

## Carbon Dioxide Removal from the Atmosphere by Weathering Minerals in a Gas-Liquid-Solid Contactor

Richard C Darton <sup>a</sup>, Aidong Yang <sup>a</sup>, Lei Xing <sup>b</sup>, Liam Bullock <sup>c</sup>

<sup>a</sup> Department of Engineering Science, University of Oxford, Oxford OX1 3PJ, United Kingdom

<sup>b</sup> Department of Chemical Engineering, Loughborough University, Loughborough, LE11 3TU, United Kingdom

<sup>c</sup> GEO3BCN-CSIC, Carrer de Lluís Solé i Sabarís, s/n, 08028 Barcelona, Spain

[richard.darton@eng.ox.ac.uk](mailto:richard.darton@eng.ox.ac.uk); [aidong.yang@eng.ox.ac.uk](mailto:aidong.yang@eng.ox.ac.uk); [L.Xing@lboro.ac.uk](mailto:L.Xing@lboro.ac.uk); [lbullock@geo3bcn.csic.es](mailto:lbullock@geo3bcn.csic.es)

**Abstract.** Limiting global warming to 1.5°C requires removal of 100-1000 GtCO<sub>2</sub> from the atmosphere this century. One option, Enhanced Weathering, removes CO<sub>2</sub> through its natural reaction with carbonate or silicate minerals and water. This could involve spreading crushed minerals on land but engineered contactors could offer faster removal and fewer unpredictable interactions with the environment. A packed bubble flow contactor was modelled, using the mineral calcite which yields aqueous calcium bicarbonate for discharge into the ocean. The removal rate was primarily controlled by gas-to-liquid mass transfer. Seawater could be used but the feed air must then be enriched with CO<sub>2</sub> because seawater is saturated with calcite. Major energy requirements were for pumping/compression and CO<sub>2</sub> enrichment, whilst energy for mining, transport and comminution of particles was minor. Optimal schemes required overall energy (work) of 5.7-8.2 MJ/kg CO<sub>2</sub>, after ocean degassing, somewhat higher than literature values for direct air capture of CO<sub>2</sub>.

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**Keywords** Carbon dioxide, absorption, mineral weathering, packed bubble column, climate change

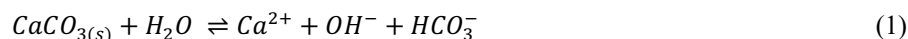
### Introduction

Proposed measures to combat climate change through reducing greenhouse gas emissions, include replacing fossil fuels with renewable energy, reducing demand for fossil fuels and improving the efficiency of their use, and capturing emitted gases at source. However, it is calculated that limiting global warming to the target of 1.5 °C *also* requires carbon dioxide removal (CDR) from the atmosphere. The amount that must be removed is huge – perhaps some 100–1000 GtCO<sub>2</sub> over the 21st century [1] – so this could become the world’s largest industry. A wide range of CDR methods has been suggested [2, 3]. Direct air capture (DAC) is the CDR process most similar to existing industrial gas treating, in which atmospheric air is contacted with an abiotic sorbent (solid or liquid) which captures the CO<sub>2</sub>. The sorbent is then regenerated to make a CO<sub>2</sub> product which must be safely sequestered and fresh sorbent that can be reused. Operating costs of DAC are mainly the costs of regeneration, and pumping and compressing the fluids [4, 5].

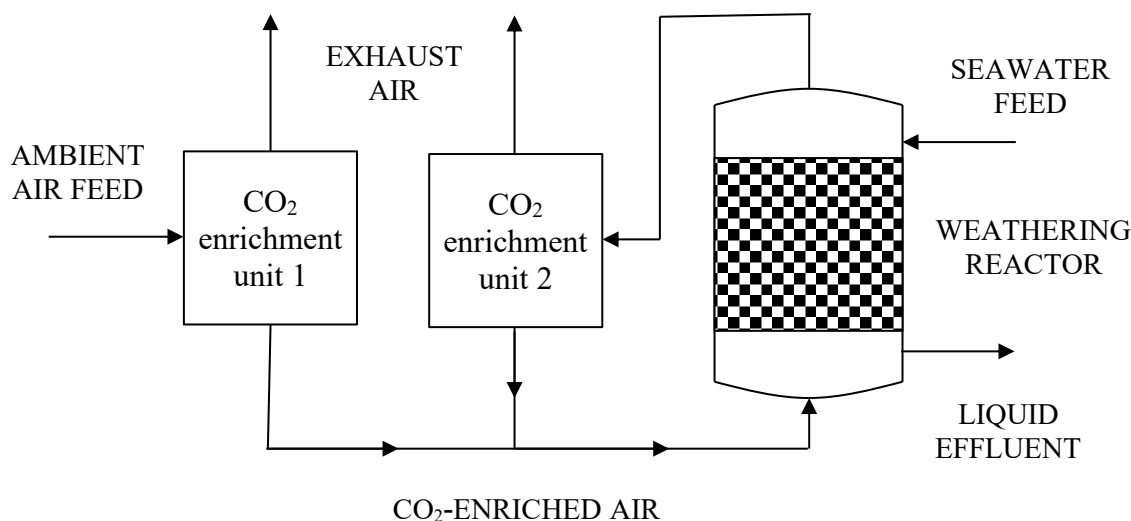
An alternative approach to CDR, by enhanced weathering (EW), is one that automatically takes care of the sequestration of the captured CO<sub>2</sub> [6]. EW of carbonate or silicate minerals aims to accelerate the slow weathering process which naturally draws down a significant amount of CO<sub>2</sub> from the atmosphere through its reaction with minerals in the rock and water. EW might be implemented by spreading crushed rock in specific locations such as on the soil [7]. Compared to such “natural” deployments, options in which mineral particles are weathered in engineered reactors [8-10], where conditions are more controlled, could lead to benefits such as higher CDR rates and fewer unpredictable interactions with the natural environment. However, such schemes might require greater energy and water consumption or involve other costs and impacts; all these must be quantified and assessed.

### Process chemistry and outline process scheme

The EW reactions of most interest when weathering carbonate minerals, the focus of this paper, can be written



Here Eq. (1) represents water attacking and dissolving the mineral surface, yielding hydroxyl and bicarbonate ions. Eq. (2) is the reaction of dissolved carbon dioxide with hydroxyl ion, which enables the absorption of more  $\text{CO}_2$  from the gas phase. These reactions generate a bicarbonate rich aqueous effluent which, it is intended, will ultimately end up in the ocean, though it may spend time first in soil or river systems. To economise on the consumption of freshwater, it is of interest to examine the use of seawater as a reactant. However, this requires the carbon dioxide concentration in the contacted gas to be raised above its value in the atmosphere, because surface seawater is already essentially at equilibrium with respect to  $\text{CO}_2$  in the atmosphere. Caldeira and Rau [11] suggested the use of power plant flue gas as a source of enriched  $\text{CO}_2$  to promote absorption into seawater. However, to maintain the principle of drawing  $\text{CO}_2$  out of the atmosphere, we take ambient air as feed and incorporate a pre-concentration step using DAC, before the weathering reaction with carbonate, as shown in Figure 1. To make optimal use of the enriched air, the reactor outlet gas is recycled following a second enrichment to maintain the reactor feed composition.



**Fig. 1** Flow scheme for capture of  $\text{CO}_2$  from air in an enhanced weathering reactor.

The weathering reaction causes the particles to shrink, and in a real operation the reactor would have to be replenished from time to time. Our calculations take account of the reduction in particle diameter, but no addition of solids is made during a modelled weathering campaign which proceeds until 63.66 kg of calcite have been consumed for every square metre of reactor cross-section. This value corresponds to the dissolution of 50 kg in a notional reactor of 1 m diameter – an arbitrarily fixed amount for comparison purposes. The capture rates and energy requirements reported here are the mean values for the simulated weathering campaigns. We used a numerical model to compare the campaigns using differently sized particles (1-10 mm diameter), various gas and liquid flowrates, bed heights (0.2-10 m) and compositions of enriched air (1-10 %  $\text{CO}_2$ ).

### The Packed Bubble Column: hydrodynamics, mass transfer and the numerical model

In earlier work we modelled EW of calcite using fresh water in a trickle flow reactor [10]. Here we use a similar mathematical model, but with seawater and a packed bubble column weathering reactor. This reactor type contains a bed of mineral particles with liquid filling most of the void space, and gas rising under buoyancy in the form of discrete bubbles. The PBC offers the potential of a larger liquid inventory than a trickle column, favouring dissolution of the solid, but also must be engineered to facilitate gas-to-liquid mass transfer. There is no settled model to be found in the literature of the hydrodynamic and mass transfer characteristics of the PBC, so we have based our calculations on literature reports, supplemented by experimental validation with a small PBC weathering reactor [12].

In a PBC bubbles which are much smaller than the particles can rise through the interstices between the particles; bubbles which are much larger than the particles can rise, rather faster, often as agglomerates, simply enveloping and

passing over the particles [13]. Several authors have observed that, in a PBC, bubbles of a certain size range can be captured in the interstices if their buoyancy is insufficient to overcome the capillary forces at points of contact with particles. A “static” gas hold-up then forms in addition to the “dynamic” gas hold-up of rising bubbles. The dynamic hold-up increases as gas flow rate increases, and there is more interaction between rising bubbles and the captured ones [14]. Coalescence then occurs and larger bubbles are formed which escape, so static hold-up plays a diminishing role as dynamic hold-up increases. To describe the interaction of the two types of gas hold-up we write

$$\varepsilon_{G,static} = \varepsilon_{G,static,0} \cdot \exp \left\{ -\frac{\varepsilon_{G,dyn}}{\varepsilon_{G,static,0}} \right\} \quad (3)$$

where the gas hold-up extrapolated to zero gas flow is  $\varepsilon_{G,static,0}$  given by the dimensional equation

$$\varepsilon_{G,static,0} = 0.055 \exp \left\{ -0.9(\sqrt{d_p, mm} - 1.7)^2 \right\} \quad (4)$$

as suggested by the data of Taghavi and Balakotaiah [15]. When the superficial liquid velocity,  $u_L$ , is relatively small, the dynamic gas hold-up  $\varepsilon_{G,dyn}$  is  $u_G/u_{b,0}$  where  $u_{b,0}$  is the bubble rise velocity for which we take a value  $0.3 \text{ ms}^{-1}$ , consistent with hold-up data [14]. The mean slip velocity,  $u_s$ , averaged over static plus dynamic hold-up is

$$u_s = \left\{ \frac{\varepsilon_{G,static}}{u_G} + \frac{1}{u_{b,0}} \right\}^{-1} \quad (5)$$

and we use this value to estimate the gas-liquid mass transfer coefficient  $k_L$  from the surface renewal theory result:

$$k_L = \sqrt{\frac{D_L u_s}{d_b}} \quad (6)$$

Here  $D_L$  is the liquid phase diffusivity and  $d_b$  is the estimated bubble diameter [16]. The above correlations for the PBC are incorporated in a calculation scheme describing the mass balances for gas and liquid phases in the bed. Reactions (1) and (2) are modelled kinetically, and all other reactions of ions in the liquid are taken to be at equilibrium, also calculated [12].

### Estimating energy requirement

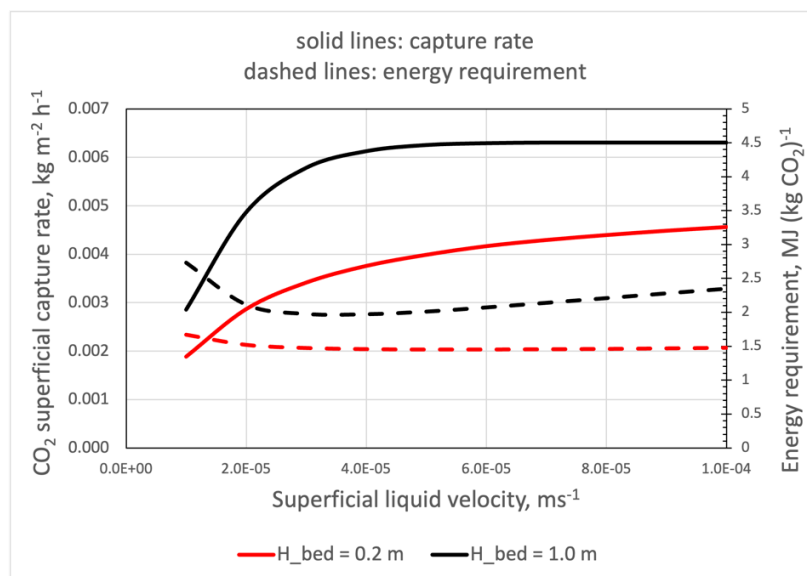
The energy required for the EW scheme is the major operating expense and it has three main components, all calculated here as electricity (work):

- Energy for supplying mineral particles.  $20 \text{ kJ/kg}_{\text{solids}}$  was allowed for excavation, drilling, blasting, and short range hauling of rock [17], and an additional  $31.6/\sqrt{d_p, mm} \text{ kJ/kg}_{\text{solids}}$  for crushing and grinding the calcite [18].
- Energy for moving liquid and gas. Once the flowrates and pressure drops have been evaluated, the energy required was calculated by standard methods assuming a mechanical efficiency of 80% for pumps and compressors.
- The energy needed for  $\text{CO}_2$  enrichment was calculated as follows. No particular technology for DAC was chosen but we note that a number of processes are being developed which might be suitable for this application. We calculated first the minimum (reversible) work requirement for the enrichment, from the total change in Gibbs free energy. Considering mainly data for flue gas scrubbing, Darton and Yang [19] found the thermal energy requirement to be about 14 times as much as the minimum work. (Applying this factor to air capture yielding pure  $\text{CO}_2$  suggests it would need thermal energy  $\sim 7.3 \text{ MJ/kg CO}_2$ , consistent with the range reported for solid sorbent DAC processes,  $\sim 4\text{--}12 \text{ MJ/kg CO}_2$  [20].) The thermal energy for sorption regeneration is generally at a level around  $100^\circ\text{C}$ , and assuming this could be provided by a heat pump with Coefficient of Performance 2.5, the electricity requirement would be a factor about  $14/2.5=5.6$  times the minimum work.

### Results

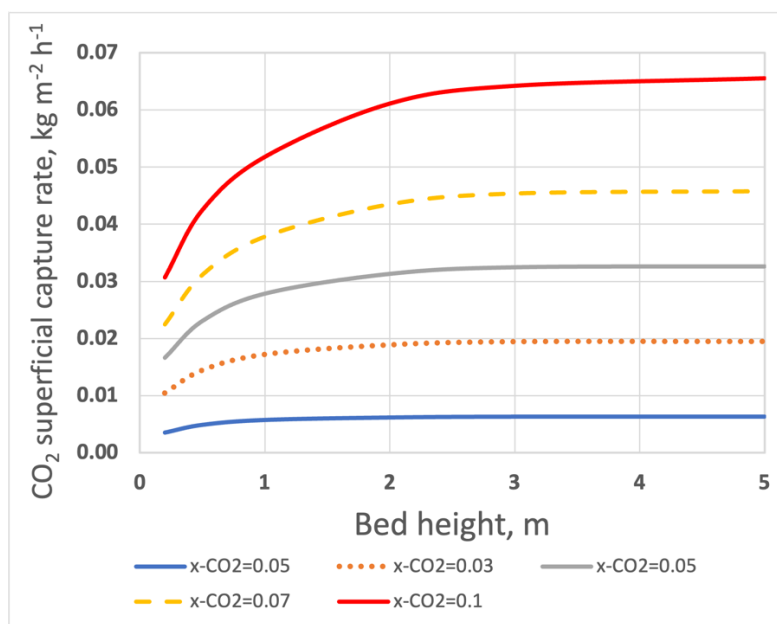
Figures 2 and 3 show typical performance of the packed bubble column. The highest superficial capture rates (per square metre of bed cross-section) are found when the bed of particles is tallest and the  $\text{CO}_2$  concentration in the feed gas is greatest, providing there is sufficient liquid flow to avoid the liquid becoming saturated. The influence of particle size was found to be relatively minor (results not presented here, but see [12]), an indication that the absorption rate is largely controlled by gas/liquid mass transfer. Achieving a high superficial capture rate is important because the ground area required for reactors is inversely proportional to this quantity. For the large amounts of  $\text{CO}_2$  that must be captured,

the land required for these reactors may limit the application of the technology. Conditions that lead to a faster capture rate also generally require more energy input.



**Fig. 2** Capture rate and energy (work) requirement as function of liquid flow rate.

Conditions:  $d_{p,0} = 1.0 \text{ mm}$ ;  $u_G = 1 \times 10^{-4} \text{ ms}^{-1}$ ;  $x_{CO_2} = 0.01$



**Fig. 3** Capture rate of CO<sub>2</sub> from enriched air with varying composition. Effect of bed height.

Conditions:  $d_{p,0} = 5.0 \text{ mm}$ ;  $u_G = 1 \times 10^{-4} \text{ ms}^{-1}$ ;  $u_L = 5 \times 10^{-5} \text{ ms}^{-1}$

Figure 4 shows how the specific energy requirement varies with the degree of enrichment, for different bed depths. Although greater enrichment itself consumes more energy, it can greatly increase effectiveness of the bed: for deeper beds, enrichment to 3-4% already leads to a significant reduction in total specific energy requirement. A thorough

investigation of the operating parameter space for the packed bubble column EW scheme (Fig. 1) suggests that a reasonable trade-off between space requirement and energy requirement can be obtained at a specific energy (work) requirement of  $\sim 2.1$ - $2.3$  MJ/kg CO<sub>2</sub>. Capture rates under these conditions vary from about 0.02 to 0.06 kg m<sup>-2</sup>h<sup>-1</sup>.

In assessing the use of EW for removing and sequestering large amounts of carbon dioxide from the atmosphere, consideration must be given to the degassing of aqueous product [8] in the ocean. When the bicarbonate-rich product from our scheme flows into the ocean it will re-equilibrate, releasing a significant fraction of the previously absorbed CO<sub>2</sub>. This degassing can be calculated by a flash calculation, taking account of the various ionic equilibria in the seawater phase, and between water and atmosphere. This shows that the sustained removal (i.e. after degassing) of CO<sub>2</sub> amounts only to  $\sim 0.55$ - $0.62$  mols of CO<sub>2</sub> for every mol of calcite dissolved. This range is consistent with that previously suggested, 0.4-0.7 mol/mol [20]. As a result, the effective overall energy (work) requirement increases to 5.7-8.2 MJ/kg CO<sub>2</sub>, and the effective capture rates decrease proportionately.

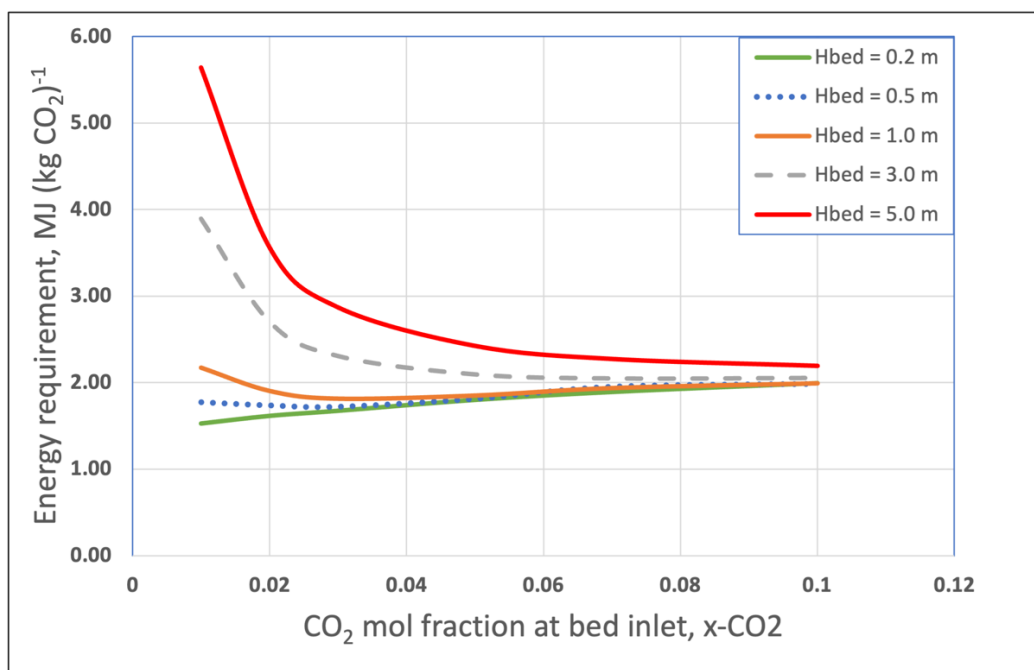


Fig. 4 Specific energy (work) requirement for EW scheme. Effect of CO<sub>2</sub> enrichment and bed height.

Conditions:  $d_{p,0} = 5.0$  mm;  $u_G = 1 \times 10^{-4}$  m s<sup>-1</sup>;  $u_L = 5 \times 10^{-5}$  m s<sup>-1</sup>

## Discussion and conclusions

The range of thermal energy requirements reported in literature for DAC,  $\sim 4$ - $12$  MJ/kg CO<sub>2</sub> [20], corresponds, again using a heat pump with CoP of 2.5, to a work requirement of  $\sim 1.6$ - $4.4$  MJ/kg CO<sub>2</sub>. The calculated optimal range of overall energy (work) requirement for EW of calcite in seawater allowing for degassing, reported here, 5.7-8.2 MJ/kg CO<sub>2</sub>, is therefore currently somewhat higher than for DAC. Absorbing CO<sub>2</sub> in a weakly alkaline liquid is a slow process dependent largely on the liquid phase mass transfer coefficient, implying significant pumping and compression costs for each kg absorbed. There is a great incentive to find ways of accelerating this absorption, by biological or other means. Several parameters on which these calculations are based are subject to uncertainty – many engineering parameters which are well-known and understood for beds of manufactured column packings can only be estimated approximately for beds of crushed rock. The properties of packed bubble columns, as a reactor class, have also been little investigated: there are some excellent studies drawing attention to interesting phenomena, such as static hold-up, but phenomenological descriptions and correlations of behaviour are largely lacking. Attention has been drawn elsewhere [4] to the importance of developing packings for DAC which have extremely low pressure drop (because of the potential need to treat very high volumes of air). We conclude that both process and equipment for the CDR industry require urgent innovation and development.

If weathering schemes like this are to be used for CO<sub>2</sub> removal, potentially at a Gt scale globally, these results imply significant demands both for power to be supplied by the future energy system and for suitable land areas for the reactors. The economic model on which the plants would be built and operated needs to be established, and also the regime for measuring and certifying the amount of CO<sub>2</sub> captured and stored. The costs of constructing and operating the reactors are not expected to be particularly high as no expensive materials or extreme operating conditions are involved. However, significant time and labour would still be needed for large-scale deployment, which could constrain the achievable rate of installation in practice. In addition, further details such as the logistics of producing and transporting minerals and the handling of waste streams (which can be particularly relevant when complex feeds such as mine tailings are processed) must be considered. Life-cycle and sustainability assessment, as well as stakeholder consultation are required to fully evaluate the potential and the implications of the up-scaling of such schemes.

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#### References

1. IPCC. *Summary for policymakers*. In: Masson-Delmotte V, Zhai P, Portner HO, et al., eds. *Global Warming of 1.5 °C. An IPCC Special Report on the Impacts of Global Warming of 1.5 °C Above Pre-Industrial Levels and Related Global Greenhouse Gas Emission Pathways, in the Context of Strengthening the Global Response to the Threat of Climate Change, Sustainable Development, and Efforts to Eradicate Poverty*. Geneva, Switzerland: World Meteorological Organization; 2018
2. *Greenhouse Gas Removal*, London: The Royal Academy of Engineering, 2018
3. National Academy of Sciences Engineering and Medicine, *Negative Emissions Technologies and Reliable Sequestration*, Washington, DC: National Academies Press, 2019.
4. D. Keith, G. Holmes, D. St. Angelo, and H. Kenton, *Joule* **2**, 1573–1594 (2018).
5. C. Beuttler, L. Charles, and J. Wurzbacher, *Frontiers in Climate*, **1**, 10 (2019).
6. J. Hartmann, A.J. West, P. Renforth, et al., *Rev. Geophys.* **51** 113–149 (2013).
7. D.J. Beerling, E.P. Kantzas, M.R. Lomas, et al., *Nature*. **583** 242–248 (2020).
8. G.H. Rau, *Environ. Sci. Technol.* **45** 1088–1092 (2011).
9. J.L. Hamilton, S.A. Wilson, B. Morgan, et al., *Econ Geol.* **115** 303–323 (2020).
10. L. Xing, R.C. Darton, A.D. Yang, *AIChE J.* **67**(5) e172020 (2021).
11. K. Caldeira, G.H. Rau, *Geophysical Research Letters*. **27**(2) 225-8 (2000 Jan 15).
12. L. Xing, H. Pullin, L. Bullock, P. Renforth, R.C. Darton and A. Yang, *Chemical Engineering Journal*, **431**, 134096 (2022).
13. J.H. Collins, A.J. Sederman, L.F. Gladden, M. Afeworki, J.D. Kushnrick, and H. Thomann, *Chemical Engineering Science*, **157**, 2-14 (2017).
14. J.G. Maldonado, D. Bastoul, S. Baig, M. Roustan, and G. Hébrard, *Chemical Engineering and Processing: Process Intensification*, **47**(8), 1190-1200 (2008).
15. M. Taghavi, V. Balakotaiah, *AIChE J.* **65** 16624 (2019).
16. K. Akita, F. Yoshida, *Ind. Eng. Chem. Res.*, **12**, 76-80 (1973).
17. P. Renforth, B.G. Jenkins, T. Kruger *Energy* **60**, 442-452 (2013).
18. F.C. Bond, *Trans Am. Inst. Mining and Metallurgical Pet. Engrs*, **193**, 484-494 (1952)
19. R.C. Darton, A. Yang, Chapter 1 in *Advances in Carbon Management Technologies*, eds. S. K. Sidkar and F. Priciotta, Boca Raton: CRC Press, 2020, 3-22.
20. F. Sabatino, A. Grimm, F. Gallucci, M. van Sint Annaland, G.J. Kramer, M. Gazzani, *Joule*, **5**(8), 2047-2076 (2021).
21. P. Renforth, G. Henderson *Reviews of Geophysics* **55**(3) 636-674 (2017).