

DRY DEPOSITION OF SULFUR TO LIMESTONE AND MARBLE :

PRELIMINARY EVALUATION OF A PROCESS BASED MODEL. M.M.

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Sulfate distributions resulting from SO₂ dry deposition and sulfur (as sulfate) transport into carbonate stone exposed to ambient conditions at several research sites in the northeastern United States are interpreted using a pore water diffusion model.

Comparison of actual sulfate distributions observed in field samples (three months to five years exposure) with those predicted by the diffusion model illustrates that the best-fit diffusion coefficients are smaller than expected for this system. Model analysis suggests that a diffusionbased mechanism is partially responsible for the observed sulfate distributions.

"PREPRINT EXTENDED ABSTRACT"

Presented Before the Division of Environmental Chemistry

American Chemical Society

Denver, CO

March 29 - April 3, 1993

DRY DEPOSITION OF SULFUR TO LIMESTONE AND MARBLE : PRELIMINARY
EVALUATION OF A PROCESS BASED MODEL

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Dry deposition of sulfur dioxide and subsequent transport of sulfur into the interior of monument and dimension carbonate stone has been observed and measured at field sites in the eastern United States (1,2). Sulfate distributions in the two stone types were determined by ion chromatography analysis of solutions prepared by dissolving powders from successive 0.25 mm thick stone layers (3). Only the bottom most three briquette layers (those on the groundward surface), hereafter termed the x, y, and z-layers will be considered here. Plots of the sulfate distributions for both stone types exhibited similar sulfate profiles with time and depth (Figures 1 and 2). For both limestone and marble, the sulfate concentration ($\mu\text{g sulfate} / \text{g stone}$) is highest in the z-layer (closest to the groundward surface) and increases with time. The successively lower sulfate concentrations in the y and x-layers also increase with time.

A predictive model for sulfur transport in this stone type was developed using Fick's second law (unsteady diffusion into a semi-infinite slab) to describe the time and spatial sulfate distribution in limestone and marble test briquettes. The diffusion model

presented here assumes that a saturated calcium sulfate dihydrate solution is present in pores at the stone surface and that sulfur (as sulfate) is transported to the stone interior by molecular diffusion from the surface reservoir (Figure 3). Application of Fick's second law with appropriate boundary conditions is shown in equations (1) through (4). Here, t is time (sec), z is depth into the stone (cm), D is the effective diffusion coefficient (cm^2/s), and c is the sulfate concentration at time t and depth z . The sulfate concentration at the stone surface (in the pore water) is given by c_a and the initial sulfate pore water concentration in the briquette interior is c_o .

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} \quad (1)$$

$$c = c_a @ t > 0, z = 0 \quad (2)$$

$$c = c_o @ t = 0, \text{ all } z \quad (3)$$

$$c = c_o @ t > 0, z \text{ approaches } \infty \quad (4)$$

Transformation to the similarity variable, n , defined as

$$n = \frac{z}{\sqrt{4 D t}} \quad (5)$$

yields the solution to the diffusion problem :

$$\frac{c - c_a}{c_o - c_a} = \frac{2}{\sqrt{\pi}} \int_0^n e^{-t^2} dt = \text{erf}(n) \quad (6)$$

Comparison of the actual sulfate distributions (Figures 1 and 2) with those predicted by the diffusion model illustrates that the model under estimates the magnitude of sulfur accumulation in the stone and that the observed diffusion coefficients are smaller than those expected for this system (Tables 1 and 2). Best-fit analysis of the field

data to the diffusion model suggests that a diffusion based mechanism is partially responsible for the observed sulfate distributions (Figures 4 and 5).

Figures 4 and 5 are plots of dimensionless sulfate concentration vs. the similarity variable (dimensionless time at a given depth) for limestone and marble. Each figure shows the actual field data and the best-fit data. The surface boundary condition and the effective diffusion coefficient used for both the actual and best-fit points were determined by the least squares fitting routine (Tables 1 and 2).

Sulfate ion is lost from the surface reservoir by both transport to the stone interior and by reaction with calcium carbonate to form gypsum. The transport term is evident in equation (1), but the reaction term is absent; the diffusion model does not account for loss of sulfate due to reaction with carbonate. A reaction term, based on the kinetics of the calcium sulfate nucleation and crystal growth reaction is needed.

The diffusion model also assumes that forced diffusion terms (resulting from potential and / or temperature gradients) are negligible. In general, this assumption is valid for dilute solutions at relatively constant pressure and temperature. In the carbonate / sulfate system investigated here, the maximum sulfate concentration is that at the surface reservoir; saturated calcium sulfate dihydrate solution. This concentration likely is low enough for the dilute assumption to hold. Temperature and pressure variations in the stone pores are expected to be small.

The diffusion model presented here assumes maintenance of charge balance in the stone interior. Sulfate anion diffusion maintains electrical neutrality in the stones pores, either by diffusion of a counter ion (such as calcium) or by counter diffusion of an anion (such as bicarbonate). Incorporation of a charge development process into the diffusion model may require the addition of a diffusion equation similar to (1) for the counter ion and simultaneous solution of the two coupled equations.

The diffusion model predicts the general character of the sulfate distributions and field data fit the parameterized diffusion model well. Other processes that may be

important and warrant inclusion in future model developments are : reactions of sulfate with calcium carbonate walls, the simultaneous pore diffusion of other ions, partially saturated diffusion in the stone pores, and precipitation / crystallization processes due to wetting and drying of the stone.

References

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3. Reimann, K.J. Chemical alteration of limestone and marble samples exposed to acid rain and weathering in the eastern United States. In *Argonne National Laboratory Report ANL - 89/34*, Argonne National Laboratory, Argonne, Il, **1991**.

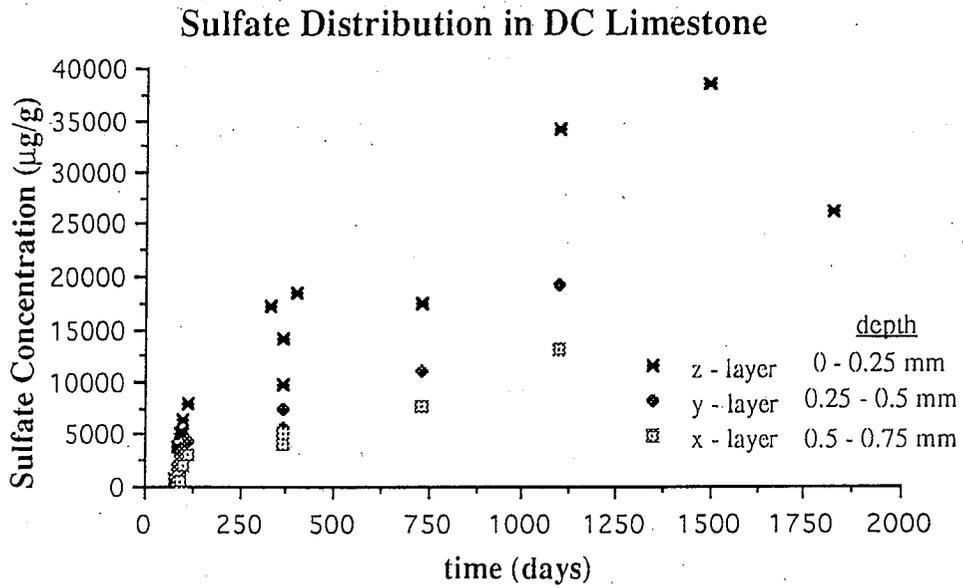


Figure 1. Sulfate distribution in limestone exposed at the field site in Washington, D.C. from 1984 to 1989.

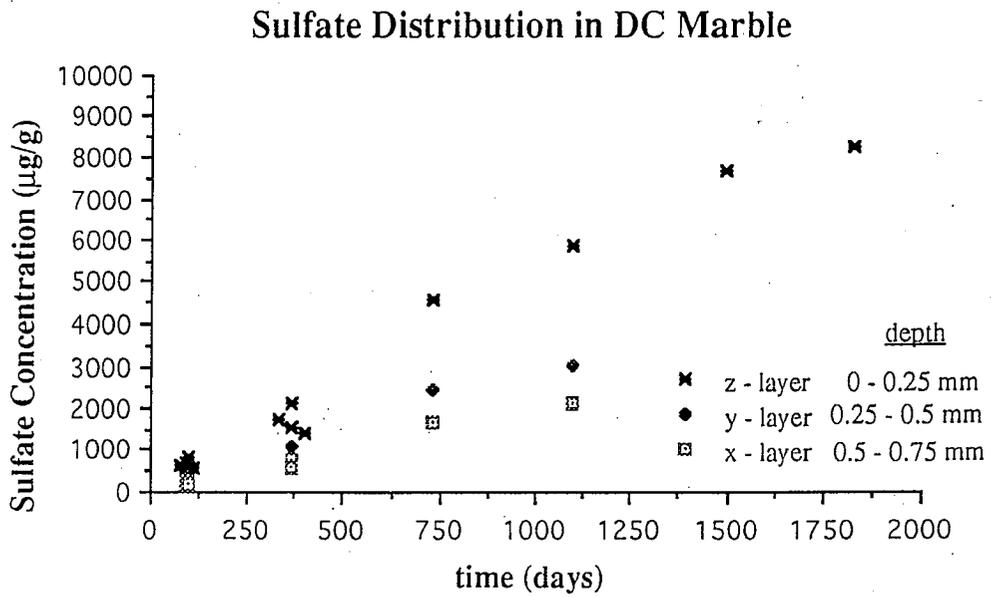


Figure 2. Sulfate distribution in marble exposed at the field site in Washington, D.C. from 1984 to 1989.

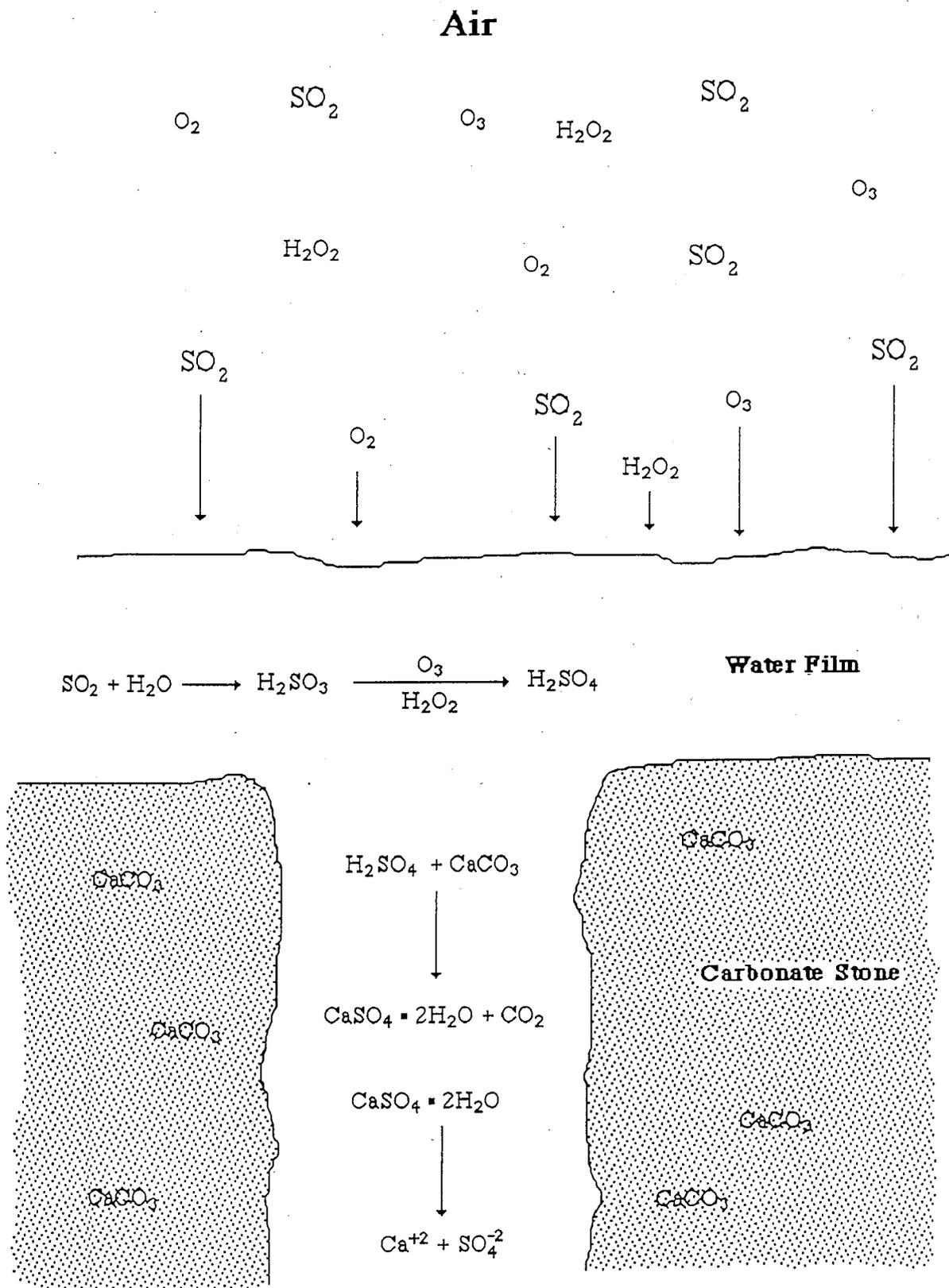


Figure 3. Dry Deposition Mechanism.

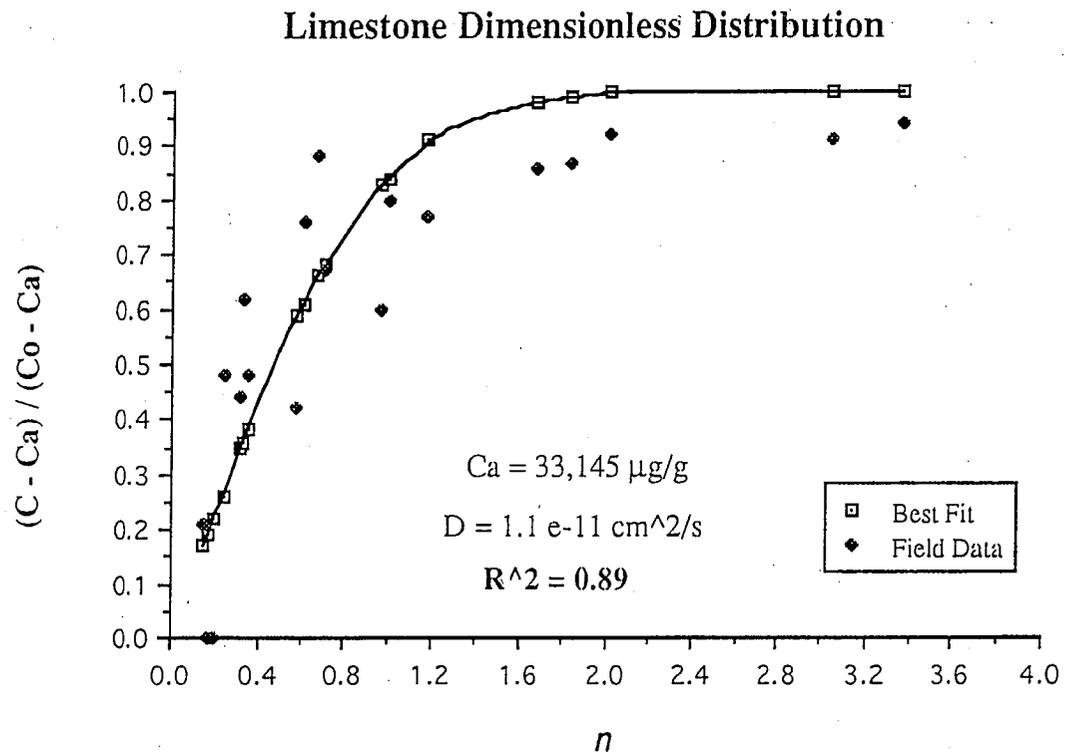


Figure 4. Dimensionless sulfate distribution in DC Limestone.

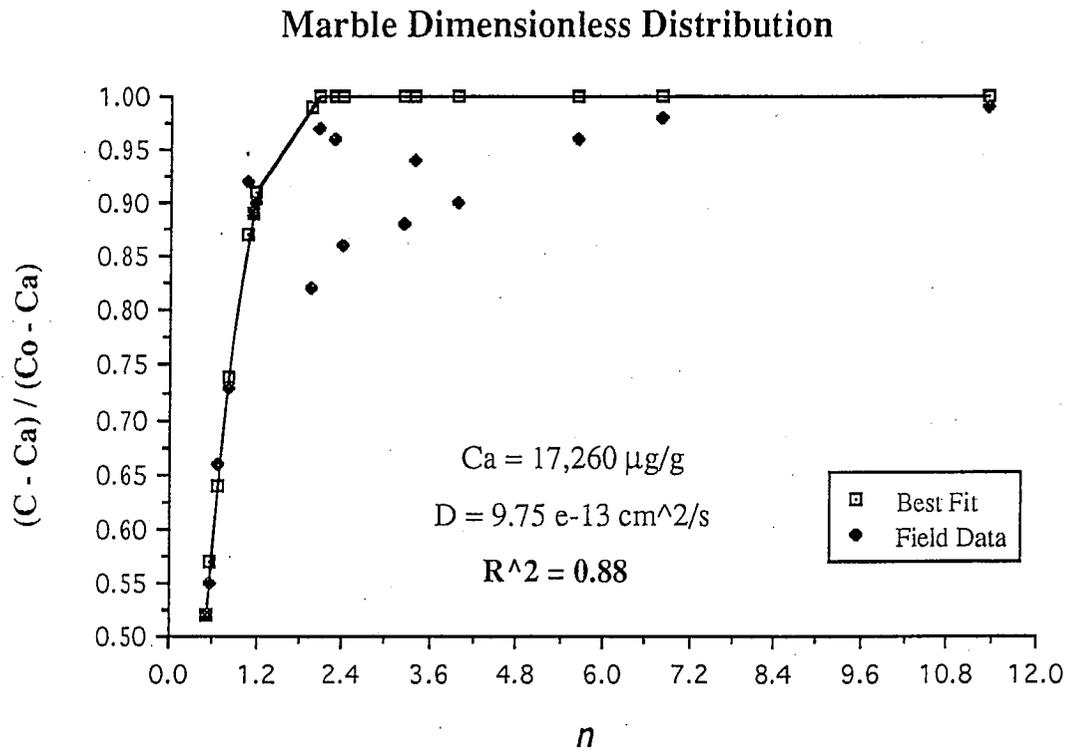


Figure 5. Dimensionless sulfate distribution in DC Marble.