Consolidating the Stone

New compounds may protect statues and buildings from weather damage

By CORINNA WU

Sometimes, even things carved in stone don't last forever. A delicate face chiseled into limestone rock slowly disintegrates into an indistinguishable blob after years of exposure to rain and sun, hot and cold. Even the grand, seemingly permanent walls of a marble building gradually turn to dust, victims of the relentless chemical attack of polluted air.

E.M. Winkler, Stone: Properties, Durability in Man's Environment

In 1908, a sandstone sculpture on Herten Castle near Recklinghausen, Germany, had eroded only slightly, leaving the features clearly visible (left). By the early 1970s, pollution had chewed away at the sculpture until it was a faceless rock (right). Although the sculpture was carved in 1702, most of its deterioration occurred after industrialization, in the mid-19th century.

Deteriorating stone sculptures and buildings are found all over the world, from churches and temples in Europe to the Maya pyramids in Mexico to the memorials in Washington, D.C. Art conservators have an obvious interest in preserving these objects, which embody decades—sometimes centuries—of history and culture. Limestone and marble are notoriously difficult materials to protect, however.

Now, scientists at Sandia National Laboratories in Albuquerque, N.M., and conservators at the Metropolitan Museum of Art in New York are using their collective expertise to tackle this problem. At first glance, Sandia, primarily a weapons laboratory, and the museum appear to be the archetypal strange bedfellows, but at a Materials Research Society (MRS) meeting a few years ago, scientists from the two institutions discovered they had a lot in common.

For many years, C. Jeffrey Brinker, a materials scientist at Sandia, had organized an MRS symposium on sol-gel processing, a method of depositing inorganic materials onto a solid surface. In solution, small building blocks of the material react with one another to form a network. When the solvent evaporates, the network remains.

"One time, we had the symposium and one fellow who came was a conservator from the Metropolitan Museum of Art," Brinker recalls. "His name was George Wheeler. He was interested in using sol-gel processing procedures to consolidate stone subjected to outdoor environments."

Much work on sol-gel chemistry involves alkoxysilanes, a class of materials that conservators since the 1920s have tried to use to strengthen and repair stone. Brinker and Wheeler decided to pool their resources and work on a method of protecting limestone and marble with alkoxysilanes.

At Sandia, it took some time for the project to come together. "I proposed this on a number of different occasions, and people laughed at me," Brinker says. About 2 years ago, a Sandia program designed to encourage basic research in unusual areas gave the project the funding it needed to get off the ground.

Although they have very different textures, limestone and marble are actually the same kind of calcium carbonate rock. Limestone is rough, and its porous surface draws in and collects water, making the rock particularly susceptible to weathering. Marble is limestone that has undergone a metamorphosis under high pressure, allowing it to take on a smooth, polished finish.

Outdoor sculptures and buildings wear via many different processes. Acid rain, which tends to plague polluted areas, eats away stone (SN: 9/7/85, p. 154). Moisture in statues can freeze and expand, weakening the rock so that chunks eventually fall off. Salt crystallization forms an unsightly crust on statues and buildings and can lead to crumbling.

The most persistent, destructive enemy of limestone and marble is a process called dry deposition, says Wheeler. Even when a statue looks dry, it may carry condensation on its surface. "Sulfur dioxide gas that's in the air interacts with stone surfaces that have a thin film of water on them," he says. The gas reacts with the calcium carbonate to form gypsum, a white, powdery mineral. Although gypsum is responsible for spectacular white sand dunes and plaster of Paris, it's the bane of a limestone statue.

Dry deposition is so insidious because it occurs continuously over long periods of time, especially during the cold hours of the night. In fact, Wheeler says, "it will occur more often and apparently more aggressively when it's not raining than when it is." A few years ago, he and his colleagues tracked condensation on the marble panels of the Lincoln Memorial in Washington, D.C. There were gypsum deposits on the inside ceiling of the structure, where no rain ever falls. "It had to have occurred by dry deposition."

Gypsum formation changes the surface of the stone, complicating efforts to find good preservation methods. "You can get white crests on the surface of the rock growing at the same time that you're dissolving [it]," says Kathryn L. Nagy, a Sandia geochemist who presented some of the project's preliminary results at the December 1996 MRS meeting in Boston. The gypsum crust also tends to accelerate absorption of the sulfur compounds, says Steven D. Leith of the University of Washington in Seattle.

Since the 1960s, art conservators have used a commercially available product to consolidate some types of stone. An alkoxysilane, this product forms a durable material that doesn't break down in sunlight, as acrylic resin glues do, Wheeler says.

Alkoxysilanes do not stick well to limestone, however. "You don't actually get any linkage between the mineral that the rock is made from and the consolidating material," Wheeler explains. Because no bond is formed, the material wears off in just a few months.

On the other hand, the product binds wonderfully to sandstone because sandstone is made of silicate materials. The atoms in the rock and in the consolidating material form chemical linkages that bridge grains of the mineral.

The research team is taking a lesson from the bonding attributes of sandstone. By looking for a molecule that will bind to calcium carbonate rock on one side and to the alkoxysilane on the other, the scientists hope to improve the alkoxysilane's properties. "What we've tried to do is come up with a mineral-specific approach to the problem," Brinker says.

The researchers wanted to conduct a rigorous approach, so they began by modeling the problem on a computer and analyzing several classes of compounds that had the appropriate dual nature. They determined how strongly the molecules would attach to a simulated limestone surface and how densely the molecules would pack together there.

With the results of the modeling in hand, the researchers chose three candidate compounds for further experiments. They coated calcium carbonate powder with the compounds alone and combined with the commercial alkoxysilane. By stirring the coated powder into a mildly acidic solution, they could measure how fast the acid dissolved the powder, Nagy says.

One particular compound, AEAPS, in combination with the alkoxysilane product slowed the dissolution rate to one-tenth that of untreated powder. "If something would take 10 years [to deteriorate] uncoated," Nagy says, "what we're suggesting is that it would take 100 years coated, based on these powder experiments." However, the powders don't accurately represent the surface of a statue or wall, so effects on limestone or marble structures may differ, she cautions.

Contrary to expectations, compounds that the modeling predicted would bind most tightly to the limestone and have the highest packing density didn't do the best job of protecting the powder from dissolution. Materials at the other end of the scale did better. The strongly bound compounds turned out to be just too strong.

"They extract the calcium right off the surface," Brinker says. "You can't just look at the overall strength of it." The researchers expect modeling to help them understand what makes some compounds bind well without yanking the calcium out of the rock.

Ideally, the bridging compound would also prevent water from penetrating the stone yet maintain its breathability, a relatively new idea in stone preservation, Wheeler says. The commercially available alkoxysilane product comes in a version that is hydrophobic, which makes the stone water-repellent, but there's disagreement among conservators as to whether a consolidating material should seal out water—because it could seal in water just as well. Moisture from the soil wicks up through statues that rest on the ground. If trapped water freezes in stone statues bound together with hydrophobic material, huge pieces could fall off.

A possible compromise would be to make the protectant repellent to liquid water but permeable to water vapor, Brinker suggests. Or it could be designed to subdivide large pores into spaces too small for ice crystals to reach the critical size needed to grow.

More testing on actual limestone rocks should help solve some of these problems. The Metropolitan Museum is providing Sandia with samples from Monk's Park in Bath, England. The researchers are coating narrow cylinders of this limestone and measuring their dissolution rate and mechanical strength.

Eric F. Hansen, a scientist at the Getty Conservation Institute in Los Angeles, would like to see the group perform tests on weathered stone. Recent studies, he says, have shown that alkoxysilanes perform much more poorly on weathered stone than on newly quarried stone. The "beautiful, golden-colored" Bath limestone, Brinker says, is "almost naturally weathered. It turns out to be quite porous and quite weak as mined."

Wheeler concurs. "The reason we use this stone is that it's terrible. It's consistently bad; it's bad in the same way all the time."


Mexico Ministry of Tourism

A limestone pyramid stands tall in the Mundo Maya Ruins in Mexico City more than 1,000 years after it was built. Art conservators are studying how to slow down the stone's deterioration.

When it comes to deterioration of outdoor statues, there currently is no good preventive medicine. Conservators don't recommend putting a protective coating on new ones, Wheeler says. "That question always comes up. 'I'm putting out my new piece of sculpture, should I squirt some stuff on?' Usually we say no."

The products available today last only a few months on limestone and could compromise the appearance of a marble piece, he says. "You don't want to have that shiny surface coating."

Wheeler sees the collaborative project as an opportunity to increase scientific rigor in the field of stone conservation. "If you do real science and you start from very basic ideas, you can make some progress," he says. Brinker foresees other potential applications for the team's work, perhaps in protecting materials used to encase toxic materials for long-term storage.

Collaboration may also be a way to increase the resources available for this kind of research. Within the art community, Wheeler says, if you have $600,000 to spend and you have to choose between buying a painting and buying scientific equipment, you're going to buy the painting.

The scientists working on art conservation intend to help art lovers focus on keeping what they've already got, because, as Brinker says, "when a sculpture is gone, it's gone forever."