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## Process integration of post-combustion CO<sub>2</sub> capture with Li<sub>4</sub>SiO<sub>4</sub>/Li<sub>2</sub>CO<sub>3</sub> looping in a NGCC plant

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### Abstract

Lithium-based sorbents require lower energy requirements for regeneration than other more studied and well known materials such as those used in the calcium looping process; however, thermodynamic assessments of these sorbents in power plants are currently missing. Accordingly, in this work, a thermal integration study of a post-combustion CO<sub>2</sub> capture plant using regenerable lithium-based high temperature solid sorbents into a natural gas combined cycle (NGCC) plant has been conducted. A process simulation study has been completed for integration of a Li<sub>4</sub>SiO<sub>4</sub>/Li<sub>2</sub>CO<sub>3</sub> looping cycle downstream of the gas turbine in a NGCC plant. A comparison between this technology and a chemical absorption capture plant with two different solvents, namely conventional monoethanolamine (MEA) and a second generation solvent (CESAR-1), has been established based on the European Benchmarking Taskforce (EBTF) methodology. The integration of post-combustion CO<sub>2</sub> capture in the power plant results in a decrease of its net electric efficiency. However, capture with Li<sub>4</sub>SiO<sub>4</sub> sorbents decreases the efficiency by 6.9 percentage points, which is lower than the 8.4 and 7.5 percentage points decrease obtained when CO<sub>2</sub> capture is based on chemical absorption with MEA and CESAR-1 solvents, respectively. Hence, Li<sub>4</sub>SiO<sub>4</sub>/Li<sub>2</sub>CO<sub>3</sub> looping is a promising alternative to amine-based systems when integrated into NGCC plants. Furthermore, additional improvements could be achieved through improved capture process heat integration and optimization.

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## 1. Introduction

In recent years, post-combustion CO<sub>2</sub> capture at high temperatures (450–700°C) based on regenerable sorbent materials has received increasing attention as an alternative to low-temperature CO<sub>2</sub> capture adsorption and conventional chemical absorption solvent systems. The use of high temperature solid looping systems involves the reversible reaction of the bulk of the solid material with CO<sub>2</sub> and they provide both high CO<sub>2</sub> adsorption capacity and selectivity. Also, in contrast with other low-temperature capture options where the temperature needs to be low (< 100°C) to favor absorption and/or ensure material integrity, CO<sub>2</sub> capture at elevated temperature avoids the need to cool or quench combustion gases. Hence, it allows for potential efficient integration within existing steam cycle concepts for power generation.

Amongst the range of different high temperature materials currently being researched, calcium based sorbents are the most developed as natural limestone (CaCO<sub>3</sub>) is a cheap raw material and CaO based sorbents present the highest theoretical (78.6%) CO<sub>2</sub> capture capacity. As a result, a substantial amount of work on CaO/CaCO<sub>3</sub> looping has been reported in the last years, which have allowed for a rapid increase of the technology technical readiness level (TRL), from basic process design level (TRL 2) in 2005 to validation in pilots operated at industrially relevant conditions (TRL 6) in 2015[1]. Solid looping systems based on CaO have been applied to post-combustion capture from coal fired power plants, Integrated Gasification Combined Cycle (IGCC) plants and more recently to NGCC power plants [2-10]. However, reported issues of the CaO based sorbents include activity loss due to cycle operation and the high temperature required for sorbents regeneration, which are substantial disadvantages of this group of materials.

### Nomenclature

AMP	2-Amino-2-Methyl-Propanol
ASU	Air Separation Unit
EBTF	European Benchmarking Task Force
EOP	Electrical Output Penalty
HRSG	Heat Recovery Steam Generator
IGCC	Integrated Gasification Combined Cycle
IP	Intermediate Pressure
LHV	Low Heat Value
LP	Low Pressure
MCR	Maximum Continuous Rating
MEA	Monoethanolamine
NGCC	Natural Gas Combined Cycle
PZ	Piperazine
TRL	Technical Readiness Level

Besides CaO based materials, lithium based sorbents have been reported to reversibly absorb CO<sub>2</sub>, with lithium orthosilicate (Li<sub>4</sub>SiO<sub>4</sub>) showing suitable reactivity and the fastest CO<sub>2</sub> sorption rate over a wide range of temperatures and CO<sub>2</sub> concentrations [11]. Although its theoretical absorption capacity (36.7%) is lower than that of calcined limestone, the lower energy requirements for regeneration and lower temperature of CO<sub>2</sub> emissions compared to CaO makes this group of solids a promising absorbent material. However, a process integration study in

order to assess the impact of these carbon capture systems on units operation of power plants or industrial facilities is still lacking.

Lithium looping technologies can be applied and integrated in power plant systems by exploiting the existing current experience on calcium looping, as the technology would be applied in the same fashion. One concern though for the full application of lithium based sorbents is that the experimental studies on capacity, absorption and stability use many different solid types, sometimes in the form of powders [11-14], which are not suited for their practical application in the continuous fluidized bed system proposed for calcium looping. However, there is a growing body of evidence that reflects that Li based solvents can be prepared as fluidizable solids and in the form of pellets, while maintaining the advantages of cyclic and thermal stability [15, 16].

Hence, this paper presents a process integration study of post-combustion CO<sub>2</sub> capture in a NGCC power plant by lithium orthosilicate sorbents, focusing on the potential advantages of regenerating the sorbents at lower temperatures than those needed for calcium looping systems. A baseline non-modified Li<sub>4</sub>SiO<sub>4</sub> solid has been chosen as the sorbent for this study. To the best of the authors' knowledge, this work has not been reported in the literature thus far.

## 2. Modelling methodology

### 2.1. Description of power plant and reference cases

A 829 MW base-load state-of-the-art NGCC power plant from the European Benchmark Task Force (EBTF)[17] report has been used as the selected reference plant for electricity production. The plant is based on two identical large-scale gas turbines, each of them equipped with a heat recovery steam generator (HRSG), which in turn feed a single steam turbine. A simplified and detailed plant flow diagram along with operational characteristics, performance and characteristics of the main streams can be found elsewhere [17]. This NGCC plant is taken as the reference power plant case without carbon capture.

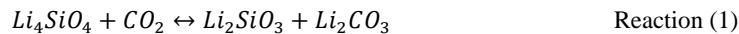
Two additional reference cases for the NGCC power plant with carbon capture have also been considered as benchmark studies where chemical absorption, as a mature and benchmark capture technology, with two different amine solvents are used. The standard 30 wt.% MEA as well as the second generation CESAR-1 solvent (23 wt.% AMP, 2-amino-2-methyl-propanol, and 12 wt.% PZ, piperazine) processes were integrated in the same manner, i.e., same degree of heat integration, into the NGCC plant. The absorber is located downstream of the HRSG, where the flue gas is further cooled down to allow for a capture process (absorber temperature) of 40°C. In both cases, solvent regeneration is achieved by extracting steam from the crossover between the IP and LP turbine. A detailed discussion on the performance of both solvent systems when integrated in a NGCC power plant has been presented before by Sanchez Fernandez and co-workers [18].

### 2.2. Integration of Li<sub>4</sub>SiO<sub>4</sub>/Li<sub>2</sub>CO<sub>3</sub> looping and modelling assumptions

The integration of the carbon capture plant based on lithium-based sorbents has been conducted following the technical assumptions and method provided by the EBTF methodology, so comparative studies can be established between different post-combustion capture technologies.

The NGCC power cycle and the new investigated case of carbon capture based on lithium looping have been simulated on a process level in steady state using Aspen Plus® commercial software. A baseline non-modified Li<sub>4</sub>SiO<sub>4</sub> solid has been chosen as the sorbent for this study, as it shows high sorption capacity and a sorption rate faster than other lithium based sorbents such as lithium zirconate (Li<sub>2</sub>ZrO<sub>3</sub>)[13, 19]. Integration of these sorbents, as opposed to chemical absorption systems, do not require cooling of the flue gas stream and the carbonator can be

located directly downstream of the gas turbine outlet. The CO<sub>2</sub> capture cycle configuration is similar to previous integration studies of calcium looping systems into NGCC power plants [3, 4]. In this case, the carbonation reaction that takes place in the carbonator yields a mixture of lithium metasilicate (Li<sub>2</sub>SiO<sub>3</sub>) and lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) following the stoichiometry of Reaction (1).



Equilibrium data for simulation of the absorber or carbonator have been taken from previous studies [20], where the equilibrium curve that relates CO<sub>2</sub> partial pressure dependence with temperature for Li<sub>4</sub>SiO<sub>4</sub> sorbents was reported. Therefore and based on those thermodynamic studies, for a CO<sub>2</sub> partial pressure of 0.04 bar, corresponding to that of the exhaust from the gas turbine, a carbonation temperature of 500°C has been selected. A 90% CO<sub>2</sub> removal is possible under those conditions, hence allowing for direct comparison with baseline capture cases with amine solvents. The absorber has been simulated as an stoichiometric reactor (RStoic model in AspenPlus®) where a fractional conversion of 0.54, calculated from previously reported kinetic data [21], is achievable.

In order to reverse Reaction (1), a desorption temperature of 708°C at atmospheric pressure is required in the desorber or calciner, which is obtained from equilibrium data under conditions of CO<sub>2</sub> partial pressure found in the calciner. Desorption in highly pure CO<sub>2</sub> at atmospheric pressure is then conducted and the heat required for the calcination reactor is supplied through internal oxy-combustion of natural gas. An Air Separation Unit (ASU) supplies the O<sub>2</sub> for the oxy-combustion process to take place and CO<sub>2</sub> is recycled and pre-mixed with the O<sub>2</sub> entering the calciner to moderate the combustion temperature. The desorber is simulated as a Gibbs reactor (RGibbs) in AspenPlus® and full sorbents regeneration is possible and assumed based on thermodynamics. The hot CO<sub>2</sub> product extracted from the calciner is used as a heat source to generate steam in a secondary HRSG. Captured CO<sub>2</sub> is then compressed to a final pressure of 110 bar before it is sent for final transportation and storage.

### 3. Results and discussion

Results for the performance of the simulated NGCC plant with integrated Li<sub>4</sub>SiO<sub>4</sub>/Li<sub>2</sub>CO<sub>3</sub> looping and corresponding data for baseline and reference cases are presented in Table 1. The net electric efficiency of the reference plant without capture is of 58.3% and the integration of post-combustion CO<sub>2</sub> capture in the power plant results in a decrease of its net electric efficiency, regardless of the capture technology being used. By using a lithium looping cycle, plant efficiency decreases to 51.4 % versus a 49.9 and 50.8% for MEA and CESAR-1, respectively. Hence, the former represents an improvement over conventional chemical absorption systems, mainly due to the fact that heat can be recovered from the carbon capture system and an additional steam cycle is generated. CO<sub>2</sub> emissions are also lower (30.6 kg/MWh) for the capture case with Li<sub>4</sub>SiO<sub>4</sub> sorbents when compared to MEA (41.1 kg/MWh) and CESAR-1 (40.4 kg/MWh) solvents. The CO<sub>2</sub> that is captured in the integrated process with lithium looping comes from capturing CO<sub>2</sub> from the gas turbines exhaust and also from the internal oxy-combustion of the natural gas that is needed to supply the heat for sorbents regeneration in the calciner.

Predicted penalty for MEA (8.4 percentage penalty points) is predominantly due to lower steam turbine power output (65% of the impact) but also additional auxiliaries. If CESAR-1 is used as the chemical solvent, the penalty gets reduced (7.5 percentage penalty points) because of lower reboiler heat duty and reduced recirculating pump consumption [18]. The penalty for the NGCC case with Li<sub>4</sub>SiO<sub>4</sub> capture is predicted as the lowest (6.9 percentage penalty points) when compared with amine solutions. Accordingly, the Electric Output Penalty (EOP) is considerable lower for the lithium looping case (343.3 kWh/tCO<sub>2</sub>) than for MEA (453.7 kWh/tCO<sub>2</sub>) and CESAR-1 (405.4 kWh/tCO<sub>2</sub>).

Table 1. Results from process simulation and comparison with baseline power plant without capture and reference carbon capture cases.

	Units	NGCC with no capture	NGCC with MEA	NGCC with CESAR-1	NGCC with Li <sub>4</sub> SiO <sub>4</sub> sorbents
Power load without capture	%fuel	100	100	100	100
Power load with capture	[%MCR]	100	86	87	115
Gross power output	MW	836.3	759.9	770.7	1010.8
Gas turbine	MW	272.2	272.1	272.1	272.2
Steam turbine	MW	292.0	215.7	226.5	291.0
Net power output	MW	829.1	709.9	722.6	950.6
Net Plant efficiency	%LHV	58.3	49.9	50.8	51.4
CO <sub>2</sub> emissions	kg/MWh	351.9	41.1	40.4	30.6
Penalty points	%		8.4	7.5	6.9
EOP	kWh/tCO <sub>2</sub>		453.7	405.4	343.3

A breakdown for the EOP is shown in Figure 1 for all three post-combustion capture technologies. For all cases, the major contribution (approx. 60%) to EOP originates from the need to extract steam within the plant, with the consequent loss of power from the turbine. Power to drive blowers, compressors, pumps and the ASU (for the lithium sorbents case) in the capture systems further reduces net output.

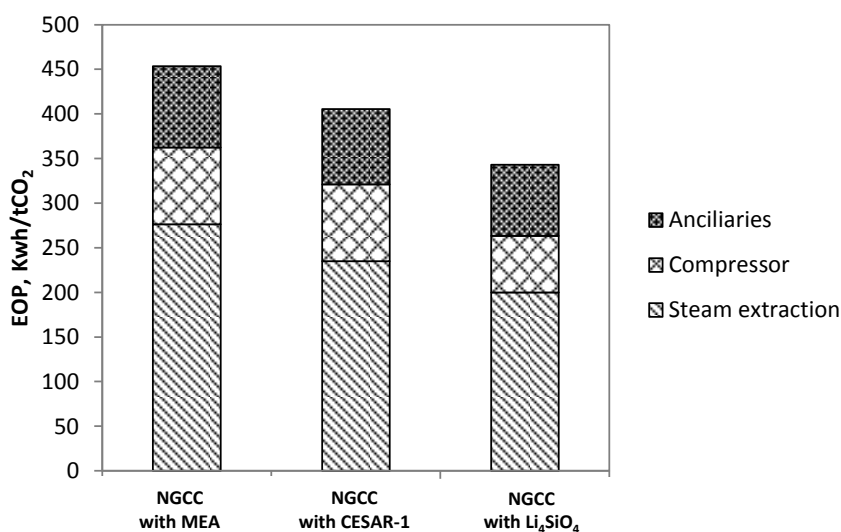


Fig. 1. EOP for evaluated post-combustion capture technologies integrated in a NGCC plant.

Previous studies on integration of calcium looping into a NGCC plant [3, 4] have explored and reported several heat integration options as well as potential efficiency increases through the use of improved (i.e. synthesized) sorbents. Net electric efficiencies (% LHV) range from 45.6 to 47.3% when no heat integration of the solid streams circulating between the carbonator and calciner is assumed. Heat recuperation is needed for energy efficiencies

higher than that for the MEA-based capture case. The greatest improvement to plant's net efficiency (53.1%) has been reported for the case with a synthetic CaO sorbent and a super-critical secondary steam cycle. Thus, the 51.4% net efficiency reported in this work for  $\text{Li}_4\text{SiO}_4$  sorbents offers a significant improvement when compared to calcium looping systems as no advanced heat integration strategies have been assumed here.

#### 4. Conclusions

Integration of lithium looping post-combustion carbon capture technology in a NGCC power plant has been conducted on a process level following the EBTF methodology. Previous studies on NGCC integration with amine-based  $\text{CO}_2$  capture technologies (conventional MEA and second generation solvent CESAR-1) have been used as a benchmark for comparison. The integrated case with lithium looping was found to have approximately 0.6 percentage points lower energy penalty when compared to the best performing (CESAR-1) chemical absorption capture system. A comparison with previous studies on calcium looping systems integration into the same power plant has also been established, with lithium sorbents offering a significant efficiency improvement. Even more, further efficiency increases are possible and will be investigated. For instance, heat recuperation between solids that circulate between the carbonator and calciner as well as more advanced heat integration options could be considered.

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