REDUCING MARBLE-SO$_2$ REACTION RATE BY THE APPLICATION OF CERTAIN SURFACTANTS

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Abstract. Sulfur dioxide (SO$_2$), prevalent in the modern urban environment of industrial countries, attacks calcite (CaCO$_3$) in marble. As a result, a gypsum (CaSO$_4 \cdot$2H$_2$O) crust is produced at rain-sheltered surfaces while areas exposed to rain experience accelerated erosion. We have investigated the effect of certain surfactants as protective agents against SO$_2$ attack. We report that the anions oxalate (C$_2$O$_4^{-2}$) and oleate (C$_{17}$H$_{33}$COO$^-$) from solutions of their highly soluble alkali salt species are able to replace carbonate (CO$_3^{-2}$) in calcite producing less reactive substrate of oxalate and oleate of calcium. Experiments to measure the protection obtained by these treatments were carried out in the laboratory and field conditions at nearly 1ppm and 10 ppb SO$_2$ concentrations, respectively. We found that these treatments provided significant protection to marble exposed in sheltered areas, up to 30% reduction of reaction rate by treatment with 2 $\times$ 10^{-4} M sodium oleate and up to 14% by a 2 $\times$ 10^{-3} M with potassium oxalate solutions, but become ineffective over long term exposure when applied to surfaces exposed to rain. Carrara marble was used in the reported study. Ion chromatography was the analytical tool, which allowed precise measurements of ionic concentrations of these salts, the amount of their uptake by marble, and the thickness of the gypsum crust. X-ray diffraction allowed determination of the new minerals formed at the marble surface by the treatment with surfactants.

Keywords: gypsum, marble, oleate, oxalate, sulfur dioxide

1. Introduction

The decay of marble in the past century in industrial countries is mainly due to sulfur dioxide as evidenced by black crust made largely of gypsum. Such crusts are formed at surfaces that are protected from rain. The crusts eventually exfoliate reducing sculptures to hunks of rock. The unprotected surfaces in such environments, however, are subjected to accelerated erosion by the scouring action of acid rain (Gauri *et al.*, 1989; Thomson and White, 1974). As a result, the inscriptions upon such surfaces become faint and the details of relief highly reduced over time. The purpose of this article is to report results of a research whereby the atmospheric attack upon stone can be reduced.

Commonly used measure to protect statues is by the application of coatings which isolate marble from atmospheric SO$_2$. Such coatings, particularly when applied upon rain-protected surfaces, have often been found more harmful than

if the marble was left untreated. The reasons for the accelerated decay include the entrapment of water and water vapor in stone whereby the rate of reaction is enhanced. Further, many coatings absorb SO_2, which also accelerates the rate of reaction. The result is that after a short period of treatment the marble surface begins to peel. In this study, based upon certain earlier work (Hanumantha *et al.*, 1988), we have used a method to protect marble by changing the surface chemistry so that the buffering capacity of the substrate is reduced while the stone surface maintains its original permeability.

2. Materials and Methods

2.1. SAMPLE PREPARATION, TREATMENT WITH SURFACTANTS, AND MEASUREMENT OF CONVERSION

Rectangular slabs, measuring $2.8 \times 1.6 \times 0.6$ cm, were cut from large blocks of Carrara marble and polished with 400-grit silicon carbide powder. The samples were then cleaned ultrasonically in deinozed water to remove fine particulate and dried at 105 °C to a constant weight, and cooled in a desiccator. The weights were then recorded to determine changes in these resulting from later experiments to determine water adsorption.

Solutions of surfactants dipotassium monohydrogen phosphate (K_2HPO_4), potassium oxalate ($K_2C_2O_4 \cdot H_2O$) and sodium fluoride (NaF) were prepared at concentrations of 2×10^{-1}, 2×10^{-2}, 2×10^{-3}, 2×10^{-4} M and that of sodium oleate ($C_{17}H_{33}COONa$) at 2×10^{-3}, 2×10^{-4}, 2×10^{-5} M. The solutions were maintained at pH 8 by adding NaOH or HCl, as needed. Marble slabs, two in each case, were immersed in 25 ml of these solutions for 4, 10, 24, 34, 48 and 72 h. and then dried. The amounts of oxalate, phosphate, and fluoride ions taken up by the marble were taken as the difference in the initial and end concentrations of these ions in the solutions, which were determined by the use of ion chromatograph (Dionex, Model DX-100). After treatment, the samples were dried at 30 °C and the mineralogical composition of the surfaces determined by X-ray diffraction.

2.2. EXPERIMENTAL METHODS

To determine the effect of the treatments on exposure to SO_2 environment, two sets of experiments were carried out with a view to measure:
  1. Change of water-vapor adsorption by the samples in a humid atmosphere, and
  2. Change in reactivity in,
      a) an artificial atmosphere with nearly 1 ppm SO_2, and
      b) in an rain-protected outdoor exposure with ambient SO_2 concentration of 10 ppb.

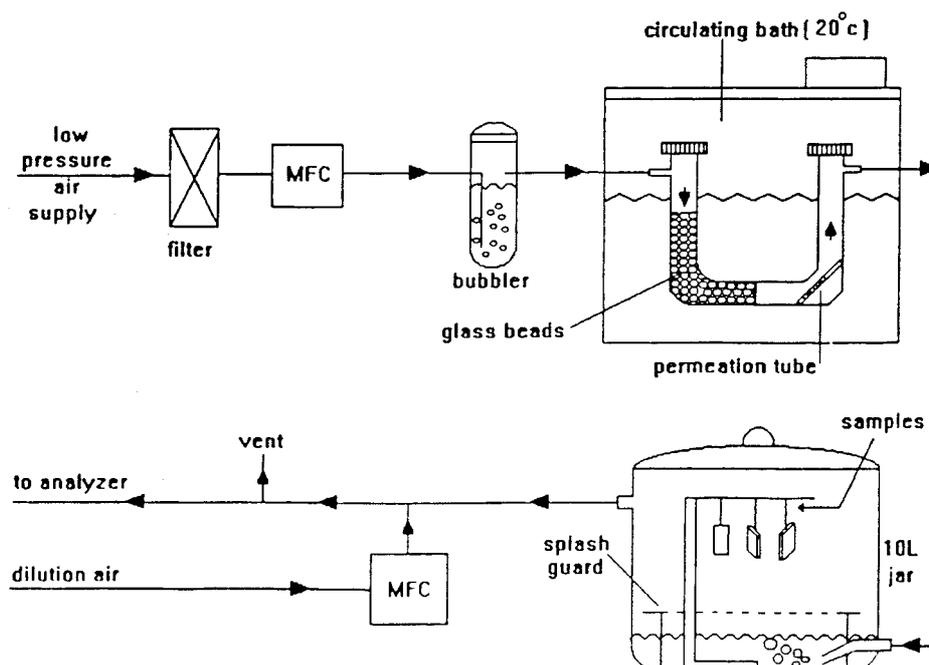In each experiment, treated and untreated samples were simultaneously exposed.

Figure 1. Reaction chamber showing generation of artificial atmosphere.

In the experiment to measure water-vapor adsorption, samples were placed upon perforated plates in a desiccator containing water at the bottom. The weight increase was recorded at time intervals until the sample weight was constant. The increase in weight was expressed as g m^{-2} of the sample surface.

In the experiment on SO$_2$ reaction, a set of samples was exposed in an atmosphere at a nearly 100% relative humidity in a reactor, which was a modified 10 L desiccator, shown in Figure 1. Some water was placed at the bottom of the reaction chamber. Moist air was passed over SO$_2$ permeation tubes, made by VICI Metronics, at a flow rate of 800 cc min^{-1}. This SO$_2$-air stream was injected in the reactor beneath the water table. After the water had reached equilibrium with the above concentration of SO$_2$, i.e., when a constant pH of the water had reached, were the samples exposed. It took several days for the water to reach the equilibrium with 1 ppm partial pressure of SO$_2$ in the atmosphere.

To expose to the SO$_2$-atmosphere, stated above, the samples were tied to a glass stand by nylon threads so that they hanged freely above the water table in the reactor. A maximum of four samples was exposed at a time in order to maintain a constant concentration of the gas in the reactor. The concentration of SO$_2$ in the reactor was determined from the permeation rate obtained from the weight loss of the permeation tube over time. This concentration was also confirmed by passing the gas mixture through a known volume of 3% hydrogen peroxide (H$_2$O$_2$) whereby

SO_2, oxidized to SO_4^{-2}, was measured by ion chromatography and converted to SO_2 mass.

Some of the exposed samples in the reaction chamber were washed in deionized water and the dried sample exposed again. The procedure was repeated several times until the effect of treatment had nearly disappeared as determined from the disappearance of sulfate ions. The data for continuous exposure over time was used to determine the rate constant of the growth of crust while that of repeated exposures and washings revealed the durability of treatment at rain-exposed sites.

In another experiment, samples were exposed outdoors under a shelter so that they were protected from rain but were exposed to free circulation of air. The maximum period of exposure was three months.
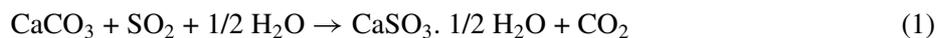
The magnitude of reaction of samples exposed in the artificial as well as in natural exposure was determined by leaching the reaction product gypsum ($CaSO_4 \cdot 2H_2O$) in deionized water and then determining its quantity from SO_4^{-2}, as transformed to gypsum by mass balance. The mass of gypsum was expressed as crust thickness, in microns (μm), by dividing the volume of this mass by the surface area of the sample; we will later give sample calculations to estimate the crust thickness.

As some quantity of calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2\ H_2O$) had also formed in the course of exposure in artificial atmosphere, the sulfite was converted to sulfate by adding H_2O_2, as stated above. 3–4 days were needed to leach the reaction product completely from samples that had been exposed for 72 h in artificial atmosphere.

3. Mechanism and Parameters Controlling the Formation of Crust

In this section we describe concisely the mechanism and the parameters controlling the rate of crust formation. A detailed treatment of the subject can be found in Gauri and Bandyopadhyay (1999).

As determined from laboratory experiments (Gauri *et al.*, 1982–83), the crust formation on marble at water-vapor less than saturated (RH 40–99%) atmosphere can be expressed by:

$$CaCO_3 + SO_2 + 1/2\ H_2O \rightarrow CaSO_3 \cdot 1/2\ H_2O + CO_2 \qquad (1)$$

$$CaSO_3 \cdot 1/2\ H_2O + 1/2\ O_2 \rightarrow CaSO_4 \cdot 2H_2O \qquad (2)$$

The first formed calcium sulfite hemihydrate oxidizes to gypsum if condensation of moisture is allowed to occur upon sample surface. In outdoor conditions, however, only gypsum is found as the reaction product, presumably due to frequent moisture condensation at night.

In a gas-solid reaction, following parameters control the rate of reaction.
- Mass transfer through boundary layer. Surrounding any solid there is a thin layer of air held stationary by friction, called boundary layer. The transfer of

SO$_2$ from the air stream through the boundary layer is a function of flow rate; a high flow rate causes turbulence, which facilitates the transfer of SO$_2$ to the stone surface. Thus, in laboratory set-ups where high flow rates are difficult to obtain, the boundary layer effect becomes significant. This, and the rate constant (see below), can be calculated by the use of programs provided by us at the Internet as ftp://ftp.wiley.com/public/sci_tech_med/limestone. In our experiment the nearly 1 ppm SO$_2$ air stream delivered about 0.6 ppm at the sample surface.

- Reaction between the gas and the solid is mainly controlled by gas concentration, buffering capacity of the solid, temperature, humidity, etc. Other factors being constant in our experiments only gas concentration will be considered to express the reaction.
- Internal diffusion. After some crust thickness has formed by surface reaction, the crust can grow by diffusion of gas through the previously formed crust or by the migration of calcium ions from within to the surface of the stone. Because the reaction reported here was carried out for a short period of time in rather low gas concentration, this factor may be ignored from further consideration.

4. Results and Discussion

The rate of the chemical reaction of marble with SO$_2$ or the deposition velocity of SO$_2$ upon marble can be considered as a function of the buffering capacity of calcite (CaCO$_3$). A reduction in this capacity by changing the mineral composition of marble surface is the key used in this investigation to protect marble. The change in the mineral composition of the marble surface alters the degree to which sample surfaces become wet when exposed to humid environment. Since the SO$_2$ deposition velocity is also determined by the wetness of the substrate, we determined the water vapor adsorption by treated samples in saturated atmospheres. In the following we describe the results from experiments obtained to estimate the efficiency of various treatments described previously.

4.1. CHANGE IN MARBLE SURFACE COMPOSITION BY SURFACTANT REACTION

By surfactant reaction we mean the reaction of calcite (marble) with the surfactant solutions. All four treatments lead to the formation of new chemical compounds at the stone surface because of the reduction of respective anions from their solutions as shown in Figure 2. In this Figure, the absence of the graph for oleate uptake, however, is due to the unavailability to us of the appropriate column for analysis of oleate by ion chromatography. Further, we determined by X-ray diffraction the nature of the product formed at the sample surface, which showed that as a result of immersion of marble slabs in solutions of potassium oxalate (K$_2$C$_2$O$_4$.2H$_2$O)
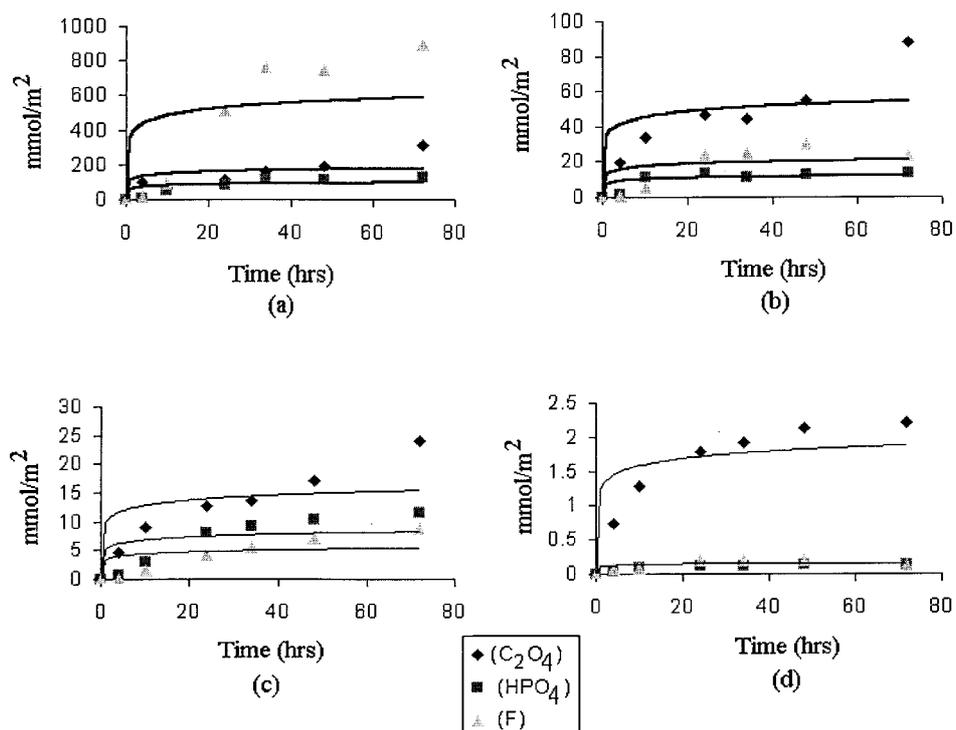
Figure 2. Adsorption of ionic species at marble surface from solutions of surfactant concentrations:
a) 10^{-1}M b) 10^{-2}M c) 10^{-3}M d) 10^{-4}M.

and sodium fluoride (NaF), calcium oxalate ($CaC_2O_4 \cdot H_2O$) and calcium fluor-
ide (CaF_2) had formed, respectively. Upon samples treated with monohydrogen
phosphate (K_2HPO_4), however, calcium phosphate was not found. This absence
can be attributed to the very small quantity of calcium phosphate formed, which
X-ray diffraction is unable to resolve. Also, calcium oleate could not be ana-
lyzed by X-ray diffraction because it is an amorphous compound. Nevertheless,
the calcite-surfactant reactions can be given by the following chemical equations:

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-} \tag{3}$$

$$Ca^{2+} + C_2O_4^{2-} \rightarrow CaC_2O_4 \cdot H_2O \tag{4}$$

$$Ca^{2+} + HPO_4^{2-} \rightarrow Ca\,HPO_4 \cdot 2H_2O \tag{5}$$

$$Ca^{2+} + 2\,F^- \rightarrow Ca\,F_2 \tag{6}$$

$$Ca^{2+} + 2\,C_{17}H_{33}COO^- \rightarrow Ca\,(C_{17}H_{33}COO)_2 \tag{7}$$

4.2. Water-vapor adsorption by treated marble

The degree of water-vapor adsorption is unique to a salt and depends further upon the quantity of the salt present. Since the amount of SO$_2$ deposition is also directly related to the wetness of the substrate, we measured the water vapor adsorption experimentally as described previously and surmised that treatments showing water vapor adsorption lesser than that of untreated marble would be a benefit for the marble.

Figure 3 shows the water-vapor adsorption by treated marble samples at 100% relative humidity. It can be seen that samples treated with various concentrations of sodium oleate adsorbed less water vapor than untreated samples. However, the treatments with oxalate, fluoride and phosphate caused moisture absorption higher than that of the untreated marble except a negligible reduction in samples treated with low M concentrations of 10^{-3} and 10^{-4}. Based on above investigations, we selected only the oleate and the oxalate treated samples with 2×10^{-4} and 2×10^{-3} M solutions, respectively, for further study by exposure in SO$_2$ atmosphere; excluding the phosphate treatment from further consideration for small quantity of the phosphate ions that replaced carbonate in the calcite structure and the fluoride treatment for its relatively large moisture adsorption.

4.3. Exposure to SO$_2$ atmosphere

As given in the method's section, samples were exposed to accelerated weathering in a nearly 1 ppm SO$_2$ atmosphere and to ambient conditions where nearly 10 ppb SO$_2$ prevailed. The results are discussed below.

In the case of exposure to 1 ppm SO$_2$ atmosphere, the result are shown in Figure 4 which shows plots of the formation of gypsum crust over time. The thickness of the gypsum crust after each period of exposure was determined by the following expression:

$$\delta_{\mathrm{p}} = \frac{W_p}{A\rho_p} \tag{8}$$

where,

δ_p = crust thickness (cm),

W_p = weight of the product, gypsum (g)

ρ_p = density (g cm^{-3}) of gypsum, 2.32

A = surface area of the sample, cm^2

W_p, the weight of the gypsum, can be obtained by mass balance from the weight of SO$_4^{2-}$ ions (W$_A$), obtained by leaching these in known volume (l) of water from the exposed sample and measuring their concentration (ppm) by ion chromatography. For example, for a sample of surface area 13.995828 cm^2 and sulfate, 7.035 ppm,
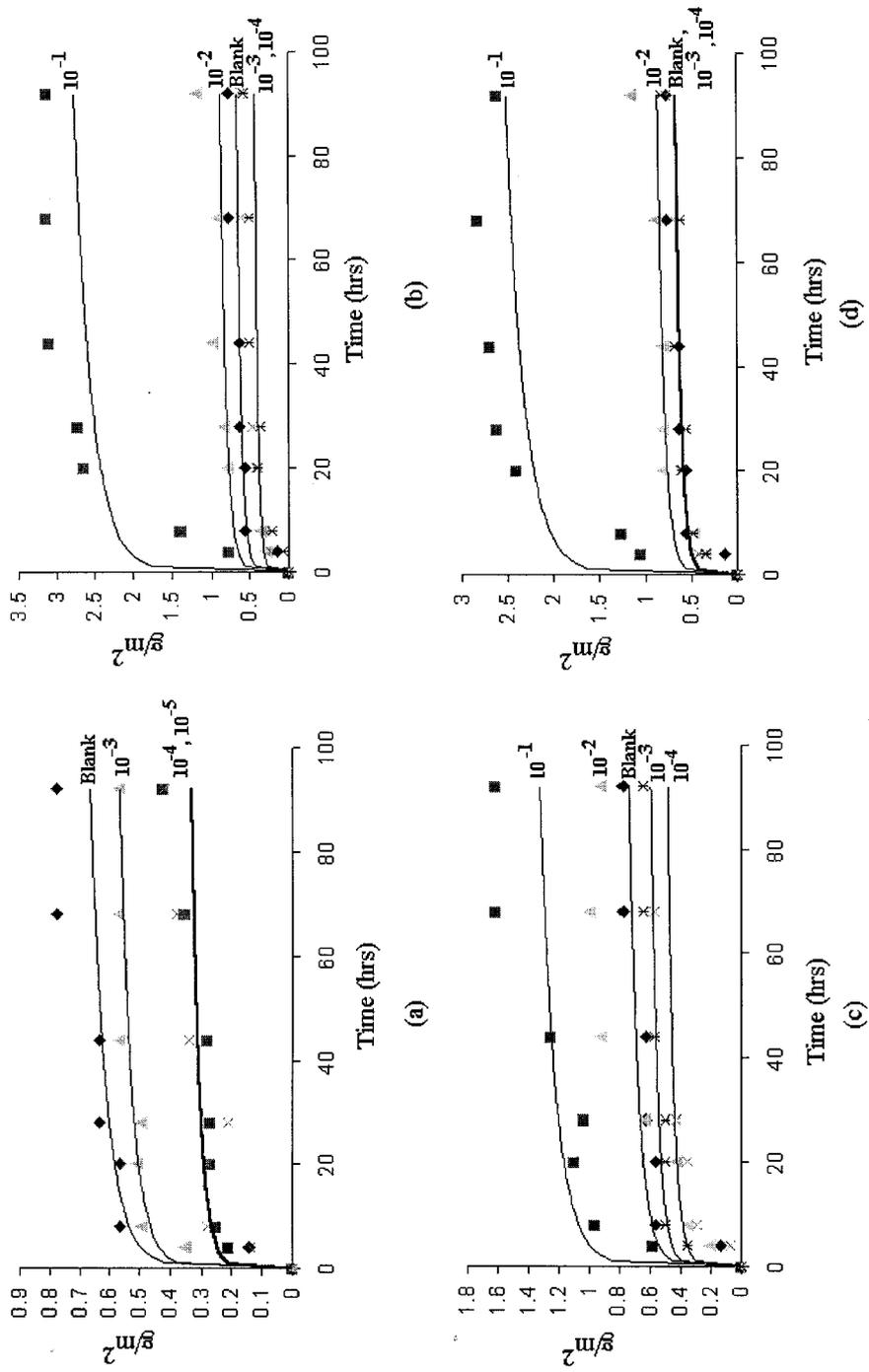
Figure 3. Water-vapor adsorption by marble samples treated with: a) oleate b) oxalate c) phosphate d) fluoride.
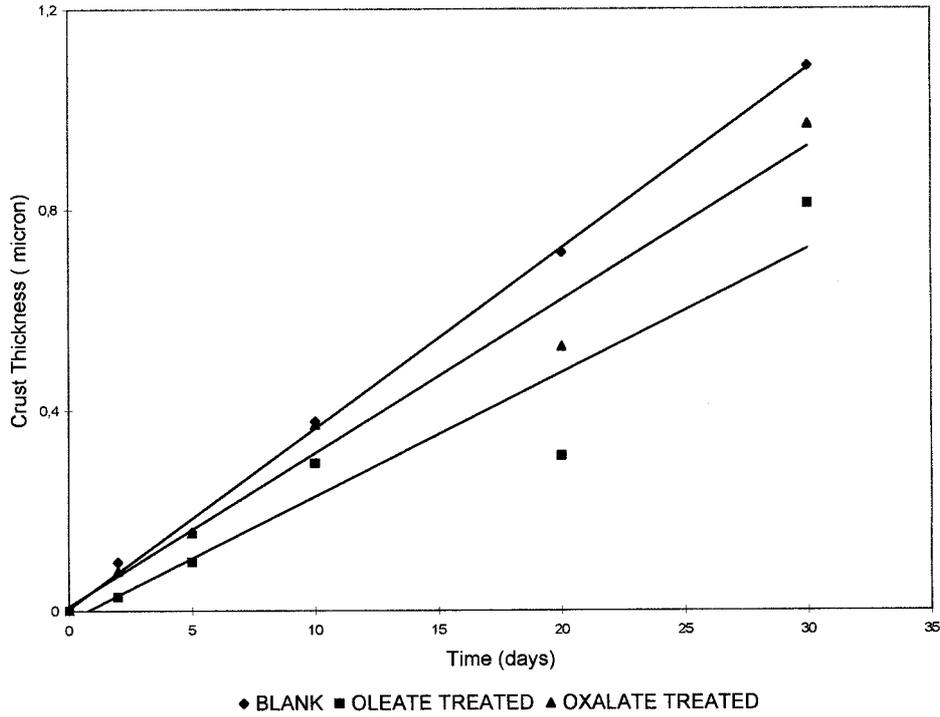
Figure 4. Formation of crust in nearly 1 ppm SO$_2$, 100% R.H. atmosphere upon blank, oleate treated (from-4M solution) and oxalate treated from 10^{-3}M solution, marble samples.

in 0.025 l of water, the weight of sulfate, gypsum and the crust thickness are:
W$_A$(sulfate) = 0.025(l) $\times$ 7.035 ppm = 0.175875 mg.

$$W_A = \frac{172.17}{96.056} \cdot 0.175875 = 0.31523 \text{ mg} = 0.00031523 \text{ g}$$

$$\delta_p = \frac{0.00031523}{13.995828 \times 2.32} = 9.70 \times 10^{-6} cm = 0.097 \mu\text{m}$$

Plotting the crust thickness against period of exposure for several exposures gives the rate curves as shown in Figure 4. Comparison of these curves shows clearly that some protection from SO$_2$ attack was obtained by the treatments with oleate and oxalate surfactants. Since these rate curves are linear, it is easy to calculate, by estimating the slope of the curve, the rate of reaction for the blank and the treated specimens. We will use the data to calculate rate constant for each case, value that is independent of SO$_2$ concentration, and use these to estimate the degree of protection obtained. The rate constant k$_s$ can be calculated from the following expression;

$$\frac{d\delta_p}{dt} = \alpha \frac{M_c}{\rho_c} k_s C_s \tag{9}$$

TABLE I

Gypsum crust thickness, calculated reaction rate and rate constant in a 1 ppm SO$_2$ artificial environment on samples exposed for 30 Days

Sample	Crust thickness (μm)	Reaction rate cm h^{-1} ($\times$ 10^{-7})	Rate constant
Untreated marble	1.086	1.50	93.2
Oleate treated marble	0.811	0.99	61.4
Oxalate treated marble	0.970	1.29	80.0

where

$$\frac{d\delta_p}{dt} = \text{reaction rate (estimated from rate curve)},$$

α = Gypsum/calcite molar volume proportionality constant, 1.72

C_s = Concentration of SO$_2$ at the sample surface, 0.6 ppm = 2.54 $\times$ 10^{-11} mol cm^{-3},

M_c = Molecular weights of marble (calcite), 100.09

ρ_c = Density (g cm^{-3}) of calcite, 2.71

C_s obtained from the concentration of SO$_2$ in the air stream ($\sim$ 1 ppm) and using relationships available at web site given previously.

By linear regression analysis of a rate data,

$$\frac{d\delta_p}{dt} = 0.001504 \ \mu\text{m h}^{-1} = 1.504 \times 10^{-7} \text{ cm h}^{-1}.$$

Solving Equation 9:

$$1.504 \times 10^{-7} = 1.72(\alpha)\frac{100.09(M_c)}{2.71(\rho_c)} \cdot 2.54 \times 10^{-11}(C_s) \cdot k_s$$

k_s = 93.210 cm h^{-1}

Finally, the rate curves are shown in Figure 4 and the crust formation, reaction rate and the rate constants (k_s) are given in Table I.

These constants suggest that the oleate and the oxalate treatments reduced the reactivity by nearly 30 and 14%.

In the case of samples exposed in ambient conditions, the rate curves cannot be drawn because the samples were exposed for a short period of three months and a perceptible change did not occur over shorter periods within this time. However, the crust formation for this period is given in Table II.

The comparison of reactivity due to SO$_2$ of untreated marble in laboratory condition (reaction rate = 1.504 $\times$ 10^{-7} cm h^{-1}.) with that in the ambient condition

TABLE II

Gypsum crust thickness and calculated reaction rate in a 10 ppb SO$_2$ ambient environment on samples exposed for 90 Days

Sample	Crust thickness (μm)	Reaction rate cm h^{-1} ($\times 10^{-9}$)
Untreated 1	0.084	3.89
Untreated 2	0.109	5.04
Oleate Treated 1	0.101	4.68
Oleate Treated 2	0.063	2.92
Oxalate Treated 1	0.067	3.11
Oxalate Treated 2	0.068	3.17

(reaction rate 3.89×10^{-9} to 5.04×10^{-9}) shows that the reaction is slower by nearly an order of magnitude in the latter case. But it should be noted that variations are very large from sample to sample even when they are exposed simultaneously, due perhaps to the heterogeneous nature of marble. The rates, therefore must be determined on a very large sample and interpreted in a statistical sense than as to what a single or two samples show.

Finally, as given in experimental section, the samples exposed in a nearly 1 ppm SO$_2$ atmosphere were washed to remove the reaction product and exposed again. The idea was to simulate the behavior of the treatment in samples if exposed to rain. The result is that the effect of the treatment was lost by nearly one third in 4 cycles suggesting that the surfactant treatments will not be useful for application to surfaces exposed to rain.

5. Conclusion

Immersion of marble samples in solutions of 10^{-3} M and 10^{-4} M potassium oxalate and sodium oleate produced calcium oxalate and calcium oleate crusts upon marble which are less vulnerable to SO$_2$ attack. Application of these treatments to marble at sites protected from rain will reduce the rate of formation of gypsum crust.

Acknowledgements

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