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Combined system of renewable heat supply and DAC based on the technical lime cycle

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ABSTRACT

A novel concept is proposed and analyzed, in which long-term thermochemical energy storage based on CaO is combined with direct air capture (DAC) by utilizing the carbonation of $Ca(OH)_2$ under ambient conditions. With a theoretical heat storage density of approximately 320 kWh/t CaO and an intrinsic DAC functionality with a CO_2 storage capacity of 44 wt%, the technical lime cycle offers two storage functions and thus promotes flexibility in energy networks with the goal to enable CO_2-negative heat supply. Since CO_2 uptake is the rate-determining step in the closed technical lime cycle, the parameters affecting the carbonation of powdered $Ca(OH)_2$ are identified and analyzed to assess the feasibility of the proposed concept. Influence of CO_2 concentration, layer thickness and air flow are experimentally investigated, each showing a dependency on the carbonation rate. With a 2.0 mm $Ca(OH)_2$ layer, 72.3% carbonation could be achieved in 62 h. Based on these experimental results, initial system estimates indicate that with a hydration efficiency of 95%, 240 kWh of heat on demand, corresponding to the heating demand of an average week, require 0.78 t of CaO and could capture up to 430 kg CO_2 from the atmosphere.

1. Introduction

In European households, almost two thirds of the final energy demand are required for the provision of space heating and hot water and yet only 27% heat were provided by renewable sources in the European Union (EU) [1,2]. As a result, provision of heat accounts for a large share of CO_2 emissions. One reason why heat supply has so far relied predominantly on fossil fuels is the fluctuating availability of renewable energy in times of heat demand, making it a challenge to shift it from times of surplus energy to times of heat demand, making long-term energy storages necessary.

At DLR, a thermochemical energy storage was developed, which can store renewable energy as chemical potential over long time periods with minimum losses to release it in periods of demand as thermal energy [3,4]. Basis is the reversible, exothermic reaction of burnt lime (CaO) and water to slaked lime ($Ca(OH)_2$), utilizing the reaction heat for space heating as well as the provision of hot water. Whenever renewable energy is available, the storage is electrically charged, releasing thermal energy whenever there is a demand. Basis for this renewable heating is lime, which is an especially suitable thermochemical energy storage material, as it is abundant, inexpensive and non-toxic [5].

For the same reasons, lime is gaining interest as material for carbon dioxide removal, which is required to achieve climate goals [6–8]. CaO has been proven as suitable CO_2 sorbent in the application of Calcium looping as a post-combustion point source carbon capture. Carbonate ($CaCO_3$) is formed in flue gas with elevated CO_2 concentrations and temperatures usually between 600–700 °C, with a subsequent regeneration in a calciner afterwards [9–11]. $Ca(OH)_2$ is already utilized in direct air capture (DAC), technologies actively removing CO_2 from the ambient air [12]. The company Carbon Engineering uses a liquid sorbent, with the capture process taking place in two cycles: in the first cycle, an alkali hydroxide solution is brought into contact with air under ambient conditions, where it absorbs CO_2. In the regeneration cycle, the formed carbonate is mixed with $Ca(OH)_2$, precipitating $CaCO_3$ and regenerating the sorbent [13,14]. The formed carbonate is regenerated with calcination at around 900–1000 °C, making it a high-temperature DAC technology [15]. Next to Carbon Engineering, which utilizes $Ca(OH)_2$ as the regeneration material in their DAC system, approaches using lime-based sorbents at lower temperatures are also being developed. The company Heirloom based in the USA utilizes $Ca(OH)_2$ powder using it as solid sorbent and allowing the carbonation to take place over longer time scales. They accelerated the rate to 85% conversion in three

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days, by spreading the material in thin layers on large trays, whereby scaling up and handling has a reduced complexity compared with the liquid sorbent approach of Carbon Engineering [16,17].

New approaches for DAC based on lime are focus of current research. Criado and Abanades investigated the use of $Ca(OH)_2$ bricks for DAC and proved their concept with a lab-scale contactor [9,18–21]. Paulsen investigated the scalability of the Heirloom technology, calling it solid calcium looping, and concluded that countries in Northern Europe meet both demands on the energy system and suitable weather conditions for passive carbonation as DAC technology [22].

DAC has the advantage to be locally independent, so it can be placed where renewable energy is cheap and area requirements are feasible. This also minimizes costs for CO_2 transport either to subsequent utilization or storage sites [23]. Other than carbon capture from point sources like flue gas, it can make up for distributed emissions like CO_2 from the transport sector. On the other hand, it faces the challenge that CO_2 concentration in the atmosphere is very low, which leads to high energy demands for separation and subsequently high costs. The minimum thermodynamic energy to separate these low CO_2 concentrations from a gas stream are approximately 20 kJ/mol CO_2 [23]. Additionally, energy penalties must be accounted for, as well as the energy required for subsequent compression, necessary for storage, which is under research itself. Samari calculated an energy requirement of almost 4 GJ/t CO_2, including subsequent compression to 100 bar which is required for sequestration, but energy requirements differ depending on the DAC technology used [14]. This leads to costs that are estimated very differently in the literature, ranging between 20–1000 USD/t CO_2 captured.

In this work, a novel concept based on lime is introduced, which combines its storage functionality for heat with the storage capacity for CO_2. In contrast to existing technologies, this approach enables the temporally decoupled thermal discharge to be utilized for heat supply before the material is subsequently used as CO_2 sorbent. Thereby, the reactor for CO_2 uptake exploits the storage time periods of the lime and can be continuously charged and discharged. The dual storage functionality enables the system to operate flexibly according to the availability of renewable electricity. Basis is the technical lime cycle, which combines three subsequent reactions: firstly, the provision of renewable heat on demand through hydration as described above. In a second step the energetically discharged $Ca(OH)_2$ is utilized as a CO_2 sorbent, forming $CaCO_3$ with atmospheric CO_2 during carbonation. With regeneration through calcination at around 900–1200 °C, the technical lime cycle is closed [5]. By combining the systems, regeneration energy is utilized for two uses: provision of renewable heating and subsequent utilization for DAC. This could not only lead to reduction in emissions caused by heat provision, but increase the overall efficiency.

The aim of this study is to provide an initial assessment of the feasibility of the proposed concept combining heat storage and DAC. Following the evaluation of the individual reaction steps, the study focuses on the carbonation, as this is considered as rate-determining step under ambient conditions for the closure of the technical lime cycle. Literature data are complemented with own experiments conducted under technically relevant conditions for the application, to identify CO_2 capture capacity, energy and material requirements and cycle time. This enables first quantifications to assess the feasibility of the proposed system.

2. Concept

Basis of the proposed concept of combined energy storage and CO_2 capture is the technical lime cycle, which is shown in Fig. 1. The exothermic reaction of quicklime with water is utilized to provide heat, while the subsequent carbonation of slaked lime with atmospheric CO_2 is utilized for DAC. Calcination separates the CO_2 and charges the material energetically, making it the regeneration step and closing the technical lime cycle.

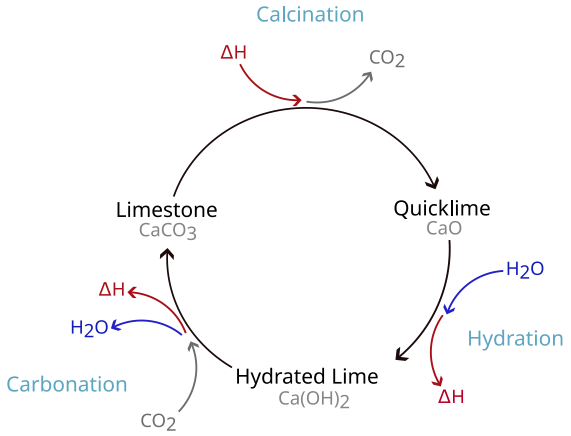

Fig. 1. Schematics of the technical lime cycle.

Limestone is an abundant material and thus inexpensive, has no environmental impact and is already widely used in industrial applications [5]. In order to use limestone as an energy storage material it needs to be burnt at temperatures of around 900–1200 °C, whereby CO_2 escapes, following Eq. 1 [5]. This calcination process is used in industrial applications worldwide, using different reactors like rotary kilns, which might be adaptable for calcination of the small particles used in this concept [5].

2.1. Calcination – energetic charging and CO_2 separation

A key factor for maximizing the CO_2 capture capacity in the concept is the carbon footprint associated with the energy used for calcination. As high temperatures are required, this requires the main energy input in the system (178 kJ/mol $CaCO_3$, calculated based on standard enthalpies according to Barin [24]). The less carbon is produced to provide this energy, the higher the efficiency of the CO_2 capture. Current state of the art in Europe is the use of shaft kilns, most commonly the parallel flow regenerative kiln (PFRK) [5]. Two parallel shafts connected with a crossover channel are used to preheat and calcine the material at 900–1100 °C, with a heat demand between 3200–4200 MJ/t $CaCO_3$ and an electricity demand of 20–41 kWh/t $CaCO_3$ [5]. Up to now, heat has mainly been generated by burning fossil fuels. This causes additional energy related emissions, as during the reaction about two third of the CO_2 is released by the chemical reaction (Eq. 1), while one third is emitted by the combustion of fossil fuels to provide high temperatures [25].

$$CaCO_3(s) + \quad \Delta H_R \rightarrow CaO(s) + CO_2(g) \tag{1}$$

As an example, in PFRKs between 0.987–1.120 t CO_2/t CaO are emitted, along with other pollutants, with more than two thirds unavoidable emissions caused by the reaction [5]. A reduction in the use of fossil fuels can therefore contribute to a reduction in emissions, but a large proportion of emissions cannot be avoided, which is why new approaches combine calcination with carbon capture.

One possibility is oxy-fuel combustion, where combustion is performed in a high purity oxygen stream, releasing a CO_2-rich exhaust stream, which can be compressed and further utilized by carbon capture and storage or utilization (CCS or CCU) [11]. A new possibility since 2020 is the use of a direct separation reactor from Calix (DSR), investigated in the Low Emissions Lime and Cement (LEILAC) project. It consists of a pre-calciner and an inner and outer reactor tube. In the outer reactor shell the burners are located, which indirectly heat the inner reactor tube. Raw material enters at the top and calcined material exits at the bottom, with the process CO_2 rising in a counterflow, recovering thermal energy [26]. This design prevents the mixing of reaction gases and exhaust gases from the combustion, and a 98%

(minimum 95%) pure CO_2 stream can exit the reactor. To prevent re-emitting into the atmosphere, it should be captured as a possibly pure gas stream, to then be compressed and either stored underground or made available for subsequent processes like production of synthetic fuels or food industry. According to Schmidt and Hahn, the potential CO_2 demand in 2030 could be around 234–423 Mt CO_2/a, exceeding the amount which can be supplied by industrial sources [27]. DSRs can be operated electrically, with the emissions then depending on the electricity mix. The most favorable case is the use of renewable energies, so that the emission value is reduced to a minimum. Thereby, thermal and electrical energy input is not expected to increase compared to conventional calcination with the LEILAC technology [26,28,29].

The overall aim of the presented concept of energy storage and DAC is combining heat on demand with CO_2 capture from the atmosphere, aiming for CO_2-negative heat supply in the future. In order to achieve this and thus maximize CO_2 capture capacity, the future goal is to exclusively use renewable energy. As their availability is highly fluctuating, using surplus energy brings the need for a dynamically operating, electrically heated calciner. With this, the combined system can work as a sector coupling technology with long-term storage option and therefore provides flexibility for a renewable energy system.

2.2. Lime slaking – energetic discharging

As the energy is chemically bound in the charged material burnt lime, it can be stored over long periods of time with almost no losses, making it a suitable long-term energy storage system. In times of heat demand, the exothermic reaction can be started by adding water to quicklime, releasing heat which can provide space heating or hot water. Stoichiometrically, 300 ml water can release 0.323 kWh/kg CaO during hydration, described in Eq. 2 (based on standard enthalpies according to Barin [24]). This equals 37% of the energy input during calcination, representing the maximum recoverable energy.

$$CaO(s) + \quad H_2O(l) \rightarrow Ca(OH)_2(s) + \quad \Delta H_R \tag{2}$$

The principle of lime-based heating is described by Schmidt et al. [3] in more detail, with their developed reactor serving as a starting point for the presented concept. A mechanically induced fluidized bed of powdered CaO is generated inside the reactor, where water is injected via a nozzle. The released reaction heat is transferred to a heat transfer fluid via the reactor shell. Operation is carried out in batch mode, so before and after hydration, the material is transported in and out the reactor via a vacuum conveyor. [3]

Theoretical efficiency is high, the real efficiency is currently under investigated in tests with a pilot plant [3]. The most important factor is the achieved conversion of the chemical reaction, but additional factors such as the energy consumption of stirrer and vacuum pump must be considered. Further designs of the hydration reactor to achieve higher temperatures or utilize CaO pellets are the subject of current research.

2.3. Carbonation – site-independent CO_2 capture

The energetically discharged, powdered $Ca(OH)_2$ then forms the basis for the extension of this thermochemical energy storage system with CO_2 capture. $Ca(OH)_2$ reacts with atmospheric CO_2 under ambient conditions, binding it chemically in $CaCO_3$ with a high storage density of 44 wt% (compare Eq. 3). The reaction is exothermic and releases heat at a low temperature level.

$$Ca(OH)_2(s) + \quad CO_2(g) \rightarrow CaCO_3(s) + H_2O(g) + \quad \Delta H_R \tag{3}$$

Carbonation has slow kinetics under ambient conditions and thus is the rate-determining step in the proposed system. However, through combination with lime-based heating, carbonation times on the order of days to weeks can still be technically feasible, as the energy storage has storage phases without heat demand and thus the material passively waiting for its use without utilizing its full potential. As heat demand fluctuates, the utilization of lime as an energy storage material fluctuates as well. From a technical perspective, the reaction should be accelerated as much as possible without compromising efficiency through additional energy input. Therefore, a detailed examination of influencing parameters affecting the kinetics of carbonation is given in the following section.

The cycle is completed by calcination as a regeneration step, to charge the material energetically and separate the stored CO_2.

3. Literature study on carbonation under ambient conditions

Carbonation under ambient conditions exhibits slow kinetics, making it the rate-determining step in the proposed concept [30,31]. Various parameters influence the reaction and its rate, important for the technical application of $Ca(OH)_2$ powder as a CO_2 sorbent material. In the following, the reaction mechanism reported in the literature, as well as results on the influence of relative humidity, temperature, CO_2 concentration, layer thickness, material characteristics and air flow are summarized.

3.1. Reaction mechanism

Previous studies have investigated the reaction mechanism, initially focusing on concrete structures due to their importance for the durability and lifespan of the construction material [32], then for the purpose of carbon capture with lime-based materials.

The reaction takes place in two steps: a fast, chemically controlled step, and a second, diffusion-controlled step [33–36]. Initially, gaseous CO_2 diffuses in the pores. The importance of water during the reaction is widely understood and reported by various authors [18,33,36–39], as CO_2 needs to dissolve in the adsorbed water and form carbonic acid and its ions, in order to react with solid $Ca(OH)_2$. With the changing pH, solid $Ca(OH)_2$ dissolves in its ions instantaneously [30], and $CaCO_3$ is precipitated [39]. The reaction mechanism is described in Eqs 4, 5, 6 and 7.

$$CO_2 + \quad H_2O \rightarrow H_2CO_3 \quad (aq) \tag{4}$$

$$H_2CO_3 \quad (aq) \quad \rightarrow 2 \quad H^+ + \quad CO_3{}^{2-} \tag{5}$$

$$Ca(OH)_2 \quad \rightarrow \quad Ca^{2+}(aq) + 2 \quad OH^- \tag{6}$$

$$Ca(OH)_2 + \quad CO_2 \rightarrow \quad CaCO_3 + \quad H_2O \tag{7}$$

The precipitated $CaCO_3$ forms a layer on the surface, which shifts the reaction towards the second, diffusion-controlled step [35,40]. Diffusion resistance for CO_2 increases with the growth of the layer as $CaCO_3$ has a larger volume and grows into free pore space, which decreases total porosity [30,36] and thus is often the limiting factor for the reaction [41].

From the reaction equation, key parameters affecting carbonation can be identified: the amount of water to start the reaction, temperature for the reaction kinetics and dissolution of CO_2, decrease in CO_2 concentration through consumption during the reaction, simultaneous growth of the carbonate layer, etc. These and others have been investigated in previous studies, but with varying materials and reaction conditions. In the following, experimental results from literature are summarized and key findings for the utilization of $Ca(OH)_2$ powder as CO_2 sorbent material in the combined system with lime-based heating are obtained.

3.2. Relative humidity

Several authors investigated the influence of water on the carbonation reaction of lime-based materials, mostly in cement materials or CaO, but as well as in porous $Ca(OH)_2$ powder. As it can be seen from the

reaction mechanism (Eq.4), water is required for the dissolution of CO_2 and thus the start of carbonation under ambient conditions. It can either already be adsorbed on the powder surface or be present in the air as relative humidity (RH). This has been confirmed by multiple experiments in the literature.

Shih et al. [36] investigated the carbonation of $Ca(OH)_2$ powder (volume mean diameter 19 μm) at 60–90 °C in humid N_2 (0–70%) for different concentrations of CO_2. Experiments were carried out in a fixed bed reactor and the samples were humidified by a humid N_2-stream prior to carbonation. Their results show that no carbonation occurred below the critical value of 8% RH in the gas stream and RH affected the reaction significantly in the tested conditions, reaching the highest conversion at the highest temperature and RH tested (90 °C, 70% RH, 34.8% in 1 h with a plateau after 10–20 min). They stated that water may be the limiting factor in the dissolution of CO_2 in the pore water during carbonation. But as the temperatures are higher, as well as the CO_2 concentration (between 3–12%), conclusions on carbonation under ambient conditions cannot be drawn without limitations. Beruto and Botter [37] tested $Ca(OH)_2$ powder with average particle size between 0.5–2 μm in lower temperatures (20 °C and 88% RH) but with elevated CO_2 concentrations of approximately 6500 ppm (0.65 kPa) and could prove in their experiments that water plays a catalytic role in carbonation under ambient temperatures.

Dheilly et al. [33] investigated carbonation of powdered $Ca(OH)_2$ in a temperature-controlled chamber with a saturation system at different RH values of 30%, 60% and 100% and 10 °C, 20 °C and 40 °C over 10 days with a CO_2 concentration of 300 ppm and 7 mm sample height. They observed different results depending on the RH present during the reaction. At the lowest RH, carbonation is low or non-existent, but with increasing RH, kinetics of carbonation increase. After 10 days, a mass gain of 13% at 60% RH and 25% at 100% RH are measured after drying, corresponding to approximately 37% and 71% carbonation degree, respectively. Koga et al. [39] also tested the influence of different RH (0%, 50% and 100%) on carbonation. They used compressed $Ca(OH)_2$ powders with 3 mm height and observed the reaction in a CO_2 reaction vessel, with an inlet stream of 200 ml/min CO_2, at room temperature for 14 days. Results show that no changes occurred at 0% RH, while at 100% RH the sample was completely converted to $CaCO_3$. At 50% RH, carbonation occurred, but no complete conversion was achieved in 14 days. They concluded that humidity is the key factor for carbonation under ambient conditions. In addition to the compressed $Ca(OH)_2$ powder, they tested a $Ca(OH)_2$ compact made from lime paste in 100% RH and results showed, that conversion was reduced compared to the compact powder. They concluded that the presence of water inside the paste may prevent diffusion and thus an optimum humidity exists for carbonation.

Erans et al. [42] investigated lime-based sorbents with the aim of using them as sorbent materials for DAC. Next to CaO, hydrated samples were prepared by spraying CaO with deionized water and using a mechanical granulator. Carbonation conditions were in ambient air inside the lab with an average temperature of 18 °C and 51% RH. After 7 days 5 mm samples achieved 50% conversion and after 12.5 days 70%. Reaction kinetics were faster than for dry CaO material, which confirms that humidity accelerates carbonation kinetics under ambient conditions. Criado et al. [18] followed the experiments and tested carbonation in the TGA with an elevated CO_2 concentration of 5 vol% CO_2 and 65 °C. In these conditions, 90% conversion was reached in 10 min. With decreasing RH, they observed that the reaction slows down but still reaches the maximum conversion in hours. Testing the gas with 0% RH, no conversions beyond 5% were achieved. They tested the same with compressed $Ca(OH)_2$ pellets and concluded that values of $>$ 80% RH promote fast reaction rates for any $Ca(OH)_2$ material.

Dependency of carbonation rate on relative humidity seems very clear from experimental studies on $Ca(OH)_2$. To conclude, Criado et al. stated that RH must be over 50% to reach carbonation over 60% and best between 80% and 100%, Beruto and Botter concluded that RH must be over 70% to significantly promote the reaction and Dheilly et al. achieved best results in RH close to 100% [18,33,37]. Moorehead did experiments with lime compacts and concluded that carbonation is maximized when 50% of the pores are filled with water [43], which may proceed at a slower rate in the larger pores of powder instead of cement material.

Pore water can not only form through the presence of RH, but can also result from hydration. This is an important aspect of the presented concept, as hydration precedes carbonation and could therefore be used to optimize subsequent carbonation. Reaction conditions influence the presence of adsorbed water on the material as well as material properties. Gillott [44] observed that $Ca(OH)_2$ made by vapor hydration carbonates at a slower rate in ambient temperature than $Ca(OH)_2$ formed by water hydration as considered in the presented concept. Dheilly et al. [33] also tested the influence of pre-hydration of $Ca(OH)_2$ samples before carbonation with humid oxygen (100% RH). Results show that carbonation occurs faster for pre-hydrated samples. In air with 300 ppm CO_2, 100% $Ca(OH)_2$ reacted to $CaCO_3$ in 25 days, with 4.5% humidity adsorbed on the sample compared to the initial dry mass. Moreno et al. [45] found that RH in storage conditions of $Ca(OH)_2$ strongly influences the later carbonation and higher RH leads to higher CO_2 capture rates. They investigated carbonation in a fluidized bed in ambient temperature and pressure with 1% CO_2 with previous RH of 24 ± 2%, 58 ± 2%, 75.5 ± 2%, 100 ± 3% during the storage period and assumed that the formation of the adsorbed water film is the most determining factor. Recently, Paulsen et al. [22] investigated the influence of different slaking ratios on the carbonation of the formed $Ca(OH)_2$ under ambient conditions in order to use the material for DAC. Best results were obtained for a slaking ratio of one, but the results are also influenced by the RH present during the following carbonation.

RH seems to influence not only the rate but possibly the reaction itself. López-Arce et al. [46] tested $Ca(OH)_2$ dispersed in isopropyl alcohol in a climate chamber at 20 °C, exposed to 33%, 54%, 75% and 90% RH in 530 ppm CO_2 for 7, 14, 21 and 28 days on its influence on the formed $CaCO_3$. Their results show that carbonation in higher RH (75–90%) leads to faster kinetics and the formation of larger particle sizes while carbonation in low RH (33–54%) leads to the formation of smaller particle sizes with lower crystallinity, which may affect subsequent reactions.

3.3. Temperature

Chemical reactions increase their kinetics with increasing temperature. However, for the carbonation reaction, an additional aspect is observed: as the initial step is the dissolution of CO_2 in pore water, the optimum is a tradeoff between fast reaction kinetics at high temperatures and the optimum temperature for solubility of CO_2 in water. Solubility of CO_2 in aqueous solutions decreases with increasing temperature, related to the temperature dependency of Henry's law [41].

Most of the studies on these opposing effects found in literature were carried out for CaO and the results for the carbonation of $Ca(OH)_2$ at low temperatures are not consistent.

In their experiments with $Ca(OH)_2$ powder Shih et al. [36] found that a temperature between 60–90 °C affects the reaction only mildly, with RH being the most important parameter. Dheilly et al. [33] investigated lower temperatures closer to ambient conditions and showed in their experiments described above that 10 °C is more favorable for the carbonation kinetics of $Ca(OH)_2$ than 20 °C or 40 °C.

Paulsen et al. [22] recently published their work on $Ca(OH)_2$ as a DAC sorbent material and found that 20 °C accelerates the reaction compared to 12 °C, but temperature does not change the overall conversion.

3.4. CO_2 concentration

CO_2 concentration in the atmosphere is very low with approximately 420 ppm and thus could be a limiting factor for the carbonation reaction [47]. In order to react with solid $Ca(OH)_2$, CO_2 needs to diffuse in the pores and dissolve in water. Thereby, the diffusion of CO_2 in water is significantly slower than in air and the dissolution is dependent on the temperature, following Henry's law [48,49].

Until now, the influence of CO_2 concentration on the carbonation under ambient conditions was mainly investigated for accelerated carbonation of cement materials as decisive for the lifespan of the construction material, and thus in higher concentrations of CO_2 as investigated in this work. The literature provides different statements on the influence of CO_2 concentration: while some authors stated a significant influence of CO_2 concentration on the carbonation under ambient conditions, others concluded that parameters like the RH are significantly more important for the carbonation kinetics.

Shih et al. [36] found that in their experiments conversions of $Ca(OH)_2$ powder are the same for 3.15, 6.30, and 12.60% CO_2 (at 60–90 °C and 0–70% RH) and that the investigated CO_2 concentrations have no influence on the reaction rate. Lower CO_2 concentrations of 300 ppm were used in the experiments by Dheilly et al. [33], with the conclusion that CO_2 partial pressure is not the dominant influencing factor and partial pressure of water dominates the carbonation at low temperatures. Van Balen [34] tested lime samples of laboratory-grade (specific surface area 14.14 m^2/g, mean particle size 4.68 μm), commercial dry $Ca(OH)_2$ (specific surface area 17.89 m^2/g, mean particle size 4.68 μm) as well as an experimental lime type with a higher specific surface area (43.73 m^2/g) but the same particle size distribution as the commercial dry $Ca(OH)_2$ in humid gas with different CO_2 concentrations (7–17 mol/m^3, corresponding to approximately 150–380 ppm CO_2). They used a closed-loop set-up with ambient conditions (20 °C) and tested for 24 h. For the studied conditions, results also showed that carbonation seems independent of CO_2 concentration.

On the other hand, Moorehead [43] found that an increase in the CO_2 concentration increases the reaction rate of carbonation in lime mortar. Visser [50] investigated the hypothesis that, following Fick's law, carbonation has to be proportional to the increase in CO_2 concentration. In the experiments, $Ca(OH)_2$ in cement was experimentally tested and it could be observed that for this material high CO_2 concentrations do not change the carbonation process for itself, as the reaction will occur instantly at the reaction surface, but will accelerate the transport of CO_2 in the air-pore solution and thus lead to faster reaction kinetics. Following this, Criado et al. [18] could show the dependency of carbonation speed and CO_2 concentration for $Ca(OH)_2$ powder experimentally. In their experiments described above, carbonation of $Ca(OH)_2$ follows Fick's law in CO_2 concentrations between 450 ppm and 12%, and thus CO_2 concentration have a direct influence on the growth of the carbonation layer. Less than 24 h was required for complete conversion of the samples for 25% RH, 80 °C and 8% as well as 12% CO_2.

3.5. Layer thickness

Carbonation starts immediately at the $Ca(OH)_2$ surface, forming a $CaCO_3$ layer, which covers the surface of the reacting material. As $CaCO_3$ has a higher volume, the growth leads to the closure of pores and reduction in porosity. Simultaneously, the carbonate layer forms around the reacting particles, making it necessary for CO_2 to diffuse through before carbonation can continue. These effects lead to a high influence of layer thickness on the carbonation rate under ambient conditions, but are reported differently in literature.

The influence of layer thickness on the carbonation under ambient conditions to utilize it in the application of DAC was investigated in more detail by Criado et al. [18]. Different $Ca(OH)_2$ mortar samples with porosities between 0.2 and 0.8 were prepared from a raw material with 5–6 μm average particle size and a layer thickness between 4–15 mm. Tests were carried out in a test room with 500 ± 25 ppm CO_2, 52 ± 3% RH and 10 ± 2 °C, with a fan in front of the sample ensuring a continuous velocity of approximately 0.5 m/s over the sample. Results show 60% carbonation in 500 h for a material with a specific surface area of 18.2 m^2/g, while high-grade $Ca(OH)_2$ with a specific surface area of 39.3 m^2/g reached 80% conversion in the same time. They compared their results with predictions of a carbonation model, which describes the limitation by diffusion following Fick's diffusion law under consideration of material and environmental influences and found good agreement between predictions and experimental tests. The same results were obtained for a $Ca(OH)_2$ material with a higher specific surface area of 39.3 m^2/g, which achieved 85–90% conversion in the same time of 500 h. To extend the capability of Fick's diffusion law, they also tested in higher CO_2 concentrations, as described above. For controllable conditions, they carried out experiments in a sealed glass container with temperatures between 20–80 °C and 200 l/h compressed air with 450 ± 35 ppm CO_2 and adjustable RH with extruded shapes of $Ca(OH)_2$ with porosities between 0.51 and 0.34. 90% conversion was achieved in > 95% RH, confirming prediction of the carbonation front is possible with known porosity, assumed maximum conversion and fitted tortuosity.

Hawrot and Renforth [51] also analyzed the influence of different layer heights, but for a significantly longer time. 2.5, 5, 10, 25 and 50 mm layers of $Ca(OH)_2$ (mean particle size of 2–6 μm, specific surface area 16–18.5 m^2/g) on sample trays were exposed to laboratory conditions (temperatures 4–26 °C, average 17 °C, and 10–89% RH, average 50%) for 184 days (six months), whereby weight and composition were regularly measured. The thinnest layer (2.5 mm) showed the fastest carbonation of 58 ± 6% in 22 days, with only minimal increase afterwards. The increase in layer thickness results in a decrease in carbonation over time. 5 mm layer converted to 53 ± 6% in 27 days, 10 mm achieved 56 ± 3%, in 55 days and 25 mm converted to 57 ± 2% in 114 days. Afterwards, a plateau is formed and only minimal increases are recorded. At the end of the experimental time, all layers reached the same $CaCO_3$ content. This confirms, that not the overall conversion, but the reaction speed are significantly determined by layer thickness of $Ca(OH)_2$.

Compared with the experiments conducted by Criado et al. [18], significantly lower reaction rates were observed. As material characteristics as specific surface area and particle sizes are comparable, this may be attributed to the highly varying reaction conditions in the laboratory environment and different experimental settings.

3.6. Material characteristics

A decisive parameter on carbonation is the material characteristics, also influencing the parameters discussed above.

Shih et al. [36] and Van Balen [34] stated that CO_2 uptake and $Ca(OH)_2$ surface area have a linear dependency, and Moreno et al. [45] emphasize that the surface of the sorbent actually exposed to the air and thus CO_2 is the main limiting factor for the carbonation. Morales-Flórez et al. [52] observed increased reaction rates with increased surface area for CaO, which was confirmed for $Ca(OH)_2$ samples by Criado et al. [18]. In their experiments, higher carbonation occurred for $Ca(OH)_2$ samples with higher specific surface area: in a test atmosphere with 500 ± 25 ppm CO_2, 19 ± 2 °C and 52 ± 3% RH and a fan located in front of the samples, porous $Ca(OH)_2$ with a specific surface area of 18.2 m^2/g achieved 60% conversion in 500 h, while high-grade $Ca(OH)_2$ with a specific surface area of 39.3 m^2/g reached 80% conversion in the same conditions [18].

Hawrot et al. [51] observed that surface area of $Ca(OH)_2$ decreased during carbonation, reducing from initially 12.89 m^2/g to 6.4 m^2/g during their experiments, with increasing particle size. This may be due to the effect that growth through carbonation proceeds inside the porous particles, which was also observed by Beruto and Botter [37]. Porosity highly influences the dependence of CO_2 concentration and RH on

carbonation kinetics, as CO_2 diffuses faster in air, but needs to dissolve in the pore water to react with solid $Ca(OH)_2$, leading to competing effects [50]. Samari et al. [14] investigated different lime-based sorbents for DAC and argued that pelletized limestone has a greater diffusivity due to its greater porosity, while Koga et al. [39] and Van Balen [34] stated that the presence of water inside the pores may prevent diffusion and thus an optimum humidity exists for carbonation.

3.7. Air flow

In DAC systems, large quantities of air are pumped through the system to compensate for the low CO_2 concentration in the atmosphere, with electrical air fans required in all commercial DAC plants [13]. Air flow is therefore an important design parameter for the air contactor. In natural conditions, carbonation has slower kinetics, raising the question of whether CO_2 is a limiting factor in the reaction and an active air flow can enhance kinetics. But to the author's knowledge, no explicit investigation of the influence of an active overflow with air on the carbonation under ambient conditions was carried out. Instead, it is not consistently clarified in most reported experiments whether an airflow was present during the experiments and may be one of the parameters explaining why experimental results differ strongly in otherwise identical conditions.

Hawrot et al. [51] observed conversion of 53 ± 6% in a 5 mm layer $Ca(OH)_2$ in 27 days (average 17 °C, 50% RH, laboratory conditions), while Erans et al. [42] achieved 70% carbonation in 300 h (12.5 days), also in laboratory conditions (18 °C, 51% RH).

Criado et al. [18] conducted experiments for a similar material in the same conditions (52 ± 3% RH, 19 ± 2 °C), but with an air velocity of 0.5 m/s over the sample through a fan, and achieved almost the same carbonation of 60% in 21 days for a material with similar properties and 90% for a high-grade $Ca(OH)_2$. This is in common with the experimental findings of Moorehead [43], where carbonation under ambient conditions was tested for 30 min, but in a pure CO_2 stream, and 71% carbonation with forced circulation and 76% without forced circulation were obtained. These results indicate that gas flow velocity on the sample surface seems to have little effect on the carbonation.

In a recent paper, Criado et al. [19] investigated different $Ca(OH)_2$ materials (compact powder with a porosity of 0.55, dried mortar in a 1:1 water ratio and extruded $Ca(OH)_2$ slurry with porosities between 0.35–0.4) in a lab-scale air contactor with air channel velocities between 0.5 – 5 m/s. Experiments took place under ambient conditions of 21 ± 3 °C, 43–80% RH and an average of 450 ppm CO_2 for 300 h. The compressed powder achieved conversion rates of 90% in 3–4 mm layers, the mortar achieved 70% in the same thickness and time. The extruded $Ca(OH)_2$ showed lower conversion of 20–30%. Their results showed that the CO_2 capture efficiency reduced with increasing air velocities, even though the average CO_2 value is higher and in theory, capture efficiency should not be influenced by the air stream.

El-Turki et al. [53], on the other hand, achieved faster reaction and a 100% degree of carbonation in 5 days with the exposure gas being passed over the sample in the reaction chamber, but with extruded $Ca(OH)_2$ paste [53]. Accordingly, these results indicate a correlation between air flow and carbonation rate.

Although several studies have already investigated carbonation under ambient conditions, their findings are often difficult to compare and, in some cases, remain inconclusive. Therefore, literature results are not directly applicable to the proposed concept and require further experimental investigation under the specific boundary conditions and material properties of the subsequent application.

4. Experimental investigation

To determine the feasibility of the proposed concept, experimental investigations of important influencing parameters are required. By combining DAC with renewable heating, carbonation is preceded by hydration, which can significantly influence reaction conditions such as humidity and moisture. Additionally, large volumes are required for the storage functionality of heat and CO_2. To investigate conditions that are representative of those in the intended later application, a test bench was built and experiments were carried out. In the following sections, the set-up is described in more detail and experimental results are summarized and discussed.

4.1. Test bench

In order to investigate the realizability of the proposed concept, key parameters which could not be determined from the literature were experimentally investigated. The aim is to determine optimal values for carbonation under ambient conditions for DAC. Therefore, a test bench was set up in the laboratory, shown in Fig. 2, with controllable reaction conditions comparable to those intended in the technical application. The reaction is intended to proceed under ambient conditions.

The key component is a scale, which records the sample mass to observe the weight increase and thus the reaction over time. Due to the CO_2 uptake of $Ca(OH)_2$ and thus the formation of carbonate, the mass can increase up to 35%. A Mettler Toledo ME4002 with a readability of 10 mg was used, suitable for small sample masses. Scale and sample are placed in a plexiglass chamber with a volume of approximately 79.2 l, in which ambient conditions can be set. Therefore, the evaporator unit CEM W−202A−330−K from Bronkhorst was installed, with a maximum water flow of 50 g H_2O /h, which is controlled by a liquid flow meter L23−PBD−11−K−30S with ± 1% accuracy. In order to pump the deionized water, an FNP1.7 pump from KNF is used. With 40% of the power, the required pre-pressure for the evaporator of 2 bar is reached. Upstream, a microfilter from Headline filters with a diameter of 12 mm and length of 32 mm and > 99.99% removal of particles < 0.1 μm is additionally installed to protect the pump from any contamination. The supplied air flow is mixed from 4.9 l_n/min compressed air and pure CO_2, depending on the testing conditions. For the reference experiment, 2 ml/min CO_2 is set, achieving approximately atmospheric CO_2 concentrations in the reaction chamber. The air flow is then directed in the chamber from above without passing directly over the sample surface. A ventilator is installed in one corner of the reaction chamber to ensure mixing of the incoming air, but is also not directed at the sample to prevent airflow over the sample.

Inside the chamber, temperature, relative humidity and CO_2 concentration of the controlled atmosphere are measured. Thermocouples Type K with ± 1 K accuracy are used. For relative humidity, two probes from Driesen + Kern were used, measuring with ± 1.8% rH accuracy in the range of 20 – 80% relative humidity. CO_2 is measured and recorded by Vaisala GMP 343, with a measuring range between 0–1000 ppm CO_2. All sensors record measurements once per minute. For evaluation, every tenth data point is used, and values are averaged over 100 data points.

4.2. Material

Material properties are currently predetermined by the hydration in the lime reactor. Fine powdered $Ca(OH)_2$ is used to serve as both heat storage material for renewable heating and CO_2 sorbent material for DAC.

Therefore, lab-grade $Ca(OH)_2$ from Honeywell with a purity of min. 96%, a max. content of 3% $CaCO_3$ and a density of 2.24 g/cm^3 was used for the experiments. The specific surface area was measured by BET using nitrogen in a Micrometrics 3Flex to 15.09 ± 0.14 m^2/g, and particle size distribution to a D_{50} of 3.52 μm by a Mastersizer3000 + from Malvern Panalytical, based on five samples.

4.3. Method

The influence of CO_2 concentration, layer thickness and an active air flow on the reaction rate of carbonation is analyzed experimentally.

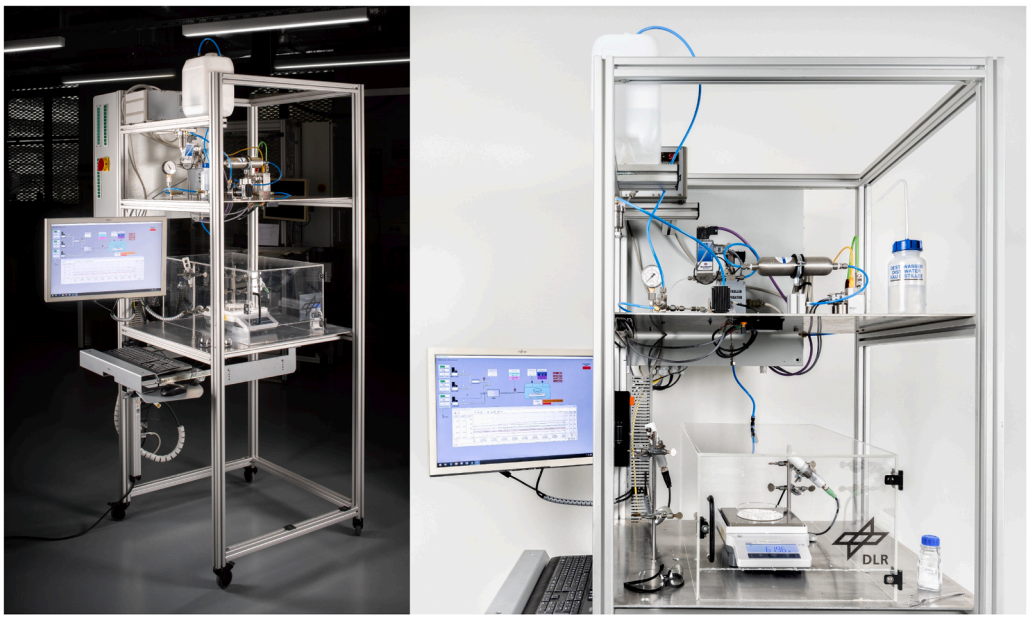

Fig. 2. Test bench for carbonation in the DLR lab, with scale to observe the reaction progress over time and adjustable relative humidity and gas compositions for controllable atmospheric conditions in the reaction chamber.

The literature reports different effects of CO_2 concentration on carbonation, particularly under the low ambient concentrations required for the proposed application, and these effects require further investigation. It is known that increasing layer heights slow down carbonation, but this is being investigated in more detail for the material used in the concept and for layer heights feasible for the technical application. This is important for determining initial material and energy flows as well as reaction time and thus area requirements, and consequently the feasibility of the concept. Given the lack of conclusive findings of an active air flow on the carbonation rate, experimental testing is necessary for the design of an air contactor.

From literature it is well known that relative humidity has a major influence on the carbonation in ambient temperatures and may even be the most dominant factor. The following experiments aim for approximately 75% RH, as a compromise of RH as high as possible and technical feasibility without condensation in the technical application as well as in the test bench, but fluctuates as the temperature is not controlled.

All samples were placed in sample holders made from stainless steel in the test bench described above, with different atmospheric conditions set. Thereby, all sample holders have the same volume of 50 cm^3, but different dimensions. After filling the $Ca(OH)_2$ powder into the sample holders, it was smoothed on the surface, to create a flat surface and guarantee the same volume of each sample. The evaporator was set to a temperature of 50 °C, and the inlet stream of air to 4.9 l_N/min. Inlet stream of water and CO_2 were adjusted, depending on the experiment. The duration of the experiments varied between 7, 14 or 28 days.

A reference experiment (0_Ref) is defined, with a gas mixture similar to atmospheric conditions and a low layer thickness of 2.0 mm. All three different influencing parameters are analyzed in the following experiments and compared with this reference experiment.

The first set of experiments investigates the influence of CO_2 concentration in the reaction chamber on the carbonation. Three different CO_2 concentrations were tested, corresponding to a possible later application: approximately 100 ppm, for low air exchange rates, approximately 400 ppm as average atmospheric condition and high CO_2 loadings of approximately 1000 ppm, for example from exhaust air in buildings. The values were calculated theoretically and then adjusted by the measured value in the sample box. The CO_2 stream mixed to the air was set to 0.35 ml/min, 2.0 ml/min and 7.0 ml/min, respectively, theoretically resulting in 70 ppm, 400 ppm and 1400 ppm. For the last experiment, the CO_2 stream was reduced to 5.0 ml/min during the experiment, as measured CO_2 concentration began to increase above 1000 ppm. In all experiments the sample holder with 2.0 mm sample height was used, as in the reference experiment.

Second tested parameter is the influence of the layer thickness on the carbonation kinetics for the fine $Ca(OH)_2$ powder used. Three different geometries of sample holders were used: 2.0 mm (reference experiment), 4.6 mm (2_4.6 mm) and 20.0 mm (2_20.0 mm) height, but differing in diameter. The small sample heights correspond to layer thickness that have already been investigated in the literature, while the 20.0 mm layer is a maximum that is being investigated for design of the technical application.

In a third experiment, the influence of an active mixing of the inlet airstream with the air in the reaction chamber was investigated by turning on the installed ventilator (3_Vent). As the reaction chamber is not airtight, the ventilator led to a loss in humidity and thus the incoming water stream was increased to 0.14 ml/min, to obtain the same values of RH.

In all experiments, the mass signal, as well as CO_2 concentration, relative humidity and temperature were measured over experimental time. From the weight increase, the degree of carbonation can be calculated at any time, following Eq. 8.

$$X_{\mathrm{Carb(m)}} = \frac{\Delta m}{\Delta m_{\mathrm{Carb,max}}} \bullet 100\% \quad (8)$$

Δm is the change in weight in grams, measured by the scale on the test bench. $\Delta m_{\mathrm{Carb,max}}$ is the maximum mass increase due to the absorption of CO_2 during carbonation. It is calculated to be 35%, according to Eq. 9.

$$\Delta m_{\mathrm{Carb,max}} = \frac{M_{\mathrm{CaCO3}} - M_{\mathrm{Ca(OH)2}}}{M_{\mathrm{Ca(OH)2}}} \bullet m_0 = 0.35 \bullet m_0 \quad (9)$$

As the weight also increases due to the adsorption and absorption of water, and since the assumption was made that pure $Ca(OH)_2$ is used in the experiments, the final sample composition was determined with thermogravimetric analysis after the experimental time for validation of the carbonation degree. Therefore, approximately 20 mg sample was homogenously mixed and placed inside an Al_2O_3 crucible in a NETZSCH STA449C. Inlet stream is set to 150 ml/min N_2 and the sample is initially heated to 110 °C with a heating rate of 10 K/min. After keeping the

temperature constant for 120 min in order to dry the sample, it was heated to 800 °C in a second step. After 20 min at the maximum temperature, the oven was cooled down.

Three steps in mass loss were identified with the software NETZSCH Proteus to calculate moisture content, then dehydration and lastly decarbonation at the highest temperatures. Stoichiometry of the reaction allows conclusions to be drawn regarding the components present in the sample. Means were calculated from triplicate samples, with one sample analyzed directly after the experiment and a high degree of reproducibility.

With the results, the degree of carbonation was calculated again, using Eq. 10.

$$X_{\mathrm{Carb(TGA)}} = \frac{x_{\mathrm{CaCO3}} - x_{\mathrm{CaCO3,Ref}}}{x_{\mathrm{CaO,Ref}} + x_{\mathrm{Ca(OH)2,Ref}}} \quad (10)$$

Here, x_{CaCO3} is the proportion of $CaCO_3$ in the sample after carbonation in %, while $x_{\mathrm{CaCO3,Ref}}$ is the percentual proportion of $CaCO_3$ in the reference sample before the carbonation. Accordingly, $x_{\mathrm{CaO,Ref}}$ and $x_{\mathrm{Ca(OH)2,Ref}}$ are the percentual share of CaO and $Ca(OH)_2$ in the starting material, respectively. The advantage of this calculation, compared to the calculation of the degree of carbonation based on the weight increase, is that the composition of the sample before the carbonation is included in the determination. Both existing $CaCO_3$ and accumulated moisture are taken into account. This is why the average degree of carbonation of the three measurements was compared with the degree of carbonation calculated from the weight increase on the test bench. However, the measured samples are only very small (20 mg from an average sample mass of 20 g) and the results can only be obtained at the end of the experiment.

For the reference experiment, the specific surface area and average particle size were measured before and after the carbonation, with a Micrometrics 3Flex in nitrogen and from five samples in a Mastersizer3000 + from Malvern Panalytical.

4.4. Results

Firstly, the results for the reference experiment *0_Ref* are presented in Fig. 3. Additionally, specific surface area and particle size distribution were determined after carbonation, for comparison with $Ca(OH)_2$ before carbonation. It could be observed that D_{50} slightly increases to 4.28 µm, while the specific surface area significantly decreases from 15.09 ± 0.14 m^2/g to 4.46 ± 0.05 m^2/g after carbonation.

A continuous increase in weight can be seen on the left, until a plateau is formed that no longer shows any change in mass. The maximum weight increase is 31.9%, corresponding to $X_{\mathrm{Carb(m)}} = 90.9\%$ after the experimental time of 28 days. The right side of Fig. 3 shows the sample composition before and after the carbonation, determined by TGA. Whereas originally 93.6% $Ca(OH)_2$ was presented, the proportion falls to 13.5%. Instead, the largest component is then $CaCO_3$, growing from 2.8% to 86.0%. Taking the determined sample composition as a basis, this results in a slightly lower carbonation degree of $X_{\mathrm{Carb(TGA)}} = 85.6\%$ (differences in the calculated degree of carbonation – based on weight increase and TGA analysis – are attributed to methodological variations and are further discussed in Section 4.5).

The first set of experiments investigated the dependency of carbonation speed and CO_2 concentration. Fig. 4 shows the weight increase over two weeks, with a maximum of 35%, for 100 ppm CO_2 and 1000 ppm CO_2 under set conditions of 20 °C and 75% RH averaged over 100 measuring points. Shown as dashed lines are 14 days of the reference experiment, which ran for a total time of 28 days at an atmospheric CO_2 concentration of 400 ppm.

As shown in Fig. 4, there is a substantial difference in the speed of carbonation. *1_low* shows a continuous, flat increase in weight over the entire experimental time, reaching a total weight increase of 16.5% after 14 days. This corresponds to $X_{\mathrm{Carb(m)}} = 46.9\%$. *1_high* achieves this carbonation degree after approximately 32 h, which corresponds to

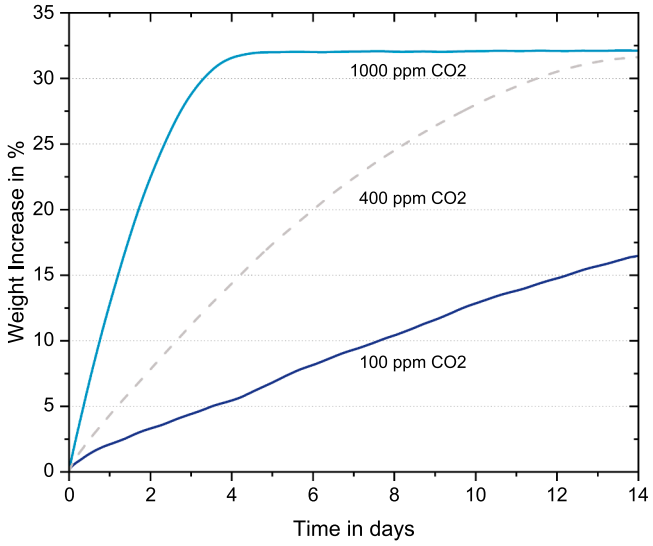

Fig. 4. Weight increase due to carbonation of a 2.0 mm layer of $Ca(OH)_2$ over two weeks under ambient conditions of approximately 22 °C and 75% RH for different CO_2 concentrations of 100 ppm (*1_low*), 400 ppm (*0_Ref*) and 1000 ppm (*1_high*).

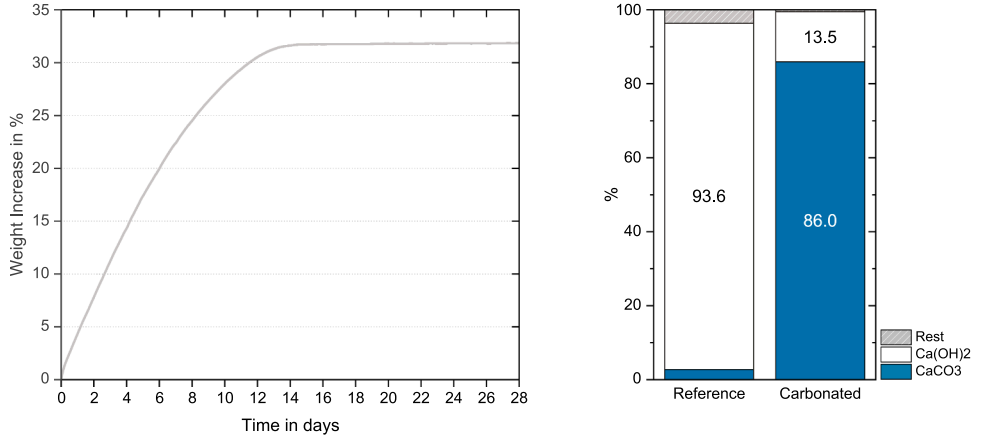

Fig. 3. Reference experiment. Left: Weight increase due to carbonation of a 2.0 mm layer of $Ca(OH)_2$ over four weeks under ambient conditions of approximately 22 °C and 71% RH in 370 ppm CO_2. Right: Sample composition before and after carbonation determined by TGA.

approximately a tenth of the time. The steep mass gain continues until it reaches a plateau of 32.0%, according to $X_{Carb(m)} = 91.2\%$ after approximately 110 h, where only small increase and fluctuations in weight of 0.14 g are observed for the rest of the experimental time. The reference experiment *0_Ref* achieves approximately the same weight gain of 31.6% in 14 days, indicating that, under the experimental conditions, the carbonation rate is affected, whereas the final degree of carbonation remains unchanged.

In a second set of experiments, the influence of the $Ca(OH)_2$ layer thickness on the carbonation speed was investigated. Fig. 5 shows the weight increase over 28 days of experimental time for a layer thickness of 2.0 mm, 4.6 mm and 20.0 mm, averaged over 100 measuring points.

Three different courses can be observed. While experiments *0_Ref* and *2_4.6 mm* reach a plateau during the experimental time, *2_20mm* with a layer thickness of 20.0 mm still gains weight after 28 days. Absolutely, *0_Ref* and *2_4.6 mm* show a weight increase of 31.9% and 31.7%, resulting in $X_{Carb(m)} = 90.9\%$ and $X_{Carb(m)} = 90.1\%$, while the *2_20mm* achieves $X_{Carb(m)} = 40.6\%$.

These results are also reflected in the determination of the sample composition at different layer heights measured by TGA. Fig. 6 shows proportion of $Ca(OH)_2$, CaO and other components in the samples, derived from the experiments.

There is a clear progression in the proportion of $Ca(OH)_2$ after carbonation at different heights of the sample. The deeper the sample was taken, the less $CaCO_3$ and the more $Ca(OH)_2$ are still present. As all experiments were carried out with the same starting material, they can be compared with the reference sample before carbonation, shown on the left. The sample composition at 20.0 mm depth shows almost no change in the proportions, which indicates that carbonation did not occur in this layer.

The third experiment shows the influence of an active airflow in the reaction chamber on the carbonation. Same conditions as in the reference experiment are set. Additionally, a small ventilator mixes the air in the reaction chamber, without directly pointing at the sample. Fig. 7 shows the difference in weight increase between the ventilator being turned on and off.

As the reaction time is decreased significantly, only one week of experimental time is shown. The weight increases fast and after approximately 2.5 days a plateau is formed at $X_{Carb(m)} = 71.0\%$, which remains constant over the rest of the experimental time with a maximum deviation of 0.4%. The dashed line shows the first week of carbonation of the reference experiment *0_Ref*, with a significantly lower gradient of weight increase and carbonation of $X_{Carb(m)} = 27.4\%$ in 2.5 days. After one week, $X_{Carb(m)} = 64.0\%$ is achieved, but still no plateau is formed, indicating that steady state is not reached.

Table 1 summarizes all experimental results and shows the carbonation degree derived from the weight increase, as well as calculated from the sample composition measured by TGA (provided in Table A.1 in the Appendix).

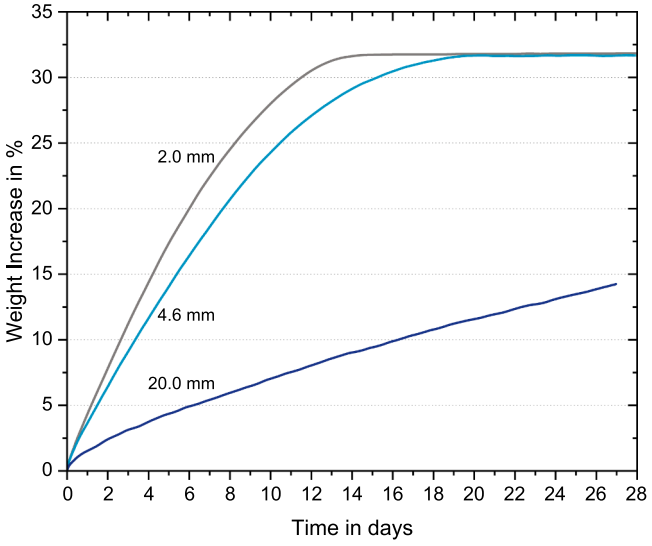

Fig. 5. Weight increase due to carbonation of $Ca(OH)_2$ over four weeks under ambient conditions of approximately 22 °C, 75% RH and ambient CO_2 concentration in different layers: 2.0 mm (*0_Ref*), 4.6 mm (*2_4.6 mm*) and 20.0 mm (*2_20.0 mm*).

4.5. Discussion of experimental results

The described test bench was built to investigate the influencing parameters of carbonation in a later technical application as CO_2 sorbent material in an air contactor. As the experimental set-up has been designed as a compromise between material investigation and representation of a later technical system, this chapter discusses the resulting unavoidable limitations.

Most importantly, carbonation degree calculated from the weight increase and by TGA show some discrepancy, as it shows slightly higher values for all experiments. This may be due to the adsorbed water on the sample surface, which can only be considered in the calculation by TGA. Additionally, the sample is not homogenous, showing different degrees of carbonation depending on the sample depth and agglomeration. Maximum deviation between carbonation degree determined by weight or TGA observed for experiments without ventilation was −6.2% in experiment *1_high*.

Weight values show slight fluctuations towards the end of the experiments. This could be due to fluctuating relative humidity and consequently varying amounts of adsorbed water on the sample surface. Humidity fluctuates because water and gas flow are controlled, whereas the temperature is not. It is influenced by the surrounding laboratory as well as temperature settings in the evaporator. The temperature and relative humidity measurements in the reaction chapter are provided in the Appendix (Figure A.1, A.2 and A.3). Humidity and temperature fluctuations also result in a small drift in the measured weight by the scale (maximum in the experiments was 0.12 g).

Results are shown as percentage weight increase, but although the sample volume was constant for all experiments, the weight varies due to differences in the powder bed.

The first set of experiments show, that CO_2 concentrating had a significant influence on the carbonation speed, at least in the range of 100–1500 ppm CO_2. In these low concentrations, CO_2 concentration seems to be the limiting factor for carbonation. Some authors stated that CO_2 concentration has no influence on the reaction, but investigated higher concentrations, like Shih et al. [36] and Visser [50]. In the experiments conducted here it seems that the atmospheric concentration of CO_2 may be the limiting factor for the rate of carbonation under ambient conditions. However, the overall conversion was not affected. It must be noted that the CO_2 measurement showed strong fluctuations, exemplary between 250 ppm and 440 ppm in the reference experiment. This may be due to the rapid absorption of CO_2 in the sample, or uneven distribution of CO_2 in the reaction chamber. The stated CO_2 concentrations are therefore calculated theoretically, even if the measured concentrations are lower. This also applies to experiment *1_high*, as the upper measuring limit of the CO_2 sensor is 1000 ppm, and measured values may differ.

Evaluating the results of the experiments with different layer thickness, it has to be considered that sample holders only exposed the sample on the surface, as bottom and sides are closed air-tightly. Results show, as expected, a clear decrease in reaction speed with an increase in sample height. Analysis of the sample composition in different layer heights shows a progression of the reaction over depth, which has been referred to as carbonation front in previous studies [18]. For the application as an CO_2 capture sorbent, that means there is a tradeoff between

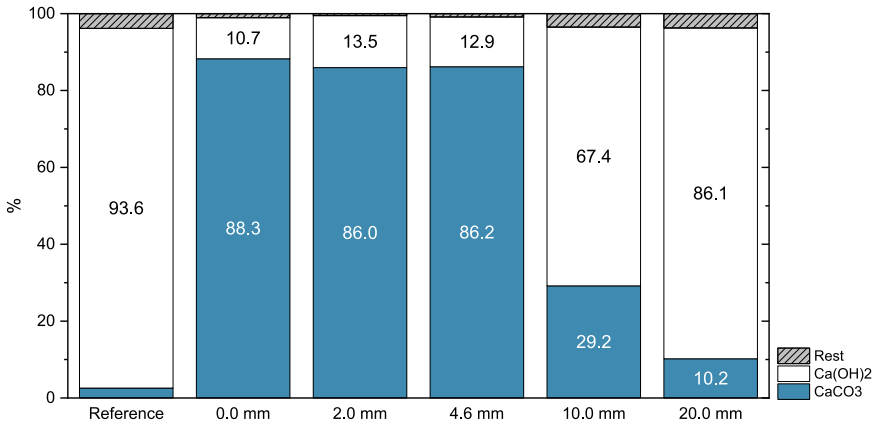

Fig. 6. Sample composition before carbonation (Reference) and after carbonation in different layer heights, with 0.0 mm being at the sample surface, determined by TGA. (Values for 2.0 mm and 4.6 mm were gained from the experiments *0_Ref* and *2_4.6 mm*, with the rest determined from *2_20mm*).

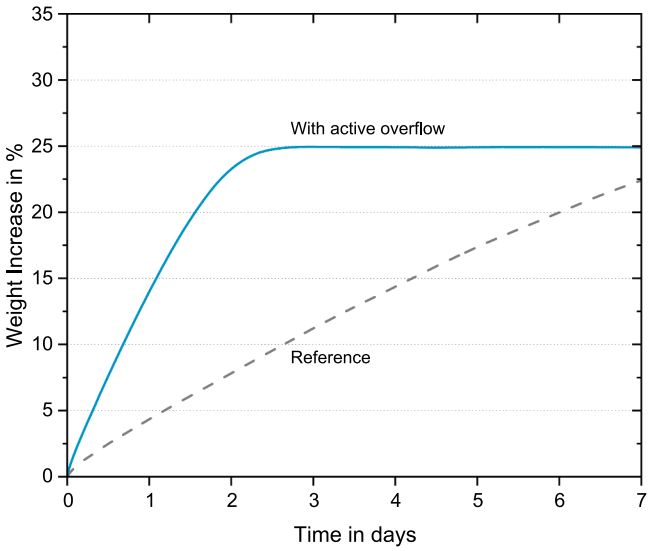

Fig. 7. Weight increase due to carbonation of a 2.0 mm layer $Ca(OH)_2$ over one week under ambient conditions of approximately 22 °C, 70–75% RH and ambient CO_2 concentration without (*0_Ref*) and with an active overflow through the ventilator.

reaction rate, material quantities and required area, making it one decisive parameter for feasibility of the overall system.

The experiment with additionally installed ventilation for active mixing of the air in the reaction chamber achieved a significant acceleration of the carbonation by 2.5 times. This may be due to two effects: the first is the faster distribution of CO_2 even in deeper layers of the sample, thereby a limitation by CO_2 diffusion would be reduced with the active transport. The air flow was not directed towards the sample, which means that there is no active air flow through the sample, however, the increased air movement can lead to forced convection. A second effect relates to the mixing of the air in the reaction chamber. If the simplified Fick's diffusion equation is used for the diffusion of CO_2 in air, the CO_2 concentration in air should equalize quickly. However, the carbonation consumes CO_2 and due to the low concentration in the air, it could create an area with even lower CO_2 concentrations. That this difference in concentration can already be a limiting factor for the reaction speed was shown in the experiments. Since the water flow to the evaporator had to be increased in this experiment to achieve a comparable relative humidity to the previous experiments, the potential influence of this change cannot be ruled out. Although installing a ventilation demonstrated a promising approach to accelerate carbonation under the given ambient conditions, this aspect requires further investigation for its potential implementation in the future technical application.

In all experiments, lab-grade $Ca(OH)_2$ powder was used. However, in the potential future application, the $Ca(OH)_2$ would be the product of the hydration of CaO, which may lead to variations in material composition due to incomplete reaction or exposure to atmospheric air. With this, the maximum achievable conversion rates may be affected, but effects of the key influencing parameters are expected to remain unchanged.

5. Discussion

The experimental results are used to give a first estimate of mass flows of the combined system of renewable heating and DAC proposed in this work to assess feasibility.

Assuming a heating period of 26 weeks, the average heating demand per person in Germany is 240 kWh per week [54]. Accordingly, Fig. 8 is normalized to 240 kWh heat supply and shows required material flows for its provision in the proposed system.

Assuming a 95% efficiency of hydration, approximately 780 kg CaO are required to cover this demand in the lime-based heating, with addition of 250 l water (based on standard enthalpies according to Barin [24]). Thereby, full utilization of the reaction enthalpy but losses due to the electrical input energy required are considered, according to

Table 1
Overview of the experimental results of carbonation under ambient conditions with averaged values for relative humidity, CO_2 and temperature over the experimental time.

Experiment	Layer	Time	Airflow	RH/%	CO_2/ppm	T/°C	$X_{Carb(m)}$/%	$X_{Carb(TGA)}$/%
0_Ref	2.0 mm	28 days	No	71.2	367.4	21.6	90.9	85.6
1_low	2.0 mm	14 days	No	75.2	109.5	22.6	46.9	42.7
1_high	2.0 mm	14 days	No	76.1	916.6	22.7	91.5	85.3
2_4.6 mm	4.6 mm	28 days	No	73.7	354.6	22.7	90.1	85.8
2_20mm	20.0 mm	28 days	No	74.5	370.0	22.5	40.6	41.1
3_Vent	2.0 mm	7 days	Yes	68.9	390.5	22.4	71.0	68.6

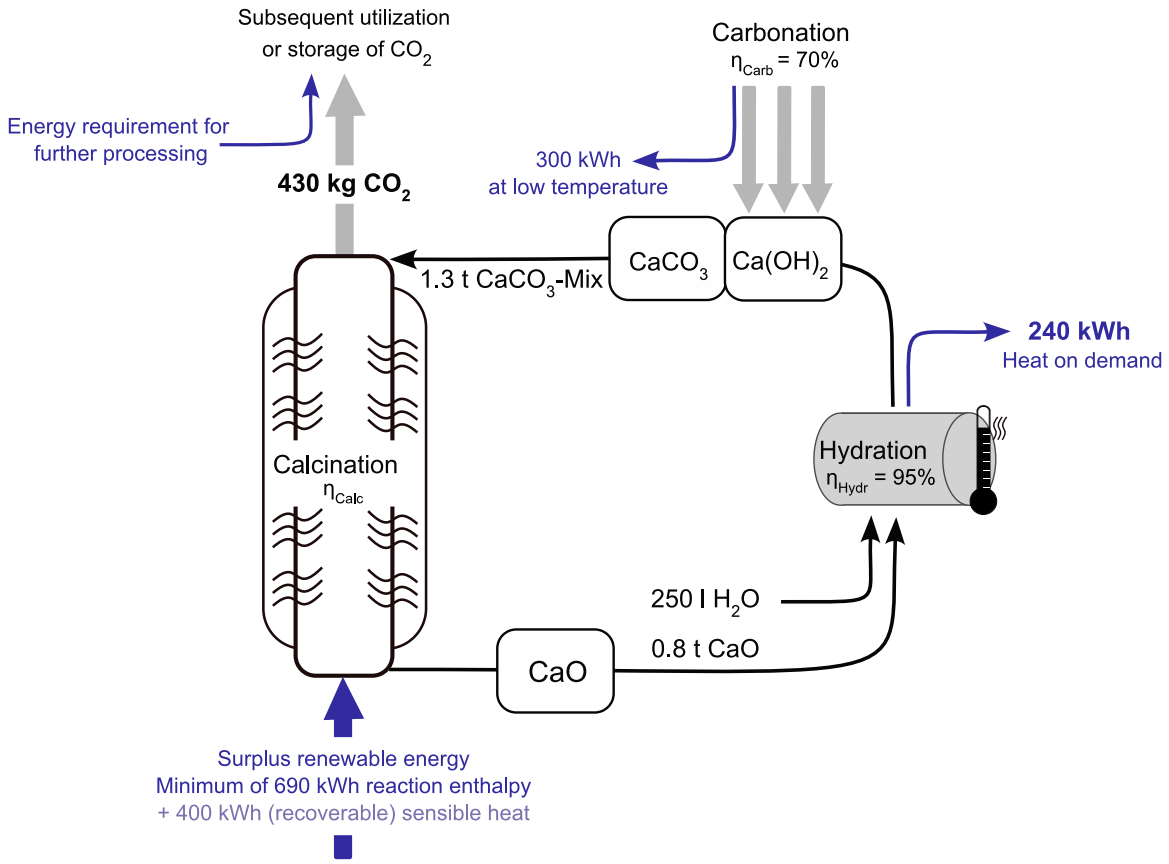

Fig. 8. Estimated material requirements for the combined system of DAC and heating including the efficiencies of each reaction, with first assessment of energy requirements, normalized to a heat demand of 240 kWh.

Schmidt et al. [3]. The efficiency of the CO_2 capture highly depends on the design of the air contactor and the time, as shown in the experimental result section. In Fig. 8, the available time for carbonation follows the heat demand, since the material is cycled within the closed cycle. In the technical application, carbonation is therefore the optimization between conversion, area requirements, time and material quantities. For this calculation, carbonation time equals the time of heat demand. Under optimal ambient conditions, as determined in the experiments, with a 2.0 mm layer and active mixing of the inlet airstream, 70% carbonation could be achieved in one week. Since the carbonation is exothermic, approximately 300 kWh of heat are released at a low temperature level during this period. In the presented concept, this heat is not utilized, but utilization could be considered in future applications.

In 1.3 t $CaCO_3$ and unreacted $Ca(OH)_2$, 430 kg CO_2 can be captured while the heat demand of one week is covered, showing synergies in the cycle times of long-term energy storage systems. To illustrate, if the entire heating demand of 6200 kWh per person were supplied by this process, the captured CO_2 would exceed 11 t CO_2, which is more than the CO_2 footprint of a person in Germany in 2025 [55]. It should be noted that this is the maximum achievable CO_2 capture capacity under the assumed boundary conditions. For an evaluation of the overall system, deductions due to CO_2 emissions from energy supply, transportation or losses must be considered.

The electrical energy input is supplied from surplus renewable energy during periods of excess power generation. Assuming the material returning material stream to the calcination consists of 1.3 t $CaCO_3$, which is calcined to CaO again to close the material cycle, a thermal energy input of approximately 690 kWh is required for the endothermal chemical reaction. An additional 400 kWh are required to sensibly heat the material, but could be reduced, for example through internal heat recovery. Incomplete carbonation reduces the energy demand due to lower energy requirements for the dehydration of $Ca(OH)_2$ compared to calcination of $CaCO_3$. Further losses are determined by the efficiency of the electrical calcination, which is currently investigated.

Since these factors depend strongly on the implementation strategy, two alternative approaches for future technical implementation are described and discussed in the following. Fig. 9 shows that starting point for both is the central electrical calcination in the middle, where the material is thermally charged and escaping CO_2 is captured as a point source for subsequent storage or utilization (CCS, CCU). From there, the material can either remain at the central site (option 1), or be transported to the end-users directly (option 2). Aspects like transport distance, storage duration, carbonation rate, etc. influence which variant is preferable and what CO_2 capture capacity can be reached.

Option 1: Central carbonation

In the first system variant, the material is stored at a central side after calcination. On demand, it is used to feed heat into a district heating network or industrial processes on site. To cover the heat demand, large amounts of material and, consequently, larger storage capacities are required. The formed slaked lime is then also stored centrally, while capturing CO_2 from the atmosphere.

The main decisive factor for the efficiency of this option is the efficiency of the district heating network. Heat losses in district heating networks increase with transport distance and amount to about 11% of the supplied heat on average, according to AGFW [56]. These energy losses must be compensated for by additional material, as the heat demand remains unchanged. On the other hand, almost no additional emissions related to transportation must be added.

Option 2: Decentral carbonation

Backbone for the second system variant is a community-based transport system, which makes it possible to transport the lime-based storage materials between centralized charging and decentralized

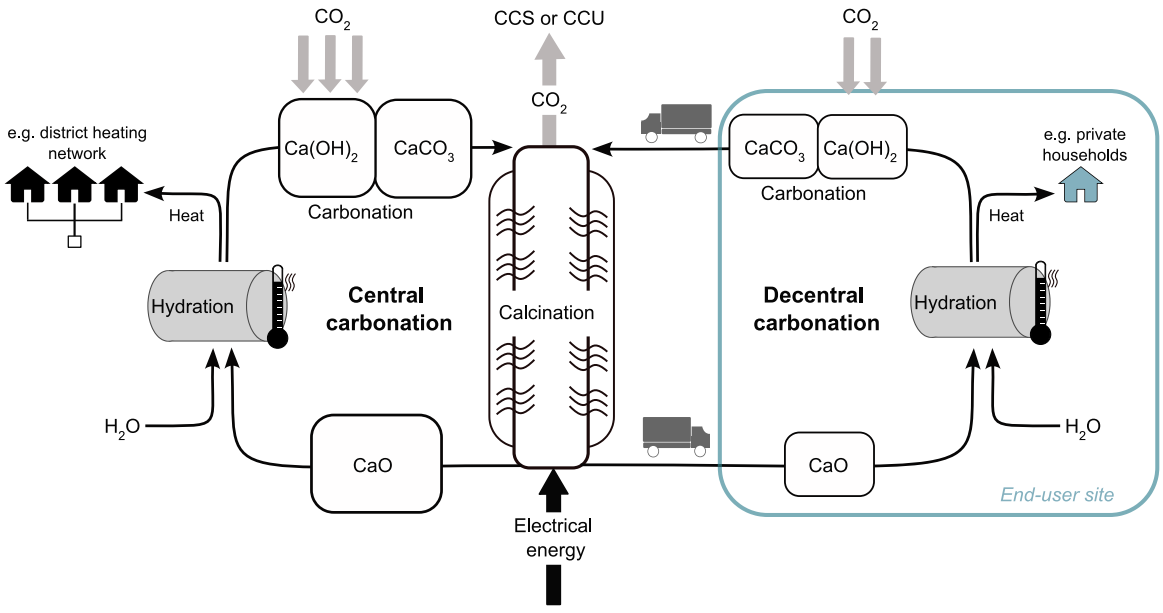

Fig. 9. Different system variants. Left: central carbonation. Right: decentral carbonation.

discharging sites. Heat provision and CO_2 capture take place at the end-user site, who receives energetically charged material and returns material with stored CO_2, giving both transportation ways a value.

Nevertheless, transport also accounts for CO_2-emissions, which must be considered in an overall evaluation of the system. The German Federal Environment Agency (Umweltbundesamt) calculated greenhouse gas emissions caused by transportation by truck to be 118 g/tkm [57], given in CO_2 equivalents. Although this value varies depending on the vehicle used, it demonstrates both the dependency on weight and transport distance. Long distances with CO_2-intensive transport decrease the CO_2 capture efficiency of the system. The energetic efficiency of the transported material remains unchanged, since the energy is stored in chemical form.

Option 3: Other variants

In addition to the two shown options, trade-offs between decentralized and centralized carbonation can also be implemented. One example is a decentralized carbonation, but in larger, thermally connected residential complexes with short transport distances.

To assess the novel system, as with any other DAC technology, it is essential to consider the overall system. Material demands and energy input can cause additional emissions and environmental impacts, which need to be taken into account and are decided by the variant of technical implementation [58]. Beyond the system boundaries, the further utilization or storage of CO_2 must be taken into account.

Additionally, material degradation plays a significant role, as the material undergoes repeated cycling in the process. It is well established that sintering can occur during the calcination, reducing the reactive surface area and porosity [10,59]. Previous studies have investigated the reactivation of CaO-sorbents through hydration in the context of calcium looping and achieved significant increase in CO_2 uptake capacity [10,60,61].

Accordingly, the material is expected to be continuously regenerated by repeatedly undergoing all three reaction steps. Any unreacted fraction is converted to CaO during calcination and remains available for carbonation in subsequent cycles.

6. Conclusion

This work proposes a novel concept for a combined system of long-term energy storage and DAC. Basis is the technical lime cycle, which offers a theoretical heat storage density of 320 kWh/t CaO and an intrinsic DAC functionality with a CO_2 storage capacity of 44 wt%. To enable a first assessment of the system and the synergies of combining thermal energy storage with DAC, literature data were supplemented with own experimental results. Carbonation under ambient conditions is the rate-determining step for operation. Therefore, three influencing parameters on the reaction were identified from the literature and experimentally investigated using fine $Ca(OH)_2$ powder: CO_2 concentration of 100 ppm, 400 ppm and 1000 ppm, layer thickness of 2.0 mm, 4.6 mm and 20.0 mm and influence of an active air ventilation. Experiments were conducted under technically relevant conditions for the intended future application, to assess conversion rates, controllability and compatibility with the thermal energy storage system.

The experiments conducted at different CO_2 concentrations showed a significant influence on the conversion rate. In the low concentrations investigated, higher CO_2 concentrations resulted in faster carbonation kinetics. $X_{Carb(m)} = 91.2\%$ was achieved after 110 h at approximately 1000 ppm, progressing about ten times faster than at 100 ppm, where $X_{Carb(m)} = 46.9\%$ was not exceeded in two weeks. Overall conversion was not affected, but the CO_2 concentration seems to substantially influence the time required for CO_2 uptake.

Layer thickness of $Ca(OH)_2$ powder is essential for the function as CO_2 sorbent, determining the area requirement in the future application. Carbonation in a 2.0 mm layer achieved $X_{Carb(m)} = 90.9\%$ in the experimental set-up, while the ten times higher layer of 20.0 mm carbonated less than half in the same time, showing a progression of carbonation with depth.

An experiment with additional installation of ventilation to mix the incoming air stream in the reaction chamber achieved promising results. The carbonation rate was significantly accelerated in the experimental set-up. $X_{Carb(m)} = 71.0\%$ conversion was achieved in contrast to $X_{Carb(m)} = 64.0\%$ without ventilation, while maintaining ambient conditions close to those in the previous experiments. These results indicate that there are influencing parameters that may accelerate carbonation even under ambient conditions significantly, and provide a basis for further investigations.

The high degrees in carbonation of $Ca(OH)_2$ powder under ambient conditions achieved during the experiments indicate that the proposed concept of combined energy storage and CO_2 capture is feasible and may offer significant advantages. A first assessment of the overall system with the experimental results shows that a maximum of 430 kg CO_2 can be captured in one week, supplying 240 kWh, the average heat demand

of one week. These results indicate that the combination of heat storage and DAC may enable the system to approach carbon negativity also when additional emissions and efficiency losses during the process are considered.

Due to its dual storage functionality for heat and CO_2, the system provides flexibility for future renewable energy systems, as it can serve as a temporal buffer, while at the same time being site-independent. Utilizing part of the regeneration heat offers an additional revenue stream for the DAC technology, increasing overall system efficiency.

CRediT authorship contribution statement

Eva Klockow: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Marc Linder:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix

Nomenclature

Abbreviation	Definition
CCS	Carbon capture and storage
CCU	Carbon capture and utilization
DAC	Direct air capture
DSR	Direct separation reactor
PFRK	Parallel flow regenerative kiln
RH	Relative humidity

Chemical abbreviation	Definition
$CaCO_3$	Calcium Carbonate
$Ca(OH)_2$	Calcium Hydroxide
CaO	Calcium Oxide
CO_2	Carbon Dioxide
H_2O	Water
(g)	Gaseous
(s)	Solid
H	Enthalpy of reaction in kJ/mol

Symbols	Definition	Unit
$X_{Carb(m)}$	Degree of carbonation, determined by weight increase	%
$X_{Carb(TGA)}$	Degree of carbonation, determined by TGA	%
Δm	Mass increase	%
$\Delta m_{Carb,max}$	Maximum mass increase due to the absorption of CO_2 during carbonation	%
x_{CaCO3}	Fraction of $CaCO_3$ in the sample after carbonation	%
$x_{CaCO3,Ref}$	Fraction of $CaCO_3$ in the reference sample before carbonation	%
$x_{CaO,Ref}$	Fraction of CaO in the reference sample before carbonation	%
$x_{Ca(OH)2,Ref}$	Fraction of $Ca(OH)_2$ in the reference sample before carbonation	%

Unit	Definition
l_N	Normliter (gas volume referenced to standard conditions, 0.00 °C and 1013.25 hPa)
tkm	Product of transported mass (t) and transport distance (km)
vol%	Volume percent
wt%	Weight percent

Experimental results of carbonation with corresponding temperature and relative humidity profiles

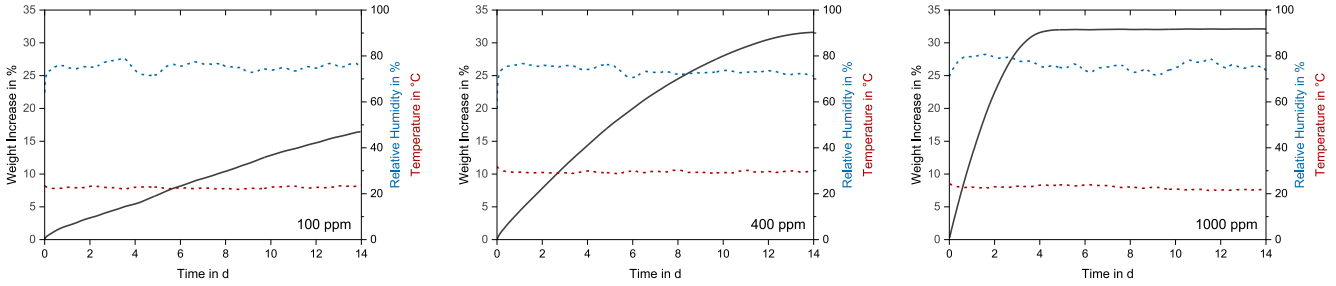

Figure A.1. Weight increase due to carbonation of a 2.0 mm layer of $Ca(OH)_2$ and corresponding temperature and relative humidity over two weeks under ambient conditions for different CO_2 concentrations of 100 ppm (*1_low*), 400 ppm (*0_Ref*) and 1000 ppm (*1_high*)

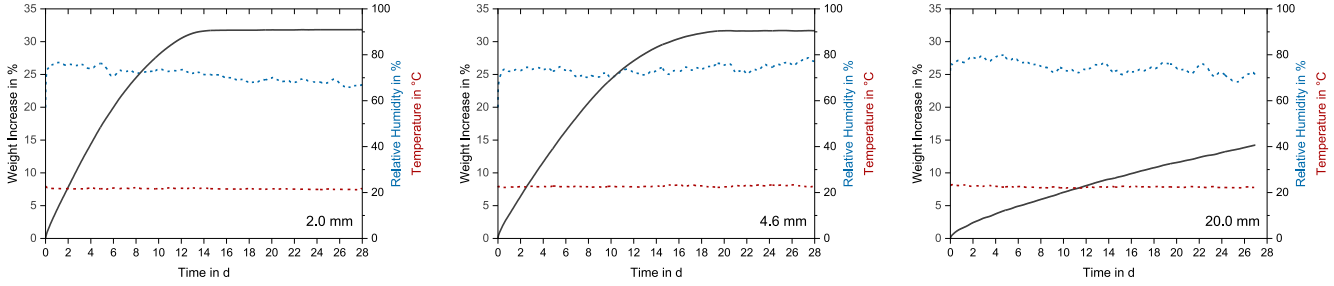

Figure A.2. Weight increase due to carbonation of $Ca(OH)_2$ over four weeks in ambient concentration with corresponding temperature and relative humidity in different layers: 2.0 mm (*0_Ref*), 4.6 mm (*2_4.6 mm*) and 20.0 mm (*2_20.0 mm*)

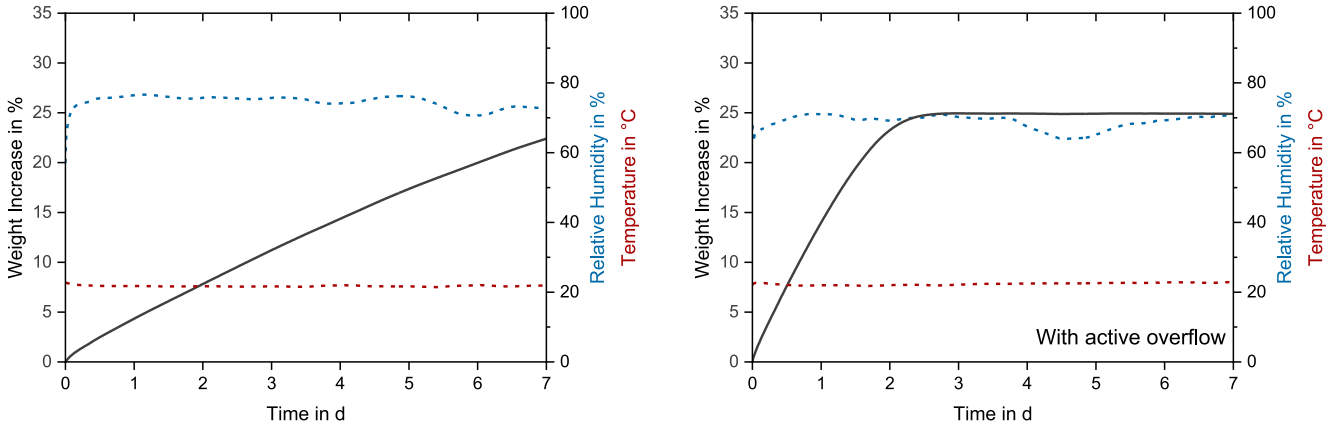

Figure A.3. Weight increase due to carbonation of a 2.0 mm layer $Ca(OH)_2$ over one week in CO_2 concentration with corresponding temperature and relative humidity for samples without (*0_Ref*) and with an active overflow through the ventilator

Experimental results of sample compositions

Table A.1
Overview of sample compositions determined by TGA before and after carbonation, with carbonated samples reported as the average of triplicate measurements

Experiment	$Ca(OH)_2$ Reference Sample			Carbonated Sample		
	$CaCO_3$	$Ca(OH)_2$	Rest	$CaCO_3$	$Ca(OH)_2$	Rest
0_Ref	2.75%	93.61%	3.64%	85.97%	13.53%	0.50%
1_low	2.80%	93.98%	3.22%	44.32%	53.78%	1.90%
1_high	2.46%	94.43%	3.11%	85.68%	13.64%	0.68%
2_4.6mm	2.59%	94.51%	2.90%	86.20%	12.94%	0.86%
2_20mm	2.39%	92.66%	4.95%	42.55%	54.70%	2.75%
3_Vent	3.50%	94.27%	2.23%	69.70%	29.57%	0.73%

Data availability

Data will be made available on request.

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