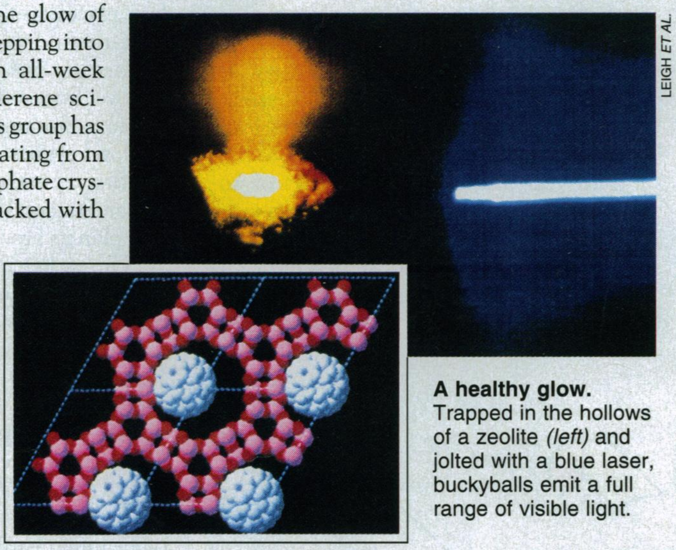
MEETING BRIEFS

Researchers Swap Material Evidence in Boston

In a mass migration of the materials research world, nearly 4000 researchers convened in Boston from 30 November through 4 December to engage in the semi-annual show-and-tell organized by the Materials Research Society (MRS). This year's meeting, with roughly 3250 technical presentations, was as big as ever. Some of the eye-catching wares in that bazaar included fullerene-packed crystals that emit light more efficiently than the tungsten filaments in incandescent lightbulbs, a possible retrotechnology transfer from ancient mining to nuclear waste disposal, and clever ways of arranging molecules in geometries that make them better at carrying electricity or harvesting solar energy.

Bottle-and-Glow Fullerenes

Fullerenes, those all-carbon molecular balls and tubes that have become a cottage industry for molecular scientists and researchers of the solid state, seem to yield surprises like a slot machine that keeps releasing unexpected surges of coins. At the MRS meeting, chemists David Leigh, Michael Anderson, and Bruce Hamilton of the University of Manchester's Institute of Science and Technology were still basking in the glow of one of the latest surprises. Stepping into a canceled time slot in an all-week symposium devoted to fullerene science, Leigh reported that his group has observed visible light emanating from a labyrinthine aluminophosphate crystal that had been loosely packed with 60-carbon buckyballs and stimulated with a laser.



LEIGH *ET AL.*

A healthy glow. Trapped in the hollows of a zeolite *(left)* and jolted with a blue laser, buckyballs emit a full range of visible light.

That glow, say Leigh and others, may point the way to new optical technologies as well as insights into the behavior of the electrons in C_{60}. And in the best buckyball tradition, the finding was serendipitous. Leigh and his colleagues were actually looking for ways to control the orientation of buckyballs so that they could do some chemistry at specific locations on the carbon ball. They tried packing buckyballs into the parallel channels of the zeolite, known as VPI-5, then studied the resulting molecular arrangement by photoluminescence: shining light of specific wavelengths onto the material and measuring the wavelengths it reemits.

When Leigh and his colleagues bathed their fullerene-packed VPI-5 in blue light from an argon laser, they expected to see slight variations on the dim infrared glow of a pure fullerene crystal. Instead, "we got a real surprise," Leigh told the meeting. "We saw a dramatic shift into the visible range of the spectrum"—strong enough to see with the naked eye. But cool, too: Unlike a lightbulb's brilliant tungsten filament, which actually emits most of the electrical energy going into it in the form of heat, the bottled buckyballs emit mostly visible light, Leigh said.

The cramped quarters of the C_{60} probably account for the luminescence, remarks organic chemist and fullerene scientist Fred Wudl of the University of California, Santa Barbara. "By putting C_{60} in [VPI-5], they improved its emission quite significantly." Why that should work, though, is "totally unclear," Leigh says. He speculates that the shift in light emission may derive from a so-called quantum confinement effect. The idea is that electrons confined in tiny spaces such as the 12.5-angstrom-wide channels of the zeolite behave differently from electrons not so confined—say, in a pure C_{60} crystal, where the electrons might hop between molecules. As a result, the quantum states of the electrons change, shifting the emissions spectrum in much the same mechanism as has been proposed for so-called porous silicon.

To R.P.H. Chang of Northwestern University's Materials Research Center, there may be a bright future in the material's technicolor glow. "If it works well, there is potential technology here," he says. That's a big if, Leigh notes; the crystals reemit at best only a hundredth of the light energy going into them from the laser, and the group has yet to show that they can emit light when pumped with electricity rather than light—a prerequisite for many technological applications. But he cautiously lists some possibilities: new kinds of lasers, optical displays, and even more far-fetched wizardry such as luminescent gels. "In theory, if you could stimulate emission with electricity [instead of light], you could prepare it as a gel, put a voltage across it, and it would glow white," Leigh muses. But he hastens to add that, even by buckyball standards, a glow-in-the-dark fullerene gel or paint is a long shot.

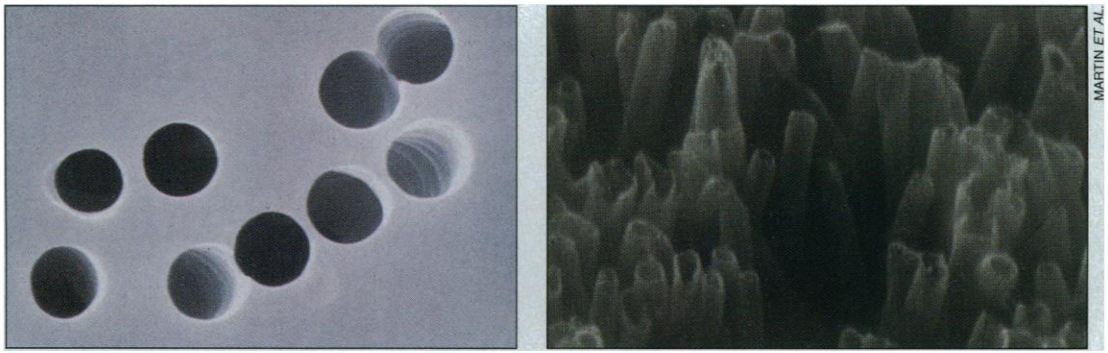
A Watertight Lesson From the Ancients?

Finding a way to contain tons of decaying nuclear waste safely for tens of thousands of years takes the materials science equivalent of a crystal ball. Advanced stainless steels, special borosilicate glasses, and a titanium-containing ceramic called synroc all remain candidates right now. But how will they fare over the millennia so that the soil and drinking water will be safe as far down the line as anyone can see? One possible answer can be found by looking 2400 years into the past, archeometallurgist Martha Goodway of the Smithsonian Institution's Conservation Analytical Laboratory told a symposium on nuclear waste containment at the MRS meeting.

Goodway's aim was to alert waste specialists to some little-known Smithsonian work, completed several years ago by a deceased colleague, on a containment material that has already withstood the test of time. Greek metallurgists of the 5th and 4th centuries BC, she said, synthesized a waterproof plaster that still does its job. "We have a material here that is proven to hold water for more than 20 centuries with absolutely no maintenance," she says. "I'd like to bring this to the attention of the nuclear waste community." And they, in turn, are welcoming this lesson from the past, which is why symposium organizers invited Goodway to speak at the meeting.

That's a remarkable twist for a material originally concocted to hold rainwater. The Greek metallurgists at lead and silver mining installations in Laurion, about 25 miles from Athens, synthesized the waterproof plaster and painted it on the network of porous cement dams, cisterns, channels, and conduits built to collect and conserve the vast amounts of water required for the mining operations. The region is arid, so seepage had to be combated—and the plaster proved so effective and durable that some of the ancient cisterns still hold water, in some cases thriving with aquatic life.

The thrifty ancients made this remarkable material from mining wastes, Goodway says. Building on preliminary analyses of the waterproof plaster done in the late 1970s by mining engineer Constantine Conophagos of the National Technical University of Athens, Goodway's Smithsonian colleague Joan Mishara, who died in 1988, did more extensive studies in the 1980s using x-ray diffraction, electron microprobe, and other analytical methods. She found that the impermeable plaster was applied in several thin layers, the underlying ones containing the mineral ganolamite. This unusual calcium lead silicate has been found to occur naturally in only two locations, New Jersey and Sweden, but is easily synthesized from a mixture of quartz, calcite, and the mineral galena, all available in abundance from the spoil of mining operations. The top coat contains another synthetic lead silicate that may also have been made from mine waste.


MARTIN *ET AL.*

Pore discipline. A polycarbonate filter with holes less than a micrometer wide *(left)* acts as a template for polypyrrole, aligning the molecules into minuscule electrically conductive tubes *(right).*

As Mishara pictured it, the raw materials were heated to high temperatures, quenched to form glassy products, and ground to a powder, which then was mixed with lime to make the water-proof plaster. Mishara never made the leap from ancient mining technology to nuclear waste disposal herself; her paper was published in 1989 in *Archeometry*, a journal virtually unknown to the nuclear waste containment crowd, Goodway points out.

Even after 2500 years, it would take a lot more testing to see whether the ancient water-proof plaster actually can inspire modern containers for liquid waste, says John Bates, a materials scientist at Argonne National Laboratory who specializes in long-term waste containment. Although he is impressed by the performance of the ancient plaster, he notes that there's a big difference between 2500 years of rainwater and 20,000 years of hot, radioactive nuclear waste. Still, he says, "historical records that provide insight into durable materials" are welcome guidance for the containment crowd as they strive to predict the future.

Molecular Crowd Control

Like good teachers, polymer scientists have always given their molecules a lot of individual attention. By altering parts of individual molecules—say, by making them longer or more rigid—a chemist might end up with a material that was more durable or stiffer than the original. But in recent years researchers have started to worry about group discipline, as well. As the presentations in an MRS symposium called Ordered Materials By Design bore witness, these researchers are trying to keep order in the molecular ranks.

They're finding, however, that it's no easier than keeping an unruly class in order. One reason: The molecules in many newly synthesized polymers tend to coil and tangle like cooked spaghetti. But there's a strong incentive to try. By controlling how a material's constituent molecules line up, polymer scientists can tailor its properties. And as several MRS reports made clear, molecular order is especially important for polymers that have attractive electrical properties, such as metal-like conductivity; electrons dashing along one polymer chain more readily hop to the next one if the molecules are aligned. That means an easier path for electric current.

Colorado State University chemist Charles R. Martin and his colleagues, for example, reported boosting the conductivity of their polymers by aligning the molecules in templates: microporous membranes similar to ones that beer makers use for filtering bacteria from their brews. When the researchers expose the membranes to a solution of the conducting polymers polypyrrole or polyaniline, the molecules settle onto the pore surfaces and aggregate into hollow microtubules or solid fibrils, depending on how long the polymerization is allowed to proceed.

The resulting molecular structure, instead of resembling coiled, cooked spaghetti, is more like the parallel strands of uncooked pasta, with the strands stacked at right angles to the pore axes. After dissolving away the surrounding membranes, the chemists harvest and pool the microtubules. Formed into sheets, the ordered polymer is 10 to 20 times more conductive than the unaligned material, Martin says.

That's one step toward what he calls "nirvana in synthetic metal research"—polymers that are as conductive as an old standard like copper. Chemist Thomas Bein of Purdue University reported another possible route to nirvana, relying on a different template. He and co-workers at Purdue University and the University of Toronto infiltrate the pores of zeolites—inorganic crystals with regular channels large enough for molecules to snuggle into—with building blocks of the conducting polymers polythiophene or polyaniline. Once inside, the building blocks link into polymeric chains oriented along the axis of the channels—what Bein and his colleagues call "molecular wires." Dissolving the zeolite with rugged agents such as hydrogen fluoride releases the zeolite-aligned polymers, which Bein says are three times more conductive than samples of unaligned polythiophene molecules.

While Bein and Martin concentrated on one-dimensional order, polymer physicist Michael Rubner of MIT and his co-workers have tried to establish a more elaborate order in their polymers—"designer surfaces," the researchers call the result. Instead of templates, Rubner and his colleagues rely on the simple fact that opposite charges attract in order to stack different, oppositely charged polymer molecules in alternating molecular layers, like a multidecker sandwich. All it takes, they say, are two $10 beakers filled with solutions of two well-chosen molecules with opposite electrical charges (for example, the conductive polymers sulfonated polyaniline and polypyridinium acetylene).

Then, by alternately dipping a glass slide or some other surface into each solution, "you can build up multilayered films of precisely controlled thickness," Rubner says. Each layer's charge makes it sticky for the next, oppositely charged layer. Moreover, by controlling the acidity, salt level, and other properties of the solutions, the researchers have found that they can dictate whether molecules newly attached to the growing stack lie flat or angle outward.

Winning that kind of control over these so-called heterostructures is the route to tailoring not only electrical properties but also optical ones, Rubner said. One long-term possibility is a heterostructure designed to harvest solar energy and channel it into electrons, in a kind of artificial photosynthesis. Before the electrons could vent their energy uselessly in the layers that spawned them, they would immediately hop to electron-accepting molecular layers above and below, where their energy could be stored like a battery. There's nothing like applying a little molecular discipline, it seems.

–Ivan Amato