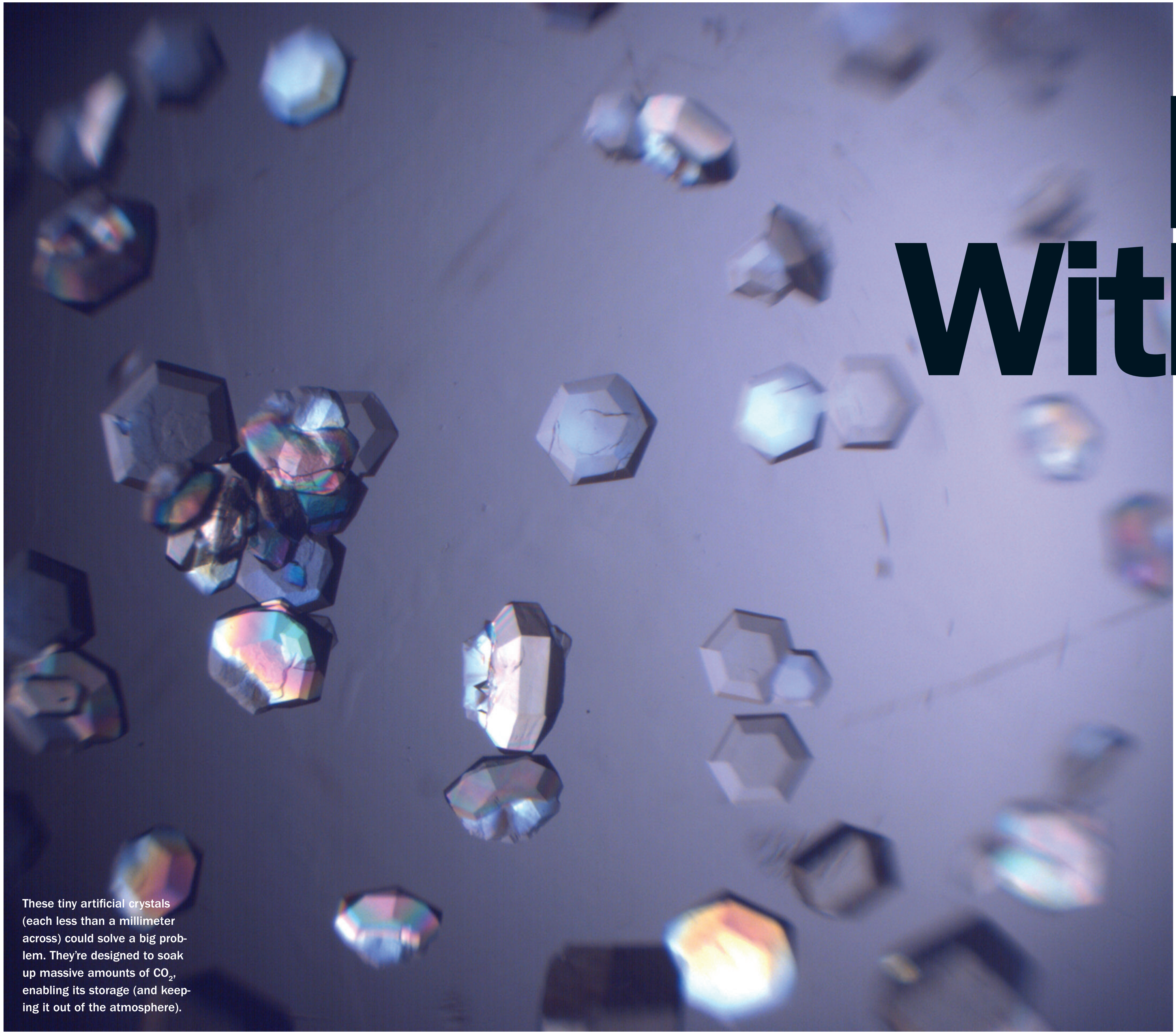

These tiny artificial crystals (each less than a millimeter across) could solve a big problem. They're designed to soak up massive amounts of CO_2, enabling its storage (and keeping it out of the atmosphere).

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Down With Carbon

Scientists work to put the greenhouse gas in its place

BY SID PERKINS

ONE MORNING EACH WEEK, a scientist takes a stroll on the barren upper slopes of Hawaii's Mauna Loa volcano, a basketball-sized glass sphere in hand. At some point, the researcher faces the wind, takes a deep breath, holds it and strides forward while twisting open a stopcock. With a whoosh lasting no more than a few seconds, 5 liters of the most pristine air on the planet replaces the vacuum inside the thick-walled orb.

Once every couple of weeks, a parka-clad researcher at the South Pole conducts the same ritual. At these remote sites and dozens of others, instruments also sniff the air, adding measurements of atmospheric chemistry to a dataset that stretches back more than 50 years. The nearly continuous record results from one of the longest-running, most comprehensive earth science experiments in history, says Ralph F. Keeling, a climate scientist at Scripps Institution of Oceanography in La Jolla, Calif. He carries on the effort his father, Charles Keeling, began as a graduate student in the 1950s.

Several trends pop out of the data, says Ralph Keeling. First, in the Northern Hemisphere the atmospheric concentration of carbon dioxide rises and falls about 7 parts per million over the course of a year. The concentration typically reaches a peak each May, then starts to drop as the hemisphere's flush of new plant growth converts the gas into sprouts, vegetation and wood. In October, the decomposition of newly fallen leaves again boosts CO_2 levels. Populations of algae at the base of the ocean's food chain follow the same trend, waxing each spring and waning each autumn.

A second trend is that each year's 7-ppm, saw-tooth variation in CO_2 is superimposed on an average concentration that is steadily rising. Today's average is more than 380 ppm, compared with 315 ppm 50 years ago. And it's still rising, about 2 ppm each year, mainly from burning fossil fuels.

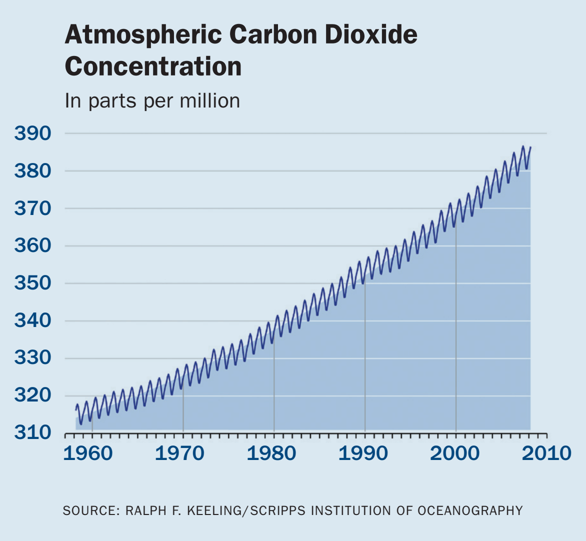
Largely because CO_2 traps heat, Earth's average temperature has climbed about 0.74 degrees Celsius over the past century (*SN: 2/10/07, p. 83*), a trend that scientists expect will accelerate. In the next 20 years, the average global temperature is projected to rise another 0.4 degrees C.

Squelching additional temperature increases depends on limiting, if not eliminating, the rise in CO_2 levels, many scientists say. And, Keeling says, "It's clear that if we want to stabilize CO_2 concentrations in the atmosphere, we need to stop the rise in fossil fuel emissions."

But halting the increase in amounts of CO_2 in the air doesn't necessarily mean doing away with fossil fuels. Many experts suggest that capturing CO_2 emissions, rather than only reducing them, could ultimately provide climate relief.

Possible solutions range from boosting natural forms of carbon capture and storage, or sequestration — fertilizing the oceans to enhance algal blooms, say, or somehow augmenting the soil's ability to hold organic matter — to schemes for snatching CO_2 from smokestacks and disposing of it deep underground or in seafloor sediments.

Success in sequestering carbon comes down to meeting two challenges: How to remove CO_2 from the air (or prevent it from getting there in the first place) and what to do with it once it has been collected.



Atmospheric Carbon Dioxide Concentration

In parts per million

SOURCE: RALPH F. KEELING/SCRIPPS INSTITUTION OF OCEANOGRAPHY

National Oceanic and Atmospheric Administration engineer Paul Fukumura-Sawada samples air atop Hawaii's Mauna Loa.

P. SATO, MAUNA LOA OBSERVATORY, NOAA

Coal-fired power plants generate about **8 billion tons** of carbon dioxide each year.

Doing it naturally

Organisms that dominate the base of the world's food chains soak up quite a bit of CO_2 — currently about 2 percent of the atmosphere's stockpile each growing season. That gas, plus sunlight and other nutrients, is converted into carbon-rich sugars and biological tissues that nourish humans and all other animals. Unfortunately, most of that carbon makes its way back to the atmosphere rather quickly: Animals metabolize their food, breathing out CO_2. Decomposition of dead plants and animals likewise produces the greenhouse gas.

Over the long haul, though, ecosystems can sequester significant amounts of carbon. About 30 percent of the carbon in the world's soil is locked in peat lands of the Northern Hemisphere, for instance, with most of that accumulating since the end of the last ice age about 10,000 years ago (*SN: 2/10/01, p. 95*).

Recent data suggest that North American ecosystems sequester, on average, 505 million metric tons of carbon each year. Some accumulates as organic material in soil, wetlands or the carbon-rich sediments deposited in the continent's rivers and lakes. More is stored in woody plants that have invaded grasslands or trees that have taken over shrublands. Most of the sequestered carbon, about 301 million tons, is locked away in North American forests or in the wood products harvested from them, notes Anthony W. King, an ecosystem scientist at Oak Ridge National Laboratory in Tennessee. He and his colleagues reported their analysis of these carbon sinks last November in an assessment issued by a consortium of ten U.S. government agencies.

"New, vigorously growing forests are where most carbon sequestration takes place," King says.

Some researchers, including Ning Zeng, an atmospheric scientist at the University of Maryland, College Park, seek to harness the prodigious carbon-storing power of forests. Right now, forest floors worldwide are lined with coarse wood — everything from twigs and limbs shed during growth to entire fallen trees — containing about 65 billion tons of carbon, says Zeng. Left undisturbed, that material would return its carbon to the atmosphere via decomposition or wildfire. Bury that wood in an oxygen-poor environment, however, and the carbon could be locked away for centuries.

Furthermore, Zeng notes, each year the world's forests naturally produce enough coarse wood to lock away about 10 billion tons of carbon. Burying just half of that amount would significantly counteract the estimated 6.9 billion tons of carbon released into the atmosphere each year via fossil fuel emissions.

While the price tag for this technique would be relatively reasonable — photosynthesis is free, and burying the wood would cost about $14 per ton — the environmental toll could be substantial. Coarse wood collected from the average square kilometer of forest could contain about 500 tons of carbon, Zeng reported in December in San Francisco at a meeting of the American Geophysical Union. That volume of wood would fill a trench 10 meters wide, 10 meters deep and 25 meters long. To sequester 5 billion tons of carbon each year, logging crews would need to dig and fill 10 million such trenches, about one every three seconds.

"This is not an environmentally friendly method" of carbon sequestration, Zeng admits.

Life at sea

In certain parts of the oceans, especially along the western coasts of large continents, nutrient-rich waters fuel the growth of algae and other phytoplankton. Their growth pulls CO_2 from the atmosphere. Many parts of the ocean, however, lack one or more vital nutrients, particularly dissolved iron, and are therefore nearly devoid of life (*SN: 8/4/07, p. 77*).

Adding iron to the surface waters in some seas could help reduce CO_2 buildup in the atmosphere and forestall climate change, some scientists suggest. In the late 1980s, oceanographer John Martin, an early proponent of this idea, boasted: "Give me half a tanker of iron, and I'll give you the next ice age."

Or maybe not. Recent studies in the North Atlantic and North Pacific confirm that natural algal blooms can indeed sequester CO_2, but in many cases the phenomenon may be only temporary, with little if any carbon making its way into deep water or seafloor sediments (*SN: 5/19/07, p. 307*). In late 2004 and early 2005, a similar study near the Crozet Islands southeast of South Africa further demonstrated that natural algal blooms result in only modest carbon sequestration.

Peter Statham, a marine biogeochemist at the National Oceanography Centre in Southampton, England, and his colleagues installed sediment traps at a depth of 2,000 meters at several spots near the islands. South of the islands, particles drifting down through a 1-square-meter area together carry only 0.087 grams of carbon each year, the researchers estimate. North of the islands, where ocean currents have carried dissolved iron and other minerals eroded from the islands, the carbon flux to deep water is almost five times higher, Statham and his colleagues reported in Orlando, Fla., in March at the Ocean Sciences Meeting.

Many uncertainties remain about how effective any artificial attempts to boost algal growth might be, says Statham. First of all, he notes, scientists aren't sure which forms of iron are the ones that marine phytoplankton find most nutritious. And the long-term effects of adding the wrong type of iron — or maybe even the right one, he adds — could damage marine ecosystems for years. "There's a huge gap in our understanding of these phenomena," he says.

Finally, fertilizing the seas to sequester carbon, even with no bad side effects, may have little if any effect on climate. "Even in the most favorable circumstances, oceans would sequester only a small fraction of the carbon dioxide that humans are emitting," Statham argues.

Down and away

Today, coal and petroleum each account for about 40 percent of global CO_2 emissions. Of the two, however, coal poses by far the larger threat to future climate. For one thing, coal produces more CO_2 per unit of energy than any other fossil fuel — about twice that generated by burning natural gas, for example. Also, coal is abundant and therefore relatively cheap: The amount of carbon found in the world's coal reserves is about triple that locked away in petroleum and natural gas deposits.

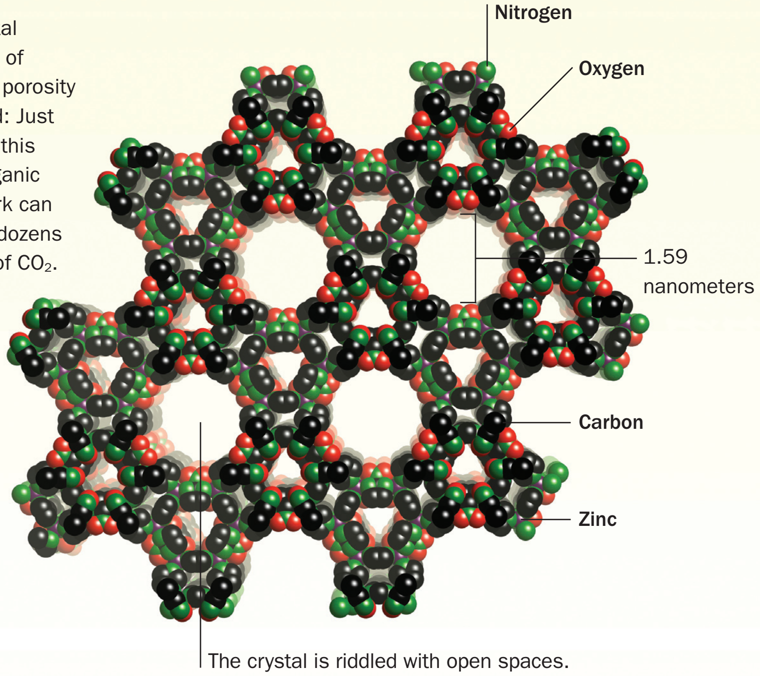
Worldwide, coal-fired power plants each year generate about 8 billion tons of CO_2, an amount that contains about 2.2 billion tons of carbon. And, says Daniel Schrag, a geochemist at Harvard University, emissions are poised to get even worse: About 150 power plants fueled by pulverized coal are now at various stages in the permitting process in the United States, and China reportedly cuts the ribbon on one such plant every week or so.

All told, the coal-fired power plants built in the next 25 years will, during their projected 50- to 60-year lifetimes, generate about 660 billion tons of CO_2, says George Peridas, an analyst with the Natural Resources Defense Council office in San Francisco. That's about 25 percent more than all the CO_2 that humans have produced by burning coal since 1751, a period that encompasses the entire Industrial Revolution.

Because coal-fired power plants are point sources of immense volumes of CO_2, they're tempting targets for sequestration efforts, says Tom Feeley, an environmental scientist at the National Energy Technology Laboratory in Pittsburgh. He and his colleagues are studying ways to capture emissions, ranging from using CO_2-hungry materials to sop

Vacancy Available

The crystal structure of ZIF-70 is porosity perfected: Just 1 liter of this metal-organic framework can soak up dozens of liters of CO_2.



The crystal is riddled with open spaces. One gram offers 1,970 square meters of surface area where CO_2 molecules can park.

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CO_2 from smokestacks to building new types of plants that burn coal altogether differently. The goal is to develop techniques for large-scale field tests by 2012 that can capture at least 90 percent of a power plant's CO_2 emissions but boost the price of its electricity by no more than 20 percent.

In current power plants, CO_2-absorbing materials would be placed in a stream of 200°C emissions, mostly nitrogen with between 3 and 15 percent CO_2. The active materials could either absorb the gas, just as a sponge sops up water, or chemically bind to it.

Materials called metal-organic frameworks (*SN: 1/7/06, p. 4*) fall into the category of CO_2 sponges. In their gaseous state, CO_2 molecules fly about at great speeds and keep a considerable distance from each other, but inside the pores of some of these crystalline sieves, the molecules line up and cram close together, says Rahul Banerjee, a chemist at the University of California, Los Angeles.

Discovering the reactions that produce a substance that effectively captures CO_2 takes time. So, Banerjee and his colleagues recently adopted a technique common in the pharmaceutical industry: They used a computer-controlled device to automatically dispense various combinations and concentrations of reactants into each of 96 tiny wells on a single plate — each well, in essence, its own 300-microliter beaker — which was then heated. The researchers then assessed the CO_2-sopping ability of the resulting crystals.

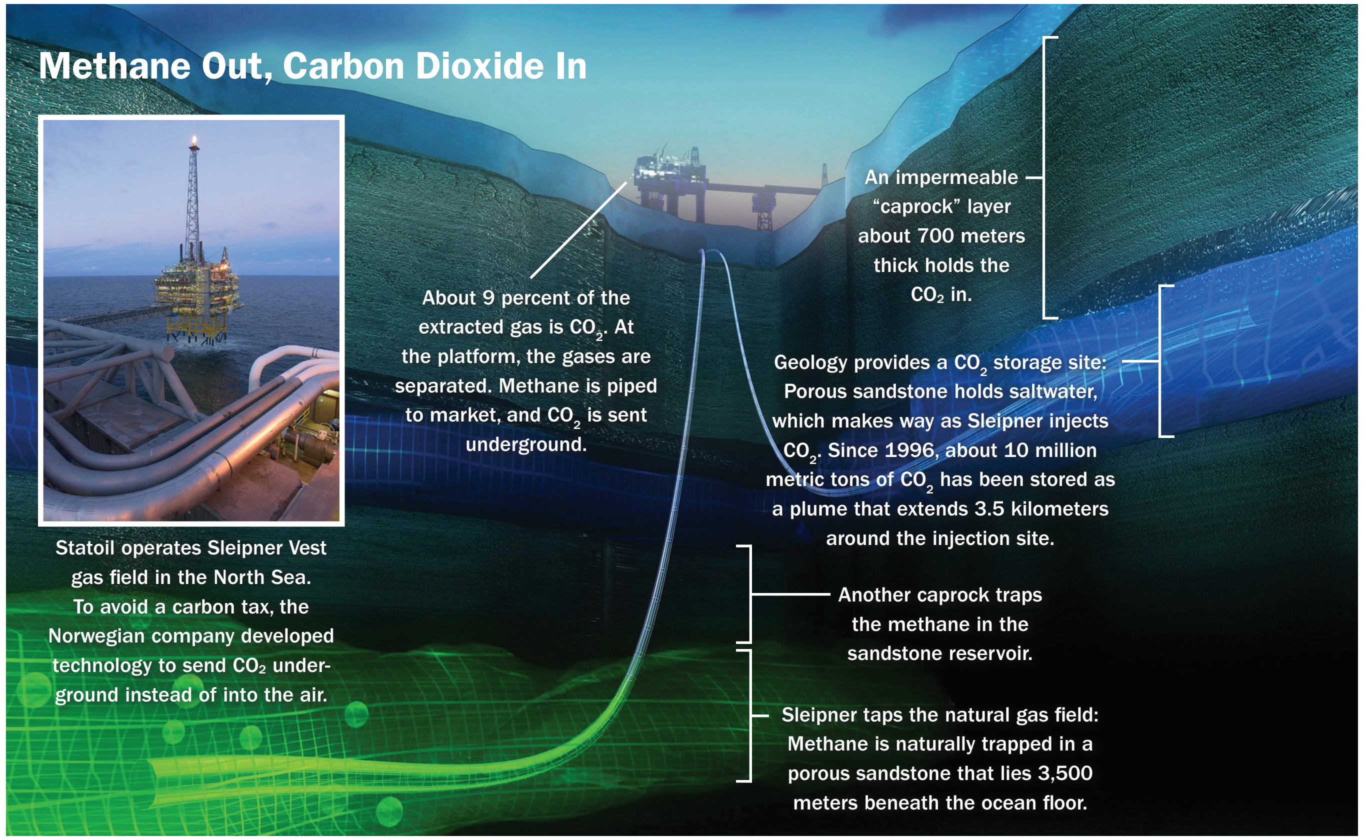
In less than three months, the researchers generated 16 new zeolites, a type of metal-organic framework composed of aluminum silicates, Banerjee and his colleagues reported in the Feb. 15 *Science*. Three of the zeolites are highly porous, with each gram of the material having a large surface area — where CO_2 molecules can attach — of between 1,000 and 2,000 square meters. A 1-liter sample of one of those supersponges, a substance dubbed ZIF-69, could hold up to 83 liters of CO_2 under normal atmospheric pressure.

Another team of scientists has produced a CO_2-absorbing substance — one that binds the gas via a chemical reaction — by painting an organic compound called aziridine on a wafer of silica. Unlike previously developed aminosilica materials, the new substance has a high storage capacity for CO_2, says Christopher W. Jones, a chemical engineer at Georgia Institute of Technology in Atlanta. The chemical reaction can be reversed by heating the CO_2-saturated material, enabling researchers to capture the gas and dispose of it. A series of lab tests indicates that the material, whose amine-rich coating is tightly bound to the silica substrate, retains its capacity to soak up CO_2 after nearly a dozen cycles, the researchers reported in the March 12 *Journal of the American Chemical Society*.

Dump sites

CAPTURING VAST AMOUNTS OF POWER plant emissions is just half the task. The next step is storage. Many scientists propose locking CO_2 underground or in the deep ocean.

Under high pressure, as in ocean depths below 500 meters, CO_2 is a dense liquid, not a gas, and doesn't mix well with water. Therefore it's possible to deep six CO_2 on the ocean floor, but many researchers have concerns about how large pools of concentrated CO_2 might affect ecosystems there (*SN: 6/19/99, p. 392*). The CO_2 might slowly dissolve into the surrounding water, creating acidic conditions.



Statoil operates Sleipner Vest gas field in the North Sea. To avoid a carbon tax, the Norwegian company developed technology to send CO_2 underground instead of into the air.

About 9 percent of the extracted gas is CO_2. At the platform, the gases are separated. Methane is piped to market, and CO_2 is sent underground.

An impermeable "caprock" layer about 700 meters thick holds the CO_2 in.

Geology provides a CO_2 storage site: Porous sandstone holds saltwater, which makes way as Sleipner injects CO_2. Since 1996, about 10 million metric tons of CO_2 has been stored as a plume that extends 3.5 kilometers around the injection site.

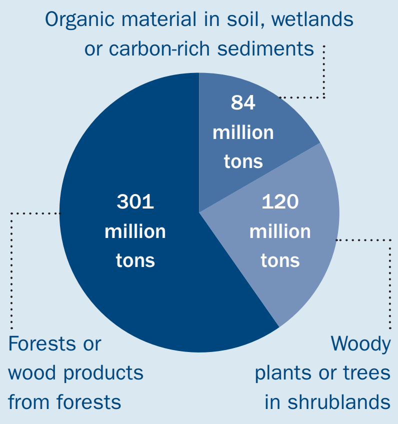
Another caprock traps the methane in the sandstone reservoir.

Sleipner taps the natural gas field: Methane is naturally trapped in a porous sandstone that lies 3,500 meters beneath the ocean floor.

GRAPHIC: ALLIGATOR FILM/BUG/STATOILHYDRO; INSET: STATOIL; INFORMATION: A. CHADWICK, BRITISH GEOLOGICAL SURVEY

From Atmosphere to Biosphere

Total carbon sequestered by North American ecosystems: 505 million metric tons of carbon each year, on average.



SOURCE: ANTHONY W. KING, OAK RIDGE NATIONAL LAB

A new and relatively simple twist on the deep-ocean technique may address many such concerns. If liquid CO_2 is blended with a mixture of seawater and pulverized limestone, the CO_2 breaks up into globules that are 200 to 500 micrometers in diameter and coated with limestone powder, says Dan Golomb, a physical chemist at the University of Massachusetts, Lowell. The resulting emulsion has a consistency between that of milk and mayonnaise. Injected into the deep sea, the limestone-veneered droplets sink about 200 meters per day, lab tests suggest. As the droplets dissolve into the surrounding water or break up as they jostle about on the seafloor, the limestone's carbonate dissolves too, buffering much of the resulting acidity, like a tiny Tums. Golomb and his colleagues described their carbon-dumping process last July in *Environmental Science & Technology*.

Immense volumes of subterranean strata are a tempting dumping ground, too. Some types of rock formations are naturally impervious to the flow of gases and liquids. In fact, some of these geological reservoirs have already proven themselves by sequestering naturally formed CO_2 for millions of years. Oil companies have been mining that CO_2, transporting it through pipelines and pumping it into the ground to enhance the recovery of petroleum from faltering oil fields for decades — an irony indeed to think that CO_2 is being pumped into the ground so that petroleum, a raw material for even more CO_2, can be extracted.

In many regions of the world, saline aquifers lie deep beneath the ground. Because that salty water isn't suitable for drinking, some of those strata, especially those sandwiched between or capped by impervious rocks, could be used to store CO_2. Scientists estimate that such reservoirs might hold hundreds of years' worth of captured emissions.

Disposal of CO_2 in ancient volcanic rocks may provide an even more secure sequestration technique. A multimillion-dollar field test soon to be under way in southeastern Washington state is designed to find out.

Lab tests suggest that liquid CO_2 will chemically react with basalt to produce various minerals, including calcium carbonate, in a matter of months, says Pete McGrail, an environmental engineer at Pacific Northwest National Laboratory in Richland, Wash. Therefore, concerns about the CO_2 escaping from its underground prison are minimized. Thick layers of basalt, the result of widespread volcanic activity in the region between 6 million and 17 million years ago, underlie the tristate area surrounding McGrail's lab. Although most think of basalt as impervious, many of these deposits are porous because they were frothy when they cooled or they cracked extensively when subsequent flows of lava heated them up or weighed them down.

Later this year, McGrail and his colleagues will inject between 1,000 and 3,000 tons of liquid CO_2 — enough, give or take, to fill an Olympic-sized swimming pool — into the porous rocks at a depth of about 1 kilometer. Then, researchers will assess the effectiveness of their sequestration by occasionally collecting fluid samples at the injection site. Analyses suggest that this volume of CO_2 will react to form carbonate minerals within five years, says McGrail.

If this sequestration technique is deemed suitable, the region's ancient basalts could hold a volume of CO_2 approaching that emitted by every coal-fired power plant in the United States over a 20- to 50-year period, McGrail and his colleagues estimate. Across the nation, deep geologic formations such as saline aquifers and coal layers could sequester 150 years' worth of worldwide power-plant emissions, possibly providing a rock-solid solution to one of the world's most pressing problems.

> One region of volcanic rock could hold as much CO_2 as every coal-fired power plant in the United States would emit over **20 to 50 years.**
>
> U.S. saline aquifers and coal layers could hold **150 years' worth** of worldwide power plant emissions.

The United States and the world need carbon sequestration—not right now, says Harvard's Schrag, but soon, and on an enormous scale. The challenge, he notes, is to ensure that carbon capture and sequestration technologies are ready when serious political action on climate change is finally taken.

And that time may be coming soon, says Oak Ridge's King. "It's beginning to dawn on people," he says, "that they can change the planet in ways larger than the planet can change itself." ■

Explore more

- "Carbon Dioxide Capture and Storage: Summary for Policymakers," IPCC Special Report, 2005. www.ipcc.ch/pdf/special-reports/srccs/srccs_summaryforpolicymakers.pdf