

## The Influence of Air-Pollution on Ancient Monuments, Buildings, and Museum Objects

### *Abstract*

The increasing negative effect of air-pollution on the cultural heritage, due to our need of energy and industrial efficiency, has the last century caused many problems for conservators and restaurators.

This paper briefly describes the deterioration of inorganic materials, such as stone and metals, as a result of air-pollution (SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>). It also briefly describes the indoor effect of air-pollution on organic material, such as leather, paper and textiles.

The need of further work, both in a preventive way, and in how to deal with the consequences of air-pollution, is of utmost importance.

The negative effects of air pollution on works of art, such as monuments, historic buildings and museum objects, outdoors as well as indoors, has been a problem for conservators and restaurators for the last century.

The Taj Mahal in India, the white marble building which is considered to be one of the greatest constructions in islamic architecture, is now endangered by the building of an oil-refinery only 30 km away. Because of the predominant north-west wind, the plant will send 25 tons of sulphur dioxide over the building per day (Fenger and Brinch Madsen, 1982). This is by no means a unique example.

The deterioration of historic buildings and monuments has accelerated with the increasing need for energy and industrial efficiency in our society, both in an economic and a political way.

What are the sources of this deterioration ?

Air pollution can be either in the form of particles, like ash or in gaseous form, like sulphur dioxide. It can come from natural sources, such as vulcanoes or from man made sources, like the chimney of a power plant.

The increasing volume of traffic, waste from industrial areas, the combustion of coal, oil-refineries etc. are the main sources of at least the outdoor deterioration of works of art, which give conservators their headaches.

## STONE

### 1. *Marble*

Historic buildings made of marble and other calcareous stones, are highly susceptible to air pollution. Sulphur dioxide coming from the sources mentioned above causes severe damage to their surfaces and, with repeated attack, it will in the end destroy the stone.

Sulphur dioxide combines with oxygen and water vapour to form sulphuric acid. The sulphuric acid penetrates the stone, dissolves the calcium carbonate, and during any subsequent heating, which could be from sunshine, the dampness and the dissolved material will be drawn to the surface of the stone to be deposited as gypsum.

Repeated wet and dry cycles will cause repeated deposition of gypsum and the porous crust which is formed has little or no attachment to the stone. The result will be crackling of the stone and exfoliation. Soot-particles, which find excellent conditions for deposition on the porous surface, give a black colouring to the crust (Fenger and Brinch Madsen, 1982).

The Marble Church in Copenhagen bears strong marks of the city's polluted air. On the four columns at the entrance to the church both white and black areas are visible. The white areas occur where rain water can run freely down the stone ; the acid water dissolves the calcium carbonate, and keeps the stone « clean ». The black areas, occur where the stone is not exposed to running water (Fig. 1).

### 2. *Granite*

Granite has hitherto been regarded as a stable material, unaffected by air-pollution. However, in recent years, we have found this view to be incorrect. Large exfoliations of granite surfaces are seen in many places in Copenhagen, especially in the footings of buildings. This might be due to the combined effects of air pollution, car exhaust fumes, and the deicing agents used on the roads (Fenger and Brinch Madsen, 1982).

### 3. *Grave monuments*

The disfiguring and damaging effects of air pollution on grave monuments has long been visible in cemeteries in Copenhagen. The Mosaic Cemetery is a rather special graveyard established in 1694. Much of it has retained a genuine Jewish character with upright flat gravestones, bearing



*Fig. 1. The crackling and exfoliation of the black crust on one of the columns of the Marble Church in Copenhagen.*

Hebrew inscriptions, facing east. Many of the gravestones are weathered by the natural processes of aging but deterioration has accelerated in recent years due to air-pollution.

Gravestones with inset marble slabs are damaged when the calcareous matrix, binding the calcium carbonate grains in the marble, is dissolved by acid rain. The marble becomes porous and is, therefore, able to absorb more water which, in winter, freezes and there fore expands, and moves the individual grains further and further apart. The marble slab forms a swelling which, at some point, will rupture (Fenger *et al.*, 1984) (Fig. 2).

#### METALS

As early as 1864, G. Magnus tried to make other people aware of the changes that had happened to the bronze statues in Berlin but at that time,



*Fig. 2. The damage caused to grave monuments at the Mosaic Cemetery in Copenhagen.*

and for many years afterwards, the corrosion was regarded as natural and protective and of great aesthetic value. It was not until 1960's, when people became aware of the severe attack on the four gilded horses of the San Marcus basilica in Venice, that one started to deal with the problem.

In the courtyard of Amalienborg Castle in Copenhagen stands F.J. Saly's equestrian statue of King Fredrik V (1723-1771), which was unveiled in 1770. Its surface varies in colour from pale, light green on all the surfaces exposed to the rain, to black on the better protected parts. The black parts exhibit a surface which is very much like the original one. In contrast, all the green parts are more or less etched in such a way that the original surface has been erased. The green corrosion layer is extremely thin and forms no protective covering for the bronze (Fenger and Brinch Madsen, 1982). Corresponding effects can be documented for many bronze sculptures in Copenhagen.



*Fig. 3. F.J. Saly's equestrian statue in bronze, from 1912.*

Figures 3-5 show the development of corrosion on the statue. Between 1912 and 1962 hardly any change can be seen but between 1962 and 1983, the change is enormous.

Metals are subject to corrosion even if there is no air-pollution, but the rate of corrosion increases considerably if the air and the rain contain sulphur dioxide or other aggressive gases or salts.

Air-pollution, both outdoors and indoors, is one factor in the deterioration of cultural objects, and works together with processes within the materials of which the objects are composed.

Among the indoor objects, organic materials such as leather, textiles and paper should be mentioned. This group of materials is also highly sensitive to sulphur dioxide and there is evidence for the influence of pollution on objects composed of them.

#### LEATHER

Sulphuric acid is often introduced to leather during its manufacture and the acid continues to accumulate in vegetable tanned leather from the sulphur dioxide in the atmosphere. In this case too, sulphuric acid is formed by the combination of sulphur dioxide, oxygen, and water vapour, in the presence of metals in the leather or under the influence of sunlight.

Sulphuric acid accumulating in the leather will break down the polypeptide bonds of the collagen, resulting in a rusty powder called red rot.

#### PAPER

Paper made from cellulose oxidizes with the oxygen in the air, but this is a slow process. This oxidation can result in the formation of peroxides,



*Fig. 4. F.J. Saly's equestrian statue in bronze, from 1962.*



*Fig. 5. F.J. Saly's equestrian statue in bronze, from 1983.*

which contribute further to the oxidation. The oxidation products can break down the molecule chains in the cellulose. In this connection ozone is a very active substance, which is destructive in small concentrations.

Sulphuric acid hydrolyzes the cellulose to glucose, with the absorption of water, and a splitting of the long polymere molecule chains occurs. The fibres become weak and brittle and, in the end, will change to dust. The hydrolysis can be caused by acid, introduced to the paper during its manufacture, or by external factors, such as air-pollution, as in this case.

#### TEXTILES

In the case of textiles, damage to the fiber is also seen.

Vegetable fibres composed of cellulose are damaged in the same way as paper. Other textile fibres, such as wool and silk, are also damaged by the

presence of sulphur dioxide in the air. Textile dyes, containing amino groups, are attacked by nitrogen dioxide which causes the textile to fade or change colour. Indigo is a dyestuff of such origin.

As we can see, there is hardly any cultural object, outdoors or indoors, which is not effected by air-pollution. Even the materials used for conserving and restoring cultural objects are being effected. It has been shown that some polymers are affected by nitrogen dioxide and by sulphur dioxide. So, the damaging effect is not only on the original object, but also on the materials added to it, and gives us reason to believe that, in the future, we will have additional problems if we do not take action.

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