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

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Abstract 8

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power plant

9 Implementation of carbon capture and storage, nuclear power stations and wide 10 utilisation of renewable energy sources have been identified as capable of reducing 11 around 42% of the energy sector's cumulative CO₂ emissions between 2009 and 12 2050. In scenarios assuming high shares of renewable energy sources in the energy 13 portfolio, the energy storage technologies and the remaining power generating 14 assets would need to flexibly balance the energy supply and demand. With nuclear 15 power plants operating at base load, this task would be handled by flexible fossil fuel 16 power plants with CO_2 capture. However, mature CO_2 capture systems were shown 17 to impose high efficiency penalties (8-12.5% points) and are better suited for base-18 load operation. An emerging calcium looping process, which has been initially 19 considered for energy storage, has been found to offer lower efficiency penalties (5-20 8% points). This study presents a concept of the calcium looping process with 21 inherent energy storage for decarbonisation of the coal-fired power plant. Analysis 22 has revealed that the possible routes for energy storage in this process include 23 CaO/CaCO₃ solids storage, CaO/Ca(OH)₂ solids storage and cryogenic O₂ storage 24 systems. Comparison of the CaO/CaCO₃ storage and cryogenic O₂ storage systems 25 revealed that implementation of the latter would result in higher turndown of the 26 entire system and would offer higher energy density. Also, the hydration reaction 27 was found to improve the energy density of the CaO/CaCO₃ energy storage system by 57.4%, from 307.2 kWh/m³ to 483.6 kWh/m³. Economic evaluation of the 28 29 proposed concepts revealed that application of the cryogenic O_2 storage system in 30 the calcium looping CO₂ capture process has the potential to increase the 31 profitability of the integrated system, even over the reference coal-fired power plant 32 without CO_2 capture.

33 Key Words: Carbon capture, calcium looping, energy storage, decarbonisation, 34 coal-fired power plant.

35 **1 INTRODUCTION**

The International Energy Agency^{1,2} has predicted that to limit the global mean 36 37 temperature increase to 2°C, around 42% of the cumulative CO₂ emission from the 38 energy sector, between 2009 and 2050, can be mitigated through implementation of 39 carbon capture and storage (CCS), nuclear power stations and utilisation of 40 renewable energy sources. The greatest challenge of such a scenario is the 41 intermittence of the renewable energy sources³, which would affect operation of the existing energy network^{4,5}, especially in cases when their share in the energy 42 portfolio would exceed 50%¹. As the nuclear power plants operate at base load, 43 44 fossil fuel power plants would need to flexibly balance energy supply and demand, 45 so that neither energy produced from renewable energy sources is wasted (high 46 renewables generation period) nor energy shortages occur (low renewables 47 generation period). Such periods of variable load operation or no operation would 48 impose energy and economic penalties on the fossil fuel power systems, especially for plants with CCS that are better suited for base-load operation⁶. 49

50 Due to their capacity of decoupling energy supply and demand⁷, energy storage 51 technologies can increase the degree of energy utilisation and thus should be widely 52 deployed along with low-emission technologies. However, the energy storage could 53 contribute to CO_2 emission reduction only in the scenario of renewables penetration^{8,9}. Otherwise, the energy storage could increase CO₂ emissions by an 54 55 extent which depends on carbon prices and share of coal-based power generation in the energy portfolio^{1,8}. For this reason, a synergy between renewable energy 56 57 sources, fossil fuel power generation and energy storage needs to be reached.

58 Presently about 145.8 GW of energy is stored globally, most of which as mechanical 59 energy in pumped hydro storage plants (97.5%), and compressed air and flywheel 60 energy storage techniques (1.0%). Interestingly, the share of thermal energy storage 61 technologies surpassed electro-mechanical storage in 2013, and now accounts for 1.2% of the global energy storage capacity¹⁰. These technologies utilise media 62 63 capable of storing thermal energy at low or high temperature, which can be recovered in the form of cold or heat depending on the process demand^{11,12}. 64 65 Moreover, thermal energy storage systems are claimed to have the potential for 66 improving the flexibility of the electricity grid, increasing the degree of the energy utilisation^{13,14}, and balancing the mismatch between energy supply and demand¹⁵. 67 68 These technologies do not have the disadvantages of pumped hydro storage and 69 compressed air storage, such as requirements of specific site topology, and relatively high capital cost, which could have a negative environmental footprint^{11,12}. 70

71 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 72 73 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 74 products is in the vapour phase¹⁹. Despite being proposed for energy storage in the 75 76 mid-1970s^{19,20}, the process involving either hydration or carbonation of CaO is still considered among the best candidates for energy storage¹⁸. A novel process design 77 78 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 79 80 comprises a single atmospheric pressure circulating fluidised bed, which can operate 81 as hydrator and regenerator, and two silos for CaO and Ca(OH)₂ storage. This study 82 revealed that, at maximum thermal output of 100 MW_{th}, the system offered an

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83 energy storage density of 260 kWh_{th}/m³ and a round-trip efficiency of 63%. Edwards and Materić²² proposed a process based on reversible carbonation of CaO in the 84 85 calcium looping process (CaL) that comprised two independent reactors -86 atmospheric pressure calciner (solar tower receiver) and pressurised fluidised bed 87 carbonator – and three reservoirs for CaO, CaCO₃ and CO₂ storage. In addition, air 88 leaving the carbonator is fed to a gas expander for power generation. The plant net 89 thermal efficiency was found to be between 40-46%. Finally, Vandersickel et al.²³ 90 proposed to integrate a process similar to the integrated gasification combined cycle 91 power plant, with the difference being that only CaO and CaCO₃ are stored, and the 92 heat for calcination is provided through oxy-combustion of syngas diverted from the 93 gas turbine. In this system, the existing Selexol unit is by-passed and the carbonator 94 is used to capture CO_2 from the syngas during the peak-demand period. 95 Nevertheless, the primary function of this system is energy storage and unloading 96 the existing CO₂ capture system. Such configuration was found to operate with a 97 round-trip efficiency of 61%, and allowed for changing the power output by +25% 98 (peak-load) and -20% (off-peak) with respect to a nominal 550 MW_{el}. However, this 99 study did not consider variation of the power generation system during part-load 100 operation, which would lead to a further reduction of the power output during the 101 calcination step.

102 Although the carbonation reaction offers nearly 50% higher theoretical energy 103 density (1222 kWh/m³) compared to that of hydration (833 kWh/m³)¹³, there are 104 some concerns that need to be resolved prior to large-scale deployment. These 105 include capability for electrical energy storage¹², reduction of sorbent activity¹⁹, and 106 requirement for temporary CO₂ storage¹⁸. Also, the CaL process was proposed by 107 Shimizu et al.²⁴ for CO₂ capture from fossil fuel power plants. Not only has this

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process been proven to impose lower net efficiency penalty (5-8% points)²⁵⁻²⁸ 108 compared to more mature CO₂ capture technologies $(8-12.5\% \text{ points})^{29-32}$, it also 109 110 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 111 112 electricity produced in the renewable energy sources to drive the air (for O_2 113 production) and CO₂ compressors and has a permanent source of CO₂ from the 114 fossil fuel power plant. Finally, it can operate with higher carbonation conversions 115 (higher energy density) when a hydration stage is employed 35 .

116 The CaL process can, therefore, be seen as a promising technology for 117 decarbonisation of the power sector as it has the ability to both decarbonise the 118 fossil fuel power plant in an efficient manner and increase power generation 119 flexibility. Hence, the fossil fuel power plant would not only meet its emission 120 reduction targets, but also operate efficiently even in the energy portfolio containing 121 large shares of intermittent renewable energy sources. In this study, the concept of 122 CaL with inherent energy storage for CO₂ capture from coal-fired power plants is 123 proposed and possible routes for energy storage in the proposed concept are 124 identified. Finally, techno-economic performance of the selected routes is evaluated 125 to analyse their degree of energy utilisation and profitability compared to the system 126 without energy storage.

127 2 CONCEPT PROCESS DESCRIPTION

128 **2.1 Calcium looping process**

129 A core of the proposed concept is the CaL process proposed by Shimizu et al.²⁴ for 130 CO_2 capture, which comprises two interconnected fluidised bed reactors operating at 131 atmospheric pressure. In the first reactor, a carbonator, CO_2 is removed from the flue 132 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. Hightemperature 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.

137 Yet, due to the decay of maximum sorbent conversion with the number of carbonation/calcination cycles³⁶, which can drop to around 5–14% after 30 cycles 138 depending on sulphur content in the flue gas and the fuel used in the calciner^{37,38}, 139 140 part of the sorbent needs to be replenished in the system. To achieve a higher 141 conversion in the carbonator, the sorbent can be reactivated through hydration (CaL-142 HYD)^{35,39,40}. As a result of 60% sorbent hydration, the maximum sorbent conversion in the carbonator is about 55% after 15 cycles⁴¹. In the concept process proposed 143 144 here, the low-pressure steam required for hydration can be extracted from the 145 secondary steam cycle. Hydrated sorbent can be directed to either the carbonator or 146 the calciner (Figure 1). However, the latter route increases the calciner heat load, 147 and although that heat can be regenerated, the need for a larger air separation unit 148 and CO₂ compression unit incurs higher capital costs, making this route less attractive. In addition, around 4–10% of sorbent⁴² could be elutriated due to attrition. 149 150 As a result, a higher fresh limestone make-up rate would be required, leading to 151 higher maximum sorbent conversions, at the expense of higher heat requirement in 152 the calciner. Yet, a higher fresh limestone make-up rate would lead to higher 153 average sorbent conversions in the carbonator, reducing the sorbent looping rate 154 required for 90% capture and thus, the heat requirement in the calciner.

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155 **2.2 Routes for energy storage and CO₂ capture**

- 156 Having analysed the process flow diagrams of the CaL process for CO₂ capture,
- 157 three viable options for energy storage have been identified (Figure 1):
- cryogenic O₂ storage (green dashed lines),
- CaO/CaCO₃ solids storage (grey dashed lines),
- CaO/Ca(OH)₂ solids storage (grey and red dashed lines, CaL-HYD only).

161 During the off-peak period, any of the identified energy storage systems can operate 162 in the charging mode, which means that liquid O₂ is produced and/or the sorbent is 163 regenerated in the calciner (in the CaL-HYD scenario reactivated sorbent is first fed 164 to the carbonator). Under such operating mode, the air separation unit, the CO_2 165 compression unit and the calciner operate at their nominal capacity, while the power 166 plant operates at its minimum load of 40%. This will lead to higher fuel consumption 167 and higher power consumption for air separation and CO₂ compression compared to 168 the system operating at 40% load without the energy storage. During the peak-169 demand period, the coal-fired power plant operates at its nominal capacity, while the 170 stored O₂ and/or regenerated sorbent is utilised to unload the air separation unit and 171 the CO_2 compression unit, reducing their power requirements, and to reduce the 172 heat requirement of the calciner. Therefore, the proposed concept would benefit from 173 using more fuel during off-peak periods, storing its chemical energy when the 174 electricity price is low, and using this energy to reduce the fuel consumption and/or 175 the system's power requirement during the peak periods characterised by higher 176 market prices for electricity. Such operation is expected to increase the flexibility and 177 the profitability of the integrated system.

178 It needs to be highlighted that the carbonator is assumed to follow the power plant 179 load changes, maintaining 90% CO_2 capture. Also, the air separation unit 180 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 181 182 three compression trains and two air separation unit trains to reach the minimum 183 load of around 40% for the entire system. Due to the same minimum constraint, 184 three compression trains are required in the CO_2 compression unit. The calciner, on 185 the other hand, can operate with a minimum load of 25%^{46,47}. It is also assumed that 186 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 unit⁴³, while the sorbent is 187 stored at high temperature in the solid storage tanks. As claimed by Arias et al.⁶, the 188 189 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. 190 191 such as ash or sand, in the insulated tanks can reach thermal efficiencies exceeding 192 99%. Such low heat losses (<1%) are a result of combined effects of highly effective 193 thermal insulation and self-insulation of the particles. Assuming short-term 194 CaO/CaCO₃ solids storage (<12h) in the tanks insulated with concrete walls and 195 refractory lining, which was also considered by Ma et al.44, heat losses are not 196 expected to affect the process performance by much and thus they are neglected in 197 this concept study. Nevertheless, at the process design stage and for long-term 198 storage (days to weeks), the effect of heat loss on process performance needs to be 199 taken into account.

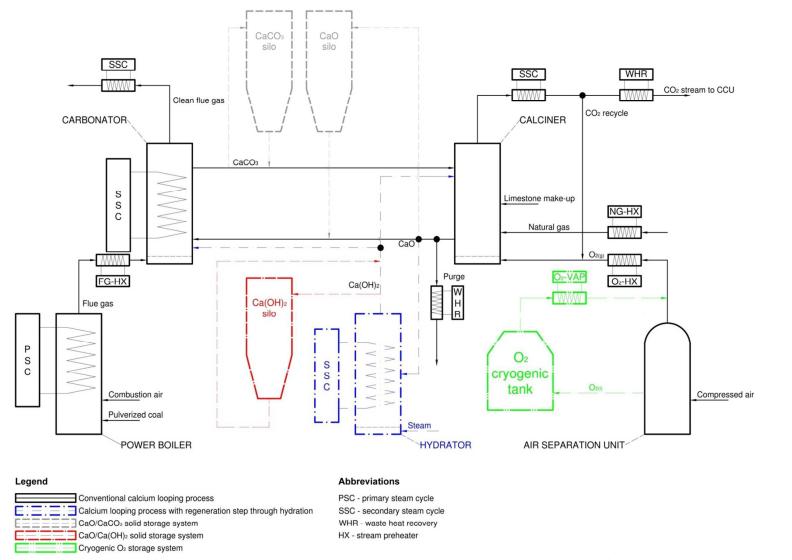


Figure 1: Schematic of coal-fired power plant retrofitted with calcium looping process for CO₂ capture and energy storage

202 3 PROOF OF CONCEPT

203 3.1 Considerations

After identifying possible routes for energy storage in the CaL plant integrated to the coal-fired power plant for CO_2 capture (Figure 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.

210 Although other routes for energy storage based on permutations of the identified 211 systems could be analysed, these are unlikely to offer any practical benefit over the 212 selected cases. This is because, in all possible cases for energy storage, the 213 minimum operating load of the calciner is limited by the minimum operating load of 214 the air separation unit and the CO_2 compression unit. Therefore, further reduction in 215 the minimum load of these systems would require additional compressors, leading to 216 higher capital costs. Nevertheless, implementation of the energy storage system 217 utilising the CaO/Ca(OH)₂ reaction for energy storage has lower energy density 218 compared to that based on CaO/CaCO₃¹³, and thus the heat storage capacity of the 219 system would be lower.

To evaluate performance of the proposed concept, a model of the entire process has been developed in Aspen Plus^{M32} 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 CO₂ compression unit were modelled in detail, to reliably assess process performance. The CO₂ capture system was scaled to remove 90% of the flue gas

225	from the reference 660 MW_{el} coal-fired power plant, the process model of which has
226	been described in detail elsewhere ⁴⁸ . As opposed to the study by Vandersickel et
227	al.23, the part-load performance of the coal-fired power plant and the secondary
228	steam cycle was evaluated in detail using the framework for part-load modelling
229	presented in Hanak et al. ⁴⁸ .

230	Table 1: Key	process model	assumptions
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Parameter		Value
Carbonator	Temperature (°C)	625
	Carbonation extent (-)	0.70
	Stoichiometric reactor. Average conversion model by Rodríguez et al. ⁴⁹ with deactivation curves derived from experimental data from Sánchez-Biezma et al. ⁵⁰ (non-hydrated sorbent) and Grasa et al. ⁴¹ (hydrated sorbent).	
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 ($\%_{vo,wetl})$	40.0
	O ₂ excess (% _{vol,dry})	2.5
	Gibbs reactor. Gibbs free energy minimisation model.	
Hydrator	Temperature (°C)	500
	Steam-to-calcium ratio (molar basis)	1.3
	Stoichiometric reactor. Complete sorbent conversion.	
Secondary	Design live/reheat steam temperature (°C)	593.3/593.3
steam cycle	Design live/reheat steam pressure (bar)	242.3/49.0

231 The capacity of energy storage technologies is usually characterised with energy 232 density (D_v) or a specific energy (D_m) defined in Eq. (1) and Eq. (2) as the ratio of the 233 energy stored (E_{stored}) and the amount of storage media stored ($m_{storage media}$), while 234 performance of the power generation systems is characterised with net power output 235 (W_{net}) and net thermal efficiency (η_{th}) , which is defined in Eq. (3) as the ratio of the 236 net power output and the heat input from fuel combustion (Q_{fuel}). Environmental 237 performance is represented as the specific CO₂ emissions (e_{CO2}) defined as the ratio 238 of CO_2 emission rate (m_{CO2}) and the net power output.

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

$$D_m = 1000 \times \frac{\dot{E}_{stored}}{\dot{m}_{storage media}}$$
(2)

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

$$e_{CO_2} = \frac{\dot{m}_{CO_2}}{\dot{W}_{net}} \tag{4}$$

239 Because energy can be stored in thermal (CaO/CaCO₃ solids) and electrical 240 (cryogenic O_2 storage) forms in the proposed concept, the above metrics cannot fully 241 represent the performance of the integrated system. Therefore, the degree of energy 242 utilisation (η_u), which is defined in Eq. (5) as the ratio of useful energy and total 243 energy input, is used as a measure of overall process performance. In Eq. (5), the 244 useful energy term comprises net power output (W_{net}) , electricity stored through 245 cryogenic O_2 storage ($W_{storage,out}$), and heat stored through CaO/CaCO₃ solids 246 storage (Q_{storage.out}), while the total energy input comprises the chemical energy input 247 from fuel combustion (Q_{fuel}), electricity input through utilisation of stored liquid O_2 248 ($W_{storage,in}$), and heat input through utilisation of stored CaO/CaCO₃ solids ($Q_{storage,in}$). 249 Although the considered forms of energy differ in quality, similar metrics, called 250 degree of fuel utilisation, have been widely applied to assess performance of 251 combined heat and power generation systems⁵¹.

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

To assess the profitability of the proposed concepts with respect to the reference coal-fired power plant without CO₂ capture, the levelised cost of electricity (*LCOE*) and the cost of CO₂ avoided (*AC*) are calculated according to Eq. (6) and Eq. (7)^{52–} ⁵⁴, respectively.

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$$LCOE = \frac{TCR \times FCF + FOM}{\dot{W}_{net} \times CF \times 8760} + VOM + \frac{SFC}{\eta}$$
(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_{CO2}), 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.

Parameter		Value
Coal-fired power plant	Reference equipment capital cost (€/kW _{el}) ^{42,52,54,57}	1100
	Reference power output (MW _{el}) ⁴²	575
Calcium looping plant	Reference equipment capital cost (€/kW _{el}) ⁵⁸	1252.3
	Reference heat input (MWth)58	534.0
	Reference reactor volume (m ³) ⁵⁸	1150.5
Cryogenic O2 storage tank	Reference equipment capital cost (€/m³) ⁴³	800000
	Reference volume (m ³) ⁴³	2500
Solid storage tank	Reference equipment capital cost (€/MW _{th,sensible}) ⁴⁴	8.0
Other economic parameters	Variable cost as a fraction of total capital cost $(\%)^{54,60}$	2.0
	Fixed cost as a fraction of total capital cost (%) ^{54,60}	1.0
	Carbon tax (€/tCO ₂) ^{54,60}	0.0
	Raw sorbent cost (€/t) ^{54,60}	6.0
	CO₂ transport and storage cost (€/tCO₂) ⁶¹	7.0
	Coal price (€/t) ^{60,62}	40.6
	Natural gas price (€/t) ⁶³	157.1
	Expected lifetime (years) ^{54,60}	25
	Project interest rate (%) ^{54,60}	8.78
	Capacity factor (%) ^{54,60}	80

In addition, considering the average electricity prices in December 2014⁵⁵, the daily
 profit is calculated. Using the approach employed by Mac Dowell and Shah⁵⁶, Eq. (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)

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270 The capital cost of the coal-fired power plant and storage equipment is determined using the exponential method function⁶⁴ with economic data presented in Table 2. 271 272 Taking the capital cost for an oxy-fuel circulating-fluidised bed system (C_0) as reference⁵⁸, Eq. (9) is employed to estimate the total capital cost of the CaL and 273 274 CaL-HYD plants (C), considering the volume of the reactors (V) and the heat input to 275 the calciner (Q_{calc}) with the scaling factors of 0.67 and 0.9, respectively. Moreover, 276 the parameter representing the fraction of the total cost of a circulating fluidised bed 277 reactor associated with the heat transfer surfaces (α) is assumed to be 0.85. It needs 278 to be highlighted that in the CaL cases, this equation reduces to the exponential function used by Romano et al.⁵⁹ 279

$$C = C_0 \left[\alpha \left(\frac{\dot{Q}_{calc}}{\dot{Q}_0} \right)^{SF,Q} + (1 - \alpha) \left(\frac{V_{calc}}{V_0} \right)^{SF,V} + (1 - \alpha) \left(\frac{V_{carb}}{V_0} \right)^{SF,V} + (1 - \alpha) \left(\frac{V_{hyd}}{V_0} \right)^{SF,V} \right]$$
(9)

Fixed and variable operating and maintenance costs are calculated as a fraction 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 (11.00pm – 5.30am), discharging mode during the morning and evening peak periods (6:00am – 9.30am and 4.30pm – 7.30pm), and CO₂ capture only mode (no energy storage) in the remaining periods (10:00am – 4:00pm and 8:00pm – 10:30pm).^a

3.2 Thermodynamic performance evaluation

296 A performance analysis conducted for the selected cases (Table 2) revealed that the 297 turndown of the reference coal-fired power plant, which is a ratio of the maximum 298 and minimum net power output reached by the system, was 2.56. Interestingly, 299 similar turndown values were estimated for Case 1 (2.62) and Case 4 (2.60), in 300 which the power plant was retrofitted with the CaL and the CaL-HYD systems for 301 CO₂ capture only, respectively. This is because integration of these systems resulted 302 not only in increase of the maximum net power output by 51.7% and 33.7%, 303 respectively, but it also caused increases in the minimum net power output of 48.3% 304 and 32.0%, respectively. Results presented in Table 2 show also that turndown of 305 the integrated system with cryogenic O_2 storage increased to 3.30 (Case 2) and 3.15 306 (Case 5), while for the integrated system with CaO/CaCO₃ solids storage it reduced 307 to 2.54 (Case 3) and 2.44 (Case 6). It should be noted that in the discharge mode, a 308 reduction in the calciner load to 40% led to reductions in fuel and O₂ requirements, 309 and thus, less high-grade heat was available for recovery from the process streams. 310 This, in turn, resulted in less high-pressure steam generation and a drop in its 311 pressure, which has been estimated according to the Stodola ellipse law⁶⁵; hence 312 lower maximum net power output. Cryogenic O_2 energy storage, therefore, appears

^a A hypothetical daily energy demand was adapted from MacDowell and Shah⁵⁶.

313 to be better suited to balance rapid changes of the energy demand, allowing for 314 immediate increases of net power output by utilising O_2 produced in the air 315 separation unit and stored in the cryogenic tank during the off-peak period. 316 Importantly, a noticeable difference in net power output between the CaL and the 317 CaL-HYD systems arose from differences in the amount of the high-grade heat 318 available for recovery in these systems. Namely, the increase in the average sorbent 319 conversion in the carbonator from 15.8% in the CaL system to 37.8% in the CaL-320 HYD system resulted in a lower solid looping rate required to achieve 90% CO₂ 321 capture in the carbonator of the latter system. This, in turn, resulted in a reduction of 322 the heat requirement for sorbent regeneration in the calciner, reducing the amount of 323 recoverable heat from the carbonator and the process streams; hence less high-324 pressure steam was generated and used for power generation in the secondary 325 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 326 327 performance of the CaL and the CaL-HYD systems.

					•••	-	-				-			
	Referenc power pla		Case 1		Case 2		Case 3		Case 4		Case 5		Case 6	
Charging (C) / Discharging (D) performance indicators	С	D	С	D	С	D	с	D	С	D	с	D	С	D
Net power output (MW _{el})	247.0	633.0	366.4	960.0	307.5	1019.5	370.3	941.5	326.1	846.6	282.4	890.8	338.3	824.8
Net thermal efficiency (%HHV)	34.5	38.8	25.7	30.1	21.6	32.0	16.3	40.2	26.2	30.4	22.7	32.0	18.1	38.2
Energy utilisation degree (%)	34.5	38.8	25.7	30.1	25.7	31.4	37.7	33.6	26.2	30.4	26.2	31.5	39.1	32.4
Net efficiency penalty	-		8.8	8.7	12.9	6.8	18.2	-1.5	8.3	8.4	11.8	6.8	16.4	0.6
Energy utilisation degree penalty (%)	-		8.8	8.7	8.8	7.4	-3.2	5.1	8.3	8.4	8.3	7.3	-4.6	6.3
CO ₂ intensity factor (gCO ₂ /kWh _{el}) Instantaneous performance indicators Net power generation	969.0	835.0	65.3	55.0	77.8	51.8	64.6	56.1	73.4	62.4	84.8	59.3	70.7	64.1
turndown (-)			2.62		3.30		2.54		2.00					
Energy density ^c (kWh/m ³)	-		-		312		307.2		-			309.8		3.6
Specific energy (kJ/kg)	ecific energy (kJ/kg)		90	00	700		-		900		1200			
Daily average performance indicators Average daily net thermal						-	00			_	00			_
efficiency (% _{HHV})	38.	.1	29.	.4	29	.5	29.	.4	29.	./	29.	8	29	./
Average daily degree of energy utilisation (%)	38.	.1	29.	.4	29	.9	33.	.0	29.	.7	30.	1	33	.0
Average daily CO ₂ intensity factor (gCO ₂ /kWh _{el})	853	3.6	56.	.4	56	.3	56.	.8	63.	.9	63.	8	64	.2
Economic performance indicators														
Levelised cost of electricity (€/MWh _{el})	37.	.2	82.	7	82	7	82.	.7	74.	.2	74.	2	74	.2
Cost of CO_2 avoided (\notin/tCO_2)	-		58.	2	58	.3	58.	.3	47.	.8	47.	8	47	.8

Table 2: Performance indicators for the considered energy storage and CO₂ capture routes^b for the proposed process 328

^b Case 1 – CaL with no ES, Case 2 – CaL with cryogenic O_2 storage, Case 3 – CaL with CaO/CaCO₃ solids storage, Case 4 – CaL-HYD with no ES, Case 5 – CaL-HYD with cryogenic O_2 storage, Case 6 – CaL-HYD with CaO/CaCO₃ solids storage. ^c The unit is kWh_{el}/m³_{O2} in Case 2 and Case 5, and kWh_{th}/m³CaCO₃ in Case 3 and Case 6.

329 Further analysis of process performance revealed that CaO/CaCO₃ solid storage 330 system would yield higher net thermal efficiencies in the discharging mode 331 $(40.2\%_{HHV})$ in Case 3 and $38.2\%_{HHV}$ in Case 6), compared to cryogenic O₂ storage 332 $(32.0\%_{HHV})$ in both Case 2 and Case 5) and even compared to the reference power 333 plant (38.8%_{HHV}). Yet, this is achieved at the expense of much lower net thermal 334 efficiencies in the charging mode (16.3%_{HHV} in Case 3 and 18.1%_{HHV} in Case 6), 335 when the solids converted in the carbonator need to be regenerated. Net thermal 336 efficiency for the cryogenic O_2 storage system operating in the charging mode would 337 result in an even lower efficiency penalty.

338 Yet, it is important to highlight that in estimation of net thermal efficiency, the net 339 power output was considered as the only source of useful work in the system, while 340 energy stored in the form of heat or electricity has not been taken into account. This 341 can also be seen as the main reason for high net thermal efficiencies estimated for 342 the discharging mode, since the energy input from the energy storage system was 343 not considered. Performance analysis of the proposed concept routes revealed that 344 the system with CaO/CaCO₃ storage has 12-13% points higher degree of energy 345 utilisation than the cryogenic O_2 storage system. Yet, this did not directly correlate to 346 system storage capacity. Estimation of energy density for both systems did not give 347 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 kWh_{th}/m³ in Case 3 and Case 6, 348 349 respectively, while for the latter it was 312.0 and 309.8 kWh_{el}/m³ in Case 2 and Case 350 5, respectively. However, direct comparison of these values cannot be used to 351 determine which system has higher energy storage capacity, due to different forms 352 of energy used in the energy density estimation. For cases with the cryogenic O_2 353 storage system, operation in the charging and discharging mode was found not to

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354 affect performance of the secondary steam cycle, compared to the system without 355 energy storage. It can be claimed that changes in net power output in these 356 operating modes were directly related to the amount of thermal energy input in the 357 boiler. By using the gross thermal efficiency of the system operating in the 358 discharging $(38.4\%_{HHV})$ and charging mode $(34.5\%_{HHV})$, the energy density of 359 cryogenic O₂ storage is recalculated to be 812.4-897.9kWh_{th}/m³, which is higher 360 than estimated values for the CaL and CaL-HYD with CaO/CaCO₃ storage. This 361 implies that to store the same amount of fuel energy, cryogenic O₂ storage would 362 require smaller volume than the CaO/CaCO₃ solids storage system, hence lower 363 capital costs.

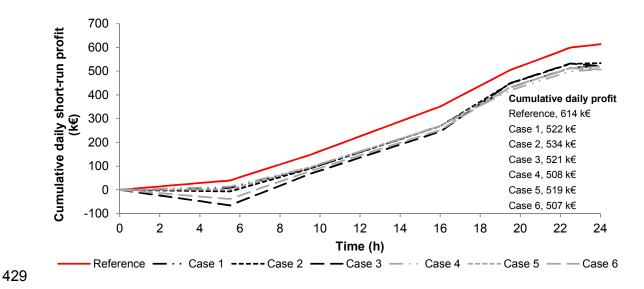
364 Incorporation of the sorbent regeneration step through hydration was found to result 365 in a 57.4% increase in energy density and 71.4% increase in specific energy. This 366 can be associated with the increase of average sorbent conversion in the carbonator 367 from 15.8% to 37.8%, resulting in a reduction of unconverted CaO in the stored 368 solids. As a result, the fraction of total thermal energy stored in the form of sensible 369 heat reduced from 39.0% (Case 3) to 24.9% (Case 6), revealing that increased 370 sorbent conversion promotes energy storage through chemical reaction. Also, it was 371 estimated here that, for each per cent of sorbent conversion improvement, energy 372 density and the specific energy can be increased by 8 kWh_{th}/m³ and 21.6 kJ_{th}/kg, 373 respectively. Therefore, not only would the systems including reactivation steps, 374 such as the investigated CaL-HYD system with CaO/CaCO₃ solids storage, or using 375 more efficient sorbents^{67,68}, require smaller reactors (hence lower capital cost), these 376 would also achieve a higher degree of energy utilisation. Moreover, the 377 CaO/Ca(OH)₂ step in the proposed concept was used to increase the energy storage 378 capacity of the CaO/CaCO₃ system by increasing the average conversion of the

379 sorbent, hence increasing the fraction of $CaCO_3$ in the stored solids. This approach differs from the system investigated by Criado et al.²¹, who proposed to use the 380 381 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 kWh_{th}/m³; 382 383 that is 57% higher than the energy density of the CaO/CaCO₃ system without 384 sorbent reactivation (307.2 kWh_{th}/m³) and 86% higher compared to the 385 CaO/Ca(OH)₂ system (260 kWh_{th}/m³) evaluated by Criado et al.²¹. As a result, 386 storage of the same amount of heat would require smaller volume in the CaO/CaCO₃ 387 system with sorbent reactivation through hydration compared to the $CaO/Ca(OH)_2$ 388 system, leading to lower capital cost of the entire CO_2 capture system with energy 389 storage, which is proven in the economic analysis presented below. The only 390 downside of using the CaL-HYD instead of the CaL system is marginally higher 391 values for CO₂ intensity factor in most of the cases investigated (Table 2). This is a 392 result of lower net power output for the regenerated system, caused by less high-393 grade heat available for recovery from the process streams.

394 Analysis of the hypothetical daily energy demand curve adapted from MacDowell and Shah⁵⁶ revealed that the daily average degree of energy utilisation in the 395 396 systems containing CaO/CaCO₃ storage (around 33%) and cryogenic O_2 storage 397 (around 30%) was higher than in systems without energy storage (29.4% for Case 1 398 and 29.7% for Case 4). This implies that the systems with energy storage capability 399 would result in higher degrees of energy utilisation. More importantly, as the periods 400 of charging and discharging were equal in the hypothetical operating schedule, the 401 average daily net thermal efficiency and the average daily CO_2 intensity factor were 402 not affected much compared to the system without energy storage. Finally, the 403 process evaluated in this study can conceptually be integrated with a solar power 404 plant or wind turbine farm to utilise excess energy for sorbent regeneration or for
405 liquid O₂ production, which can be utilised later to increase net thermal efficiency and
406 the degree of energy utilisation.

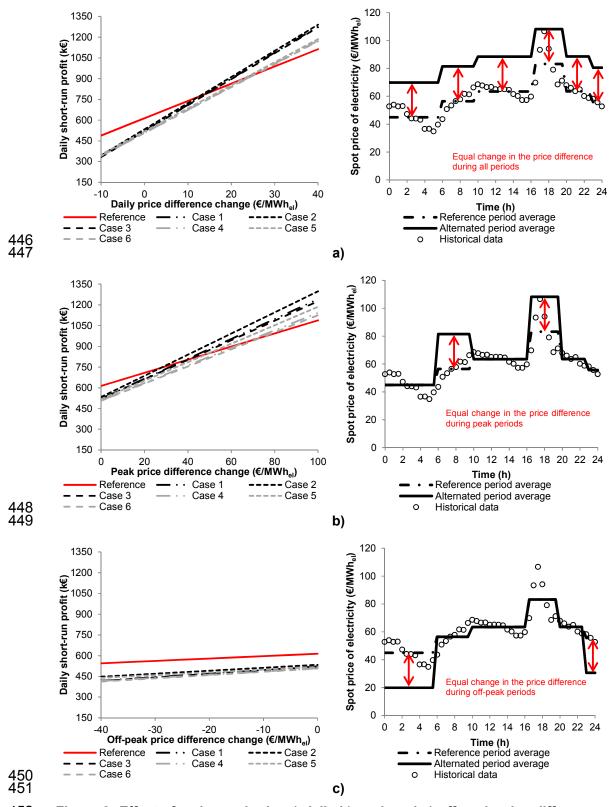
407 **3.3 Economic performance evaluation**

408 The specific capital costs of the reference coal-fired power plant, the CaL system 409 (Case 1) and the CaL-HYD system (Case 4) have been estimated to be 1206.5 410 €/kW_{el.gross}, 2981.6 €/kW_{el.gross} and 2776.4 €/kW_{el.gross}, respectively. This is in 411 agreement with other studies, which assumed the specific capital costs for coal-fired 412 power plants of 1200 €/kW_{el.cross} and for the CaL system of 2500-3000 €/kW_{el gross}^{25,52–54}. Moreover, specific capital cost of the integrated CaL and CaL-HYD 413 414 systems was estimated to be 2023.4 €/kW_{el,aross} and 1799.1 €/kW_{el,aross}, respectively, 415 which is close to the range 1250–1740 €/kW_{el.gross} estimated in other studies^{42,52,54}. A 416 slightly higher specific capital cost obtained in this study is caused by the assumption 417 of maximising heat recovery for power generation in the CaL and CaL-HYD plants. 418 Also, the higher energy density due to sorbent regeneration in Case 6, compared to 419 Case 3, reduces the specific capital cost of the entire system. An additional capital 420 cost associated with cryogenic O₂ storage and CaO/CaCO₃ solid storage increases 421 the specific captial cost of the integrated CaL system only by 0.6 €/kW_{el.gross} (Case 2) 422 and 2.3 €/kW_{el.gross} (Case 3), and of the CaL-HYD by 0.6 €/kW_{el.gross} (Case 5) and 1.4 423 €/kW_{el.gross} (Case 6). Hence, addition of energy storage capability does not change 424 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 425 426 avoided (Table 2). Therefore, the inherent energy storage ability of the CaL and CaL-427 HYD systems is available at a very low additional capital cost to the CO₂ capture 428 system.



430 Figure 2: Comparison of the daily short-run profit

431 Implementation of the CaL (Case 1) and the CaL-HYD (Case 4) plants for CO₂ 432 capture will reduce the daily short run profit by 15.0% and 17.2% (Figure 2), 433 respectively, regardless of the better thermodynamic performance of Case 4 434 identified previously. This is due to 7.2% lower net power output in Case 4 with 435 respect to Case 1 and thus lower expected revenue from electricity sales. 436 Furthermore, addition of the cryogenic O_2 storage was found to increase the daily 437 short-run profit of the CaL (Case 2) and CaL-HYD (Case 5) plants by 2.3% and 438 2.2%, respectively. Conversely, addition of the $CaO/CaCO_3$ solid storage system 439 was found to slightly reduce the daily short-run profit of the CaL (Case 3) and CaL-440 HYD (Case 6) by 0.1% and 0.2%, respectively; yet it will increase the plant flexibility. 441 Therefore, it appears as if the cryogenic O_2 storage system was more economically 442 substantiated. Yet, with the secondary steam cycle designed for normal operating 443 mode without energy storage, part-load opeartion of the calciner in discharging mode 444 reduces the amount of recoverable heat that results in reduction of net power output 445 in Case 3 and Case 6 by 0.2% and 0.3%, respectively.



452 Figure 3: Effect of a change in the a) daily b) peak and c) off-peak price difference on 453 daily short-run profit

454 As electricity prices are subject to annual fluctuations and to seasonal changes, the 455 effect of the price difference, which is defined as change of the electricity price with 456 respect to the reference value over the considered period, on the daily short-run 457 profit, is evaluated. On increasing the daily price difference (Figure 3a), it was found 458 that the concepts proposed in Case 2 and Case 3 would generate the same daily 459 short-run profit as the reference coal-fired power plant without CO₂ capture if the 460 daily price of electricity increases by 12.5 €/MWh_{el} and 14.8 €/MWh_{el} respectively, 461 while the CaL plant without energy storage will break even at the 14.4 €/MWh_{el} 462 increase in price difference. For the cases with sorbent regeneration through 463 hydration, higher daily short-run profit would be achieved on increased price 464 difference of 22.6–26.0 €/MWh_{el}, with the lowest increase associated to Case 5. 465 Moreover, increased peak price difference (Figure 3b) of more than 27.4 €/MWh_{el} 466 and 49.2 €/MWh_{el}, would make the CaL (Case 2) and the CaL-HYD (Case 5) more 467 economical than the reference coal-fired power plant. In addition, it was found that 468 reduction of off-peak prices (Figure 3c) will not bring any additional benefit, as the 469 loss of profit in the charging mode during low electricity price periods outweighs the 470 benefits of discharging mode operated at peak times with higher prices. 471 Nevertheless, this analysis revealed that the proposed concept, in particular the CaL 472 plant with cryogenic O_2 storage system (Case 2), could generate daily short-run 473 profit higher than the reference coal-fired power plant depending on the daily spot 474 prices of electricity. Further increase of the profit can be achieved on determination 475 of the optimal charging and discharging times, using optimisation methodology developed by Barbour et al.⁶⁹. 476

477 Finally, economic performance of the proposed concepts is highly dependent upon478 the economic climate, as it is predicted that the carbon tax may vary between 10–

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150 €/tCO₂^{70,71}. Moreover, economic performance will vary depending on whether 479 480 the produced CO_2 is transported and stored (the costs for which vary between 2.5– 36 €/tCO2^{62,72} depending on the CO2 transport method and storage location), or 481 used, for example, for enhanced oil recovery at a supply price of 12-15 \in /tCO₂^{73,74} 482 483 Figure 4a reveals that the daily short-run profit of the reference coal-fired power plant 484 is highly affected by increases in the carbon tax, while it is hardly affected in the 485 remaining cases with 90% CO₂ capture. Importantly, when the carbon tax exceeds 486 8.3 \in /tCO₂ for Case 2 (which is lower than the average price of 8.5 \in /tCO₂ for the European emission allowances in November 2015⁷⁵), and 11.1 €/tCO₂ for Case 6, 487 488 the proposed concepts become more profitable than the reference coal-fired power 489 plant. This implies that the proposed concept (Case 2) is already more profitable 490 than the reference coal-fired power plant without CO₂ capture.

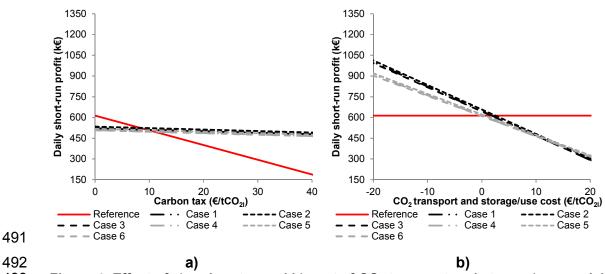


Figure 4: Effect of a) carbon tax and b) cost of CO₂ transport and storage/use on daily
short-run profit

Furthermore, it can be seen in Figure 4b that for the specific cost for CO_2 capture and transport of 2.5 \in /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 $€/tCO_2$, which corresponds to negative values in Figure 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.

503 4 CONCLUSIONS

In this study, a concept for the CO_2 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 involving the requirement of temporary CO_2 storage and sorbent deactivation were identified. These were resolved in the proposed system as the power plant acts as a permanent source of CO_2 and hydration was used as a means for sorbent regeneration.

511 Analysis of the process revealed that possible routes for energy storage include 512 $CaO/CaCO_3$ solids storage, $CaO/Ca(OH)_2$ solids storage and cryogenic O_2 storage 513 systems. The comparison of CaO/CaCO₃ and cryogenic O_2 storage systems 514 revealed that implementation of the latter would result in higher turndown of the 515 entire system and offer higher energy density, hence requiring lower capital cost. 516 Although performance of the integrated system with energy storage through a 517 CaO/Ca(OH)₂ loop was not evaluated here due to the lower energy density of such 518 system, the reactivation step was found critical in improving the performance of the 519 $CaO/CaCO_3$ energy storage system. Not only did it increase net thermal efficiency, it 520 increased the energy density by 57.4% and specific energy by 71.4% leading to a 521 higher degree of energy utilisation. Importantly, the proposed CaL-HYD system with

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522 CaO/CaCO₃ energy storage was found to offer 86% higher energy density than the 523 conventional CaO/Ca(OH)₂ energy storage system. An increase in the energy 524 density was found to be important from the economic perspective, as storing the 525 same amount of heat in a lower volume would result in the specific capital cost of the 526 CaL-HYD system lower by 6.8% compared to the CaL system.

527 The economic performance evaluation conducted in this section revealed that the 528 addition of energy storage capability to the CaL and the CaL-HYD plants for CO₂ 529 capture from the coal-fired power plant has a low impact on the total capital cost and 530 thus on the levelised cost of electricity and the cost of CO_2 avoided. Moreover, 531 analysis of the daily short-run profit revealed that Case 2, in which the CaL plant was 532 equipped with the cryogenic O₂ storage system, will reduce the daily short-run profit 533 of the coal-fired power plant by 15.0%. This case was found to have the lowest 534 impact on system profitability. Yet, the proposed concept (Case 2) can generate 535 higher profit when the carbon tax exceeds $8.3 \notin tCO_2$. As the price of the European 536 emission allowances in November 2015 was 8.5 \in /tCO₂, the proposed concept is 537 already more profitable than the reference coal-fired power plant without CO₂ 538 capture.

539 Further studies will aim to provide a detailed design of the proposed concepts of CO₂ 540 capture with inherent energy storage for decarbonisation and to optimise the 541 charging and discharging times to maximise the daily short-run profit. Also, the 542 applicability of the proposed concepts in natural gas combined cycle power plants 543 will be assessed. Finally, the inherent energy storage capability of other clean power 544 technologies, such as chemical looping combustion and oxy-combustion, will be 545 assessed.

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546 Nomenclature

AC	Cost of CO ₂ avoided	€/tCO ₂
С	Capital cost of calcium looping system	€/kW _{el}
C ₀	Reference capital cost of oxy-fuel circulating fluidised bed system	€/kW _{el}
CE	CO ₂ emission cost	€
CF	Capacity factor	-
CTS	CO ₂ transport and storage cost	€
D_V	Energy density	kWh/m ³
D_m	Specific energy	kJ/kg
e_{CO_2}	Specific CO ₂ emission	gCO ₂ /kWh _{el}
\dot{E}_{stored}	Rate of energy to storage	MW
FC	Fuel cost	€
FCF	Fixed charge factor	-
FOM	Fixed operating and maintenance cost	€
LCOE	Levelised cost of electricity	€/MWh
\dot{m}_{CO_2}	Rate of CO ₂ emission	kg/s
ṁ _{storage media}	Rate of media to storage	kg/s
R	Revenue from electricity sales	€
SC	Sorbent make-up cost	€
SCF	Specific fuel cost	€/MWh
SF,Q	Scaling factor for reactor heat input	-
SF,V	Scaling factor for reactor volume	-
SRP	Daily short run profit	€
TCR	Total capital requirement	€
\dot{Q}_0	Reference heat input	MW _{th}
\dot{Q}_{calc}	Heat input to the calciner	MW _{th}
\dot{Q}_{fuel}	Chemical energy input from fuel combustion	MW
$\dot{Q}_{storage,in}$	Heat input from CaO/CaCO ₃ solids storage	MW
$\dot{Q}_{storage,out}$	Heat stored through CaO/CaCO ₃ solids storage	MW
V	Volume of reactors	m ³
V ₀	Reference volume of reactor	m ³
VOM	Variable operating and maintenance cost	€/MWh
\dot{W}_{net}	Net power output of the integrated system	MW
Ŵ _{storage,in}	Electricity input from cryogenic O ₂ storage	MW
Ŵ _{storage,out}	Electricity stored through cryogenic O ₂ 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

547

548 **Abbreviations**

CaL	Calcium looping process
CaL-HYD	Calcium looping process with sorbent reactivation step through hydration
CCS	Carbon capture and storage

549

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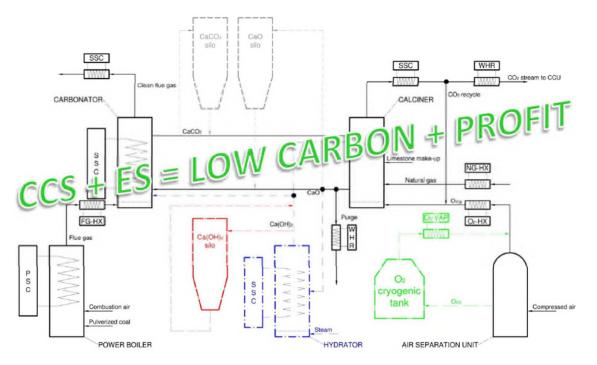
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Graphical Abstract

Carbon capture and storage (CCS) with energy storage (ES) systems increase flexibility and profitability of fossil-fuel-fired power systems.



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 challenge for 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 CO_2 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.