A MATERIAL LOSS

Acid rain is leaving its mark on buildings, statues, automobiles and other man-made structures

By IVARS PETERSON

In the high plateau lands of southwestern Colorado, the ancient stone cities of the Anasazi Indians are slowly wearing away. Brilliant sunlight, dusty winds, stinging rain and swirling snow take turns assaulting the sandstone blocks that make up the remains of these elaborate cliff dwellings.

But the stones may be eroding more quickly now than they were a few decades ago. Carried by wind or concentrated in rain and snow, air pollutants from several power plants and a nearby smelter continually wash over the site.

To test this postulated acceleration of natural erosion, a team of researchers last year began a careful study of sandstone deterioration at Mesa Verde National Park, where the Anasazi dwellings are located. For their project, the researchers used fragments of local sandstone to construct two test walls similar to those built by the Anasazi centuries before.

With photographic and other techniques, the researchers now regularly check for signs of wear on the stone walls. At the same time, they track the weather and measure the concentrations of various pollutants in the air. They are looking for a correlation between the rate of erosion and the presence of pollutants.

The Mesa Verde project is only one of several ongoing studies designed to examine the effects of acid deposition on materials. Concern is mounting that acidic pollutants cause widespread damage to paint, stone, wood, fabrics, masonry, concrete and metals.

"Economically, one of the most serious effects of acid deposition is on materials," says James H. Gibson of Colorado State University in Ft. Collins. According to the Environmental Protection Agency (EPA), recent estimates of the annual cost of repairing or replacing structures damaged by acid deposition start at $5 billion and go up from there.

Reflecting this growing concern, more than 125 scientists and engineers from a variety of disciplines earlier this year attended a symposium on the "Degradation of Materials due to Acid Rain." The meeting, sponsored in Arlington, Va., by the American Chemical Society, was the first to focus on this specific issue.

"The materials problems are really formidable," says Robert Baboian, meeting chairman and head of the corrosion laboratory at Texas Instruments, Inc., in Attleboro, Mass. Not only may the damage be extensive, he notes, but very little is known about how the damage occurs and what can be done to prevent it.

Limestone and marble are particularly vulnerable because acids attack their principal constituent, calcium carbonate. These reactions produce water-soluble substances that easily leach out and weaken the structure. The worn faces of marble tombstones (SN: 11/17/84, p. 313), limestone monuments and ancient buildings like the Acropolis in Athens all show the effects of air pollution and acid rain.

To investigate the weathering of these materials, the National Park Service has established four sites where slabs of Salem limestone from Indiana and Shelburne marble from Vermont are exposed to the elements. After granite, limestone is the most commonly used building stone in the United States. Salem limestone, widely used for more than 100 years, makes up much of the Empire State Building in New York City. Shelburne marble has been used

D. Doskel/Ill. State Water Survey

This test wall, one of two constructed from types of sandstone used by the Anasazi, sits exposed to wind and rain (above). Microphotography (right) is one technique being used to track surface deterioration.

to face structures like the Jefferson Memorial in Washington, D.C.

For the next 10 years, researchers will analyze the chemistry of runoff water, monitor color changes, measure weight losses and perform other experiments in comparing protected and unprotected stone samples. Early results from the site at Research Triangle Park, N.C., show that even one heavy rainfall contains enough acid to wear away a few microns of the highly polished marble surface.

Much less is known about the effect of acid deposition on Portland cement and concrete. Nevertheless, the small amount of information available suggests that acids "significantly affect the durability of concrete," says Ronald P. Webster of Brookhaven National Laboratory in Upton, N.Y. Substances like sulfur dioxide, nitrogen oxides and hydrochloric acid are also known to accelerate the corrosion of steel rods used to reinforce concrete.

Crumbling brick may signal acid rain damage as strongly as cracking and flaking concrete. Acid rain affects brick masonry by selectively dissolving the glassy fabric that holds the silica grains of a brick together. The resulting soluble sodium and calcium salts, carried by water, migrate through the porous brick. Salts are deposited wherever the water evaporates, leaving a white, powdery film that appears to ooze out of the masonry. Eventually, all that's left of a brick is a weakened "silica sponge."

Chemist A. Elena Charola of the Metropolitan Museum of Art in New York, however, warns that acid rain shouldn't be blamed for everything. In the case of bricks, neutral rainwater can be more damaging than acid rain. Rain by itself carves channels across the exposed faces of bricks, she says. "It's not the acid but the water that does the damage."

The problem is particularly serious for modern bricks, says Charola, because these are typically fired only long enough to create a thin glassy surface layer. Once this layer is gone, a brick quickly disintegrates. Twelfth-century Venetian bricks, in contrast, sat in kilns much longer to create a glassy matrix throughout. These bricks, she says, have held up very well for centuries, despite high levels of pollution.

Much of the building-wall damage now seen has been caused by efforts to clean or repair masonry, Charola says. Don't clean brick, she recommends. "It will last longer if you leave it dirty."

Likewise, attempts to seal brick walls by applying a coating that is impermeable to water are almost invariably unsuccessful. If water somehow enters the wall, perhaps from the interior side, the coating along with a portion of the brick will pop off in large flakes.

Even replacing mortar must be done carefully. If the replacement mortar is less porous than the bricks in a wall, the bricks will deteriorate faster than the mortar, says Charola. Instead, a more porous mortar should be used. In this way, the mortar rather than the brick will lose its strength first. It's usually cheaper to replace missing or cracked mortar than to rebuild a brick wall, she notes.

The picture is just as complicated for wood and paint. Factors other than immersion in occasional acid showers also contribute to deterioration. In some cases, the combination of acid rain and ultraviolet light from sunlight is much worse than either one by itself.

Wood is a composite material made up of cellulose and hemicellulose fibrils held together by a natural glue called lignin.


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A bronze lion drips corroded metal, staining its masonry resting place.

Chemically, the fibrils and the lignin behave quite differently. Cellulose, a polymeric sugar, is very sensitive to moisture and acids. Acid rain weakens these fibrils. On the other hand, lignin, a phenolic polymer, is susceptible to ultraviolet light. In bright sunlight, lignin decomposes, allowing the wood to start falling apart.

How well paint protects a wooden surface depends a great deal on the state of the wood, the flexibility of the paint and the bond between the paint and the wood, says R. Sam Williams of the Forest Products Laboratory in Madison, Wis. The worst problems occur when a newly erected wooden fence or building is left unpainted for a month or so during the summer, he says. By that time, both sunshine and rain have had a good chance to start breaking down the wood.

Peeling, cracked or discolored paint and disintegrating wood are not the only visible signs of possible acid rain damage. The rusting of reinforcing steel in bridge decks and other structures, ragged holes in metal automobile panels and the various ills of bronze and copper statues (SN: 6/29/85, p. 404) also signal problems that may be exacerbated if not directly caused by acid rain.

In a recent study of automobile corrosion in Montreal, Detroit, Boston and Dallas, Montreal cars seemed to suffer the highest level of "body rot" although considerable corrosion damage also showed up in Detroit and Boston. Montreal happens to have highly acidic rain and allows heavy use of road salt during the winter. Laboratory tests, says Baboian, who conducted the survey, confirm that the combination of acidic moisture and salts like


Courtesy: R. Baboian

Robert Baboian examines the Statue of Liberty's copper sandal for signs of deterioration. Measurements of the copper skin's thickness provide a benchmark for tracking future corrosion.

calcium chloride cause much more damage than either factor alone.

Car manufacturers have already tried to solve the problem by using galvanized steel in vulnerable spots. The zinc coating on the steel sacrifices itself to keep the steel from corroding. This delays the onset of acid and salt penetration into the steel. Car bodies have also been redesigned so that cavities where debris can be trapped have been eliminated. But, says Baboian, other corrosion problems persist.

What makes the whole question of materials durability extremely complicated are the numerous factors that can contribute to weathering. For one thing, pollutants reach surfaces in various forms — as molecules of gases, as particles or in raindrops, dew and fog. In each case, the chemical effects may be different.

Furthermore, rain itself may alter weathering rates by wetting surfaces to allow the occurrence of chemical reactions that don't necessarily involve acidity. It may also wash away encrusted pollutants and dirt so that less damage occurs. Alternatively, rain could periodically provide a fresh surface for renewed corrosion.

Even in unpolluted environments, moisture, atmospheric oxygen, carbon dioxide, sunlight, temperature fluctuations, frost and the action of microorganisms (SN: 7/20/85, p. 42) all contribute to the deterioration of materials. Separating out the effects of acid deposition is a difficult problem.


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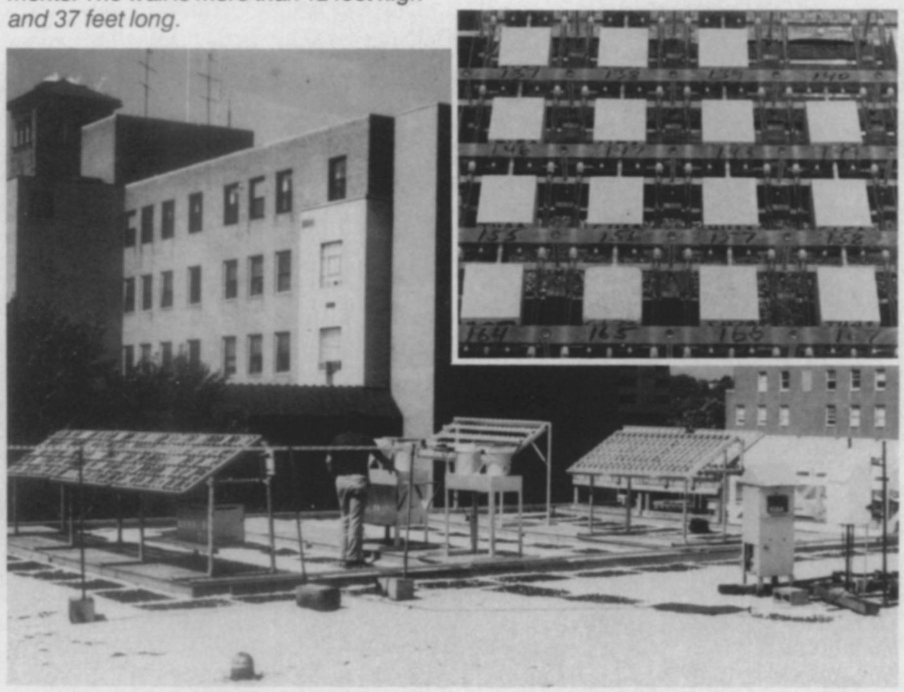
Now sitting on a grassy hilltop in Gaithersburg, Md., after being moved in 1978 from a site in Washington, D.C., this test wall at the National Bureau of Standards is made up of 2,400 stone samples. After almost 40 years, some samples, especially sandstones, are beginning to crumble, crack or flake away (see detail). Many limestones have developed a surface texture clearly showing fossil fragments. The wall is more than 12 feet high and 37 feet long.

A second difficulty is the wide range of materials used for man-made products. There are dozens of types of concrete and steel, plastics and glass, sealants and coatings. All are subject to some type of chemical degradation.

"Architects need to understand the combined effect of all pollutants on an entire building, not just how man-made products react in a continuous bath of acid rain," says William E. Evans of Cooper Lecky Architects in Washington, D.C. "Designers need lots of information," he says, so that they can identify the architectural details that either encourage or inhibit damage.

Is it better, for example, to construct overhanging eaves to keep rainwater away from stone carvings on a building's wall, Evans asks, or will this create other problems? Clear answers to questions of this kind are still hard to find.



National Park Service

As part of a 10-year study of acid rain's effect on materials, pieces of Indiana limestone and Vermont marble (inset) sit on a rooftop in Washington, D.C.

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This exposed limestone sculpture near the entrance to a church in New York City shows the weathering effect of rain and air pollution.

As far as materials are concerned, one answer to the acid rain problem is to learn to live with it by changing designs or using acid-resistant materials. Automobiles, for example, are now less likely to corrode over the average lifetime of a car because manufacturers use special metal alloys. Similarly, architects are beginning to see how the shape, orientation and pitch of a copper roof is related to how quickly it deteriorates.

However, on a national scale, the expense of constant repairs and replacements along with the use of new designs and better materials may outweigh the cost of stricter controls on emissions of sulfur dioxide and nitrogen oxides from power plants and other pollutant sources (SN: 7/28/84, p. 58). In this case, it would be cheaper to change the environment. But the costs and benefits involved are hard to compute.

One difficulty is that EPA and the federal government don't have a clear mandate for dealing with materials damage caused by acid deposition, says Roger C. Dower of the Environmental Law Institute in Washington, D.C. The Clean Air Act, for instance, emphasizes effects on human health rather than damage to objects.

In addition, more needs to be done to merge the growing volume of scientific, technical and economic data now becoming available, says Dower. This should be translated into dollar terms, he suggests, so that people can begin to understand the extent of materials damage.

Yet the figures remain elusive, and scientific and technical uncertainties are not the only reasons. How is it possible, for example, to measure and factor in the value of a symbol like the Statue of Liberty or of a historic site like the Mesa Verde dwellings of the Anasazi Indians?

"This is an important issue," says economist Thomas D. Crocker of the University of Wyoming in Laramie, and one that is also far from being resolved. □