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Computer Model Studies of the Atmospheric Corrosion of Copper

Pollution and Corrosion

Copper has been used in Europe as a roofing material for centuries. Initially brown, its surface gradually changes to a pale and attractive blue-green color. If built up slowly and uniformly, this surface patina is relatively stable over time. In the early part of the 20th century, the time needed for a natural patina layer to form was two or three decades, as exemplified by a Danish saying: "When a young architect covers his roof with copper, it will turn green when his hair turns gray"[1]. That transition time is now much shorter in many areas, typically about a decade. [2] The change is universally regarded as due to an increase in airborne pollution.

Conceptually, corrosion can be related to the agent or agents that cause it by a "damage function" or "dose-response function" of the type

$$CR = f \text{ (Causative Agents)}$$

where CR is a measure of the corrosion rate.[3] In defining a damage function, the first step is to determine the identity of the corrosive agents. In the case of metal and stone, airborne sulfur dioxide, particulate matter, and water have been so identified for two-thirds of a century.[4] Near the seacoast, sea salt is implicated as well.[5] More recent laboratory and field studies have suggested that ozone and nitrogen dioxide should be added to the list since they accelerate the corrosion process.[6]

The suite of causative agents thus suggests a generalized damage function of the type

$$CR = A(H_2O)^\alpha \, B(SO_2)^\beta \, C(\text{Particulate Matter})^\chi \, D(\text{Sea Salt})^\delta \\ E(NO_2)^\epsilon \, F(O_3)^\vartheta$$

where the function is integrated over time and where A-F and α-ϕ are constants to be determined. Whether the individual terms take additive, multiplicative, or other forms is, however, poorly understood.[3] Until the form of the damage function is reliably established for each material of interest, little progress can be made in predicting the quantitative corrosion rates of the future.

Computer Models of Metal Corrosion

As a tool to explore the interactions among atmospheric gases and particles, water, and metal surfaces, a computer simulation model has been developed.[7] It addresses the six distinct regimes that may need to be treated theoretically, as shown in Figure 1: G(gas), I(interface), L(liquid), D(deposition layer), E(electrodic regime) and S(solid), so models treating such systems may be designated GILDES models. Within the regimes chemical reactions can occur to change the constituents. Transport of chemical species of interest between regimes can occur, as can condensation and dissolution; all must be assessed. The products of

the chemical reactions are susceptible to transport and deposition or volatilization just as are the reactants.

For the six regimes, mathematical formulations must be specified to describe the transitions and transformations that occur. Some can be developed from first principles, while in other cases parameterization from data is indicated. This conceptual framework draws on the knowledge of a number of different disciplines and incorporates the insightful work of many specialists in relevant scientific fields, as follows: gas layer – atmospheric chemistry; interface layer – mass transport engineering and interface science; liquid layer – freshwater, marine, and brine chemistry; deposition layer – colloid chemistry and mineralogy; electrodic layer – electrochemistry; and solid layer – solid state chemistry.

The Atmospheric Corrosion of Copper

One of the applications of the GILDES model has been to study the corrosion chemistry of copper.[8, 9] It is known that the blue-green copper patina consists largely of cupric hydroxysulfate salts, thereby demonstrating that sulfur in some form (almost certainly SO_2) is involved in the corrosion process.[2] According-

Fig. 1. A schematic representation of the six regimes and the transitions and transformations that make up the GILDES model of aqueous environmental chemistry. In the figure, the circles indicate initial reactants and the squares indicate reaction products. Solid lines connecting reactants and/or products denote processes that can be readily described by formulations based on first principles. Dashed lines indicate processes whose details are less straightforward and which are described by parameterized coefficients based on experimental data. The dotted line indicates that liquid phase chemistry can be described by first principles at low ionic strength but must be parameterized at high ionic strength. The dashed-dotted line indicates that chemical transformations in the solid state are not included in the current GILDES formulation, as they are thought not relevant to the problems of interest
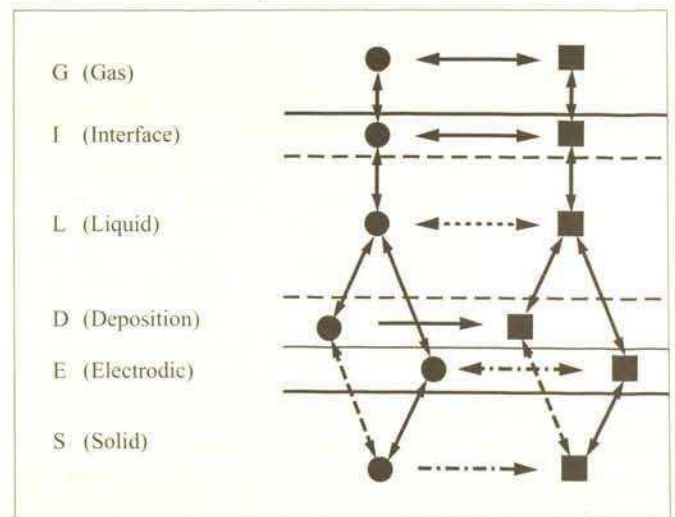
ly, the model has the research of Persson and Leygraf as its experimental counterpart, chosen because that work has generated time-resolved quantitative data for the initial formation of sulfites on copper.[10] While the practical implications of this comparison are limited, since sulfates rather than sulfites are detected as natural corrosion products, it is a natural choice for comparison with the initial calculations since it treats the first step of the corrosion process.

In the base set developed for the model, 95 reactions in 39 species were considered. The resulting calculation enabled the discovery of the dominant species and the major chemical pathways for the corrosion of the copper surface. Figure 2 shows a summary of this analysis, in which the numbers on the reaction paths are the reaction rates 59 simulated minutes into the calculation. The numbers inside the boxes indicate the concentrations of the corresponding species, also after 59 minutes.

Consider first the surface species in Fig. 2, where the concentrations of $S = Cu^+$ and $S = CuSO_3^-$ are very similar. (The notation $S = x$ indicates a surface species.) The concentration behavior is a consequence of the charge balance requirement. In solution there turns out to be an excess positive charge, mainly due to the dominance of Cu^{2+}. The positive net charge in solution is balanced by the negative surface charge arising from the small but significant difference in the concentrations of $S = Cu^+$ and $S = CuSO_3^-$. The overall corrosion rate is limited by the rate of delivery of gas-phase SO_2 to the system. This delivery rate in turn depends on the SO_2 concentration, the deposition velocity, and the liquid layer thickness.

Once the charged surface complexes are dissolved into the liquid layer, the Cu(I) ions have two possible long-term fates, precipitation, or oxidation to Cu(II) followed by precipitation. The latter turns out to be more important than the former under the circumstances of the calculation.

The experimental data relevant to the calculations are shown in Fig. 3 together with two of the calculational results, those from the base set and those from another calculation that produced a lower corrosion rate. In all cases the total amount of sul-

Fig. 3. Total amount of S(IV) as a function of time of exposure. The experimental points (dotted line) are from Persson and Leygraf[10] and the bottom curve from a calculation in which the dissolution rates for $S = Cu^+$ and $S = CuSO_3^-$ were decreased by a factor of ten compared with the base set

fite is given as a function of time. It is apparent that the model produces a reasonable simulation of the overall corrosion rate. It is notable, however, that after a relatively constant growth during the first three hours, the experimental data show a transition to a significantly lower deposition rate. Such a transformation in process is a detail not adequately described by the model in its initial formulation. However, it is clear that various model calculations, using reaction rate constants within the uncertainties in their magnitudes, can produce corrosion rates that bracket the actual experimental results that incorporate the initial and subsequent corrosion processes.

The results of the computer model show that chemical reactions within the thin water layer on the copper surface are less important than the direct reactions of dissolved atmospheric species with the surface. The rates with which those surface reactions proceed are, however, poorly known, so further research on these specific reactions is indicated. In a subsequent study,

Fig. 2. Significant species, their concentrations and their principal reaction networks, with rates for the base reaction set after 59 minutes of exposure. Copper and sulfur species concentrations are given in either ppb = parts per billion (1 x 10^-9) by volume, or ml = monolayers
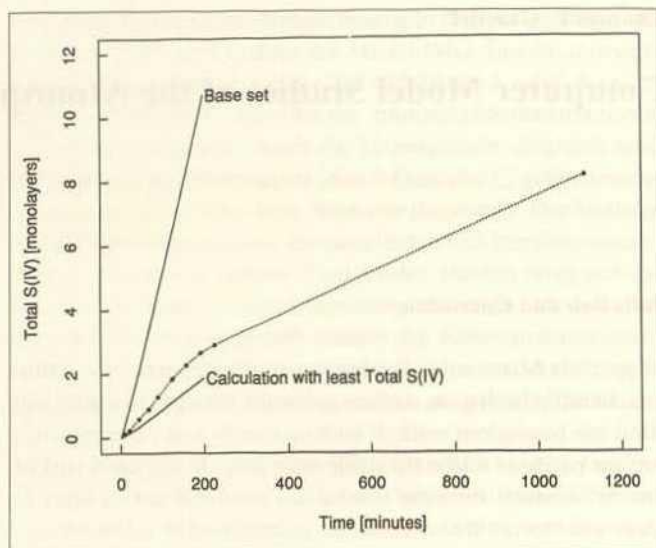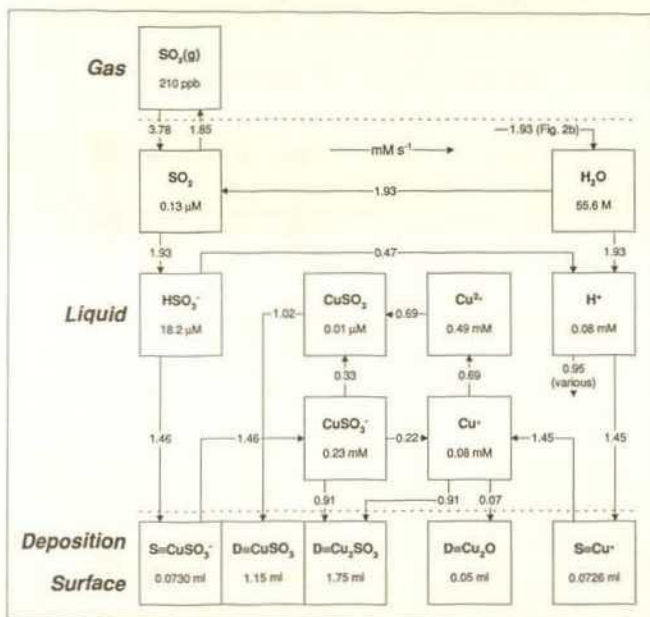
Fig. 4. Time curves from the GILDES model of copper corrosion showing precipitated amounts (in equivalent monolayers) of the dominant corrosion products cuprite (D=Cu$_2$O), chalcocyanite (D=CuSO$_4$), and antlerite (D=Cu$_3$(OH)$_4$SO$_4$). The late precipitation of chalcocyanite and cuprite relative to antlerite reflects the fact that they are much more soluble, reaching saturation only as the water film on the copper surface nears total evaporation
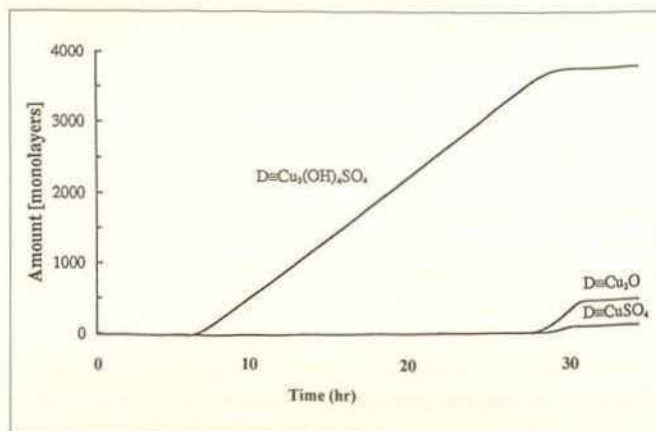
the effects on copper corrosion of ammonium sulfate particles, known to be common in the atmosphere, were evaluated. [11] It was found that the cupric hydroxysulfates formed were a function of the particle concentration, and that a large fraction of the corrosion products forms near the end of the surface drying phase (Fig. 4). These results reproduce, at least qualitatively, existing laboratory and field data on the corrosion of copper.

Calculations including as reactants the gases NO_2 and O_3 and sea salt particles remain to be performed. In studies of zinc chemistry, however, both NO_2 and O_3 have been shown by experiments and GILDES calculations to accelerate the corrosion process. [12] It is anticipated that similar results will be achieved when these species are added to the copper chemistry model.

With the availability of the GILDES model, now increasingly guided by careful experimental data, the development of a damage function for copper seems within reach in a few years. [10,13]

21st Century Corrosion of Copper Statues and Monuments

One of the most useful characteristics of computer models is that once they have been validated against present conditions, they can be used to make predictions for hypothetical corrosion scenarios of interest. At this stage of model development, it is too early to have confidence in such predictive capability. Nonetheless, one can look forward to that possibility and make a few predictions.

In the case of the atmospheric corrosion of copper, the damage function contains two types of terms: the A-F and α-ϕ constants that must be determined by computer model studies that draw upon relevant laboratory and field data, and the concentrations of the causative corrosion agents. Just as corrosion rates are related to the atmospheric concentrations of corrosive species, so those concentrations are related to the rates of emission of those species. Sulfur dioxide is probably the most important agent, and oxides of nitrogen probably next. Although SO_2 and NO_x have some natural sources, most emissions are from the combustion of fossil fuels and other human activities. [14] The degree to which these activities occur in the vicinity of or upwind from statues and monuments will have a major impact on the longevity of those objects of art and heritage.

Since objects of culture and art are perceived as having been created for existence over long periods of time, it is instructive to ask what changes can be foreseen in SO_2 and NO_x in the coming several decades. The consensus of experts is that anthropogenic emissions of SO_2, now at about 65 megatonnes of sulfur per year, will at least double over the next century, largely as a result of increased combustion of sulfur-containing coal. [15] In the case of NO_x, now at 21 megatonnes of nitrogen per year [14], the increases will be at least as high and probably higher. [16] Spatially, the increase will be far from uniform. The largest reserves of coal, the fastest growing populations, and the most rapid rate of industrialization all occur in Southeast Asia. Accordingly, emissions will grow strongly in that region. Figure 5 shows a projection of emissions of SO_2 and NO_x for the year 2020 on each of Earth's continents. [17] It is obvious that if these predictions are even approximately correct, the statues and monuments of Southeast Asia will be those most at risk in the 21st century.

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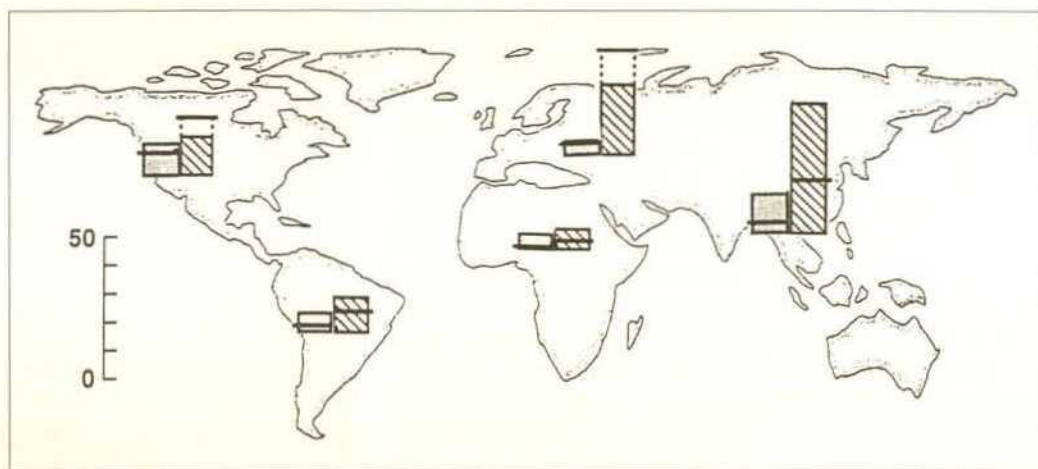17 J. N. GALLOWAY, Water, Air, and Soil Pollution, 85 (1995), p. 15.

Fig. 5. The anthropogenic emission rates of SO_2 (right bars) and NO_x (left bars) to the atmosphere on each continent, projected for the year 2020. The units are Tg (10^{12} g S or N) per year; the horizontal bars indicate 1990 emission rates (adapted from reference) [17]