

## **THE CONTROL OF GYPSUM FORMATION ON CALCAREOUS STONE SURFACES**

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### **Abstract**

This study examines the possibilities of slowing down the sulphation reaction of calcium carbonate by using some materials in the pure calcium carbonate matrix which have a decreasing effect on the solubility of calcium carbonate in water. For this purpose, three types of surfactants; Abil Quat 3270 (cationic type), sodium oleate (anionic type), Tween 20 (non-ionic type) and disodium monohydrogen phosphate were used in the pure calcium carbonate powder matrix or on the calcium carbonate disks prepared from the same powder.

Effects of these compounds on the sulphation reaction of calcium carbonate with SO<sub>2</sub> have been followed by the laboratory simulation experiments. The reaction was examined by qualitative and quantitative determinations of the sulphation products using Fourier Transform Infrared Spectroscopy (FTIR). The reaction path was followed by weight increase of the samples in time. In the presence of orthophosphates and surfactants used, considerable decrease have been observed in the total amount of sulphation and calcium sulphite hemihydrate was the main sulphation product. The decrease in the sulphation has been explained by the lowering effect of these compounds on the solubility of calcium carbonate in the water film, where the sulphation reaction is taking place.

### **Introduction**

The reaction of calcium carbonate with sulphur dioxide has been an important subject of conservation science for the purpose of the protection of historical buildings affected from atmospheric pollution. Intensive researches on this reaction have been done in the field and in the laboratory since few decades. In some of the recent studies, critical role of water film on the surface during the

sulphation reaction has been pointed out (Böke et al<sup>1</sup>., Elfving et al<sup>2,3</sup>.,). In this water film, the surface controlled dissolution of calcium carbonate (Caner et al<sup>4</sup>.,) during sulphation seems to be highly probable. It has been found that the presence of phosphates, oxalate and some surfactants in the solution reduce the solubility of calcium carbonate possibly by blocking the active sites during its dissolution (Simon et al<sup>5</sup>., Ivanova and Shcukin<sup>6</sup>.,). This study examines the roles of these compounds during the sulphation reactions of calcium carbonate.

## Experimental

The experimental apparatus was built in our laboratory and used for the simulation experiments (Göktürk et al<sup>7</sup>.,). The dynamic atmosphere of SO<sub>2</sub> with the desired concentrations was generated by passing compressed SO<sub>2</sub> and air mixtures over the samples in the reaction chamber with a flow rate of 0.25 lpm. The relative humidity of approximately 85 was provided by placing a saturated solution of zinc sulphate in the chamber. All experiments were carried out at room temperature of 20 °C.

Extra pure calcium carbonate powder (Merck) and pressed disks of this powder were used as the matrix of the samples. The pure calcium carbonate disks with 13 mm diameter and 1mm thickness were prepared by pressing the powder (Böke<sup>8</sup>).

In the first group of the experiments, 1.5% and 0.5% disodium monohydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>) concentrations by weight were used in the matrix. Aqueous solution of Na<sub>2</sub>HPO<sub>4</sub> was added to the carbonate matrix and was dried at 40 °C prior to the sulphur dioxide exposure. At different time intervals, composition of the samples were analyzed by FTIR both qualitatively and quantitatively (Böke et al<sup>9</sup>.,). Detailed experimental conditions are given in Table 1.

In the experiments with the surfactants, Abil Quat 3270 (diquarternary polydimethyl siloxanes), Sodium Oleate (C<sub>17</sub>H<sub>33</sub>COONa) and Tween-20 (polyoxyethylene (20) sorbitan mono-oleate) aqueous solution of 1.5% concentration by weight were applied to the disk surfaces by brush and then dried at room temperature. At certain time intervals, the discs were weighed using a Gibertini balance of 0.01 mg readability and these discs were brought to powder form for FTIR analysis. Detailed experimental conditions are shown in Table 2.

**Table 1. Experimental conditions used with pure calcium carbonate powder samples containing with disodium monohydrogen phosphate**

**FIRST RUN**

Concentration of Disodium Monohydrogen Phosphate: 1.5 % by weight
SO <sub>2</sub> Concentration : 1000 ppm
Total Exposure Time: 210 Hours
Determinations: FTIR: At the end of 45, 114, 210 hours exposures Weight Increase: At various time intervals during the course of exposure

**SECOND RUN**

Concentration of Disodium Monohydrogen Phosphate : 0.5 % by weight
SO <sub>2</sub> Concentration : 1000 ppm
Total Exposure Time: 150 Hours
Determinations: FTIR: At the end of 79, 103, 150 hours exposures Weight Increase: At various time intervals during the course of exposure

**Table 2. Experimental conditions used with pure calcium carbonate disks containing some surfactants on the surfaces.**

Surfactants Used : Abil Quat, Sodium Oleate, Tween 20,
Concentration of Surfactants : 1.5 % by weight (In water)
SO <sub>2</sub> Concentration : 1000 ppm
Total Exposure Time: 546 hours
Determinations: FTIR: At the end of 48, 117, 210, 378, 546 hours exposures Weight Increase: At various time intervals during the course of exposure

**Results and Discussion**

The results obtained from the two groups of experiments concerning the effects of orthophosphates and surfactants are given in the following sections:

**Experiments by Using 1.5% and 0.5 % Disodium Monohydrogen Phosphate (Na<sub>2</sub>HPO<sub>4</sub>) in Pure Calcium Carbonate Powder**

Powder calcium carbonate samples containing 1.5% disodium monohydrogen phosphate impurity by weight were exposed to 1000 ppm sulphur dioxide atmosphere for approximately 210 hours. The weight increases (Figure 1) do not reveal the changes in the sulphation reaction due to considerable molecular weight differences of sulphation products however FTIR results (Figure 2) indicate a decrease in the sulphation reaction of phosphate containing samples, that is the retardation of sulphation reaction by about 35 percent. Another

significant point is the formation of gypsum along with the main sulphation product calcium sulphite hemihydrate in all the phosphate containing samples.

These experiments were repeated with 0.5% phosphate containing samples to check the concentration effects of these additives. At this concentration, the only sulphation product observed was calcium sulphite hemihydrate (Figure 3). In addition to that total sulphation has decreases only by about 10 percent. In this case, percent weight change results also reveal these facts as only one sulphation product is involved in the reactions (Figure 4).

The observed decrease by monohydrogen phosphate ions may be due to the decrease in the solubility of calcium carbonate by inorganic phosphate compounds which may have been adsorbed on the calcium carbonate surface (Morse<sup>10</sup>, Suzuki et al<sup>11</sup>, Simon et al<sup>5</sup>.), as any factor which cause a decrease in the solubility of calcium carbonate may cause a decrease in the extend of sulphation process. These evidences support the idea of the presence of a liquid film on the surface of calcium carbonate matrix (Böke et al<sup>1</sup>.,)

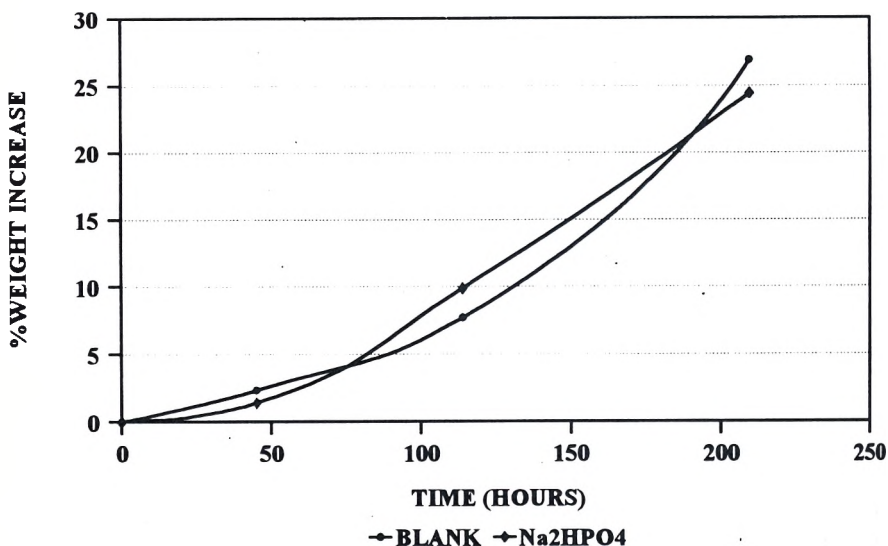
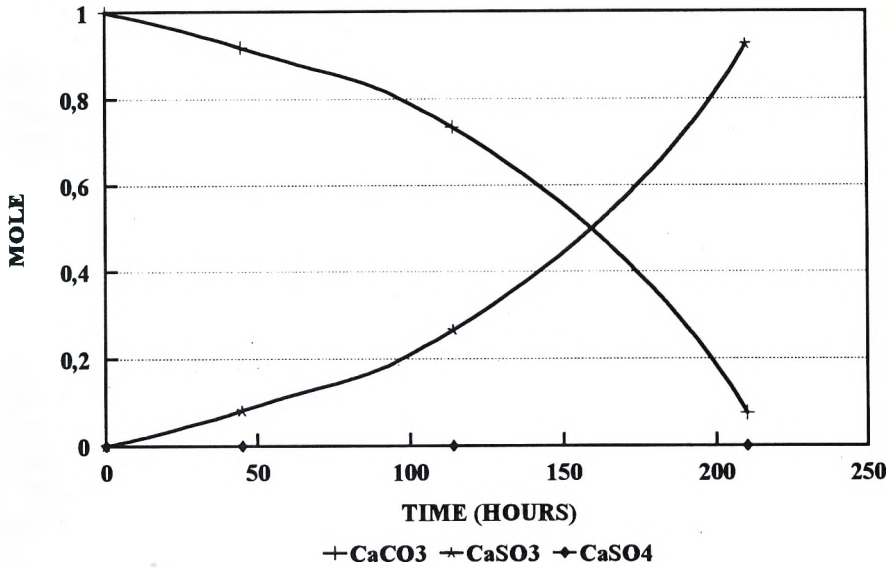


Figure 1. Percent weight changes in time; pure calcium carbonate samples and samples containing 1.5% Disodium monohydrogen phosphate

a) PURE CALCIUM CARBONATE



b) 1.5% Na<sub>2</sub>HPO<sub>4</sub>

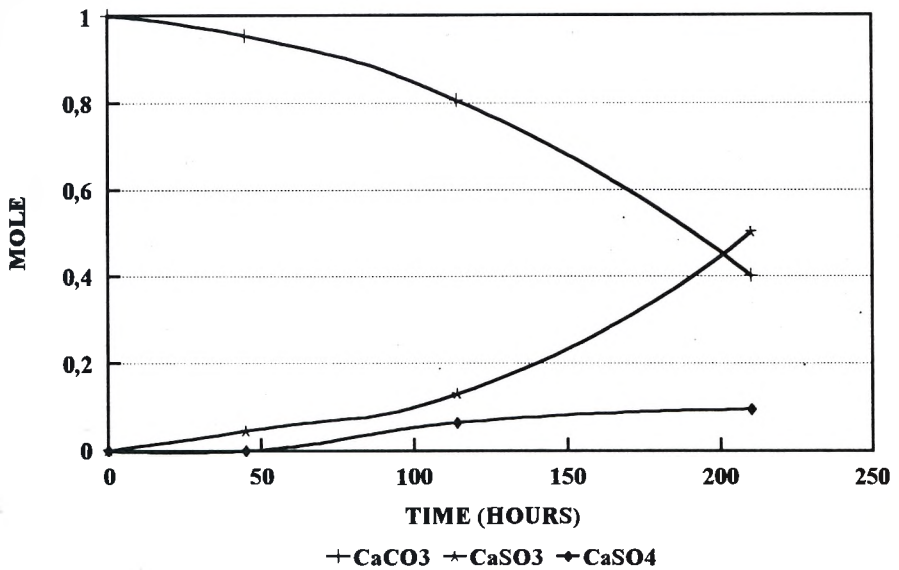


Figure 2. Relative Molar Composition of a) pure calcium carbonate sample  
b) calcium carbonate sample containing 1.5% disodium monohydrogen phosphate

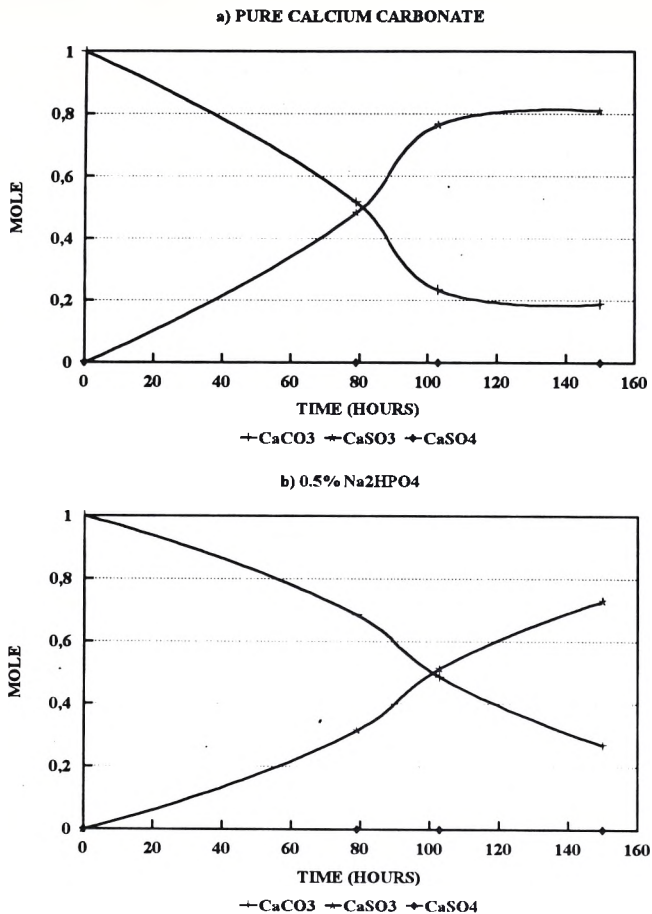


Figure 3. Relative molar compositions of a) pure calcium carbonate samples b) calcium carbonate samples containing 0.5% disodium monohydrogen phosphate

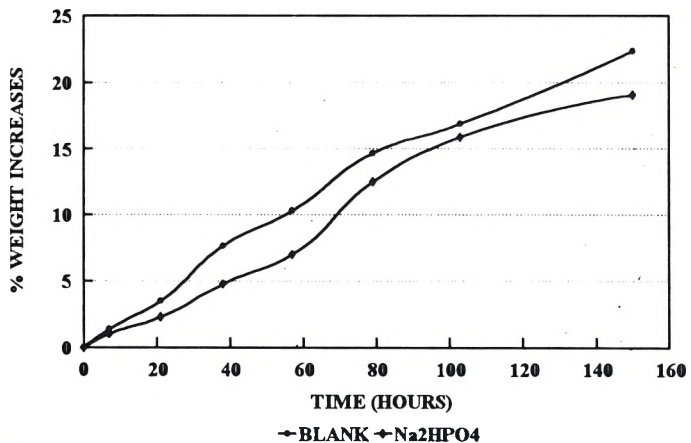
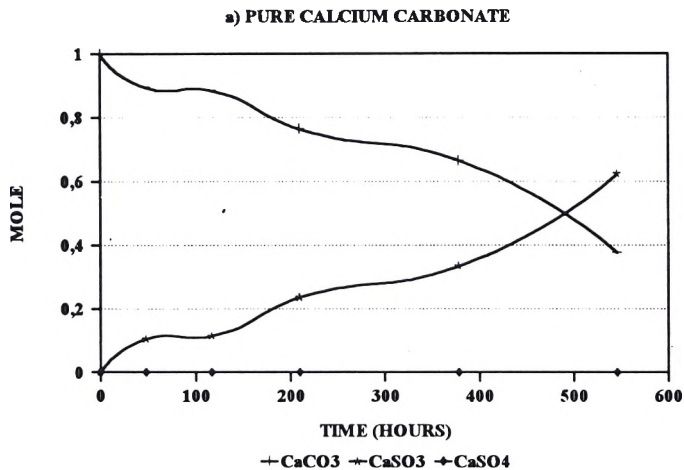


Figure 4. Percent weight changes in time; pure calcium carbonate samples and calcium carbonate samples containing %0.5 disodium monohydrogen phosphate

### Experiments by Using Surfactants on the Calcium Carbonate Discs

The effects of some surfactants in the pure calcium carbonate powder matrix have been already studied and their considerable decreasing effect on the sulphation reaction has been observed in a previous study (Böke et al<sup>12</sup>,.). In this study, the experiments were repeated by using disc samples prepared with pure calcium carbonate powder since they were thought to represent the building stones better than the powder ones. 1.5% surfactant containing aqueous solutions were applied to discs surfaces with brush by a single application. Then these discs were exposed to 1000 ppm SO<sub>2</sub> dynamic atmosphere, at 85 relative humidity, for about 546 hours.

The main sulphation product observed is calcium sulphite hemihydrate in all samples (Figure 5). There is a considerable increase in the sulphation reaction by the use of some surfactants (Figure 5,6). The decrease was about 75 percent in Tween 20 containing samples and by about 60 percent in Abil quat ones. It was less in sodium oleate containing samples which was about 30 percent. These results are in good agreement with the ones obtained from powdered samples (Böke et al<sup>12</sup>,.).



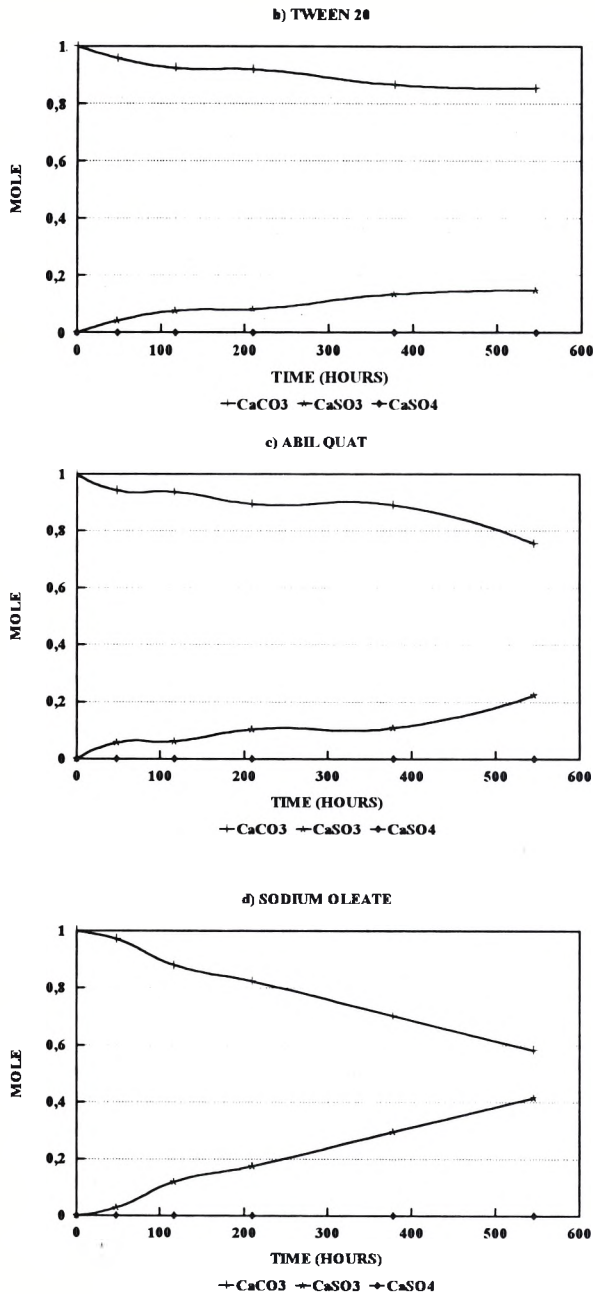


Figure 5. Relative molar compositions of a) pure calcium carbonate samples and pure calcium carbonate discs applied b) Tween 20, c) Abil Quat d) Sodium oleate



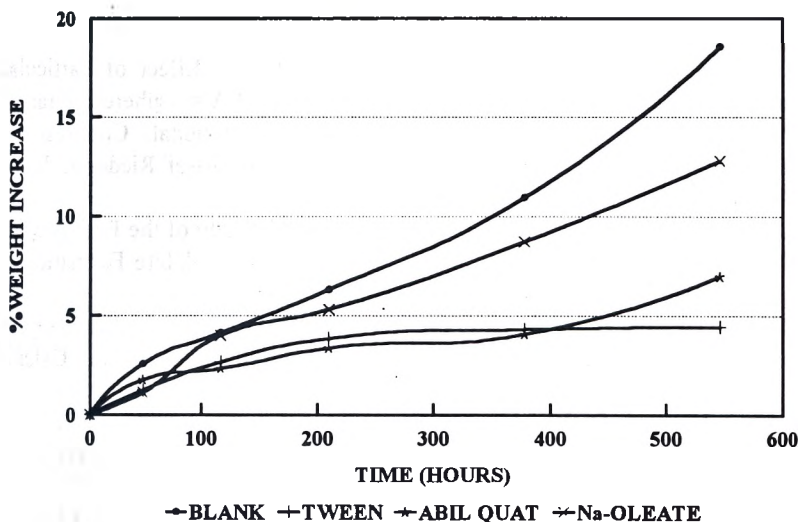


Figure 6. Percent weight changes in time; 1.5% Tween 20, Abil Quat and sodium oleate applied pure calcium carbonate discs

### Conclusion

Some decrease observed in the extent of sulphation reaction by the use of di sodium monohydrogen phosphate and considerable decrease in sulphation by the use of some surfactants may be due to their influence on the solubility of calcium carbonate. This fact reveals the existence of water, probably as a film on the surface of calcium carbonate crystals during the reaction.

Mono hydrogen phosphate ion has a decreasing effect on the total sulphation by about forty percent and that effect gets smaller at its lower concentrations. In addition, higher concentrations of this compound promote the oxidation of calcium sulphite hemihydrate to gypsum.

The surfactants, Tween-20 and Abil Quat have decreased the total sulphation by about 75 and 60 percent respectively. The decreasing effect of sodium oleate was only about 30 percent. None of the surfactants had any effect on the oxidation of calcium sulphite hemihydrate into gypsum at the concentrations studied.

These results show that it is probable to reduce the sulphation reaction by the addition of some surfactants. The materials which reduce the solubility of calcium carbonate in the water film or in the aqueous solution should therefore must be studied further.

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