

Process design and energy requirements for the capture of carbon dioxide from air

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Abstract

A process to capture carbon dioxide from air to reduce its atmospheric concentration and to mitigate climate change is studied. It is based on the absorption of carbon dioxide in a sodium hydroxide solution, its precipitation as calcium carbonate, and its release as pure gas stream through oxy-fuel calcination. The process utilizes existing commercial technologies wherever possible, particularly in the case of the absorber, whose design is carried out in detail. The analysis allows deriving material and energy balances for the whole process and determining energy demands that can be used for a technical, economical, and environmental feasibility evaluation of the technology. In particular, it indicates that the real specific energy demand is larger than the heat released to emit the same amount of CO₂ by the combustion of coal, and smaller than that of methane. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

The atmospheric concentration of carbon dioxide, i.e. the most critical greenhouse gas, has increased from 280 ppm in the pre-industrial age to more than 370 ppm now, and is expected to increase above 500 ppm by the end of this century [1]. This is recognized to be due to anthropogenic activities, particularly burning of fossil fuels and land-use changes, and has been accompanied by a corresponding increase of the earth's average temperature. According to all socio-economical-technological models, such global warming is predicted to continue and expected to cause adverse impacts on the socio-economic sectors, the ecological systems, and the human health.

Instruments to reduce greenhouse gas emissions are being debated worldwide, and some legislative actions are being taken. These include the Kyoto protocol, entered into force after Russia's signature in October 2004, and the European Union's greenhouse gas emission trading scheme started on January 1st, 2005.

Present strategies rely on improving the efficiency in energy use, on reducing fossil fuel consumption, and on using renewable energy sources or nuclear power plants. However, the continuing increase of the world population together with the concomitant growth in energy consumption and the industrial development in developing countries like China and India conflict with the efforts to reduce greenhouse gas emissions. Moreover, the inertia of the “spaceship earth” will lead to much higher final CO₂ concentrations in the atmosphere, average temperatures and sea levels than those reached at the time when the CO₂ emissions peak [1].

Thus, the inevitable way to keep within this century the overall CO₂ load of the atmosphere and hydrosphere below unbearable levels is that of complementing emission reduction efforts by techniques to capture CO₂ from point sources before emission or to capture it from the air after emission, and to store it permanently outside the atmosphere. Carbon dioxide capture and storage (CCS) does not exempt us from developing a sustainable and efficient energy system fuelled dominantly by renewable energy sources, but it is the only possible bridge technology towards it.

There exist several approaches to capture CO₂. Some rely on capturing CO₂ close to the source of emissions, other rely on recapturing CO₂ out of the atmosphere, possibly long after its

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emissions. Some need to make use of new technologies, yet to be engineered; Others rely on exploiting and managing natural mechanisms or some combination of both.

To capture CO₂ from large point sources, three engineering techniques are pursued. The first is an end-of-pipe approach whereby carbon dioxide is recovered from the flue gas by scrubbing it with an aqueous solution, e.g. of amines (post-combustion capture). The second approach is called pre-combustion, and is associated to the use of hydrogen as an energy carrier; in this case the fossil fuel is converted into hydrogen through reforming and water gas shift reaction, and CO₂ is recovered from the product stream. The last approach uses oxygen instead of air in the burner (oxy-fuel combustion), and requires air separation upstream of combustion. The post-combustion capture is the technology closest to implementation, whereas the other options require more research to reduce costs.

Once captured in gas form and compressed, carbon dioxide can be transported to storage sites, which could be a suitable geological formation. Ocean storage is also discussed, yet faces strong opposition because of ecological concerns. Several geological storage solutions are being tested in different countries in the world. Suitable sites are deep saline aquifers, where CO₂ slowly dissolves and reacts with the cap rock (see the Sleipner project in Norway [2]), oil reservoirs, where pumping CO₂ can enhance oil or gas production (the so called EOR, enhanced oil recovery), as for instance at Weyburn in Canada [2], or in unminable coal seams, where CO₂ displaces methane (ECBM, or enhanced coal bed methane recovery) and remains adsorbed on the coal bed (see the EU project Recopol) [2]. Another approach aims at mimicking natural weathering, by letting CO₂ react fast enough with natural silicates, e.g. ophiolite rocks, or alkaline industrial wastes to be fixed into carbonates [2].

It is well known that large point sources contribute to no more than 50% of the overall carbon dioxide emissions, the rest being due to distributed emissions, mainly transportation and heating systems. The above mentioned capture strategies do not address the distributed emissions. For this reason there is an increasing interest in exploring the possibility of extracting carbon dioxide directly from air, as vegetation does with the help of solar irradiation. Such an approach, if feasible, would have a number of significant advantages, namely that distributed emissions would be addressed, that capture and sequestration could be carried out in the same location by exploiting the earth atmosphere for the transport of carbon dioxide to the capture site, that it would allow for a direct reduction of carbon dioxide concentration in the atmosphere if a critical level were overcome.

Recapturing CO₂ from air after emission could be considered as a “visionary” approach. This is in fact the only technique that can be still operational to reduce the atmospheric load long after the peak in emissions, i.e. when atmospheric CO₂ concentrations are expected to be still growing due to the inertia in the climate system. In other words, even if we should be able to develop technologies for a near zero-emission energy system fuelled by renewable energies in the mid-term (2100), it is likely that the CO₂ levels and the temperature reached at that point will already be dangerously large. Moreover, the envisaged

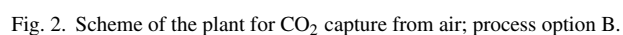
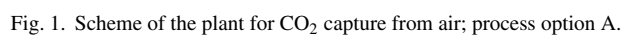
new energy systems with minimum greenhouse gas emissions will allow deploying technologies to recapture CO₂ from the atmosphere, which appear today to be too energy intensive.

A process for the capture of carbon dioxide from air has been proposed by Lackner et al. [3,4], whereby carbon dioxide is absorbed by a sodium hydroxide solution forming sodium carbonate that is then precipitated as calcium carbonate by adding calcium hydroxide, obtained by slaking of quicklime. Thereafter the precipitate is conveyed to a calciner, where quicklime and carbon dioxide are obtained, whereas the sodium hydroxide containing mother liquor is recycled back to the absorption column. Such proposition has initiated a debate between advocates of CO₂ capture from air insisting on its feasibility [4] and sceptics due to its excessive energetic costs [5]. However, most of the discussion has been based on conceptual estimates of costs and energy penalties rather than on a straightforward design of the proposed process based on mass and energy balances.

The aim of this work is to provide such a design, namely the design of a system for carbon dioxide capture from air and compression, which is based on the scheme of Lackner and utilizes existing technologies for most process steps, namely CO₂ absorption, carbonate precipitation, sludge dewatering train, calcination, slaking, oxygen purification, and CO₂ compression. In other words, we intend to provide a baseline design that can be used for economical and energetic evaluations that will have to be based on socio-economical and technological scenarios, but are beyond the scope of this paper.

2. Process design criteria

The process, whose scheme is reported in Figs. 1 and 2 in two different implementations as discussed later, aims at capturing and concentrating carbon dioxide from air. The objective of such a process is of course CO₂ capture with the best possible economics, keeping in mind that in the context of and at the scale of interest for carbon dioxide capture and storage the minimization of the consumption of energy and of other chemicals is of paramount importance. A thorough discussion about the general design criteria adopted for carbon dioxide absorption and concentration is presented here, whereas the detailed design and the relevant mass and energy balances for each unit operation are reported in Section 3. It is worth noting that the efficiency of all energy transfer operations is assumed to be unitary, hence the calculated energy requirements represent lower-bound estimates of the values of an industrial plant. Based on available references, the energy requirements given in this work should be increased, accounting at least for 70% efficiency for pumps and compressors [6] and an average 90% efficiency for heat transfer units [7]. Nevertheless, a more accurate and definitive evaluation of the actual energy requirements can be done only after performing the thermal rating of heat transfer equipment and the design or selection of pumps and compressors. For the same reasons it is not possible to price the equipment, hence to estimate the capital cost accurately enough to include it in our analysis. Therefore, in the following we will confine our study to the energy requirements, which are related to the running costs of the process.



2.1. Capturing carbon dioxide

There are several commercial processes that capture CO₂ from a gas stream. Among these, absorption of carbon dioxide in MEA (mono-ethanolamine) solutions is applied at moderate CO₂ partial pressures, typically encountered in combustion flue gases. On the contrary, the Selexol solvent is preferred in Integrated Gasification Combined Cycle (IGCC) power plants, where CO₂ is captured from a syngas at rather high partial pressure. Neither process can be applied for CO₂ capture from air, whereas an aqueous solution of calcium hydroxide might be considered, since this solvent would effectively enhance absorption of CO₂ by converting it readily to carbonate ions. The main drawback of such absorption process would be the low solubility of calcium carbonate that would cause scaling on the surfaces of the gas–liquid contactor. In order to overcome this problem, and following the approach discussed by Greenwood and Pearce [8] with reference to the air scrubbing process to be positioned upstream low temperature air separation plants, the use of sodium hydroxide instead of calcium hydroxide has been proposed, since the enhancement of CO₂ absorption is still effective, but no scaling occurs due to the high solubility of sodium carbonate [4]. Therefore, with reference to the process scheme shown in Fig. 1 (and 2 also, since this part of the process is in common), carbon dioxide in air (stream 1A) is conveyed to an absorption column (Unit 1) where it is absorbed into a sodium hydroxide solution (stream 1C), thus yielding a stream containing carbon dioxide mainly in the form of carbonate ions (stream 1D).

The main problems in designing such absorption column arise from the very low concentration of CO₂ in air and the large throughput required in order to make such process meaningful in view of capturing atmospheric CO₂ to a meaningful extent. These considerations have induced scientists to claim either the unfeasibility of CO₂ capture from air [5] or the need for a brand new CO₂ absorber, that has been proposed and denominated wind-scrubber [4]. In spite of that, in this work we propose the use of state-of-the-art absorption columns equipped with commercial structured packings, e.g. those manufactured by Koch–Glitsch (Wichita, United States) or Kühni (Allschwil, Switzerland) or Sulzer Chemtech (Winterthur, Switzerland), which are designed to deal with absorption operations requiring at the same time low pressure drop and high throughput. This is indeed what is needed here. A detailed analysis of the absorption unit is reported in Appendix A, where its suitability for the extraction of carbon dioxide from air is also demonstrated.

2.2. Concentrating carbon dioxide

The design of this part of the process has to fulfil two requirements. On the one hand a concentrated carbon dioxide stream is required for CO₂ storage; on the other hand the recovery of the reactants used in the absorption process has to be maximized. Two existing processes have been considered due to their similarity to our application, namely the Kraft process in the paper industry [9] and the lime-soda softening process in water treatment systems [10]. Both processes deal with a sodium carbonate solution that needs to be converted to a sodium hydroxide solu-

tion. In both cases this is obtained by reacting sodium carbonate with lime, i.e. Ca(OH)₂, which is formed through quicklime hydration, i.e. by the reaction $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$. Upon exchange of sodium and calcium cations in a precipitator, calcium carbonate is obtained as the precipitate, which can then be calcined to quicklime and carbon dioxide for recycle and for pressurization and storage, respectively. This scheme can be applied also to our case, provided the calcining step takes place in a kiln where pure oxygen is used, thus allowing to obtain flue gases containing carbon dioxide at rather high partial pressure, and water vapour, that can be easily separated in a condenser.

The slaker is designed in accordance to standard practice, by selecting the ratio between water and quicklime in order to control the process temperature at its set-point [11]. Temperature is the most important process variable, since it controls the product characteristics, i.e. the higher the temperature and the energy demand, the smaller the particle size and the greater the specific surface of the particles [11]. In the present case, instead of the usual 80–85 °C interval, the slaker is operated at a temperature of 95 °C, which is optimal from the product quality point of view. For the sake of simplicity, all calculations reported in the following have been carried out assuming no impurities in the Ca-rich streams and complete conversion of all reactive steps involving quicklime, lime and calcium carbonate. The water required for the slaking process can either be provided by an external source or, as in the scheme reported in Figs. 1 and 2, it can be a small part of the outlet stream from the absorption column (stream 2A), which is conveyed to the slaking unit (2), where quicklime (stream 7G) is hydrated. The latter choice avoids the consumption of fresh water and the associated dilution effect.

Calcium carbonate precipitation can be carried in two different ways that are illustrated in Figs. 1 and 2, respectively.

In the first approach, after cooling the calcium hydroxide solution (stream 3A) is mixed in Unit 3 with the sodium carbonate solution from the absorber (stream 3B), thus forming calcium carbonate that precipitates. This step could also be performed in the same tank where also the first clarification step takes place, but for the sake of clarity it appears as an independent step in the scheme reported in Fig. 1. Clarification of the supernatant, together with separation and thickening of the sludge containing calcium carbonate, has been dealt with by comparison with what is done in the lime-soda softening process. Even though calcium carbonate dewatering properties are far better than those exhibited by activated sludge for instance, common thickening technologies do not allow obtaining solids with water content below 30–35% [10]. Further dewatering may be in this case obtained only by drying with hot air. Therefore, the slurry containing calcium carbonate (stream 3C) is conveyed to a clarification tank (Unit 4), where a clarified liquid (stream 4A) and a sludge (stream 4B) with approximately 1% solid content, i.e. a rather conservative value, are obtained. As commonly done to soften sludge that contains mainly calcium and magnesium carbonates, the sludge at 1% solid content is further thickened in a gravity thickener (Unit 5), thus yielding a sludge with 30% solid content (stream 5B). This is further dewatered in a filter press or a rotary vacuum filter (Unit 6), thus reaching a final solid content of 65% in stream 6B. The supernatants from the

sludge dewatering units (streams 4A, 5A and 6A) are sodium hydroxide solutions that can be recycled back to the absorption column.

The second approach is illustrated in Fig. 2 and is based on using a Pellet Reactor to precipitate calcium carbonate. This reactor type, commercialized by DHV as Crystalactor® [12] consists of a cylindrical vessel, partially filled with suitable seed material, e.g. filter sand or possibly calcium carbonate itself. The water is pumped through the reactor in the bottom up mode at such a velocity (40–120 m/h) that the pellet bed is kept in the fluidized state and a sharp phase separation between the fluidized bed and the supernatant is guaranteed. The fluidized bed suspension provides a rather large crystallization surface where virtually all precipitation events occur, thus yielding pellets with a moisture content of only 5–10% after atmospheric drying. While growing, the pellets gradually move to the bottom of the reactor due to their increasing weight. Periodically, part of the largest pellets is discharged, while new seed material is added in order to keep the number of pellets constant. Therefore, in this second process option, after cooling the calcium hydroxide solution from the slaker (stream 3A in Fig. 2) is mixed in the Pellet reactor (Unit 3) with the sodium carbonate solution from the absorber (stream 3B). Calcium carbonate pellets are produced (stream 6B), already at 10% moisture content, i.e. 90% solid content, together with a supernatant sodium hydroxide solution (stream 3C) that can be directly recycled back to the absorber. For the sake of simplicity, the atmospheric drying step has not been explicitly accounted for at this stage of the analysis.

Whatever option is chosen, i.e. either the scheme in Fig. 1 or that in Fig. 2, the calcium carbonate in sludge or pellet form, respectively, (stream 6B) is conveyed to the kiln (Unit 7) where it is calcined to quicklime. This operation differs from the one usually performed in the cement industry because there is no reason to increase the temperature up to 1500 °C, since our goal is not to obtain clinker. A temperature of 900–1000 °C should be high enough for the purpose of producing good quality quicklime, as recognized also by producers of kilns for lime manufacturing from calcium carbonate [11]. Yet, the energy requirements for the calciner remain very high, at least when considering the first option, since the sludge contains approximately 30% of water that has to be evaporated. Another peculiar feature of this technology is that calcination in the kiln shall be carried out using pure oxygen rather than air in order to avoid the difficult separation of CO₂ from nitrogen after calcination. To our knowledge, there is no industrial experience on oxy-combustion in kilns for lime production; it can be expected that operating with pure oxygen is doable but presents specific process design issues that require additional R&D work and that are anyhow beyond the scope of this study. A possible solution for the mechanical design of the kiln could be to use a fluidized-bed system, which was already proposed and investigated in previous works [7,13]. For the sake of simplicity, a pure oxygen stream obtained from an oxygen separation unit has been used for the following calculations, thus leading to flue gases from the calciner containing only water vapour and CO₂ (stream 7E). A Pressure Swing Adsorption process has been selected for oxygen production,

considering that in the calciner oxygen is required in the gas phase, whereas a cryogenic process would produce liquid oxygen with an unnecessary additional energy cost. The flue gas (stream 7E) needs further processing in order to obtain pure CO₂ according to the process specifications. Following the literature [14], first most of the water vapour is removed in a condenser (Unit 8); then the gas stream is conveyed to a compression unit (Unit 9) where its pressure is increased to above 58 bar to obtain almost pure liquefied carbon dioxide. The quicklime from the kiln (stream 7F) is recycled back to the slaker. A calcium carbonate make-up (stream 7C) is necessary to compensate for solid losses in the kiln (stream 7D).

In the following sections, mass and energy balances for each process unit are performed, in order to evaluate the material and energy requirements for both process options.

3. Mass and energy balances

As outlined above, the process for CO₂ capture from air can be divided in two main sections. The first one, aimed at absorbing CO₂ from air, consists of the absorption column. The second section is constituted of several unit operations, and is aimed at extracting and concentrating CO₂ from the aqueous solution leaving the absorber, in order to obtain a pure CO₂ stream to be sent to storage. It is worth pointing out that for both process options in Figs. 1 and 2, the design of the second section of the process, and the corresponding mass and energy balances, depends on the operation of the absorption column, whose design has therefore been carried out first (see Section 3.1). In other words, the other unit operations have been designed (see Sections 3.2–3.7) based upon the flow rate and composition of the liquid stream leaving the absorption column (stream 1D in Figs. 1 and 2). The resulting mass balances are reported in Table 1 for the section of the process common to both options A and B, whereas those corresponding to the second section of the process are reported in Tables 2 and 3, for process options A and B, respectively. The energy requirements of the different units, including both heat and work terms, calculated through mass and energy balances for each unit, are reported in Table 4.

3.1. Absorption column

As discussed in Appendix A, a column equipped with Sulzer Mellapak 500Y packing has been selected, to absorb carbon dioxide from air from an inlet concentration of 500 ppm, to an outlet value of 250 ppm, using a 2 M sodium hydroxide solution. The absorber has been designed for an allowable pressure drop of 100 Pa/m and a liquid to gas ratio $L/G = 1.44$. Such a column design resulted in a 2.8 m height, and a specific cross section equal to 18,500 m²/(tCO₂/min). Such units have been used since, when assuming to operate the column for 7000 h/y, i.e. approximately 300 d/y, the capture rate of one tCO₂/min corresponds to about 0.42 MtCO₂/y. This is the same order of magnitude of the largest carbon dioxide capture and storage projects running today, namely Sleipner, In-Salah, and Weyburn [2]. Therefore, a plant for the CO₂ capture from air of a similar size would require an absorber cross section of about 20,000 m², corresponding to

Table 1

Material balances for the process part, which is common to both process options A and B

Stream	Flow rate (m ³ /h)	Flow rate (kg/h)	CO ₂ (kg/h)	CaO (kg/h)	Na ⁺ (kg/h)	CO ₃ ²⁻ (kg/h)	T (K)
1A air	817115	–	734 ^a	–	–	–	298
1B air	817115	–	367 ^b	–	–	–	298
1C liquid	864	864000	–	–	60480 ^e	100.0 ^c	298
1D liquid	864	864000	–	–	60480 ^e	600.0 ^d	298
2A liquid	1.876	1876	–	–	130 ^e	600.0 ^d	298
2B liquid	–	2343	–	467	130	600.0 ^d	368
3A liquid	–	2343	–	467	130	600.0 ^d	308
3B liquid	862.1	862124	–	–	60350 ^e	600.0 ^d	298

^a CO₂ concentration: 500 ppm.^b CO₂ concentration: 250 ppm.^c CO₃²⁻ concentration: 0.1158 kg/m³.^d CO₃²⁻ concentration: 0.6948 kg/m³.^e Na⁺ concentration: 70 kg/m³ (2 M).

about four soccer fields. However, for practical reasons a single absorption column cannot have a diameter exceeding 12 m, i.e. a cross section of 113 m², corresponding to a carbon dioxide capture rate of 0.366 t/h. All the calculations reported in this paper refer to a single absorber of this size as far as material balances and energy balances are concerned. However, all energy requirements will also be expressed per unit mass of captured CO₂ in such a way that the results can be applied in general.

3.2. Slaker

The slaker is the unit where calcium oxide (quicklime) from the calciner is hydrated to obtain calcium hydroxide (hydrated lime), using for this purpose a fraction of the solution leaving

the absorber. This reaction is strongly exothermic:



Choosing a slaking temperature of 95 °C and a 4:1 weight ratio between water and quicklime, and assuming that the heat required for heating quicklime is negligible [11], it is found that the heat generated by the slaking reaction is completely used to heat the solution to the slaking temperature. Thus, the only heat available from this unit is what can be recovered by cooling the stream leaving the slaker (stream 2B); however, this is a low-grade heat that is very difficult to exploit.

Assuming a residence time of 10 min [11], the slaker volume is 0.33 m³. The corresponding power required for mixing is 0.5 kW [15], resulting in a specific energy requirement, that is negligible with respect to other requirements in the plant.

Table 2

Material balances for the process option A (Fig. 1); process section (a) upstream and (b) downstream of the calciner

Stream	Flow rate (m ³ /h)	Flow rate (kg/h)	CaO (kg/h)	Na ⁺ (kg/h)	CO ₃ ²⁻ (kg/h)	CaCO ₃ (kg/h)	CaCO ₃ (wt.%)	<i>T</i> (K)
(a) Upstream of the calciner								
3C liquid	864.0	864467	—	60480	100.05	833.0	0.096	298
4A liquid out	781.1	781167	—	54677 ^a	90.45 ^a	—	—	298
4B sludge out	83.60	83300	—	5852 ^a	9.68 ^a	833.0	1.0	298
5A liquid out	80.52	80523	—	5636 ^a	9.32 ^a	—	—	298
5B sludge out	2.252	2777	—	136 ^a	0.23 ^a	833.0	30	298
6A liquid out	1.495	1495	—	104.6 ^a	0.173 ^a	—	—	298
6B sludge out	0.798	1282	—	31.4 ^a	0.052 ^a	833.0	65	298
7C make up	—	84	—	—	—	84	—	298
7D solid dust	—	84	—	—	—	84	—	1000
7F solid out	—	467	467	—	—	—	—	473 ^b
Stream	Flow rate (kg/h)	Flow rate (kmol/h)	H ₂ O (kmol/h)	CO ₂ (kmol/h)	CH ₄ (kmol/h)	O ₂ (kmol/h)	<i>T</i> (K)	
(b) Downstream of the calciner								
7A fuel in	81.6	5.1	—	—	5.1	—	298	
7B air in	360.6	11.27	—	—	—	11.27	298	
7E flue gas	1260.4	48.09	35.2 ^c	13.43 ^d	—	1.12	473 ^b	
8A gas	637.7	15.15	0.61	13.43	—	1.12	303	
8B liquid	622.7	34.6	34.6	—	—	—	303	
9A liquid	591	—	—	13.43	—	—	—	

^a Na⁺ concentration: 70 kg/m³ (2 M); CO₃²⁻ concentration: 0.1158 kg/m³.^b After cooling.^c 25 kmol/h from sludge water plus 10.2 kmol/h from combustion.^d 8.33 kmol/h from calcining plus 5.1 kmol/h from combustion.

Table 3

Material balances for the process option B (Fig. 2); process section (a) upstream and (b) downstream of the calciner

Stream	Flow rate (m ³ /h)	Flow rate (kg/h)	CaO (kg/h)	Na ⁺ (kg/h)	CO ₃ ²⁻ (kg/h)	CaCO ₃ (kg/h)	CaCO ₃ (wt.%)	T (K)
(a) Upstream of the calciner								
3C liquid out	863.5	863542	–	60445 ^a	100.00 ^a	–	–	298
6B pellets out	N/A	925	–	35 ^a	0.05	833.0	90	298
7C make up	–	84	–	–	–	84	–	298
7D solid dust	–	84	–	–	–	84	–	1000
7F solid out	–	467	467	–	–	–	–	473 ^b
Stream	Flow rate (kg/h)	Flow rate (kmol/h)	H ₂ O (kmol/h)	CO ₂ (kmol/h)	CH ₄ (kmol/h)	O ₂ (kmol/h)	T (K)	
(b) Downstream of the calciner								
7A fuel in	55.5	3.47	–	–	3.47	–	298	
7B air in	244.1	7.63	–	–	–	7.63	298	
7E flue gas	760.96	24.64	12.08 ^c	11.80 ^d	–	0.76	473 ^b	
8A gas	554.50	13.17	0.61 ^e	11.80 ^d	–	0.76	303	
8B liquid	206.46	11.47	11.47	–	–	–	303	
9A liquid	519.20	11.80	–	11.80	–	–	–	

^a Na⁺ concentration: 70 kg/m³ (2 M); CO₃²⁻ concentration: 0.1158 kg/m³.^b After cooling.^c 5.14 kmol/h from sludge water plus 6.94 kmol/h from combustion.^d 8.33 kmol/h from calcining plus 3.47 kmol/h from combustion.^e Calculated assuming 4% residual moisture content in the gas phase.

3.3. Calcium carbonate precipitation and dewatering

The two process options proposed in this work differ in the way calcium carbonate is precipitated. Namely, in Option A precipitation and dewatering of the calcium carbonate sludge is accomplished using standard technology commonly adopted in water treatment systems [10]; in Option B a rather innovative

pellet reactor is used. The different choices lead to different mass balances, which are reported in Tables 2 and 3 for options A and B, respectively, as discussed in the following.

3.3.1. Process option A

The precipitation and dewatering train is constituted of four units, namely a precipitator (Unit 3 in Fig. 1), a clarification unit (4), a thickener (5), and a filter press (6). The first and the second unit can also be merged into one. In order to determine mass and energy balances, we assume that all units behave ideally, i.e. the mother liquor in the precipitator is a saturated solution with respect to both calcium carbonate and calcium hydroxide, and the supernatant from all units (streams 4A, 5A and 6A) does not contain any suspended solids. Moreover, the concentration of suspended solids in the sludge streams from Units 4, 5 and 6 are specified to be 1 wt.% (stream 4B), 30 wt.% (stream 5B), and 65 wt.% (stream 6B), respectively. The energy requirements associated to these steps in the process have been calculated to be negligible with respect to the other contributions. Therefore, the wet calcium carbonate stream (6B) to the calciner contains 35 wt.% of water that is to be evaporated in the calciner, thus adding to its energy load.

3.3.2. Process option B

The pellet reactor (Unit 3 in Fig. 2) allows to obtain a very efficient dewatering of the calcium carbonate, which leaves the unit and is conveyed to the calciner (stream 6B) as solid pellets with 10 wt.% residual water content. The clarified supernatant (stream 3C) can be recycled to the absorption unit.

3.4. Kiln

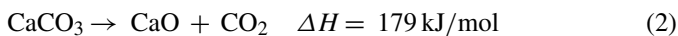
In the kiln calcium carbonate is calcined through the following endothermic reaction:

Table 4

(a) Heat and (b) work requirements for carbon dioxide recovery from air for process options A and B

Operation	Heat (GJ/tCO ₂)	
	Option A	Option B
(a) Heat requirements		
Slake cooling	–1.28	–1.28
CaCO ₃ heating	2.19	2.19
CaCO ₃ drying	4.59	0.94
CaCO ₃ calcining	4.47	4.47
Air heating	1.13	0.77
CaO cooling	–0.96	–0.96
Flue gas cooling	–2.61	–1.36
Water condensation	–3.97	–1.31
Total net heat requirement ^a	8.8	6.04
Operation	Work (GJ/tCO ₂)	
	Option A	Option B
(b) Work requirements		
Air blowing to absorber	0.625	0.625
Water pumping to absorber	0.065	0.065
Clarifier/pellet reactor	0.11	0.11
Slaker	0.0049	0.0049
O ₂ purification (PSA)	0.620	0.419
CO ₂ compression	0.416	0.360
Total work requirement	1.794	1.584

^a Water condensation and slake cooling not considered in the total net heat requirement.



In the proposed process, this reaction is carried out in an oxy-fuelled kiln, fired by natural gas that for sake of simplicity was considered 100% methane. Carbon dioxide in the outlet gas stream (7E) can be easily separated from water, recovered pure (stream 8A), and compressed (stream 9A). The solid product from the kiln (7F) consists of calcium oxide and is recycled to the slaker. In both process options, A and B, the calcium carbonate flow rate has been set at a value 10% higher than the stoichiometric one, to compensate for possible losses in the kiln (see Tables 2 and 3). Stream 7C provides the corresponding calcium carbonate make-up.

The heat requirements reported in Table 4 have been calculated for a 900 °C temperature in the calciner, including the contributions needed for the heating and drying of the feed streams. Process option B has a lower heat requirement for CaCO₃ drying, which is clearly due to the lower water content of the incoming solid.

Two heat recovery terms have also been considered, corresponding namely to cooling of solid quicklime (stream 7F) and flue gases (stream 7E) leaving the kiln from 900 to 200 °C. These have been assumed to be indeed recoverable since the kiln temperature is rather high.

3.5. Water condenser

In the water condenser the flue gas stream (7E) is cooled from 200 to 30 °C, and the water is condensed. We assume that the flue gas leaving the condenser (stream 8A) has a 4 vol.% residual amount of water, which is equivalent to a partial pressure of approximately 30 mmHg. It is worth pointing out that the low-grade heat released in this unit is difficult to recover, and it will be considered lost in the overall energy balance of Table 4. Not only cannot this heat be recovered, but also the water condenser can be a critical bottleneck of the process since a large amount of cooling water is required.

3.6. Compressor

According to the pressure–enthalpy diagram, the pressure to achieve carbon dioxide liquefaction at ambient temperature (20 °C) is equal to 58 bar [14]. This will possibly require a further cooling step, whose heat contribution can be neglected. A multi-stage compressor is required to reach 58 bar, where the residual is condensed in the first stage. The energy requirement for compression reported in Table 4b has been calculated based on literature data [14]. The work requirement for process option B is lower than for process option A, since in the first case the flue gas flow rate (stream 7E) is smaller. Namely, in both cases the flue gas stream (7E) contains the same amount of CO₂ from calcining, but a different amount of CO₂ (and water) produced by the fuel combustion needed to dry the inlet calcium carbonate, whose amounts differ since the residual water contents in the two process options differ.

3.7. O₂ purification (PSA)

A reasonable estimate of the energy requirement for oxygen purification, provided by PSA manufacturer [16] is 0.4 kWh/Nm³, equivalent to 0.9 MJ/Nm³. It is worth noting that the oxygen flow rate in process option A is larger than in process option B (see Tables 2 and 3), and so is the corresponding PSA energy requirement (see Table 4b), for the same reason discussed in Section 3.6.

4. Discussion and conclusions

The energy requirements of the process for carbon dioxide capture from air are summarized in Table 4. The total net heat requirement in Table 4a is calculated without considering the major contribution from water condensation (stream 8B) and slake cooling (stream 2B), i.e. 5.3 and 2.6 GJ/tCO₂ captured in case of options A and B, respectively, since both these terms represent low-grade heat, which is difficult to recover.

When analyzing the different contributions to the energy demand, calcination of calcium carbonate represents the largest, unavoidable part, i.e. 4.5 GJ/tCO₂ captured. It is also worth underlining that a technology for calcination using oxygen rather than air (oxy-fuel calciner) is not available and should be developed from scratch for this and other applications, e.g. a zero-emission cement plant. In order to tackle the challenge posed by the calcination reaction, recently the use of a solar reactor has been proposed, thus making it possible to exploit non-fossil fuel energy for the energy-intensive step of the CO₂ capture from air process [17].

The other large contributions to the energy demand are heating of calcium carbonate and of air, as well as drying of calcium carbonate, whose impact can be drastically reduced by adopting process option B. Other important contributions are due to CO₂ compression and to air separation to obtain pure oxygen, as well as to the energy demand associated to the absorption column. It is however worth noting that the last contribution is less than 10% of the total energy requirement, even though standard absorption technology and equipment have been considered, i.e. nothing specifically designed for carbon dioxide capture from air.

The total specific energy requirement is 10.6 GJ/tCO₂ captured (8.8 GJ/tCO₂ thermal plus 1.8 GJ/tCO₂ mechanical) for the process option A, whereas it reduces to 7.6 GJ/tCO₂ captured (6.0 GJ/tCO₂ thermal plus 1.6 GJ/tCO₂ mechanical) if option B is chosen. Assuming 35% efficiency for electricity generation and 75% efficiency for the direct utilization of thermal energy, the real energy demand is about 17 and 12 GJ/tCO₂ captured for process options A and B, respectively. These figures should be compared with the heat released by combustion, which is 9 or 20 GJ per tonne of CO₂ released to the atmosphere in the case of coal or methane, respectively. It can readily be observed that for both process options the energy demand is larger than the heat released by the combustion of coal, and smaller than that of methane. It is clear that the large energy demands that have been calculated in this work based on a non-conservative set of assumptions make the economical and environmental feasibility of the technology questionable. Even if capital costs associated

to the process were estimated and the trade-offs between running and capital costs were accounted for, it would be difficult to improve the economic feasibility of the process. To make the process feasible, its energy efficiency should be improved or non fossil-fuel energy, e.g. solar, nuclear, hydro, wind, should be used. Based on the analysis presented here, the energy efficiency of the process can be significantly improved only by finding ways to recover the heat of the slaking reaction. The use of steam, rather than water, as proposed by Lackner, could be a solution to the problem, but as far as we know a suitable technology has yet to be developed.

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Appendix A. Design and analysis of the CO₂ absorber

A.1. Design criteria

The absorber design (Unit 1) is based upon the use of state-of-the-art commercial structured packing, e.g. that manufactured by Koch-Glitsch (Wichita, United States) or Kühni (Allschwil, Switzerland) or Sulzer Chemtech (Winterthur, Switzerland). Such packing is specifically suited for absorption operations requiring low pressure drop and high throughput. For the sake of simplicity, but without loss of generality, in the following we consider Mellapak Y packing from Sulzer Chemtech (Winterthur, Switzerland).

The column performances have been evaluated by numerically solving the material balance for carbon dioxide in the gas phase:

$$dy = \frac{K_G a_e}{G} P(y - y^*) dz \quad (\text{A.1})$$

where y is the carbon dioxide mole fraction in the bulk gas phase, y^* the carbon dioxide mole fraction in equilibrium with the bulk liquid phase, and dy is the mole fraction change taking place in a column section of height dz . Moreover, P is the column pressure, K_G represents the global mass transfer coefficient in terms of gas phase composition, a_e the packing effective specific area, and G is the gas phase molar flux, assumed to be constant through the column. The resulting change in carbon dioxide content of the solution is readily calculated as:

$$dx = \frac{G}{L} dy \quad (\text{A.2})$$

where L is the liquid phase molar flux, also considered to be constant, and x is the sum of the mole fractions of all carbonic species in solution, i.e. dissolved CO₂, carbonic acid, and carbonate and bicarbonate ions.

Eqs. (A.1) and (A.2) are typically used to calculate the height of the absorption column for a given set of data, namely carbon dioxide inlet concentration, sodium hydroxide inlet concentration, and L/G ratio, and for a given specification, i.e. the maximum carbon dioxide outlet concentration.

These material balances can be solved when coupled with constitutive equations defining the term $K_G a_e$ and the equilibrium carbon dioxide mole fraction y^* . In the following, the methods used for this purpose are briefly outlined.

The equilibrium gas phase CO₂ mole fraction, y^* , is calculated from the CO₂ mole fraction in solution, which depends on the solution speciation to be determined by considering all the dissociation equilibria in solution, using the Henry constant corrected for the presence of electrolytes [18].

The overall mass transfer coefficient K_G is readily obtained in terms of the mass transfer coefficients in the two phases. The gas phase mass transfer coefficient, k_g , is calculated using the following correlation valid for structured packing [19]:

$$k_g = (0.0338 Re_G^{0.8} Sc_G^{1/3}) \frac{D_{CO_2,G}}{d_h} \quad (\text{A.3})$$

where $D_{CO_2,G}$ is the diffusivity of carbon dioxide in the gas phase, d_h is a packing-specific parameter [20], and the Reynolds and Schmidt numbers are defined as follows:

$$Re_G = \frac{\rho_G v_G d_h}{\mu_G} \quad (\text{A.4})$$

$$Sc_G = \frac{\mu_G}{\rho_G D_{CO_2,G}} \quad (\text{A.5})$$

with ρ_G , μ_G and v_G being the gas phase density, viscosity and effective velocity, respectively.

The liquid phase mass transfer coefficient has to take into account the reaction of carbon dioxide with the hydroxyl ions, i.e. a fast irreversible reaction, through the introduction of the enhancement factor, E [21]. Therefore, the liquid phase mass transfer coefficient, k_L , is obtained by multiplying the coefficient for physical mass transfer, i.e. in the absence of reaction:

$$k_L^o = 2 \sqrt{\frac{D_{CO_2,L}}{\pi t}} \quad (\text{A.6})$$

and the enhancement factor E , calculated as follows [22]:

$$\left[\frac{1}{E-1} \right]^{1.35} = \left[\frac{1}{E_i-1} \right]^{1.35} + \left[\frac{1}{E_1-1} \right]^{1.35} \quad (\text{A.7})$$

$$E_i = 1 + \left[\frac{C_{OH,L} D_{OH,L}}{2 D_{CO_2,L} C_{CO_2,i}} \right] \quad (\text{A.8})$$

$$E_1 = \frac{\sqrt{M}}{\tanh \sqrt{M}} \quad (\text{A.9})$$

$$M = \frac{D_{CO_2,L} k_2 C_{OH,L}}{(k_L^o)^2} \quad (\text{A.10})$$

where t (Eq. (A.6)) is the gas–liquid contact time that is set equal to the travelling time for liquid flowing from one packing intersection to another [20]; $C_{OH,L}$ is the hydroxyl ion concentration in the bulk liquid phase and $C_{CO_2,i}$ is the carbon dioxide molar concentration at the gas–liquid interface; $D_{OH,L}$ and $D_{CO_2,L}$ are the hydroxyl ions and carbon dioxide liquid phase diffusion coefficients, respectively. The kinetic constant of the reaction

between carbon dioxide and hydroxyl ions, k_2 , is calculated using the following equation [18]:

$$\log k_2 = 11.895 - \frac{2382}{T} + 0.0221I_C - 0.016I_C^2 \quad (\text{A.11})$$

where I_C and T are the ionic strength and temperature of the absorbing solution, respectively.

The effective surface area of the packing available for mass transfer, a_e , is evaluated using the Onda equation [22]:

$$a_e = a_p \left[1 - \exp \left(-1.45 \left(\frac{\sigma_c}{\sigma_L} \right)^{0.75} Re_L^{0.1} Fr_L^{-0.05} We_L^{0.2} \right) \right] \quad (\text{A.12})$$

where a_p is the packing surface area, whereas σ_L and σ_c are the liquid and critical surface tension, respectively. The value of the latter depends on the construction material of the absorption column packing. In this work a packing in steel material was selected, with a critical surface tension of 75 dynes/cm [23]. The dimensionless groups in Eq. (A.12) are defined as follows:

$$Re_L = \frac{L_m}{a_p \mu_L} \quad (\text{A.13})$$

$$Fr_L = \frac{L_m^2 a_p}{\rho_L^2 g} \quad (\text{A.14})$$

$$We_L = \frac{L_m}{\rho_L \sigma_L a_p} \quad (\text{A.15})$$

where L_m is the mass liquid flux through the absorption column, whereas ρ_L and μ_L are the liquid density and viscosity, respectively.

The column is assumed to be isothermal, since thermal effects due to carbon dioxide absorption and water evaporation can be neglected.

A.2. Sensitivity analysis

As analyzed in the next sections of this appendix, the design of the absorption column depends on three parameters, namely the process specification, i.e. the required outlet carbon dioxide concentration, the inlet concentration of sodium hydroxide in the absorbing solution, and the L/G ratio. Two different Mellapak packings are used, namely 250Y and 500Y. Although the values obtained will apply specifically to this packing material, we believe that the observed trends bear a more general validity and apply to other packing types as well. All simulations have been performed by considering a CO_2 concentration in the inlet air of 500 ppm (today this is 380 ppm), which is a reasonable value for the time when this technology would be attractive on a large scale. We require that the pressure drop in the column be 10 mbar/m (100 Pa/m), and the L/G ratio and the gas flux G are selected based on the Sulzer Chemtech technical data (see Fig. 7 of [24]) in order to fulfil this constraint.

In this work no thorough optimization of the absorber is carried out, but we limit our study to a rather straightforward parametric and sensitivity analysis of the effect of different operating conditions on the absorber design and performance. Based

on this analysis, an educated choice is made about a possible design for the absorber, i.e. the one used in Section 3.1 of this paper.

A.3. Sodium hydroxide inlet concentration and carbon dioxide outlet concentration

The data reported in Tables A.1 and A.2 show the effect of changing sodium hydroxide inlet concentration and CO_2 outlet concentration on height and energy consumption of the absorber, which is mostly needed for blowing air and is given as power per rate of CO_2 capture, i.e. $\text{GW}/(\text{tCO}_2/\text{s})$. All calculations reported in these tables apply to the 250Y Mellapak packing, and have been carried out at $L/G = 0.37$ and $G = 0.18 \text{ kmol s}^{-1} \text{ m}^{-2}$. Such low L/G ratio has been selected in order to have a large air flux through the column with a column cross section as small as possible for a given amount of captured carbon dioxide; this parameter will be analyzed more in detail in Appendix A.4. It is worth noting that the sodium hydroxide solution enters the absorption column at conditions corresponding to saturation with respect to calcium carbonate, since in the process under consideration this solution is the supernatant obtained from the precipitation and dewatering section of the plant (see Figs. 1 and 2).

The results demonstrate that an increase of column height and of air fan specific power is required to absorb more carbon dioxide per pass, as expected. On the other hand, for all outlet carbon dioxide concentration levels there is an optimal $[\text{Na}^+]$ value, for which the column length and the specific power consumption are minimum. The best value among those considered here is $[\text{Na}^+] = 3 \text{ M}$, with a rather shallow minimum. The presence of the minimum is due to two counteracting effects occurring when $[\text{Na}^+]$ increases. On the one hand, the enhancement factor increases as to Eq. (A.8), thus improving mass transfer and enhancing CO_2 absorption. On the other hand, the saturation carbonate concentration in the solution entering the column also increases, thus making more difficult to absorb more carbon dioxide.

The effect of the CO_2 outlet concentration is less dramatic on the specific power consumption than on the column height. The reason is that for the same amount of CO_2 captured, more air has to be fanned when the outlet concentration is lower, and this compensates the effect of the shorter column.

As far as the design of the absorber is concerned, it is worth noting that the absorber cross section needed to capture a given amount of CO_2 per unit time is inversely proportional to the product of the gas flux, G , and the CO_2 concentration change between inlet and outlet. Therefore, since at constant gas flux the cross section increases from right to left in both Tables A.1 and A.2, whereas the absorber height behaves in the opposite way, the size of the absorber is determined based on a trade off between height and diameter. It can also be noticed that the height of the absorber is approximately proportional to the CO_2 concentration change between inlet and outlet. Hence the volume of the absorber is approximately independent of this change and proportional to the reciprocal of the gas flux. Without going into a thorough cost analysis, we have selected for our further calcula-

Table A.1

Column height calculated at different operating conditions as a function of sodium hydroxide concentration and outlet carbon dioxide content

[Na ⁺] _{in} (M)	Column height (m)				
	[CO ₂] _{out} = 490 ppm	[CO ₂] _{out} = 450 ppm	[CO ₂] _{out} = 400 ppm	[CO ₂] _{out} = 350 ppm	[CO ₂] _{out} = 250 ppm
0.1	1.07	5.54	12.11	20.28	44.31
1.0	0.38	1.92	4.05	6.50	12.71
2.0	0.31	1.56	3.29	5.26	10.27
3.0	0.30	1.50	3.16	5.05	9.84
4.0	0.31	1.57	3.31	5.29	10.30
8.0	0.66	3.33	6.99	11.18	21.74

L/G: 0.37; *G*: 0.18 kmol s⁻¹ m⁻²; inlet CO₂ concentration: 500 ppm. Packing type: Mellapak 250Y.

Table A.2

Air fan specific power calculated at different operating conditions as a function of sodium hydroxide concentration and outlet carbon dioxide content

[Na ⁺] _{in} (M)	Specific power for air blowing (MW/(tCO ₂ /min))				
	[CO ₂] _{out} = 490 ppm	[CO ₂] _{out} = 450 ppm	[CO ₂] _{out} = 400 ppm	[CO ₂] _{out} = 350 ppm	[CO ₂] _{out} = 250 ppm
0.1	99.5	103.0	112.5	125.7	164.7
1.0	35.5	35.7	37.7	40.3	47.2
2.0	29.0	29.2	30.5	32.7	38.2
3.0	27.8	28.0	29.3	31.3	36.5
4.0	29.2	29.3	30.7	32.8	38.3
8.0	61.7	61.8	65.0	69.2	80.8

L/G: 0.37; *G*: 0.18 kmol s⁻¹ m⁻²; inlet CO₂ concentration: 500 ppm. Packing type: Mellapak 250Y.

tions a reasonable absorber design, namely that corresponding to a carbon dioxide outlet concentration of 250 ppm and a sodium hydroxide inlet concentration of 2 M.

A.4. *L/G* ratio and packing type

Table A.3 analyses the effect of the *L/G* ratio at constant gas pressure drop per unit length (namely 100 Pa/m) on the height, cross section, volume and power consumption of the absorber. The calculations are carried out for two different packing types, namely Sulzer Mellapak 250Y and 500Y in the recommended *L/G* range, by keeping the values of carbon dioxide outlet concentration and of sodium hydroxide inlet concentration at the values chosen in Appendix A.3. In all simu-

lations, the global mass transfer coefficient in terms of gas-phase composition multiplied by the specific packing area, $K_{Ga}a_e$, was between 1.1×10^{-2} and 2.0×10^{-2} kmol m⁻³ s⁻¹ atm⁻¹ for both Mellapak packing types. Despite the fluid-dynamic conditions were different, these values are comparable with those measured by Greenwood and Pearce [8] in an absorption tower packed with Raschig and Lessing rings and fed with a 2.5 N NaOH solution, that ranged between 4.5×10^{-3} and 1.8×10^{-2} kmol m⁻³ s⁻¹ atm⁻¹.

It can be readily observed the Mellapak 500Y outperforms 250Y in both investment costs, i.e. the absorber height and volume, and in energy consumption. As to the latter, the data in Table A.3 demonstrate that blowing air is much more energy intensive than pumping water, as expected. Increasing the *L/G*

Table A.3

Size and energy requirements for an absorption column equipped with different packing types and operated at different *L/G* ratios

Packing type	<i>L/G</i>	<i>G</i> (kmol m ⁻² s ⁻¹)	Column height (m)	Column cross section (m ² /(tCO ₂ /min))	Column volume (m ³ /(tCO ₂ /min))	Specific power for air blowing (MW/(tCO ₂ /min))	Specific power for water pumping (MW/(tCO ₂ /min))
Mellapak 250Y	0.37	0.180	10.3	8400	86700	38.2	1.04
	0.43	0.173	9.7	8700	85000	36.2	1.13
	0.58	0.161	8.8	9400	82800	32.5	1.38
	0.87	0.146	7.6	10400	78900	28.3	1.80
	1.16	0.137	6.9	11100	76300	25.8	2.19
	1.44	0.118	6.0	12800	77000	21.7	2.35
Mellapak 500Y	0.37	0.125	4.8	12000	57600	17.8	0.48
	0.43	0.119	4.5	12700	57100	16.7	0.52
	0.58	0.110	4.0	13800	55200	15.0	0.64
	0.87	0.099	3.5	15300	53500	12.8	0.82
	1.16	0.092	3.1	16500	51100	11.7	0.99
	1.44	0.0821	2.8	18500	51800	10.3	1.09

[Na⁺]: 2 M; carbon dioxide concentration—inlet: 500 ppm; outlet: 250 ppm.

ratio leads to shorter columns and lower energy consumption, but also to larger values of the absorber cross section. However, the absorber volume is less sensitive to L/G , and exhibits a shallow minimum at L/G of about 1.16.

Based on these data, we can conclude that Mellapak 500Y is the packing of choice and we select $L/G = 1.44$ for our further calculations, since this minimizes energy consumption and column height, while requiring a column volume very close to the minimum.

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