

# Pollution and the Deterioration of Materials

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Atmospheric pollutants that cause the deterioration of materials can be considered under three main headings:

1. The first are the acidic pollutants of which sulphur dioxide,  $\text{SO}_2$ , is the most important.
2. The second are the oxidants that are associated with photochemical smog of which ozone,  $\text{O}_3$ , seems to be the most destructive.
3. The third are the airborne particles which cause soiling and abrasion, and which combine with the acidic pollutants to make them even more destructive.

The emissions of these pollutants are largely from motor cars, other forms of transportation, heat and power generation, and heavy industrial activity. The total weight of air pollution emissions into the Australian atmosphere in 1971 was estimated<sup>1</sup> to weigh 12 million tons. On a per capita basis this amounts to 0.94 tons of emissions per Australian. The figure for the United States in 1968 was about the same at 0.96 tons per American. The effects of airborne pollutants on the deterioration of the materials of art, architecture, and documentation have been studied in the large cities of America, Europe and Japan. Most of the literature on this subject has originated in these countries. In order to obtain an estimate of the extent of the damage that atmospheric pollution is causing in Australia, it is useful to compare the concentrations of pollutants in our city atmospheres with those in overseas cities.

## Sources of Pollution

The major sources of sulphur dioxide pollution in large cities are from the burning of fossil fuels

such as coal, coke, fuel oil, and motor spirit. Australian coal and motor spirit have a much lower sulphur content than the fossil fuels that are used in America and Europe<sup>2</sup>, and this is reflected in the lower sulphur dioxide concentrations in the atmospheres of our cities (Table 1)<sup>3, 4</sup>. Typical annual average sulphur dioxide concentrations in the atmospheres of Sydney and Melbourne are about one-tenth of the average concentrations that are found in New York and Chicago. In the disastrous December 1962 smog in London, peak sulphur dioxide concentrations reached 1.95 parts per million over a three day period. Sulphur dioxide pollution is more severe in our smelting towns such as Port Kembla and Port Pirie where metal sulphide ores are roasted<sup>3</sup> in air. Country air has about one-fiftieth the concentration that is found in Sydney. As will be pointed out later, an annual average sulphur dioxide concentration of 0.02 parts per million, that is found in Sydney, is enough to cause extensive damage to property.

Oxidant gases such as ozone and nitrogen dioxide increase in concentration in association with photochemical smog, which occurs in cities with high traffic densities during calm sunny weather. This kind of smog has been associated with the city of Los Angeles for more than thirty years. Both Sydney and Melbourne have experienced many photochemical smogs since 1967. Canberra can expect a number of days of pollution by photochemical oxidants in the 1980s, according to a report on air quality in Canberra by Dr Neil Daly and Mr Paul Steele of the Australian National University<sup>5</sup>.

Table 1  
Some Selected SO<sub>2</sub> Concentrations in  
Air in Parts-per-million by Volume 3, 4

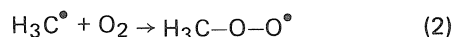
Place	Annual Averages	Highest 24 hr Average	Peak Reading
Country Air	0.0004	—	—
Brisbane, Qld.	0.01	—	—
Adelaide, S.A.	0.01	0.04	—
Melbourne, Vic.	0.02	—	—
Sydney, N.S.W.	0.02	—	—
Redfern, N.S.W. 1973	0.05	0.13	—
Port Kembla, N.S.W. 1973	0.05	0.44	1.0
Port Pirie, S.A. 1966	—	0.27	0.9
Los Angeles, U.S.A.	0.02	—	—
New York, U.S.A.	0.24	—	—
Chicago U.S.A.	0.18	—	1.36
London, U.K. 1962	—	—	1.95
W.H.O. Long-Term Limit	0.02	—	—

The main ingredients essential to the occurrence of photochemical smog are unburnt hydrocarbons, nitrogen monoxide, nitrogen dioxide, ozone, and sunlight. Figure 1 shows the order in which these gases reach peak concentrations during a typical day of smog in Los Angeles<sup>6</sup>. The hydrocarbons and nitrogen monoxide are products of internal combustion in motor vehicles and are put into the atmosphere as exhaust emissions. The hydrocarbons are unburnt residues of motor spirit, and the nitrogen monoxide is formed as a result of reaction between atmospheric nitrogen, N<sub>2</sub>, and atmospheric oxygen, O<sub>2</sub>, at the high temperatures of the combustion chamber,



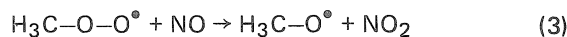
Nitrogen monoxide reaches its peak concentration during the early morning peak hour traffic flow.

By a complex series of reactions in the atmosphere, the exhaust hydrocarbons are broken down into alkyl radicals, such as the methyl radical H<sub>3</sub>C•, which collide with atmospheric oxygen to form alkyl peroxide radicals<sup>7</sup>,



These peroxide radicals become a source of atomic oxygen which is transferred in a chain of events to

NO and finally to O<sub>2</sub>,



Reactions such as (3) cause a decrease in the NO concentration, and cause an increase in the NO<sub>2</sub> concentration which reaches its peak in mid-morning. In the presence of sunlight nitrogen dioxide is rapidly photo-dissociated into NO and atomic oxygen,



Atomic oxygen is rapidly consumed in the formation of ozone, O<sub>3</sub>

CONCENTRATION (ppm).

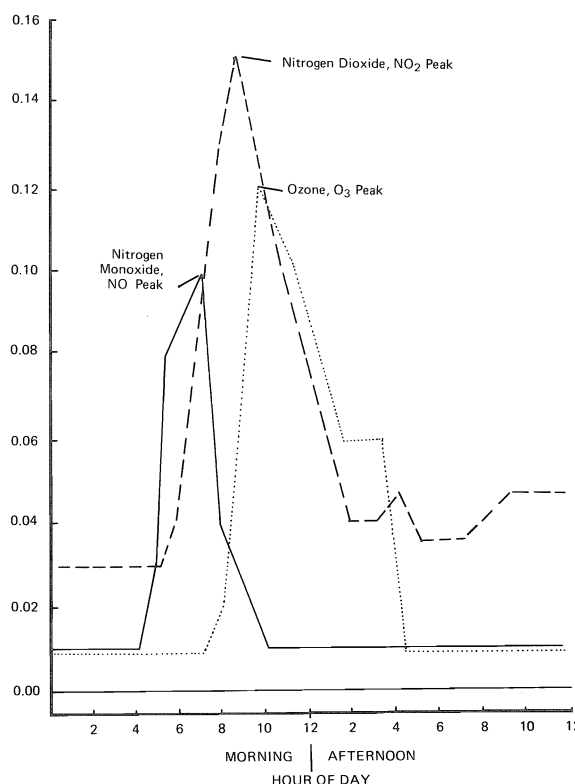
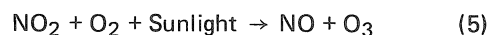
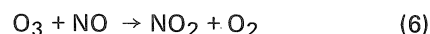


Figure 1. The variation of the NO, NO<sub>2</sub>, and O<sub>3</sub> concentrations in the atmosphere of Los Angeles on a typical day of photochemical smog<sup>6</sup>.



Ozone reaches its peak concentration at about midday. In the absence of sunlight reaction (5) is automatically reversed with the ozone rapidly decomposing,



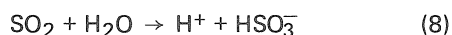
Typical peak values on a bad day of smog reach concentrations of from 0.15 to 0.20 ppm (Table 2)<sup>8, 9</sup>. These concentrations have been exceeded in Sydney and Melbourne in recent years. Los Angeles began having photochemical smogs in 1943, and



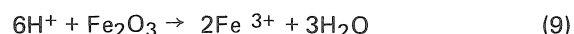
## Acidic Gases

Acidic gases commonly found in polluted atmospheres are  $\text{CO}_2$ ,  $\text{NO}_2$  and  $\text{SO}_2$ . These gases cause deterioration in a wide range of materials because they render rain water and moisture adsorbent materials more acidic. Acid rains are known to occur in the large cities of North America and Europe, where rainfall can register pH values as low as pH4. At this low pH alkaline building materials dissolve, and metals become subject to rapid corrosion.

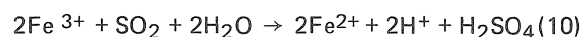
Atmospheric sulphur dioxide is particularly damaging because it can be oxidised into the highly corrosive and persistent sulphuric acid. The destruction of nylon stockings as they are worn by pedestrians in polluted cities is attributed to the presence of sulphuric acid aerosols in the city atmosphere. Sulphur dioxide gas tends to be adsorbed by suspended aerosol particles which contain metal oxides that were released into the atmosphere as a result of the combustion of motor spirit and emissions from smoke stacks<sup>15</sup>. These metal oxides can speed up the atmospheric oxidation of sulphur dioxide into sulphuric acid, Sulphur dioxide when dissolved in water forms sulphurous acid,



The  $\text{H}^+$  ions dissolve some of the iron (III) oxide present to release  $\text{Fe}^{3+}$  ions,



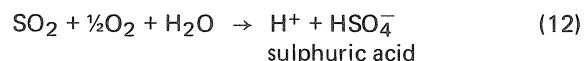
The  $\text{Fe}^{3+}$  ions oxidise the sulphur dioxide into sulphuric acid,



Though  $\text{Fe}^{3+}$  is consumed in reaction (10), it is rapidly regenerated by reacting with atmospheric oxygen,



This two step process in reactions (10) and (11) is much more rapid than the direct conversion,



This rapid conversion of sulphur dioxide to sulphuric acid may also occur in materials that absorb moisture and sulphur dioxide and which contain traces of iron oxides. Leather is such a material.

Leather loses its strength and disintegrates in atmospheres containing sulphur dioxide. Book-bindings made of leather crack at the top inside hinge of books and eventually disintegrate into a red powder<sup>14</sup>. Michael Faraday in 1843 came to the conclusion that rotting leather on arm chairs in a London club was the result of sulphur compounds in the atmosphere of the club<sup>16</sup>. In a recent investigation leather was found to accumulate as

much as 7% sulphuric acid by weight when exposed to  $\text{SO}_2$  atmospheres<sup>14</sup>.

## Paper

Paper is another material that has the capacity to absorb sulphur dioxide and moisture. Paper made prior to 1750 is not seriously affected by sulphur dioxide<sup>14</sup>. These papers, even newsprint, were made from cotton or linen rags by slow processes, largely by hand, and few if any chemical additives were used. In the quest for a cheap paper during the nineteenth century, ground woodpulp and chemical woodpulp were introduced especially for newsprint.

That sulphur dioxide is harmful to modern grades of paper has been shown since at least 1898 when the Committee of the Royal Society of Arts on the Deterioration of Paper reported that illuminating gas causes deterioration of all grades of paper<sup>17</sup>. In a series of gas chamber tests, a pile of paper sheets exposed to sulphur dioxide showed that at the more exposed edges, the paper was more seriously embrittled, had a lower pH, had a higher acid content and a greater sulphate content than the less exposed parts in the centre of the pile<sup>17</sup>. Paper has been found to accumulate as much as 1% by weight in its fibers of sulphuric acid<sup>14</sup>. Sulphuric acid degrades the cellulose fibers to such an extent that the mechanical properties of the paper, such as folding endurance, are lost. Research has shown conclusively that the presence of acid impurities is one of the major factors that severely reduces the useful life and permanence of papers<sup>12</sup>. Small amounts of impurities such as iron and copper in modern grades of paper may be responsible for the rapid conversion of absorbed sulphur dioxide into sulphuric acid.

The long term pick-up rate of sulphur dioxide over two to sixty days has been tested for a number of grades of paper<sup>18</sup>. The purest rag papers showed an extremely slow pick-up rate of sulphur dioxide; but the commercial newsprint tested showed a pick-up rate that was one hundred times greater. Addition of rosin size to a paper increased markedly the long term pick-up rates, but the addition of alum and aluminoferric alum did not make much difference.

Cellulose based textiles such as cotton, linen, and rayon are also subject to the same chemical degradation as is paper. Cotton and rayon fabrics were tested in an atmosphere containing 0.1ppm sulphur dioxide and were found to suffer a loss of breaking strength as a result<sup>19, 20</sup>. A large loss of strength of cellulose textiles in urban atmospheres has been found due to the presence of acid pollutants such as sulphur dioxide<sup>12</sup>.

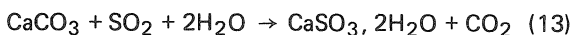
## Metals

The serious corrosive effects of sulphur oxides on metals are manifest even when the atmospheric humidity is as low as 60%. In unpolluted atmospheres at relative humidities of up to 75%, corrosion of the useful metals is almost negligible<sup>21</sup>. According to a survey of eight North American cities, the annual average sulphur dioxide concentrations in a city appears to be a good indicator of the rate of corrosion of metals. The annual average sulphur dioxide concentrations ranged from 0.02 ppm in Los Angeles to seven times as much in Chicago<sup>4</sup>. The rate of corrosion of metal specimens in Los Angeles was up to one-third the rate for metal specimens in Chicago. The annual average sulphur dioxide concentrations in Sydney and Melbourne are also at 0.02 ppm. Assuming that the rate of corrosion in our two largest cities is about the same as is found in Los Angeles, sulphur dioxide pollution in the atmospheres of our largest cities must be causing extensive damage through corrosion to metallic objects and structures.

Another survey in Great Britain in sixteen different locations found almost perfect correlation between the amount of sulphur dioxide measured by the lead peroxide method and the weight loss of some zinc and steel specimens through corrosion<sup>22</sup>. Old bronzes are threatened in polluted atmospheres particularly if cast with alloys rich in lead. Modern bronzes which contain tin, zinc and only a little lead, however, were found to be much more resistant<sup>23</sup>. Controlled laboratory experiments indicate that particulate matter is an important factor in the rapid electrochemical corrosion of metals especially in the presence of acid gas pollutants<sup>14</sup>. Particles that settle on metal surfaces attract sulphur dioxide and moisture from the atmosphere and are often responsible for the initial sites of corrosion. Major airborne solid pollutants that have the effect of accelerating corrosion are carbon, silicate dust, ammonium sulphate, and ferric oxide.

## Building Materials

Though sulphur dioxide was found to have little effect on dry hard paint films, fresh paint surfaces can be damaged by it. Extended pigments containing calcium carbonate are affected<sup>14</sup> because calcium carbonate is decomposed by sulphur dioxide,

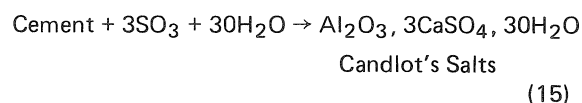
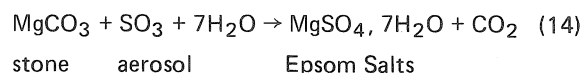


Brunswick green in fresh paints was bleached to pale blue by sulphur dioxide, owing to the reduction of yellow lead chromate to lead sulphate<sup>14</sup>.

Sulphuric acid aerosols can transform ferric oxide pigments such as ochres into rust brown  $\text{FeOOH}$ <sup>15</sup>. Copper based pigments such as blue

azurite, green malachite, and emerald green can be slowly decomposed into basic copper sulphate<sup>15</sup>.

Contact of sulphur polluted air with materials containing calcium carbonate such as limestone, marble, plaster, mortar, cement, etc leads to the decomposition of the calcium carbonate into calcium sulphite and sulphate (reaction 13). Magnesian limestone, containing magnesium carbonate, is damaged by conversion of the carbonate into magnesium sulphate, which is well known as Epsom Salts. The British House of Commons building is constructed of magnesian limestone which is crumbling away in the London atmosphere.



In cement and concrete Candlot's Salts are also decomposition products<sup>15</sup>. Decomposition of limestone calcium carbonate can cause rapid deterioration of sandstones which consist of silica or sand particles bound together by a matrix of calcium carbonate. The loss of a very small amount of calcium carbonate results in the loss of a large number of silica grains. Cologne cathedral has been severely damaged by acidic air pollutants especially where sandstones have been used. Huge pieces of sandstone have fallen from the building on to the paved public walks. The most severely threatened parts are the labyrinth of buttresses which knit the structure together. More than half of the 106 main buttresses are on the point of collapse<sup>24</sup>.

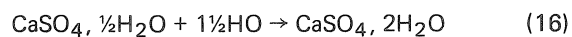
A famous example of the decomposition of marble is found in the Acropolis where the five Caryatid statues have been removed by the Greek authorities to the protection of a museum. The atmospheric pollutants from the burning of high sulphur fuels in nearby apartment blocks were decomposing the marble into plaster. The rapid decay of the Giotto frescoes in the Scrovegni Chapel at Padua is another famous example. In frescoes<sup>12</sup> the pigment is bonded to the surface with calcium carbonate. Pigmented lime plaster is first applied and atmospheric carbon dioxide slowly converts the lime into a matrix of calcium carbonate which cements the pigment into position. Conversion of calcium carbonate into calcium sulphate causes loss of adhesion of the pigment.

Another important cause of stone decay is the presence of salts such as sodium chloride, and the sulphates of calcium, magnesium, and sodium in the pores of the stone. The repeated recrystallisation and efflorescence of these salts causes a pow-

dering of the stone surface and in the case of magnesium sulphate the formation of deep cavities<sup>25</sup>. The resistance of limestone to crystallisation damage is dependent on the pore size distribution. The durability decreases as the proportion of fine pores increases<sup>25</sup>. Salts in a confined pore space may undergo three types of change creating stresses which would lead to stone disintegration<sup>26</sup>:

1. pressures produced by growth of crystals from solution;
2. differences in thermal expansion between crystal and stone;
3. and hydration of salts such as calcium sulphate which leads to crystal growth and expansion in confined pore spaces<sup>26</sup>.

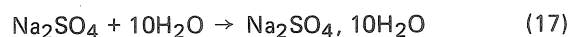
The conversion of plaster into crystalline gypsum in a humid atmosphere leads to an expansion in crystal volume of 32%,



plaster gypsum

The conversion from anhydrous sodium sulphate to Glauber crystals brings about a 308% increase in

volume<sup>15</sup>,



sodium Glauber's Salt  
sulphate

The transformation of magnesium sulphate into Epsom salt produces a 170% increase in volume,



When a growing crystal, that is trapped inside a coarse pore, fills that pore, it will continue to grow on all surfaces of the crystal drawing moisture from surrounding smaller pores<sup>25</sup>. This causes a pressure build-up between the crystal and the walls of the pore which eventually causes the walls to break up. Conversion of plaster into gypsum under these circumstances for example may cause a pressure of 2000 atmospheres between crystal and pore wall before the crystal ceases to grow larger<sup>27</sup>.

An excellent review for conservators of atmospheric pollution and the methods of controlling pollution in museum air has been published by Garry Thomson<sup>12</sup>.

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