

Carbonation of lime-based materials under ambient conditions for direct air capture

María Erans^{1,2}, Seyed Ali Nabavi¹, Vasilije Manović^{1,}*

¹Power Engineering Centre, Cranfield University, Bedford, Bedfordshire, MK43 0AL, UK.

²Department of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham, Nottingham, NG7 2RD, United Kingdom

*Corresponding author: Vasilije Manović (v.manovic@cranfield.ac.uk)

Abstract

Carbonation of lime-based materials at high temperatures has been extensively explored in the processes for decarbonisation of the power and industrial sectors. However, their capability to capture carbon dioxide from air at realistic ambient conditions in direct air capture technologies is less explored. In this work, lime and hydrated lime samples are exposed to ambient air for prolonged durations, as well as to calcination/ambient-carbonation cycles, to assess their carbonation performance. It is shown that the humidity plays a key role in carbonation of lime under ambient conditions. Furthermore, faster weathering and higher conversions are demonstrated by hydrated lime, showing a carbonation conversion of 70% after 300 h. Importantly, it was found that there was a negligible difference in the carbonation conversions during five calcination/ambient-carbonation cycles, which can be explained by simultaneous reactivation of cycled material by moist air. These findings indicated that lime-based materials are suitable for carbon dioxide capture from ambient air employing cyclic processes, in a practical time-scale, and that humidity of air plays a key role.

Keywords: Climate change; Direct air capture; Negative emissions; Limestone; Hydration; Carbonation

Nomenclature and abbreviations

BECCS	Bio-energy with carbon capture and storage
CCS	Carbon capture and storage
DAC	Direct air capture
DAC-IN	Direct air capture inside building
DAC-OUT	Direct air capture outside building
DAC-HYD	Direct air capture by hydrated lime
DAC-CIN	Direct air capture - cyclic inside building
DAC-COUT	Direct air capture - cyclic outside building
ESEM	Environmental scanning electron microscopy
SEM	Scanning electron microscopy
SI	Supporting information
SOFC	Solid oxide fuel cell
TGA	Thermogravimetric analysis
UNFCCC	United Nations Framework Convention on Climate Change
Xcarb	Carbonation conversion
Xhyd	Hydration conversion
Xtot	Total conversion

1. Introduction

The Paris agreement, achieved at the 21st Conference of the UNFCCC Parties, recommended that the global mean temperature increase should be kept below 2° C. Moreover, it was established that efforts should be undertaken to limit the rise to 1.5° C above pre-industrial levels (Tollefson, 2015). Reducing CO₂ emissions in order to mitigate climate change has been investigated thoroughly over the last decades (Dovì et al., 2009; Zou et al, 2017). In order to tackle CO₂ emissions in the power sector, a combination of technologies such as carbon capture and storage (CCS) (Aminu et al., 2017), biomass-fired power plants with CCS (BECCS) (Fajardy et al., 2018) and renewable sources need to be deployed (IEA, 2017). On the other hand, the decarbonisation of industrial processes imposes even greater challenges since CO₂ emissions are not only associated with the combustion of fossil fuels but also the process itself (Bains et al., 2017). However, the reduction targets on CO₂ emissions might not be achieved even with complete decarbonisation of the power and industrial sectors due to emissions from distributed CO₂ sources, such as transportation and small-scale distributed heat and power generation. Therefore, it has been proposed that negative emissions technologies should be potentially deployed in order to remove the CO₂ directly from the atmosphere (Obersteiner et al., 2018; Rogelj et al., 2015). Direct air capture (DAC) is one of the potential approaches that can reduce the concentration of CO₂ already in the atmosphere (Goeppert et al., 2012), and could account for distributed CO₂ emissions (Bollini et al., 2011; Jones, 2011). It is important to highlight that distributed emission sources account for approximately one half of anthropogenic CO₂ emissions (Goeppert et al., 2012; Wurzbacher et al., 2016). It is key to note that the concentration of CO₂ in the atmosphere is very low (~400 ppm) (Sanz-Pérez et al., 2016); therefore, the cost associated with CO₂ capture from air is estimated to be in the range of £400-£800/t CO₂ (House et al., 2011; Keith et al., 2006). However, it has been suggested by

some authors that DAC could be competitive with point-source CCS, as the actual cost of the transportation can be minimised (Fasihi et al., 2019).

Solid oxides such as MgO and CaO undergo carbonation in the presence of CO₂ and form stable carbonates. This chemical reaction is considered as a carbon storage technology since the CO₂ is permanently fixed under ambient conditions (Lackner, 2002; IPCC, 2005; Stephens and Keith, 2008). Carbonation of CaO and the effect of moisture on this reaction have been studied thoroughly in concrete applications (Alexander et al., 2008), with some studies taking into account the effect of climate change on the carbonation of concrete (Talukdar and Banthia, 2013; Yoon et al., 2007). The carbonation of CaO and Ca(OH)₂ has also been investigated for other applications, such as for extravehicular activities during space missions (Colombo, 1973). CaO-based materials are also typically used for CO₂ capture as solid sorbents in high-temperature looping cycles. This technology was first proposed by Shimizu et al. (1999) and has been researched thoroughly by investigating fundamental phenomena (Manovic and Anthony, 2010), conceptual solutions (Abanades et al., 2005) and demonstrated at various scales such as 10 kW_{th} (Charitos et al. 2010) and 1.7 MW_{th} (Arias et al., 2013). It has been reported that hydrating lime is beneficial for CO₂ capture due to enhanced sorbent morphology. The reason for this reactivity increase is attributed to the formation of cracks during hydration of the material, which result in higher pore volume (Wu et al., 2007). Hydration can also be used as a reactivation technique for spent sorbent. Two main methods have been investigated for hydration: water (Coppola et al., 2014; Yin et al., 2012) and steam (Arias et al., 2010; Han et al., 2009). Also, Fennell et al. (2007) proposed exposing spent limestone to humid air as a reactivation approach, demonstrating that the carrying capacity could be restored. The most effective method for hydrating spent sorbent is hydration by water; however, the conditions are less than ideal due to the energy requirements for drying the wet hydrated material (Erans et al., 2016). Therefore, steam hydration has been proposed as the best method for reactivation

(Arias et al., 2010; Han et al., 2009). A key property of hydrated materials is that their carbonation occurs faster than that of non-hydrated CaO-based materials (Jia and Anthony, 2000; Manovic et al., 2008).

The use of CaO-based materials for DAC has also been proposed as an effective way of removing CO₂ from air. Lackner et al. (1999) investigated the feasibility of using calcium hydroxide as a DAC sorbent. However, this concept was considered inefficient due to the required high energy demand in order to regenerate the saturated sorbent. Alternatively, a solution of sodium hydroxide was proposed while calcium hydroxide was utilised for its regeneration in order to causticise the sodium carbonate solution and precipitate the calcite (Zeman and Lackner, 2004). Nikulshina et al. (2009) proposed using lime in a fluidised bed for DAC, where the heat of regeneration was provided by solar energy. They reported that this system would achieve higher CO₂ capture than those using Na-based sorbents, as long as the air entered the reactor at higher temperature (~375° C). Stolaroff et al. (2005) investigated the DAC capability of a saturated solution using a Ca-rich industrial waste stream. The concept presented in their work consisted of an aqueous Ca-rich solution being recirculated continuously and reacting with CO₂ when CaCO₃ is precipitated. Hanak et al. (2017) proposed a system for simultaneous power generation and CO₂ capture from air using carbonate materials. The sorbent regeneration temperature was achieved through utilisation of the high-grade heat from a solid oxide fuel cell (SOFC). The advantages of this process are simultaneous generation of electricity by the fuel cell, CO₂ capture from ambient air using calcined sorbent, and production of a concentrated CO₂ stream that can be stored or used. Also, Hanak and Manovic (2018) performed a techno-economic analysis on the SOFC-DAC system, demonstrating its feasibility even under uncertainties in the market conditions, considering this process as carbon-negative-ready since produced lime can be sold in the market if there is no economic incentive for DAC. Also, the economic evaluation showed that the proposed concept

is competitive with other low-carbon power generation and DAC technologies (Hanak et al., 2017; Hanak and Manovic, 2018). However, the suitability of the materials for the proposed DAC process needs to be further assessed as the application of the proposed concept depends highly on the ability of the sorbent to remove CO₂ from air under realistic ambient conditions and in a practical time-scale. Namely, in the previous studies, the DAC performance of CaO-based sorbents was typically tested under controlled laboratory conditions, e.g., in packed beds with a humidifier to maintain humidity of air circulated through the reaction system by compressor (Samari et al., 2019).

In this work, the capability of lime and hydrated lime for DAC were investigated as a proof of the concept under realistic conditions by exposing CaO-based material to ambient air, without conditioning it and then circulating it through an adsorption/absorption reactor. This is so-called ‘passive DAC by lime’ with the aim to avoid the operating costs (energy requirement for conditioning and compressing air) as well as to minimise capital costs (reactors and equipment such as compressors). Therefore, the samples were exposed to ambient conditions under a series of scenarios, namely, inside the building (low humidity), outside the building (high humidity) and water hydration after calcination using a mechanical pelletiser to assess their DAC performance. The carbonation and hydration conversions were measured over a prolonged time, and morphological variations were assessed using a scanning electron microscope (SEM). Finally, cycling calcination/ambient-carbonation experiments were also performed for months under different ambient conditions in order to assess the reactivity performance of the sorbents when used in a closed-loop process for DAC in a practical time-scale.

2. Experimental Section

The DAC tests in this study are performed using natural limestone which was calcined and exposed to ambient air for prolonged time in order to capture CO₂.

2.1. Materials

The lime samples used were obtained by calcination of Longcal limestone (Longcliffe Ltd., UK) containing a minimum of 98.25% calcium carbonate with a particle size range from 100-500 μm. A thin layer (~ 5 mm) of the limestone was placed on a stainless steel rectangular tray (45 cm x 35 cm). In order to achieve complete calcination, the material was first heated for 2 h at 850 °C in a muffle furnace (Carbolite GPC 12/81) in an air atmosphere containing CO₂ released due to calcination. The calcined material was cooled to 300 °C inside the furnace, and then exposed to air under the testing conditions.

2.2. Experimental Procedure

A preliminary test and three series of experiments were performed to explore the time-scale required for CO₂ capture from ambient air by lime, the level of carbonation and hydration conversions over time, as well as the cyclic calcination/re-carbonation under realistic weathering conditions. The experiments were performed under variable ambient air temperature and humidity conditions, typical for Northern Europe, in order to simulate their weathering performance during prolonged exposure to air. During each set of experiments, the ambient temperature and relative humidity were recorded every hour using a data logger (EL-USB-2-LC, Lascar). The hydration and carbonation conversions were determined by thermogravimetric analysis (TGA), which allows one to distinguish the individual amounts of CaO, Ca(OH)₂ and CaCO₃ in a given sample, and the morphology of the samples was analysed by scanning electron microscopy (SEM). A schematic of the experimental procedure is provided in Figure 1.

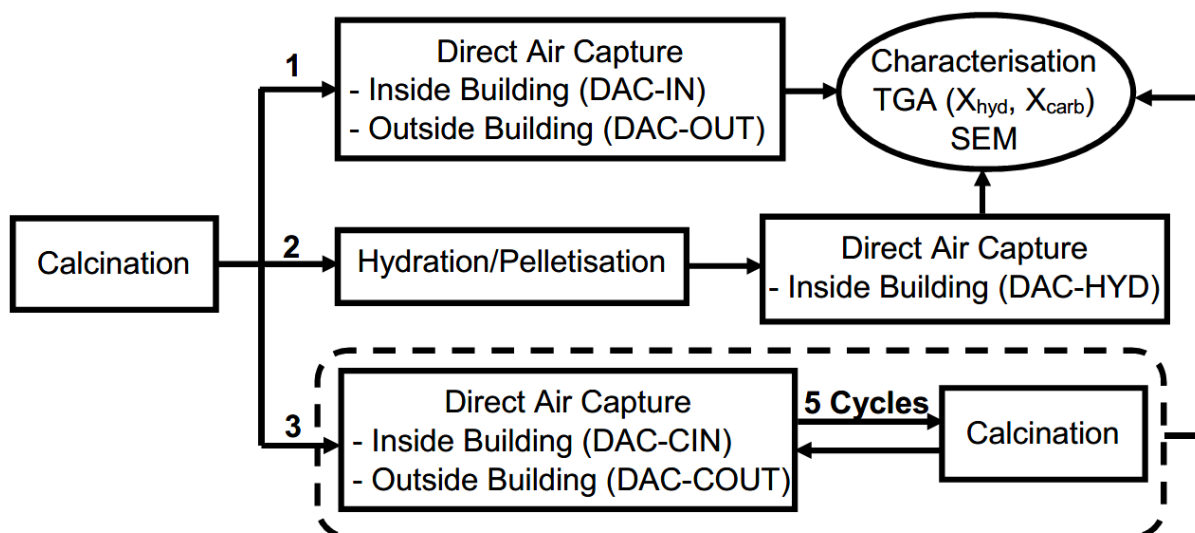


Figure 1. Schematic of the experimental procedure.

Preliminary DAC time-scale. A preliminary experiment was performed to anticipate the time-scale required for the DAC process using lime. After the calcination, a tray with 1.5 kg lime was exposed to the ambient air inside the building (closed laboratory room), where the humidity is relatively low, i.e., average relative humidity was ~45% during the test. The weight of the tray with lime was recorded throughout the experiment until a plateau was reached.

1. Ambient hydration-carbonation. In the first series of experiments, the extent of ambient carbonation-hydration of the CaO-based materials over time was studied by exposing 1.0 kg calcined material in a thin layer (~5 mm) to different ambient conditions. Although the thickness of the material can affect the results in the initial stages of weathering, considering the time-scale of a month, the diffusion effects on the conversions due to this layer thickness are considered negligible. In the first test, a tray with lime was exposed to the ambient air inside the building (DAC-IN) where humidity variations were relatively small. It should be noted that the CO₂ concentration in buildings varies in the range of 350-2,500 ppm, and the main source of CO₂ is its occupants, with ventilation also being a key factor (Seppänen et al., 1999). In this study, the experiments were performed in an empty laboratory building, which was ventilated

by extraction hoods. Therefore, it can be assumed that CO₂ concentration (400 ppm) did not significantly vary during the experiments. In the second test, a tray with lime was exposed to the ambient air outside the building (DAC-OUT), where the material experienced considerable variations in temperature and humidity. For the DAC-OUT test, the tray was placed under a roof structure to avoid any direct contact of the material with rain. In both cases, small amounts of sample were collected periodically for over a month for further characterisation to determine hydration/carbonation conversions and morphology. In order to ensure that the samples collected were representative of the entire material in the tray, they were taken from top to bottom and mixed thoroughly before the analysis.

2. Ambient carbonation of pre-hydrated lime. In this experiment the extent of carbonation conversion was measured when hydrated samples were used (DAC-HYD). The limestone samples were calcined and left to cool overnight in sealed containers. Then, they were hydrated using a mechanical granulator (TMG 1/6, Glatt GmbH) and a spray of deionised water. Further information on the experimental procedure for the hydration and pelletisation of lime using the mechanical granulator is provided by Manovic et al. (2012). The hydrated samples were then exposed to ambient air inside the laboratory building, and the samples for characterisation were collected in the same manner as those of the DAC-IN test.

3. Cyclic calcination/ambient re-carbonation. In these sets of experiments the effect of cyclic calcination/ambient re-carbonation on the performance of CaO-based material for ambient CO₂ capture was assessed. Cyclic tests were performed for samples exposed to air inside (DAC-CIN) and outside the building (DAC-COUT) for 14 days. Subsequently, the weathered samples were calcined in a muffle furnace for 2 h at 850 °C, and again exposed to the same ambient conditions. The cycles were repeated five times for each test, and samples for further characterisation were collected periodically. The number of cycles was selected as a compromise between reasonable duration of the tests, which is, in this case, more than 2

months, and previous findings on reactivity decay. Namely, the reactivity decay, if any, can obviously be observed during the first five cycles (Manovic et al. 2009; Fennell et al., 2007).

A summary of the experimental conditions reported in Figures S1-S5 of the Supplementary Information (SI) is shown in Table 1, where the minimum, maximum, and average temperatures, and relative humidity profiles are presented for each set of experiments.

Table 1. Experimental conditions for the direct air capture (DAC) tests by lime.

Test	Time (day)	Temperature (°C)			Relative humidity (%)		
		Minimum	Maximum	Average	Minimum	Maximum	Average
DAC-IN	40	4	24	13	25	62	45
DAC-OUT	31	4	23	14	32	95	70
DAC-HYD	20	12	27	18	37	62	51
DAC-CIN	68	9	29	17	31	62	48
DAC-COUT	68	0	23	10	32	100	78

Notation: DAC – direct air capture, IN – inside the building, OUT – outside the building, HYD – hydrated sample, CIN – cyclic test inside the building, and COUT – cyclic test outside the building.

2.3. Material Characterisation

Thermogravimetric Analysis (TGA). The carbonation/hydration conversions of the collected samples were measured by calcination of the reacted material using a Pyris 1 Perkin Elmer thermogravimetric analyser (TGA). In each test, 20-30 mg of the material was heated from ambient temperature to 900 °C with a heating rate of 30 °C/min under a nitrogen flow rate of 20 mL/min, and maintained at 900 °C for a further 5 min. The accuracy of the TGA is ± 0.001 mg, which negligibly contributes to the experimental error of measuring the sample

conversions. All measurements were performed twice and the discrepancy in the results was typically less than 5%.

Scanning Electron Microscopy (SEM). An FEI XL30 Philips environmental scanning electron microscope (ESEM) was used to assess the morphology of the samples. The SEM images were taken at an accelerated voltage of 20 keV. Prior to scanning, the samples were coated with gold to prevent electrostatic charges on the particles.

3. Results and Discussion

The preliminary test showed an increase in weight of the tray with lime when exposed to ambient air inside the building, where the humidity is relatively low. Initially, there was a sharp weight gain, and the weight reached a maximum after ~30 days, with no noticeable increase afterwards. Therefore, it was concluded that the reactions were finished in this period considering practical application for DAC, and this time-scale was considered for the further experiments.

Figure 2 presents the hydration, carbonation and total conversions of lime exposed to the ambient air inside the building (DAC-IN) over time. It can be seen that there is an initial regime with relatively fast hydration, when the hydration conversion reached 72% in the first 140 h, and then decreased due to carbonation of $\text{Ca}(\text{OH})_2$ ($\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$). On the other hand, carbonation was relatively slow during this period, and reached only 6% conversion. This is expected as the reaction is limited by the disparity in moisture and CO_2 concentrations in ambient air, which causes the difference in time needed for the hydration and carbonation reactions. The carbonation conversion increased steadily and reached a maximum of ~78% after 740 h. No noticeable changes in the conversion of carbonation and hydration reactions were seen after 740 h. These results are consistent with previous findings, and it implies that carbonation of already hydrated samples is controlled by two steps: (i) the diffusion

of the atmospheric CO₂ into the reactive material, followed by (ii) chemical reaction of diffused CO₂ with Ca(OH)₂ (Van Balen, 2005). The process progresses through the formation of a H₂O/OH⁻ interface controlled by intrinsic chemical reaction. This reaction takes place over the surface not covered by CaCO₃ (Mess et al., 1999; Shih et al., 1999). Subsequently, the build-up of a CaCO₃ layer shifts the reaction mechanism towards a step controlled by diffusion in the product layer (Mess et al., 1999; Nikulshina et al., 2007).

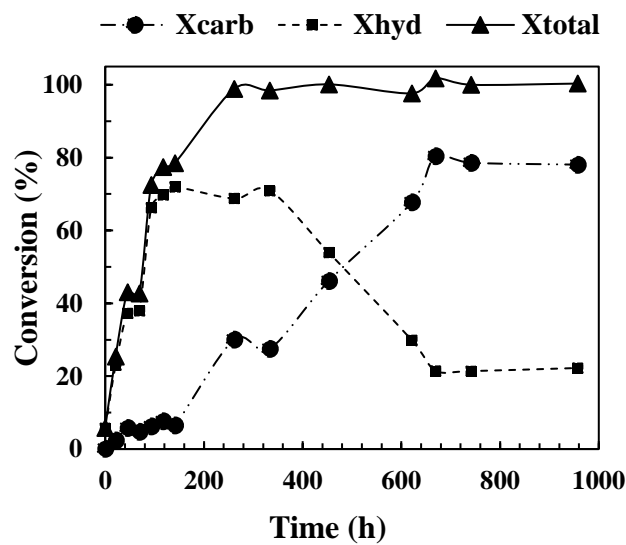


Figure 2. Carbonation (Xcarb), hydration (Xhyd) and total (Xtotal) conversions of DAC-IN sample over time.

The time-conversions profiles for the sample DAC-OUT can be seen in Figure 3. It is important to note that the only difference between DAC-IN and DAC-OUT tests was the average relative humidity of air, 45% and 70%, respectively, but the average air temperature was similar, 13°C and 14°C, respectively, which can be seen in Figures S1 and S2 of the SI. The trends are similar to those of DAC-IN. The initial carbonation conversion rates are lower for DAC-IN with the carbonation of the Ca(OH)₂ starting to increase at ~330 h, while at ~100 h for DAC-OUT. The hydration conversion at the beginning was higher for DAC-OUT, reaching a maximum after

100 h, while the DAC-IN reached the maximum hydration conversion after 140 h. This indicates that moisture in the air under the low-humidity conditions is a limiting factor for the reaction.

It has been reported that moisture in air promotes CO₂ capture from these sorbents under ambient conditions (Beruto and Botter, 2000; Shih et al., 1999). The mechanism of this capture process comprises dissolution of CO₂ in the water that is in contact with the surface of the material, forming carbonic acid (Pontiga et al., 2013). This phase aids carbonation via the formation of movable spherules. It is important to note that, due to the hydration process, DAC-HYD sample contained more non-bound water than DAC-IN and DAC-OUT, which promoted the carbonation reaction. Also, it has been previously claimed that water acts as a catalyst, promoting the carbonation reaction due to presence of Ca²⁺ and OH⁻ ions (Beruto and Botter, 2000). This phenomenon has been observed by varying relative humidity and CO₂ concentration at ambient temperature (Van Balen, 20015), under controlled humidity and temperature conditions (Morales-Flórez et al., 2015), and using wollastonite as CaO-based sorbent (Daval et al., 2009).

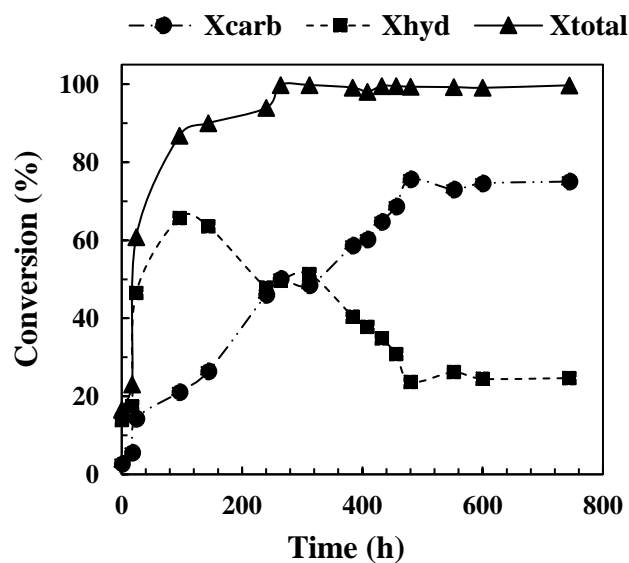


Figure 3. Carbonation (X_{carb}), hydration (X_{hyd}) and total (X_{total}) conversions of DAC-OUT over time.

The conversions of the DAC-HYD sample over time are shown in Figure 4, while the temperature and relative humidity data are provided in Figure S3 of the SI. It can be seen that the hydrated sample carbonates faster, reaching around 50% carbonation conversion in 168 h, compared to DAC-OUT (50% conversion in 264 h, Figure 3) and DAC-IN (50% conversion in 453 h, Figure 2). It is suggested that this faster carbonation is caused by two separate phenomena. Namely, the increase in moisture in the material helps with the CO_2 dissolution at the gas/solid interface. The instant hydration in the mechanical granulator also contributed greatly to an earlier onset of the carbonation reaction due to the larger molar volume of $Ca(OH)_2$, which induces cracks in the material, creating and exposing fresh unreacted lime for further carbonation (Manovic and Anthony, 2008; Nikulshina et al., 2009).

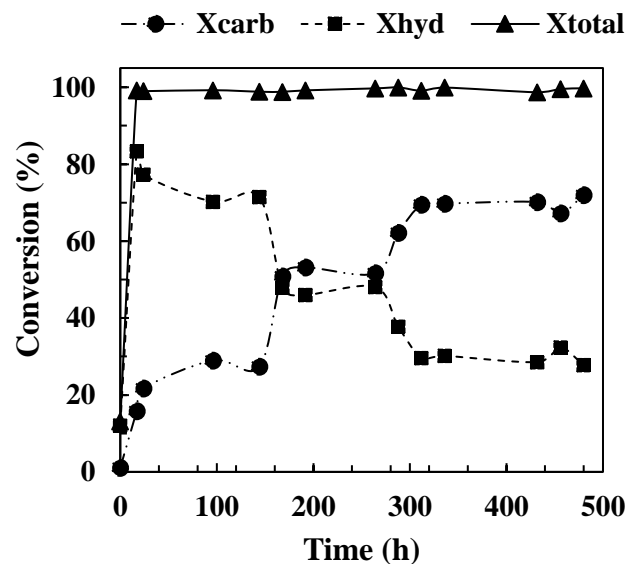


Figure 4. Carbonation (X_{carb}), hydration (X_{hyd}) and total (X_{total}) conversions of DAC-HYD over time.

The DAC experiments were performed for five cycles of calcination/ambient-carbonation in two sets of tests designated as DAC-CIN and DAC-COUT. The conversions for the cyclic experiments over time for DAC-CIN and DAC-COUT are shown in Figure 5 and Figure 6, respectively, where higher carbonation conversions are achieved during the cycles. The data for the temperature and relative humidity of DAC-COUT are presented in Figure S4 and S5 of the SI. The results on conversions are consistent with those of DAC-OUT (Figure 3) highlighting again the importance of moisture in air for ambient carbonation of CaO-based sorbents. DAC performance seems unaffected by the number of cycles as stable carbonation conversion profiles are obtained over the course of five cycles. Therefore, it can be concluded that the cycling has a negligible effect on CaO-based materials under the DAC conditions. The reason behind this superior performance is the simultaneous reactivation of the cycled material when in contact with humid air. Namely, it has been suggested that humid ambient air reactivates CaO-based materials exposed to calcination/carbonation cycles and enables the carrying capacity to be restored (Fennell et al., 2007). This finding is important since the technology can be deployed at large scale if CaO-based sorbent is used in a cyclic mode. Also, sorbent reactivation and using it in longer series of capture cycles aids the economics of the proposed DAC system since the economic performance of the process is strongly affected by the sorbent cost and activity (Hanak and Manovic, 2018).

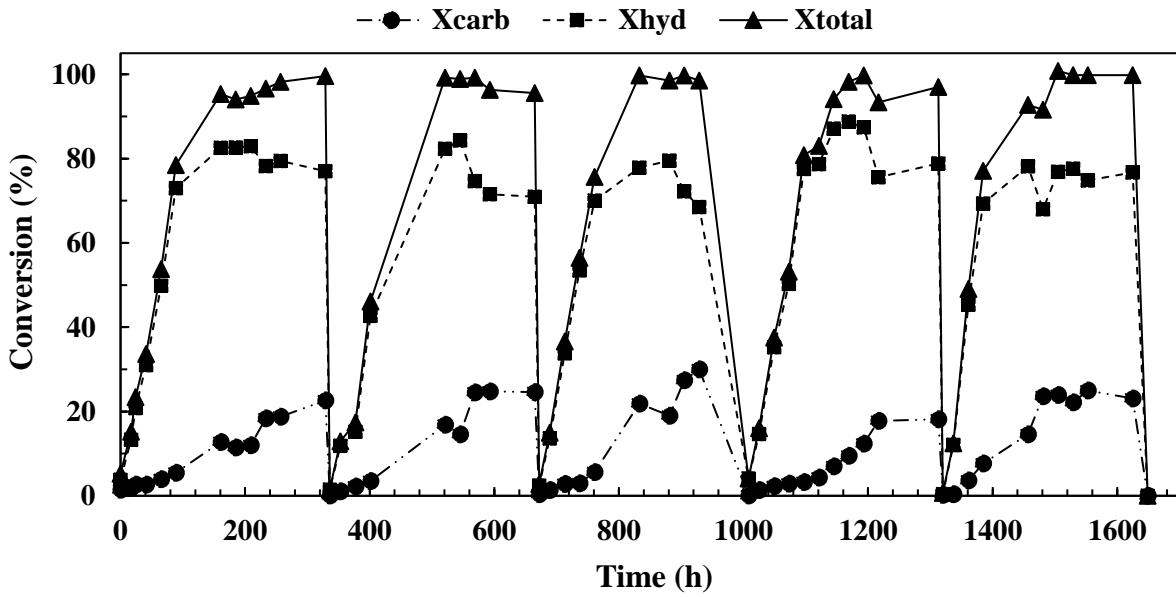


Figure 5. Carbonation (X_{carb}), hydration (X_{hyd}) and total (X_{total}) conversions of DAC-CIN sample over five repetitive cycles.

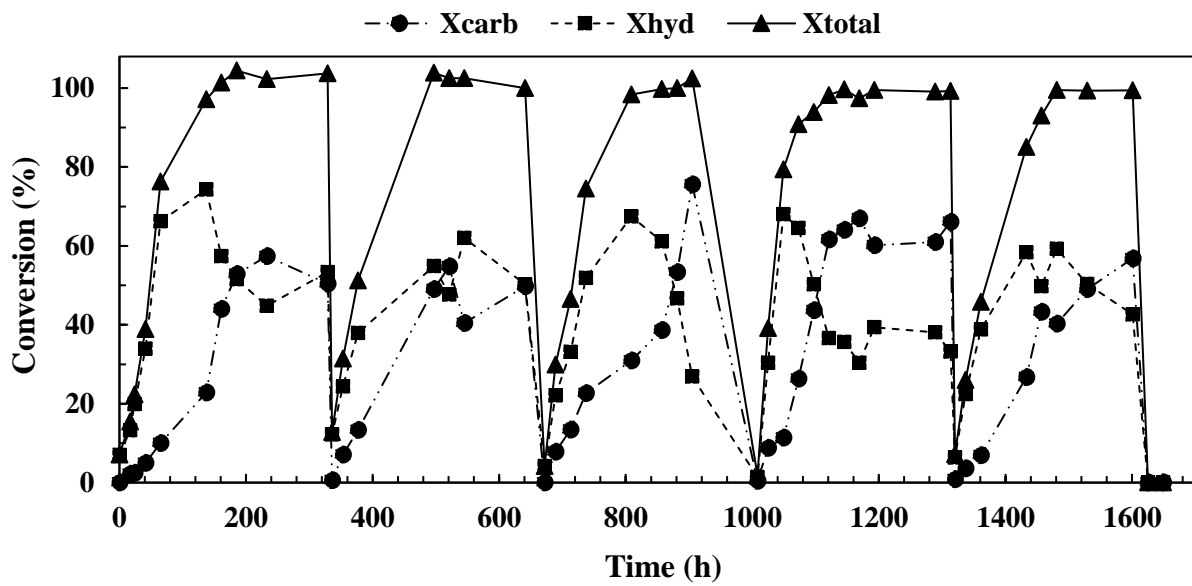


Figure 6. Carbonation (X_{carb}), hydration (X_{hyd}) and total (X_{total}) conversions of DAC-COUT sample over five repetitive cycles.

The SEM images of the samples at different stages are presented in Figures 7 and 8. It can be seen that there is no substantial difference between DAC-IN (Figure 7a) and DAC-OUT

(Figure 7b) at the end of their exposure to air. Their morphology appears to be similar and most of the pores are closed due to CaCO_3 formation. This is consistent with the results on conversion as both of these samples had almost the same carbonation conversions at the end of the exposure to air (744 h for DAC-OUT and 957 h for DAC-IN). Figure 7 also presents the images of DAC-HYD after hydration (Figure 7c) and after exposure to air (Figure 7d). These two morphologies differ greatly with the first one being very compact and dense after lime reacted with water. The sample presented in Figure 7d appears to have a similar morphology to those of DAC-IN and DAC-OUT (Figures 7a and 7b, respectively). This can be expected since carbonation conversions of these samples are very similar at the end of their exposure to air.

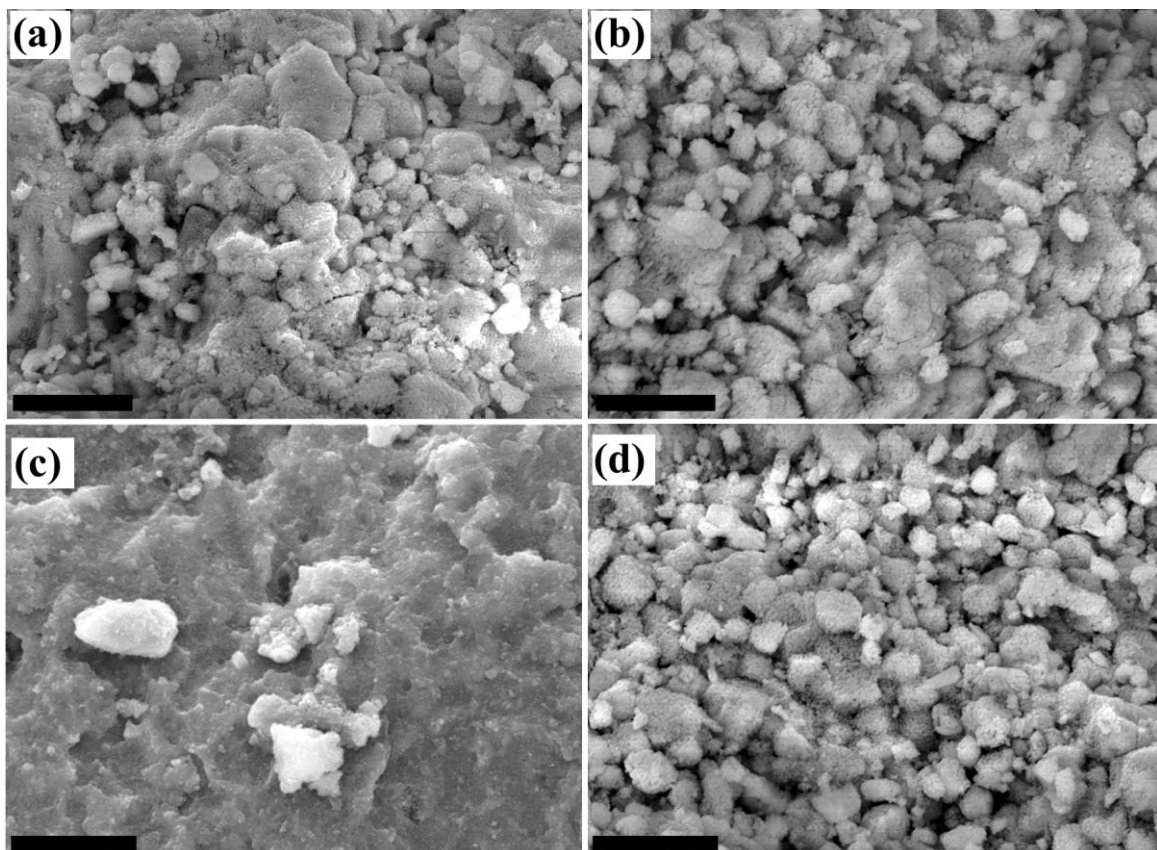


Figure 7: SEM images of tested lime samples (a) DAC-IN and (b) DAC-OUT after exposure to air, (c) DAC-HYD after hydration, and (d) DAC-HYD after exposure to air. All scale bars are 10 μm .

In Figure 8, the SEM images of DAC-CIN (8a and b) and DAC-COUT (8c and d) before and after the third cycles are presented. In this case, subtle differences can be found in the morphology with DAC-COUT having lower porosity, due to CaCO_3 formation, than that of DAC-CIN. Namely, carbonation conversion after the cycles was substantially lower for DAC-CIN than for DAC-COUT, i.e., 29% compared to 53%, respectively, at the end of the third cycle.

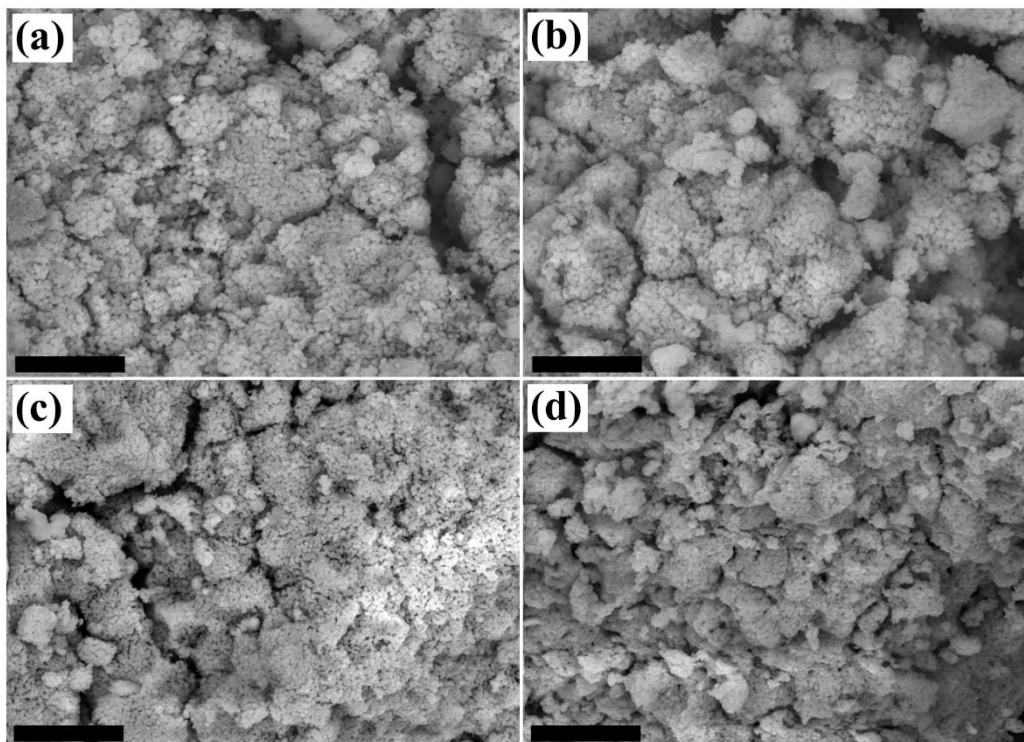


Figure 8. SEM images of cycled lime samples: (a) calcined DAC-CIN prior to exposure to the ambient air; (b) DAC-CIN sample after third carbonation; (c) calcined DAC-COUT prior to exposure to the ambient air; and (d) DAC-COUT after third carbonation. All scale bars are 10 μm .

4. Conclusions

DAC technologies are expected to be essential in the future in order to capture CO₂ that cannot be removed via large point-source CCS. One of the main challenges of DAC processes is the associated costs, which are often regarded as the main obstacle for scaling-up DAC processes. This work presents a novel DAC process utilising a cheap and environmentally friendly sorbent without the need of costly equipment or reactors. CaO-based materials are a viable solution for DAC by means of exposing them to ambient air in a thin layer. High levels of carbonation by ambient air (~ 75%) can be achieved in a time-scale of weeks to months, which is acceptable from an engineering point of view if these materials are used in the proposed DAC process. Importantly, there has been no loss of activity during the cycles, which implies that the DAC process requires neither additional reactivation nor disposal of cycled material, which is explained by simultaneous reactivation by humid air, which can significantly enhance the economics of the process and its technical feasibility. Also, it should be highlighted that limestone is cheap, environmentally friendly and widely available, making it a suitable candidate for DAC technologies considered in our recent studies. However, the availability of land should be further investigated as it could be one of the constraints of the DAC process explored in this study. In order to aid the scale-up of this technology, DAC processes should be developed looking at the future practical applications of the technology. Investigations on the suitability of these sorbents under variable realistic atmospheric conditions and geographic locations are scarce and thus necessary, as are techno-economic analysis and the investigation of other suitable sorbents.

ASSOCIATED CONTENT

Supporting Information

The temperature and relative humidity profiles throughout the experiments are shown in Figures S1-S5.

AUTHOR INFORMATION

Corresponding Author

*Corresponding author: Tel.: +44 1234 754649; E-mail address: v.manovic@cranfield.ac.uk (V. Manović).

Notes

The authors declare no competing financial interest.

Acknowledgments

This work is part of the “Balanced Energy Network” project supported by InnovateUK Integrated Supply Chains for Energy Systems Grant (InnovateUK reference: 102624). The consortium consists of ICAX Ltd., London South Bank University, Terra Firma Ground Investigations Ltd., Upside Energy Ltd., Mixergy Ltd., Origen Power Ltd., and Cranfield University. The authors would like to thank Mr Howard Smith for his kind help and support during this work.

References

Abanades, J.C., Anthony, E.J., Wang, J., Oakey, J.E., 2005. Fluidized bed combustion systems integrating CO₂ capture with CaO. *Environ. Sci. Tech.* 39, 2861-2866. DOI: 10.1021/es0496221

Alexander, M.G., Beushausen, H.D., Dehn, F., Moyo, P., 2008. Concrete Repair, Rehabilitation and Retrofitting II: 2nd International Conference on Concrete Repair, Rehabilitation and Retrofitting, ICCRRR-2, 24-26 November 2008, Cape Town, South Africa. CRC Press.

Aminu, M.D., Nabavi, S.A., Rochelle, C.A., Manovic, V., 2017. A review of developments in carbon dioxide storage. *Appl. Energy.* 208, 1389–1419. DOI: [10.1016/j.apenergy.2017.09.015](https://doi.org/10.1016/j.apenergy.2017.09.015)

Arias, B., Grasa, G.S., Abanades, J.C., 2010. Effect of sorbent hydration on the average activity of CaO in a Ca-looping system. *Chem. Eng. J.* 163, 324–330. DOI: 10.1016/j.cej.2010.08.009

Arias, B., Diego, M.E., Abanades, J.C., Lorenzo, M., Diaz, L., Martínez, D., Alvarez, J., Sánchez-Biezma, A., 2013. Demonstration of steady state CO₂ capture in a 1.7 MWth calcium looping pilot. *Int. J. Greenh. Gas Con.* 18, 237-245. DOI: 10.1016/j.ijggc.2013.07.014

Bains, P., Psarras, P., Wilcox, J., 2017. CO₂ capture from the industry sector. *Prog. Energy Combust. Sci.* 63, 146–172. DOI: 10.1016/j.pecs.2017.07.001

Beruto, D.T., Botter, R., 2000. Liquid-like H₂O adsorption layers to catalyze the Ca(OH)₂/CO₂ solid–gas reaction and to form a non-protective solid product layer at 20° C. *J. Eur. Ceram. Soc.* 20, 497–503. DOI: [10.1016/S0955-2219\(99\)00185-5](https://doi.org/10.1016/S0955-2219(99)00185-5)

Bollini, P., Didas, S.A., Jones, C.W., 2011. Amine-oxide hybrid materials for acid gas separations. *J. Mater. Chem.* 21, 15100–15120. DOI: 10.1039/c1jm12522b

Charitos, A., Hawthorne, C., Bidwe, A.R., Sivalingam, S., Schuster, A., Spliethoff, H., Scheffknecht, G., 2010. Parametric investigation of the calcium looping process for CO₂ capture in a 10 kWth dual fluidized bed. *Int. J. Greenh. Gas Con.* 4(5), 776-784. DOI: [10.1016/j.ijggc.2010.04.009](https://doi.org/10.1016/j.ijggc.2010.04.009)

Colombo, G. V., 1973. Study of CO₂ sorbents for extravehicular activity. NASA-CR-114632, MDC-G4778

Coppola, A., Salatino, P., Montagnaro, F., Scala, F., 2014. Reactivation by water hydration of the CO₂ capture capacity of a calcium looping sorbent. *Fuel* 127, 109–115. DOI: [10.1016/j.fuel.2013.09.059](https://doi.org/10.1016/j.fuel.2013.09.059)

Daval, D., Martinez, I., Corvisier, J., Findling, N., Goffé, B., Guyot, F., 2009. Carbonation of Ca-bearing silicates, the case of wollastonite: experimental investigations and kinetic modeling. *Chem. Geol.* 265, 63–78. DOI: [10.1016/j.chemgeo.2009.01.022](https://doi.org/10.1016/j.chemgeo.2009.01.022)

Dovì, V.G., Friedler, F., Huisingsh, D., Klemeš, J.J., 2009. Cleaner energy for sustainable future. *J. Clean. Prod.*, 17(10), 889-895. DOI: [10.1016/j.jclepro.2009.02.001](https://doi.org/10.1016/j.jclepro.2009.02.001)

Erans, M., Manovic, V., Anthony, E.J., 2016. Calcium looping sorbents for CO₂ capture. *Appl. Energy*. 180, 722-742. DOI: [10.1016/j.apenergy.2016.07.074](https://doi.org/10.1016/j.apenergy.2016.07.074)

Fasihi, M., Efimova, O., Breyer, C., 2019. Techno-economic assessment of CO₂ direct air capture plants. *J. Clean. Prod.*, 224, 957-980. DOI: [10.1016/j.jclepro.2019.03.086](https://doi.org/10.1016/j.jclepro.2019.03.086)

Fajardy, M., Chiquier, S., Mac Dowell, N., 2018. Investigating the BECCS resource nexus: delivering sustainable negative emissions. *Energy Environ. Sci.* 11, 3408-3430. DOI: [10.1039/C8EE01676C](https://doi.org/10.1039/C8EE01676C)

Fennell, P.S., Davidson, J.F., Dennis, J., Hayhurst, A.N., 2007. Regeneration of sintered limestone sorbents for the sequestration of CO₂ from combustion and other systems. *J. Energy Inst.* 80, 116–119. DOI: [10.1179/174602207X189175](https://doi.org/10.1179/174602207X189175)

Goeppert, A., Czaun, M., Surya Prakash, G.K., Olah, G.A., 2012. Air as the renewable carbon source of the future: An overview of CO₂ capture from the atmosphere. *Energy Environ. Sci.* 5, 7833–7853. DOI: [10.1039/c2ee21586a](https://doi.org/10.1039/c2ee21586a)

Han, L., Wang, Q., Ma, Q., Guan, J., Luo, Z., Cen, K., 2009. Hydration reactivation of CaO-based sorbent for cyclic calcination-carbonation reactions, in: *Proceedings of the 20th International Conference on Fluidized Bed Combustion*. Springer, 726–731. DOI: [10.1007/978-3-642-02682-9_112](https://doi.org/10.1007/978-3-642-02682-9_112)

Hanak, D.P., Jenkins, B.G., Kruger, T., Manovic, V., 2017. High-efficiency negative-carbon emission power generation from integrated solid-oxide fuel cell and calciner. *Appl. Energy* 205, 1189–1201. DOI: [10.1016/j.apenergy.2017.08.090](https://doi.org/10.1016/j.apenergy.2017.08.090)

Hanak, D.P., Manovic, V., 2018. Combined heat and power generation with lime production for direct air capture. *Ener. Conv. Manag.*, 160, 455-466. DOI: [10.1016/j.enconman.2018.01.037](https://doi.org/10.1016/j.enconman.2018.01.037)

House, K.Z., Baclig, A.C., Ranjan, M., van Nierop, E.A., Wilcox, J., Herzog, H.J., 2011. Economic and energetic analysis of capturing CO₂ from ambient air. *Proc. Natl. Acad. Sci.* 108, 20428–20433. DOI: [10.1073/pnas.1012253108](https://doi.org/10.1073/pnas.1012253108)

IEA, 2017. *Tracking Clean Energy Progress*. Paris, France.

IPCC, 2005. *Special report on carbon dioxide capture and storage*. In: Metz B, Davidson O, de Coninck HC, Loos M, Meyer LJ (eds). Cambridge University Press, Cambridge, United Kingdom/New York, NY, USA.

Jia, L., Anthony, E.J., 2000. Pacification of FBC ash in a pressurized TGA. *Fuel* 79, 1109–1114. DOI: [10.1016/S0016-2361\(99\)00248-3](https://doi.org/10.1016/S0016-2361(99)00248-3)

Jones, C.W., 2011. CO₂ capture from dilute gases as a component of modern global carbon management. *Annu. Rev. Chem. Biomol. Eng.* 2, 31–52. DOI: [10.1146/annurev-chembioeng-061010-114252](https://doi.org/10.1146/annurev-chembioeng-061010-114252)

Keith, D.W., Ha-Duong, M., Stolaroff, J.K., 2006. Climate strategy with CO₂ capture from the air. *Clim. Change* 74, 17–45. DOI: [10.1007/s10584-005-9026-x](https://doi.org/10.1007/s10584-005-9026-x)

Lackner, K., Ziock, H.J., Grimes, P., 1999. Carbon dioxide extraction from air: Is it an option? (No. LA-UR-99-583). Los Alamos National Lab., NM (US).

Lackner, K.S., 2002. Carbonate chemistry for sequestering fossil carbon. *Annu. Rev. Energy Environ.* 27, 193–232. DOI: [10.1146/annurev.energy.27.122001.083433](https://doi.org/10.1146/annurev.energy.27.122001.083433)

Manovic, V., Anthony, E.J., 2008. Sequential SO₂/CO₂ capture enhanced by steam reactivation of a CaO-based sorbent. *Fuel* 87, 1564–1573. DOI: [10.1016/j.fuel.2007.08.022](https://doi.org/10.1016/j.fuel.2007.08.022)

Manovic, V., Lu, D., Anthony, E.J., 2008. Steam hydration of sorbents from a dual fluidized bed CO₂ looping cycle reactor. *Fuel* 87, 3344–3352. DOI: [10.1016/j.fuel.2008.04.035](https://doi.org/10.1016/j.fuel.2008.04.035)

Manovic, V., Charland, J.P., Blamey, J., Fennell, P.S., Lu, D.Y., Anthony, E.J., 2009. Influence of calcination conditions on carrying capacity of CaO-based sorbent in CO₂ looping cycles. *Fuel* 88(10), 1893-1900. DOI: [10.1016/j.fuel.2009.04.012](https://doi.org/10.1016/j.fuel.2009.04.012)

Manovic, V., Anthony, E.J., 2010. Carbonation of CaO-based sorbents enhanced by steam addition. *Ind. Eng. Chem. Res.* 49(19), 9105-9110. DOI: [10.1021/ie101352s](https://doi.org/10.1021/ie101352s)

Manovic, V., Wu, Y., He, I., Anthony, E.J., 2012. Spray water reactivation/pelletization of spent CaO-based sorbent from calcium looping cycles. *Environ. Sci. Technol.* 46, 12720–12725. DOI: [10.1021/es303252j](https://doi.org/10.1021/es303252j)

Mess, D., Sarofim, A.F., Longwell, J.P., 1999. Product layer diffusion during the reaction of calcium oxide with carbon dioxide. *Energy Fuels* 13, 999–1005. DOI: [10.1021/ef980266f](https://doi.org/10.1021/ef980266f)

Morales-Flórez, V., Santos, A., Romero-Hermida, I., Esquivias, L., 2015. Hydration and carbonation reactions of calcium oxide by weathering: kinetics and changes in the nanostructure. *Chem. Eng. J.* 265, 194–200. DOI: [10.1016/j.cej.2014.12.062](https://doi.org/10.1016/j.cej.2014.12.062)

Nikulshina, V., Galvez, M.E., Steinfeld, A., 2007. Kinetic analysis of the carbonation reactions for the capture of CO₂ from air via the Ca(OH)₂–CaCO₃–CaO solar thermochemical cycle. *Chem. Eng. J.* 129, 75–83. DOI: [10.1016/j.cej.2006.11.003](https://doi.org/10.1016/j.cej.2006.11.003)

Nikulshina, V., Gebald, C., Steinfeld, A., 2009. CO₂ capture from atmospheric air via consecutive CaO-carbonation and CaCO₃-calcination cycles in a fluidized-bed solar reactor. *Chem. Eng. J.* 146, 244–248. DOI: [10.1016/j.cej.2008.06.005](https://doi.org/10.1016/j.cej.2008.06.005)

Obersteiner, M., Bednar, J., Wagner, F., Gasser, T., Ciais, P., Forsell, N., Frank, S., Havlik, P., Valin, H., Janssens, I.A., Peñuelas, J., Schmidt-Traub, G., 2018. How to spend a dwindling greenhouse gas budget. *Nat. Clim. Chang.* 8, 7–10. DOI: [10.1038/s41558-017-0045-1](https://doi.org/10.1038/s41558-017-0045-1)

Pontiga, F., Valverde, J.M., Moreno, H., Duran-Olivencia, F.J., 2013. Dry gas–solid carbonation in fluidized beds of Ca(OH)₂ and nanosilica/Ca(OH)₂ at ambient temperature and low CO₂ pressure. *Chem. Eng. J.* 222, 546–552. DOI: [10.1016/j.cej.2013.02.067](https://doi.org/10.1016/j.cej.2013.02.067)

Rogelj, J., Luderer, G., Pietzcker, R.C., Kriegler, E., Schaeffer, M., Krey, V., Riahi, K., 2015. Energy system transformations for limiting end-of-century warming to below 1.5 °C. *Nat. Clim. Chang.* 5, 519–527. DOI: [10.1038/nclimate2572](https://doi.org/10.1038/nclimate2572)

Samari, M., Ridha, F., Manovic, V., Macchi, A., Anthony, E. J., 2019. Direct capture of carbon dioxide from air via lime-based sorbents. *Mitig. Adapt. Strateg. Glob. Chang.*, in press, DOI: 10.1007/s11027-019-9845-0

Sanz-Pérez, E.S., Murdock, C.R., Didas, S.A., Jones, C.W., 2016. Direct capture of CO₂ from ambient air. *Chem. Rev.* 116, 11840–11876. DOI: 10.1021/acs.chemrev.6b00173

Seppänen, O.A., Fisk, W.J., Mendell, M.J., 1999. Association of ventilation rates and CO₂ concentrations with health and other responses in commercial and institutional buildings. *Indoor Air.* 9(4), 226-252. DOI: 10.1111/j.1600-0668.1999.00003.x

Shih, S.-M., Ho, C.-S., Song, Y.-S., Lin, J.-P., 1999. Kinetics of the reaction of Ca(OH)₂ with CO₂ at low temperature. *Ind. Eng. Chem. Res.* 38, 1316–1322. DOI: [10.1021/ie980508z](https://doi.org/10.1021/ie980508z)

Shimizu, T., HIRAMA, T., Hosoda, H., Kitano, K., Inagaki, M., Tejima, K., 1999. A twin fluid-bed reactor for removal of CO₂ from combustion processes. *Chem. Eng. Res. Des.* 77(1), 62-68. DOI: 10.1205/026387699525882

Stephens, J.C., Keith, D.W., 2008. Assessing geochemical carbon management. *Clim. Change* 90, 217. DOI: 10.1007/s10584-008-9440-y

Stolaroff, J.K., Lowry, G. V, Keith, D.W., 2005. Using CaO- and MgO-rich industrial waste streams for carbon sequestration. *Ener. Conv. Manag.*, 46, 687–699. DOI: 10.1016/j.enconman.2004.05.009

Talukdar, S., Banthia, N., 2013. Carbonation in concrete infrastructure in the context of global climate change: Development of a service lifespan model. *Constr. Build. Mater.* 40, 775–782. DOI: 10.1016/j.conbuildmat.2012.11.026

Tollefson, J., 2015. The 2 ° C dream. *Nature* 527, 436–438. DOI: 10.1016/j.ecoenv.2014.01.038

Van Balen, K., 2005. Carbonation reaction of lime, kinetics at ambient temperature. *Cem. Concr. Res.* 35, 647–657. DOI: [10.1016/j.cemconres.2004.06.020](https://doi.org/10.1016/j.cemconres.2004.06.020) Wu, S.F., Beum, T.H., Yang, J.I., Kim, J.N., 2007. Properties of Ca-base CO₂ sorbent using Ca(OH)₂ as precursor. *Ind. Eng. Chem. Res.* 46, 7896–7899. DOI: 10.1021/ie070135e

Wurzbacher, J.A., Gebald, C., Brunner, S., Steinfeld, A., 2016. Heat and mass transfer of temperature-vacuum swing desorption for CO₂ capture from air. *Chem. Eng. J.* 283, 1329–1338. DOI: 10.1016/j.cej.2015.08.035

Yin, J., Zhang, C., Qin, C., Liu, W., An, H., Chen, G., Feng, B., 2012. Reactivation of calcium-based sorbent by water hydration for CO₂ capture. *Chem. Eng. J.* 198–199, 38–44. DOI: 10.1016/j.cej.2012.05.078

Yoon, I.S., Çopuroğlu, O., Park, K.B., 2007. Effect of global climatic change on carbonation progress of concrete. *Atmos. Environ.* 41, 7274–7285. DOI: 10.1016/j.atmosenv.2007.05.028

Zeman, F.S., Lackner, K.S., 2004. Capturing carbon dioxide directly from the atmosphere. *World Resour. Rev.* 16, 157–172.

Zou, H., Du, H., Wang, Y., Zhao, L., Mao, G., Zuo, J., Liu, Y., Liu, X., Huisingh, D., 2017. A review of the first twenty-three years of articles published in the *Journal of Cleaner Production*: With a focus on trends, themes, collaboration networks, low/no-fossil carbon transformations and the future. *J. Clean. Prod.*, 163, 1-14. DOI: 10.1016/j.jclepro.2017.04.157