiencies refer to the CO<sub>2</sub> entering the separation section. On a whole-plant carbon basis, the feed carbon of 19.60 kmol C/h contained in CO and CO<sub>2</sub> is recovered to approximately 85 % in the cryogenic route and 93 % in the calcium-looping route, the difference being the carbon leaving as unconverted CO, 2.01 and 0.87 kmol C/h respectively; the smaller quantity of unconverted CO in the calcium-looping route reflects the partial conversion of residual CO in the carbonator. In accordance with the system boundary defined in Section 4.6, this stream is exported to the steelworks fuel-gas network and combusted outside the battery limits, so that the associated EU-ETS liability is attributed to the receiving installation. Had it been vented on site, the corresponding 713 t CO<sub>2</sub>/y for the cryogenic route and 309 t CO<sub>2</sub>/y for the calcium-looping route would add approximately 68,000 and 29,000 EUR/y, equivalent to about 11 and 5 EUR/t respectively. The penalty is therefore larger for the cryogenic route, so that accounting for the exported CO on site would widen rather than narrow the difference between the two routes.

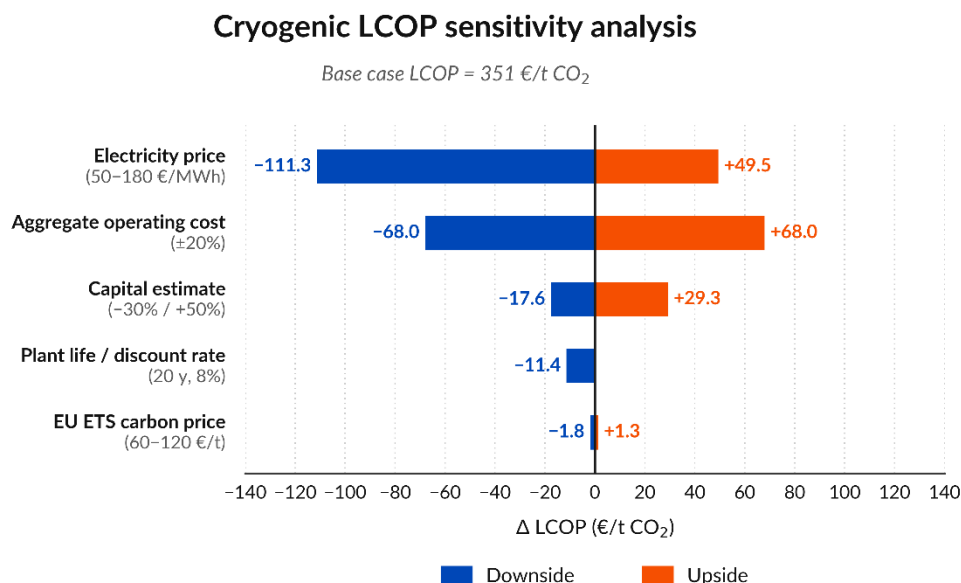
Doubling the carbon price from 60 to 120 EUR/t increases the cryogenic LCOP by only 3 EUR/t (349.5 - 352.5 EUR/t) and the calcium-looping LCOP by 1.4 EUR/t (392.3-393.7 EUR/t). Despite the widespread perception that carbon pricing is the primary economic driver for carbon capture, its influence is negligible in this case because both technologies capture 95 % or more of the incoming CO<sub>2</sub>. As a result, very little carbon remains subject to ETS charges, which is making the economics largely insensitive to carbon-price fluctuations. While high capture efficiency effectively reduces exposure to carbon-price risk, it also means that higher carbon prices alone are insufficient to make either process economically viable. The combined sensitivity results establish a clear hierarchy of the economic drivers affecting both technologies, which is shown in **Table 5.13**.

**Table 5.13** Comparison of LCOP sensitivity to selected economic parameters for the cryogenic and calcium-looping processes.

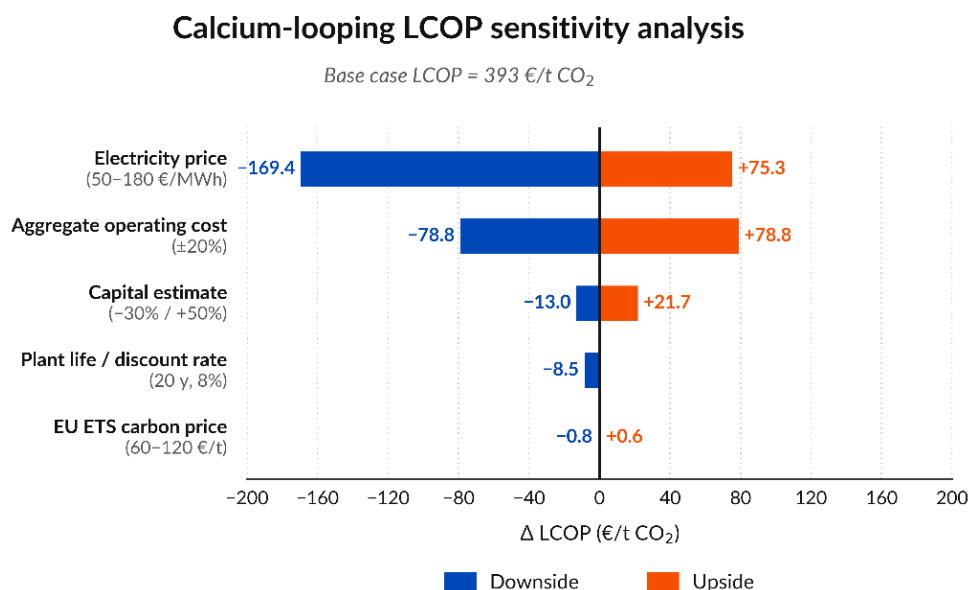
| Driver (range)                         | Cryogenic $\Delta$ LCOP (EUR/t) | Calcium-looping $\Delta$ LCOP (EUR/t) |
|----------------------------------------|---------------------------------|---------------------------------------|
| Aggregate operating cost ( $\pm 20$ %) | -68.0 / +68.0                   | -78.8 / +78.8                         |
| Electricity price (50–180 EUR/MWh)     | -111.3 / +49.5                  | -169.4 / +75.3                        |
| Capital estimate (-30 %/+50 %)         | -17.6 / +29.3                   | -13.0 / +21.7                         |
| Plant life & discount rate             | -11.4                           | -8.5                                  |

|                                    |             |             |
|------------------------------------|-------------|-------------|
| EU ETS carbon price (60-120 EUR/t) | -1.8 / +1.3 | -0.8 / +0.6 |
|------------------------------------|-------------|-------------|

Aggregate operating cost includes electricity and all other operating expenses; therefore, its sensitivity should not be interpreted as additional to the separate electricity-price sensitivity. The sensitivity analysis identifies operating cost, particularly electricity, as the dominant economic driver for both technologies. In contrast, capital cost, financing assumptions and carbon price have only a minor influence on the LCOP and do not alter the relative ranking of the two routes. The cryogenic process is close to economic viability under favorable operating conditions, whereas calcium looping remains structurally uneconomic. These findings are consistent with the thermodynamic analysis, which identifies electricity demand as the principal determinant of techno-economic performance. Sensitivity results are also presented as a tornado diagram in **Figure 5.13** and **Figure 5.14**.



**Figure 5.13** Sensitivity analysis of the cryogenic route showing the effect of key economic parameters on the base-case LCOP (351.1 €/t CO<sub>2</sub>).



**Figure 5.14** Sensitivity analysis of the calcium-looping route showing the effect of key economic parameters on the base-case LCOP (393.1 €/t CO<sub>2</sub>).

### 5.4.3 Scale-up and economies of scale

The base case of 1,000 Nm<sup>3</sup>/h corresponds to only about 0.9 MW on a BFG lower-heating-value basis, which is one to two orders of magnitude smaller than industrial CO<sub>2</sub> capture facilities. To

distinguish the intrinsic process performance from the penalty of a laboratory-scale design, the techno-economic assessment was repeated at 68,500 and 274,000 Nm<sup>3</sup>/h, representing 25% and 100% of a reference blast furnace gas stream. As described in the methodology, total investment was scaled using the 0.65 power-law relationship, variable operating costs were assumed proportional to throughput, while fixed costs were recalculated from the scaled capital investment and plant staffing. The resulting CO<sub>2</sub> production was assumed to scale linearly with feed rate. The results are summarized in **Table 5.14**.

**Table 5.14** Scale-up results. TIC and OPEX in M EUR; LCOC in EUR/t; product prices held at 260 (cryo) and 80 (CaL) EUR/t.

| Metric                                                  | 1,000 Nm <sup>3</sup> /h | 68,500 Nm <sup>3</sup> /h | 274,000 Nm <sup>3</sup> /h |
|---------------------------------------------------------|--------------------------|---------------------------|----------------------------|
| <b>Cryogenic Route - product 260 EUR/t, ≥ 99.9 %</b>    |                          |                           |                            |
| CO <sub>2</sub> captured (t/y)                          | 5,929                    | 406,147                   | 1,624,588                  |
| Total investment, TIC (M EUR)                           | 2.58                     | 40.22                     | 99.03                      |
| Annual OPEX (M EUR)                                     | 2.02                     | 103.99                    | 410.50                     |
| LCOC (EUR/t CO <sub>2</sub> )                           | 348.9                    | 221.6                     | 213.3                      |
| Margin vs 260 EUR/t                                     | -88.9                    | +38.4                     | +46.7                      |
| Annual profit (M EUR/y)                                 | -0.53                    | +15.6                     | +75.9                      |
| <b>Viable?</b>                                          | <b>No - loss</b>         | <b>Yes- profit</b>        | <b>Yes - profit</b>        |
| <b>Calcium Looping Route - product 80 EUR/t, ≥ 95 %</b> |                          |                           |                            |
| CO <sub>2</sub> captured (t/y)                          | 6,491                    | 444,614                   | 1,778,457                  |
| Total investment, TIC (M EUR)                           | 2.09                     | 32.66                     | 80.41                      |
| Annual OPEX (M EUR)                                     | 2.56                     | 142.80                    | 566.40                     |
| LCOC (EUR/t CO <sub>2</sub> )                           | 391.4                    | 286.1                     | 279.8                      |
| Margin vs 80 EUR/t                                      | -311.4                   | -206.1                    | -199.8                     |
| Annual profit (M EUR/y)                                 | -2.02                    | -91.6                     | -355.3                     |
| <b>Viable?</b>                                          | <b>No - loss</b>         | <b>No - loss</b>          | <b>No - loss</b>           |

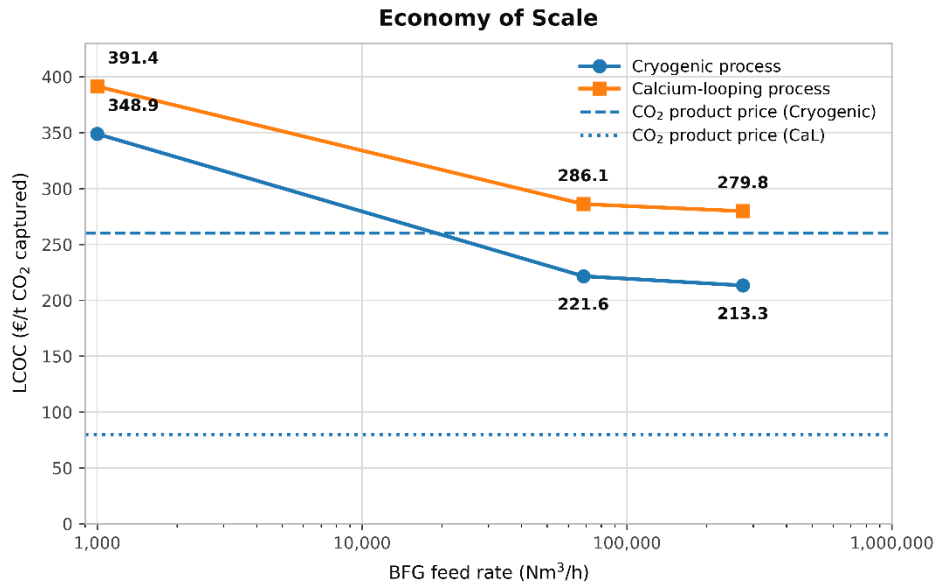
The scale-up analysis demonstrates fundamentally different economic behavior for the two capture technologies. Owing to economies of scale, the cryogenic route exhibits a substantial reduction in levelized cost of capture (LCOC), decreasing from 348.9 EUR/t at the base case to 221.6 EUR/t at 68,500 Nm<sup>3</sup>/h and 213.3 EUR/t at 274,000 Nm<sup>3</sup>/h. Since the assumed liquid CO<sub>2</sub> selling price remains constant at 260 EUR/t, the intermediate and full-scale cases become profitable, generating annual profits of 15.6 and 75.9 M EUR, respectively. Although capital investment increases from 2.58 to 99.03 M EUR, it grows much more slowly than throughput because of the power-law scaling, reducing the capital cost per tonne of CO<sub>2</sub> captured. The relatively small LCOC reduction between the intermediate and full-scale cases (222 to 213 EUR/t) indicates that most economy-of-scale benefits are already realized around 68,500 Nm<sup>3</sup>/h.

In contrast, calcium looping remains economically unattractive throughout the investigated capacity range. The LCOC decreases from 391.4 to 279.8 EUR/t as plant size increases, reflecting the same capital-scaling effect observed for the cryogenic process. However, these values remain far above the assumed CO<sub>2</sub> selling price of 80 EUR/t, resulting in increasingly negative annual profits as throughput rises, as also shown in **Figure 5.15**. Unlike the cryogenic process, the dominant operating cost is the electricity demand of the electrically heated calciner, which scales almost directly with CO<sub>2</sub> production and therefore cannot be substantially reduced through economies of scale. Consequently, increasing plant capacity only magnifies the operating losses.

Overall, the scale-up study shows that plant size is the key economic limitation for the cryogenic route but not for calcium looping. Cryogenic CO<sub>2</sub> separation becomes economically viable once operated at industrially relevant throughput, whereas the current calcium-looping configuration remains uneconomic even at full scale. Achieving economic viability for calcium looping would therefore require a fundamental reduction in calcination energy cost, such as alternative heat supply or improved heat integration, together with access to a higher-value CO<sub>2</sub> market.

Although the present calcium-looping configuration remains economically unattractive, this result should be interpreted in the context of the specific process design evaluated in this study rather than as a general limitation of calcium-looping technology. The process considered here is a standalone system employing an electrically heated calciner and producing a horticultural-grade CO<sub>2</sub> product. Consequently, the economic performance differs substantially from many published techno-economic assessments, which typically report capture costs in the range of 20-60 EUR/t depending on the industrial application.[145] A key distinction is that most literature studies integrate calcium looping with large industrial facilities, such as cement plants or power stations, and employ oxy-fuel-fired calciners rather than direct electric heating. These configurations reduce external energy demand, enable recovery of high-temperature waste heat, and achieve higher overall thermal efficiency, resulting in significantly lower capture costs than those obtained in the present study.

Furthermore, the assumed CO<sub>2</sub> selling price of 80 EUR/t reflects a horticultural-grade product and is considerably lower than the value of high-purity merchant-grade CO<sub>2</sub> adopted in many economic assessments. Consequently, the economic performance reported here reflects the combined effects of process configuration, energy supply, thermal integration, and product specification, rather than an intrinsic limitation of calcium-looping technology itself.



**Figure 5.15** Economy of scale effect on the LCOC of the cryogenic and calcium-looping processes.

## 5.5 Uncertainties and limitations

The techno-economic results are a study-level estimate and carry the uncertainties normal to a Class 4 AACE estimate. The most significant sources of uncertainty are discussed below because they influence the quantitative results and, in some cases, the apparent economic competitiveness of the evaluated processes. The largest single uncertainty on the revenue side is the hydrogen by-product credit, because the hydrogen yield depends on the oxygen-carrier phase representation adopted for the steam-oxidation reactor. The economic evaluation uses the non-stoichiometric wüstite design value of 70.1 t/yr, which is the yield obtained from the adopted oxidation model. An alternative, idealized stoichiometric FeO representation of the oxidation step gives a more conservative 16.6 t/yr, and the hydrogen credit can therefore be regarded as bounded by these two representations. Adopting the lower, FeO-based value raises the cryogenic LCOP from 351 to 387 EUR/t and widens the gap to the assumed product price from about 91 to 127 EUR/t. This uncertainty does not change the ranking of the two capture routes, as calcium looping remains substantially more expensive on either basis, but it does affect the apparent nearness of the cryogenic route to viability. Hence, phase-consistent oxygen-carrier representation or a process-specific hydrogen credit is recommended for future refinement. Three modeling assumptions carry disproportionate weight. First, the electricity price of 0.14 EUR/kWh is an assumed industrial grid tariff rather than a contracted, site-specific price, and because electricity is by far the most influential driver, this single input largely determines the outcome. The cryogenic route would meet its 260 EUR/t product price at an electricity price of approximately 66 EUR/MWh, so the finding that it is not viable at the base scale is as much a statement about the assumed tariff as about the capture technology itself. Second, the blast-furnace gas is charged at its full 22.8 EUR/t opportunity cost rather than treated as a credited avoided-emissions stream.

This assumption is conservative and increases the LCOP by approximately 42 €/t CO<sub>2</sub>. If CO<sub>2</sub> were instead treated using a shadow-price approach, the cryogenic LCOP would decrease to approximately 309 €/t CO<sub>2</sub>, substantially reducing the gap to the assumed product price, although the process would still not reach break-even under the base-case conditions. Despite these uncertainties, the relative ranking of the two capture technologies is considered robust. The principal conclusions are governed by the large differences in CO<sub>2</sub> product value and electricity intensity between the two configurations, which substantially exceed the uncertainty associated with a Class 4 cost estimate. Consequently, while the absolute values of the techno-economic indicators may change following further process refinement, the comparative conclusions of this study are unlikely to be affected.

## 5.6 Literature comparison and benchmarking

The two separation processes are benchmarked against published data for their respective technologies and against the industrial reference for post-combustion capture, monoethanolamine (MEA) absorption. [85], [145], [146] Three key boundary conditions explain most of the differences between the present results and the literature. First, plant scale differs substantially. The base-case design processes 1,000 Nm<sup>3</sup>/h of blast furnace gas (approximately 0.9 MWth), corresponding to annual CO<sub>2</sub> capture rates of 5,929 t for the cryogenic route and 6,491 t for calcium looping. In contrast, the benchmark studies generally evaluate industrial-scale systems. Second, the economic metric differs. The present study reports the levelized cost of capture (LCOC) for a pressurized, saleable CO<sub>2</sub> product produced in conjunction with the shared iron chemical-looping front end, whereas most published studies report the cost of CO<sub>2</sub> avoided at the plant gate. Third, the energy supply differs. Both capture configurations investigated here are powered entirely by grid electricity at an assumed price of 0.14 EUR/kWh, whereas the benchmark systems are typically supplied by low-grade steam or fuel combustion. Accordingly, direct cost comparisons should be interpreted with caution, and greater emphasis is placed on comparing transferable performance indicators, including CO<sub>2</sub> purity, capture efficiency, and specific energy consumption.

The cost of CO<sub>2</sub> avoided relates the additional cost of the capture plant to the net reduction in emissions relative to an unabated reference plant, and therefore accounts for the emissions associated with the energy consumed by the capture process itself; the cost of CO<sub>2</sub> captured, by contrast, relates the annualized cost of the plant to the quantity of CO<sub>2</sub> delivered as product, as defined in Eq. (4.18). No avoided cost is calculated in this work because no unabated reference plant was defined, and the literature values are reproduced on the avoided basis on which their authors report them, since they remain the only published figures available for these technologies. As the avoided cost of a given plant necessarily exceeds its captured cost, the comparison presented here is conservative with respect to the present study.

**Table 5.15** Comparison of the cryogenic process performance in this study with literature cryogenic and MEA-based CO<sub>2</sub> capture systems.

| Parameter                                | This study (cryogenic)  | Published cryogenic                                      | MEA (literature)             |
|------------------------------------------|-------------------------|----------------------------------------------------------|------------------------------|
| CO <sub>2</sub> purity (mol%)            | 99.9                    | 99.9 [133], [134],                                       | >99                          |
| Capture efficiency CO <sub>2</sub> (%)   | 95.0                    | 90-99 [133], [134]                                       | ~ 90                         |
| Specific energy (GJ/t)                   | 4.45                    | 1.08 [133]                                               | 3.2- 4.2 (steam) [17]        |
| Cost of CO <sub>2</sub> avoided (€/t)    | -                       | ≈74-111(dilute), ≈23-46 at 60-95 % CO <sub>2</sub> [133] | 100-115 (steel); 104.6 [109] |
| Cost of CO <sub>2</sub> captured (EUR/t) | LCOC 349 → 213 at scale | -                                                        | -                            |

Regarding the transferable indicators, the cryogenic process modeled in this study performs at the top of the published range. Its simulated CO<sub>2</sub> purity of 99.9 mol% and capture efficiency of 95.0 % are consistent with the high-recovery cryogenic systems reviewed by Luberti et al. (2024), whose energy is dominated by refrigeration and compression rather than by any chemical duty, as also shown in **Table 5.15**. [133] The literature reports that distillation-based cryogenic capture consumes roughly 0.30 MWh/t CO<sub>2</sub> (1.08 GJ/t) and costs about 74-111 €/t for dilute post-combustion streams, but that these costs fall steeply as feed concentration rises, for streams of 60-95 % CO<sub>2</sub> the specific refrigeration duty per tonne drops by a factor of three to five, bringing cryogenic costs to about 23-46 €/t, competitive with absorption [133]. This concentration dependence is central to the present result, because the iron-looping front end enriches the BFG-derived stream to roughly 39-40 mol% CO<sub>2</sub>, placing the separation the exact concentrated-feed regime the literature identifies as favorable. The base-case LCOC of 349 EUR/t lies above the published band, but this is a scale effect rather than a technology penalty. The scale study of Section 5.4.3 shows the LCOC falling to 213 EUR/t at industrial throughput, converging toward the literature once the sub-commercial penalty is removed. One point requires explicit reconciliation: the specific electricity of the present model, 1.24 MWh/t, is higher than the ≈0.30 MWh/t reported for the cited cryogenic systems. This reflects the wider system boundary adopted here, which includes compression of the product to 43 bar together with the shared iron-looping front end rather than a less efficient separation.

Benchmarked directly against MEA, the difference is one of energy form. MEA regeneration requires 3.2-4.2 GJ/t CO<sub>2</sub>. [17] But this is overwhelmingly low-grade steam at about 120 °C plus a small electricity demand, whereas the cryogenic process draws 4.45 GJ/t entirely as premium electricity. Because a host plant already possesses low-grade heat, MEA's energy is intrinsically cheaper, which is reflected in the reported cost of avoided CO<sub>2</sub> for amine scrubbing in the iron-and-steel sector with its full commercial maturity. About 100-115 €/t, reaching €104.6/t and identified as the least feasible option for iron and steel in the comparative review of Santos and Hanak (2022). [109] Against this, the cryogenic process offers advantages the headline cost omits: it uses no chemical solvent and therefore avoids the solvent degradation, corrosion, reclaiming, and amine-emission burdens that dominate real MEA operating cost. It delivers a high-purity liquid already at 43 bar, saving downstream compression and decisively, its economics improve with CO<sub>2</sub> concentration, whereas MEA is

optimized for dilute (3-15 mol%) flue gas and gains little from enrichment. For the concentrated, pressurizable stream produced by the looping front end, the cryogenic route is therefore the better physical match, and because the steel-sector MEA benchmark (100-115 €/t) is far higher than the cement or power figures often quoted, the present cryogenic LCOC of 213 EUR/t at scale is much closer to the mature reference than the dilute-flue-gas literature would suggest. MEA retains the advantage only where cheap steam is abundant; the stream is dilute, and commercial certainty is paramount.

**Table 5.16** Comparison of the proposed calcium-looping process with literature solid-looping and MEA-based CO<sub>2</sub> capture systems.

| Parameter                                   | This study<br>(calcium looping) | Published solid<br>looping (BFG)     | MEA (literature)         |
|---------------------------------------------|---------------------------------|--------------------------------------|--------------------------|
| Capture efficiency CO <sub>2</sub><br>(%)   | 97.6 (carbonator)               | 90-99 [138], [139]                   | ~ 90                     |
| Calciner heat supply<br>(kW)                | Electric, 1,025                 | Oxy-fuel / fuel-fired                | -                        |
| Specific energy (GJ/t)                      | (6.8, electric)                 | 0.8-1.4 [36], [109]                  | 3.2-4.2 (steam) [17]     |
| Cost of CO <sub>2</sub> avoided<br>(€/t)    | -                               | 30-50 [109], [185];<br>≈27- 46 [110] | 100-115 (steel)<br>[109] |
| Cost of CO <sub>2</sub> captured<br>(EUR/t) | LCOC 391 → 280<br>at scale      | -                                    | -                        |
| Maturity (TRL) 2026                         | ~6-7                            | 6-7 [37]                             | Commercial               |

The calcium-looping process modeled here reproduces the performance reported in the literature, but not its cost, and the divergence is attributable to configuration rather than to the technology. Its simulated carbonator capture of 97.6 % is at or above the range reported for solid-looping systems, whose markedly lower energy penalty relative to amine scrubbing is 0.8-1.4 GJ/t against 3.2-4.2 GJ/t for MEA, as indicated in **Table 5.16**. [36], [109], [17] On cost, the comparative review of Santos and Hanak (2022) places CO<sub>2</sub> avoidance for solid looping applied to blast-furnace gas at 30-50 €/t, roughly one-third to one-half the cost of amine scrubbing for the steel industry and Thiedemann and Wark estimate calcium-looping costs at ≈ 27-46 €/t (29-50 \$/t), about 50 % cheaper than amine capture. [109], [110] The present LCOC of 391 EUR/t lies far above this band, and the reason is that the configuration modeled here supplies the 1,025 kW calcination endotherm at 900 °C electrically, which is 48 % of the operating cost, whereas the competitive literature fires the calciner by oxy-fuel or otherwise fuel-fired combustion and recovers the reaction heat. The consequence is legible in the specific energy as 6.8 GJ/t of high-value electricity here, against the largely fuel-based energy of the integrated cases. Because it substitutes premium electricity for the low-grade heat that fuel-fired designs consume, the all-electric configuration is intrinsically penalized at any scale, and the scale study lowers the LCOC only to 280 EUR/t. The comparison therefore does not indict calcium looping as a technology; it indicates the electrically heated, standalone configuration. Fuel-fired or oxy-fuel calcination with heat recovery and industrial integration would be required to approach the 30-50 EUR/t capture costs reported in the literature. Against MEA, the present electric configuration is more expensive because it uses premium electricity instead of low-cost steam and lacks integration benefits. This comparison is configuration-specific, as integrated fuel-fired calcium looping has been reported to cost only 30-50 €/t versus 100-115 €/t for MEA. Although less mature than MEA, calcium-looping technologies for steel have reached TRL 6-7 by 2026, as demonstrated by a packed-bed pilot

treating up to 300 Nm<sup>3</sup>/h of real blast-furnace gas [37] and a techno-economic study of a Ca–Cu looping process integrated with CO<sub>2</sub> separation by partial condensation. [185]

## 5.7 Technology selection and recommendation

For the concentrated, pressurizable blast furnace gas stream investigated in this thesis, the evidence identifies the cryogenic route as the most immediately promising option and calcium looping as the stronger long-term candidate once reconfigured. On performance, the cryogenic process delivers the highest purity (99.9 mol%) and a capture efficiency (95.0 %) equal to the best cryogenic literature and above typical MEA (~90 %), and at industrial scale, an LCOC of 213 EUR/t against a steel-sector MEA benchmark of 100-115 €/t. [109] The recommendation is nevertheless conditional on the two variables identified as decisive in the sensitivity analysis. The cryogenic route is preferred where a concentrated CO<sub>2</sub> stream can be pressurized, as in the present H2Loop configuration, where a high-purity, high-pressure product is required, and where low-cost, low-carbon electricity is available. These conditions are expected to become increasingly common as electricity grids decarbonize. MEA remains the safer choice for dilute, atmospheric-pressure flue gas served by cheap steam and where commercial certainty is paramount. Calcium looping becomes preferable and indeed the cheapest option reported for blast-furnace gas - only in an oxy-fuel, heat-integrated form with a clinker or heat outlet. On balance, for the specific context of this study, an enriched, pressurizable CO<sub>2</sub> stream at an integrated steelworks with access to electricity, the cryogenic separation process is recommended for near-term deployment, while calcium looping is identified as the more promising route for long-term industrial integration, contingent on converting its calciner from electric to fuel-fired heating.

## 6 Conclusion

This thesis assessed the most technically and economically appropriate route for separating the concentrated CO<sub>2</sub> produced by the H2Loop chemical-looping process from blast-furnace gas at an integrated steelwork. Two capture technologies, cryogenic distillation and calcium looping, sharing a common iron chemical-looping front end (reduction at 850 °C, steam-oxidation at 700 °C), were modeled in Aspen Plus at a 1,000 Nm<sup>3</sup>/h design point and subjected to a consistent techno-economic assessment, benchmarked against the mature reference technology, monoethanolamine absorption.

At the process level, both routes met and exceeded the  $\geq 95$  mol% purity and  $\geq 90$  % capture design targets. The cryogenic route delivered a 99.9 mol% liquid CO<sub>2</sub> product at 43 bar with 95.0 % capture, and calcium looping a  $\approx 100$  mol% product at 21 bar with 97.6 % capture, while the shared front end enriched the feed to roughly 39-41 mol% CO<sub>2</sub> and co-produced 70.1 t/yr of hydrogen. Both configurations are fully electrified, and their energy consumption dominates their economics. The cryogenic route consumes 1.24 MWh/t of CO<sub>2</sub>, with front-end reactor heating representing the largest electricity demand (42%), followed by the distillation-column auxiliaries (22%) and compression and refrigeration (18%). In contrast, calcium looping consumes 1.88 MWh/t of CO<sub>2</sub>, with the electrically heated calciner alone accounting for 48% of the total operating cost.

Economically, at the sub-commercial 1,000 Nm<sup>3</sup>/h base scale, neither route is profitable. The levelized cost of capture is 349 EUR/t for the cryogenic route against a 260 EUR/t product price, and 391 EUR/t for calcium looping against 80 EUR/t. However, sensitivity analysis identifies electricity price and plant scale as the dominant economic drivers, whereas capital cost, financing terms and carbon price have a comparatively smaller influence. This is confirmed by the scale analysis, in which the cryogenic LCOP falls to 213 €/t CO<sub>2</sub> at industrial throughput, reaching economic viability while calcium looping remains uneconomic at 280 €/t CO<sub>2</sub> because the cost of its electrically heated calciner is largely scale-invariant. Compared with MEA (100-115 €/t CO<sub>2</sub> avoided), the difference is fundamentally one of energy form, with MEA relying on low-cost steam, whereas the electrified routes depend on premium electricity, making their competitiveness primarily dependent on electricity price and carbon intensity.

On this evidence, the cryogenic separation route is recommended as the most immediately promising option for the concentrated, pressurisable blast-furnace-gas stream investigated in this study. It delivers the highest product purity, a capture efficiency equal to the best in the literature and above typical MEA and it is the only route that reaches viability at industrial scale, exploiting the concentrated-feed regime in which physical separation is thermodynamically favored and requiring no chemical solvent. Calcium looping is identified as the stronger long-term candidate, but only if its electric calciner is replaced with oxy-fuel or fuel-fired heating, its high-grade reaction heat is recovered for power generation, and it is integrated with a host process that can utilize clinker or waste heat. Under these conditions, the literature reports costs of 30-50 EUR/t CO<sub>2</sub>, making it competitive with amine scrubbing.

The principal contribution of this work is a systematic Aspen Plus and techno-economic comparison of cryogenic distillation and calcium looping for the H2Loop concentrated CO<sub>2</sub> stream at a steelwork, including valorization of the hydrogen co-product. The main limitations are the use of equilibrium reactor models, the steady-state representation of a cyclic process, the AACE Class 4 ( $-30\%/+50\%$ ) cost accuracy, and the sensitivity of hydrogen production to the oxygen-carrier phase representation. Future work should incorporate kinetic and transient reactor models validated against pilot data, optimize heat integration and waste-heat recovery, particularly for calcium looping, evaluate higher-value CO<sub>2</sub> utilization pathways, refine the economic assessment with vendor data, and complement

the techno-economic analysis with a life-cycle assessment to account for the carbon intensity of the electricity supply.

The quantitative results of this study are accordingly to be read as a bounded range. The upper-bound (adopted) case yields 39–41 mol% CO<sub>2</sub> to the separation step, 70.1 t/y of hydrogen and up to 95.0 % single-pass CO<sub>2</sub> recovery, the latter conditional on the vapour–liquid-equilibrium assumption of the column model, while the phase-consistent wüstite case defines the lower bound with 32.6 % CO conversion and approximately 12.9 kmol/h of CO<sub>2</sub> to the separation step. The qualitative findings are robust across this range: the electric-calcination penalty of the calcium-looping route and the concentrated-feed advantage of cryogenic separation persist in both bounds, and the ranking of the two routes is unchanged. On a whole-plant carbon basis, capture amounts to approximately 85 % for the cryogenic and 93 % for the calcium-looping route once the carbon leaving as unconverted CO is counted. As the scale-up cases inherit the upper-bound base case, the scale-up results constitute a conditional screening rather than absolute cost predictions.

## 7 Optimization and Future Directions

In addition to the directions discussed in this chapter, the following model refinements are required to convert the bounded estimates of Chapters 5 and 6 into realistic figures:

- Phase-consistent re-simulation of the iron-oxide loop using a single solid phase, ideally a non-stoichiometric wüstite model, with a closed Fe/O balance in both routes and in the techno-economic assessment; this is expected to reduce the CO conversion toward approximately 50–57 % and the CO<sub>2</sub> flow to the separation step accordingly.
- An equilibrium checks on the cryogenic column at the frost point, together with the design and costing of an anti-sublimation or defrost section, for example a Clodic-type switching desublimating exchanger [168], required to recover the vapour–liquid-equilibrium bound of 95 % single-pass recovery.
- A thermodynamically consistent calciner basis, comprising a pressure and temperature combination satisfying Eq. (4.12), or steam-sweep operation with downstream condensation, which would also address the nitrogen-purge and purity issue.
- Low, central and high blast-furnace-gas feed-composition cases, and an assessment of the effect of trace components removed in the upstream cleaning system on carrier and sorbent life, corrosion and product purity.
- Equipment-specific scale exponents in place of the global 0.65 exponent, and a CO<sub>2</sub> offtake and price study covering route-specific market scenarios, including merchant sale, permanent storage and temporary utilisation with the corresponding EU-ETS obligations.
- A sensitivity study on sorbent residual conversion and service life, confirmation of the installed versus purchased basis of the equipment cost data, alignment of the reactor pressures reported in Section 4.5 and a quantitative techno-economic comparison of multistage membrane configurations on the post-front-end composition.

The techno-economic assessment demonstrates that cryogenic distillation and calcium looping face fundamentally different barriers to commercialization. Cryogenic distillation is primarily constrained by plant scale and electricity price, whereas calcium looping is limited by the configuration of the process itself, particularly the electrically heated calciner. Consequently, the cryogenic process can be optimized through deployment decisions, while calcium looping requires more fundamental process redesign before it can become economically competitive.

For cryogenic distillation, plant scale is the principal optimization lever. Scale-up reduced the levelized cost from 349 €/t CO<sub>2</sub> at 1,000 Nm<sup>3</sup>/h to 220 €/t at 68,500 Nm<sup>3</sup>/h, making the process economically attractive under the assumed CO<sub>2</sub> selling price of 260 €/t. Because electricity remains the largest operating cost (1.24 MWh/t CO<sub>2</sub>) and more than half of it is consumed by front-end reactor heating rather than by the separation itself, access to low-cost renewable electricity and further heat integration on the front end provide the main remaining opportunities to reduce operating expenditure. Given its commercial maturity, successful deployment therefore depends primarily on industrial-scale implementation and favorable electricity procurement rather than further technological development.

In contrast, calcium looping cannot achieve economic viability through incremental optimizations alone because the electrically heated calciner dominates operating costs. Replacing the electric calciner with a fuel-fired or oxy-fuel configuration, coupled with recovery of high-temperature process

heat, represents the most effective route to improving economic performance and is consistent with the integrated calcium-looping configurations reported in the literature. The economics of both capture routes could be further enhanced through product valorization, with the H2Loop hydrogen providing an additional annual revenue of approximately 0.28 M€ and higher-value CO<sub>2</sub> utilization pathways, such as mineralization, synthetic fuels or construction materials, offering greater returns than the horticultural application assumed in the present study.

Beyond these model refinements, future research should focus on improving both the technical fidelity and economic confidence of the present assessment. The equilibrium reactor models employed in this study provide thermodynamic upper bounds and should be extended to rate-based kinetic models incorporating gas-solid reaction kinetics, sorbent deactivation, and oxygen-carrier degradation. Likewise, the steady-state representation should be replaced by dynamic simulations capable of capturing the cyclic operation of the reduction-oxidation and carbonation-calcination processes and validated against pilot-scale experimental data. From an engineering perspective, the preliminary pinch analysis should be developed into a detailed heat-exchanger-network synthesis with combined heat and power integration, particularly for calcium looping, where significant high-temperature heat remains available for recovery. In addition, the techno-economic assessment should be refined from the current AACE Class 4 estimate through detailed equipment design and vendor quotations, while experimental validation of hydrogen production, CO<sub>2</sub> capture performance and long-term material stability, together with a life-cycle assessment, would provide a more comprehensive evaluation of the technical, economic and environmental performance of the proposed capture systems.

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## 9 Appendices

**Table 9.1** Top six blast furnace (BF) iron-producing countries in 2024, including pig iron production, BF ironmaking capacity, share of global BF capacity and fleet status.

| Rank | Country     | Pig iron (BF route) 2024 [Mt] | BF ironmaking capacity [Mtpa] | Share of global BF capacity [%] | Fleet status                                                         |
|------|-------------|-------------------------------|-------------------------------|---------------------------------|----------------------------------------------------------------------|
| 1    | China       | 851.7                         | 898                           | 55                              | Relatively young fleet (avg. ~13 yr), most capacity added post 2000s |
| 2    | India       | 144.9                         | 152                           | 9                               | Young fleet: ≥72% installed in last two decades; ~11% >40 yr         |
| 3    | Japan       | 61.0                          | 86                            | 5                               | Mature fleet; heavy reliance on BF–BOF, several units under relining |
| 4    | Russia      | 59.0                          | 71                            | 4                               | Older fleet with Soviet-era units; some modernized                   |
| 5    | South Korea | 44.1                          | 45                            | 3                               | Modern, state-of-the-art (POSCO/Hyundai operations)                  |
| 6    | USA         | ~20                           | ~25                           | 2                               | Oldest fleet globally (avg. operating age ~74 yr)                    |

**Table 9.2** Economic and financial basis used throughout the assessment

Source: Assumptions; the discounting factors  $\phi$ ,  $\psi$  and  $\phi/\psi$  and the construction phasing are defined in Section 4.6.

| Parameter                                       | Symbol      | Value        | Unit                  | Basis                                    |
|-------------------------------------------------|-------------|--------------|-----------------------|------------------------------------------|
| Discount rate                                   | $i$         | 5.0          | %                     | Screening basis                          |
| Plant operating life                            | $n$         | 10           | years                 | 2029–2038                                |
| Capital recovery factor                         | CRF         | 0.1295046    | –                     | $i(1+i)^n / [(1+i)^n - 1]$               |
| Annuity factor                                  | AF          | 7.721735     | –                     | $[1 - (1+i)^{-n}] / i$                   |
| Construction phasing                            | –           | 20 / 40 / 40 | %                     | 2026 / 2027 / 2028                       |
| Construction PV factor                          | $\phi$      | 0.943764     | –                     | $0.2 + 0.4/(1+i) + 0.4/(1+i)^2$          |
| Operating PV factor                             | $\psi$      | 7.003841     | –                     | $AF / (1+i)^2$                           |
| Capital charge rate                             | $\phi/\psi$ | 0.1347495    | –                     | –                                        |
| Electricity price                               | –           | 0.14         | EUR/kWh               | Industrial tariff                        |
| Annual operating hours                          | –           | 8,059.2      | h/yr                  | 92 % availability × 8,760 h              |
| CO <sub>2</sub> price - cryogenic product       | –           | 260          | EUR/t                 | Food/merchant grade, ≥99.9 mol%          |
| CO <sub>2</sub> price - calcium-looping product | –           | 80           | EUR/t                 | Horticultural grade, ≥95 mol%            |
| Hydrogen price                                  | –           | 4,000        | EUR/t                 | By-product credit                        |
| EU ETS price                                    | –           | 95           | EUR/t CO <sub>2</sub> | Uncaptured slip only                     |
| BFG opportunity price                           | –           | 22.83        | EUR/t                 | LHV 3.20 MJ/Nm <sup>3</sup> × 35 EUR/MWh |
| Steam price                                     | –           | 42.5         | EUR/t                 | Process steam                            |
| Maintenance                                     | –           | 5.0          | % FCI/yr              | Factorial                                |
| Insurance and local taxes                       | –           | 1.15         | % FCI/yr              | Factorial                                |
| Operating labour rate                           | –           | 85,000       | EUR/person/yr         | 3 operators at base scale                |

| Parameter          | Symbol | Value | Unit | Basis                                |
|--------------------|--------|-------|------|--------------------------------------|
| Corporate tax rate | –      | 29.9  | %    | German combined rate (financed case) |
| Escalation         | –      | 2.0   | %/yr | ECB target (financed case)           |

**Table 9.3** Reactor heat duties from Aspen Plus

| Block                       | Description                       | Temperature     | Duty (kW)      | Sign            |
|-----------------------------|-----------------------------------|-----------------|----------------|-----------------|
| R-101                       | Reduction reactor                 | 850 °C          | 517.0          | Endothermic (+) |
| R-102                       | Steam-oxidation reactor           | 700 °C          | 158.0          | Exothermic (–)  |
| <b>Net front-end duty</b>   | R-101 – R-102                     | –               | <b>359.0</b>   | Endothermic     |
| Electrical input            | net duty / 0.95 heater efficiency | –               | <b>377.9</b>   | –               |
| R-103                       | Carbonator                        | 650 °C, 1.5 bar | 898            | Exothermic (–)  |
| R-104                       | Calciner                          | 900 °C, 1 bar   | 1,024.4        | Endothermic (+) |
| Electrical input (calciner) | 1,024.4 / 0.95                    | –               | <b>1,078.3</b> | –               |
| HXST                        | Surplus-heat recovery exchanger   | 491.8 → 40 °C   | 99.8           | Recovered       |

**Table 9.4** Cryogenic route - equipment, design basis and installed cost (RG-H<sub>2</sub> internal data).

| Tag      | Equipment                             | Design basis                   | Cost (EUR)       |
|----------|---------------------------------------|--------------------------------|------------------|
| R-101    | Reduction reactor                     | 2 m <sup>3</sup>               | 150,000          |
| R-102    | Steam-oxidation reactor               | 2 m <sup>3</sup>               | 150,000          |
| FV-101   | Knock-out drum                        | 2.4 m <sup>3</sup>             | 26,500           |
| HX-101   | Feed/effluent recuperator             | 50 m <sup>2</sup>              | 77,625           |
| HX-102   | Product gas cooler                    | 1 m <sup>2</sup>               | 14,000           |
| HX-103   | Cold-box exchanger                    | 1 m <sup>2</sup>               | 14,000           |
| HX-104   | Cryogenic pre-cooler                  | 2 m <sup>2</sup>               | 25,000           |
| M-CP-101 | Four-stage CO <sub>2</sub> compressor | 138.5 kW                       | 350,000          |
| DC-01    | Distillation column package           | sum: column+condenser+reboiler | 350,000          |
| REF-UNIT | Mechanical refrigeration              | 15.3 kW                        | 125,000          |
| MS-101   | Molecular-sieve dryer                 | 0.65 scaling                   | 105,000          |
| AC-101   | Air cooler                            | 122 kW                         | 31,000           |
| HE-101   | Electric trim heater                  | 98 kW                          | 75,500           |
| HE-102   | Electric trim heater                  | 10 kW                          | 30,000           |
| —        | Switching-valve manifold              | 8 valves                       | 8,000            |
|          | <b>Bare erected cost (BEC)</b>        |                                | <b>1,531,625</b> |

**Table 9.5** Calcium-looping route - equipment, design basis and installed cost (RG-H<sub>2</sub> internal data).

| Tag    | Equipment                              | Design basis               | Cost (EUR) |
|--------|----------------------------------------|----------------------------|------------|
| R-101  | Reduction reactor                      | 2 m <sup>3</sup>           | 150,000    |
| R-102  | Steam-oxidation reactor                | 2 m <sup>3</sup>           | 150,000    |
| R-103  | Fixed-bed carbonator (650 °C)          | 2 m <sup>3</sup>           | 240,000    |
| R-104  | Calciner (900 °C, electric)            | 2 m <sup>3</sup> ; €120/kW | 240,000    |
| HX-01  | Feed/effluent recuperator              | 2.2 m <sup>2</sup>         | 31,000     |
| HX-02  | Inter-stage cooler                     | 1.2 m <sup>2</sup>         | 16,500     |
| HX-03  | Heat-recovery exchanger                | 1.7 m <sup>2</sup>         | 23,500     |
| HX-04  | Product gas cooler                     | 1.3 m <sup>2</sup>         | 17,500     |
| HX-05  | Condenser                              | 1 m <sup>2</sup>           | 14,000     |
| MC-101 | Three-stage CO <sub>2</sub> compressor | 72 kW (21 bar)             | 240,000    |
| HE01   | H-T electric heater                    | 40 kW                      | 27,500     |
| HE02   | H-T electric heater                    | 10 kW                      | 30,000     |
| —      | Switching-valve manifold               | 16 valves                  | 16,000     |
| —      | Steam-reactivation package             | lump sum                   | 40,000     |
|        | Bare erected cost (BEC)                |                            | 1,236,000  |

**Table 9.6** Factorial build-up from bare erected cost to total investment

Source: RG-H<sub>2</sub> CAPEX workbooks (cryogenic and calcium-looping routes).

| Step                         | Factor                      | Cryogenic (EUR) | Calcium looping (EUR) |
|------------------------------|-----------------------------|-----------------|-----------------------|
| Bare erected cost, BEC       | Σ installed equipment       | 1,531,625       | 1,236,000             |
| Land                         | 3 % of BEC                  | 45,949          | 37,080                |
| EPC services                 | 15 % of BEC                 | 229,744         | 185,400               |
| Process contingency          | 10 % of (BEC + EPC)         | 176,137         | 142,140               |
| Project contingency          | 20 % of (BEC + EPC + proc.) | 387,501         | 312,708               |
| Licensing                    | 3 % of BEC                  | 45,949          | 37,080                |
| Total plant cost, TPC        | sum                         | 2,416,904       | 1,950,408             |
| Commissioning                | 5 % of TPC                  | 120,845         | 97,520                |
| Working capital              | inventory lump              | 40,000          | 45,000                |
| <b>Total investment, TIC</b> | TPC + comm. + WC            | 2,577,749       | 2,092,928             |
| <b>Fixed capital, FCI</b>    | TPC + comm. – land          | 2,491,801       | 2,010,848             |

**Table 9.7** Electricity consumption - cryogenic route

| Tag          | Equipment                                    | Calculation basis                                                  | Demand (kW)  | Annual (kWh/yr)  | Cost (EUR/yr)    |
|--------------|----------------------------------------------|--------------------------------------------------------------------|--------------|------------------|------------------|
| DC-01 aux    | Column condenser / reboiler                  | Condenser via Luyben (2017) power ratio; reboiler on cooling water | 198.0        | 1,595,722        | 223,401          |
| R-101/102    | Front-end reactor heating                    | net 359 kW / 0.95                                                  | 377.9        | 3,045,572        | 426,380          |
| M-S-COMP     | CO <sub>2</sub> compressor, 4-stage → 43 bar | Shaft power                                                        | 145.8        | 1,175,031        | 164,504          |
| HE-101       | Trim heater (electric)                       | Trim duty                                                          | 103.3        | 832,515          | 116,552          |
| HE-102       | Steam superheater                            | Steam superheating                                                 | 6.7          | 53,997           | 7,560            |
| MS-101       | Molecular-sieve regeneration + blower        | Regeneration duty                                                  | 57.9         | 466,628          | 65,328           |
| REF-UNIT     | Refrigeration, -35 °C pre-cool               | Cold duty 15.31 kW × Luyben power ratio                            | 18.2         | 146,677          | 20,535           |
| AC-101       | Air-cooler fans                              | 1.5 % of 122.4 kW duty                                             | 2.1          | 16,924           | 2,369            |
| <b>Total</b> |                                              |                                                                    | <b>909.9</b> | <b>7,333,066</b> | <b>1,026,629</b> |

\*Specific electricity:  $7,333,066 \text{ kWh} \div 5,929.15 \text{ t} = 1,237 \text{ kWh/t CO}_2$  (1.24 MWh/t)

**Table 9.8** Electricity consumption - calcium-looping route

| Tag          | Equipment                                    | Calculation basis       | Demand (kW)     | Annual (kWh/yr)   | Cost (EUR/yr)    |
|--------------|----------------------------------------------|-------------------------|-----------------|-------------------|------------------|
| CAL-101      | Electric calciner                            | Calcination duty / 0.95 | 1,078.3         | 8,690,235         | 1,216,633        |
| R-101/102    | Front-end reactor heating                    | net 359 kW / 0.95       | 377.9           | 3,045,572         | 426,380          |
| M-COM01      | CO <sub>2</sub> compressor, 3-stage → 21 bar | Shaft power             | 52.7            | 424,720           | 59,461           |
| HE-02        | Steam superheater                            | Steam superheating      | 6.7             | 53,997            | 7,560            |
| HE-01        | Feed-preheat trim heater                     | Trim duty               | 0.45            | 3,627             | 508              |
| <b>Total</b> |                                              |                         | <b>1,516.05</b> | <b>12,218,150</b> | <b>1,710,541</b> |

Specific electricity:  $12,218,150 \text{ kWh} \div 6,490.72 \text{ t} = 1,882 \text{ kWh/t CO}_2$  (1.88 MWh/t)

Calciner share of electricity:  $1,078.3 / 1,516.05 = 71.1 \%$

**Table 9.9** Annual operating-cost breakdown at the base scale

Source: RG-H<sub>2</sub> OPEX workbooks (cryogenic and calcium-looping routes).

| Component                        | Cryogenic (EUR/yr) | Calcium looping (EUR/yr) | Basis                                    |
|----------------------------------|--------------------|--------------------------|------------------------------------------|
| BFG feedstock (opportunity cost) | 250,760            | 250,760                  | 22.83 EUR/t on 10,983.9 t/yr             |
| Electricity                      | 1,026,629          | 1,710,541                | Preceding two tables                     |
| — of which electric calciner     | —                  | 1,216,633                | CAL-101                                  |
| — of which front-end heating     | 426,380            | 426,380                  | shared, identical                        |
| Steam                            | 57,885             | 60,351                   | Process steam                            |
| Process / cooling water          | 96,710             | 873                      | Make-up + circulation                    |
| Carrier, sorbent and ETS on slip | 40,132             | 22,654                   | Consumables + uncaptured CO <sub>2</sub> |
| Fixed costs                      | 542,996            | 513,417                  | Next table                               |
| <b>Gross OPEX</b>                | <b>2,015,113</b>   | <b>2,558,596</b>         |                                          |

Specific operating cost: cryogenic 339.9 EUR/t, calcium looping 394.2 EUR/t

**Table 9.10** Derivation of the fixed operating costs for both routes

Source: RG-H<sub>2</sub> OPEX workbooks (cryogenic and calcium-looping routes).

| Item                         | Formula              | Cryogenic (EUR/yr) | Calcium looping (EUR/yr) |
|------------------------------|----------------------|--------------------|--------------------------|
| Operating labour             | 3 operators × 85,000 | 255,000            | 255,000                  |
| Supervision                  | 15 % of labour       | 38,250             | 38,250                   |
| Laboratory / QC              | Allowance            | 15,000             | 15,000                   |
| Plant overheads              | 30 % of labour       | 76,500             | 76,500                   |
| Maintenance                  | 5.0 % × FCI          | 124,590            | 100,542                  |
| Insurance and local taxes    | 1.15 % × FCI         | 28,656             | 23,125                   |
| Permits / ETS administration | Allowance            | 5,000              | 5,000                    |
| <b>Total fixed</b>           |                      | <b>542,996</b>     | <b>513,417</b>           |

FCI is 2,491,801 EUR (cryogenic) and 2,010,848 EUR (calcium looping); both routes use identical staffing and identical percentage rates, so the difference arises solely from the capital-based items.

**Table 9.11** Annual revenue streams for both routes

Source: RG-H<sub>2</sub> OPEX workbooks (cryogenic and calcium-looping routes).

| Stream                    | Quantity                 | Unit price     | Cryogenic (EUR/yr) | Calcium looping (EUR/yr) |
|---------------------------|--------------------------|----------------|--------------------|--------------------------|
| CO <sub>2</sub> product   | 5,929.15 / 6,490.72 t/yr | 260 / 80 EUR/t | 1,541,580          | 519,257                  |
| Hydrogen by-product       | 70.115 t/yr              | 4,000 EUR/t    | 280,460            | 280,460                  |
| Spent CaO to cement plant | 14.53 t/yr               | 10 EUR/t       | —                  | 145                      |
| Waste-heat export (HXST)  | 2,895.5 GJ/yr            | 3 EUR/GJ       | —                  | 8,687                    |
| <b>Total revenue</b>      |                          |                | <b>1,822,040</b>   | <b>808,549</b>           |

**Waste-heat export:** 99.8 kW × 8,059.2 h × 3.6 MJ/kWh = 2,895.5 GJ/yr at 3 EUR/GJ.

The hydrogen credit is booked on the harmonised wüstite front end (70.115 t/yr), the basis shared by both routes; the FeO variant as originally modelled yields 16.6 t/yr.

**Table 9.12** Worked derivation of the levelised cost of capture

$$\text{Levelised cost} = (\text{CRF} \times \text{TIC} + \text{gross OPEX} - \text{non-CO}_2 \text{ revenues}) \div \dot{m}$$

**Cryogenic**

| Term                             | Value                                  |
|----------------------------------|----------------------------------------|
| CRF × TIC                        | $0.1295046 \times 2,577,749 = 333,830$ |
| Gross OPEX                       | 2,015,113                              |
| Less non-CO <sub>2</sub> revenue | - 280,460                              |
| Numerator                        | 2,068,483                              |
| ÷ CO <sub>2</sub> captured       | ÷ 5,929.15                             |
| <b>Result</b>                    | <b>348.9 EUR/t</b>                     |

**Calcium looping**

| Term                             | Value                                  |
|----------------------------------|----------------------------------------|
| CRF × TIC                        | $0.1295046 \times 2,092,928 = 271,044$ |
| Gross OPEX                       | 2,558,596                              |
| Less non-CO <sub>2</sub> revenue | - 289,292                              |
| Numerator                        | 2,540,348                              |
| ÷ CO <sub>2</sub> captured       | ÷ 6,490.72                             |
| <b>Result</b>                    | <b>391.4 EUR/t</b>                     |

**Table 9.13** Worked derivation of the levelised cost of product

$$\text{Levelised cost} = (\text{TIC} \times \phi/\psi + \text{gross OPEX} - \text{non-CO}_2 \text{ revenues}) \div \dot{m}$$

**Cryogenic**

| Term                             | Value                                  |
|----------------------------------|----------------------------------------|
| TIC × $\phi/\psi$                | $0.1347495 \times 2,577,749 = 347,350$ |
| Gross OPEX                       | 2,015,113                              |
| Less non-CO <sub>2</sub> revenue | - 280,460                              |
| Numerator                        | 2,082,003                              |
| ÷ CO <sub>2</sub> captured       | ÷ 5,929.15                             |
| <b>Result</b>                    | <b>351.1 EUR/t</b>                     |

**Calcium looping**

| Term                             | Value                                  |
|----------------------------------|----------------------------------------|
| TIC × $\phi/\psi$                | $0.1347495 \times 2,092,928 = 282,021$ |
| Gross OPEX                       | 2,558,596                              |
| Less non-CO <sub>2</sub> revenue | - 289,292                              |
| Numerator                        | 2,551,325                              |
| ÷ CO <sub>2</sub> captured       | ÷ 6,490.72                             |
| <b>Result</b>                    | <b>393.1 EUR/t</b>                     |

**Difference LCOP - LCOC (cryogenic):**  $(0.1347495 - 0.1295046) \times 2,577,749 \div 5,929.15 = +2.3 \text{ EUR/t}$  - the phased construction period.

**Table 9.14** Screening cash flow - cryogenic route

| Year        | CAPEX     | OPEX      | Revenue   | Net cash   | Cumulative | DF (5 %) | PV                 |
|-------------|-----------|-----------|-----------|------------|------------|----------|--------------------|
| 2026        | 515,550   | –         | –         | –515,550   | –515,550   | 1.000    | –515,550           |
| 2027        | 1,031,100 | –         | –         | –1,031,100 | –1,546,650 | 0.952    | –982,000           |
| 2028        | 1,031,100 | –         | –         | –1,031,100 | –2,577,749 | 0.907    | –935,238           |
| 2029        | –         | 2,015,113 | 1,822,040 | –193,073   | –2,770,822 | 0.864    | –166,783           |
| 2030        | –         | 2,015,113 | 1,822,040 | –193,073   | –2,963,895 | 0.823    | –158,841           |
| 2031        | –         | 2,015,113 | 1,822,040 | –193,073   | –3,156,967 | 0.784    | –151,277           |
| 2032        | –         | 2,015,113 | 1,822,040 | –193,073   | –3,350,040 | 0.746    | –144,074           |
| 2033        | –         | 2,015,113 | 1,822,040 | –193,073   | –3,543,112 | 0.711    | –137,213           |
| 2034        | –         | 2,015,113 | 1,822,040 | –193,073   | –3,736,185 | 0.677    | –130,679           |
| 2035        | –         | 2,015,113 | 1,822,040 | –193,073   | –3,929,258 | 0.645    | –124,456           |
| 2036        | –         | 2,015,113 | 1,822,040 | –193,073   | –4,122,330 | 0.614    | –118,530           |
| 2037        | –         | 2,015,113 | 1,822,040 | –193,073   | –4,315,403 | 0.585    | –112,886           |
| 2038        | –         | 2,015,113 | 1,822,040 | –193,073   | –4,508,476 | 0.557    | –107,510           |
| <b>NPV</b>  |           |           |           |            |            |          | <b>–3,785,037</b>  |
| <b>LCOP</b> |           |           |           |            |            |          | <b>351.1 EUR/t</b> |

**Table 9.15** Screening cash flow - calcium-looping route

| Year        | CAPEX   | OPEX      | Revenue | Net cash   | Cumulative  | DF (5 %) | PV                 |
|-------------|---------|-----------|---------|------------|-------------|----------|--------------------|
| 2026        | 418,586 | –         | –       | –418,586   | –418,586    | 1.000    | –418,586           |
| 2027        | 837,171 | –         | –       | –837,171   | –1,255,757  | 0.952    | –797,306           |
| 2028        | 837,171 | –         | –       | –837,171   | –2,092,928  | 0.907    | –759,339           |
| 2029        | –       | 2,558,598 | 808,549 | –1,750,049 | –3,842,977  | 0.864    | –1,511,758         |
| 2030        | –       | 2,558,598 | 808,549 | –1,750,049 | –5,593,026  | 0.823    | –1,439,769         |
| 2031        | –       | 2,558,598 | 808,549 | –1,750,049 | –7,343,074  | 0.784    | –1,371,209         |
| 2032        | –       | 2,558,598 | 808,549 | –1,750,049 | –9,093,123  | 0.746    | –1,305,913         |
| 2033        | –       | 2,558,598 | 808,549 | –1,750,049 | –10,843,172 | 0.711    | –1,243,727         |
| 2034        | –       | 2,558,598 | 808,549 | –1,750,049 | –12,593,221 | 0.677    | –1,184,502         |
| 2035        | –       | 2,558,598 | 808,549 | –1,750,049 | –14,343,269 | 0.645    | –1,128,097         |
| 2036        | –       | 2,558,598 | 808,549 | –1,750,049 | –16,093,318 | 0.614    | –1,074,378         |
| 2037        | –       | 2,558,598 | 808,549 | –1,750,049 | –17,843,367 | 0.585    | –1,023,217         |
| 2038        | –       | 2,558,598 | 808,549 | –1,750,049 | –19,593,415 | 0.557    | –974,493           |
| <b>NPV</b>  |         |           |         |            |             |          | <b>–14,232,294</b> |
| <b>LCOP</b> |         |           |         |            |             |          | <b>393.1 EUR/t</b> |

**Table 9.16** Financed cash flow - cryogenic route

| Year        | OPEX      | Revenue   | Interest | Principal | Deprec. | Tax | Net cash | Cumulative | PV                 |
|-------------|-----------|-----------|----------|-----------|---------|-----|----------|------------|--------------------|
| 2026        | –         | –         | –        | –         | –       | –   | 0        | 0          | 0                  |
| 2027        | –         | –         | –        | –         | –       | –   | 0        | 0          | 0                  |
| 2028        | –         | –         | –        | –         | –       | –   | 0        | 0          | 0                  |
| 2029        | 2,015,113 | 1,822,040 | 128,887  | 257,775   | 257,775 | 0   | –579,735 | –579,735   | –500,797           |
| 2030        | 2,055,415 | 1,858,481 | 115,999  | 257,775   | 257,775 | 0   | –570,708 | –1,150,443 | –469,523           |
| 2031        | 2,096,523 | 1,895,650 | 103,110  | 257,775   | 257,775 | 0   | –561,758 | –1,712,200 | –440,152           |
| 2032        | 2,138,454 | 1,933,563 | 90,221   | 257,775   | 257,775 | 0   | –552,886 | –2,265,087 | –412,572           |
| 2033        | 2,181,223 | 1,972,235 | 77,332   | 257,775   | 257,775 | 0   | –544,095 | –2,809,182 | –386,678           |
| 2034        | 2,224,847 | 2,011,679 | 64,444   | 257,775   | 257,775 | 0   | –535,386 | –3,344,569 | –362,371           |
| 2035        | 2,269,344 | 2,051,913 | 51,555   | 257,775   | 257,775 | 0   | –526,761 | –3,871,330 | –339,555           |
| 2036        | 2,314,731 | 2,092,951 | 38,666   | 257,775   | 257,775 | 0   | –518,221 | –4,389,551 | –318,143           |
| 2037        | 2,361,026 | 2,134,810 | 25,777   | 257,775   | 257,775 | 0   | –509,768 | –4,899,318 | –298,051           |
| 2038        | 2,408,246 | 2,177,507 | 12,889   | 257,775   | 257,775 | 0   | –501,403 | –5,400,722 | –279,200           |
| <b>NPV</b>  |           |           |          |           |         |     |          |            | <b>–3,807,041</b>  |
| <b>LCOP</b> |           |           |          |           |         |     |          |            | <b>357.6 EUR/t</b> |

**Table 9.17** Financed cash flow – calcium-looping route

| Year        | OPEX      | Revenue | Interest | Principal | Deprec. | Tax | Net cash   | Cumulative  | PV                 |
|-------------|-----------|---------|----------|-----------|---------|-----|------------|-------------|--------------------|
| 2026        | –         | –       | –        | –         | –       | –   | 0          | 0           | 0                  |
| 2027        | –         | –       | –        | –         | –       | –   | 0          | 0           | 0                  |
| 2028        | –         | –       | –        | –         | –       | –   | 0          | 0           | 0                  |
| 2029        | 2,558,596 | 808,549 | 104,646  | 209,293   | 209,293 | 0   | –2,063,986 | –2,063,986  | –1,782,949         |
| 2030        | 2,609,768 | 824,720 | 94,182   | 209,293   | 209,293 | 0   | –2,088,522 | –4,152,509  | –1,718,233         |
| 2031        | 2,661,964 | 841,215 | 83,717   | 209,293   | 209,293 | 0   | –2,113,759 | –6,266,267  | –1,656,185         |
| 2032        | 2,715,203 | 858,039 | 73,252   | 209,293   | 209,293 | 0   | –2,139,709 | –8,405,976  | –1,596,684         |
| 2033        | 2,769,507 | 875,200 | 62,788   | 209,293   | 209,293 | 0   | –2,166,388 | –10,572,364 | –1,539,611         |
| 2034        | 2,824,897 | 892,704 | 52,323   | 209,293   | 209,293 | 0   | –2,193,809 | –12,766,173 | –1,484,856         |
| 2035        | 2,881,395 | 910,558 | 41,859   | 209,293   | 209,293 | 0   | –2,221,988 | –14,988,162 | –1,432,314         |
| 2036        | 2,939,023 | 928,769 | 31,394   | 209,293   | 209,293 | 0   | –2,250,941 | –17,239,102 | –1,381,882         |
| 2037        | 2,997,803 | 947,345 | 20,929   | 209,293   | 209,293 | 0   | –2,280,681 | –19,519,783 | –1,333,467         |
| 2038        | 3,057,759 | 966,291 | 10,465   | 209,293   | 209,293 | 0   | –2,311,225 | –21,831,008 | –1,286,977         |
| <b>NPV</b>  |           |         |          |           |         |     |            |             | <b>–15,213,158</b> |
| <b>LCOP</b> |           |         |          |           |         |     |            |             | <b>397.9 EUR/t</b> |

**Table 9.18** Sensitivity of LCOP to electricity price – worked values

$LCOP_{(p)} = LCOP_{base} + (p - 0.14) \times E_s$  where  $E_s = 1,236.8$  kWh/t (cryogenic) and 1,882.4 kWh/t (calcium looping)

| Case               | Cryogenic $\Delta$ LCOP                  | LCOP         | Calcium-looping $\Delta$ LCOP            | LCOP         |
|--------------------|------------------------------------------|--------------|------------------------------------------|--------------|
| 50 EUR/MWh         | $(0.05 - 0.14) \times 1,236.8 = -111.31$ | <b>239.8</b> | $(0.05 - 0.14) \times 1,882.4 = -169.42$ | <b>223.7</b> |
| 90 EUR/MWh         | $(0.09 - 0.14) \times 1,236.8 = -61.84$  | <b>289.3</b> | $(0.09 - 0.14) \times 1,882.4 = -94.12$  | <b>299.0</b> |
| 140 EUR/MWh (base) | —                                        | <b>351.1</b> | —                                        | <b>393.1</b> |
| 180 EUR/MWh        | $(0.18 - 0.14) \times 1,236.8 = +49.47$  | <b>400.6</b> | $(0.18 - 0.14) \times 1,882.4 = +75.30$  | <b>468.4</b> |

\* Break-even electricity price (cryogenic, LCOP = 260):  $0.14 + (260 - 351.15) \div 1,236.8 = 0.0663$  EUR/kWh = **66 EUR/MWh**

**Table 9.19** Sensitivity of LCOP to aggregate operating cost - worked values

$*LCOP_{(f)} = LCOP_{base} + f \times (gross\ OPEX \div \dot{m})$ , specific OPEX = 339.87 EUR/t (cryogenic), 394.19 EUR/t (calcium looping)

| f    | Cryogenic $\Delta$ LCOP         | LCOP         | Calcium-looping $\Delta$ LCOP   | LCOP         |
|------|---------------------------------|--------------|---------------------------------|--------------|
| -30% | $-0.30 \times 339.87 = -101.96$ | <b>249.2</b> | $-0.30 \times 394.19 = -118.26$ | <b>274.8</b> |
| -20% | $-0.20 \times 339.87 = -67.97$  | <b>283.2</b> | $-0.20 \times 394.19 = -78.84$  | <b>314.2</b> |
| -10% | $-0.10 \times 339.87 = -33.99$  | <b>317.2</b> | $-0.10 \times 394.19 = -39.42$  | <b>353.7</b> |
| Base | -                               | <b>351.1</b> | -                               | <b>393.1</b> |
| +10% | $+0.10 \times 339.87 = +33.99$  | <b>385.1</b> | $+0.10 \times 394.19 = +39.42$  | <b>432.5</b> |
| +20% | $+0.20 \times 339.87 = +67.97$  | <b>419.1</b> | $+0.20 \times 394.19 = +78.84$  | <b>471.9</b> |
| +30% | $+0.30 \times 339.87 = +101.96$ | <b>453.1</b> | $+0.30 \times 394.19 = +118.26$ | <b>511.3</b> |

\* Reduction required to reach the product price:  $(351.15 - 260) \div 339.87 = 26.8\%$  (cryogenic);  $(393.07 - 80) \div 394.19 = 79.4\%$  (calcium looping)

**Table 9.20** Sensitivity of LCOP to the capital estimate (AACE Class 4, -30 % / +50 %)

Capital contribution =  $TIC \times (\phi/\psi) \div \dot{m} = 58.58$  EUR/t (cryogenic), 43.45 EUR/t (calcium looping)

| Case | Cryogenic $\Delta$ LCOP       | LCOP         | Calcium-looping $\Delta$ LCOP | LCOP         |
|------|-------------------------------|--------------|-------------------------------|--------------|
| -30% | $-0.30 \times 58.58 = -17.58$ | <b>333.6</b> | $-0.30 \times 43.45 = -13.03$ | <b>380.0</b> |
| Base | —                             | <b>351.1</b> | —                             | <b>393.1</b> |
| +50% | $+0.50 \times 58.58 = +29.29$ | <b>380.4</b> | $+0.50 \times 43.45 = +21.72$ | <b>414.8</b> |

**Table 9.21** Effect of a 20-year life at 8 % on the annualised capital charge

| Term                         | Substitution                           | Value                       |
|------------------------------|----------------------------------------|-----------------------------|
| AF (20 yr, 8 %)              | $[1 - 1.08^{-20}] \div 0.08$           | 9.81815                     |
| $\phi$ (8 %)                 | $0.2 + 0.4/1.08 + 0.4/1.08^2$          | 0.913306                    |
| $\psi$ (8 %)                 | $9.81815 \div 1.08^2$                  | 8.41748                     |
| $\phi/\psi$                  | $0.913306 \div 8.41748$                | <b>0.108501</b>             |
| K, cryogenic                 | $2,577,749 \times 0.108501 + 5,929.15$ | 47.17 EUR/t (base 58.58)    |
| K, calcium looping           | $2,092,928 \times 0.108501 + 6,490.72$ | 34.99 EUR/t (base 43.45)    |
| <b>LCOP, cryogenic</b>       | $351.15 - (58.58 - 47.17)$             | <b>339.7 EUR/t (-11.41)</b> |
| <b>LCOP, calcium looping</b> | $393.07 - (43.45 - 34.99)$             | <b>384.6 EUR/t (-8.46)</b>  |

**Table 9.22** LCOP sensitivity to the EU ETS carbon price

The ETS is charged on the uncaptured slip only: 311.9 t/yr (cryogenic), 152.4 t/yr (calcium looping).

$\Delta\text{LCOP} = (p - 95) \times \text{slip} \div m = (p - 95) \times 0.05260$  (cryogenic);  $(p - 95) \times 0.02348$  (calcium looping)

| Case            | Cryogenic $\Delta\text{LCOP}$ | LCOP         | Calcium-looping $\Delta\text{LCOP}$ | LCOP         |
|-----------------|-------------------------------|--------------|-------------------------------------|--------------|
| 60 EUR/t        | $-35 \times 0.05260 = -1.84$  | <b>349.3</b> | $-35 \times 0.02348 = -0.82$        | <b>392.3</b> |
| 95 EUR/t (base) | —                             | <b>351.1</b> | —                                   | <b>393.1</b> |
| 120 EUR/t       | $+25 \times 0.05260 = +1.32$  | <b>352.5</b> | $+25 \times 0.02348 = +0.59$        | <b>393.7</b> |

**Table 9.23** Comparison of LCOP sensitivity to the selected economic parameters

| Driver (range)                             | Cryogenic $\Delta\text{LCOP}$ (EUR/t) | Calcium-looping $\Delta\text{LCOP}$ (EUR/t) |
|--------------------------------------------|---------------------------------------|---------------------------------------------|
| Electricity price (50–180 EUR/MWh)         | -111.3 / +49.5                        | -169.4 / +75.3                              |
| Aggregate operating cost ( $\pm 20$ %)     | -68.0 / +68.0                         | -78.8 / +78.8                               |
| Capital estimate ( $-30$ % / $+50$ %)      | -17.6 / +29.3                         | -13.0 / +21.7                               |
| Plant life and discount rate (20 yr @ 8 %) | -11.4 / 0.0                           | -8.5 / 0.0                                  |
| EU ETS carbon price (60–120 EUR/t)         | -1.8 / +1.3                           | -0.8 / +0.6                                 |

**Table 9.24** Scale-up analysis – cryogenic route (product 260 EUR/t)

| Metric                          | 1,000 Nm <sup>3</sup> /h | 68,500 Nm <sup>3</sup> /h | 274,000 Nm <sup>3</sup> /h |
|---------------------------------|--------------------------|---------------------------|----------------------------|
| CO <sub>2</sub> captured (t/yr) | 5,929                    | 406,147                   | 1,624,588                  |
| Total investment, TIC (M EUR)   | 2.58                     | 40.22                     | 99.03                      |
| Annual OPEX (M EUR)             | 2.0                      | 103.99                    | 410.50                     |
| LCOC (EUR/t)                    | 348.9                    | 221.6                     | 213.3                      |
| Margin vs 260 EUR/t             | -88.9                    | 38.4                      | 46.7                       |
| Annual profit (M EUR/yr)        | -0.53                    | 15.6                      | 75.9                       |
| <b>Viable?</b>                  | <b>NO - loss</b>         | <b>YES - profit</b>       | <b>YES - profit</b>        |

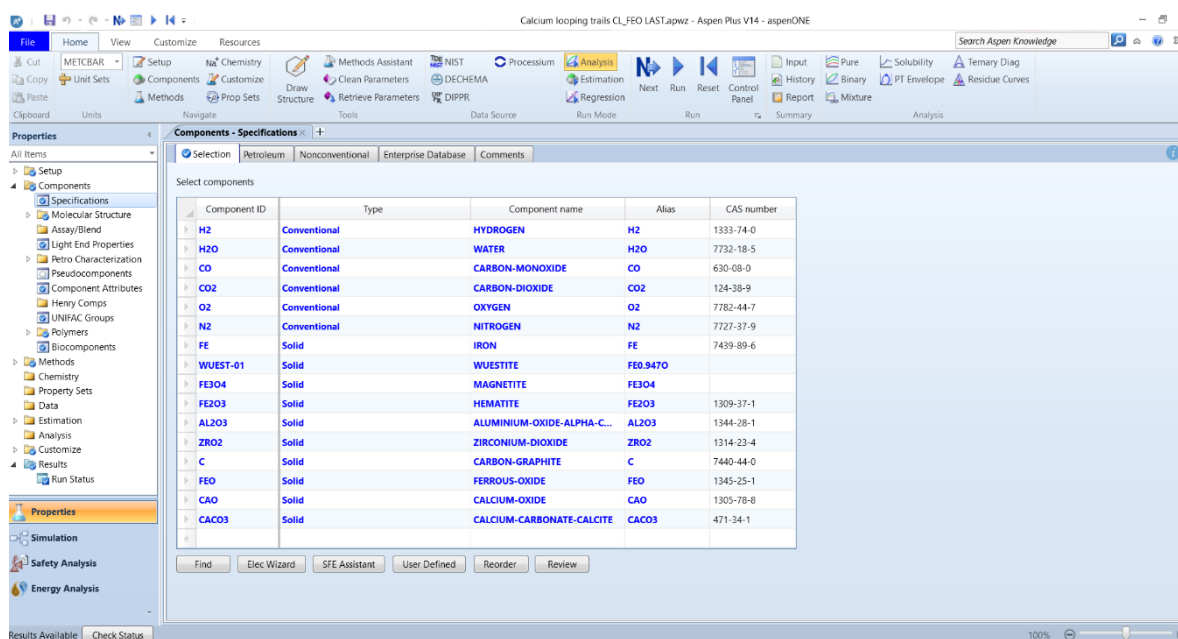
**Table 9.25** Scale-up analysis – calcium-looping route (product 80 EUR/t)

| Metric                          | 1,000 Nm <sup>3</sup> /h | 68,500 Nm <sup>3</sup> /h | 274,000 Nm <sup>3</sup> /h |
|---------------------------------|--------------------------|---------------------------|----------------------------|
| CO <sub>2</sub> captured (t/yr) | 6,491                    | 444,614                   | 1,778,457                  |
| Total investment, TIC (M EUR)   | 2.09                     | 32.66                     | 80.41                      |
| Annual OPEX (M EUR)             | 2.56                     | 142.78                    | 566.38                     |
| LCOC (EUR/t)                    | 391.4                    | 286.1                     | 279.8                      |
| Margin vs 80 EUR/t              | -311.4                   | -206.1                    | -199.8                     |
| Annual profit (M EUR/yr)        | -2.02                    | -91.6                     | -355.3                     |
| <b>Viable?</b>                  | <b>NO - loss</b>         | <b>NO - loss</b>          | <b>NO - loss</b>           |

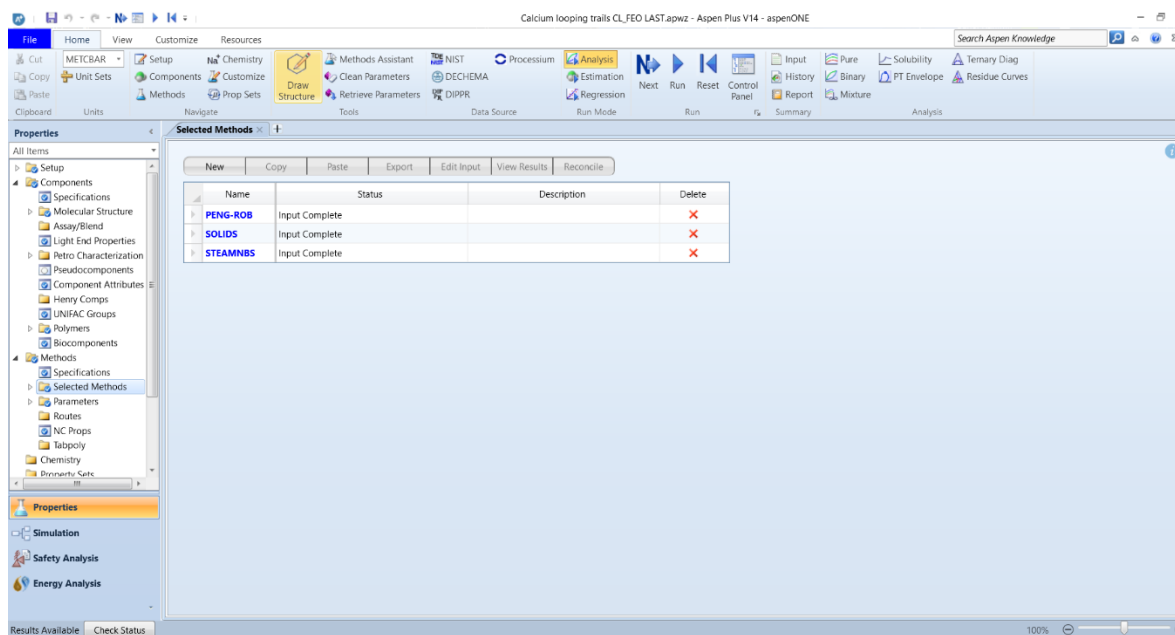
**Table 9.26** Internal consistency checks on the cost tables

| Check                           | Result                                                                           |
|---------------------------------|----------------------------------------------------------------------------------|
| Cryogenic OPEX column sum       | 2,015,113 = gross OPEX 2,015,113 ✓                                               |
| Calcium-looping OPEX column sum | 2,558,596 = gross OPEX 2,558,596 ✓                                               |
| Cryogenic revenue sum           | 1,541,580 + 280,460 = 1,822,040 ✓                                                |
| Cryogenic electricity sum       | 909.9 kW over eight items ✓                                                      |
| Calcium-looping electricity sum | 1,516.05 kW over five items ✓                                                    |
| Cryogenic fixed-cost sum        | 542,996 ✓                                                                        |
| Front-end symmetry              | R-101/102 charged at 377.9 kW in both routes ✓                                   |
| LCOP – LCOC (cryogenic)         | $(0.1347495 - 0.1295046) \times 2,577,749 \div 5,929.15 = +2.28 \text{ EUR/t}$ ✓ |
| Capital charge rate             | $\phi/\psi = 0.943764 \div 7.003841 = 0.1347495$ ✓                               |

Figures are reported to the precision carried in the workbook; column sums close exactly.



**Figure 9.1** List of chemical components used in the Aspen Plus simulation



**Figure 9.2** Thermodynamic Property Method Selected in Aspen Plus

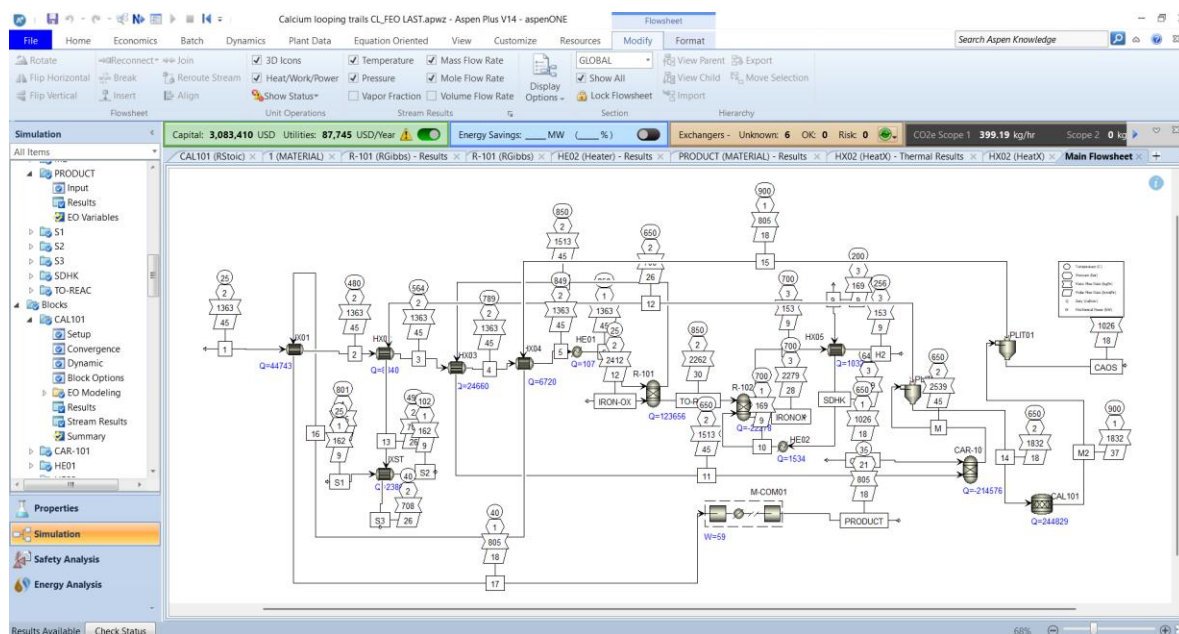


Figure 9.3 Aspen Plus process flow diagram of the calcium looping CO<sub>2</sub> capture process with the FeO oxygen carrier

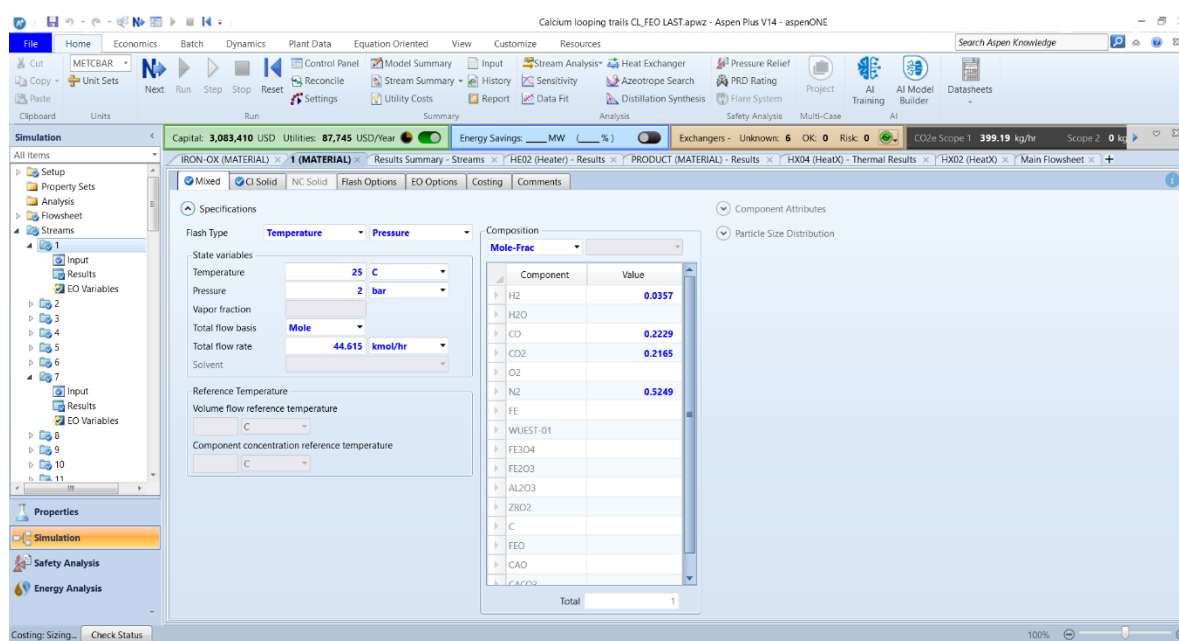


Figure 9.4 Feed stream composition specified in Aspen Plus for the calcium looping simulation

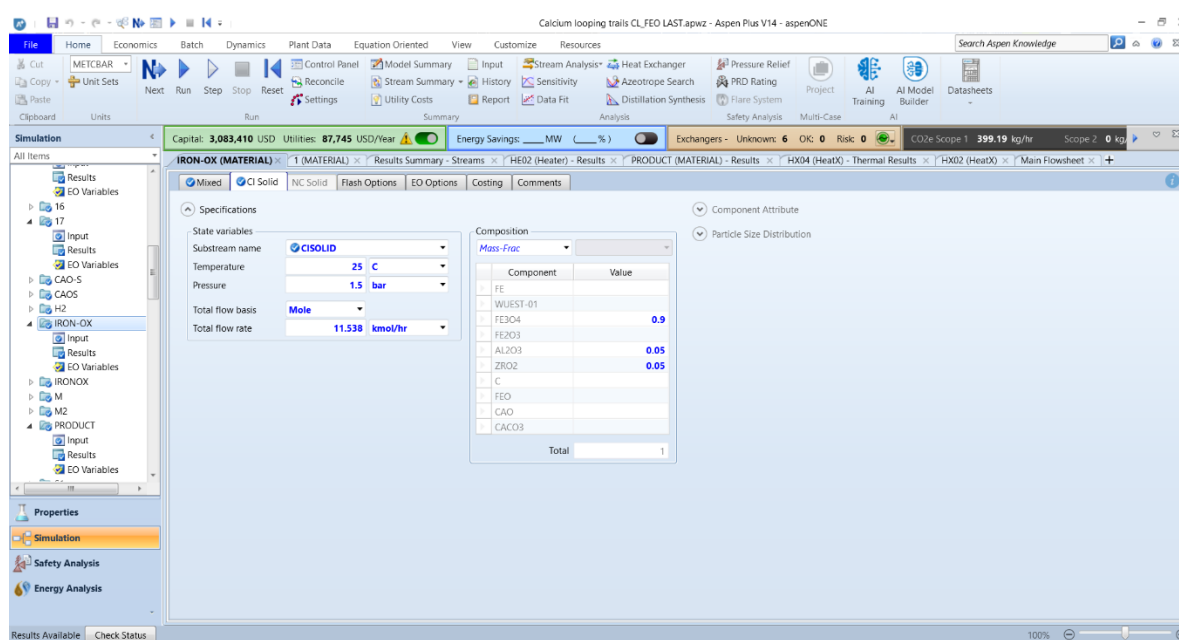


Figure 9.5 Composition of the iron-based oxygen carrier specified in Aspen Plus

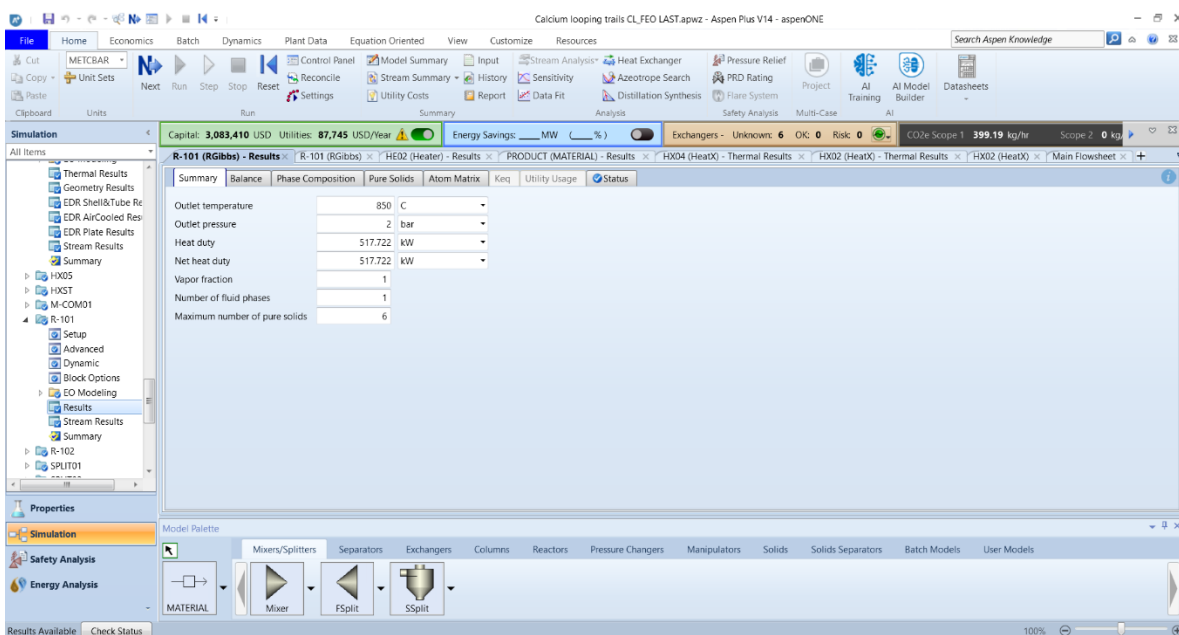


Figure 9.6 Operating specifications of reactor R-101 in the Aspen Plus calcium looping model

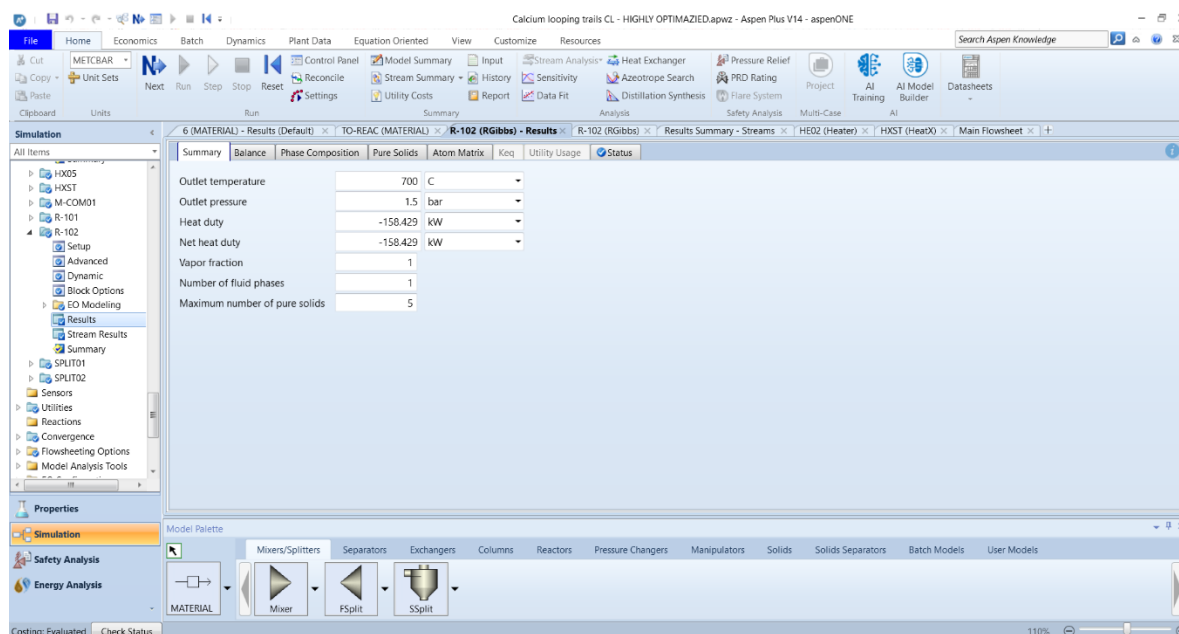


Figure 9.7 Operating specifications of reactor R-102 in the Aspen Plus model using wüstite

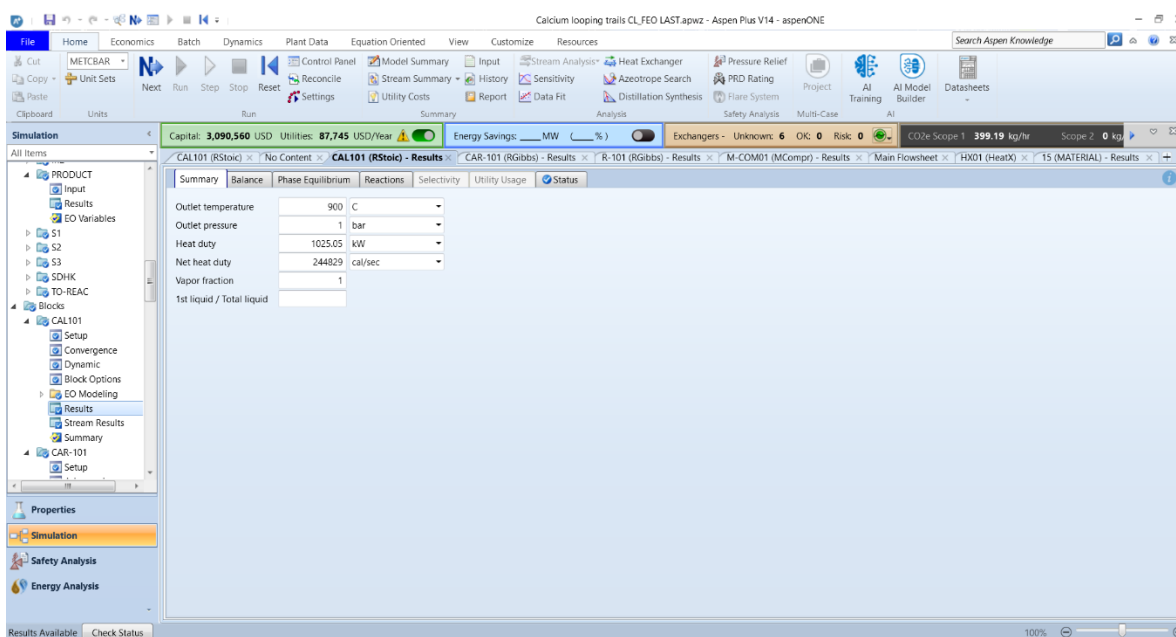
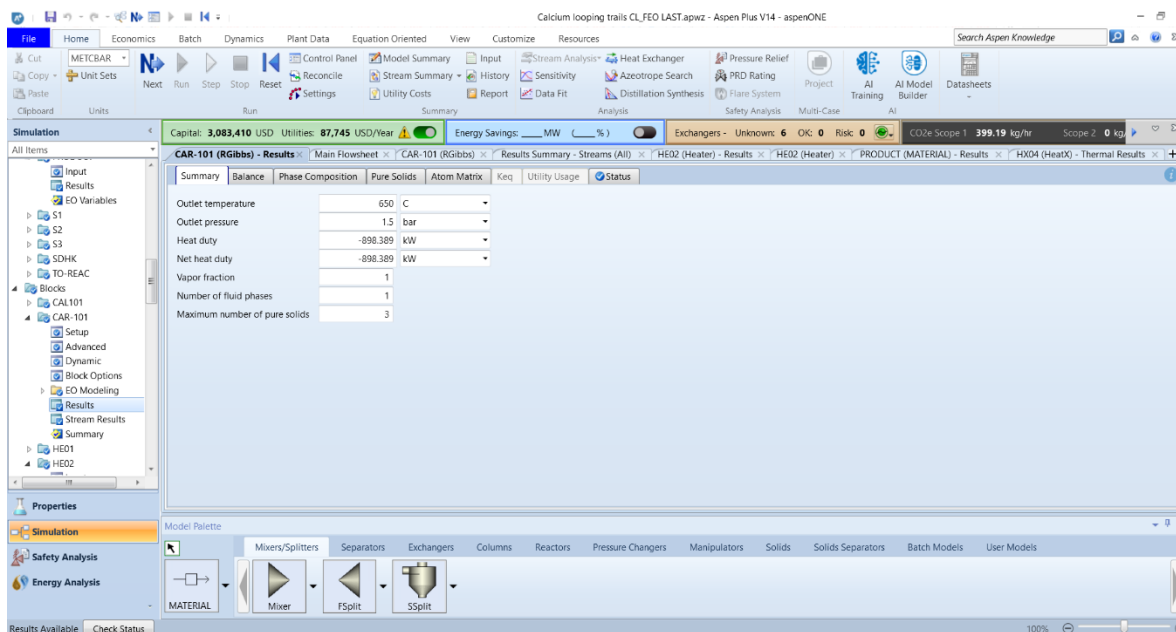
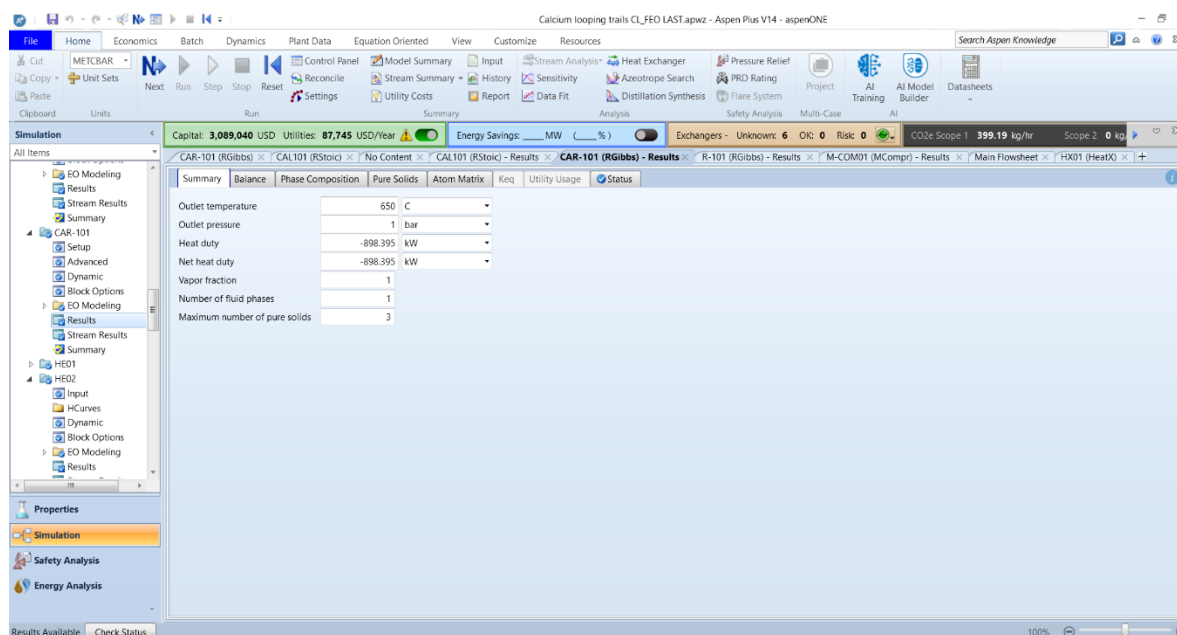


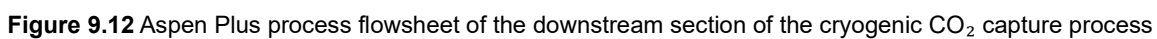
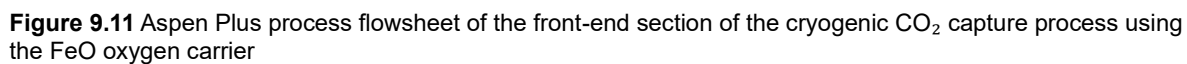
Figure 9.8 Operating specifications of the calciner R-104 reactor in the Aspen Plus calcium looping model

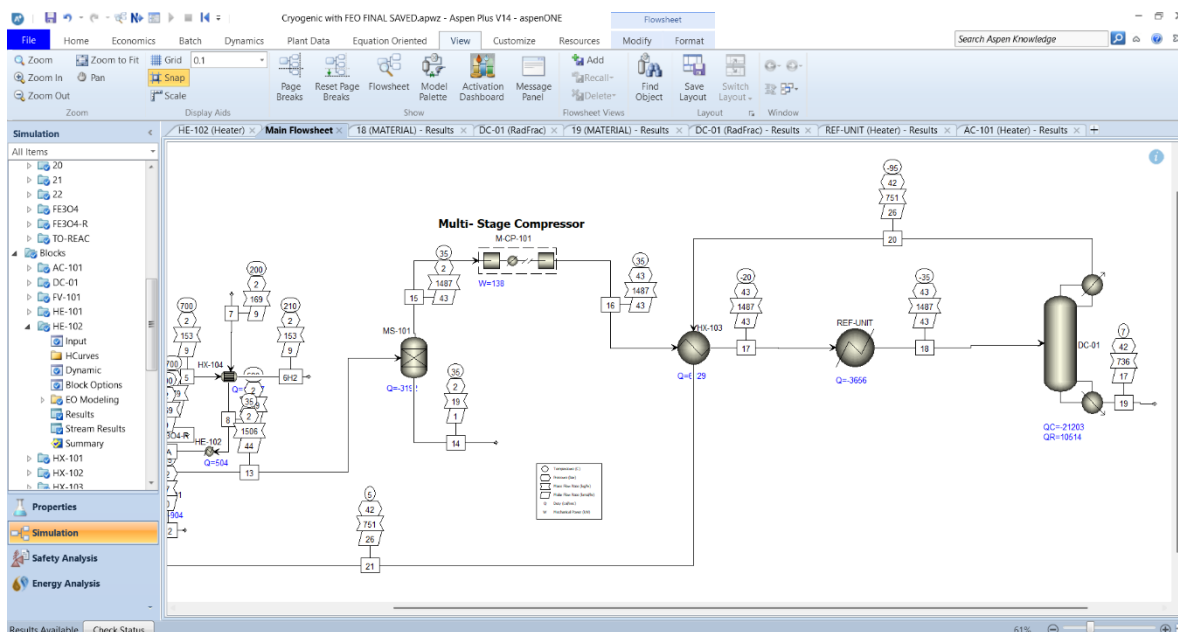


**Figure 9.9** Operating specifications of the carbonator (R-103) in the Aspen Plus calcium looping model at 1.5 bar, the pressure adopted in the reported case. The carbonator duty is -898.389 kW, against -898.395 kW at atmospheric pressure, confirming that the carbonation equilibrium is insensitive to this difference.

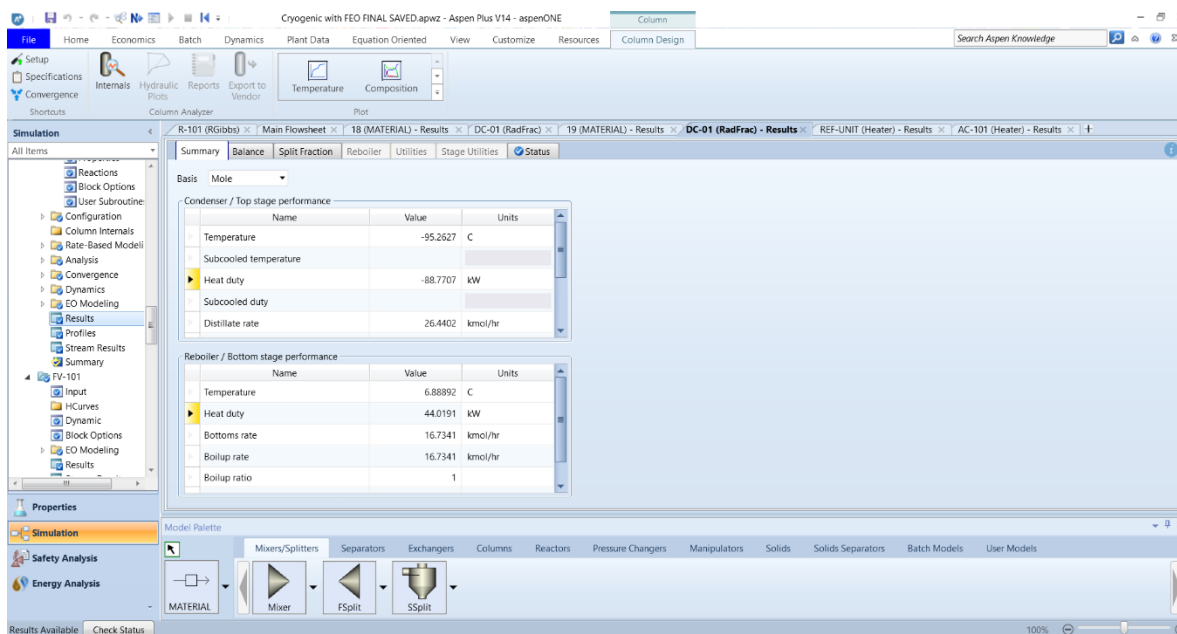


**Figure 9.10** Operating specifications of the carbonator (R-103) in the Aspen Plus calcium looping model at atmospheric pressure





**Figure 9.13** Aspen Plus simulation results for the cryogenic CO<sub>2</sub> capture process, showing stream properties and equipment duties



**Figure 9.14** Condenser and reboiler performance results for the RadFrac distillation column (DC-01) in Aspen Plus

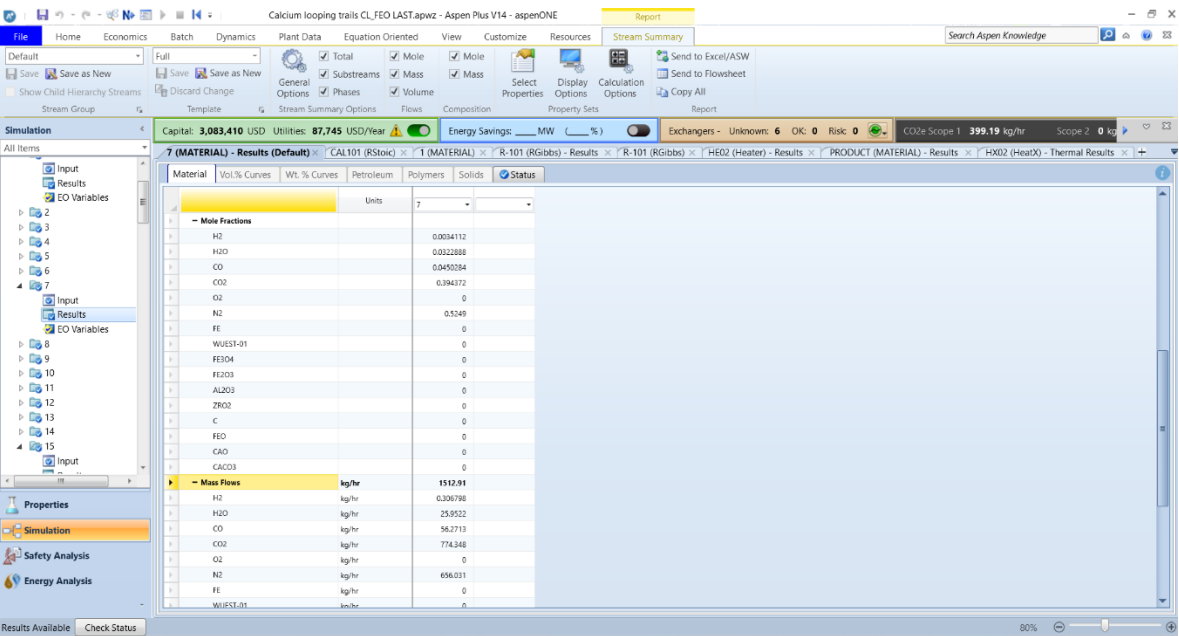


Figure 9.15 Stream summary results for the feed stream in the Aspen Plus calcium looping model

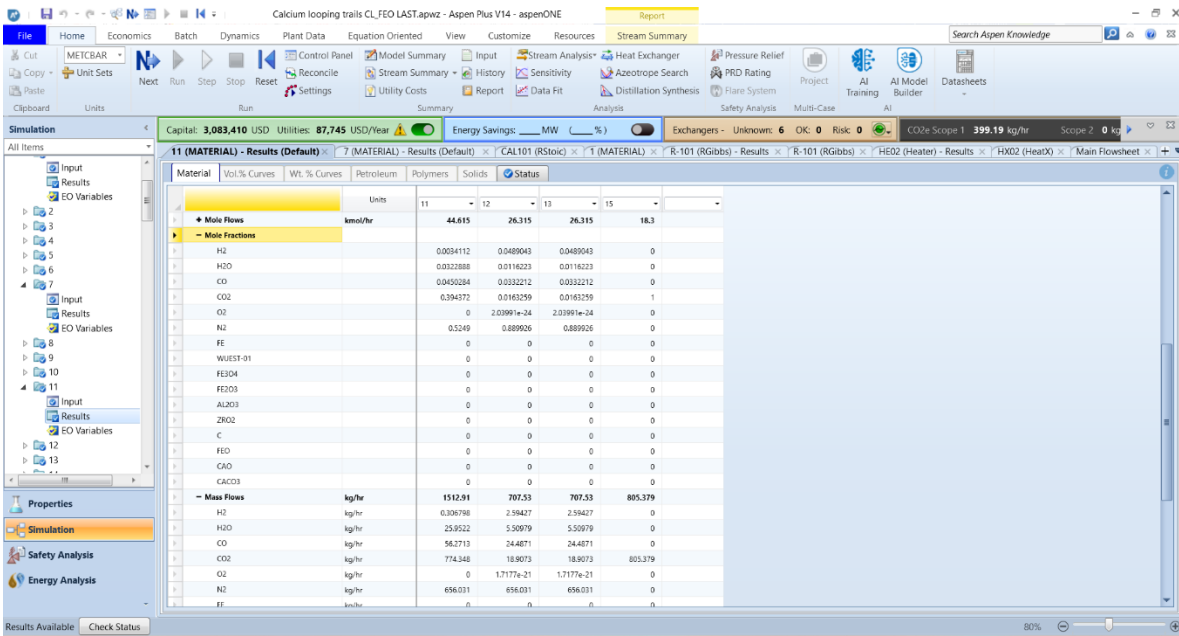


Figure 9.16 Aspen Plus stream summary for selected process streams in the calcium looping model

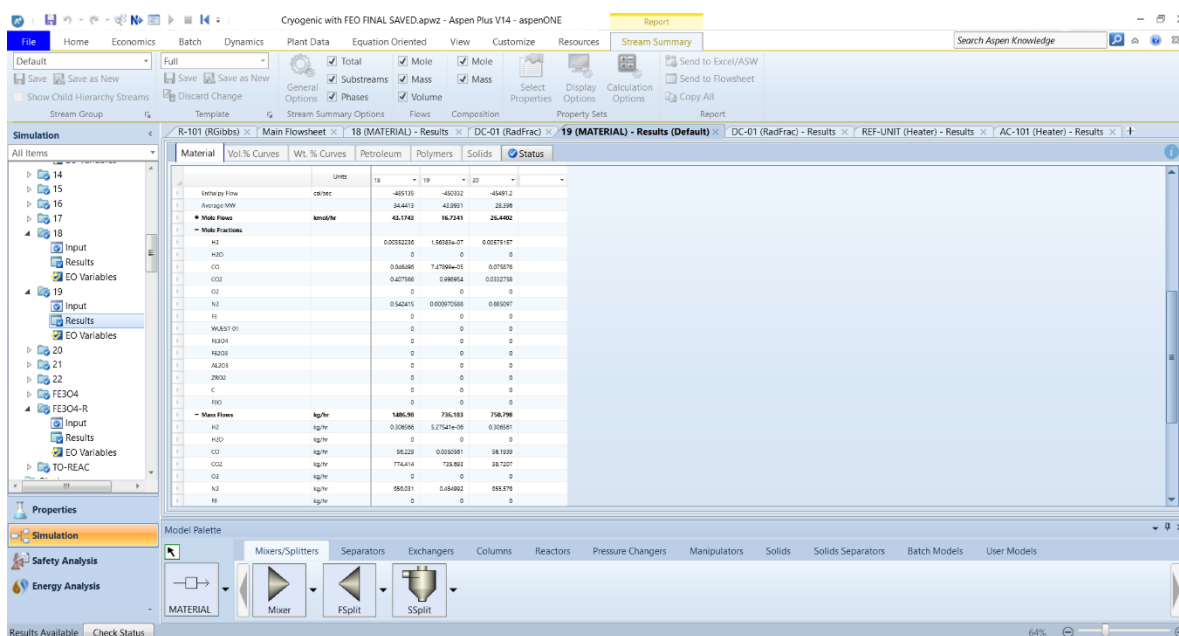


Figure 9.17 Aspen Plus stream summary for selected process streams in the cryogenic CO<sub>2</sub> capture model

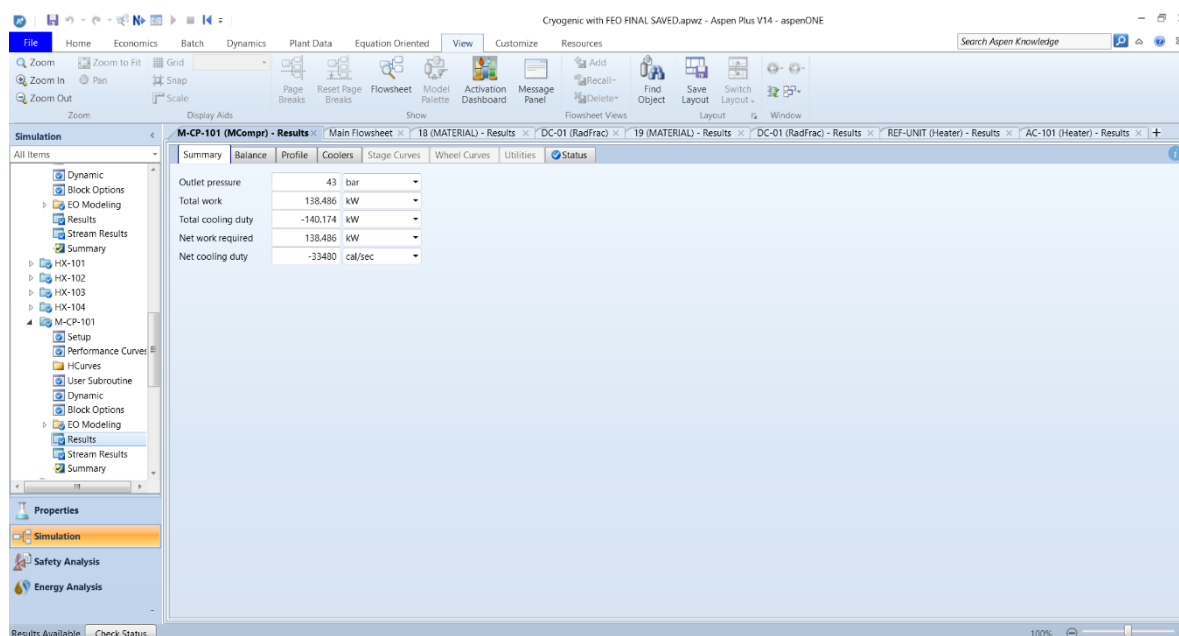


Figure 9.18 Performance summary of the multi-stage compressor (M-CP-101) in the Aspen Plus cryogenic CO<sub>2</sub> capture model