COPPER IN TODAY'S ATMOSPHERE

By David L. Hunt

Several months ago, an article appeared in a magazine for roofing professionals that could be misinterpreted to indicate that copper is no longer a good building material. The author's comments were based on personal observation, unsupported by independent testing or data.

In Europe, copper has been used as a building material since the Middle Ages. The oldest known copper roof is on the cathedral in Hildesheim, Germany, built in the 1200s. Records vary as to the date of construction; according to some, the roof was installed in 1230 by order of Bishop Konrad. Other records place construction in 1280. In any event, the roof was untouched until partially destroyed by aerial bombs in March 1945.

Following the war, the cathedral was reconstructed. Those portions of the roof that were unharmed remain today as they were when installed over 800 years ago. Where possible, repairs involved re-forming and reinstalling the original copper sheets.

To imply that copper is less suitable for roofing and flashing today than it was 40 or 50 years ago is ridiculous. Admittedly, no building material is perfect. No material – not even copper – is suitable for all applications in all environments. However, to reject a roofing material simply on the basis of unsupported opinion or "old wives' tales" is unprofessional and potentially dangerous.

The purpose of this article is not to promote copper, nor is it intended to be a thesis detailing the intricacies of corrosion. The corrosion of copper and its alloys has been widely studied for decades – perhaps centuries. For those interested in a scientific dissertation, there are many excellent publications by ASM International – The Materials Information Society, ASTM International, the U.S. Department of Commerce, and others.

Rather, it is hoped that this article will remind the roofing profession that good decisions are based on fact, not supposition. A secondary purpose is to provide factual information about weathering and atmospheric corrosion of copper as a building material.

Any evaluation of corrosion of roofing materials should begin with, or at least encompass, a review of those conditions believed to contribute to corrosion. The evaluation should also consider whether deterioration is:

- Of consequence or cosmetic (aesthetic) only.
- The result of one item, event, or material; or the result of two or more.
- A short-term event or a continuing event that will lead to failure.

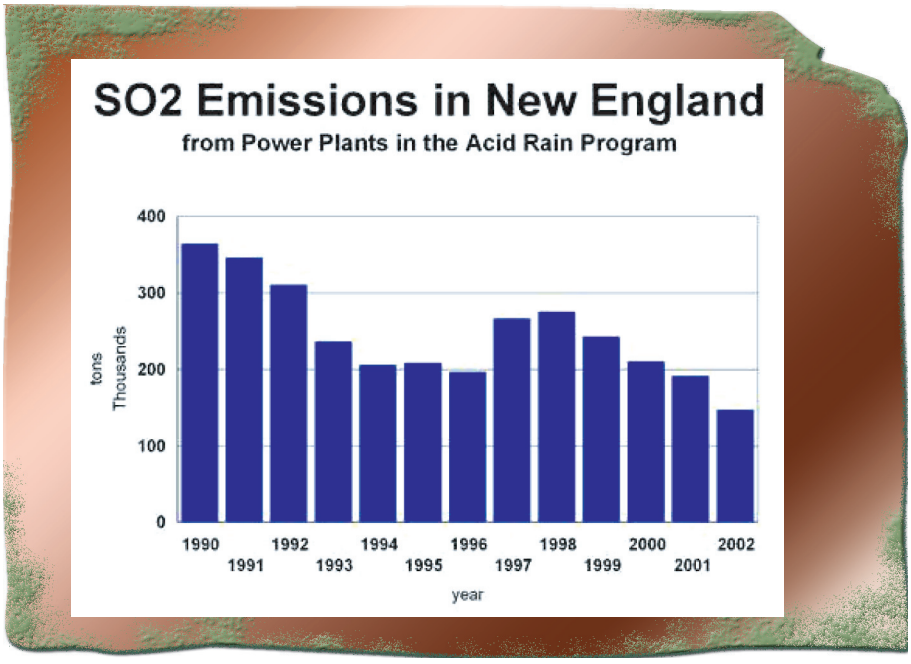
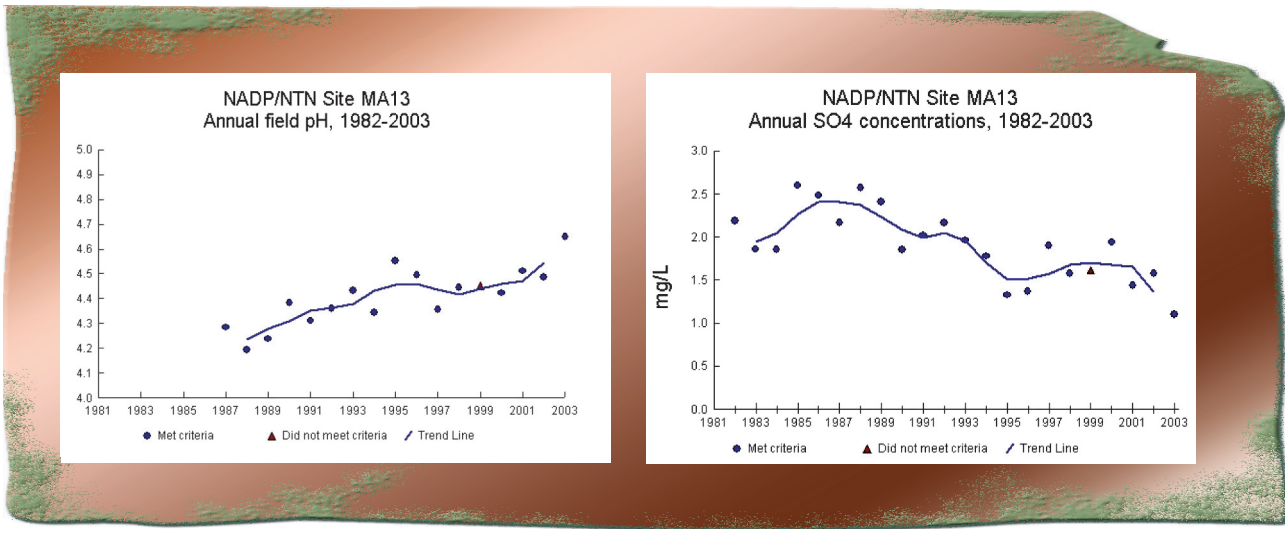


Figure 1: SO_2 emission in New England from power plants in the acid rain program. Source: U.S. EPA.



Figures 3 and 4: The pH of precipitation has risen. The concentration of SO_4 has decreased.

Acid rain - trends and measurements

To begin an investigation of corrosion with the premise that air quality in the United States today is worse than it was 50 or 100 years ago is incorrect. Due to enforcement of EPA and state clean air regulations, since the mid 1980s, sulfate ion concentration (SO_4^{-2} mg/L) has been significantly reduced throughout the United States.

Visit the U.S. Environmental Protection Agency website at **http://www.epa.gov/region01/eco/acid rain/trends.html.** There, one can find the statement, "SO_2 and NO_X emissions from power plants in New England have decreased since 1990." (See *Figure 1.*) Charts on the website also plot the reduction.

Obviously, acid rain is not a local phenomenon. The fact that New England power plants have "cleaned up their act" does not automatically mean that the air in Boston is better. Just as smoke from a neighbor's fire can drift into one's yard, so too can airborne pollutants cross state and national borders.

Visiting the website of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) can provide a better understanding of air quality (acid rain) for the entire United States.

The website – **http://nadp.sws.uiuc.edu** – states, "NADP/NTN is a nationwide network of precipitation monitoring sites. The network is a cooperative effort among many different groups, including the State Agricultural Experiment Stations, U.S. Geological Survey, U.S. Department of Agriculture, and numerous other governmental and private entities. The NADP/NTN has grown from 22 stations at the end of 1978 to over 200 sites spanning the continental United States, Alaska...Puerto Rico, and the Virgin Islands... The purpose of the network is to collect data on the chemistry of precipitation for monitoring of geographical and temporal long-term trends."

An interesting feature of the NADP/NTN website is the isopleth maps that trace the history of SO_4, NO_3 and NH_4 in the atmosphere. On this site, one may also find information about monitoring sites in the Bay State – MA01, MA08, and MA13. (See *Figure 2.*)

Site MA13, located at the State Agricultural Experimental Station, has collected rainfall data since 1982. Over the past 22 years, the pH of the precipitation has risen while the concentration of SO4 has decreased (*Figures 3* and *4*).

Admittedly, this is more information than most roofing professionals want or need to evaluate and select materials. But it is necessary to fully understand the micro-environment and how it can affect the durability and performance of materials.

Of consequence or cosmetic?

Assuming that the data presented above and visits to the referenced websites convince most people that the air quality in the United States is improving, we should move on to the next question: Does acid rain hurt copper?

The answer is: *not really.*

As part of a 20-year study of atmospheric corrosion, ASTM members exposed nine different coppers and copper alloys to rural, urban, and marine environments. Corrosion rates observed for alloy C11000 and C12000 (historically the designations for copper used for architectural purposes) were as shown in the table on page 44.[1]

A monograph on atmospheric corrosion by E. Mattsson and R. Holm for the Electrochemical Society reported that the following corrosion rates have been determined for copper:[2]

Atmosphere	Corrosion Rate (µm/yr)
Rural	~0.5
Urban	1 to 2
Marine	~1

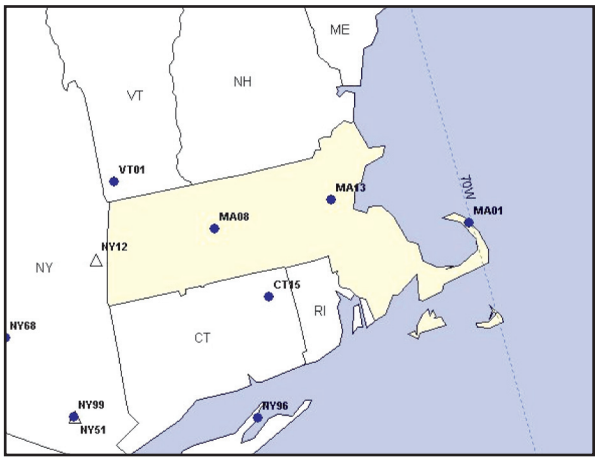


Figure 2: Monitoring sites in Massachusetts. Site MA13 is at the State Agricultural Experimental Station in the eastern part of the state.

Corrosion Rates - µm/yr						
Alloy	Altoona, PA	New York, NY	Key West, FL	La Jolla, CA	State College, PA	Phoenix, AZ
C11000	1.40	1.38	0.56	1.27	0.43	0.13
C12000	1.32	1.22	0.51	1.42	0.36	0.08

Mathematically, if 16-ounce (0.0216" thick) copper is subject to atmospheric corrosion at a constant rate of 1.50 µm per year, it will take over 360 years before it is perforated. There are, however, studies that indicate a decrease in the rate of corrosion as protective films (patina) form.[3]

Further, as noted by Einar Mattsson, head of the Swedish Corrosion Institute, at Corrosion/82, "If the atmosphere is low in pollution, the patina may take an extremely long time to form – hundreds of years – due to scarce supply of anions for the formation of basic copper salt."[4] This is why many people in the Mountain States believe "copper doesn't turn green here." The problem is not with the copper, it is just that the people have not watched it long enough – and probably will not live long enough to do so.

This is not to say that a copper roof will or will not last a given number of years; only that for most architectural applications, atmospheric corrosion is not significant.

There are, however, cases where it appears that copper is corroding faster than expected. These include locations where copper is installed below other roofing materials. It is not unusual to see bright, angry, orange, icicle-shaped discolorations in copper valleys, eave snow slides, etc., below wood, composition shingles, or slate. Are such streaks or discolorations reason for concern? Perhaps – but perhaps not.

Many roofing products can leach relatively weak acids when they are new and first installed. These compounds can – and often do – act like copper cleaners and remove the naturally forming tarnish (oxide) as it forms. This results in uneven weathering or discoloration of the copper.

"Does Acid Rain Hurt Copper?

The answer is:

Not really."

Figure 5 shows uneven weathering that is caused by the flow of rainwater from an asphaltic-based roof covering onto standing seam copper. This is typical of the appearance of copper subjected to mild, surface corrosion.

Figure 5: Uneven weathering caused by the flow of rainwater from an asphaltic-based roof covering onto standing seam copper.

In general, compounds that leach from wood and composition shingles are weak when the shingles are new. As the shingles age, the amount of leachate decreases. In most cases, after several months to a few years, the leaching ceases completely, the orange "icicles" disappear, and a natural patina forms. With the passage of more time, the assembly assumes a uniform coloration with no hint of the previous discolorations. In these cases, the early discoloration is purely cosmetic and of no consequence.

A caveat, however, is that the flow shown in *Figure 5* is through a scupper and it impinges on the copper. As will be discussed later, impingement can cause problems. This roof should be monitored regularly and corrective action taken if thinning is noted.

This is not to say that copper can be installed below wood (cedar) or composition shingles with no concern for serious corrosion. Many roofing professionals have observed copper flashings that are completely perforated at the shingle butt line. The first reaction – that this is the result of compounds leaching from the shingle – is incorrect.

Studies conducted by the U.S. Department of Commerce Bureau of Standards almost 75 years ago identified this form of corrosion as "line corrosion."[5] Research Paper No. 123, "Corrosion of Open Valley Flashings," published December 1929 notes:

> "...line corrosion is an interesting case of the type of attack occurring with differential aeration..." and "...in general, when a metal is exposed to a solution, part of which is aerated and part nonaerated, the metal under the nonaerated portion will be anodic to that under the aerated portion and will be corroded."

Figure 6, from Research Paper No. 123, "...is a diagram showing, on a large scale, approximately the relation between roofing, flashing, and retained liquid and the location of line corrosion."

Conclusions from the Bureau of Standards test include:

1. "Wood shingles are *not* [emphasis added] the primary cause of line corrosion.
2. "Line corrosion may occur not only with wood shingles, but also with slate, asbestos shingles, composition shingles, and, under exceptional circumstances, even when one sheet of copper overlaps another.

3. "On all open valleys ...a batten strip should be inserted between the flashing and the roofing. ...There is reason to believe that if this precaution is followed, *no perceptible line corrosion will occur in 50 years or more* [emphasis added] on a roof under the severe conditions such as are found in New York City and its environs."

For more than 50 years, Revere and the copper industry have published installation details and specifications showing the butt end of shingles raised above copper flashings to allow air circulation and drying. This minimizes the possibility of line corrosion.

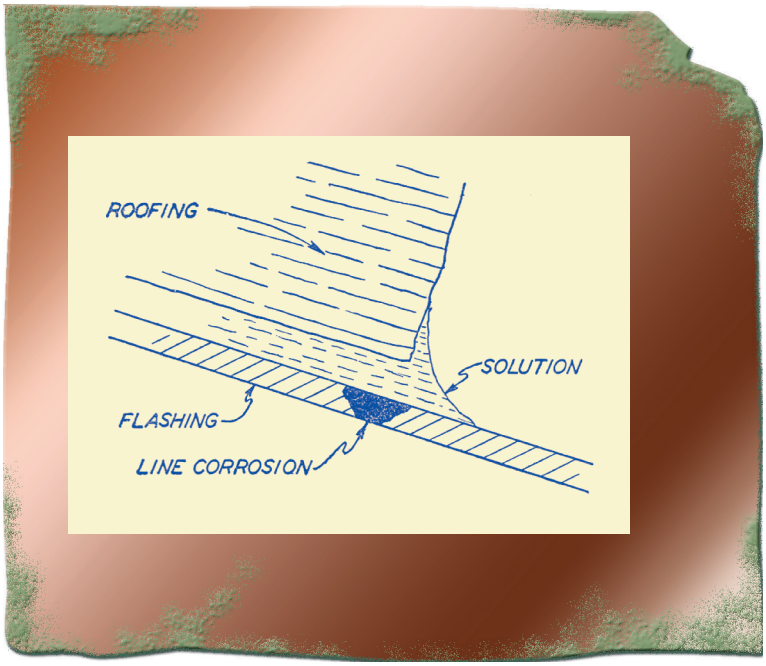


Figure 6 from Research Paper No. 123 is a diagram of open-valley flashing, illustrating the manner in which line corrosion occurs.

One or multiple causes?

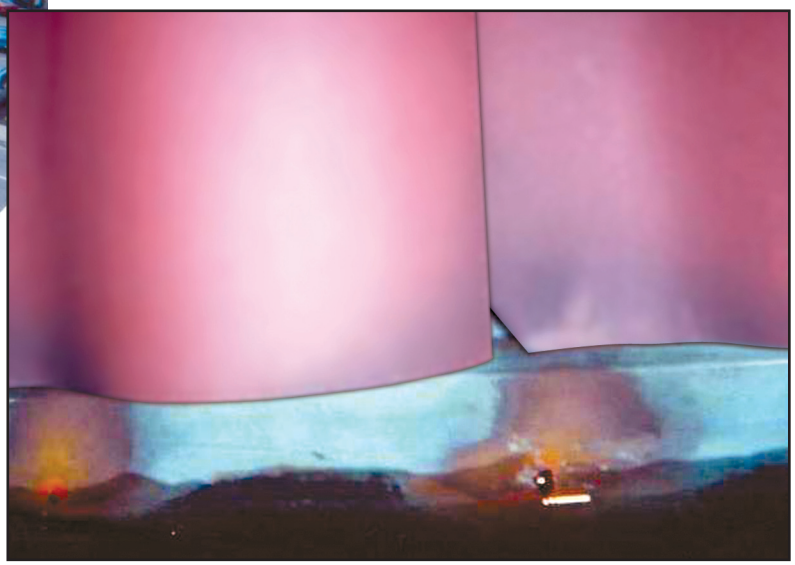
Bright orange "icicles" or spots can occur when copper's protective oxide is mechanically removed by high-velocity, turbulent rainwater. It can also be removed by the flow of abrasive water over copper. This type of attack on copper is generally referred to as "erosion-corrosion" or impingement attack.

The former is the consequence of runoff from slate, tile, etc. that contains abrasive particles that continually sand or polish the copper. The latter can occur when water is permitted to fall from an upper element (roof) onto a lower one with sufficient velocity to remove the copper's surface. In either case, deterioration (thinning) of the copper may be aggravated if the water is sufficiently acidic or contains other elements that are corrosive to copper.

As noted above, if erosion-corrosion is severe and it appears the copper is being thinned, corrective action is required. Usually this can be accomplished by installing a "sacrificial strip" of copper at the area of impingement. If this is not possible, it may be necessary to reroute the flow through gutters and downspouts.

Erosion-corrosion can also occur where concentrated flow from slate or tile roofs empty into a copper gutter, valley, etc. *Figures 7* and *8* show how this can occur with Spanish clay tile. The low points (valleys) of the tiles not only are the point of concentrated flow, but also the channel for moisture from heavy dewfalls and mists. Depending upon the type and amount of pollutants that accumulate on the tile before they are washed off, these small amounts of water may be very corrosive to copper.

In cases like these, use of heavier copper and/or installation of a "sacrifice strip" will prolong the life of the assembly, but



Figures 7 and 8: Runoff from clay tiles can be corrosive to copper, causing "erosion-corrosion."

Figures 9 and 10: Only the initial aesthetics are affected by this natural but unusual weathering. With time, the copper should take on a uniform brown, bronze, and eventually blue-green color of natural patina.

periodic monitoring is required to protect against perforation and leaks.

Erosion-corrosion can also occur in copper downspouts – especially at abrupt changes in direction. Wherever possible, sharp, 90-degree bends in downspouts should be avoided.

More often than atmospheric corrosion, erosion and erosion-corrosion result in the premature failure of copper assemblies. However, with a little forethought and care, most cases can be mitigated, if not eliminated, so as not to adversely affect the assembly.

Is failure imminent or likely?

Is the discoloration an early warning of failure? Sometimes yes – sometimes no. Each case has to be judged independently.

Although the owners of the properties in *Figures 9* and *10* may not be especially pleased with the appearance of the copper wall cladding, only the initial aesthetics are affected. The coloration is simply the result of natural – if somewhat unusual – weathering. With time and additional weathering, there is every reason to believe the copper will take on a uniform brown or bronze tone and eventually the blue-green color of natural patina. However, since the air quality in the United States is considerably better now than it was 25 years ago, they may have to wait many years.

In summary

Years ago the United Textile Workers had a jingle that advised you to "Look for the union label." In reviewing reports about roofing materials, "Look for the supporting data."

References

(1) Thompson, D.H.; Tracy A.W.; Freeman, J.R., "The Atmospheric Corrosion of Copper – Results of 20-Year Tests," *Symposium on Atmospheric Corrosion of Non-Ferrous Metals,* 1956.

(2) Mattsson, W.; Holm, R., *Atmospheric Corrosion of Copper and its Alloys,* Electrochemical Society Monograph on Atmospheric Corrosion, 1982.

(3) Thompson, D.H.; Tracy, A.W.; Freeman, J.R.; "The Atmospheric Corrosion of Copper," ASTM, 1943.

(4) Mattsson, E., "The Atmospheric Corrosion Properties of Some Common Structural Metals – A Comparative Study," National Association of Corrosion Engineers, 1982.

(5) Beij, K.H., Research Paper No. 123, Corrosion of Open-valley Flashings," 1929.

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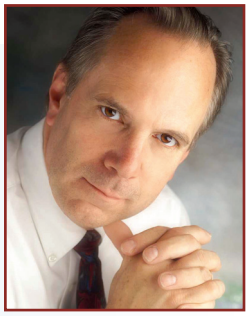

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