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SHORT COMMUNICATION

IN SITU IR STUDY ON THE INITIAL SULPHITION AND CARBONATION OF $Ca(OH)_2$ AND CaO BY SO_2 POLLUTED AIR

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Abstract—Absorptions of SO_2 and CO_2 to fresh and aged forms of CaO and $Ca(OH)_2$ are investigated at dry and humid conditions. Sulphite formation on $Ca(OH)_2$ is found to be fairly independent of the relative humidity, while surface water is found to be a necessary condition for the corresponding carbonation reaction. Results supportive of $Ca(OH)_2$ sulphition to be strongly preferred before carbonation at humid conditions are produced. Marked improvements in SO_2 adsorption are seen for the fresh substrates. The observations are put in perspective of an on-going effort to understand the roles of SO_2 in the deterioration of calcareous stone monuments, and are relevant to the chemistry of building materials. Copyright © 1996 Elsevier Science Ltd

Key word index: $Ca(OH)_2$, CaO, sulphite formation, carbonation, *in situ* DRIFT.

1. INTRODUCTION

The deterioration of historical monuments results from the interplay between exposures to periodic and non-periodic changes in the physical and chemical environments of each monument. The generally accepted overall understanding of this process is that the monument surface is continuously being exposed to a chemically more or less aggressive atmosphere which tends to weaken the material, and that the resulting surface is subsequently degraded by rain, wind and temperature changes (Amoroso and Fassina, 1983; Rosvall, 1988).

The strategy of the present approach to understand the initial steps in the degradation process is to try to isolate the chemical components of the material and focus on their surface chemistry at close to natural conditions. Thus the accelerated deterioration of calcareous stone monuments is generally believed to result from the increased abundance of SO_2 in the atmosphere. In an initial study, the reactivity of precipitated calcite to SO_2 at dry and humid conditions was addressed (Elfving *et al.*, 1994a). The surface product was characterised with a new sample preparation technique for Diffuse Reflectance Infrared Fourier Transform spectrometry (DRIFT), and argued to be similar to $CaSO_3 \cdot 0.5H_2O$. No surface sulphite was found at dry conditions. In a subsequent work (Elfving *et al.*, 1994b), exposure of surface sulphite to O_3 was found to rapidly form surface sulphate. In addition, NO_2 was found to act as a catalyst for sulphite oxidation by O_2. The efficiency of the catalytic process was found to increase with the amount of sulphate at the surface, suggesting an activated complex involving SO_3^{2-}, SO_4^{2-}, NO_2 and O_2. No sulphate formation was observed in the absence of O_3 and NO_2. In a third study, the increased tendency of iron- or manganese-containing calcareous stones to form surface gypsum was addressed. Mixtures of $CaCO_3$ and Fe_2O_3 or MnO_2 were argued to be valid models for surfaces of calcareous stones containing these transition metals (Elfving *et al.*, 1994c), and surface sulphate was found to form upon exposure to air polluted with SO_2. The catalytic process was located to the solid phase.

The reaction between a calcite surface and SO_2 progresses by necessity via a CO_3^{2-} surface ion decomposition, whereby CO_2 is removed to make room for the incoming SO_2 molecule. This reaction was found to depend strongly on the presence of surface water. The present study aims to produce more information as to the role of water in this system.

The model systems chosen are CaO and $Ca(OH)_2$. As in previous works, the choices of model systems are governed by the pursuit of conclusive chemical understanding. Hence, any comparisons of these model systems' chemistry to the actual deterioration processes are *ad hoc* at this stage.

The characteristic reactivity of CaO(s) and $Ca(OH)_2$ has long been exploited, e.g. as fusing agents in Pozzolanic cement (Taylor, 1990). Also, calcium hydroxide is mixed in concrete in order to protect the reinforcement from corroding (Schiessl, 1988). Calcium sulphate formation in these materials is believed to be a major initial step in several reactions that ultimately lead to weathering (Tuutti, 1980). Hence, a chemically related and relevant subject is whether any negative effects on the durability of materials in modern buildings can be correlated to the amounts of unreacted $Ca(OH)_2$, in conjunction with the present abundance of air pollutants in general and SO_2 in particular. The sulphition of $Ca(OH)_2$ formed by hydrolysis of components in cement was addressed by Tischer (1980), and the ability of moisture containing SO_2 to penetrate the material and react was also discussed.

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The reactivity of CaO(s) is believed to be strongly surface-dependent. The porosities of calcined $CaCO_3$ and $Ca(OH)_2$ have been shown to increase by 35–40% and to react more rapidly with water vapour than non-porous CaO (Beruto *et al.*, 1980). The property of calcined limestone to react with SO_2 at elevated temperatures to form calcium sulphate is well-known and it is exploited in coal furnaces to reduce the SO_2 concentration in the flue gas (Borgwardt, 1970). Aspects on the relevance of this reaction to the sulphite formation on calcite at room temperature are studied and discussed below.

2. EXPERIMENTAL

Three techniques were applied in the present study. Hence, samples were subjected to short-term exposure experiments with an on-line SO_2 or a CO_2 analyser, *in situ* DRIFT spectrometry (Elfving *et al.*, 1994a–c) and X-ray diffractometry. A brief account of the experimental set-up is provided below.

2.1. *Chemicals*

CaO powder (Fisher) was used as received. The $Ca(OH)_2$ were produced by exposing the sample in a desiccator at 50% RH until all CaO was transformed to $Ca(OH)_2$, verified gravimetrically. In order to produce a more reactive CaO, precipitated $CaCO_3$ (p.a. Merck) was calcined in an inert atmosphere at 800°C for 3 h. One part of the sample was thereafter converted to $Ca(OH)_2$ as above.

2.2. *Experimental set-up*

The reactive gas was produced by letting purified and dried air pass through two channels. One part was saturated with water vapour at 22°C, and the other part passed through a chamber containing an SO_2 permeation tube. The concentration of SO_2 was kept at 1 ppm. The two flows were regulated in order to achieve the desired relative humidity, 0 or 90% RH. The purification system includes a 3.5 Å filter which reduces the CO_2 content to about 6 ppm.

The powdered sample was placed in the sample holder of an *in situ* diffuse reflectance absorption cell (HVC-DRI, Harrick) in an FT-IR spectrometer (Perkin-Elmer 1800). The sample was used pure in order to avoid any possible interference with a diluting substance which would obscure the final analysis, especially at high relative humidities. By using neat samples the assumptions made in the Kubelka–Munk transformation equations do not apply, particularly at a high surface coverage of absorbed species (Brimmer and Griffiths, 1988). Hence, all spectra are plotted as reflectance spectra. The sample was heated in the sample holder to 120°C for 10 min and thereafter cooled to room temperature, in order to standardise the initial conditions. The reaction gas was introduced into the cell and single beam spectra were acquired intermittently during the exposure experiment. The first spectrum was used as reference and subtracted from the subsequent spectra. Spectra were acquired with 4 cm^{-1} resolution over the range 4000–750 cm^{-1}. Measurements with 256 co-added interferograms were performed.

In the on-line SO_2 and CO_2 exposure experiments the sample was placed in a glass chamber on a glass filter and the reactive gas was allowed to pass through the sample bed. The SO_2 and CO_2 uptake was monitored continuously with an SO_2 fluorescence instrument (Environnement s.a AF 21M) and a CO_2 infrared absorption instrument, respectively (Binos 100).

3. RESULTS AND DISCUSSION

The aim of the present series of experiments was to explore the reactions of CaO and $Ca(OH)_2$ with SO_2 polluted air. The two factors of particular interest were to understand further the roles of water in the sulphition and carbonation processes, and to compare the sulphite formation of aged and fresh CaO and $Ca(OH)_2$ at room temperature.

3.1. *Carbonate formation on* $Ca(OH)_2$

Aged calcium hydroxide was exposed to air with 6 ppm CO_2 at dry and humid conditions. Only minor CO_2 adsorption was observed at dry conditions, while rapid carbonation was seen at 90% RH (Fig. 1). The crucial role of water suggests the mechanism for carbonation to be

$$CO_2(g) + H_2O(surface) \rightarrow H_2CO_3(aq) \qquad (1)$$

$$Ca(OH)_2(s) + H_2CO_3(aq) \rightarrow CaCO_3(surface) + 2H_2O(surface). \qquad (2)$$

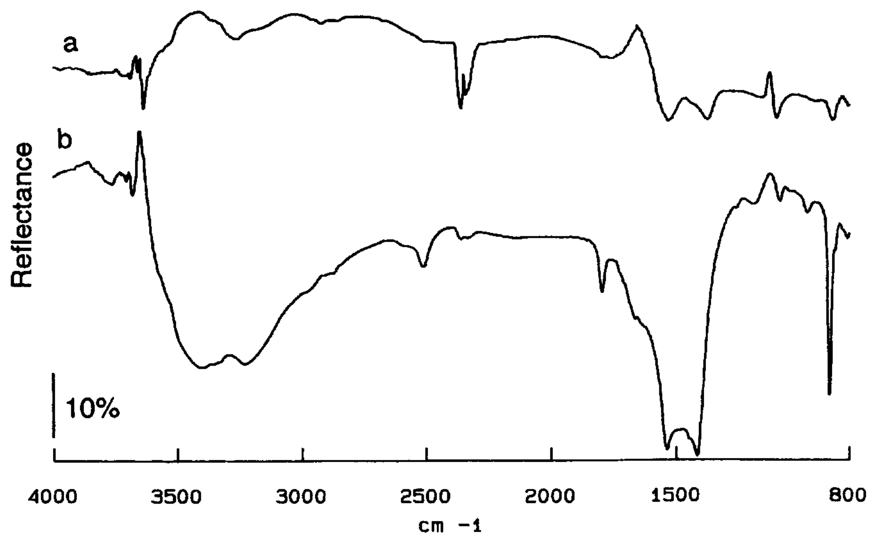

Fig. 1. $Ca(OH)_2$ exposed to 6 ppm CO_2 at 22°C at (a) 0% RH and at (b) 90% RH for 20 h. The prominent absorption band at 2350 cm^{-1} is due to $CO_2(g)$.

Hence, the IR reflectance pattern at 1550–1400 cm^{-1} would correspond to carbonate formation. A small absorption band corresponding to water formation could be claimed in Fig. 1, i.e. the feature at 3300–3500 cm^{-1}, and is expected from equations (1) and (2). Although this absorption is systematic, such a conclusion is highly uncertain due to the experiment being performed at an elevated relative humidity.

This experiment is central to the interpretation of the DRIFT spectra for calcareous stone, since it localises the carbonate bands. Its importance is accentuated by the fact that water has a strong IR absorption in this energy region. Thus, distortions of the surface water spectrum that could easily be interpreted as methodological anomalies are presently explained by surface carbonate being formed or decomposed.

3.2. *Sulphite formation on* $Ca(OH)_2$

Aged calcium hydroxide is found to adsorb small amounts of SO_2 in contrast to the calcium hydroxide formed from fresh calcined $CaCO_3$ for the first 20 h at dry conditions. Fresh calcined $CaCO_3$ is initially an ideal adsorber of SO_2. This drastic increase in SO_2 uptake cannot be ascribed solely to an increased porosity in the material. Rather, imperfections in the crystalline material, observed by XRD, are proposed to contribute significantly to the reactivity of the material. The disorders would result from the fact that the fresh $Ca(OH)_2$ is formed from calcined calcite (see Section 2.1) rather than, e.g. by precipitation.

DRIFT spectra reveal surface sulphite to be the sole product when $Ca(OH)_2$ is exposed to 1 ppm SO_2 at dry conditions (Fig. 3). The negative reflectance band in the interval 1550–1400 cm^{-1} is due to desorption of CO_2 (*vide supra*).

When the sample is exposed to air with 90% RH and 1 ppm SO_2, reflections associated with the formations of both CO_3^{2-} and SO_3^{2-} are detected. The deposition of SO_2 and CO_2 is approximately 0.1 and 2 mg, respectively, on the $Ca(OH)_2$ sample of 0.03 g. Thus the absorptivities of the sulphite and carbonate bands are very different. Comparison to the dry SO_2 exposure experiment reveals no dramatic increase in sulphite formation (Fig. 2), assuming similar reflection behaviour at dry and humid conditions. The SO_2 deposition is approximately 0.06 mg/0.03 g $Ca(OH)_2$. These spectra bear great resemblance to those of sulphite on calcite in both the sulphite and water IR absorption regions. This was proposed to result from the formation of a $CaSO_3 \cdot 0.5H_2O$ surface analogue (Elfving *et al.*, 1994a). In order to further test the validity of this characterisation, $Ca(OH)_2$ was allowed to age in dry SO_2 atmosphere for 100 h. Upon investigation by XRD, crystalline $CaSO_3 \cdot 0.5H_2O$ was indeed seen to form on fresh $Ca(OH)_2$.

A similar interpretation of the sulphition of $Ca(OH)_2$ as was made for the carbonation (*vide supra*), taking into account that the reaction takes place both at dry and conditions, suggests the following sulphition mechanism:

$$2\ Ca(OH)_2(\text{surface}) + SO_2 \rightarrow 2\ CaSO_3 \cdot 0.5H_2O(\text{surface}) + H_2O. \qquad (3)$$

The fact that no sulphate is produced is in line with previous studies (Elfving *et al.*, 1994a–c) that show O_2 to be too weak an oxidant to oxidise sulphite both at calcite surfaces and in aqueous solution. The sulphation was found to be mediated by catalysts such as iron ions, manganese ions or NO_2.

3.3. SO_2 *adsorption by* CaO

Sulphition of calcium oxide upon exposure to dry SO_2 at room temperature has been observed previously by Martin *et al.* (1987) and Zawadski (1993). The surface of aged calcium oxide displays surface carbonation. This system is well suited to demonstrate the preference of surface sulphite before carbonate. Hence, exposure to 1 ppm SO_2 at dry conditions seems to result in a replacement of surface carbonate by sulphite (Fig. 4). The ability of fresh CaO to

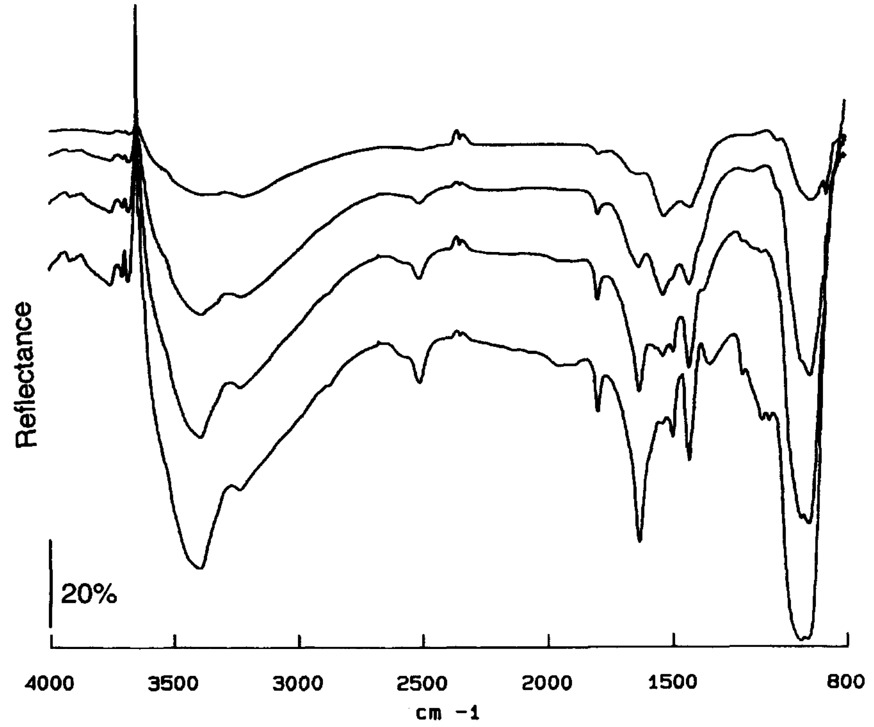

Fig. 2. DRIFT spectra of $Ca(OH)_2$ exposed to 1 ppm SO_2 and 6 ppm CO_2 at 90% RH. The spectra were acquired after 1, 5, 10 and 20 h exposure (top to bottom).

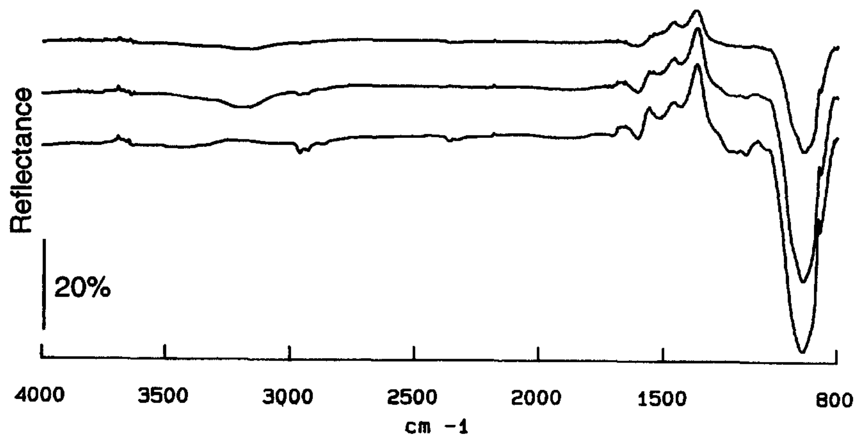

Fig. 3. DRIFT spectra of $Ca(OH)_2$ exposed to 1 ppm SO_2 and 6 ppm CO_2 at 0% RH. The spectra were acquired after 1, 5 and 20 h exposure (top to bottom).

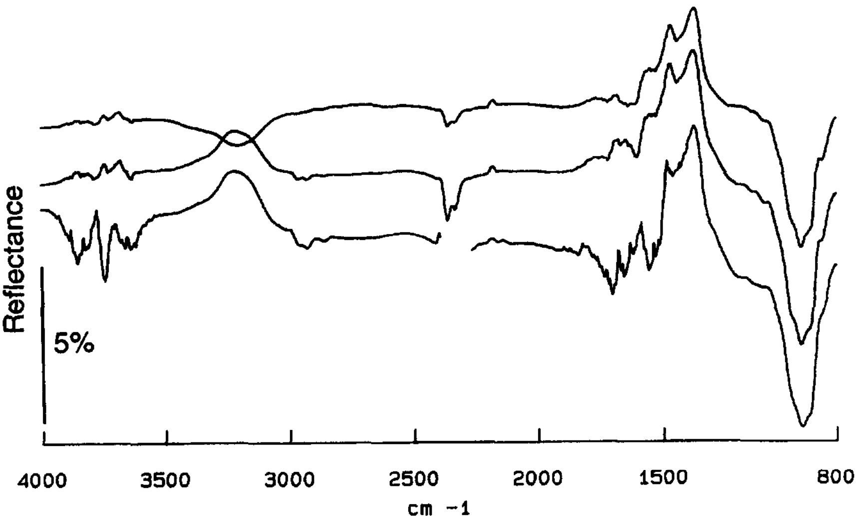

Fig. 4. DRIFT spectra of CaO exposed to 1 ppm SO_2 and 6 ppm CO_2 at dry conditions, 1, 5 and 20 h exposure (top to bottom).

adsorb SO_2 was also investigated. Thus, calcite was calcined at 800°C in N_2 atmosphere and the sample was subsequently exposed to SO_2 at dry conditions. A drastic increase in SO_2 absorption was detected, which implies the SO_2 adsorption by pure CaO(s) to form anhydrous calcium sulphite. Small negative IR reflections corresponding to the desorption of CO_2 that can be seen in the spectrum (Fig. 4) imply rapid initial carbonation and stresses the substrate preference for sulphite before carbonate. As in the case of $Ca(OH)_2$, the marked increase in reactivity is believed to be due to an increase in particle porosity but also to disorders in the fresh material. The fact that no crystalline $CaSO_3$ could be detected by XRD after long-time exposure is in contrast to the result for fresh $Ca(OH)_2$ (*vide supra*), and hence the qualitative difference in abilities of aged CaO and $Ca(OH)_2$ to absorb SO_2 is seen also for the fresh materials.

4. SUMMARY AND CONCLUSION

The physical effects of water in porous building materials have been extensively investigated previously, while a detailed understanding of the chemistry has been lacking. Calcium hydroxide is a key ingredient in many traditional building materials such as plasters, and its reaction with CO_2 to form calcium carbonate is a main reason for its importance. The competition between carbonation and sulphition was addressed. Also, decarbonation of calcium carbonate upon exposure to SO_2 was modelled, and argued to be crucial for the understanding of the deterioration of calcareous stone monuments, since calcium carbonate constitutes the main chemical component in this material.

Below is a summary of the achievements of the present study.

- The initial formation of surface $CaCO_3$ on $Ca(OH)_2$ was monitored, and surface water was shown to be a necessary condition for carbonation.
- The reactivity of calcium hydroxide to SO_2 depends strongly on the history of the material. Aged $Ca(OH)_2$ is a moderate adsorbent, while the fresh substance reacts readily to form $CaSO_3 \cdot 0.5H_2O$. The reaction rates are only weakly coupled to the relative humidity.
- Sulphition of calcium hydroxide is preferred as compared to carbonation. Thus the former dominates despite the relative concentrations being 1 : 6 (1 : 60) in the experimental atmosphere.

- The preference of sulphition before carbonation was also demonstrated with CaO as substrate.

These results point to the sensitivity of calcium hydroxide to SO_2 attack, and the favoured sulphition before carbonation. Hence, the wanted carbonation occurs only at humid conditions, while sulphition is less affected by the relative humidity.

This study also produces an additional clue to the understanding of the sulphite formation on calcite, which is proposed to be the key step in the deterioration of calcareous stone. In a previous study water was shown to be necessary for surface sulphite formation on calcite. While the formation of crystal water in $CaSO_3 \cdot 0.5H_2O$ was indicated to be the main reason, the result of the present work suggests the role of water to be twofold, in being a necessary prerequisite for decarbonation as well. The preference for sulphition before carbonation in the subsequent step leads to the final product.

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