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Calcium looping with inherent energy storage for decarbonisation of coal-fired power plant*

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Implementation of carbon capture and storage, nuclear power stations and wide utilisation of renewable energy sources have been identified as capable of reducing around 42% of the energy sector's cumulative CO₂ emissions between 2009 and 2050. In scenarios assuming high shares of renewable energy sources in the energy portfolio, energy storage technologies and the remaining power generating assets would be required to flexibly balance energy supply and demand. With nuclear power plants operating at base load, this task would be handled by flexible fossil fuel power plants with CO₂ capture. However, mature CO₂ capture systems were shown to impose high efficiency penalties (8-12.5% points) and are better suited for base-load operation. An emerging calcium looping process, which has also been considered for energy storage, has been found to offer lower efficiency penalties (5-8% points). This study presents a concept of the calcium looping process with inherent energy storage for decarbonisation of the coal-fired power plant. Analysis has revealed that the possible routes for energy storage in this process include CaO/CaCO₃ solids storage, CaO/Ca(OH)₂ solids storage and cryogenic O₂ storage systems. Comparison of the CaO/CaCO₃ storage and cryogenic O₂ storage systems revealed that implementation of the latter would result in higher turndown of the entire system and would offer higher energy density. Also, the hydration reaction was found to improve the energy density of the CaO/CaCO₃ energy storage system by 57.4%, from 307.2 kW_{th} h m⁻³ to 483.6 kW_{th} h m⁻³. Economic evaluation of the proposed concepts revealed that application of the cryogenic O₂ storage system in the calcium looping CO₂ capture process has the potential to increase the profitability of the integrated system, even over the reference coal-fired power plant without CO2 capture.

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Broader context

Fossil fuel power plants with CO₂ capture, nuclear power stations and renewable energy sources have been identified as capable of reducing around 42% of the energy sector's cumulative CO₂ emissions between 2009 and 2050. However, the increasing share of intermittent renewable energy sources in the energy portfolio will be a challenge for the balance of the energy network. Therefore, the fossil fuel power plants are expected to be decarbonised and to flexibly balance energy supply and demand to avoid energy wastage and shortages. Implementation of energy storage is seen as an alternative option to counterbalance the intermittent nature of renewables. In this study we present a concept of CO₂ capture systems based on calcium looping with inherent energy storage. We demonstrated that such systems, in addition to decarbonisation of power plants, can increase the degree of energy utilisation at very small additional capital costs. In the realistic future energy portfolio/policy scenarios, the fossil fuel energy systems based on the proposed concept can generate higher profit than current fossil fuel power plants without CO₂ capture. In other words, integration of carbon capture and storage with energy storage can enable decarbonisation of power and other carbon-intensive industries with no economic penalties.

1. Introduction

The International Energy Agency^{1,2} has predicted that to limit the global mean temperature increase to 2 $^{\circ}$ C, around 42% of the cumulative CO₂ emission from the energy sector, between 2009

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and 2050, can be mitigated through implementation of carbon capture and storage (CCS), nuclear power stations and utilisation of renewable energy sources. The greatest challenge of such a scenario is the intermittence of the renewable energy sources,³ which would affect operation of the existing energy network,^{4,5} especially in cases when their share in the energy portfolio exceeds 50%.¹ As the nuclear power plants operate at base load, fossil fuel power plants would need to flexibly balance energy supply and demand, so that neither energy produced from

renewable energy sources is wasted (high renewables generation period) nor energy shortages occur (low renewables generation period). Such periods of variable load operation or no operation would impose energy and economic penalties on the fossil fuel power systems, especially for plants with CCS that are better suited for base-load operation.

Due to their capacity of decoupling energy supply and demand, energy storage technologies can increase the degree of energy utilisation and should thus be widely deployed along with low-emission technologies. However, the energy storage could contribute to CO₂ emission reduction only in the scenario of wide renewables penetration.^{8,9} Otherwise, energy storage may increase CO2 emissions by an extent that depends on carbon prices and the share of coal-based power generation in the energy portfolio.^{1,8} For this reason, a synergy between renewable energy sources, fossil fuel power generation and energy storage needs to be reached.

Presently about 145.8 GW of energy is stored globally, most of which as mechanical energy in pumped hydro storage plants (97.5%), and compressed air and flywheel energy storage techniques (1.0%). Interestingly, the share of thermal energy storage technologies surpassed electro-mechanical storage in 2013, and now accounts for 1.2% of the global energy storage capacity. 10 These technologies utilise media capable of storing thermal energy at low or high temperature, which can be recovered in the form of heat depending on the process demand. 11,12 Moreover, thermal energy storage systems are claimed to have the potential of improving the flexibility of the electricity grid, increasing the degree of the energy utilisation, 13,14 and balancing the mismatch between energy supply and demand. 15 These technologies do not have the disadvantages of pumped hydro storage and compressed air storage, such as requirements of specific site topology, and relatively high capital cost, which could have a negative environmental footprint. 11,12

Thermal energy storage systems can be classified as sensible heat, latent heat, and thermochemical energy systems. 13,16,17 The last mechanism, in which heat is used to sustain an endothermic chemical reaction and is released in the reverse reaction, is claimed to offer high energy densities, 13,18 especially if one of the regeneration stage products is in the vapour phase. 19 Despite being proposed for energy storage in the mid-1970s, 19,20 the process involving either hydration or carbonation of CaO is still considered among the best candidates for energy storage. 18 A novel process design based on the reversible CaO hydration reaction for storing heat from a concentrated solar field has been recently analysed by Criado et al.21 The proposed configuration comprises a single atmospheric pressure circulating fluidised bed, which can operate as hydrator and regenerator, and two silos for CaO and Ca(OH)2 storage. This study revealed that, at maximum thermal output of 100 MWth, the system offered an energy storage density of 260 kW h_{th} m⁻³ and a round-trip efficiency of 63%. Edwards and Materić²² proposed a process based on reversible carbonation of CaO in the calcium looping process (CaL) that comprised two independent reactors atmospheric pressure calciner (solar tower receiver) and pressurised fluidised bed carbonator - and three reservoirs for CaO,

CaCO₃ and CO₂ storage. In addition, air leaving the carbonator was fed to a gas expander for power generation. The plant net thermal efficiency was found to be between 40-46%. Finally, Vandersickel et al.23 proposed to integrate a similar process to the integrated gasification combined cycle power plant, with the difference being that only CaO and CaCO3 are stored, and the heat for calcination is provided through oxy-combustion of syngas diverted from the gas turbine. In this system, the existing Selexol unit is by-passed and the carbonator is used to capture CO₂ from the syngas during the peak-demand period. Nevertheless, the primary function of this system is energy storage and unloading the existing CO2 capture system. Such configuration was found to operate with a round-trip efficiency of 61%, and allowed for changing the power output by +25% (peak-load) and -20%(off-peak) with respect to a nominal 550 MW_{el}. However, this study did not consider variability of the power generation system during part-load operation, which would lead to a further reduction of the power output during the calcination step.

Although the carbonation reaction offers nearly 50% higher theoretical energy density (1222 kW h m⁻³) compared to that of hydration (833 kW h m⁻³), ¹³ there are some concerns that need to be resolved prior to large-scale deployment. These include capability for electrical energy storage, 12 reduction of sorbent activity, 19 and requirement for temporary CO2 storage. 18 Also, the CaL process was proposed by Shimizu et al.24 for CO2 capture from fossil fuel power plants. Not only has this process been proven to impose lower net efficiency penalty (5-8% points)²⁵⁻²⁸ compared to more mature CO₂ capture technologies (8-12.5% points), 29-32 it also has the ability to increase the net power output of the integrated system by more than 50%. 28,33,34 More importantly, this system can accept an excess amount of electricity produced in the renewable energy sources to drive the air (for O2 production) and CO2 compressors and has a permanent source of CO₂ from the fossil fuel power plant. Finally, it can operate with higher carbonation conversions (higher energy density) when a hydration stage is employed.35

The CaL process can, therefore, be seen as a promising technology for decarbonisation of the power sector as it has the ability to both decarbonise the fossil fuel power plant in an efficient manner and increase power generation flexibility. Hence, the fossil fuel power plant would not only meet its emission reduction targets, but also operate efficiently even in the energy portfolio containing large shares of intermittent renewable energy sources. In this study, the concept of CaL with inherent energy storage for CO₂ capture from coal-fired power plants is proposed and possible routes for energy storage in the proposed concept are identified. Finally, techno-economic performance of the selected routes is evaluated to analyse their degree of energy utilisation and profitability compared to the system without energy storage.

2 Concept process description

2.1 Calcium looping process

A core of the proposed concept is the CaL process proposed by Shimizu et al.²⁴ for CO₂ capture, which comprises two interconnected fluidised bed reactors operating at atmospheric pressure.

In the first reactor, a carbonator, CO_2 is removed from the flue gas stream via calcium-based sorbent. In the second reactor, a calciner, the sorbent is regenerated at a high temperature, provided through oxy-combustion of fuel. High-temperature operation of the CaL process allows for recovery of high-grade heat from the carbonator and the process streams. As a result high-pressure steam can be generated and utilised for power generation in a secondary steam cycle.

Yet, due to the decay of maximum sorbent conversion with the number of carbonation/calcination cycles, 36 which can drop to around 5–14% after 30 cycles depending on sulphur content in the flue gas and the fuel used in the calciner, 37,38 part of the sorbent needs to be replenished in the system. To achieve a higher conversion in the carbonator, the sorbent can be reactivated through hydration (CaL-HYD). 35,39,40 As a result of 60% sorbent hydration, the maximum sorbent conversion in the carbonator is about 55% after 15 cycles. 41 In the concept process proposed here, the low-pressure steam required for hydration can be extracted from the secondary steam cycle. Hydrated sorbent can be directed to either the carbonator or the calciner (Fig. 1). However, the latter route increases the calciner heat load, and although that heat can be regenerated, the need for a larger air separation unit and CO_2 compression unit incurs higher

capital costs, making this route less attractive. In addition, around 4–10% of sorbent⁴² could be elutriated due to attrition. As a result, a higher fresh limestone make-up rate would be required, leading to higher maximum sorbent conversions, at the expense of higher heat requirement in the calciner. Yet, a higher fresh limestone make-up rate would lead to higher average sorbent conversions in the carbonator, reducing the sorbent looping rate required for 90% capture and thus, the heat requirement in the calciner.

2.2 Routes for energy storage and CO₂ capture

Having analysed the process flow diagrams of the CaL process for CO₂ capture, three viable options for energy storage have been identified (Fig. 1):

- cryogenic O2 storage,
- CaO/CaCO₃ solids storage,
- CaO/Ca(OH)₂ solids storage.

During the off-peak period, any of the identified energy storage systems can operate in the charging mode, which means that liquid O_2 is produced and/or the sorbent is regenerated in the calciner (in the CaL-HYD scenario reactivated sorbent is first fed to the carbonator). Under such operating mode, the air separation unit, the CO_2 compression unit and the calciner operate at their

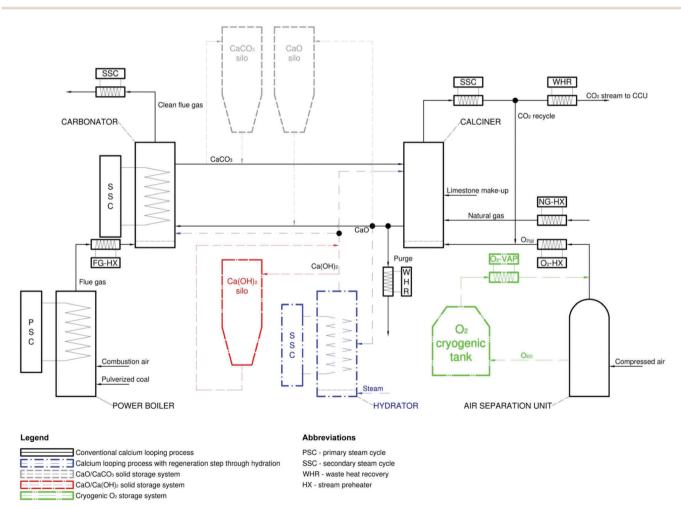


Fig. 1 Schematic of coal-fired power plant retrofitted with calcium looping process for CO₂ capture and energy storage.

nominal capacity, while the power plant operates at its minimum load of 40%. This will lead to higher fuel consumption and higher power consumption for air separation and CO₂ compression compared to the system operating at 40% load without the energy storage. During the peak-demand period, the coal-fired power plant operates at its nominal capacity, while the stored O2 and/or regenerated sorbent is utilised to unload the air separation unit and the CO₂ compression unit, reducing their power requirements, and to reduce the heat requirement of the calciner. Therefore, the proposed concept would benefit from using more fuel during off-peak periods, storing its chemical energy when the electricity price is low, and using this energy to reduce the fuel consumption and/or the system's power requirement during the peak periods characterised by higher market prices for electricity. Such operation is expected to increase the flexibility and the profitability of the integrated system.

It needs to be highlighted that the carbonator is assumed to follow the power plant load changes, maintaining 90% CO2 capture. Also, the air separation unit compressors can operate with a minimum load of 75% without recycling or venting, while the cold box operates at a minimum load of 50%. 45 This implies the need for three compression trains and two air separation unit trains to reach the minimum load of around 40% for the entire system. Due to the same minimum constraint, three compression trains are required in the CO₂ compression unit. The calciner, on the other hand, can operate with a minimum load of 25%. 46,47 It is also assumed that liquid O2 is stored in the cryogenic tank at 1.2 bar at around -182 °C, which is maintained by the waste N_2 leaving the air separation unit,43 while the sorbent is stored at high temperature in the solid storage tanks. As claimed by Arias et al., 6 the heat losses in the solid storage tanks, characterised by a low surface-to-volume ratio, are negligible. Ma et al. 44 showed that storing energy using solid materials, such as ash or sand, in the insulated tanks can reach thermal efficiencies exceeding 99%. Such low heat losses (<1%) are a result of combined effects of highly effective thermal insulation and self-insulation of the particles. Assuming short-term CaO/CaCO3 solids storage (<12 h) in the tanks insulated with concrete walls and refractory lining, which was also considered by Ma et al., 44 heat losses are not expected to affect the process performance by much and thus they are neglected in this concept study. Nevertheless, at the process design stage and for long-term storage (days to weeks), the effect of heat loss on process performance needs to be taken into account.

3 Proof of concept

3.1 Considerations

After identifying possible routes for energy storage in the CaL plant integrated to the coal-fired power plant for CO₂ capture (Fig. 1), the performance of the following scenarios is evaluated:

 CaL (Case 1) and CaL-HYD (Case 4) systems without energy storage;

- CaL (Case 2) and CaL-HYD (Case 5) systems with cryogenic O₂ storage;
- CaL (Case 3) and CaL-HYD (Case 6) systems with CaO/CaCO₃ solids storage.

Although other routes for energy storage based on permutations of the identified systems could be analysed, these are unlikely to offer any practical benefit over the selected cases. This is because, in all possible cases for energy storage, the minimum operating load of the calciner is limited by the minimum operating load of the air separation unit and the CO₂ compression unit. Therefore, further reduction in the minimum load of these systems would require additional compressors, leading to higher capital costs. Nevertheless, implementation of the energy storage system utilising the CaO/Ca(OH)₂ reaction for energy storage has lower energy density compared to that based on CaO/CaCO₃, ¹³ and thus the heat storage capacity of the system would be lower.

To evaluate performance of the proposed concept, a model of the entire process has been developed in Aspen Plus^{TM32} with the key assumptions presented in Table 1. In addition to modelling of the CaL or CaL-HYD system, the air separation unit and the $\rm CO_2$ compression unit were modelled in detail, to reliably assess process performance. The $\rm CO_2$ capture system was scaled to remove 90% of the flue gas from the reference 660 MW_{el} coal-fired power plant, the process model of which has been described in detail elsewhere. As opposed to the study by Vandersickel *et al.*, the part-load performance of the coal-fired power plant and the secondary steam cycle was evaluated in detail using the framework for part-load modelling presented in Hanak *et al.* 48

The capacity of energy storage technologies is usually characterised with energy density $(D_{\rm v})$ or a specific energy $(D_{\rm m})$

Table 1 Key process model assumptions

Parameter		Value				
Carbonator	Temperature (°C)					
	Carbonation extent (–) Stoichiometric reactor. Average conversion model by Rodríguez <i>et al.</i> ⁴⁹ with deactivation curves derived from experimental data from Sánchez-Biezma <i>et al.</i> ⁵⁰ (non-hydrated sorbent) and Grasa <i>et al.</i> ⁴¹ (hydrated sorbent)	0.70				
Calciner	Temperature (°C)	900				
	Calcination extent (–)	0.95				
	Relative make up (fresh limestone/sorbent circulation rate) (–)	0.04				
	O ₂ concentration in the calciner fluidising gas (% _{vo,wet})	40.0				
	O ₂ excess (% _{vol,dry}) Gibbs reactor. Gibbs free energy minimisation model	2.5				
Hydrator	Temperature (°C)	500				
·	Steam-to-calcium ratio (molar basis) Stoichiometric reactor. Complete sorbent conversion.	1.3				
Secondary steam cycle	Design live/reheat steam temperature (°C)					
scam cycle	Design live/reheat steam pressure (bar)	593.3 242.3/ 49.0				

defined in eqn (1) and (2) as the ratio of the energy stored $(E_{\rm stored})$ and the amount of storage media stored $(m_{\rm storage\ media})$, while performance of the power generation systems is characterised with net power output $(W_{\rm net})$ and net thermal efficiency $(\eta_{\rm th})$, which is defined in eqn (3) as the ratio of the net power output and the heat input from fuel combustion $(Q_{\rm fuel})$. Environmental performance is represented as the specific ${\rm CO}_2$ emissions $(e_{{\rm CO}_2})$ defined in eqn (4) as the ratio of ${\rm CO}_2$ emission rate $(m_{{\rm CO}_2})$ and the net power output.

$$D_{\rm V} = \frac{\dot{E}_{\rm stored}}{3.6 \times \dot{m}_{\rm storage\,media}} \rho_{\rm storage\,media} \tag{1}$$

$$D_{\rm m} = 1000 \times \frac{\dot{E}_{\rm stored}}{\dot{m}_{\rm storage media}} \tag{2}$$

$$\eta_{\rm th} = \frac{\dot{W}_{\rm net}}{\dot{O}_{\rm fuel}} \tag{3}$$

$$e_{\text{CO}_2} = \frac{\dot{m}_{\text{CO}_2}}{\dot{W}_{\text{net}}} \tag{4}$$

Because energy can be stored in thermal (CaO/CaCO₃ solids) and electrical (cryogenic O2 storage) forms in the proposed concept, the above metrics cannot fully represent the performance of the integrated system. Therefore, the degree of energy utilisation $(\eta_{\rm u})$, which is defined in eqn (5) as the ratio of useful energy and total energy input, is used as a measure of overall process performance. In eqn (5), the useful energy term comprises net power output (Wnet), electricity stored through cryogenic O2 storage (W_{storage,out}), and heat stored through CaO/CaCO₃ solids storage ($Q_{\text{storage,out}}$), while the total energy input comprises the chemical energy input from fuel combustion (Q_{fuel}) , electricity input through utilisation of stored liquid O2 (Wstorage,in), and heat input through utilisation of stored CaO/CaCO3 solids $(Q_{\text{storage,in}})$. Although the considered forms of energy differ in quality, similar metrics, called degree of fuel utilisation, have been widely applied to assess performance of combined heat and power generation systems.51

$$\eta_{\rm u} = \frac{\dot{W}_{\rm net} + \dot{Q}_{\rm storage, out} + \dot{W}_{\rm storage, out}}{\dot{Q}_{\rm fuel} + \dot{Q}_{\rm storage, in} + \dot{W}_{\rm storage, in}}$$
(5)

To assess the profitability of the proposed concepts with respect to the reference coal-fired power plant without CO_2 capture, the levelised cost of electricity (LCOE) and the cost of CO_2 avoided (AC) are calculated according to eqn (6) and (7)^{52–54} respectively.

$$LCOE = \frac{TCR \times FCF + FOM}{\dot{W}_{net} \times CF \times 8760} + VOM + \frac{SFC}{\eta}$$
 (6)

$$AC = \frac{LCOE_{capture} - LCOE_{ref}}{e_{CO_2,ref} - e_{CO_2,capture}}$$
 (7)

These parameters allow assessing the economic viability of the proposed concept through correlating thermodynamic performance indicators, such as net power output, net thermal efficiency (η) , capacity factor (CF) and specific emissions $(E_{\rm CO_2})$,

with economic performance, such as total capital requirement (TCR), variable (VOM) and fixed (FOM) operating costs, specific fuel cost (SFC), and the fixed charge factor (FCF), which considers the system's lifetime and project interest rate.

In addition, considering the average electricity prices in December 2014, 55 the daily profit is calculated. Using the approach employed by Mac Dowell and Shah, 56 eqn (8) allows calculating the daily short-run profit (SRP) as the difference between the daily revenue from electricity sales (R) and daily operating costs associated with fuel consumption (FC), sorbent make-up (SC), CO₂ transport and storage (CTS), and CO₂ emissions (CE).

$$SRP = R - (FC + SC + CTS + CE)$$
 (8)

The capital cost of the coal-fired power plant and storage equipment is determined using the exponential method function 64 with economic data presented in Table 2. Taking the capital cost for an oxy-fuel circulating-fluidised bed system (C_0) as ref. 58, eqn (9) is employed to estimate the total capital cost of the CaL and CaL-HYD plants (C), considering the volume of the reactors (V) and the heat input to the calciner ($Q_{\rm calc}$) with the scaling factors of 0.67 and 0.9, respectively. Moreover, the parameter representing the fraction of the total cost of a circulating fluidised bed reactor associated with the heat transfer surfaces (α) is assumed to be 0.85. It needs to be highlighted that in the CaL cases, this equation reduces to the exponential function used by Romano *et al.* ⁵⁹

$$C = C_0 \left[\alpha \left(\frac{\dot{Q}_{\text{calc}}}{\dot{Q}_0} \right)^{\text{SF},Q} + (1 - \alpha) \left(\frac{V_{\text{calc}}}{V_0} \right)^{\text{SF},V} + (1 - \alpha) \left(\frac{V_{\text{carb}}}{V_0} \right)^{\text{SF},V} + (1 - \alpha) \left(\frac{V_{\text{hyd}}}{V_0} \right)^{\text{SF},V} \right]$$

$$(9)$$

Fixed and variable operating and maintenance costs are calculated as fractions of total capital cost, while operating costs associated with fuel and sorbent consumption, and CO₂ storage, transport and emission are determined based on process simulation outputs using economic data from Table 2.

Finally, performance of the selected cases for the proposed concept is assessed in the following operating modes:

- Charging mode in which the power plant operates at 40% load, while the considered energy storage system operates at 100% load,
- Discharging mode in which the power plant operates at 100% load, while the considered energy storage system operates at 40% load,
- Daily variable load operation in which the system operates in the charging mode during the off-peak period (11.00 pm 5.30 am), discharging mode during the morning and evening peak periods (6.00 am 9.30 am and 4.30 pm 7.30 pm), and CO_2 capture only mode (no energy storage) in the remaining periods (10:00 am 4:00 pm and 8:00 pm 10:30 pm).‡

 $[\]ddagger$ A hypothetical daily energy demand was adapted from Mac Dowell and Shah. 56

Table 2 Economic model assumptions

Parameter	Value			
Coal-fired power	Reference equipment capital cost $(\mathcal{E} \text{ per kW}_{el})^{42,52,54,57}$			
plant	Reference power output $(MW_{el})^{42}$	575		
Calcium looping	Reference equipment capital cost (€ per kW _e) ⁵⁸	1252.3		
plant	Reference heat input $(MW_{th})^{58}$ Reference reactor volume $(m^3)^{58}$	534.0 1150.5		
Cryogenic O ₂ storage tank	Reference equipment capital cost $(\in \text{per } m^3)^{43}$ Reference volume $(m^3)^{43}$	800 00 2500		
Solid storage tank	Reference equipment capital cost $\left(\in \text{ per } MW_{th,sensible} \right)^{44}$	8.0		
Other economic	Variable cost as a fraction of total capital cost (%) ^{54,60}	2.0		
parameters	Fixed cost as a fraction of total capital cost (%) ^{54,60}	1.0		
	Carbon tax (€ per tCO ₂) ^{54,60}	0.0		
	Raw sorbent cost (€ per t) ^{54,60}	6.0		
	CO ₂ transport and storage cost (€ per tCO ₂) ⁶¹	7.0		
	Coal price (€ per t) ^{60,62}	40.6		
	Natural gas price (€ per t) ⁶³	157.1		
	Expected lifetime (years) ^{54,60}	25		
	Project interest rate $(\%)^{54,60}$ Capacity factor $(\%)^{54,60}$	8.78 80		

3.2 Thermodynamic performance evaluation

A performance analysis conducted for the selected cases (Table 3) revealed that the turndown of the reference coal-fired power plant, which is a ratio of the maximum and minimum net power output reached by the system, was 2.56. Interestingly, similar turndown

values were estimated for Case 1 (2.62) and Case 4 (2.60), in which the power plant was retrofitted with the CaL and the CaL-HYD systems for CO2 capture only, respectively. This is because integration of these systems resulted not only in increase of the maximum net power output by 51.7% and 33.7%, respectively, but it also caused increases in the minimum net power output of 48.3% and 32.0%, respectively. Results presented in Table 3 show also that turndown of the integrated system with cryogenic O2 storage increased to 3.30 (Case 2) and 3.15 (Case 5), while for the integrated system with CaO/CaCO₃ solids storage it reduced to 2.54 (Case 3) and 2.44 (Case 6). It should be noted that in the discharge mode, a reduction in the calciner load to 40% led to reductions in fuel and O₂ requirements, and thus, less high-grade heat was available for recovery from the process streams. This, in turn, resulted in less high-pressure steam generation and a drop in its pressure, which has been estimated according to the Stodola ellipse law;65 hence lower maximum net power output. Cryogenic O2 energy storage, therefore, appears to be better suited to balance rapid changes of the energy demand, allowing for immediate increases of net power output by utilising O₂ produced in the air separation unit and stored in the cryogenic tank during the off-peak period. Importantly, a noticeable difference in net power output between the CaL and the CaL-HYD systems arose from differences in the amount of the high-grade heat available for recovery in these systems. Namely, the increase in the average sorbent conversion in the carbonator from 15.8% in the CaL system to 37.8% in the CaL-HYD system resulted in a lower solid looping rate required to achieve 90% CO2 capture in the carbonator of the latter system. This, in turn, resulted in a

Table 3 Performance indicators for the considered energy storage and CO₂ capture routes^a for the proposed process

	Reference power plant		Case 1		Case 2		Case 3		Case 4		Case 5		Case 6	
Charging (C)/Discharging (D) performance indicators	C	D	C	D	C	D	C	D	C	D	C	D	C	D
Net power output (MW _{el}) Net thermal efficiency (% _{HHV}) Energy utilisation degree (%) Net efficiency penalty (% _{HHV}) Energy utilisation degree penalty (%) CO ₂ intensity factor (gCO ₂ per kW _{el} h)	247.0 34.5 34.5 — — 969.0	633.0 38.8 38.8	366.4 25.7 25.7 8.8 8.8 65.3	960.0 30.1 30.1 8.7 8.7 55.0	307.5 21.6 25.7 12.9 8.8 77.8	1019.5 32.0 31.4 6.8 7.4 51.8	370.3 16.3 37.7 18.2 -3.2 64.6	941.5 40.2 33.6 -1.5 5.1 56.1	326.1 26.2 26.2 8.3 8.3 73.4	846.6 30.4 30.4 8.4 8.4 62.4	282.4 22.7 26.2 11.8 8.3 84.8	890.8 32.0 31.5 6.8 7.3 59.3	18.1 39.1 16.4	824.8 38.2 32.4 0.6 6.3 64.1
Instantaneous performance indicators Net power generation turndown (–) Energy density ^b (kW h m ⁻³) Specific energy (kJ kg ⁻¹)	2.56 — —		2.62 		3.30 312.0 900		2.54 307.2 700		2.60 — —		3.15 309.8 900		2.44 483.6 1200	
Daily average performance indicators Average daily net thermal efficiency (% _{HHV}) Average daily degree of energy utilisation (%) Average daily CO ₂ intensity factor (gCO ₂ per kW _{el} h)	38.1 38.1 853.6		29.4 29.4 56.4		29.5 29.9 56.3		29.4 33.0 56.8		29.7 29.7 63.9		29.8 30.1 63.8		29.7 33.0 64.2	
Economic performance indicators Levelised cost of electricity (\in per MW _{el} h) Cost of CO ₂ avoided (\in per tCO ₂)	37.2 —		82.7 58.2		82.7 58.3		82.7 58.3		74.2 47.8		74.2 47.8		74.2 47.8	

^a Case 1 - CaL with no ES, Case 2 - CaL with cryogenic O₂ storage, Case 3 - CaL with CaO/CaCO₃ solids storage, Case 4 - CaL-HYD with no ES, Case 5 - CaL-HYD with cryogenic O₂ storage, Case 6 - CaL-HYD with CaO/CaCO₃ solids storage. ^b The unit is kW_{el} h m⁻³_O, in Case 2 and Case 5, and kW_{th} h m⁻³ CaCO₃ in Case 3 and Case 6.

reduction of the heat requirement for sorbent regeneration in the calciner, reducing the amount of recoverable heat from the carbonator and the process streams; hence less high-pressure steam was generated and used for power generation in the secondary steam cycle. The results obtained for the integrated system without energy storage were found to be consistent with the predictions by Wang *et al.*, ⁶⁶ who compared performance of the CaL and the CaL-HYD systems.

Further analysis of process performance revealed that the CaO/CaCO₃ solid storage system would yield higher net thermal efficiencies in the discharging mode (40.2%_{HHV} in Case 3 and 38.2%_{HHV} in Case 6), compared to cryogenic O₂ storage (32.0%_{HHV} in both Case 2 and Case 5) and even compared to the reference power plant (38.8%_{HHV}). Yet, this is achieved at the expense of much lower net thermal efficiencies in the charging mode (16.3%_{HHV} in Case 3 and 18.1%_{HHV} in Case 6), when the solids converted in the carbonator need to be regenerated. Net thermal efficiency for the cryogenic O₂ storage system operating in the charging mode would result in an even lower efficiency penalty.

Yet, it is important to highlight that in estimation of net thermal efficiency, the net power output was considered as the only source of useful work in the system, while energy stored in the form of heat or electricity has not been taken into account. This can also be seen as the main reason for high net thermal efficiencies estimated for the discharging mode, since the energy input from the energy storage system was not considered. Performance analysis of the proposed concept routes revealed that the system with CaO/CaCO₃ storage has 12-13% points higher degree of energy utilisation than the cryogenic O2 storage system. Yet, this did not directly correlate to system storage capacity. Estimation of energy density for both systems did not give a clear answer as to which system has higher energy storage capacity; for the former it was estimated to be 307.2 and 483.6 kW_{th} h m⁻³ in Case 3 and Case 6, respectively, while for the latter it was 312.0 and 309.8 kW_{el} h m⁻³ in Case 2 and Case 5, respectively. However, direct comparison of these values cannot be used to determine which system has higher energy storage capacity, due to different forms of energy used in the energy density estimation. For cases with the cryogenic O2 storage system, operation in the charging and discharging mode was found not to affect performance of the secondary steam cycle, compared to the system without energy storage. It can be claimed that changes in net power output in these operating modes were directly related to the amount of thermal energy input in the boiler. By using the gross thermal efficiency of the system operating in the discharging (38.4%_{HHV}) and charging mode (34.5%_{HHV}), the energy density of cryogenic O2 storage is recalculated to be 812.4–897.9 kW_{th} h m⁻³, which is higher than estimated values for the CaL and CaL-HYD with CaO/CaCO3 storage. This implies that to store the same amount of fuel energy, cryogenic O2 storage would require smaller volume than the CaO/CaCO3 solids storage system, hence lower capital costs.

Incorporation of the sorbent regeneration step through hydration was found to result in a 57.4% increase in energy density and 71.4% increase in specific energy. This can be associated with the increase of average sorbent conversion in

the carbonator from 15.8% to 37.8%, resulting in a reduction of unconverted CaO in the stored solids. As a result, the fraction of total thermal energy stored in the form of sensible heat reduced from 39.0% (Case 3) to 24.9% (Case 6), revealing that increased sorbent conversion promotes energy storage through chemical reaction. Also, it was estimated here that, for each percent of sorbent conversion improvement, energy density and the specific energy can be increased by 8 kW_{th} h m⁻³ and 21.6 kJ_{th} kg⁻¹, respectively. Therefore, not only would the systems including reactivation steps, such as the investigated CaL-HYD system with CaO/CaCO₃ solids storage, or using more efficient sorbents, ^{67,68} require smaller reactors (hence lower capital cost), these would also achieve a higher degree of energy utilisation. Moreover, the CaO/Ca(OH)₂ step in the proposed concept was used to increase the energy storage capacity of the CaO/CaCO3 system by increasing the average conversion of the sorbent, hence increasing the fraction of CaCO₃ in the stored solids. This approach differs from the system investigated by Criado et al., 21 who proposed to use the CaO/Ca(OH)₂ system as the primary energy storage system. This approach was found to increase the energy density of the CaO/CaCO₃ system to 483.6 kW_{th} h m⁻³; that is 57% higher than the energy density of the CaO/CaCO3 system without sorbent reactivation (307.2 kW_{th} h m⁻³) and 86% higher compared to the CaO/Ca(OH)₂ system (260 kW_{th} h m⁻³) evaluated by Criado et al.21 As a result, storage of the same amount of heat would require smaller volume in the CaO/CaCO₃ system with sorbent reactivation through hydration compared to the CaO/Ca(OH)2 system, leading to lower capital cost of the entire CO2 capture system with energy storage, which is proven in the economic analysis presented below. The only downside of using the CaL-HYD instead of the CaL system is marginally higher values for CO₂ intensity factor in most of the cases investigated (Table 3). This is a result of lower net power output for the regenerated system, caused by less high-grade heat available for recovery from the process streams.

Analysis of the hypothetical daily energy demand curve adapted from Mac Dowell and Shah⁵⁶ revealed that the daily average degree of energy utilisation in the systems containing CaO/CaCO₃ storage (around 33%) and cryogenic O₂ storage (around 30%) was higher than in systems without energy storage (29.4% for Case 1 and 29.7% for Case 4). This implies that the systems with energy storage capability would result in higher degrees of energy utilisation. More importantly, as the periods of charging and discharging were equal in the hypothetical operating schedule, the average daily net thermal efficiency and the average daily CO₂ intensity factor were not affected much compared to the system without energy storage. Finally, the process evaluated in this study can conceptually be integrated with a solar power plant or wind turbine farm to utilise excess energy for sorbent regeneration or for liquid O2 production, which can be utilised later to increase net thermal efficiency and the degree of energy utilisation.

3.3 Economic performance evaluation

The specific capital costs of the reference coal-fired power plant, the CaL system (Case 1) and the CaL-HYD system (Case 4) have

been estimated to be 1206.5 € per kW_{el,gross}, 2981.6 € per kW_{el,gross} and 2776.4 $\ensuremath{\varepsilon}$ per $kW_{el,gross}\text{,}$ respectively. This is in agreement with other studies, which assumed the specific capital costs for coal-fired power plants of 1200 $\ensuremath{\varepsilon}$ per $kW_{el,\mathrm{gross}}$ and for the CaL system of 2500–3000 \in per kW_{el,gross}. ^{25,52–54} Moreover, specific capital cost of the integrated CaL and CaL-HYD systems was estimated to be 2023.4 € per kW_{el,gross} and 1799.1 € per kW_{el,gross}, respectively, which is close to the range 1250–1740 € per kW_{el.gross} estimated in other studies. 42,52,54 A slightly higher specific capital cost obtained in this study is caused by the assumption of maximising heat recovery for power generation in the CaL and CaL-HYD plants. Also, the higher energy density due to sorbent regeneration in Case 6, compared to Case 3, reduces the specific capital cost of the entire system. An additional capital cost associated with cryogenic O2 storage and CaO/CaCO3 solid storage increases the specific capital cost of the integrated CaL system only by 0.6 € per kW_{el,gross} (Case 2) and 2.3 € per kW_{el,gross} (Case 3), and of the CaL-HYD by 0.6 € per kW_{el,gross} (Case 5) and 1.4 € per kW_{el.gross} (Case 6). Hence, addition of energy storage capability does not change the levelised cost of electricity, the value of which is in agreement with results from Romano et al. 59 and Yang et al., 54 and has a negligible effect on the cost of CO2 avoided (Table 3). Therefore, the inherent energy storage ability of the CaL and CaL-HYD systems is available at a very low additional capital cost to the CO2 capture system.

Implementation of the CaL (Case 1) and the CaL-HYD (Case 4) plants for $\rm CO_2$ capture will reduce the daily short run profit by 15.0% and 17.2% (Fig. 2), respectively, regardless of the better thermodynamic performance of Case 4 identified previously. This is due to 7.2% lower net power output in Case 4 with respect to Case 1 and thus lower expected revenue from electricity sales. Furthermore, addition of the cryogenic $\rm O_2$ storage was found to increase the daily short-run profit of the CaL (Case 2) and CaL-HYD (Case 5) plants by 2.3% and 2.2%, respectively. Conversely, addition of the CaO/CaCO₃ solid storage system was found to slightly reduce the daily short-run profit of the CaL (Case 3) and CaL-HYD (Case 6) by 0.1% and 0.2%, respectively; yet it will increase the plant flexibility. Therefore, it appears as if the cryogenic $\rm O_2$ storage system was more economically substantiated. Yet, with the secondary steam cycle designed for normal

operating mode without energy storage, part-load operation of the calciner in discharging mode reduces the amount of recoverable heat that results in reduction of net power output in Case 3 and Case 6 by 0.2% and 0.3%, respectively.

As electricity prices are subject to annual fluctuations and to seasonal changes, the effect of the price difference, which is defined as change of the electricity price with respect to the reference value over the considered period, on the daily shortrun profit, is evaluated. On increasing the daily price difference (Fig. 3a), it was found that the concepts proposed in Case 2 and Case 3 would generate the same daily short-run profit as the reference coal-fired power plant without CO2 capture if the daily price of electricity increases by 12.5 € per MWel h and 14.8 € per MW_{el} h, respectively, while the CaL plant without energy storage will break even at the 14.4 € per MW_{el} h increase in price difference. For the cases with sorbent regeneration through hydration, higher daily short-run profit would be achieved on increased price difference of 22.6-26.0 € per MWel h, with the lowest increase associated to Case 5. Moreover, increased peak price difference (Fig. 3b) of more than 27.4 € per MW_{el} h and 49.2 € per MW_{el} h, would make the CaL (Case 2) and the CaL-HYD (Case 5) more economical than the reference coalfired power plant. In addition, it was found that reduction of off-peak prices (Fig. 3c) will not bring any additional benefit, as the loss of profit in the charging mode during low electricity price periods outweighs the benefits of discharging mode operated at peak times with higher prices. Nevertheless, this analysis revealed that the proposed concept, in particular the CaL plant with cryogenic O2 storage system (Case 2), could generate daily short-run profit higher than the reference coalfired power plant depending on the daily spot prices of electricity. Further increase of the profit can be achieved on determination of the optimal charging and discharging times, using optimisation methodology developed by Barbour et al.69

Finally, economic performance of the proposed concepts is highly dependent upon the economic climate, as it is predicted that the carbon tax may vary between 10– $150 epr tCO_2$. The Moreover, economic performance will vary depending on whether the produced CO_2 is transported and stored (the costs for which vary between 2.5– $36 epr tCO_2$ depending on the CO_2 transport

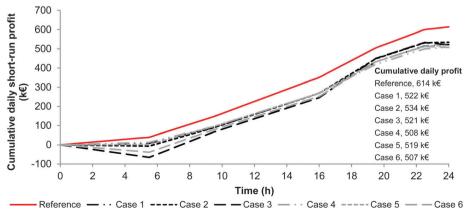


Fig. 2 Comparison of the daily short-run profit

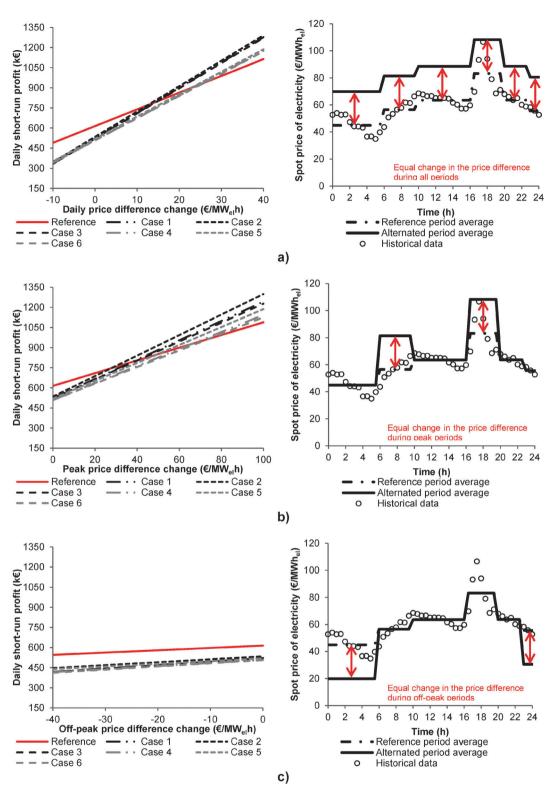
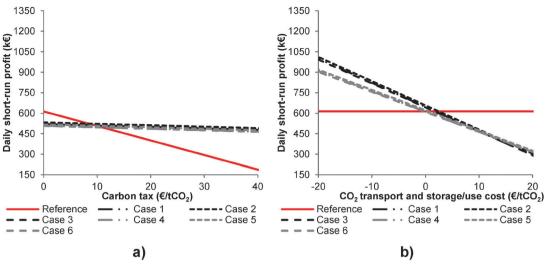


Fig. 3 Effect of a change in the (a) daily (b) peak and (c) off-peak price difference on daily short-run profit.

method and storage location), or used, for example, for enhanced oil recovery at a supply price of 12–15 € per tCO₂. ^{73,74} Fig. 4a reveals that the daily short-run profit of the reference coal-fired power plant is highly affected by increases in the carbon tax, while it is hardly affected in the remaining cases with 90% CO₂ capture. Importantly, when the carbon tax exceeds 8.3 € per tCO₂ for Case 2 (which is lower than the average price of 8.5 € per tCO₂ for the European emission allowances in November 2015⁷⁵), and 11.1 € per tCO₂ for Case 6, the proposed concepts become more profitable than the reference coal-fired



Effect of (a) carbon tax and (b) cost of CO₂ transport and storage/use on daily short-run profit.

power plant. This implies that the proposed concept (Case 2) is already more profitable than the reference coal-fired power plant without CO2 capture.

Furthermore, it can be seen in Fig. 4b that for the specific cost for CO₂ capture and transport of 2.5 € per tCO₂, the daily short-run profit for Case 2 is equal to that generated by the reference coal-fired power plant. On the other hand, for Case 6 to become more profitable than the reference coal-fired power plant, CO2 would need to be sold for industrial use at prices higher than 0.3 € per tCO₂, which corresponds to negative values in Fig. 4b. This shows that the profitability of the proposed concepts could greatly exceed that of the reference coal-fired power plant, if pure CO2 produced in the proposed concepts is industrially utilised, even at low price.

4. Conclusions

In this study, a concept for the CO₂ capture plant based on CaL with inherent energy storage is proposed and evaluated in the coal-fired power plant retrofit scenario. The CaL was previously proposed for energy storage from solar power plants; however, challenges such as the requirement for temporary CO₂ storage and sorbent deactivation were identified. These were resolved in the proposed system as the power plant acts as a permanent source of CO₂ and hydration was used as a means for sorbent regeneration.

Analysis of the process revealed that possible routes for energy storage include CaO/CaCO3 solids storage, CaO/Ca(OH)2 solids storage and cryogenic O2 storage systems. The comparison of CaO/CaCO3 and cryogenic O2 storage systems revealed that implementation of the latter would result in higher turndown of the entire system and offer higher energy density, hence requiring lower capital cost. Although performance of the integrated system with energy storage through a CaO/Ca(OH)2 loop was not evaluated here due to the lower energy density of such system, the reactivation step was found critical in improving the performance of the CaO/CaCO₃ energy storage system. Not only did it increase net thermal efficiency, it increased the energy density by 57.4% and specific energy by 71.4% leading to a higher degree of energy utilisation. Importantly, the proposed CaL-HYD system with CaO/ CaCO₃ energy storage was found to offer 86% higher energy density than the conventional CaO/Ca(OH)2 energy storage system. An increase in the energy density was found to be important from the economic perspective, as storing the same amount of heat in a lower volume would result in the specific capital cost of the CaL-HYD system lower by 6.8% compared to the CaL system.

The economic performance evaluation conducted revealed that the addition of energy storage capability to the CaL and the CaL-HYD plants for CO2 capture from the coal-fired power plant has a low impact on the total capital cost and thus on the levelised cost of electricity and the cost of CO2 avoided. Moreover, analysis of the daily short-run profit revealed that Case 2, in which the CaL plant was equipped with the cryogenic O₂ storage system, will reduce the daily short-run profit of the coal-fired power plant by 15.0%. This case was found to have the lowest impact on system profitability. Yet, the proposed concept (Case 2) can generate higher profit when the carbon tax exceeds 8.3 € per tCO₂. As the price of the European emission allowances in November 2015 was 8.5 € per tCO2, the proposed concept is already more profitable than the reference coal-fired power plant without CO2 capture.

Further studies will aim to provide a detailed design of the proposed concepts of CO2 capture with inherent energy storage for decarbonisation and to optimise the charging and discharging times to maximise the daily short-run profit. Also, the applicability of the proposed concepts in natural gas combined cycle power plants will be assessed. Finally, the inherent energy storage capability of other clean power technologies, such as chemical looping combustion and oxy-combustion, will be assessed.

Nomenclature

ACCost of CO₂ avoided, € per tCO₂ CCapital cost of calcium looping system, € per kWel $\begin{array}{ccc} C_0 & & \text{Reference capital cost of oxy-fuel circulating} \\ & & \text{fluidised bed system, } \in \text{per kW}_{\text{el}} \\ \text{CE} & & \text{CO}_2 \text{ emission cost, } \in \\ \text{CF} & & \text{Capacity factor, } -- \end{array}$

CTS CO_2 transport and storage cost, \in

 $D_{\rm V}$ Energy density, kW h m⁻³ $D_{\rm m}$ Specific energy, kJ kg⁻¹

 e_{CO_2} Specific CO₂ emission, gCO₂ per kW_{el} h

 \dot{E}_{stored} Rate of energy to storage, MW

FC Fuel cost, €

FCF Fixed charge factor, —

FOM Fixed operating and maintenance cost, \in LCOE Levelised cost of electricity, \in per MW h

 \dot{m}_{CO_2} Rate of CO₂ emission, kg s⁻¹ $\dot{m}_{\text{storage media}}$ Rate of media to storage, kg s⁻¹
Revenue from electricity sales, €
SC Sorbent make-up cost, €
SCF Specific fuel cost, € per MW h

SF,*q* Scaling factor for reactor heat input, — SF,*v* Scaling factor for reactor volume, —

SRP Daily short run profit, \in TCR Total capital requirement, \in \dot{Q}_0 Reference heat input, MW_{th} Heat input to the calciner, MW_{th}

 \dot{Q}_{fuel} Chemical energy input from fuel combustion, MW $\dot{Q}_{\mathrm{storage,in}}$ Heat input from CaO/CaCO $_{3}$ solids storage, MW Heat stored through CaO/CaCO $_{3}$ solids storage,

MW

V Volume of reactors, m³

 V_0 Reference volume of reactor, m³

VOM Variable operating and maintenance cost,

€ per MW h

 \dot{W}_{net} Net power output of the integrated system, MW $\dot{W}_{\mathrm{storage, out}}$ Electricity input from cryogenic O₂ storage, MW $\dot{W}_{\mathrm{storage, out}}$ Electricity stored through cryogenic O₂ storage,

MW

α Fraction of the total cost of a circulating fluidised

bed reactor associated with the heat transfer

surfaces, —

 η_{th} Net thermal efficiency, — η_{u} Degree of energy utilisation, —

Abbreviations

CaL Calcium looping process

CaL-HYD Calcium looping process with sorbent reactivation

step through hydration

CCS Carbon capture and storage

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