

# Dry deposition of sulfur to limestone and marble: preliminary evaluation of a process based model

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## Abstract

Dry deposition of sulfur dioxide and transport of sulfur into the interior of monument and dimension carbonate stone has been observed widely. In this paper we describe a predictive model for sulfur transport in limestone and marble developed using Fick's second law (unsteady diffusion into a semi-infinite slab). Comparison of actual sulfate distributions with those predicted by the diffusion model illustrates that the model underestimates the magnitude of sulfur accumulation in the stone and that the observed diffusion coefficients are smaller than those expected. The diffusion model predicts the general character of the sulfate distributions and field data fit the parameterized diffusion model well.

## Keywords

Limestone, marble, dry deposition, sulfur, sulfur dioxide, stone damage

## Introduction

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 (Baedeker et al., 1990 and 1992). 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 (Reimann, 1991). Only the bottommost three briquette layers (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 / g stone) is

highest in the z-layer (closest to the groundward surface) and generally increases with time. The successively lower sulfate concentrations in the y and x-layers also increase with time.

## Model

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 temporal and spatial surface distribution of sulfate in limestone and marble test briquettes. The diffusion model described 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's interior by molecular diffusion from the surface reservoir (Figure 3). Application to 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 ( $\text{cm}^2/\text{s}$ ), 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  $c_s$  and the initial sulfate pore water concentration in the briquette interior is  $c_0$ .

$$\delta c / \delta t = D(\delta^2 c / \delta z^2) \quad (1)$$

$$c = c_s \text{ @ } t > 0, z = 0 \quad (2)$$

$$c = c_0 \text{ @ } t = 0, \text{ all } z \quad (3)$$

$$c = c_0 \text{ @ } t > 0, z \text{ approaches } \infty \quad (4)$$

Transformation to the similarity variable,  $\eta$ , defined as

$$\eta = z / (4Dt)^{1/2} \quad (5)$$

yields the solution to the diffusion problem:

$$\frac{c - c_0}{c_\infty - c_0} = \frac{2}{\sqrt{\pi}} \int_0^\eta e^{-t^2} dt = \text{erf}(\eta) \quad (6)$$

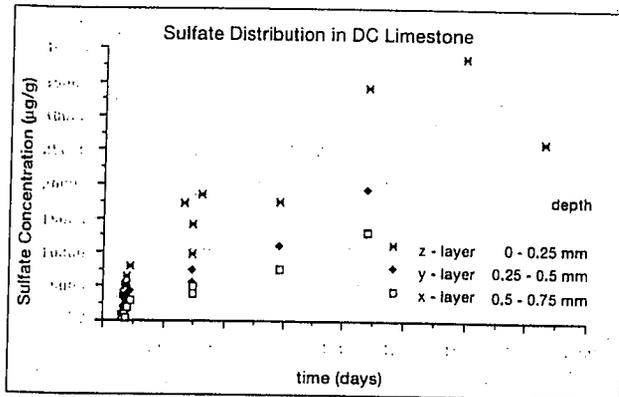


Fig. 1 - Sulfate distribution in limestone exposed at a field site in Washington, D.C. from 1984 to 1989.

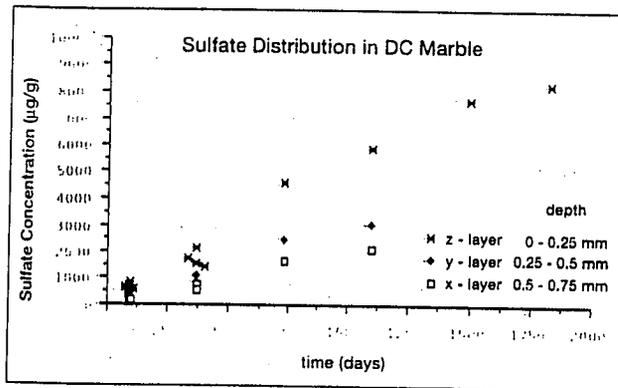


Fig. 2 - Sulfate distribution in marble exposed at a field site in Washington, D.C. from 1984 to 1989.

## Results and discussion

Comparison of the actual sulfate distributions (Figures 1 and 2) with those predicted by the diffusion model illustrates that the model underestimates 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 partly responsible for the observed sulfate distributions (Figures 4 and 5).

Figures 4 and 5 are plots of dimensionless sulfate concentration versus the similarity variable (dimensionless

time at 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 contained 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 (the concentration of the 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 mainte-

| Stone Type | Ca@95% confidence (µg/g) | Standard Deviation (µg/g) | Ca-model (µg/g) |
|------------|--------------------------|---------------------------|-----------------|
| Limestone  | 33,150+/-8,900           | 4200                      | 150             |
| Marble     | 17,250+/-8,600           | 4000                      | 2.0             |

Table 1 - Sulfate surface boundary conditions of Washington, D.C. stone from least squares minimization of differences between diffusion model predictions and field data.

| Stone Type | D @ 95% confidence (cm <sup>2</sup> s)                 | Standard Deviation (cm <sup>2</sup> /s) | D-model calculated* (cm <sup>2</sup> /s) |
|------------|--|---|--|
| Limestone  | 1.1 X 10 <sup>-11</sup><br>+/- 8.98X10 <sup>-12</sup>  | 4.22 X 10 <sup>-12</sup>                | 1.0 X 10 <sup>-8</sup>                   |
| Marble     | 9.75 X 10 <sup>-13</sup><br>+/- 6.94X10 <sup>-13</sup> | 3.28 X 10 <sup>-13</sup>                | 1.0 X 10 <sup>-8</sup>                   |

\* As determined by the stone porosity and tortuosity

Table 11 - Sulfate ion diffusion coefficients of Washington, D.C. stone from least squares minimizations of differences between diffusion model predictions and field data.

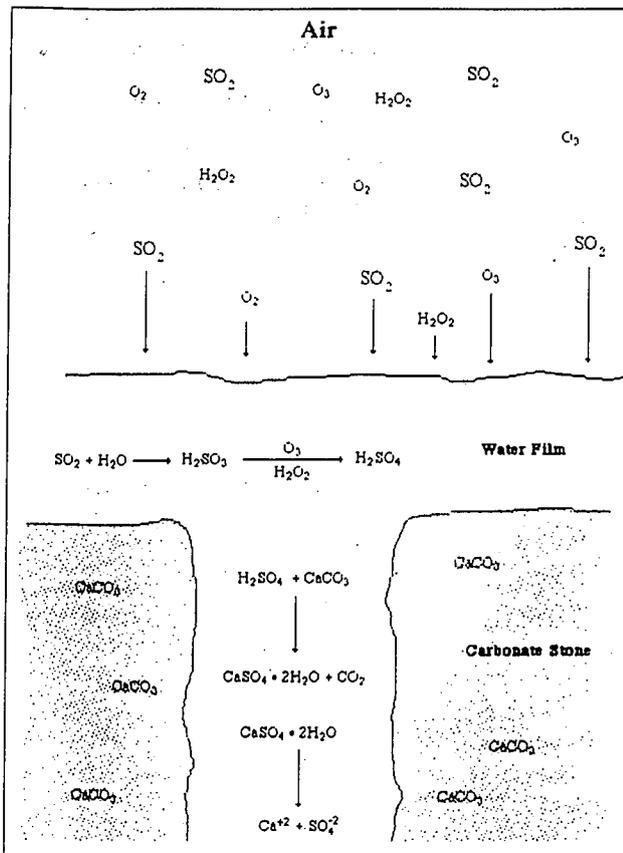


Fig. 3 - Dry deposition mechanism.

nance of charge balance in the stone interior. Sulfate anion diffusion maintains electrical neutrality in the stone 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 (Leith, 1993).

### Conclusion

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 pore 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 (Leith, 1993).

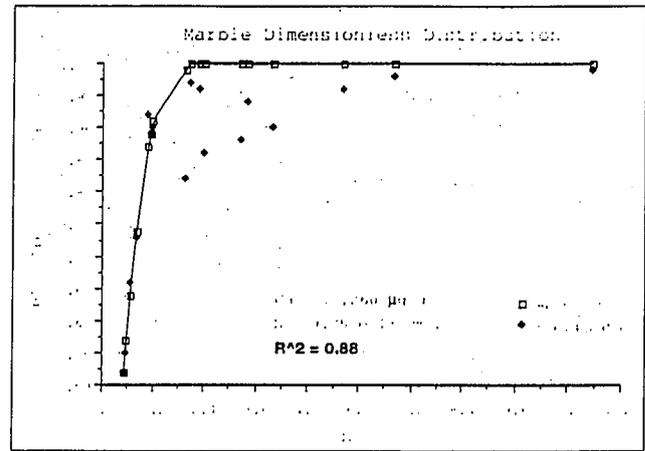


Fig. 4 - Dimensionless sulfate distribution in limestone exposed at a field site in Washington, D.C. from 1984 to 1989.

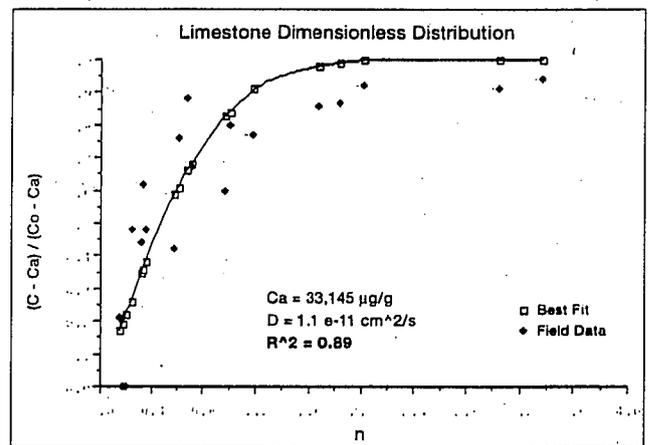


Fig. 5 - Dimensionless sulfate distribution in marble exposed at a field site in Washington, D.C. from 1984 to 1989.

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