



ELSEVIER

December 2002

Materials Letters 57 (2002) 935–939

**MATERIALS
LETTERS**

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Effect of some surfactants on SO₂–marble reaction[☆]

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Received 18 January 2002; received in revised form 8 May 2002

Abstract

In the polluted atmosphere, sulphur dioxide (SO₂) reacts with calcite (CaCO₃) in marble producing calcium sulphite hemihydrate (CaSO₃·0.5 H₂O) and gypsum (CaSO₄·2H₂O). Gypsum develops crust at rain-sheltered surfaces and then, being more soluble, accelerates erosion at areas exposed to rain. Eventually, all these lead to significant deformations in the appearance and structure of marble surfaces. Clearly, some precautions must be taken to stop or at least to slow down this deterioration process which destroys our cultural heritage. In this study, we have investigated the possibilities of preventing the SO₂–marble reaction by using water-soluble surfactants: Abil Quat 3270 and Tween 20. Experiments for measuring their effects have been carried out at conditions simulating the dry deposition of SO₂. Infrared spectrometry and scanning electron microscopy were used to analyze the mineralogical composition and morphology of the reaction products. The extent of sulphation reaction was calculated by determining calcium sulphite hemihydrate and gypsum quantitatively by an IR approach and also by weight increases observed during the progress of SO₂–marble reaction. A 10% decrease is observed in the total sulphation with both surfactant applications. The results have been discussed in relation to the possible stages of sulphation reaction and surface reactions of calcite.

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Keywords: Sulphur dioxide; Marble; Gypsum; Calcium sulphite hemihydrate; Surfactant; IR

1. Introduction

In the polluted urban atmosphere, deterioration of historic buildings and monument stones have been accelerated to a great extent over the last decades. The main atmospheric pollutant affecting the building materials is primarily SO₂ which is very reactive

and corrosive. Among the large variety of building stones, calcareous stones such as limestone, marble and travertine have been studied more due to their high reactivity with SO₂. The main part of change observed in the structure is due to sulphur dioxide gas going into reaction with calcareous stone. The final product of the chemical reactions is gypsum which is more soluble and occupies more volume than the original matrix, calcium carbonate. As a result, calcareous stone is easily eroded and disintegrated.

In the recent past, calcareous stone–SO₂ reaction has been the subject of many investigations, ranging from the field studies to laboratory investigations

[☆] In the memory of Dr. Ertuğrul Onat

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using enriched SO₂ atmosphere and rather simple matrices [1–4]. In several cases, the airborne particles collected on stone surfaces have been considered to enhance gypsum crust formation [4–6]. Aiming to cure the deterioration, some laboratory studies have been carried out to convert the formed gypsum back to calcium carbonate by chemical precipitation [7]. The results were not promising since the calcite crystals recreated rested as powder on the surface. In another group of study, various types of polymer coatings have been used both in laboratory conditions and in situ for preventing gypsum formation on calcareous stones [8]. The results obtained are still in debate from the point of view of complying with the generally accepted conservation principles as well as their probable damages to the monuments in time.

In the work presented, the effects of some surfactants, Abil Quat 3270 and Tween 20 in preventing sulphation on marble surface were investigated. It is already known that these two surfactants have reducing effects on the solubility of calcite in aqueous media [9,10]. Natural marble from Marmara Island was used as the calcite matrix to control the applicability of these surfactants in marble conservation.

2. Experimental

2.1. Sample preparation and treatment with surfactants

Rectangular plates, with 17×10×2 mm dimensions, were cut from large blocks of Marmara marble. These plates were then cleaned ultrasonically in deionized water to remove fine particles from their surfaces, dried at 105 °C, and then cooled in a desiccator to the room temperature.

Aqueous solutions of surfactants Abil Quat 3270 (diqartenary polydimethyl siloxanes, cationic) and Tween 20 (polyoxyethylene 20 sorbitan mono oleate, nonionic) were prepared at concentrations of 1.5% by weight and were applied on the marble surfaces by brush. After treatment, samples were dried at 30 °C.

2.2. Experimental set up

Marble plates, with and without surfactants on their surfaces, were exposed in a dynamic 1000 ppm

SO₂-enriched atmosphere at 25 °C and at 90% relative humidity (RH) conditions for 540 h. SO₂ concentration was chosen as 1000 ppm for practical reasons in order to shorten the reaction periods. Reaction chamber was a modified 10-l desiccator [4]. Sulphur dioxide atmosphere was generated by introducing compressed sulphur dioxide and dry air gas mixture of the proper combinations at a constant rate of 250-ml min⁻¹. SO₂-air stream was injected into the reaction chamber by bubbling it through a washing bottle containing water. Plates were reacted in the chamber only after this water had been equilibrated with the given concentration of the gas.

2.3. Experimental methods

The blank- and surfactant-treated plates exposed to SO₂ were removed from the reaction chamber at the end of 540 h. The weight increases due to the formation of sulphation products on marble samples were determined using a Gibertini balance of 0.01-mg readability. IR analysis were then carried out on powder samples scrubbed from marble surfaces by a Nicolet Model 510 FTIR spectrometer. The results were used to quantify the calcium sulphite hemihydrate and gypsum formed on marble surfaces. For this purpose, a calibration curve was prepared by plotting the absorbance ratio of gypsum to calcium sulphite hemihydrate as a function of their concentration ratio [4]. Using the calibration curve and corresponding weight increase results, the amount of calcium sulphite hemihydrate and gypsum were accurately calculated. Scanning electron microscopy analysis has also been carried out for investigating the crystal morphology and composition. The instrument was a JSM-6400 model scanning electron microscope equipped with an Energy Dispersive X-ray (EDX) analyzer.

3. Results and discussion

FTIR analyses (Fig. 1) show that calcium sulphite hemihydrate and gypsum are the reaction products in marble plates with and without surfactant layers. In a study by Elfving et al. [3], SO₂-calcite reaction is described as proceeding in a water film when con-

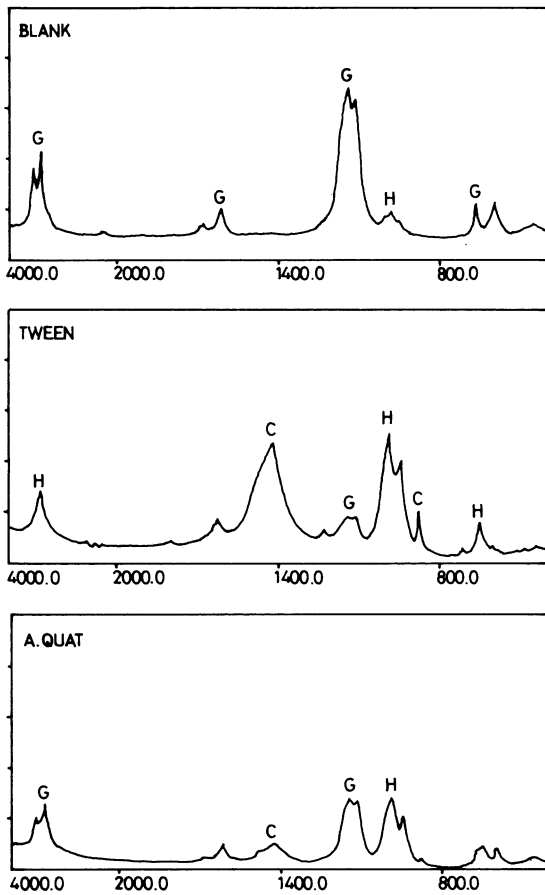


Fig. 1. IR spectra of surfactant free marble (blank), Tween 20 and Abil Quat 3270 applied marble surfaces at the end of 540 h of exposure. G: Gypsum, H: calcium sulphite hemihydrate, C: calcite.

densation is favourable on calcite surface. Sulphation mechanism under these conditions can be explained by successive stages of gas–liquid–solid interfacial reactions [4] as follows:

- diffusion of the SO_2 from the gas phase into aqueous phase present on marble surface,
- dissolution of SO_2 in aqueous phase,
- dissolution of calcite in aqueous phase,
- precipitation of calcium sulphite hemihydrate in aqueous phase,
- partial dissolution of calcium sulphite hemihydrate in aqueous phase,

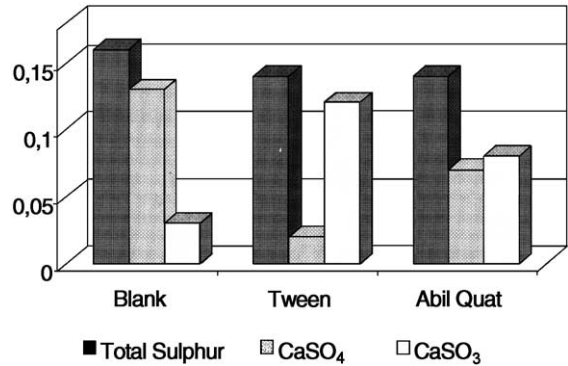


Fig. 2. Moles of sulphation products (mol/m^2) on surfactant free marble (blank), Tween 20 and Abil Quat 3270 applied marble plates at the end of 540 h of exposure.

- formation of gypsum by oxidation of sulphite ions present in aqueous phase.

Detailed discussions and related chemical reactions are given elsewhere [4].

On Abil Quat and Tween 20 applied surfaces, quantitative IR analyses of the sulphation products indicate a 10% decrease in total sulphur content compared to those of exposed but surfactant-free marble surfaces (Fig. 2). Formed crystals and their habits were examined by SEM-EDX analysis. As it is seen in Fig. 3, unexposed surfactant-free marble consists only fine calcite crystals of 10–300- μm size.

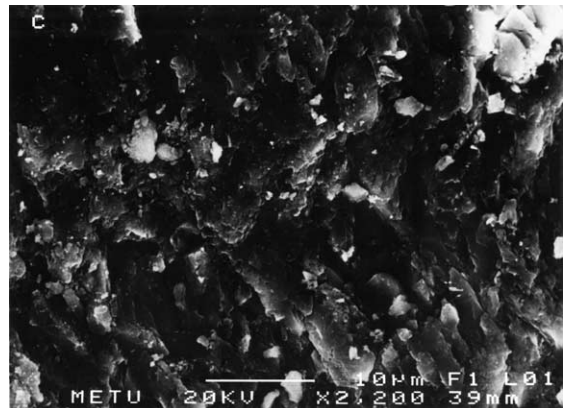


Fig. 3. SEM view of the unexposed surfactant-free marble surface with fine calcite crystals ($\times 2200$).

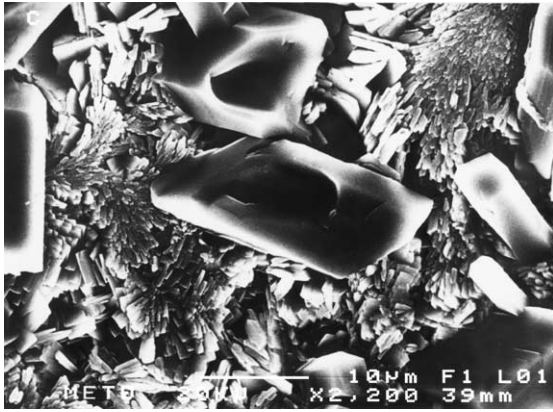


Fig. 4. SEM view of surfactant free Marmara marble at the end of 540 h of SO_2 exposure with aggregates of calcium sulphide hemihydrate and prismatic gypsum crystals ($\times 2200$).

At the end of exposure period, monoclinic gypsum crystals of 10–30- μm size were observed as tabular, long prismatic and rarely in twinned forms on these surfaces (Fig. 4). On Abil Quat 3270 applied plates, aggregates of 1–5- μm size hemihydrate crystals and the 10–30- μm size prismatic gypsum crystals were almost equally distributed on the surface after exposure (Fig. 5). On Tween 20, applied surfaces calcium sulphite hemihydrate crystals were much more abundant compared to that of gypsum crystals (Fig. 6). This may indicate that Tween 20 is more effective in

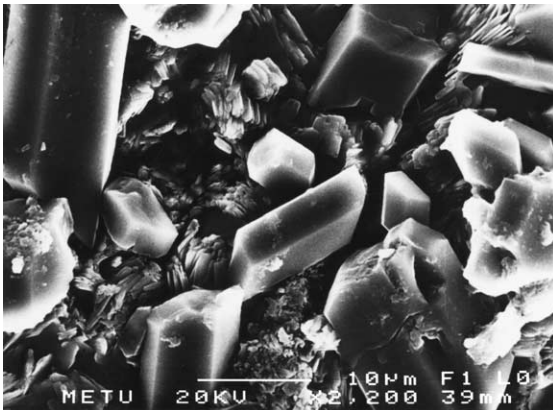


Fig. 5. SEM view of Abil Quat-treated marble surface after 540 h of exposure. Aggregates of calcium sulphide hemihydrate and prismatic gypsum crystals ($\times 2200$).

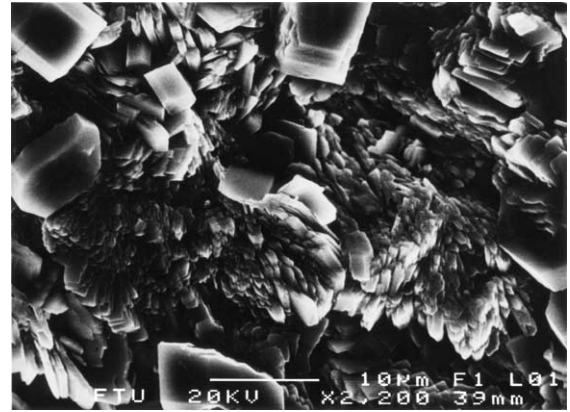


Fig. 6. SEM view of Tween 20-treated marble surface after 540 h of exposure. Aggregates of calcium sulphide hemihydrate and prismatic gypsum crystals ($\times 2200$).

keeping the sulphation reaction at sulphite formation stage.

4. Conclusions

In the polluted atmosphere, the final SO_2 –marble reaction product is gypsum. Gypsum formed, being more soluble than calcite, is easily eroded and washed out from the marble surface causing serious deformations on its outer appearance and structure. The use of surfactants, particularly Tween 20, seems to be promising in reducing the degree of sulphation and altering the extent of oxidation of calcium sulphite hemihydrate into gypsum. Our observations indicate that when these agents are applied as protective layers to the marble surfaces, they decrease the solubility of calcium carbonate in water film. Their effects to the marble surface in the long run, however, must be clarified. In any case, their use as protective agents deserves further investigations. A more significant decrease in the degree of total sulphation may probably be achieved by different application techniques which may create more homogeneous surfactant layers on the stone surface.

Acknowledgements

The authors thank Dr. M. Volkan, Dr. A. Türkmenoğlu and Miss S. Kahveci for their valuable

help and discussions during the experimental stage of this work.

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