GYPSUM CRUSTS ON BUILDING STONES. A SCANNING ELECTRON MICROSCOPY STUDY

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ABSTRACT

The gypsum crusts of some of the most outstanding monuments of Seville, Spain, has been studied. They include the Giralda (a Moorish tower), the Cathedral and the City Hall. Sulphur dioxide-polluted air and airborne carbon particles from car emissions are important factors in the formation of these crusts.

The deteriorating quality of urban and urban-industrial atmospheres has greatly accelerated the decay rate of the natural stone of buildings and monuments.

Natural building stones may be obtained from igneous, sedimentary or metamorphic rocks. Sedimentary rocks provide the main Spanish building stones: limestones and sandstones. The original deposit from which they were formed consisted of loose, uncemented particles produced by the weathering of earlier rock, by accumulation of animal skeletons or by chemical deposition in lakes and seas. In the course of time, the sediments become cemented together to form porous, coherent masses. Limestones consist mainly of calcium carbonate; sandstones of quartz.

In nature, the alteration of calcium carbonate is brought about by solution due to the action of rain water directly at the surface and, especially, of water circulating underground. This action is enhanced by the presence of acidic oxides (CO₂, SO₂, SO₃, NOₓ). According to Stambolov (1967) combustion of sulphur-containing materials produces, besides sulphur dioxide, sulphur trioxide also, but normally in the ratio 10:1. Various
oxidation mechanisms in the atmosphere are likely to change this ratio in favour of the sulphur trioxide proportion. Catalysts like transition metal ions—Fe(III), Mn(II), Cu(II), Co(III)—bring about a considerable oxidation of SO₂ to SO₃. Sunlight and moisture may also be the cause of oxidation. In contact with water, sulphur dioxide and sulphur trioxide form respectively sulphurous and sulphuric acids. More recently, Tomasi et al. (1975) have shown that the concentration of sulphate ions observed in the atmosphere is the result of chemical reactions occurring inside the atmospheric system constituted by SO₂, liquid water and NH₃. Airborne particles also play a fundamental role in the catalytic reaction of SO₂ in water.

Contact of sulphur dioxide-polluted air with calcium carbonate produces on their exposed surfaces a dirty, hard crust of gypsum. The dark colour is due to the incorporation of sand, soot, tar and fly ash particles.

This paper reports preliminary work on the black crusts of some of the most outstanding monuments of Seville, Spain. They include the Giralda (a Moorish tower), the Cathedral and the City Hall.

The three monuments are in the centre of the town, an area with intensive car traffic, which produces an atmosphere of carbon monoxide, oxides of nitrogen, hydrocarbons, lead-containing compounds and other substances from the car fumes, along with high smoke and sulphur dioxide levels, which often occur in urban areas.

In the urban centre of Seville there are a few sulphur dioxide and smoke recording gauges which have been in operation since 1975. The data are a very significant collection of relevant material, which appears to be valid for the understanding of the effect of pollution on monuments. Table 1 shows mean season sulphur dioxide and smoke concentrations for 1976-80 and mean season relative humidity, maximum and minimum temperatures and total rainfall for 1961-80.

| TABLE 1. | Climatic and environmental conditions in Seville |
| season | SO₂ ug/m³ | smoke ug/m³ | RH % | T max °C | T min °C | total rainfall (mm) |
| Spring | 93 | 143 | 61 | 25.8 | 12.4 | 110 |
| Summer | 84 | 141 | 54 | 34.2 | 17.4 | 25 |
| Autumn | 87 | 210 | 74 | 20.3 | 9.1 | 237 |
| Winter | 84 | 203 | 76 | 17.0 | 6.7 | 254 |

It is noteworthy that sulphur dioxide levels were almost constant through the year, with no significant seasonal variations. It has been stated for other cities,
as Milan for instance, that the sulphur dioxide level falls drastically during the summer, confirming that the main source of this contaminant in urban areas is domestic heating (Tomasi et al., 1975). This is not the case for Seville where heating is mainly by electric power, which may explain the absence of seasonal fluctuations.

Scanning electron microscopy has been proved to be a valuable technique for diagnosis of diseased stone and for studying the mechanisms of formation of inorganic substances on stone surfaces (Lewin and Charola, 1978; Charola and Lewin, 1979).

For this study, fragments of the crusts were cemented to sample stubs, coated with carbon and then with gold and examined in a scanning electron microscope (Hitachi model HHS-2R) interfaced with an energy dispersive analyser of X-rays (EDAX). The results were as follow:

The Giralda. The building stones of the belfry of the Giralda are of different limestone types. The balustrade stone mostly consists of a conglomerate of microfossils cemented by a calcareous matrix. The dissolution of a part of the matrix caused by the acid rain in exposed areas gives rise to a relief of fossils. These eroded parts can be observed in the stones uncolonized by lichens (Saiz-Jimenez, 1981).

Undecayed stone samples from the belfry walls showed a thick layer of compact calcium carbonate (calcite) crystals. EDAX analysis also gave minor amounts of Al, Si, Cl, K and Fe as elemental constituents. Sheltered surfaces are covered by a black, compact, homogeneous crust, detached in many cases. Analysis of this crust yielded as the major component calcium sulphate (gypsum), although crystals of potassium chloride and calcium chloride were found in a few cases. Quartz and aluminosilicates (EDAX analysis provided Al, Si, K, Ca and Fe) also appeared. In one case, a small grain containing Si, Ca and Ti was observed, probably titanite (sphene) sometimes associated with limestones.

Some examples of crusts are presented in figures 1-4. Figure 1 shows a rough, deeply bored surface from which EDAX mostly displays Ca and smaller peaks of S and Si. Traces of Al and Fe are also present. A higher magnification of the hole border reveals gypsum and quartz grains (figure 2). The rough crust may be created by acid rain water dissolution of original calcite. The acid leaches out the calcium ions from the surface, causing it to crumble away, generating channels and cracks and uncovering the more acid-resistant quartz grains that are embedded in the limestone. The drying out of the stone results in the formation and growth of new
crystals on the surfaces and at the pores and channels. As
these crystals grow they exert expansive stresses on
the surrounding stone and crumble and crack the crust,
or the crust flakes away.

Figure 3 discloses a model of gypsum crystal growth
on the crust surface and figure 4 presents the oriented
crystals at higher magnification. This growth is probably
induced by alterations or structural modifications in the
stone, and the gypsum crystals nucleate and grow in the
zones which show clear structural defects. In fact, Badan
et al. (1976) have stated that in places where defects
and structural and macroscopic discontinuities are
present, gypsum is formed and grows differently from the
other areas and generally tends to form crystal growing
in predetermined directions.

In other crust samples (not shown here) were found
either a thick layer of small, compact, randomly oriented
crystals or growth in acicular configurations. Also, some
crusts exhibit either a network of small cracks or very
large fissures (see also figure 3).

Several samples were colonized by very long and
scattered fungal hyphae, which is striking because this
habitat does not seem favourable to microbial growth. A
fungal hypha can also be discerned in figure 1 crossing
over a hole.

The Cathedral. The area studied is mostly constituted
by sandstone, although some limestone is also present.
Two processes can be observed in this stone decay. One of
them is the presence of stone blocks which appear worn
away even to a depth of about 10 cm. Also there is
formation of deep cavities, the surface of which are
covered by stone powder. This is the typical form of
decay called by the French specialists "maladie
alveolaire". It seems that the principal factors involved
are the presence of soluble salts and hygrometric
variations (Pauly, 1976). The process consists in the
mechanical disgregation of the surface layers of the
stone by repeated crystallisation of salts brought by the
wetting-drying cycles. Furthermore, wind, acting
mechanically on the disgregated surface and/or by
conveying humidity and heat, plays a role in this
deterioration mechanism (Rossi-Manaressi and Ghezzo,
1978).

Another possibility is that in stones that are
frequently wetted by rain, the repeated crystallisation
of the calcium sulphate dislodges particles of stone
which are subsequently washed off, together with the
calcium sulphate, during heavy rainfall. The surface of
the stone therefore erodes gradually. In most sheltered
parts, the gypsum remains in position to form a hard and
dirty skin, which eventually blisters to reveal an
underlying layer of crumbling debris.

The black crust of the stones of the Cathedral are characterized by the high gypsum content (as evidenced by the EDAX analysis of the crystals). Total analysis of the crust gave as major elements Ca, S and Si, and as minor elements Al and Fe. Scattered quartz grains are also present. Figure 5 shows an example of this crust, exclusively composed of gypsum. Figure 6 presents together with gypsum and quartz a few fungal hyphae, which are covered by mineral matter. Fungal hyphae and spores were also observed in different samples of this crust.

The City Hall. This limestone building shows the same problems as those previously described for the Cathedral. The crust showed as major elements (determined by EDAX analysis) Ca, S and Si, and Al, Fe, Na, Cl and K as minor elements. In one case Zr was found. Major compound was gypsum, together with a small amount of sodium and calcium chlorides, some calcium carbonate, quartz and aluminosilicates.

Surfaces present cracks and fissures. Figure 7 discloses a typical picture in which gypsum is the major component, with some sodium chloride crystals in the lower part of the micrograph.

To study the composition of the black constituents of the crusts the procedure of del Monte et al. (1980) was adopted. Crusts were ground and then dissolved in 10 N HCl. The insoluble material was washed several times with distilled water and recovered by centrifugation. The material was found to be composed of quartz and aluminosilicates together with airborne carbon particles of spherical shape, rough surface, high porosity and irregular pore distribution (figure 8) as described also by the above mentioned authors. EDAX analysis gave as major elements Si, Ca and S, and as minor elements Zn, Fe and Cu. Cheng et al. (1976) identified these airborne particles with particulate matter emitted from oil fired power plants, but in our case these most probably arise from car emissions. These particles may also be an important deteriorating agent because they contain sulphates, sulphites and sulphur dioxide adsorbed on the surface and bonded to it in different ways (Craig et al., 1974).

From the results reported in this paper it appears evident that sulphur dioxide-polluted air is one of the most important factors in the deterioration of the monuments located in the urban centre of Seville, as is suggested by the almost uniform black gypsum crust covering these monuments. The combined action of all air pollutant (gases and solid particles) blackens the buildings and cover them with blisters and scales, which
are subsequently removed by erosive agents or by
generation of stresses due to salt crystallisation within
the pores of the stones.

The action of air pollutants is undoubtedly increased
by the typical street configuration of the urban centre,
with very narrow and sheltered streets with intensive car
traffic and high rising damp in walls. This favours a
long-term effect of the sulphuric acid on the stones.

It is clear that some of the most outstanding
monuments of Seville, Spain are seriously damaged and
cleaning, consolidation and protection work is urgently
needed. Unfortunately, this work is only being carried
out on the Giralda, but the Cathedral and the City Hall,
which show higher weathering rates seem not to be
included among the Spanish monuments to be restored in
the near future.

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Figure 1. Gypsum crust of the Giralda. x50

Figure 2. Detail of figure 1. x2100

Figure 3. Gypsum crystal growth. Crust of the Giralda x400

Figure 4. Detail of figure 3. x1600
Figure 5. Gypsum crust of the Cathedral. x800

Figure 6. Gypsum and fungal hyphae. Crust of the Cathedral. x400

Figure 7. Gypsum crust of the City Hall. x1500

Figure 8. Airborne carbon particle. x1800