PAPER

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An air CO2 capture system based on the passive carbonation of large Ca(OH)2 structures

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Direct Air Capture (DAC) requires contacting a vast flow of air with a functional surface, which must be accommodated in a large and costly CO_2 capture device (*i.e.* at least 0.2–0.4 m^3 of the reactor volume per t_{CO_2} per year). We propose in this paper a low-cost alternative that involves contactor volumes that are one or two orders larger, but require only the passive CO_2 carbonation of purpose-built porous structures of $Ca(OH)_2$. Such low-cost materials can be manufactured from natural limestone and/or from recycled carbonated structures by using oxy-calcination technologies, and then simply stacked in such a way as to leave gaps for air to pass through. On the basis of an analysis of the rate controlling factors of the carbonation reaction, we employed as the structural element sintered $Ca(OH)_2$ plates with an area of 2 × 2 m^2 and 3 cm thick with a porosity of 0.5, which can be fully carbonated in about 6 months. The cost of CO_2 captured from air is estimated to be between 140 and 340 $ per t_{CO_2} depending on assumed cost values for fuel, land use, structural materials manufacture & transport, and process and project contingencies.

1. Introduction

Direct CO_2 capture from air (DAC), combined with permanent CO_2 storage, is one of the negative emission technologies (NETs) that may be needed in the future to limit global warming to 1.5 °C.[1,2] The first conceptual designs of DAC systems were proposed 20 years ago,[3] and research into novel concepts and materials is still continuing today.[3–22] The direct capture of CO_2 from air requires vast contacting surfaces with a great affinity and selectivity towards CO_2 (*i.e.* through a gas–liquid interface, the internal surface of a solid sorbent or through a membrane). Absorption methods generally use a strong alkaline aqueous solvent solution such as $Ca(OH)_2$,[3,10,11] $NaOH$[12–14] or KOH[15] that reacts with CO_2 to yield carbonated salts. Such alkaline solutions are corrosive, require costly gas–liquid contactors and require a large amount of energy for their regeneration.[8,16] Adsorbent solids with a high selectivity for CO_2, such as amines supported on porous materials, ion-exchange resins, metal–organic frameworks, zeolites or activated carbons, have also been explored.[8,9,17,18] Other gas–solid contact options are membranes combined with KOH solutions,[19] dispersed amines or ion-exchange resins.[20] An entirely different approach is to extract CO_2 from large flows of seawater by electrodialysis, after which the water is returned to the ocean to reabsorb more CO_2 from the air.[21,22]

Some DAC technologies are being tested on increasingly larger scales to assess their technical and economic viability.

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Carbon Engineering operates a pilot plant designed to capture around 300 t CO_2 per year using aqueous solutions of $NaOH$ or KOH coupled to a $Ca(OH)_2/CaCO_3$ loop.[15] The estimated cost of the CO_2 captured in this process is around 230 $ per ton of CO_2 (in the case of "no revenues" for the CO_2 captured) depending on the type of fuel used, the cost of electricity or the fate of the CO_2 (storage or fuel synthesis).[15] Climeworks has built a modular plant able to capture almost 1000 ton CO_2 per year using filters made up of porous granulates modified with amines. The process can deliver pure CO_2 for subsequent use in greenhouses or for geological storage/use at a cost of around 600 $ per tCO_2.[23] The largest DAC plant built to date, which is operated by Global Thermostat,[24] has been designed to capture around 4000 tCO_2 per year.[25] This facility is equipped with amine-based ceramic honeycombs able to produce a CO_2-rich gas of 98% purity.[26]

The references to costs noted above were provided by developers and they are subject to a great degree of uncertainty. As pointed out in several studies dedicated to the analysis of the viability and cost of advanced DAC systems,[27–34] there are strong arguments for claiming that the cost of CO_2 captured from air will be in the range of 500–1000 $ per tCO_2, which is about one order of magnitude higher than that of their counterpart technologies for CO_2 capture from flue gases. Particularly relevant to the discussion in this work is the cost of the enormous capture device required to achieve the close contact of highly diluted molecules of CO_2 in the air with the surface of the material with a high affinity and selectivity towards CO_2. Fig. 1 represents the mass balance for a generic air capture device where 1 $MtCO_2$ per year is captured. As can be seen, a huge flow of air (about 45 000
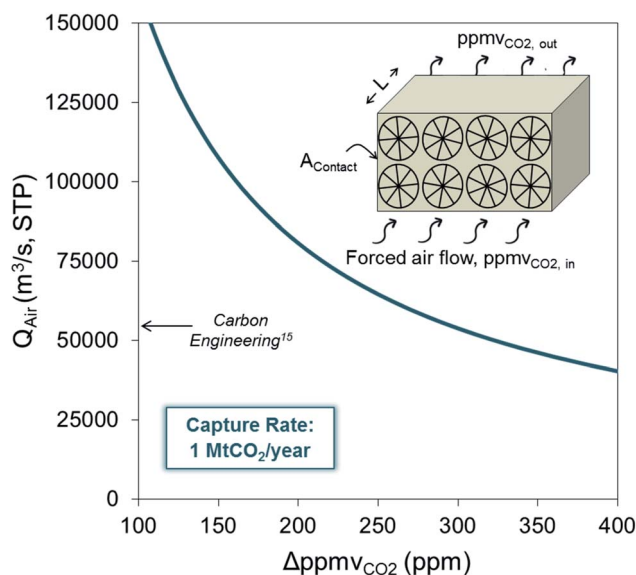
Fig. 1 Volumetric flow of air (Q_{air} in $m^3 \, s^{-1}$ STP) required to achieve a CO_2 capture rate of 1 $MtCO_2$ per year for a reduction in the CO_2 concentration of $\Delta ppmv_{CO_2}$ (=$ppmv_{CO_2 in}$ − $ppmv_{CO_2 out}$) in air as it circulates through the CO_2 capture system (arrow marks the particular design point of Carbon Engineering,[15] in the design of Climeworks[36] the air flows range between 67 000 and 150 000 $m^3 \, s^{-1}$).

$m^3 \, s^{-1}$ STP) must flow through the DAC device even if a large capture efficiency ($\Delta ppmv_{CO_2} \approx 400$ ppm between the inlet and the outlet will require deep reactors) is assumed. The reduction of the cross-sectional area of the contactor ($A_{contact}$) by increasing the air velocity will be limited by kinetic constraints at the gas/sorbent (or solvent) interface, by the pressure drop along the contactor, and by other phenomena such as water and solvent losses due to evaporation or entrainment.[35]

In an attempt to overcome the costly barrier entailed by the capture device in large scale DAC systems, we propose in this work a passive CO_2 capture system involving the carbonation of large purpose-built porous structures of low-cost $Ca(OH)_2$. A basic cost analysis, which is mainly based on relatively well-known costs of oxy-combustion and hydration processes for obtaining $Ca(OH)_2$ from $CaCO_3$, demonstrates the economic feasibility of the proposed DAC process for a capture target of 1 $MtCO_2$ per year.

2. Passive direct air capture process concept

Fig. 2 shows the general scheme of the concept investigated in this work. The design target is to estimate the necessary volume and cost of the porous passive carbonation infrastructure (represented as a blue box on the left-hand side of Fig. 2), which is aimed at capturing 1 $MtCO_2$ per year, and the size, cost and energy requirements of the units needed to manufacture such structures in a continuous manner.

It should be noted that although in Fig. 2 we use the expression "CO_2 for storage or use", the negative emission character of DAC technologies necessarily requires the

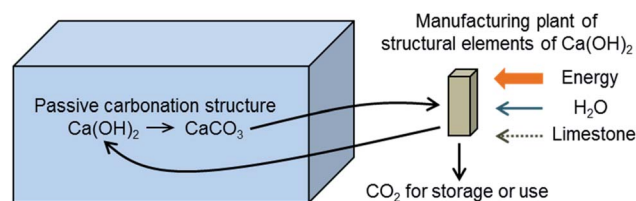Fig. 2 The concept of passive CO_2 capture from air by the carbonation of a suitable structure of solid $Ca(OH)_2$ exposed to ambient air.

permanent storage of CO_2, which must be added as a cost to account for avoided cost.[37] If CO_2 was used for the production of synthetic fuels with renewable energy, this would only lead to a maximum of 50% CO_2 captured,[38] which might be insufficient in future scenarios demanding negative emission technologies.[2]

The DAC concept shown in Fig. 2 is based on the known tendency of porous $Ca(OH)_2$ solids to slowly carbonate in contact with ambient air. Anecdotally, the passive carbonation of solid beds composed of $Ca(OH)_2$ is already commercially exploited for removing ambient CO_2 in order to preserve fruit in storage halls.[39,40] As a climate mitigation tool, the ambient carbonation of concrete and alkaline wastes obtained from steel, cement, lime and other solids containing free CaO and $Ca(OH)_2$ is another passive method for sequestering CO_2.[2,41–49] However, to our knowledge, a comprehensive design and cost analysis of a purpose-built passive DAC system, such as that represented in Fig. 2, has not yet been reported in the literature. As will be explained below in more detail, the very low specific cost and widespread geographical availability of natural limestone make it possible to manufacture derived calcium-based materials cheaply by means of calcination and hydration. In this study, porous $Ca(OH)_2$ has been chosen as the functional material for CO_2 capture due to its suitable mechanical stability when pelletized and favorable carbonation kinetics compared to CaO.[47,50,51]

The slow kinetics of large porous carbonating structures can be modelled[52] by accounting for the advance rate of a neat carbonation front according to Fick's law. In our case, where CO_2 diffuses through the porous $CaCO_3$ layer resulting from the carbonation of $Ca(OH)_2$, assuming that there is no expansion of the porous solid during carbonation (i.e. $\rho_{CaCO_3}(1 - \varepsilon_{CaCO_3}) = \rho_{Ca(OH)_2}(1 - \varepsilon_{Ca(OH)_2})$), the mass balance can be represented as follows:

$$\rho_{Ca(OH)_2}\left(1 - \varepsilon_{Ca(OH)_2}\right) X_{CaCO_3} \frac{dz_{CaCO_3}}{dt}$$
$$= -\frac{D_{CO_2}\left(1 - \rho_{Ca(OH)_2}\left(1 - \varepsilon_{Ca(OH)_2}\right)\middle/ \rho_{CaCO_3}\right) C_{CO_2}}{z_{CaCO_3}} \quad (1)$$

or in its integrated form:

$$z_{CaCO_3} = \sqrt{\frac{2 D_{CO_2}\left(1 - \rho_{Ca(OH)_2}\left(1 - \varepsilon_{Ca(OH)_2}\right)\middle/ \rho_{CaCO_3}\right) C_{CO_2} t}{\rho_{Ca(OH)_2}\left(1 - \varepsilon_{Ca(OH)_2}\right) X_{CaCO_3}}} \quad (2)$$

where z_{CaCO_3} is the thickness of the carbonated product layer (m), D_{CO_2} is the diffusion coefficient of CO_2 in the pores (m^2

s^{-1}), $\rho_{Ca(OH)_2}$ and ρ_{CaCO_3} are the molar densities (*i.e.* 29.9 and 27.1 kmol m^{-3}), respectively, $\varepsilon_{Ca(OH)_2}$ and ε_{CaCO_3} are the corresponding porosities, C_{CO_2} is the CO_2 concentration at the external surface of the porous solid (*i.e.* assuming zero the concentration of CO_2 in the reaction front) and X_{CaCO_3} is the maximum carbonation conversion of the $Ca(OH)_2$ material. The advance of the carbonation with time represented in eqn (2) has been experimentally validated in several studies on the carbonation of concrete on time scales of years to decades.[44,53–55]

Fig. 3 shows the evolution with time of the carbonated layer in a $Ca(OH)_2$-based solid according to eqn (2) for different values of $Ca(OH)_2$ solid porosity, $\varepsilon_{Ca(OH)_2}$, and assuming a ppmv$_{CO_2}$ gradient of 400 ppm ($C_{CO_2} = ppmv_{CO_2}/(RT \times 10^6)$ in mol m^{-3}) between the external surface and the carbonation front. As can be seen, individual $Ca(OH)_2$ solids of thickness 5 mm (assuming $\varepsilon_{Ca(OH)_2} = 0.5$) would require around 15 days to approach total carbonation. This timescale is consistent with the experimental results of Erans *et al.*,[47] who obtained carbonation conversions of around 70% after 12.5 days in particles of hydrated lime exposed to ambient air in layers of 5 mm thickness. Fig. 3 extends to an arbitrary scale of 1 year the results for thicker and less porous solids.

To take full advantage of such a slow passive carbonation process in a DAC system targeting 1 MtCO$_2$ per year, amounts of calcium-based sorbent on a megaton scale will be required. Such a carbonating material could take in principle many different forms, ranging from a vast number of pellets of several centimeters thick, simply dispersed on the ground, to purpose-designed porous structures/buildings for passive carbonation and eventual recycling. In the first case, the manufacture of non-recoverable $Ca(OH)_2$ pellets would involve the calcination of natural limestone to generate CaO (and eventually $Ca(OH)_2$) and a pure stream of CO_2 for permanent geological storage. Although there is evidence that soil liming provides nutrients for plant growth and contributes to acidity correction,[56] further experimental investigation would be required to determine the environmental implications of this option, and the possible constraints related to land availability. For this reason, the present work focuses on large-scale structural alternatives (*e.g.* stacked plates, beams *etc.*) that entail the recovery and regeneration of the carbonating solids once they have been completely carbonated. There are already commercial processes for manufacturing solid structures with a high porosity (as in the case of pervious concrete[57]) and high mechanical stability (provided by the incorporation of cement-type additives[58,59]). Consequently, details about the structural and mechanical properties of the porous solids have not been discussed in depth in this work. Similarly, the operations designed to produce CaO and a separated stream of pure CO_2 from limestone or carbonated solids are sufficiently well known from recent developments in clinker production with oxy-combustion[60,61] and CO_2 capture by Calcium Looping[62,63] and so will only be discussed in the cost section.

3. Estimation of the volume of passive carbonation structures

Of the wide range of possible arrangements for the $Ca(OH)_2$ structures, we have selected, for the purpose of illustration from the results of Fig. 3, flat plates 0.03 m thick with both sides exposed to the atmosphere and with a porosity $\varepsilon_{Ca(OH)_2} = 0.5$ that can achieve total carbonation in approximately 6 months. An external exposed area of 50.7×10^6 m^2 of such solids would be needed to capture 1 MtCO$_2$ per year or, in other words, 761 000 m^3 of porous plates. With a specific minimum capture contactor volume of almost 0.8 m^3 per tCO$_2$ per year, this configuration is already 2–4 times larger than other competing air capture devices noted in the Introduction. However, it is possible to envisage recycling schemes (analogous to those already in operation for glass, metals, plastics *etc.*) promoting the deployment of disperse, but very large passive carbonation systems. In societies aiming at zero emission objectives, a person could reduce by 1 tCO$_2$ per year his per capita emissions by participating in such a recycling scheme, if he/she were responsible for maintaining exposed to the atmosphere (*i.e.* on a house, in a garden, terrace or on the roof of a building) 25.4 m^2 of plates exposed on both sides, and replaced approximately every 6 months. Much smaller surfaces or volumes of solids could also be considered if the thicknesses of the plates were reduced and the frequency of recycling was increased (see Fig. 3).

For the case of larger and centralized schemes, an important constraint affecting these carbonating structures is that they must be arranged in such a way that a continuous and renovated flow of air is in contact with the structure. To ensure this, further assumptions on the dimensions and the way the plates are stacked, including additional resistances other than those
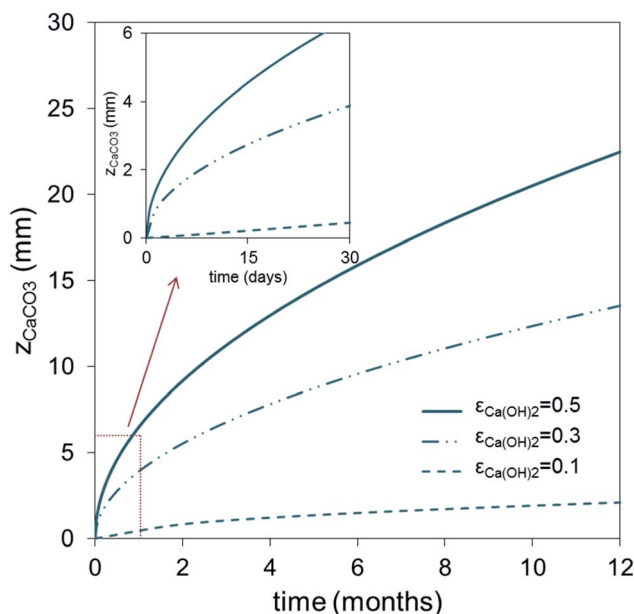

Fig. 3 Evolution with time of the carbonated layer (z_{CaCO_3}) in carbonated solids according to eqn (2), for different porosities ($\varepsilon_{Ca(OH)_2}$) and assuming a CO_2 concentration gradient of 400 ppmv at 20 °C.

strictly related to the carbonation process inside the porous solids, must be taken into account (see Fig. 4).

The volume of the overall structure increases as additional free space is required to facilitate the access of CO_2 from air to the external surface of each plate. Although the design decisions may differ considerably depending on local conditions (*i.e.* availability of wind and other atmospheric convective phenomena), the target is to design structures that are sufficiently expanded to ensure a high concentration of CO_2 on the external surface of each individual plate (large dot in Fig. 4). The volume occupied by the stacks of plates will be $V_{stack} = V_{carb}/(1 - \varepsilon_2)$, where ε_2 is the volume fraction of the plates. In an oversimplification, it is assumed that CO_2 is transported horizontally by wind velocity (u_1) to the carbonating stacks. The actual velocity of the air circulating between the plates (u_2) is given by the net dynamic pressure exerted by the wind (at a velocity u_1) on the surface of the structure. This can be calculated by means of Bernoulli's equation and taking into account the friction factor and the geometry of the channel.[64] With the aim of achieving a value of $u_2 > 0.5u_1$, we have chosen squares that measure 2×2 m^2, arranged horizontally one on top of the other in the form of open structures 10 m high, with a space in between each plate that is twice their thickness (*i.e.* $\varepsilon_2 = 0.67$). With these dimensions, and a front open stack cross-section of 0.8 Mm^2 ($=L_{plate}H\varepsilon_2 N_{stacks}$), wind velocities u_1 below 0.8 m s^{-1} (*i.e.* 3 km h^{-1}) are high enough to sustain an overall carbonation process controlled by Fick's diffusion as in Fig. 4 (since ppmv$_3$ − ppmv$_0$ will exceed 50 ppmv$_{CO_2}$ for $u_1 > 0.8$ m s^{-1}). In many open field regions, average wind velocities of between 3 and 7 m s^{-1} are common.[65,66] This will ensure a sufficient supply of air to the carbonating surfaces (except at the very beginning of the carbonation period, where z_{CaCO_3} is close to zero and the rate of carbonation may be limited by the value of u_1). Therefore, assuming a utilization factor for the carbonation structures of 1,

a mass of 0.84 Mton of $Ca(OH)_2$ will need to be replaced every 6 months to remove from air 1 Mton of CO_2 per year. This amount of material will occupy a volume of about 761 000 m^3 of porous plates, which is equivalent to around 2.3 Mm^3 of open stacks. Finally, when the stacked plates are arranged in a specially assigned open field (left hand side of Fig. 4), an extra-large volume of the overall structure ($V_{structure} = V_{carb}/((1 - \varepsilon_2)(1 - \varepsilon_1))$) will be needed to take into account the resistance linked to Eddy diffusion, which is perceptible in large CO_2 sink areas, such as forests, where variations in the CO_2 concentration of between 25 and 35 ppm occur.[67,68] A value for ε_1 of 0.95 may be required to ensure that there is sufficient separation between the stacks to allow isolated roughness flow.[69] This will ensure the continuous renovation of CO_2 in the vicinity of the stacked plates. The DAC system will therefore need to occupy a total volume of 45.7 Mm^3 which means 4.6 Mm^2 of land use when considering the height of stacked plates (*i.e.* $H = 10$ m).

To sum up, the specific contactor volumes necessary for the proposed passive air capture (which will range from 2.3 to 45.7 m^3 per tCO$_2$ per year) for highly dispersed stacked structures and for a purpose-designed DAC field, respectively, will be between one and two orders of magnitude higher than the values reported for the competing DAC systems referred to in the Introduction. However, as it will be claimed in the next section, this DAC scheme could be sufficiently competitive in the context of a carbon-constrained world.

4. The cost of the full DAC system

To estimate the cost of capturing and removing from the atmosphere a tonne of CO_2 using the full DAC system shown in Fig. 2 we consider the following three main cost elements:

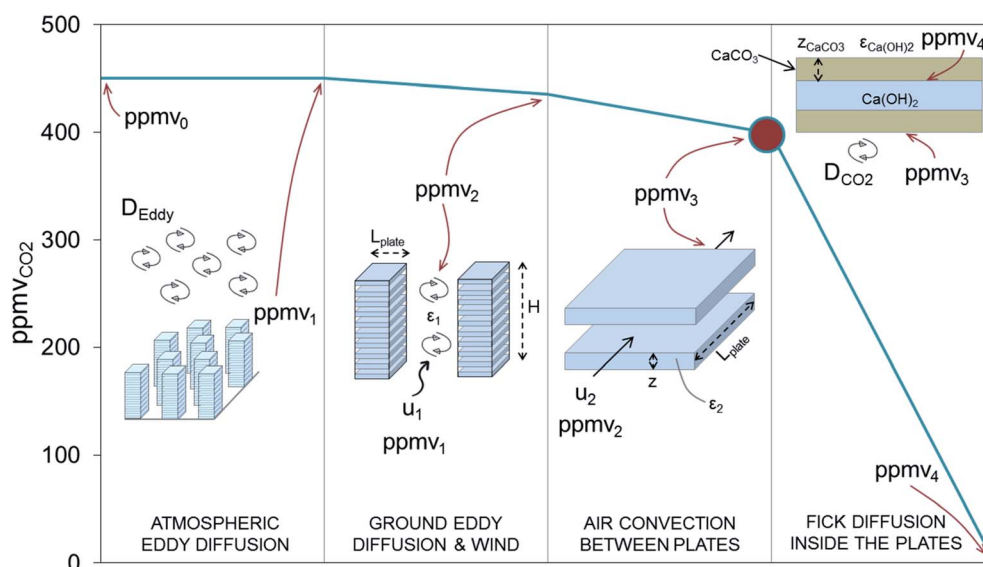(i) The specific cost of capturing and storing CO_2 from the calcination of $CaCO_3$, which includes the total capital

Fig. 4 Evolution of the CO_2 concentration in air through the different CO_2 transport/diffusion stages, taking place at increasing scales from right to left: interior of a plate, individual plates, stacked plates and numerous stacked plates arranged in a field.

requirements (TCRs) for the purchase of the oxy-combustion equipment for calcination, energy recovery and compression and purification, all amortized at a certain capital charge factor (CCF). Also, following the standards in major CO_2 capture and storage (CCS) cost studies[37,70] the CCS cost includes terms for the fixed and variable operating cost (FOM and VOM), the fuel cost (FC), and the cost of transport and permanent geological storage of CO_2 ($C_{CO_2\ T\&S}$).

(ii) The specific cost linked to the handling and transport of structural elements ($C_{handling}$) as well as their manufacturing cost ($C_{manufacture}$) from CaO generated in (i) and water.

(iii) The specific cost of the land occupied by the infra-structure ($V_{structure}/H)C_{land}$, which is amortized as other capital requirements in (i).

Therefore:

$$\text{Cost per tCO}_2 \text{ captured} = \left[\frac{\text{TCR} \times \text{CCF} + \text{FOM}}{\text{CF} \times t_{CO_2}} + \text{VOM} \right.$$
$$\times 8760 \times \text{MW}_{th}/t_{CO_2} + \text{FC}$$
$$\times \text{GJ}/t_{CO_2} + C_{CO_2\ T\&S} \left] + \left[\right. C_{handling} \right.$$
$$\times M_{CaCO_3}/M_{CO_2} + C_{manufacture}$$
$$\times M_{Ca(OH)_2}/M_{CO_2} \left] + \right. \left[C_{land} \right.$$
$$\times (V_{structure}/H) \times \text{CCF}/t_{CO_2} \right]$$

$$(3)$$

To gain transparency in the cost analysis carried out in this work, a set of minimum and maximum values of the specific cost of each cost component is adopted and justified below using references available in the literature, together with contingencies and other assumptions.

The specific cost of producing pure CO_2 and CaO from $CaCO_3$, and then transporting and storing geologically the captured CO_2, can be estimated from a basic simulation of the required oxy-combustion process (see Fig. 5). Oxy-fired Circulating Fluidized Bed (CFB) technology has been chosen for the calcination operation, due to the substantial amount of information available in the literature on the cost of these systems for power generation,[63,71] Calcium Looping processes[62] or even cement plants.[61,72] However, other types of calciners (*e.g.* rotary kilns, entrained beds *etc.*) with CO_2 capture capability and different energy sources (*i.e.* gas, biomass, H_2 or solar energy) may be available for consideration in the future.

Fig. 5 represents a basic scheme of the proposed process. A flow of 72 kg s^{-1} of $CaCO_3$ needs to be calcined to achieve the DAC capture target of 1 MtCO$_2$ per year. Following the cost estimation method reported by Guandalini *et al.*,[63] mass and energy balances have been solved, indicating energy requirements for the oxy-calcination operation of 225 MW$_{th}$ (equivalent to 7.1 GJ per tCO$_2$ captured from air), assuming calcination at 900 °C, no-preheating of the inlet streams, biomass as a fuel (assuming a LHV value of 20 MJ kg^{-1} and 41.4%C for these calculations) burnt with 10 vol% of excess O_2, including the use of the Air Separation Unit, ASU, and Compression and Purification Unit, CPU, of 210 kW h$_e$ per tO$_2$ and 90 kW h$_e$ per tCO$_2$,
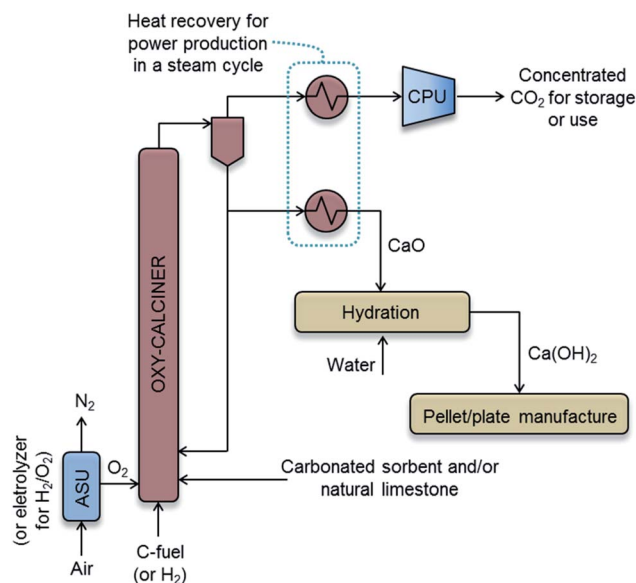

Fig. 5 General process scheme of the oxy-fired CFB calcination system and Ca(OH)$_2$ manufacture.

respectively, and including also the consumption of about 2.3% fuel input in the auxiliary units.[63] The waste heat extracted from the outlet CaO and CO_2-rich gas streams (assumed to be at 900 °C) drives a stream cycle (not shown in Fig. 5 for the sake of simplicity) that generates 34 MW$_e$, which is a sufficient power to cover the electricity consumed in the ASU, CPU and other auxiliary units. In other words, the system shown in Fig. 5 is designed as a small oxy-fired combustion boiler where parasitic power losses (mainly ASU and CPU electricity consumption) equal the gross power output, so that no electric power is exported or imported to run the system.

Reference costs for a typical oxy-combustion plant have been taken from Guandalini *et al.*[63] and have been updated assuming an inflation rate of 1.7%/annually.[73] The specific cost of a reference oxy-combustion plant of 550 MW$_e$ (or 1697 MW$_{th}$) has been estimated to be about 4349 $ per kW$_e$ (or 1626 $ per kW$_{th}$), which results in a total capital requirement (TCR) in 2011 USD of 2392 M$ (ref. 63) including process and project contingencies. Thus, when a scale factor of 0.7 is applied and the cost is updated to 2020 USD, the TCR for the proposed oxy-combustion system of 225 MW$_{th}$ amounts to 671 M$. Assuming a capital charge factor (CCF) of 10.88% per year (ref. 63) and a capacity factor (CF) of 0.9, the CAPEX of the oxy-combustion plant amounts to 81 $ per tCO$_2$. Similarly and by comparison with the cost reported by Guandalini *et al.*,[63] a reference cost of 12 M$ per year has been calculated for fixed operation costs (FOM) by considering a scale factor of 0.65 and 1 for the labor and property taxed and insurance terms, respectively, resulting in a OPEX fixed of 14 $ per tCO$_2$. The variable costs (VOM) reported, without including the limestone cost, are about 9 $ per MW h$_e$,[63] resulting in about 3 $ per MW h$_{th}$ when the electric efficiency and the inflation rate are applied. Considering that for a capture target of 1 MtCO$_2$ per year are required 225 MW$_{th}$, a variable OPEX of 7 $ per tCO$_2$ has been calculated.

Table 1 Summary of the minimum and maximum costs of the main components of a passive CO_2 capture process, following the notation of eqn (3). All costs in 2020 US dollars

Cost component	Reference values				Cost CO_2 captured ($ per tCO_2)		%Total min–max
		Min	Max	Units	Min	Max	
Oxy-combustion plant CAPEX	TCR	671	805	M$	81	113	59–33
Oxy-combustion plant OPEX fixed	FOM	12	15	M$ per year	14	20	10–6
Oxy-combustion plant OPEX variable	VOM	3	4	$ per MW h_{th}	7	10	5–3
Fuel	FC	2	10	$ per GJ	14	71	10–21
CO_2 transport & storage	$C_{CO_2 \text{ T&S}}$	5	15	$ per tCO_2	5	15	4–4
Handling & transport of structural elements	$C_{handling}$	4	25	$ per $tCaCO_3$	9	57	6–17
Pellets/plates manufacture	$C_{manufacture}$	5	30	$ per $tCa(OH)_2$	8	50	6–15
Land use	C_{land}	0	10	$ per m^2	0	5	0–1
Total cost of CO_2 captured in $ per tCO_2					**138**	**341**	

Contingency factors as high as 40–60% are used to account for cost uncertainties in other DAC systems.[29,35] We consider for this purpose, a maximum contingency factor of 40%, as the CAPEX and OPEX cost data used from Guandalini *et al.*[63] already include standard process and project contingencies and there is direct industrial experience in oxy-calcination, solids handling and all the energy recovery operations represented in Fig. 5. Note that the CAPEX range (min value of 81 and max 113 $ per tCO_2 in Table 1) can be considered conservative cost estimations compared to the CAPEX of the oxy-combustion calciner reported by Keith *et al.*[15] claiming a cost at around 36 $ per tCO_2.

On the other hand, different fuels can be considered to cover the thermal requirements in the oxy-calciner and their cost will vary depending on their type and resource availability. Thus a fuel cost (FC) of between 2 and 10 $ per GJ has been taken as reference numbers, resulting in 14 to 71 $ per tCO_2 when considering that 7.1 GJ per ton of CO_2 captured from air are required in the subsystem of Fig. 5. Finally for the cost of the CO_2 transport and storage ($C_{CO_2 \text{ T&S}}$), 5 and 15 $ per tCO_2 have been taken to be consistent with published values.[70]

Regarding those cost elements in Table 1 and eqn (3) linked to land use and handling and manufacture of structural elements, the similarity with other existing unit operations facilitates cost estimations. The US average market value of crushed limestone is about 8.4 $ per t.[74] Thus the minimum cost has been assumed as half the market value, accounting for a favourable scenario where $CaCO_3$ is provided directly from the quarry with a very short distance transport. Meanwhile, the maximum value for the sensitivity analysis is arbitrarily taken by multiplying by three this figure to 25 $ per t of carbonated material (or 57 $ per tCO_2 captured from air).

Regarding the manufacture of the $Ca(OH)_2$ structural elements or pellets, the cost is subjected to larger uncertainties (*e.g.* small pellets with modest mechanical stability or large porous structures with improved mechanical properties or other design characteristics). A wide cost range from 5 to 30 $ per ton of $Ca(OH)_2$ has been adopted as the manufacture cost ($C_{manufacture}$), which results in 8 to 50 $ per tCO_2.

Finally, since there are no special demands on the land to be used for the infrastructures, other than that of facilitating the exposure of a large volume of solids to the atmosphere, the minimum capital cost linked to land use can be assumed as zero. However, for more conservative scenarios, a royalty of C_{land} = 10 $ per m^2 has been taken as the upper bound, consistent with the land cost of extensive energy infrastructures in the US.[75] This results only in an increase of 5 $ per tCO_2 when the same CCF as for the oxy-combustion plant is applied.

As can be seen in Table 1, the cost of the passive CO_2 capture process from air will be between 140 and 340 $ per tCO_2. As expected, the main cost driver of the DAC system is the capture and storage of CO_2 generated from the oxy-combustion of $CaCO_3$, with a contribution to the total cost of between 67 and 88%. Thus, since there is substantial industrial experience in the operations involved in such operation, the system investigated in this work will be relatively insensitive to additional cost contingencies when compared to other proposed DAC systems involving large contactors for the CO_2 capture as discussed in Fig. 1.

5. Conclusions

The cost of Direct Air Capture (DAC) technologies is strongly influenced by the capital cost of a large device (*i.e.* about 0.2–0.4 m^3 of the reactor volume per tCO_2 per year) that is needed to bring a vast flow of air into contact with a functional material with an affinity for CO_2. In an attempt to overcome this cost barrier, we have proposed design rules for a large-scale, purpose-built, passive carbonation system made up of porous structures of $Ca(OH)_2$ (*i.e.* plates or pellets with a thickness of 0.03 m and a porosity of 0.5). A DAC system of this type could adopt different forms of viability: from widely dispersed approaches involving the irreversible dissemination of $Ca(OH)_2$ pellets in the soil, or the public recycling of pellets/plates, to centralized schemes where vast structures of elements are stacked up in open fields. In the latter case, the volume of the structures must be able to increase (to up to 46 m^3 per tCO_2 per year) to ensure that there are enough wind and natural

atmospheric convection currents to sustain a given average rate of carbonation. However, the key advantage of the proposed scheme is that the required materials are available at an extremely low cost (*i.e.* limestone and/or recycled carbonated structures from the DAC scheme) and that the technology required to manufacture them, while generating a pure stream of CO_2, is already available (oxy-fuel combustion technologies for $CaCO_3$ calcination). The overall cost estimation of this DAC scheme is between 140 and 340 $ per tCO_2 captured, which is considerably less (subject to contingencies) than that of other competing DAC technologies.

Nomenclature

$A_{contact}$	Air contactor cross-sectional area perpendicular to the air flow, m^2
CCF	Capital charge factor, per year
C_{CO_2}	CO_2 concentration at the external surface of the porous solid, mol m^{-3}
$C_{CO_2\ T\&S}$	Cost of transport and permanent geological storage of CO_2, $ per tCO_2
CF	Capacity factor
$C_{handling}$	Specific cost linked to the handling and transport of carbonated structural elements, $ per $tCaCO_3$
C_{land}	Specific cost linked to the land use occupied by the DAC system, $ m^{-2}
$C_{manufacture}$	Specific cost linked to manufacturing pellets/plates, $ per $tCa(OH)_2$
D_{CO_2}	Diffusion coefficient of CO_2, $m^2\ s^{-1}$
D_{Eddy}	Eddy diffusion coefficient, $m^2\ s^{-1}$
FC	Fuel cost, $ per GJ
FOM	Fixed operation costs of the oxy-combustion plant, M$ per year
H	Height of the stacked plates, m
LHV	Lower heating value of the fuel used in oxy-combustion, MJ kg^{-1}
L_{plate}	Length of the plates, m
M_i	Molecular weight of the compound i, kg $kmol^{-1}$
MW_{th}	Required thermal input to the oxy-combustion plant, MW_{th}
N_{stacks}	Number of stacks in the DAC system
$ppmv_0$	Atmospheric CO_2 concentration, ppm
$ppmv_1$	CO_2 concentration in the vicinity of the overall structure, ppm
$ppmv_2$	CO_2 concentration outside the stacked plates, ppm
$ppmv_3$	CO_2 concentration at the surface of the plates, ppm
$ppmv_4$	CO_2 concentration in the carbonation reaction front in the interior of the porous plates or pellets, ppm
Q_{air}	Volumetric air flow, $m^3\ s^{-1}$ STP
R	Universal gas constant, atm L $mol^{-1}\ K^{-1}$
T	Temperature, K
t_{CO_2}	CO_2 capture rate, $MtonCO_2$ per year
TCR	Total capital requirements of the oxy-combustion plant, M$
u_1	Wind velocity outside the stacked plates, m s^{-1}
u_2	Velocity of air moving in the space between the plates, m s^{-1}
VOM	Variable operation costs, $ per MW h_{th}
V_{stack}	Volume occupied by the stacks of plates, m^3
$V_{structure}$	Volume of the overall DAC structures
X_{CaCO_3}	Maximum carbonation conversion of the $Ca(OH)_2$ material
z	Flat plate thickness, m
z_{CaCO_3}	Thickness of the carbonated product layer, m
ε_1	Volume fraction between stacks
ε_2	Volume fraction between plates
$\varepsilon_{Ca(OH)_2}$	Porosity of the $Ca(OH)_2$ layer
ε_{CaCO_3}	Porosity of the $CaCO_3$ layer
$\Delta ppmv_{CO_2}$	Reduction in the CO_2 concentration, ppm
$\rho_{Ca(OH)_2}$	$Ca(OH)_2$ molar density, mol m^{-3}
ρ_{CaCO_3}	$CaCO_3$ molar density, mol m^{-3}

Conflict of interest

There are no conflicts of interest to declare.

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