L. Cimitan
P.P. Rossi
G. Torraca

375

Accelerated sulphation of calcareous materials in a climatic chamber: Effect of protective coatings and inhibitors

Accelerated sulphation of calcareous materials in a climatic chamber. Effect of protective coatings and inhibitors

Lucio Cimitàn*, Pier Paolo Rossi*, Giorgio Torraca**
*ISMES SpA, Divisione Geomeccanica. 24068 Seriate BG, Italy
**Facoltà d'Ingegneria Università di Roma "La Sapienza". 00184 Roma RM, Italy

Abstract

A series of experiments allowed to determine the conditions required to produce an accelerated sulphation of calcareous stone and mortars in a climatic chamber. The chamber operated temperature cycles between 10° and 45°C under high humidity (98% r.h.) in a sulphur dioxide enriched (10 ppm) atmosphere and in the presence of nitrogen dioxide and ultraviolet radiation.

$CaCO_3$ powder and disks, the latter made of crushed white marble and lime, were exposed in the chamber and the amount of calcium sulphate formed was measured at regular intervals. The reaction shows a very slow start (induction period) before proceeding at a lively pace; in our interpretation, this fact indicates that some time is required in order to create on the surface of the calcareous material the proper conditions for the catalytic oxidation of sulphur dioxide.

The hypothesis was then advanced that some chemical compounds might act as inhibitors, further delaying the onset of the sulphation of the carbonatic material, since such effects are well known in the field of heterogeneous catalysis.

Five compounds were tested in the chamber by adsorbing them on $CaCO_3$ powder; two of them delayed the start of the reaction and reduced its rate.

Experiments conducted on the mortar disks showed that the application of a silicone coating did not cause a reduction in the rate of the sulphation process; this is consistent with the hypothesis that sulphur dioxide molecules should be able to pass through a thin protective coating to be adsorbed at suitable receptor points on the carbonate surface. The formation of calcium sulphate would require also the passage of molecules of oxygen, water and nitrogen dioxide on the same path.

The successive growth of calcium sulphate hydrate (gypsum) crystals under the surface film would then cause its progressive disruption and premature failure. Observation of the surface of the disks at the S.E.M. during the development of the sulphate crystals brought some support to this hypothesis.

The application of an inhibitor under the protective film, as a sort of primer, should cause a delay in the growth of the sulphate crystals and so prolong the life of the film; experiments on mortar disks showed that this is indeed true but that the efficiency of the inhibitor is not improved, but rather slightly reduced, by the application of a silicone coating on top of it.

Keywords

Accelerated weathering test, climatic chamber, acid atmosphere, chemical deterioration of stone, sulphation, sulphur dioxide oxidation, protective coating, failure of coating, oxidation inhibitor, stone corrosion inhibitor.

Introduction

Observations made both in the field and in the course of accelerated weathering tests led us to advance the hypothesis that, in polluted atmospheres, the service life of protective coatings applied on carbonate-rich stone or mortar might be considerably shorter than in the case of a carbonate-free material.

As an example, we observed a considerable difference of behaviour between coatings applied on Sarnico sandstone (which is almost carbonate free) and those applied on travertine from the Rome area (mostly calcium carbonate) in the course of weathering tests performed under an artificial atmosphere, enriched in gaseous SO_2. These experiments, which were intended to allow a comparison of the efficiency of various protective materials, do not constitute a proof of our hypothesis because there was a distance in time between them and the operation of the climatic chamber had been modified in the meanwhile; also the coating materials came from different sources.

There was a hint, anyway, that the failure of protective coatings on calcareous surfaces might depend upon a

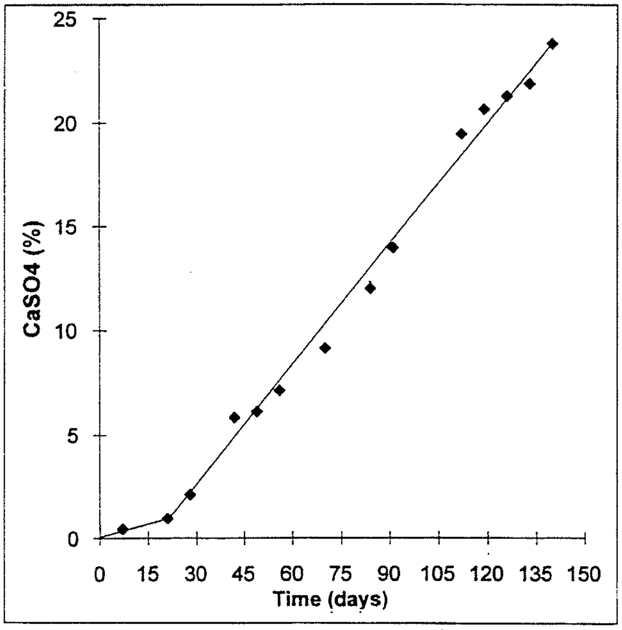

Fig. 1 - Progressive sulphation of calcium carbonate powder in the climatic chamber. Abscissa: time (days) - ordinate: $CaSO_4$ *%.*

special mechanism and this appeared to be a promising line of research.

Another interesting information that prompted the start of the present project was gathered from the analysis of the calcium carbonate powder which was introduced in the climatic chamber in each run to determine the efficiency of the weathering cycle and so to assess the comparability of the results obtained in different runs. The analysis of the sulphur content of the powder showed that the initial rate of reaction was extremely slow in all cases, starting to increase after some days to reach an almost constant value in about three weeks (see figure 1).

The fact that a certain amount of time is required before the sulphation may proceed at a reasonable rate, suggests that the reaction must overcome some energy barrier, most probably in the phase of the oxidation of sulphur dioxide. According to the literature, the heterogeneous catalytic oxidation of SO_2[1] in the initial phase should involve the adsorption of the reactant molecules on the surface of the solid catalyst; SO_2 at electron acceptor positions and O_2 at electron donor position[2].

One of several suggested schemes for the oxidation of SO_2 on a metal oxide catalyst is shown here below:

1. $O_2 + 2\,(\;) \Rightarrow 2\,(O)$
2. $SO_2 + 2\,(O) \Rightarrow (SO_4)$
3. $SO_2 + (SO_4) \Rightarrow 2\,SO_3 + (O)$

The species written between brackets are adsorbed on the surface and are supposed to be charged negatively[3].

The most active catalyst (among oxides) is vanadium pentoxide, but also iron oxide (Fe_2O_3) shows considerable activity. Another material which shows catalytic properties is carbon. Both carbon and iron oxide are frequently present on building surfaces in polluted atmospheres; in our experiments their absence is compensated by the addition of nitrogen dioxide to the gaseous mixture in the chamber and by the activation energy provided by ultraviolet radiation.

On a calcium carbonate surface it is not likely that reaction **3** will have a chance to proceed to any great extent; it is more probable that sulphate ions formed in reaction **2** be combined with calcium ions and water molecules to form gypsum.

If this mechanism is accepted, the surface reaction might then be inhibited by molecules containing electron acceptor, or donor, groups (or both) which could interfere with the adsorption processes taking place on the solid surface. Corrosion inhibitors act on metal surfaces according to a similar mechanism.

A list of chemicals to be submitted to screening tests was formed selecting either well known "poisons" of catalysts or molecules whose structure showed the possibility of a certain mobility of electrons (e.g. aromatic molecules, with nitrogen-containing substituent groups, or heterocyclic rings) or well known corrosion inhibitors. The screening tests were carried out adsorbing a solution of the presumed inhibitor on calcium carbonate powder and exposing the powder, with periodical mixing, in the climatic chamber.

Up to the present moment, however, only five products have been tested; the slow development of the project being due to the intensive use of the equipment for the evaluation of protective materials and to the frequent maintenance operations which are required because of the corrosive conditions prevailing in the test chamber.

The limited series of screening tests indicated anyway two potential inhibitors one of which was submitted to further testing on disks of an artificial calcareous stone made up with crushed marble and lime.

The use of the disks allows to study the behaviour of films applied on the surface. In the disk test the build-up of the sulphate concentration in the mass of the sample is obviously slower than in the case of the powder because the internal material is reached with greater difficulty by the reactive gases; on the whole, however, this is a more realistic test than the powder one.

A series of disks was also prepared including a water repellant in the formulation of the mortar, the purpose being that of testing the effect of hydrophobic properties in a plaster, or a stucco; this experiment, however, failed because it produced the surprising result that the sulphation rate of the hydrophobic material in the climatic chamber was greater than that of the plain lime-marble mortar.

The climatic chamber and the "acid" weathering cycle

The conditions under which sulphur dioxide reacts with the surface of a calcareous material to produce calcium sulphate (at a rate acceptable for the use in accelerated weathering tests) was be determined mostly by trial and error since only one reference in the technical literature did provide relevant information[4].

The experiments were carried out in a CLIMATEST equipment (manufacturer: Mazzali, Monza, Italy) provided with a 300 litres chamber. For the use with a corrosive atmosphere this space was reduced to 120 litres by the insertion of an airtight stainless steel container. The apparatus is provided with heating, cooling and humidifying systems controlled by solid state devices to produce the desired temperature and relative humidity conditions.

Inflow of air (and reactive admixtures) is controlled by a flow regulator. In our present operating conditions, filtered and washed air is admitted at a velocity of 6 litres/minute; air containing 2000 ppm sulphur dioxide is added from a cylinder to reach a 10 ppm concentration in the airflow.

Nitrogen dioxide is added as a catalyst, by injecting in the airflow a minimal amount of air containing 500 ppm NO_2; ultraviolet radiation is also provided by a lamp (Helios Italquartz 125w, total spectrum from 180 mμ upwards) which, according to the manufacturer, stimulates the production of ozone. Both catalyst and radiation are required to achieve a reasonable reaction rate.

The outflowing air is washed accurately in water to remove all corrosive gases or aerosols before being recycled into the climatic chamber.

The samples are placed flat on the bottom of the airtight container, while temperature and humidity are regulated in such a way that moisture condensation is allowed to take place in each cycle on their surface.

One weathering cycle includes:

a. 1 hour at 45°C, 98% r.h.
b. fast cooling to 10° C (1/2 hours)
c. 2 hours at 10°C, 98% r.h.
d. heating to 45°C (1/2 hours).

As one complete cycle takes 4 hours time, 6 cycles may be performed every day since all controls are automatic. U.V. radiation is always active.

Experiments with powder samples

Powder samples were prepared by weighing 10g of dry $CaCO_3$ and putting the powder in a 20 mm Petri dish.

Possible "inhibitors" were tested by dissolving 0,1g of the solid in a suitable solvent and pouring the solution in the Petri dish; after thorough mixing the solvent was allowed to evaporate.

A blank sample (pure $CaCO_3$ powder) is included in every run of the chamber and allows some sort of calibration of the efficiency of the equipment.

The test was intended to last 35-40 days. In the first 15 days the Petri dishes were removed daily, the powder was carefully mixed and a small amount was withdrawn for analysis. In the next 25 days samples for analysis were taken twice every week.

The only analysis performed on the powders was total sulphur, carried out by means of a "Sulphur Determinator 532-500" (LECO Corp. St. Joseph, Michigan, USA); in this apparatus the sample is burnt (1200°C) and the gases are gurgled inside a potassium iodide solution. The dissolved SO_2 is then titrated with potassium iodate until free iodine is formed.

The results otained in three runs of the chamber, each including three "inhibitors" undergoing the test and one blank, are shown in the figures 2, 3, 4, 5.

In each graph all measurements executed in the course of three experiments have been recorded and straight lines were drawn, attempting an approximate best fit to the recorded points; the slopes of the lines provide therefore an indication of the reaction rate in the various phases of the reaction.

The approximate reaction rates calculated from the approximate best fit lines are listed in table 1.

The conclusion which may drawn from these three tests is that p-nitro aniline does actually interfere with the sulphate formation in the calcium carbonate powder, delaying the start of the sulphur fixation and reducing the reaction rate once the reaction is started.

Sample	Initial rate	Intermediate rate	Final rate
A0 blank	1st-9thday 0.04%/day	10th-19th day 0,14%/day	20th-30th day 20th-0,31%/day
A1 lead acetate	1st-5th day 0,01%/day	6th-17th day 0,10%/day	17th-35th day 0,28%/day
A2 thiourea		1st-17th day 0,11%/day	18th-32th day 0,23%/day
A3 p-nitroaniline	1st-5th day 0,0005%/day	6th-19th day 0,04%/day	20th-35th day 0,07%/day

The materials undergoing the test were:
A0 pure calcium carbonate (figure 2)
A1 calcium carbonate + lead acetate (dissolved in water) (figure 3)
A2 calcium carbonate + thiourea (dissolved in water) (figure 4)
A3 calcium carbonate + p-nitro aniline (dissolved in acetone) (figure 5).

Table 1 - Sulphation rates of calcium carbonate powders with various admixtures.

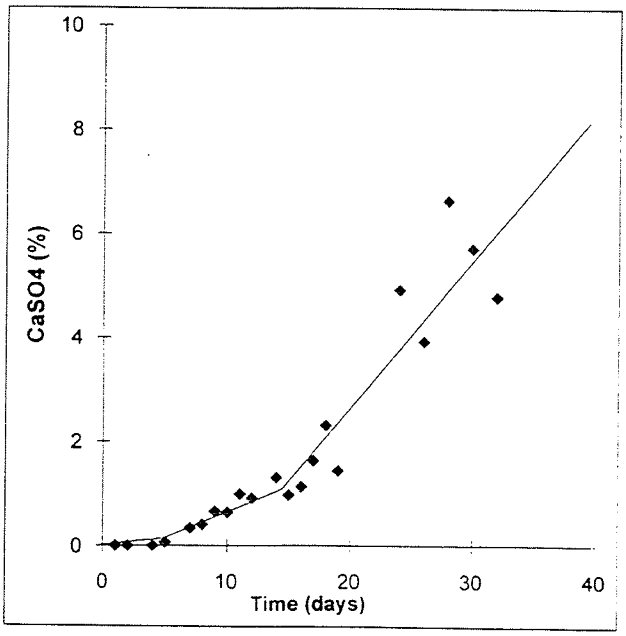

Fig. 2 - Screening tests of possible inhibitors on calcium carbonate powder. Sulphation rate of the blank (results of three different runs). Abscissa: time (days) - ordinate: $CaSO_4$ %.

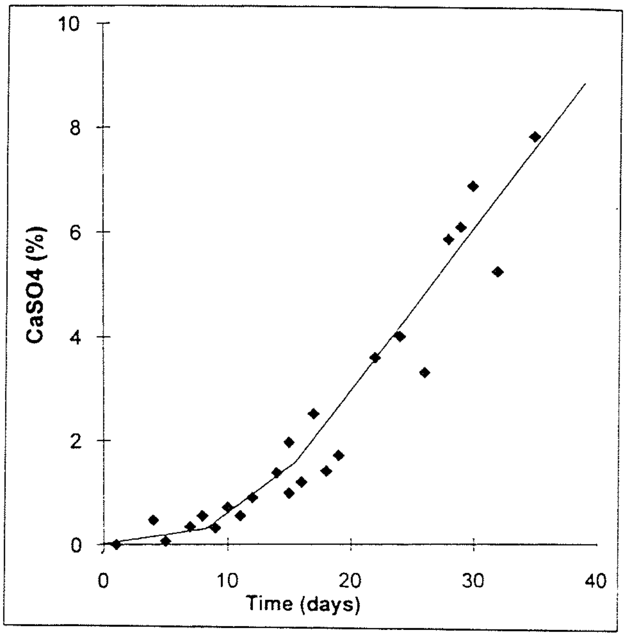

Fig. 4 - Screening tests of possible inhibitors on calcium carbonate powder. Sulphation rate in the presence of thiourea (results of three different runs). Abscissa: time (days) - ordinate: $CaSO_4$ %.

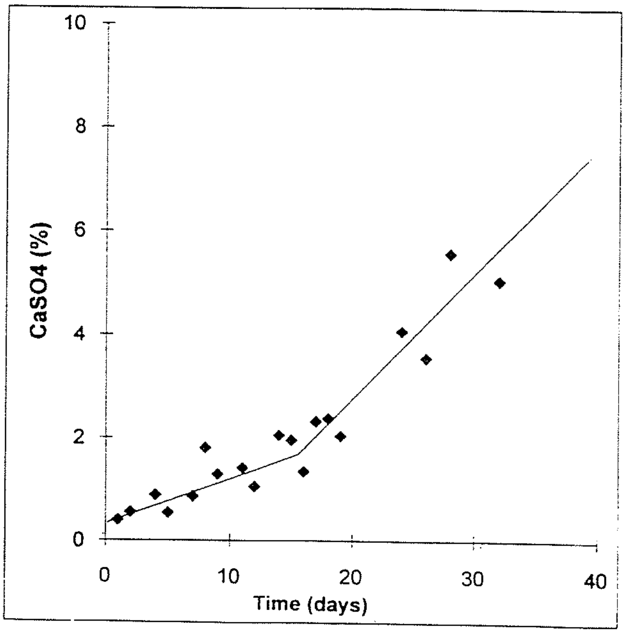

Fig. 3 - Screening tests of possible inhibitors on calcium carbonate powder. Sulphation rate in the presence of lead acetate (results of three different runs). Abscissa: time (days) - ordinate: $CaSO_4$ %.

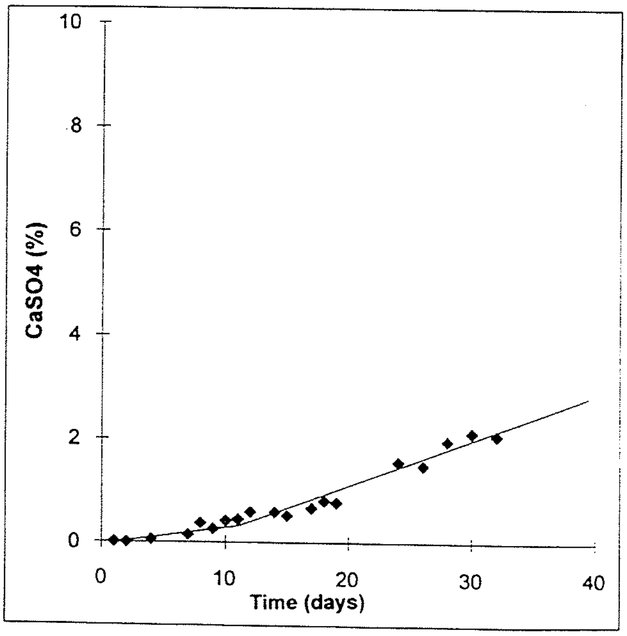

Fig. 5 - Screening tests of possible inhibitors on calcium carbonate powder. Sulphation rate in the presence of p-nitroaniline (results of three different runs). Abscissa: time (days) - ordinate: $CaSO_4$ %.

In the other two cases, although some influence is detectable, the compounds tested do not appear to be promising as inhibitors; thiourea actually appears to shorten up the induction period, even if later the reaction rate remains below the value it has in the blank.

Two other compounds were tested quite recently on powder samples: benzotriazole and 3-5-DTB-4-anisole. The first, as could be expected from its efficiency as a metal corrosion inhibitor, showed a definite delaying effect and a reduction of the sulphate formation rate while the second appeared to be totally inactive.

The present condition of the Climatest equipment, which is undergoing a complete revision after several years of operation and is also heavily scheduled for routine weathering tests, will not allow us still for some time to complete the planned series of screening tests of perspective sulphation inhibitors; we hope, however, to install soon a second identical chamber which will allow a much faster completion of our screening programme.

Experiments with mortar disks

Mortar disks were prepared according to the following formula:

Carrara marble, ground (0-2 mm)	3000 g
Calcium hydroxide 96%	500 g
Distilled water	600 g

After mixing, the paste was compressed in molds to form disks of 10 mm thickness and 100 mm diameter. After 60 days ageing, inhibitors and/or protective coatings were applied on one side only, by brushing a solution, and the disks were allowed to stay 28 days more before the testing cycle was started. Climatic conditions in the storage area were approximately 20°C and 50% relative humidity. The hardened disks are shown in figure 6.

P-nitroaniline was applied by brushing a 1% solution in acetone (one coat only).

The protective silicone coating (Rhodorsil RP 224) was applied by brushing a 7% solution in white spirit either directly on the disk or on top of the adsorbed p-nitroaniline.

Hydrophobic mortar disks were prepared according to the same formula, but adding 10 g of a polysiloxane (Rhodorsil RP 224) at the moment of mixing.

The weathering cycle in the climatic chamber was the same that had been used in the screening tests (see the preceding paragraph).

The progress of the sulphate formation was determined by withdrawing samples after 3, 7, 14, 28 days and analyzing soluble sulphates according to the Italian specification Normal 13/83 which requires extraction in water at 110°C for 4 hours followed by determination of the sulphate ion in the solution by ionic chromatography.

The results are presented graphically in figure 7 and numerical results of the analyses are reported in table 2.

These results suggest several considerations

a. Sample B1 (p-nitroaniline).

The delaying effect caused by p-nitroaniline is quite evident, as it was in test A3 on the $CaCO_3$ powder. In B1 the sulphate concentration is 6% of that of the blank at the end of the first week. From the second week, however, the reaction rate increases in B1 more than it did in A3, so after 28 days the sulphate concentration reaches 60% of the blank (the sulphate concentration was about 30% of the blank in A3 at the same time).

In both A3 and B1 it appears that the inhibitor loses progressively its efficiency, but the decay is faster in the disk test. The discrepancy between the disk and the powder experiments, aside from the general problem of the quantitative reproducibility of the accelerated ageing process, may be ascribed to the different conditions of the tests, and in particular:

- the fact that in the disk the inhibitor remains always on the surface (exposed to u.v.radiation) while the powder is mixed after each sampling operation;
- the influence of possible residues of calcium hydroxide (lime still uncarbonated after 98 days) on the stability of the inhibitor and, further, the effect of the resulting higher pH on the sulphation rate.

Anyway, if one considers the extremely harsh condition of the exposure, the delay in the start and the initial slow progress of the sulphation process may still constitute a successful performance.

b. Sample B2 (Rhodorsil RP 224).

At the end of the first week the sulphation rate is somewhat below that of the blank (59%) but in the second week the sulphate concentration gets closer (81%) to overshoot the blank finally (109%) after the fourth week.

Such a behaviour is not a complete surprise because other cases are known in which protective coatings on stone cause an initial improvement in some property (e.g. water adsorption on Swiss sandstone[5]) but produce in the long run a result which is worse than that of the untreated material.

The cause of this may be the progressive detachment of the protective film from the inorganic material induced by the presence of liquid water at the interface, a phenomenon well studied in the case of structural adhesives applied on metals and denominated "preferential wetting". After the film is detached, capillary suction in the gap between film and surface can make the situation even worse than in the case the surface of the porous material is left free.

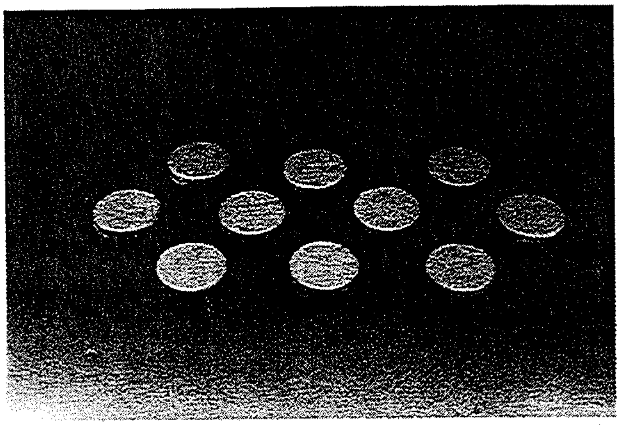

Fig. 6 - Mortar disks made of lime and crushed white marble.

c. Sample B3 (p-nitroaniline + Rhodorsil RP 224).

The application of p-nitroaniline under the silicone coating delays considerably the start of the reaction with respect to the coating alone and later the concentration of the sulphate remains always below that of the blank (14% of blank after a week, 48% after two weeks and 72% after four weeks). It must be noted, however, that the reaction rate is slightly larger than in the case of the inhibitor alone.

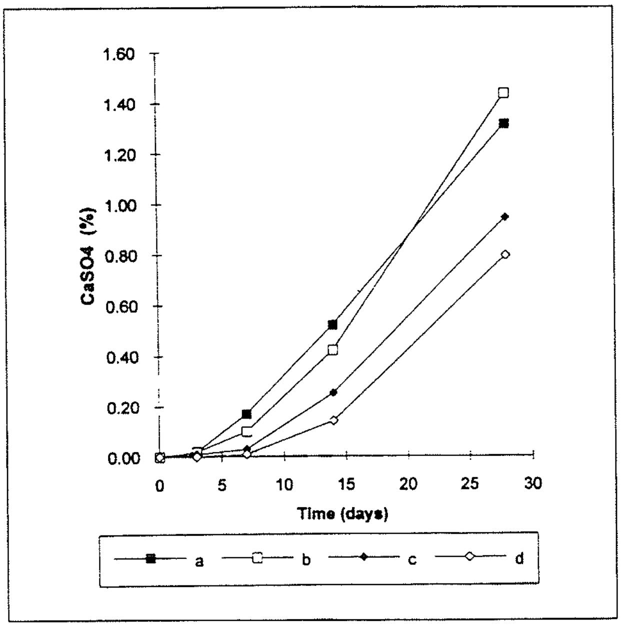

Fig. 7 - Test of a coating and an inhibitor on mortar disks.
a. blank; b. Rhodorsil RP 224 coating;
c. p-nitroaniline + Rhodorsil RP 224 coating;
d. p-nitroaniline. Abscissa: time (days) - ordinate: CaSO$_4$ %.

Sample	CaS04 3 days	CaS04 7 days	CaS04 14 days	CaS04 28 days
B0 blank	0,02%	0,17%	0,52%	1,31%
B1 p-nitroaniline	0,00%	0,01%	0,14%	0,79%
B2 Rhodorsil 224	0,02%	0,10%	0,42%	1,43%
B3 p-nitroaniline + Rhodorsil224	0,00%	0,03%	0,25%	0,94%
B0-HF hydrophobic mortar	0,10%	0,37%	0,77%	2,26%

The following materials were tested:

B0	Blank; mortar disk.
B1	Mortar disk + p-nitroaniline.
B2	Mortar disk + Rhodorsil 224 coating.
B3	Mortar disk + p-nitroaniline + Rhodorsil RP 224 coating.
B0-HF	Hydrophobic mortar disk.

Table 2 - Sulphation of calcium carbonate mortar disks.

The fact might be explained either by some interaction between the molecules of the coating material and those of the inhibitor or by a general tendency of the coating to favour the sulphur fixation. The difference, however, is relatively small and the data available are very few; confirmation therefore is required before a deeper analysis is attempted.

d. Samble BO-HF (hydrophobic mortar).

This sample behaves worse than the blank from the start of the exposure; the induction period is practically cancelled and the sulphate concentration after the fourth week is 173% of that the blank.

A possible explanation is that the carbonation process of the lime in the mortar might have been delayed by the presence of the silicone; as a consequence the hydrophobic mortar samples at the moment of the test would contain a larger concentration of calcium hydroxide with respect to the plain mortar ones. A higher pH may well explain an increased reactivity of the mortar.

Microscopic observations

Examination under the Scanning Electron Microscope (S.E.M.) of samples B2 (Rhodorsil RP 224 coating) and B3 (p-nitroaniline + Rhodorsil RP 224 coating) shows ocasionally phenomena which support the idea that the formation of gypsum crystal in the course of the sulphation reaction might begin under the hydrophobic coating which would be later broken and destroyed by the growth of the crystals.

It must be pointed out, however, that in our weathering

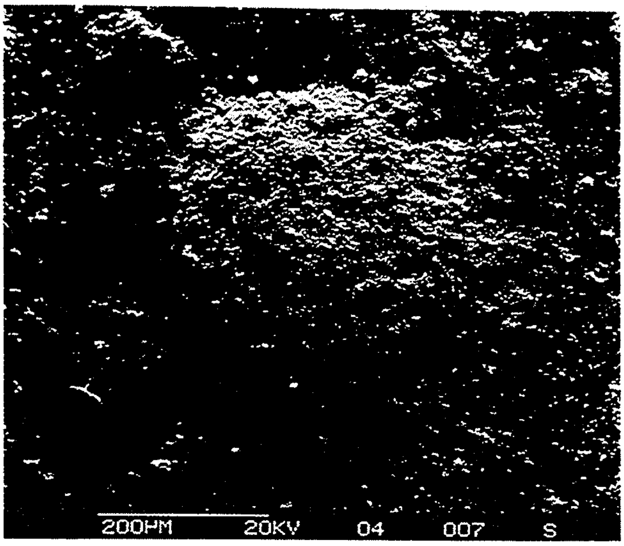

Fig. 8 - Accelerated sulphation test, S.E.M. image of the surface of disk sample B2 (Rhodorsil RP 224). Blistering of the protective coating.

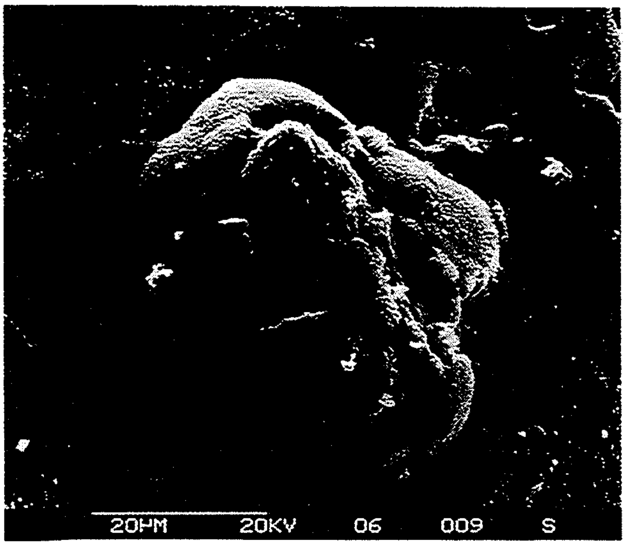

Fig. 9 - Accelerated sulphation test, S.E.M. image of the surface of disk sample B2 (Rhodorsil RP 224). Swelling and break of the protective coating.

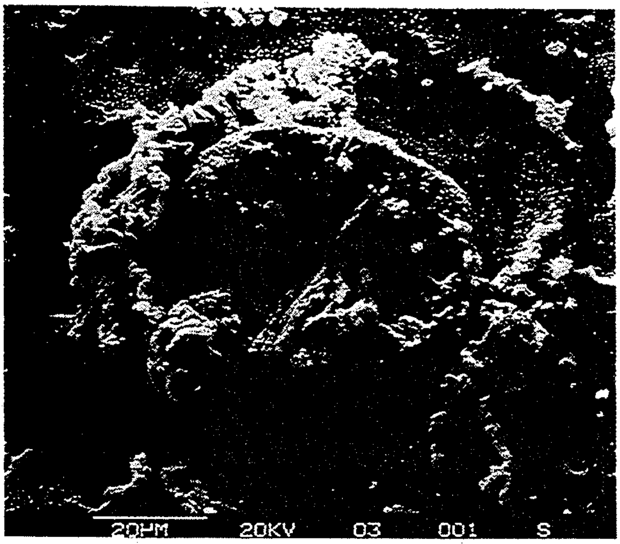

Fig. 10 - Accelerated sulphation test, S.E.M. image of the surface of disk sample B2 (Rhodorsil RP 224). Film break and growth of gypsum crystals.

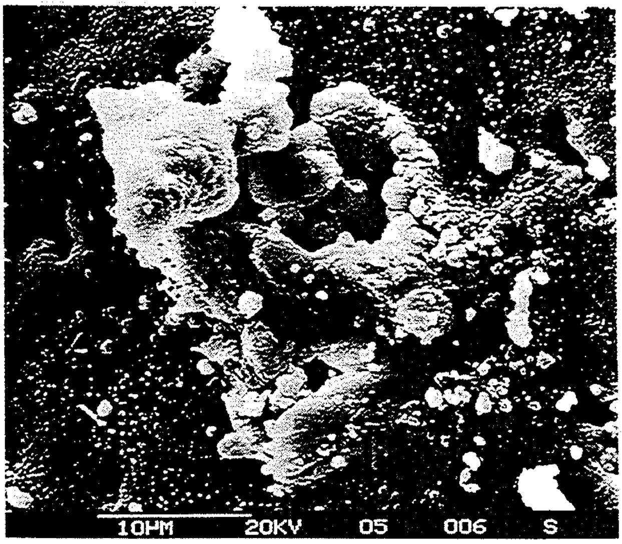

Fig. 11 - Accelerated sulphation test, S.E.M. image of the surface of disk sample B2 (Rhodorsil RP 224). Growth of gypsum crystals out of the film.

cycle condensation takes place four times every day and therefore liquid water takes an active part in the process, besides the gaseous reactants, causing some recrystallization and displacement of the slightly soluble gypsum crystals as soon as the hydrophobic coating is broken.

The observation of undisturbed occurrencies of crystal growth is not so frequent, therefore our interpretation although supported by some images is still to be considered an hypothesis requiring confirmation.

The photographs in figures 8, 9, 10 and 11, taken on sample B2, illustrate cases of swelling of the film and initial breaks accompanied by crystal growth. In figure 12 the film is practically destroyed, few remains floating on a compact layer of gypsum crystals.

Figure 13, referring to sample B3 in which p-nitroaniline was applied under the coating, shows a peculiar type of failure of the film, with a minor growth of crystals, which

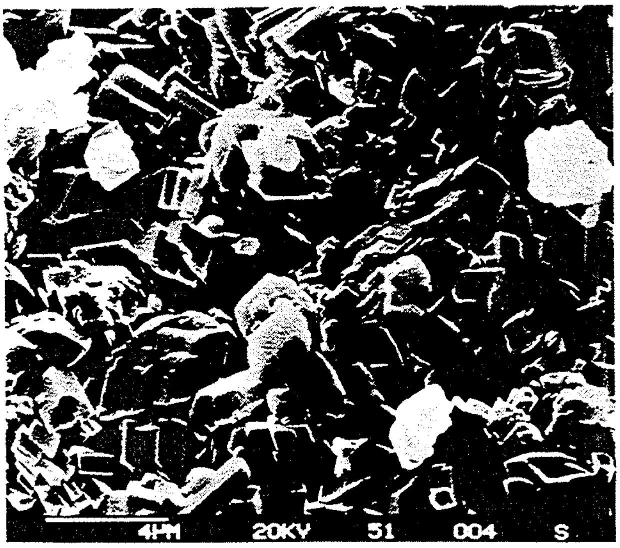

Fig. 12 - Accelerated sulphation test, S.E.M. image of the surface of disk sample B2 (Rhodorsil RP 224). Complete destruction of coating, only residues still visible on top of a gypsum crystals layer.

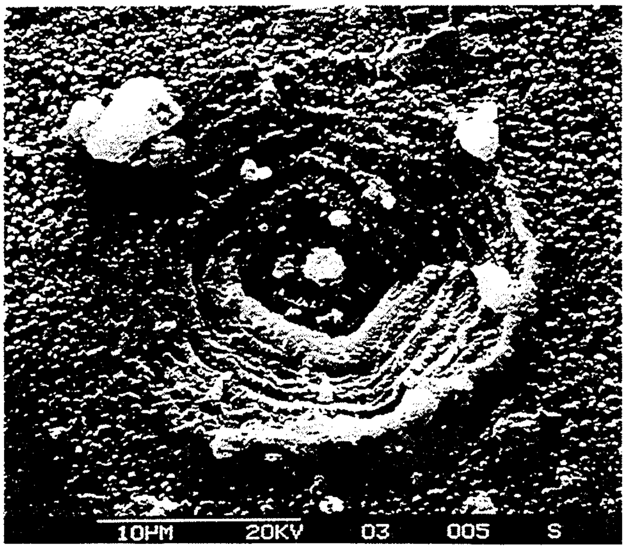

Fig. 13 - Accelerated sulphation test, S.E.M. image of the surface of disk sample B2 (Rhodorsil RP 224). Break of film and growth of gypsum, possibly hindered by p-nitroaniline.

might be connected with the partial inhibition of the sulphation reaction.

Conclusion

The results of the experiments carried out in a climatic chamber under conditions which induce an accelerated sulphation of calcium carbonate by gaseous sulphur dioxide, support the hypothesis that in such conditions protective films on calcareous materials may break down because of the start of a chemical reaction at the film-carbonate interface.

It is obvious, however, that at the present moment it is not possible to affirm that the mechanism proposed is active also under the much milder conditions prevailing in a polluted urban atmosphere.

As the reaction at the interface requires the passage of gaseous molecules through the surface coating, the mechanism proposed would entail the consequence that the protective films, contrary to the current belief, should not be permeable to gases, or anyway should be as little permeable as possible, in order to achieve a prolonged service life.

The experiments also prove that it is possible to delay the sulphation of calcareous materials by the application on their surfaces of suitable substances (inhibitors) which can interfere with the adsorption and the catalytic oxidation of sulphur dioxide.

A possibility exists therefore that the service life of protective coatings on calcareous stones, or mortars, might be prolonged by an appropriate use of sulphation inhibitors but further experiments are required in order to assess the merits and drawbacks of the use of such inhibitors in actual field conditions.

Materials

- *calcium carbonate RP NORMAPUR* 99,5%, Carlo Erba, Milano, Italy
- *calcium hydroxide RP* 96%, Carlo Erba, Milano, Italy
- Carrara marble, crushed sieved 0 - 2 mm, $CaCO_3$ >99%, commercial
- *lead tetraacetate (pfs)* Sigma Chimica (A Division of Sigma Aldrich) Gallarate, Milano, Italy
- *p-nitroaniline (pfs)* Sigma Chimica (A Division of Sigma Aldrich) Gallarate, Milano, Italy
- *Rhodorsil RP 224* Rhône Poulenc Italia SpA, Milano, Italy
- *thiourea (psf)* Sigma Chimica (A Division of Sigma Aldrich) Gallarate, Milano, Italy

References

Golodets, G.I. (1983) Heterogeneous catalytic reactions involving molecular oxygen (translation and editing by Ross, J.R.H.) Studies in Surface Catalysis 15, Elsevier Amsterdam, Oxford, New York, pp. 120-122 and 366-372.

Golodets, G.I. ibid. p. 373.

Golodets, G.I. ibid. p. 120.

Johnson,J.B., Haneef, S.J., Dickinson, C., Thompson, G.E. and Wood, G.C. (1991) Laboratory exposure chamber studies: pollutant and acid rain presentation rates and stone degradation Science, Technology and European Cultural Heritage Baer, N.S., Sabbioni, C. and Sors, A.I. editors, Butterworth-Heinemann Oxford, pp. 474-476.

Furlan, V. and Pancella, R. (1981) Propriétés d'un grès tendre traité avec des silicates d'éthyle et un polymère acrylique The Conservation of Stone II Rossi Manaresi, R. editor, Centro per la Conservazione delle Sculture all'Aperto, Bologna.