Salt, not acid rain, may mottle Ms. Liberty

Caretakers of the aging Ms. Liberty need never worry that she will develop wrinkles, but they do express concern about the streaks and freckles that mar her splendid green complexion. Six years ago, restoration scientists working on the century-old statue concluded that acid rain was damaging her thin copper skin, making the metal more susceptible to decay and darkening its color.

Now, geochemist Richard A. Livingston reports that even New York City's most acidic storms lack the acidity needed to disrupt the chemical processes occurring on the statue's surface. "It's just not possible for the acid rain to have an effect on the statue at all," he told SCIENCE NEWS.

Livingston, of the University of Maryland in College Park, describes a chemical scenario that runs counter to that put forth in 1986. A reduction in sulfur dioxide pollution since 1940 has increased the statue's susceptibility to the harbor's salty air, he asserts in the August ENVIRONMENTAL SCIENCE AND TECHNOLOGY.

Shiny copper dulls as it reacts with moisture and chemicals in the atmosphere. This corrosion eventually leads to the formation of a green patina, usually a copper sulfate mineral called brochantite ($Cu_4(OH)_6SO_4$). However, scientists noticed in 1986 that the surface also contained lots of a sulfur-enriched mineral called antlerite ($Cu_3(OH)_4SO_4$), which dissolves and washes away more easily than brochantite, exposing the darker layer below (SN: 12/20&27/86, p.392).

Because the patina protects the underlying copper from further corrosion, the discovery of the antlerite raised concern. Researchers blamed antlerite's presence on acidic rain, dew, fog and particulates, which made the statue's surface too acidic for brochantite to remain stable, says Robert Baboian, a corrosion scientist at Texas Instruments, Inc., in Attleboro, Mass., who studied the statue's patina.

In 1985, Livingston noticed that pictures of the statue's east side resembled photo negatives: Shadowed areas looked light, while well-lit surfaces appeared quite dark. This phenomenon, coupled with an earlier study showing that the patina contained a copper chloride mineral, prompted him to investigate the various conditions under which the patina's different minerals form.

He calculated the thermodynamics involved when copper and its minerals are exposed to the various ions present in air and water. These ions compete to react with the copper-based materials, and their success depends on their concentrations and the reaction environment. "Every chemical reaction has a characteristic energy, and you can use this to determine which ones will happen and under what conditions," Livingston explains. "It's a theoretical [model], but it's a fairly good predictor of what's going to happen."

With this technique, he ruled out acid rain because it lacked the acid concentrations required for antlerite to form. He then concluded that the buildup of chlorides from salt spray could affect the surface chemistry where rain failed to regularly rinse away these salts. Thus, where rainwater flows, the statue stays light green; elsewhere, a copper chloride mineral gives it a darker, olive hue.

"It's a thorough analysis of the subject, but I disagree with his conclusions," says Baboian. "I don't believe sea salts have anything to do with it [the dark color]."

He argues that Livingston failed to consider that as acid rain evaporates, it becomes acidic enough to cause antlerite to form. Moreover, Baboian's X-ray analyses of the patina showed no signs of copper chloride even where the statue looked darker. "This is a very complex, dynamic system," he adds. "It's not something that can be treated with thermodynamics."

While the darker areas might alter the statue's aesthetics, they do not seem to wear away any faster than lighter parts, Baboian says. Even so, the National Park Service plans to trace the history of the patina by looking at photographs taken over the past 100 years, says Park Service architect E. Blaine Cliver of Washington, D.C., who directed the statue's 1986 restoration. In this way, Cliver hopes to get a better understanding of how the color has changed through time and what conditions might affect it.

J.T. Lowe/Library of Congress

Sea salt may darken Liberty's complexion in areas sheltered from rain, such as the lee side of the statue or the region under the crown. This photo was taken in natural light.

Cliver worries less about the darkening than about a trouble spot where runoff from the statue's crown seems to have created a black streak that reaches down in front of one ear. A green patina should form from that black layer, but Cliver fears that the corrosion will occur too rapidly for the green to appear. "If the black gets eroded, then it will expose the bright copper, and we will lose copper," he says.

"It would be hard to protect against these effects," Livingston adds. "It would probably involve some kind of wrapping, which nobody wants to do." — *E. Pennisi*

Heart drug trial cut short

Federal officials have halted a large-scale clinical trial — originally designed to see whether any of three drugs could increase long-term survival of people with mild arrhythmia following a heart attack — after finding evidence that the lone drug remaining in the trial increased volunteers' risk of death during the study period. In April 1989, researchers had stopped testing the study's two other drugs for the same reason (SN: 4/29/89, p.260).

The National Heart, Lung, and Blood Institute (NHLBI) announced this week that it notified researchers on Aug. 2 to warn their patients to stop taking moricizine, made by Du Pont Pharmaceuticals in Wilmington, Del.

Researchers in the Cardiac Arrhythmia Suppression Trial (CAST II) had recruited 1,346 men and women who had survived a heart attack but developed mild rhythm irregularities due to damaged ventricles, the lower heart chambers. During the study, each volunteer took one of three daily doses of moricizine or placebo pills.

On July 30 of this year — 18 months into the trial — a review of the data revealed a disturbing trend: 97 people in the moricizine group had died, compared with 74 in the placebo group. Although researchers have not yet established the cause of each death, study director Lawrence M. Friedman says the preliminary findings suggest that moricizine itself can trigger life-threatening episodes of arrhythmia in such patients. NHLBI ended the trial because the apparent risks of the treatment outweighed any possible benefits.

In an Aug. 9 letter sent to more than 100,000 U.S. physicians, Du Pont's medical marketing director, John N. Hurley, states that the study's results apply only to people with mild arrhythmia. He adds that physicians can continue to prescribe moricizine (Ethmozine) for people with life-threatening arrhythmias, pointing out that the FDA approved the drug specifically for such cases in 1990. □