

From Respiration

A Livermore project is building on a natural catalyst to grab carbon dioxide before it hits the atmosphere.

to Carbon Capture

OUR lungs separate, capture, and transport carbon dioxide (CO₂) out of blood and other tissues as part of the normal respiration process. The catalyst that initiates this natural response in the lungs is carbonic anhydrase, the fastest operating natural enzyme known.

Other enzymes play an “energy” role in our bodies as well. For example, ribulose-1,5-bisphosphate carboxylase oxygenase, more commonly known as RuBisCO, catalyzes the first major step of carbon fixation. In that process, molecules of atmospheric CO₂ are made available to organisms in the form of energy-rich molecules such as glucose. Methane monooxygenase, or MMO, oxidizes the carbon-hydrogen bond in methane.

Medical researchers have used these enzymes as guides for designing synthetic catalysts that speed up chemical reactions. Now, a collaboration led by Lawrence Livermore is examining carbonic anhydrase as the basis for a new molecule that does for coal-fired power plants what the enzyme does for our bodies: quickly separate CO₂. But instead of transporting it out of blood or tissue, the catalyst will remove the greenhouse gas before a power plant emits it to the atmosphere. (See box on p. 7.)

“Developing a synthetic molecule to replace CO₂ scrubbing processes that use amines could greatly speed up carbon capture,” says geochemist Roger Aines, the principal investigator for the catalyst project. “Current analysis indicates that

efficient catalysts might increase the capture rate for CO₂ separation by as much as 1,000 times.”

It Takes a Team

In 2010, the collaboration, which involves researchers from Lawrence Livermore, Babcock & Wilcox Company, and the University of Illinois, received funding from the Department of Energy’s Advanced Research Projects Agency–Energy (ARPA-E). The team’s goal is to develop robust, small-molecule catalysts that mimic the behavior of carbonic anhydrase and can be adapted to capture CO₂ from power-plant emissions.

Each institution brings different expertise to the three-year project.

Computational biologists and synthetic chemists in Livermore's Physical and Life Sciences Directorate are working with the Laboratory's powerful supercomputers to computationally design hundreds of molecular compounds and synthesize the most-promising candidates for laboratory testing. Babcock & Wilcox's Power Generation Group, a leading supplier of steam-generation and environmental equipment for the electric utility market, will provide benchtop and full-scale testing and process modeling to determine which molecules can be implemented in existing and new processes. The University of Illinois will design and fabricate specific applications for the catalysts selected.

Before the ARPA-E project began, Livermore was already working on methods to design and synthesize such a catalyst through Laboratory Directed Research and Development funding. Results from this early effort showed that key technologies must be improved for global air-capture systems to be feasible. In particular, researchers must speed up the

chemistry of the CO₂ removal process to keep the capture device to a manageable size. If a new molecule is tough enough, it might also enable the direct capture of CO₂ from such emission sources as airplanes and home heating systems.

Supercomputers Aid the First Steps

Experiments by others show that adding a carbonic anhydrase enzyme to CO₂ interactions dramatically enhances the kinetics of carbon capture. In the ARPA-E project, researchers want to modify the enzyme, making it less chemically complex than the native protein and better able to withstand the high pressures and temperatures of the flue gas from a coal-fired power plant.

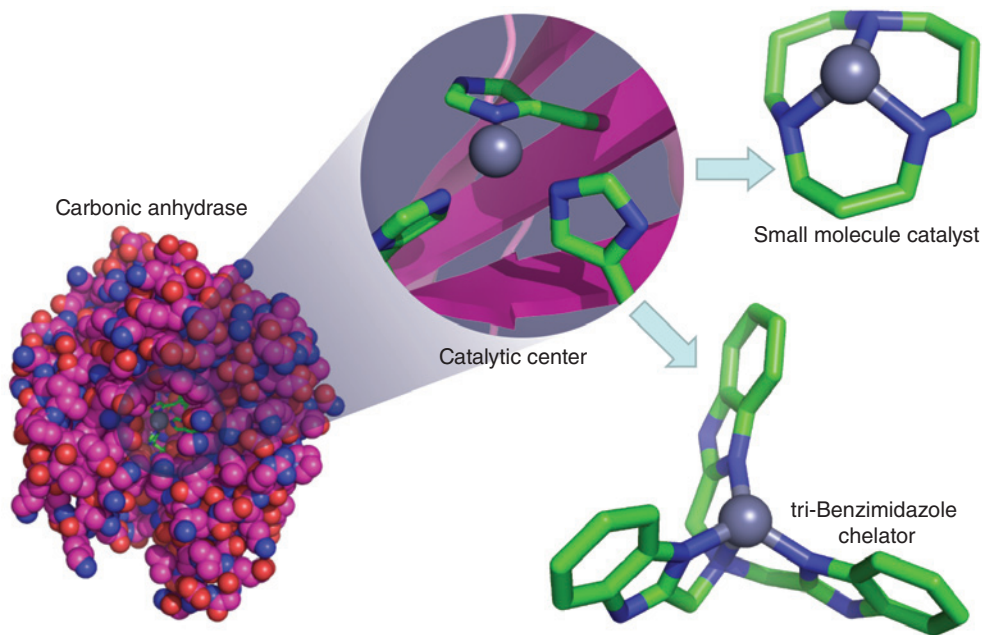
Felice Lightstone, a computational biologist at Livermore, is leading the initial effort to evaluate potential candidates. "We are developing a computational library of molecules, all of which are designed to protect the zinc ion that activates the catalyst," says Lightstone. "Using quantum molecular

calculations, we can experiment with different configurations, placing nitrogen atoms at various angles and distances from the zinc. The idea is to build scaffold structures that protect the metallic ion in a power plant's harsh operating environment and optimize the molecule for capturing CO₂." The computational team, which includes Sergio Wong, Lawrence Fellow Yosuke Kanai, and Donghwa Lee, also examined cobalt as a replacement for zinc but found it to be less effective in many configurations.

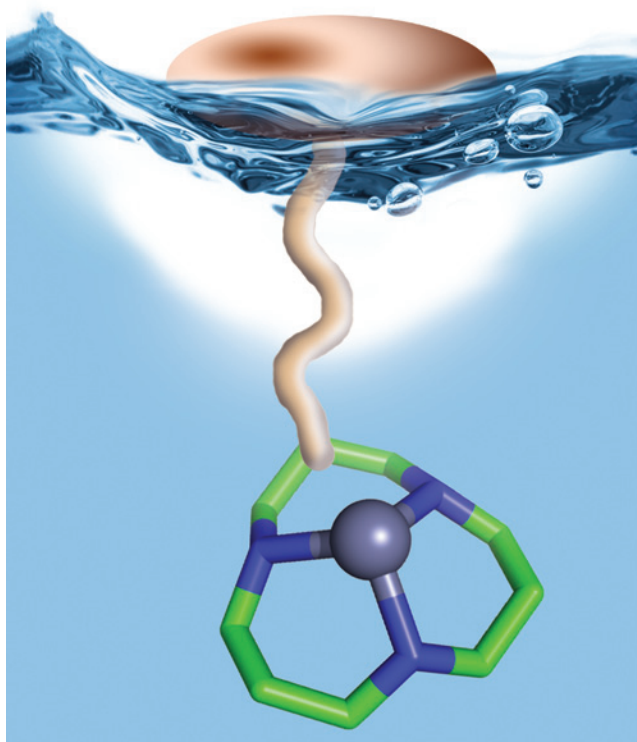
Quantum molecular calculations can predict activity at the electronic scale—a dimension comparable to about 1/50,000 of a slice of human hair—allowing scientists to examine processes occurring at dimensions that experiments often cannot create. Kanai and Lee are applying density functional theory (DFT) to model the atomic motion and complex dynamics of each candidate's material interactions. DFT starts from first principles. That is, it uses the laws of quantum mechanics without any ad hoc assumptions to describe the electronic density of a molecular or condensed system.

Kanai notes, however, that at the scale of molecular vibrations, chemical reactions are rare events. A simple application of first-principles molecular-dynamics simulations does not allow researchers to investigate reaction kinetics, which largely determine catalytic reactivity. "To address this challenge, we interface DFT with other computational tools such as the 'nudged elastic band' and 'string' methods to locate the reaction coordinates and obtain the reaction barrier."

The ARPA-E team is examining two possible molecular designs. One is a relatively simple dissolved catalyst system that could be applied immediately in industrial practice. This technology, known as regenerable solvent absorption technology, or RAST, is being developed largely by Babcock & Wilcox. The second, a Livermore design, is a "tethered" molecule that holds the catalyst at the air-liquid interface where the CO₂



Chemical scaffolds are designed to protect the zinc ion in carbonic anhydrase, which is critical for capturing carbon dioxide (CO₂).



"Tethered" molecules, such as the model shown at left, will cling to the gas–water interface much as mosquito larvae (above) hang from the surface of still water. (Photo courtesy of James Gathany, Centers for Disease Control and Prevention.)

transfer typically takes place. The tethered molecule looks much like mosquito larvae floating just below the surface of water. This approach promises very high efficiency, but using it in power plants may require changes in industrial practices.

Challenges to Overcome

Several challenges remain to make the synthetic catalysts suitable for a commercial CO₂ capture process. First, the molecular scaffolding must be structurally stable to preserve the metal ion in the catalytic pocket under high temperatures and pressures.

Addressing structural robustness and fast catalytic rates would normally be a slow, expensive process. Because of Livermore's computational and synthetic chemistry capabilities, the ARPA-E team can quickly evaluate hundreds of candidate compounds computationally, synthesize dozens, and test the most promising ones in the laboratory. Aines estimates that in just two years, the team will be ready to conduct long-term stability experiments

Keeping Carbon Dioxide Out of the Atmosphere

About 50 percent of electricity consumed in the U.S. comes from coal-fired power plants. In 2006, these plants accounted for 83 percent of the carbon dioxide (CO₂) emitted during the process of electricity generation. Capturing CO₂ before it enters the atmosphere could have enormous environmental benefits, yet to date, no CO₂-capture technology has advanced to the demonstration phase. The costs for the postcombustion process are still very high at about \$60 per ton of CO₂, and precombustion capture technology has stalled because of increasing capital costs to retrofit or redesign power plants.

The current method for CO₂ removal involves scrubbing the flue gas with amines, or nitrogen compounds, but this process uses copious quantities of water to heat and cool the gas. The energy required to strip CO₂ from the amine solvent is as much as 2.1 billion British thermal units per hour (or more than 0.6 gigawatts). "Considering additional equipment such as pumps, fans, and heat, we estimate that an optimal scrubbing system consumes 15 percent of the energy produced by the power plant," says Livermore geochemist Roger Aines.

And coal-fired power plants are just one of many facilities that emit CO₂ to the atmosphere. Natural gas plants, refineries, steel mills, cement plants, even home heating appliances produce this greenhouse gas. Substantially increasing the rate of CO₂ separation would reduce the size and cost of industrial processes designed to reduce CO₂ emissions.

For years, researchers have considered adapting the natural CO₂ lung catalyst carbonic anhydrase to capture carbon emitted in industrial operations. "An effective catalyst would make the separation process much more efficient," says Aines, "although at this point we can't project how much energy could be saved." The limiting factor with carbonic anhydrase is the difficulty of maintaining a viable enzyme in the intense conditions of industrial processes. Because hot, high-pH flue gas quickly degrades the molecule, modifying the catalyst to make it more robust is essential.

Livermore chemist Carlos Valdez synthesizes molecules based on the elemental structures proposed by the computational team. Thus far, only a few have offered the structural stability and ease of construction that would make them candidates for CO₂ capture.



on candidate molecules in large-scale testing facilities.

In addition, catalysts for the tethered molecule design must remain within about 100 micrometers of the gas–water interface, where they are most effective. If the catalyst is distributed throughout the solvent, more of it must be produced overall. The team is investigating an approach that adds a hydrophobic molecule to tether the molecule at the gas–water interface. Livermore’s preliminary calculations show that such tethers do not deform the catalyst and should preserve full functionality. Another design possibility uses very small particles containing the catalyst on their surface. These particles move with the solvent and can be easily extracted before thermal desorption.

As candidate molecules move closer to commercialization, team members at Livermore and Babcock & Wilcox will work together to balance the cost of

catalyst production with the molecule’s expected lifetime. “For now, we are estimating that a catalyst will live at least a few days, possibly longer,” says Aines. “Surviving the high temperature is the greatest challenge in designing an effective catalyst and will be the limiting factor with this technology.”

Molecules Made to Order

Synthetic chemist Carlos Valdez notes that the desired catalyst must be easily assembled in a concise operation. A reaction scheme should involve two to five steps to keep costs down and facilitate commercialization. The catalyst’s structure must also be amenable to further chemical enhancement so that properties such as solubility, thermal stability, surface attachment, and efficiency can be improved when necessary.

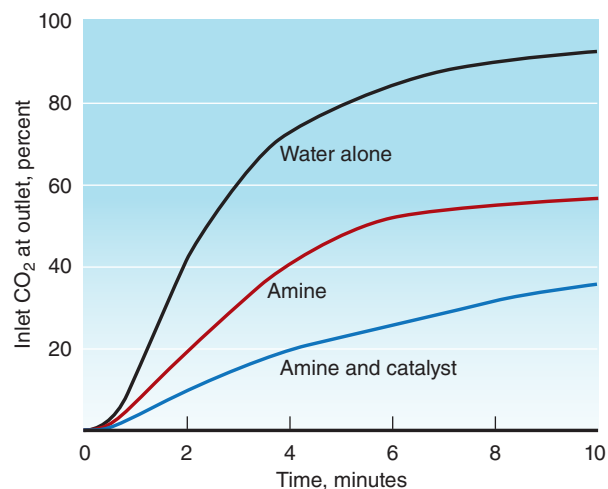
For this project, Valdez is applying what he learned during his postdoctoral

research at the Scripps Research Institute under K. Barry Sharpless, who in 2001 won the Nobel Prize in Chemistry. Sharpless is the father of “click chemistry,” a process designed to speed up drug discoveries by building chemical libraries and rapidly screening them for molecules with a desired activity. Click chemistry changed the search for effective drug formulas from a needle-in-a-haystack operation, in which numerous attempts led to only a few successes, into a winnowing process that more quickly identifies a successful candidate.

The ARPA-E researchers want to achieve a similar advance with their combinatorial approach. Their goal is to ensure that each reaction in the multistep synthesis process is fast, efficient, and highly predictable. “The computational aspect of the project involves arbitrarily shuffling and arranging atoms around the metal center,” says Valdez. “For the



Chemists Roger Krueger (left) and Sarah Baker operate the wetted wall apparatus. This Livermore-designed test device measures the combined rates of all chemical and mass-transfer processes, including the concentration of CO₂ being vented.



Initial experiments indicate that adding the carbonic anhydrase enzyme would dramatically reduce the amount of CO₂ emitted during the combustion process compared with the amount captured using scrubbing processes that use only amine or water.

synthetic chemistry phase, I use an array of scaffolds that have been developed without regard for their linkage stability or synthetic tractability.”

Combinations that are not stable or would require an extensive construction process are eliminated from the list of candidates for synthesis. Only about 2 percent of the computationally derived scaffolds have made it to the synthesis stage, which is currently under way.

Synthesized molecules go through two tests, run by Livermore chemist Sarah Baker, to evaluate how well the candidates actually work. In the first test, a stopped-flow spectrophotometer determines a candidate’s absolute hydration kinetics and stability. The spectrophotometer heats the dissolved catalyst to 80°C and mixes it with CO₂ gas in less than 500 microseconds. The color of the resulting solution indicates the rate of CO₂ capture. In the second test, a wetted wall apparatus built at

Livermore measures the combined rates of all chemical and mass-transfer processes, including the concentration of CO₂ emitted by the operation.

The Process Continues

The feedback loop is constant. If a candidate cannot be synthesized, the computational team will take another look at its molecular structure. If laboratory tests are unsuccessful, similar analysis may reveal the problem. “We currently have a ‘map’ showing the expected performance of hundreds of structures based on each one’s bond length and angle around the zinc atom,” says Aines. “We’ve also synthesized 16 candidates, including 6 molecules previously identified.”

Even when combinations of bond length and angles cannot be synthesized, computational methods such as click chemistry allow the team to consider options more quickly. “We originally

thought we could synthesize five new molecules a year,” says Aines. “By combining advanced computation and experimental tools, we now expect to test up to 20 specific examples a year. The synergy exhibited in our team’s multidisciplinary approach is critical to our success.”

Aines notes that one day, the technology could be fast enough to remove CO₂ directly from the atmosphere. Until then, researchers will focus on capturing this greenhouse gas at the source—removing it from the numerous industrial processes we rely on every day.

—Katie Walter

Key Words: carbon capture, carbon dioxide (CO₂), carbonic anhydrase, density functional theory (DFT), greenhouse gas.

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