centrates the cells and less space is needed for methane conversion, Peot says. "Without that [amount of savings] we would not have been able to afford the digesters," he says.

Waste streamlined

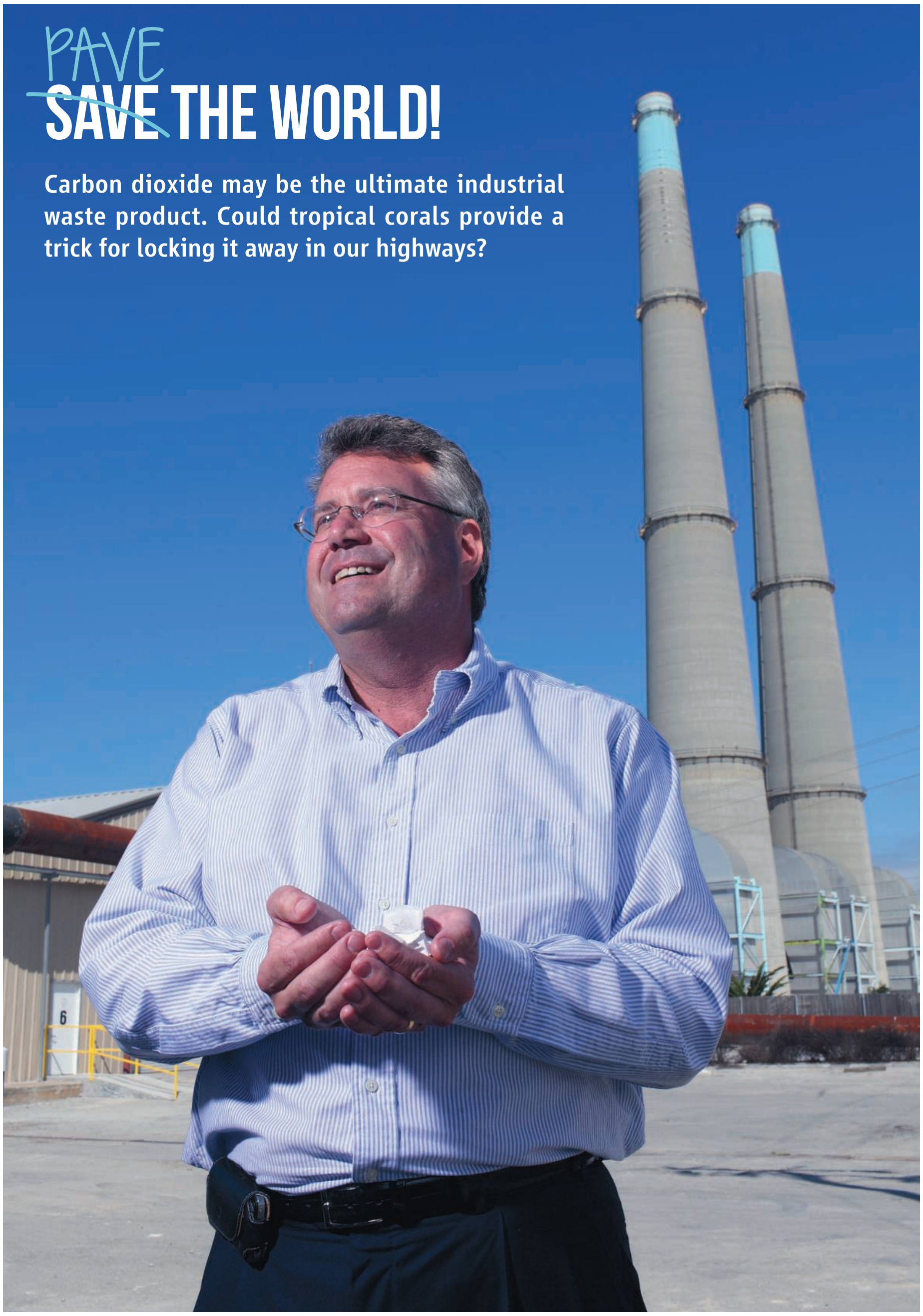
A second Blue Plains project, being undertaken in conjunction with two other treatment plants in Austria and Virginia, is coming up with a better way to remove nitrogen compounds from wastewater. Ironically, part of the nitrogen problem is created by the methane-producing digesters; the microbes release a lot of ammonia into the wastewater stream. At first, Peot and his colleagues considered taking that water and putting it through the entire treatment process again to remove the ammonia. But that multistep process, which involves aerobic bacteria and methanol, is costly, in part because sustaining the bacteria requires aerating, or adding oxygen, to the water, which accounts for almost one-quarter of the Blue Plains plant's power use. The process also yields carbon dioxide, increasing the plant's carbon footprint.

Instead, they decided to use an increasingly popular bacterial process, called anammox or deammonification, to get rid of the nitrogen compounds (*Science*, 7 May 2010, p. 702). To start with, Blue Plains will use anammox on only the ammonia-rich water coming out of the digesters. But if the process works as advertised, Peot envisions using it for the entire waste stream. And "if we are successful," he says, Blue Plains will cut its power use for aeration by two-thirds and, together with other energy-saving measures, almost get by on just the power generated using its own methane. "Our goal is to investigate ways to become energy neutral or even energy positive," he says.

Other plants are finding that reaching that goal is possible. In 2004, for example, anammox combined with other measures enabled a plant in Strass, Austria, to become energy self-sufficient. A similar multifaceted approach is enabling the East Bay Municipal Utility District, which serves part of the greater San Francisco area in California, to use various types of organic waste, including chicken blood and cheese waste, to generate enough power to run its treatment process as well as 13,000 homes. As the East Bay's director of wastewater, David Williams, puts it, "We've turned wastes into commodities." It's an achievement Blue Plains and other waste-treatment plants hope to emulate. **–ELIZABETH PENNISI**

~~SAVE~~ PAVE THE WORLD!

Carbon dioxide may be the ultimate industrial waste product. Could tropical corals provide a trick for locking it away in our highways?



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Researchers who think about how best to stave off the worst impacts of climate change often have their favorite way of disposing of one prominent industrial waste product: carbon dioxide (CO_2). Some urge planting trees to soak up the greenhouse gas; others say capture it and pump it underground. For Brent Constantz, the solution is pavement, and lots of it.

Drawing on the chemistry that corals use to build their rock-hard shells, the California entrepreneur and biomineralization expert hopes to combine simple seawater with CO_2 to manufacture cement and concrete that would devour vast amounts of the greenhouse gas. "I honestly don't think we can address the carbon problem any other way," says Constantz, a consulting associate professor at Stanford University in Palo Alto, California.

It's an audacious idea he's already tried to commercialize once—with mixed results and plenty of criticism. And his peers are divided on the prospects for seawater cement. "Brent has been too optimistic about these kinds of processes in the past and too glib about the challenges," says Roger

Concrete plans. Brent Constantz hopes to use advances in biotechnology to make cement the way coral do and in the process lock up billions of tons of CO_2 before it can reach the atmosphere.

Aines, a geochemist at Lawrence Livermore National Laboratory in California. But Constantz is "a brilliant man" with "a very interesting idea," says Barry Blackwell, president and CEO of Akermin, a start-up in St. Louis, Missouri, that also works with CO_2.

Abundant waste

There is certainly plenty of work needed to deal with humanity's most abundant waste product. In simple numbers, burning fossil fuels generates nearly 35 billion metric tons of CO_2 per year. Roughly 40% of that CO_2 comes from some 5000 power plants that burn coal and natural gas to produce electricity.

The likely impact of that waste is well known. Since 1750, the amount of CO_2 in the atmosphere has risen from 280 to nearly 400 parts per million (ppm) today. By 2100 it's expected to reach 500 to 1000 ppm, depending on progress in cutting emissions. That's expected to lock in a global average temperature increase of up to 5.2°C, trigger sea-level rise, and boost ocean acidity by as much as 150%.

The world won't have a prayer of limiting the CO_2 buildup unless nations find ways to either prevent or lock up billions of tons of CO_2 emissions per year. Constantz, for one, doesn't see many ways to prevent emissions quickly at that large of a scale. Although he says it is critical to improve energy efficiency and develop low-carbon energy sources—such as wind and solar—he doesn't think that will be enough. And he believes that carbon capture and storage technologies—separating carbon dioxide from industrial emissions, liquefying it, and injecting it underground—will be too costly to be widely adopted.

If researchers can develop a valuable product that gobbles up CO_2 during manufacture, however, that would dramatically lower the cost barrier to megascale carbon capture, he says. And for Constantz, the most obvious candidates are cement, concrete, and the mix of sand and gravel known as aggregate, all of which are used to build infrastructure, from bridges to buildings. The world today produces some 2.5 billion tons of Portland cement annually, for example, as well as 12.5 billion tons of concrete and 32 billion tons of aggregate. Using those mountains of material to trap carbon is "a properly scaled solution to the problem," Constantz says.

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Copycat. Marine corals, such as this reef in the North Pacific, inspired the idea for seawater cement.

To achieve that solution, however, Constantz needs to turn the current concretemaking process upside-down. Today, manufacturing the materials actually produces—rather than traps—huge quantities of CO_2. Making a ton of concrete, for example, generates a ton of CO_2. Overall, in fact, concrete production accounts for about 5% of all carbon emissions globally.

Tropical inspiration

Constantz, 53, says the idea of transforming concrete from a carbon source into a carbon sink came from his early academic work studying how tropical corals make their shells. But he quickly turned to the corporate world. When he was 27, he used his experience studying marine calcification to come up with and commercialize a novel cement that revolutionized the repair of bone fractures in hospitals around the globe. In 2002, he revised his recipes to develop a stronger and faster-setting cement. He now holds nearly 100 patents in cement-making technology.

As he mixed his boutique medical cements, however, Constantz began to wonder whether it might be possible to turn waste CO_2 into the minerals that form the basis of structural cement and concrete. In principle, the idea is straightforward. When dissolved in water, CO_2 reacts with water to make bicarbonate ions, which under the right circumstances are transformed into carbonate ions. When carbonate meets up with calcium and magnesium ions present in seawater, they readily combine to form calcium and magnesium carbonates; those form the same minerals used by many marine organisms to build their shells, as well as what is found in standard industrial Portland cement.

In 2007, Constantz got the chance to turn his idea into a company called Calera. Backed by Khosla Ventures, a Silicon Valley venture-capital firm, it raised $182 million to build a pilot cement plant next to a power station in Moss Landing, on the California coast. A pipe from the plant carried CO_2-rich flue gas into the base of a 33.5-meter-high tower. The gas then streamed up through the tower, where it met droplets of seawater raining down. Calcium and magnesium carbonates formed as the gas and water collided and then sifted down in a fine white powder that was dried and used to make cement. Instead of producing CO_2, however, the company said the process actually sequestered one-half ton of CO_2 per ton of concrete. The upshot, they argued, was that humanity could solve its CO_2 problem by using seawater cement to build more roads and buildings.

Outsiders, however, were far from convinced. Some critics argued that the company was too secretive about its process, and that something else must be going on for the chemistry to work. One outspoken critic was Ken Caldeira, a climate scientist at the Carnegie Institution for Science at Stanford University. Caldeira argued that getting calcium and magnesium ions to bind with CO_2 to precipitate out of water isn't easy. That's because carbonate ions are stable in water only if the pH is above 9.5 (far more alkaline than the 8.1 pH value of seawater). In natural seawater, the lower pH causes carbonate ions to pick up an extra H+ to become bicarbonate. Many shell-building organisms get around this by creating microenvironments with high pH to precipitate out their needed minerals.

Caldeira was right. It turned out Calera engineers were adding sodium hydroxide or other strong bases to their seawater to make

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it more alkaline, driving the pH as high as 12 or 13. The higher pH allows more CO_2 to dissolve into the water and then speeds the precipitation of calcium and magnesium carbonates. The problem is that alkalinity isn't free. And although the Moss Landing site had a ready source of alkalinity—piles of magnesium hydroxide left over from the plant's former life of making metal for World War II bombs—most power plants do not (although Constantz estimates that 10% of coal and natural gas power plants worldwide are located next to plentiful sources of alkalinity).

In the end, despite early demonstration successes, Calera's cementmaking process turned out to be too expensive to be broadly applicable. And last year, the company replaced Constantz as president, shifting its focus to using the process to make other, higher-value chemicals. "That's not why I founded Calera," Constantz says of the specialty chemicals business. "I founded it to sequester gigaton levels of CO_2."

A second try

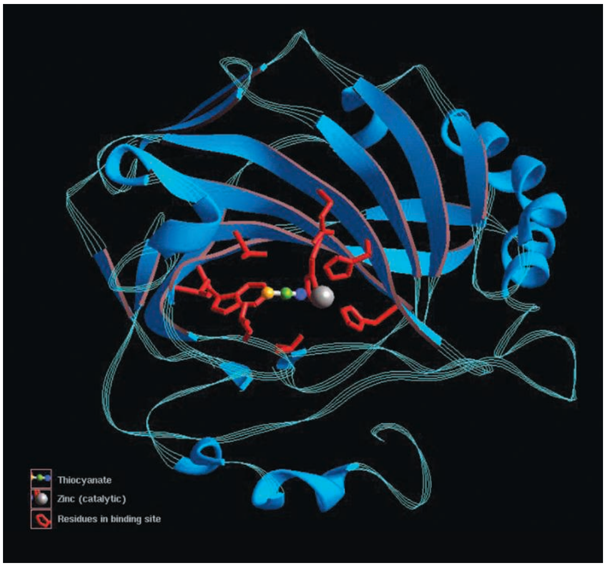
Now, Constantz is back at Stanford University, working on what he calls his generation-2 approach. Like the earlier effort, Constantz envisions bubbling CO_2 into seawater to bind it into solid minerals. But this time he hopes to run the process with a gentler and, he hopes, cheaper chemistry.

The key, Constantz now believes, is carbonic anhydrase (CA), an enzyme that whisks CO_2 out of our blood and into our lungs to be exhaled. Corals use their own version of CA to pull CO_2 out of seawater to build their shells. This process happens slowly without the enzyme. But CA speeds it up as much as 1 million–fold. And speed is the key for industrial reactions. A fast reaction, for instance, could dramatically reduce the size of the tower used to mix water and CO_2. Instead of a 33.5-meter tower, for example, the process might need one just 3.5 meters high. That, Constantz hopes, will significantly reduce the capital costs of setting up seawater cement plants.

Speeding up the reaction might also help reduce the need to add so much alkalinity. Even at a pH of 9.5 without CA, few bicarbonate ions turn into carbonate and become available to bind with calcium and magnesium to form calcium and magnesium carbonates. That's why Calera was forced to add powerful bases, to pump the pH up above 12 and accelerate the reaction. The addition of CA could change all that.

Most CAs have a zinc atom at their core surrounded by four amino acids called histidines. The histidines help zinc bind to a water molecule. Once it does, the protein's core essentially splits water (H_2O) into a hydroxyl group (OH–) and a proton (H+). The hydroxyl quickly binds with CO_2, forming bicarbonate (HCO_3–), and the H+ floats off into solution. The fastest CAs can perform this little molecular dance 1 million times a second, fast enough to turn lots of CO_2 into bicarbonate, which then goes on to form carbonate if the pH is 9.5 or higher.

But there's a catch. "For this reaction to continue, you need to maintain this pH," says Alex Zaks, a biochemist and Akermin's chief technology officer. But if H+ ions continue to stream into the seawater, they will steadily drive down the pH, increasing the water's acidity (pH is the measure of available H+ ions in solution). And if the pH drops too low, only bicarbonate will be stable in solution, not carbonate. That means even with CA, engineers will still have to add chemical bases continually. But Constantz says he's hopeful that CA will enable them to use less strong, and less expensive, bases such as coal ash, a waste product from coal-fired electric plants. "The logic does make sense," Zaks says. However, until he sees a working demonstration plant and the numbers to go with it, he's remaining noncommittal.



Take two. By adding the protein carbonic anhydrase, researchers hope to make seawater cement more affordable.

Constantz and others will also need to make other improvements to CA to enable it to work in an industrial setting. For starters, CAs are fragile proteins that fall apart in hours to days at about 40°C, well below the temperature of a normal power plant flue gas. Some companies have already taken steps to make them hardier. Researchers at Akermin, for example, have shown that by encapsulating a CA variant in a CO_2-permeable polymer, they can keep their enzyme stable and highly active for at least 90 days even above 40°C. Aines and his colleagues, meanwhile, reported online 6 June in *Inorganic Chemistry* that they've made a synthetic CA mimic that withstands temperatures up to 100°C. Although the catalytic activity of the mimic is more than 10-fold slower than natural CA, Aines says his team is now working on versions that are faster. Finally, Codexis, a Redwood City, California–based company, reported last month that one of their engineered CAs remained stable during a field test at a coal plant in which temperatures reached as high as 82°C.

Other companies are also exploring CA to make seawater cement. Last year, for example, Quebec City, Canada–based CO_2 Solutions teamed up with Codexis and aluminum maker Alcoa to pursue a similar strategy. However, last month the companies announced that they put their pilot project on hold because they couldn't meet their timeline from the U.S. Department of Energy, which was funding much of the work.

That means, for now, most companies working on CA are looking at using it to develop a cheaper method of purifying CO_2 from flue gases. Their hope is either to pump the purified CO_2 into old oil wells to push out additional oil, or to feed it to algae to produce plant oils that can be converted into transportation fuel.

Such work underscores that Constantz is not alone in his hope to use CA to convert billions of tons a year of CO_2 waste into something valuable. And for now, Constantz's dream of using CA to pave his way to saving the world remains just that. But geologist Gordon Brown, a Stanford colleague, says people would be premature to dismiss Constantz. "He's often prescient and sees things before others do," he says. And anyone hoping to curb climate change is probably hoping Constantz's dream comes true.

–ROBERT F. SERVICE

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