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A Molecular Perspective on Carbon Capture

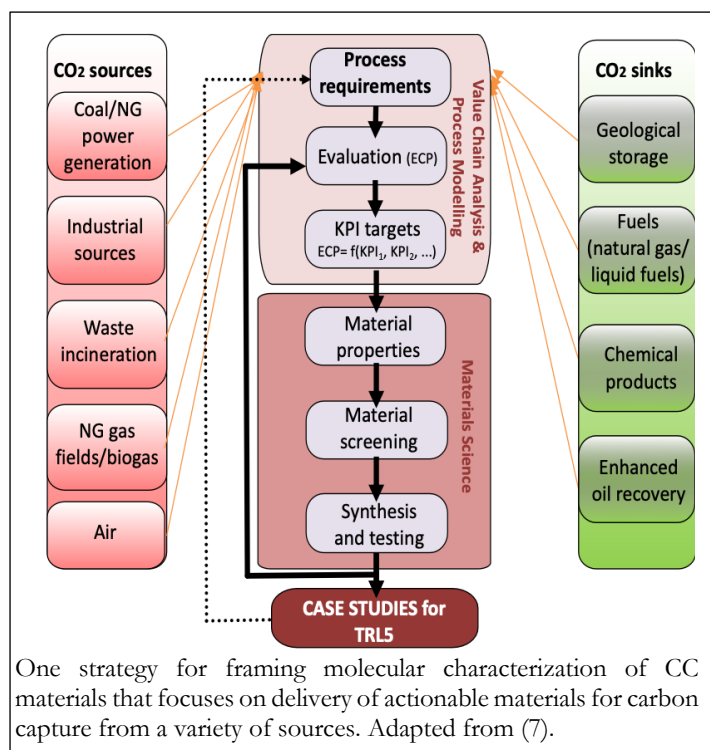
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The atmosphere is changing. This change is due to humans combusting hydrocarbons to provide themselves with mobility, power, and goods. The Earth responds in many ways to our changing atmosphere via the carbon cycle, and in a few hundred thousand years these anthropogenic changes will be absorbed within that cycle. In the meantime, the changed atmosphere is increasing the temperature of the planet via changes in radiative forcing. There are consequences of a warming planet throughout the physical and biological ecosystems, and these consequences are not visited equally amongst the nations. Indeed, the extraction of hydrocarbon resources typically does not economically benefit local peoples (a problem of *environmental justice*), or the outcomes of a changing atmosphere disproportionately affect peoples that lack resources to deal with those consequences (a problem of *climate justice*). The lack of environmental and climate justice is an ethical shortcoming and thus a legal and governance problem for all humans. Moreover, failure to support disadvantaged peoples, and indeed the creation of circumstances which furthers their disadvantage, is a moral failing that is contrary to the world religions of which this author is aware.

World response to this ethical and moral crisis is captured well in the 6th Assessment Report of the Intergovernmental Panel on Climate Change (IPCC) (1). The role of carbon capture and sequestration/utilization (CCUS) in this milieu of responses to radiative forcing is summarized in review articles (2), though these discussions sidestep questions often heard in public discourse, such as *why not shut down carbon emitting industries and replace them with green processes*, or *why don't you support rapid transition to nuclear power?* These are important questions, yet virtually all IPCC reports strongly advocate CCUS technologies to mitigate industrial emissions before transitions can take place, and increasingly advocate using CCUS as a *negative emissions technology* whereby the carbon content of the atmosphere is reduced. This worldwide endorsement of CCUS supports a variety of research, from the molecular details of carbon capture to unit operations and design for such functions, from technoeconomic analyses and life cycle studies to plant-scale deployment and utilization for defossilization. Basic research in all these areas has been, or is, emerging throughout the world (3); what appears to be lacking, however, is functional governance (particularly in the USA) that affirms public policy and support for deployment of CCUS. This lack of action is due in part to neo-liberal economics that fail to account for the social cost of carbon (4) and the propensity for policy-making institutions to distance themselves from local perception of environmental change (5).

Despite lack of action on national and international scales, fundamental research on CCUS continues with strong financial support from a variety of sectors, and carbon capture technologies imagine several non-biological strategies for removal of CO₂ from industrial or direct air sources (2, 6). The important question for researchers that deploy molecular level characterization of carbon-capture materials is how to embed their studies into the larger questions posed above, and in particular focus their studies so as to contribute to actionable carbon capture materials. The figure below details one such strategy (7) and serves as a useful paradigm for molecular perspectives on carbon capture. Here



the question of materials characterization begins with a “meta” view of CO₂ sources (including direct air) and the sink for this captured CO₂. The input and output requirements, then, dictate the requirements of a capture process (e.g., adsorption, absorption, membrane, looping). The process requirements provide key performance indicators (KPI) for the process, which in turn make certain demands on the material properties. The subset of all materials that meet these properties are discerned by “genomic” screening, with *actionable* materials dictated *in silico* for subsequent synthesis and testing. It is in this latter step that molecular level characterization should be focused.

An example illustrates this approach (8). Here the authors make analogy with drug

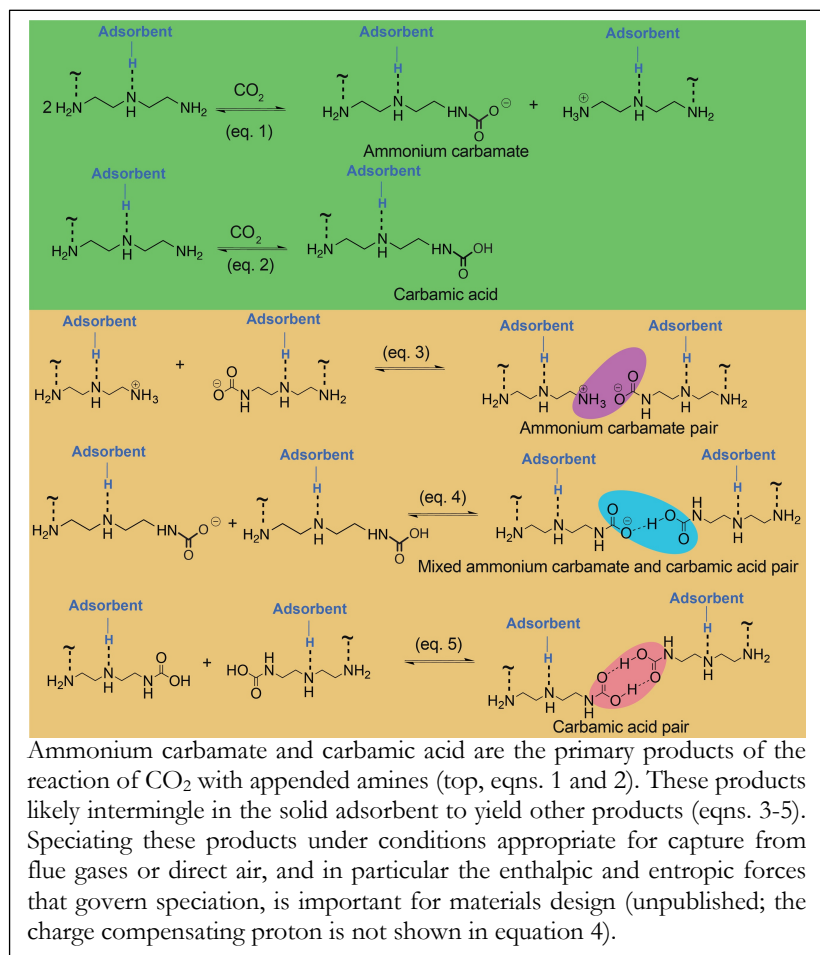
design wherein pharmacophores are discerned *in silico* for optimal binding to target biological macromolecules. The proposal for an *adsorbaphore* is the inverse: discern an optimal atomic arrangement to bind CO₂ with the exclusion of dinitrogen and water under the specific conditions of coal-fired power plant (CFPP) flue gas. Monte Carlo screening of >300,000 metal-organic frameworks (MOFs) discerns a space of working capacity (a KPI for costs of, e.g., temperature programmed desorption) versus selectivity against dinitrogen (a KPI for efficacy of the adsorbent). About 8,000 MOFs that meet KPIs for these metrics have their CO₂ binding sites analyzed by graph theory to bin the sites into adsorbaphore structural types (e.g., parallel aromatic rings spaced by 0.7-0.8 nm), then further screened by Monte Carlo methods for water affinity versus CO₂ affinity. Further KPIs, such as cost, recyclability, and abundance of the MOF metals, led to the net result of 35 structures that, according to computer studies, would be optimal for CC from a CFPP. Combinatorial synthetic strategies led to two aluminum-based MOFs that could actually be synthesized. Here the molecular level characterization affirmed that the structures synthesized were actually what the computer had imagined, and that the binding sites for CO₂, and its exclusion of water, were in fact realized as the computer had predicted. In the presence of humidified flue gases, the materials outperformed commercial materials for carbon capture.

Specifying the source of CO₂ may seem obvious for determining the capture process requirements. Steel and cement manufacture, for example, have exhaust streams of very different temperatures than those from a power plant, or even direct air. The sinks are equally important, however. For example, underground sequestration of CO₂ involves pipeline transport of supercritical CO₂, and such pipelines must be protected against corrosion via impurities (e.g., water) in the fluid stream. Use of captured CO₂ for manufacture of chemicals (“defossilization”) may have very stringent requirements for purity owing to the sensitivity of downstream catalysts for reduction of CO₂.

It is a long-held notion in the chemical sciences that discerning *mechanism* leads to optimal materials design. A particularly challenging aspect of discerning mechanism for carbon capture is the plethora

of chemistry that may occur within the capture material. *Adsorption* on solid materials, for example, is often aided by incorporating amines within the materials, advantaging carbon capture through the use of long-understood reversible reactions of CO₂ with amines to form carbamates. In the context of porous materials hosting amine functionalities, there are a host of reactions that may occur, and these reactions are expected to be influenced by process temperature, pressure, and water partial pressure. While vibrational spectroscopies may provide analyses of which atoms are bonded to each other, the *intermingling* of molecules or functional groups may be important for understanding mechanism. Such intermingling may be discerned by aggressive scattering methods (e.g., single crystal neutron scattering), but in the case of amorphous materials, or disordered environments within powders, nuclear magnetic resonance (NMR) has been decisively employed. For example, at least three different structures for CO₂ adsorbed within amine-appended MOFs have been enumerated: within the channels of amine-appended MOFs are ammonium carbamate chains, carbamic acid chains, or mixed ammonium carbamate/carbamic acid chains (9). In some cases, the presence of water interconverts these species (10).

The molecular subtleties of CO₂ adsorption onto *amorphous* porous materials are illustrated in the figure below where we imagine an adsorbent material imbibed with amines so as to produce carbamates and carbamic acid (reactions 1 and 2). Here the host adsorbent is a polymeric material that can afford the intermingling of carbamate and carbamic acid species to yield (to a first approximation) pairs of carbamates and carbamic acid



moieties (equations 3-5). Neither scattering methods nor vibrational spectroscopy can characterize and enumerate these functions in the amorphous matrix. Here solid-state NMR methods become particularly useful. Proton, carbon, and nitrogen chemical shifts identify carbamates from carbamic acids, and heteronuclear recoupling methods (HETCOR) allow the proton-carbon dipolar couplings to be used as a ruler to measure spatial proximity. In this way the authors (submitted for publication) determined that ammonium carbamate pairs, along with carbamate-carbamic acid pairs, were the final products formed under CFPP flue gas conditions. This material was found to be stable after multiple adsorption/desorption cycles.

Motivation for thesis work aimed at molecular-level events in carbon capture is very high amongst entering doctoral students at Berkeley, and likely elsewhere. Such motivations are understandable as a new generation of world citizens seeks to ameliorate the damage resulting from changes in radiative forcing - past, present and future. Consideration of such thesis projects in the context of systems and processes that can deliver technological action is a valuable imperative for such work.

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