Process Integration of Lithium Based High Temperature CO$_2$ Capture in Power and Industrial Plants

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School of Engineering and Physical Sciences
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ABSTRACT

Lithium orthosilicate (Li$_4$SiO$_4$) sorbents have been reported to show relatively high CO$_2$ capture capacity, high stability and require lower regeneration temperatures than other high-temperature sorbents. Based on these properties, a CO$_2$ capture plant concept could be envisaged, aiming for achieving as low as possible CO$_2$ capture penalties. Accordingly, this work presents a conceptual process integration study and techno-economic assessment that evaluates the integration of Li$_4$SiO$_4$-based looping systems into a Natural Gas Combined Cycle (NGCC) power plant and Sorption Enhanced Steam Methane Reforming (SESMR) H$_2$ Production plant for CO$_2$ capture. Based on previously obtained experiment results, absorption and regeneration temperatures of 525-550 and 700 °C, respectively, and a sorbent fractional conversion of 0.2, were used to build NGCC and SESMR plants process models. The process integration results showed that implementation of a Li$_4$SiO$_4$-based high temperature carbon capture (HTCC) system into a NGCC power plant reduces the plant efficiency by 9.2% penalty points. The techno-economic assessment resulted in a levelized cost of electricity (LCOE) and a cost of CO$_2$ avoided equal to 73.9£/MWh and 75.6 £/tCO$_2$, respectively. For the SESMR plant, an equivalent net hydrogen production efficiency penalty of 8.2% was obtained after the integration of the Li-based carbon capture plant. A levelized cost of hydrogen (LCOH) and cost of CO$_2$ avoided equal to 159.3 £/kNm$^3$ and 72.7 £/tCO$_2$, respectively, were obtained using the same techno-economic assessment method applied in the NGCC case study. For both case studies, the Li$_4$SiO$_4$-based HTCC integration performance is compared to other capture technologies, including amine-based solvents and Calcium looping (CaL) systems, for benchmarking purpose. A parametric sensitivity analysis was conducted for each case study by varying several techno-economic parameters and by evaluating the impact of the variation on the plant Key Performance Indicators (KPIs). Finally, recommendations and guidelines for possible future work are suggested.
DEDICATION

This Thesis is dedicated
to
my father & my mother

with love and eternal appreciation,

to

my lovely wife,

my brother and sisters

for their huge support and encouragement.

I will always appreciate all what they have done.
ACKNOWLEDGEMENT

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Dr. Susana Garcia and Prof. M. Mercedes Maroto-Valer

And to

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<td>ASU</td>
<td>Air separation unit</td>
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<td>BEIS</td>
<td>UK Department for Business, Energy and Industrial Strategy</td>
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</tr>
<tr>
<td>Ppmv</td>
<td>Part per million vapour</td>
</tr>
<tr>
<td>PSA</td>
<td>Pressure swing adsorption</td>
</tr>
<tr>
<td>S/C</td>
<td>Steam to carbon ratio</td>
</tr>
<tr>
<td>SE</td>
<td>Specific CO₂ emissions</td>
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<tr>
<td>Acronym</td>
<td>Definition</td>
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<tr>
<td>SESMR</td>
<td>Sorption Enhanced Steam Methane Reforming</td>
</tr>
<tr>
<td>SI</td>
<td>Specific Investment</td>
</tr>
<tr>
<td>SMR</td>
<td>Steam methane reforming</td>
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<tr>
<td>SPECCA</td>
<td>Specific primary energy consumption for CO₂ avoided</td>
</tr>
<tr>
<td>Syngas</td>
<td>Synthesis gas</td>
</tr>
<tr>
<td>TDA</td>
<td>Top down approach</td>
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<tr>
<td>TGA</td>
<td>Thermogravimetric analyser</td>
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<tr>
<td>TPD</td>
<td>Temperature programmed Desorption</td>
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<tr>
<td>TSA</td>
<td>Temperature swing adsorption</td>
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<tr>
<td>USD</td>
<td>United States Dollars</td>
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<td>WGR</td>
<td>Water gas shift reactor</td>
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<td>WGS</td>
<td>Water gas shift</td>
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<tr>
<td>CCRₚₑₜ</td>
<td>Equivalent carbon capture ratio</td>
</tr>
<tr>
<td>SCEₚₑₜ</td>
<td>Equivalent specific CO₂ emissions</td>
</tr>
<tr>
<td>SPECCAₚₑₜ</td>
<td>Equivalent Specific Primary Energy Consumption for CO₂ avoided</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
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LIST OF PUBLICATIONS

Journal Publications


Journal Publications in preparation


Conference Presentations

The Trondheim Conference on Carbon Capture, Transport and Storage (TCCS-9), Norway, 2017 (Oral Presentation)

Institute of Mechanical, Process and Energy Engineering (IMPEE) conference, Edinburgh, UK- 2017 (Oral Presentation)

UK Chemeng Day conference, Heriot-Watt University, Edinburgh, UK 2019 (Oral Presentation)
1.1 Background Literature

Limiting global warming to 1.5°C is considered as one of the greatest worldwide challenges nowadays. To achieve such target, several pathways are proposed and developed to reduce greenhouse gases (GHGs) by controlling the increase of the atmospheric levels of Carbon dioxide (CO$_2$), as CO$_2$ is considered the main dominant factor of long-lived climate forcers (LLCFs) [1]. Carbon capture and storage (CCS) was found to be one of the promising solutions to achieve the global warming mitigation pathway [2-4]. Although renewables have been proposed as an alternative solution for clean energy, the problem of energy storage is highly affecting their reliability [5]. In CCS, the CO$_2$ is captured from large flue gas sources, such as power plants, refineries and industrial plants, and followed by CO$_2$ transportation to storage locations. There are various technological methods for CO$_2$ capture. The most extensively investigated ones are liquid solvents (especially amine-based), solid sorbents and membranes [6]. Although amine-based technology is considered the closest to market, it suffers from a large energy penalty when integrated in power and industrial plants due to low working temperature and high regeneration energy [7, 8].

Sorbent adsorption has emerged in recent years as a viable and attractive technology option to capture CO$_2$ from gaseous streams [9]. One of the key advantages of the solid absorption technology is that alkali-based solid sorbents can capture CO$_2$ at elevated temperature, higher than 400°C, in contrast with other capture options like amine solvent based absorption or membrane separation, avoiding therefore the energy penalty associated to cooling or quenching combustion gases while recovering the heat from the flue gas and convert it to power [10]. This is attractive to both the power and industry sectors, where, depending on technology, combustion gases can have temperatures that exceed 500°C. Moreover, due to the thermal resistance of solid sorbents, they can be used for direct CO$_2$ capture from reforming or gasification processes with potential enhancement of the process yield due to a shift in equilibrium conditions towards the production of products [11, 12].
Among the high temperature solid sorbents materials, lithium orthosilicate (Li$_4$SiO$_4$) showed a relatively good performance under high temperature flue gas conditions [13]. Li$_4$SiO$_4$ could achieve a maximum theoretical capacity of 36.7% and lower regeneration temperatures, regeneration energy requirements and higher cyclic stability compared to most commonly considered high temperature solid sorbents such as CaO. That makes this group of solids a promising absorbent material [14].

1.2 Knowledge gaps

There are numerous literature studies investigating the reactivity and stability of lithium based sorbents [13, 15-23] for CO$_2$ capture applications. Although some experimental studies are based on powder-like solids, which are not suited for practical application in continuous fluidized bed systems, there is a growing body of evidence that reflects that Li-based sorbents can be prepared as fluidizable solids and in the form of pellets, while maintaining the advantages of cyclic and thermal stability [17, 24]. This suggests that this group of solids can be applied and integrated using the same technology as the calcium looping [24]. Nevertheless, the studies of Li-based sorbents integration into power and industrial plants are far more limited than those for CaO based sorbents, which limits the comparison with other alkali based and metal oxide sorbents. For the purpose of guiding material development, there is a need for analysing the potential benefits of lower regeneration temperature and energy requirements with respect to energy penalty, and identifying the application that could benefit the most from the development of a capture technology based on Li-sorbents. That can be achieved by investigating the process integration of Li-based sorbents in power and industrial plants for CO$_2$ capture.

1.3 Research Aim and Objectives

The aim of this research is to investigate the process integration of high temperature Li$_4$SiO$_4$ based sorbents for CO$_2$ capture from power and industrial plants. A natural gas combined cycle (NGCC) plant, and a H$_2$ steam methane reforming (SMR) plant, as two power and industrial case studies, have been selected for this work.

The specific research objectives are the ones below:

1. Evaluate Li$_4$SiO$_4$ sorbents CO$_2$ capture performance under the relevant flue gas conditions for each case study.
2. Assess the potential impact of integrating a Li₄SiO₄ / lithium carbonate (Li₂CO₃) looping system on the performance of a NGCC power plant, and a H₂ SMR plant.

3. Optimize the integration of a Li₄SiO₄ / Li₂CO₃ looping system in each case study by using relevant experimental sorbent performance data and by comparing the process performance with existing solvent and CaO based capture technologies.

4. Perform a techno-economic evaluation for each case study and investigate the impact of different process parameters on identified Key Performance Indicators (KPIs).

5. Benchmark the obtained results from the integration of Li₄SiO₄ based capture looping systems for each case study versus conventional solvent-based and CaO-based capture technologies integrated in the same reference plants.

1.4 Thesis structure

In order to present how the aim and objectives of this work were achieved, this thesis has been structured as follows:

First, chapter 2 covers the related literature review for CO₂ capture technologies in general, and in particular, the application of high temperature solid sorbents for CO₂ capture from power and industrial applications. Chapter 3 then describes the methodology that was followed to achieve the research objectives described in Section 1.3, including the details tasks performed to achieve each objective. Next, Chapters 4 and 5 show the results and analysis of the process and techno-economic assessment for the integration of a Li₄SiO₄ / Li₂CO₃ looping system in the first case study, a NGCC power plant. The process modelling and techno-economic results and analysis of the integration of a Li₄SiO₄ / Li₂CO₃ looping system in the second case study, a H₂ SMR plant, is then presented in Chapters 6 and 7. Finally, Chapter 8 concludes the analysis and discussions in previous chapters and provides recommendations for future work.
Chapter 2 LITERATURE REVIEW

2.1 Introduction

There has been a continuous global increase in energy consumption levels in recent decades and, as reported by the International Energy Agency’s World Energy Outlook 2019, there will be a rise in energy demand by 1.3% each year to 2040 [25]. Up to date, the conventional fossil fuels resources have been considered as one of the most reliable sources of energy. However, the continuous dependence on conventional fossil fuel resources have resulted in a notable growth in atmospheric levels of greenhouse gases (GHG) such as carbon dioxide (CO₂) and other harmful gases which are considered the main reason for the observed worldwide climate change. Consequently, an increase in global temperature has been observed which in turn resulted in many undesirable natural changes such as ice melting and rising of sea levels. In the period between 1880 and 2012, the average surface temperature of the earth, based on combining land and ocean temperatures, was raised by 0.85°C, as depicted in figure 2.1 [26-28].

Figure 2.1: Relationship between global mean surface temperature increase and aggregate global CO₂ emissions [28]

2.2 UK efforts to Mitigate GHG emissions by 2050

To cope with the international and European requirements for GHG reduction, the UK government has set a new target for UK’s GHG reduction, which is net zero emissions for long-lived gases like CO₂, to reach by 2050 [29]. On the other hand, Scotland has set more stringent target which aims to reach net zero emissions target by 2045 [30], while
Wales set a target of 95% emissions reduction by 2050. For Northern Ireland, they are included in UK Long-term targets [31]. Since the fossil fuels are considered the main sources for GHG, reducing the consumption of fossil fuels for electricity and energy generation was considered an important action to abate GHG emissions. Figure 2.2 shows the UK projection for the primary energy demand by fuel up to 2035 [32].

As shown in figure 2.2, a decline in solid fuel consumption is expected after 2016 and only 4 Mtoe of primary energy demand is projected to be met by coal by 2035. As a summary for the UK’s primary energy projection, it was reported that the UK’s primary energy demand is expected to fall by a total of 6% after 10 years, and it will rise again to 2% above current levels by the end of 2035 [32, 33]. UK government has set several scenarios to cope with the projected energy demand while achieving the UK’s GHG 2050 net zero emissions targeting different intermediate and final emission limits based on

\[ \text{Mtoe: Million tonnes of Oil Equivalent} \]
availability of energy sources, viability of application of advanced technologies and implementation cost of each pathway [34].

Recent reports about balancing climate - forcing emissions, stated that GHG emissions target limits can be achieved through the development and implementation of a powerful integrated group of solutions such as: expanding renewable energy and bioenergy dependency; adding new nuclear power stations; using clean fuel vehicles; increasing energy efficient processes in industry, and implementation of advanced highly efficient carbon capture and storage (CCS) systems for refineries, industrial processes and power stations[35]. Figure 2.3 illustrates the UK greenhouse gas emissions breakdown as reported in 2018 [36] and it shows that CO₂ gas emissions contribute with 81% to the overall UK greenhouse gas emissions in 2018. Figure 2.4 presents the actual and projected UK territorial CO₂ emissions in MtCO₂e recently reported.

Figure 2.3: UK greenhouse gas emissions in 2018 [36]
As shown in Figure 2.4, the overall CO₂ emissions have fallen in 2016 and are expected to fall more by 2035 due to applying CO₂ emissions reduction strategies. However, the emissions projections are considered uncertain due to economic, social trends and technological barriers which may affect the implementation of the CO₂ emissions reduction scenarios. In order to meet the UK’s 2050 net zero emissions target, it is required to implement a combination of four main options/alternatives: nuclear power generation, large-scale renewable energy, biomass energy and carbon capture and storage (CCS) technologies [37].

As per UK latest statistics [36], large amounts of CO₂ are released in the air due to transport, energy supply including electricity generation, residential including district heating, business including fuel combustion and other industrial process. Figure 2.5 shows the breakdown of UK 2018 CO₂ emissions in MtCO₂e, data extracted from [36].
Since CO₂ is the main contributor among GHG emissions, power and industrial decarbonization approaches became the key solution to achieve the UK’s 2050 emissions target. Decarbonization approaches include several technological options such as low-carbon electricity production, low-carbon industries, replacing the conventional hydrocarbon fuels by hydrogen. However, social, technological and financial constrains should be solved before the implementation of such solutions in large scale.

Carbon Capture and Storage (CCS) is considered the process of separating and collecting carbon dioxide from industrial and power generation CO₂ sources and transporting it to an appropriate safe location to store it for long term or utilize it in other industrial related activities [38]. Currently, consideration is given to CO₂ capture from large CO₂ sources points such as natural gas or coal power plants and oil and gas refineries. Following the capture and the transportation step, the CO₂ is injected into geological formations either for storage, such as in depleted oil and gas fields, or for utilization in the process of enhanced oil recovery in low pressure oil fields [39].

In the following sections, carbon capture applications and technologies will be discussed focusing on different capture systems since they are considered the most costly part of the CCS process, with a contribution to 70-80% of the total cost of full CCS system including capture, transport and storage [40].
2.3 Carbon capture applications

2.3.1 Carbon capture Technologies

As mentioned previously, low-carbon energy supply is considered one of the important key solutions to achieve the UK’s 2050 emissions target. Hence, the focus of this section is on the application of carbon capture systems in power and industrial plants.

For carbon capture systems, there are three main paths to achieve CO₂ capture from fossil-fuel based power plants: a) pre-combustion Capture, b) post-combustion capture and c) oxy-combustion capture, as illustrated in figure 2.6. For industrial processes, the design of the capture system depends on the type of the industrial process.

![Figure 2.6: Types of Carbon Capture Systems [38]](image)

The selection of the best suitable carbon capture system normally depends on many factors which are [38]: concentration of CO₂ in the flue gas, flue gas pressure, flue gas temperature and fuel type / power plant type / process type. The following subsection will discuss briefly each carbon capture technology pathway.

2.3.1.1 Pre-combustion capture

Pre-combustion capture involves reacting a fuel (coal or gas) with oxygen or air and/or steam to yield a ‘synthesis gas (syngas)’ or ‘fuel gas’ composed mainly of carbon monoxide and hydrogen. Carbon monoxide is converted to carbon dioxide in another reaction occurring in a shift reactor. CO₂ is finally separated by different methods based on operation conditions and process design. CO₂ concentration in the mixture is ranging
from 15 – 60% (dry basis) at a total pressure of 2 – 7 MPa [38, 41, 42]. The governing chemical reactions in the pre-combustion capture process are:

- Steam reforming or partial oxidation
  
  i. Steam reforming reaction: steam is reacted with hydrocarbon fuel.

\[
C_xH_y + xH_2O \leftrightarrow xCO + (x + \frac{y}{2})H_2 \quad (R3.1)
\]

ii. Partial oxidation / gasification reaction: oxygen is reacted with hydrocarbon fuel.

\[
C_xH_y + x/2O_2 \leftrightarrow xO + \left(\frac{x}{2}\right)H_2 \quad (R3.2)
\]

- Water gas shift reaction: converting CO to CO\(_2\) by adding more steam.

\[
CO + H_2O \leftrightarrow CO_2 + H_2 \quad (R3.3)
\]

Capturing CO\(_2\) during a steam methane reforming process helps reducing the reaction temperature while maintaining high values of H\(_2\) production and fuel conversion and hence, reduces the cost of the reactor material. Furthermore, the combination of CO\(_2\) capture with fuel reforming step was reported to enhance the overall process efficiency and reduce the efficiency penalty due to CO\(_2\) capture, reducing the overall cost accordingly [43, 44].

The main disadvantage of the pre-combustion capture system is that the systems are reported to have an overall investment cost relatively higher than the cost of the same plant with other capture technologies [42]. In addition to that, application of pre-combustion capture needs high integration between system components which reduces enormously the availability of the power plant [45]. Figure 2.7 shows a basic conceptual schematic for pre-combustion capture systems in power plants [38, 41].
2.3.1.2 Post-combustion Capture

In a post-combustion capture system, CO₂ is separated from the flue gas produced by combustion of a primary fuel (coal, natural gas, oil or biomass) in air to produce energy. Post-combustion capture flue gases / stack gases pressures are normally above atm (1.01 bara) with a CO₂ content ranging from 3-4 % volume for NGCC plants and up to 14 % volume for coal fired combustion plants [38, 46, 47].

The main design problem and consideration in a post-combustion capture system is that the impurities, such as nitrogen oxides and sulphur oxides, should be eliminated from the flue gas by different methods before applying CO₂ capture system. Figure 2.8 shows a schematic design of a CO₂ post-combustion capture system in fossil fuel-based power plants.
2.3.1.3 Oxy-Fuel combustion CO₂ Separation

Oxy-fuel combustion capture involves fuel combustion with 95 mol% pure oxygen [48], after removing nitrogen from air, to produce required heat. In oxy-fuel combustion, the gas exhaust is comprised mainly of CO₂ (up to 60 - 70 % volume) and H₂O. Due to the high combustion temperatures (up to 3500°C), if pure O₂ is used, a portion of CO₂ and steam is recycled back to the combustion chamber to achieve an overall oxygen level of 30-35 vol.% [49]. That, in turn, helps to reduce the temperature of combustion to the industrial accepted limits by lowering the temperature of the flame [38, 50]. Oxy-fuel combustion flue gases associated products are reported to achieve 75 % reduction in combustion flue gases volume and NOₓ volumes in flue gases compared to conventional air – fired combustion. Due to lower flue gas volumes in oxy-fuel Combustion, the flue gas pollutants, such as SOₓ and NOₓ, can be easily removed, and at a lower cost compared to post combustion capture technologies. The CO₂ concentration in the net gas stream, after H₂O separation, ranges from 80-98 % based on the type of fuel and configuration of the Oxy-fuel combustion process [38, 50].

Oxy-fuel combustion system consists mainly of three major units:
• Air separation unit (ASU) for separating N\textsubscript{2} from O\textsubscript{2}.
• Fuel - heat conversion unit (combustion chamber) which converts fuel and O\textsubscript{2} into heat.
• CO\textsubscript{2} purification and compression unit.

Figure 2.9: shows typical schematic of an Oxy-fuel combustion CO\textsubscript{2} capture system for Pulverized Coal (PC) power plant.

![Schematic diagram of an oxy-fuel, PC fired power plant. GGH is gas-gas heater and RFG is the recycled flue gas][51]

Oxy-fuel combustion capture system is claimed to have relatively higher efficiency and lower cost compared to other CO\textsubscript{2} capture technologies [52]. As an example, for a PC power plant with 1200MW\textsubscript{e} without capture, integrating oxy-fuel CO\textsubscript{2} capture process has shown to be 5 % better overall plant efficiency and 9% lower investment cost compared to amine based post-combustion capture from the same reference plant [53].

2.3.1.4 CO\textsubscript{2} capture from industrial plants

Several types of industrial plants produce CO\textsubscript{2}. These CO\textsubscript{2} emissions are resulted from burning fuel (gas, coal and biomass) or / and from the industrial process itself. Cement and steel production plants are considered the industrial processes which produce one of the largest amounts of CO\textsubscript{2} in the atmosphere [54, 55]. Depending on the nature of the manufacture / industrial process, one of the previous three types of CO\textsubscript{2} capture processes can be chosen to be integrated into the industrial plant to reduce amount of CO\textsubscript{2} resulted emissions.
2.3.2 CO₂ Capture / separation Methods

In the previous section, the main types of carbon capture processes were discussed. Each process or technology route (i.e. pre or post-combustion capture) should involve a CO₂ capture / separation method to achieve the final separation of CO₂ from the gas stream. CO₂ separation methods include absorption, adsorption, membrane and cryogenic technologies. CO₂ capture and separation methods should be chosen carefully to maintain high system integration and overall plant efficiency. In this section, different methods used to capture CO₂ from flue gas, produced from industrial / power plants, are presented.

2.3.2.1 Absorption

In absorption process, a liquid solvent is utilized to capture CO₂ from the gas stream. The CO₂ capture solvent should have selectivity for CO₂ compared to N₂ in order to achieve capture for large quantities of CO₂. The absorption process is normally performed through tall columns (scrubbers) where the CO₂ is separated from the flue gas. The separation process is followed by solvent regeneration process which aims to desorb the captured CO₂ and regenerate the solvent so that it can be used again in further capture cycles. The solvent regeneration process takes place in a “stripper column” by adding heat using steam and / or by reducing the pressure. The stripped solvent is routed back to the scrubber column and the CO₂ is separated from CO₂ / steam mixture by cooling down the mixture and condensing the steam which results in a highly concentrated CO₂ stream suitable for compression and transportation [40, 56].

Carbon capture using an absorption process normally suffers from high operating cost resulting from the high energy consumption since heat is required for steam generation and warming up of the solvent [57]. In PC power plants, the low-pressure steam, needed for solvent regeneration, is extracted before the last stage of the steam turbine. In natural gas combined cycle (NGCC) plants, solvent regeneration steam is recovered from the last stage of the heat recovery steam generator (HRSG) [56]. Extracting steam from the turbine / HRSG also results in reducing the overall power output of the plant.

Conventional CO₂ Capture using absorption processes operates at capture temperatures of 40-60°C and 1 bara of pressure and regeneration temperatures of 100-140°C and 1.5 to 1.8 bara pressures [38, 58]. Typical CO₂ capture solvents include Monoethanolamine (MEA), Diethanolamine (DEA), potassium carbonate and ammonia [40, 56]. The process of CO₂ capture using absorption depends on different connected factors which affect the
overall cost of the absorption process such as equipment, absorbent kinetics and thermodynamics and operating cost [59].

2.3.2.2 Membrane Technology

Membrane technologies have been used to capture CO₂ from natural gas in natural gas process plants. The theory behind membrane CO₂ capture technology is that the membrane’s permeable / semi permeable material allows only CO₂ to pass through without the rest of gas components. By using developed membrane CO₂ capture systems, high capture efficiencies of up to 88% could be achieved [40, 60, 61].

The main advantages of using a membrane CO₂ capture system, compared to conventional absorption process, are that there is no need for regeneration since there is no solvent used. That means that membrane systems can be easily integrated into power plants and easy to be scaled up with less space requirement [59]. Despite the advantages, individual membrane CO₂ capture selectivity cannot accomplish the required CO₂ capture limit alone. Hence, several stages and recycle streams are usually added to achieve the desired level of separation, which results in more complicated systems with higher capital cost and higher energy consumption [60]. Brunetti et al have concluded in their report that CO₂ capture systems based on membranes are highly influenced by the flue gas conditions (overall pressure and CO₂ concentration) and at low pressure / CO₂ concentration, the CO₂ capture performance is very low. Due to the aforementioned limitations, using membrane systems in CO₂ capture in post-combustion processes are considered an undesirable solution [62].

To overcome the previous mentioned limitations, a hybrid membrane – absorption capture system was investigated recently for carbon capture. In a hybrid membrane systems, CO₂ separation from the flue gas takes place in two stages (absorber and membrane) which can achieve 90 % CO₂ removal from flue gas at laboratory scale, as reported by Freeman et al [63]. Using a hybrid membrane design system helps eliminating flue gas impurities from the amine solvent part. That in part reduces the amine loss resulted from the formation of salts [39]. In addition, a hybrid membrane system has a relatively smaller stripper footprint compared to conventional solvent stripper column [63].

Similar to an absorption process, the overall cost of the membrane process depends on the system components and other factors such as type of membrane material and energy requirements. All these factors can be optimized to achieve optimum process design.
2.3.2.3 Cryogenic technology

Cryogenic gas separation technology is a gas separation process which involves gas distillation (gas separation due to boiling points differences) at low temperatures and / or high pressures [59]. In cryogenic CO₂ separation processes, the CO₂ rich flue gas is cooled to low temperatures (-100 to -135°C), lower than the CO₂ triple point temperature, to solidify the CO₂ molecules and separate them from the other flue gas constituents. The separated CO₂ is then compressed to high pressures (100-200 atm) achieving 90-95% CO₂ recovery from the flue gas. This process consumes higher energy since it operates at very low temperatures and high pressures [40].

2.3.2.4 Adsorption

As opposed to an absorption process, adsorption processes use a solid sorbent to capture CO₂ molecules onto its surface. In CO₂ adsorption processes, solid sorbents provide large adsorption area, high selectivity for CO₂ over the other flue gas constituents and higher ability for sorbent regeneration. There are several types of solid sorbents which can be used in CO₂ capture processes such as activated carbons, zeolites, metal organic frames (MOFs), calcium oxides and alkali based sorbents [40].

To desorb the captured CO₂ and regenerate the sorbent, pressure swing adsorption (PSA) or temperature swing adsorption (TSA) methods are usually used. In a TSA process, the flue gas stream passes through the adsorption bed at adsorption temperature \( T_1 \) and CO₂ partial pressure \( P_1 \). The maximum CO₂ captured loading of \( x_1 \) can be achieved provided that equilibrium is reached in the reactor. Figure 2.10 illustrates a TSA desorption method configuration and loading profile, respectively [59]. To regenerate the sorbent either the sorbent is circulated to another column for regeneration, or the same column can be switched from adsorption to regeneration mode. To start the regeneration, the column bed temperature needs to be raised to desorption temperature \( T_2 \) by directly adding heat to the bed using a heat exchanger or a hot purge stream. By reaching equilibrium in the regeneration column and removal of captured CO₂, the partial CO₂ pressure and the sorbent CO₂ loading is decreased to \( P_2 \) and \( x_2 \) respectively. The net sorbent working capacity \( (\Delta x) \) can be estimated by calculating the difference between \( x_2 \) and \( x_1 \).
In a pressure swing adsorption (PSA) process, similarly to a TSA process, the flue gas stream passes through the adsorption bed at adsorption temperature $T_1$ and CO$_2$ partial pressure $P_1$ to achieve CO$_2$ captured loading, $x_1$. Before starting the regeneration mode, either the sorbent is circulated to another column, or the same column can be switched from adsorption to regeneration mode. In a PSA process sorbent regeneration is achieved by reducing the partial pressure of CO$_2$ from $P_1$ to $P_2$ by lowering the overall pressure of the gas load inside the column. The period required to complete the PSA cycle including adsorption and desorption normally takes from seconds to several minutes, which makes the PSA process more applicable for bulk gas separation applications.

Similar to the absorption and membrane processes, CO$_2$ capture using adsorption depends on different connected factors which affect the overall cost of the adsorption process such as system components, energy consumption, sorption rate and cost of the material [59].

Since CO$_2$ capture using adsorption is currently gaining high attention as an alternative to the conventional absorption process, the following section will focus on the different types of solid sorbents and their advantages and disadvantages.

2.4 CO$_2$ Capture by solid sorbents

Although using solvent based CO$_2$ capture system has proved good performance in treating large volumes of gases, there are numbers of drawbacks in these systems such as slow reaction, material erosion problems, high rate of heat consumption, low removal rate

Figure 2.10: Temperature swing adsorption configuration and adsorption loading profile [59]
and large equipment footprint. These drawbacks have opened the window for using other capture technologies such as dry sorbents.

2.4.1 **Dry Solid sorbents as a novel solution**

Several studies [64-68] promoted solid dry sorbents as new heat efficient candidates, which are suitable for post and pre-combustion capture processes and consequently, could reduce the operation cost due to less heat requirement.

Dry sorbent processes in general require relatively simpler equipment design and easier in operation. Also, dry sorbents can provide a very good solution in terms of high heat management and improving energy efficiency compared to chemical absorption processes, as the latter ones require very high heat consumption during the solvent regeneration step (for example MEA solvent consumes not less than 3MJ/kg CO$_2$) [66]. Moreover, the solid sorption reaction can be considered as a reversible reaction (easy regeneration) and the sorption efficiency can be enhanced by adjusting the dry sorbent structure or doping the sorbent with other materials [69]. Additionally, all current solvent capture technologies cannot work at high temperatures, higher than 400°C, which leads to cooling requirements for high temperature applications and thus loosing heat and efficiency. In contrast, solid sorbents were found suitable for moderate and high temperature applications which leads to higher energy savings. For example, in post combustion power generation plants, the flue gas temperature produced after the combustion of fossil fuels in a turbine usually ranges between 427 and 627°C [70]. To implement a post combustion CO$_2$ capture system using amine solvents, the flue gas should be cooled to the amine solvent operating temperature range (40-150°C) resulting in further energy losses. In contrast, several solid sorbents were recently investigated to work under high temperature conditions such as lithium orthosilicate and lithium zirconate and they have shown good CO$_2$ capture capacity even at low CO$_2$ concentration. Consequently, solid sorbents can be considered as good candidates competing with traditional amine solvents especially for high temperature applications [71-73].

For a better understanding of solid sorbents nature and their best working conditions, different classifications of solid sorbents materials will be discussed in the following subsections:

2.4.2 **Sorbents classification based on type of interaction**

There are several studies in literature discussing the classification of solid sorbents based on the type of reaction which is taking place between solid sorbents and CO$_2$ molecules.
In general, when a solid sorbent is exposed to flue gas containing CO$_2$, the CO$_2$ molecules will be adsorbed by the sorbent in one of two different mechanisms (chemical or physical adsorption) based on the type of the sorbent. In CO$_2$ physi-sorption, CO$_2$ molecules are held to the adsorbent surface by weak intermolecular forces. On the contrary, in CO$_2$ chemisorption, CO$_2$ molecules are held to the sorbent surface through strong covalent bonding. The physi-sorption process is usually accompanied with heat of adsorption lower than 10-15 kcal/mol. On the other hand, the chemisorption process is usually accompanied with heat of adsorption higher than 15 kcal/mol [59, 74]. Both physi- and chemi-sorption processes are described in detail in the following subsections:

2.4.2.1 Chemical adsorption

Chemical adsorption, i.e. chemisorption, is an adsorption process, forced by chemical reactions which take place at the exposed sorbent surface. Chemical adsorbents usually exist in two forms of compounds: metal oxides such as CaO and MgO, and metal salts such as lithium silicate and lithium zirconate [75]. In chemisorption, the adsorbed gas (CO$_2$) binds to the chemi-sorbent using covalent chemical reaction which results in a great heat of adsorption, which is approximately equal to heat of reaction. As mentioned before, the heat of adsorption of chemi-sorbs is usually higher than physi-sorbs due to the existence of strong covalent bonding resulted from chemical adsorption [59, 76].

2.4.2.2 Physical adsorption

Physical adsorption is an adsorption process, driven by physical interaction between carbon dioxide and sorbent molecules. As reported in literature, the main CO$_2$ physical adsorbents include activated carbon and inorganic porous materials such as zeolites [75]. CO$_2$ physiosorption selectivity, from gas mixture, is achieved due to the Van der Walls attraction between molecules of carbon dioxide and the adsorbent surface, also by the pole-pole and pole-ion interactions between the fixed quadrupole of the CO$_2$ molecule and the polar and ionic sites of the adsorbent surface [77]. The adsorbed gas molecules are attached to the surface of pore walls within the physi-sorb by Van der Waals forces which result in a low heat of adsorption that is slightly higher than heat of sublimation of the adsorbate [76]. Physi-sorbs normally operate at relatively low temperatures (≤100°C) as it was found that physi-sorbs lose CO$_2$ capacity and selectivity at high temperatures [77].
2.4.3 Dry Sorbent classification based on working temperature

Since the pre and post-combustion CO\textsubscript{2} capture processes have different configurations and deal with a wide range of temperatures ranging from high temperature to ambient, there is a great benefit of classifying the sorbents based on working temperatures. This classification helps matching the best suited sorbent for a specific application (based on pressure and temperature working conditions). Hence, an efficient heat management, low heat loss and high overall plant efficiency could be achieved.

Dry sorbents can be classified based on their working temperatures as: low temperature sorbents, medium temperature sorbents and high temperature sorbents. Each of these sorbents types is discussed in detail in the following subsections.

2.4.3.1 Low Temperature sorbents

The sorption process is achieved at relatively low temperature, \( \leq 100^\circ \text{C} \). These kinds of sorbents are not recommended for high temperature applications since there will be a high heat loss due to the requirement of cooling down the flue gas to the sorption low temperature. Examples for low temperature sorbents are:

a) Zeolites: porous crystalline silicate materials which are naturally existing and their pore sizes ranges from 0.5 to 1.2 nm [59, 69, 78].

b) Metals Organic Frameworks (MOFs): are widely synthesized by constituting strong bonds during merging of inorganic and organic materials. Around 20,000 MOFs with specific surface areas ranges from 1000 to 10,000 \( m^2/g \) were investigated in literature as solid sorbent candidates for CO\textsubscript{2} capture [59, 69, 79].

c) Activated Carbons: are extensively used as CO\textsubscript{2} sorbents in a large commercial scale as they have high surface area due to large mesopore and micropore volumes [74]. Activated carbons have low cost and low energy generation requirements compared to zeolites [80] which made activated carbons a more attractive option for CO\textsubscript{2} capture.

2.4.3.2 Medium temperature Sorbents

Medium temperature sorption process is usually achieved at relatively medium temperatures, ranging from 100°C to 400°C. Examples of medium temperature sorbents are:
Metal Oxides such as MgO: MgO – CO$_2$ sorption is taking place at a temperature range of 150 - 400°C and 1 bara pressure. MgO has been shown to be a good candidate for CO$_2$ capture due to its abundance and low toxicity [69].

Alkali-metal based sorbents: potassium (K) and sodium (Na) based alkali metal sorbents have low to medium sorption and regeneration temperatures (below 200°C). As an example, for Na$_2$CO$_3$ and K$_2$CO$_3$ sorbents, the CO$_2$ sorption temperatures are 60 and 110°C at 1 bara to achieve 41.5 wt% and 31.8 wt % CO$_2$ capture from pure CO$_2$ stream, respectively [69].

2.4.3.3 High temperature Sorbents

The high temperature sorption process takes places at temperatures higher than 400°C which leads to less heat loss since there is no need for further cooling of the feed flue gas stream to meet the sorbent capture temperatures. These sorbents present a novel solution for the high heat loss experienced in most of the carbon capture systems [50, 69].

High temperature sorbents can be mainly classified as three types of sorbents:

- Calcium oxide Sorbents: CaO is considered a high capacity high temperature CO$_2$ sorbent. CaO can achieve a CO$_2$ theoretical capacity up to 75 wt %, in the first operation cycle, at temperatures > 600°C and regeneration temperature > 900°C [77]. CaO is obtained from a very cheap raw material (CaCO$_3$). However, calcium oxide normally degrades after a low number of cycles and needs a large amount of makeup which tremendously affects the overall cost of capture process. In addition, it has been reported that CaO suffers from slow chemical reaction and requires high-energy consumption due to its high regeneration temperatures [38, 69, 77].

- Sodium-based high temperature sorbents: Sana et al [81, 82] investigated the suitability of sodium carbonate / fly ash sorbents at high temperatures up to 700°C and the sorbents have shown good carbon capture capacity which can reach up to 11 wt % in presence of 12 % H$_2$O and 12.5 % CO$_2$. Such CO$_2$ capture capacity is considered higher than the amine solvent benchmarking capacity (8%) [82].

- Lithium-based high temperature sorbents: lithium-based high temperature sorbents such as lithium orthosilicate (Li$_4$SiO$_4$) and lithium zirconate (Li$_2$ZrO$_3$) have shown good carbon capture capacity, up to 35 wt % at relatively high temperatures (500-700°C) and low sorbent volume change during sorption – desorption cycles [83, 84].
As mentioned previously, the main advantage of high temperature sorbents is in reducing energy penalties compared to solvent based process, as there is no need to cool down the flue gas to the solvent capture temperature. In addition, high temperature sorbents can work at high temperatures which allows for several options of heat integration inside the plant at several locations which leads to more efficient plant with less power penalty.

Despite the advantages described previously, for high temperature sorbents, some disadvantages were found such as high cost of sorbent for lithium based sorbents, high cost of reactor material due to dealing with higher temperatures up to 900°C in case of CaO and overall performance need to be proven in a large scale over repeated cycles.

Based on the advantages mentioned above, in this thesis, high temperature Li-based sorbents will be further investigated as good candidate for high temperature CO₂ capture applications and process integration in power and industrial applications.

2.5 Review of Li-based sorbents as good candidates for CO₂ capture

Li-based sorbents have been investigated by numerous previous workers [20, 71, 81, 85-87] as good candidates for CO₂ capture and they have shown high sorption / desorption stability and relatively good kinetics at high temperatures [87]. The main considered problem with lithium based sorbents is that the initial cost of the sorbent raw material is very high compared to sodium based sorbents or calcium oxide based sorbents [20]. However, this drawback can be compensated with the high durability and less make up requirement that Li-based sorbents generally have recorded until now. Furthermore, another general drawback of lithium based sorbents is the toxicity nature of lithium carbonate, that is used widely in synthesis of lithium based sorbents [81].

In order to prove that lithium based sorbents are economically competitive, Duo et al proposed that the durability of the sorbent should be checked over 10000 cycles of sorption / desorption [43]. Further details on the different existing types of Li-based sorbents will be discussed in the following sections.

2.5.1 Performance of Li-based sorbents

2.5.1.1 Lithium Zirconate

Lithium zirconate has high sorption selectivity, since it does not react with N₂ [71], good capture capacity up to 20 wt % at a temperature range of 450-550°C and slow adsorption process (e.g. 250 min under exposure to 100% CO₂ stream) [71]. It was reported that
lithium zirconate, with additives such as K$_2$CO$_3$ and small particle size, achieved much faster sorption rates compared to original lithium zirconate material [71]. Lithium zirconate is considered the most expensive lithium based sorbents as the zirconia material is considered more costly, 1400 $/imported$ metric ton for 2013 prices [88, 89], compared to silica material [69, 90]. Lithium zirconate reacts with CO$_2$ molecules as per the following reaction:

$$Li_2ZrO_3 + CO_2 \rightarrow Li_2CO_3 + ZrO_2$$  \hspace{1cm} \text{R(2.1)}

### 2.5.1.2 Lithium Orthosilicate (Li$_4$SiO$_4$)

Lithium orthosilicate (Li$_4$SiO$_4$) is a white ceramic material, which is synthesised by heat treatment of a mixture of SiO$_2$ and Li$_2$CO$_3$ [84]. The CO$_2$ can be captured by Li$_4$SiO$_4$ as per the following reaction:

$$Li_4SiO_4 + CO_2 \leftrightarrow Li_2SiO_3 + Li_2CO_3$$  \hspace{1cm} \text{R(2.2)}

Li$_4$SiO$_4$ is relatively cheaper than Li$_2$ZrO$_3$ [69, 90] and has shown higher sorption capacity (up to 36.7 wt %) compared to Li$_2$ZrO$_3$ at high temperatures of 427°C to 627°C [69]. Li$_4$SiO$_4$ has shown sorption rate 30 times faster than Li$_2$ZrO$_3$ at 20% CO$_2$ stream and 500°C and 1 bara [13]. In addition, Li$_4$SiO$_4$ was reported to capture CO$_2$ at 500°C in 2% CO$_2$ stream and Lithium zirconate showed very poor CO$_2$ capture capacity at same conditions[13]. Also, Quinn et al reported that presence of water vapor enhanced the absorption rate of Li$_4$SiO$_4$ without affecting the sorption capacity[23]. Table 2.1 illustrates detailed examples of CO$_2$ capture using Li$_4$SiO$_4$ based sorbents at high temperature and different CO$_2$ concentrations.

### Table 2.1: CO$_2$ capture capacity for Li$_4$SiO$_4$ at different CO$_2$ concentrations and conditions, $P_{ads} = P_{des} = 1$ atma.

<table>
<thead>
<tr>
<th>$T_{ads}$, °C</th>
<th>additives</th>
<th>CO$_2$ (vol %)</th>
<th>Heat Rate, °C/min</th>
<th>Adsorption Time (min)</th>
<th>CO$_2$ capture level, wt %</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>Potassium and titanium tracings</td>
<td>15</td>
<td>NA</td>
<td>25</td>
<td>22</td>
<td>[23]</td>
</tr>
<tr>
<td>700</td>
<td>none</td>
<td>100</td>
<td>NA</td>
<td>150</td>
<td>35</td>
<td>[84]</td>
</tr>
<tr>
<td>580</td>
<td>30 wt % K$_2$CO$_3$</td>
<td>4</td>
<td>10</td>
<td>120</td>
<td>9</td>
<td>[73]</td>
</tr>
</tbody>
</table>

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2.5.1.3 Lithium Oxosilicate (Li$_8$SiO$_6$)

Lithium oxosilicate (Li$_8$SiO$_6$) can be prepared using solid-state reaction of silicon dioxide (SiO$_2$) and lithium oxide (Li$_2$O) [93]. The following reactions were proposed to explain Li$_8$SiO$_6$ reaction with CO$_2$ [93]:

\[
\text{Li}_8\text{SiO}_6 + 2 \text{CO}_2 \rightarrow 2 \text{Li}_2\text{CO}_3 + \text{Li}_4\text{SiO}_4 \quad \text{at} \ (300 – 700^\circ\text{C}) \tag{R(2.3)}
\]

\[
\text{Li}_4\text{SiO}_4 + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{Li}_2\text{SiO}_3 \quad \text{at} \ (400-580^\circ\text{C}) \tag{R(2.2)}
\]

By combining, the previous two reactions at temperature range 400-580°C, it will result in:

\[
\text{Li}_8\text{SiO}_6 + 3 \text{CO}_2 \rightarrow 3 \text{Li}_2\text{CO}_3 + \text{Li}_2\text{SiO}_3 \quad \text{at} \ (400-580^\circ\text{C}) \tag{R(2.4)}
\]

Li$_8$SiO$_6$ has shown the highest CO$_2$ sorption capacity among lithium-based sorbents at high temperatures (up to 51 wt. % under 700°C, 1 bara and 100% CO$_2$). Also, at 600°C, it showed higher adsorption kinetics compared to Li$_4$SiO$_4$ [94]. Despite the high carbon capture capacity, that Li$_8$SiO$_6$ has shown, it was not fully analysed to prove high durability through large number of cycles. Table 2.2 illustrates some examples of CO$_2$ capture using Li$_8$SiO$_6$ based sorbents at high temperatures.

Table 2-2: CO$_2$ capture capacity for Li$_8$SiO$_6$ at different conditions

<table>
<thead>
<tr>
<th>$T_{ads}$, °C</th>
<th>$P_{ads}$</th>
<th>Material</th>
<th>CO$_2$ (vol %)</th>
<th>Heat Rate, °C/min</th>
<th>Adsorption Time (min)</th>
<th>CO$_2$ Capture, wt %</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>1 bara</td>
<td>Li$_8$SiO$_6$</td>
<td>100</td>
<td>NA</td>
<td>180</td>
<td>30</td>
<td>[94]</td>
</tr>
<tr>
<td>700</td>
<td>1 bara</td>
<td>Li$_8$SiO$_6$</td>
<td>100</td>
<td>5</td>
<td>180</td>
<td>51</td>
<td>[93]</td>
</tr>
</tbody>
</table>

2.5.2 Chemi-sorbents theoretical Capacity for CO$_2$ Capture

The first step to investigate the sorption capacity and performance of a specific sorbent is normally achieved by calculating the theoretical adsorption capacity through the

---

| 580 | 30 wt % K$_2$CO$_3$ with 20 wt % cellulose fibres | 4 | 10 | 120 | 15 | [73] |
| 700 | none | 100 | 25 | 30 | 33 | [91] |
| 580 | 20 wt % K$_2$CO$_3$ | 4 | NA | 120 | 22 | [92] |
stoichiometric balance for the chemical reaction. The following equations represent the chemical reaction of CO₂ adsorption for Li-based high temperature sorbents:

\[ \text{Li}_2\text{ZrO}_3 + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{ZrO}_2 \]  
\[ 153.2 + 44 \rightarrow 74 + 123.2 \]  
\[ \text{Capacity} = (44/153.2) \times 100\% = 28.7\text{ wt\%} \]

\[ \text{Li}_4\text{SiO}_4 + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{Li}_2\text{SiO}_3 \]  
\[ 120 + 44 \rightarrow 74 + 90 \]  
\[ \text{Capacity} = (44/120) \times 100\% = 36.6\text{ wt\%} \]

\[ \text{Li}_8\text{SiO}_6 + 3 \text{CO}_2 \rightarrow 3 \text{Li}_2\text{CO}_3 + \text{Li}_2\text{SiO}_3 \]  
\[ 180 + 132 \rightarrow 222 + 90 \]  
\[ \text{Capacity} = (132/180) \times 100\% = 73.3\text{ wt\%} \]

It is common for adsorption capacity to be quoted as mmol CO₂/g solid. In this thesis, the carbon capture capacity from the stoichiometric reaction equation is calculated as a wt %. Values from references have been recalculated to follow this terminology as showed in the above reactions.

From the previous stoichiometric calculation, it can be concluded that Li₈SiO₆ sorbent showed the highest theoretical capacity (73.3 wt %) followed by lithium orthosilicate, with a capture capacity of 36.6 wt %, and finally, the lowest theoretical capture capacity is the one for lithium zirconate, which is of 28.7 wt %. Although the previous capacities represent the theoretical capacities for the sorbents, these capacities can be considered only as a preliminary indicator for the sorbent CO₂ capacity. However, additional information based on the experiments data obtained from several test cycles should also be considered to achieve a fair comparison between sorbents.

2.5.3 Alkali-sorbents Double Shell Sorption Mechanism

When a solid chemi-sorbent is exposed to CO₂ at an appropriate adsorption temperature, CO₂ is adsorbed by the sorbent through chemical reaction happening between the sorbent and carbon dioxide followed by diffusion of CO₂ into the sorbent material. The nature of the reaction, the rate of the reaction and rate of diffusion can be defined based on the sorbent type. Several studies have observed that alkali based sorbents shared the same sorption kinetics processes when exposed to CO₂ at appropriate sorption temperature which is called double shell adsorption mechanism [71, 82, 93, 95, 96]. The combination of CO₂ capture by chemical reaction and product layer diffusion was initially proposed by Ida et al to illustrate the sorption kinetics for lithium zirconate and it was called shell sorption mechanism [96]. Double shell mechanism was used afterwards to describe the
sorption mechanism of wide alkali-based sorbent based on different experimental results for each sorbent. The concept of the double shell sorption mechanism is that the sorption process is divided into two steps. The first step includes the formation of alkali carbonate layer followed by the alkaline and CO₂ diffusion through the external layer (second step) [71, 95]. Figures 2.11 depicts typical double shell mechanism for lithium Silicate based sorbents.

![Double Shell Mechanism Diagram](image)

*Figure 2.11: CO₂ double shell sorption mechanism for lithium silicate[95]*

**2.6 High Temperature sorbents comparison summary**

For a clear understanding of differences between high temperature sorbents, a detailed comparison between Ca-based sorbents, lithium based and sodium-based sorbents is presented in table 2.3.

The current thesis focuses on lithium orthosilicate based sorbents as they can provide a novel solution for CO₂ capture at high temperatures due to obtaining a good CO₂ capture capacity, up to 36.7 wt. %[97], and lower regeneration temperature (< 750°C) when compared to other high temperature sorbents such as CaO-based sorbents [14, 84, 98, 99]. Even though there are numerous studies investigating the reactivity and stability of lithium-based sorbents [15-19], both in powder and pellet forms, that proof their cyclic and thermal stability [17, 24], their potential to decrease the energy penalty of the capture system is yet to be established. To the author’s knowledge, there are no comprehensive studies of Li-based capture systems integrated into either power or industrial plants. The current thesis would enable the comparison to other capture technologies as well as to conventional CaO based capture technologies and could provide useful guidance for the
development and possible application of synthetic lithium-based sorbents. Consequently, $\text{Li}_4\text{SiO}_4$ sorbents are discussed in detail in the following sections / sub-sections, with a focus on the conceptual process integration of high temperature CO$_2$ capture into power and industrial plants.
Table 2-3: Detailed comparison between high temperature sorbents.

<table>
<thead>
<tr>
<th>Compared factor</th>
<th>CaO</th>
<th>Li₄SiO₄</th>
<th>Li₂ZrO₃</th>
<th>Li₄SiO₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost of precursor materials</td>
<td>Very cheap</td>
<td>Quite expensive but cheaper than Li₂ZrO₃</td>
<td>Li based sorbents are quite expensive</td>
<td>Quite expensive but cheaper than Li₂ZrO₃</td>
</tr>
<tr>
<td>Toxicity [38]</td>
<td>Nontoxic</td>
<td>Toxic</td>
<td>Toxic</td>
<td>Toxic</td>
</tr>
<tr>
<td>Carbonation Temp @ ( P_{atm} )</td>
<td>&gt;600°C</td>
<td>427-627°C</td>
<td>400-627°C</td>
<td>300-700°C [93]</td>
</tr>
<tr>
<td>Regeneration Temp @ ( P_{atm} )</td>
<td>≥850°C [82]</td>
<td>≥627°C</td>
<td>≥627°C</td>
<td>≥700°C [93]</td>
</tr>
<tr>
<td>Max achieved capacity</td>
<td>75 wt % [77]</td>
<td>36.7 wt % [69]</td>
<td>21 wt % [77]</td>
<td>42 - 51.9 % wt [69, 93]</td>
</tr>
<tr>
<td>( N_{cycles} ) that half of sorbents can complete without deactivation [100]</td>
<td>13</td>
<td>8299 for lithium carbonate</td>
<td>8299 for lithium carbonate</td>
<td>8299 for lithium carbonate</td>
</tr>
<tr>
<td>Advantages</td>
<td>Highest uptake at high temperatures [69]</td>
<td>• Faster sorption – desorption kinetics compared to sodium based sorbents [82]</td>
<td>• Achieved relatively stable performance over several sorption – desorption cycles [104]</td>
<td>• Highest stoichiometric CO₂ capture capacity (73 wt%) among Li-based sorbents [94]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Provide higher sorption capacity compared to Lithium Zirconate at low ( CO_2 ) concentration [101]</td>
<td>• Moderate CO₂ capture capacity and lower desorption temperature (&lt; 750°C) [101]</td>
<td>• Suitable for high pressure and high temperature applications (up to 1052°C and 20 bara) [94]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Relatively high sorption capacity and high cyclic performance [93]</td>
<td>• Ongoing research to prepare it from low cost non-toxic materials such as vermiculite and fly ash [102, 103]</td>
<td>• Requires higher energy input for regeneration at high temperatures compared to Li₄SiO₆ and Li₂ZrO₃ [94]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Li₂CO₃ is toxic and expensive [81]</td>
<td>• Li-based sorbents performance should be examined through ~10,000 cycles to prove suitability for large scale application [43]</td>
<td>• It has not been yet fully analysed [93]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Li-based sorbents performance should be examined through ~10,000 cycles to prove suitability for large scale application [43]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Disadvantages [38, 77]</td>
<td>Poor cyclic performance and requires high regeneration energy [69]</td>
<td>Li₂CO₃ is toxic and expensive [81]</td>
<td>Li-based sorbents performance should be examined through ~10,000 cycles to prove suitability for large scale application [43]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>High regeneration temperature &gt; 850°C [82]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CaO reacts with SO₂ which affects sorbent deactivation [105]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.7 Integration of high temperature CO\textsubscript{2} capture looping processes

As mentioned earlier, the CO\textsubscript{2} capture process from flue or industrial gases is considered the main source of cost penalties associated with CCS technologies. For sorbent-based capture technologies, the main criteria in sorbents R&D is to find how to use a lower cost sorbent while achieving less energy penalties compared to other sorbents / solvents applications. The calcium looping process in CO\textsubscript{2} post combustion capture, as an example of high temperature solid-based capture technology, has offered a promise to achieve a low cost CO\textsubscript{2} capture, since many heat streams could be integrated inside the plant achieving higher efficiencies and less penalties [106]. Calcium oxide, as a sorbent for CO\textsubscript{2} post combustion capture systems, has been investigated widely in many power / industrial plants. In this section, different applications of Ca looping system in post combustion capture are reviewed, with a focus on the application of lithium silicate-based sorbents as substitutes to calcium oxide sorbents.

In previous studies, calcium looping was investigated to be applied in post combustion capture of coal power plants [107, 108] and natural gas combined cycle (NGCC) plants [47, 66, 109]. Also, it was investigated for integration in industrial plants such as cement plants [110, 111] and hydrogen production steam methane reforming plants[112-114].

Although, Li\textsubscript{4}SiO\textsubscript{4} based sorbents have been studied quite extensively on lab scale but there is a lack of comprehensive studies that evaluate their integration into power and industrial plants for high temperature CO\textsubscript{2} capture.

The following subsections review integration studies of the CaL process in a NGCC power plant and a H\textsubscript{2} SMR plant, as potential case studies to investigate in the current thesis. Also, the following subsections discuss the potential of integrating Li\textsubscript{4}SiO\textsubscript{4} based sorbents into the same plants similar to CaL system.

2.7.1 Natural Gas Combined Cycle (NGCC) Plants

Natural gas combined cycle plants have many advantages compared to coal power plants which make them more favourable to apply carbon capture integration. NGCC plants have the highest plant efficiencies, 44.71-49.6\% L.H.V, while producing less carbon dioxide content, 4-6 vol \% and specific emissions around 350 kg/MWh, compared to coal power plants [47, 66]. The following diagram illustrates an example of a pre-designed NGCC plant with CO\textsubscript{2} capture using CaL.
From the plant configuration, illustrated in figure 2.12, it is observed that NGCC plant modification with the sorbent looping unit integration can be favourable from a construction point of view since it can be considered as a pure modular modification. These modifications could be much easier as there is no heat integration / major modifications inside the main equipment [47].

Despite the previous mentioned advantage of the design in figure 2.12, it is worth mentioning that this design is recommended only when designing a new NGCC plant with carbon capture. The reason for that recommendation is that bypassing the exhaust gases from the point between the gas turbine and the HRSG in an existing NGCC plant is considered difficult as the gas turbine and HRSG normally come as one unit connected together. Different designs could be followed to retrofit CO$_2$ capture systems inside active NGCC plant as the CO$_2$ capture system can be placed after the main HRSG unit to avoid any major change in the existing plant [109].

In the design illustrated in figure 2.12, the following design conditions were applied to integrate the sorbent looping unit into the NGCC plant [47]:

- A fluidized bed carbonator was used for CO$_2$ capture and an oxy–natural Gas calciner (regenerator) was used for CaCO$_3$ decomposition.
• A CO₂ recirculation stream was taken from the calciner CO₂ discharge stream. This recirculation stream helps to moderate the flame temperature inside the calciner, maintain the reactor fluidized and improve oxygen and fuel consumption.

• Heat recovered from the lean CO₂ flue gas stream is used to generate steam in the primary HRSG.

• Heat recovered from the exothermic reaction inside the carbonator and heat recovered from the hot pure CO₂ stream discharged from the calciner were used to generate steam in secondary HRSG.

• Heat recuperation was applied between the two solids stream between the carbonator and the calciner to heat up the solid stream entering the calciner which improves the calciner heat consumption.

• CO₂ conditioning unit performs multi-stage compression and water knock out up to 500 ppm water content.

For Li₄SiO₄ based CO₂ capture system, this can be integrated into a NGCC power plant using a similar process design as applied with CaL system but with different working temperatures. The Li₄SiO₄ based CO₂ capture working temperatures, ie. absorption and regeneration should be defined based on Li₄SiO₄ / CO₂ best performance working temperature from sorbent lab tests under NGCC relevant flue gas conditions. Further details on the integration of Li₄SiO₄ based CO₂ capture system, inside NGCC power plant, are described in chapter 4.

2.7.2 Hydrogen production plants:

High concentrated hydrogen is considered as an essential gas for chemical and petroleum plants. Recently, H₂ has shown attractiveness as one of the clean energy solutions [115]. Hydrogen is currently being produced from more than 20 resources based on the graphical location and availability of natural resources [116]. Hydrogen production based on fossil fuels (coal and natural gas) is considered one of the common processes for H₂ production [115, 117, 118] which in turn results in CO₂ emissions to the atmosphere due to the emissions from fuel burning [115].

Numerous reports and studies, in literature, discuss in detail how to use amine based solvents to remove CO₂ from the gas products from hydrogen production plants based on steam methane reforming (SMR) process [118-120]. SMR process is designed mainly based on the conversion of CH₄, in the presence of high-pressure steam, to H₂ and CO₂.
CO₂ can be removed from the SMR process from different locations as illustrated in figure 2.13 [119].

![Figure 2.13: Schematic Diagram for possible CO₂ capture options from SMR H₂ production plant [119]](image)

CCS integration with SMR based Hydrogen production plants was investigated for CO₂ captures technologies different to amine based solvents such as membranes [121, 122] and solid sorbents as part of Sorption Enhanced Steam Methane Reforming (SESMR) process [120].

This section focuses on CO₂ capture from H₂ SMR plants using high temperature sorbent looping systems in the process called SESMR.

Figure 2.14 shows the block flow diagram for the SMR process [120] with solvent based CO₂ capture.

![Figure 2.14: SMR with solvent based CO₂ capture [120]](image)
In the SMR process, illustrated in figure 2.14, the NG reacts with steam in a reformer and the heat required for the reaction is provided by burning the tail gas produced from PSA unit. After the reformer, the syngas will pass through a shift reactor to complete the conversion, followed by a Methyl diethanolamine (MDEA) unit for CO₂ capture and the final syngas stream is sent to PSA unit to produce pure H₂.

High temperature sorbent looping systems, such as CaL, can be integrated in the SMR process to capture CO₂ and replace the water gas shift reactor (WGR), MDEA and MEA units as per the following block flow diagram:

![Figure 2.15: SMR process with CaL integration [120]](image)

In the previous system, illustrated in figure 2.15, there is no need to modify the main steam methane reformer and only the WGR is eliminated from the main SMR equipment along with the solvent based CO₂ capture system [120]. CaL system was investigated to be integrated with SMR process in sorption enhanced steam methane reforming (SESMR) process which needs a major modification in plant equipment [123, 124]. Figure 2.16 illustrates a simplified schematic diagram for CaL system integrated in SESMR process.
The process configuration, illustrated in figure 2.16, was proposed by Gracia-Lario et al [123] as a modification for SMR process to eliminate the WGR and amine based CO\textsubscript{2} capture units and achieve CO\textsubscript{2} capture and steam methane reforming in one step inside the SESMR reformer. After completing the sorption enhanced reforming process at a suitable temperature (650-700°C), the sorbent is directed to the regenerator to get regenerated under oxy fuel combustion conditions.

Similar to the integration of CaL system in the SESMR process, a Li\textsubscript{4}SiO\textsubscript{4} / Li\textsubscript{2}CO\textsubscript{3} looping system could then be integrated in the plant by adjusting the syngas temperature to the required capture temperature. As a result, Li-based sorbents could be used in a SESMR reactor with the advantage of requiring a lower carbonation temperature (500-550°C) [125, 126] compared to CaL system (650-700°C) [123] and such saved energy can be thermodynamically integrated somewhere else in the plant to reduce the energy penalty or to generate steam and electricity.

Integrating Li\textsubscript{4}SiO\textsubscript{4}-based CO\textsubscript{2} capture system in SESMR process is discussed in detail in chapter 6.

2.8 Conclusion

CO\textsubscript{2} capture based on high temperature solid sorbents is an important option to reduce CO\textsubscript{2} emissions in exhaust gases from power and industrial plants. A key advantage of such technology is its capacity to capture CO\textsubscript{2} at the temperature of exhaust gases,
avoiding the need to quench or cool gases and the high potential for heat integration within the process of the main plant.

Lithium orthosilicate (Li$_4$SiO$_4$) based sorbents have shown good potential to be used as CO$_2$ capture sorbents. As shown through the extensive literature screening, Li$_4$SiO$_4$ has a relatively good sorbent capacity, conversion and durability. However, the sorbent needs to be investigated further with respect to its potential use in CO$_2$ capture systems for power and industrial applications. Hence, the sorbent should be tested and regenerated under the relevant flue gas conditions for particular applications, in case the test data is not reported in the literature. With respect to process integration studies of Li$_4$SiO$_4$ based sorbents, there are no studies that evaluate the process integration of those sorbents into power and industrial plants. Consequently, this research will focus on investigating the technical and economic impact of process integration of a novel sorbent technology based on lithium orthosilicate into NGCC power plants and H$_2$ SMR plant for CO$_2$ capture.

For NGCC power plant process, high temperature, Li$_4$SiO$_4$/Li$_2$CO$_3$, looping system is proposed as a potential candidate to capture CO$_2$ from the NGCC flue gas at high temperatures without the need to cool down the gas. To achieve that, the NGCC process should be modified by integrating high temperature solid sorbent looping system, with oxy fuel regenerator. Due to the high working temperature of oxyfuel system inside the regenerator (up to 700°C), the hot CO$_2$ stream exiting the regenerator could be used in an additional heat recovery system to generate high pressure steam and electricity. That in turn helps to reduce the plant efficiency and energy penalties associated with the integration of the high temperature CO$_2$ capture system.

For H$_2$ SMR plant, Li$_4$SiO$_4$/Li$_2$CO$_3$ looping based SESMR system is proposed as a replacement for the conventional SMR system. The high temperature Li$_4$SiO$_4$ SESMR would be integrated following the same concept explained earlier for integration CaL SESMR system in SMR H$_2$ plant by combining the CO$_2$ capture and steam methane reforming processes in one reactor while the sorbent regeneration is performed in a separate reactor, regenerator, under oxy fuel combustion atmosphere. Such design would result in eliminating several equipment such as WGR and MEA based solvent system inside the plant.
Investigating the process integration for Li$_4$SiO$_4$ based CO$_2$ capture system, into the aforementioned power and industrial plants, followed by techno-economic assessment in each case, would help to prove the Li$_4$SiO$_4$ based sorbents suitability to be integrated in power and industrial plants for high temperature CO$_2$ capture from conceptual process and techno-economic point of views. It could give further guidance for material and future development.

Chapter 3, will introduce the methodology used to investigate the process and techno-economic assessment of integrating Li$_4$SiO$_4$ / Li$_2$CO$_3$ looping system in the following plants for CO$_2$ capture:

- NGCC plant
- H$_2$ SMR reforming plant
Chapter 3 METHODOLOGY

This chapter describes the methodology used in the current study to perform the technical and economical assessment for the integration of Li$_4$SiO$_4$ / Li$_2$CO$_3$ capture looping systems into power and industrial plants. The current study presents two different case studies, which target two different type of plants: Natural gas combined cycle (NGCC) power plant and Hydrogen steam methane reforming (SMR) plant. The analysis of those two case studies would help to investigate the sorbent suitability for both pre- and post-combustion high temperature capture processes for power and industrial applications.

The methodology in the current Thesis was designed to achieve the research objectives mentioned in chapter 1 for each case study. Figure 3.1 illustrates the workflow that has been followed and shows the methodology adopted in this thesis including the following tasks:

1. Sorbent and process screening
2. Testing sorbent under relevant flue gas conditions
3. Building full plant model with and without capture in Aspen Plus
4. Process optimization and results analysis
5. Compare performance results and penalties to other CO$_2$ capture technologies and perform technical sensitivity analysis
6. Fluidized bed sizing and costing
7. Estimate techno-economic assessment KPIs for each plant
8. Perform techno-economic sensitivity analysis and compare results to other capture technologies.

First, Li$_4$SiO$_4$ sorbent and CO$_2$ capture process technology screening was performed to identify the sorbent performance under relevant flue/industrial gas conditions and determine potential options for process level integration. Second, a two reference cases were chosen for the process integration of the Li$_4$SiO$_4$ / Li$_2$CO$_3$ capture looping system. With respect to sorbent performance, one of the key novelty of the research is that the sorbent is tested under the relevant flue or industrial gas conditions where data does not exist in literature.
Figure 3.1: Workflow indicating the research methodology followed in this study
The sorbent lab test aims to identify CO$_2$ capture performance and kinetics which are used in designing the CO$_2$ capture Li$_4$SiO$_4$/Li$_2$CO$_3$ looping system for each case study. Next, a process model is built in Aspen Plus V.9 for each reference case with and without capture. Following the development of the process model, the model is optimized to improve plant’s efficiency and reduce the heat / energy loss. The optimized process modelling results are used to evaluate the impact of the process integration of the CO$_2$ capture system, and to estimate the power, energy and performance penalties associated with the CO$_2$ capture process. For performance benchmarking, the Li$_4$SiO$_4$/Li$_2$CO$_3$ looping system for each case study is compared to other capture technologies applied for the same reference plant.

Following the previous steps, fluidized bed detailed sizing and costing is performed to estimate the direct equipment cost for the fluidized bed system. After that, direct equipment costing is performed for the rest of plant equipment. Next, a techno-economic assessment is carried out by estimating capital and operational costs for each case study before and after capture, which is followed by estimation of the techno-economic KPIs. Finally, sensitivity analysis for several techno-economic parameters is performed as part of the techno-economic assessment. The following sub sections explain each of the steps within the followed methodology.

### 3.1 Sorbent and process screening

The purpose of this task was to define the sorbent performance under several flue/industrial gas conditions.

This task mainly focused on reviewing the literature and screening the sorbent capture capacity, cyclic performance and kinetics under 100% CO$_2$ concentration to give an initial indication about the sorbent performance as a high temperature chemi-sorbent and estimate its suitability for integration in high temperature power and industrial applications. In parallel to sorbent screening, several power and industrial processes were investigated to ascertain their potential integration with high temperature solid sorbent looping systems for CO$_2$ capture. Due to the similarity of the capture looping technology, the integration of Li$_4$SiO$_4$ based sorbents was decided to follow a similar approach to that for conventional Calcium looping (CaL) systems since it has been applied in several pilot plants [127].

For both case studies, NGCC and H$_2$ SMR plants, reported Li$_4$SiO$_4$ performance lab tests in literature, had already shown relatively good promise [84, 98, 128-130] for its CO$_2$
capture application. Any missing sorbent performance data from the literature was estimated from conducting additional CO\textsubscript{2} capture experimental tests under the relevant flue/industrial gas conditions (see next section). A detailed study for each process was performed to define the sorbent key performance data required as an input for the process model. These data included sorbent conversion as well as absorption and regeneration working temperatures required to achieve the best possible process integration.

### 3.2 Testing sorbent under relevant flue gas conditions

For the NGCC case study, several lab tests were designed to evaluate the expected sorbent performance under relevant conditions. For the SESMR case study, since Li\textsubscript{4}SiO\textsubscript{4} performance data under relevant conditions was available in literature, only one lab test was further required. A typical SESMR gas stream was mimicked to identify the sorbent conversion under SESMR flue gas composition. Sorbent CO\textsubscript{2} capture performance testing was conducted in the lab in a thermogravimetric analyser (TGA). Thermogravimetric analysis (TGA) is an analytical technique used to estimate the material thermal stability by measuring its weight change against time and temperature [131]. The technique can be used in turn to estimate the amount of CO\textsubscript{2} captured and sorbent/CO\textsubscript{2} capture kinetics by measuring the sorbent mass increase against time and temperature when passing a non-adsorbing gas, N\textsubscript{2}, containing a specific amount of the adsorbing gas, CO\textsubscript{2} [132]. Figure 3.2 shows the TGA instrument used in the analysis of Li\textsubscript{4}SiO\textsubscript{4} sorbents under relevant flue/industrial gas conditions.

![Figure 3.2: Thermogravimetric Analysis Instrument (TGA Q500)](image-url)
For the NGCC case study, TGA tests were designed to evaluate the sorbent CO₂ capture capacity, conversion and best absorption and regeneration temperatures under flue gas conditions (composition, temperature, pressure) similar to those of a NGCC plant. Sorbent cyclability was also tested to prove the sorbent durability. For the SESMR case, TGA tests were used to estimate the CO₂ capture capacity and conversion of Li₄SiO₄ under relevant SMR syngas conditions.

For performance testing purposes, pure lithium orthosilicate was prepared as per the best optimized synthesis procedures previously reported [133]. The lab test matrix is detailed in table A.1.1 in appendix A.1, and it was designed to fulfil the following purposes:

1. Verify the synthesized sorbent capture capacity with the values available in literature under 95% CO₂ concentration.
2. Compare sorbent capture capacity with CaO and commercial Li₄SiO₄ under 95% CO₂
3. Identify the best sorbent pre-treatment / activation temperature / conditions
4. Identify the best absorption temperature under NGCC flue gas conditions
5. Compare sorbent cyclic performance with CaO
6. Identify the best regeneration temperature under oxyfuel flue gas conditions
7. Testing the sorbent stability under NGCC/ oxyfuel absorption and desorption cyclic conditions.
8. Estimate sorbent capture capacity and performance under SESMR Syngas CO₂ concentration.

Initially, the synthesized sorbent performance was validated by comparison with previously reported values in the literature. Next, the sorbent was tested under NGCC flue gas concentration, i.e., 4% CO₂. Testing the sorbent under NGCC conditions helped to identify sorbent optimum absorption / regeneration temperatures, cyclic performance and sorbent fractional conversion.

These data were used to build the integrated NGCC Aspen Plus V.9 model. From testing the sorbent under SESMR conditions, the sorbent fractional conversion was defined and compared to results reported in literature under similar conditions. Table 3.1 summarizes the data obtained from the thermogrametric analysis of the Li₄SiO₄ under different CO₂ capture conditions.
<table>
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<tr>
<th>Test Phase</th>
<th>Data</th>
<th>Application</th>
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</thead>
<tbody>
<tr>
<td>Absorption under 4 and 14% CO₂</td>
<td>Sorbent capture capacity and sorbent conversion factor ($X_{carb}$) for both NGCC and SESMR cases</td>
<td>Sorbent conversion factor $X_{carb}$ will be used to build the absorber reactor model in Aspen Plus.</td>
</tr>
<tr>
<td>Temperature programmed Absorption under 4% CO₂ concentration</td>
<td>Identify best absorption temperature under 4% CO₂ concentration for NGCC case</td>
<td>Define the optimum carbonation temperature to be used in building Aspen Plus model</td>
</tr>
<tr>
<td>Temperature programmed Desorption (TPD) under oxyfuel combustion conditions</td>
<td>Identify best regeneration temperature under oxyfuel flue gas conditions</td>
<td>Define the optimum sorbent regeneration temperature desorption temperature to be used in building the Aspen Plus model for both case studies</td>
</tr>
</tbody>
</table>

The equation used to estimate the sorbent conversion factor, $X_{LiASIO4}$, was similar to that used by Puccini et al [134] as following:

$$X_{LiASIO4} \% = \frac{\Delta W}{F_{LiASIO4} \cdot r_s}$$  \hspace{1cm} Eq (3.1)

Where $\Delta W$ is the observed percentage weight change during absorption process, $F_{LiASIO4}$ is the weight fraction of the Li₄SiO₄ in the sorbent and $r_s$ represents the stoichiometric uptake of CO₂ by Li₄SiO₄.
3.3 Building the integrated Process Aspen Plus V.9 Model with the Li₄SiO₄/Li₂CO₃ looping system

The purpose of this task is to build a rigorous Aspen Plus V.9 model for each case study before and after the process integration of the Li₄SiO₄/Li₂CO₃ looping system in order to investigate the thermodynamic, performance and technical impact of the integration of the Li-based CO₂ capture system. This task can be divided into the following subtasks:

3.3.1 Plant Pre-modelling

In this task, a detailed study of the mechanical, chemical and thermodynamic performance of NGCC and SESMR plants was performed. That was achieved by reviewing similar integration studies and solutions applied for other sorbents to identify the possible options to integrate the high temperature sorbents into the reference plant. That helped in choosing the two reference case studies and defining modelling assumptions for each case.

3.3.2 Plant modelling with and without CO₂ capture integration

This task includes building each reference plant steady state process model without capture in Aspen Plus V.9. Next, each reference case process model is built with Li₄SiO₄ based looping system integrated. The high temperature CO₂ capture (HTCC) system was built in Aspen Plus V.9 based on sorbent lab test data obtained under each reference case CO₂ concentration. Each case plant performance is compared with and without the integration of high temperature CO₂ capture (HTCC) system to evaluate the impact of the HTCC system integration.

3.4 Process Optimization and results analysis

The purpose of this task is to optimize and improve the plant performance and efficiency after the integration of HTCC system. That aims reducing the performance and energy penalties associated with the integration of HTCC system.

After the optimization of plant parameters and performance, plant performance results are analysed to identify the key performance factors which are affecting the plant efficiency after integration of HTCC system and give an indication about the possible future improvement to the sorbent / process configuration.

The sub-tasks performed under this section, can be summarized as follows:

- Generate mass balance, heat balance and performance calculation sheets.
• Optimize the heat integration solutions between the HTCC unit and the rest of the plant to achieve the most efficient plant performance.

• Estimate overall plant efficiency (η) and Specific primary energy consumption for CO\(_2\) avoided (SPECCA) to account for the performance and energy penalties associated with CO\(_2\) capture.

• Analysing the thermodynamic impact of the HTCC system integration in each case study. Followed by sensitivity analysis for HTCC operating parameters to check the most affecting parameters on plant performance.

• Benchmarking Li\(_4\)SiO\(_4\) CO\(_2\) capture process performance against other capture processes. That was done by comparing plant process integration results and performance to other CO\(_2\) capture technologies, such as amine-based solvents and calcium looping, integrated in similar type of reference cases.

Following this task, the technical plant performance data is used for calculating equipment cost and plant techno-economic, as described in the following section.

3.5 Techno-economic analysis and benchmarking

This task includes performing the techno-economic evaluation for each case study to calculate several Techno-economic Key Performance Indicator (KPI) parameters. For instance, for NGCC, specific investment, levelized cost of electricity (LCOE) and cost of CO\(_2\) avoided were chosen to be investigated. For the SESMR plant case study, levelized cost of hydrogen (LCOH) and cost of CO\(_2\) avoided were chosen to be investigated as SESMR techno-economic KPIs.

For the NGCC case study techno-economic assessment, two methods were applied in order to investigate the effect of changing the techno-economic assumptions on the final evaluation. The first method applied was the one used in the European Benchmarking Task Force (EBTF) assessment [135]. The second applied method is based on the latest recommendations followed by the UK Department for Business, Energy and Industrial Strategy (BEIS) for assessing and benchmarking new CO\(_2\) capture technologies for power and industrial plants [136]. For the SESMR case study, only the BEIS estimation method for integrating novel CO\(_2\) capture technologies in SMR H\(_2\) production plant was employed.
Before applying techno-economic assessment methods, fluidized bed system sizing and costing is performed based on plant operational data in each case study. Direct equipment costing for rest of plant equipment / units followed, based on published costing tables / charts / correlations for different equipment. After estimating equipment direct costing, techno-economic assessment methods were applied for each case study before and after integration of the CO₂ capture unit. The techno-economic assessment included estimation of capital expenditures (CAPEX) and operational expenditures (OPEX) for each case study before estimating the techno-economic KPIs with each assessment method.

In the BEIS method, carbon taxes are included to estimate the impact of adding the carbon emissions cost to the techno-economic assessment and techno-economic KPIs. Following the initial techno-economic assessment, a sensitivity analysis was performed for several techno-economic factors, using BEIS method without considering carbon tax, to identify the most affecting parameter on plant economics.

Lastly, recommendations for future possible improvements with respect to sorbent and capture unit configuration and integration are provided.

3.6 Summary Table for methodology tasks and relevant objectives

The following table summarizes the relation between the different tasks in the methodology, thesis objectives and relevant thesis chapters.

<table>
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<td>3</td>
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<td>4 &amp; 5</td>
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Chapter 4  PROCESS INTEGRATION CASE 1-NGCC PLANT

4.1 Introduction

Lithium Orthosilicate ($\text{Li}_4\text{SiO}_4$) based sorbents have been studied numerously in literature investigating the reactivity and stability of lithium-based sorbents [16, 92, 98, 128, 137, 138]. This suggests that this group of solids can be applied and integrated using the same technology as the calcium looping [139]. As mentioned in chapters 2 & 3, studies of Li-based capture systems integration into power plants are far more limited than those for CaO-based sorbents, which limits the comparison with other alkali based and metal oxide materials. That means that the sorbent has been barely tested or studied under relevant industrial / practical applications.

As mentioned previously, the key advantage of this technology is its capacity to capture $\text{CO}_2$ from exhaust gases at high temperature, e.g. 500 to 600°C, avoiding excessive cooling. Lab experiment has shown that lithium orthosilicate ($\text{Li}_4\text{SiO}_4$) has a relatively lower regeneration temperature, much higher cyclic stability and relatively higher residual capacity compared to other high temperature solid sorbents. Analysing the Li based sorbents potential of lower regeneration temperature and energy requirement to decrease the energy penalty of this capture system, could provide useful guidance for the future development of synthetic sorbents and improving the system overall technology readiness level. Accordingly, this chapter shows the conceptual process integration study to evaluate thermal integration principles of $\text{Li}_4\text{SiO}_4$ sorbents looping system into an NGCC power plant making use of obtained experiment results evaluated under NGCC flue gas relevant conditions.

The evaluation focused on demonstrating the advantages derived from regenerating the sorbents at lower temperatures compared to those needed in CaO based capture system.

Prior to the process integration assessment, several lab tests were performed on inhouse synthesized $\text{Li}_4\text{SiO}_4$ solid sorbent to choose the most suitable operating temperature under $\text{CO}_2$ concentration, 4%, similar to that for NGCC flue gas. After evaluating the best sorbent operating temperatures, cyclic tests were performed under 4% $\text{CO}_2$ concentration, for absorption, and 70% $\text{CO}_2$ concentration, for the desorption, to reflect the real condition of a HTCC $\text{Li}_4\text{SiO}_4$ looping system. Lab test results are discussed on section 4.3 of the current chapter.
To investigate the impact of varying technical parameters on plant efficiency, sensitivity analysis was performed by varying the sorbent conversion, make up ratio, regeneration temperature and excess O$_2$ in the calciner. The process simulation and sensitivity analysis results are discussed in section 4.5. Other sensitivity analysis was performed to evaluate the impact of using different HTCC configuration such as using heat recuperator between solid streams and using solid steam heat exchanger. This analysis can be found in section 4.6 for possible future improvements, at which potential future improvements were discussed to improve the plant efficiency and lower the capture penalties.

### 4.2 Sorbent thermodynamic assessment

Before starting the modelling and integration of Li$_4$SiO$_4$ based HTCC system into a NGCC plant, the sorbent performance should be evaluated under the plant flue gas conditions to provide more accurate results and give a reliable indication about the real sorbent performance when it is integrated in such application.

In order to identify optimum CO$_2$ capture working conditions under NGCC flue gas (4% CO$_2$ concentration), the CO$_2$ partial pressure – temperature equilibrium was defined as following:

From the definition of the change in Gibbs Energy:

$$\Delta G = \Delta G^0 + RT \ln Q$$  \hspace{1cm}  \text{Eq (4.1)}$$

Where $\Delta G$ is the change in Gibbs energy, $\Delta G^0$ is the change in Gibbs energy at standard conditions, T is temperature in Kelvin, R is the universal gas constant = 8.314 J/mol-K, Q is the reaction quotient of Li$_4$SiO$_4$/CO$_2$ reaction.

As stated by Kotz et al [140], at equilibrium $\Delta G = 0$ and Q=K where K is the equilibrium constant of Li$_4$SiO$_4$ / CO$_2$ reaction. By substituting in Eq (4.1), the following correlation can be obtained:

$$0 = \Delta G^0 + RT \ln K$$

$$\Delta G^0 = -RT \ln K$$  \hspace{1cm} \text{Eq (4.2)}$$

but $\Delta G^0$ can also be substituted as a function of temperature as per the fundamental definition of Gibbs free Energy at standard conditions:

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$  \hspace{1cm} \text{Eq (4.3)}$$

from equations 4.2 and 4.3, the following equation will be resulted:
\[
\Delta H^0 - T \Delta S^0 = -RT \ln K \quad \text{Eq (4.4)}
\]

As reported by Chowdhury et al. [24], the equilibrium constant, \(K\), for a heterogeneous reaction can be obtained from Le Chatelier’s principle [141]:

\[
K(T) = \prod_{i=1}^{\Delta} a_i^{v_i} = \frac{a_p^0 \cdot a_q^0}{a_p^q \cdot a_q^p} \quad \text{Eq (4.5)}
\]

Where \(a_i\) is the activity coefficient and \(v_i\) is the stoichiometric coefficient of species \(i\).

Activity coefficients for solids are generally set =1 [24] and for gases can be defined from the following correlation:

\[
a_i = \frac{f_i^c}{f_i^0} \quad \text{Eq (4.6)}
\]

Where \(f_i^c\) is the fugacity of the gas species in the mixture and \(f_i^0\) is the fugacity of the gas species at standard conditions.

For \(\text{Li}_4\text{SiO}_4/\text{CO}_2\) desorption reaction, the stoichiometric coefficients of each component \(v_i\) can be substituted with 1. By applying Eq (4.5), the equilibrium constant for the desorption reaction can be obtained as following:

\[
K_{\text{des}}(T) = \frac{a_{\text{CO}_2} \cdot a_{\text{Li}_4\text{SiO}_4}}{a_{\text{Li}_2\text{CO}_3} \cdot a_{\text{Li}_2\text{SiO}_3}} \quad \text{Eq (4.7)}
\]

As per [142], since the reaction is heterogenous, the activity coefficients for \(\text{Li}_4\text{SiO}_4\), \(\text{Li}_2\text{SiO}_3\) and \(\text{Li}_2\text{CO}_3\) are equal to 1 and for \(\text{CO}_2\), the activity coefficient is obtained from:

\[
a_{\text{CO}_2} = \frac{f_{\text{CO}_2}}{f_{\text{CO}_2}^0} \quad \text{Eq (4.8)}
\]

where \(f_{\text{CO}_2}\) is the \(\text{CO}_2\) fugacity in the mixture and \(f_{\text{CO}_2}^0\) is the \(\text{CO}_2\) fugacity at standard conditions. By applying the values of the fugacity in Eq (4.7), we get:

\[
K_{\text{des}}(T) = a_{\text{CO}_2} = \frac{f_{\text{CO}_2}}{f_{\text{CO}_2}^0} \quad \text{Eq (4.9)}
\]

Eq (4.9) is identical to the correlation derived by Chowdhury et al. [24], and with the consideration of \(\text{CO}_2\) fugacity at standard condition: \(f_{\text{CO}_2}^0 = P^0 = 1\) bara = 1 atm, and fugacity at mixture conditions:

\[
f_{\text{CO}_2} = y_{\text{CO}_2} P_{\text{mix}} f_{\text{CO}_2} \quad \text{Eq (4.10)}
\]

where \(y_{\text{CO}_2}\) is the molar fraction of the \(\text{CO}_2\) in the mixture, \(P_{\text{mix}}\) is the gas total pressure in the mixture, \(f_{\text{CO}_2}\) is the \(\text{CO}_2\) fugacity coefficient.
By substituting with $f_{CO_2}^0$ and $f_{CO_2}^{-}$ in Eq (4.9), activity CO₂ coefficient can be written as following:

$$a_{CO_2} = y_{CO_2}P_{mix}\phi_{CO_2}$$  \hspace{1cm} \text{Eq (4.11)}

which can be rewrittten using CO₂ partial pressure as:

$$a_{CO_2} = P_{CO_2}\phi_{CO_2}$$  \hspace{1cm} \text{Eq (4.12)}

Presuming that CO₂ is considered as an ideal gas, the gas fugacity coefficient can also be substituted with 1 [142], i.e.:

$$a_{CO_2} = P_{CO_2}$$  \hspace{1cm} \text{Eq (4.13)}

By substituting in Eq (4.9):

$$K_{des}(T) = P_{CO_2}$$  \hspace{1cm} \text{Eq (4.14)}

At the end, by combining Eq. (4.4) and (4.14) and rearranging terms, the relationship between $P_{CO_2}$ and T can be defined from:

$$lnP_{CO_2} = \frac{\Delta H^0 - T\Delta S^0}{RT}$$  \hspace{1cm} \text{Eq (4.15)}

The values of $\Delta H^0$ and $\Delta S^0$ of the CO₂ desorption reaction were estimated based on [143] as $\Delta H^0 = 141.963 \text{ kJ/mol}$ and $\Delta S^0 = 164.646 \text{ J/K} \cdot \text{mol}$.

Figure 4.1 shows the CO₂ pressure - temperature equilibrium curve for the Li₂SiO₄/CO₂ reaction. From this equilibrium curve, it can be noticed that the equilibrium temperature for low CO₂ concentration, such as 4% CO₂, is lower than the values resulted from previously cited works [24, 94, 144-146]. Although Chowdhury, M.B.I et al and Seggiani, M. et al [24, 144] applied the same approach to solve the Gibbs Energy equation, there is an inconsistency between their equilibrium curve results themselves. The reason for such differences can be due to different thermodynamic data used to obtain values of $\Delta H^0$ and $\Delta S^0$. From the work of Zhang, S., et al. and Lopez Ortiz, A., et al. [145, 146], the equilibrium curves were obtained using commercial softwares and it is highly expected to get different results due to using different approaches. Similarly, the results obtained from [94] have been calculated based on the variation of chemical potential of the reaction ($\Delta \mu$).

Focusing on NGCC flue gas conditions, according to figure 4.1, the inversion temperatures for a 0.04 bara CO₂ partial pressure is 470 °C which is much lower than the value obtained from the equilibrium curve in Seggiani et al. [144] as they have obtained 590°C inversion temperature under the same CO₂ concentration.
Hence, we can notice that predicting CO$_2$ - Sorbent equilibrium using thermodynamics cannot give accurate results at lower CO$_2$ concentration such as NGCC flue gas conditions. Based on these finding, we carried out sorbent performance and equilibrium assessment, under NGCC flue gas conditions, using TGA lab test as will be discussed in next section.

4.3 Sorbent performance assessment

Following to the results of thermodynamic assessment of the sorbent under NGCC flue gas condition, 4% CO$_2$ concentration, several tests were performed the Li$_4$SiO$_4$ sorbent under similar gas conditions to decide the suitable practical operating conditions to be used inside the process model. The sorbent used in the lab test was a pure Li$_4$SiO$_4$ in house synthesized sorbent. The sorbent was optimized and synthesized as per the procedures mentioned by Izquierdo, M., et al. [133]. After successfully synthesized the sorbent, several tests were performed using thermogravimetric analysis machine TGA Q500.

The details of performed lab tests were covered in table A.1.1 in appendix A.1. As mentioned earlier, several absorption, desorption and cycling tests were performed on the sorbent at 4 % CO$_2$ gas concentrations to check the sorbent suitability for the NGCC application. For sake of comparing sorbent stability to CaO based sorbents, under similar conditions, pure CaO based sorbent was prepared and tested as well. The results of the
The results for the different lab tests performed with Li$_4$SiO$_4$ sorbent are detailed in the following subsections.

### 4.3.1 Synthesized sorbent pre-assessment

In the beginning of material testing and characterisation, the synthesized sorbent was compared to the commercial Li$_4$SiO$_4$ and CaO prepared sorbent. All samples were tested under 92.5% CO$_2$ concentration gas stream. The CO$_2$ capture capacity was normalized for each sorbent theoretical capture capacity ie 36.7% and 78% for Li$_4$SiO$_4$ and CaO respectively.

![Figure 4.2: Normalized CO$_2$ capture capacity for 1 – Prepared CaO, 2-in house synthesized sorbent, 3- Commercial Li$_4$SiO$_4$. 600°C carbonation temperature. Continuous and dashed lines: sorbents with 600°C pre-treatment and 700°C respectively](image)

As shown in figure 4.2, the in-house synthesized Li$_4$SiO$_4$ based sorbent (sample 2) achieved the highest normalized CO$_2$ capture capacity compared to the prepared CaO sorbent and commercial Li$_4$SiO$_4$ sorbent. This gave an initial indication about the synthesized sorbent reliability under different pre-treatment temperatures. With respect to the performance comparison with the commercial Li$_4$SiO$_4$ sorbent, the optimised procedures for sorbent preparation, adopted from Izquierdo, M., et al. [133], have resulted in better sorbent CO$_2$ capture capacity.

Following to the previous test, a cyclic test under 92.5% CO$_2$ concentration was performed on prepared CaO and synthesized Li$_4$SiO$_4$. The purpose of this test was to get
an indication about the sorbent durability when tested for multiple cycles (more than 10) and compare it to CaO performance under the same conditions. Both sorbents were tested under 600°C carbonation temperature and 92.5% CO₂ concentration and 700°C desorption temperature under 100% N₂.

![Graph of CO₂ absorption and desorption cyclic performance](image)

*Figure 4.3: CO₂ absorption – desorption cyclic performance for a) prepared CaO and b) synthesized Li₄SiO₄ sorbent*

As see from figure 4.3, there is a noticeable decay in the CaO based sorbent cyclic performance compared to the synthesized Li₄SiO₄ which showed a relative stability under 700°C regeneration temperature, within the same 3000 min cyclic time.

### 4.3.2 Determining the sorbent optimum working conditions under NGCC flue gas

The next step following to the cyclic test was to identify the most suitable working conditions for Li₄SiO₄ sorbent under NGCC flue gas condition. Based on that, a temperature programmed CO₂ capture experiment was performed at 4 % CO₂ concentration to identify the best absorption temperature. Figure 4.4 illustrates the temperature programmed CO₂ absorption of synthesized Li₄SiO₄ sorbent under 4% CO₂ concentration.
As seen in figure 4.4, the onset temperature for peak of the absorption process was defined at temperature = 525°C where the maximum carbonation can take place. From this result, we can notice that there is a remarkable difference between the theoretical calculated inversion temperature and that measured from TPA - CO₂ test.

Following to the TPA - CO₂ absorption test and after obtaining an indication about the optimum absorption temperature, three absorption tests were performed to check the sorbent performance under 4% CO₂ at three different temperatures around the onset temperature. The three absorption temperatures were 500, 525 and 550°C. The purpose of this test was to confirm that 525°C was the optimum temperature by comparing the uptake profile to other two temperatures. Figure 4.5 shows the uptake comparison between the three absorption temperatures under 4% CO₂.
Figure 4.5 shows that the highest CO₂ uptake the sorbent occurred at 525°C absorption temperature, this is consistent with the results obtained from the TPA - CO₂ test.

In line with previous results, 525°C, would be considered as the optimum absorption temperature and would be used in the following experiments and in the process model as well.

Following to the TPA - CO₂ test, the sorbent was tested for 4 cycles under 4% CO₂ concentration and temperature of 525°C for absorption and 100%N₂ atmosphere and 700°C to get an indication about sorbent durability under such absorption conditions. Figure 4.6 shows the sorbent performance for 4 cycles under the previous mentioned conditions:

![Figure 4.6: Cyclic test for Li₄SiO₄ sorbent under 4% CO₂ concentration / temperature of 525°C for absorption and 100% N₂ / temperature of 700°C for desorption](image)

From figure 4.6, it can be noticed that the sorbent is stable and was able to be almost fully regenerated at several cycles at temperature of 700°C which is much lower than the normal regeneration temperature of CaO sorbents which is around 850-900°C.

After identifying the optimum absorption temperature and obtaining an indication about sorbent stability under conditions close to NGCC flue gas conditions, it was important to identify the best desorption operating temperature in order to optimize the heat duty in the regenerator. This was achieved by applying the same rationale used to identify the best absorption temperature.
Hence, an absorption experiment was performed under 4% CO$_2$ concentration and 525$^\circ$C. Following to the absorption test, temperature programmed CO$_2$ desorption experiment (TPD - CO$_2$) were performed using TGA under 70% CO$_2$ concentration which is similar to the concentration of the flue gas resulted from oxyfuel combustion inside the calciner. The upper limit for the TPD test was set to 710$^\circ$C which is lower than the Li$_2$CO$_3$ melting temperature at 723$^\circ$C. The TPD - CO$_2$ test results are shown in figure 4.7:

![Figure 4.7: TPD - CO$_2$ for Li$_4$SiO$_4$ sorbent under 4% CO$_2$ concentration](image)

Figure 4.7 shows that the maximum desorption took place at onset temperature around 660$^\circ$C and this value is considered close to that, 675$^\circ$C, obtained from other studies [24, 144, 145] under 70% CO$_2$ concentration. Following to the TPD test, the Li$_4$SiO$_4$ was tested for several cycles under the optimized absorption and regeneration temperatures resulted from TPA and TPD tests. Figure 4.8 shows the cyclic performance for Li$_4$SiO$_4$ under 4% CO$_2$ concentration and 520$^\circ$C for absorption and 70% CO$_2$ concentration and 675$^\circ$C for desorption. It is observed from figure 4.8 that the sorbent CO$_2$ capture capacity is achieved during the cycles and the sorbent can be considered almost fully regenerable in all cycles.
It is worthy to mention that this is considered the first kind of study which includes testing of Li$_4$SiO$_4$ under practical conditions for CO$_2$ capture and regeneration.

Hence based on the lab test results showed in figure 4.8, we can find that the sorbent has shown stability under NGCC absorption conditions and oxyfuel combustion regeneration conditions. In line with these findings, it was decided to choose temperatures of 525°C and 700°C as the working conditions for absorber and regenerator respectively to achieve best plant performance under NGCC relevant conditions. As the sorbent has been tested for several experiments at 525°C absorption temperature and 4% CO$_2$ concentration showing relatively good capture uptake (more than 10% wt) and regenerated at temperatures between 675 to 700°C for several cycles under different concentrations (70% CO$_2$ & 100% N$_2$) showing high stability and the ability to be fully regenerated.

**4.3.3 Identifying sorbent kinetics under NGCC flue gas conditions**

After identifying the optimum sorbent working conditions, it was important to identify the sorbent kinetics input to the model i.e how much practical conversion the sorbent can achieve under NGCC relevant conditions. The conversion has a direct impact on absorber sizing and volume, volume of sorbent recirculation required, and amount of heat required inside the regenerator to regenerate the sorbent. All these factors have a direct impact on the plant as we will be discussed in the modelling section.

For Calcium looping (CaL), Berstad et al [48] have considered 0.2 sorbent conversion when CaL is integrated in NGCC plant. This value was considered taking into consideration the sorbent decay during several cycles. In our case study, we will consider the same conversion of 0.2 and the relevant sorbent residence time to this conversion.
The conversion was calculated based on the lab TGA test data obtained for Li$_4$SiO$_4$ under 4% CO$_2$ concentration and 525°C absorption temperature. The correlation used to sorbent conversion factor $X_{Li4SiO4}$ was similar to that used by Puccini et al [134] described in chapter 3. Figure 4.9 shows the profile of the Li$_4$SiO$_4$ fractional conversion under 4% CO$_2$ concentration and 525°C absorption conditions:

![Figure 4.9: Li$_4$SiO$_4$ sorbent fractional conversion under 4% CO$_2$ concentration and 525 °C absorption temperature](image)

As we see in figure 4.9, at 0.2 sorbent fractional conversion, the sorbent needs 20 minutes residence time inside the reactor.

After identifying the sorbent optimum working conditions and kinetics under NGCC flue gas conditions, these data were used as an input to build the Aspen Plus process model as will be explained in next section.

### 4.4 Process Integration of Li$_4$SiO$_4$ based HTCC into NGCC plant

#### 4.4.1 Modelling approach

For the current study, the CO$_2$ absorption has been modelled based on a fixed value of the fractional conversion of reaction of Li$_4$SiO$_4$ / CO$_2$ reaction. As shown in figure 4.9, under an absorption temperature of 525°C and 0.04 bara CO$_2$ partial pressure and after 20 minutes of contact between the gas and the solid a fractional conversion of 0.2 on molar basis is obtained. Since that CO$_2$ partial pressure is similar to the CO$_2$ partial pressure in the GT exhaust gas, this value has been used in this study.
A precise approach for the simulation of the HTCC plant integration into a NGCC power plant is mandatory to achieve acceptable energy penalties. The case study modelling was performed based on the NGCC power plant are as per European Benchmarking Task Force (EBTF) common framework [135]. A rigorous NGCC model was built in Aspen Plus steady state model and it was used to estimate the plant streams heat and mass balance. For NGCC plant, two main models were created, with and without capture, to estimate the carbon capture associated penalties such as efficiency, power and other electrical penalties. The following subsections includes detail description of each model for this case study.

4.4.2 Base case without capture

The base case plant is based on NGCC power plant which mainly comprises of a gas turbine, heat recovery steam generator and steam turbine. Figure 4.10 shows the conceptual design of a NGCC power plant.

![Figure 4.10: Conceptual design of NGCC power plant](image)

Figure 4.11 shows the process flow diagram of the studied NGCC Power Plant which is considered as a state-of-the-art large-scale power plant. The NGCC reference plant has two identical largescale gas turbine generators (GTGs). Each one of the two units consists of an “F Class” individual gas turbine (GT). The flue gas from the GT is then passed by an HRSG which in turn consists of three pressure levels. The steam generated from each HRSG unit is combined and sent to a single three pressure level steam turbine. In this work, the denotation of 2x1 plant configuration means two gas turbines connected to a single steam turbine. For each HRSG unit, a single medium pressure reheat is considered.
to reheat the intermediate pressure steam before passing through the intermediate steam turbine. The GT natural gas fuel is preheated to 160°C before entering the gas turbine combustion chamber using hot water extracted from the intermediate pressure section in the HRSG. Through the simulation, the GT air-to-fuel ratio is adjusted to be constant and the plant is running under full load operation mode. The location of the plant was considered as an inland location in centre of Europe with cooling towers as the cooling system.

Figure 4.11: Process flow diagram of the state of the art 2x1 NGCC power plant reference case. Single gas turbine and HRSG are illustrated in the process flow diagram

4.4.3 HTCC plant and possible heat integration

Following the generic scheme for CO₂ capture based on high temperature CO₂ capture (HTCC) solids looping, the following Li₄SiO₄/Li₂CO₃ high temperature looping system was conceptually chosen to be integrated in NGCC power plant similar to the high temperature CaL CO₂ capture in previous NGCC integration studies [47, 148, 149]. As illustrated in figure 4.12, the Li₄SiO₄ based sorbent is circulated between absorber (C-1) and regenerator (C-2) for CO₂ capture and regeneration respectively as per reaction R(2.2) with no consideration of any heat recuperation between the circulated solid sorbent streams between the two reactors. As mentioned in the lab test section, 525 and 700 °C were chosen to be the optimum working conditions for CO₂ capture and sorbent regeneration respectively based on experiment result have been obtained from testing Li₄SiO₄ under NGCC relevant conditions [150].
For the current case study, the temperature of the flue gas ($T_1 = 600^\circ C$) is higher than the absorption temperature ($T_{abs} = 525^\circ C$). Thus, it was required to cool the flue gas down to a temperature of 525°C and recover heat. The recovered heat is used to generate high pressure steam through the primary heat recovery system (E-1). After E-1, the CO$_2$ rich flue gas is directed towards the CO$_2$ absorption column (C-1) filled with the regenerated Li$_4$SiO$_4$ received from the regenerator column (C-2). The regenerated lithium sorbents enters the absorber at temperature equal to the regenerator working temperature ($T_{reg} = 700^\circ C$) while the CO$_2$ absorption reaction takes place at absorption temperature of 525°C. Inside the absorber, excess heat is generated from the highly exothermic Li$_4$SiO$_4$ carbonation reaction (142 kJ/mol) [24] besides the temperature difference between the recycled regenerated sorbent and the absorber working temperature. For best utilization of such excess heat, an in-boiler heat exchanger (E-2) was chosen to be integrated inside the absorber. This heat exchanger helps to control the temperature inside the absorber and utilizes the excess heat to heat up/ boil water in the secondary steam cycle.

As mentioned, the sorbent regeneration takes place in the regenerator (C-2) where the CO$_2$ is recovered for transportation. During each carbonation – decarbonation cycle, the
fluidized sorbent is directed to the regeneration column after completing the proper residence time inside the absorber. Direct oxyfuel combustion is used in the regenerator to supply the heat required for the sorbent regeneration without dilution of CO₂ stream. For sorbent fluidization and cycling, the sorbent is considered to be fluidized using the plant flue gas and pure CO₂, in the absorber and regenerator respectively, similar to the design applied in CaL system [151].

To reduce the fuel consumption inside the regenerator, several options of indirect heating and heat integration have been studied in literature as an alternative to oxyfuel combustion. These options were not considered in our model but will be discussed in the possible improvements section.

For sorbent deactivation, although the sorbent has been shown relative stability for multiple cycle under NGCC conditions [150], the model considered a fresh lithium orthosilicate make up stream to be added to the absorber to cover for any minor sorbent deactivation with the consideration of the option of preheating the fresh sorbent with hot CO₂ stream leaving the regenerator. The deactivated / spent sorbent is extracted from the regenerator.

The main concept of the heat integration, with such configuration, is to divide the plants between heat sources and heat sinks, then heat sources and sinks are connected together to achieve the most possible heat integration. The hot pure, CO₂ leaving the regenerator, is directed to a secondary heat recovery system (E-4) to produce steam and generate electricity. An innovative heat integration design was considered to utilize part of the hot CO₂ stream heat to pre-heat the fuel and oxygen feed streams through (E-5) and (E-6) respectively before being fed to the regenerator column. Integrating such HTCC configuration in a NGCC plant results in flexibility in the modes of the operation of the plant. For instance, the primary steam cycle can operate with / without the capture unit working whenever needed. In addition to that and as mentioned, several heat integration sources are available in such system which helps to achieve optimum heat recovery and minimize the penalties associated with CO₂ integration.

4.4.4 **NGCC Plant model with HTCC plant integrated (Base case with capture)**

In this model, a 2x1 combined cycle identical to the base case was considered for Li₄SiO₄ based HTCC plant integration. Figure 4.13 illustrates the block flow diagram for the base NGCC case with capture.
Figure 4.13: Conceptual Integration of CO₂ Post Combustion capture in NGCC Plant

The HTCC is integrated to the plant to capture CO₂ from the hot flue gas stream exiting the gas turbine. The flue gas temperature at the GT exit is around 600°C, which is higher than the absorber chosen operating temperature, $T_{abs} = 525°C$. For the best utilization of the hot flue gas heat and to minimize the plant modification, the hot flue gas is extracted from the primary HRSG after the intermediate pressure (IP) superheaters at the temperature of 525°C and passed through the HTCC unit. After capturing CO₂ from the hot flue gas, the clean flue gas exiting the absorber will be directed back to the primary HRSG at the temperature of 525°C to complete the heat recovery in the primary HRSG. The hot CO₂ exiting the regenerator is utilized to generate steam and electricity through the secondary HRSG and secondary steam turbine.

Figure 4.14 shows detailed process flow diagram for the NGCC power plant after integration of HTCC plant.
As shown in figure 4.14, the configuration of the capture unit is based on the scheme for HTCC unit as mentioned previously and showed in figure 4.12.

The sorbent is regenerated in the regenerator (C-2) by providing the heat required to reverse the reaction R (2.2) towards the reactants. Oxyfuel combustion is used to provide the required heat for sorbent regeneration in the regenerator which in turn requires the addition of extra natural gas to be burned with oxygen inside the regenerator. For oxygen production, a typical air separation unit (ASU) is used to produce a 95% pure O$_2$ stream. The ASU was assumed to consume 200 kWh/t O$_2$ as per (Berstad et al., 2012). The oxygen-to-fuel ratio in the regenerator was set to achieve 3% excess oxygen for the fuel combustion reaction. The oxyfuel combustion temperature inside the regenerator was adjusted by dilution of the 95% pure O$_2$ stream with a CO$_2$ recycle stream extracted from the hot CO$_2$ stream exiting the regenerator, to achieve final 35% O$_2$ purity (mol basis) before entering the regenerator[152, 153].

The main hot CO$_2$ exiting the regenerator is passed by single pressure HRSG unit to generate high pressure superheated steam. For further details, please refer to the material balance in appendix A.2.
A single train 3 pressure stages steam turbine is used to generate electricity from the high pressure (HP) steam generated in secondary HRSG. The intermediate pressure (IP) steam exiting the HP steam turbine (K-6) is being directed to IP reheat system where part of the hot CO$_2$ heat is used to reheat the IP steam before entering the IP steam turbine (K-7). The low pressure (LP) steam exiting the IP steam turbine is passed through the LP steam turbine (K-8) to complete the electricity generation in the secondary steam cycle. The final steam exiting the LP turbine (K-8) is being condensed using cooling water system before being pumped back to the secondary HRSG. In this design, a novel heat integration was considered by utilizing part from the heat of hot CO$_2$ stream in heating up the fuel and oxygen in E-11 and E-12, respectively before entering the regenerator. This helped to optimize the sorbent regeneration energy consumed inside the regenerator.

As mentioned earlier, excess heat from the HTCC unit and absorption exothermic reaction heat is recovered in a secondary HRSG using HPE-3 and HPB-2 heat exchangers similar to the case study of (Berstad et al., 2012 [48]). Extraction of the heat from the absorber using two heat exchangers helps to control the temperature inside the absorber equal to the absorption temperature $T_{abs} = 525 \, ^\circ C$. The steam generated from the absorber heat exchangers is passed to a high-pressure super heater to achieve more superheating before entering the HP steam turbine.

Before final CO$_2$ compression train, the hot CO$_2$ stream is passed to another heat exchanger (E-9) to heat up the make-up stream before being fed to the absorber to minimize the energy penalty in HTCC unit.

The final CO$_2$ stream, leaving the secondary HRSG, is compressed using 4 stage compressor train to achieve 110 bara final transportation pressure as per EBTF [154]. Figure 4.15 illustrates the process flow diagram of the 4 stages CO$_2$ compression train with intercooling to 30ºC after each stage similar to the cooling scheme followed in base case. A knock-out drum (KOD) is used after each intercooler, to eliminate any water condensate from entering the next compression train.
The conceptual design of the HTCC plant was done with the following assumptions: a) very small sorbent makeup flow rate (0.01 kg fresh sorbent / kg circulated regenerated sorbent) and as a result, no heat recovery was considered from the spent sorbent; b) no heat integration with the CO₂ compression train was considered; c) The absorption heat is generated at fixed temperature (525°C) and is used in pre-heating the high-pressure feed water and generate superheated steam; d) A single intermediate pressure re-heat was considered to achieve low pressure steam dryness fraction (> 90%) at the low-pressure steam turbine exhaust and improve steam cycle efficiency in the secondary HRSG.

The absorber was modelled in Aspen Plus as a stoichiometric reactor with fixed sorbent fractional conversion (20% on molar basis) which was considered similar to the conversion value used for the integration of CaO sorbents in NGCC plants [148]. The absorber performance was set to achieve 90% fixed CO₂ capture at absorber working temperature of 525°C.

The absorber unit operating pressure was set to be 1 bara and a solid gas separator was considered at the absorber exit to separate the suspended solids from flue gas stream with 100% assumed efficiency, similar to the assumption of Astolfi et al [218]. The regenerator was modelled using a Gibbs reactor which is based on Gibbs free energy minimization. The regenerator was set to operate at 1 bara pressure as well and full sorbent regeneration was assumed. Similar to the absorber, a solid-gas separator unit is considered at the regenerator exit to split any suspended solids from the hot CO₂ stream with 100% assumed separation efficiency. The following sections will discuss the model evaluation parameters and integration. For summary of the assumptions, please refer to appendix A.2.
4.4.5 Model and HTCC integration assessment parameters

Based on the previous mentioned assumptions, the following efficiency related terms were calculated to evaluate the impact of the HTCC plant on NGCC power plant performance after the integration and to compare to other CO$_2$ capture technologies:

4.4.5.1 Net Plant efficiency ($\eta$) was estimated as follows:

$$\eta = \frac{W_1 + W_2}{(m_1 + m_2) \cdot H_c}$$

Eq (4.16)

At which, $W_1$ is the net power output of the gas turbine and primary steam cycle in (MW$_{th}$) and $W_2$ is the net power output of secondary steam cycle in (MW$_{th}$), $m_1$ and $m_2$ are the natural gas mass flows (kg/s) to the gas turbine combustion chamber and the regenerator respectively, and $H_c$ is the low heat value of the fuel (L.H.V) in (MJ/kg).

4.4.5.2 Specific Primary Energy consumption for CO$_2$ avoided (SPECCA):

The specific primary energy consumption for CO$_2$ avoided (SPECCA) in GJ/tCO$_2$ was calculated from the following formula [155]:

$$SPECCA = \frac{HR_{CC} - HR_{REF}}{E_{REF} - E_{CC}} = \frac{3600 \cdot \frac{1}{\frac{1}{E_{CC}} - \frac{1}{E_{REF}}}}{E_{REF} - E_{CC}}$$

Eq(4.17)

Where $HR_{CC}$ and $HR_{REF}$ are the heat rate (kJ/kWh) for the plant with the capture unit and reference plant, i.e. before integrating the capture unit, respectively, and $E_{CC}$ and $E_{REF}$ are CO$_2$ emission rate in (kgCO$_2$/kWh) for the plant with the capture unit and reference plant, respectively.

4.4.5.3 Electricity output penalty (EOP):

As explained in [156], EOP is equivalent to the total net power reduction, after integrating the HTCC unit, in kWh/tCO$_2$. EOP estimation takes into consideration all power losses from all plants units per unit mass flow of CO$_2$ to final transportation pipeline. The following formula explains the EOP:

$$EOP = \frac{(m_1 + m_2) H_c}{\eta_{ref}} \frac{(W_1 + W_2)}{m_{CO2}}$$

Eq(4.18)

Where, $\eta_{ref}$ is the reference plant efficiency (58.3 % L.H.V), before integrating HTCC unit, and $m_{CO2}$ is the CO$_2$ mass flow to the final transportation pipeline in (t/h).
4.4.5.4 Marginal thermal efficiency of the oxyfuel coombustion in the regenerator:

This parameter measures the thermal efficiency of the additional consumed natural gas in oxy-combustion generator as explained by Díaz, A.G., et al. [157] and is defined by the following formula:

\[ \eta_{\text{marg}} = \frac{W_2}{m_2H_e + H_r} \]  

Eq(4.19)

Where \( H_r \) is the heat of \( \text{Li}_4\text{SiO}_4/\text{CO}_2 \) reaction in (MW)

4.5 Integration results and discussion

In this section, the results of the simulation are discussed including the simulation results of the reference case with and without capture. Also, the result of sensitivity analysis of technical parameters is discussed as well. The sensitivity analysis investigated the impact of the \( \text{CO}_2 \) capture integration on power plant’s efficiency and specific energy demand. The following technical parameters were varied to perform the sensitivity analysis:

- Sorbent fractional conversion
- Sorbent make up ratio
- Excess \( \text{O}_2 \) in the \( \text{CO}_2 \) stream exiting the regenerator
- Sorbent regeneration temperature.

As a possible improvement for heat integration, two extra cases were modelled with solid-solid heat recuperator and solid steam heat exchangers, respectively. The integration impact is investigated with respect to net plant efficiency and specific energy demand in the HTCC unit. The simulation results are also compared to other capture technologies reported in the literature. Finally, possible future possible improvements to the model are discussed to be considered in future studies.

4.5.1 Evaluation of Net plant efficiency after HTCC integration

The simulation results for the reference case with and without HTCC unit integration is summarized in table 4.1.

As we can see in table 4.1, net plant efficiency, \( \text{CO}_2 \) emissions, EOP and SPECCA were calculated before and after the \( \text{CO}_2 \) capture integration. Table 4.1 also includes a breakdown for the gross power output from the overall plant including the gross power from gas turbine, primary and secondary HRSGs, and overall net plant power output after
deducting the power consumed by the ancillaries and auxiliaries equipment inside the plant such as CO₂ compression train, ASU and cooling pumps. All these parameters were used to compare the modelling results with other technologies.

Table 4-1: Summary of modelling results for NGCC base case before and after the integration of HTCC unit operating at 525 °C absorption temperature, 700°C regeneration temperature, 0.2 fractional conversion and 0.01 make up ratio and excess 3 % O₂.

<table>
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<tr>
<th>Parameter</th>
<th>Unit</th>
<th>NGCC base case</th>
<th>NGCC with capture</th>
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<tr>
<td>Fuel flow rate</td>
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<td>Gross power output</td>
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<td>Gas turbine output (x1)</td>
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<td>275</td>
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<td>Primary Steam turbine output</td>
<td>MW</td>
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<td>287.7</td>
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<tr>
<td>Secondary steam turbine power output</td>
<td>MW</td>
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<td>266.3</td>
</tr>
<tr>
<td>Net power output</td>
<td>MW</td>
<td>829.9</td>
<td>1001.6</td>
</tr>
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<td>kWh/tCO₂</td>
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</tbody>
</table>

As seen in table 4.1, the net and gross plant power output has been increased compared to the original values of the plant without capture. The increment of the plant power output is due to the addition of the secondary steam cycle and steam turbines which supplement the gross plant power output with 266.3 MW. However, from the other hand,
the net plant efficiency for the NGCC power plant with HTCC unit integration has dropped to 49.1% with a 9.2% points reduction of net efficiency comparing to the base modelling case without CO₂ capture, 58.3%. This efficiency reduction is mainly due the increase of fuel consumption due to oxyfuel sorbent regeneration in addition to the electricity consumed by the ASU and CO₂ compressors.

In addition to net plant efficiency reduction, other electricity and power penalties were calculated using EOP and SPECCA. For the plant with HTCC integrated, EOP and SPECCA were estimated to be 455.6 kWh/tCO₂ and 3.6 GJ/tCO₂ respectively. On the other hand, the CO₂ emissions were reduced from 351.6 to 30.7 kg/MWh which achieves a reduction of 91% of the CO₂ emissions after capture.

By analysing the energy penalties associated with the HTCC integration, it was found that the extra fuel consumption, due to oxyfuel sorbent regeneration in the regenerator, is the largest contributor to the efficiency penalty. Figure 4.16 shows breakdown of EOP.

![Figure 4.16: EOP breakdown in kWh/tCO₂](image)

As shown in figure 4.16, fuel penalty contributes to the major part of EOP followed by CO₂ compressors. For the rest of the ancillaries, ASU is the most power consuming units inside the plant due to it high energy consumption (200kWh/tCO₂), compared to the rest of the ancillaries such as pumps and blowers.

This means that the overall plant efficiency after the capture can be improved if the main energy / power consumers are optimized. For instance, if a lower power consumption ASU can be developed and integrated, then the ancillary power consumption could be...
reduced and in turn, the CO₂ capture integration penalty. Similarly, the CO₂ compressors power consumption could be optimized and reduced by applying a lower inter-cooling temperatures compression scheme where the final CO₂ stream is cooled below its critical point (25.5°C at 84.3 bara). Such CO₂ compression scheme can be applied using sea water cooling option to achieve final CO₂ stream in liquid phase and pump it through the final CO₂ transportation pipeline.

### 4.5.2 Technical feasibility of HTCC integration on power plant

To achieve a feasible HTCC integration into power plant, several aspects should be considered such as thermodynamic impact, mechanical integration impact and the final cost impact. In this section, we will discuss the impact of CO₂ capture integration with respect to overall plant thermodynamics and potential of mechanical modification in original plant. This could help to prove the feasibility of achieving such integration in NGCC plant.

As described in section 4.4, to capture CO₂ from the flue gas, the flue is being directed towards the absorber at temperature equal to the absorption temperature \( T_{abs} = 525 \) °C). After the CO₂ being captured, the clean flue gas is being directed back to the main HRSG at a temperature almost equal to the same extraction temperature (525°C) to avoid any disturbance in the heat integration in the rest of heat exchangers in the main HRSG. However, due to the reduction of CO₂ emissions in the flue gas by 90%, the mass flow of the returned flue gas is lower than that of the original flue gas. As a result, the heat capacity of the returned flue gas would be slightly lower than its value for the flue gas before CO₂ capture. To investigate the effect of the change of the flue gas heat capacity on the primary HRSG, T-Q curves for the primary HRSG are shown in figure 4.17.

Figure 4.17 illustrates the primary HRSG T-Q curves a) before the integration of HTCC unit and b) after the integration of HTCC unit. From figure 4.17, we can notice that for the main flue gas TQ line (red line), the slope has been slightly changed after the integration of HTCC unit. This is due to the lower specific heat the flue gas has after the extraction of CO₂ in the absorber and also due to the slight difference between the temperature of the flue gas before and after the absorber. In addition to that, we can notice that the pinch points at low, medium and high pressure levels have been slightly decreased.

Despite previous changes, all these changes could be considered minor changes and their thermodynamic impact on the primary HRSG performance is negligible.
This means that it is still viable to modify the primary HRSG, to do the CO₂ capture integration, from a thermodynamic point of view without a major impact on HRSG performance.

Regarding equipment modifications and mechanical integration, as a conceptual design, there are several options to mechanically integrate the capture unit inside the NGCC plant. For considering designing a new NGCC plant with carbon capture integrated, the primary HRSG could be divided in two modules with the capture unit in between so that the temperature of flue gas (600°C) can be used in the primary HRSG to super heat / reheat the steam before the CO₂ capture process at 525°C.

For existing NGCC plant retrofitting:

- Either existing primary HRSG is modified to accommodate the absorber and regenerator columns, which seems to be a challenging modification due to the space limitation inside the main HRSG
- Or the Gas Turbine flue gas could be used in superheating high pressure steam generated from the secondary HRSG to reduce the flue gas temperature to the absorption temperature (525°C) before entering the absorber.

The latter case needs to reheat the treated flue gas exiting the absorber at 525°C to 600°C by exchanging heat with hot CO₂ stream leaving the regenerator at (700°C) so that the
flue gas can enter the primary HRSG at its original HRSG flue gas inlet temperature of 600°C, similar to HRSG design for the base case without capture as showed in figure 4.11. Although, there is no modification required in the primary HRSG if this option is applied, but it needs mechanical modification in the GT exhaust bypass system to divert the flue gas to the capture unit instead. In addition to that, there will be an energy penalty due to cooling and heating up of the flue gas before the primary HRSG.

4.5.3 Comparison to other capture technologies

This section compares the NGCC power plant with HTCC integration with other CO₂ capture technology integrated in the same NGCC reference plant. Table 4.2 shows the comparison between Li₄SiO₄ based HTCC integration into NGCC power plant and different CO₂ capture systems applied to the same reference plant. The other applied CO₂ technologies are MEA which is the basic amine-based solvents, CESAR-1 which is an advanced solvent consists of a blend of two amines. The third technology compared is CO₂ capture using CaO based high temperature sorbents.

Table 4.2 shows the gross and net power output for each technology with gross power breakdown. Also, it shows the Net plant efficiency, SPECCA, EOP and CO₂ emissions to get an indication about the penalties associated with the integration of each technology and final amount of final CO₂ emissions. From the results shown in table 4.2, the gross power output of the Li₄SiO₄ HTCC integration case (1104.0 MW) is much higher all other technologies due to the nature of the integration or the configuration of the original plant.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Base case</th>
<th>MEA</th>
<th>CESAR-1</th>
<th>CaCO₃</th>
<th>Li₄SiO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>[-]</td>
<td>[158]</td>
<td>[158]</td>
<td>[148]</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>Gross power output</td>
<td>MW</td>
<td>837.3</td>
<td>759.9</td>
<td>770.7</td>
<td>627.6</td>
<td>1104.0</td>
</tr>
<tr>
<td>Gas turbine (x1)</td>
<td>MW</td>
<td>274.6</td>
<td>272.1</td>
<td>272.1</td>
<td>270.2</td>
<td>275</td>
</tr>
<tr>
<td>Steam turbine</td>
<td>MW</td>
<td>288.1</td>
<td>215.7</td>
<td>226.5</td>
<td>135.0</td>
<td>287.7</td>
</tr>
<tr>
<td>2nd Steam turbine</td>
<td>MW</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>222.4</td>
<td>266.3</td>
</tr>
</tbody>
</table>

Table 4-2: Comparison of integration results into NGCC plant for different capture technologies
<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Net power output</strong></td>
<td>MW</td>
<td>829.9</td>
<td>709.9</td>
<td>722.6</td>
<td>559.5</td>
</tr>
<tr>
<td><strong>Net Plant efficiency</strong></td>
<td>%L.H.V</td>
<td>58.3</td>
<td>49.9</td>
<td>50.8</td>
<td>45.6</td>
</tr>
<tr>
<td><strong>CO₂ removal efficiency</strong></td>
<td>% of Flue gas CO₂</td>
<td>NA</td>
<td>90</td>
<td>90</td>
<td>90.3</td>
</tr>
<tr>
<td><strong>CO₂ emissions</strong></td>
<td>kg/MWh</td>
<td>351.6</td>
<td>41.1</td>
<td>40.4</td>
<td>30.6</td>
</tr>
<tr>
<td><strong>Penalty points</strong></td>
<td>%</td>
<td>8.4</td>
<td>7.6</td>
<td>12.5</td>
<td>9.2</td>
</tr>
<tr>
<td><strong>SPECCA</strong></td>
<td>GJ/tCO₂</td>
<td>3.4</td>
<td>2.9</td>
<td>5.4</td>
<td>3.6</td>
</tr>
<tr>
<td><strong>EOP</strong></td>
<td>kWh/tCO₂</td>
<td>456.9</td>
<td>408.6</td>
<td>659.7</td>
<td>455.6</td>
</tr>
</tbody>
</table>

For instance, for MEA and CESAR-1, the base case without capture is identical to the case we applied the Li₄SiO₄ HTCC to, i.e. the same plant size, but no secondary steam cycle was considered for any of the two amines based solvent integration cases. For the CaO based sorbent, a secondary HRSG and steam cycle was considered, and the case followed the EBTF guidelines for the reference case except that the original modelled reference plant is based on a 1 x 1 gas turbine – steam turbine configuration while 2 x 1 arrangement has been considered for the other technologies.

Although Li₄SiO₄ HTCC integration case achieved the highest gross and net power output, but it could not achieve the highest efficiency and lower penalties compared to the rest of technologies. As noticed from table 4.2, the Li₄SiO₄ HTCC integration case achieved higher net plant efficiency and lower SPECCA and EOP when compared to CaO based technology with 90% CO₂ capture rate.

However, when the Li₄SiO₄ based system is compared to the MEA and CESAR-1 technologies, we could find the Li₄SiO₄ HTCC based system achieved a net plant efficiency (49.1% L.H.V) lower than that obtained from CAESAR-1 solvent (50.8% L.H.V) and very close to that obtained from basic amine solvent technology (49.9% L.H.V).

For the specific primary energy consumption for CO₂ avoided (SPECCA), the Li₄SiO₄ integration case has achieved a value of 3.6 GJ/tCO₂ which is lower than that of CaO based sorbent (5.4 GJ/tCO₂) and higher than the SPECCA values obtained from amine and CAESAR-1 systems (3.4 and 2.9GJ/tCO₂ respectively).
For the electricity output penalty (EOP), the $\text{Li}_4\text{SiO}_4$ based case achieved lower EOP (455.6 kWh/tCO$_2$) compared to CaL and basic amine solvent systems (659.7 and 456.9 kWh/tCO$_2$ respectively) but higher than that obtained from CESAR-1 integration case (408.6 kWh/tCO$_2$).

Looking at the calcium looping technology, the CaO based CO$_2$ capture system was found to have higher power and energy penalties, compared to $\text{Li}_4\text{SiO}_4$ based system, since CaO based sorbent has a relatively low sorbent residual capacity after being exposed several carbonation / regeneration cycles. In addition, the CaO based sorbents are generally regenerated under high temperatures (around 900°C) compared to $\text{Li}_4\text{SiO}_4$ regeneration temperature (around 700°C).

For $\text{Li}_4\text{SiO}_4$ based sorbents, if they can be synthesized and produced at large scale with the same performance achieved at the lab scale, it is possible that the sorbent can be integrated in NGCC with optimum regeneration conditions achieving almost zero make up [159]. In similar case, the overall plant efficiency and CO$_2$ capture integration penalties could be similar to the those obtained from this work.

Also, it is worth mentioning that the power and electricity penalties associated with $\text{Li}_4\text{SiO}_4$ and CaO based CO$_2$ capture systems could be further improved if heat recuperator is considered between the two fluidized sorbents streams exiting the absorber and regenerator similar to that proposed by Berstad et [159]. This design was not considered in our base case model, but it is modelled separately as a possible improvement scenario. This will be discussed at the end of this chapter.

With respect to the amine-based technology, MEA and CESAR-1, both perform better than the $\text{Li}_4\text{SiO}_4$ with respect to net plant efficiency and SPECCA. However, for EOP, $\text{Li}_4\text{SiO}_4$ has achieved better EOP (455.6 kWh/tCO$_2$) compared to basic MEA (456.9 kWh/tCO$_2$). The main reason of the lower EOP value, compared to MEA system, is that MEA system needs to extract part of the generated steam to regenerate the solvent in the regenerator which had a direct impact on the plant electricity output and EOP.

Although amine technology capture systems have shown relatively better plant efficiency and lower energy penalties, they have issues with respect to solvent and degradation products emissions which could result in a potential environmental hazard [160].

Also, it is worth mentioning that better process integration results could be obtained if better $\text{Li}_4\text{SiO}_4$ sorbent is synthesized to capture CO$_2$ with better kinetics and lower
regeneration temperatures. Hence, the Li$_4$SiO$_4$ sorbent-based solution could be an attractive alternative to other CO$_2$ capture technologies.

To have a better assessment for the proposed technology, technology readiness level should be discussed as well. For amine solvent CO$_2$ capture systems, they have been demonstrated already at medium to large scale (ca. 150 MW [161]) and for CaO based CO$_2$ capture system, it has been implemented in a pilot scale of 2MW$_{th}$[162]. On the other hand, Li$_4$SiO$_4$ high temperature sorbents have only been tested at small laboratory scale. However, based on CaL existing technology knowledge, Li$_4$SiO$_4$ based capture system could be developed faster to reach the application stage and readiness level following similar steps to the CaL technology.

4.5.4 Energy demand analysis

To achieve the required Li$_4$SiO$_4$ based HTCC integration into the NGCC plant as explained in section 4.4 with lowest energy penalties, it is required to recover the maximum amount of heat from all available sources of heat inside the plant. That can be implemented by recovering the heat available in hot CO$_2$-lean flue gas leaving the absorber and hot CO$_2$ rich stream leaving the regenerator in addition to the exothermic heat generated in the absorber. All the heat recovered should be used in steam production and electricity production.

For sorbent regeneration, the energy required inside the regenerator should cover the heat input required to force R(2.2) reaction towards the reactants side and also it should provide the required sensible heat to raise the solids and gaseous streams to the regenerator operating temperature. For CO$_2$ capture inside the absorber, the model was configured to achieve 90% fixed CO$_2$ capture during absorption on molar basis. As per this configuration, the endothermic heat, required inside the regenerator to reverse the reaction R (2.2), is considered to be constant as well.

With respect to the additional sensible heat required to increase the solids and unburned gases inside the regenerator to 700°C, it can be estimated for the following sensible heat general formula:

$$Q_{sens} = m \cdot C_p \cdot \Delta T$$  \hspace{1cm} \text{Eq (4.21)}

To apply this equation on the solid sorbent, m would be the solid sorbent flow rate, $C_p$ would be the specific heat for the solids and $\Delta T$ is the difference between the absorber and regenerator working temperatures. For the oxyfuel gases, m is considered the mass
flow rate of the unburned O2-CO2 mixture, \( C_p \) is the specific heat of the O2-CO2 gas mixture, \( \Delta T \) is the difference between the regenerator working temperature and temperature of gases entering the regenerator. Based on Eq (4.21), the main factors affecting the energy demand in the oxyfuel regenerator are the regenerator working temperature, the mass flow rate of the circulated sorbent and the amount of oxygen entering the regenerator. Any variation in these factors, is expected to result in a remarkable change in fuel consumption which is in turn affecting the overall plant efficiency.

Since the main affecting parameter in plant efficiency is highly correlated with amount of recovered heat and how it was converted to electricity besides the amount of extra fuel consumed due to the integration. In order to identify the most affecting technical parameters with respect to net plant efficiency and electricity and energy penalties, sensitivity analysis was applied to different technical parameters in line with previous energy demand analysis. The chosen sensitivity parameters are sorbent regeneration temperature, sorbent fractional conversion during the absorption process, sorbent make up ratio and amount of excess oxygen in oxyfuel gases exiting the regenerator. All parameters were investigated against the net plant efficiency (L.H.V), specific energy demand in the regenerator and SPECCA in GJ/tCO2.

The sensitivity analysis was performed by varying each parameter above and below the value used in the base case model. For instance, for sorbent fractional conversion, a variation of ±25% from the base case value of 0.2 (i.e., 0.15, 0.25) was considered. For regenerator working temperature and sorbents make up ratio, variations of ±2% (i.e., 685, 715°C) and ±50% (i.e., 0.05, 0.015) with respect to base case model values were applied, respectively. For excess O2 value, variation of ±33% (i.e., 2%, 4 %) with respect to base case model value, 3%.

Figures 4.18, 4.19, 4.20 and 4.21 illustrate the impact of variation of sorbent fractional conversion, regeneration temperatures, make up ratio and excess O2 in oxyfuel combustion on net plant efficiency, specific regeneration requirements, SPECCA and EOP respectively.
Figure 4.18: Effect of changing HTCC plant parameters on Net plant efficiency

Figure 4.19: Effect of changing HTCC plant parameters on sorbent specific regeneration energy demand in GJ/ton CO₂.
Figure 4.20: Effect of varying HTCC unit parameters on SPECCA in GJ/tCO₂

Figure 4.21: Effect of varying HTCC unit parameters on EOP in kWh/tCO₂
From previous figures, we can conclude that the regenerator working temperature is the most affecting parameter and has the biggest impact on plant efficiency, SPECCA, EOP and sorbent regeneration energy. This can be observed from the slope of each line in each graph as the desorption temperature effect has the highest slope amongst all other parameters with respect to plant efficiency, electricity and energy penalties as seen in previous figures.

Also, we can observe that the sorbent fractional conversion has the second highest impact on performance measuring parameters.

This observation is in agreement with the earlier discussion in the beginning of current section. Reducing the desorption temperature results in reducing the term $\Delta T$ in Eq (4.21), when applied for both sorbent and oxyfuel combustion gases sensible heat equations. This will in turn reduce the required sensible heat which then lead to reducing the regeneration energy consumptions inside the regenerator. Additionally, regenerating the sorbent at lower temperature leads to reduce the amount of fuel consumed in regenerator. This directly leads to improve the overall net plant efficiency.

Looking at the second highest affecting parameter, the fractional conversion, since it is considered as a measure for the amount of Li$_4$SiO$_4$ conversion to Li$_2$CO$_3$ during absorption process and hence it has a direct link with the amount of CO$_2$ captured during absorption process i.e more CO$_2$ is captured. Looking back at the absorber modelling assumption that 90% of CO$_2$ molar basis from the flue gas is captured inside the absorber, this means that sorbent with higher fractional conversion can achieve the 90% CO$_2$ capture with less amount of sorbent compared to sorbent with lower fractional conversion. This means that the higher sorbent fractional conversion, the lower sorbent flow rate required to achieve the CO$_2$ capture target. As a result, optimizing the sorbent and absorption conditions to achieve higher sorbent fractional conversion could result in reducing the sorbent regeneration energy consumption during desorption process and hence more energy is saved. In addition to that, reducing the sorbent inventory in HTCC unit leads in turn to minimize the fuel consumed to bring the sorbent to the regeneration temperature during the regeneration process. That results directly in higher plant efficiency.

For variation of the sorbent make up rate, similar to the discussion of the sorbent fractional conversion, to increase the makeup ratio, it is required to increase the amount of fresh sorbent batch entering the absorber. This leads to a higher energy consumption
to bring the fresh sorbent to the absorption temperature which means more loss in energy and more consumption of fuel and lower plant efficiency.

For the last parameter, the amount of oxyfuel excess O\textsubscript{2}, it was found that reducing the excess O\textsubscript{2} by 33\% would lead to direct reduction in EOP and hence a direct increase in the net plant efficiency. This is normally due to the reduction in electricity consumption in ASU due to lower O\textsubscript{2} consumption. Besides, lower O\textsubscript{2} inside the regenerator would reduce the sensible heat required to raise the oxyfuel gases to the regenerator temperature.

Figures 4.18 – 4.21 have shown also that the desorption temperature is a strong contributor to the overall efficiency and energy and electricity penalties. However, the desorption temperature cannot exceed upper and lower limits. Since the desorption temperature cannot exceed a temperature of 723°C as there is a risk that the lithium carbonate would melt which may lead to operational issues inside the fluidized bed. Also, the lower desorption temperature should not go below 660°C based as showed by lab test results performed under 70% CO\textsubscript{2} concentration Li\textsubscript{4}SiO\textsubscript{4} regeneration conditions and obtained from by Izquierdo et al [163].

On the other hand, from figures 4.18-4.21, the Li\textsubscript{4}SiO\textsubscript{4} fractional conversion can be varied in a larger limit and can also be further improved, for instance by altering the sorbent preparation procedures [164]. This could help to achieve a notable impact on plant efficiency and regeneration energy consumption. Based on the obtained results, the effect of varying fractional conversion only would be further investigated in the following section.

\textbf{4.5.5 Heat integration in the secondary HRSG and impact of different sorbent fractional conversions}

To recover heat from the process a single pressure steam cycle is used as illustrated in figure 4.14 and briefly introduced in section 4.4. The absorption heat is supplied at constant temperature (525°C) and is used to pre-heat the high-pressure feed water, generate and super-heated steam. Additional superheating of the steam is possible using the excess heat from the CO\textsubscript{2} product stream. A single re-heat of the intermediate pressure steam is used to achieve suitable values of dryness fraction at the low-pressure steam turbine exhaust and improve steam cycle efficiency. During the sensitivity analysis, the live steam and condenser pressures have kept constant (149 bara and 0.048 bara, respectively) in all cases. Moreover, the inlet pressure of intermediate pressure and low-pressure turbines were kept fixed. For secondary HRSG heat exchangers, the operating
conditions (temperature and pressure) for all the water/steam–CO$_2$ heat exchangers were nearly kept constant in all simulations. The water/steam flow rate was adjusted for each case study to accommodate the exothermic energy change in the absorber resulted from varying the sorbent recirculation rates as described previously. The considered isentropic efficiencies for the high, intermediate and low pressure turbines are 0.92, 0.94 and 0.88 respectively as per EBTF guidelines [165].

Figure 4.22 shows the enthalpy-entropy diagram of the secondary steam cycle at different fractional conversion values.

![Figure 4.22: Enthalpy-entropy diagram for secondary HRSG for different fractional conversions](image)

As shown in figure 4.22, changing the fractional conversion had a minimal effect on secondary HRSG enthalpy-entropy diagram since the steam pressures were fixed for all turbines and secondary HRSG heat exchangers were operating under same pressures and temperatures. Another important aspect of this process is the need to optimize the
regeneration energy demand. Part of the excess heat in the CO₂ product stream is used to pre-heat the gaseous streams before entering the oxyfuel regeneration column (heat exchangers E-5 and E-6) in figure 4.23. This is most appreciable in figure 4.24, where the composite temperature-heat lines of the secondary HRSG are provided for the fractional conversions 0.15, 0.2 and 0.25 respectively. Figure 4.24 shows the heat inputs to the cycle (absorber heat and CO₂ product stream) and the temperature-heat profile of the secondary steam cycle. From figure 4.24, we can observe that the heat input requirement is decreased when the sorbent conversion is increased. For instance, for sorbent conversion of 0.15, the accumulated heat input was around 350 MW. While for sorbent conversion of 0.25, the accumulated heat input was around 270 MW. This finding is in line with the energy analysis discussed in section 4.5.4 for the effect of varying the sorbent conversion and its relation to the heat requirement inside the HTCC.

Figure 4.23: HTCC integrated with secondary HRSG system

Figure 4.24: T-Q composite diagram of the secondary HRSG, a) for fractional conversion 0.15, b) for fractional conversion 0.2, c) for fractional conversion 0.25. The regeneration temperature is 700°C and absorption temperature is 525°C
For hot CO$_2$ stream, green line, there is a gap in the CO$_2$ temperature-heat profile as the CO$_2$ hot stream was used to heat up the oxygen and fuel lines before oxyfuel combustion. The temperature level needed to efficiently pre-heat the fuel and oxygen streams is between 400$^\circ$C and 385 $^\circ$C in the three simulation cases. The CO$_2$ stream at this temperature is split for recycle to the regenerator. The remaining CO$_2$ stream is used to heat the natural gas up to 240$^\circ$C and the oxygen stream up to 280 - 300$^\circ$C to optimise the regeneration energy demand in each simulation case. The remaining energy in the CO$_2$ stream is then used to pre-heat the feed water from the condenser and preheat the sorbent make up stream before entering the absorber.

For further investigation of effect of varying sorbent conversion on plant performance after the HTCC integration, figure 4.25 shows the marginal efficiency of the oxyfuel regenerator and secondary HRSG.

![Figure 4.25: Marginal efficiency of the secondary HRSG as a function of sorbent fractional conversion](image)

The marginal HRSG efficiency decreases with decreasing the sorbent fractional conversion. Consequently, further improvements in the fractional conversion can lead to more efficient secondary HRSG and lower CO$_2$ associated penalties.
4.6 Possible future improvements

As explained in energy demand analysis section, sorbent fractional conversion and sorbent regeneration temperature were found to have the greatest effect on the fuel, energy and electricity penalties resulted from the integration of CO₂ capture inside the plant. Further improvements / modification to the Li₄SiO₄ sorbent, as discussed in [22, 97, 166, 167], can be applied to improve the sorbent performance would help to reduce the heat and energy penalties and hence achieve better heat plant efficiency. With respect to process modelling, further improvements could be applied to the process model by considering a kinetic model inside the reactor. With regards to the heat integration inside HTCC unit, an improved heat integration level inside the HTCC can be improved by introducing new heat exchange concepts such as solid – steam heat exchangers or solid – solid heat recuperators. These two heat exchanging options were modelled separately based on reference NGCC base case with Li₄SiO₄ based CO₂ capture system integrated. The model results for these new cases showed better net plant efficiency and lower penalties as illustrated in table 4.3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Base case</th>
<th>Base case with HTCC integrated</th>
<th>Base case with Solid Heat recuperator</th>
<th>Base case with solid steam HE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gross power output</td>
<td>MW</td>
<td>837.3</td>
<td>1104.0</td>
<td>1015.3</td>
<td>1100.5</td>
</tr>
<tr>
<td>Gas turbine (x1)</td>
<td>MW</td>
<td>274.6</td>
<td>275</td>
<td>275</td>
<td>275</td>
</tr>
<tr>
<td>Steam turbine</td>
<td>MW</td>
<td>288.1</td>
<td>287.7</td>
<td>287.7</td>
<td>287.7</td>
</tr>
<tr>
<td>2nd Steam turbine</td>
<td>MW</td>
<td>NA</td>
<td>266.3</td>
<td>177.6</td>
<td>262.9</td>
</tr>
<tr>
<td>Net power output</td>
<td>MW</td>
<td>829.9</td>
<td>1001.6</td>
<td>933.2</td>
<td>999.1</td>
</tr>
<tr>
<td>Net Plant efficiency</td>
<td>%L.H.V</td>
<td>58.3</td>
<td>49.1</td>
<td>50.9</td>
<td>49.4</td>
</tr>
<tr>
<td>Penalty points</td>
<td>%</td>
<td>9.2</td>
<td>7.4</td>
<td>8.9</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Table 4-3: Comparison of integration results into NGCC plant for different HTCC configurations
The model with solid-solid heat recuperator option results showed a net plant efficiency of 50.9 % which is better than the efficiency obtained when advanced amine, CESAR-1, is used (50.8 %). Also, the option with solid steam heat exchangers showed an improvement in plant efficiency penalty with 0.3 % points compared to the base case with CO₂ capture.

Although the noticeable improvements in plant efficiency when these heat integration options are applied, these options are not well demonstrated and need to be approved for large scale practical applications.

In addition to the previous improvements, other options could be applied with respect to sorbent regeneration to achieve lower heat and energy consumption during the regeneration process. In literature, many options were studied to replace the direct oxy fuel heating with indirect heating options. These options are conceptually based on applying heat transfer between the main power plant combustor and the sorbent regenerator [168], heat transfer between the hot regenerated solid stream exiting the regenerator and the colder solids stream exiting the absorber [169, 170] and the use of a double looping system to regenerate the sorbent in the regenerator [171]. These indirect heating options are still also at the conceptual design stage and requires further development before being available for large scale practical implementation.

If these heat integration options and such technologies are approved for large scale application, a wide horizon for high temperature Li₄SiO₄ based sorbents utilization, could be created as an energy efficient solution for CO₂ capture.

4.7 Conclusion

High temperature solid sorbents CO₂ capture solution has been investigated as an important option to abate the exhaust gases CO₂ emissions result from fossil fuel combustion in power and industrial processes. For such technologies, the key advantage is the possibility of capture CO₂ at relatively high capacity without the need to cool down the flue gases to low temperatures. This provides a high potential for heat integration from the HTCC unit and between the HTCC unit and the plant. This chapter evaluated the integration of a novel Li₄SiO₄ based CO₂ capture technology into NGCC power plants.

Due to the Li-based solids high sorbent cyclic performance obtained, a process design could be achieved with minimum amount of sorbent the make-up flow that only needed to compensate the physical degradation of the solids through attrition.
A steady-state Aspen Plus model was built for a NGCC power plant with a Li$_4$SiO$_4$ sorbent HTCC integrated. European Benchmarking Task Force (EBTF) common framework basis and assumptions were followed and applied in process modelling. The base case model with HTCC was developed with 525 °C and 700 °C absorption and regeneration temperatures, respectively, Li$_4$SiO$_4$ fractional conversion of 0.2 and sorbent make up ratio of 0.01. The model results showed a net power plant efficiency penalty of 9.2% points after HTCC plant integration. The obtained efficiency penalty is slightly higher than that obtained from a MEA-based system (8.4% penalty points), applied for the same reference plant and under the same conditions, and lower than the one for CaCO$_3$ sorbent-based HTCC integration (12.5% penalty points), which also was applied to the same reference plant under the same conditions.

Sensitivity analysis were performed to investigate the effect of the desorption temperature, Li$_4$SiO$_4$ fractional conversion, sorbent make up ratio and amount of oxyfuel excess O$_2$ on net plant efficiency, specific regeneration energy demand, EOP and SPECCA.

Model results showed a significant reduction in sorbent regeneration energy consumption by reducing the desorption temperature by 2% from its original temperature. This in turn has led to a 0.6% higher net plant efficiency. Similarly, increasing the sorbent conversion by 25% resulted in a 1.2% increase in the net plant efficiency. This was linked to the lower sorbent circulation requirements in such case.

With respect to the oxyfuel excess O$_2$, it was found that reducing the oxyfuel excess O$_2$ by 33%, results in 0.15% increase in net plant efficiency. Finally, for the sorbent make up ratio, it has showed the lowest effect on net plant efficiency and power penalties. When the make-up ratio was reduced by 50%, it resulted only in 0.2% increase in net plant efficiency.

According to the obtained simulation and sensitivity results, further efforts should be spent to reduce the sorbent CO$_2$ desorption temperature and increase the sorbent fractional conversion to achieve lower energy penalties and higher net plant efficiencies.

With respect to the heat integration inside the plant, better integration results can be obtained by using a solid – solid heat recuperator or solid-steam heat exchangers in HTCC unit and it can be further improved by incorporating indirect heating options inside the
regenerator. However, all these options are subjected to the demonstration and their availability to be applied practically in large scale applications.

The next step in Li$_4$SiO$_4$ based CO$_2$ capture technology evaluation should focus on evaluating the economic impact of the HTCC on NGCC plant. Consequently, a full techno-economic evaluation for the integrated plant is performed and discussed in the next chapter to prove the feasibility of the application of Li-based HTCC into NGCC plant.
Chapter 5    TECHNO-ECONOMIC ANALYSIS CASE 1 – NGCC PLANT

5.1 Introduction

Assessing the integration of novel CO₂ capture technologies into power and industrial plants requires both technical and economic analysis for the studied plants. The integration of Li₄SiO₄ based HTCC into a NGCC plant, have showed a net power plant efficiency penalty of 9.2% points after HTCC plant integration, which is slightly higher than that obtained from a MEA-based system (8.4% penalty points) and lower than the one for CaO sorbent-based HTCC integration (12.5% penalty points). However, a full evaluation of the integration of this technology requires a detailed techno-economic assessment to assess the economics and guide future developments.

The main objective of the techno-economic assessment is to investigate the techno-economic feasibility of the integration of the novel sorbent-based CO₂ capture system. The thermodynamic properties of the main GT flue gas, hot CO₂ stream, sorbent fluidization, fluidized bed working conditions and heat duties were used to estimate equipment cost and techno-economics. For the techno-economic calculation, detailed costing of the HTCC equipment was obtained besides the costing for the rest of the power plant, and all costing was estimated based on 2017 values.

Based on the described objective, the following Key Performance Indicators (KPIs) are estimated for the plant to give an indication about the final cost impact:

- Specific Investment [£/kW]
- Cost of CO₂ avoided [£/tCO₂]
- Levelized Cost of electricity output [£/kWh]

In the current study, a class 4 accuracy on costing estimates is assumed (-30% to + 50 %) based on 1% to 15% full project definition [172], which is identical to the conceptual design stage for the process [173]. Figure 5.1 illustrates the techno-economic assessment workflow that has been followed in this study.
Figure 5.1: Workflow chart for Techno-economic assessment
Mass and heat balances were obtained from the process model along with the main process parameters. The Aspen Plus model process parameters were used for equipment costing / scaling, final techno-economic assessment and KPIs estimation. For equipment costing, a combination of bottom up and top down approaches are used. In the top down approach (TDA), TDA tends to focus on the bulky items or the main units of the plant to derive the cost estimation. Using TDA, the equipment cost was being scaled using a formula based on an allocation factor such as equipment capacity, power consumption etc. Conversely, the bottom up approach (BUA) tends to be a more accurate method for cost estimation since it includes detail costing for each and every component of process equipment based on available process data [174].

It is worth mentioning that the TDA is applied for costing of standard process equipment which are well defined in the industry such as pumps, compressors, blowers etc[175]. For non-standard equipment such as the fluidized bed CO\textsubscript{2} capture system, detailed BUA was used to estimate the equipment direct cost, as will be explained later. For HTCC unit, detailed costing using bottom up approach was performed. Detailed fluidized bed reactors design and sizing were performed then used in HTCC unit costing estimation.

After estimating the direct cost for all the equipment, capital and operational expenditures were calculated, the techno-economic KPIs were evaluated using two different methods for the sake of comparison between both methods [136, 176]. Also, the same KPIs were estimated for the same reference plant integrated with CaL system for sake of comparison. At the end of the chapter, techno-economic sensitivity analysis were performed by varying several technical and economical parameters, such as sorbent cost, fuel cost, capital investment, operating and maintenance cost, plant capacity factor, discount rate.

### 5.2 Equipment Direct Costing

#### 5.2.1 Equipment Direct Costing Basis

For fluidized bed CO\textsubscript{2} capture systems with Li-based sorbents, there was no detailed costing available. As a result, a detailed design for the fluidized bed system was performed followed by detailed costing for each component inside the fluidized bed system.

For rest of the plant equipment, direct cost was calculated using the following scaling equation [177]:

\[
C = C_0 \cdot \left(\frac{S}{S_0}\right)^n
\]

Eq (5.1)
Where C is the inside battery limit (ISBL) capital cost of the new package / equipment, 
$C_0$ is the ISBL capital cost of the reference package / equipment, $S$ is the new equipment 
capacity or rating, $S_0$ is the reference equipment capacity or rating and $n$ is the scaling 
factor.

The reference scaling parameter $S_0$, reference cost $C_0$ and scaling factor $n$ are same to 
those used in NGCC case study techno-economic analysis in EBTF [135]

It is worth mentioning that 2017 was assumed to be the reference year for the start of the 
project and all pricing values are converted to USD prices and rescaled to 2017 USD 
prices using Chemical Engineering Plant Cost Index (CEPCI). CEPCI gives an indication 
about the reflection of the inflation and other cost changes affecting the overall cost of 
the plant compared to a reference year. CEPCI of 562.1 was used for 2017. For CEPCI 
historical data, please refer to figure A.2.1 in appendix A.2. All equipment costs were 
finally converted from 2017 USD prices to GBP using a 0.77 conversion factor based on 
the average GBP exchange rates in 2017 published by the Bank of England [178].

Tables 5.1, 5.2 & 5.3 illustrate the main process parameters extracted from the model and 
used in the equipment sizing and costing for Absorber, regenerator and rest of plant 
equipment:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Used in</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue Gas volumetric flow rate ($V_g$)</td>
<td>1475.11 m$^3$/s</td>
<td>Absorber sizing and costing</td>
</tr>
<tr>
<td>Flue gas mol flow rate</td>
<td>84610.37 kmol/h</td>
<td>Absorber costing</td>
</tr>
<tr>
<td>Flue Gas density ($\rho_g$)</td>
<td>0.451 kg / m$^3$</td>
<td>FB Sizing and Costing</td>
</tr>
<tr>
<td>Gas viscosity ($\mu_g$)</td>
<td>3.6 $ \times 10^{-5}$ pa. s</td>
<td>FB Sizing and Costing</td>
</tr>
<tr>
<td>Gas Reversible compressibility ($\gamma_g$)</td>
<td>1.3</td>
<td>FB Sizing and Costing</td>
</tr>
<tr>
<td>Flue gas inlet temperature ($T_{abs}$)</td>
<td>525°C</td>
<td>Absorber Design and Costing</td>
</tr>
<tr>
<td>$P_{flue Gas}$</td>
<td>1 bara</td>
<td>Absorber Design and Costing</td>
</tr>
<tr>
<td>Mass flow rate of sorbent at absorber exit ($G_s$)</td>
<td>533.4 kg/s</td>
<td>Absorber Sizing and Costing</td>
</tr>
<tr>
<td>$Q_{carb_tot}$</td>
<td>239.55 MW</td>
<td>H. Ex Costings</td>
</tr>
</tbody>
</table>
Table 5-2: Process model simulation parameters used in regenerator sizing (per train – two trains are used)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Used in</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ volumetric flow rate ($V_{CO₂}$)</td>
<td>297.4 m³/s</td>
<td>FB Sizing and Costing</td>
</tr>
<tr>
<td>CO₂ mol flow rate</td>
<td>13415.3 kmol/h</td>
<td>Regenerator costing</td>
</tr>
<tr>
<td>CO₂ density ($\rho_g$)</td>
<td>0.426 kg/m³</td>
<td>Regenerator Sizing and Costing</td>
</tr>
<tr>
<td>CO₂ viscosity ($\mu_g$)</td>
<td>3.88 . 10⁻⁵ pa.s</td>
<td>Regenerator Sizing and Costing</td>
</tr>
<tr>
<td>CO₂ Reversible compressibility ($\gamma_g$)</td>
<td>1.2</td>
<td>Regenerator Sizing and Costing</td>
</tr>
<tr>
<td>Mass flow rate of sorbent at absorber exit ($G_s$)</td>
<td>533.4 kg/s</td>
<td>Regenerator Sizing and Costing</td>
</tr>
<tr>
<td>$P_{CO₂}$</td>
<td>1 bara</td>
<td>Regenerator Sizing and Costing</td>
</tr>
<tr>
<td>Sorbent Regeneration Temp</td>
<td>700°C</td>
<td>Regenerator Sizing and Costing</td>
</tr>
<tr>
<td>Regenerator heat duty</td>
<td>307 MW</td>
<td>Oxy fuel combustion costing</td>
</tr>
</tbody>
</table>

Table 5-3: Process model simulation parameters used in costing for rest of plant equipment

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Used in</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressor Power Consumption</td>
<td>24.8 MW</td>
<td>Compressor Costing</td>
</tr>
<tr>
<td>ASU Power Consumption</td>
<td>16.1 MW</td>
<td>ASU Costing</td>
</tr>
<tr>
<td>GT net power</td>
<td>275 MW</td>
<td>GT Costing</td>
</tr>
<tr>
<td>Primary HRSG UA</td>
<td>8.84 MW/K</td>
<td>Primary HRSG Costing</td>
</tr>
<tr>
<td>Secondary HRSG UA</td>
<td>1.35 MW/K</td>
<td>Secondary HRSG Costing</td>
</tr>
<tr>
<td>Primary steam turbine</td>
<td>144 MW</td>
<td>Steam turbine costing</td>
</tr>
<tr>
<td>Secondary steam turbine</td>
<td>133 MW</td>
<td>Steam turbine costing</td>
</tr>
<tr>
<td>Rejected Heat $Q_{cond}$</td>
<td>235.5 MW</td>
<td>Cooling tower costing</td>
</tr>
</tbody>
</table>

5.2.2 Fluidized bed design and Costing

A techno-economic assessment for the integration of HTCC technology in a NGCC power plant requires to have a detailed design of the fluidized bed system. That should include identifying the dimensions of the reactors, pressure drop across the vessel and mean particle residence time in reactor. In addition, the results of the detailed design would be used in the evaluation of the basic capital cost of the fluidized bed and hence calculate the detailed costing of the HTCC unit.
Hence, this section presents the detailed design and sizing for the fluidized bed reactors to provide all the technical data required for costing such as equipment dimensions and weight.

5.2.2.1 Fluidized bed design assumptions and correlations

Sizing the fluidized bed system requires the following parameters for absorber and regenerator: vessel diameter, vessel height, pressure drop across the vessel and mean particle residence time in reactor. That would be applied for both the absorber and regenerator reactors using Kunii and Levenspiel (KL) method [179].

For both reactors sizing, the following assumptions were followed:
Table 5-4: Assumptions and design rationale for absorber and regenerator

<table>
<thead>
<tr>
<th>Assumptions</th>
<th>Range</th>
<th>Value (Unit)</th>
<th>Ref</th>
<th>Assumptions</th>
<th>Range</th>
<th>Value (Unit)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>No of Absorber per train (n_{abs})</td>
<td>NA</td>
<td>8</td>
<td>Design</td>
<td>Pellets Sphericity (ϕ) Based on Pellet shape</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>optimization</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No of regenerators per train (n_{reg})</td>
<td>NA</td>
<td>4</td>
<td>Design</td>
<td>Bed voidage at minimum fluidization conditions ε_{mf}</td>
<td>Based on particle size and shape</td>
<td>ε_{mf} = 0.48 based on particle size 100 µm and round sand shape with ϕ = 0.86</td>
<td>[179]</td>
</tr>
<tr>
<td>Superficial velocity (U_{0})</td>
<td></td>
<td></td>
<td></td>
<td>For fast fluidization: U_{0} &gt;&gt; U_{i} and U_{0} &gt; 0.5 m/s</td>
<td>Pressure drop across the distributor ΔP_d</td>
<td>0.1-0.3 of the bed pressure drop</td>
<td>0.1 * ΔP_b</td>
</tr>
<tr>
<td>Dense bed height – to diameter (H_d/D)</td>
<td>1</td>
<td>1</td>
<td>[180]</td>
<td>Heat transfer coefficient (U)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dense bed Height (H_d)</td>
<td></td>
<td>0.3 to 15 m</td>
<td>[180]</td>
<td>Reactor Material</td>
<td>NA</td>
<td>SS304</td>
<td>Spec NO SA-182 SS304, ASME BPVC Section II part D</td>
</tr>
<tr>
<td>Solid mean particle size (d_{m})</td>
<td>50-300 µm</td>
<td>for good fluidization</td>
<td>100 µm</td>
<td>The maximum allowable stress (S) in bar</td>
<td>NA</td>
<td>186.2 bara</td>
<td>ASME BPVC Section II part D</td>
</tr>
<tr>
<td>Solid density</td>
<td>2400</td>
<td>2400 kg/m³</td>
<td>[182]</td>
<td>the welding coefficient (α)</td>
<td>.75-1</td>
<td>1 with a complete Xray</td>
<td>[183]</td>
</tr>
<tr>
<td>Decay constant α from the value of (α . U_{0})</td>
<td>5 for Geldart AB Zone</td>
<td>5</td>
<td>[184]</td>
<td>Corrosion allowance</td>
<td>NA</td>
<td>8mm</td>
<td>ASME BPVC Section II part D</td>
</tr>
<tr>
<td>Gas Transport Carrying capacity (f^*)</td>
<td>≤ 0.02 for Geldart A zone</td>
<td>0.01</td>
<td>[184]</td>
<td>Skirt Height</td>
<td>3-5 m</td>
<td>3 m</td>
<td>[183]</td>
</tr>
<tr>
<td>Solid fraction in the dense region (f_{d})</td>
<td>≤ 0.02 for pneumatic transport</td>
<td>0.02</td>
<td>[184]</td>
<td>Skirt Thickness</td>
<td>8-12 mm</td>
<td>10 mm</td>
<td>[183]</td>
</tr>
</tbody>
</table>
The following equations are solved together to estimate the final reactors dimensions:

For reactor height \( H_t \); \( H_t = H_l + H_d \) \hspace{1cm} Eq (5.2)

Where \( H_l \) and \( H_d \) are the heights for lean and dense beds respectively. For illustration, please refer to appendix A.2

Assuming \( H_d/D = 1 \)

\( H_d = D \) \hspace{1cm} Eq (5.3)

To estimate \( D \), continuity equation is used:

\[ Q = A \cdot U_0 \] \hspace{1cm} Eq (5.4)

where \( Q \) is the gas volumetric flow rate in \( \text{m}^3 \text{s}^{-1} \), \( A \) is the reactor cross sectional area in \( \text{m}^2 \) and \( U_0 \) is the gas superficial velocity in \( \text{m} \text{s}^{-1} \).

To calculate the height of the fluidized lean region \( (H_l) \), the Kunni and Levenspiel model for Fast Fluidized CFB is used [184]. The lean Height \( H_l \) is calculated from the following equation:

\[ H_l = \frac{1}{a} \ln \left( \frac{f_d - f^*}{f_{ex} - f^*} \right) \] \hspace{1cm} Eq (5.5)

Where as \( a, f_d, f_{ex} \), \( f^* \) are constants that depend on solids fluidization conditions as following: and depends on the sorbent Geldart classification

\[ f_{ex} = \frac{g_s}{\rho_s(U_0 - U_t)} \] \hspace{1cm} Eq (5.6)

\[ U_t = U_t^* \left[ \frac{\mu (\rho_s - \rho_g) g}{\rho_g^2} \right]^{1/3} \] \hspace{1cm} Eq (5.7)

\( U_t^* \) is the dimensionless terminal velocity and can be calculated from the following equation assume sphere sorbent particles:

\[ U_t^* = \left[ \frac{18}{(d_p^*)^2} + \frac{0.591}{(d_p^*)^{1/2}} \right]^{-1} \] \hspace{1cm} Eq (5.8)

Where \( d_p^* \) is the dimensionless particle size and can be calculated from:

\[ d_p^* = d_p \left[ \frac{\rho_g (\rho_s - \rho_g) g}{\mu^2} \right]^{1/3} \] \hspace{1cm} Eq (5.9)

For blower duty calculation,
\[-W_{s,\text{ideal}} = \frac{\gamma}{\gamma - 1} P_1 v_1 \left[\left(\frac{P_1}{P_2}\right)^{\frac{\gamma - 1}{\gamma}} - 1\right]\]  
Eq (5.10)

\[-W_{\text{actual}} = -\frac{W_{(s,\text{ideal})}}{\eta}\]  
Eq (5.11)

Where:

$W_{s,\text{ideal}}$ is the ideal compressor work in W.

$\gamma$ is the adiabatic reversible compression of the flue gas and can be calculated from Aspen simulation results.

$P_1$ is the initial pressure for the flue gas before the reactor.

$v_1$ is the inlet flue gas volumetric flow rate.

$P_2$ = the required pressure to overcome pressure drop.

$\eta$ is the compressor efficiency (mechanical).

$P_2 = P_1 + \Delta P_t$  
Eq (5.12)

$\Delta P_t = \Delta P_d + \Delta P_b$  
Eq (5.13)

$\Delta P_b$ is the pressure drop across the fluidized bed and can be obtained from the balance of the sorbent weight inside the reactor and fluidization force [180]:

$\Delta P_b = 9.8 \frac{W_s}{A}$  
Eq (5.14)

Where $W_s$ is the sorbent weight inside the reactor and $A$ is the reactor cross sectional area. For $\Delta P_d$ calculation, it is assumed to be 10% of the pressure drop across the bed as per:

$\Delta P_d = 0.1 \ \Delta P_b$  
Eq (5.15)

$W_s = W_l + W_d$  
Eq (5.16)

To calculate $W_s$, the weight of solids in lean zone, $W_l$, and in dense zone, $W_d$ should be identified first from the following equations:

$W_l = A \rho_s H_l f_l^-$  
Eq (5.17)

$f_l^- = f^* + \frac{f_d^- f_{ex}}{a H_l}$  
Eq (5.18)

$W_d = A \rho_s H_d f_d$  
Eq (5.19)
For Sorbent residence time, the following equation obtained from Kunii et al [179] is used:

\[ t_{mr} = \frac{W}{\epsilon_s} \]  

\text{Eq (5.20)}

For heat exchanger area in absorber:

\[ Q = UA\Delta T \]  

\text{Eq (5.21)}

shell weight calculation

The minimum wall thickness of the vessel can be determined from the formula:

\[ t = \frac{PR}{\alpha S - 0.6P} \]  

\text{Eq (5.22)}

P is the internal pressure in bara, R is the radius in mm, S is the maximum allowable stress in bara, \( \alpha \) is the welding coefficient.

For the empty reactor weight calculations, the following equation is used [183, 185]:

\[ W_{tv} = W_v + W_{sk} + W_h \]  

\text{Eq (5.23)}

For vessel weight calculation in kg, the following equation is used [183, 185]:

\[ W_v = 24.7 D H_t t \]  

\text{Eq (5.24)}

\( W_v \) is the vessel weight without heads, D is the vessel diameter in m, \( H_t \) is the total height in m, \( t \) is the wall thickness in mm. The same equation is used to estimate the skirt weight, \( W_{sk} \).

For the combined weight of heads, \( W_h \), the following equation is used [183, 185]:

\[ W_h = W_{1mm} t \]  

\text{Eq (5.25)}

Where \( W_{1mm} \) is the combined weight of two elliptical 1mm thick elliptical vessel heads

\textbf{5.2.2.2 Fluidized bed design results}

Based on the previous assumptions, sizing and design optimization, the HTCC fluidized bed train was designed to have 8 absorbers designed based on superficial velocity \( U_0 = 8 \text{ m.s}^{-1} \) and 4 regenerators designed based on superficial velocity \( U_0 = 6 \text{ m.s}^{-1} \). Table 5.5 presents the sizing results for individual absorbers and regenerators.
Table 5-5: Sizing results for absorber and regenerator

<table>
<thead>
<tr>
<th>Design variables</th>
<th>Absorber Values</th>
<th>Regenerator Values</th>
<th>Derived from</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter</td>
<td>5.4 m</td>
<td>4 m</td>
<td>Eq (5.4)</td>
</tr>
<tr>
<td>Terminal velocity ( (U_t) )</td>
<td>0.33 m/s</td>
<td>0.30 m/s</td>
<td>Eq (5.7) to (5.9)</td>
</tr>
<tr>
<td>Total vessel height</td>
<td>10.5 m</td>
<td>10 m</td>
<td>Eq (5.2)</td>
</tr>
<tr>
<td>Dens bed height</td>
<td>5.4 m</td>
<td>4 m</td>
<td>Eq (5.3)</td>
</tr>
<tr>
<td>Lean bed height</td>
<td>5.1 m</td>
<td>6 m</td>
<td>Eq (5.5-5.6)</td>
</tr>
<tr>
<td>Pressure drop</td>
<td>4.8 kPa</td>
<td>3.9 kPa</td>
<td>Eq (5.13-5.15)</td>
</tr>
<tr>
<td>Fluidization power</td>
<td>1 MW</td>
<td>0.31 MW</td>
<td>Eq (5.10-5.11)</td>
</tr>
<tr>
<td>Residence time</td>
<td>2.6 minutes</td>
<td>0.6 minutes</td>
<td>Eq (5.20)</td>
</tr>
<tr>
<td>Heat exchanger Area</td>
<td>11 m²</td>
<td>NA</td>
<td>Eq (5.21)</td>
</tr>
<tr>
<td>Sorbent Weight</td>
<td>10.2 tonne</td>
<td>4.5 tonnes</td>
<td>Eq (5.16-5.19)</td>
</tr>
<tr>
<td>Min Wall thickness</td>
<td>23 mm</td>
<td>19 mm</td>
<td>Eq (5.22)</td>
</tr>
<tr>
<td>(incl corrosion allowance)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weight (no solids)</td>
<td>50 tonnes</td>
<td>27 tonnes</td>
<td>Eq (5.23-5.25)</td>
</tr>
<tr>
<td>Weight (with solids)</td>
<td>60.2 tonnes</td>
<td>31.5 tonnes</td>
<td>Eq (5.16, 5.23)</td>
</tr>
</tbody>
</table>

5.2.2.3 Fluidized bed costing

The fluidized bed system is based on bottom up approach [186] which covers the costing for the components of the fluidized bed system as per following:

- Fluidized Bed Reactor vessel Costing using functional module method and costing Equation proposed Chauvel et al 2003 [185].

The following equation represents the base cost for fluidized bed reactors based on pressure, flow rate, fluidization power and residence time in 1985 French franc:

\[
\ln P_B = 2.5776 + 0.2839 \ln (DEB) + 0.2369 \ln(TS) + 0.1606 \ln(CV) + 0.1441 \ln (PRES) \quad \text{Eq (5.26)}
\]
Where DEB is the gas flow rate in kmol/hr, TS is the residence time in s, CV is the fluidization power in kW and PRES is the pressure in bar.

The final reactor cost was converted in USD in 1985 first quarter rates using rates available in [187] then it was rescaled to 2017 GBP values using CEPCI as explained before in 5.2.1. Using process data from the Aspen Plus model and sizing data from sizing section for absorber and regenerator with applying material correction factor for SS304 = 1.8 [187], the final direct vessel cost was calculated as showed in table 5.6.

- Fluidized Bed Blower / compressor costing based on power consumption [185].
- Using Air / Hydrogen compressor costing curves from [185]

To estimate the cost of 1 MW and 0.31 MW compressors, for each absorber and regenerator reactor respectively, including the driver cost in mid-2000 Euros. By rescaling the price using the 6th power method and converting the prices to 2017 £ million.

For cyclones costing, the cyclones costing curves from [185] was used. The chosen individual cyclone capacity is 100,000 m³ h⁻¹ which costs €300,000 in mid-2000 prices.

- Heat Exchanger Costing (Absorber reactor)

The cost of the absorber heat exchangers was estimated based on the designed heat exchanger area per reactor, 11 m², using the costing chart from the IChemE costing book, cost of carbon steel tubular heat exchanger [188], and by converting the cost to 2017 values the total cost of heat exchangers for 8 absorber reactors was £0.11 million.

- Oxyfuel combustion cost in regenerator using the method from [189]:

Using pre estimation cost data available from Towler and Sinnot [189] and substituting in the following equation:

\[ C_e = C \times S^n \]  \hspace{1cm} \text{Eq (5.27)}

Where \( C_e \) is the purchase cost in $, C is cost constant which is equal to 560 $ mid 2004 prices for box furnace, S is the maximum unit size = 10^5 KW, n is the costing index = 0.77 for box furnace.

The purchase cost of 100 MW furnace = 4M US$ – 2004 prices.

Since the design contains 4 regenerators, then the heat duty for each absorber = 77 MW

The previous cost is then rescaled based on furnace heat duty using six tenth rule [189] to calculate the cost of 77 MW regenerator oxy fuel combustor and converted to 2017
prices values using CEPCI. The final cost of the regenerator combustor (2017) = £13 million.

- Cost of sorbent inventory:

For cost of the raw material of the Li₄SiO₄, based on latest prices of lithium silicate precursors, reported by Mineral Commodity Summaries 2014 and 2013 Mineral year Books (Lithium and silica) [88, 190, 191], the cost of 1 kg of Li₄SiO₄ for 2013 was considered equal to 4.5 $/kg. Hence, the final cost of the initial sorbent inventory is calculated based on the weight of sorbent required inside each absorber reactor as mentioned in table 5.5. Hence, the total weight of sorbent required for each train of 8 absorber= 82 tonne. That results in 0.3 M£ sorbent cost to be added to the capital cost of the fluidized bed system.

- Summary of fluidized bed cost

Table 5.6 presents summary of the fluidized bed costing, per train of HTCC unit, based on previously explained costing methods. The presented prices are in 2017 £ million.

*Table 5-6: Summary of fluidized components costing in 2017 £ million.*

<table>
<thead>
<tr>
<th>Costing methods</th>
<th>Unit Cost / No of units</th>
<th>Total Cost results in £ million</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absorber</td>
<td>Regenerator</td>
</tr>
<tr>
<td></td>
<td>£ million</td>
<td>No</td>
</tr>
<tr>
<td>Reactor column</td>
<td>[185]</td>
<td>0.43</td>
</tr>
<tr>
<td>Fluidization power</td>
<td>[185]</td>
<td>0.5</td>
</tr>
<tr>
<td>Cyclones</td>
<td>[185]</td>
<td>0.04</td>
</tr>
<tr>
<td>Heat Exchanger</td>
<td>[188]</td>
<td>0.014</td>
</tr>
</tbody>
</table>
5.2.3 Direct cost estimation for rest of plant equipment

The current section covers basic capital cost calculation for rest of plant equipment which was estimated using relevant costing data for similar standard equipment, as explained previously.

Starting with the main NGCC plant without capture, direct cost of the equipment was estimated using bottom up approach and top down approach for sake of comparison. Following the comparison, NGCC reference case BUA costing is applied to calculate the basic capital cost of the NGCC plant with HTCC integrated using the costing results selected from previous section for HTCC unit.

In BUA, the costing is performed for main packages inside the plant. Table 5.7 summarizes the main packages used in the calculation, sizing parameter used with Eq (5.1) to rescale the cost of each package and reference equipment cost in £-2017 prices and presents the costing for the NGCC reference plant without capture using the BUA.

The following figure shows the cost break down in % of the total cost for the reference plant without capture using BUA:

<table>
<thead>
<tr>
<th>Oxy fuel combustor</th>
<th>[189]</th>
<th>0</th>
<th>0</th>
<th>3.3</th>
<th>4</th>
<th>0</th>
<th>13.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorbent inventory</td>
<td>[88, 190, 191]</td>
<td>0.04</td>
<td>8</td>
<td>0</td>
<td>0</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td>Total equipment cost in 2017 M£</td>
<td>9.9</td>
<td>15.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total fluidized bed Equipment direct cost with initial solid inventory £ million</td>
<td>25.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 5.2: NGCC reference plant without capture Capital Cost break down in % from the total equipment direct cost without installation**
Table 5-7: Summary of the costing for the NGCC reference plant without capture using the BUA

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Scaling criteria</th>
<th>Scaling factor</th>
<th>Reference Equipment rating (S0)</th>
<th>Reference Equipment Cost (C0) in euro million</th>
<th>Reference year</th>
<th>New equipment rating / capacity</th>
<th>Rescaled cost in 2017 £ million</th>
<th>No of units</th>
<th>Final Cost in 2017 £ million</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Turbine</td>
<td>GT net power – MW</td>
<td>1</td>
<td>272.12</td>
<td>49.4</td>
<td>2008</td>
<td>274.6</td>
<td>55.06</td>
<td>2</td>
<td>110.1</td>
<td>[135, 192, 193]</td>
</tr>
<tr>
<td>Primary HRSG, ducting and stack</td>
<td>U x A MW/k</td>
<td>0.67</td>
<td>12.9</td>
<td>32.6</td>
<td>2008</td>
<td>7.924</td>
<td>26</td>
<td>2</td>
<td>52</td>
<td>[1, 2, 6]</td>
</tr>
<tr>
<td>Steam turbine, generator and auxiliaries</td>
<td>Gross Power – MW</td>
<td>0.67</td>
<td>200</td>
<td>33.7</td>
<td>2008</td>
<td>288.1</td>
<td>47.5</td>
<td>1</td>
<td>47.5</td>
<td>[135, 192, 193]</td>
</tr>
<tr>
<td>Cooling water system and BOP</td>
<td>Q_rejected – MW_{th}</td>
<td>0.67</td>
<td>470</td>
<td>49.6</td>
<td>2008</td>
<td>472.13</td>
<td>55</td>
<td>1</td>
<td>55</td>
<td>[135, 192, 193]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Total direct cost = 264.6 £ million</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The reference plant without capture costing was repeated using TDA by re-adjusting the prices of the base case in 2017 £ million, which gives a final value =262.3 £ million i.e. with an error less than 1 % compared to the BUA costing.

For the capital cost calculation for the NGCC case after integration of the HTCC, the direct cost calculation for the capture unit and all associated equipment using BUA was summarized in 5.2.2. The cost for secondary HRSG, Steam turbines, cooling water system and CO\textsubscript{2} compression system was scaled and adjusted to 2017 M£ using costing figures available in a EBTF study for similar equipment [135]. For ASU cost, the cost was rescaled using the estimated cost for the ASU applied in benchmark 5 IGCC plant in AMEC Fosterwheeler report for Benchmarking state-of-the-art and next generation CO\textsubscript{2} capture technologies [136]. The cost of the O\textsubscript{2} and NG preheaters is similar to the costing of heat exchangers followed in the detailed BUA study for the fluidized bed based on the heat exchangers costing charts obtained from [188]. Table 5.8 summarizes the costing results for the NGGC plant case after integration of HTCC. The costing figures in the table 5.8 includes the costing of two trains of HTCC fluidized beds as described previously:

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Cost in 2017 £ million</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost of NGCC reference plant (GT and primary HRSG)</td>
<td>264.6</td>
<td>[1, 2, 6]</td>
</tr>
<tr>
<td>Cost of Capture unit (including solid inventory)</td>
<td>50.9</td>
<td>Table 5.6</td>
</tr>
<tr>
<td>Cost of secondary HRSG</td>
<td>12.6</td>
<td>[1, 2, 6]</td>
</tr>
<tr>
<td>Cost of Steam Turbines</td>
<td>45.1</td>
<td>[1, 2, 6]</td>
</tr>
<tr>
<td>Cost of Cooling water system and BOP (For 351 MW Q\textsubscript{eq})</td>
<td>45.1</td>
<td>[1, 2, 6]</td>
</tr>
<tr>
<td>Cost of CO\textsubscript{2} compression and condenser</td>
<td>27</td>
<td>[135, 194]</td>
</tr>
<tr>
<td>Cost of fuel / O\textsubscript{2} preheaters</td>
<td>0.5</td>
<td>[188]</td>
</tr>
<tr>
<td>Cost of ASU</td>
<td>69</td>
<td>[136]</td>
</tr>
<tr>
<td>Total Direct cost</td>
<td>£515.6 million</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.3 shows the equipment cost break-down in percentage for the NGCC plant after capture in % from the overall cost.

As shown in figure 5.3, the cost of the GT and primary HRSG system contributes to 51.3% of the overall plant capital cost and it represents the cost of the original NGCC reference plant. Following to the GT and primary HRSG cost, it was found that the ASU recorded the second highest capital cost, with 13.5% of the overall capital cost, followed by the HTCC capital cost which recorded 9.9% of the overall capita cost. For CO₂ compression train, it was found that it contributes to 5.2% of the overall capital cost. For secondary HRSG, steam turbine and cooling system, it was found that overall capital cost of theses equipment contributes to 19.8% of the overall capital cost. Further discussion for the capital cost results, is available in results discussion, section 5.4.
5.3 Techno-economic Assessment

5.3.1 General Techno-economic assumptions

The following assumptions were used to perform the techno-economic assessment:

- Two methods are applied to estimate the plant techno-economics for HTCC integration and each of them has its own assumptions. However, common direct cost of equipment is used for both studies before applying each study related assumptions.
- The main techno-economic KPIs mentioned in section 5.1 are applied for both methods.
- Specific investment (SI) is calculated for the plant for each method before and after the integration of the HTCC plant. SI is calculated by estimating the ratio between the total capital cost and net power output from the plant.
- Levelized cost of electricity generation (LCOE) is the discounted ownership cost of using the power plant transferred into equivalent cost of generation in £/MWh or p/kWh.[195]. In other words, levelized cost of electricity represents the lifecycle assessment of the power plant from the cradle to grave. Levelized cost of electricity will be calculated for the same NGCC plant before and after the integration of CO₂ capture unit.
- Cost of CO₂ avoided is the measure for the cost spent to capture CO₂ emissions from the reference plant in £/t CO₂ [194]. Cost of CO₂ avoided can be calculated from the following formula: Cost of CO₂ avoided = \( \frac{(\text{COE})_{\text{cc}} - (\text{COE})_{\text{ref}}}{E_{\text{Ref}} - E_{\text{cc}}} \) in £/t CO₂ where COE is cost of electricity in £/MWh and E is the CO₂ emission rate in kgCO₂/ kWh and Ref stands for the reference case without capture and CC for case with capture.
- The actual power output of the plant over the life of the plant is calculated based on the capacity factor assumed for each method. The plant capacity factor describes the average output over the year relative to the maximum rated capacity.

5.3.2 Techno-economic Assessment – method 1 (EBTF)

This method was constructed based on EBTF study assumptions [135] for CAPEX and OPEX calculation. For Levelized cost of electricity and cost of CO₂ avoided, the guidelines mentioned in Mott MacDonald Electricity Cost Update report [195] were followed. The assumptions followed in method 1 assessment are listed in appendix A.2
5.3.2.1 Method 1 results

Table 5.9 shows the final calculation for the total plant cost without capture including installation cost, indirect cost, Owner’s Costs and Contingencies:

Table 5-9: Summary of the total plant cost without capture

<table>
<thead>
<tr>
<th>Summary of total plant cost without capture</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Gross power output</td>
<td>MW</td>
<td>837.3</td>
</tr>
<tr>
<td>Net Power Output</td>
<td>MWe net</td>
<td>829.9</td>
</tr>
<tr>
<td>Total Direct cost</td>
<td>M£</td>
<td>264.6</td>
</tr>
<tr>
<td>Installation Cost</td>
<td>M£</td>
<td>178.0</td>
</tr>
<tr>
<td>Total Plant direct cost (M£)</td>
<td>M£</td>
<td>442.6</td>
</tr>
<tr>
<td>Indirect cost (14 %)</td>
<td>M£</td>
<td>62.0</td>
</tr>
<tr>
<td>EPC Cost</td>
<td>M£</td>
<td>504.5</td>
</tr>
<tr>
<td>Owner’s Costs and Contingencies (15 % of EPC)</td>
<td>M£</td>
<td>75.7</td>
</tr>
<tr>
<td>TPC</td>
<td>M£</td>
<td>580.2</td>
</tr>
<tr>
<td>Specific Investment - Gross</td>
<td>£/kWgross</td>
<td>693.0</td>
</tr>
<tr>
<td>Specific Investment – Net</td>
<td>£/kWnet</td>
<td>699.1</td>
</tr>
</tbody>
</table>

Table 5.10 shows the final calculation for the total plant cost with HTCC integration including installation cost, indirect cost, Owner’s Costs and Contingencies:

Table 5-10: Summary of the total plant cost with capture

<table>
<thead>
<tr>
<th>Summary of total plant cost with capture</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Gross power output</td>
<td>MW</td>
<td>1104.0</td>
</tr>
<tr>
<td>Net Power Output</td>
<td>MWe net</td>
<td>992</td>
</tr>
<tr>
<td>Total Direct cost</td>
<td>£ million</td>
<td>515.6</td>
</tr>
<tr>
<td>Installation Cost power part</td>
<td>£ million</td>
<td>294.4</td>
</tr>
<tr>
<td>Installation cost CO₂ capture section</td>
<td>£ million</td>
<td>64.4</td>
</tr>
<tr>
<td>Total Installation Cost</td>
<td>£ million</td>
<td>358.8</td>
</tr>
<tr>
<td>Total Plant direct cost</td>
<td>£ million</td>
<td>874.4</td>
</tr>
<tr>
<td>Indirect cost (14 %)</td>
<td>£ million</td>
<td>122.4</td>
</tr>
<tr>
<td>EPC Cost</td>
<td>£ million</td>
<td>996.8</td>
</tr>
<tr>
<td>Owner’s Costs and Contingencies (15 % of EPC)</td>
<td>£ million</td>
<td>149.5</td>
</tr>
</tbody>
</table>
For operating and maintenance cost, the assumptions mentioned previously in this section were followed. Also, for the utilities variable cost, the cost was scaled based on the cost of the utilities of the basic plant in EBTF and rescaled using 0.67 scale factor using Eq (5.1), and then transferred to 2017 £ using CEPCI. For sorbent cost, basic cost of the sorbent was assumed to be 4.5 USD in 2013 based on the basic sorbent costing calculation done previously; next, the cost was transferred to £ in 2017. Tables 5.11 and 5.12 present the operating and maintenance cost calculation before and after integration of the capture unit, respectively:

### Table 5-11: Operating and Maintenance cost before capture

<table>
<thead>
<tr>
<th>O&amp;M Cost</th>
<th>Unit</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fixed Operation Cost</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maintenance and repair (2.5 % x TPC)</td>
<td>£ million pa</td>
<td>14.5</td>
</tr>
<tr>
<td>Operating Labour (40% from Maintenance cost)</td>
<td>£ million pa</td>
<td>5.8</td>
</tr>
<tr>
<td>Supervision (30 % labour cost)</td>
<td>£ million pa</td>
<td>1.7</td>
</tr>
<tr>
<td>Laboratory Test (10% of labour cost)</td>
<td>£ million pa</td>
<td>0.6</td>
</tr>
<tr>
<td>Insurance (1.5 % TPC)</td>
<td>£ million pa</td>
<td>8.7</td>
</tr>
<tr>
<td>Plant Overhead Cost (60 % M+OL)</td>
<td>£ million pa</td>
<td>13.6</td>
</tr>
<tr>
<td><strong>Total Fixed O&amp;M Cost</strong></td>
<td>£ million pa</td>
<td>44.9</td>
</tr>
<tr>
<td><strong>Variable Cost:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sorbent Yearly Cost</td>
<td>£ million pa</td>
<td>0</td>
</tr>
<tr>
<td>Utilities (Process water)</td>
<td>£ million pa</td>
<td>4.3</td>
</tr>
<tr>
<td><strong>Total Variable O&amp;M Cost</strong></td>
<td>£ million pa</td>
<td>4.3</td>
</tr>
<tr>
<td><strong>Total O&amp;M cost</strong></td>
<td>£ million pa</td>
<td>49.2</td>
</tr>
</tbody>
</table>
Table 5-12: Operating and Maintenance cost after capture

<table>
<thead>
<tr>
<th>O&amp;M Cost</th>
<th>Unit</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed Operation Cost</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maintenance and repair (2.5% x TPC)</td>
<td>£ million pa</td>
<td>28.7</td>
</tr>
<tr>
<td>Operating Labour (40% from Maintenance cost)</td>
<td>£ million pa</td>
<td>11.5</td>
</tr>
<tr>
<td>Supervision (30% Labour cost)</td>
<td>£ million pa</td>
<td>3.4</td>
</tr>
<tr>
<td>Laboratory Test (10% of labour test)</td>
<td>£ million pa</td>
<td>1.1</td>
</tr>
<tr>
<td>Insurance (1.5% TPC)</td>
<td>£ million pa</td>
<td>17.2</td>
</tr>
<tr>
<td>Plant Overhead Cost (60% M+OL)</td>
<td>£ million pa</td>
<td>26.8</td>
</tr>
<tr>
<td>Total Fixed O&amp;M Cost</td>
<td>£ million pa</td>
<td>88.7</td>
</tr>
</tbody>
</table>

Variable Cost:

<table>
<thead>
<tr>
<th></th>
<th>£ million pa</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ Storage Cost</td>
<td>58.3</td>
<td></td>
</tr>
<tr>
<td>Sorbent Yearly Cost</td>
<td>8.8</td>
<td></td>
</tr>
<tr>
<td>Utilities (Process water)</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>Total Variable O&amp;M Cost (per year)</td>
<td>£ million pa</td>
<td>72.2</td>
</tr>
<tr>
<td>Total O&amp;M cost</td>
<td>£ million pa</td>
<td>161</td>
</tr>
</tbody>
</table>

For LCOE and Cost of CO₂ avoided, the assumptions explained earlier in this section were followed. Table 5.13 shows the LCOE calculations for plant without capture and with capture respectively:

Table 5-13: Summary of economic parameters

| Summary of economic parameters for NGCC 830 MW Case using BUA |
|-------------------------|----------------|----------------|
| Parameter               | Unit           | Without Capture | With Capture  |
| Gross Electricity output| MW             | 837.3           | 1104          |
| Net Electricity output  | MWe net        | 829.9           | 991.8         |
| Efficiency              | %              | 58.3            | 47.4          |
| CO₂ emissions           | kg/MWh         | 351.6           | 30.7          |
| Total Plant Cost        | £ million      | 580.2           | 1146          |
Specific Investment - Gross £/kWgross 693.0 1038
Specific Investment - net £/kWnet 699.1 1155.8
Annual Fuel Cost £ million pa 185.9 266.5
Fixed O&M £ million pa 44.9 88.7
Variable O&M £ million pa 4.3 72.2
Cost of Electricity £/MWh 42.3 67.5
Cost of CO₂ avoided £/tCO₂ avoided - 78.7

5.3.3 Techno-economic Assessment – method 2 (BEIS)

The cost method 2 follows the costing methodology presented in [136] to benchmark the application of different technologies for CO₂ capture in power and industrial plants in UK. This cost method is prepared based on American Association of Cost Engineers (AACE) class 4 which aims to achieve (-30% to + 50 %) accuracy. The method was used to calculate CAPEX, OPEX, Levelized cost of electricity and cost of CO₂ avoided for the plant before and after the integration of High temperature CO₂ capture unit. All cost calculations were obtained based on 2017 prices in GBP. This method depends on BUA costing for fluidized bed system using the basic equipment costing results from section 5.2. The assumptions followed in method 2 assessment are listed in appendix A.2.

5.3.3.1 Method 2 results

Table 5-14: Summary of the total plant cost without capture using method 2

<table>
<thead>
<tr>
<th>Summary of total plant cost without capture</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Gross power output</td>
<td>MW</td>
<td>837.3</td>
</tr>
<tr>
<td>Net Power Output</td>
<td>MWe net</td>
<td>829.9</td>
</tr>
<tr>
<td>EPC Contract cost</td>
<td>£ million</td>
<td>442.6</td>
</tr>
<tr>
<td>Infrastructure connection cost</td>
<td>£ million</td>
<td>22.5</td>
</tr>
<tr>
<td>Owner’s Cost</td>
<td>£ million</td>
<td>31</td>
</tr>
<tr>
<td>Pre-Licensing, Technical &amp; Design</td>
<td>£ million</td>
<td>4.4</td>
</tr>
</tbody>
</table>
Table 5.15 shows the final calculation for the total plant cost with HTCC integration including installation cost, indirect cost, Owner’s Costs and other relevant costs:

<table>
<thead>
<tr>
<th>Summary of total plant cost without capture</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gross power output</strong></td>
</tr>
<tr>
<td><strong>Net Power Output</strong></td>
</tr>
<tr>
<td><strong>EPC Contract cost</strong></td>
</tr>
<tr>
<td><strong>Infrastructure connection cost</strong></td>
</tr>
<tr>
<td><strong>Owner’s Cost(^2)</strong></td>
</tr>
<tr>
<td><strong>Pre-Licensing, Technical &amp; Design</strong></td>
</tr>
<tr>
<td><strong>Regulatory, Licensing &amp; Public Enquiry</strong></td>
</tr>
<tr>
<td><strong>TPC</strong></td>
</tr>
<tr>
<td><strong>Specific Investment - Gross</strong></td>
</tr>
<tr>
<td><strong>Specific Investment – Net</strong></td>
</tr>
</tbody>
</table>

For operating and maintenance cost, the assumptions mentioned previously in this section were followed to obtain O&M total cost to £ in 2017 without the consideration of carbon

\(^2\) Owner’s Costs are miscellaneous additional costs directly incurred by the owner of a project such as owner’s staff, land, permitting, environmental reporting and facilities
and fuel prices. Tables 5.16 and 5.17 present the operating and maintenance cost calculation before and after capture respectively:

Table 5-16: Operating and Maintenance cost before capture

<table>
<thead>
<tr>
<th>Fixed Operation Cost</th>
<th>Unit</th>
<th>Cost</th>
<th>Variable Cost:</th>
<th>Unit</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Labour</td>
<td>£ million pa</td>
<td>2.4</td>
<td>CO₂ Storage Cost</td>
<td>£/tonne CO₂</td>
<td>£ million pa</td>
</tr>
<tr>
<td>General Overheads</td>
<td>£ million pa</td>
<td>2.2</td>
<td>Cats &amp; Chems Consumption</td>
<td>£ million pa</td>
<td>0</td>
</tr>
<tr>
<td>Insurance and Local Taxes</td>
<td>£ million pa</td>
<td>8.9</td>
<td>Other</td>
<td>£ million pa</td>
<td>0.2</td>
</tr>
<tr>
<td>Power Island Maintenance</td>
<td>£ million pa</td>
<td>11.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Connection &amp; Use of System (£/MW/y)</td>
<td>£ million pa</td>
<td>2.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Fixed O&amp;M Cost</td>
<td>£ million pa</td>
<td>27.2</td>
<td>Total Variable O&amp;M Cost</td>
<td>£ million pa</td>
<td>0.2</td>
</tr>
<tr>
<td>Total O&amp;M cost excl carbon and fuel price</td>
<td>£ million pa</td>
<td>27.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5-17: Operating and Maintenance cost after capture

<table>
<thead>
<tr>
<th>Fixed Operation Cost</th>
<th>Unit</th>
<th>Cost</th>
<th>Variable Cost:</th>
<th>Unit</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Labour</td>
<td>£ million pa</td>
<td>3.1</td>
<td>CO₂ Storage Cost</td>
<td>£/tonne CO₂</td>
<td>£ million pa</td>
</tr>
<tr>
<td>General Overheads</td>
<td>£ million pa</td>
<td>4.4</td>
<td>Cats &amp; Chems Consumption</td>
<td>£ million pa</td>
<td>8.8</td>
</tr>
<tr>
<td>Insurance and Local Taxes</td>
<td>£ million pa</td>
<td>17.5</td>
<td>Other</td>
<td>£ million pa</td>
<td>0.2</td>
</tr>
</tbody>
</table>
### Table 5.18: Summary of economic parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Without Capture</th>
<th>With Capture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gross Electricity output</td>
<td>MW</td>
<td>837.3</td>
<td>1104.0</td>
</tr>
<tr>
<td>Net Electricity output</td>
<td>MWe net</td>
<td>829.9</td>
<td>991.9</td>
</tr>
<tr>
<td>Efficiency</td>
<td>%</td>
<td>58.3</td>
<td>48.6</td>
</tr>
<tr>
<td>CO₂ emissions</td>
<td>kg/MWh</td>
<td>351.6</td>
<td>30.7</td>
</tr>
<tr>
<td>Total Plant Cost</td>
<td>£ million</td>
<td>510.3</td>
<td>1000</td>
</tr>
<tr>
<td>Specific Investment - Gross</td>
<td>£/kW gross</td>
<td>615</td>
<td>905.7</td>
</tr>
<tr>
<td>Specific Investment - net</td>
<td>£/kW net</td>
<td>609.4</td>
<td>1008</td>
</tr>
<tr>
<td>Fixed O&amp;M</td>
<td>£ million pa</td>
<td>27.2</td>
<td>46.7</td>
</tr>
<tr>
<td>Variable O&amp;M</td>
<td>£ million pa</td>
<td>0.2</td>
<td>67.2</td>
</tr>
<tr>
<td>Levelized Cost of Electricity (LCOE) excl carbon price</td>
<td>£/MWh</td>
<td>49.6</td>
<td>73.9</td>
</tr>
</tbody>
</table>

Table 5.18 illustrates the summary of the economic parameters using method 2 including LCOE and cost of CO₂ avoided.
<table>
<thead>
<tr>
<th>Cost of CO₂ avoided excl. carbon price</th>
<th>£/tCO₂ avoided</th>
<th>0</th>
<th>75.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Levelized Cost of Electricity (LCOE) including carbon price</td>
<td>£/MWh</td>
<td>80</td>
<td>76.4</td>
</tr>
<tr>
<td>Cost of CO₂ avoided including carbon price</td>
<td>£/tCO₂ avoided</td>
<td>0</td>
<td>-11.2</td>
</tr>
</tbody>
</table>

5.3.4 **NGCC reference case with CaL system integrated**

In this section, method 2 was used to calculate the LCOE and cost of CO₂ avoided for CaL system when it is applied to the same base case study. Table 5.19 illustrate the technical parameters extracted from NGCC model with an integrated CaL system.

*Table 5-19: Summary of NGCC with CaL integrated technical parameters*

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1176</td>
<td>1030.5</td>
<td>550</td>
<td>287.7</td>
<td>338.5</td>
<td>10.5</td>
<td>59.4</td>
<td>51.6</td>
<td>20.4</td>
<td>48</td>
<td>46.2%</td>
</tr>
</tbody>
</table>

For CaL system, the absorber and regenerator sizing and costing were performed based on the method previously followed for Li-based HTCC system. For Summary of Fluidized bed sizing parameters and sizing results for CaL system, please refer to appendix A.2, table A.2.3. Table 5.20 shows summary for the direct cost of NGCC with CaL integrated without installation cost:
Table 5-20: Summary of direct cost of NGCC plant with CaL integrated

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Cost in 2017 £ million</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost of basic plant</td>
<td>264.6</td>
<td>[1, 2, 6]</td>
</tr>
<tr>
<td>Cost of Capture unit (including solid inventory)</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>Cost of secondary HRSG</td>
<td>9.6</td>
<td>[1, 2, 6]</td>
</tr>
<tr>
<td>Cost of Steam Turbines</td>
<td>45</td>
<td>[1, 2, 6]</td>
</tr>
<tr>
<td>Cost of Cooling water system and BOP</td>
<td>56.8</td>
<td>[1, 2, 6]</td>
</tr>
<tr>
<td>Cost of CO$_2$ compression and condenser</td>
<td>27</td>
<td>[135, 194]</td>
</tr>
<tr>
<td>Cost of ASU</td>
<td>110</td>
<td>[136]</td>
</tr>
<tr>
<td><strong>Total Direct cost</strong></td>
<td><strong>568.1</strong></td>
<td><strong>£ million</strong></td>
</tr>
</tbody>
</table>

Following to capital cost calculation, methods 1 and 2 were applied for NGCC plant with CaL system integrated. The results for the techno-economics for NGCC with CaL are presented in the following section.

5.3.5 **Summary of techno-economic assessment results**

The techno-economic results estimated for the NGCC with Li-based and CaL HTCC system using methods 1 and 2 are presented in this section. Table 5.21 summarizes the results of both costing methods for Li based and CaL based systems integrated in NGCC plant. Section 5.4 discusses techno-economic results for Li-based HTCC integration and comparison to HTCC CaL system.
### Table 5-21: Summary of techno-economic estimation for NGCC case with Li based and Ca based sorbents looping integrated

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>NGCC without capture</th>
<th>NGCC with Li$_2$SiO$_3$ HTCC</th>
<th>NGCC with CaL HTCC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Method 1</td>
<td>Method 2</td>
<td>Method 1</td>
</tr>
<tr>
<td>Total Plant Cost</td>
<td>£ million</td>
<td>580.2</td>
<td>510.3</td>
<td>1146</td>
</tr>
<tr>
<td>Specific Investment – Gross</td>
<td>£/kW gross</td>
<td>693.0</td>
<td>609.4</td>
<td>1038</td>
</tr>
<tr>
<td>Specific Investment – net</td>
<td>£/kW net</td>
<td>699.1</td>
<td>615</td>
<td>1156</td>
</tr>
<tr>
<td>Fixed O&amp;M</td>
<td>M£/year</td>
<td>44.9</td>
<td>27.2</td>
<td>88.7</td>
</tr>
<tr>
<td>Variable O&amp;M</td>
<td>M£/year</td>
<td>4.3</td>
<td>0.2</td>
<td>72.2</td>
</tr>
<tr>
<td>LCOE excl carbon price</td>
<td>£/MWh</td>
<td>42.3</td>
<td>49.6</td>
<td>67.5</td>
</tr>
<tr>
<td>Cost of CO$_2$ avoided excl carbon price</td>
<td>£/tCO$_2$ avoided</td>
<td>-</td>
<td>0</td>
<td>78.7</td>
</tr>
<tr>
<td>LCOE incl carbon price</td>
<td>£/MWh</td>
<td>-</td>
<td>80</td>
<td>-</td>
</tr>
<tr>
<td>Cost of CO$_2$ avoided incl carbon price</td>
<td>£/tCO$_2$ avoided</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

Before proceeding to the results discussion section, sensitivity analysis for several parameters is performed for Li-based HTCC integration case to have a further assessment for the technology integration as will be described in following section.

#### 5.3.6 Sensitivity Analysis

In this section, different economic and technical parameters were varied to investigate the effect of their variation on the LCOE before and after capture and on Cost of CO$_2$ avoided. All parameters were varied by ±25 % of it’s original value except the sorbent regeneration
temperature which was varied between 685 to 715°C. LCOE and Cost of CO₂ were estimated using calculation method 2 explained in 5.3.3, without the consideration of the carbon tax.

The following techno-economic parameters were considered in the sensitivity:

- Specific Investment (SI) net
- O&M Cost
- Fuel Price
- Discount cash flow factor
- Sorbent Cost
- Plant Capacity factor
- Net Plant efficiency

Figure 5.4, presents the impact of changing the previous techno-economic parameters on LCOE before and after the integration of Li-based HTCC system. Figures 5.5 and 5.6, summarize the results of varying techno-economic parameters ±25% on LCOE in % from the reference plant base case LCOE and cost of CO₂ avoided respectively.
Figure 5.4: Impact of varying SI, O&M cost, Fuel price, DF and capacity factor by ±25% on LCOE before and after the integration of Li-based CO₂ capture system and impact of varying Plant efficiency and sorbent cost, by ±25%, on LCOE after the integration of Li-based CO₂ capture system.
Figure 5.5: Effect of varying techno-economic parameters ±25% on LCOE in % from the NGCC plant reference case LCOE

Figure 5.6: Effect of varying techno-economic parameters ±25% on cost of CO$_2$ avoided in % from the NGCC plant reference case cost of CO$_2$ avoided
5.4 Results and discussion

For equipment direct cost calculations, all plant equipment except the fluidized bed was scaled and transferred to 2017 £ million, as shown in tables 5.7 and 5.8. For the fluidized bed system, a detailed bottom up approach was followed using the equipment sizing results to estimate the capital cost for each component, as shown in table 5.6. A direct cost of 51£ million for the fluidized bed system with the initial solid inventory was calculated without including the cost of the ASU, which was estimated separately. Figure 5.3 showed the break down for the NGCC plant direct cost after the integration of the Li-based looping system. Figure 5.3 showed that the cost of the GT and primary HRSG system contributes to 51.3% of the overall plant capital cost and they represent the cost of the original NGCC reference plant. Following to the reference plant equipment cost, it was found that the ASU recorded the second highest capital cost, with 13.5% of the overall capital cost, followed by the cost of the HTCC which recorded 9.9% of the overall capita cost. For CO₂ compression train, it was found that it contributes to 5.2% of the overall capital cost. For secondary HRSG, steam turbine and cooling system, it was found that overall capital cost of these equipment contributes to 19.8% of the overall capital cost.

For the techno-economic analysis, as explained in section 5.3, two methods were used and applied to the reference case study and also to the case with the integrated CaL technology for the same reference case. The advantage of using both methods is to give an indication about the impact of the techno-economic assumptions on the results of the techno-economic analysis. Method 1 mainly followed the EBTF methodology while Method 2 was based on the latest published guidelines for techno-economic calculations for new CO₂ capture technologies to be applied in UK.

Table 5.21 shows the techno-economic results for NGCC reference case without capture and with integrated Li-based and CaL based systems by using both evaluation methods. As seen in table 5.21, different calculation methods and assumptions result in different techno-economic evaluation results. For instance, the LCOE increased from 42.3 to 49.6 £/MWh for the reference plant when Method 2 was used, which is about +17% increase in the LCOE compared to Method 1. Also, for cases with Li and CaL capture systems, the LCOE increased from 67.5 to 73.9 and 67.8 to 77.1 £/MWh, respectively, when Method 2 is used instead of Method 1 for NGCC. The main reason of such discrepancies is the different assumptions between Methods 1 and 2. For instance, for NGCC with Li-based system integrated, the total project cost was estimated be 1146 £ million using
method 1 assumptions while the same total project cost was estimated to be 1000 £ million using method 2 assessment.

Although the capital and O&M cost for method 1 are estimated to be more than method 2, the final values for method 2 are higher due to the difference in some significant parameters such as fuel cost, no of years assumed for capital split and working capital allowances. For example, for method 1, the total fuel cost over the project life was estimated to be 5899 £ million while method 2 estimated a cost of 8044 £ million, which is 36.4% higher than the values resulted in Method 1. Also, for Method 2, working capital allowance was assumed and estimated to be 762 £ million over the life of the project while it was not considered in the calculation of method 1. For further reference to the methods assumptions, please refer to appendix A.3.

Also, considering the cost of CO$_2$ emissions, which was applied in Method 2 only, it was found that it had a great impact on cost of CO$_2$ avoided. For instance, for NGCC with Li-system integrated, it was found that by considering the carbon cost, the cost of CO$_2$ avoided dropped from 75.6 to -11.2 £/tCO$_2$. That means that the policies and regulations had a great impact on the viability and techno-economic assessment of the integration of novel carbon capture technologies such as Li-based CO$_2$ capture systems.

When comparing the results with those obtained for the integration of a CaL system, it was found that applying the same design constraints and economical evaluation parameters on the same NGCC power plant, the CaL integrated system will lead to a higher LCOE, 67.8 and 77.1 £/MWh, for Methods 1 and 2, respectively without considering the carbon tax. The cost of CO$_2$ avoided was estimated to be 82.5 and 88.9 £/tCO$_2$ for Methods 1 and 2, respectively, without considering any carbon tax. Those values were found to be higher than the values obtained for the Li-based case. The reason behind such results, is that the efficiency of CaL system, 46.2% L.H.V, is lower than that obtained for Li-based system, 48.6% L.H.V. Also, the emissions footprint for CaL system, 42.3 kg CO$_2$/MWh, is higher than that estimated for Li-based system, 31 kg CO$_2$/MWh, which affects the Cost of CO$_2$ avoided calculation. Additionally, the CO$_2$ storage cost for the CaL case, 61.8 £ million pa, is higher than that estimated for Li-based case, 58.3 £ million pa because the fuel consumption in CaL case is higher than that required for Li-based case and hence, resulted in higher CO$_2$ flow rate and hence higher CO$_2$ storage cost.
For the sensitivity analysis, a parametric change of ±25% of several techno-economic parameters was performed to investigate the effect of the main parameters on LCOE and cost of CO₂ avoided. Figures 5.4 to 5.6 show the effect of varying the selected parameters on LCOE and Cost of CO₂ avoided.

From the sensitivity results, it was found that net plant efficiency has the major impact on LCOE and cost of emissions. That is obvious from the nature of the plant, since the final product is electricity and improving the plant efficiency will lead to higher production of electricity with the same amount of fuel and CO₂ emissions. Hence, improving the net plant efficiency will lead to a massive reduction in LCOE and Cost of CO₂ avoided. Following plant efficiency, both the fuel price and capacity factors had the largest impact on LCOE, and cost of CO₂ avoided. For fuel cost, it was previously observed to have a great impact on LCOE and cost of CO₂ avoided as explained earlier in this section and showed that it was one of the main reason to have higher techno-economic figures when using method 2 rather than method 1. The capacity factor, similar to the plant efficiency, affects directly the net exported power and hence affect the final product of the plant.

The parameter that had the smallest effect on both, LCOE and cost of CO₂ avoided, was found to be the cost of sorbent. This result suggests that by improving other technical and economical parameters the high cost for Li-based sorbents can be overcome and lead to better plant techno-economics.

5.5 Conclusion

Li₄SiO₄/Li₂CO₃ high temperature looping CO₂ capture solution has been investigated as an important option to abate the exhaust CO₂ emissions resulting from NG fuel combustion in NGCC power plant. As a continuation for the assessment of the integration of novel high temperature Li-based sorbent capture technologies in a NGCC plant, a techno-economic study was performed to estimate the economic feasibility of integrating a Li₄SiO₄/Li₂CO₃ looping system in the plant.

Prior to performing the techno-economic analysis, a detailed design and sizing for the fluidized bed system was performed using the process modelling data obtained from the process integration study discussed in Chapter 4. The fluidized bed system was optimized based on splitting the GT flue gas between 8 absorbers connected with 4 regenerators for sorbent regeneration. The final optimized sizes were 5.4m x 10.5m and 4m x 10m for absorber and regenerator, respectively.
Following the fluidized bed sizing, a detailed bottom up approach was followed to estimate the direct cost for the fluidized bed system in 2017£ values. The cost for the rest of plant equipment was obtained and scaled from reference equipment costing data / curves available in literature and all values were also transferred to 2017£ values.

Two techno-economic methods were applied with different assumptions, to evaluate the levelized cost of electricity (LCOE), cost of CO$_2$ avoided and specific investment (SI) for the NGCC plant before and after the integration of a Li-based CO$_2$ capture system. Techno-economic Method 1 assumptions were obtained from the EBTF study and those for Method 2 were obtained from the latest UK published techno-economic guidelines for benchmarking new CO$_2$ capture technologies. Both methods were also applied to a CaL system integrated in the same reference NGCC plant.

It was found that by using Method 1, LCOE increased from 42.3 to 67.5 £/MWh and 67.8 £/MWh when applying Li-based and CaL based capture systems, respectively. The reason behind such increase in both cases is the expansion in capital and operational cost after the integration of the capture unit. With respect to cost of CO$_2$ avoided, it was found that the Li-based case achieved 78.7 £/tCO$_2$ while the CaL case achieved 82.5 £/tCO$_2$.

For Method 2, the techno-economic estimates are higher than those values obtained from Method 1 for all cases, i.e. reference case, Li-based CO$_2$ capture case and CaL CO$_2$ capture case. For instance, after applying Method 2, the LCOE for the base case without capture increased from 42.3 to 49.6 £/MWh. For the Li-based capture case, the LCOE increased from 67.5 to 73.9 £/MWh and the Cost of CO$_2$ avoided slightly decreased from 78.7 to 75.6 £/tCO$_2$. The reason behind this decrease is that the LCOE for the reference case was increased as well after applying the Method 2 assumptions which resulted in slightly lower Cost of CO$_2$ avoided when compared to Method 1.

Finally, to investigate the effect of the most relevant parameters on the process techno-economic, sensitivity analysis was conducted for 7 parameters, including SI, Plant efficiency, Discount factor, plant capacity factor, O&M cost, sorbent cost and fuel cost. The sensitivity analysis was performed on the Li-based case using Method 2 and the impact of the parameters on LCOE and Cost of CO$_2$ avoided was investigated. From the sensitivity analysis, it was found that the plant efficiency is the parameter that affected the most the LCOE and cost of CO$_2$ avoided, followed by fuel price and capacity factor. It was also found that the sorbent cost was the parameter that affected the least. These results showed that even if the cost of the sorbent is initially high, such as the case of
Li$_4$SiO$_4$, that cost can be offset with other advantages obtained from the sorbent properties such as stability and relatively good capture and integration performance.
Chapter 6  PROCESS INTEGRATION: CASE 2 – SMR 
H₂ PRODUCTION PLANT

6.1 Introduction

This chapter presents the process integration of a carbon capture system based on Li₄SiO₄ sorbent into a steam methane reforming (SMR) hydrogen production plant in a process known as sorption enhanced steam methane reforming (SESMR). Similar to the NGCC case, the Li-based sorbent will be integrated inside the H₂ SMR plant in a way that it can capture CO₂ during the process of H₂ production at relatively high temperature. A conceptual process integration study was conducted by making use of literature and lab obtained experiment results evaluated under SMR flue gas relevant conditions. The evaluation focused on demonstrating the advantages derived from regenerating the sorbents at lower temperatures than those needed in CaO-based capture systems and, their ability to capture CO₂ at higher temperature than amine-based solvents. Prior to the process integration study, lab tests were performed with inhouse synthesized Li₄SiO₄ in order to examine the sorbent performance under the relevant CO₂ concentration (14%) present in the syngas coming from the SMR reformer.

Also, as a part of the process integration assessment, the results of the Li₄SiO₄ based SESMR process are compared to CaO based SESMR and amine based solvent capture systems integrated into the same reference SMR H₂ plant. The comparison is established based on equivalent plant H₂ plant efficiency, equivalent CO₂ emissions and energy consumption for each technology.

Lastly, potential future improvements are proposed and discussed to improve the plant efficiency and lower the capture penalties.

6.2 Process Integration of Li₄SiO₄ based HTCC into SESMR plant

6.2.1 Modelling approach

The base case study model was performed based on 100,000 Nm³ h⁻¹ SMR H₂ production plant described in IEAGHG Technical report[196]. A rigorous SMR model was built in Aspen Plus steady state mode and it was used to estimate the plant streams heat and mass balances. Two main process models were created, with and without capture, to estimate the carbon capture integration penalties such as efficiency, energy and other electrical penalties.
The SESMR process has been modelled in this study based on the sorbent performance data obtained from lab test and literature under steam methane reforming conditions, as will be discussed in section 6.2.3. The SESMR unit has been modelled using a black box concept, where a combination of Gibbs and Stochiometric reactors were arranged to mimic the equilibrium shifted reaction for SESMR using Li-based sorbents. The black box SESMR reformer model was optimized to match the performance of the Li-based sorbents under SESMR conditions. For instance, CO\(_2\) absorption was modelled based on a fixed value of the sorbent fractional conversion for the Li\(_4\)SiO\(_4\)/CO\(_2\) reaction of 0.2. That conversion corresponds to 5 minutes residence time in SESMR, as reported by Essaki et al [128].

The following subsections includes further details for the base case with and without the integration of the capture system.

### 6.2.2 Base case without capture

The base case plant is based on a SMR H\(_2\) production plant with integrated power plant which mainly comprises of a gas turbine, heat recovery steam generator and steam turbine. Figure 6.1 shows the conceptual design of a SMR H\(_2\) production plant.

![Figure 6.1: Block Flow diagram for a Hydrogen production process using the SMR process](image)

The base case was a state of the art SMR plant with 100,000 Nm\(^3\)/h of pure hydrogen production operating in standalone mode without being integrated in any other process [119, 197]. NG is used as a fuel and feedstock for the plant. The base case includes a
feedstock pretreatment process, pre-reforming process, reforming process and a Pressure Swing Adsorption (PSA) unit for H₂. Figure 6.2 illustrates the process flow diagram for the SMR reference case.

As shown in figure 6.2, NG is fed and preheated to 135°C using hot syngas exiting the water gas shift reactor (WGR). The NG feed is split between feedstock stream and reactor furnace feed stream, which is sent to the main reformer furnace to provide the heat required for the reforming process. The feedstock is then mixed with the H₂ recycle stream before entering the desulphurization unit for H₂S removal. The convection section of the reformer exhaust section is used to preheat the feedstock entering the pre-reformer and the syngas before the reformer using the hot flue gas resulted from the NG burning in the reformer furnace.

The treated NG stream after the desulphurization unit is mixed with HP superheated steam before being heated in the convection section of the reformer to 370°C. The steam is mixed with NG stream to maintain a Steam to Carbon (S/C) ratio of 2.7 - 2.8 (molar basis). The residual amount of C₂ + components in the syngas after the pre-reformer should not exceed 500 ppmv. The low-carbon NG exiting the pre-reformer is also mixed with HP Superheated steam before being preheated to a temperature (around 700 °C) that is suitable to start the main reforming reaction in the reformer. The reformer working temperature is normally between 800-900°C. The amount of unreacted CH₄ in the syngas exiting the reformer should not exceed 3.3 to 4% dry molar basis. The following reaction represents the reforming reaction inside the reformer.

Reforming: \( \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \Delta H_{298} = 206 \text{kJ mol}^{-1} \quad \text{R(6.1)} \)

The convection section of the reformer is made up of a system of different coils which include: the feedstock preheater coil, pre-reformer preheater, reformer feed preheater, steam production (water boiler), and steam superheater.

The furnace part of the reformer is responsible for burning the fuel and providing the required heat to the steam methane reforming reactor. The outlet temperature of the flue gas exiting to the convection section is normally 800-900°C.

The syngas after the reformer is then passed to reformer waste heat boiler to be cooled to 320°C and generate HP saturated steam to be sent to the super heater coil.
Figure 6.2: Process flow diagram for 100,000 Nm$^3$/h SMR H$_2$ production plant$^3, 4$

$^3$ BL: Plant battery limits at which the H$_2$ is exported
$^4$ BFW: Boiler feed water
Following the reformer and waste heat boiler, the syngas is sent to WGR at which the excess steam converts CO to CO₂ and H₂ following the reaction R(7).

\[
\text{WGS: } CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_{298} = -41 \text{ kJ/mol} \quad \text{R(6.2)}
\]

The residual CO from the reformer is 2.5-3.5 % on a dry basis. The resulting H₂ rich stream is then passed through several heat exchangers to be cooled before entering a separator that condenses water out before it is passed to a PSA unit to remove impurities such as CH₄, CO₂, CO to produce H₂ with a purity > 99.9 %. The tail gas generated from the PSA unit is recycled and mixed with the reformer NG fuel to be burned in the reformer burner. A recycle stream of H₂ is compressed and sent back to be mixed with the reformer feed. HP steam is produced as a byproduct from the plant at 4.23 MPa and 395°C, which is sent to the steam turbine for electricity generation. Steam is produced in the hydrogen plant from the following locations:

- Reformer waste heat boiler (produces HP saturated steam - 64 % of the steam is produced here)
- HT shift waste heat boiler (produces HP saturated steam – 20% of the steam is produced here)
- Steam generation coil in the convection section of the reformer (16% of the steam is produced here)

The boiler feed water (BFW) required for steam generation comes from:

- Condensate from the turbine in the cogeneration unit.
- Condensate from the process condensate separator.
- Make up demi water from the demi water plant (See figure 6.2)

### 6.2.3 Base case with integrated carbon capture plant: H₂ SESMR plant

#### 6.2.3.1 Sorbent Thermodynamic assessment

Prior to the modelling and integration of Li₄SiO₄ based HTCC system into SMR plant, the performance of Li₄SiO₄ needs to be evaluated under the same conditions as the flue gas in the industrial SESMR process. That obtained data from lab tests are used as an input for the process model.
Previous studies on the performance of SMR plants with a capture unit based on Li₄SiO₄ pellets [128] have shown that the operating temperature for the reformer after the integration of a Li₄SiO₄ based capture system should be approximately 550°C. In that SESMR plant, the lithium-based pellets were tested under S/C of 3.5 at 1 bara and achieved maximum CH₄ conversion of 80% and a H₂ yield of 3.5 in 5 minutes. For a CO₂ flue gas concentration of 14% CO₂, the inversion temperature will be around 525°C which is close to the optimum operation temperature of 550°C obtained by Esaki et al [128]. Further lab tests using TGA were performed on pure lithium orthosilicate material to estimate the value of sorbent conversion under relevant conditions. The sorbent was tested under 14% CO₂ concentration and 525°C and the equation used to estimate sorbent conversion $X_{Li_4SiO_4}$ was similar to that used by Puccini et al [134] described in chapter 3. Figure 6.3 shows the Li-based sorbent conversion profile as a function of time in mol % at 525°C, atmospheric pressure and 14 % CO₂ concentration.

![Figure 6.3: Li₄SiO₄ fractional conversion under 14% CO₂ concentration and 525°C absorption temperature](image)

After 15 minutes reaction time, the Li₄SiO₄ sorbent achieves 20% mole basis conversion. It is worth mentioning that the same conversion was obtained in Essaki et al [98] under 15% CO₂ concentration, but after only 5 minutes and a working temperature of 550 °C. The same sorbent fractional conversion is also consistent with the results from Lee et al [198] after 5 minutes uptake and cyclic test under 15% CO₂ concentration and 550°C. Thus, an initial conversion value of 20% was considered in the SESMR process design.
6.2.3.2 \( \text{Li}_4\text{SiO}_4 \) based SESMR process modelling and integration

Based on previous process integration studies, the \( \text{Li}_4\text{SiO}_4 / \text{Li}_2\text{CO}_3 \) high temperature looping system was conceptually integrated in the SMR \( \text{H}_2 \) plant similar to the high temperature SESMR concept \([112, 113, 124, 199, 200]\) as will be described later in this section. By integrating the sorbent in the reformer through the SESMR process, the equilibrium of the steam methane reforming process (Reaction R-6.1) and water gas shift reaction (Reaction R-6.2) is shifted towards hydrogen production, and high quality hydrogen ( > 90% concentration) can be produced at relatively lower temperatures (550°C) than the conventional SMR process (700-950°C). Another advantage is the elimination of the WGS reactor which will help towards reducing the overall cost impact of the plant \([128, 200]\). In addition to that and similarly to the NGCC case, heat integration is possible in such system, which helps to achieve optimum heat recovery and minimize the penalties associated with the \( \text{CO}_2 \) capture process. Figure 6.4 illustrates the concept design of HTCC \( \text{Li}_4\text{SiO}_4/\text{Li}_2\text{CO}_3 \) looping based SESMR system.

![Figure 6.4: Schematic diagram for conceptual design of a HTCC \( \text{Li}_4\text{SiO}_4/\text{Li}_2\text{CO}_3 \) looping based Plant for integration with SESMR process based \( \text{H}_2 \) plant](image)

As explained in the SESMR concept, the SESMR process is mainly based on the following reactions:

Reforming: \( \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \Delta H_{298} = 206\text{kJ mol}^{-1} \)  \( \text{R}(6.1) \)
\[ \text{WGS: } CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_{298} = -41 \text{ kJ/mol} \quad \text{R(6.2)} \]

\[ CO_2 \text{ capture: } Li_4SiO_4 + CO_2 \leftrightarrow Li_2SiO_3 + Li_2CO_3 \quad \Delta H_{298} = -142 \text{ kJ/mol} \quad \text{R(6.3)} \]

\[ CH_4 + 2H_2O + Li_4SiO_4 - \text{Catalyst} \rightarrow Li_2CO_3 + Li_2SiO_3 + 4H_2 \quad \Delta H_{298} = 23 \text{ kJ/mol} \quad \text{R(6.4)} \]

As illustrated in figure 6.4, the Li\textsubscript{4}SiO\textsubscript{4} sorbent is circulated between the sorption enhanced steam methane reformer (SESMR, C-1) and regenerator (C-2) for CO\textsubscript{2} capture and regeneration, respectively (Reaction R-6.4). Heat recuperation between the circulated solid sorbent streams between the two reactors is not considered. Temperature values of 550ºC and 700 ºC were chosen to be the optimum working conditions for the SESMR process and sorbent regeneration, respectively, based on experiment results under SESMR relevant conditions.

Prior to entering the SESMR unit, the NG feed is combined with low pressure steam with a steam to carbon ratio of 3.5, to match the reference Li\textsubscript{4}SiO\textsubscript{4} lab test data under SESMR conditions [98]. Since the SESMR working temperature is 550ºC, the hot H\textsubscript{2} rich syngas, exiting the reformer at \( T_3 = 550 \) ºC, is used to generate HP Steam through the syngas HP HRSG heat exchangers (E-3). For sorbent regeneration and catalyst oxidation, the sorbent and catalyst are circulated to the regenerator column C-2. The Ni/AL\textsubscript{2}O\textsubscript{3} catalyst is sent along with the sorbent to the regenerator since the atmosphere in the regenerator is oxidation atmosphere due to high temperature and availability of O\textsubscript{2} [128]. Part of the NG feed is circulated to the regenerator along with oxygen feed for oxyfuel combustion. The oxyfuel combustion is used to regenerate the sorbent at the chosen working temperature (\( T_{\text{reg}} = 700\)ºC), similar to the regenerator in the NGCC case study (Chapter 4).

The regenerated lithium sorbents and oxidized catalyst enter the SESMR at a temperature equal to the regenerator working temperature (\( T_{\text{reg}}=700\)ºC), while the SESMR reaction...
takes place at a temperature of 550°C. Inside the reformer, excess heat is generated from the temperature difference between the recycled regenerated sorbent and the reformer working temperature. For best utilization of such excess heat, two in-boiler heat exchangers (E-4 and E-6) were chosen to be integrated inside the reformer. These help to control the temperature inside the reformer and utilize the excess heat to heat up/ boil / reheat water.

As mentioned previously, the sorbent regeneration takes place in C-2 where the CO₂ is recovered for transportation. During each carbonation – regeneration cycle, the fluidized sorbent is directed to the regeneration column after completing the required residence time inside the reformer. For sorbent fluidization and cycling, the sorbent is fluidized using the reformer feed gas and pure CO₂ in the reformer and regenerator, respectively, similar to the design applied in a CaL system [151].

To account for sorbent and catalyst deactivation, sorbent and catalyst makeup feed are added to the absorber. The deactivated catalyst / spent sorbent are extracted from the regenerator.

The hot CO₂ pure stream exits the regenerator at temperature \( T_1 = T_{\text{reg}} \) and part of the hot CO₂ stream exiting the regenerator is used to super heat the HP steam, before entering the HP steam turbine, through E-5. After E-5, the hot CO₂ stream is used to preheat the reformer feed to the required reforming temperature \( T_r = T_3 = 550°C \) through E-2. The remaining energy in hot CO₂ stream is used to generate LP steam, required for reformer feed charge, through E-2 by heating up the low-pressure water (LPW) return from the steam turbines. It is worth mentioning that the reforming reaction of methane \( R(6.1) \) is endothermic and needs heat to be added. However, this heat could be compensated by the heat generated from the capture and water gas shift reactions as well as the heat exchanged from the hot sorbent and catalyst coming from calciner at a temperature of 700°C. This heat integration helps to cover the heat requirement of the reformer, especially after heating up the feed charge to the reformer working temperature.

The overall \( \text{Li}_4\text{SiO}_4 \) SESMR \( \text{H}_2 \) production plant conceptual process model is presented in figure 6.5, which shows the block flow diagram for the \( \text{H}_2 \) SESMR case with CO₂ capture.
The SESMR is fed with a mixture of Li₄SiO₄ and commercial Ni/Al₂O₃ catalyst (NiO 18% wt.) along with the pretreated NG. The catalyst to sorbent ratio is kept equal to 0.3 as per the case of [113]. Figure 6.6 shows detailed process flow diagram for the Li₄SiO₄ based SESMR H₂ production plant.

As seen in figure 6.6, the integration of the Li₄SiO₄ based system into SMR H₂ plant is done based on the configuration of the HTCC scheme described in figure 6.4 and the conceptual integration block diagram in figure 6.5.

For process model description, further details are described in the following subsection.
Figure 6.6: Process flow diagram for the Li$_3$SiO$_4$ SESMR H$_2$ Production Plant
6.2.4 $H_2$ SESMR plant Process model description

A rigorous Aspen Plus model was built for the SESMR $H_2$ production plant. The NG feed is fed to the plant at the same conditions than those for the reference SMR reforming case without capture, i.e. at 9°C and 70 bara. The NG feed is throttled to 37 bara before being heated to 200°C using the hot CO$_2$ through the NG heater before entering the sulphur removal unit. A recycle from the final pure $H_2$ stream is sent to the sulphur removal to perform the hydrodesulphurization process. The de-sulphurated NG Feed is then passed by a turbo expander to reduce the pressure to the reformer working temperature while generating electricity from the gas expansion. The expanded NG feedstock is passed by another heat exchanger before being mixed with LP steam to produce the reformer feedstock with the S/C ratio of 3.5. The LP steam mixed with the NG is extracted from the LP steam return from the steam turbines and LP steam generated from the LPW process recycle. LPW recycle comes from the $H_2$ compressor KOD along with the LPW make up feed. The LPW feed is then pumped through LPFW Pump to the LPW preheater and LP boiler respectively to generate LP steam at 226°C to be mixed with the LP steam returned from the steam turbine before finally mixed with the de-sulphurated NG feed. The final reformer feedstock is further heated in reformer feed preheater and heater respectively to achieve a reformer feedstock with a temperature of 550°C similar to the reformer working temperature.

As described in section 6.2.1, the SESMR was modelled using a black box to overcome the Aspen Plus limitation of modelling the SESMR by using one reactor. Figure 6.7 shows the Aspen Plus configuration for the black box.

The SESMR process was designed to perform the CH$_4$ reforming / CO$_2$ capture processes, described in reactions (6-9), to achieve 75% CH$_4$ conversion and 3.5 $H_2$ yield in 5 minutes operation time [98, 128]. The reformer and the regenerator are working at a pressure of 1.2 bara, close to atmospheric.
Figure 6.7: Aspen Plus Process flow diagram for the SESMR black box
The sorbent is regenerated in the calciner by providing the required heat to reverse reaction R (6.3) towards the reactants. Oxyfuel combustion is used to provide the required heat for sorbent regeneration in the calciner which in turn requires the addition of extra natural gas to be burned with oxygen inside the calciner. For oxygen production, an air separation unit (ASU) is assumed to produce a 95% pure O$_2$ stream with 159 kWh/t O$_2$ similar to the cases reported in [201-203]. The oxygen-to-fuel ratio in the regenerator was set to achieve 3% excess oxygen. The oxyfuel combustion temperature inside the regenerator was adjusted by dilution of the 95% pure O$_2$ stream with a CO$_2$ recycle stream extracted from the hot CO$_2$ stream exiting the regenerator.

The main hot CO$_2$ exits the calciner at temperature of 700°C and heat is recovered from it in two stage heat exchanger operating at two pressures. The hot CO$_2$ stream passes first through a HP superheater to superheat the HP steam before entering the HP steam turbine. Following the HP steam super heater, the hot CO$_2$ is sent to two heat exchanger systems, one for heating up the NG and reformer feed to achieve a reformer feedstock with 550°C. The other heat exchanger system is used to produce LP steam required to achieve the designed S/C ratio of 3.5 in the reformer feed. After the CO$_2$ / LPW preheater, part of the CO$_2$ stream is recycled to dilute the pure O$_2$ before entering the regenerator to achieve 3% excess oxygen, as mentioned previously. The remaining CO$_2$ is further cooled before being compressed to the final transportation pressure, as will be explained later at the end of the current section.

The hot H$_2$ rich stream exits the reformer at 550°C and the heat is in a single stage HP heat recovery system through HPE -01, 02 & 03. After the H$_2$ heat recovery system, the H$_2$ stream is passed by a knockout drum (KOD) to remove any water content before being compressed through a multistage compressor. This compression is required to reach the PSA working pressure of 20 bara to meet the H$_2$ transportation requirements. The tail gas resulted from the PSA unit is recycled to the regenerator to contribute in the oxy fuel combustion required to regenerate the sorbent.

The knocked-out water from the H$_2$ compressor (KOD) is mixed with the LPW make up feed to be distributed in LP and HP water/steam systems. An HP pump is used to pressure part of the LP recycled water to 161 bara to be suitable for steam turbines and electricity generation. The HP water is heated up and partially boiled through the H$_2$ hot heat...
exchangers. Following the hot H₂ heat exchangers, an SESMR in-boiler high pressure heat exchanger, HPB-02, is used to recover the extra heat generated inside the SESMR unit. The HP steam generated from the SESMR in-boiler, HPB, is then passed by HP steam super heater using the hot 700°C CO₂ stream generated from the calciner. The HP super-heated steam leaves the super heater at 647°C before entering two pressure stage steam turbines. In the HP steam turbine, the steam pressure is reduced to 16 bara. The IP steam with 16 bara pressure is being reheated in an in-boiler steam re heater placed inside the SESMR to reheat the steam to 500°C before entering the second steam turbine. The steam leaves the second turbine at 1 bara pressure to be mixed with LP steam used in the reformer feed as described before.

For CO₂ compression to 110 bara, a multistage compression and auto-refrigeration train is used with a design similar to conceptual auto-refrigerated system [204] to achieve final liquid CO₂ stream, ready for transportation [196], with a purity of 94% mole basis.

Figure 6.8 illustrates the process flow diagram for the CO₂ compression and auto-refrigeration train. As it is shown in figure 6.8, the final CO₂ stream is further cooled to 25°C before being compressed to a pressure of 30 bara through two stages compression train with 25°C intercooling. The pressurized CO₂ stream is cooled again to 25°C before entering a molecular sieve dehydration unit to remove the remaining water in the CO₂ stream to a level below 1 ppmv [204]. After the molecular sieve, the dry CO₂ stream passes through a multi-stream heat exchanger unit. The function of the multi-stream heat exchanger is to further cool down the dry CO₂ stream to -55°C to achieve partial CO₂ condensation and hence two-phase cold CO₂ stream at -55°C and 30 bara. The two-phase CO₂ stream passes through two phase separator to split the rich CO₂ liquid stream from the CO₂ lean vapour stream. The rich CO₂ liquid stream is then expanded through a valve to a pressure of 25 bara reforming a two-phase low temperature CO₂ stream at -56°C. This stream is then used inside the multi-stream heat exchanger as an auto-refrigerant which provides refrigeration to the initial dry CO₂ stream entering the multi-stream Heat exchanger.
Figure 6.8: Configuration of CO₂ Compression train
For the vapor lean CO₂ stream, it also works an auto-refrigerant inside the multi-stream heat exchanger by cooling the dry CO₂ feed. The resulted reheated CO₂ rich liquid stream is then compressed to 81 bara through 5 stages compressor with intercooling system. The final 81 bara CO₂ stream is cooled to 22°C prior to condensate the rich CO₂ stream. The condensed CO₂ stream is finally pumped to a pressure of 110 bara through the CO₂ transportation pump to achieve final HP dense CO₂ stream as per the transportation requirements. For summary of process modelling assumptions, please refer to appendix A.5.

6.2.5 Process modelling and HTCC integration assessment parameters

Based on the process description and in order to evaluate the impact of the integration of HTCC system inside SESMR plant, several performance parameters were defined. The aim of these parameters was to assess the performance of the Li₄SiO₄/Li₂CO₃ looping SESMR H₂ plant and enable the performance comparison with the reference case without capture and with other CO₂ capture technologies. Figure 6.9 illustrates a simplified diagram for the SESMR plant inputs and products.

![Diagram of SESMR plant inputs and products](image)

*Figure 6.9: Simplified diagram for the main inputs / outputs in SESMR H₂ plant*

The SESMR plant is expected to import electricity due to the electricity consumption in the H₂/CO₂ compression trains and ASU. Hence, the demand for imported electricity needs to be considered to provide a fair plant performance assessment. In order to count for that input, several “equivalent” parameters such as the equivalent Hydrogen production efficiency and equivalent energy consumption are defined and will be discussed below. The equivalent emissions and equivalent fuel consumed in a NGCC
power plant without capture to generate the required imported electricity are calculated and incorporated in the “equivalent” metrics defined below.

**Hydrogen production efficiency (\(\eta_{H2}\))**:

Hydrogen production efficiency is defined as the ratio between the Hydrogen output energy based on L.H.V and the natural gas L.H.V energy input to the plant including reformed NG and heating NG. The following equation is used to calculate the hydrogen production efficiency [113]:

\[
\eta_{H2} = \frac{m_{H2} \cdot L.H.V_{H2}}{m_{in-NG} \cdot L.H.V_{NG}} \quad \text{Eq (6.1)}
\]

Where \(m_{H2}\) is the final \(H_2\) stream mass flow rate in kg/h, \(L.H.V_{H2}\) is the Hydrogen lower heating value which is 119.96 MJ/kg [196], \(m_{in-NG}\) is the mass flow rate of the natural gas feed to the reactor in kg/h, \(L.H.V_{NG}\) is the lower heating value for the NG feed and estimated to be 46.5 MJ/kg, similar to the value used in Chapter 4.

**\(H_2\) yield**:

\(H_2\) yield is used as an indication of the progress of the overall SESMR reaction and \(H_2\) production efficiency. It is calculated from the following formula:

\[
\text{\(H_2\) yield (mol} = \frac{\text{mol} - H_2}{\text{mol} - CH_4} = \frac{C_{H2, out} \cdot F_{tot, out}}{F_{CH4, in}} \quad \text{Eq(6.2)}
\]

Where \(C_{H2, out}\) is the \(H_2\) mole fraction in the outlet stream from the reactor in dry basis; \(F_{tot, out}\) is the total dry gas molar flow in kmol/h at the reactor outlet, and \(F_{CH4, in}\) is the molar flow rate of the methane, kmol/h, at the reactor inlet.

**\(CH_4\) conversion**:

\(CH_4\) conversion can be obtained from the following formula:

\[
\text{\(CH_4\) conversion} \% = (1 - \frac{C_{CH4, out} \cdot F_{tot, out}}{F_{CH4, in}} ) \times 100 \quad \text{Eq (6.3)}
\]

where \(C_{CH4, out}\) is the \(CH_4\) mole fraction in dry basis at the reactor outlet.

**Hydrogen Equivalent production efficiency**:

Considering the \(H_2\) production from the base case, 100,000 Nm\(^3\)/h, the hydrogen equivalent production efficiency can be estimated. It covers the electrical and hydrogen
production efficiencies by converting the produced / consumed electricity to an equivalent NG fuel input as per the following equation [205]:

$$\eta_{H2,eq} = \frac{m_{H2}.LHV_{H2}}{m_{NG, eq}.LHV_{NG}}$$  \quad \text{Eq (6.4)}

where \( m_{NG,eq} \) is the equivalent NG fuel input considering the hydrogen and electricity production. The equivalent NG fuel input \( (m_{NG,eq}) \) can be calculated from the following formula:

$$m_{NG,eq} = m_{in-NG} - \frac{W_{el}}{\eta_{el}.LHV_{NG}}$$  \quad \text{Eq (6.5)}

and assuming \( \eta_{el} = 58.3\% \) based on Natural gas combined cycle power plant efficiency [206].

\( \eta_{H2,eq} \) is a useful term in comparing the hydrogen plant before and after capture based on the combination of electrical and hydrogen production.

**Carbon Capture Ratio (CCR):**

The Carbon Capture ratio (CCR) is calculated from the ratio between the mass flow rate of the captured CO\(_2\) and mass flow rate of the CO\(_2\) resulted from the natural gas feed to the plant. The following formula is used to estimate the CCR:

$$CCR = \frac{m_{T-CO2}}{m_{NG, Feed}.LHV_{NG}.E_{NG}.001}$$  \quad \text{Eq (6.6)}

where \( m_{T-CO2} \) is the final mass flow rate of the CO\(_2\) in the transportation pipeline, \( m_{NG, Feed} \) is the total amount of NG feed to the plant and \( E_{NG} \) is the specific CO\(_2\) emissions per unit of energy input of NG. The value of \( E_{NG} = 57 \text{ gCO}_2/\text{MJ}_LHV_{NG} \) based on the initial composition of the NG feed as per the base case data [113, 197].

**Specific CO\(_2\) emissions (SE):**

The Specific CO\(_2\) emissions (SE) are expressed in gCO\(_2\) per MJ of H\(_2\) and represent the amount of CO\(_2\) emissions produced in grams per each MJ of H\(_2\) produced to the battery limit. This parameter can be obtained from the following equation:

$$SE = \frac{m_{v-CO2}}{m_{H2}.LHV_{H2}} .1000$$  \quad \text{Eq (6.7)}

where \( m_{v-CO2} \) is the mass flow of the vented CO\(_2\) to the atmosphere in kg/h.
To account for the equivalent produced emissions, the equivalent carbon capture ratio ($CCR_{eq}$) and equivalent specific CO$_2$ emissions ($SCE_{eq}$) can be calculated.

**Equivalent carbon capture ratio:**

The equivalent carbon capture ratio ($CCR_{eq}$) can be calculated from the following equation:

$$CCR_{eq} = \frac{m_{T-CO2}}{m_{NG, eq} \cdot LHV_{NG} \cdot E_{NG} \cdot 0.001}$$

Eq (6.8)

**Equivalent Specific CO$_2$ Emissions**

Similar to $CCR_{eq}$, Equivalent specific CO$_2$ emissions ($SCE_{eq}$) can be calculated from the following equation:

Equivalent specific CO$_2$ emissions ($SE_{eq}$) = \( \frac{m_{NG, eq} \cdot LHV_{NG} \cdot E_{NG} \cdot 0.001 - m_{T-CO2}}{m_{H2} \cdot LHV_{H2}} \) . 1000

Eq (6.9)

**Equivalent Specific Primary Energy Consumption for CO$_2$ avoided:**

The Equivalent Specific Primary Energy Consumption for CO$_2$ avoided ($SPECCA_{eq}$) estimates the equivalent consumed thermal energy to avoid 1 kg of CO$_2$ emissions. That parameter is calculated by comparing the thermal energy of the plant after the integration of the Li-based capture unit with the thermal energy consumption in the reference case without capture. The following equation is used to calculate the $SPECCA_{eq}$:

$$SPECCA_{eq} = \frac{1}{\eta_{H2,eq}} \frac{1}{SCE_{eq,ref}}$$

Eq (6.10)

Where $\eta_{H2,eq,ref}$ & $SCE_{eq,ref}$ are the reference case equivalent hydrogen production efficiency and specific CO$_2$ emissions, respectively.

6.3 Results and Discussion

In this section, the results of the process modelling and integration are discussed including the simulation results of the reference case with and without capture. The simulation results are also compared to other capture technologies. Finally, possible future possible improvements to the model are discussed to be considered in future studies.
6.3.1 Evaluation of SESMR plant performance parameters

The simulation results for SMR H₂ production plant, with and without the integration of Li₄SiO₄ / CO₂ capture system (SESMR), are summarized in table 6.1. Previously described performance and energy parameters were estimated. A breakdown for the gross power output and consumption from the overall plant is also presented. All these parameters were used to compare the modelling results with other technologies. As shown in table 6.1, the hydrogen production efficiency for the plant before and after capture are 75.9% and 72.2%, respectively. The SESMR H₂ production efficiency is reduced by 3.7% points of efficiency compared to the base case while achieving 99% carbon capture ratio (CCR). The reason behind the efficiency reduction, for the SESMR case, is that the total hydrogen produced in the SESMR plant (8.6 t/h) is lower than that produced from the base case (9.0 t/h), while the natural gas feedstock is fixed for both cases. Also, the sorbent regenerating by oxyfuel combustion, has led to slightly higher NG fuel consumption, 4.4 t/h, compared to the fuel consumed in the base SMR case for heating the reformer, 4.3 t/h.

Table 6-1: Summary of modelling results for SMR / SESMR cases. SESMR operates at 550°C for reforming temperature, 700°C regeneration temperature, 0.2 fractional conversion and excess 3 % O₂

<table>
<thead>
<tr>
<th>Plant Performance Data</th>
<th>Units</th>
<th>Base case</th>
<th>SESMR Plant</th>
</tr>
</thead>
<tbody>
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<td>Natural Gas Feed Stock</td>
<td>t/h</td>
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<td>26.2</td>
</tr>
<tr>
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<td>t/h</td>
<td>4.3</td>
<td>4.4</td>
</tr>
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<td>MJ/Kg</td>
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<tr>
<td>Total Energy Input</td>
<td>MW</td>
<td>394.8</td>
<td>395.7</td>
</tr>
<tr>
<td>Plant Output Summary</td>
<td></td>
<td></td>
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<tr>
<td>Hydrogen Production to BL</td>
<td>t/h</td>
<td>9.0</td>
<td>8.6</td>
</tr>
<tr>
<td>Hydrogen Production to BL</td>
<td>Nm³/h</td>
<td>100000</td>
<td>95387.5</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-------</td>
<td>--------</td>
<td>---------</td>
</tr>
<tr>
<td>Hydrogen L.H.V</td>
<td>MJ/Kg</td>
<td>120.0</td>
<td>120</td>
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<tr>
<td>Total Energy in the product</td>
<td>MW</td>
<td>299.7</td>
<td>285.7</td>
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**Power Balance**

<table>
<thead>
<tr>
<th></th>
<th>MW</th>
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</thead>
<tbody>
<tr>
<td>Gross Power output from the steam turbines</td>
<td></td>
<td>11.5</td>
<td>27</td>
</tr>
<tr>
<td>Power output from expanders</td>
<td></td>
<td>0.0</td>
<td>4.3</td>
</tr>
<tr>
<td>Hydrogen Plant power Consumption</td>
<td>MW</td>
<td>1.2</td>
<td>16.7</td>
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<tr>
<td>Utilities + BOP</td>
<td>MW</td>
<td>0.4</td>
<td>1.2</td>
</tr>
<tr>
<td>CO₂ capture (ASU+...)</td>
<td>MW</td>
<td>0.0</td>
<td>7.7</td>
</tr>
<tr>
<td>CO₂ compression</td>
<td>MW</td>
<td>0.0</td>
<td>9.2</td>
</tr>
<tr>
<td>Excess electricity to the grid</td>
<td>MW</td>
<td>9.9</td>
<td>-3.7</td>
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**Fuel Consumption**

<table>
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<tr>
<th></th>
<th>GJ/1000 Nm³ H₂</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Natural Gas as a feedstock</td>
<td></td>
<td>12.2</td>
<td>12.8</td>
</tr>
<tr>
<td>Natural Gas as a fuel</td>
<td></td>
<td>2.0</td>
<td>2.1</td>
</tr>
<tr>
<td>Feed + Fuel</td>
<td></td>
<td>14.2</td>
<td>14.9</td>
</tr>
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</table>

**Emissions**

<table>
<thead>
<tr>
<th></th>
<th>t/h</th>
<th></th>
<th></th>
</tr>
</thead>
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<tr>
<td>CO₂ final Emissions to air</td>
<td></td>
<td>80.9</td>
<td>1.1</td>
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<tr>
<td>CO₂ to pipeline</td>
<td>t/h</td>
<td>0.0</td>
<td>80.1</td>
</tr>
<tr>
<td>Specific CO₂ captured</td>
<td>t/1000 Nm³ H₂</td>
<td>0.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Specific CO₂ Emissions (SE)</td>
<td></td>
<td>75.0</td>
<td>1.1</td>
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</table>

Performance parameters
<p>| | | | |</p>
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<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>S/C Ratio</td>
<td>-</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Overall CO₂ capture Ratio (CCR)</td>
<td>%</td>
<td>0.0</td>
<td>99</td>
</tr>
<tr>
<td>Hydrogen Production Efficiency (η₇₂)</td>
<td>% L.H.V</td>
<td>75.9</td>
<td>72.2</td>
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<tr>
<td>H₂ Yield</td>
<td>-</td>
<td>3.5</td>
<td>3.4</td>
</tr>
<tr>
<td>CH₄ Conversion</td>
<td>%</td>
<td>84.5</td>
<td>75</td>
</tr>
</tbody>
</table>

**Equivalent efficiencies**

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalent NG Flow (mₙGₜₜₑq)</td>
<td>t/h</td>
<td>29.2</td>
<td>31.1</td>
</tr>
<tr>
<td>H₂ Equivalent Efficiency (η₇₂ₑq)</td>
<td>%L.H.V</td>
<td>79.3</td>
<td>71.1</td>
</tr>
<tr>
<td>Equivalent Carbon capture ratio (CCRₑq)</td>
<td>%</td>
<td>0.0</td>
<td>97.1</td>
</tr>
<tr>
<td>Specific CO₂ Equivalent Emissions (SEₑq)</td>
<td>gCO₂/MJH₂ₑq</td>
<td>71.8</td>
<td>2.4</td>
</tr>
<tr>
<td>SPECCAₑq</td>
<td>MJ/kgCO₂</td>
<td></td>
<td>2.1</td>
</tr>
</tbody>
</table>

For the plant Specific CO₂ Emissions (SE), it was found that the SE dropped from 75.0 (base case) to 1.0 gCO₂/MJH₂, achieving almost 99% reduction in the specific emissions. Similar to the H₂ production efficiency, both the hydrogen yield and methane conversion were reduced in the SESMR case. The hydrogen yield dropped from 3.5, for the base case, to 3.4 for the SESMR case, whereas methane conversion decreased from 84.5 % to 75 %. The main reason for the obtained reductions is that the reforming conversion reaction R(6) is favored at high temperature[113, 114, 205, 207]. Hence, lowering the reforming temperature in the SESMR case (from 900°C to 550°C) would lead to a decrease in the reforming efficiency. However, such decrease is partially compensated by the effect of combining the CO₂ capture reaction R(6.3) with R(6.1) and R(6.2) as the continuous CO₂ removal from the system will promote the overall reaction R(9) to be shifted towards the products side [113, 128] leading to enhancing the methane reforming process. It is worth mentioning, that performing the reforming process at a lower pressure of 1.2 bara, compared to the original reforming pressure of 28 bara, also helps to increase the reforming performance as the methane reforming reaction R(6.1) is favored at low pressure [114, 207].
A full assessment of the plant performance after the integration of CO\textsubscript{2} capture system also requires counting for electricity and power consumption / production. For electricity and power production consumption, we can see that the SMR base case produces 11.5 MW from the HP steam enters the steam turbines and after considering the different power consumers and auxiliaries inside the plant, there is an excess electricity of 9.9 MW exported to the grid. For SESMR, the design of the cogeneration plant turbines generates 27 MW electricity from the HP superheated steam enters the turbine. However, due to the large number of auxiliaries and power consumers inside the plant, there is a requirement for importing 5.5 MW from the grid. The reasons behind the power shortage, is the high-power demand requirements for the hydrogen compressors and CO\textsubscript{2} compressors which is almost equal to 26 MW. The requirement of the hydrogen compressors existed due to generating the hydrogen at SESMR process at low pressure, 1.2 bara, at which the final Pressure swing adsorption unit, PSA, cannot work since it is designed to work at high pressures, 20 - 25 bara[113, 197]. Also, the ASU consumes around 7.7 MW which lead to a further shortage in the plant power consumption after considering the utilities and BOP power consumptions. Figure 6.10 shows breakdown of power production / consumption in MW for SESMR.

![Figure 6.10: Power production / consumption breakdown in MW for SESMR plant](image-url)
After counting for the power consumptions inside the SESMR plant, the equivalent parameters are estimated to count for the emissions coming from producing electricity required for the plant consumption and its effect on the overall plant efficiency, as explained in 6.2.3. That was reflected in the equivalent performance parameters: $m_{NG,eq}$, $\eta_{H2,eq}$, $CCR_{eq}$, $SE_{eq}$ and finally the equivalent specific primary energy consumption for CO₂ avoided ($SPECCA_{eq}$). Looking at the equivalent values for the SMR plant base case, it was found that base case SMR plant consumes an equivalent value of NG flow of 29.2 t/h which is almost 4.3 % lower than the original NG consumption, 30.6 t/h. The reason behind that equivalent fuel consumption reduction is that the plant is exporting electricity to the grid equal to 9.9 MW. That means that the equivalent NG used to produce the pure hydrogen at the battery limit is equal to 29.2 t/h. It is worth mentioning that $m_{NG,eq}$ for the SMR plant, is higher than the reformer NG feed, 26.2 t/h, by 11.5%. The reason behind this is that 1.6 MW of the generated electricity from the turbines, has been used inside the SMR process. That resulted in such increment in the equivalent NG feed when compared to the initial NG feed value to the reformer. Based on the equivalent NG consumptions, an equivalent $H_2$ efficiency ($\eta_{H2,eq}$) of 79.3% was estimated for SMR plant achieving an increase of 3.4% points of efficiency compared to the net $H_2$ production efficiency, due to the reduction of the equivalent NG feed after considering the exported electricity. Similar to the plant equivalent efficiency, $\eta_{H2,eq}$, the plant equivalent specific emissions, $SE_{eq}$, has been improved as it has been reduced by 4.2% achieving 71.5 gCO₂ / MJH₂eq emissions. The reason for the reduction is that part of the emissions from the natural gas feed is omitted due to exporting the electricity. For SESMR equivalent values, it was found that base case SESMR plant consumes an equivalent value of NG flow of 31.1 t/h which is almost 1.6% and 18.6 % higher than the original overall NG consumption, 30.6 t/h, and the reforming NG feed, 26.2 t/h, respectively. The reason behind those increment, is that the SESMR imports electricity from the grid equal to 3.7 MW to cover the shortage in plant power consumption. The imported electricity has been translated into equivalent NG value based on the assumption that that amount of electricity is produced by a NGCC plant with an efficiency of 58.3 % as explained earlier. For the SESMR plant equivalent specific emissions, $SE_{eq}$, unlike the SMR base case, $SE_{eq}$ has been increased from 1.1 to 2.4 gCO₂ / MJH₂eq after counting for the emissions coming from the imported electricity. Similar to $SE_{eq}$, the $CCR_{eq}$ have been reduced to 97.1% instead of 99% capture rate. To count for the equivalent energy consumption and similar
to the calculations in chapter 4, $SPECCA_{eq}$ was calculated based on the equivalent efficiencies and equivalent emissions for the SMR and SESMR plants as explained earlier achieving 2.1 MJ/kgCO$_2$. That means there is an energy equivalent penalty of 2.1 MJ for each kg of CO$_2$ captured.

6.3.2 Technical feasibility of Li4SiO4 SESMR integration

To achieve a feasible SESMR integration, several aspects should be considered such as thermodynamic impact, mechanical integration impact and the final cost impact. In this section, we will discuss the impact of SESMR integration with respect to overall plant thermodynamics. This could help to prove the feasibility of achieving such integration and modification for the SMR process.

To investigate the thermodynamic effect of changing the plant design to accommodate the SESMR system, Figures 6.11 & 6.12 show the TQ curves for the heat recovery systems in the original SMR plant and SESMR plant, respectively.

Figure 6.11: a) $T$-$Q$ curves for reformer convection heat recovery system in SMR plant. b) $TQ$ curves for syngas heat recovery system in SMR plant

Figure 6.11 illustrates the T-Q curves a) for reformer convection section and b) for the hot syngas heat recovery after the water gas shift (WGR) reactor. From figure 6.11-a and, as explained in the SMR description, the PSA tail gas is mixed with NG fuel and burned in the reformer combustion chamber along with air to provide the heat required for the
reforming process. The generated flue gas exits the reformer burners at 1 bara and 900°C. The generated flue gas is passed by a series of heat exchangers located inside the reformer convection section and exits the reformer at 112°C as can be seen in the hot flue gas red line in figure 6.11 a). In the reformer convection section, the heat exchangers were arranged, from colder to hotter flue gas sides, as per the following: air preheater, steam generator, feed preheater, HP steam superheater, pre-reformer pre-heater and finally reformer preheater as shown in the PFD for the SMR plant in figure 6.2. The hot 900°C flue gas is used to generate HP superheated steam for the reformer feed through steam generator and steam superheater heat exchangers. The Boiler feed water feed is pumped through HP pump to 42 bara before passes through a BFW heater, in the syngas heat recovery system, before being split into two streams. The HP water is divided into three streams to be heated in three heat exchangers distributed between the reformer and syngas heat recovery systems. For reformer convection section, 23.5 t/h HPFW is feed to the steam generator at 195°C and 42 bara to generate part of the HP steam required for the reformer feed. The generated steam leaves the steam generator at 245°C. The HP steam generated from the reformer convection section is combined with the HP steam generated from the syngas section to form a final HP steam flow of 142 t/h. The combined HP steam flow is passed by the steam superheater, in the reformer convection section, to generate super-heated HP steam at 400°C. Since the flow rate of steam, generated from the reformer steam generator and steam super heater, are different, a change in the HP steam slope of the two HP steam (light orange) lines can be observed in the TQ curve for the reformer convection section. Part of the HP super-heated steam is sent to steam turbines to generate 11.5 MW of electricity. The remaining superheated steam, 95 t/h, is split between the pre-reformer and the reformer feed streams. A steam flow rate of 76 t/h is being mixed with the pre-reformer feed after leaving the sulphur removal unit. The pre-reformer feed (light green TQ line) is being initially heated to a temperature of 370° at the feed preheater before entering the sulphur removal unit. The pre-reformer feed mixed with steam (green TQ line) is then being heated to 500°C before entering the pre-reformer. The resulted syngas leaves the pre-reformer at 447°C and 34 bara before being mixed with 19 t/h of HP super-heated steam. The final reformer feed (purple TQ line) is then passed by a reformer preheated to heat it up to 700°C before entering the reformer for final reforming. For the combustion air pre-heater (light blue line), the combustion air used in the reformer burner, is being preheated to 254°C before entering the reformer
burner. Preheating the air helps to reduce the fuel consumption inside the reformer to reach the required reforming temperature.

Figure 6.11-b represents the heat recovery section after the high temperature (HT) shift reactor. The purple TQ line represents the hot syngas exiting the HT shift reactor at 417°C and 28 bara. The syngas exits the syngas heat recovery system at temperature of 134°C after heating up the NG feed and boiler feed recirculated water. The syngas heat recovery system includes 4 heat exchangers: Shift waste heat boiler, BFW heater, NG feed preheater-1 and condensate heater. The NG feed preheater-1 is used to heat the NG feed (Light green TQ line) to 135°C before being sent to the reforming section.

For water / steam system, LP steam exits the turbine at 78°C and 0.4 bara and is condensed before being mixed with boiler feed water (BFW) make-up. The BFW recirculated stream is then mixed with the water condensate extracted in the separator unit before the PSA. The final BFW condensate stream is passed by a condensate heater (light blue line) to heat it up to 150°C before being pumped through the HP pump to 42 bara. The HP water feed stream then enters a BFW heater to heat it up to 195°C (Dark blue line). The heated HP BFW stream is then split between three steam generators: the reformer convection section steam generator, shift waste heat boiler and the reformer waste heat boiler. The orange line in figure 6.11-b represents the HP BFW being heated in the shift waste heat boiler. It is worth mentioning that in figure 6.11-b, the syngas slope has been changed twice. The reason behind this is that energy content of the syngas stream has changed due to the condensation of water content, mixed in the syngas stream, during the heat recovery process, hence changing the heat capacity flow rate.

Figure 6.12 shows the TQ curves for the Hot CO₂ section leaving the regenerator (a) and for the hot syngas leaving the SESMR unit (b).
In figure 6.12-a, the hot CO\textsubscript{2} leaves the regenerator at 700°C and then directed towards a series of heat exchangers to make use of the energy content. The hot CO\textsubscript{2} stream exits the series of heat exchangers at a temperature of 170°C. The red line in figure 6.12-a represents the TQ line for the hot CO\textsubscript{2} stream. The function of the hot CO\textsubscript{2} heat recovery section is to generate the LP steam required for the SESMR process, preheat the NG fuel feed and preheat the final SESMR feed before entering the reforming unit. Also, part from the energy content of the hot CO\textsubscript{2} stream is used to superheat the HP steam before entering the HP steam turbine for electricity generation. For LP water system, the LP water knocked out from the PSA compressor knock out drum (KOD) is mixed LPW feed makeup before being pumped to the LPW preheater. The LPW feed is being heated in the LPE preheater to 105°C. The heated LPW feed is then passed by LPB to generate LP steam at 226°C. The generated LP steam is then mixed with LP steam that exits the turbines at a temperature of 162°C. The combined LP steam stream is then superheated in the LPST-SH to a temperature of 432°C. It is worth mentioning here as well that due to the change of the LP steam flow rate, the slope of the superheated steam TQ line is different from the slope of the LP steam generated in the LP boiler. The superheated steam is then mixed with the preheated NG feed exiting the sulphur removal unit to prepare the SESMR unit feed.

For the NG feed, it is being fed at 70 bara and 9°C similar to the SMR base case condition. The NG feed is then throttled to 37 bara and -10°C. The throttled NG feed is then passed by a NG-H to 200°C. The heated NG feed is then directed to a sulphur removal unit at
which it is mixed with H₂ recycle to remove the sulphur content from the NG feed. The desulphurized NG feed is then passed by a turbo expander to generate electricity while expanded to the SESMR working pressure of 1.4 bara. The depressurized NG feed is then passed by another NG feed heater (Fuel-H) to heat it up to 363°C. The heated NG feed is then mixed with the LP superheated steam to form the SESMR feed charge with 3.54 S/C ratio. The reactor feed is then further heated to 424°C and 550°C in the reformer feed preheater and reformer feed heater respectively (dark green TQ line). The final heated reformer feed enters the SESMR at 550°C.

As mentioned previously, the LP steam is being generated in the hot CO₂ heat recovery system while the HP steam is mainly generated from the hot Syngas Heat recovery system and SESMR in-boiler heater. The generated HP steam from the SESMR in-boiler heaters is then directed to HP steam superheater, which is fed by the hot CO₂ exiting the regenerator cyclones, for further superheating. The HP superheated steam exits the superheater at a temperature of 650°C then it is directed to the steam turbines for electricity generation. The light orange TQ line represents the TQ line for the HP superheated steam.

Figure 6.12-b represents the TQ lines for the heat recovery system using the heat extracted from the regenerator after regenerating the sorbent at 700°C and heat extracted from the hot syngas leaving the reactor at 550°C (red lines). The orange lines represent the TQ lines for HP water/Steam system. Through the high-pressure feed water (HPFW) pump, the feed water is pumped to 161 bara before passing through the first HP economizer, HPE-01. The HPFW is heated in HPE-01 to 122°C. The heated HP feed water is then further heated in another heat exchanger, which is located at the start of the CO₂ compression train, to 156°C. The heated HPFW is then returned back to pass through the hot syngas heat recovery system, in HPE-02 and HPE-03 to heat it up to 337°C before entering the SESMR in-boiler HPB to generate HP steam at 437°C and 138 bara. The HP steam is then superheated in HP superheater to 650°C before entering the HP steam turbine for electricity generation.

From the above discussion, it is obvious that the plant thermodynamics have changed due to major modifications in the plant equipment. However, based on the TQ curves showed in figure 6.12, it can be concluded that the Li₄SiO₄ based SESMR H₂ process is feasibly from a thermodynamic and heat integration point of view.
Regarding equipment modifications and mechanical integration, as a conceptual design, the SESMR design is proposed to be applied for newly built plants since it requires major modifications in the plant equipment. It is worth mentioning that SESMR would work at low pressure which will lead to a more simplified equipment design and potentially lower costs. Also, the elimination of the water gas shift reactor and pre-reformer reactors contribute to further savings of capital cost. The techno-economics of the proposed SESMR will be discussed in the next chapter.

6.3.3 Comparison to other capture technologies

This section compares the Li-based SESMR H₂ production plant with other CO₂ capture technologies integrated in the same H₂ reference plant.

Table 6.2 shows the comparison between Li₄SiO₄ based SESMR Plant and different CO₂ capture systems applied to the same reference plant. The other CO₂ capture technologies are MDEA, which is the based-on amine-based solvents, and CaO based SESMR design. The Li₄SiO₄ SESMR integration case achieved an H₂ production efficiency of (72.2%) which is lower than that for CaO (79.9 %) and close to that for MDEA technology (73.5%). The reason behind that the H₂ production efficiency in case of Li₄SiO₄ is lower than CaO, is that the performance of the Li₄SiO₄ SESMR is lower than that for CaO with respect to hydrogen production since the CaO SESMR case is based on 600°C reforming temperature and 31% CO₂ conversion inside the reactor while Li-SESMR operates at 550°C and considered 20% CO₂ conversion inside the reformer. For the case of MDEA, the H₂ production efficiency is higher than both SESMR cases since there is no change in the original plant as the MDEA capture unit was added downstream of the reformer.

Looking at the emissions reduction performance for each technology, both Li₄SiO₄ and CaO SESMR cases achieved very low specific CO₂ emissions, 1.1 gCO₂/MJH₂, compared to 31.2 gCO₂/MJH₂ for MDEA. The reason for this is that the concept of the design of SESMR aims to achieve high capture rate, up to 99% CO₂ capture, while the MDEA technology does not cover all the CO₂ sources inside the plant as it only capture CO₂ from the reformer flue gas achieving 55.7% CO₂ capture rate.
Table 6-2: Comparison of integration results into H\textsubscript{2} SMR plant for different capture technologies

<table>
<thead>
<tr>
<th>Performance Parameters</th>
<th>Unit</th>
<th>Reference Case without capture</th>
<th>SMR Plant with MDEA</th>
<th>CaO-based SESMR</th>
<th>Li-based SESMR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[196]</td>
<td>[113]</td>
<td>This Work</td>
<td></td>
</tr>
<tr>
<td>Total natural Gas Consumption</td>
<td>t/h</td>
<td>30.6</td>
<td>31.6</td>
<td>8.7</td>
<td>30.6</td>
</tr>
<tr>
<td>Hydrogen Production to BL</td>
<td>t/h</td>
<td>9.0</td>
<td>9.0</td>
<td>2.7</td>
<td>8.6</td>
</tr>
<tr>
<td>Gross Power output from the steam turbines</td>
<td>MW</td>
<td>11.5</td>
<td>6.7</td>
<td>5.1</td>
<td>26.9</td>
</tr>
<tr>
<td>Power output from expanders</td>
<td>MW</td>
<td>0.0</td>
<td>0.0</td>
<td>1.4</td>
<td>4.3</td>
</tr>
<tr>
<td>Total Power consumption</td>
<td>MW</td>
<td>1.6</td>
<td>5.2</td>
<td>11.2</td>
<td>34.9</td>
</tr>
<tr>
<td>Excess electricity to the grid</td>
<td>MW</td>
<td>9.9</td>
<td>1.5</td>
<td>-5.0</td>
<td>-3.7</td>
</tr>
<tr>
<td>NG Specific Consumption</td>
<td>GJ/1000 Nm\textsuperscript{3} H\textsubscript{2}</td>
<td>14.2</td>
<td>14.7</td>
<td>13.5</td>
<td>14.9</td>
</tr>
<tr>
<td>S/C Ratio</td>
<td></td>
<td>3.5</td>
<td>3.5</td>
<td>3.2</td>
<td>3.5</td>
</tr>
<tr>
<td>Reforming Temperature</td>
<td>C</td>
<td>900.0</td>
<td>900.0</td>
<td>600.0</td>
<td>550.0</td>
</tr>
<tr>
<td>Equivalent NG Flow (m\textsubscript{NG,eq})</td>
<td>t/h</td>
<td>29.2</td>
<td>31.4</td>
<td>9.4</td>
<td>31.1</td>
</tr>
<tr>
<td>H\textsubscript{2} Equivalent Eff (\eta\textsubscript{H2,eq})</td>
<td>% L.H.V</td>
<td>79.3</td>
<td>76.7</td>
<td>74.3</td>
<td>71.1</td>
</tr>
<tr>
<td>Equivalent Carbon capture ratio (CCR\textsubscript{eq})</td>
<td>%</td>
<td>0.0</td>
<td>56</td>
<td>91.5</td>
<td>97.1</td>
</tr>
<tr>
<td>Specific CO\textsubscript{2} Equivalent Emissions (SCE\textsubscript{eq})</td>
<td>gCO\textsubscript{2}/MJH\textsubscript{2}, eq</td>
<td>71.8</td>
<td>33.9</td>
<td>6.5</td>
<td>2.4</td>
</tr>
<tr>
<td>SPECCA\textsubscript{eq}</td>
<td>MJ/kgCO\textsubscript{2}</td>
<td></td>
<td></td>
<td></td>
<td>2.1</td>
</tr>
</tbody>
</table>
As explained before, calculating equivalent parameters would give a better indication about the overall plant performance. To do that, equivalent NG consumption has been calculated for each case to count for the emissions generated / saved from imported / exported electricity for each case. For instance, Li$_4$SiO$_4$ SESMR was found to consume 31.1 t/h equivalent NG, with 1.6% increment after considering the consumed NG to generate the 3.7 MW imported electricity. Similarly, for CaO case, was found to consume 9.4 t/h equivalent NG with 13.3 % increment to count for 5 MW imported power. On the other hand, the base case and MDEA technology were found to have less equivalent NG consumption, 29.2 & 31.4 t/h, compared to the original NG consumptions in both cases, 30.6 & 31.6 t/h respectively. The reason for the reduction in both cases, is that both plants are exporting electricity.

With respect to equivalent H$_2$ efficiency, specific emissions and energy consumption for CO$_2$ avoided, it can be observed that the equivalent efficiencies for Li and CaO based SESMR cases are lower than the original values, due to the increase of fuel consumption when considering the imported electricity. For instance, the equivalent H$_2$ production efficiency of Li$_4$SiO$_4$ based SESMR plant was found to be 71.1% after counting for the emissions coming from the imported electricity. Similarly, in CaO SESMR case, the equivalent H$_2$ production efficiency was found to be 74.3% with 5.6 efficiency points reduction. Although the scale of the a CaO SESMR reference case is 30,000 N Nm$^3$ H$_2$ plant, which is smaller than the main 100,000 Nm$^3$ H$_2$ plant, it was found that the imported electricity in CaO based SESMR plant was 5 MW. That is almost 40% higher than the imported electricity in Li-based SESMR. That was reflected in SPECCA$_{eq}$ for both cases. For instance, for Li-based SESMR, the SPECCA$_{eq}$ was found to be 2.1 MJ/kgCO$_2$ while for CaO SESMR case, it was found to be 2.4 MJ/kgCO$_2$. The reason for SPECCA$_{eq}$ to be lower in Li-SESMR case compared to CaO SESMR case, is that the case of CaO SESMR imports more electricity to achieve the high efficiency which affects the equivalent emissions. For instance, the Equivalent Carbon capture ratio (CCR$_{eq}$) and Specific CO$_2$ Equivalent Emissions (SE$_{eq}$) for CaO case are 91.5% and 6.5 gCO$_2$/MJH$_2$eq respectively. From the other hand, for Li – based SESMR, CCR$_{eq}$ and SE$_{eq}$ were found to be 97.1% and 2.4 gCO$_2$/MJH$_2$eq respectively.

For MDEA case, the equivalent H$_2$ production efficiency was found to be 76.7%, achieving an increment of 3.2 points of efficiency with respect to it is original H$_2$ production efficiency, 73.5%. The reason for this improvement is the equivalent reduction
in NG fuel consumption due to exporting 1.5 MW of electricity. However, the equivalent emissions in MDEA case are much higher than those obtained by the Li-SESMR design. For example, for MDEA case, the Equivalent Carbon capture ratio (CCR_{eq}) and Specific CO\textsubscript{2} Equivalent Emissions (SE_{eq}) are 56\% and 33.9 gCO\textsubscript{2}/MJH\textsubscript{2eq} respectively. However, the SPECCA\textsubscript{eq} for MDEA case was found to be 1.1 MJ/kgCO\textsubscript{2} which is lower than that obtained by Li-SESMR case. The reason for a lower SPECCA\textsubscript{eq} value is that the MDEA based system provides a relatively high equivalent H\textsubscript{2} production efficiency, 76.7\%, while reducing the emissions by more than 50\%.

In summary, when comparing the results of Li-based SESMR with other solvent and CaO-based integration cases, Li\textsubscript{4}SiO\textsubscript{4} SESMR based H\textsubscript{2} production process has showed relatively good performance, (\eta_{H2,eq} = 71.1\%), compared to the CaO based SESMR process, (\eta_{H2,eq} = 74.3\%), and MDEA based SMR plant, (\eta_{H2,eq} = 76.7\%), while yielding the highest equivalent capture rate (CCR_{eq}), 97.1\% , compared to that obtained by CaO based SESMR, 91.5\%, and MDEA SMR plant, 56\%. That in turn resulted on the Li-based SESMR system showing the lowest specific CO\textsubscript{2} equivalent emissions (SE_{eq}), 2.4 gCO\textsubscript{2}/MJH\textsubscript{2eq}, compared to 6.5 and 33.9 gCO\textsubscript{2}/MJH\textsubscript{2eq} for CaO-based SESMR plant and MDEA SMR plant, respectively.

Based on the previous obtained results, further efforts could then be directed to improve the overall Li-based SESMR process performance. The following section suggests the possible future improvements for the Li\textsubscript{4}SiO\textsubscript{4} SESMR process.

\textbf{6.4 Possible future improvements}

Although the integration of Li-based SESMR on the process of H\textsubscript{2} production has shown relatively good performance with respect to emissions reduction and energy consumption, further improvements in the design of the Li-SESMR system would lead to lower equivalent emissions and higher plant equivalent efficiency. For instance, improving the sorbent conversion under the SESMR conditions would lead to higher equivalent hydrogen production efficiency and lower the energy penalties since the same amount of CO\textsubscript{2} can be captured by less amount of sorbent, as explained in Chapter 4. Also, testing the sorbent under higher temperatures for the SESMR process and proving its suitability could lead to improvements on the hydrogen production efficiency because the reforming process is favored at higher temperatures.
With respect to energy and electricity penalties, new solutions to optimize the heat / fuel / steam consumption inside the plant and energy consumption could lead to further improvements in the plant performance. For example, integrating the SESMR with heat rejected from a nuclear reactor [208] or using solar / sorption enhanced steam methane reforming [209] could achieve a better performance and further reductions in equivalent energy penalties. Also, considering other hybrid methods such as membrane-SESMR processes [210] can help optimizing the steam consumption in the SESMR process.

For heat integration, similar to the Li$_4$SiO$_4$ looping system in the NGCC case, better integration results can be obtained by using a solid – solid heat recuperator between the SESMR and regenerator. It could also be further improved by incorporating indirect heating options inside the regenerator.

With respect to the overall SESMR application, considering the integration between SESMR and a gas turbine combined cycle would result in relatively good plant performance, while capturing CO$_2$, compared to a conventional NGCC plant [124].

### 6.5 Conclusion

High temperature lithium orthosilicate solid sorption enhanced steam methane reforming has been investigated as a novel option to abate the CO$_2$ emissions resulting from H$_2$ SMR production plants. For the proposed technology, the key advantage is the possibility of capturing CO$_2$ at a very high capture rate, 99%, while performing the steam methane reforming process within the same step. The SESMR design is based on the concept that the CO$_2$ capture process helps shifting the reforming reaction towards the hydrogen production side. That results in a major reduction in the plant high pressure equipment since the process can be carried out in just one low pressure reformer and without a need for the pre-reforming unit or water gas shift reactor. Hence, potential reductions in the plant capital cost and cost of hydrogen production could be achieved.

A steady-state Aspen Plus model was built for a Li$_4$SiO$_4$ based SESMR H$_2$ plant. A 100,000 Nm$^3$ H$_2$ reference plant was considered and assumptions were followed and applied in process modelling based on the IEGHG case study [119]. The base case model with SESMR was developed with a 550°C reforming temperature and 700 ºC regeneration temperature. A Li$_4$SiO$_4$ fractional conversion of 0.2 was considered inside the reactor. The model results showed an equivalent net hydrogen production efficiency
The obtained efficiency penalty points were found to be higher than those obtained from a CaO-based SESMR H₂ production plant (5% penalty points). However, the Li-based SESMR process achieved a higher equivalent carbon capture ratio (CCReq=97.1%) and lower Specific CO₂ Equivalent Emissions (SCEeq=2.4 gCO₂/MJH₂eq) compared to those obtained by CaO based SESMR process (CCReq=91.5% and SCEeq=6.5 gCO₂/MJH₂eq). The Li₄SiO₄ SESMR plant equivalent H₂ efficiency was also found to be lower than that obtained by MDEA integration (76.3%), which was also applied to the same reference plant, but it achieved lower carbon capture rates, 56%. According to the obtained simulation and technology comparison results, further efforts should be focused on increasing the sorbent CO₂ SESMR working temperature and the sorbent fractional conversion to achieve lower energy penalties and higher net plant H₂ efficiencies. With respect to integration heat and electricity penalties, integrating the SESMR plant with heat rejected from a nuclear reactor, using solar / sorption enhanced steam methane reforming or considering other methods of integration such as membrane-SESMR process could achieve a better performance and further reductions in equivalent energy penalties. With respect to the heat integration inside the plant, better integration results can be obtained by using a solid – solid heat recuperator or indirect heating options inside the regenerator. However, all the abovementioned options are subjected to the demonstration and their availability to be applied practically in large scale applications. The next step in the assessment of Li₄SiO₄ based SESMR processes should focus on evaluating the economic impact of the CO₂ capture plant integration on the H₂ production plant. Consequently, a full techno-economic evaluation for the integrated plant is performed and discussed in the next chapter to prove the feasibility of the application of Li-based SESMR H₂ production plants.
Chapter 7  TECHNOECONOMI ANALYSIS: CASE 2 – SMR H₂ PRODUCTION PLANT

7.1 Introduction

As mentioned in Chapters 4, 5 and 6, the assessment of the integration of novel CO₂ capture technologies into power and industrial plants requires both a technical and economic analysis for the studied plants. The integration of Li₄SiO₄ based HTCC into H₂ SESMR plants, have showed a net Hydrogen Production Efficiency penalty of 3.7% after HTCC plant integration, which is slightly higher than that obtained for a MDEA-based system (2.4% penalty points). However, a full evaluation of the integration of Li-based SESMR technology, requires a detailed techno-economic assessment.

Following the technical and thermodynamic assessment, the techno-economic assessment is performed in this chapter. The main objective of the techno-economic assessment is to investigate the technological feasibility of the integration of the novel sorbent-based CO₂ capture system and economical assessment for the cost impact which is quite affected by the technological feasibility.

The process modelling data for the SMR and SESMR plants were used to estimate equipment cost and techno-economics. For techno-economic calculation, detailed costing of the Li-based looping equipment was evaluated along with the costing for the rest of the hydrogen plant and all costing was estimated based on 2017 values.

Based on the described thesis objective, the following KPIs are estimated for the plant to give an indication about the final cost impact:

- Cost of CO₂ avoided [£/tCO₂]
- Levelized Cost of Hydrogen [£/kNm³ of H₂]
- Levelized Cost of Hydrogen [£/kWth]

In the current study, costing estimates accuracy class 4 is assumed (-30% to + 50 %) based on 1% to 15% full project definition [172] which is matching with the conceptual design stage for the process [173].

Similar to NGCC case in chapter 5, the mass and heat balance were extracted from the process model along with the main process parameters. The Aspen Plus model process parameters are used for equipment costing / scaling and final KPIs estimation. For equipment costing, a combination of bottom up and top down approaches are used. It is
worth mentioning that top down approach is applied for costing of standard process equipment which are well defined in the industry such as pumps, compressors, blowers etc[175]. For non-standard equipment such as the fluidized bed CO₂ capture system, detailed bottom up approach is used to estimate the equipment direct cost similar to NGCC power plant case.

After estimating the direct cost for all equipment items, capital and operational expenditures were calculated followed by calculating KPI terms using method 2 explained in chapter 5. A sensitivity analysis was performed, using the most affecting technical and economical parameters, such as sorbent cost, fuel cost, capital investment, operating and maintenance cost, plant capacity factor, discount rate, is performed.

7.2 Equipment Direct Costing

7.2.1 Equipment Direct Costing Basis

For fluidized bed reformers costing with Li-based sorbents, there was no detailed costing for such system. As a result, a detailed design for the fluidized bed system is performed followed by detailed costing for each component inside the fluidized bed system.

For rest of the plant equipment, direct cost was calculated using the scaling equation Eq (5.1) used in chapter 5.

All pricing values were converted to USD prices and rescaled to 2017 USD prices using Chemical Engineering Plant Cost Index (CEPCI) of 562.1 for 2017. All equipment the costs are finally converted from 2017 USD prices to GBP using 0.77 conversion factor based on the average GBP exchange rates in 2017 published by the bank of England [178]. Tables 7.1, 7.2 & 7.3 illustrate the main process parameters extracted from the model and used in the equipment sizing and costing for SESMR reactor, regenerator and rest of plant equipment:
Table 7-1: Process model simulation parameters used in SESMR reactor sizing

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Used in</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue Gas volumetric flow rate ($V_g$)</td>
<td>129.8 m³/s</td>
<td>SESMR reactor sizing and costing</td>
</tr>
<tr>
<td>Flue gas mole flow rate</td>
<td>8208 kmol/h</td>
<td>SESMR reactor costing</td>
</tr>
<tr>
<td>Flue Gas density ($\rho_g$)</td>
<td>0.16 kg/m³</td>
<td>FB Sizing and Costing</td>
</tr>
<tr>
<td>Gas viscosity ($\mu$)</td>
<td>3.02 * 10^{-5} pa s</td>
<td>FB Sizing and Costing</td>
</tr>
<tr>
<td>Gas Reversible compressibility ($\gamma$)</td>
<td>1.00014</td>
<td>FB Sizing and Costing</td>
</tr>
<tr>
<td>Flue gas inlet temperature ($T_{abs}$)</td>
<td>550°C</td>
<td>SESMR reactor Design and Costing</td>
</tr>
<tr>
<td>Flue Gas Pressure at SESMR reformer</td>
<td>1.1 bara</td>
<td>SESMR reactor Design and Costing</td>
</tr>
<tr>
<td>Q_{carb_tot}</td>
<td>38 MW</td>
<td>H. Ex Costing</td>
</tr>
</tbody>
</table>

Table 7-2: Process model simulation parameters used in regenerator sizing

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Used in</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ volumetric flow rate ($V_{CO2}$)</td>
<td>191 m³/s</td>
<td>FB sizing and costing</td>
</tr>
<tr>
<td>CO₂ mole flow rate</td>
<td>10084.2 kmol/h</td>
<td>Regenerator costing</td>
</tr>
<tr>
<td>CO₂ density ($\rho_g$)</td>
<td>0.465 kg/m³</td>
<td>Regenerator sizing and costing</td>
</tr>
<tr>
<td>CO₂ viscosity ($\mu$)</td>
<td>4.2 * 10^{-5} pa s</td>
<td>Regenerator sizing and costing</td>
</tr>
<tr>
<td>CO₂ reversible compressibility ($\gamma$)</td>
<td>1.00005</td>
<td>Regenerator sizing and costing</td>
</tr>
<tr>
<td>Mass flow rate of sorbent at SESMR reactor exit ($G_s$)</td>
<td>213.6 kg/s</td>
<td>Regenerator sizing and costing</td>
</tr>
<tr>
<td>CO₂ pressure in the regenerator</td>
<td>1.1 bara</td>
<td>Regenerator sizing and costing</td>
</tr>
<tr>
<td>Sorbent Regeneration Temp</td>
<td>719°C</td>
<td>Regenerator sizing and costing</td>
</tr>
<tr>
<td>Regenerator heat duty</td>
<td>100 MW</td>
<td>Oxy fuel combustion costing</td>
</tr>
</tbody>
</table>
Table 7-3: Process model simulation parameters used in costing for rest of plant equipment

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Used in</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$ compressor Power Consumption</td>
<td>16.7 MW</td>
<td>Compressor costing</td>
</tr>
<tr>
<td>CO$_2$ compression package</td>
<td>9.2 MW</td>
<td>CO$_2$ compression package costing</td>
</tr>
<tr>
<td>power consumption</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASU power consumption</td>
<td>8.2 MW</td>
<td>ASU costing</td>
</tr>
<tr>
<td>Qcarb_tot</td>
<td>38 MW</td>
<td>H. Ex costing</td>
</tr>
<tr>
<td>Total HRSG UA</td>
<td>1.1 MW/K</td>
<td>HRSG costing</td>
</tr>
<tr>
<td>Steam turbine</td>
<td>27 MW</td>
<td>Steam turbine costing</td>
</tr>
<tr>
<td>Rejected heat Q$_{cond}$</td>
<td>317 MW</td>
<td>Cooling tower costing</td>
</tr>
</tbody>
</table>

7.2.2 Fluidized bed design and Costing

Similar to NGCC case, a detailed design of the fluidized bed system is performed to achieve a bottom approach costing model. The design includes dimensions of the reactors, pressure drop across the vessel and mean particle residence time in reactor. The results of the detailed design would be used in the evaluation of the basic capital cost of the fluidized bed and hence calculate the detailed costing of the HTCC unit.

7.2.2.1 Fluidized bed design assumptions

For fluidized bed system design and sizing, Kunii and Levenspiel (KL) method [179] was used similar to the NGCC case discussed in chapter 5. Table 7.4 illustrates the assumption followed in H$_2$ SESMR plant case study:
### Table 7-4: Assumptions and design rationale for SESMR reactor and regenerator

<table>
<thead>
<tr>
<th>Assumptions</th>
<th>Range</th>
<th>Value (Unit)</th>
<th>References</th>
<th>Assumptions</th>
<th>Range</th>
<th>Value (Unit)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>No of SESMR reactor per train ( (n_{abs}) )</td>
<td>NA</td>
<td>1</td>
<td>Design optimization</td>
<td>Bed voidage at minimum fluidization conditions ( \epsilon_{mf}) Based on particle size and shape</td>
<td>Based on particle size and shape with ( \phi = 0.86 )</td>
<td>( \epsilon_{mf} = 0.48 ) based on particle size 100 µm and round sand shape</td>
<td>[179]</td>
</tr>
<tr>
<td>No of regenerators per train ( (n_{reg}) )</td>
<td>NA</td>
<td>1</td>
<td>Design optimization</td>
<td>Pressure drop across the distributor ( \Delta P_d ) ( 0.1-0.3 ) of the bed pressure drop</td>
<td>( 0.1 * \Delta P_d )</td>
<td>6.4 for fast fluidization</td>
<td>[179]</td>
</tr>
<tr>
<td>Superficial velocity ( (U_0) )</td>
<td>For fast fluidization: ( U_0 &gt;&gt; U_t ) and ( U_0 &gt; 0.5 \text{ m s}^{-1} )</td>
<td>7 m/s</td>
<td>[179]</td>
<td>Heat transfer coefficient ( (U) ) ( 10.15 \text{ kW m}^2\text{C}^{-1} )</td>
<td>10.15 kW m$^2$C$^{-1}$</td>
<td>6.4 for fast fluidization</td>
<td>[181]</td>
</tr>
<tr>
<td>Dense bed height – to – diameter ( (H_d/D) )</td>
<td>1</td>
<td>1</td>
<td>[180]</td>
<td>Reactor Material ( ) NA</td>
<td>SS304</td>
<td>Spec NO SA-182 SS304, ASME BPVC Section II part D</td>
<td></td>
</tr>
<tr>
<td>Dense bed height ( (H_d) )</td>
<td>0.3 to 15 m</td>
<td>5</td>
<td>[180]</td>
<td>The maximum allowable stress ( (S) ) in bara NA</td>
<td>186.2 bara</td>
<td>ASME BPVC Section II part D</td>
<td></td>
</tr>
<tr>
<td>Solid mean particle size ( (d_p) )</td>
<td>50-300 µm for good fluidization</td>
<td>100 µm</td>
<td>[127, 180]</td>
<td>the welding coefficient ( (\alpha) ) ( 0.75-1 )</td>
<td>1 with a complete Xray</td>
<td>[183]</td>
<td></td>
</tr>
<tr>
<td>Decay constant ( \alpha ) from the value of ( (\alpha .U_0) )</td>
<td>7 for Geldart A Zone</td>
<td>7</td>
<td>[184]</td>
<td>Corrosion allowance ( ) NA</td>
<td>8mm</td>
<td>ASME BPVC Section II part D</td>
<td></td>
</tr>
<tr>
<td>Gas Transport Carrying capacity ( (f^+) )</td>
<td>( \leq 0.02 ) for Geldart A zone</td>
<td>0.01</td>
<td>[184]</td>
<td>Skirt Height ( (H) ) 3-5 m</td>
<td>3 m</td>
<td>[183]</td>
<td></td>
</tr>
<tr>
<td>Solid fraction in the dense region ( (f_d) )</td>
<td>( \leq 0.02 ) for pneumatic transport</td>
<td>0.02</td>
<td>[184]</td>
<td>Skirt Thickness ( (H) ) 8 -12 mm</td>
<td>10 mm</td>
<td>[183]</td>
<td></td>
</tr>
</tbody>
</table>
For fluidized bed sizing results, equations 5.2 to 5.25 are solved together to estimate the final reactors dimensions.

### 7.2.2.2 Fluidized bed design results

Based on the previous assumptions, sizing and design optimization, the fluidized bed system is designed based on superficial velocity $U_0 = 7 \text{ m.s}^{-1}$ for both SESMR reactor and regenerator. Table 7.5 presents the sizing results for SESMR reactor and regenerator.

#### Table 7-5: Sizing results for SESMR reactor and regenerator

<table>
<thead>
<tr>
<th>Design variables</th>
<th>SESMR reactor Values</th>
<th>Regenerator Values</th>
<th>Derived from</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter</td>
<td>5 m</td>
<td>5.9 m</td>
<td>Eq (5.4)</td>
</tr>
<tr>
<td>Terminal velocity $(U_t)$</td>
<td>0.49 m/s</td>
<td>0.35 m/s</td>
<td>Eq (5.7) to (5.9)</td>
</tr>
<tr>
<td>Total vessel height</td>
<td>7.1 m</td>
<td>8.2 m</td>
<td>Eq (5.2)</td>
</tr>
<tr>
<td>Dens bed height</td>
<td>5 m</td>
<td>5.9 m</td>
<td>Eq (5.3)</td>
</tr>
<tr>
<td>Lean bed height</td>
<td>2 m</td>
<td>2.3 m</td>
<td>Eq (5.5-5.6)</td>
</tr>
<tr>
<td>Pressure drop</td>
<td>4 kPa</td>
<td>4.7 kPa</td>
<td>Eq (5.13-5.15)</td>
</tr>
<tr>
<td>Fluidization power</td>
<td>0.56 MW</td>
<td>1 MW</td>
<td>Eq (5.10-5.11)</td>
</tr>
<tr>
<td>Residence time</td>
<td>0.6 minutes</td>
<td>1 minute</td>
<td>Eq (5.20)</td>
</tr>
<tr>
<td>Heat exchanger Area</td>
<td>13.3 m$^2$</td>
<td>NA</td>
<td>Eq (5.21)</td>
</tr>
<tr>
<td>Sorbent Weight</td>
<td>7 tonnes</td>
<td>12 tonnes</td>
<td>Eq (5.16-5.19)</td>
</tr>
<tr>
<td>Min Wall thickness (incl corrosion allowance)</td>
<td>22 mm</td>
<td>24 mm</td>
<td>Eq (5.22)</td>
</tr>
<tr>
<td>Weight (no solids)</td>
<td>36 tonnes</td>
<td>40 tonnes</td>
<td>Eq (5.23-5.25)</td>
</tr>
<tr>
<td>Weight (with solids)</td>
<td>43 tonnes</td>
<td>52 tonnes</td>
<td>Eq (5.16, 5.23)</td>
</tr>
</tbody>
</table>
7.2.2.3 Fluidized bed costing

The fluidized bed system is based on bottom up approach [186] which covers the costing for the components of the fluidized bed system as per following:

- Fluidized Bed Reactor vessel Costing using functional module method and costing Equation proposed Chauvel et al 2003 [185]
- Fluidized Bed Blower / compressor costing based on power consumption [185]
- Using Air / Hydrogen compressor costing curves from [185] to estimate the cost of blower for each reactor respectively, including the driver cost
- For cyclones costing, the cyclones costing curves from [185] were used.
- Heat Exchanger Costing (SESMR reactor reactor) based on the designed heat exchanger area per reactor, using the costing chart from the IChemE costing book, cost of carbon steel tubular heat exchanger [188]
- Oxyfuel combustion cost in regenerator using the method from [189]
- Cost of sorbent inventory

The cost of sorbent is considered as one of the most important factors affecting the overall evaluation. The cost of sorbent itself depends on many aspects such as price of the sorbent or price of the sorbent raw material in case of synthesizing sorbent, and amount of required make up and capture capacity, which is affecting the overall amount of sorbent.

To calculate the cost of the sorbent inventory inside the fluidized bed reactor, the weight of the sorbent required inside the reactor was calculated based on SESMR reactor sizing data obtained from solving the Kunii and Levenspeil model for the SESMR reactor. Based on KL model, the weight of sorbent required inside the SESMR reactor is 7 tons including catalyst. For cost of the raw material of the $\text{Li}_4\text{SiO}_4$, based on latest prices of lithium silicate precursors, reported by Mineral Commodity Summaries 2014 and 2013 Mineral year Books (Lithium and silica) [88, 190, 191], 4.5 $/kg was considered as the cost of 1 kg of $\text{Li}_4\text{SiO}_4$.

$\text{Al}_2\text{O}_3\text{NiO}$ Catalyst cost was estimated based on the price of pure Ni in 2013 [22-23] approximated with average cost 11 $/kg in 2013.

Hence, the final cost of the initial sorbent/catalyst inventory is 0.03 £ million and will be added to the capital cost of the fluidized bed system. Table 7.6 presents summary of the fluidized bed costing, based on previously explained costing methods. The presented prices are in 2017 £ million.
Table 7-6: Summary of fluidized components costing in 2017 M£

<table>
<thead>
<tr>
<th>Costing methods</th>
<th>Component cost</th>
<th>SESMR reactor</th>
<th>£ million</th>
<th>Regenerator</th>
<th>£ million</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor column [185]</td>
<td></td>
<td>0.7</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluidization power [185]</td>
<td></td>
<td>0.4</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclones cost [185]</td>
<td></td>
<td>0.2</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat Exchanger cost [188]</td>
<td></td>
<td>0.014</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxy fuel combustor [189]</td>
<td></td>
<td>0</td>
<td>3.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial sorbent inventory inside the SESMR reactor [88, 190, 191]</td>
<td></td>
<td>0.03</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total equipment cost in 2017 M£</td>
<td></td>
<td>1.1</td>
<td>4.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total fluidized bed Equipment direct cost with initial solid inventory £ million</td>
<td></td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

7.2.3 Direct cost estimation for rest of plant equipment

As mentioned previously, the capital cost for the SMR plant equipment and SESMR plant equipment was estimated using reference equipment costing data available in literature for similar case studies.

Starting with the main SMR plant without capture, direct cost of the equipment was estimated using bottom up approach and are compared to the values estimated by previous study for similar plant [197]. Following to the comparison, SMR reference case BUA costing was applied to calculate the basic capital cost of the SESMR plant using the costing results obtained from the fluidized bed sizing and costing section.

Table 7.7 summarizes the main packages used in the calculation of SMR plant equipment direct cost, sizing parameters to rescale the cost of each package and reference equipment cost in £ million - 2017 prices.
Table 7.7: Summary of SMR reference plant costing using BUA

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Scaling criteria</th>
<th>Scaling factor</th>
<th>Reference Equipment Cost (C0) in M€/M$</th>
<th>reference year</th>
<th>New equipment rating / capacity</th>
<th>Rescaled cost in £ million -2017</th>
<th>No of units</th>
<th>Final Cost in £ million 2017</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur removal, performer, Reformer, WGR, PSA</td>
<td>Thermal plant input (MW)</td>
<td>0.67</td>
<td>1916</td>
<td>2005</td>
<td>395</td>
<td>0.63</td>
<td>1</td>
<td>24</td>
<td>[211]</td>
</tr>
<tr>
<td>Reformer Convection H-Ex</td>
<td>U x A MW/k</td>
<td>0.67</td>
<td>12.9</td>
<td>2008</td>
<td>.93</td>
<td>6.2</td>
<td>1</td>
<td>6.2</td>
<td>[135]</td>
</tr>
<tr>
<td>H-ex after the reformer</td>
<td>U x A MW/k</td>
<td>0.67</td>
<td>12.9</td>
<td>2008</td>
<td>1.024</td>
<td>6.5</td>
<td>1</td>
<td>6.5</td>
<td>[135]</td>
</tr>
<tr>
<td>Steam turbine, generator and auxiliaries</td>
<td>ST Gross Pow – MW</td>
<td>0.67</td>
<td>200</td>
<td>2008</td>
<td>11.7</td>
<td>5.6</td>
<td>1</td>
<td>5.6</td>
<td>[135, 192, 193]</td>
</tr>
<tr>
<td>Cooling water system and BOP</td>
<td>Q_rejected – MW</td>
<td>0.67</td>
<td>470</td>
<td>2008</td>
<td>117</td>
<td>22</td>
<td>1</td>
<td>22</td>
<td>[135, 192, 193]</td>
</tr>
</tbody>
</table>

Total direct Cost: 64 £ million
The equipment direct capital cost for the SMR plant is estimated to be 64 £ million. For installation cost, an installation factor of 147% was assumed for reformers, which has been previously used for SMR units [211] and a factor of 67.25% was assumed for power section (heat exchangers, turbines, cooling), similar to EBTF assumption[135]. So, total installation cost without contingencies= 126.2 £ million. If this value is compared to the value estimated for the reference case [119, 197], after transferring the base case cost to 2017 £ million values, the total capital cost including installation cost would be =133.5 £ million with error of - 5.5 % compared to the BUA calculation. Figure 7.1 shows Equipment direct cost break down for SMR H₂ plant.

![Figure 7.1: SMR H₂ reference Plant without capture direct capital cost break down in % from the total equipment direct cost without installation](image)

For the capital cost calculation for the SESMR with HTCC integrated, the direct cost calculation for the capture unit and all associated equipment using BUA was summarized in 7.2.2. The cost for heat recovery system, steam turbines, cooling water system and CO₂ compression system was scaled and adjusted to 2017 £ million using costing figures available in EBTF study for similar equipment [135]. For the ASU, this cost was rescaled using the estimated cost for the ASU applied in benchmark 5 IGCC plant used by Tarrant et al 2018 [136]. For H₂ compression train, the cost was scaled from [185] and adjusted
to 2017 £ million values. For Sulphur removal unit, PSA and expanders the cost was scaled from [212, 213]. For the heat exchangers, costing charts from [188] was used. For installation cost, an installation factor of 147% was assumed for reformers including SESMR [211] similar to base case and a factor of 67.25% was assumed for power section (heat exchangers, turbines, cooling) and factor of 82.7% for PSA unit as part of chemical part similar to EBTF assumption [135] followed in NGCC case. Table 7.8 summarizes the SESMR plant direct cost of the plant equipment in 2017 £ million.

Figure 7.2 shows the equipment cost break-down in percentage for the SESMR plant after capture in % from the overall direct equipment cost.

![Pie Chart](image)

**Figure 7.2: Capital cost break down in percentage for the SESMR H₂ plant in % from the overall equipment direct cost**
<table>
<thead>
<tr>
<th>Equipment</th>
<th>Scaling criteria</th>
<th>Scaling factor</th>
<th>Reference Equipment rating (S0)</th>
<th>Reference Equipment Cost (C0) in M€</th>
<th>Reference year</th>
<th>New equipment rating / capacity</th>
<th>rescaled cost in M€ -2017</th>
<th>No of units</th>
<th>final Cost in M€ 2017</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur removal</td>
<td>Thermal plant input (MW)</td>
<td>0.67</td>
<td>413.8</td>
<td>0.66</td>
<td>2011</td>
<td>396</td>
<td>0.6</td>
<td>1</td>
<td>0.6</td>
<td>[212]</td>
</tr>
<tr>
<td>SESMR</td>
<td>Detailed fluidized bed costing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSA</td>
<td>Inlet flow rate (kmol/h)</td>
<td>0.6</td>
<td>17069</td>
<td>27.96</td>
<td>2007</td>
<td>5197</td>
<td>16.5</td>
<td>1</td>
<td>16.5</td>
<td>[212]</td>
</tr>
<tr>
<td>Expander 1</td>
<td>Expander power in MW</td>
<td>0.67</td>
<td>200</td>
<td>33.7</td>
<td>2007</td>
<td>3.6</td>
<td>0.9</td>
<td>1</td>
<td>0.9</td>
<td>[213]</td>
</tr>
<tr>
<td>Expander 2</td>
<td>Expander power in MW</td>
<td>0.67</td>
<td>200</td>
<td>33.7</td>
<td>2007</td>
<td>0.7</td>
<td>0.9</td>
<td>1</td>
<td>0.9</td>
<td>[213]</td>
</tr>
<tr>
<td>H₂ compressor</td>
<td>Power consumption (MW)</td>
<td>0.6</td>
<td>1</td>
<td>0.5</td>
<td>2000</td>
<td>16.7</td>
<td>2.8</td>
<td>1</td>
<td>2.8</td>
<td>[185]</td>
</tr>
<tr>
<td>Hex after the reformer</td>
<td>U x A MW/k</td>
<td>0.67</td>
<td>12.9</td>
<td>32.6</td>
<td>2008</td>
<td>0.6</td>
<td>4.4</td>
<td>1</td>
<td>4.4</td>
<td>[135]</td>
</tr>
<tr>
<td>Syn Gas H-exch</td>
<td>U x A MW/k</td>
<td>0.67</td>
<td>12.9</td>
<td>32.6</td>
<td>2008</td>
<td>0.6</td>
<td>4.4</td>
<td>1</td>
<td>4.4</td>
<td>[135]</td>
</tr>
<tr>
<td>Rest of H-exch</td>
<td>Area</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.03</td>
<td>[188]</td>
</tr>
<tr>
<td>Steam turbine, generator and auxiliaries</td>
<td>ST_Gross power – MW</td>
<td>0.67</td>
<td>200</td>
<td>33.7</td>
<td>2008</td>
<td>27</td>
<td>9.7</td>
<td>1</td>
<td>9.7</td>
<td>[135, 192, 193]</td>
</tr>
<tr>
<td>Cooling water and BOP</td>
<td>Q_rejected – MW</td>
<td>0.67</td>
<td>470</td>
<td>49.6</td>
<td>2008</td>
<td>317</td>
<td>42.1</td>
<td>1</td>
<td>42.1</td>
<td>[135, 192, 193]</td>
</tr>
<tr>
<td>CO₂ compression</td>
<td>Power consumption (MW)</td>
<td>0.67</td>
<td>13</td>
<td>9.95</td>
<td>2008</td>
<td>9.2</td>
<td>8.7</td>
<td>1</td>
<td>8.7</td>
<td>[135, 194]</td>
</tr>
<tr>
<td>ASU</td>
<td>Power consumption (MW)</td>
<td>0.67</td>
<td>88.9</td>
<td>143.7</td>
<td>2017</td>
<td>8.2</td>
<td>29</td>
<td>1</td>
<td>29</td>
<td>[136]</td>
</tr>
</tbody>
</table>

| Total direct Cost               |                          |                |                                 |                                     |                |                                 |                          |             | 128 M€               |     |
As shown in figure 7.2, the cost of the BOP and cooling system contributes to 32.9% of the overall plant capital cost. Following to the cooling water system and BOP, it was found that the ASU recorded the second highest direct capital cost, with 22.7% of the overall capital cost, followed by the PSA direct cost which recorded 12.9% of the overall direct cost. For CO\textsubscript{2} compression train, it was found that it contributes to 6.8% of the overall direct cost, while the H\textsubscript{2} compressors contribute to 2.2% of the overall cost. For heat recovery systems and steam turbines, it was found that overall direct capital cost of heat recovery system 1 and 2 is equal to 6.9% of the overall direct cost, while the steam turbines contribute to 7.6% of the overall direct cost. Further discussion for the capital cost results, are available in results discussion section, 7.4. Following to the calculation of the equipment direct cost, techno-economic assessment was performed as will be explained in the following section.

7.3 Techno-economic Assessment

7.3.1 General Techno-economic assumptions

The following assumptions were used to perform techno-economic assessment:

- One method is applied to estimate the plant techno-economics for HTCC integration into SMR H\textsubscript{2} plant using direct cost of equipment estimated in previous section.
- The main techno-economic KPIs mentioned in section 7.1 are applied for both methods.
- Levelized cost of Hydrogen (LCOH) represents the selling price for the hydrogen with the consideration of the net present value (NPV) of the project over its lifecycle from cradle to grave is equal to 0. The levelized cost of hydrogen is calculated in both £/kNm\textsuperscript{3} of H\textsubscript{2} and £/kWth similar to the assessment in [136]. The LCOH values are calculated for the reference SMR and SESMR H\textsubscript{2} production plants.
- Cost of CO\textsubscript{2} avoided is the measure for the cost spent to capture CO\textsubscript{2} emissions from the reference plant in £/t CO\textsubscript{2} [194]. Cost of CO\textsubscript{2} avoided can be calculated from the following formula, similar to NGCC case:
  \[
  \text{Cost of CO}_2 \text{ avoided} = \frac{(\text{LCOH})_{cc} - (\text{LCOH})_{ref}}{E_{Ref} - E_{cc}} \text{ in £/t CO}_2 \text{ where LCOH is cost of Hydrogen in £/kNm}^3 \text{ and E is the CO}_2 \text{ emission rate in kgCO}_2/\text{kNm}^3 \text{ and Ref stands for the reference case without capture and CC for case with capture.}
  \]
- The actual hydrogen production of the plant over the life of the plant is calculated based on the capacity factor assumed.
7.3.2 Techno-economic Assessment – method (BEIS)

The cost method followed the costing methodology presented in [136] to screen the application of different technologies for CO$_2$ capture in Hydrogen SMR Plant in UK. This cost method was prepared based on American Association of Cost Engineers (AACE) class 4 which aims to achieve ±30% estimation accuracy. The method was used to calculate CAPEX, OPEX, LCOH and cost of CO$_2$ avoided for the plant before and after the integration of High temperature CO$_2$ capture unit. All cost calculations were obtained based on 2017 prices in £. This method depends on BUA costing for fluidized bed system using the basic equipment costing results from section 7.2. The assumptions followed are listed in appendix 7.6

7.3.2.1 Method results

<table>
<thead>
<tr>
<th>Summary of total SMR plant cost without capture</th>
<th>£ million</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Production to BL t/h</td>
<td>9</td>
</tr>
<tr>
<td>Total Energy in the product MW</td>
<td>301.3</td>
</tr>
<tr>
<td>Excess electricity to the grid MW</td>
<td>9.8</td>
</tr>
<tr>
<td>EPC Contract cost (including installation cost)</td>
<td>126.2</td>
</tr>
<tr>
<td>Infrastructure connection cost £ million</td>
<td>3.8</td>
</tr>
<tr>
<td>Owner’s Cost £ million</td>
<td>8.8</td>
</tr>
<tr>
<td>Pre-Licensing, Technical &amp; Design £ million</td>
<td>1.3</td>
</tr>
<tr>
<td>Regulatory, Licensing &amp; Public Enquiry £ million</td>
<td>2.7</td>
</tr>
<tr>
<td>TPC £ million</td>
<td>142.8</td>
</tr>
</tbody>
</table>

Table 7-9: Summary of the total plant cost without capture

Table 7.10 shows the final calculation for the total SESMR plant cost including installation cost, indirect cost, Owner’s Costs and other relevant costs:
Table 7-10: Summary of the total SESMR plant cost

<table>
<thead>
<tr>
<th>Summary of total SESMR plant cost</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Production to BL</td>
<td>t/h</td>
</tr>
<tr>
<td>Total Energy in the product</td>
<td>MW</td>
</tr>
<tr>
<td>Excess electricity to the grid</td>
<td>MW</td>
</tr>
<tr>
<td>EPC Contract cost (including installation cost)</td>
<td>£ million</td>
</tr>
<tr>
<td>Infrastructure connection cost</td>
<td>£ million</td>
</tr>
<tr>
<td>Owner’s Cost</td>
<td>£ million</td>
</tr>
<tr>
<td>Pre-Licensing, Technical &amp; Design</td>
<td>£ million</td>
</tr>
<tr>
<td>Regulatory, Licensing &amp; Public Enquiry</td>
<td>£ million</td>
</tr>
<tr>
<td>TPC</td>
<td>£ million</td>
</tr>
</tbody>
</table>

For operating and maintenance cost, the assumptions mentioned in appendix A.4 were followed to obtain O&M total cost to £ in 2017 without the consideration of carbon and fuel prices. Tables 7.11 and 7.12 present the operating and maintenance cost calculation before and after capture respectively:

Table 7-11: Operating and Maintenance cost before capture

<table>
<thead>
<tr>
<th>O&amp;M Cost excl carbon and fuel price</th>
<th>Unit</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed Operation Cost</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Direct Labour</td>
<td>£ million  pa</td>
<td>0.9</td>
</tr>
<tr>
<td>General Overheads</td>
<td>£ million  pa</td>
<td>0.6</td>
</tr>
<tr>
<td>Insurance and Local Taxes</td>
<td>£ million  pa</td>
<td>2.5</td>
</tr>
<tr>
<td>Syngas Unit Maintenance</td>
<td>£ million  pa</td>
<td>2.7</td>
</tr>
<tr>
<td>Other Units Maintenance</td>
<td>£ million  pa</td>
<td>0.5</td>
</tr>
<tr>
<td>Total Fixed O&amp;M Cost</td>
<td>£ million  pa</td>
<td>7.3</td>
</tr>
<tr>
<td>Variable Cost:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ Storage Cost £/tonne CO₂</td>
<td>£ million  pa</td>
<td>0</td>
</tr>
<tr>
<td>Cats &amp; Chems Consumption</td>
<td>£ million  pa</td>
<td>0.7</td>
</tr>
<tr>
<td>Electricity Import Cost</td>
<td>£ million  pa</td>
<td>-5.6</td>
</tr>
<tr>
<td>Total Variable O&amp;M Cost</td>
<td>£ million  pa</td>
<td>-5</td>
</tr>
<tr>
<td>Total O&amp;M cost excl carbon and fuel price</td>
<td>£ million  pa</td>
<td>2.4</td>
</tr>
</tbody>
</table>
Table 7-12: Operating and Maintenance cost after capture

<table>
<thead>
<tr>
<th>O&amp;M Cost excl carbon and fuel price</th>
<th>Unit</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fixed Operation Cost</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Direct Labour</td>
<td>£ million pa</td>
<td>1</td>
</tr>
<tr>
<td>General Overheads</td>
<td>£ million pa</td>
<td>1.1</td>
</tr>
<tr>
<td>Insurance and Local Taxes</td>
<td>£ million pa</td>
<td>4.4</td>
</tr>
<tr>
<td>Syngas Unit Maintenance</td>
<td>£ million pa</td>
<td>2.2</td>
</tr>
<tr>
<td>Other Units Maintenance</td>
<td>£ million pa</td>
<td>2.2</td>
</tr>
<tr>
<td><strong>Total Fixed O&amp;M Cost</strong></td>
<td>£ million pa</td>
<td>11</td>
</tr>
<tr>
<td><strong>Variable Cost:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ Storage Cost £/tonne CO₂</td>
<td>£ million pa</td>
<td>12</td>
</tr>
<tr>
<td>Cats &amp; Chems Consumption, sorbent make up</td>
<td>£ million pa</td>
<td>2.2</td>
</tr>
<tr>
<td>Electricity Import Cost</td>
<td>£ million pa</td>
<td>3</td>
</tr>
<tr>
<td><strong>Total Variable O&amp;M Cost</strong></td>
<td>£ million pa</td>
<td>17.2</td>
</tr>
<tr>
<td><strong>Total O&amp;M cost excl carbon and fuel price</strong></td>
<td>£ million pa</td>
<td>28.3</td>
</tr>
</tbody>
</table>

The techno-economic results estimated for the SMR H₂ reference plant and SESMR H₂ plant with Li-based HTCC system integrated, based on techno-economic method 2 assessment, are summarized in table 7.13.

Table 7-13: Summary of economic estimation for SMR 100000 Nm³/h Case before and after integration of HTCC unit

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>SMR Plant</th>
<th>SESMR Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Production to BL</td>
<td>t/h</td>
<td>9</td>
<td>8.6</td>
</tr>
<tr>
<td>Excess electricity to the grid</td>
<td>MWe net</td>
<td>9.9</td>
<td>-5.2</td>
</tr>
<tr>
<td>H₂ equivalent Efficiency (L.H.V)</td>
<td>%</td>
<td>79.3</td>
<td>71</td>
</tr>
<tr>
<td>Specific CO₂ emissions</td>
<td>t/1000 Nm³ H₂</td>
<td>0.81</td>
<td>0.03</td>
</tr>
<tr>
<td><strong>Total Plant Cost</strong></td>
<td>M£</td>
<td>142.8</td>
<td>253.2</td>
</tr>
<tr>
<td>Fixed O&amp;M</td>
<td>£ million pa</td>
<td>7.3</td>
<td>11</td>
</tr>
<tr>
<td>Variable O&amp;M</td>
<td>£ million pa</td>
<td>-5</td>
<td>17.2</td>
</tr>
<tr>
<td>Levelized Cost of Hydrogen (LCOH) excl carbon price</td>
<td>£/kNm³</td>
<td>102.3</td>
<td>159.3</td>
</tr>
<tr>
<td></td>
<td>£/kWth</td>
<td>34.1</td>
<td>53.2</td>
</tr>
<tr>
<td>------------------------------------------------</td>
<td>-------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>Levelized Cost of Hydrogen (LCOH) excl carbon price</td>
<td>£/kWth</td>
<td>34.1</td>
<td>53.2</td>
</tr>
<tr>
<td>Levelized Cost of Hydrogen (LCOH) excl carbon price</td>
<td>£/kg H₂</td>
<td>1.1</td>
<td>1.8</td>
</tr>
<tr>
<td>Cost of CO₂ avoided excl carbon price</td>
<td>£/tCO₂ avoided</td>
<td>0</td>
<td>72.7</td>
</tr>
<tr>
<td>Levelized Cost of Hydrogen (LCOH) incl carbon price</td>
<td>£/kNm³</td>
<td>169</td>
<td>160.2</td>
</tr>
<tr>
<td>Levelized Cost of Hydrogen (LCOH) incl carbon price</td>
<td>£/kWth</td>
<td>56.4</td>
<td>53.5</td>
</tr>
<tr>
<td>Levelized Cost of Hydrogen (LCOH) incl carbon price</td>
<td>£/kg H₂</td>
<td>1.9</td>
<td>1.8</td>
</tr>
<tr>
<td>Cost of CO₂ avoided including carbon price</td>
<td>£/tCO₂ avoided</td>
<td>0</td>
<td>-11.2</td>
</tr>
</tbody>
</table>

Following the techno-economic assessment for SMR reference case and SESMR H₂ plant case, sensitivity analysis for several economical parameters was performed for the SESMR plant with Li-based HTCC integration as will be described in the following section.

### 7.3.3 Sensitivity Analysis

In this section, different economic and technical parameters were varied to investigate the effect of their variation on the LCOH before and after capture and on Cost of CO₂ avoided. All parameters were varied by ±25 % of its original value in base case. LCOE and Cost of CO₂ were estimated using calculation method explained previously without the consideration of the carbon tax. The following techno-economic parameters were considered in the sensitivity:

- Capital Cost
- O&M Cost
- Fuel Price
- Electricity Selling Price
- Discount cash flow factor
- Sorbent Cost
- Plant Capacity factor
Figure 7.3: Impact of varying capital cost, O&M cost, Fuel price, Electricity Price, DF and capacity factor and sorbent cost by ±25%, on LCOH before and after the integration of Li-based CO₂ capture system
Figure 7.4: Effect of varying techno-economic parameters ±25% on LCOH in % from the base case LCOH

Figure 7.5: Effect of varying techno-economic parameters ±25% on cost of CO₂ avoided in % from the base case cost of CO₂ avoided
7.4 Results and Discussion

As explained in sections 7.2, the design for the fluidized beds was optimized to achieve a feasible and constructible equipment dimension as showed in table 7.5. The SESMR reactor is designed to have 5m diameter and 7.1m total vessel height. While the regenerator was designed to have 5.9m diameter with 8.2m vessel height. The residence time of the sorbent inside the SESMR and regenerator reformers was set to be 0.6 and 1 minutes respectively in order to apply fast fluidization system. The fluidization power was calculated for each reactors and the sum of the power consumption was estimated to be equal 1.6 MW and used to adjust the plant performance data obtained in chapter 6 from the process modelling which lead to final H₂ plant equivalent efficiency of 70.7 % instead of 71.1 % L.H.V.

For equipment direct cost calculation, all plant equipment except the fluidized bed was scaled and transferred to 2017 M£ as shown in tables 7.7 and 7.8. For fluidized bed system, detailed bottom up approach was followed using the equipment sizing results to estimate the capital cost for each component in the fluidized bed system as shown in table 7.6 resulting in direct cost of 6M£ for the fluidized bed system with the initial solid inventory and without the consideration of ASU which was estimated separately. Figure 7.1 showed the equipment cost breakdown for reference plant without capture. As shown in figure 7.1, the plant reactors are the costliest equipment, 37% of the overall direct cost, followed by cooling system and BOP, which contributes to 34% of the overall direct cost. Figure 7.2 showed the cost breakdown for SESMR plant. It showed that BOP and cooling systems are contributing to 32.9% of the direct equipment cost and considered the costliest equipment followed by ASU and PSA units which contributes to 22.7% and 12.9% of the overall direct cost respectively. It is also well observed from figure 7.2, that the cost of reactors, including SESMR and sulphur removal units, have been reduced to 5.2 % only from the overall direct equipment cost compared to the reference case. That is well understood from the major change of the design of the plant when SESMR system is applied as explained in chapter 6.

For the techno-economic assessment, as explained in section 7.3, the estimation method followed in [136] was used and applied to the SMR and SESMR plants cases. This method was based on the latest published guidelines for techno-economic calculation for new CO₂ capture technologies to be applied in UK.
Table 7.13 illustrated the techno-economic results for SMR and Li-based SESMR H₂ production plants with and without the consideration of the carbon taxes. As seen in table 7.13, the hydrogen production to the BL has been reduced by 4% from its original value, 9 t/h, recorded for the original SMR plant. Also, the new SESMR was found to need 5.2 MW electricity import after adding the equipment electricity consumption inside the plant which resulted in overall H₂ equivalent efficiency of 70.7% compared to 79.3% for the SMR base case. The reduction in performance and total produced hydrogen was discussed in chapter 6. The effect of the such performance reduction on the plant techno-economics is discussed below.

For total plant cost (TPC), the cost of plant equipment, including installation and other capital cost parameters, are detailed in tables 7.9 and 7.10, has increased by 77% from the TPC, 142.8 £ million, estimated for SMR plant. The reason behind this is the major change in the plant design and addition of extra high cost packages such as ASU, CO₂ compression & H₂ compression packages. In addition to that, the water-cooling system requirement for the SESMR has greatly increased from 117 MW to 317 MW in SESMR. This results in a significant impact on the direct capital cost of the plant as the direct equipment cost for the cooling system and BOP increased by 90% for SESMR when compared to its original value in SMR, 22.2 £ million as shown in tables 7.7 and 7.8.

For operation and maintenance costs, it is observed that both fixed and variable O&M cost have been increased also for SESMR plant when they are compared to the original estimated values for SMR plant. As shown in table 7.12, the fixed O&M has increased from 7.3 to 11 £ million / year after modifying the plant to SESMR system. The reason behind that is that most of the fixed O&M parameters were calculated, based on assumptions on appendix A.4, as a percentage from plant capital cost which in turn has greatly increased for SESMR case compared to SMR case. For variable O&M cost, it was increased from -5, for SMR plant, to 17.2 £ million / year for SESMR. The reason behind such massive increase is due to addition of cost of electricity, 3£ million / year and cost of CO₂ storage, 12 £ million / year besides the increment of catalysts and chemicals consumption from 0.7 £ million / year to 2.2 M£/year after considering the yearly cost for sorbent make up. The increase in fixed and variable O&M costs lead to an overall increase in the total O&M cost, without the consideration for fuel consumption cost, from 2.4 £ million / year for SMR to 28.3 £ million / year which is more than one order of magnitude. The increase of capital and O&M costs for SESMR plant compared to SMR plant has a
noticeable impact on the calculation for the net present value for levelized cost of Hydrogen (LCOH) and hence affecting the cost of CO₂ avoided.

For LCOH and Cost of CO₂ avoided calculation, the calculations were estimated for both cases with and without the consideration of carbon taxes. The carbon taxes were estimated based on a variable carbon cost distributed over the lifetime of the project with an average cost of 95.6 £/ tonne CO₂.

For estimation without considering carbon taxes prices, as showed in table 7.13, LCOH has increased from 102.3 £/kNm³, 34.1 £/kWth & 1.1 £/kg H₂ for SMR to 159.3 £/kNm³, 53.2 £/kWth & 1.8 £/kg H₂ for SESMR plant. For cost of CO₂ avoided, it was estimated to be equal to 72.7 £/tCO₂ avoided.

After applying carbon emissions taxes, it was found that the LCOH has been reduced from 169 £/kNm³, 56.4 £/kWth & 1.9 £/kg H₂ for SMR to 160.2 £/kNm³, 53.5 £/kWth & 1.8 £/kg H₂ for SESMR plant. For cost of CO₂ avoided, it was estimated to drop to -11.2 £/tCO₂ avoided. The reason behind the changes in the LCOH and cost of CO₂ values, with and without the consideration of carbon taxes, is due to considering the cost of CO₂ emissions resulted from those emitted from the SMR plants and those avoided in SESMR plant.

From previous results, it is showed clearly that the carbon emissions policies and regulation such as carbon taxes can change the feasibility of new capture technologies when integrated in SMR similar H₂ plants.

For sensitivity analysis, a parametric change of ±25% of several techno-economic parameters were performed to investigate the effect on LCOH in £/kNm³ and cost of CO₂ avoided in £/tCO₂ avoided without the consideration of carbon taxes. Figures 7.3 to 7.6 show the effect of varying the selected parameters on LCOH and Cost of CO₂ avoided.

From figure 7.3, it was found that effect of increasing most of the parameters has the same trend, ie increase, for the LCOH except for electricity price and capacity factor. For electricity price, it was observed that there is a small change, ± 0.6 %, from the original LCOH value when varying the electricity price by ±25%. The reason for such trend is that the electricity is not the main product of the plant opposite to the NGCC case discussed in chapters 4 & 5. For capacity factor, it was found that by reducing the capacity factor by 25% will result in increasing the LCOH for SESMR by 12%.
Comparing the impact of all parameters on LCOH for SESMR, it was found that the fuel price has the major impact on the LCOH. For instance, increasing the average fuel cost by +25% would lead to 13% increase in the LCOH. Following to the fuel price, capacity factor recorded the second highest impact on LCOH. The reason behind that, the capacity factor affects directly the net exported hydrogen and hence affect the final product of the plant. It is interesting to mention that changing the capacity factor in SESMR is affecting on several parts of the calculation of NPV for the hydrogen such as cost of imported / exported electricity, cost of selling hydrogen and cost of CO\(_2\) storage.

For Cost of CO\(_2\) avoided, it was found that varying the O&M cost had the highest impact on cost of CO\(_2\) avoided. For instance, by increasing the O&M cost by 25%, the cost of CO\(_2\) avoided would increase by 16% from its original value for SESMR plant. The reason behind this is due to the big difference between the O&M for SMR and SESMR plants. As explained above, the O&M cost for SESM is higher than that for SMR plant by more than one order of magnitude. Changing the O&M cost for the SMR will results in less impact on LCOH compared to SESMR as we could see in figure 7.3, since the cost of CO\(_2\) avoided is based on the difference between the LCOH for SMR and SESMR plants as per the definition of Cost of CO\(_2\) avoided explained in section 7.3.1. Hence, the difference between the impact on LCOH for SMR and SESMR would result in such effect on the cost of CO\(_2\) avoided. It was also found that following to the O&M cost, the capacity factor has the second highest impact on cost of CO\(_2\) avoided as shown in figure 7.5.

Regarding the lowest affecting parameter for LCOH and cost of CO\(_2\) avoided, it was found that for LCOH, Sorbent cost and electricity price had the lowest impact, ±0.5% & ±0.6%, respectively. For Cost of CO\(_2\) avoided, also the cost of sorbent has recorded the lowest impact, ±1.3%. Following the sorbent cost, fuel price was found to have lower impact, ±1.7, on cost of CO\(_2\) avoided compared to electricity price, ±5. The reason behind this is thought to be due to that electricity cost is affecting the O&M cost which was found to have the biggest impact on cost of CO\(_2\) avoided as explained previously.

### 7.5 Conclusion

Li\(_4\)SiO\(_4\)/Li\(_2\)CO\(_3\) high temperature looping CO\(_2\) capture solution has been investigated as an important option to abate the exhaust CO\(_2\) emissions resulting from an SMR H\(_2\) production plant. As a continuation for the novel high temperature Li-based sorbent technology assessment, the techno-economic study was performed to estimate the
economic feasibility of applying Li$_4$SiO$_4$/Li$_2$CO$_3$ SESMR looping system as a solution to reduce CO$_2$ emissions from conventional SMR H$_2$ production plant.

Similar to NGCC case in chapter 5 and prior to performing techno-economic analysis, detailed design and sizing for the fluidized bed system was performed using the process modelling data obtained from the process integration study discussed in chapter 6. The fluidized bed system was sized and optimized to be in a single train with sorbent and catalyst looping between SESMR and regenerator units. The final optimized sizes were: 5m x 7.1m & 5.9m x 8.2m for SESMR and regenerator respectively.

Following to the fluidized bed sizing, the detailed bottom up approach was followed to estimate the direct cost for the fluidized bed system in 2017£ values. The cost for the rest of plant equipment was obtained and scaled from reference equipment costing data / curves available in literature and all values were transferred to 2017£ values.

BEIS techno-economic method and assumptions were applied, to evaluate the levelized cost of hydrogen (LCOH), in £/kNm$^3$ & £/kWth, cost of CO$_2$ avoided, in £/tCO$_2$ avoided, for SMR and SESMR plants with and without considering the cost of CO$_2$ emissions. Techno-economic method assumptions were obtained from the latest UK published techno-economic guidelines for benchmarking new CO$_2$ capture technology. It was found that, LCOH has increased from 102.3 £/kNm$^3$ and 34.1 £/kWth for SMR to 159.3 £/kNm$^3$ and 53.2 £/kWth for SESMR plant. For cost of CO$_2$ avoided, it was estimated to be equal to 72.7 £/tCO$_2$ avoided.

After applying carbon emissions taxes, it was found that the LCOH has been reduced from 169 £/kNm$^3$ and 56.4 £/kWth for SMR to 160.2 £/kNm$^3$ and 53.5 £/kWth for SESMR plant. For cost of CO$_2$ avoided, it was estimated to drop to -11.2 £/tCO$_2$ avoided. The reason behind the changes in the LCOH and cost of CO$_2$ values, with and without the consideration of carbon taxes, is due to considering the cost of CO$_2$ emissions resulted from those emitted from the SMR plants and those avoided in SESMR plant.

Finally, to investigate the most affecting parameters on the Li$_4$SiO$_4$/Li$_2$CO$_3$ looping based SESMR process techno-economic, a parametric change of ±25% was done for 7 parameters, including capital cost, O&M cost, fuel cost, electricity selling price, Discount factor and plant capacity factor, The sensitivity analysis was performed to investigate the impact of changing the chosen parameters on LCOH and Cost of CO$_2$ avoided without considering the carbon emissions cost.
From sensitivity analysis, it was found that the fuel price is the most affecting parameter on LCOH followed by capacity factor while, sorbent cost and electricity selling price were found to be the lowest affecting parameters on LCOH. For cost of CO₂ avoided, it was found that varying the O&M cost had the highest impact on cost of CO₂ avoided. The reason behind this is due to the big difference between the O&M for SMR and SESMR plants. Following to O&M cost, capacity factor was found to have the second highest impact on Cost of CO₂ avoided similar to the observation for the impact on LCOH.

For the lowest affecting parameter for LCOH and cost of CO₂ avoided, it was found that Sorbent cost had the lowest impact, ±0.5% & ±1.3%, on LCOH and Cost of CO₂ avoided respectively.

From previous findings, we could conclude that applying the Li₄SiO₄/Li₂CO₃ SESMR looping system as a solution to reduce CO₂ emissions from conventional SMR H₂ production plant is considered feasible with an impact of 55.8% increase from the original price for LCOH and 72.7 £/tCO₂. However, such cost impact can be overcome when applying the cost of CO₂ emissions on similar hydrogen production plants. Moreover, by applying such policies, the reverse trend on LCOH and cost of CO₂ avoided could be observed as LCOH is reduced for SESMR resulting in negative values for cost of CO₂ avoided.

Similarly to the NGCC Case Study, the sensitivity analysis showed that even if the cost of the sorbent is initially high, such as the case of Li₄SiO₄, such cost can be compensated with other advantages obtained from the sorbent properties such as stability and relatively good capture and integration performance.
Chapter 8  GENERAL DISCUSSION AND FINAL REMARKS

8.1  Research Context, Gaps in Knowledge and Methodology

Lithium orthosilicate (Li$_4$SiO$_4$) based sorbents have shown good potential to be used as CO$_2$ capture sorbents, since they have a relatively good sorbent capacity, conversions and durability. However, despite their potential and to the best of the author’s knowledge, there are no previous extensive studies which evaluate the process integration of Li-based sorbents into power and industrial plants. Consequently, two reference plants, a Natural Gas Combined Cycle (NGCC) power plant and a Steam Methane Reforming (SMR) H$_2$ production plant, were chosen to investigate the process integration of Li$_4$SiO$_4$/Li$_2$CO$_3$ looping systems for CO$_2$ capture to assess their feasibility for large scale application.

The current study evaluated the thermal integration of Li$_4$SiO$_4$ based sorbent capture looping systems into the selected reference plants based on a conceptual evaluation of its equilibrium absorption and regeneration properties. Next, the technical and economic impact of the integrated process was assessed. The proposed conceptual techno-economic study covered plant performance, energy, efficiency penalties and potential economic impact of the high temperature CO$_2$ capture (HTCC) unit integration when applied in selected reference plants.

In this thesis, chapters 1 and 2 discussed: 1) previous work conducted for several carbon capture systems and technologies, focusing on the application of Li-based sorbents; 2) presented current research gaps in knowledge, and; 3) formulated the aim and objectives for this work. Chapter 3 highlighted the methodology followed to achieve the objectives of the thesis.

To achieve the aim of this study, the performance of the sorbent was first experimentally evaluated under relevant flue/industrial gas conditions for both, absorption and regeneration steps. The data obtained from the lab tests was used in building rigorous steady state Aspen Plus models. After building the process model for each case study, process optimization was performed to achieve the maximum possible heat integration / utilization inside the plant and hence, reduce the penalties associated with the integration of the CO$_2$ capture process.

Following the process modelling optimization, a techno-economic analysis was conducted to estimate the economic impact of the integrated model on a set of Key
Performance Indicators (KPIs) chosen for each reference case, such as the levelized cost of electricity and hydrogen and cost of CO₂ avoided.

Results for the process integration for the two case studies were presented and discussed in chapters 4 and 5 for the NGCC plant, and Chapters 6 and 7 for the SMR plant.

8.2 Case Study 1: NGCC process integration results

8.2.1 Modelling results

A steady-state Aspen Plus model was built for a NGCC power plant with a Li₄SiO₄ sorbent HTCC integrated. The European Benchmarking Task Force (EBTF) common framework basis and assumptions were followed and applied in process modelling. The base case model with HTCC was developed with 525°C and 700 °C absorption and regeneration temperatures, respectively, a Li₄SiO₄ fractional conversion of 0.2 and sorbent make up ratio of 0.01. The model results showed a net power plant efficiency penalty of 9.2% after HTCC plant integration. The obtained efficiency penalty is slightly higher than that obtained from a MEA-based system (8.4% penalty points), applied for the same reference plant and under the same conditions, and lower than the one for CaCO₃ sorbent-based HTCC integration (12.5% penalty points), which also was applied to the same reference plant under the same conditions.

Sensitivity analysis was conducted to investigate the effect of the regeneration temperature, Li₄SiO₄ fractional conversion, sorbent make up ratio and amount of oxyfuel excess O₂ on net plant efficiency, specific regeneration energy demand, EOP and SPECCA. Model results showed a significant reduction in sorbent regeneration energy consumption by reducing the regeneration temperature by 2% from its original value. This in turn led to a 0.6 % higher net plant efficiency. Similarly, increasing the sorbent conversion by 25% resulted in a 1.2% increase in the net plant efficiency. This was linked to the lower sorbent circulation requirements in such case.

With respect to the oxyfuel excess O₂, it was found that reducing the oxyfuel excess O₂ by 33%, results in 0.15 % increase in net plant efficiency.

Finally, the change in sorbent make up ratio was shown to have the lowest effect on net plant efficiency and power penalties. When the make-up ratio was reduced by 50%, it resulted in only 0.2 % increase in net plant efficiency.
8.2.2 Techno-economic results

Detailed design and sizing for the CO₂ capture fluidized bed system was performed using the process modelling data obtained from the process integration study discussed in chapter 4. The fluidized bed system was optimized based on splitting the GT flue gas between 8 absorbers connected with 4 regenerators for sorbent regeneration. The final optimized sizes were 5.4m x 10.5m and 4m x 10m for absorber and regenerator, respectively.

Following the fluidized bed sizing, a detailed bottom up approach was followed to estimate the direct cost for the fluidized bed system in 2017£ values. The cost for the rest of plant equipment was obtained and scaled from reference equipment costing data / curves available in literature and all values were also transferred to 2017£ values.

Two techno-economic methods were applied with different assumptions, to evaluate the levelized cost of electricity (LCOE), cost of CO₂ avoided and specific investment (SI) for the NGCC plant before and after the integration of a Li-based CO₂ capture system. Techno-economic Method 1 assumptions were obtained from the EBTF study and those for Method 2 were obtained from the latest UK published techno-economic guidelines for benchmarking new CO₂ capture technologies. Both methods were also applied to a CaL system integrated in the same reference NGCC plant.

It was found that by using Method 1, LCOE increased from 42.3 to 67.5 £/MWh and 67.8 £/MWh when applying Li-based and CaL based capture systems, respectively. The reason behind such increase in both cases is the expansion in capital and operational cost after the integration of the capture unit. With respect to cost of CO₂ avoided, it was found that the Li-based case achieved 78.7 £/tCO₂ while the CaL case achieved 82.5 £/tCO₂.

For Method 2, the techno-economic estimates are higher than those values obtained from Method 1 for all cases, i.e. reference case, Li-based CO₂ capture case and CaL CO₂ capture case. For instance, after applying Method 2, the LCOE for the base case without capture increased from 42.3 to 49.6 £/MWh. For the Li-based capture case, the LCOE increased from 67.5 to 73.9 £/MWh and the Cost of CO₂ avoided slightly decreased from 78.7 to 75.6 £/tCO₂. The reason behind this decrease is that the LCOE for the reference case was increased as well after applying Method 2 assumptions, which resulted in a slightly lower Cost of CO₂ avoided when compared to Method 1.

Finally, to investigate the effect of the most relevant parameters on the techno-economics of the process, a sensitivity analysis was conducted for 7 parameters, including Specific
Investment (SI), Plant efficiency, Discount factor, plant capacity factor, O&M cost, sorbent cost and fuel cost. The sensitivity analysis was performed on the Li-based case using Method 2, and the impact of the parameters on LCOE and Cost of CO₂ avoided was investigated. From the analysis, it was found that the plant efficiency is the parameter that affected the most the LCOE and cost of CO₂ avoided, followed by fuel price and capacity factor. It was also found that the sorbent cost was the parameter that affected the least. These results showed that even if the cost of the sorbent is initially high, such as the case of Li₄SiO₄, that cost can be offset with other advantages obtained from the sorbent properties such as stability and relatively good capture and integration performance.

8.3 Case Study 2: Hydrogen SMR plant process integration results

8.3.1 Modelling results

A steady-state Aspen Plus model was built for a Li₄SiO₄ based SESMR H₂ plant. A 100,000 Nm³ H₂ reference plant was considered and assumptions were followed and applied in process modelling based on the IEGHG case study [119]. The base case model with SESMR was developed with a 550°C reforming temperature and 700 ºC regeneration temperature A Li₄SiO₄ fractional conversion of 0.2 was considered inside the reactor. The model results showed an equivalent net hydrogen production efficiency penalty of 8.2% points after integrating the SESMR plant. The obtained efficiency penalty points were found to be higher than those obtained from a CaO-based SESMR H₂ production plant (5% penalty points). However, the Li-based SESMR process achieved a higher equivalent carbon capture ratio (CCReq=97.1%) and lower Specific CO₂ Equivalent Emissions (SCEeq=2.4 gCO₂/MJH₂eq) compared to those obtained by a CaO based SESMR process (CCReq=91.5% and SCEeq=6.5 gCO₂/MJH₂eq). The Li₄SiO₄ SESMR plant equivalent H₂ efficiency was also found to be lower than that obtained by MDEA integration (76.3 %), which was also applied to the same reference plant, but it achieved lower carbon capture rates, 56%.

8.3.2 Techno-economic results

Detailed design and sizing for the fluidized bed system was performed using the process modelling data obtained from the process integration study discussed in chapter 6. The fluidized bed system was sized and optimized to be in a single train with sorbent and catalyst looping between the SESMR and regenerator units. The final optimized sizes were: 5m x 7.1m and 5.9m x 8.2m for SESMR and regenerator, respectively.
Following the fluidized bed sizing, the detailed bottom up approach was followed to estimate the direct cost for the fluidized bed system in 2017£ values. The cost for the rest of plant equipment was obtained and scaled from reference equipment costing data / curves available in literature and all values were transferred to 2017£ values.

The techno-economic method and assumptions were applied to evaluate the levelized cost of hydrogen (LCOH), in £/kNm³ and £/kWth, and cost of CO₂ avoided, in £/tCO₂ avoided, for the SMR and SESMR plants with and without considering the cost of CO₂ emissions. The techno-economic method assumptions were obtained from the latest UK published techno-economic guidelines for benchmarking new CO₂ capture technologies. It was found that, LCOH increased from 102.3 £/kNm³ and 34.1 £/kWth for SMR to 159.3 £/kNm³ and 53.2 £/kWth for SESMR plant. The cost of CO₂ avoided was estimated to be equal to 72.7 £/tCO₂ avoided.

After applying carbon emissions taxes, it was found that the LCOH was reduced from 169 £/kNm³ and 56.4 £/kWth for SMR to 160.2 £/kNm³ and 53.5 £/kWth for SESMR plant. The cost of CO₂ avoided dropped to -11.2 £/tCO₂ avoided. The reason behind the changes in the LCOH and cost of CO₂ values, with and without the consideration of carbon taxes, is the fact of considering the cost of CO₂ emissions resulted from those emitted from the SMR plants and those avoided in the SESMR plant.

Finally, to investigate the most affecting parameters on the Li₄SiO₄/Li₂CO₃ looping based SESMR process techno-economics, a parametric change of ±25% was done for 7 parameters, including capital cost, O&M cost, fuel cost, electricity selling price, Discount factor and plant capacity factor. The sensitivity analysis was conducted to investigate the impact of changing the chosen parameters on LCOH and Cost of CO₂ avoided without considering the carbon emissions cost.

From the sensitivity analysis, it was found that the fuel price is the most affecting parameter on LCOH followed by capacity factor, while sorbent cost and electricity selling price were found to be the lowest affecting parameters on LCOH. For cost of CO₂ avoided, it was found that varying the O&M cost had the highest impact on cost of CO₂ avoided. The reason behind this is the big difference between the O&M for SMR and SESMR plants. Following to O&M cost, the capacity factor was found to have the second highest impact on Cost of CO₂ avoided, similar to the observation for the impact on LCOH. Sorbent cost had the lowest impact on LCOH, and cost of CO₂ avoided, ±0.5% and ±1.3%, respectively.
From all the findings, we could conclude that applying the Li$_4$SiO$_4$/Li$_2$CO$_3$ SESMR looping system as a solution to reduce CO$_2$ emissions from conventional SMR H$_2$ production plant is considered feasible, with an impact of 55.8% increase from the original price for LCOH and 72.7 £/tCO$_2$. However, such cost impact can be overcome when applying the cost of CO$_2$ emissions on similar hydrogen production plants. Moreover, by applying such policies, the reverse trend on LCOH and cost of CO$_2$ avoided could be observed as LCOH is reduced for SESMR, resulting in negative values for cost of CO$_2$ avoided.

Similarly, to the NGCC Case Study, the sensitivity analysis showed that even if the cost of the sorbent is initially high, such cost can be compensated with other advantages obtained from the sorbent properties such as stability and relatively good capture and integration performance.

Looking at hydrogen production from other technologies, it was found that the cost of hydrogen production varies from £1.1 / kg H$_2$ for Indirect bio-photolysis process upto £17.6 / kg H$_2$ for solar PV electrolysis as illustrated in table 8-1[219]:

*Table 8-1 Comparison between cost of hydrogen for SESMR / SMR processes from this study and other technologies from [219].*

<table>
<thead>
<tr>
<th>Process</th>
<th>Feedstock</th>
<th>Hydrogen Cost £ / kg H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMR (the current study)</td>
<td>Natural Gas</td>
<td>1.1</td>
</tr>
<tr>
<td>SESMR (the current study)</td>
<td>Natural Gas</td>
<td>1.8</td>
</tr>
<tr>
<td>Methane pyrolysis</td>
<td>Natural Gas</td>
<td>1.2-1.3</td>
</tr>
<tr>
<td>Biomass pyrolysis</td>
<td>Woody biomass</td>
<td>1.7</td>
</tr>
<tr>
<td>Biomass gasification</td>
<td>Woody biomass</td>
<td>1.5</td>
</tr>
<tr>
<td>Direct bio-photolysis</td>
<td>Water + algae</td>
<td>1.6</td>
</tr>
<tr>
<td>Indirect bio-photolysis</td>
<td>Water + algae</td>
<td>1.1</td>
</tr>
<tr>
<td>Dark fermentation photo-fermentation</td>
<td>Organic biomass</td>
<td>1.9</td>
</tr>
<tr>
<td>solar PV electrolysis</td>
<td>Water</td>
<td>4.4-17.6</td>
</tr>
<tr>
<td>solar thermal electrolysis</td>
<td>Water</td>
<td>3.8-7.9</td>
</tr>
<tr>
<td>wind electrolysis</td>
<td>Water</td>
<td>4.4</td>
</tr>
<tr>
<td>Nuclear electrolysis</td>
<td>Water</td>
<td>3.1-5.3</td>
</tr>
<tr>
<td>Process</td>
<td>Reactant</td>
<td>Cost ( £ / kgH₂)</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------</td>
<td>------------------</td>
</tr>
<tr>
<td>Nuclear thermolysis</td>
<td>Water</td>
<td>1.6</td>
</tr>
<tr>
<td>Solar thermolysis</td>
<td>Water</td>
<td>6</td>
</tr>
<tr>
<td>Photo-electrolysis</td>
<td>Water</td>
<td>7.8</td>
</tr>
</tbody>
</table>

As showed in table 8-1, producing Hydrogen by Li-based SESMR process has not scored the lowest cost of production. However, it shows a relatively low-cost solution, 1.8 £ / kgH₂ comparing to most of other clean H₂ production technologies such as wind, 4.4 £ / kgH₂, or solar PV electrolysis, 4.4 to 17.6 £ / kgH₂.

8.4 Recommendations for future work

The investigated sorbent, Li₄SiO₄, has showed good potential for its CO₂ capture process integration in NGCC power plants and SESMR plants. The process models for each case study were mainly built based on sorbent process data obtained from small scale lab experimental tests. For instance, for the NGCC case, the sorbent was tested on a lab scale by thermogravimetric analysis, i.e., mg scale. Hence, to advance the sorbent to a higher TRL level, the sorbent should be tested under similar flue gas conditions, for each case study, but at larger scale. The next stage should be to test the sorbent in a structured form on circulating fluidized beds, at lab scale, using flue gas conditions for each case study and for several cycles. The lab scale fluidized bed should be designed using the same sizing method followed in the techno-economic assessment.

Following to testing the sorbent on fluidized bed at lab scale, it can be tested in pilot fluidized beds [214, 215] previously built for Calcium looping to test the feasibility and cyclic durability of the sorbent under large volume of flue gases.

With respect to sorbent kinetics and its capture capacity, doping the sorbent with additives would help to increase the sorbent conversion inside the absorber and hence reduce the amount of solid inventory required to achieve 90% CO₂ capture in each case study. That would lead to reduce the reactors footprint and fluidization power, which in turn are expected to improve the plant performance and techno-economics for the integrated process.

With regards to process design and thermodynamic performance of the plant, other sorbent regeneration options could be investigated to achieve lower heat and energy consumption during the regeneration process. For instance, the replacement of direct oxy
fuel heating with indirect heating options. These options are conceptually based on applying heat transfer between the main power plant combustor and the sorbent regenerator [168], heat transfer between the hot regenerated solid stream exiting the regenerator and the colder solids stream leaving the absorber [169, 170], and the use of a double looping system to regenerate the sorbent in the regenerator [171]. These indirect heating options are also still at the conceptual design stage and require further development before being available for large scale practical implementation.

For the process design of NGCC plants, the combination between the Li-based looping system with a NGCC plant with selective exhaust gas recirculation could be considered [216]. For the SMR H$_2$ production application, other novel integration options could be investigated for Li-based high temperature looping system into similar plants such as:

- Li$_4$SiO$_4$-based sorption Enhanced water gas shift reaction application
- The application of Li$_4$SiO$_4$-based Sorption Enhanced Steam methane reforming combined with membrane reactor
- The integration of Li$_4$SiO$_4$-based SESMR process in a combined cycle power plant
- The integration of solar salt heat carriers into Li$_4$SiO$_4$-based SESMR to heat up the reformer feed to the reformer temperature.

Also, both case studies were investigated and evaluated for full load operation. Further investigation of other plant operation scenarios, i.e., plants running on part load operation, would be beneficial for further improvement of sorbent technology readiness level and techno-economic evaluation.

In addition to that, since the current study discussed steady state simulation only, a dynamic modelling for each case study using the current produced models, would be a valuable contribution to the technology assessment.

With respect to the high temperature Li-based sorbents, the same methodology followed in the current study and same simulation and techno-economic models could be modified to adapt the usage of other high temperature sorbents to give more wider evaluation for the integration of high temperature sorbent based CO$_2$ capture process in power and industrial plants.

Finally, it is worth mentioning that, as indicated by the techno-economic studies, the implementation of carbon tax policies and low emissions regulations would have a great impact on the feasibility of carbon capture and storage technologies. A collaboration
between government, industry, energy producers and consumers to apply such policies is very much needed to open the horizon for the application of several novel CO₂ capture technologies.
References


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Appendices

Appendix A.1

A.1.1 Experimental Scope and Design of Experiment (DOE)

Experimental Scope

The experimental plan was designed to cover the following[147]:

- General Sorbent CO₂ capture performance test:
  a) Test sorbent under 95% CO₂ to check the maximum sorbent capacity.
  b) Perform cyclic test (10 cycles) under 95% CO₂ for both Lithium Silicate and CaO sorbents to compare sorbent stability and cyclic performance.

- Testing the sorbent under NGCC flue gas conditions:
  a) Performing temperature-programmed CO₂ uptake under CO₂ concentration of 4% to define the optimum absorption temperature at which the maximum uptake can be achieved.
  b) Performing temperature programmed desorption (TPD) under 70% CO₂ to mimic the actual sorbent regeneration conditions for oxyfuel combustion and estimate the best desorption temperature at which the maximum sorbent regeneration is achieved.
  c) Perform one cycle for lithium orthosilicate under NGCC relevant conditions
  d) Performing multiple cyclic test for the lithium orthosilicate sorbent under the optimized absorption and desorption temperatures and NGCC flue gas conditions.

- Testing the sorbent under SESMR flue gas conditions:
  a) Perform one CO₂ capture test for lithium orthosilicate under SESMR flue gas conditions with 14% CO₂ concentration

Design of Experiment (DOE)

Name of Equipment: Thermal Gravimetric Analysis (TGA)

Sample: Inhouse optimized lithium orthosilicate powder / synthesized CaO.

Sample activation atmosphere: 100% N₂

Sample activation heating rate: 20°C/min

Intermediate activation temperature: 110°C
Intermediate activation isotherm duration: 30 min
Final activation isotherm duration: 10 min
Absorption test precooling rate: 25°C/min
Absorption test precooling temperature: 110°C
Absorption test heating rate: 10°C/min
Adsorption flue gas concentration: 95% CO$_2$, 5%N$_2$ / 4 % CO$_2$, 30% N$_2$ / 14% CO$_2$, 85% N$_2$
Desorption flue gas: 100% N$_2$ and for oxyfuel regeneration 70 % / 30% CO$_2$/N$_2$
<table>
<thead>
<tr>
<th>No</th>
<th>Test</th>
<th>Sample</th>
<th>Preheating Temp °C</th>
<th>Absorption test</th>
<th>Regeneration Test</th>
<th>No of Runs</th>
<th>Total time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>T_{abs.} °C</td>
<td>Atmosphere</td>
<td>T_{reg.} °C</td>
<td>Heating rate °C/min</td>
</tr>
<tr>
<td>1</td>
<td>TPA under 4 % CO₂</td>
<td>Li₄SiO₄</td>
<td>700</td>
<td>110 -600</td>
<td>4% CO₂</td>
<td>100% N₂</td>
<td>600 -725</td>
</tr>
<tr>
<td>2</td>
<td>Absorption</td>
<td>Li₄SiO₄</td>
<td>600</td>
<td>525</td>
<td>4% CO₂</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>3</td>
<td>Absorption</td>
<td>Li₄SiO₄</td>
<td>700</td>
<td>525</td>
<td>4% CO₂</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>4</td>
<td>Absorption</td>
<td>Li₄SiO₄</td>
<td>700</td>
<td>500</td>
<td>4% CO₂</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>5</td>
<td>Absorption</td>
<td>Li₄SiO₄</td>
<td>700</td>
<td>550</td>
<td>4% CO₂</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>6</td>
<td>Absorption for TPD</td>
<td>Li₄SiO₄</td>
<td>700</td>
<td>525</td>
<td>4% CO₂</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>7</td>
<td>TPD at 700</td>
<td>Li₄SiO₄</td>
<td>NA³</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>70% CO₂/30% N₂</td>
</tr>
<tr>
<td>8</td>
<td>Abs / Des cyclic test</td>
<td>Li₄SiO₄</td>
<td>700</td>
<td>525</td>
<td>4% CO₂</td>
<td>120</td>
<td>100% N₂</td>
</tr>
<tr>
<td>9</td>
<td>Abs / Des cyclic test</td>
<td>Li₄SiO₄</td>
<td>600</td>
<td>525</td>
<td>4% CO₂</td>
<td>120</td>
<td>100% N₂</td>
</tr>
<tr>
<td>10</td>
<td>Abs / Des cyclic test</td>
<td>Li₄SiO₄</td>
<td>700</td>
<td>525</td>
<td>4% CO₂</td>
<td>120</td>
<td>100% N₂</td>
</tr>
<tr>
<td>11</td>
<td>Abs / Des cyclic test</td>
<td>Li₄SiO₄</td>
<td>700</td>
<td>600</td>
<td>92% CO₂</td>
<td>120</td>
<td>100% N₂</td>
</tr>
<tr>
<td>12</td>
<td>Abs / Des cyclic test</td>
<td>CaO</td>
<td>700</td>
<td>600</td>
<td>92% CO₂</td>
<td>120</td>
<td>100% N₂</td>
</tr>
<tr>
<td>13</td>
<td>Abs test</td>
<td>CaO</td>
<td>600</td>
<td>525</td>
<td>4% CO₂</td>
<td>120</td>
<td>NA</td>
</tr>
<tr>
<td>14</td>
<td>Abs test</td>
<td>Li₄SiO₄</td>
<td>600</td>
<td>525</td>
<td>14% CO₂</td>
<td>30</td>
<td>NA</td>
</tr>
</tbody>
</table>

Total number of hours 203 Hrs

³ NA: not applicable since that kind of test focused only on absorption or desorption.
Appendix A.2

A.2.1 Plant assumptions and model input data for NGCC Plant

The guidelines of the EBTF have been followed [154]

The process conditions for Air and Natural Gas (NG) Streams:

Table A.2.1: Air feed to GT. Process conditions and composition

<table>
<thead>
<tr>
<th>Stream</th>
<th>G (kg/s)</th>
<th>T (ºC)</th>
<th>P (bara)</th>
<th>Composition mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Feed to GT</td>
<td>650</td>
<td>15</td>
<td>1.013</td>
<td>H₂O 0.0099, O₂ 0.2079, N₂ 0.7822</td>
</tr>
</tbody>
</table>

Table A.2.2: NG Feed Stream. Process conditions and composition

<table>
<thead>
<tr>
<th>Stream</th>
<th>G (kg/s)</th>
<th>T (ºC)</th>
<th>P (bara)</th>
<th>CO₂</th>
<th>N₂</th>
<th>CH₄</th>
<th>C₂H₆</th>
<th>C₃H₈</th>
<th>n-Butane</th>
<th>n-Pentane</th>
</tr>
</thead>
<tbody>
<tr>
<td>NG Feed to GT</td>
<td>15.3</td>
<td>160</td>
<td>70</td>
<td>.02</td>
<td>.0089</td>
<td>0.89</td>
<td>0.07</td>
<td>0.01</td>
<td>0.001</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

Gas turbine operational conditions

Table A.2.3: Operational parameters used in the modelling of the gas turbine

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Temperature</td>
<td>15</td>
<td>ºC</td>
</tr>
<tr>
<td>Air Pressure</td>
<td>1.013</td>
<td>bara</td>
</tr>
<tr>
<td>Air Flow rate per gas turbine</td>
<td>650</td>
<td>kg/s</td>
</tr>
<tr>
<td>Compressor Pressure Ratio</td>
<td>18.1</td>
<td>[-]</td>
</tr>
<tr>
<td>TIT (turbine inlet temperature)</td>
<td>1277</td>
<td>ºC</td>
</tr>
<tr>
<td>Fuel Flow rate per gas turbine</td>
<td>15.3</td>
<td>kg/s</td>
</tr>
<tr>
<td>Isentropic efficiency of the compressor</td>
<td>84.5 %</td>
<td>[-]</td>
</tr>
<tr>
<td>Mechanical efficiency of the compressor</td>
<td>99.6 %</td>
<td>[-]</td>
</tr>
<tr>
<td>Overall gas turbine efficiency</td>
<td>38.6 %</td>
<td>[-]</td>
</tr>
</tbody>
</table>
Heat recovery steam generator (HRSG) operational assumptions:

Table A.2.4: Equipment Pressure drops for primary and secondary heat recovery steam generators (HRSG)

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Pressure drop (as percentage of inlet pressure)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRSG- Cold Side</td>
<td>3% per heat Exchanger</td>
</tr>
<tr>
<td>Total Reheat- Cold Side</td>
<td>10%</td>
</tr>
<tr>
<td>Steam-Pipe-valve Losses</td>
<td></td>
</tr>
<tr>
<td>HP</td>
<td>7%</td>
</tr>
<tr>
<td>IP</td>
<td>9%</td>
</tr>
<tr>
<td>LP</td>
<td>12%</td>
</tr>
</tbody>
</table>

The pinch point temperature was considered as the main factor affecting the selection of equipment duties for each pressure stage inside the HRSG. The minimum pinch point followed is 8 ºC.

Steam Turbines and ancillaries’ conditions for primary and secondary steam cycles:

Turbine efficiencies:

- HP Turbine Isentropic Efficiency: $\eta_{HP} = 92 \%$
- IP Turbine Isentropic Efficiency: $\eta_{IP} = 94 \%$
- LP Turbine Isentropic Efficiency: $\eta_{LP} = 88 \%$
- Turbines Mechanical Efficiency: $\eta_{Turbine-Mech} = 99.6 \%$

General Pump Efficiency: 75 %

CO₂ compression train

The compression discharge pressure of each train was selected as per following:

- 1st Stage: 0.435 MPa
- 2nd Stage: 1.865 MPa
- 3rd Stage: 8.0 MPa
- 4th stage: 11 MPa

The Polytropic Efficiencies for Compression Stages are:
• 1st Stage: 80 %
• 2nd Stage: 80 %
• 3rd Stage: 75 %
• 4th stage: 75 %

The compressor driver efficiency is 95%.

**Summary of High Temperature CO\textsubscript{2} Capture (HTCC) unit modelling assumptions:**

• Absorber is modelled as a conversion reactor with 0.2 sorbent fractional conversion and 525°C working temperature.
• An in-boiler heat exchanger is assumed to extract the exothermic heat from the absorber.
• Regenerator is modelled as a Gibbs reactor working at 700°C.
• 1 bara was assumed as the working pressure for absorber and regenerator.
• Direct oxyfuel combustion is used in the regenerator to supply the heat required for the sorbent regeneration.
• A typical air separation unit (ASU) is modelled as a component splitter to produce a 95% pure O\textsubscript{2} stream with 200 kWh/t O\textsubscript{2} power consumption.
• Oxygen-to-fuel ratio in the regenerator was set to achieve 3% excess oxygen for the fuel combustion reaction.
• A CO\textsubscript{2} recycle is used to dilute the pure O\textsubscript{2} stream to achieve final 35% O\textsubscript{2} purity (mol basis) before entering the regenerator.
• A solid gas separator was considered at the absorber and regenerator exits to separate the suspended solids from flue gas stream with 100% assumed efficiency.
## A.2.2 Material balance for NGCC plant with HTCC integration

<table>
<thead>
<tr>
<th>Description</th>
<th>Units</th>
<th>AIR-1</th>
<th>AIR-2</th>
<th>NG-1</th>
<th>NG-1-3</th>
<th>NG-2</th>
<th>O₂</th>
<th>CO₂-1</th>
<th>CO₂-2</th>
<th>CO₂-3</th>
<th>FGAS-1</th>
<th>FGAS-2</th>
<th>HPS-1</th>
<th>IPS-1</th>
<th>LPS-1</th>
<th>LPFW-01</th>
</tr>
</thead>
<tbody>
<tr>
<td>From</td>
<td>V-9</td>
<td>E-11</td>
<td>E-12</td>
<td>V-3</td>
<td>C-2</td>
<td>V-4</td>
<td>E-8</td>
<td>GT</td>
<td>K-2</td>
<td>LPE-1</td>
<td>V-7</td>
<td>V-6</td>
<td>V-5</td>
<td>E-3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>To</td>
<td>V-1</td>
<td>ASU</td>
<td>V-2</td>
<td>C-2</td>
<td>GT</td>
<td>C-2</td>
<td>HPS-4</td>
<td>V-9</td>
<td>CO₂</td>
<td>Comp</td>
<td>HPS-1</td>
<td>Air</td>
<td>K-3</td>
<td>K-4</td>
<td>K-5</td>
<td>H-4</td>
</tr>
<tr>
<td>Temp</td>
<td>C</td>
<td>15</td>
<td>15</td>
<td>10</td>
<td>240</td>
<td>160</td>
<td>368</td>
<td>700</td>
<td>395</td>
<td>76</td>
<td>608</td>
<td>85</td>
<td>570</td>
<td>546</td>
<td>368</td>
<td>30</td>
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<tr>
<td>Press</td>
<td>bara</td>
<td>1.013</td>
<td>1.013</td>
<td>70</td>
<td>76</td>
<td>68.6</td>
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<td>1.013</td>
<td>1.013</td>
<td>1.04</td>
<td>1.04</td>
<td>106.13</td>
<td>13.514</td>
<td>3.95</td>
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<tr>
<td>Mole Flows</td>
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<td>8.44</td>
<td>5.08</td>
<td>11.11</td>
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</tbody>
</table>

### Mole Fractions

<table>
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<th>Description</th>
<th>Units</th>
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<th>AIR-2</th>
<th>NG-1</th>
<th>NG-1-3</th>
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<th>CO₂-1</th>
<th>CO₂-2</th>
<th>CO₂-3</th>
<th>FGAS-1</th>
<th>FGAS-2</th>
<th>HPS-1</th>
<th>IPS-1</th>
<th>LPS-1</th>
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### Description

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### Mole Fractions

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<th>CO₂-3</th>
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Appendix A.3

A.3.1 Design and costing Figures

Figure A.3.1: CEPCI values from 2003 to 2017

Figure A.3.2: Geldart Particle Classification Chart[179]
A.3.2 Techno-economic assessment method 1 assumptions

This method assumptions can be summarized in the following:

A) Assumptions for Total Capital Cost expenditure (CAPEX) evaluation:
   - Installation cost is assumed to be 67.25 % for power part and 82.7% for the chemical part as a percentage from the total capital cost.
   - Total direct cost (TDC) = capital cost + installation cost
   - Indirect cost is assumed = 14% from the total direct cost
   - EPC cost = TDC + indirect cost
   - Owner’s Costs and Contingencies = 15 % of EPC cost
   - Total Plant cost (TPC) = EPC cost + Owner’s Costs and Contingencies
   - Cost of the initial solids inventory is added to the capital cost of the CO₂ capture unit
   - All capital costs are assumed to be spitted between the 3 years before 1ˢᵗ year of operation:

Figure A.3.3: fluidized bed design assumption with respect to solid distribution [179]
B) Assumptions for Operation cost expenditure (OPEX) calculations:

- operation and maintenance (O&M) cost will be divided into fixed O&M cost and variable O&M cost
- Fixed O&M is calculated as following:
  a. Maintenance and repair cost = 2.5% of TPC
  b. Operating Labour cost = 40% of Maintenance cost
  c. Supervision cost = 30% of labour cost
  d. Laboratory Test cost = 10% of labour cost
  e. Insurance = 1.5 % of TPC
  f. Plant overhead cost = 60% of Maintenance and repair cost, labour and supervision cost and laboratory test cost
- Variable O&M cost covers the yearly cost of sorbent, process water and make up water
- Fuel cost was assumed to be 4.2 £/GJ based on average prices of NG purchased by power producers during 2017 [217]

C) Assumptions for levelized cost of electricity and cost of CO\textsubscript{2} avoided calculations:

- Plant life is 25 years
- Capacity factor is assumed to be 0.65 in the first year and 0.9 for the rest of the years till the end of lifetime of the plant. This is aimed to cover any technical or operational issues with the plant in the first year that may affect the electricity production.
- Discounted cash flow (DCF) rate is a valuation method used to estimate the attractiveness of an investment opportunity. DCF analyses use future free cash flow projections and discounts them, using a required annual rate, to arrive at present value estimates. In this study, 8% DCF was used similar to EBTF [135].
• Levelized cost of electricity will be calculated for the same NGCC plant before and after the integration of CO₂ capture unit.

• Cost of CO₂ storage is counted based on the Figure provided by BEIS in their recent studies which is equal to 19£ per tonne CO₂ [136].

A.3.3 Techno-economic assessment method 2 assumptions

This method assumptions can be summarized in the following:

A) Assumptions for Total Capital Cost expenditure (CAPEX) evaluation:
• All capital costs are assumed to be spitted between the 4 years before 1st year of operation:

<table>
<thead>
<tr>
<th>Year</th>
<th>Capital Cost split</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15%</td>
</tr>
<tr>
<td>2</td>
<td>35%</td>
</tr>
<tr>
<td>3</td>
<td>40%</td>
</tr>
<tr>
<td>4</td>
<td>10%</td>
</tr>
</tbody>
</table>

• Capital Cost = EPC cost + infrastructure connection cost
• EPC Cost is calculated based on Direct cost of equipment including installation cost
• Infrastructure connection cost is added from experience and rescaled based on plant power output (base case was scaled from wood base case and capture case was scaled from wood capture case).
• Indirect Cost is calculated as per the following:
  Indirect Cost = Pre-Licensing cost, Technical & Design Cost + Licensing & Public Enquiry + 0.04 * infrastructure connections

Where pre-Licensing, Technical & Design Cost = 1 % of EPC, Regulatory, Licensing & Public Enquiry = 2% of EPC.

• Owners’cost is assumed = 7 % of EPC cost
• Startup phase is taking place in 1 year before the 1st year of operation
• Start up cost = (no labour startup months * annual labour cost + startup maintenance months * annual maintenance cost + no of consumable start up months * annual cost of consumables) / 12 in £M
• 3 startup months are assumed for labour, maintenance and consumables cost calculation as a part of the startup cost
• Startup cost is added to the capital cost of the year of starting up
• Yearly working capital allowance is a 30 days cash-flow of the consumables and 30 days fuel consumption
• Cost of working capital = difference between last year capital allowance and this year capital allowance
• Cost of the initial solids inventory is added to the capital cost of the CO\(_2\) capture unit

B) Assumptions for Operational Cost Expenditure (OPEX) evaluation:
• Fixed OPEX = (Direct Labour Cost + General Overheads + Insurance and Local Taxes + Power Island Maintenance + Other Units Maintenance + Connection & Use of System in (£/MW/y))
• Direct Labour Cost based on total number of plant manpower scaled from NG power plant reference case with average salary of 53700 £ pa.
• General Overheads = 5 % EPC direct cost
• Insurance and Local Taxes = 2 % EPC direct cost
• Power Island Maintenance = 2.5 % Power Island Direct Cost
• Other Units Maintenance = 1.5 % (ASU + CO\(_2\) Capture & Compression + Utilities Direct cost)
• Connection & Use of System (M£ pa) = 3280 * 10\(^{-6}\) £ / MW / y * Net power output in MW
• Variable OPEX = (CO\(_2\) Storage Cost £/tonne CO\(_2\) + Sorbent Make-up Cost + other consumables)
• CO\(_2\) Storage Cost 19 £/tonne CO\(_2\)
• Sorbent make up cost based on sorbent costing model
• Other consumables Cost (0.2 £ pa)

C) Assumptions for levelized cost of electricity and cost of CO\(_2\) avoided:
• Year 2025 is the first year of operation

*Discounted Cash flow* = \[ \frac{\text{Projected Annual Cash flow}}{(1 + \text{discount rate})^{\text{current year-2017}}} \]

• Discount rate = 8%
• Projected annual cash flow = fuel cost + carbon price + fixed operating cost + variable operating cost + cost of working capital + capital cost including start-up cost
• Sales of electricity, operating and capital costs are escalated forward to 2017
• First year production rate is 60%
• Overall plant operating factor is 90%
• LCOE was calculated for each plant based on Net present value (NPV) using goal seek function
• Cost of CO₂ avoided have been calculated using the same formula used in method 1
• There are two values for cost of CO₂ avoided: one that considered the effect of a carbon price, and one that doesn’t consider a carbon price
• Fuel and carbon prices are calculated on a year-by-year, 2017 real cost basis.

A.3.4 Summary of CaL fluidized bed parameters

*Table A.3.3: Summary of Fluidized bed sizing parameters using KL model*

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<th>Absorber</th>
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<td>Sorbent Flow rate (kg/s)</td>
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<td>Average Particle size (µm)</td>
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<td>Flue gas superficial speed (m/s)</td>
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<td>H (m)</td>
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Appendix A.4

A.4.1 Techno-economic assessment assumptions

This method assumptions can be summarized in the following:

A) Assumptions for Total Capital Cost expenditure (CAPEX) evaluation:

- All capital costs are assumed to be spitted between the 4 years before 1st year of operation:

<table>
<thead>
<tr>
<th>Year</th>
<th>Capital Cost split</th>
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<td>3</td>
<td>40%</td>
</tr>
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<td>4</td>
<td>10%</td>
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- Capital Cost = EPC cost + infrastructure connection cost
- EPC Cost is calculated based on Direct cost of equipment including installation cost
- Infrastructure connection cost is added from experience and rescaled based on plant power output (base case was scaled from wood base case and capture case was scaled from wood capture case).
- Indirect Cost is calculated as per the following:
  Indirect Cost = Pre-Licensing cost, Technical & Design Cost + Licensing & Public Enquiry + 0.04 * infrastructure connections)
  Where pre-Licensing, Technical & Design Cost = 1% of EPC, Regulatory, Licensing & Public Enquiry = 2% of EPC.
- Owners’cost is assumed = 7% of EPC cost
- Startup phase is taking place in 1 year before the 1st year of operation
  Start up cost = (no labour startup months * annual labour cost + startup maintenance months * annual maintenance cost + no of consumable start up months * annual cost of consumables) / 12 in £M
- 3 startup month s are assumed for labour, maintenance and consumables cost calculation as a part of the startup cost
- Startup cost is added to the capital cost of the year of starting up
• Yearly working capital allowance is a 30 days cash-flow of the consumables and 30 days fuel consumption

• Cost of working capital = difference between last year capital allowance and this year capital allowance

• Cost of the initial solids inventory is added to the capital cost of the CO₂ capture unit

B) Assumptions for Operational Cost Expenditure (OPEX) evaluation:

• Fixed OPEX = (Direct Labour Cost + General Overheads + Insurance and Local Taxes + Power Island Maintenance + Other Units Maintenance + Connection & Use of System in (£/MW/y))

• Direct Labour Cost based on total number of plant manpower scaled from NG power plant reference case with average salary of 53700 £ pa.

• General Overheads = 5% EPC direct cost

• Insurance and Local Taxes = 2% EPC direct cost

• Power Island Maintenance = 2.5% Power Island Direct Cost

• Other Units Maintenance = 1.5% (ASU + CO₂ Capture & Compression + Utilities Direct cost)

• Connection & Use of System (M£ pa) = 3280 * 10⁻⁶ £ / MW / y * Net power output in MW

• Variable OPEX = (CO₂ Storage Cost £/tonne CO₂ + Sorbent Make-up Cost + other consumables)

• CO₂ Storage Cost 19 £/tonne CO₂

• Sorbent make up cost based on sorbent costing model

• Other consumables Cost (0.2 £ pa)

C) Assumptions for levelized cost of electricity and cost of CO₂ avoided:

• Year 2025 is the first year of operation

• Discounted Cash flow = \( \frac{\text{Projected Annual Cash flow}}{(1+\text{discount rate})^{\text{(current year - 2017)}}} \)

• Discount rate = 8%

• Projected annual cash flow = fuel cost + carbon price + fixed operating cost + variable operating cost + cost of working capital + capital cost including start-up cost

• Sales of electricity, operating and capital costs are escalated forward to 2017
• First year production rate is 60%
• Overall plant operating factor is 90%
• LCOH was calculated for each plant based on 0 Net present value (NPV) using goal seek function
• There are two values for cost of CO₂ avoided: one that considered the effect of a carbon price, and one that doesn’t consider a carbon price
• The carbon taxes were estimated based on a variable carbon cost distributed over the lifetime of the project with an average cost of 95.6 £/ tonne CO₂.
• Fuel and carbon prices are calculated on a year-by-year, 2017 real cost basis.
• Indirect emissions from power input is assumed based on NGCC power plant as mentioned in chapter 6.
A.5.1 SESMR Modelling Assumptions

- The SESMR unit has been modelled using a black box concept.
- In the SESMR black box a combination of Gibbs and stochiometric reactors were arranged to mimic the Li-based equilibrium shifted reaction.
- CO₂ absorption inside the stochiometric reactor was modelled based on a fixed value of the sorbent fractional conversion for the Li₄SiO₄ / CO₂ reaction of 0.2.
- Operating temperature of 550°C is used inside the SESMR reformer.
- The NG feed is combined with low pressure steam to achieve a steam to carbon ratio of 3.5 before entering the SESMR reactor.
- Oxyfuel combustion is used to regenerate the sorbent at the chosen working temperature (T_{reg} = 700°C), similar to the regenerator in the NGCC case study.
- For best utilization of excess heat, two in-boiler heat exchangers (E-4 and E-6) were chosen to be integrated inside the SESMR reformer.
- The reformer and the regenerator are working at a pressure of 1.2 bara.
- For oxygen production, an air separation unit (ASU) is assumed to produce a 95% pure O₂ stream with 159 kWh/t O₂.
- A CO₂ multistage compression and auto-refrigeration train is used with auto-refrigerated system to achieve final liquid CO₂ stream, ready for transportation with a purity of 94% mole basis at 110 bara.

A.5.2 SESMR H₂ plant material balance
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<th>CO₂ to Comp</th>
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<th>H₂ -Recycle</th>
<th>H₂ TO BL</th>
<th>HP-Steam -01</th>
<th>Reheated Steam</th>
<th>LP-Steam</th>
<th>LPW-Feed</th>
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<td>PSA</td>
<td>HP Super Heater</td>
<td>Sr- Reheater</td>
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<td>Preheater</td>
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