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## EXPERIMENTAL STUDY OF LIMESTONE AND SANDSTONE SULPHATION IN POLLUTED REALISTIC CONDITIONS: THE LAUSANNE ATMOSPHERIC SIMULATION CHAMBER (LASC)

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**Abstract**—The Lausanne Atmospheric Simulation Chamber (LASC) has been constructed with the aim of studying the SO<sub>2</sub> effects on different materials. It allows the carrying out of numerous measurements on large stone samples simultaneously and on line. The behaviour of two carbonatic stone types (limestone and sandstone), either naked or covered with fly ash or soot particles, exposed at the following conditions, SO<sub>2</sub> = 125 ppb (340 µg m<sup>-3</sup>), NO<sub>2</sub> = 50 ppb (98 µg m<sup>-3</sup>), relative humidity = 79%, temperature = 13°C, has been studied. This experiment has been carried out over a 1 yr period. It has been observed that SO<sub>2</sub> deposition velocity decreases with time and in different ways for each of the two stone types, naked or covered with fly ash or soot particles. During the first four months, the deposition velocity is higher on naked stones; later on, it is higher on the stone samples covered with fly ash. Throughout the experiment the SO<sub>2</sub> deposition velocity on stone samples covered with soot particles is lower than on naked samples and those covered by fly ash. Finally, the values of SO<sub>2</sub> deposition velocity are confirmed by the chemical analysis of sulphur in the samples. Sulphur is present from the stone surface down to about 0.8 mm depth. Copyright © 1996 Elsevier Science Ltd

**Key word index:** Atmospheric simulation chamber, sulphur dioxide, limestone, sandstone, fly ash, soot particles, SO<sub>2</sub> deposition velocity, sulphur fixation.

### INTRODUCTION

Gaseous pollutants (SO<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub>, etc.), microparticulate carbonaceous matter (particularly fly ash), and water are, according to the literature, today's most active factors in the deterioration of building stone surfaces in areas where air quality is bad. In these areas and for materials containing calcium carbonate, the most important degradation is identified with sulphation.

The sulphation has been described by some authors as a development of black crusts (Kieslinger, 1932; Jeannette, 1981; Camuffo *et al.*, 1982; Del Monte and Sabbioni, 1984; Ausset *et al.*, 1991). These crusts are found mainly in areas protected from rain wash-out and their thickness grows as the air pollution increases.

Other authors observed stone sulphation with no formation of black crusts, as if stones could have the capacity of drawing and storing sulphur without any visible transformation of the surfaces concerned (Winckler, 1966; Braun and Wilson, 1970; Furlan and Girardet, 1988).

These two phenomena can be easily observed in the natural environment but are very difficult to be interpreted and above all to be quantified. Sulphation depends on numerous factors including the stone type, the concentration of polluting elements (gas, particles), temperature and humidity. It is difficult to identify the role played by these different factors and it is therefore necessary to carry out simulations in laboratories, under very precise conditions, in order to understand their activity.

In the literature there are some studies simulating the stone alteration caused by sulphur dioxide. Speeding (1969) and Breccia *et al.* (1975) have reproduced in a simulation chamber the degradation of limestones and marbles under the effect of <sup>35</sup>SO<sub>2</sub> with high humidity. After some hours of exposition the formation of Ca<sup>35</sup>SO<sub>4</sub> has been observed. Judeikis and Stewart (1976) and Cobourn *et al.* (1993) showed that the deposition velocity of SO<sub>2</sub> varies, depending on the nature of exposed materials (marbles and dolomites). Similar studies (Serra and Strarace, 1978) on calcium carbonate and SO<sub>2</sub> demonstrated



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that not only is an important quantity of carbonate transformed into calcium sulphate, but that this reaction does not occur completely in the absence of humidity. The works by Spiker *et al.* (1992a, b) show that the deposits of SO<sub>2</sub> on limestones and marbles increase exponentially when the relative humidity increases. Johansson *et al.* (1988) show that limestones exposed to a gaseous mixture of SO<sub>2</sub>-NO<sub>2</sub> and at a relative humidity of 90% form gypsum on their surface: according to these authors, NO<sub>2</sub> acts as a catalyst of oxidation of sulphur dioxide on the stone surfaces.

In addition to these experiments in simulation chambers, numerous studies on black crusts have been performed. These crusts, besides their gypsoous nature, contain fly ash emitted during fuel oil and coal combustion. Camuffo *et al.* (1983) and Del Monte and Sabbioni (1984) also assert that a small amount of gypsum forming sulphur and calcium could be carried by microparticulate aerosol carbonaceous matter and particularly by fly ash. The same authors (Del Monte *et al.*, 1984) observed in the laboratory the growth of inorganic crystals on black carbons from fuel oil combustion (fly ash) exposed to 60–100% relative humidity and at room temperature. Among these authigenic minerals, gypsum is the most abundant mineralogical phase.

Few studies, in the literature, concern the interaction between stones, sulphur dioxide and carbonaceous microparticulate matter. Cheng *et al.* (1987) show that fly ash covering marble in a simulation chamber with humid air and a high SO<sub>2</sub> concentration (100 ppm) induce gypsum formation in a much higher quantity than on naked stone in the same climatic conditions. Hutchinson *et al.* (1992), on the contrary, demonstrate that neither the fly ash produced by fuel oil nor that emitted by coal fire combustion increase the gypsum formation on limestone surfaces.

While the experiments regarding the interaction stone-SO<sub>2</sub>-fly ash are very poor, the studies on the interaction fly ash-SO<sub>2</sub> are, on the contrary, the object of important literature. All these studies demonstrate a high fly ash reactivity. Craig *et al.* (1974) indicate, by XPS-ESCA, that these particles contain numerous chemical elements, and sulphur compounds, especially sulphates.

Novakov *et al.* (1974) demonstrate that the carbonaceous particles catalyse the oxidation of SO<sub>2</sub> to SO<sub>3</sub> at room temperature. Tartarelli *et al.* and Liberti *et al.*, in 1978, demonstrate the capacity of carbonaceous particles adsorbing and converting SO<sub>2</sub> into sulphates. This oxidation process is magnified by the presence of NO<sub>2</sub> and O<sub>3</sub> (Cofer *et al.*, 1980, 1981). All these authors furthermore agree that high relative humidity is a relevant factor for these transformations.

Taking into account these different considerations and because of little experience on the reactivity of stones in the presence of gas and especially of fly ash and soot particles, we have developed an atmospheric

simulation chamber reproducing urban pollution in order to study the different factors leading to stone sulphation. Contrary to the previous authors, with the exception of Spiker *et al.* (1992a, b), we chose much lower SO<sub>2</sub> concentrations which are similar to the ones in urban polluted atmospheres.

The stones chosen for the experiment are a limestone and a sandstone, the behaviour of which has been previously studied in the field (Furlan and Girardet, 1992). These rocks were utilized both naked and covered with fly ash (produced by heavy fuel oil combustion) or soot particles (from light fuel oil combustion in diesel motors). Both types of particles are present in relevant quantities in polluted urban atmospheres.

The aim of this experience was to study:

- (1) the behaviour of the two types of stones and of an inert substrate (quartz fibres) in the presence of gas: SO<sub>2</sub>, NO<sub>2</sub> and H<sub>2</sub>O<sub>vap</sub>,
- (2) the behaviour of fly ash and of soot particles with the same atmospheric gaseous pollutants and H<sub>2</sub>O<sub>vap</sub>,
- (3) the behaviour of stones in contact with microparticulate carbonaceous matter, gaseous pollutants and H<sub>2</sub>O<sub>vap</sub>,
- (4) the products resulting from these different interactions, and
- (5) how the different materials contribute to the formation of the alteration products.

This paper deals with the first three points only: the last two will be developed in a later paper. Before considering these steps, a description of the simulation chamber and of its working system is given.

#### THE LAUSANNE ATMOSPHERIC SIMULATION CHAMBER (LASC)

The simulation chamber is made up of three units (Fig. 1): a system of gas injection, a main part with cells containing stone samples, and a measuring and monitoring control unit.

##### Gas injection system

Dry air is filtered on active charcoal (1) and then moisturized above a water bath (2) with temperature control to obtain a relative humidity between 10 and 95% ± 1%. The air is filtered again at its exit (3) before the addition of SO<sub>2</sub> and NO<sub>2</sub> (4). The dilution is regulated by means of mass flow meters (5). SO<sub>2</sub> and NO<sub>2</sub> concentrations as well as the diluted gas flux can be regulated for each cell within the limits of 3–500 ppb and 1–20 l min<sup>-1</sup>, respectively.

##### The main part

The main part (3.5 × 2.2 × 1.4 m) contains 10 cells (6) with a volume of 22 l each made of borosilicate glass. These cells are equipped with d.c. fans (7) passing at full charge 17 l s<sup>-1</sup> of air with an inlet power of

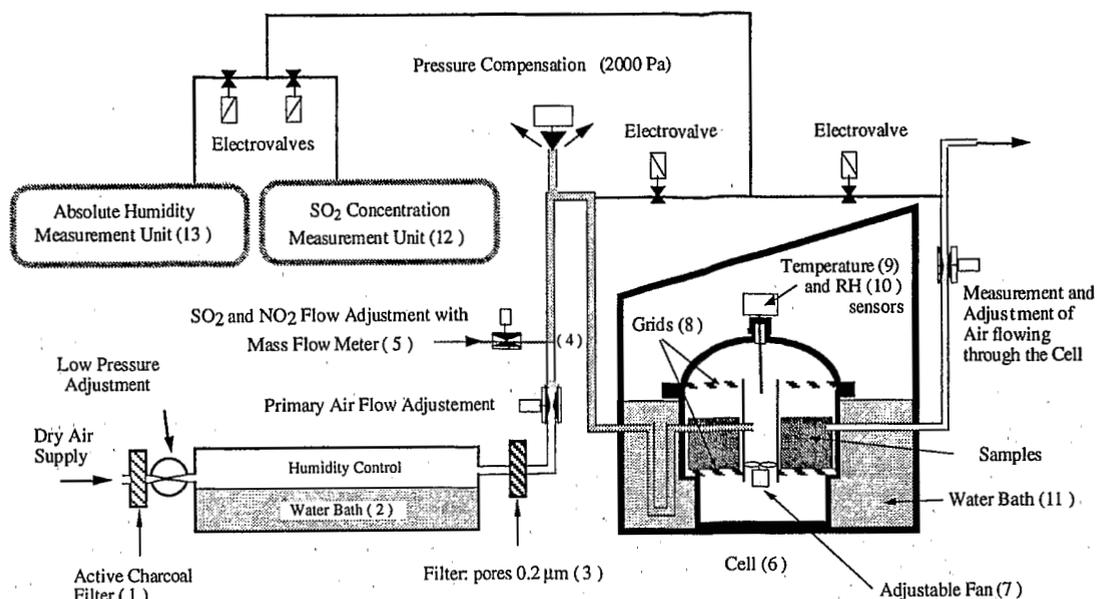


Fig. 1. Scheme of one of the 10 cells and of its running: gas injection system (1 to 5), main part (6 to 11) and measurement system (12 and 13).

7.2 W. Grids (8) assure atmospheric homogenizing. The speed of the fans is adjustable for each cell. This enables the resistance of the boundary layer to be regulated between 1 and 4  $\text{s cm}^{-1}$  after setting. These values have been determined experimentally by means of test samples of fibreglass impregnated with a solution of potassium carbonate in glycerol. Since the superficial resistance of the materials in experimental conditions is practically nonexistent, the measured values correspond to the transferring resistance of air. Although some air speeds do not exceed  $300 \text{ mm s}^{-1}$ , the weak air speeds measured allow us to suppose that the boundary layer is very thin and the exchange with the surface of the stone samples occurs in turbulent conditions. In laminar flow, notably higher values were found (Spiker *et al.*, 1992 a, b). The temperature and relative humidity adjustment is the same for all cells. It is achieved by a thermoresistance Pt 100 (9) and a capacitive probe (10) placed inside an empty reference cell. The cell inner temperature is adjustable between 5 and  $30^\circ\text{C} \pm 0.2^\circ\text{C}$ ; its stability is assured by the immersion of cells in a thermostatic water bath (11). All cell forming materials have been chosen by their chemical inertia; the metallic parts have been coated with PTFE.

#### Measure system

The concentration measures of water and SO<sub>2</sub> in air are carried out by aspiration inlet and outlet of each cell three times an hour. The concentration of SO<sub>2</sub> is measured by means of an analyser with a UV fluorescence detection Horiba AP5H (12), and the absolute humidity by a dew point instrument MBW Electronics/DP3 D (13). The measure of NO<sub>2</sub> concen-

tration is performed at the inlet of each cell only. A set of programmed measures as well as periodical setting of the measure instruments are enabled by a control unit. A microcomputer works out all operating data.

#### EXPERIMENTAL CONDITIONS

The experimental conditions were fixed with the aim of:

(i) getting products of interaction between pollutant gases and exposed materials which can be easily identified and quantified throughout the experiment;

(ii) operating in realistic conditions: we opted therefore for temperature values, relative humidity and SO<sub>2</sub> concentration measured in Milan urban area, a good example of an industrialized European town where SO<sub>2</sub> concentration was particularly high in the last decades. We chose temperature and relative humidity corresponding to the annual average of this town in the 3 last decades (from 1931 to 1960) and, although SO<sub>2</sub> concentrations are decreasing over the last years, we decided to experiment with the values of the 1972 annual average ( $125 \text{ ppb} = 340 \mu\text{g m}^{-3}$ ), i.e. a year when the pollution peaks were very high. Besides, in order to take into consideration the synergic role of NO<sub>2</sub> (Johansson *et al.*, 1988) we introduced it into the cells with the concentration measured in Milan in the same year (1972:  $50 \text{ ppb} = 98 \mu\text{g m}^{-3}$ ). A boundary layer resistance value ( $r_{\text{air}}$ ) of  $1.3 \text{ s cm}^{-1}$  is representative for the relatively well-protected areas of a building, according to our measurement. This experiment is developed over 1 yr with quarterly drawings of samples and carried out in total darkness in order to limit the photochemical effects and the development of some microorganisms. The utilized experimental conditions allow us to compare the results obtained by LASC with those obtained by Furlan and Girardet (1992) in the field (see Table 1).

In Fig. 2 the variations of temperature and relative humidity in the reference cell during the 12 experimental months

Table 1. Physical and chemical parameters inside each cell

Temperature	$13 \pm 0.2^\circ\text{C}$
Relative humidity	$79 \pm 1\%$
SO <sub>2</sub> concentration	$125 \pm 5 \text{ ppb} = 340 \pm 13 \mu\text{g m}^{-3}$
NO <sub>2</sub> concentration	$50 \pm 2 \text{ ppb} = 98 \pm 4 \mu\text{g m}^{-3}$
Boundary layer resistance	$1.3 \text{ s cm}^{-1}$
Exposure	3, 6, 9 and 12 months

are recorded. It shows the good stability of the system, with the exception of some accidents which we will comment upon later.

#### THE MATERIALS EXPOSED IN THE CHAMBER

Two kinds of stones were selected according to their relevant capacity of fixing sulphur in polluted urban areas (Furlan and Girardet, 1988): Jaumont limestone and Berne sandstone. As it is known in the literature, fly ash is always present inside gypsum crusts (Del Monte and Sabbioni, 1984; Camuffo *et al.*, 1983; Ausset *et al.*, 1994): they contain S, sulphate compounds and metallic catalysts (Fe, V, Ni, etc.) (Novakov *et al.*, 1974) which facilitate the reaction of sulphation of carbonatic rocks in particular conditions of temperature and air humidity (Del Monte *et al.*, 1984). This is the reason why we put fly ash in the presence of some of our stone samples utilized in LASC. Finally, the abundance of soot particles (also containing S and metals) in the atmosphere of towns with heavy traffic permits us to deduce that they could take part, as does fly ash, in the reactions of sulphation (Novakov *et al.*, 1974; Chang *et al.*, 1981). Therefore, in our experiment we also put soot particles on some of our stone samples.

#### The stones

The Jaumont limestone (calcite = 94%; quartz = 2.5%) is an oolitic bioclastite with microspartic

cement. The porosity of this limestone derives from the addition of a macroporosity and a microporosity with low connectivity. Macroporosity consists of large pores of about 200  $\mu\text{m}$  deriving from the dissolution of bioclasts edges. Petrophysical studies show that all macroporosity is trapped. Microporosity in porous areas either in the centre of bioclasts or in microspartic cement is a free porosity.

The Berne sandstone is a calcareous sandstone (calcite = 23%; quartz = 40%). Two types of porosities affect it. Microporosity derives from uneven contact among the grains, from microporosity of feldspars altered to clay minerals and from clay matrix: it is a free porosity. Macroporosity consists of intergranular spaces which are not occupied by calcareous cement and clay matrix. They are seldom larger than 50  $\mu\text{m}$ : it is a trapped porosity.

#### The fly ash and the soot particles

In 1991 a sampling was carried out in the Porcheville power plant (France) that utilizes heavy fuel oil. The samples were collected at the outlet of the boiler, on the electrostatic precipitators: coarse particles with a diameter of several mm, of various colours (green, brown, red), were found. They were mixed with very small particles which could be recognized by microscopical methods only. Considering the great variety of these particles, a splitting of the sample by sieving (Norm DIN 4195) was performed. In order to approach the real conditions of atmospherical pollution as much as possible the fraction composed of particles with a diameter lower than 100  $\mu\text{m}$  was kept: these particles could be carried to great distances and interact with all surfaces, including building stones.

These fly ash belong to two morphological categories: the first category consists of more or less spherical and spongy microparticles representing 97% of the total sample. The greatest part has a diameter between 50 and 100  $\mu\text{m}$ . (They are found within carbonaceous particles as reported in the

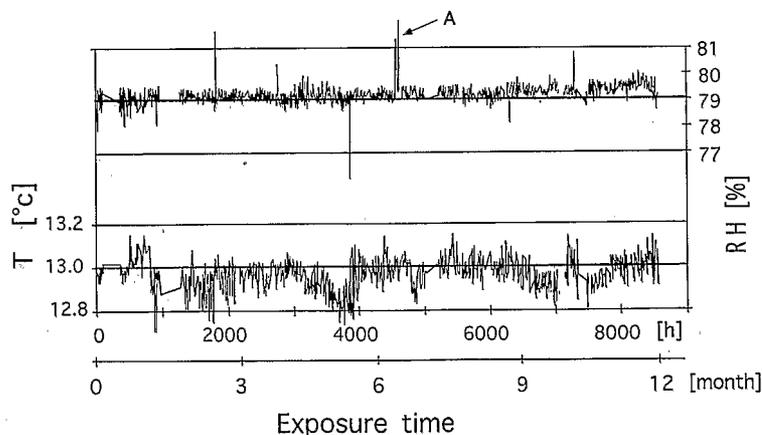


Fig. 2. Variation of temperature and relative humidity in the reference cell during 12 experimental months (A: accidental increase of relative humidity at 4600 hours).

nomenclature given by Fischer *et al.* (1978)). The second category consists of spherical and smooth particles and represents about 3% of the total population. Their diameter varies from a few  $\mu\text{m}$  to 50  $\mu\text{m}$ . Referring to the Fischer *et al.* (1978) nomenclature, they are classified as solid spheres and cenospheres.

Soot particles were drawn from the wall of an exhaust pipe of a motor installed on the test bench of the Institut Francais du Pétrole (Rueil-Malmaison, France). Soots sampled correspond to the combustion products of different fuels of various qualities as in the case of exhausts of diesel motors in polluted urban areas. They are black and covered by a film of oil. This sampling did not undergo any preliminary sieving, as happened with the previous one. The soot particles have a diameter of about 0.1  $\mu\text{m}$ . The Analytical Transmission Electron Microscope (ATEM) demonstrates that they are carbonaceous spherical particles, assembled in clusters. Few particles have a higher diameter (40–70  $\mu\text{m}$ ) and are formed of spongy and carbonaceous particles which are very similar to those observed in heavy fuel oil combustion.

#### The inert support

A filter manufactured by the Whatman® Company is used as an inert support. This type of filter is realized for the air filtration in the controlling stations of atmospheric pollution. It consists of 95% of ultra-pure quartz microfibrils and 5% of borosilicated glass microfibrils. It does not contain alkaline-earth metals and its use is recommended in environments rich in  $\text{SO}_2$  and  $\text{NO}_2$ ; also the technical instructions state that the risk of reaction of sulphation and nitration is non-existent. This material is completely inert in relation to atmospheric microparticles which can be easily observed.

#### PREPARATION OF THE TEST SAMPLES AND APPLICATION OF THE FLY ASH AND SOOT PARTICLES

The test samples were drawn from cores of quarry blocks. They were cut up, squared and washed with demineralized water and dried at 60°C to constant weight. In consideration of the petrographical heterogeneity of stones, the difficulty in obtaining a homogeneous dispersion of fly ash and soot particles on their surface, and with the aim of quantifying and interpreting the results, the test samples were prepared to sufficient size, i.e. 0.1 × 0.1 × 0.02 m. The Jaumont limestone or the Berne sandstone, as well as the inert support, were exposed in the cells naked or covered with fly ash or with soot particles. Each cell contained only one type of preparation to avoid any interaction between samples. It contained eight similar samples in a same geometrical disposition (total: 72 samples). Every three months, two samples were drawn out of each cell.

The homogeneous distribution of particles on the exposed surface of the stone samples is a delicate

process. We spread 7.5  $\text{g m}^{-2}$  of fly ash on the exposed surface (0.01  $\text{m}^{-2}$ ) and then pressed them lightly to fix the particles. For the soot we spread 50 mg (5  $\text{g m}^{-2}$ ) on each stone sample. The result of this application was that the fly ash thickened mostly in the largest pores of the stone samples, especially in the Jaumont limestone, and, in contrast, the soot formed a continuous layer on the surface of the samples.

After applying fly ash and soot, the stone samples were assembled and bound two by two by a PTFE tape around the edges. In this way, only one side of the stone samples was exposed to the atmospheric simulation chamber.

#### RESULTS

##### Variation of $\text{SO}_2$ concentration in the cells

Since the homogeneity of atmosphere was assured by fans,  $\text{SO}_2$  concentration measured at the cell exit was considered the same as on the stone samples. This concentration depended on the inlet concentration, on the gaseous flow and on the material reactivity.

The reactivity variations of the materials during the experiment and the change of number of stone samples in the cell entailed resetting of the inlet concentrations in order to keep the  $\text{SO}_2$  concentration constant at the exit. They were carried out periodically when the variation in relation to the fixed value (125 ppb of  $\text{SO}_2$ ) became too high, and every three months when a set of stone samples was drawn out from the cells (Fig. 3). Figure 4 shows the variations of  $\text{SO}_2$  concentration in the cells containing the Berne sandstone samples naked and covered with fly ash or with soot. The same variations can be observed on the Jaumont limestone samples and on the inert support.

##### Deposition velocity of $\text{SO}_2$

The deposition velocity of sulphur dioxide ( $v$ ) is calculated starting from the flux ( $F$ ) and the concentration ( $C$ ):

$$v \text{ (m s}^{-1}\text{)} = \frac{F \text{ (g m}^{-2}\text{s}^{-1}\text{)}}{C \text{ (g m}^{-3}\text{)}}$$

In the simulation chamber, the flux is determined from the difference of  $\text{SO}_2$  concentration between the inlet and the outlet and from the gaseous flow for the surface unit of each stone sample. The deposition velocities of  $\text{SO}_2$  for the three naked materials, covered with fly ash or with soot particles, were determined during the 12 test months.

The following observations can be made:

- (1) The deposition velocity of  $\text{SO}_2$  for the filters of quartz microfibrils is, in all cases, very weak, between 0.005 and 0.01  $\text{cm s}^{-1}$  (Fig. 5).
- (2) The deposition velocity of  $\text{SO}_2$  on the Berne sandstone (Fig. 6) varies from 0.40 to 0.20  $\text{cm s}^{-1}$ , while for the Jaumont limestone (Fig. 7) these velocities vary from 0.45 to 0.15  $\text{cm s}^{-1}$ .

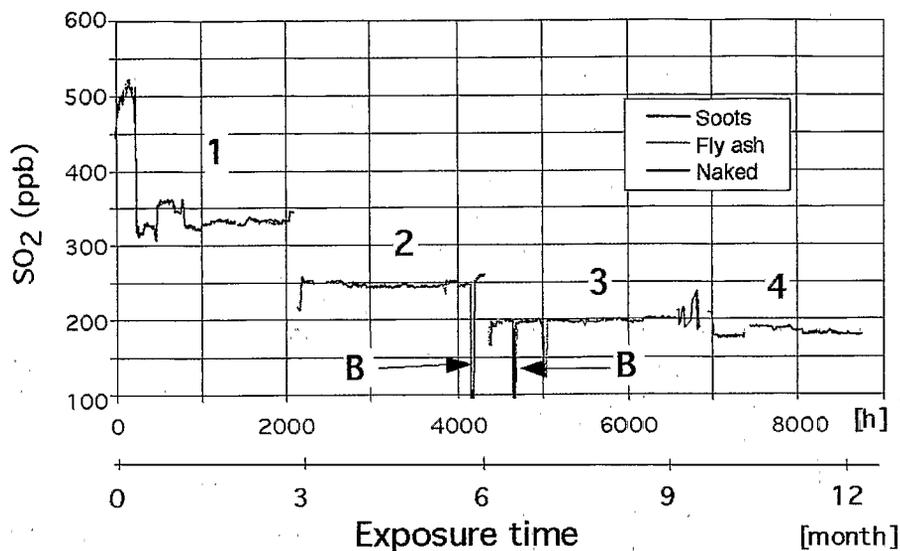


Fig. 3. Variation of the  $\text{SO}_2$  inlet concentration in three cells containing Berne samples naked, covered with fly ash or with soot particles. The very weak differences among the three curves indicate the good working of the  $\text{SO}_2$  dilution and measurement system. The four flats correspond to the periodical adjustments of the inlet concentration because of the decrease of the number of stone samples in the cells after the quarterly drawings (B: drop of the concentration as a consequence of an accidental stop of  $\text{SO}_2$  injection).

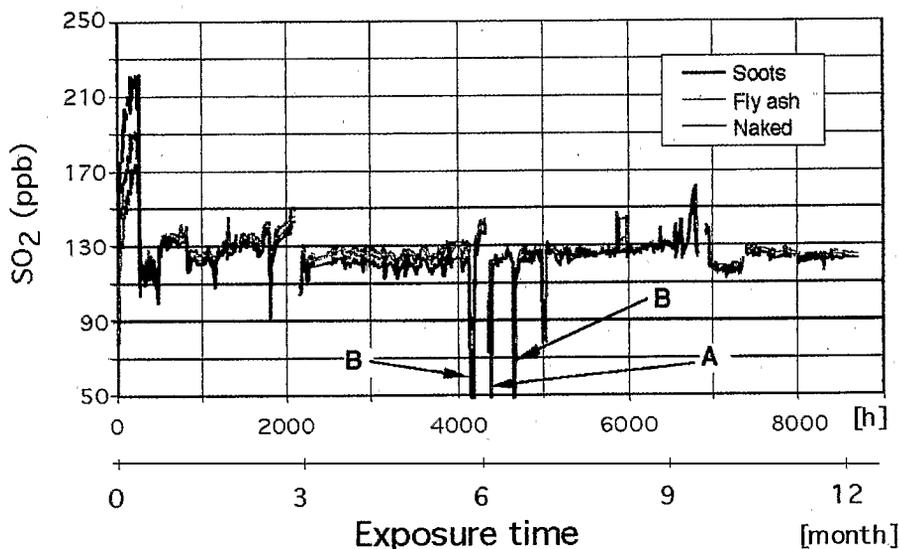


Fig. 4. Variation of  $\text{SO}_2$  concentration over 1 yr at the exit of the three cells containing Berne samples naked, covered with fly ash or with soot particles. The concentration decrease (A) corresponds to the increase of  $\text{SO}_2$  deposition velocity for the materials relating to an accidental increase in the relative humidity in the cells. The peaks B were caused by an accidental interruption of  $\text{SO}_2$  injection.

(3) In the Jaumont limestone (Fig. 7) a higher difference among the three deposition velocities (naked, with fly ash or with soot particles) can be observed than in the Berne sandstone (Fig. 6). These differences tend to decrease with time.

(4) In both cases, but especially for the Jaumont limestone, the deposition velocity decreases with time.

(5) The deposition velocity on the Berne sandstone is similar to the average deposition velocity observed on stones exposed in Milan (M in Figs 6 and 7) (Furlan and Girardet, 1992). The deposition velocity on the Jaumont limestone is considerably different from that on the Berne sandstone, especially during the first six months.

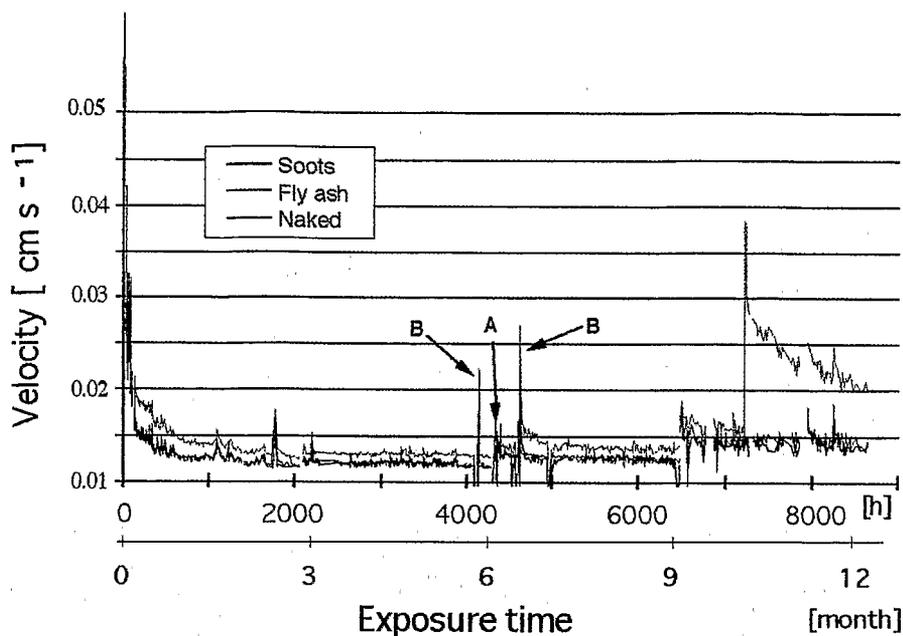


Fig. 5. Deposition velocity of  $\text{SO}_2$  on the quartz filter, naked, covered with fly ash or with soot particles during the 12 experimental months (A: accidental increase in relative humidity; B: accidental interruption of  $\text{SO}_2$  injection in the cells). The velocity scale is magnified 10 times in relation to the same at Figs 6 and 7.

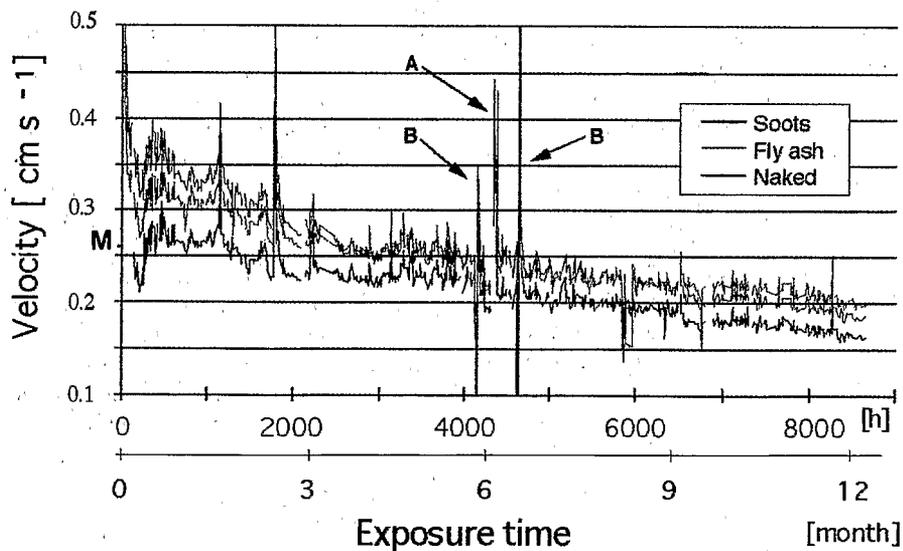


Fig. 6. Deposition velocity of  $\text{SO}_2$  on Berne sandstone, naked, covered with fly ash or with soot particles during the 12 experimental months (A: accidental increase in relative humidity; B: accidental interruption of  $\text{SO}_2$  injection in the cells; M: average annual deposition velocity of  $\text{SO}_2$  measured in Milan (Furlan and Girardet, 1992).

(6) After more or less four months of exposition the fly ash particles have an activating role, especially when they are on the Jaumont limestone.

(7) For the stone samples covered with soot particles, the deposition velocities are lower than for the naked or covered with fly ash stones, at least during the first nine months.

After nine months, the differences between the deposition velocities became lower and lower.

Although all basic parameters, i.e. temperature, relative humidity, concentration and gaseous flow, were kept within narrow limits, the velocity of  $\text{SO}_2$  deposition showed some sudden variations of high amplitude which can be seen in the diagrams (A and B

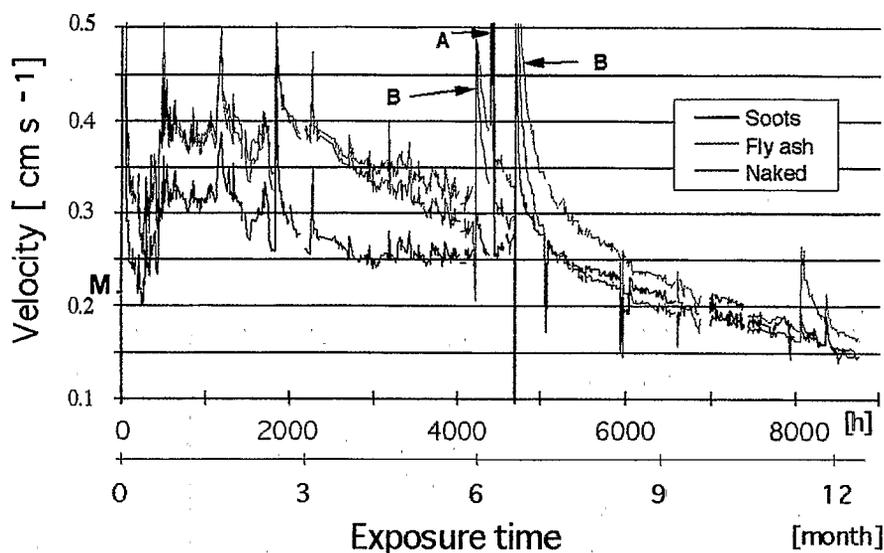


Fig. 7. Deposition velocity of  $\text{SO}_2$  on the Jaumont limestone, naked, covered with fly ash or with soot particles during the 12 experimental months (A: accidental increase in relative humidity. B: accidental interruption of  $\text{SO}_2$  injection in the cells; M: average annual deposition velocity of  $\text{SO}_2$  measured in Milan) (Furlan and Girardet, 1992).

in Figs 5, 6 and 7). The peaks correspond to abnormal and short variations in humidity or  $\text{SO}_2$  concentration. These accidents do not seem to have a long incidence on the deposition velocity on the Berne sandstone. They have, on the contrary, a very remarkable effect on the Jaumont limestone; a drop of  $\text{SO}_2$  concentration of some hours caused an activation of the deposition velocity for several hundreds of hours. This fact indicates that the two materials have a remarkable difference in their behaviour when they are moved from a stationary condition: the explanation lies in their different physical and chemical properties.

In the case of humidity variations, the deposition velocity attains its previous speed quickly again.

#### Determination of sulphur deposition

A set of two sample stones were drawn out from each cell every three months. The preparation of stone samples for analysis was performed by milling  $10 \text{ cm}^2$  of the surface of the stones in subsequent steps of  $0.1 \text{ mm}$  on  $2.5 \text{ mm}$  depth. The sulphur concentrations were determined by pyrolysis and Infra Red (elementary analyser of C and S: CSA 2003 Leybold-Heraeus) directly on small amounts of powder.

The results for the 3, 6, 9 and 12 months of exposition for each stone, naked or covered with fly ash or with soot are reported in Fig. 8. The values plotted in these diagrams correspond to the S quantity actually fixed, i.e. after deducting the sulphur contained in the stones, fly ash or soot particles. A regular decrease of

Table 2. Flux of fixed sulphur on the two stones ( $\text{g m}^{-2} \text{ yr}^{-1}$ ), after 3, 6, 9 and 12 months of experiment for the three different situations

Stones	Time (month)	Naked	Fly-ash	Soot particles
Jaumont Limestone	3	3.0	2.7	2.2
	6	7.1	6.7	4.5
	9	8.3	9.6	5.6
	12	10.0	10.3	7.2
Berne Sandstone	3	2.6	2.6	1.9
	6	4.9	4.7	3.5
	9	6.7	6.2	5.0
	12	8.3	8.5	6.3

sulphur fixation from the surface towards the depth can be observed in the case of the Berne sandstone. On the contrary, for the Jaumont limestone a weaker sulphur fixation in the first layer (100  $\mu\text{m}$ ) than in the second one is systematically observed. This last result can be explained by the structure of the stone material which shows on its surface large open pores with an average diameter of 200  $\mu\text{m}$ . Inside the pores,  $\text{SO}_2$ ,  $\text{NO}_2$  and  $\text{H}_2\text{O}$  concentrations are slightly higher and, because of a higher number of active sites, there is a higher probability that the reaction of  $\text{SO}_2$  fixation occurs.

Table 2 indicates the total sulphur fluxes calculated starting from the preceding data, by integrating the different distribution curves of Fig. 8.

It can be observed that:

- (1) The flow increases with time but not in a linear way: the speed increase lessens, depending on time, whatever the nature of stone is or if it is coated or not.
- (2) The Jaumont limestone is, in any case, more reactive than the Berne sandstone. This is quite obvious if we consider that the active mineralogical surface of the Jaumont limestone is much higher than that of Berne sandstone (94% and 23% calcite, respectively): the probability that one  $\text{SO}_2$  molecule interacts with one of  $\text{CaCO}_3$  and fixes as  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is much higher on the first. Besides, the large pores acting as traps further increase the probability of reaction in the Jaumont limestone.
- (3) After six months, the fly ash has an activating role.
- (4) The soot particles, on the contrary, protect the stones surface all over the experiment.
- (5) The sulphur deposition in relation to depth in the stone samples (Fig. 8) and the flow calculations of deposited sulphur (Table 2) agrees with the measure of  $\text{SO}_2$  deposition velocity (Figs 6 and 7).
- (6) The curve trend of Fig. 8 correspond to the ones determined on test samples of the same stones in the field of Milan between 1986 and 1987 (Furlan and Girardet, 1992). Figure 9 is, for example, the sulphur distribution on Berne sandstone after a yearly exposition in Milan.
- (7) The flow values up to 12 months also confirm that Jaumont limestone covered with fly ash is more reactive than the same material naked.

### CONCLUSIONS

The Lausanne Atmospheric Simulation Chamber (LASC) enables us to achieve artificial atmospheric conditions with fixed parameters that remain stable over long periods of time. Its 10 independent cells permit numerous simultaneous investigations, thus reducing the time needed to obtain results. The wide volume of the cells enables us to test numerous stone samples of sufficient size as to hide petrographic and petrophysic heterogeneity of the stone. Moreover, the

measurement method allows us to quantify the atmosphere-material exchanges on each cell instantaneously and on line.

The analysis of the first results concerning the behaviour of the exposed materials, i.e. Jaumont limestone and Berne sandstone, over a 1 yr period and under conditions similar to reality, points out remarkable modifications. Such modifications can be compared with the ones produced on the same materials in a polluted urban area.

Jaumont limestone and Berne sandstone have different  $\text{SO}_2$  deposition velocities when exposed naked. This can be explained by their different chemico-mineralogical and petrophysical characteristics.

As far as  $\text{SO}_2$  deposition velocity is concerned, fly ash particles do not change the behaviour of Jaumont limestone, during the first three or four months. From this time, the  $\text{SO}_2$  deposition velocity increases. The same behaviour can be observed on the Berne sandstone, but the increase of  $\text{SO}_2$  deposition velocity caused by fly ash is less revealing.

Throughout the experiment, the  $\text{SO}_2$  deposition velocity on stones covered with soot particles is lower, especially during the first six months. Soot particles seem to play an important screening role during this time interval.

In general, a decrease of  $\text{SO}_2$  deposition velocity can be observed in all cases, i.e. in samples exposed naked or covered with fly ash or soot. It shows a passivation phenomenon that decreases sulphation velocity with time.

Sulphur deposition into the stones occurs from the surface down to about 0.8 mm depth. In samples exposed naked or covered with fly ash or soot, this sulphur fixation tends to decrease with time. These measurements seem to indicate a decrease of stone sulphation with time too.

The above reported results show, according to Winkler (1966), Braun and Wilson (1970) and Furlan and Girardet (1988), the capacity of the two stone types to fix sulphur but, according to Judeikis *et al.* (1976) and Cobourn *et al.* (1993), at a different  $\text{SO}_2$  deposition velocity. We demonstrate, like Cheng *et al.* (1987), but with  $\text{SO}_2$  concentrations three orders of magnitude lower, that fly ash plays a role in stone sulphur fixation. On the contrary, our first results on the fly ash do not agree with Hutchinson *et al.* (1992) who also utilized carbonatic stones covered with fly ash, but using much higher  $\text{SO}_2$  values (0.5 ppm).

The aim of future publications will be the study of:

- (i) the products of the reaction between the two stone types,  $\text{SO}_2$  and the microparticulate carbonaceous particles;
- (ii) the link between the reaction products and the properties of the stones: chemical, mineralogical and petrophysical parameters.

These data will allow a better understanding of the preliminary results reported in the present paper.

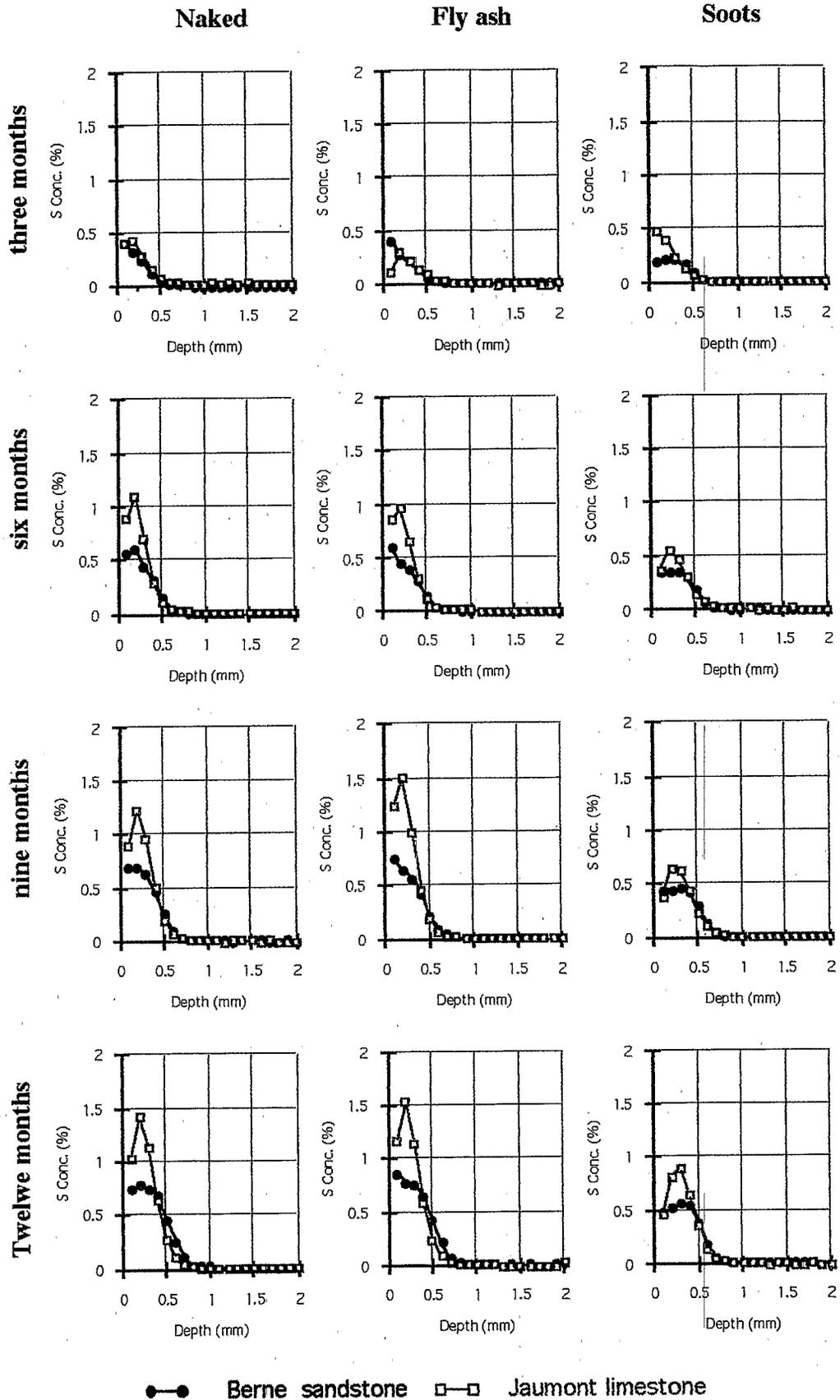


Fig. 8. Depth sulphur distribution in the Berne and Jaumont samples after 3, 6, 9 and 12 months of experiment.

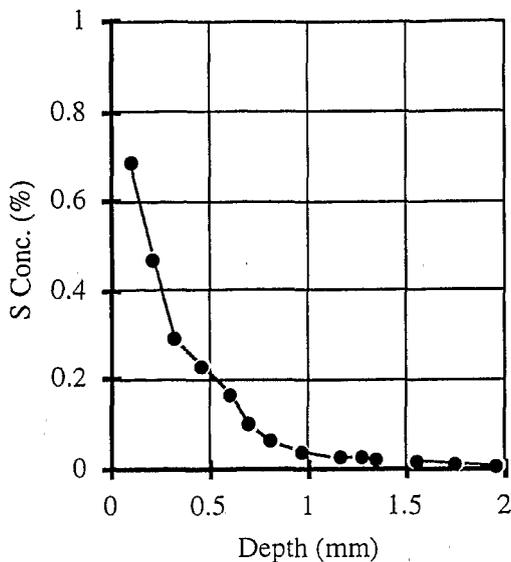


Fig. 9. Curve of sulphur distribution in relation to depth in a naked Berne sample exposed in Milan over 1 yr (1986–1987).

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