

MARBLE DISCOLORATION AT THE TAJ MAHAL: A PROPOSED EXPLANATION

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INTRODUCTION

The Taj Mahal is a World Heritage Site, located in a predominantly agricultural landscape, dotted with small lime kilns burning high-sulfur coal, and in an environment conducive to frequent heavy dewfall. The construction is almost entirely of marble and other decorative stones. The prospect of pollution-related damage to the Taj is of considerable social and economic concern, and has generated a number of research programs to document pollution-related decay and to identify specific causes of observed discoloration.

Because of its orientation and of its design, the building offers a range of exposure situations that are of special interest in studies of the role of surface wetness as a promoter of the exchange of pollutants from the air to the surface. The Taj is oriented such that the direct beam of the sun can strike obliquely across the northern side at sunrise. Close inspection of marble discoloration patterns at the Taj reveals evidence compatible with the hypothesis that air pollutants are most efficiently transferred to the surface of the Taj in the early morning, when the structure is wetted by dew and when atmospheric mixing is adequate to bring pollutants into contact with the surface of the building. Figure 1 is a drawing illustrating the pattern of discoloration evident in a niche on the northern side of the Taj. The hypothesis concerning the relevant transfer processes and the evidence supporting the hypothesis are discussed below.

THE ROLE OF TIME-OF-WETNESS

The concept of "time of wetness" is basic to studies of pollution damage to materials surfaces. The origin of time-of-wetness (ToW) as a concern appears to lie mainly with considerations of corrosion of metals. Vernon (1931, 1935) reports, for example, that clean metal surfaces do not corrode significantly when the relative humidity is below about 60% (approximately), but when $RH > \text{about } 80\%$, surface wetness can accelerate metal corrosion due to the presence of relatively small amounts of atmospheric sulfur dioxide. Existing standards refer to ToW accordingly, as the proportion of the exposure period for which the environmental relative humidity exceeds some predetermined critical value, typically 85% for metals (see Guttman and Sereda, 1968). Extension to the case of stone degeneration is complicated by the fact that the electrochemical corrosion mechanisms that are promoted by the presence of surface moisture on metals may have no close analog in the case of stone. Specifically, the critical value for the relative humidity to start the process of stone degeneration may differ substantially from the value appropriate for metals. Nevertheless, field data show that ToW is important in the corrosion of stone (e.g. see Martin and Price, 1981), although perhaps with an important secondary role of temperature.

Moisture supplied by rainfall presents a substantially different problem. A major effect is to cleanse exposed surfaces of deposited particles and salts formed by surface reactions with atmospheric trace gases. In addition, there is convincing evidence of the direct interaction of "acid rain" with carbonate rock (see Reddy et al., 1986). The product of the chemical reaction is partially soluble, and tends to be washed from the surface. In this regard, we might expect to find surfaces exposed to direct impact of precipitation to be cleaner but possibly more eroded than surfaces that are sheltered from rain.

THE RESISTANCE MODEL

It is instructive to consider the time variability of the processes that cause ToW to be a critical concern in the context of damage to stone. In order for pollutants in the air to be transferred to a material surface, it is necessary to have (a) efficient turbulent transfer through the atmosphere, (b) easy exchange across the thin layer of air in immediate contact with the surface and (c) rapid uptake at the surface itself. These three factors may be considered in terms of a multiple-resistance model, in which there are three major resistance components (R_a , R_b and R_c ; typically in units of seconds/cm) corresponding respectively to aerodynamic transfer, transfer across the near-surface laminar layer and transfer to the surface from air in contact with it. These resistances are thought of as elements in an electrical circuit, through which the current flow is considered to be an analog of the flux of pollutant (F ; g/m²/s) to the surface. The technique is widely used for studies of pollutant deposition to vegetation (Wesely and Hicks, 1977, and as under the U.S. National Acid Precipitation Assessment Program; see Hicks, 1985). Here, the philosophies in current vogue for studies of deposition of sulfur dioxide to plants are extended to the case of materials surfaces.

In this multiple-resistance approach, the conductance (k ; cm/s) associated with the net transfer from the atmosphere to an individual surface exposed in it is then expressed in terms of the total effective resistance:

$$k = 1/(R_a + R_b + R_c).$$

It should be noted that this conductance relates deposition at a specific surface to air concentrations at some distant point. Atmospheric scientists refer to a "deposition velocity" defined similarly to k , but in which R_b and R_c represent spatial average characteristics of the atmosphere-surface boundary. In both cases, the role of surface wetness is to modify the surface resistance, R_c . For sulfur dioxide, a liquid water film on the surface will promote uptake unless the liquid is acidic (pH < 3.5, approximately) or is enriched in dissolved sulfur dioxide. Such enrichment might occur in the case of falling rain, when the droplets arriving at building level contain dissolved sulfur dioxide in equilibrium with the air through which they fell, or in the case of extended exposure to sufficient atmospheric concentrations that sulfur dioxide concentrations in the liquid phase reach equilibrium with the gas phase, which then limits further transfer. Neither constraint is likely to be applicable in the case of substrates for which oxidation of sulfur dioxide to sulfate occurs in solution, such as for a wet marble surface.

Even though the presence of surface moisture undoubtedly reduces R_c to near-zero for sulfur dioxide, it does not mean that uptake rates are high

unless the other contributing resistances (R_a and R_b) are also small and concentrations of sulfur dioxide are high. Figure 2 presents a hypothetical time sequence of all of the relevant quantities. The curves are intended to represent typical behavior patterns (drawn to illustrate the importance of time simultaneity of different processes, as is emphasized here), not detailed characteristics for any particular circumstance.

For the case of the aerodynamic resistance, R_a , the curve drawn in Figure 2 illustrates the large resistances imposed by the stratified atmosphere at night, the rapid reduction in resistance following dawn (assumed here to be at about 0600, with sunset at about 1800), the low resistance associated with daytime convection, the rapid increase in resistance starting a couple of hours before sunset, and a short period of extremely stable stratification that typically follows sunset. For R_b , direct linking to the near-surface wind speed is assumed, with near-calm conditions at night.

The effects of dewfall are represented in Figure 2 by plotting the proportion (W) of the surface that is wetted, and by estimating the consequences of this wetting on the surface resistance R_c (assumed to be relevant to the case of sulfur dioxide exchange; see Judeikis and Stewart, 1976). The values of the three resistances are combined to produce overall conductance values (not shown in the diagram), which are then applied to a hypothetical concentration distribution in order to estimate surface deposition rates F . The concentration "data" are meant to correspond to an area surrounded by low-level sources that typically inject emissions into a level some hundred meters above ground level (after accounting for appropriate plume rise) and maintain night-time near-surface concentrations at about 50% of daytime values. Fumigation is a common phenomenon which causes near-surface concentrations to increase as the mixed layer grows in the morning and finally draws to the surface pollutants that remained aloft overnight. A fumigation event is assumed to occur soon after dawn.

The consequences of all of these various environmental patterns are evident in the plot of the resulting deposition rate, F . The peak in the deposition rate evident in the early morning dominates the overall transfer of pollutants to the marble surface. This peak is due to several coincident phenomena, but primarily to the fact that surface wetness due to overnight dewfall persists long enough for pollutants from aloft to be transported and deposited to the surface by the increased vertical mixing caused by surface heating following sunrise. There is reason to suspect, therefore, that surface wetness occurring at night is not as important as wetness lasting through the daytime.

SOME VISUAL EVIDENCE AT THE TAJ MAHAL

Several factors combine to make the Taj Mahal an intriguing and instructive subject for investigation. In particular, its location is such that dewfall is frequent, and the common burning of high-sulfur coal in local lime kilns ensures high ambient concentrations of sulfur dioxide. Moreover, discoloration of the Taj is clearly evident in some locations, especially where sheltered from falling rain.

Figure 1, presented earlier, illustrates localized discoloration of marble evident at the Taj Mahal, in an area where it appears likely that direct sunlight at dawn can evaporate dew from some areas but not from others. The view is looking upwards, late in the afternoon, at the underside of a niche in a northern wall that is sheltered from direct

rainfall. Areas in the right side of the niche can receive the direct solar beam in the morning and hence dry rapidly after deposition of dew at night; they are less discolored than are areas to the left that are shaded from the morning sun.

DISCUSSION AND CONCLUSIONS

The variations represented in Figure 2 are intended to approximate the probable environment affecting the Taj. Observations made in January, 1986, and reports of local observers, confirm the frequent and typical presence of morning dewfall on exposed surfaces near the Taj, lasting several hours after sunrise. The low-level emission of sulfur dioxide from lime kilns in the surrounding area is undisputed. However, the hypothesis presented here to explain the link between environmental factors and the visible pattern of discoloration remains to be fully explored.

Other explanations for the observations are possible, and have not been rejected. Such alternative explanations include the effects of past cleaning of the surface, promotion of deposition of sulfur dioxide due to the presence of particles already deposited in some areas, effects associated with local turbulence, etc. It has not been the purpose here to explore all of these alternatives, but instead to present a hypothesis that is of potential general importance, in the hope that independent verification of its validity will be possible, and in the belief that the concept of "time-of-wetness" should be refined to include consideration of simultaneity between elevated pollutant concentrations and surface moisture.

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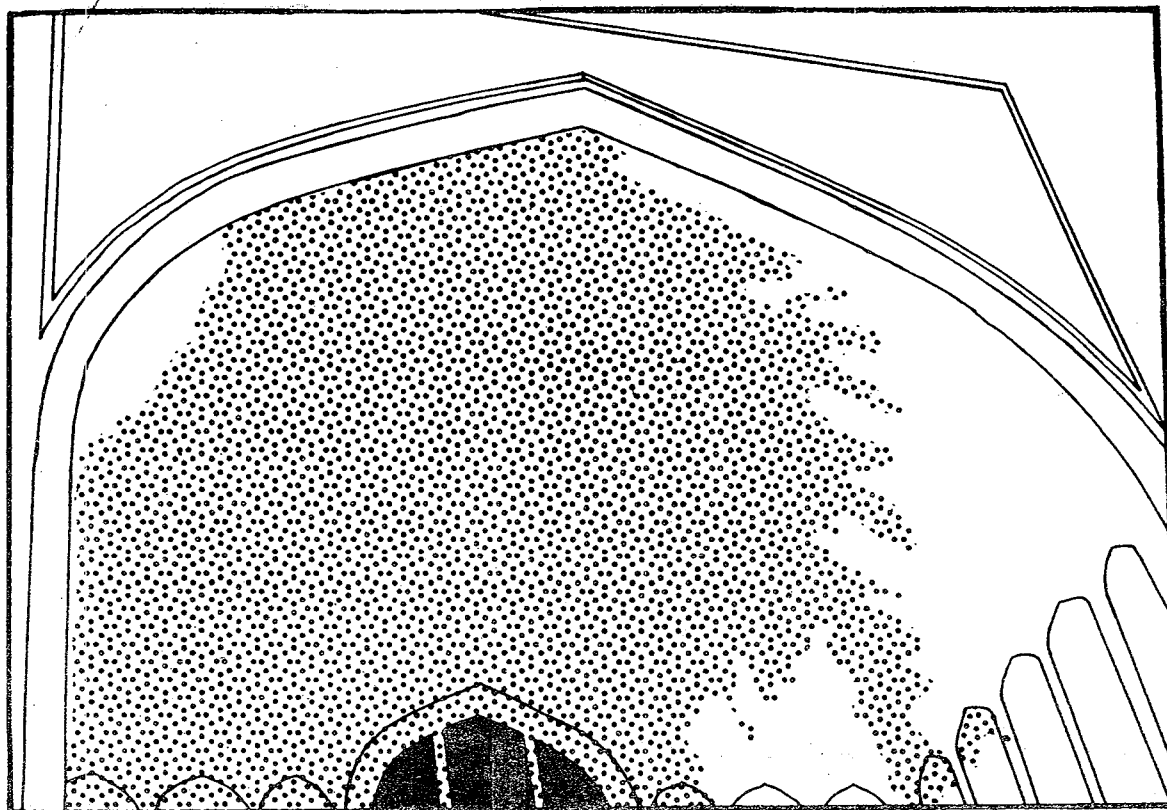


Figure 1. A view of a niche on the northern wall of the Taj Mahal, with clearly evident discoloration in an area that is most shaded from direct morning sun. The other side is not so discolored.

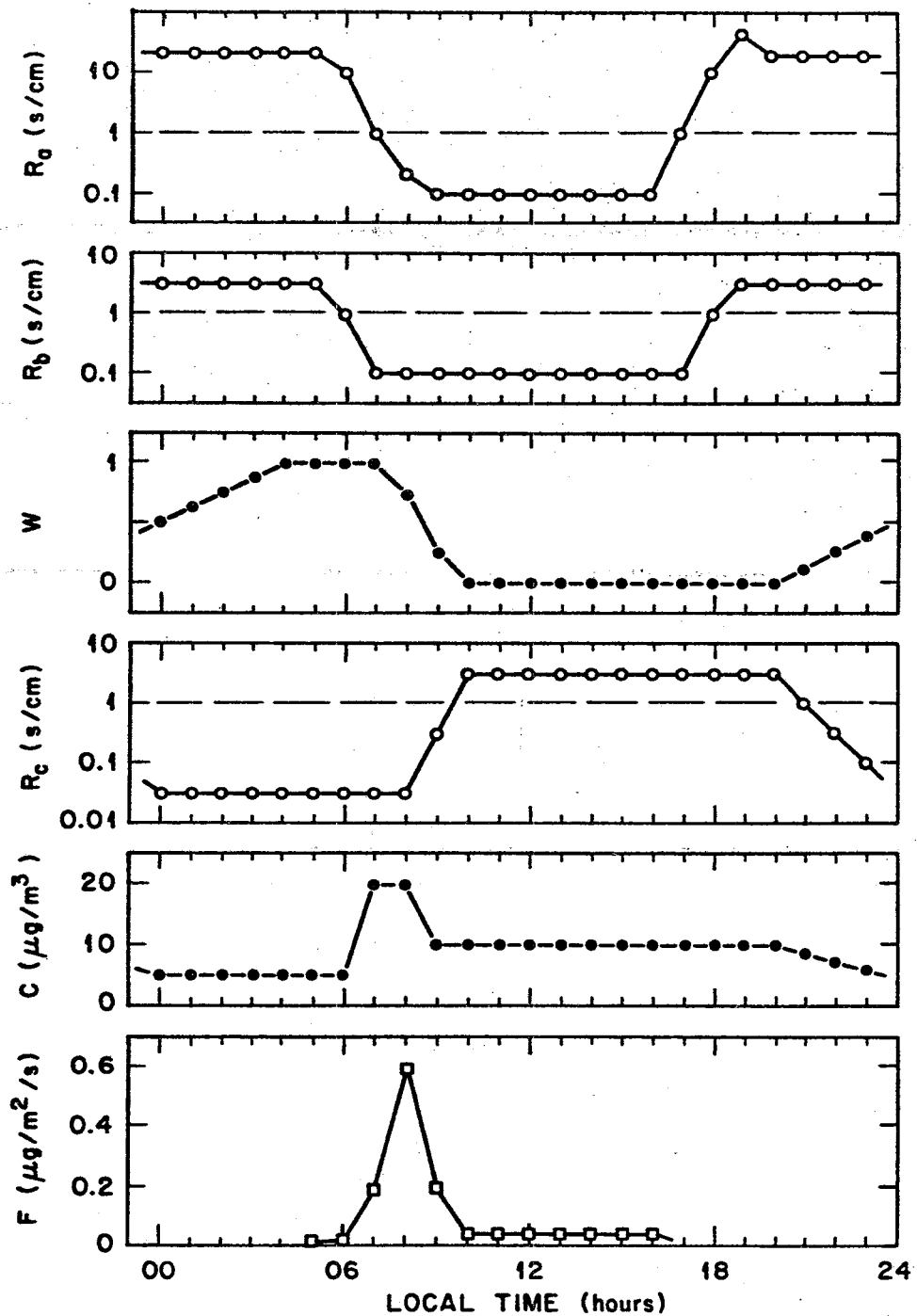


Figure 2. Hypothetical diurnal cycles of aerodynamic resistance (R_a), quasi-laminar boundary layer resistance (R_b), the proportion of the surface that is wetted (W), the surface resistance (R_c), atmospheric sulfur dioxide concentrations (C), and the flux of sulfur dioxide to relevant exposed surfaces (F). Sunrise is assumed to be at 0600; sunset is at 1800. The diagram is constructed to emphasize the importance of simultaneity among the contributing factors.

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SUMMARY

The pattern of marble discoloration at the Taj Mahal, Agra, India, appears to be most prevalent in areas that are both shaded from early morning sun and protected from rainfall. An explanation, based on atmospheric modelling concepts, will be presented that attributes, at least in part, the discoloration to the simultaneous occurrence of high concentrations of pollutants and condensation on the marble surfaces in the early morning.

Surface moisture, formed during the night, will remain longest on stone surfaces that are not exposed to the early morning sun. Pollution in the vicinity of the Taj Mahal stems from both low-level sources, especially small lime kilns, and tall stacks, e.g. the Mathura Oil Refinery. Pollution is thus released throughout the lower atmosphere in the area surrounding the Taj. At night, there is little mixing of the atmosphere and wind movement is minimal. These conditions do not favor pollution deposition. However, soon after sunrise, surface warming is known to cause a rapid increase in turbulent mixing, which draws the pollutants to the surface of the building. Since wet surfaces enhance the deposition of gaseous pollutants such as sulfur dioxide, it is hypothesized that the areas of marble still wetted by surface condensation will preferentially take up an early morning "pulse" of pollutants. This phenomenon could help explain the discoloration observed in areas shaded from the early morning sun, and should be considered along with other possibilities.

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La Décoloration du Marbre au Taj Mahal:
Une Proposition d'Explication

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Résumé

La décoloration du marbre au Taj Mahal à Agra, Indes semble suivre certaines conditions, notamment elle s'accroît dans les zones privées de soleil matinal et abritées de la pluie. Une explication basée sur les "atmospheric modelling concepts" sera présentée, attribuant, du moins en partie, la décoloration au double fait de la concentration élevée des polluants et de la condensation sur les surfaces de marbre tôt le matin.

L'humidité de surface, accumulée pendant la nuit, restera le plus longtemps sur des surfaces qui ne sont pas exposées aux premiers rayons du soleil. La pollution aux alentours du Taj Mahal provient à la fois des fours à chaux à bas niveau et des hautes cheminées comme celles de la raffinerie de Mahtura. Ainsi la pollution circule à travers la basse atmosphère autour du Taj. Pendant la nuit l'atmosphère est calme et il y a peu de vent. Ces conditions ne favorisent pas le dépôt de polluants. Néanmoins, juste après le lever du soleil, on sait que l'échauffement de la surface de la terre occasionne une rapide augmentation qui pousse les polluants à se déposer sur la surface du bâtiment. Comme les surfaces humides attirent les polluants gazeux tel que le sulfure de dioxyde, on formule l'hypothèse que les parties de marbre encore mouillées par la condensation accapareront les polluants de début de la matinée. Ce phénomène pourrait expliquer la décoloration observée dans les parties protégées du soleil matinal et devrait être pris en considération entre autres possibilités.