The effects of ozone and NO\textsubscript{x} on the deterioration of calcareous stone

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Abstract

This paper looks at the changes in urban air quality and the effect on building materials with particular regard to their deterioration arising from pollution due to vehicles. The paper aims to review basic information on the likely effect of NO\textsubscript{x} and ozone on calcareous building materials (limestone, marble, dolomite, calcareous cemented sandstone) by examining experimental and fieldwork relating to the principle reaction of the oxidation of the sulphite to sulphate. NO\textsubscript{2} is only one of many possible oxidants present in the urban and rural environment. A brief synopsis of the effects of other oxidants and inhibitors is given along with a review of the processes involved in aqueous phase oxidation, which seems to be the phase where the reactions take place. Controlling factors in the reaction and oxidation of sulphite to sulphate are the type and porosity of the stone, the level of humidity, the nature of the oxidants and to a lesser extent the presence of other extraneous reactants, e.g. metal oxides, chlorine and ammonia salts. For freshly cut stone unpolished marble is much less reactive than porous limestone and the degree of activity has different relative humidity thresholds. Reaction of the stone with the gaseous compounds occurs during the process of absorption onto the surface. The oxidation is accelerated at the gas–water interface by the presence of NO\textsubscript{x}, and seems to depend on the NO\textsubscript{2} component but it is clear that NO\textsubscript{x} is only one of many possible oxidants in the urban and rural environments. Correlation studies of the damage to stone materials are unlikely to pick up the effects of NO\textsubscript{x} due to the nature of their duration and the rather transient nature of the appearance and removal of nitrates on the stone. Presence of other oxidants and catalysts such as H\textsubscript{2}O\textsubscript{2}, O\textsubscript{2} (catalysed by Fe\textsuperscript{3+} and Mn\textsuperscript{2+}), OH, HSO\textsubscript{3}, SO\textsubscript{4}\textsuperscript{2-}, O\textsubscript{3}, HO\textsubscript{2}, NO\textsubscript{2}, NO\textsubscript{3}, O\textsubscript{2} and PAN, plus the fact that the reactions are pH and ionic strength sensitive, add greatly to the complications of determining what affects the oxidation rate. These difficulties are further compounded by the presence of trace elements in the chemical reagents, particulate matter and the stone itself (such as Mn\textsuperscript{2+} or Vn\textsuperscript{3+}). In conclusion there is sufficient evidence that NO\textsubscript{x} has a role to play in the oxidation of sulphite. However, the magnitude of influence NO\textsubscript{x} and related compounds have in the environment is far from

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clear due to the prevalence of other stronger oxidants (ozone and hydrogen peroxide), the intricately linked NOx and ozone chemistry in relation to their diurnal cycle and the diurnal humidity variations, seasonal variations, the presence of metal oxide catalysts (Fe and Mn) in the stone and environment, and the possibility of organic oxidation inhibitors. © 1999 Building Research Establishment. Published by Elsevier Science B.V. All rights reserved.

**Keywords:** Ozone; NOx; Stone deterioration; Vehicles; Urban environment; Oxidation

1. Introduction

During the past decade there has been a growing concern about the changes in urban air quality. Much of this concern has focused on public health issues. A complementary issue is the effect on building materials particularly their deterioration and maintenance arising from pollution. Presently those concerns relate specifically to the rise of pollution from vehicles. This paper aims to provide basic information on the likely effects of NOx and ozone on buildings with particular emphasis on contributions from vehicles.

Response to the health hazard legislation implemented through the clean air acts has resulted in a fairly rapid reduction of the levels of sulphur dioxide, smoke and the elimination of the thick smog of the early 1950s (Fig. 1). Further reductions are anticipated to arise from the 1994 UN-ECE directive which stipulates a 50% reduction by 2000, a 70% reduction by 2005 and 80% reduction from the 1980 values. During this time of

![Fig. 1. Changes in gas concentrations at Sheffield and national emissions.](image-url)
rapid reduction in sulphur dioxide and smoke there has been a rise in the amount of traffic with accompanying emissions of black smoke particulate, which is different from those due to coal and oil burning, and nitrous oxides (NOx) (Fig. 1).

Putting these emissions in context the national changes in NOx and black smoke emissions show that the general contribution to NOx from traffic is some 40% of the UK emissions and similarly 30% of the UK emissions for black smoke. Thus, the output from vehicles contributes to the general scenario but is not the major component when viewed purely as an emission total.

Fig. 2 shows the principle pathways by which airborne pollutants can be transported from source. Many of these such as domestic, commercial, industrial, power generation, and shipping tend to be positioned away from major conurbations. This enables the pollutants to disperse and react. Similarly there is a dispersion of vehicle emissions arising from the general road network.

However, there is a greater concentration of vehicles in cities where vehicles tend to have lower speeds resulting in significant emission sources in close proximity to buildings. Slower vehicles and congestion result in higher emissions of pollutants. This changes the balance of contributions. It has been estimated that up to 80% of the black smoke and NOx levels in London arises from vehicles. It is this rise in gaseous and particulate contributions within the urban areas that is of direct concern regarding building deterioration. However, it should be borne in mind that, both the background and local sources contribute to the gaseous and particulate composition at a specific location and they are in turn are controlled by the local meteorological conditions. This leads to a very complex scenario for the

Fig. 2. Principle pathways for pollution (reproduced from ‘acid rain’ and London; Laxen and Schwar, 1985).
distribution and transport of airborne pollutants onto the surface of a building.

1.1. Effects on buildings

Airborne pollutants affect buildings in two ways — decay and soiling. Soiling is the discoloration of a building whilst decay results in the destruction of the building fabric. In order to understand these processes we need to look at the chemical interaction and the physical changes occurring at the building surface.

Sulphur dioxide and nitrogen oxides are gaseous components which react directly with the stone surface by forming acids in the presence of water and oxidising agents. These acids react with the stone to form salts which either crystallise out within the stonework resulting in physical damage or they are washed away resulting in a loss of material. This is the primary damage mechanism which, since it is a chemical reaction, continues at all sulphur dioxide concentrations. Nitrate salts are more soluble and expand less than salts of sulphate, leading to little, if any, damage by this mechanism. Thus, a reduction in the erosion rates would be anticipated with the reduction in sulphur dioxide. This trend can be seen even with quite modest levels of sulphur dioxide as has been demonstrated by field measurements in the National Materials Exposure Programme (NMEP) (Butlin et al., 1992) and estimated recession rates at a number of locations in London (Table 1).

There is a sulphur dioxide component in vehicle emissions but it is far smaller than the sulphur dioxide levels from other sources. Modern fuels have concentrated on eliminating sulphur dioxide and pressure for environmentally acceptable fuels will maintain the reductions.

A further factor relevant to nitrogen oxide levels relates to their importance as catalysts which increase the rate of oxidation of the sulphate compounds in the conversion of the gaseous and particle forms to acids. Thus, the levels of NOX generated by traffic could contribute to this effect. The catalytic effect has been demonstrated in special laboratory test chambers at extreme concentrations of both sulphur dioxide and NOX. However, field exposure trials, where material is left out to weather naturally, have failed to demonstrate that NOX has a significant catalytic effect.

It is worth noting that NOX emissions from vehicles have doubled during the period 1950–1985 whilst over the same period recession rates for calcareous stone have dropped by a factor of 10 (Fig. 1 and Table 1). The NMEP has demonstrated that there is a linear relationship between material weight loss and sulphur dioxide levels down to sulphur dioxide values of 10 μg/m3. This suggests that the actual catalytic effect must be fairly slight. UNECE (United Nations Economic Commission for Europe), who implement the convention on transboundary air pollution, are presently of the opinion that there is no observable effect within the various international field exposure trials they have conducted. However, the effect of NOX still remains a matter of much debate within the scientific community.

1.2. The urban environment

The urban environment is a very complex system with varying concentrations of pollution and fluctuating temporal variations. Observation of single reactions, conjectured reactions and sample measurements have to be considered against this complex backdrop. It is almost impossible to focus in on one facet of the problem without other areas encroaching on the discussion. This is entirely true of the NOX and SO2 system.

The oxidation of the SO2 aqueous phase is the key step in the formation of gypsum on the surface of the stone. This is affected by a number of different catalysts which may be present in the system. NOX is only one of a possible number of oxidants and oxidation catalysts. Given that in the urban environment the major source of the NOX

### Table 1

<table>
<thead>
<tr>
<th>Period</th>
<th>Location</th>
<th>Recession Rate</th>
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<tbody>
<tr>
<td>1955–1965</td>
<td>Whitehall</td>
<td>76–109 μm/year</td>
</tr>
<tr>
<td>1981–1983</td>
<td>St Paul’s</td>
<td>22 μm/year</td>
</tr>
<tr>
<td>1987–1991</td>
<td>Elephant &amp; Castle</td>
<td>11 μm/year</td>
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is from vehicles and with this there is an associated increase in the amount of particulate matter (carbonaceous, VOC, iron and manganese), which can act as catalysts, it is very difficult to determine the precise effect of NO₂ on its own.

Atmospheric concentrations of NOx are strongly linked to the amount of O₃, another major oxidant within the system (Photochemical Oxidants Review Group PORG, 1997), during daylight hours since the reaction between the two is mediated by the amount of sunlight. The balance between the two is also affected by the presence of free radicals. The principle reaction at night time is the formation of NO₃ and N₂O₅, accompanied by a reduction in O₃. N₂O₅ is a moderately strong oxidising agent and readily removed by water vapour to form the acid HNO₃.

A further complicating factor is the dry deposition of the various non-gaseous species and their reaction products onto the surface of the stone with the possibility that the dry deposition includes catalysts and reagents that greatly affect the adsorption and desorption of the gases (Amoroso and Fassina, 1983).

A fall in the SO₂ levels means that more subtle effects may begin to come into play, e.g. NO₂. Rising NOx emissions (Fig. 1) are a cause for concern yet there is some evidence that the urban NOx burden can decrease with the introduction of catalytic converters (Sjödin et al., 1996). However, experience from monitoring in the UK has shown that the effects of introducing catalytic converters has yet to make an impact on the kerbside measurements of NO₂ (ENDS Report 280, 1998).

It is against this rather dynamic and complex backdrop that the influence of NOX on the oxidation of sulphite at a stone surface is to be considered. The principle research methods are to examine specimens from field studies or conduct laboratory work using exposure chambers or pure chemistry techniques. Neither techniques can be considered satisfactory, the latter because the conditions regarding concentrations and the physical environment are not the same as the natural environment and the former due to the rather uncontrolled natural exposure conditions.

2. Chamber and laboratory work

Much of the early work on the deterioration of stonework was carried out with very high gaseous concentrations (> 10–100 times those of ambient levels which are 10–100 ppb). For example:

- Gauri et al. (1973): stones to gaseous atmospheres

Elfving (1994) comments that the high SO₂ concentrations will alter the pH of the surface water films slowing the formation of sulphate and thus favouring the production of sulphite. The variety of exposure chambers, presentation rates, type of measurements taken and the condition of the samples make the comparison of measurements in chamber studies very difficult.

Detection methods such as X-ray diffraction or IR studies have different sensitivities (> 2% and > 2–5%, respectively) and require different quantities of material for analysis which therefore affect the degree of detection, particularly in the detection of the reaction products for NO₃. Nevertheless, there are some common strands which emerge.

Judeikis and Stewart (1976) carried out measurements of SO₂ depositions and Judeikis and Stewart (1978) incorporated NOx to show that SO₂ was converted to surface reaction products with NOx during the initial period of exposure after which the gas NO was formed. They concluded that the removal of the reactive NOx gases (NO + NO₂) by deposition occurs by ground level interaction of the NOX. Moisture is important in enhancing the conversion processes with SO₂ but the deposition of NOx is independent of the relative humidity.

A study on the interaction of SO₂ and NOx by Johansson et al. (1988) suggested that the presence of NOx greatly enhanced the conversion of SO₂. They postulated the slow conversion of the sulphite CaSO₃·2H₂O to sulphate was enhanced by the presence of NOx, since the resulting corro-
sion products were predominantly gypsum. This is in reasonable agreement with the observations of other experimenters that sulphite is formed first and then converted to sulphate (and gypsum) occurs later. The role of NO$_2$ in this conversion is, however, not clear.

Peleg et al. (1989) studied the effects of NO and SO$_2$ (at 300 ppm). Again the oxidation of the SO$_2$ was determined to be the most important rate step towards the formation of gypsum and is greatly influenced by humidity. The formation of Ca(NO$_3$)$_2$ is unaffected by relative humidity but the oxidation of NO is affected by the presence of hydrocarbons.

Ausset et al. (1996) and Girardet et al. (1996) demonstrated that measurements could be made at realistic conditions (125 ppb SO$_2$, 50 ppb NO$_2$ at 79% RH and 13°C) but required the test period to be extended to 1 year. No attempt was made to explore changes in the NO$_2$ concentration. In addition they dosed the samples with fly-ash or soot. The soot seemed to protect the surface whilst the fly-ash enhanced the SO$_2$ deposition rate slightly. The effect of RH was found to be linear for some stones and exponential with others.

Spiker et al. (1992, 1995) demonstrated that the uptake of SO$_2$ was exponentially related to the RH and controlled by the amount of water absorbed on the surface for Indiana limestone and Vermont marble.

De Santis et al. (1994) demonstrated that the enhancement due to NO$_2$ was sensitive to the RH — at 90% RH the reaction was increased but below 50% RH there was no effect.

These dependencies of SO$_2$ and NO$_2$ deposition on their interaction, moisture levels and type of stone were demonstrated by Johnson et al. (1991), where NO$_2$ was shown to greatly influence the deposition of SO$_2$. Further work by the same team (Hutchinson et al., 1992a) cited the relevance of Fe$_2$O$_3$ and sheet silicate minerals (clays, mica and chlorites) in catalysing the oxidation process. Johnson et al. (1996) looked at the co-deposition of HCl, SO$_2$, NO$_2$ and O$_3$ gas in conjunction with coal and diesel coated samples using mass change and water soluble reaction products as the measure of deterioration. They conclude that HCl acts addictively with all combinations of the gases and again observe the marked increase in the amount of deterioration when SO$_2$, NO$_2$ and O$_3$ are combined. They noted a slight reduction in the amount of reaction products with the diesel and smoked samples which they attributed to decreasing the number of active calcite sites. Hutchinson et al. also noticed a reduction in the reactivity of samples which had been exposed on the NMEP (Butlin et al., 1992). Gas concentrations were of the order of 2–0.5 ppm, water was applied by means of a drip feed onto the specimens and RH was maintained at 84% for the majority of the experiments.

Work using ground powders in a variety of reaction devices tend to confirm the findings relating to porosity, RH and stone type. These and the other laboratory studies have also enabled some estimation of reaction kinetics to be made.

Gwinn and Popli (1982) suggest a linear reaction rate which results in a diffusion limited reaction on the surface of the stone. Katsanos and Vassilakos (1991), Vassilakos et al. (1992) and Vassilakos and Salta (1993) use reverse gas flow chromatography to analyse the reaction of powders — they conclude that the rate is dependant on the flow rate of the gas, NO$_2$ reacts at a rate that is three orders of magnitude smaller than SO$_2$. For the combination of SO$_2$ and NO$_2$, at 372.5 K, they conclude there is no synergistic effect on the adsorption of SO$_2$ but the desorption of SO$_2$ decreases by a factor of 10. Gauri et al. (1989) and Tambe et al. (1994) looked at experimental data and outdoor exposure conditions for dolomite and concluded that they could be modelled using a half-order and first-order reaction model, respectively.

Elfving et al. (1994a,b) used IR at gas concentrations of 1 ppm to establish the effect of both NO$_2$ and O$_3$ in the process of sulphation. For SO$_2$ alone there is an immediate formation of sulphite at the surface of the calcite under humid conditions. No sulphite is formed in dry conditions. The surface sulphite gradually deteriorates under humid conditions. On preconditioned sulphite surfaces formed on calcite NO$_2$ is less efficient than O$_3$ in oxidising the sulphite — NO$_2$
requires moisture to be present whilst the O_3 operates in both moist and dry conditions albeit at slower rates for the latter condition. Exposing calcite to SO_2 and O_3 simultaneously demonstrated that sulphate is the preferred reaction product. Simultaneous exposure to SO_2 and NO_2 demonstrated that a catalytic reaction takes place which increases the rate of sulphate production after 30-h exposure. The authors’ conclusions from this experimentation are:

- Ozone reacts rapidly with surface sulphite to form sulphate both at dry and humid conditions.
- Simultaneous exposure of calcite to O_3 and SO_2 at dry conditions does not result in any sulphite nor sulphate formation at the surface.
- Simultaneous exposure of calcite to O_3 and SO_2 at humid conditions results in rapid sulphate formation.
- The rate of degradation of prepared surface sulphite on calcite at humid conditions was found to be faster than the sulphate formation in the presence of NO_2.
- Surface sulphite is stable at dry conditions and no sulphate formation is seen in the presence of NO_2.
- At dry conditions neither sulphite nor sulphate is formed on a clean calcite surface when simultaneously exposed to SO_2 and NO_2.
- Initial surface sulphite formation and an accelerated amount of surface sulphate are observed at a calcite surface during the simultaneous exposure to SO_2 and NO_2 in a humid atmosphere.

This suggests that the reaction occurs at the surface of the calcite and not in the gaseous phase and the increased production of sulphate is by an activated complex involving the surface water film, NO_2, SO_2^+, SO_4^- and O_2. The time span for the conversion from sulphite to sulphate occurred over 5–70 h, depending on the conditions. The O_3 is much more efficient than NO_2 at oxidation.

Elfving et al. (1996) continued their studies using the IR technique to look at the sulphation and carbonation of Ca(OH)_2 and CaO by SO_2. They report that sulphation is preferable to carbonation for both Ca(OH)_2 and CaO. The connection with the decay of limestone is that the work suggests that water is involved in the decarbonation as well as the formation of the sulphite.

3. Field work

With the difficulties in the variations in stone type, presentation rates, turbulence, object shape, and factors generally beyond the control of the experiment the identification and influence of NO_3 is far from certain. Even the detection of the formation of nitrite salt is far from positive.

A number of field studies, both large and small, have taken place over the past two decades. The deposition velocities for SO_2 range from 2 to 20 mm/s for a variety of stone types, exposure conditions and duration. Few of these tests related to the interaction of SO_2 and NO_2 or to experimental chamber work.

Peleg et al. (1989) studied SO_2 and NO_2 in an exposure chamber and 10 m above street level in Jerusalem. He concluded that the deterioration rates established in the chamber tests could not be linearly extrapolated to the conditions prevailing in the street.

4. Other sources of oxidation

Adema and Heeres (1995) examined the dry deposition of SO_2 onto a film of water in a wind tunnel. They concluded that the transfer was controlled by the oxidation stage using either O_2 or O_3 and an activated HSO_3^- or HS_2O_5^- surface complex. The results suggested that this took place at the gas–liquid interface and the presence of NH_3 or catalysts is not necessary for the oxidation.

Böke et al. (1996) looked at the interaction of different particles such as clay, activated carbon, metal oxides and chlorides on the sulphation of carbonate powder at very high concentrations of 3500 ppm SO_2 at 85% RH. The clay had little effect and the activated carbon some effect, the metal chlorides (Mn, Cu, Co) increased sulphation by 10% but their action was concentration-dependant. Iron, nickel and sodium chlorides also
increase sulphation to the sulphite. Complete sulphation through to the gypsum was achieved for MnO, V₂O₅, whilst little difference occurred with TiO₂, NiO, Fe₂O₃ and SiO₂.

Benner et al. (1992) examined the oxidation process taking place at the water film due to ammonia (NH₃). They observed that the reaction did not take place in the gas phase but when the gases were absorbed on to the surface. They observed that regardless of the type of surface (Teflon, glass, quartz or stainless steel) the formation of sulphate was increased when the available surface was increased. The reaction was not catalysed by the surfaces themselves. They conclude that the reaction takes place in the moist thin surface films. Oxidation in the thin films was an order of magnitude greater than in bulk water for the SO₂ and O₂ reaction.

Hutchinson et al. (1992b) describe the effects of other sources of catalysts. They comment that the stone itself may contain metal oxide catalysts (specifically that Portland stone contains 0.1% iron oxide, 0.04% MnO as well as MgCO₃, SiO₂, Al₂O₃, K₂O, TiO₂ and P₂O₅ in discrete phases) and smoke or soot is known to catalyse the SO₂ reaction. In addition to this rainfall also contains cations which are known to assist oxidation. The authors conclude from studies of seeding Portland and Monks Park limestone with fly-ash and oxides that these additions do not significantly affect the production of elemental sulphur on the surface of the stone. The measurements were taken using EDX and the control of the moisture films on the samples was not very rigorous. This could explain why the results conflict with the observations that the rate of sulphation is increased in the presence of suitable oxidants.

Elfving (1994) cites work on the oxidation of SO₂ in the aqueous phase which supports the view that the first row of transition metals are effective catalysts, particularly Fe(III) and Mn(II). Trace amounts of metal are known to catalyse the reaction whereas pure water and ambient oxygen do not. The presence of ozone and hydrogen peroxide also increase the rate of oxidation. He also considers heterogeneous oxidation by non-catalytic reaction with the metal oxides, such as Fe₂O₃, Al₂O₃ and MnO₂, which are also effective oxidants occurring on carbon particles. His experimental work indicated that of the metal oxides MnO₂ and Fe₂O₃, at representative concentrations to that found in the stone, MnO₂ was more efficient than Fe₂O₃ with regard to oxidation and oxidation depended on the initial concentrations of the oxides. The sulphates are formed on the metal oxides and then migrate by a diffusion process in the aqueous phase onto the calcite. Additional experiments showed that MnCO₃ to be as efficient as MnO₂ with regard to oxidation. For the reaction to be truly catalytic the reduced metal oxides would have to be oxidised for the process to continue. Whilst manganese occurs in very small amounts in stone the increased oxidation efficiency means that it dominates the reaction in preference to the more prevalent iron oxides, which also act as suitable oxidants.

Sikiotis and Kirkitsos (1995) examine the effects of HNO₃ gas on marble. They consider this to be at least as significant as SO₂ and NO₂ gas in locations with high levels of sunshine during the summer months, e.g. the Acropolis, Athens. However, it should be noted that their experimental technique removed the effects of particulate deposition and concentrated on the gaseous components. Further work of Kirkitsos and Sikiotis (1996) looking at the effects of NO₂ alone show that the stones considered are not good sinks for NO₂ in comparison to HNO₃. Synergistic effects were not examined but the work does indicate the effects of other species on the decay which add further complications to establishing in situ effects.

Fenter et al. (1995) examine the reaction of HNO₃ gas on calcite in much more detail, and confirmed calcite as an extremely good sink. The reaction proceeds by absorption of the gas on the surface and is highly dependant on the presence of water. Carbon dioxide and water are products of the reaction but there is a delay in the desorption process. Porosity does not seem to be a major factor since the HNO₃ gas is absorbed at the mouth of the pores with great efficiency and there is no opportunity for the gas to diffuse into the pore system. Measurements of the probability of uptake of HNO₃ gas on calcite were made.
The authors comment on the affinity of HNO$_3$ gas on the apparatus surfaces and the fact that HNO$_3$ gas can be considered to be a very sticky gas with regard to its diffusive properties.

Rodriguez-Navarro and Sebastian (1996) demonstrate the effect of diesel and gasoline particulate in accelerating the formation of gypsum on limestone at 100 ppm. They hypothesise that the metal content (Cu, Pb and Zn) plus the carbon are the chief proponents. The composition of the crusts on the Cathedral of Granada are compared with the chemical analysis of particulate emitted from vehicles. Vehicle exhaust emissions are virtually the only source of pollution in Granada. The work does not differentiate between different elements and oxides in the particulate regarding their individual potency. However, diesel car-engine exhaust particulate are far more potent than gasoline exhaust particulate. The reason for this is not clear. He also comments on the effects of dust in retaining moisture, which is essential for the sulphation reaction, and providing a minor source of reaction components (mainly iron).

5. Aqueous reactions

Much of the literature cited above indicates that the reaction is activated by the presence of moisture. This would seem to suggest that the reactions take place in the aqueous phase. Martin (1984) describes the aqueous oxidation of sulphite in water in quite some detail at natural concentration levels (ppb). These reactions are highly dependant on the pH of the solution which governs the form SO$_2^{\text{aq}}$, HSO$_3^{-}$, or SO$_3^{2-}$. The convention is to examine $[\text{S(IV)}] = [\text{SO}_2^{\text{aq}}] + [\text{HSO}_3^{-}] + [\text{SO}_3^{2-}]$ in experiments. At low concentrations the gas liquid transfer is very fast and the limiting step are the redox reactions. Martin comments that mass transfer can be a severe problem at higher concentrations. This has the effect of speeding up the chemical kinetics so that chemistry is no longer the rate limiting step. There is also firm evidence that these aqueous reactions also change order as concentrations are increased or reduced.

The indication is that there is no oxidation with ambient oxygen and that the reaction is greatly increased in the presence of iron and manganese at very low concentrations ($10^{-11}$ mol/l). It is most likely that such minor reactions that are observed at ultra low concentrations are still due to catalysts. Additions of a metal ion complexing agent (EDTA) or an iron-complexing agent completely stops the reaction.

Reaction with ferric iron depends on the pH since ferric iron readily changes form with pH and is unstable for pH values greater than pH 4. At low pH (0–3) the rate is affected by temperature changing by at least a factor of 10 over 10–25°C and is first order with respect to iron and S(IV) and inversely related to pH. In the higher pH range the instability of the ferric ion changes the reaction to second order with respect to S(IV). The details of the process are far from clear due to the complexity of the ferric ion reaction. The sensitivity to the presence of iron is also highlighted by the effect of iron-complexing agents cited above.

Manganese oxidation has zero order behaviour with S(IV), second order with manganese and an inverse hydrogen ion dependance. The zero order behaviour seen in the laboratory would lead to infinite conversion rates in the environment which is quite disconcerting. At submicromolar concentrations the rate changes to a first order dependance on manganese and S(IV). As the pH rises the manganese hydroxide is still stable and therefore much easier to deal with experimentally. Martin reports that there is a synergism between the ferric ion and manganese which increases the first order ferric ion reaction rate by a factor of 100 or more at high S(IV) concentrations (> $10^{-6}$ M, similar to values found in plumes). This results in a loss of S(IV) from the system of approximately 3–10 times greater than without the synergism. The lower concentration regime has not been explored but there is evidence that this also demonstrates increased rates. He comments that no other metal synergisms were found for Cu, Co, Zn, Sn, Co, V, Ni or Pb and a mixture of all these ions only gave the same Fe–Mn reaction.

Some work on the catalytic rate of carbon in aqueous suspension is quoted which shows carbon to be an effective oxidant which is independent of
the pH. Work on fly-ash concludes that leached iron is likely to be the major catalytic agent. Organics can also have an effect on the rate, e.g. moderate inhibition toluene, hexene, α-pinene and hydroquinone; no inhibition ethanol, acetone, acetic acid and formaldehyde. A major source of toluene in the environment is petrol exhaust fumes (QUARG, 1993) so it might be possible that residues on the particulate initially act as inhibitors to oxidation. Organics can also take part in the formation of ozone, which is a very efficient oxidant, thus the very local inhibition effect might well be counteracted by the increased production of ozone.

Martin continues to discuss the very fast oxidation due to ozone, hydrogen peroxide and nitrous acid. These are the dominant processes in the atmosphere due to the rapid absorption of the gases into water and fast reaction kinetics.

Ozone is 100 times or more faster than the catalytic action of iron and manganese with O₂. In so far as the present discussion is concerned the reaction rate is not sensitive to iron or manganese catalytic activity. Hydrogen peroxide is even more efficient, being many orders of magnitude faster at low pH (3–5), and present in rainwater in hundreds of ppb. The exceedingly high reaction rate means that hydrogen peroxide dominates the low pH oxidation process. Whereas ozone dominates the process above 5 pH. Nitric acid is reported not to provide any oxidation even in the presence of Fe, Mn, Cu, Co, Pb or V; whilst nitrous acid had reaction rates which were comparable to ozone at low pH (0–3) which remained uncatalysed by Fe, Mn or V. The difficulty with the comparisons between NOx compounds in the context of vehicular pollution is that the effect of gaseous NO₂, an effective oxidant in its own right, cannot be discounted in the real urban environment.

Nitrogen dioxide readily dimerizes in aqueous solution to form nitrogen tetroxide which is a moderately strong oxidising agent. The relative effect of NO₂ and associated compounds depends on the product of Henry's law constant and the partial pressure. Within the urban situation the interaction between the species NO, NO₂ and O₃ is very complex. It is largely activated by daylight and the chemical reaction pathways change during night time (Hoffmann and Jacob, 1984).

Martin (1994) reviews the state-of-the-art regarding aqueous oxidation mechanisms in the light of a decade of further research. This reveals that there are some very subtle changes occurring with the iron-catalysed oxidation which affect the rate of the oxidation reactions:

1. Inhibition by ionic strength;
2. Inhibition by sulphur(VI);
3. Self-inhibition (i.e. by sulphur(IV)); and
4. Inhibition by organics at high pH but not at low pH.

Investigations at high pH (≥4) were much more difficult due to the fact that the oxidation of the sulphur causes the pH to drop and the use of buffers inhibits the reaction. The solubility of the iron(III) above a pH of 3.6 also causes special experimental problems. Consequently the effects of ionic strength, sulphate ion and sulphur(IV) have not been assessed. The experiments show that only the dissolved iron acts as a catalyst and at pH 5 the rate is second order rather than first order once the iron is below saturation.

The effect of manganese is re-examined (Martin, 1994) and found to depend on the ionic strength of the solution and not on pH as some have mistakenly reported. The synergism between iron and manganese for low sulphur concentrations is first order for both iron and manganese. The fresh evidence shows that the low concentration rate depends on the ionic strength of the solutions. As noted in the 1984 work, higher concentrations lead to very complex relationships with the manganese rate becoming second order, the iron forming various iron complexes and possibly a switch between molecular to free radical processes.

With regard to organic inhibition the greatest inhibition occurs at high pH and is non-existent at low pH (2) for the organic acids formic, acetic and trichloroacetic and three alcohols ethyl, isopropyl and allyl.

Martin observes that some revision has taken place in the ‘fast’ oxidation process for ozone — the rate is found to be dependant on the reactivi-
ties of the three sulphur(IV) species \( \text{SO}_4^{2-} \), \( \text{HSO}_4^- \), and \( \text{SO}_3^{2-} \) rather than their sum as previous cited. Results for the rate with hydrogen peroxide are similar to the previously cited work with the exception of the removal of acid catalysis effects in the mid pH region.

6. Conclusion

Controlling factors in the reaction and oxidation of sulphite to sulphate are the type and porosity of the stone, the level of humidity, the nature of the oxidants and to a lesser extent the presence of other extraneous reactants, e.g. metal oxides, chlorine and ammonia salts. Marble is much less reactive than porous limestone and the degree of activity has different relative humidity thresholds.

The majority of the chamber studies use what might be termed ‘bulk’ chemistry techniques, i.e. weight changes, analysis of solutes and X-ray diffraction to detect the changes occurring on the stones. An exception to this is the use of infrared (IR) which can be used to track the reaction at the surface. Reaction of the stone with the gaseous compounds occurs during the process of absorption onto the surface. This produces sulphite which is subsequently oxidised to sulphate. This process of oxidation is accelerated by the presence of \( \text{NO}_2 \), and seems to depend on the \( \text{NO}_2 \) component. It is perhaps a mute point as to whether the stone is considered ‘damaged’ at the point of sulphite formation or after the subsequent conversion to gypsum. The rate of dissolution is certainly enhanced by the conversion since gypsum is some 150 times more soluble. Certainly the \( \text{NO}_2 \) accelerates the conversion process after the sulphite has formed by the interaction at the gas–water interface but it is clear that \( \text{NO}_2 \) is only one of many possible oxidants in the urban and rural environment.

Correlation studies of the damage to stone materials are unlikely to pick up the effects of \( \text{NO}_2 \) due to the nature of their duration and the rather transient nature of the appearance and removal of nitrates on the stone.

Presence of other oxidants and catalysts (Benner et al., 1992) such as \( \text{H}_2\text{O}_2 \), \( \text{O}_2 \) (catalysed by Fe\(^{3+} \) and Mn\(^{2+} \)), OH, \( \text{H}_2\text{SO}_4^- \), \( \text{SO}_4^{2-} \), \( \text{O}_3 \), \( \text{HO}_2 \), \( \text{NO}_2^- \), \( \text{NO}_3^- \), \( \text{O}_2^- \) and PAN, all of which are present in the natural environment, plus the fact that the reactions are pH and ionic strength sensitive, add greatly to the complications of determining what affects the oxidation rate. These difficulties are further compounded by the presence of trace elements in the chemical reagents, particulate matter and the stone itself (such as Mn\(^{2+} \) or Vn\(^{2+} \)).

In conclusion there is sufficient evidence that \( \text{NO}_2 \) has a role to play in the oxidation of sulphite. However, the magnitude of influence \( \text{NO}_2 \) and related compounds have in the environment is far from clear due to the prevalence of other stronger oxidants (ozone and hydrogen peroxide), the intricately linked \( \text{NO}_2 \) and ozone chemistry in relation to their diurnal cycle and the diurnal humidity variations, the presence of metal oxide catalysts (Fe and Mn) in the stone and the environment and the possibility of organic oxidation inhibitors.

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