

A conceptual design for integrating lithium-based carbon capture looping systems into Natural Gas Combined Cycle power plants

*Ahmed. Saleh, E. Sanchez Fernandez, M. M. Maroto-Valer and Susana Garcia**

Research Centre for Carbon Solutions (RCCS), Heriot-Watt University,

EH14 4AS, Edinburgh, United Kingdom

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ABSTRACT

Lithium Orthosilicate (Li₄SiO₄) based sorbents have been reported to show relatively high CO₂ capture capacity, high stability and require lower regeneration temperatures than other high-temperature sorbents. Based on these properties, a capture plant concept could be envisaged, aiming for achieving as low as possible CO₂ capture penalties. Accordingly, this work presents a conceptual AspenPlus® process simulation study that evaluates the thermal integration of Li₄SiO₄-based looping systems into a Natural Gas Combined Cycle (NGCC) power plant with the addition of a secondary oxyfuel combustion system and a secondary steam cycle. Based on previously obtained experiment results, absorption and desorption temperatures of 525 and 700°C,

respectively, a sorbent fractional conversion of 0.2 in the absorber and a sorbent make up ratio of 0.01, were used in the model. The results show that implementation of a Li_4SiO_4 -based high temperature carbon capture (HTCC) system into a NGCC power plant reduces the plant efficiency by 9.2% penalty points. This energy penalty is close to the one obtained from the integration of first-generation amine-based capture technologies, 8.4% penalty points, and lower than the one for CaO-based HTCC plants (12.5 % points), which were evaluated under the same assumptions as those used in this work. A sensitivity analysis on the impact of varying different process parameters on plant efficiency and integration penalties has been performed. Sorbent regeneration temperature was observed as the most affecting parameter. However, it was found to be constrained by upper and lower limits. In line with the current findings, using improved Li_4SiO_4 sorbents, could lead to further reduction in CO_2 capture penalties.

1. Introduction

Limiting the global warming to 1.5°C is considered as one of the greatest worldwide challenges nowadays. To achieve such target, several pathways were 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 dioxide capture and storage (CCS) was found to be one of the promising solutions to achieve the global warming mitigation pathways²⁻⁴. 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 or injection locations. There are various technological methods for CO_2 capture. The most extensively investigated ones are liquid solvents (especially amine-based), solid sorbents and membranes⁵. 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 energy⁶⁻⁷. For example, Sanchez et al⁸, reported that the net plant efficiencies of coal and natural gas power plants have been decreased by 11.7 and 8.4 % points respectively when conventional amine based technologies are applied for CO₂ capture. Also, oxyfuel combustion was frequently proposed as a solution for CO₂ emissions from NGCC plants in a process called semi-close oxygen combustion combined (SCOC-CC) cycle. Such oxyfuel plants were reported to have efficiencies ranging from 36.7%⁹ up to 53.9%¹⁰ for a 1400°C class oxyfuel gas turbine. However, these oxyfuel plants face several technical issues such as the high temperature at the turbine outlet, which needs an efficient cooling system for the gas turbine blades¹¹. Also, from an operational point of view, the oxyfuel working conditions for the gas turbine combustor are significantly different from the air blown gas turbine combustor conditions¹² due to the different flue gas properties.

As an alternative option, solid sorbents based processes have been investigated as an energy efficient separation technology for CO₂ capture, especially for high temperature applications¹³⁻¹⁴ such as NGCC plants. Their main advantage is that they can capture CO₂ at high (>400 °C) working temperatures with no need to cool down the flue gas to ambient temperature. This will potentially help saving energy and improving the plant efficiency especially when utilizing the hot extracted CO₂ stream inside the plant as a heat source^{6,15}.

In recent years, the utilization of regenerable lithium metal oxide sorbents as high temperature CO₂ acceptors in the temperature range of 450-700°C was extensively investigated¹⁶⁻²⁰. Among the investigated sorbents lithium orthosilicate, Li₄SiO₄, is considered a promising material for high temperature CO₂ capture applications due to

a good CO₂ capture capacity, up to 36.7 wt. %¹⁹, and lower regeneration temperature (< 750°C) when compared to other high temperature sorbents such as CaO-based sorbents^{16, 21-23}. When Li₄SiO₄ is exposed to a CO₂ stream at appropriate temperature, CO₂ is absorbed by the sorbent through the following reversible chemical reaction:



Based on the stoichiometry of reaction R(1), the maximum CO₂ absorption capacity of these sorbents is 36.7 wt.%, which is higher than the amine benchmark (8%)²⁴. Even though there are numerous studies investigating the reactivity and stability of lithium-based sorbents²⁵⁻²⁹, both in powder and pellet forms, that prove their cyclic and thermal stability^{27, 30}, their potential to decrease the energy penalty of the capture system is yet to be established. To the best of authors' knowledge, there are no comprehensive studies so far of the integration of Li-based capture systems into either power or industrial plants. These studies would enable the comparison to other capture technologies as well as to second-generation alkali-based materials and could provide useful guidance for the development and possible application of synthetic lithium-based sorbents.

In this work, the process integration of a high temperature Li₄SiO₄-based CO₂ capture system is investigated as a potential energy efficient solution. The process is performed through AspenPlus® software and the study aims to investigate the energy penalty due to the integration of the capture plant and it also evaluates how to achieve a reduction in the energy demand for regeneration. Hence, this work analyses the thermal integration of Li-based sorbents into a Natural Gas Combined Cycle (NGCC) power plant with the addition of a secondary oxyfuel combustion system and a secondary

steam cycle. The study focusses on the potential advantages of using Li-based sorbents, which regenerate at lower temperatures and show a higher stability than those sorbents used in calcium looping systems. Section 2 in this paper describes the principles of the capture technology based on solid sorbents, its energy requirements and summarizes the integration concepts that could be applied to Li-based sorbents based on what it has been developed in the past for the calcium looping process. Section 2 also covers modelling methodology and assumptions for the reference case with and without CO₂ capture. Section 3 discusses the integration results with respect to Plant efficiency and associated penalties. The results are then compared to other technologies including calcium looping, standard monoethanolamine (MEA) and more advanced amine-based solvents when integrated in the same plant. Section 3 also presents the impact of varying several process parameters, such as regeneration temperature, sorbent fractional conversion and make up ratio, on net plant efficiency and energy penalties along with possible future improvements. Obtained results could be used as guidance for future experimental and kinetic testing studies on the absorption and regeneration of Li-based sorbents so further improvements on net plant efficiencies could be achieved.

The next step from this work is the technoeconomic assessment of the proposed integration of a Li-based High temperature looping CO₂ capture system into NGCC plants. This technoeconomic assessment is outside the scope of this work and will be presented in a follow-up study.

2. Modelling methodology and assumptions

2.1 Cases process description

The process design for NGCC power plant was done as per European Benchmarking Task Force (EBTF) common frame work ³¹. The NGCC plant was modelled with and without capture to evaluate efficiency, power and electrical penalties associated with carbon capture. Model details and assumptions are discussed in section 2.2. Each case is described separately in the following sub sections.

2.1.1 Base case

The considered NGCC Power Plant, illustrated in Figure 1, is a state-of-the-art large-scale power plant which consists of two large scale identical Gas Turbine (GT) generators.

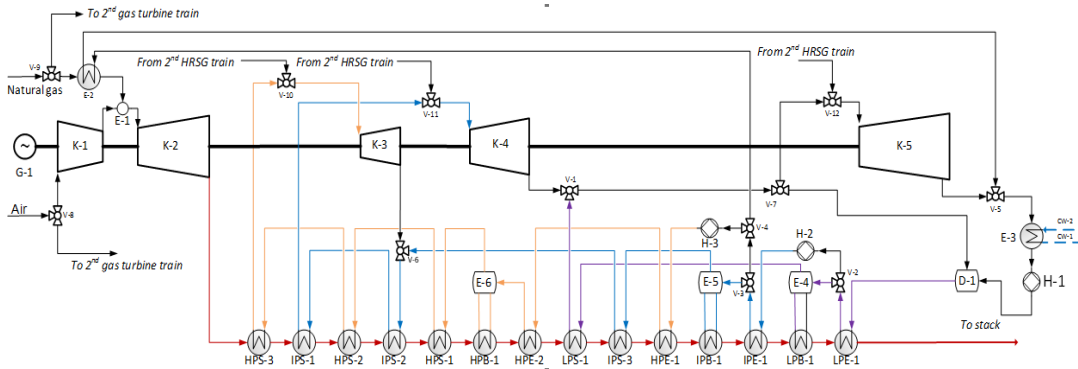


Figure 1. Process flow diagram of the 2x1 NGCC power plant base case. Only one GT and HRSG are illustrated in the figure.

Each unit has a single GT “F Class” and a three-pressure level Heat Recovery Steam Generator (HRSG) connected with a single steam turbine. In the current work, the plant configuration is denoted as 2x1, i.e., two gas turbines and a single steam turbine.

As seen in figure 1, the air is being compressed in an air compressor, K-1, before being burned with the NG fuel in the GT combustor. The high-pressure hot flue gas resulted from the combustion is directed to the turbine K-2 to generate electricity.

The hot flue gas existing the turbine K-2 is passed to a HRSG unit for heat recovery. The HRSG generates steam at three different pressure levels: low pressure - purple color streams, medium pressure - blue color streams and high pressure - orange color streams. Each pressure stage has an economizer, which helps to reduce the energy consumption and preheat the water, boiler, which generates the steam at each stage, and superheater, to generate superheated steam.

Since the plant with 2 x 1 design contains only one three pressure stage steam turbine, the steam generated from each pressure stage in each HRSG is combined before entering the relative pressure steam turbine. In figure 1, K3, K4 & K4 represents high, intermediate and low-pressure steam turbines respectively.

The HRSG has a single reheat for the intermediate pressure steam at which the intermediate pressure steam is reheated in IPS-1 & 2 to increase the temperature of the superheated intermediate steam before entering the intermediate steam turbine, K-4. Hot water is extracted from intermediate pressure section at V-4 in the HRSG to preheat the natural gas fuel to 160°C, in E-2, before entering the combustor. The gas turbine air-to-fuel ratio is kept constant and simulations are carried out for full load operation. An inland location in central Europe and a cooling system based on cooling towers and considering the ISO standard for ambient conditions are assumed. The LP steam exiting the LP steam turbine, K-5, is being cooled and condensed in the condenser, E-3, before being pumped to the deaerator drum, D-1, to remove any dissolved gases from the water before being circulated to the HRSG unit. On the other hand, the final flue gas stream, red stream, exits the HRSG low pressure stage to the stack.

2.1.2 HTCC plant and possible heat integration

The $\text{Li}_4\text{SiO}_4 / \text{Li}_2\text{CO}_3$ HTCC conceptual plant design (Fig. 2) was chosen to be like the one previously envisaged for high temperature calcium looping (CaL) systems integrated in NGCC plants source^{15, 32-33}.

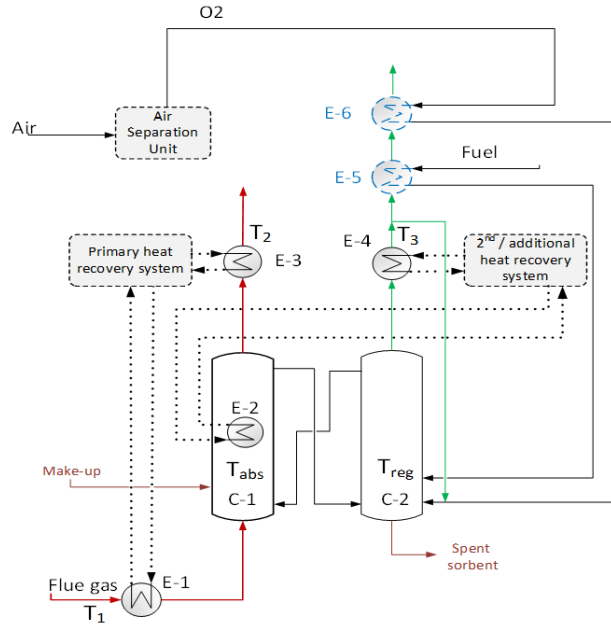


Figure 2. Conceptual design of a Li_4SiO_4 -based HTCC Plant.

As seen in Figure 2, in a $\text{Li}_4\text{SiO}_4 / \text{Li}_2\text{CO}_3$ HTCC looping system, the $\text{Li}_4\text{SiO}_4 / \text{Li}_2\text{CO}_3$ solids are circulated between two reactors, absorber and regenerator without any heat recuperation between the two fluidized solids streams. The CO_2 capture takes place in the absorber (C-1) following the reaction R(1) to the right direction. The sorbent is then regenerated at the required temperature in the regenerator (C-2) following the reverse reaction of R(1). Sorbent absorption and regeneration working temperatures of 525 and 700 °C, respectively, were chosen based on previously obtained experimental data on Li_4SiO_4 under NGCC flue gas conditions³⁴. The best operating temperature for each reactor was selected after performing temperature programmed adsorption / desorption lab tests under the operational conditions of each reactor, respectively. For the absorption process, the temperature programmed absorption test was performed under

4% CO₂ concentration and it was found that 525°C is the best absorption temperature at which the maximum CO₂ uptake takes place. Similarly, for desorption process, temperature programmed desorption test was performed under 70% CO₂ concentration, which is similar to oxyfuel combustion conditions. It was found that a desorption temperature higher than 660°C was required to achieve full regeneration. In line with the previous mentioned results, absorption and desorption temperatures of 525 and 700°C, respectively, were chosen as the optimum cyclic operational temperatures for the HTCC unit.

To integrate the HTCC looping system in a NGCC plant, the capture system should be placed downstream the GT outlet as can be seen from figure 3, which illustrates the process flow diagram of the NGCC power plant after the integration of HTCC unit.

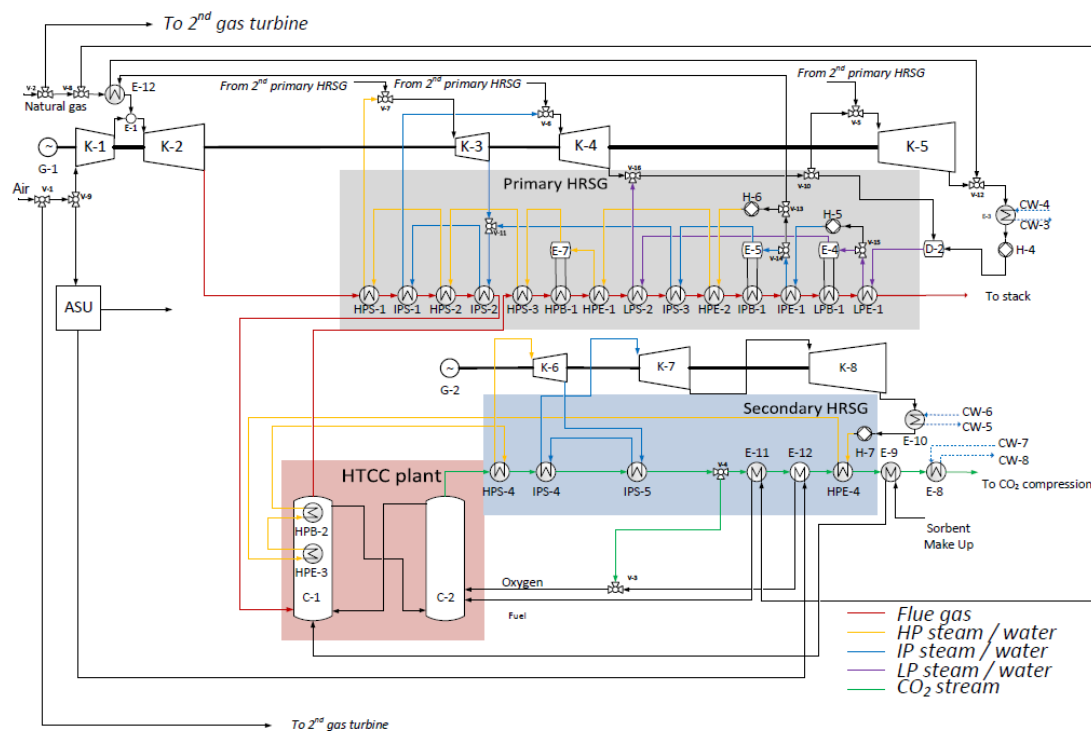


Figure 3. Conceptual integration of a Li₄SiO₄ based HTCC plant into the NGCC power plant base case.

In such case, the temperature of the GT flue gas (T_1) is normally around 600°C which is higher than the required absorption temperature of 525 °C. The excess heat in the flue gas could be best utilized for electricity production in the primary energy recovery system heat exchanger (E-1), as shown in Figure 2. After E-1, flue gas containing the CO₂ is contacted in the carbonator (C-1), at temperature = T_{abs} , with the lithium sorbents (Li₄SiO₄) coming from the regenerator (C-2). These sorbents enter the absorber at the regeneration temperature ($T_{\text{reg}}=700^\circ\text{C}$) and the carbonation reaction takes place at the absorption temperature (T_{abs}). Since the carbonation is highly exothermic (142 kJ/mol)³⁰, a fluidized bed reactor with in-bed heat transfer equipment (E-2) was chosen, to allow for temperature control and heat recovery in the absorber. The design of the in-bed heat transfer system, (E-2), is similar to the design of the in-bed temperature cooling system followed in the 200kW fluidized bed pilot scale³⁵ at which two heat exchangers were added to the dense and lean region, respectively, to cool down the fluidized bed and control the temperature inside the fluidized bed.

During absorption, the sorbent is fluidized using the plant flue gas. This is similar to fluidized bed designs previously used in similar CaL systems³⁶.

To regenerate the carbonated lithium sorbents and recover CO₂ ready for storage or utilization, the fluidized sorbent is directed to the regenerator. To avoid dilution inside the regenerator, direct oxyfuel combustion is used where the oxyfuel combusted gas is acting as the fluidizing medium in the desorber. Heat is recovered from the hot CO₂ stream, leaving the desorber, to generate electricity through a secondary HRSG (E-4). A novel heat integration scheme has been proposed, where a fraction of the excess heat in the CO₂ stream is used to pre-heat both the natural gas stream and the oxygen rich stream in (E-5) and (E-6) respectively before being supplied to the regeneration column. To overcome sorbent deactivation, fresh Li₄SiO₄ is added to the absorber with

possibility of preheating by using the CO₂ hot stream coming from the desorber. The spent sorbent is extracted from the desorber.

Integrating this HTCC design in a NGCC plant yields more flexibility in the plant modes of operation, since it allows for the primary steam cycle to operate with the capture unit turned on or off whenever needed. In addition to that, this configuration offers several sources for potential heat recovery, such as the exothermic reaction inside the absorber and hot CO₂ stream exiting the desorber. From these sources, the heat can be recovered which results in reducing the energy penalties associated with the CO₂ capture process.

2.1.3 Base case with HTCC plant

This case comprises a 2x1 combined cycle identical to the base case in which a Li₄SiO₄ based HTCC plant has been integrated. The capture unit configuration is based on the one previously presented in Fig. 2. The process flow diagram for the base case with the integrated HTCC plant is illustrated in Fig. 3. The conceptual design of the HTCC plant is done with the following assumptions:

- The make-up flow rate is very small (0.01 Kg fresh Li₄SiO₄/ Kg circulated Li₄SiO₄), so there is no need to use heat exchangers with spent sorbent. That was decided based on the high stability of the sorbent observed during cyclic test of the sorbent under NGCC flue gas absorption condition and oxy-fuel combustion desorption condition as observed by M.T. Izquierdo et al ³⁴.
- The final CO₂ stream before the compression train is by passed to another heat exchanger (E-9) to heat up the make-up stream before being fed to the absorber. That helps to improve the secondary steam cycle efficiency by

transferring part of the hot CO₂ stream heat to the absorber through the sorbent make up flow which is being recover in turn in the in-bed heat exchangers.

- Heat integration with the CO₂ compression excess heat has not been considered. That was decided to have an equal comparison to other capture technologies applied to the same NGCC reference case as will be discussed in section 3.
- The absorption heat is supplied at constant temperature (525°C) and is used to pre-heat the high-pressure feed water and generate superheated steam. That was assumed in line with the utilization of the in-bed heat exchangers to control the temperature inside the absorber as described in section 2.1.2.
- Additional superheating of the steam is possible using the excess heat from the CO₂ product stream and a single re-heat of the intermediate pressure steam is used to achieve suitable values of the dryness fraction (> 90%) at the low-pressure steam turbine exhaust and improve steam cycle efficiency in the secondary HRSG.

In Figure 3, the absorber C-1 was adjusted to achieve 90% CO₂ capture at a sorbent fractional conversion of 0.2 and 525°C absorption temperature by adjusting the sorbent recirculation rates. On the other hand, the regenerator C-2 was considered to achieve full sorbent regeneration which is consistent on the sorbent regeneration results obtained from testing Li₄SiO₄ under NGCC flue gas absorption condition and oxy-fuel combustion desorption condition as described in ³⁴. To provide the required heat for sorbent regeneration, an oxyfuel combustion takes place in the desorber at 700°C. A conventional air separation unit (ASU) with power consumption of 200 kWh/t O₂ ³² is assumed to produce a 95% pure O₂ stream required for combustion.

The absorption heat and excess heat from the HTCC unit is recovered in a secondary high pressure (HP) HRSG with single reheat for steam generation as in the case of Berstad et al ³².

The main advantage of having a second steam cycle is that it gives more flexibility from plant operational point of view. This flexibility enables to achieve full bypass to the HTCC system, in case of peak hours operation or maintenance shutdown, without affecting the primary steam cycle and electricity production from the original plant. In addition to that, the main equipment in the primary steam cycle, i.e. steam turbine and HRSG heat exchangers, have a design limitation with respect to turbine load and HRSG heat exchange area and any modification in this equipment would affect the plant integrity.

Although, adding a secondary steam cycle is more favorable from a plant operational and integrity point of view, it is worth mentioning that it would lead to an increase in capital investment and operational cost as well which in turn affects the final price of electricity.

For the secondary steam cycle, the heat is extracted from the absorber using two heat exchangers integrated inside the absorber to provide superheated steam at temperature of 518°C using the exothermic energy resulted from R(1). Dividing the extracted heat from the absorber between two heat exchangers helps to have a constant temperature distribution across the absorber so that the absorption process takes place at a fixed temperature equal to 525°C. The steam generated from the absorber heat exchangers is directed to a HP super heater for more superheating at 578°C. The pure CO₂ stream exiting the regenerator at 700°C is passed through the secondary HRSG to generate steam and electricity before entering the compression and transportation train. As seen

in figure 3, the hot CO₂ stream is used first to superheat the HP steam to 578°C before entering the HP turbine. The steam exits the HP turbine at temperature around 368°C and is passed through a two-stage single pressure reheat system using the hot CO₂ stream to generate intermediate pressure (IP) steam at temperature of 578°C. After the reheaters, the CO₂ is used to preheat the HP boiler feed water to 483°C before entering the absorber in-bed heat exchangers.

After the secondary HRSG, the final CO₂ product stream, at 76°C, is cooled down to 30°C before being compressed to 110 bars for transportation. The final compression pressure and compression pressure ratios for each compression stage are as per EBTF frame work recommendations ³¹. As shown in Figure 4, the compression train consists of 4 compression stages with intercooling to 30°C after each stage based on the cooling system described in section 2.1.1 for the base case.

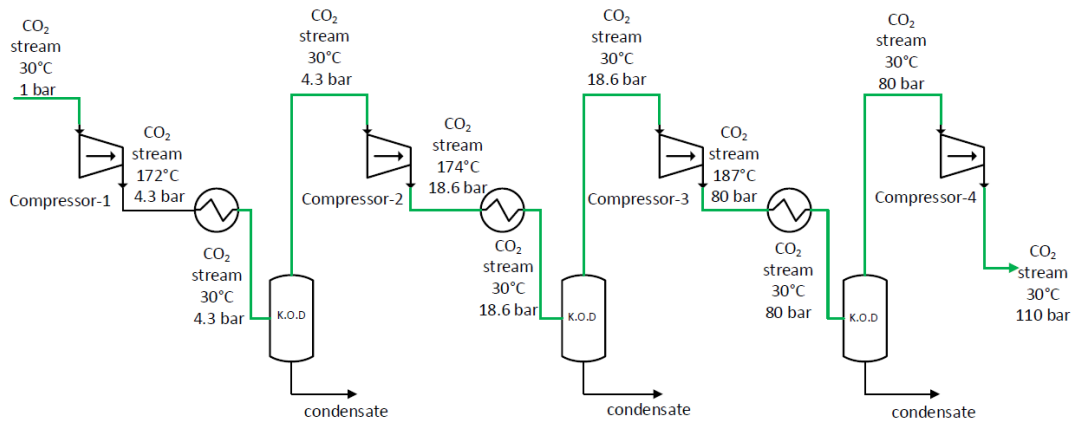


Figure 4. Configuration of CO₂ Compression train in modelling base case. KOD indicates a water knock-out drum.

2.2 Modelling Assumption

The modelling basis and assumptions for the NGCC power plant are as per European Benchmarking Task Force (EBTF) common frame work ³¹ and are available in the

supporting information to this article. AspenPlus® software has been used to build a rigorous steady state plant model and calculate heat and mass balances for all plant streams. The absorber was modelled using a stoichiometric reactor based on a fixed value of fractional conversion (0.2 on molar basis) which was considered similar to the one used for the integration of CaO sorbents in NGCC plants ³². The 0.2 molar basis fractional conversion was extracted from the lab Thermogravimetric Analysis (TGA) test results of the sorbent under NGCC flue gas absorption conditions (4% CO₂ concentration) and 525°C absorption temperature. A solid-gas contact time of 20 minutes was assumed to achieve the 0.2 molar basis fractional conversion based on the lab results (Figure 5).

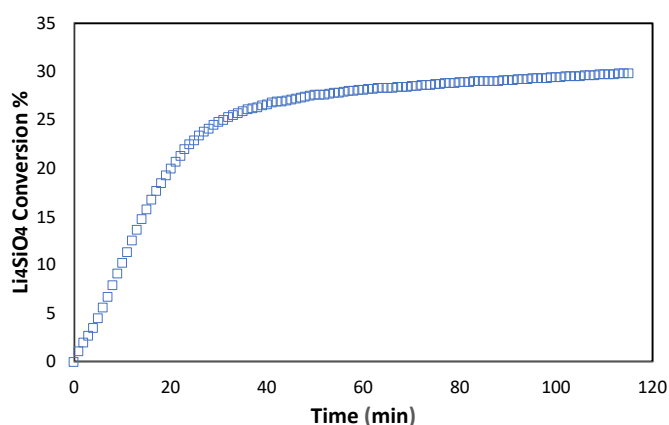


Figure 5: Li₄SiO₄ sorbent fractional conversion under 4% CO₂ concentration and 525°C absorption temperature.

High sorbent cyclic stability was assumed inside the absorber based on the sorbent cyclic test under NGCC flue gas absorption condition and oxy-fuel combustion desorption condition observed by M.T. Izquierdo et al ³⁴.

The absorber unit was set to operate at 1 bar outlet pressure, absorption temperature of 525°C and a solid gas separator unit was added at the absorber exit to split the gas stream from any suspended solid particles with 100% assumed efficiency. The regenerator was modelled using a Gibbs reactor which is based on Gibbs free energy

minimization similar to calciner modelling assumptions followed in several studies in literature ³⁷⁻⁴⁰. It is set to operate at 1 bar pressure and regeneration temperature of 700°C.). A solid-gas separator unit is also added at the regenerator exit to split the gas stream from any suspended solid particles with 100% assumed efficiency.

For oxyfuel combustion, the oxygen-to-natural gas ratio was adjusted to achieve 3% excess oxygen. The temperature of the oxyfuel combustion was moderated by dilution of the O₂ stream of 95% purity with a fraction of the rich CO₂ stream exiting the regenerator, to achieve 35% O₂ purity (mol basis). A Polytopic CO₂ compression train was modelled for CO₂ compression and final CO₂ transportation.

2.3 Modelling evaluation parameters

The following parameters are calculated to evaluate plant performance and associated penalties after the integration of HTCC unit including electricity power and electricity penalties. These parameters include the net plant efficiency, which is a measure of the total plant fuel input energy converted into net power output, Specific Primary Energy consumption for CO₂ avoided (SPECCA), Electricity Output Penalty (EOP), which show the energy and electricity penalties associated with the integration of HTCC into NGCC plant, and Marginal thermal efficiency of the oxyfuel combustion, which evaluates the thermal efficiency of the oxyfuel combustion used to regenerate the sorbent in the desorber.

These parameters are also used to compare the Li₄SiO₄ HTCC integration results with other CO₂ capture technologies. Based on the previously mentioned assumptions, the modelling evaluation parameters were calculated as following:

Net Plant efficiency (η) was calculated as:

$$\eta = \frac{W_1 + W_2}{(m_1 + m_2) \cdot LHV} \quad \text{Eq (1)}$$

In the formula above, W_1 and W_2 are the net power output of the primary and secondary steam cycles respectively (MW), obtained from the Aspen model after deducting ASU, CO₂ compressors and other auxiliary power consumptions, m_1 and m_2 are the natural gas mass flows (kg/s) to the gas turbine and the oxyfuel regenerator respectively, and LHV is the low heat value of the fuel in (MJ/kg).

Specific Primary Energy consumption for CO₂ avoided (SPECCA): The specific primary energy consumption for CO₂ avoided (SPECCA) in GJ/tCO₂ was calculated from the following formula ⁸:

$$SPECCA = \frac{HR_{CC} - HR_{REF}}{E_{REF} - E_{CC}} = \frac{3600 \cdot \left(\frac{1}{\eta_{CC}} - \frac{1}{\eta_{REF}} \right)}{E_{REF} - E_{CC}} \quad \text{Eq(2)}$$

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. HR_{CC} includes the energy from the primary GT and secondary oxyfuel combustion systems, whereas HR_{REF} includes the energy from the primary GT combustion system only.

E_{CC} and E_{REF} are CO₂ emissions rate in kg CO₂/kWh for the plant with the capture unit and reference plant, respectively. η_{cc} and η_{ref} are the net plant efficiency (LHV) with and without the integration of capture unit, respectively.

Electricity output penalty (EOP): as defined in ⁴¹, it is adopted here as the total net loss in plant power output, in kWh/tCO₂, after integration of the CO₂ capture unit, taking into consideration all power penalties resulted from ASU, CO₂ compression and oxy-combustion in desorber per unit mass flow of CO₂ to pipeline transportation. It follows the formula:

$$EOP = \frac{\left((m_1 + m_2) \cdot LHV \cdot \eta_{ref} - (W_1 + W_2) \right) \cdot 1000}{m_{CO_2}} \quad \text{Eq(3)}$$

Where, η_{ref} is the reference plant efficiency (58.3 % LHV), before integration of the capture unit, and m_{CO_2} is the mass flow of CO₂ to the pipeline (t/h).

Marginal thermal efficiency of the oxyfuel regenerator: this parameter measures the thermal efficiency of the additional natural gas combustion as described in [42] and follows the formula:

$$\eta_{marg} = \frac{W_2}{m_2 \cdot LHV + \Delta H_r} \quad \text{Eq (4)}$$

Where ΔH_r is the overall heat of reaction in the absorber in (MW). ΔH_r can be calculated from the following formula:

$$\Delta H_r = H_r * m_{R-Li_4SiO_4} \quad \text{Eq(5)}$$

As H_r is the molar heat of reaction of Li₄SiO₄ with CO₂ in kJ/mol and $m_{R-Li_4SiO_4}$ is the sorbent recirculation rate between the absorber and desorber in kmol/s.

3. Results and discussion

In this section, the results of the simulation are presented and discussed covering the modelling of base case without capture, base case with capture and sensitivity analysis. The net plant efficiency and energy demand of the HTCC plant are evaluated for each model. The impact of the HTCC integration on power plant's efficiency is subsequently analyzed for selected values of fractional conversion, make up ratio and regeneration temperature and compared to other capture technologies. Finally, possible improvements to the model are described for consideration in subsequent studies.

3.1 HTCC integration into NGCC power plant

3.1.1 Evaluation of efficiency performance

Table 1 summarizes modelling results for the base case with and without capture based on 525 °C and 700 °C absorption and desorption temperatures, respectively.

Performance evaluation parameters include the gross power output from the overall plant, gas turbine, primary and secondary HRSGs, and net power output from the plant after deducting the power consumed by plant auxiliaries and ancillaries such as CO₂ compressors, ASU and cooling pumps. Table 1 also shows net plant efficiency, CO₂ emissions, EOP and SPECCA. All these parameters are used to compare the simulation results with other technologies. For CO₂ purity and final flue gas composition, table 2 illustrates the composition of the Gas Turbine (GT) flue gas, before and after CO₂ capture, and final CO₂ stream composition before entering transport pipeline.

Table 1. Summary of simulation results for base case (NGCC plant without capture) and NGCC plant with an integrated HTCC unit operating at 700°C regeneration temperature, 0.2 fractional conversion and 0.01 make up.

Parameter	Unit	NGCC base case	NGCC with capture
Gross power output	MW	837.3	1104
Gas turbine output (x1)	MW	274.6	275
Primary Steam turbine output	MW	288.1	287.7
Secondary steam turbine power output	MW	NA	266.3
ASU Power consumption	MW	NA	38
Auxiliaries for main power plant	MW	7.4	7.4
Auxiliaries for secondary steam cycle	MW	NA	7.4
CO ₂ compression power consumption	MW	NA	49.6
Net power output	MW	829.9	1001.6
Fuel thermal Input	MW _{th(LHV)}	1423.0	2039.7
Net Plant efficiency	%LHV	58.3	49.1

CO ₂ emissions	kg/MWh	351.6	30.7
Penalty points	%	-	9.2
EOP	kWh/tCO ₂	-	455.6
SPECCA	GJ/tCO ₂	-	3.6

Table 2. GT flue gas and final CO₂ Streams. Process conditions and composition

Stream	G	T	P	Composition Mol %					
	(Kg/S)	(°C)	(Bar)	CO ₂	N ₂	H ₂ O	O ₂	CH ₄	CO
GT Flue Gas at GT exit	665.3	608	1.04	3.9	75.3	8.3	12.5	0	2.619e-05
GT Flue gas before being released to atmosphere	628.8	85	1.04	0.4	78.1	8.6	12.9	0	2.714e-05
Final CO ₂ stream before entering transportation pipeline	57.3	54	110	92	3.6	0.2	4.2	0	1.254e-8

From table 1, The net plant efficiency for the NGCC power plant case with CO₂ capture is 49.1%, i.e. there is a 9.2 % points reduction in efficiency when compared to the base case simulation without capture, 58.3%. Also, after integrating the HTCC plant, EOP of 455.6 kWh/tCO₂ and SPECCA of 3.6 GJ/tCO₂ were obtained. On the other hand, the CO₂ emissions were reduced from 351.6 to 30.7 kg/MWh achieving 90% emissions reduction after capture. In line with the net plant efficiency drop due to the HTCC integration, it was found that there is a slight drop in the primary steam cycle electricity output by 0.4 MW due to the extraction of CO₂ from the gas turbine flue gas. Further details about the integration impact are discussed in the next sub section.

With regards to the main energy consumers inside the plant after the HTCC integration, it was found that the largest contributor to the efficiency penalty was the fuel penalty incurred when the combustion of natural gas takes place in the regenerator and not in the gas turbine, as shown in the EOP breakdown in Fig. 6.

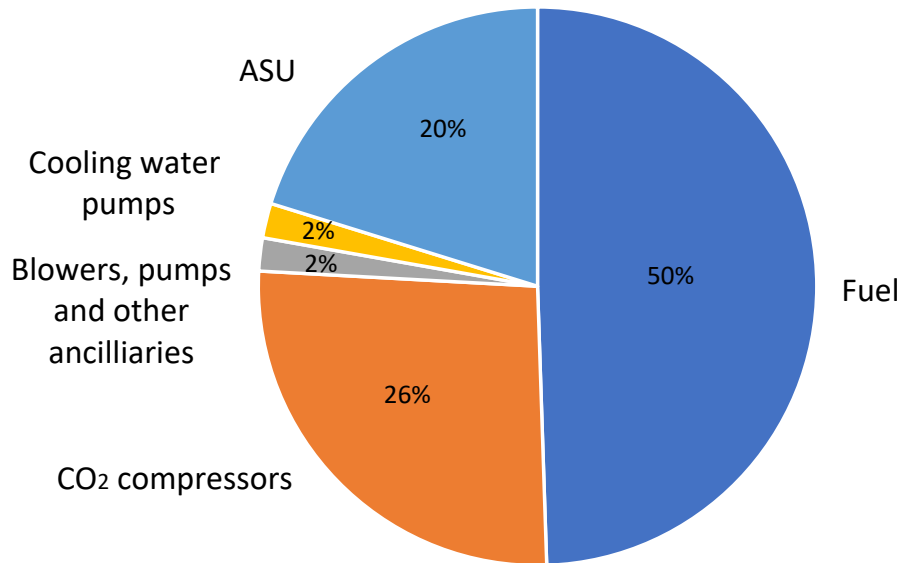


Figure 6. EOP breakdown in kWh/tCO₂.

With respect to power, CO₂ compression train and ASU are the most power consuming units inside the plant, compared to the rest of the ancillaries such as pumps and blowers. This can be observed from the breakdown of the power consumption inside the plant after the integration of the HTCC unit as shown in table 1. As per table 1, the CO₂ compressors are the main power consumer inside the plant as they consume 49.6 MW followed by the ASU which consumes 38MW.

For ASU power consumption, if an ASU with a power consumption lower than 200 kWh/t O₂ can be used, similar to the case of an ASU with 159 kWh/tO₂ power consumption reported in ⁴³⁻⁴⁵, then the ancillary power consumption could be reduced and in turn, the integration penalty. For better understanding of the effect of improving

ASU power consumption, the result of a modelling case with lower ASU power consumption will be presented and discussed in the future improvement section. With regards to the power consumption in the final CO₂ compression train, it could also be optimized and reduced by implementing a compression scheme where lower inter-cooling temperatures, below the critical point of the final CO₂ stream (25.5°C at 84.3 bar), could be used to liquify the final CO₂ stream entering the last compression train. Such CO₂ compression can be done using sea water cooling option to liquify the final CO₂ stream after the third compression train before pumping it through the transportation pipeline. This option is subjected to the availability of sea water close to the plant location.

With respect to the oxyfuel combustion in the desorber, table 2 shows the effect of capturing CO₂ from the GT flue gas stream. That can be observed from the lower CO₂ concentration obtained after the integration of HTCC unit as 90% reduction in the flue gas CO₂ concentration has been achieved. Regarding the use of an ASU with 95% O₂ purity, the results in table 2 shows that using an ASU with 95% O₂ purity will lead to final CO₂ stream with 92 mol % purity which is within the accepted transportation limits mentioned in EBTF common frame work ³¹. In case there is a specific requirement to increase the CO₂ concentration in the final CO₂ transportation pipeline, several options can be applied to increase the CO₂ concentration such as adding a high pressure CO₂ distillation⁴⁶⁻⁴⁷ unit which could achieve up to 99% final CO₂ purity. Also, using an ASU which can produce O₂ purity higher than 95%, as the one which is reported to produce 99% O₂ purity, could improve the final CO₂ purity in the transportation pipeline. Such high O₂ purity will lead to reduce the inert gases concentrations in the final pipeline and hence increase the final CO₂ concentration. However, these options

are outside the scope of this paper since the final CO₂ purity obtained from the current study is within the EBTF common frame work³¹ transportation limits.

3.1.2 Technical feasibility of HTCC integration into NGCC power plant

The technical feasibility of integrating the capture plant into the NGCC power plant is subject to several aspects such as thermodynamic, equipment modification and final cost impacts. In this section, the thermodynamic and equipment modification impacts are discussed briefly to give an indication about the feasibility of applying the proposed thermodynamic integration into NGCC Plants.

The integration concept evaluated in this work (Figure 3) requires the extraction of the flue gas from an intermediate section in the main HRSG, where the flue gas temperature is as closed as possible to the absorption temperature (525°C). After CO₂ capture the flue gas is re-conducted to the main HRSG for heat recovery. As a result, the flue gas mass flow is reduced, due to CO₂ removal and its heat capacity is slightly changed.

Figure 7 illustrates T-Q curves of the primary HRSG before (a) and after (b) the integration of the carbon capture unit into the NGCC plant. From Figure 7, it can be observed that the slope of the TQ curve of the flue gas (red line) has slightly changed after the capture unit integration (Figure 7-b), as the flue gas stream, exiting the absorber, has a lower specific heat capacity due to the extraction of CO₂ in the carbon capture unit. In addition, the pinch points for most of the pressure levels have changed and decreased. However, from the thermodynamic perspective, those changes are minor and have a negligible impact on the performance of the main HRSG.

From a mechanical and equipment modification point of view, as a conceptual design, there are several options to mechanically integrate the capture unit inside the NGCC plant as following:

For newly-built NGCC plants with carbon capture, the design of the primary HRSG could consist of two modules with the capture unit in between so that the temperature of flue gas (600°C) can be used to super heat / reheat the steam in the primary HRSG before the CO₂ absorption process, which takes place at 525°C. That gives a flexibility to the plant operation since 100% CO₂ capture unit bypass can be achieved in case of peak electricity production or capture unit shutdown due to maintenance.

To retrofit the same design within an existing NGCC plant, either the existing primary HRSG is modified to accommodate the absorber and desorber columns, which might prove challenging due to limited space, or, alternatively, the GT flue gas will need to be cooled from 600°C to the absorption temperature (525°C), before being directed to the absorber. This can be done by using the GT hot stream in superheating high-pressure steam generated from the secondary HRSG. For the latter case, the CO₂-lean flue gas exiting the absorber at 525°C needs to be reheated to 600°C so it can enter the primary HRSG at the same temperature as per the base case design without capture. This heating could be achieved by exchanging heat with the hot CO₂ stream leaving the desorber at (700°C). The latter option needs no modifications in the primary HRSG but needs mechanical modification in the GT exhaust bypass system to divert the flue gas to the capture unit and there will be also an energy penalty due to cooling and heating of the flue gas before the primary HRSG. This option is considered less flexible from operational point of view as 100% CO₂ capture unit bypass is not possible with no energy penalties due to the mechanical modification in the GT bypass system.

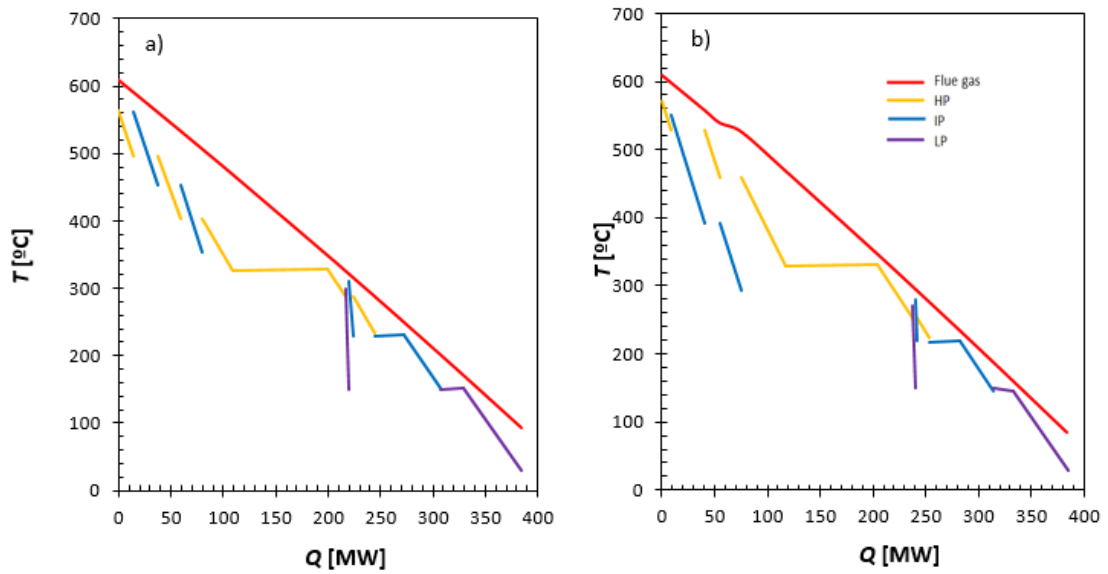


Figure 7. a) TQ curves for primary HRSG for NGCC plant base case without capture. b) TQ curves for primary HRSG for NGCC plant base case with capture unit integrated.

Based on previous discussion in this section, the retrofitting option of HTCC unit in NGCC is not recommended due to mechanical modification limitations and to avoid the disturbance of the integrity of the equipment in the original plant. Thus, the proposed process design of an NGCC with HTCC integrated is recommended to be applied for newly built plants.

3.2 Comparison to other capture technologies

This section compares the results of this work with data from other existing capture technologies. Table 3 shows the comparison with two amine-based capture technologies (MEA and CESAR-1, a blend of two amines) and the CaCO_3 technology when integrated into NGCC power plants. The table compares the gross power output with power breakdown, net power output, net plant efficiency, CO_2 emissions, SPECCA and EOP for each technology. Both, MEA and CESAR-1 cases, have been implemented into the same base case adopted here. However, due to the addition of electricity produced from the secondary HRSG, the power output of the Li_4SiO_4 -based

HTCC integration case is significantly higher (1001.6 MW) compared to base case without capture (729.9 MW), MEA case (709.9 MW) and CESAR-1 case (722.6 MW). The CaCO_3 integration case also follows the EBTF guidelines but it is based on a 1x1 (one gas turbine and one steam turbine) arrangement rather than on a 2x1 arrangement as in the other cases. Hence, that is the reason the net power output (559.5 MW) for this case is lower than in other cases.

As seen in Table 3, based on the assumptions followed in this work, the Li_4SiO_4 -based HTCC technology achieved lower net efficiency penalty, energy and electricity penalties (9.2 % point reduction, 3.6 GJ/tCO₂ and 455.6 kWh/tCO₂, respectively) than the calcium looping technology (12.5 % point reduction, 5.4 GJ/tCO₂ and 660 kWh/tCO₂ respectively). The higher energy penalty of the calcium looping technology is mainly due to the low residual sorption capacity of CaO after undergoing a significant number of carbonation / calcination cycles and the higher regeneration temperature compared to Li_4SiO_4 as explained earlier in section 2 with reference to the obtained lab test results from ³⁴. If Li-sorbents can be manufactured with the stability characteristics reported so far at laboratory scale, it is possible to foresee a design where the optimum regeneration energy corresponds to a situation with nearly zero make-up ¹⁵. In such case, the gains with respect to lower penalties are indicated by the results of this work. It should be noted that lower penalty points are possible with both the CaO and Li_4SiO_4 technologies by including a recuperator between the solid's streams leaving and entering the absorber and regeneration columns. This is similar to the design proposed by David Berstad et al ¹⁵ which was not considered in our model.

When compared to amine-based cases, the net plant efficiency penalty points and energy penalty achieved by Li_4SiO_4 HTCC technology are slightly higher than those reported for MEA (8.4 % points reduction and 3.4 GJ/tCO₂ respectively), but a lower

electricity penalty (455.6 kWh/tCO₂ versus 456.9 kWh/tCO₂ for the MEA case) was found. The obvious improvement in EOP, compared to MEA case, is due to absence of steam extraction in Li-based sorbent case. However, even though both, MEA and CESAR-1, cases show lower energy penalties than the Li₄SiO₄ case, they may present significant issues with respect to solvent and degradation products emissions that could pose a potential environmental hazard. Also, comparable or improved results to those reported for amine-based technologies could be obtained if data from modified Li₄SiO₄ sorbents, i.e. better kinetics and lower regeneration temperatures, are used. Therefore, the sorbent technology could be an attractive alternative.

Table 3. Comparison of integration results into NGCC plant for different capture technologies.

Parameter	Unit	Base case	MEA	CESAR-1	CaCO ₃	Li ₄ SiO ₄
Reference	[-]	⁸			³²	This work
Gross power output	MW	837.3	759.9	770.7	627.6	1104.0
Gas turbine (x1)	MW	274.6	272.1	272.1	270.2	275
Steam turbine	MW	288.1	215.7	226.5	135.0	287.7
2 nd Steam turbine	MW	NA	NA	NA	222.4	266.3
Net power output	MW	829.9	709.9	722.6	559.5	1001.6
Net Plant efficiency	%LHV	58.3	49.9	50.8	45.6	49.1
CO ₂ removal efficiency	%	-	90	90	90.3	90
CO ₂ emissions	kg/MWh	351.6	41.1	40.4	30.6	30.7
Penalty points	%	-	8.4	7.6	12.5	9.2
SPECCA	GJ/tCO ₂	-	3.4	2.9	5.4	3.6
EOP	kWh/tCO ₂	-	456.9	408.6	659.7	455.6

With respect to technology readiness, amine solvent systems have been demonstrated already at medium to large scale (ca. 150 MW⁴⁸) and calcium looping is being scaled up to 2MW scale. Li-based sorbents have only been tested at small laboratory scale. However, based on the knowledge already existing for CaCO₃ technologies, Li-sorbent capture units could see a fast development to application following similar steps to the CaO technology. Another important aspect of the comparison is, obviously, the cost. Although the economic evaluation of the Li-sorbent based capture technology is outside the scope of this paper, it is worth mentioning that the sorbent material is anticipated to be more expensive than CaCO₃. However, its higher stability and lower energy penalty could balance the solid inventory costs.

3.3 Exergy, energy demand and sensitivity analysis

The integration of the Li₄SiO₄ based HTCC plant into the reference case described in section 3 requires not only the availability of the necessary energy for regeneration, but also the recovery of the CO₂-lean (from the absorber) and hot CO₂ stream (from the desorber) excess heat for electricity production. The energy supplied for regeneration needs to provide the heat required to reverse the carbonation reaction R(1) and the sensible heat necessary to bring the solids and the gaseous streams entering the regeneration column up to the required temperature.

Since the efficiency of CO₂ capture inside the absorber is assumed to be fixed at 90% of the CO₂ in the flue gas on molar basis, the amount of CO₂ capture is assumed to be constant and consequently, the endothermic heat required to reverse reaction R(1) is fixed as well during the regeneration process. Additional regeneration energy requirements include the sensible heat required to bring the solids and unburned O₂-CO₂ mixture to the regeneration temperature. The sensible heat can be described by the following equation:

$$Q_{sens} = m C_p \Delta T \quad \text{Eq (6)}$$

For sorbents, m is the sorbent solids flow rate, C_p is the specific heat for the solids and ΔT is the difference between the absorption and desorption temperature. For the oxyfuel gas mixture, m is the unburned O_2 - CO_2 mixture flow rate, C_p is the specific heat of the gas mixture, ΔT is the difference between the regeneration temperature and temperature of gases entering the desorber.

Based on equation (6), there are two main factors affecting the energy demand in the desorber which are the regeneration temperature and sorbent flow rate. Any change in these two factors will lead to a change in fuel consumption which is in turn affecting the amount of O_2 - CO_2 mixture entering the desorber, and hence affecting the sensible heat required to bring the gas mixture to the regeneration temperature, and overall gas stream leaving the desorber.

A parametric sensitivity analysis was then conducted to evaluate how variations on regeneration temperature as well as on sorbent fractional conversion in the absorber, solids make up ratio and excess O_2 would affect the performance of the integrated plant. The sensitivity analysis was conducted by varying one single parameter at a time. For sorbent fractional conversion, a variation of $\pm 25\%$ (i.e., 0.15, 0.2, 0.25) with respect to the integrated base case model was considered. For regeneration temperature and sorbents make up ratio variations of $\pm 2\%$ (i.e., 685, 700, 715°C) and $\pm 50\%$ (i.e., 0.05, 0.01, 0.015) with respect to base case model values were investigated, respectively. The sensitivity range for the desorber temperature is so low due to the restrictions imposed by observed minimum and maximum limiting regeneration temperature values, which were obtained from relevant testing experiments, as will be explained below.

For the excess O_2 in the desorber oxyfuel combustion, a variation of $\pm 33\%$ (i.e., 2%, 3%, 4%) was investigated as well.

Figures 8, 9 and 10 show the results from the sensitivity analysis on net plant efficiency, specific regeneration requirements and SPECCA, respectively.

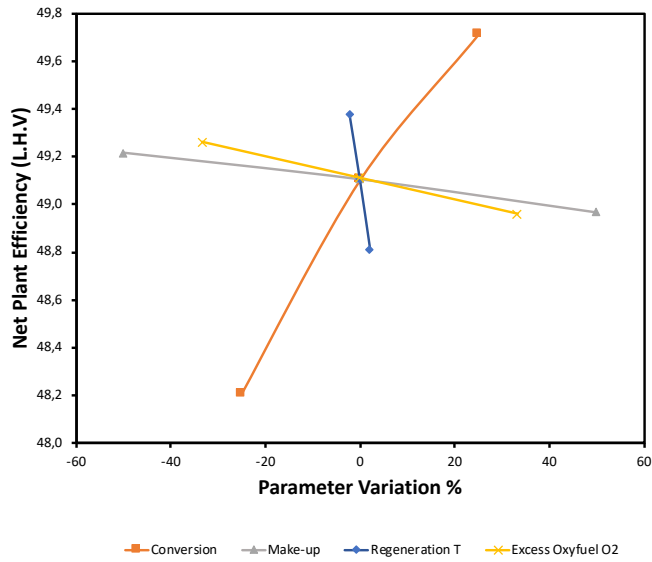


Figure 8. Effect of changing HTCC plant parameters on Net plant efficiency.

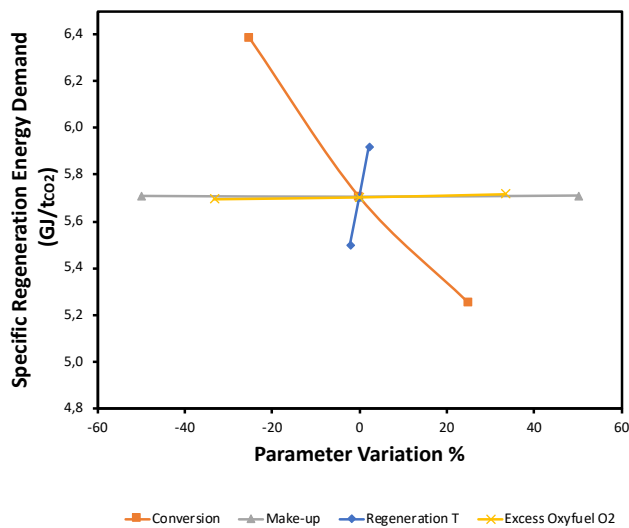


Figure 9. Effect of changing HTCC plant parameters on sorbent specific regeneration energy demand in GJ/tCO₂.

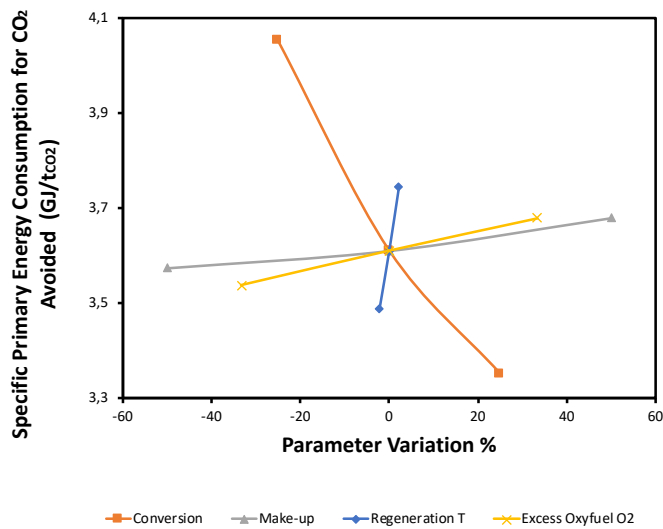


Figure 10. Effect of changing HTCC plant parameters on Specific Primary Energy Consumption for CO₂ Avoided (SPECCA).

The change in regeneration temperature shows the highest impact on the results, followed by changes on sorbent fractional conversion and excess O₂.

Although sensitivity analysis results show that the regeneration temperature is the parameter that affects most net plant efficiency and energy demand, it is worth pointing out that this parameter is constrained by upper and lower limits. Sorbent regeneration is conducted under internal oxyfuel combustion conditions, where the expected CO₂ concentration in the desorber is around 70% CO₂¹⁵. Based on lab test results where the solids are regenerated under the same conditions as the ones modelled in this work³⁴, it was found that Li₄SiO₄ sorbents cannot be regenerated at a temperature lower than 660°C. Likewise, the upper limit is dictated by a temperature of 723°C as the melting temperature of lithium carbonate. On the other hand, the fractional conversion has

larger limits for variation and improvements and at the same time it achieved a notable impact on plant efficiency and regeneration energy consumption.

For regeneration temperature, a reduction of only 2% on the regeneration temperature will change the net plant efficiency, sorbent specific energy demand and SPECCA by +0.6, -3.4 and -3.4 %, respectively. This finding is consistent with the earlier discussion in this section. A reduction in regeneration temperature results in reducing the term ΔT in equation (6), hence reducing the required sensible heat and regeneration energy demand inside the desorber. Moreover, reducing the T_{reg} leads to lower fuel consumption in the desorber which leads to an overall improvement in the net plant efficiency. Lowering the fuel consumption and the regeneration energy requirement results, in turn, in reducing the energy penalty from the integration of the HTCC unit as can be observed from the SPECCA results.

For the fractional conversion, variations of +25% will change the net plant efficiency, sorbent specific energy demand and SPECCA by +1.2, -7.5 and -7.2%, respectively. In the model, the molar amount of CO₂ required to be captured inside the absorber is set to be 90% of the CO₂ entering the absorber; hence, sorbents with higher conversion values will require less sorbent inventory (i.e., lower sorbent flowrate) than sorbents with lower conversion. Therefore, an increasing sorbent conversion leads to reduce the sorbent recirculation rates and overall inventory, which leads to reduce the heat regeneration requirements inside the desorber, save more energy, achieve higher plant efficiency and lower overall energy consumption.

Reducing the oxyfuel combustion excess O₂ by 33.3% was found to change the net plant efficiency, sorbent specific energy demand and SPECCA by +0.3, -1.3 and -2%, respectively. Looking at the power consumption prospective, the lower excess O₂, the lower power consumption in ASU due to reducing the production rate of the pure

oxygen stream. Since the ASU was selected to provide 95% O₂ purity, there are some inert gases, such as nitrogen, produced in the pure oxygen stream. Such inert incondensable gases lead to higher CO₂ compression duties^{15, 32}. Hence, reducing the amount of excess O₂, result also in lower CO₂ compression duties. The reduction in ASU and CO₂ compression power consumption leads, in turn, in improving the net plant efficiency and reducing the specific primary energy consumption for CO₂ avoided, SPECCA. With respect to the sorbent regeneration energy and referring to earlier discussion about equation (6), the lower mas of O₂-CO₂ gases entering the absorber, the lower energy required to heat up the gas mixture to the desorber working temperature. That explained the reduction in the specific regeneration energy requirement when the amount of excess O₂ is reduced.

For sorbent make-up ratio, increasing the make-up ratio by 50% will result in a lower net plant efficiency by 0.3%, a higher sorbent specific demand by 0.08% and a higher SPECCA by 1.9%. These results are due to the higher energy and fuel consumption required to heat up the increased amount of fresh sorbent entering the absorber. That leads to fuel and energy penalty inside the desorber and hence reduce the overall net plant efficiency. At this point, it is worth mentioning that the initial base case value of the make-up ratio, 0.01, is considered relatively low, due to sorbent high cyclic stability, and hence have minimum effect on improving the sorbent conversion inside the reactor. That is why the sorbent conversion inside the reactor was considered fixed while varying the sorbent make up ratio.

The abovementioned results indicate that changing sorbent make up ratio was found to have the lowest impact on net plant efficiency and the specific regeneration duty compared to sorbent fractional conversion, desorption temperature and excess O₂ since

the sorbent has high cyclic durability, as explained earlier, and the expected amount of sorbent make up flow is relatively low.

3.4 Possible future improvements

As described previously, sorbent fractional conversion and sorbent regeneration temperature have the greatest impact on the energy penalty associated with the integration of the HTCC unit in the plant. If latest improvements and modifications on Li_4SiO_4 sorbents kinetics and performance^{19, 49-51} were considered in the model, further improvements could be achieved in terms of energy savings and higher net efficiencies could be obtained for the integrated plant.

Additionally, further degrees of heat integration inside the HTCC plant can be achieved by introducing new heat exchange concepts such as solid – solid heat recuperators or solid – steam heat exchangers inside the HTCC. Also, with respect to reducing power consumption inside the secondary combustion system, more power can be saved, as discussed earlier, in case of using an ASU with lower power consumption such as that with 159kWh/tO₂.

These three options were modelled separately based on the base case with the integrated HTCC unit and results showed a better net plant efficiency for both cases when compared with the base case. Table 4 illustrates the modelling results for the proposed configurations and models.

Table 4. Comparison of integration results into NGCC plant for different HTCC configurations and advanced low power ASU.

Parameter	Unit	Base case	Base case with	Base case with Solid	Base case with	Base case with
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			HTCC integrated	Heat recuperator	solid steam HE	advanced low power ASU
Gross power output	MW	837.3	1104.0	1015.3	1100.5	1104.0
Gas turbine (x1)	MW	274.6	275	275	275	275
Steam turbine	MW	288.1	287.7	287.7	287.7	287.7
2 nd Steam turbine	MW	-	266.3	177.6	262.9	266.3
Net power output	MW	829.9	1001.6	933.2	998.7	1009.4
Net Plant efficiency	%LHV	58.3	49.1	50.9	49.3	49.5
Penalty points	%	-	9.2	7.4	9	8.8

The model with a solid-solid heat recuperator achieved the highest net plant efficiency, 50.9 %, which is even better than the efficiency obtained when advanced amine systems, CESAR-1, are used (50.8 %) for the same reference case. Although, the model with a solid-solid heat recuperator generates less net power output compared to the base case without solid-solid heat recuperator, the overall achieved efficiency was higher by 1.8% points. The reason behind such high efficiency is due to that heat integration between the circulated solid's steams between the absorber and desorber. Such heat integration lead to increase the temperature of the circulated CO₂ saturated sorbent before entering the desorber for regeneration. That, in turn, results in reducing the energy required to bring the sorbent to the regeneration temperature, 700°C, which resulted in lower fuel and O₂ consumption in the oxyfuel combustion inside the desorber. The lower O₂ consumption lead to lower ASU power duty as there is a need

to generate less quantity of O₂. The lower fuel and O₂ consumptions lead as well to lower CO₂ compression power consumption as the CO₂ resulted from the oxyfuel combustion will have less flow rate and less inert gases to compress as discussed in the sensitivity analysis section. All these power and fuel savings lead to higher overall net plant efficiency in case of solid-solid heat recuperator.

For the option with solid steam HE, it achieves a net plant efficiency of 49.3% which is very close to that achieved by basic amine solvents (49.9%) for the same reference case and higher than that obtained for the same base case without solid steam HE, 49.1%. The reason behind the efficiency improvement in this case is that using part of heat from the hot 700°C Li₄SiO₄ regenerated sorbent stream, exiting the desorber, to superheat the steam generated from the absorber in-bed boilers to a temperature of 572°C before entering the final steam superheater prior to entering the HP steam turbine. The previous two options achieved relatively better net plant efficiency and lower penalties; however, these two heat exchange technologies need to be proven for large scale practical applications with lithium orthosilicate material.

With respect to the model with an advanced low power ASU and as seen in table 4, the model with lower ASU power consumption, 159 kWh/tO₂, achieved better net plant efficiency, 49.5%, compared to the original model with higher power consumption ASU. That can be observed from the net plant electricity output as it has been increased from 1001.6 MW, in the base case without an advanced ASU, to 1009.4 MW due to the power consumption reduction in the ASU since the ASU power consumption was reduced from 38MW to 30.2 MW resulting in higher net plant efficiency, 49.5%.

Further improvements could be also obtained from different sorbent regeneration strategies in the regenerator. For instance, many options were studied in literature to

replace the direct oxyfuel heating with indirect heating options. These options consider the heat transfer between the main power plant combustor and the regenerator ⁵², heat transfer between the hot regenerated solids leaving the regenerator and the colder solids leaving the absorber ⁵³⁻⁵⁴ and the use of a double looping system to transfer heat indirectly to the regenerator ⁵⁵. These strategies are still at the conceptual formulation stage and would need to be further developed and demonstrated prior to their implementation. Also, utilizing the compression heat, from ASU and CO₂ transport train, in the secondary steam cycle, could reduce the overall power consumption and improve the net plant efficiency ⁵⁶⁻⁵⁷.

Proving the abovementioned technologies and solutions could create new horizons for Li-based solid sorbents utilization as an energy efficient solution for CO₂ capture at high temperatures.

4. Conclusion

CO₂ capture based on high temperature solid sorbents is an important option to abate CO₂ emissions in exhaust gases from combustion and other industrial processes. A key advantage of this technology is its capacity to capture CO₂ at the temperature of exhaust gases, avoiding the need to quench or cool gases and the high potential for heat integration from the HTCC unit. This work evaluates the integration of a novel sorbent technology based on lithium orthosilicate into NGCC power plants. Due to the high stability exhibited by Li-based solids, it is foreseen that a design could be achieved where the make-up flow is very small and only needed to cover the physical degradation of the solids through attrition.

A steady-state model has been developed for a NGCC power plant where a Li-based sorbent HTCC plant has been integrated. The modelling basis and assumptions for the

NGCC power plant are as per European Benchmarking Task Force (EBTF) common framework. Absorption and regeneration temperatures of 525 °C and 700 °C, respectively, a fractional conversion of 0.2 and sorbent make up ratio of 0.01 have been used in the model. The results indicate a reduction in power plant efficiency of 9.2% penalty points due to the integration of the HTCC plant. This penalty is slightly higher than the one for a MEA-based system (8.4% penalty points), evaluated under the same conditions and reference plant, and lower than the penalty incurred by a CaCO₃ sorbent-based system (12.5% penalty points), which also followed the same evaluation guidelines.

Sensitivity analysis on the impact of the regeneration temperature, sorbent fractional conversion, oxyfuel excess O₂ and sorbent make-up ratio on net plant efficiency, specific regeneration energy demand and SPECCA has been performed. Results showed that by decreasing the regeneration temperature by only 2 %, significant savings in regeneration energy consumption could be achieved, which resulted in a 0.6 % higher net plant efficiency. Likewise, an increase in sorbent conversion by 25% leads to 1.2% increase in the net plant efficiency, mainly due to lower sorbent circulation requirements. Varying the make-up ratio showed the lowest impact on net plant efficiency and power penalties as reducing the make-up ratio by 50% led to only 0.2% points increase in net plant efficiency. According to these results, future improvements on high temperature capture technologies that make use of Li-based sorbents should pursue further efforts on reducing the sorbent regeneration temperature and increasing their fractional conversion to achieve lower energy penalties and higher net plant efficiencies.

From the heat integration viewpoint, further improvements can be achieved by incorporating a solid – solid heat recuperator or solid-steam heat exchangers in HTCC

unit or by applying indirect heating options inside the desorber, but these options are subjected to the demonstration and availability of those technologies for large scale applications. Future work should also focus on conducting a full techno-economic evaluation for the integrated plant to prove the feasibility of the process and technology.

ASSOCIATED CONTENT

Supporting Information

Section 1, Integration Block Diagrams: Figure 1, Conceptual design of NGCC power plant; Figure 2, Conceptual Integration of CO₂ Post Combustion capture in NGCC Plant. Section 2, Plant assumptions and model input data: Table 1, Air feed to GT. Process conditions and composition; Table 2, NG Feed Stream. Process conditions and composition; Table 3, Operational parameters used in the modelling of the gas turbine; Table 4, Equipment Pressure drops for primary and secondary heat recovery steam generators (HRSG); Steam Turbines and ancillaries conditions for primary and secondary steam cycles; CO₂ compression train.

AUTHOR INFORMATION

Corresponding Author

*Email: S.Garcia@hw.ac.uk. Phone: +44 131 451 8083

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

NGCC, Natural Gas Combined Cycle; HTCC, High Temperature CO₂ Capture; LLCFs, long-lived climate forcers; GHG, Green House Gases; CCS, Carbon Dioxide Capture and Storage; MEA, monoethanolamine; EBTF, European Benchmarking Task Force; GT, Gas Turbine; HRSG, Heat Recovery Steam Generator; CaL, Calcium Looping; KOD, Knock Out Drum; LHV, Low Heat Value; SPECCA, Specific Primary Energy Consumption for CO₂ Avoided, EOP, Electricity Output Penalty; ASU, Air Separation Unit.

LIST OF SYMBOLS

T_{abs} : absorption temperature

T_{reg} : regeneration temperature

η : net plant efficiency

W_1 : net power output of the primary steam cycle (MW)

W_2 : net power output of the secondary steam cycle (MW)

m_1 : natural gas mass flow to the gas turbine (Kg/s)

m_2 : natural gas mass flow to the oxyfuel generator (Kg/s)

HR_{CC} : the heat rate for the plant with the capture unit (kJ/kWh)

HR_{REF} : the heat rate for the reference plant (kJ/kWh)

E_{CC} : CO₂ emissions rate for the plant with the capture unit (kg CO₂/kWh)

E_{REF} : CO₂ emissions rate for the reference plant (kg CO₂/kWh)

η_{cc} : the net plant efficiency with and without the integration of capture unit

η_{ref} : the net plant efficiency without the integration of capture unit

m_{CO_2} : the mass flow of CO₂ to the pipeline (t/h)

η_{marg} : marginal thermal efficiency of the oxyfuel regenerator

ΔH_r : the heat of reaction in absorber (MW)

Q_{sens} : sensible heat

m : mass flow rate

C_p : the specific heat

ΔT : the difference between the absorption and desorption temperature

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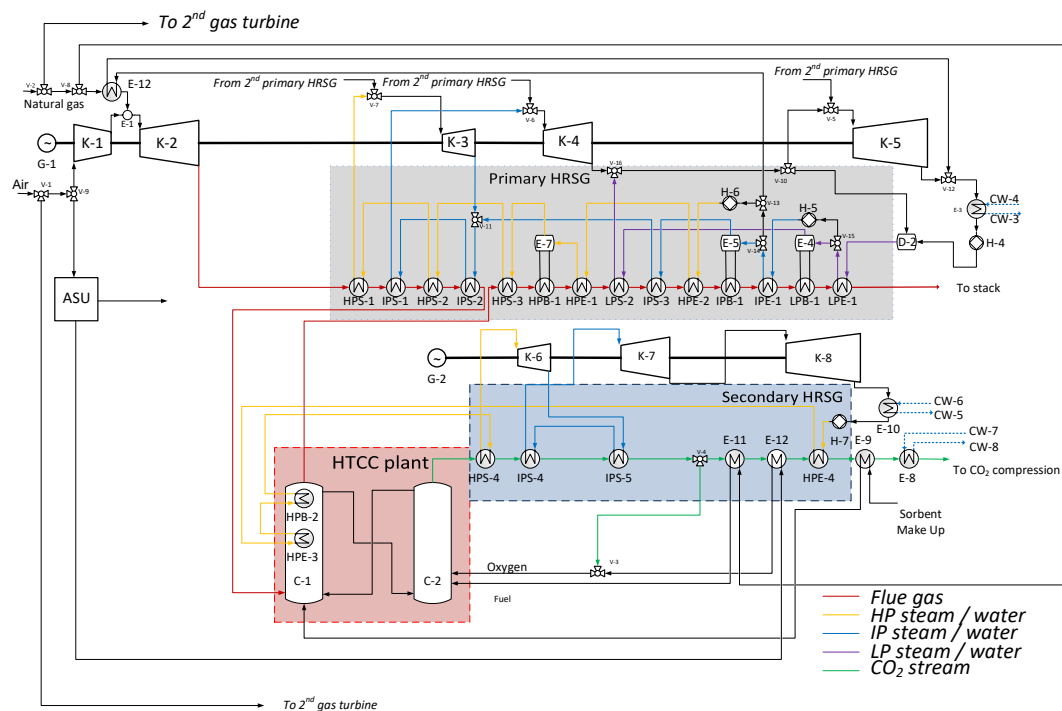
Graphical Abstract

A conceptual design for integrating lithium-based carbon capture looping systems into Natural Gas Combined Cycle power plants

Ahmed. Saleh, E. Sanchez Fernandez, M. M. Maroto-Valer and Susana Garcia

Research Centre for Carbon Solutions (RCCS), Heriot-Watt University,

EH14 4AS, Edinburgh, United Kingdom



Conceptual integration of a Li_4SiO_4 -based HTCC plant into the NGCC power plant base case