MODELING LIMESTONE DISSOLUTION BY ACID RAIN

Michael M. Reddy, United States Geological Survey, Denver Federal Center, Lakewood, CO. 80225

Susan Sherwood, Preservation Assistance Division, United States Park Service, Washington, D.C.

Bruce Doe, United States Geological Survey, 12201 Sunrise Valley Drive, Reston, VA. 22092

Summary

Acid precipitation has been related to environmental and ecological damage; however, the extent to which acid deposition will attack materials is unclear. In this paper we demonstrate the use of chemical models, based on equilibrium and kinetic expressions, to define the limiting cases of acid rain damage to calcium carbonate building stone. Two cases were examined: (1) Limestone dissolution to equilibrium by a fixed volume of rain (equilibrium control) and (2) Limestone dissolution by a fixed composition solution (kinetic control).

Three rain pH values, bracketing the range of acid precipitation commonly encountered, were used for the calculation. Limestone dissolution and associated surface corrosion increase with decreasing pH under equilibrium control. This change reflects the increasing calcite solubility with decreasing rain pH. Limestone dissolution is much greater and exhibits a more pronounced pH dependence under kinetic control. Factors, such as material aspect and runoff hydrodynamics, regulate whether dissolution is by equilibrium or kinetic processes; thus they are important in evaluating acid-precipitation damage to susceptible materials. This analysis suggests that, where material loss is regulated by kinetic processes, relatively small decreases in precipitation pH will lead to significant increase in material damage.

The chemical modeling techniques discussed briefly here appear to have application in assessing the potential for acid rain damage to stone structures and monuments. Field exposure of representative stone at carefully monitored sites has been incorporated into the study plan. Experimental weathering data from these sites is currently being collected. It is our hope to relate these weathering rates to important acid rain and air pollution characteristics.

Introduction

Air pollution and acid rain have been related to environmental and ecological problems in urban and rural areas of Europe and North America. These environmental contaminants also may accelerate deterioration of stone historic monuments and cultural resources.[1-3] Indeed, recent investigations by Doe and others (U.S. Geological Survey, oral commun., 1984) are documenting damage to monuments and other stone structures in Washington, D.C.

An understanding of the physical and chemical processes involved in stone deterioration is important in identifying sources of damage, proposing regulation and developing effective protection measures. Unfortunately, several gaps exist in our understanding of damage to these resources. For example, it is unclear to what extent acids present in rainfall (e.g. sulfuric and nitric acids) and air pollutants (e.g. sulfur and nitrogen oxides, ozone and particulates) contribute separately or synergistically to the observed cultural resource damage. The interaction of climatological and meteorological factors with ambient pollutant levels is also an area of uncertainty.

As a preliminary step in assessing the impact of acid rain on susceptible cultural resources we present here an application of chemical models to two hypothetical situations involving acid rain interaction with limestone. Chemical equilibrium and kinetic models of the calcium carbonate dissolution process by dilute solutions of sulfuric acid are used to estimate the extent of damage as a function of rain pH. A brief description of a field exposure program, planned to give field verification to the model results, is presented as well.

Procedures

Dissolution Calculations

Equilibrium

The aqueous model PHREEQE has been used to calculate the changes in rain composition following reaction with a limestone surface.[4,5] The calculation assumed that a calcite surface reacted to equilibrium with acid rain of varying initial pH with the system open or closed to atmospheric exchange of carbon dioxide.

Kinetic Limitation

The second limiting dissolution rate was based on the kinetics of calcite dissolution.[6] For this case initial rates of reaction are calculated and are assumed to apply over the period of reaction. This corresponds to a situation where negligible reaction has occurred; thus, solution composition remains constant. It is assumed that a sufficiently large amount of precipitation reacts with the limestone surface. The extent of reaction is limited only by the forward rate of the calcite dissolution process at the initial pH of the

rain.

Field Exposure

The research design for field experiments was adopted by analogy with a design for metals exposure (David Flynn, U.S. Dept. of Interior, personal communication). This design, which minimized extraneous experimental variability, allowed identification of the major processes involved in stone deterioration.

A wide variety of physical and chemical techniques are available to characterize damage to stone cultural resources.[7] Techniques selected for use in this program are well suited for quantitative damage assessment over short time intervals.

An overview of the Stone Exposure Program has been recently presented by Sherwood and Doe.[8] Limestone and marble were selected as the first carbonate stones for study because these materials comprise a significant cultural resource in acid-rain impacted areas, and resources fabricated from these materials would be susceptible to acid-rain damage. Also, it was possible to expose research stones representative of material currently at risk.

Exposure Sites

Stone exposure sites were positioned along a gradient (David Flynn, U.S. Dept. of Interior, personal communication) in precipitation acidity in the Eastern United States: Chester, N.J.; Newcomb, N.Y.; Research Triangle Park, N.C. and Washington, D.C. Meteorological and air quality data are monitored at each site.

Research Stone

Ross and Knab have recently summarized the procurement and characterization of specimens used for field exposure.[9] The stone study blocks, 3.5 feet by 4 feet by 9 feet in size, were limestone from Bedford, Indiana (Salem Limestone) and marble from Danby, Vermont (Shelbourne Marble). These specimens were cut and commercially finished into slabs measuring one foot by two feet by two inches at mills, located near each quarry. Slabs from the mid-portions of each study block were selected for field exposure. All aspects of stone quarrying and fabrication were supervised by project personnel. Sample inventory and exposure history of all research stones involved in the program is coordinated by A. Youngdahl of the Argonne National Laboratory.

Chemical Analyses

Field and laboratory analytical procedures were adapted, in so far as possible, from the recommendations of the National Atmospheric Deposition Program. A detailed description of the instrumental specifications and techniques for pH and conductance measurements are given elsewhere.[10]

Samples underwent an extensive suite of chemical analyses by Inductively Coupled Plasma Atomic Emission Spectrometry for metal ion determinations and Ion Chromatography for anion determinations.[11,12]

Insoluble residues resulting from weathering, such as clays or iron minerals, are not being examined. Future investigations of changes in the stone surface chemistry and mineralogy by M. Ross may yield information about these substances.

Estimates of precision and accuracy for the analytical procedures were obtained by analyzing standard reference water samples coincidental with rainfall and runoff. For example, reference water samples were diluted to a concentration range similar to that of rainfall. Recovery values calculated for this diluted standard reference sample ranged from 97 percent to 106 percent with a coefficient of variation of 2 percent for cation determinations and 5 percent for anion determinations. Other checks on laboratory data quality included: calculation of ion balances, analyses of blank samples and analyses of minor constituents.

Results and Discussion

Dissolution Calculations

Equilibrium

Details of the basic assumptions and mathematical techniques involved in solving problems dealing with multicomponent chemical equilibria are presented, with a comparison of the results of several frequently used computer programs, by Nordstrom and others.[13]

Runoff pH values for each of three rainfall pH's, and the corresponding equilibrium calcium concentrations are presented in Table 1. All acid present is assumed to be sulfuric acid. Erosion rates are expressed in units of millimeters of calcium carbonate removed per millimeter of rainfall for the limiting case of very long contact time before runoff. The last column in Table 1 shows the limestone material loss rate converted to microns of calcite removed from the test stone for an arbitrary annual rain fall (using a calcium carbonate density of 2.4 grams per cubic centimeter). Dissolution rates in Table 1 treat the input rainfall as a fixed amount of acid that reacts to equilibrium with the limestone. This situation would be analogous to a limestone surface receiving only wet precipitation with sufficient contact time to allow equilibrium. The equilibrium material loss will be reduced by kinetic and hydrodynamic factors.

This equilibrium calculation assumes that all acid present in rainfall reacts with the exposed stone surface. If these conditions are

not met, less material will be lost.

Calcium carbonate dissolution in equilibrium with atmospheric carbon dioxide (Table 1) exhibits a final runoff pH of approximately 8.2 over a rainfall pH range of 3 to 5; in the absence of atmospheric carbon dioxide, runoff solutions have a pH of 8 to 10.

Kinetic Limitation

Calcium carbonate dissolution rates were determined using an aqueous model and the kinetic rate expression of Plummer and others for a fixed set of solution conditions.[6] The calculation yields depth of material removed as a function of precipitation pH. This situation is analogous to a steeply-sloping stone surface receiving runoff from a relatively large drainage area in a high rainfall location. Results of this calculation, which assume a uniform rate of weathering over the stone surface, are given in Table 2. The forward reaction rate is given in units of millimoles per square centimeter of exposed surface per second. Rates of surface loss are given in units of millimeters per second and in units of micrometers per year.

The reaction rate calculated in this way is strongly dependent on the hydrogen ion rate constant, k_1, a transport rate constant. Because of the dependence of transport rate on solution hydrodynamics, the value of k_1 could vary (from the value used here to 1/5 that value) over the stone surface. An additional complication is that at impact k_1 values would be large, but as a laminar film slides off the stone surface the value of k_1 would decrease (N. Plummer, personal communication).

The kinetic model differs from the equilibrium model in an important way. In the equilibrium model, (as mentioned above) a fixed amount of rainfall reacts with the stone surface to reach chemical equilibrium. However, in the limiting kinetic model the composition of the solution phase is held constant allowing dissolution to be governed only by the reaction rate. In most practical applications, this rate, determined for circumstances equivalent to stone surface continually wetted by acid precipitation, is too great. Most surfaces are wetted only a fraction of their exposure time, and most surfaces have sufficient reaction contact time with rainfall to neutralize much of the acidic deposition. However, it does not seem impossible for some selective areas in buildings and monuments to be susceptible to kinetically limited dissolution. Under these situations the potential for material damage, with slight changes in the average rainfall pH, would seem to be pronounced. Selective erosion of carbonate surfaces may be a practical example of kinetically limited dissolution.

The role of sulfate in calcium carbonate building material weathering may be important.

A gypsum skin forming on a calcium carbonate surface may alter both the equilibrium and kinetic aspects of that surface's weathering. Several investigators are actively looking into this process (M. Kingston, personal communication).

A comparison of the material loss in Tables 1 and 2 illustrates the difference between the equilibrium and kinetic limiting rates over the rainfall pH range of interest. These results point out the overriding importance of material orientation and precipitation flow on damage. Erosion rates calculated using the equilibrium rate, show a moderate pH dependence. On the other hand, for a material under kinetic control the loss per year at pH 5 would be more than three orders of magnitude greater than under equilibrium control.

Field Exposure

To obtain a perspective on which acid-rain dissolution mechanism may be most appropriate for material damage a field exposure program was begun in August, 1983. The first year of this project involved selection of an experimental design, and establishment of the four sites. Installation of the field experiment was begun in May, 1984. Only limited field data are presently available. This report addresses initial results and their relation to the assessment of acid rain damage to limestone and marble.

Rainfall Collection Efficiency

Rainfall collection by the exposure racks (Figure 1) has been calculated from the interception area and has been measured from an unoccupied collector (referred to as the blank sample).

The runoff volume from the blank and each of the stone slabs is linearly related to the rainfall amount during the collection interval as determined by a standard raingage. In each case, the linear relationship had a correlation coefficient value greater than 0.95. Runoff volume from marble was within one percent of runoff volume calculated from the interception area. Collection efficiency for the limestone was smaller than that for marble, because of the more porous nature of the limestone, and because of a faster evaporation rate from the rough limestone surface.

Comparison of Field and Laboratory Measurements of pH and Conductance

Several rainfall and stone-runoff chemical characteristics were measured both at the time of sample collection and in the laboratory at the start of sample analyses.

For summer 1984 samples from North Carolina, field pH values of runoff samples ranged from 4.06 to 5.55 for blank samples, from

7.96 to 8.94 for limestone and from 7.05 to 8.45 for marble. Field mean pH values (standard deviations) were 4.46 (0.72) for the blank, 8.06 (0.27) for limestone and 7.65 (0.23) for marble. Laboratory pH values measured in Denver, Colorado, differed significantly from field pH values because of changes in sample carbon dioxide partial pressure during transit. The mean difference between field and laboratory pH measurements was greater for the limestone runoff (1.0 pH units) than for the marble sample (0.4 pH units) or the blank (-0.45 pH units). Conductance values measured onsite and in the laboratory were also significantly different at greater than the 95% confidence level.

Composition of Runoff from Stone Slabs

Chemical analyses were completed for rainfall and runoff samples from several sites. Discussion of variation in rainfall and runoff chemistry with climatological, meteorological and air quality site parameters must await verification and merging data bases for each site. However, several observations can be made from initial chemical analyses of the runoff samples. Calcium ion was the predominant cation in precipitation as well as in the stone runoff. Stone runoff calcium ion concentrations were ten to one hundred times greater than concentrations seen in rainfall. Magnesium ion also showed a greater than ten fold increase in stone-runoff concentration compared to rainfall.

Other major and trace metal ions had less pronounced differences between rainfall and runoff chemistry. Sulfate ion concentrations were increased in the stone runoff relative to rainfall; other anionic component concentrations were similar in rainfall and stone runoff.

Approach to Chemical Equilibrium

Runoff from the experimental stones reflected the dissolution reaction of acid present in rain with the basic calcium carbonate surface. During this dissolution reaction, and the concomitant approach to calcite equilibrium, carbon dioxide may participate in the reaction; carbon dioxide may either be taken up or lost by the runoff solution. Approach to chemical equilibrium can therefore be examined both from the perspective of: 1) calcite equilibrium (which regulates the dissolution of the carbonate-mineral surface); or 2) carbon dioxide equilibrium between the runoff solution and the atmosphere.

Both the calcite and carbon dioxide equilibria can be examined by using chemical models such as WATEQF.[14] Input data for the program were field pH, total dissolved calcium concentration and total alkalinity. Calcite equilibrium often is monitored by calculating the ratio of the ion activity product (IAP) of calcium and carbonate ions in solution to the

calcite solubility product (K_{sp}). This ratio, the calcite subsaturation, Ω_c ($\Omega_c = IAP/K_{sp}$), indicates the approach of the reaction to equilibrium. Subsaturation values calculated for preliminary-runoff experiments range from near equilibrium for limestone to subsaturation values one fiftieth of the equilibrium value for marble.

Carbon dioxide equilibrium is related to the calcium carbonate dissolution process, the rates of gas transfer, and carbon dioxide formation. For the preliminary runoff experiment carbon dioxide partial pressures appeared to be most strongly influenced by the final runoff solution pH. Carbon dioxide partial pressures in the runoff solution ranged from one tenth to five times the atmospheric value.

Differences between limestone and marble dissolution appear significant. These differences may arise because of greater surface roughness and (or) porosity of the Salem Limestone in comparison with the Shelbourne Marble. It is noteworthy that even though the Salem Limestone may have greater net dissolution, the Shelbourne Marble may exhibit the first perceptible material damage, i.e., the loss of polish.

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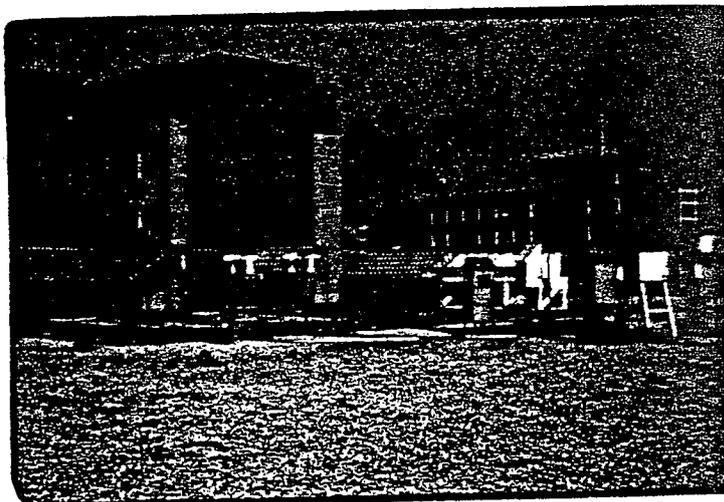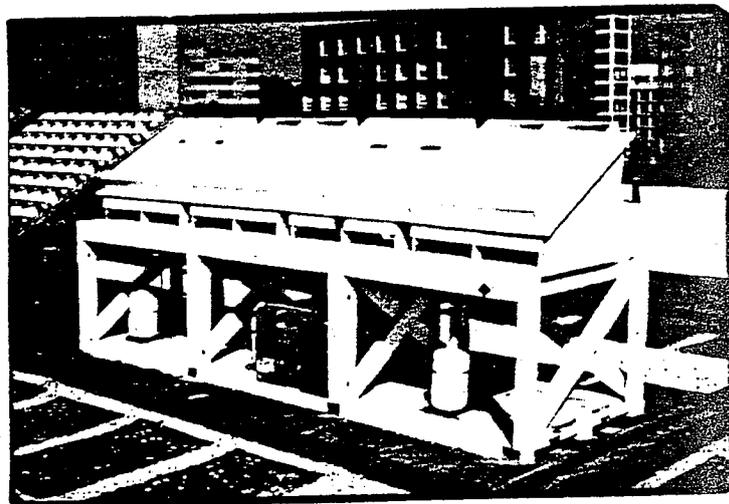
Figure 1. Research stone exposure racks at the Martin Luther King Public Library, Washington, D.C.

Table 1. Calcium carbonate dissolution by dilute sulfuric acid solutions. Dissolution amount calculated for equilibrium of 30 inches rainfall on the research stone specimen.

Initial rainfall pH	Equilibrium runoff pH	Equilibrium runoff calcium concentration, millimoles per liter	Surface Recession	
			millimeters of calcium $\underline{carbonate}$ X 10^6 millimeter of rainfall	micrometers of calcium carbonate $\underline{lost}$ 30 inches of rainfall
A. System in equilibrium with atmospheric carbon dioxide. *				
3.03	8.14	0.91	38	29
4.00	8.23	0.55	23	17
4.98	8.24	0.51	22	16
B. System closed to carbon dioxide exchange. **				
3.03	8.03	0.99	41	32
4.00	9.56	0.17	7	5
5.00	9.87	0.12	5	4

* Carbon dioxide partial pressure assumed to be $10^{-3.46}$ atmospheres.
** Assuming no carbon dioxide gas present in starting solution.

Table 2. Calcium carbonate dissolution by dilute sulfuric acid solutions. Dissolution amount and rate determined from an initial rate based on the equation of Plummer and others.[6]

Initial rainfall pH	Initial dissolution rate, R_f, $\dfrac{millimoles}{cm^2 \cdot sec.}$ x 10^6	Surface recession	
		$\dfrac{millimoles}{second}$ x 10^6	$\dfrac{micrometers}{year}$ x 10^{-3}
3.0	51.3	21.4	674.
4.0	5.23	2.18	69.
5.0	0.63	0.26	8.3

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