

Industrial CO₂ Removal Using Carbonic Anhydrase: Potential, Promise and Challenges

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Atmospheric concentrations of greenhouse gases (GHG) such as carbon dioxide (CO₂), chlorofluorocarbons, methane, and nitrous oxide have been rising considerably due to human-induced processes [1]. One of the most abundant of the GHG is CO₂, and a main contributor to a rise in global temperatures [2]. The burning of fossil fuels has sharply increased the concentration of atmospheric CO₂ and has been correlated with increased global temperatures over the past century [3,4]. This presents a global threat that has recently been addressed by world leaders in the *Paris Climate Talks* [5] promoting an extensive effort to limit CO₂ production in industrial processes and to slow the rate of climate change. Despite the recognition of these issues, implementation of large scale CO₂ removal from the burning fossil-fuels has been limited [6]. Most of this is due to the use of harsh chemical processes and extreme temperatures to remove CO₂, which translates to an energy and cost inefficient process [4,7]. Therefore, more efficient CO₂ removal processes must be implemented. One such potential avenue is the utilization of enzymatic CO₂ sequestration [8]. Specifically, the use of the enzyme, carbonic anhydrase (CA) for CO₂ removal (CDR) has shown promise for its catalytic efficiency and its ability to be produced in large quantities from recombinant technology [7,9-11].

However, for a successful CA-mediated CDR, the enzyme must maintain its catalytic efficiency in extreme conditions, such as high temperature (up to 80°C), pressure, extreme pH levels (between pH 3 – 11), and more recently, resistance to anionic inhibition [10,12-16]. Furthermore, a mechanism to feasibly incorporate a CA-mediated CDR step in the fossil-fuel combustion process needs to be developed. To date, several possibilities have come in the form of CO₂ absorbers containing immobilized CA resins, or bioreactors containing algae that over express CA, all of which have been extensively reviewed by Frost and McKenna et al. [17]. A model depicting a CA-mediated CO₂ absorber is depicted in Figure 1 with favorable biochemical and biophysical characteristics of the enzyme highlighted.

Our group and others, have made efforts to characterize CAs from organisms that thrive in extreme environments [15,18] and utilize these biochemical and biophysical characteristics to engineer thermal and pH stable CA variants [11,19-21], to address the need for a suitable bio-catalytic CDR agent. Previously it has been shown: that truncating surface loops, the presence of an intramolecular disulfide bond, and dimerization allows CA to maintain its catalytic activity at 70°C, and a range of pH (from pH 5-9) [15,20]. In addition, it has been shown that the presence of charged residues in the catalytic site of CA can contribute to the reduction in anionic inhibition (common anions found in fossil-fuel by-products and their CA inhibition constants are shown in Table 1). Although these parameters still fall short of the ideal characteristics of a CA-mediated CDR agent, they provide us with avenues which we can further exploit to engineer a useful candidate to reduce fossil-fuel produced CO₂ emissions. Future studies will include implementing an enzymatic design of an oligomeric and compact CA, that exhibits resistance to anionic inhibition, and retains its activity in a range of pH from 3-11 and temperatures up to 80°C (Figure 1) [13-16,18]. These results can further be combined with current designs to

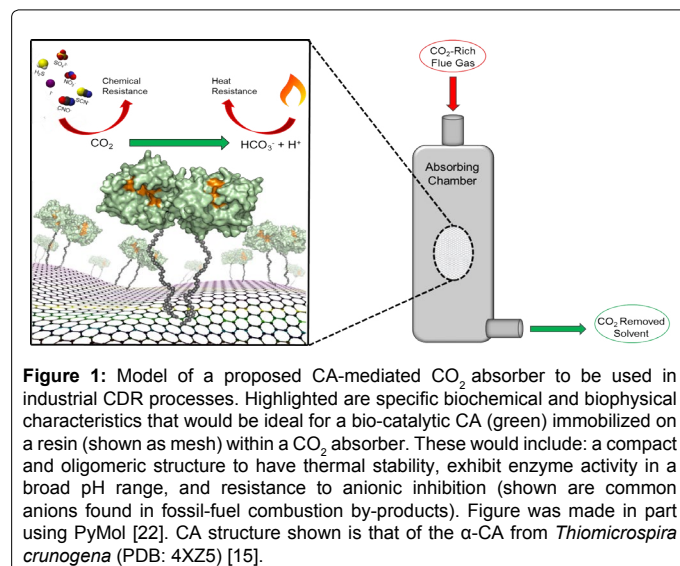


Figure 1: Model of a proposed CA-mediated CO₂ absorber to be used in industrial CDR processes. Highlighted are specific biochemical and biophysical characteristics that would be ideal for a bio-catalytic CA (green) immobilized on a resin (shown as mesh) within a CO₂ absorber. These would include: a compact and oligomeric structure to have thermal stability, exhibit enzyme activity in a broad pH range, and resistance to anionic inhibition (shown are common anions found in fossil-fuel combustion by-products). Figure was made in part using PyMol [22]. CA structure shown is that of the α-CA from *Thiomicrospira crunogena* (PDB: 4XZ5) [15].

Anion	TcrUCA	hCA II	SspCA
	K _i (mM) ^a		
Hg ²⁺	8.40	0.85	0.77
HSO ₃ ⁻	0.97	89	21.1
SO ₃ ²⁻	7.6	7.5	2.3
HS ⁻	0.70	0.04	0.58

TcrUCA: α-CA isolated from *Thiomicrospira crunogena* XL2 [15]; hCA II: α-CA from humans (isoform II); SspCA: α-CA isolated from *Sulfurihydrogenibium yellowstonense* YO3AOP1 [18]; ^aInhibition constants adapted from Mahon et al. [14]

Table 1: Selected anion inhibition constants of CAs suggested as CDR-agents.

implement a CA-mediated CDR system and provide an energy and cost efficient process to limit atmospheric CO₂. With the current global dependency on fossil-fuels for energy production, CA may provide a means to reduce human induced climate change.

References

- Hansen J, Sato M, Ruedy R, Lacis A, Oinas V, et al. (2000) Global warming in the twenty-first century: an alternative scenario. *Proc Natl Acad Sci USA* 97: 9875-9880.

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2. Shakun JD, Clark PU, He F, Marcott SA, Mix AC, et al. (2012) Global Warming Preceded by Increasing Carbon Dioxide Concentrations during the Last Deglaciation. *Nature* 484: 49-54.
3. Canadell JG, Le Quéré C, Raupach MR, Field CB, Buitenhuis ET, et al. (2007) Contributions to accelerating atmospheric CO₂ growth from economic activity, carbon intensity, and efficiency of natural sinks. *Proc Natl Acad Sci USA* 104: 18866-18870.
4. Intergovernmental Panel on Climate Change (2005) IPCC Special Report on Carbon Dioxide Capture and Storage; Metz, B., Ed, Cambridge University Press, for the Intergovernmental Panel on Climate Change: Cambridge.
5. Cesare C (2015) Paris Climate Talks, Day 12: What We're Reading. *Nature* 2015.
6. Leung DY, Caramanna G, Maroto-Valer MM (2014) An Overview of Current Status of Carbon Dioxide Capture and Storage Technologies. *Renew Sustain Energy Rev* 39: 426-443.
7. Pierre AC (2012) Enzymatic Carbon Dioxide Capture. *ISRN Chem. Eng.* 2012: 1-22.
8. Boone CD, Gill S, Habibzadegan A, McKenna R (2013) Carbonic Anhydrase: An Efficient Enzyme with Possible Global Implications. *Int J Chem Eng* 2013: 1-6.
9. Favre N, Christ ML, Pierre AC (2009) Biocatalytic Capture of CO₂ with Carbonic Anhydrase and Its Transformation to Solid Carbonate. *J Mol Catal B Enzym* 60: 163-170.
10. Boone CD, Habibzadegan A, Gill S, McKenna R (2013) Carbonic anhydrases and their biotechnological applications. *Biomolecules* 3: 553-562.
11. Boron WF (2010) Evaluating the role of carbonic anhydrases in the transport of HCO₃⁻-related species. *Biochim Biophys Acta* 1804: 410-421.
12. Savile CK, Lalonde JJ (2011) Biotechnology for the acceleration of carbon dioxide capture and sequestration. *Curr Opin Biotechnol* 22: 818-823.
13. Mahon BP, Díaz-Torres NA, Pinard MA, Tu C, Silverman DN, et al. (2015) Activity and Anion Inhibition Studies of the α -Carbonic Anhydrase from *Thiomicrospira Crunogena* XCL-2 Gammaproteobacterium. *Bioorg Med Chem Lett* 25: 4937-4940.
14. Mahon BP, Bhatt A, Vullo D, Supuran CT, McKenna R, et al. (2015) Exploration of Anionic Inhibition of the α -Carbonic Anhydrase from *Thiomicrospira Crunogena* XCL-2 Gammaproteobacterium: A Potential Bio-Catalytic Agent for Industrial CO₂ Removal. *Chem Eng Sci* 138: 575-580.
15. Díaz-Torres NA, Mahon BP, Boone CD, Pinard MA, Tu C, et al. (2015) Structural and Biophysical Characterization of the α -Carbonic Anhydrase from the Gammaproteobacterium *Thiomicrospira Crunogena* XCL-2: Insights into Engineering Thermostable Enzymes for CO₂ Sequestration. *Acta Crystallogr D Biol Crystallogr* 71: 1745-1756.
16. Vullo D, Bhatt A, Mahon BP, McKenna R, Supuran CT, et al. (2015) Sulfonamide Inhibition Studies of the α -Carbonic Anhydrase from the Gammaproteobacterium *Thiomicrospira Crunogena* XCL-2, TcrUCA. *Bioorg Med Chem Lett*.
17. Frost SC, McKenna R (2014) Carbonic Anhydrase Mechanism, Regulation, Links to Disease, and Industrial Applications. Springer.
18. Capasso C, De Luca V, Carginale V, Cannio R, Rossi M, et al. (2012) Biochemical Properties of a Novel and Highly Thermostable Bacterial α -Carbonic Anhydrase from *Sulfurihydrogenibium Yellowstonense* YO3AOP1. *J Enzyme Inhib Med Chem* 27: 892-897.
19. Yu Y, Chen B, Qi W, Li X, Shin Y, et al. (2012) Enzymatic conversion of CO₂ to bicarbonate in functionalized mesoporous silica. *Microporous Mesoporous Mater* 153: 166-170.
20. Boone CD, Habibzadegan A, Tu C, Silverman DN, McKenna R (2013) Structural and Catalytic Characterization of a Thermally Stable and Acid-Stable Variant of Human Carbonic Anhydrase II Containing an Engineered Disulfide Bond. *Acta Crystallogr D Biol Crystallogr* 69: 1414-1422.
21. Mirjafari P, Asghari K, Mahinpey N (2007) Investigating the Application of Enzyme Carbonic Anhydrase for CO₂ Sequestration Purposes. *Ind Eng Chem Res* 46: 921-926.
22. Schrodinger LLC. The PyMOL Molecular Graphics System, Version 1.2r3pre, Schrödinger, LLC.