

Chapter 9

The atmospheric chemistry of sulphur and nitrogen in power station plumes

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Abstract

Emissions of sulphur and nitrogen compounds from power stations represent a significant fraction of the total emissions of these elements to the atmosphere. Understanding their subsequent chemical reactions in the atmosphere is of fundamental importance as without it, a quantitative assessment of their contribution to local and regional scale air pollution is not possible. Here the atmospheric chemistry of sulphur dioxide and the oxides of nitrogen, and their resultant likely behaviour in the plumes of power stations are reviewed.

1. Introduction

At least 90% of the sulphur present in fossil fuel enters the gas phase in the form of sulphur dioxide (SO₂) during combustion, and, unless it is deliberately removed from the flue gas, is emitted to the atmosphere, leading to the global anthropogenic emission of about 65 Tg SO₂ (as S) yr⁻¹ (Benkovitz et al., 1996; Spiro et al., 1992). Globally, an increasing proportion of this reactive sulphur is emitted from power plants, as power generation becomes more and more concentrated on large units. High-temperature combustion processes also inevitably produce oxides of nitrogen (NO_x = NO + NO₂), leading to the global emission of about 21–25 Tg NO_x (expressed as N) yr⁻¹ (Benkovitz et al., 1996; Dignon, 1992). SO₂ and NO_x are important air pollutants with both environmental and health effects attributed to them. Both compounds may lead to the deposition of acidity (“acid deposition” or “acid rain”) on the regional scale and NO_x takes part in chemical reactions that lead to the formation of ozone (O₃) in the troposphere, also on the regional scale. However, here the

focus is on the processes that affect SO_2 and NO_x oxidation in power station plumes, particularly with respect to how these processes influence the concentrations of the primary pollutants and their products in the relatively near field, for example at receptor sites located tens of kilometres from the source.

2. Review of the chemistry of sulphur dioxide and the oxides of nitrogen in the atmosphere

A very considerable body of literature exists on the atmospheric chemistry of sulphur and nitrogen occurring inside power station plumes. This is derived from theoretical and experimental studies of the chemistry of S and N compounds in the gas and aerosol phases, supplemented by observations of concentration changes in the atmosphere, both inside and outside of power station plumes.

2.1. Gas-phase oxidation of sulphur dioxide

In the gas phase, SO_2 can potentially be subject to a large number of reactions involving reactive transient oxidants (Calvert et al., 1978). These reactions, shown in Table 1, are all thermodynamically possible in the atmosphere under ambient conditions of temperature and pressure, but have widely differing elementary rate constants, ranging from about 10^{-12} to $\sim 10^{-20} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. Coupled with the wide range of concentrations of these various oxidants in the atmosphere, this variation in rate constants ensures that only very few of these possible reactions play any appreciable role in the oxidation of SO_2 in the atmosphere. In fact, the reactions of SO_2 with oxygen atoms and ozone are unlikely to be important in the gas phase, with the possible exception of the reaction with the $\text{O}(^3\text{P})$ atom in the very early stages of stack gas dispersion. $\text{O}(^3\text{P})$ is formed by the photodissociation of NO_2 , and under conditions of very high NO_2 concentrations, such as might exist in a plume close to the point of emission, it is possible that significant $\text{O}(^3\text{P})$ concentrations may result in appreciable SO_2 oxidation rates. However, as plume dilution with background air occurs, the instantaneous rate of this reaction will quickly fall.

Oxidation of SO_2 by ozone (O_3) is highly exothermic ($\Delta H = -242 \text{ kJ mol}^{-1}$). However with a gas-phase rate constant of $k = \sim 8 \times 10^{-24} \text{ m}^3 \text{ molec}^{-1} \text{ s}^{-1}$ and a maximum likely ozone concentration of $\sim 5 \times 10^{12} \text{ molec cm}^{-3}$ there will normally be insignificant SO_2 oxidation by this route ($< 1.4 \times 10^{-5} \% \text{ h}^{-1}$). Although the rate of the gas-phase reaction of SO_2 with ozone is extremely slow, the addition of an alkene to a dilute O_3 - SO_2 mixture in air results in the significant oxidation of the SO_2 (Cox and Penkett, 1971, 1972). The mechanisms behind this enhancement in oxidation rate are not fully elucidated but

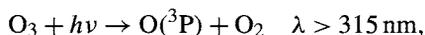
Table 1. Enthalpy changes and rate constants for potentially important reactions of ground state SO₂ and SO₃ molecules in the lower atmosphere (adapted from Calvert, 1984)

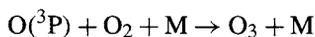
Reaction	$-\Delta H^\circ$ (kJ mol ⁻¹)	25°C k (cm ³ molec ⁻¹ s ⁻¹)
O ₂ (¹ Δ _g) + SO ₂ → SO ₄ (biradical)	105	3.9 × 10 ⁻²⁰
O ₂ (¹ Δ _g) + SO ₂ → SO ₄ (cyclic)	~ 117	
O ₂ (¹ Δ _g) + SO ₂ → SO ₃ + O(³ P)	-56.5	
O ₂ (¹ Δ _g) + SO ₂ → SO ₂ (³ Σ _g ⁻) + SO ₂	94	
O ₂ (¹ Σ _g ⁺) + SO ₂ → SO ₄ (biradical)	167	6.6 × 10 ⁻¹⁶
O ₂ (¹ Σ _g ⁺) + SO ₂ → SO ₄ (cyclic)	180	
O ₂ (¹ Σ _g ⁺) + SO ₂ → SO ₃ + O(³ P)	6.3	
O ₂ (¹ Σ _g ⁺) + SO ₂ → SO ₂ + O ₂ (¹ Δ _g)	62.8	
O(³ P) + SO ₂ (+M) → SO ₃ (+M)	347	5.7 × 10 ⁻¹⁴
SO ₃ + SO ₂ → O ₂ + SO ₃	241	< 8 × 10 ⁻²⁴
NO ₂ + SO ₂ → NO + SO ₃	41.4	8.8 × 10 ⁻³⁰
NO ₃ + SO ₂ → NO ₂ + SO ₃	136	< 7 × 10 ⁻²¹
ONOO + SO ₂ → NO ₂ + SO ₃	~ 126	< 7 × 10 ⁻²¹
N ₂ O ₅ + SO ₂ → N ₂ O ₄ + SO ₃	100	< 4 × 10 ⁻²³
HO ₂ + SO ₂ → HO + SO ₃	69.9	
HO ₂ + SO ₂ (+M) → HO ₂ SO ₂ (+M)	29.3	< 1 × 10 ⁻¹⁸
CHO ₃ O ₂ + SO ₂ → CHO ₃ O + SO ₃	~ 113	< 1 × 10 ⁻¹⁸
CHO ₃ O ₂ + SO ₂ (+M) → CHO ₃ O ₂ SO ₂ (+M)	~ 130	~ 1.4 × 10 ⁻¹⁴
(CH ₃) ₃ CO ₂ + SO ₂ → (CH ₃) ₃ CO + SO ₃	~ 109	
(CH ₃) ₃ CO ₂ + SO ₂ → (CH ₃) ₃ CO ₂ SO ₂	~ 126	< 7.3 × 10 ⁻¹⁹
CHO ₃ COO ₂ + SO ₂ → CH ₃ CO ₂ + SO ₃	~ 138	
CHO ₃ COO ₂ + SO ₂ → CH ₃ COO ₂ SO ₂	~ 155	< 7 × 10 ⁻¹⁹
HO + SO ₂ (+M) → HOSO ₂ (+M)	~ 155	1.1 × 10 ⁻¹²
CHO ₃ O + SO ₂ (+M) → CH ₃ OSO ₂ (+M)	~ 100	~ 5.5 × 10 ⁻¹³
SO ₃ + H ₂ O → H ₂ SO ₄	24.8	9.1 × 10 ⁻¹³

are most likely due to the formation of the Criegee intermediate (CH₂O₂) and its reaction with SO₂. However, the significance of this reaction in the real atmosphere is difficult to assess, since the effect of addition of NO to the reaction mixture, and competition between NO and SO₂ for reaction with CH₂O₂, is not fully known.

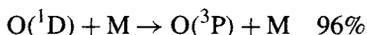
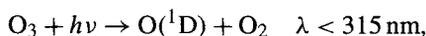
By far the most important route of oxidation of SO₂ in the gas phase is by reaction with the hydroxyl radical, OH (e.g. McAndrew and Wheeler, 1962; Harris and Wayne, 1975; Castleman and Tang, 1976; Atkinson et al., 1976; Davis et al., 1979a, b; Cox and Sheppard, 1980; Harris et al., 1980; Leu, 1982).

In the unpolluted atmosphere, OH is produced by the photolysis of O₃ and the subsequent reaction of oxygen atoms with water vapour:

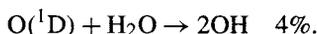




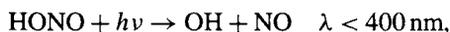
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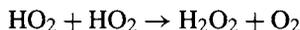
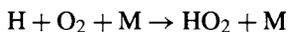
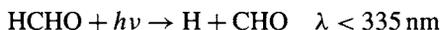
but



In polluted air, the photolysis of nitrous acid (HONO) and hydrogen peroxide (H₂O₂) produce OH directly



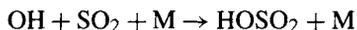
Under more polluted conditions, OH radicals are produced by the photolysis of the products of the incomplete combustion of fossil fuels, especially aldehydes, ketones and other oxygenated organic compounds. For example, formaldehyde photolysis leads to



then



Hydroxyl then rapidly reacts with SO₂ by addition:

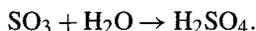
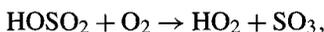


where M is another molecule (usually N₂) that is required to absorb excess kinetic energy from the reactants. At the pressures pertaining in the lower atmosphere the rate of this reaction is independent of the concentration of M and hence it is effectively a second-order reaction.

Many attempts have been made to measure the rate constant for the OH–SO₂ reaction in the laboratory (e.g. Cox, 1975; Castleman and Tang, 1976;

Atkinson et al., 1976; Cox and Sheppard, 1980; Harris et al., 1980) and rather a wide range of values have been obtained. However, Atkinson and Lloyd (1984) recommend an effective bimolecular rate constant at 1 atm and 298 K of $9 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, with an uncertainty of around $\pm 50\%$. For an average ambient OH concentration of $1 \times 10^6 \text{ radicals cm}^{-3}$ (Hewitt and Harrison, 1985) the lifetime of SO_2 with respect to this one gas phase reaction will be $\sim 13 \text{ d}$ in the "typical" troposphere.

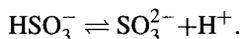
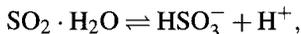
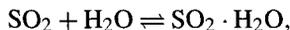
Once formed, the free radical HOSO_2 will rapidly react with oxygen to form SO_3 , which in turn will rapidly react with water vapour to form sulphuric acid, H_2SO_4 (Goodeve et al., 1934; Cox and Penkett, 1971; Calvert et al., 1978; Stockwell and Calvert, 1983):



Eatough et al. (1994) point out that the rate of conversion of SO_2 to sulphate by OH will increase with both increasing temperature and relative humidity. In practise, the rate of the homogeneous gas-phase conversion of SO_2 to sulphate can vary from much less than $1\% \text{ h}^{-1}$ up to a probable maximum of $10\% \text{ h}^{-1}$ under optimum atmospheric conditions.

2.2. Aqueous phase oxidation of sulphur dioxide

The presence of aqueous droplets in the atmosphere offers another phase in which oxidation of SO_2 can occur. After transport of the gas to the surface of the droplet and transfer of the gas across the air-liquid interface, SO_2 can dissolve in water and establish an equilibrium with its ionic products, with the aqueous-phase concentrations described at equilibrium by the Henry's law constant. As a result, dissolved SO_2 actually consists of three species, hydrated SO_2 ($\text{SO}_2 \cdot \text{H}_2\text{O}$), the bisulphite ion (HSO_3^-) and the sulphite ion (SO_3^{2-}):



The predominant form depends upon the acidity of the solution in which the SO_2 dissolves, since the hydrogen ion concentration will drive the equilibrium either to the left or right (Martin and Damschen, 1981). The oxidation state of the sulphur in the various products is +4, and hence S(IV) is used to denote all

these forms of sulphur taken together. In contrast, the oxidised form of sulphur (i.e. H_2SO_4 and SO_4^{2-}) is in the +6 oxidation state and hence is referred to as S(VI). There are several possible routes of oxidation of S(IV) to S(VI) and these are now briefly considered.

Molecular oxygen may oxidise S(IV) to S(VI) but in the absence of a catalyst the reaction is insignificant. Although both iron (III) and manganese (II) appear to catalyse the reaction it is still relatively slow and unlikely to be of significance (e.g. Huss et al., 1982; Martin and Good, 1991; Martin et al., 1991).

As noted above, O_3 reacts very slowly with SO_2 in the gas phase, but in the liquid phase the reaction is rapid (e.g. Penkett et al., 1979):



At ambient gas-phase concentrations of 30–60 ppb and a Henry's law constant of $0.01 \text{ mol l}^{-1} \text{ atm}^{-1}$, the expected aqueous-phase equilibrium concentration of O_3 will be around $(3\text{--}6) \times 10^{-10} \text{ mol l}^{-1}$. Although this concentration is around 6 orders of magnitude lower than that for dissolved O_2 , oxidation of S(IV) by O_3 is much more important under most conditions because of the much higher rate constant for the reaction, which is pH dependent (e.g. Lagrange et al., 1994; Botha et al., 1994). At a pH greater than around 4 this is likely to be an important route of oxidation of S(IV) in water droplets.

Hydrogen peroxide has been shown to oxidise S(IV) relatively rapidly in solution and in fact is one of the most effective oxidants of S(IV) in solution (Penkett et al., 1979). Because of its high solubility, with a Henry's law constant of $1 \times 10^5 \text{ M atm}^{-1}$, a 1 ppb gas-phase concentration of H_2O_2 would produce an equilibrium aqueous-phase concentration at 298 K of around $1 \times 10^{-4} \text{ mol l}^{-1}$, or 6 orders of magnitude greater than the solution-phase equilibrium O_3 concentration. The rate constant for the reaction of H_2O_2 and S(IV) is largely pH independent, and at a gas-phase H_2O_2 concentration of 1 ppb is around $300 \times 10^{-6} \text{ M h}^{-1} (\text{ppb SO}_2)^{-1}$. Organic peroxides have also been proposed as potential aqueous phase S(IV) oxidants but have lower Henry's law constants and lower gas-phase concentrations than does H_2O_2 and are considered to normally be of minor importance in this regard (Lind et al., 1987).

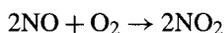
The different routes of aqueous-phase oxidation of S(IV) can be compared as a function of pH and temperature (Seinfeld and Pandis, 1998), using starting conditions of, for example, 5 ppb SO_2 , 1 ppb NO_2 , 1 ppb H_2O_2 , 50 ppb O_3 , $0.3 \mu\text{M Fe(III)}$ and $0.03 \mu\text{M Mn(II)}$. Under practically all conditions, oxidation by dissolved H_2O_2 is the predominant pathway for sulphate formation. Only at pH values greater than 5 does oxidation by O_3 start to dominate, and at pH 6 this route is around 10 times faster than that by H_2O_2 . Assuming a liquid cloud water content of 1 g m^{-3} , the rate of oxidation by H_2O_2 can exceed $500\% \text{ h}^{-1}$. In contrast to the homogeneous gas-phase reactions of SO_2 the

aqueous-phase process is therefore largely controlled by mixing and reactant limitations, rather than kinetic considerations (Eatough et al., 1994).

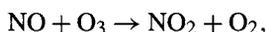
2.3. Gas-phase oxidation of the oxides of nitrogen

Homogeneous formation of nitric acid by the oxidation of NO and NO₂ appears to be a much less complicated, and better understood process than the formation of sulphuric acid from sulphur dioxide. Most work on NO_x oxidation has been carried out in polluted air and this may hinder extrapolation of predicted oxidation rates to the case of power station plumes. NO and smaller amounts of NO₂ are formed during high temperature combustion processes, with power stations emitting NO_x (the sum of NO and NO₂) as ~ 95% NO and ~ 5% NO₂.

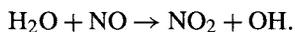
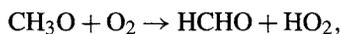
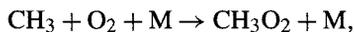
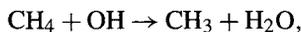
The termolecular reaction of NO with O₂:



is very slow at atmospheric temperatures and, except at extremely high NO concentrations, is insignificant compared with the reactions of NO with O₃, OH, HO₂ (hydroperoxy) and RO₂ (alkylperoxy):



The peroxyradicals, HO₂ and RO₂, are formed in chain reactions in the atmosphere, initiated by the attack of hydroxyl on reactive hydrocarbons. For example, in the simplest (but slowest) case involving methane



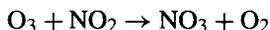
There is some observational evidence that the termolecular reaction with O_2 may play a role in the rapid oxidation of NO to NO_2 in highly polluted urban air in the wintertime, when the concentrations of the photochemically produced oxidants O_3 , OH , HO_2 and RO_2 are likely to be very low. However the role of free radical chemistry is also now thought to be significant, even in wintertime smog episodes (Harrison and Shi, 1996; Shi and Harrison, 1997; Harrison et al., 1998).

Overall, then, the predominant fate of emitted NO is oxidation to NO_2 which can then react with OH during the daytime:

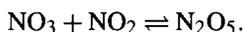


A great variety of experimental studies support the view that this reaction is relatively rapid, with an effective 2nd order rate constant at 1 atm in air of around $1.1 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson and Lloyd, 1984), approximately ten times the rate of the SO_2 - OH reaction.

A second potentially important source of nitric acid involves the reaction of the nitrate radical, NO_3 , with some organic compounds. The nitrate radical is formed in the presence of NO_2 and O_3 and is in equilibrium with N_2O_5 in the atmosphere:



$$k = 3.2 \times 10^{-17} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \text{ (Atkinson and Lloyd, 1984)}$$

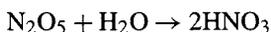


NO_3 reacts relatively rapidly with a variety of organics, and in the case of alkanes and aldehydes, the reaction is believed to proceed by hydrogen abstraction to form nitric acid:



In polluted urban air, alkane concentrations (excluding CH_4) are typically around 100 ppb ($2.5 \times 10^{12} \text{ molec cm}^{-3}$) and total aldehyde concentrations are of the order of tens of ppb. Using an estimated NO_3 concentration of 100 ppt, the calculated rate of formation of HNO_3 formation by this route would be around 0.3 ppb h^{-1} . This can be compared to the daytime rate of formation of HNO_3 by reaction of NO_2 with the OH radical of around 2 ppb h^{-1} , at an NO_2 concentration of 50 ppb and an average OH concentration of $1 \times 10^6 \text{ cm}^{-3}$ (Hewitt and Harrison, 1985). Thus the rate of nighttime formation of HNO_3 is likely to be rather insignificant relative to the rate of daytime formation.

Another potential source of nitric acid is the hydrolysis of N_2O_5 (Platt and Perner, 1980):



where $k < 1.3 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ (Tuazon et al., 1983). This rate constant is sufficiently large to ensure that this reaction may contribute significantly to HNO_3 formation in the polluted atmosphere. In fact, Tuazon et al. (1983) estimated a formation rate of 0.3 ppb h^{-1} at NO_2 and NO_3 concentrations of 3 ppb and 100 ppt, respectively, at 50% relative humidity. This is similar to the rate of formation due to the reactions of the nitrate radical with alkanes and aldehydes. Other studies, including Jones and Seinfeld (1983) and Richards et al. (1981, 1983) confirm this.

2.4. Aqueous phase oxidation of the oxides of nitrogen

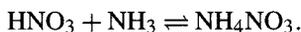
Some field studies (e.g. Lazrus et al., 1983) have indicated appreciable formation of nitric acid in the aqueous phase in the atmosphere (NO_2 conversion rates of $\sim 8\% \text{ h}^{-1}$, Gertler et al., 1984), but laboratory studies are less conclusive. In fact, aqueous phase oxidation of the oxides of nitrogen probably proceeds far too slowly under ambient conditions to contribute to either the significant removal of these gas-phase compounds or to cloud-water acidification (rate constants of 2×10^{10} and $1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, for the reactions of NO and NO_2 with OH , respectively).

2.5. Sulphuric and nitric acids compared

Once formed in the atmosphere sulphuric and nitric acids show very different behaviours, both physically and chemically. Nitric acid is more volatile and hence exists in significant concentrations in the gas phase, while sulphuric acid has a very low vapour pressure under ambient conditions and hence exists in the form of aerosol phase particles.

Both nitric acid and sulphuric acid will react with alkaline substances in the atmosphere to produce salts, the most important of these under ambient conditions being the ammonium compounds resulting from reactions with ammonia (APEG, 1999; Lee and Atkins, 1994; Langford et al., 1992).

When HNO_3 reacts with NH_3 an equilibrium is established (Hidleman et al., 1984):



The ammonium nitrate exists as a solid if the relative humidity is less than that of deliquescence. At higher relative humidities it will exist as aerosol droplets. However at elevated temperatures, above $\sim 310 \text{ K}$, little NH_4NO_3 will exist in

the atmosphere, since the dissociation constant is temperature dependent and the above reaction will move to the left (Mozurkewich, 1993).

In polluted air, where high concentrations of both NO_x and SO_2 are present, the oxidation chemistries of these compounds become intertwined. As NO_x concentrations increase, so the gas-phase concentration of OH will decrease, hence lowering the rate of oxidation of SO_2 . Similarly, high concentrations of NO_x will lead to a decrease in the rate of formation of H_2O_2 as the NO molecules will compete for reaction with HO_2 , so reducing the number of HO_2 radicals available for the self-reaction needed to produce H_2O_2 .

2.6. Removal of sulphur and nitrogen by wet and dry deposition processes

Both the primary pollutants, SO_2 and NO_x , and their secondary products, H_2SO_4 , HNO_3 , SO_4^{2-} and NO_3^- , as well as their further reaction products, e.g. $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 , are subject to continuous removal from the boundary layer by the process of dry deposition to the Earth's surface. This process may be parameterized by the use of a deposition velocity, the magnitude of which varies from compound to compound and with environmental conditions and the nature of the surface. A typical range of deposition velocities reported for various pollutants and surfaces is $0.1\text{--}2\text{ cm s}^{-1}$. Additionally, intermittent deposition may occur for soluble gases and particles by the process of wet deposition. Although wet deposition may be extremely efficient, it is, by its nature, sporadic.

The current understanding of dry deposition has recently been authoritatively reviewed by Wesely and Hicks (2000) while recent measurements of the deposition velocity of SO_2 include those of Horvath et al. (1998), who found values of $0.19\text{--}0.20\text{ cm s}^{-1}$ over short vegetation. However, it is recognized that more direct measurements of deposition fluxes and deposition velocities are required for the improved parameterization of deposition models. Such models (e.g. those contained within the Acid Deposition and Oxidant Model (ADOM: Pleim et al., 1984), the Regional Acid Deposition Model (RADM: Walmsley and Wesely, 1996) and the Routine Deposition Model (RDM: Brook et al., 1999) appear to give a reasonable description of pollutant deposition integrated over time and space (e.g. monthly deposition fluxes on a $10\text{ km}\times 10\text{ km}$ grid) but their utility in describing removal rates from a plume as it rapidly moves over complex and varying terrain are very limited (Park, 1998). Similarly, wet deposition, resulting from cloud and precipitation scavenging, can be very effective in removing pollutants (Martin, 1984; Prupacher and Klett, 1978; Bidleman, 1988) but is extremely difficult to model for a plume, due to its intermittent nature.

3. Power station plume chemistry

3.1. Observations

A large number of field studies have been carried out with the aim of validating the understanding of sulphur and nitrogen pollution chemistry obtained theoretically or in the laboratory and/or with the aim of obtaining observational estimates of the rate of oxidation of sulphur and nitrogen (and hence the rate of formation of sulphate and nitrate) in power station plumes. The oxidation rates observed in plumes may well be expected to differ from those predicted or observed in ambient or background air for a number of reasons, including the possibility of enhanced concentrations of catalysts and the rapid depletion of oxidants (e.g. removal of O_3 by reaction with NO) within the plume. However, very few studies have procured sufficient simultaneous measurements of SO_2 and NO_x concentrations to allow a full understanding of the relative rates of removal of these gases from discrete plumes. This poses a major limitation on the conclusions that can be drawn.

The SO_2 oxidation rates seen in plumes from point sources vary from nearly zero to more than $16\% h^{-1}$. In urban plumes even higher oxidation rates, up to $30\% h^{-1}$, have been reported. Part of this variation may be attributable to uncertainties in data collection and interpretation, but the wide variations in plume compositions and background conditions, both chemical and meteorological, are also important.

As already noted above, heterogeneous oxidation of SO_2 may be very rapid under certain conditions and will depend on the amount of water vapour available for the formation of droplets. Additionally, experimental studies (e.g. Haury et al., 1977) and modelling of the $H_2SO_4-H_2O$ gas-phase binary system have shown that the rates of nucleation and condensation and hence of the rate of formation of sulphate aerosol is largely controlled by the concentration of water vapour present. However, most field studies of plume chemistry, particularly those involving aircraft, have been conducted in conditions where the aqueous-phase reactions were not favoured. The SO_2 oxidation rates discussed below are summarised in Table 2. Although the focus of most early field studies was the formation of sulphate and nitrate (in the frame of a general concern about acid deposition and environmental acidification), more recently the focus has shifted somewhat to the role of power plant plumes to the formation of ozone and other oxidants in the lower atmosphere. For example, Gillani et al. (1998a, b), Ryerson et al. (1998), Luria et al. (1999, 2000), Sillman (2000), St. John and Chameides (2000) and Nunnermacker et al. (2000) all studied the formation of O_3 in power plant plumes, rather than, explicitly, sulphate and nitrate formation.

Table 2. Oxidation rates of S(IV) in plumes (adapted from Harter, 1985)

Location of source	Plume age (h)	Stack distance (km)	Travel time (h) of sampling	Month and year rate	Oxidation data (% h ⁻¹)	No of rate points	Average (% h ⁻¹)	Rate derivation, method comments	Reference
<i>Coal fired power plants</i>									
Cumberland, TN, USA	1.5–10	8–160	1.67–12	Aug. 1978	< 0.1–7.5	19	3	Particulate S/total S ratio	Gillani et al. (1977, 1978, 1981, 1983)
Johnsonville, TN, USA	6–8	56–160	6–8	Aug. 1978	0.8–8.5	6	3	Dry conditions only	
Cumberland, TN, USA	1.3–10.7		2.15–4.77	Jul./Aug. 1976	1.1–8.5	5	5.5	Average daytime rate	Zak (1981)
	0–7		1.35–7.03	Aug. 1978	0.4–16.7	5	6.1	Stack to first measurement Particulate S/gaseous S ratio	
Keystone, PA, USA			0.5–2.67	Apr./May/Sep./ Oct. 1978	0.01–5.92	13	0.05	At r.h 42–64%	Dittenhoeffer and De Pena (1980)
							0.78	At r.h 65–90%	
							3.31	At r.h 91–100%	
Paradise, KY, USA			0.2–3.8	Jun.	0–1.3	5		Particulate S/total S ratio	Meagher et al. (1981)
Colbert, AL, USA		7–50	0.28–5.20	May/Jun.	0.78–2.79	12	1.3	Morning rate	Meagher and Luria (1982)

Table 2. (Continued)

Location of source	Plume age (h)	Stack distance (km)	Travel time (h) of sampling	Month and year rate	Oxidation data (% h ⁻¹)	No of rate points	Average (% h ⁻¹)	Rate derivation, method comments	Reference
Widows Creek, AL, USA		2-49.3	0.43-6.01	Aug.	0.34-3.41	17	1	Morning rate	
							2.4	Afternoon rate	
Cumberland, TN, USA	0.76-9	11-200		Aug. 1978	0.1-7	21	3	Particulate S/total S ratio Late morning & afternoon	Forrest et al. (1981)
							0.5	Night & early morning	
							2	Average diurnal rate	
Bowen, GA, USA			0.12-3.33	Dec. 1979	0-2.3	7	< 0.2	Particulate S/total S ratio	Liebsch and De Pena (1982)
Breed, IN, USA	1.3-6.8			Jun./Nov. 1977	0-3.7	7	1	Particulate S/total S ratio	Easter et al. (1980)
Cobb, MI, USA	1.1-3			May/Nov. 1977	0.2-8.4	6	2.6		
Labadie, MO, USA	0.8-12	12-320	0.83-12	Jul. 1976	0.3-3.2	17	1-3	Particulate S/total S ratio	Gillani and Wilson (1980)
Labadie, MO, USA	0.7-12.5	14-360		Aug. 1974/Jul. 1976	0.1-4.8	50	1.6	Particulate S/total S ratio Rate 1-4% h ⁻¹ d ⁻¹ , < 0.5 night	Husar et al. (1978)
Leland-Olds, ND, USA			0.38-1.08	Jun. 1978	0-0.06	4		Change in total particle volume & particulate S/total S ratio	Hegg and Hobbs (1980)

Table 2. (Continued)

Location of source	Plume age (h)	Stack distance (km)	Travel time (h) of sampling	Month and year rate	Oxidation data (% h ⁻¹)	No of rate points	Average (% h ⁻¹)	Rate derivation, method comments	Reference
Big Brown, TX, USA			0.63-1.32	Jun. 1978	0.15-5.7	4			
Sherburne Co. MN, USA			0.17-2.7	Jun. 1978	0-2.2	4			
Centralia, WA, USA			0.03-1.42	Mar./Oct. 1976	0.03-0.56	5		Change in total particle volume	Hobbs et al. (1979)
Four Corners, NM, USA			0.78-0.87	Sep./Oct. 1977	0.34-6.6	3			
Navajo AZ, USA	3-6.1			Jun./Jul. 1979	0.7-13	22	1.9	Rate at noon	Wilson and McMurry (1981)
							0.9	Diurnal average Particle volume/ Total S ratio	
Great Basin, NV, USA	0.36-10.5			Jul./Aug. 1979	1-7	16		Particulate S/total S ratio	Eatough et al. (1981)
Navajo, AZ, USA	2.5-11	25-115	2.67-10.92	Jul./Dec. 1979	0-0.8	13		Particulate S/total S ratio	Richards et al. (1981)
Four Corners, NM, USA		2-90	0.3-12.5	Jun. 1978	0.15-0.5	3		Varies with stack distance CN production/ SO ₂ ratios	Mamane and Poeschel (1980)
Nanticoke Ont., Canada	0.15-1.93	3-43		Jun. 1978	0-8.7	7	4	Plume age < 2 h with fumigation Particulate S/total S ratio	Anlauf et al. (1982)

Table 2. (Continued)

Location of source	Plume age (h)	Stack distance (km)	Travel time (h) of sampling	Month and year rate	Oxidation data (% h ⁻¹)	No of rate points	Average (% h ⁻¹)	Rate derivation, method comments	Reference
Nanticoke Ont., Canada	0.07-2.9	2-93		Nov. 1975	0.32-12.6	19		Varies with stack distance Particulate S/total S ratio	Melo (1977)
<i>Oil fired power plants</i>									
Anclote, FL, USA		0.50	0-1.67	Aug. 1976/Feb. 1977			≤ 0.25	Steady state rate Particulate S/total S ratio	Forrest et al. (1979b)
Andrus, MS, USA	1.2-6.6			May/Oct. 1977	0-5.1	9	2.2	Particulate S/total S ratio	Easter et al. (1980)
Northport, NY, USA	0-3.3		0-2	Various, over 3 yr		60	< 1	Rate essentially incalculable Particulate S/total S ratio	Garber et al. (1981)
<i>Metal smelters</i>									
Mt Isa, Qld, Australia	0.08-14.83	2-256		Jun. 1977	0.06-0.45	65	0.25	Diurnally averaged rate Gaseous S/total S ratio	Roberts and Williams (1979)
Mt Isa, Qld, Australia	2.2-42.5	60-1001		Jul. 1979			0.15	Diurnally averaged rate	Williams et al. (1981)

Table 2. (Continued)

Location of source	Plume age (h)	Stack distance (km)	Travel time (h) of sampling	Month and year rate	Oxidation data (% h ⁻¹)	No of rate points	Average (% h ⁻¹)	Rate derivation, method comments	Reference
<i>Urban plumes</i>									
St Louis, MO, USA				Aug. 1975	10-14	18		Gaseous S/total S ratio	Alkezweeny and Powell (1977)
Milwaukee, WI, USA			0-3	Aug. 1976/Jul. 1977	1-9		4	Sulphate and light scattering	Miller and Alkezweeny (1980)
St Louis, MO, USA				Jun. 1976	0-4			Measurements	Forrest et al. (1979a)
Budapest Hungary		50	~3h	Jul./Aug. 1978	3-31	8	10	Particulate S/total S ratio	Horvath and Bonis (1980)
<i>Long-range transport trajectories</i>									
Sweden		900-1900	23-61	Summer (Apr.-Sep.)	0.3-5.2	12	1.4	Particulate S/gaseous S ratio	Traegaardh (1980)
		1300-2500	27-55	Winter (Oct.-Mar.)	0.4-1.3	4	0.8		

One of the first airborne investigations of SO₂ oxidation in the plume of a power station was that of Flyger et al. (1978), who used an SF₆ tracer to monitor dispersion and deposition from the plume emitted from a 122 m high stack. They estimated that half the SO₂ was lost from the plume within 45 km of the source, corresponding to a travel time (and half-life) of about 90 min.

Gillani et al. (1978) studied the gas-to-particle conversion rate of sulphur emitted from a coal fired power station in Kansas. They observed that the ratio of particle phase to total sulphur was related linearly to the total solar radiation dose experienced by the plume. This resulted in the amount of sulphur lost by deposition to the ground surface being about 25% in the first 200 km of travel, comparable to the amount of particulate sulphate formed. The maximum rate of particulate sulphur formation was less than 3% h⁻¹ and only occurred during the daytime. Further analysis of the same data set was carried out by Husar et al. (1978) who concluded that SO₂ oxidation rates were 1–4% h⁻¹ during the daytime and < 0.5% h⁻¹ during the night. In a further re-examination of these data, Gillani and Wilson (1980) concluded that the condition of the background air mass which receives the plume, the extent of plume – background air interactions and photochemical processes are the most important factors in determining the SO₂ oxidation rate. This is probably because of the dominant role of O₃, both directly and as a source of OH. Additionally, the entrainment of non-methane hydrocarbons from polluted background air can provide a source of peroxy radicals (HO₂ and RO₂), allowing replenishment of the O₃ removed by reaction with NO in the plume.

Put together, the Kansas experiment suggests that sulphate aerosol forms relatively rapidly during the daytime when sufficient oxidants (OH, HO₂ and RO₂), are available in the plume. Initially, close to the point of emission, oxidant depletion occurs rapidly within the plume by consumption of O₃ by emitted NO, thus limiting the concentrations of OH (which is formed by the photolysis of O₃). If sufficient mixing with background air occurs, O₃ concentrations will recover, either by mixing in of O₃ or of non-methane hydrocarbons, which can in turn form peroxy radicals. These can both contribute to O₃ formation, by rapidly converting NO to NO₂ without consumption of O₃, and can directly offer a route of oxidation of SO₂.

Clearly, SO₂ oxidation rates in the bulk plume are likely to be lower than in background air due to oxidant limitation. However, it is possible that at the plume top and edges, where plume dilution is greatest, conversion rates may be significantly enhanced. Zak (1981) observed daytime conversion rates up to 5.5% h⁻¹ in a plume edge. Similarly, when the plume top is in contact with clouds, fast liquid-phase reactions will enhance the SO₂ oxidation rate, up to 10% h⁻¹ (Gillani et al., 1981).

Another important consideration is the SO₂/NO_x ratio. This is a critical parameter in determining sulphate formation rates because SO₂ and NO_x compete

for the same oxidising radicals, and oxidation of NO_2 by OH is much faster ($\times 10$) than that of SO_2 . Hence the presence of NO_x in a plume will inhibit SO_2 oxidation rates (and sulphate formation rates) relative to the rates in background air.

Mamane and Pueschel (1980) used the concentrations of particles in the plume of the Four Corners power station to estimate an SO_2 oxidation rate of about $0.15\% \text{ h}^{-1}$ in the first 0.3 h, increasing to $0.5\% \text{ h}^{-1}$ in the next two hours of travel time, decreasing again to $\sim 0.3\% \text{ h}^{-1}$. Outside the Four Corners plume, Davis et al. (1979a, b) estimated SO_2 oxidation rates due to reaction with OH of $0.2\% \text{ h}^{-1}$ in the early morning and $2.3\% \text{ h}^{-1}$ around noon, with an average conversion rate of $0.7\% \text{ h}^{-1}$.

Dittenhoeffer and De Pena (1978) found that gas-phase photochemical reactions were the dominant sulphate formation mechanisms during the daytime in a power station-plume at Keystone, Pennsylvania, at low relative humidities. However, when the plume merged with a cooling tower plume, liquid-phase oxidation predominated. In a later study of the Keystone plume they found an average SO_2 oxidation rate of about $1\% \text{ h}^{-1}$ in the first 2 h of plume travel, rising to $6\% \text{ h}^{-1}$ when the plume encountered clouds (Dittenhoeffer and De Pena, 1982).

Meagher et al. (1977) used an instrumented aircraft to determine the rate of SO_2 oxidation within the plume of the Cumberland Valley coal-fired power station in Tennessee. Most of the oxidation of SO_2 that was observed appeared to occur in the immediate vicinity of the power plant. Beyond 10 km, an average oxidation rate of $0.2\% \text{ h}^{-1}$ was found. In a later modelling study, Meagher and Luria (1982) simulated the chemistry of a plume from a power station of similar size and location to the Cumberland Valley plant. Hydroxyl was found to be the most important oxidant of SO_2 , except when high background concentrations of hydrocarbons were used, in which case oxidation by HO_2 and RO_2 became significant. Rapid attenuation of oxidation rates were observed, as oxidant limitation became significant, following the removal of O_3 by NO, and plume dilution by incorporation of background air was required before radical chemistry became established. Forrest et al. (1981) found a daytime average conversion rate of $3\% \text{ h}^{-1}$ in summer, varying with time of day, and an average of $0.5\% \text{ h}^{-1}$ at night. The Cumberland Valley plant was studied more recently, during the 1995 Southern Oxidant Study, when Gillani et al. (1998a, b) found nitrate formation rates of $10\text{--}15\% \text{ h}^{-1}$ and a high differential loss rate of nitrogen species (relative to SO_2) of about 0.12 h^{-1} .

Summer and wintertime oxidation rates of SO_2 were obtained in the plume from a northern Alberta power station by Lulis et al. (1978). In February the oxidation rate was found to be low (less than $0.5\% \text{ h}^{-1}$), increasing to $1\text{--}3\% \text{ h}^{-1}$ in June, again suggesting the role played by photochemical processes. Another wintertime study (Liebsch and De Pena, 1982), this time of the

Bowen, Georgia, power station plume, found that the highest conversion rate was $0.2\% \text{ h}^{-1}$, except when high relative humidity was observed, when the conversion rate increased to $2.3\% \text{ h}^{-1}$. Meagher and Luria (1981) also observed increased conversion rates, up to $2.8\% \text{ h}^{-1}$, in periods of high relative humidity.

Data obtained from five different coal-fired power stations in the western USA at times favourable to gas-phase photochemical reactions gave SO_2 to SO_4^{2-} conversion rates of $0\text{--}5.7\% \text{ h}^{-1}$ for travel times of 10–162 min (Hegg and Hobbs, 1980). In a later study carried out in Arizona, they failed to find measurable conversion rates in four flights out of five (Hegg and Hobbs, 1983), while in another study on the plume from the coal-fired Mohave station, an SO_2 to particle conversion rate of $0.6\% \text{ h}^{-1}$ was estimated (Hegg et al., 1985).

Anlauf et al. (1982) found an average summertime SO_2 to SO_4^{2-} oxidation rate of $4\% \text{ h}^{-1}$ in the plume of the Nanticoke coal-fired power station in Ontario at distances downwind from the stack of 3–43 km at relative humidities of 30–50%. Eatough et al. (1982) studied sulphur chemistry in the plume of the Kennecott copper smelter in Utah and found SO_2 to sulphate conversion rates as high as $6\% \text{ h}^{-1}$ in hot, dry and sunny summer conditions.

Luria et al. (1983) attempted to obtain SO_2 oxidation rates by airborne sampling of the plume from the coal-fired Colbert Steam Plant, Alabama, and by studying stack gases from the plant in a reaction chamber. Quite good agreement was obtained between the two methods of estimation, with an SO_2 to SO_4^{2-} oxidation rate of $2.2\% \text{ h}^{-1}$ found on the first day of study. On the second day the power station plume merged and mixed with an urban plume and an enhanced oxidation rate of $4.1\% \text{ h}^{-1}$ was seen, presumably because of enhanced free radical chemistry occurring as a result of the presence of reactive hydrocarbons. This study also provided one of the very few estimates of NO_x oxidation rates obtained from plume observations and a first-order rate coefficient for NO_x removal of $27\% \text{ h}^{-1}$ was found.

Cheng et al. (1987) studied the plume from an oil sand extraction plant in Alberta. This contained relatively high aerosol concentrations close to the source, and the aerosol surface was believed to be wet. SO_2 to SO_4^{2-} conversion rates of $0\text{--}2.8\% \text{ h}^{-1}$ in winter, and $0\text{--}6\% \text{ h}^{-1}$ in summer, were found. Heterogeneous processes were believed to be appreciable on the wet aerosol surfaces close to the point of emission.

The heterogeneous oxidation of SO_2 in power station plumes has also been studied in field experiments. Gillani and Wilson (1983) used measurements made under wet conditions from three plumes in Missouri and Tennessee when the power station plumes interacted with clouds and during light rain. Variable oxidation rates were observed, but during light rain the liquid-phase rate was around $8\% \text{ h}^{-1}$. In a modelling study of plume–cloud interactions, Gillani et

al. (1983) estimated a daytime liquid-phase sulphate formation rate of about $(12 \pm 6)\% \text{ h}^{-1}$.

In one of the few European field studies of plume sulphur chemistry, Clark et al. (1984) followed the chemical composition of cloud water in a power station plume over the North Sea in winter. The plume was trapped in a shallow layer filled with stratocumulus cloud, restricting dilution and allowing total depletion of O_3 in the boundary layer. An SO_2 conversion rate of about $1\% \text{ h}^{-1}$ was estimated at 5 h travel time, comparable to an estimated rate of $4.3\% \text{ h}^{-1}$ in background air over the same period.

3.2. Other plume observations

The occurrence and chemistry of sulphur, and to a lesser extent, nitrogen, compounds has been studied in plumes other than those from coal-fired power stations. Oil-fired stations, metal smelters and urban plumes have all been studied, and have yielded some information relevant to understanding plume chemistry. However, since the chemical composition of emissions from these types of plumes will be different to those from coal-fired power stations, so the dominant routes of oxidation and their rates will be different. For example, the concentrations of trace metals will be different, giving rise to different rates of catalysis (Garber et al., 1981). Newman (1981) observed sulphur oxidation rates five times greater in an oil-fired power station plume than in a coal-fired station plume, but this has not been borne out by more recent work.

Forrest et al. (1979a) studied the Anclote oil-fired power station in Florida and measured an SO_2 oxidation rate of $< 0.25\% \text{ h}^{-1}$. Garber et al. (1981) measured a similarly low rate in a variety of meteorological conditions in the Northport, NY, oil-fired plume. However, Eatough et al. (1981) found no significant differences in SO_2 oxidation rate in an oil-fired plume to that from a coal-fired station. Somewhat higher rates ($3.1 \pm 0.8\% \text{ h}^{-1}$) were observed by Eatough (1984) in the plume from a Pacific coast oil-fired power station, with a rate of oxidation of $30 \pm 4\% \text{ h}^{-1}$ when the plume passed through a fog bank. Enger and Hoegstoem (1979) qualitatively describe a similarly enhanced SO_2 oxidation rate under conditions of very high relative humidity in Sweden.

The rate of conversion of SO_2 to sulphate aerosol particles was determined by a comprehensive measurement programme in the plume emitted from an oil sands extraction plant at Fort McMurray in Alberta (Cheng et al., 1987). A single parcel of air was tracked and sampled by an aircraft and conversion rates of $0\text{--}2.8\% \text{ h}^{-1}$ were observed in winter and $0\text{--}6\% \text{ h}^{-1}$ in summer. It was suggested that heterogeneous processes were responsible for the oxidation in winter and close to the point of emission when the aerosol particles in the plume were wet.

Plumes from metal smelters might be expected to contain relatively high concentrations of trace metals and hence have elevated SO₂ oxidation rates due to catalytic effects. However, Roberts and Williams (1979) found an SO₂ conversion rate of only 0.15% h⁻¹ in a smelter plume at Mt Isa, Australia, and Eatough et al. (1981, 1982) found similarly low rates.

Urban plumes differ from point source plumes in having relatively higher NO_x and hydrocarbon concentrations, derived from vehicle exhausts. In general it might be expected that higher oxidation rates of SO₂ and NO_x will be experienced in an urban plume than in a point source plume, due to the more reactive nature of a hydrocarbon-rich plume (Winchester, 1980; Ellestad, 1980). The St Louis, Missouri, plume was extensively studied in the 1970s. Alkezweeny and Powell (1977) found S(IV) conversion rates of 10–14% h⁻¹ in the summertime while Zak (1981) estimated a daytime rate of 8.5 ± 4% h⁻¹ and a nighttime rate of 1.1 ± 0.5% h⁻¹. In a study of the Milwaukee urban plume a rate of 6–8% h⁻¹ was seen on one day and < 1% h⁻¹ on the following day, in similar meteorological and precursor conditions (Miller and Alkezweeny, 1980; Alkezweeny et al., 1982). Recently, the urban plumes of Atlanta (e.g. St. John and Chameides, 2000) and Nashville (e.g. Nunnermacker et al., 2000) and other major conurbations have been extensively studied, but with a clear focus on O₃ formation.

3.3. Plume fringe activity

It is quite clear from the above review of sulphur and nitrogen chemistry and of power station plume studies that the oxidation of SO₂ and NO₂ is likely to be rather slower in a power station plume than in ambient air, since the supply of oxidants will quickly become limiting, at least in clear air where homogeneous photochemically driven gas-phase reactions predominate. Primary emissions of NO will soon eliminate O₃ from the plume, so cutting off the production of OH. However, the situation is likely to be somewhat different at the fringes of the plume where the plume mixes with ambient air. Increased chemical reactivity on the fringes of a power station plume was first observed by Davis and Klauber (1975) who saw an increase in the O₃ concentration at the edges of a power station plume, which they erroneously attributed to photochemical reactions involving SO₂. In fact O₃ formation in the plume fringe is almost certainly due to the photochemical reactions of NO, NO₂ and hydrocarbons, the latter derived largely from the background air, as described by Calvert et al. (1978). Such O₃ enhancements in plume fringes have now been repeatedly observed (e.g. Gillani et al., 1978; Lulis et al., 1978; Miller et al., 1978; Forrest et al., 1979b).

3.4. Model calculations

As well as the experimental studies summarised above, several attempts have been made to estimate sulphur and nitrogen oxidation rates in power station plumes using models of the gas and aerosol phase chemistry believed to be occurring in such plumes. Eltgroth and Hobbs (1979) developed an early model, supported by data, that suggested that homogeneous gas to particle conversion of SO_2 to SO_4^{2-} is greatest at the edges of a plume, due to the mixing in of ambient air. Hov and Isaksen (1981) developed a comprehensive plume model where the chemistry and meteorology of the boundary layer interact with a power station plume, which was given spatial resolution in the cross wind direction. The model predicted the formation of O_3 in the plume fringes, with chemical activity enhanced in the fringes, but becoming more pronounced towards the centreline of the plume with time. SO_2 to SO_4^{2-} oxidation rates varied ($1\text{--}5\% \text{h}^{-1}$), with nitric acid formation proceeding more rapidly. Depletion of NO and NO_2 occurred very rapidly, with about 80% of the NO_x being converted to HNO_3 and NO_3 within three hours.

Seigneur (1982) modelled sulphate aerosol formation in power station plumes, using a gas and aerosol phase chemistry scheme and a particle growth model. Rather slow SO_2 oxidation rates were predicted: $0.5\% \text{h}^{-1}$ by homogeneous processes. Importantly, the rate was found to be sensitive to the background hydrocarbon and NO_x concentrations, as well as to humidity and to the photolysis rate of NO_2 . A similar dependence on the background hydrocarbon and NO_x concentrations was found in the plume chemistry model of Meagher and Luria (1982). SO_2 oxidation rates of $1\text{--}2\% \text{h}^{-1}$ were predicted during the spring and summer, reducing in winter.

Joos and Mendonca (1986) integrated a chemistry model with a comprehensive model of secondary aerosol formation processes, with validation of the output using observational data from a plume study. The sulphate formation rate was found to be: very sensitive to relative humidity (increasing with relative humidity); sensitive to temperature only at high relative humidities, where SO_2 solubility decreases as the temperature increases; very sensitive to solar intensity; and not very sensitive to background O_3 concentration. The formation rate of nitrate aerosol in the plume was found to be: very sensitive to temperature, because the $\text{HNO}_3/\text{NH}_3/\text{NH}_4\text{NO}_3$ equilibrium is temperature dependent; not very sensitive to relative humidity, although model limitations may make this conclusion invalid; very sensitive to solar irradiation; and slightly more sensitive to the background ozone concentration than is the SO_2 oxidation rate. The relative insensitivity of this model to background O_3 is important since it implies that the OH radical concentrations in the plume depend more upon NO_x /reactive hydrocarbon photochemical reactions in the plume than on the amount of O_3 mixed into the plume. In addition, the model showed that the

net contribution of the plume to sulphate aerosol concentrations was always significant, but that the plume contribution to nitrate aerosol was only significant when there was a relatively low background NO_x concentration and a reactive hydrocarbon/ NO_x ratio greater than 10.

Recently, a reactive plume model incorporating transport, chemistry and aerosol dynamics has been used by Karamchandani and Seigneur (1999) to simulate sulphate and nitrate chemistry in power station plumes. They made simulations for winter and summer emissions with travel times of 8 and 10 h, respectively, and with different start times. NO_x and SO_2 emission rates were held constant at 88 and 161 ton d^{-1} respectively. The effects of changes in the chemical composition of the background air were investigated by varying ambient O_3 , hydrocarbon and PAN concentrations, the hydrolysis rate of N_2O_5 and the horizontal and vertical dispersion coefficients.

The model results very largely confirmed the many earlier predictions of plume chemistry: oxidation rates in the plume are lower than in background air; excess nitrate concentrations in the plume were 4–7 times greater than the excess sulphate concentrations (i.e. NO_x removal was 4–7 times greater than SO_2 removal in the same travel time); conversion of NO_x and SO_2 was at a maximum in the daytime in summer and at a minimum during the night and in winter; NO_x conversion proceeded at night in clear air by the hydrolysis of N_2O_5 whereas SO_2 conversion did not; and in the presence of clouds SO_2 is rapidly oxidised during both the day and night. Background O_3 , reactive hydrocarbon and PAN concentrations had significant effects on the SO_2 and NO_x conversion rates.

Duncan et al. (1995) demonstrated the possible use of emission inventories coupled with chemistry and transport modelling as a tool for apportionment of the sources of NO_x and SO_2 measured at particular locations. Since the sulphur content of gasoline differs from that of coal and of heavy fuel oil, plumes from mobile and point sources should be identifiable by their characteristic SO_2 to NO_x ratios. However, since these ratios will vary over time, due to the different oxidation rates of these species in the atmosphere, and will vary with ambient conditions, as one or other of the multitude of possible NO_x and/or SO_2 oxidation routes becomes dominant, this is not a trivial task. In this study, these changes over time were ignored and an average SO_2/NO_x ratio of 0.05 was used for mobile sources and 2.67–4.56 for power station plumes. This was justified on the grounds that the study was confined to a relatively small area with plume travel times of 3–10 h at maximum. They concluded that the four major power stations in the study area accounted for about 15% of the ambient NO_x at the surface measurement sites on average, but that in the short term this value was extremely variable, due to the intermittent nature of plume fumigation.

3.5. Summary of plume chemistry

As can be seen from the foregoing review of SO_2 and NO_x chemistry, the field observations of concentration changes in plumes and the theoretical modelling studies, there is now significant convergence in our understanding and prediction of processes affecting the removal of SO_2 and NO_x and the formation of sulfate and nitrate in power station plumes. This understanding can be summarised as:

- (a) In non-cloudy conditions, SO_2 removal in power station plumes occurs primarily during the daytime by reaction with the OH radical, whereas NO_x removal occurs both during the daytime, by fast reaction with OH, and at nighttime by the $\text{NO}_3/\text{N}_2\text{O}_5$ pathway.
- (b) In non-cloudy conditions, NO_x removal will occur much more rapidly (~ 10 times faster) than SO_2 removal.
- (c) In cloudy conditions, SO_2 will be removed rapidly by reactions in the aqueous phase, but NO_x will not.
- (d) The dry deposition velocity of SO_2 is greater than that of NO_x leading to more rapid removal of SO_2 by this process. Conversely, nitrate aerosol is likely to be removed more rapidly by dry deposition than is sulphate aerosol.
- (e) These differences in removal rates will cause changes in the ratios of S and N concentrations with time of travel from the point of emission. In clear air, as the plume travels downwind, the SO_2/NO_x ratio will increase. Conversely, the ratio of sulphate aerosol to nitrate aerosol concentration will decrease downwind. In cloudy conditions, where aqueous-phase reactions become important and photochemical processes become less important, SO_2 oxidation will proceed faster than NO_x oxidation and hence the SO_2/NO_x ratio may decrease.
- (f) SO_2 and NO_x removal rates will normally be lower in a plume than in background air, due to oxidant limitations, in both the gas and aerosol phases, with plume fringes offering an intermediate oxidation environment.
- (g) Absolute oxidation rates of SO_2 and NO_x will vary with plume and background air composition and ambient conditions. In sunny conditions a maximum SO_2 conversion rate of around $3\% \text{ h}^{-1}$ and a maximum NO_x conversion rate of around $30\% \text{ h}^{-1}$ might be expected. However, lower rates may be expected in a "normal" power station plume as oxidant supply becomes diminished by consumption of O_3 , although the rate of oxidation of NO_x will remain ~ 10 times that of SO_2 in photochemically active conditions.

Unfortunately, however, there do remain significant restrictions in our ability to translate these points into a complete description of SO_2 and NO_x be-

haviour in a power station plume. These arise because of the lack of field data of NO_x oxidation rates inside discrete plumes, a poor understanding of the effects of oxidant limitation on NO_x oxidation and a poor understanding of the rapidity with which oxidant limitation can be reversed once a plume encounters polluted urban air or mixes with background air. Despite these limitations, it is clear that ground level SO_2/NO_x ratios may vary with travel time and ambient conditions. In conditions of simple meteorology and plume dynamics, with clear air and adequate sunlight, the photochemical removal of NO_x will proceed up to 10 times faster than that of SO_2 . At night, SO_2 conversion will be effectively zero in clear air while NO_x conversion proceeds. In cloudy conditions the opposite effect will pertain, as the SO_2 conversion rate will be increased, but the NO_x conversion rate will be reduced. Whether or not the resultant ratio changes are observable in the ground-level concentrations of the plume will depend upon the travel time, the ambient conditions and on the nature and magnitude of other sources of SO_2 and NO_x .

3.6. Source apportionment using ratios of S/N

The discussion above of the atmospheric chemistry of SO_2 and NO_x clearly suggests that when elevated concentrations of these pollutants are observed at ground level as a result of emissions from multiple sources, the unambiguous identification of these sources, from consideration of the ratios of their concentrations, is not straightforward. Indeed, such unambiguous source apportionment is not likely without use of a sophisticated chemical and transport model of the atmosphere and then only under ideal conditions. However, in an idealised dry atmosphere with simple photochemistry occurring and in the absence of other sources of the pollutants, an observable increase in the SO_2/NO_x ratio in a power station plume as it travels downwind may be expected. In fact, such elevated ratios of SO_2/NO_x measured downwind could be taken as evidence that power station emissions were responsible for the elevated concentrations of SO_2 . However, if other sources of pollutants are present then this idealised pattern of changing ratios could be distorted. In particular, vehicular or other sources of NO_x could substantially reduce the SO_2/NO_x ratio below that expected for a power station plume. Thus high SO_2/NO_x ratios ($> \sim 5$) are almost certainly indicative of pollution from major combustion processes, but low SO_2/NO_x ratios ($< \sim 5$) do not unambiguously rule out power stations as being the source of the SO_2 . In wet weather, when liquid phase chemical conversion processes will occur, the situation is much more complex. In both wet and dry conditions it is necessary to correct for background concentrations of the pollutants before consideration of the ratios.

4. Conclusions

Pollution by the products of fossil fuel combustion remains a major environmental issue, with ecological, health and material damage effects well documented. As well as the direct effects of SO₂ and NO_x and their indirect effects on acid deposition and visibility reduction, consideration is now being given to the role of power plant plumes to O₃ formation. Current understanding of the chemistries of SO₂ and NO_x in plumes is sufficiently advanced to allow the broad description and prediction of their behaviour under ideal or near-ideal conditions. However, the effects of oxidant limitation and of more complicated atmospheric conditions cause major problems to the prediction of plume behaviour in the ambient atmosphere. Chemical models of plume behaviour require integration with models of the physical dispersion and transport of the plume if a full description of concentration changes is to be effected. The need for large-scale integrated field experiments for the validation of chemistry-transport models remains.

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