Uptake of Air Pollutants by Paper

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UPTAKE OF AIR POLLUTANTS
BY PAPER

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FoU-projektet för papperskonservering
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Preface

"FoU-projektet för papperskonservering" (R&D project on paper preservation) is a national cooperative project conducted by major Swedish institutions responsible for the preservation of archive materials and books.

It is generally known that the storage conditions – temperature, humidity and air pollutants – affect the degradation of paper. With regard to pollutants, the effects of sulphur dioxide are fairly well established. The effects of other common pollutants, such as nitrogen dioxide and ozone and especially their combined effects, are much less known.

In previous studies within the Swedish project on paper preservation, effects of nitrogen dioxide on non-deacidified papers, and of sulphur dioxide and nitrogen dioxide on deacidified papers have been investigated (Reports No. 5 and 6).

In the present study, investigations of the deposition of air pollutants on non-deacidified papers and the synergistic effects on the deposition of pollutants are reported. The investigations have been performed by Anna Johansson and Oliver Lindqvist at the Department of Inorganic Chemistry, Göteborg University, and by Petter Kolseth at STFI (Swedish Pulp and Paper Research Institute). J. Anthony Bristow has contributed with valuable comments and the linguistic revision of the text.

Investigations of the deposition of air pollutants and their effects on mass deacidified papers have been carried out by the two above-mentioned institutions within the framework of the STEP project The Effects of Air Pollutants on the Accelerated Ageing of Cellulose Containing Materials, in which the Swedish project on paper preservation has been involved.

Uppsala, June 1998

Ingmar Fröjd
Project Coordinator
Contents

ABSTRACT......................................................................................................................... 1

1 INTRODUCTION............................................................................................................. 2

2 EXPERIMENTAL.......................................................................................................... 4

2.1 Deposition test equipment .................................................................................. 4

2.2 Paper samples used in the study ....................................................................... 6

2.3 Test piece preparation ......................................................................................... 9

2.4 Evaluation of data .............................................................................................. 9

3 RESULTS .................................................................................................................. 10

3.1 Deposition of sulfur dioxide ............................................................................. 10

3.1.1 Influence of relative humidity ..................................................................... 10

3.1.2 Influence of sulfur dioxide concentration ................................................. 12

3.1.3 The effect of the presence of nitrogen dioxide ........................................... 13

3.1.4 The effect of the presence of ozone ............................................................ 16

3.2 Deposition of nitrogen dioxide on paper ............................................................ 17

3.3 Consumption of ozone on paper ...................................................................... 18

4 DISCUSSION ......................................................................................................... 19

4.1 The influence of relative humidity on the deposition of sulfur dioxide ........... 20

4.2 The influence of concentration on the deposition of sulfur dioxide ................. 21

4.3 The effect of nitrogen dioxide on the deposition of sulfur dioxide ................. 22

4.4 The effect of ozone on the deposition of sulfur dioxide .................................... 24

4.5 The consumption of alkali reserve due to the uptake of sulfur dioxide ........... 24

5 CONCLUSIONS .................................................................................................. 25

REFERENCES ....................................................................................................... 26
ABSTRACT

The objectives of the study have been to investigate the uptake of air pollutants (SO₂, NO₂ and O₃), especially synergistic effects when these pollutants are present together, and effects of climate.

The initial dry deposition of the pollutants onto a paper surface was studied using on-line gas analysis. The paper samples were exposed to synthetic atmospheres with careful control of pollutant concentrations, relative humidity and flow conditions. The concentration levels used corresponded to those found under ambient conditions in a moderately to heavily polluted environment.

The depositions of NO₂ and O₃ were judged to be insignificant in the present study. The investigated papers showed a low tendency to pick up SO₂ alone. The deposition of SO₂ was however enhanced by the presence of the other pollutants, and also by a high relative humidity. The addition of NO₂ increased the pick-up of SO₂ at high relative humidities, while the addition of O₃ increased the pick-up of SO₂ also at intermediate humidities.

The presence of CaCO₃ favoured a high pick-up of SO₂ on the alkaline papers. However, it was found that the alkaline papers responded differently to SO₂. This may indicate that the alkali reserve under adverse conditions is either too rapidly consumed or passivated, probably due to the paper manufacturing process and the origin of the filler.
INTRODUCTION

There is little doubt today that the presence of acidic species in paper is the main cause of paper deterioration. An increase in the acidity in a paper accelerates the hydrolysis of cellulose by a cleavage of the glycosidic linkages between the glucose subunits of cellulose. The paper then loses strength and turns brittle.

Acidity may originate from several sources. One of the most important is papermaker’s alum, Al₂(SO₄)₃·18 H₂O, that was introduced into the manufacture of paper in the early 19th century and is still being used by some papermakers. Factors such as humidity, temperature, light etc. contribute to the degradation processes and may increase the overall acidity in paper (Fellers et al. 1989). Results also indicate that the rate of pick-up of acidic pollutants such as SO₂ in paper is enhanced by humidity.

The effects of environmental pollution on the ageing stability of archival materials have been addressed in several investigations (Kimberly 1932; Langwell 1953; Langwell 1955; Langwell 1956; Lyth Hudson 1967; Lyth Hudson et al. 1964; Lyth Hudson, Milner 1961a; Lyth Hudson, Milner 1961b). The studies have been focused mainly on the interaction between paper and sulfur dioxide since this pollutant has been predominant from a historical point of view due to the combustion of sulfur-containing fossil fuels. The impact of nitrogen oxides and ozone on the degradation processes has attracted less interest in the field of paper conservation.

It is suggested that SO₂ adsorbed in papers is held in two ways, either reversibly or irreversibly. SO₂(g) is physically adsorbed on the paper surface, is dissolved in available moisture in the paper structure and is eventually converted into sulfite S(IV):

\[
\text{SO}_2(g) + H_2O \leftrightarrow \text{SO}_3^{2-}(\text{ads}) + 2\text{H}^+(\text{ads})
\]

The sulfite is reversibly bound to the surface and can readily be desorbed as gaseous SO₂. However, four-valent sulfur is not thermodynamically stable but is known to oxidize to form sulfate S(VI):

\[
\text{SO}_3^{2-}(\text{ads}) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{SO}_4^{2-}(\text{ads})
\]

This transformation into sulfate is irreversible, and SO₂ cannot then be desorbed from the paper. Damage to the paper is probably related to this chemical change. Studies on several materials exposed to SO₂ have demonstrated the role of NOₓ and ozone as catalysts and/or oxidants for the oxidation of S(IV) to S(VI) (Johansson et al. 1988; Mangio, Johansson 1989; Svensson, Johansson 1993) and it may be expected that similar processes are important in paper degradation.

Typical concentrations of SO₂, NO₂ and O₃ in polluted urban air are given in Table 1. NOₓ is produced from reactions between N₂ and O₂ in air during high temperature combustion processes. Automotive exhaust is one of the main sources. The only man-made source of O₃ is in reactions involving NO/NO₂.
European NO\textsubscript{x} emission has increased from rather low values one hundred years ago to the present value. Since 1940 the atmospheric emission of NO\textsubscript{x} has increased markedly relative to that of SO\textsubscript{2}, and this stresses the increasing importance of NO\textsubscript{x} emission. There is often a similarity between indoor and outdoor variations for the pollutants even though the concentrations of the pollutants are considerably lower indoors. Both NO\textsubscript{2} and O\textsubscript{3} often occur at higher concentrations than SO\textsubscript{2} (Hisham Mohamed, Grosjean 1991; Lanting 1990).

Table 1  Typical peak concentrations of SO\textsubscript{2}, NO\textsubscript{2} and O\textsubscript{3} in the troposphere over the continents (Finlayson-Pitts, Pitts 1986).

<table>
<thead>
<tr>
<th>Type of area</th>
<th>Concentration of pollutant, ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SO\textsubscript{2}</td>
</tr>
<tr>
<td>Rural</td>
<td>1–20</td>
</tr>
<tr>
<td>Moderately polluted</td>
<td>20–200</td>
</tr>
<tr>
<td>Heavily polluted</td>
<td>200–500</td>
</tr>
</tbody>
</table>

As already mentioned, SO\textsubscript{2} is by far the most studied air pollutant with regard to the exposure of paper. It was early shown that the edges of books contained more sulfuric acid than the middle areas of the pages (Jarrell et al. 1936; Jarrell et al. 1938; Langwell 1956). Old books from the 17th and 18th centuries stored in a highly polluted area were more acid than books of the same edition stored in a rural environment (Lyth Hudson 1967). It is probable that the higher acidity in these books is an effect of air pollution.

A number of investigations have been carried out in which the uptake of SO\textsubscript{2} by paper has been measured. Lyth Hudson and Milner (1961b) investigated the sulfur uptake on different types of pulp fibres during exposure to 0.5% SO\textsubscript{2} for different times. In general, pulps with low contents of lignin and hemicellulose have a lower uptake of sulfur. Edwards et al. (1968) found that the relative humidity affects the initial uptake of SO\textsubscript{2} (<48 hours). Initially, a higher relative humidity leads to a greater SO\textsubscript{2} uptake, but after 48 hours the SO\textsubscript{2} uptake is independent of the moisture content. The rate of pick-up of SO\textsubscript{2} is apparently proportional to the square root of the partial pressure of the gas. Atherton et al. (1973) concluded that transition metal ions may catalyse the oxidation of sulfur dioxide, thereby increasing its uptake rate.

Recent studies have focused on the influence of NO\textsubscript{2}, alone or in combination with SO\textsubscript{2}. Daniel et al. (1990) and Palm (1991) studied the ageing of deacidified paper exposed to SO\textsubscript{2} + NO\textsubscript{2}. They showed that it is difficult to draw conclusions regarding ageing due to air pollution using data related to mechanical properties of paper. Iversen and Kolar (1991) measured the mechanical and optical properties of different types of paper after exposure to NO\textsubscript{2}. They found that acid-sized chemical pulp paper deteriorated quickly but that neutral-sized
rag and chemical pulp papers containing CaCO₃ showed no loss of mechanical strength.

Most studies of the effects of air pollutants on paper have used concentrations of the pollutants ranging from 10 ppm to 0.5%, i.e. considerably higher concentrations than those found even in a heavily polluted urban atmosphere. The degradation of paper due to hydrolysis of cellulose is a slow and temperature-dependent process. It is not therefore easy to detect any changes in mechanical properties as a result of exposure to air pollution at sub-ppm levels.

Although investigations in high concentrations of pollutants yield rapid results, there may be additional effects which lead to ambiguities in interpretation. One problem noted by Williams II and Grosjean (1992) is that in air at ambient humidity and with a high SO₂ concentration, sulfuric acid aerosol may be formed and the damage observed in paper may be due to the uptake of H₂SO₄ rather than SO₂. They investigated the nature and yields of the reaction products from the exposure of untreated and deacidified paper to ambient levels of SO₂ and NO₂. The study of reaction products is clearly an important way of gaining information about potentially aggressive atmospheric pollutants but there is little to be learned from such studies about the parameters which govern the deterioration processes.

We have chosen in our study to investigate the first stage in paper deterioration, i.e. the initial dry deposition of pollutants onto a paper surface. Dry deposition includes the deposition of the pollutant in a gaseous form as well as in a particle form. This is probably the dominating route for the deposition of pollutants in an indoor environment. The rate of deposition depends on several factors, including the composition of the paper, and environmental parameters such as relative humidity, the mixture of pollutants, temperature etc.

We have investigated the dependence on humidity and SO₂-concentration, and the influence of NO₂ and O₃ on the SO₂ deposition on different paper grades. The rates of deposition of NO₂ and O₃ on the papers were also studied. The concentration levels used were those of ambient conditions in a moderately to heavily polluted environment. The depositions of NO₂ and O₃ were judged to be insignificant in the present study. The deposition of SO₂ was however enhanced by the presence of these pollutants, and also by a high relative humidity. The total uptake of air pollutants in the paper samples was so low that no deterioration in paper properties such as strength could be detected.

2 EXPERIMENTAL

2.1 Deposition test equipment

The experiments were carried out using time-resolved analysis of the deposition (TRAD) of SO₂, NO₂ and O₃. Figure 1 shows the experimental set-up. The equipment was designed specially for deposition studies. The main advantages of the equipment were the high accuracy in the control and regulation of
temperature, gas flow, relative humidity and concentrations of gaseous pollutants such as SO₂ and NO₂. The apparatus was made entirely of glass and Teflon (Eriksson, Johansson 1991).

**Figure 1** Experimental set-up.

The system was immersed in a thermostated water tank. The polluted atmosphere was created by allowing purified and dried air to enter through two different channels. One part was saturated with water vapour at the exposure temperature (22°C). The temperature in the laboratory was kept above the temperature in the water tank in order to avoid water condensation after the humidifier. The other part was used as a carrier for the pollutants. SO₂ and NO₂ were added from permeation tubes which contained the pollutants in liquid form. The concentration of the gaseous pollutants was controlled to within 2 ppb. O₃ was produced by allowing dry air to flow past an adjustable ozone generator that uses UV radiation to form atomic oxygen from molecular oxygen which then reacts with undissociated oxygen molecules to form O₃. The O₃ concentration was held to within ±5% of the desired concentration. The relative humidity was adjusted within an accuracy of ±0,3% by mixing measured amounts of dry and humidified air.

The gas flows were then mixed and thermostated and the resulting gas was passed through the exposure chamber. The tubular exposure cell had an inner diameter of 48 mm. The gas flow through the cell was 1,00 dm³/min, resulting in a laminar flow speed of 0,9 cm/s in the cell (Re = 12). The paper test piece
was suspended by a nylon string in the middle of the chamber so that the direction of flow was parallel to the test piece.

The gas emanating from the exposure chamber was analysed continuously. SO₂ was determined using a fluorescence instrument (Environment AF21M) which had a sensitivity of 0.001 ppm and a time constant of one minute. NO₂ was determined with a chemiluminescence instrument (Environment AC230 M) which had a sensitivity of 0.002 ppm and a time constant of one minute. O₃ was monitored with a UV photometric O₃ analyser (Dasibi 1108) with a detection limit of 1 ppb. Instrument calibrations involved the use of permeation tubes for SO₂ and NO₂.

The concentrations of SO₂ and NO₂ were calculated from the weight loss of the permeation tube and from the flow rate. The deposition of air pollutants was calculated from the difference in concentration between inlet and outlet. In the case of ozone, the gas may decompose at the sample surface. Since this reaction cannot be distinguished from a true uptake in the sample, the consumption of ozone is reported rather than the deposition or uptake.

Before the start of the experiment, the interaction of the pollutants with the chamber walls had reached a steady state, and the effect of the absorption of pollutants by the apparatus could therefore be disregarded.

2.2 Paper samples used in the study

Five commercially available papers, four copy papers and one archive paper, were chosen to represent different paper grades (Table 2). Paper is a material with a rather high porosity and a high specific surface, and the surface that may be exposed to air pollutants is therefore much larger than the macroscopic sheet surface (Table 3). The table also gives the content of metal ions that may already have been present in the native fibres, introduced with different papermaking additives, or could emanate from the pulping and papermaking process equipment. These metal ions may play a significant role in the uptake of air pollutants. The equilibrium moisture content in the papers at different RH levels is given in the final part of the table.

The open structure of paper is illustrated in the photomicrographs showing cross sections of two of the investigated paper samples.
Table 2  Characteristics of the paper samples.

<table>
<thead>
<tr>
<th>Code</th>
<th>Grade</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>A acid wood-free</td>
<td>Acid lignin-free copy paper</td>
<td>Bleached kraft pulp (SW 40%, HW 60%), 18% kaolin, rosin sized</td>
</tr>
<tr>
<td>B alkaline wood-free</td>
<td>Alkaline lignin-free copy paper</td>
<td>Bleached sulfite pulp (SW 60%, HW 40%), 18–20% CaCO₃ (chalk), neutral sized</td>
</tr>
<tr>
<td>C acid groundwood</td>
<td>Acid lignin-containing copy paper</td>
<td>Groundwood pulp (SW 35%), bleached chemical pulp (SW 30%, HW 35%), rosin sized</td>
</tr>
<tr>
<td>D alkaline CTMP</td>
<td>Alkaline lignin-containing copy paper</td>
<td>Groundwood pulp (SW 52%), bleached CTMP (aspen 26%), bleached chemical pulp (SW 20%, HW 2%), 2–3% CaCO₃, neutral sized</td>
</tr>
<tr>
<td>E alkaline cotton</td>
<td>Archive paper</td>
<td>Bleached cotton (linters and combers), 2–3% CaCO₃, 0.5–1% TiO₂, neutral sized</td>
</tr>
</tbody>
</table>

SW = softwood, HW = hardwood, CTMP = chemi-thermomechanical pulp

Table 3a  Grammage, porosity, specific surface and metal ion content of the paper samples.

<table>
<thead>
<tr>
<th>Code</th>
<th>Grammage, g/m²</th>
<th>Spec surface (BET), m²/g</th>
<th>Metal ions (AAS), μg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>A acid wood-free</td>
<td>80</td>
<td>1.37</td>
<td>0.7 55.1 1.2</td>
</tr>
<tr>
<td>B alkaline wood-free</td>
<td>80</td>
<td>0.95</td>
<td>3.9 91.4 26.5</td>
</tr>
<tr>
<td>C acid groundwood</td>
<td>75</td>
<td>nd</td>
<td>nd nd nd</td>
</tr>
<tr>
<td>D alkaline CTMP</td>
<td>75</td>
<td>1.53</td>
<td>4.6 209 6.0</td>
</tr>
<tr>
<td>E alkaline cotton</td>
<td>80</td>
<td>0.90</td>
<td>1.4 13.8 4.0</td>
</tr>
</tbody>
</table>

nd = not determined

Table 3b  Pore volume, porosity, characteristic pore radius and specific surface of the paper samples determined by mercury porosimetry.

<table>
<thead>
<tr>
<th>Code</th>
<th>Pore vol, cm³/g</th>
<th>Porosity, %</th>
<th>Char radius, R₀,50v, μm</th>
<th>Spec surface*, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>A acid wood-free</td>
<td>0.395</td>
<td>34</td>
<td>1.63</td>
<td>0.95</td>
</tr>
<tr>
<td>B alkaline wood-free</td>
<td>0.416</td>
<td>34</td>
<td>1.72</td>
<td>0.86</td>
</tr>
<tr>
<td>D alkaline CTMP</td>
<td>0.702</td>
<td>44</td>
<td>2.51</td>
<td>1.35</td>
</tr>
<tr>
<td>D alkaline cotton</td>
<td>0.419</td>
<td>32</td>
<td>1.57</td>
<td>0.87</td>
</tr>
</tbody>
</table>

*(R ≥ 0.1 μm)*
Table 3c  Equilibrium moisture content of the paper samples at different relative humidities.

<table>
<thead>
<tr>
<th>Code</th>
<th>Equilibrium moisture content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15% RH</td>
</tr>
<tr>
<td>A acid wood-free</td>
<td>3.0%</td>
</tr>
<tr>
<td>B alkaline wood-free</td>
<td>3.0%</td>
</tr>
<tr>
<td>C acid groundwood</td>
<td>3.8%</td>
</tr>
<tr>
<td>D alkaline CTMP</td>
<td>3.3%</td>
</tr>
<tr>
<td>E alkaline cotton</td>
<td>2.9%</td>
</tr>
</tbody>
</table>

Photo 1  Cross section of the acid lignin-free copy paper.

Photo 2  Cross section of the alkaline lignin-containing copy paper.
2.3 Test piece preparation

All the investigated papers were of A4 size. The paper test pieces for exposure were taken from the centres of the sheets and cut into strips, 3x10 cm. The geometrical exposure area of the test piece was 60 cm$^2$ as both sides of the paper were exposed to the gas. The weight of the test piece was 0.24 g which implies that the entire exposed area was approximately 2400 cm$^2$. The test pieces were preconditioned in desiccators containing saturated salt solutions giving the desired humidity for at least five hours prior to exposure. Only one test piece was exposed at one time and the uptake of the gases was recorded continuously. One exposure lasted until a steady state was reached or for at least 20 hours.

2.4 Evaluation of data

Figure 2 schematically shows a deposition curve. The deposition rate is defined as the amount of the gaseous pollutant deposited on the test piece surface per unit time per unit mass of exposed sample, and is calculated from the difference between the input and output concentrations of the pollutants. The deposition rate can also be presented as the amount of gas deposited per unit time per unit area.

Figure 2  A deposition curve for a paper test piece showing deposition rate as a function of time.

The deposition rate in all the graphs is given with respect to unit mass of paper. In all the experiments, the resolution of the SO$_2$ concentration measurement was 1 ppb, which in relation to the flow rate and sample weight corresponds to a SO$_2$ deposition rate of 0.18 ng·s$^{-1}$·g$^{-1}$. Calculated with respect to sample area, this is 0.72 pg·s$^{-1}$·cm$^{-2}$. The deposition rate must be considered in relation to the deposition velocity to an ideal absorbing surface. The deposition velocity, $v_d$, is defined as the deposition per unit area per unit time (Garland 1978), i.e. the flux $F$ divided by the concentration $c$ of the gas:

$$v_d = \frac{F}{c}$$

where

- $F$ = the flux of the gaseous pollutant to the surface per unit time
- $c$ = average concentration of the pollutant in the air
The concentration of the pollutant is taken as the mean of the input and output concentrations in the cell. The deposition velocity in all experiments was calculated when the deposition rate had reached an apparently steady state.

The flux to the surface may be described as being retarded by an aerodynamic resistance and by a surface resistance. The aerodynamic resistance may be estimated by measuring the deposition velocity to a surface with no surface resistance – an ideal absorber. This mass-transfer-limited deposition rate of SO\textsubscript{2} to the test piece surface, was found to be 3.8 mm/s at 85% RH and 107 ppb SO\textsubscript{2}. The ideal absorber was prepared by soaking a paper test piece in 0.1 M NaOH, and then drying it between filter papers before exposure.

3 RESULTS

3.1 Deposition of sulfur dioxide

The influence of different parameters on the SO\textsubscript{2} deposition rate was investigated and the results are here presented in the following order:

- Influence of humidity: 15, 50 and 85% RH.
- Concentration dependence of SO\textsubscript{2} at 50% RH.
- Influence of NO\textsubscript{2} at 50% and 85% RH.
- Influence of O\textsubscript{3} at 50% and 85% RH.

The deposition velocity at a steady state deposition rate was calculated when the decrease in the deposition rate was less than 1 ppb in 5 hours. For most runs, a steady state was reached after approximately 20 hours of exposure.

3.1.1 Influence of relative humidity

Table 4 shows the calculated deposition velocities on papers exposed to 107 ppb SO\textsubscript{2} at different relative humidities. At 15% relative humidity, the SO\textsubscript{2} deposition rate was low on all papers (Figure 3). The initial deposition rate was almost the same regardless of paper type. Alkaline CTMP (D) was the only paper which still had a measurable deposition rate of SO\textsubscript{2} when the exposure was interrupted after 20 hours.

<table>
<thead>
<tr>
<th>Code</th>
<th>Deposition velocity (v_d), mm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15% RH</td>
</tr>
<tr>
<td>A acid wood-free</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>B alkaline wood-free</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>C acid groundwood</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>D alkaline CTMP</td>
<td>0.07</td>
</tr>
<tr>
<td>E alkaline cotton</td>
<td>&lt;0.03</td>
</tr>
</tbody>
</table>

* after 25 h
Figure 3  The SO₂ deposition rate on papers exposed to 107 ppb SO₂ at 15% RH.

At 50% RH, the initial SO₂ deposition rate was higher than at 15% RH on all papers (Figure 4). Differences in SO₂ uptake on the papers due to paper quality was noted primarily during the initial stage of exposure. The decrease in deposition rate with time was lower on alkaline CTMP (D) and the deposition rate at steady state on this paper was almost five times higher than the rate at 15% RH.

Figure 4  The SO₂ deposition rate on papers exposed to 107 ppb SO₂ at 50% RH.

At 85% RH, the uptake of SO₂ was substantially higher on all papers (Figure 5). Just as at lower humidities, alkaline CTMP (D) differed from the other paper grades. Instead of a fast rate decline during the first 10 hours of
exposure, which was the case for the rest of the paper grades, a steady-state was reached from the start of the exposure on this paper.

![Graph showing SO2 deposition rate on papers exposed to 107 ppb SO2 at 85% RH.](image)

**Figure 5** The SO2 deposition rate on papers exposed to 107 ppb SO2 at 85% RH.

### 3.1.2 Influence of sulfur dioxide concentration

The concentration dependence of the deposition rate of SO2 was investigated at four different concentrations of SO2: 69, 107, 289 and 465 ppb at 50% RH. Table 5 shows the calculated deposition velocities on *acid wood-free* (A) and *alkaline cotton* (E) exposed to different concentrations of SO2.

**Table 5** The deposition velocity of SO2 at different gas concentrations at 50% RH.

<table>
<thead>
<tr>
<th>Code</th>
<th>Deposition velocity $v_d$, mm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>69 ppb</td>
</tr>
<tr>
<td>A acid wood-free</td>
<td>&lt;0,03</td>
</tr>
<tr>
<td>E alkaline cotton</td>
<td>0,23</td>
</tr>
</tbody>
</table>

The deposition rate during the first minutes of exposure onto *acid wood-free* (A) was proportional to the SO2 concentration, but the rate dropped rapidly (Figure 6). After 5 hours of exposure, no significant deposition rate could be measured at any concentration of SO2.
Figure 6  The SO$_2$ deposition rate on acid lignin-free copy paper exposed to different concentrations of SO$_2$ at 50% RH.

Figure 7 shows that the initial deposition rate of SO$_2$ on alkaline cotton (E) had the same concentration dependence as that on acid wood-free (A). The rate decline was faster at higher concentrations of SO$_2$. The steady-state deposition rates were at the same level regardless of the SO$_2$ concentration.

Figure 7  The SO$_2$ deposition rate on archive paper exposed to different concentrations of SO$_2$ at 50% RH.

3.1.3 The effect of the presence of nitrogen dioxide
Table 6 shows the deposition velocities for SO$_2$ in the presence of 350 ppb NO$_2$. The deposition rate curves in Figure 8 are similar to those in Figure 4, i. e. there was no significant influence of NO$_2$ on the SO$_2$ uptake on paper during exposure at 50% RH.
Table 6  The deposition velocity of 107 ppb SO$_2$ in 350 ppb NO$_2$ at different relative humidities.

<table>
<thead>
<tr>
<th>Code</th>
<th>Deposition velocity $v_d$, mm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50% RH</td>
</tr>
<tr>
<td>A acid wood-free</td>
<td>0,03</td>
</tr>
<tr>
<td>B alkaline wood-free</td>
<td>0,06</td>
</tr>
<tr>
<td>D alkaline CTMP</td>
<td>0,27</td>
</tr>
<tr>
<td>E alkaline cotton</td>
<td>0,13</td>
</tr>
</tbody>
</table>

* after 25 h

![Graph showing SO$_2$ deposition rate over time](image)

Figure 8  The SO$_2$ deposition rate on papers exposed to 107 ppb SO$_2$ and 350 ppb NO$_2$ at 50% RH.

At 85% RH, the presence of NO$_2$ increased the rate of deposition of the SO$_2$ at steady state for all papers with the exception of the alkaline CTMP (D) (Figure 9). The effect of NO$_2$ was most pronounced on alkaline wood-free (B). The decrease in the deposition rate with time on alkaline cotton (E) was much slower than during exposure to SO$_2$ alone; after 20 hours, the deposition rate was almost three times higher. The exposure was continued for five more hours and the rate of deposition of SO$_2$ did not change during this time, but remained at approximately 2.5 ng.s$^{-1}$.g$^{-1}$. A significantly higher SO$_2$ uptake on acid wood-free (A) was noted in the presence of NO$_2$. The initial rate decline was slower than in the corresponding run with SO$_2$ alone.
Since the synergism between SO$_2$ and NO$_2$ was so pronounced on *alkaline wood-free* (B) at 85% RH, additional runs at 70% RH were carried out at an SO$_2$ concentration of 107 ppb. Figure 10 shows that an increase in humidity from 50 to 70% RH primarily enhanced the initial SO$_2$ uptake. Results of corresponding runs with the addition of 350 ppb NO$_2$ are shown in Figure 11. The strong synergetic effect of NO$_2$ at 85% RH was not found at 70% RH.

**Figure 9** The SO$_2$ deposition rate on papers exposed to 107 ppb SO$_2$ and 350 ppb NO$_2$ at 85% RH.

**Figure 10** The SO$_2$ deposition rate on alkaline lignin-free copy paper exposed to 107 ppb SO$_2$ at different relative humidities.
Figure 11  The SO$_2$ deposition rate on alkaline lignin-free copy paper exposed to 107 ppb SO$_2$ and 350 ppb NO$_2$ at different relative humidities.

3.1.4 The effect of the presence of ozone
Table 7 shows the deposition velocities in the presence of ozone at 50% and 85% RH. The SO$_2$ concentration was 107 ppb and the O$_3$ concentration was 230 ppb.

Table 7  The deposition velocity of 107 ppb SO$_2$ in 230 ppb O$_3$ at different relative humidities.

<table>
<thead>
<tr>
<th>Code</th>
<th>Deposition velocity $v_d$, mm/s</th>
<th>50% RH</th>
<th>85% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>A acid wood-free</td>
<td>0.09</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>B alkaline wood-free</td>
<td>0.13</td>
<td>0.68*</td>
<td></td>
</tr>
<tr>
<td>D alkaline CTMP</td>
<td>0.70</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>E alkaline cotton</td>
<td>0.18</td>
<td>0.38*</td>
<td></td>
</tr>
</tbody>
</table>

* after 25 h

Ozone accelerated the rate of deposition of SO$_2$ on all paper grades at 50% RH (Figure 12). The SO$_2$ uptake at steady state was three times higher in the acid wood-free (A) and twice as high in the alkaline CTMP (D), but was only slightly higher in the alkaline wood-free (B) and alkaline cotton (E).
3.2 Deposition of nitrogen dioxide on paper

Figure 14 shows the NO₂ deposition on different paper grades. The papers were exposed to 350 ppb NO₂ at 85% RH. The NO₂ deposition rate was very low, or non-detectable (below the detection limit of 2 ppb), in all the papers. Acid wood-free (A) picked up a minor amount of NO₂ during the first hours of exposure, but
the deposition rate decreased rapidly and, after three hours' exposure, no further deposition of NO₂ could be detected. Alkaline CTMP (D) differed from the rest of the paper grades in that a low but invariable NO₂ deposition was recorded on this paper during the 20 hours of exposure.

![Figure 14](image)

**Figure 14** The NO₂ deposition rate on papers exposed to 350 ppb NO₂ at 85% RH.

### 3.3 Consumption of ozone on paper

Figure 15 shows the rate of consumption of ozone on different papers exposed to 290 ppb O₃ at 50% RH. Ozone consumption was recorded on all the exposed papers during the first 15 hours, but it decreased rapidly. After 20 hours of exposure, it was below the detection limit of the ozone analyser on alkaline wood-free (B) and alkaline cotton (E) whereas the consumption rate on acid wood-free (A) and alkaline CTMP (D) had reached a steady state level of approx. 2 ng·s⁻¹·g⁻¹.

![Figure 15](image)

**Figure 15** The ozone consumption rate on papers exposed to 290 ppb ozone at 50% RH.
Figure 16 shows the ozone consumption on different papers exposed to 230 ppb O$_3$ at 85% RH. High humidity affected the interaction with *alkaline CTMP (D)* where the ozone consumption was increased three times. The consumption rate at 20 hours on *acid wood-free (A)* seemed to be unaffected by the humidity. A small but significant consumption of O$_3$ was detected on the alkaline papers, *alkaline wood-free (B)* and *alkaline cotton (E)*.

\[ \text{Figure 16} \quad \text{The ozone consumption rate on papers exposed to 230 ppb ozone at 85\% RH.} \]

4 DISCUSSION

The uptake of NO$_2$ seemed to be insignificant in the present study. At higher concentrations, chemical reactions may of course occur between NO$_2$ and paper compounds (Iversen, Kolar 1991), but this was judged to be of minor importance at the concentrations studied in this work. The experimental results indicated that O$_3$ may react with paper at sub-ppm levels, but at the present time we cannot judge whether this should be attributed to decomposition of O$_3$ at the paper surface or to direct chemical reaction with the material. The higher ozone consumption on *alkaline CTMP* could be attributed to reactions with lignin (Eriksson, Gierer 1985; Kratzl et al. 1976), but further experiments are needed if possible reactions between O$_3$ and paper components are to be clarified. This discussion has therefore focused on the uptake of SO$_2$, and the effects of relative humidity, concentration of SO$_2$ and the presence of NO$_2$ and O$_3$ on this uptake.

The intention of this study has not been to establish meticulous relations between the exact composition of the different paper grades and the uptake of air pollutants. Instead, we concentrate the discussion on the overall differences between the selected papers such as pulp composition and inorganic fillers and from that point of view discuss parameters that potentially govern the uptake of gaseous pollutants in paper.
4.1 The influence of relative humidity on the deposition of sulfur dioxide

Humidity primarily influenced the initial SO₂ deposition (<15 hours) on paper. This is in agreement with Edwards et al. (1968). The initially enhanced uptake of SO₂ at higher humidity was probably only an effect of the higher moisture content which resulted in more SO₂ (g) dissolved in a greater amount of adsorbed water. The moisture content at a given RH did not differ greatly between the paper samples (Table 3c) and this could not therefore explain the large differences in deposition rates. When an equilibrium between SO₂ (g) and SO₂ (ads) was achieved, the uptake of SO₂ slowed down markedly for all papers. According to Edwards et al. (1968), the pick-up of SO₂ is independent of the moisture content after 48 hours. This is in keeping with our results provided that the papers did not contain additives whose reactions with SO₂ are governed by the presence of water. The influence of humidity on the SO₂ uptake at a steady state is best illustrated by the two extremes of acid wood-free and alkaline CTMP, the former being almost resistant to SO₂ at any humidity whereas the deposition rate of SO₂ on the alkaline CTMP was highly humidity dependent. Apart from the different pulp compositions of the two papers, alkaline CTMP contained CaCO₃ as filler whereas acid wood-free contained kaolin.

The uptake of SO₂ on alkaline wood-free, alkaline cotton and alkaline CTMP was probably related to the calcite content. The reaction mechanisms of SO₂ and calcite have been thoroughly investigated in numerous studies related to accelerated deterioration of cultural buildings, statues etc. (Amoroso, Fassina 1983; Haneef et al. 1994). Even though the reaction mechanisms for the attack of SO₂ on calcareous stone are far from clarified, it is our belief that similar processes occur in CaCO₃-filled papers.

CaCO₃ reacts with SO₂ and forms gypsum which is the thermodynamically stable end product according to:

\[ \text{SO}_2(\text{ads}) + \text{CaCO}_3 + \frac{1}{2}\text{H}_2\text{O} \leftrightarrow \text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O} + \text{CO}_2(\text{g}) \quad (4) \]

\[ \text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O} \xrightarrow{\text{ox/cat}} \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \quad (5) \]

At room temperature, however, the reaction of SO₂ with CaCO₃ is very slow. The reaction rate increases when the adsorbed water layer on the CaCO₃ particles increases with relative humidity (Elfving 1994; Mangio 1991). Since the intermediate reaction product calcium sulfite, eq. (4), forms a fairly stable layer on the surface of calcium carbonate in a humid SO₂ atmosphere, it hinders SO₂ from reacting with the underlying CaCO₃ with a decreasing reaction rate of SO₂ as a consequence. In the presence of an oxidizer/catalyst, calcium sulfite is readily oxidized to calcium sulfate, eq. (5), which is less dense than the sulfite and allows passage of SO₂ to the underlying CaCO₃.

This may be a possible explanation for the different behaviours of the three alkaline papers which contain calcite as a filler. The high reaction rate of SO₂ on the alkaline CTMP at 85% RH may have been due to the presence of
additives with a catalytic effect. Atherton et al. (1973) noted that the occurrence of metal ions such as Cu(II) and Mn(II) strongly accelerates the uptake of SO₂ in paper. Investigations by Elfving et al. (1994) demonstrated the catalytic sulfation of calcite in the presence of Fe₂O₃ and MnO₂.

A more plausible explanation would be the high mechanical pulp content in combination with the alkaline filler in the alkaline CTMP. It has been shown that SO₂(g) reacts with lignin in a mechanical pulp (Svensson et al. 1994). Any acidic products formed should be neutralised by reaction with calcite which also reacts directly with SO₂ according to eqs. (4) and (5).

An increasing deposition rate with increasing humidity was also recorded on acid groundwood, although it was somewhat lower than on alkaline wood-free and alkaline cotton. As this paper contains approx. 30% mechanical pulp, the higher SO₂ deposition rate compared to that on acid wood-free can probably be assigned to sulfonation of lignin.

Of the papers investigated, only the kaolin-filled acid wood-free showed a low deposition rate of SO₂ at all humidities (vₐ < 0,03 mm/s) after 20 hours. Kaolin has no buffer capacity towards acidic species and provides no protection of the fibres. The pick-up of SO₂ is therefore to a higher degree related to reactions with cellulose than in the calcite-filled papers. The rate-controlling step is probably the conversion of adsorbed S(IV) to S(VI). Efforts have been made to prove the presence of S(IV) species in paper (Williams II, Grosjean 1992). Due to the instability of SO₃²⁻ in aqueous medium, wet chemical analysis methods are unfortunately too vigorous and subsequently only SO₄²⁻ has been isolated. It is however probable that the deposition rate of SO₂(g) is related to the oxidation of S(IV) species adsorbed on the fibre. This process is obviously slow in ambient concentrations of SO₂ at room temperature and is independent of humidity.

Since the calcite in alkaline cotton probably shields the fibres from reacting with SO₂, we cannot comment upon the stability of cotton cellulose towards dry deposition of SO₂. The uptake of SO₂ on pure cotton cellulose was however studied in a parallel investigation (Johansson, Lindqvist 1994). A similar behaviour was then found for cotton cellulose as for acid wood-free, i.e. SO₂ at ambient concentrations did not react at any significant rate with cotton cellulose at any of the humidities studied.

4.2 The influence of concentration on the deposition of sulfur dioxide

The exposures at different concentrations of SO₂ were performed at a moderate humidity i.e. 50% RH. This climate was chosen since the humidity in most archives and libraries is kept close to 50% whereas the SO₂ concentration may vary with season, traffic etc.

Figure 17 shows the momentary deposition of SO₂ on acid wood-free (A) and alkaline cotton (E) at the start of the exposure. The initial adsorption of SO₂ to the fresh paper surface was directly proportional to the concentration of SO₂.
i.e. to the partial pressure of the gas, the surface being rapidly saturated. When all favourable adsorption sites had been covered, the deposition rate dropped to a low and nearly constant value within a few hours (cf. Figures 6 and 7). The steady state rate of SO2 deposition was then apparently independent of the concentration. Acid wood-free (A) showed no significant reaction with SO2 at any concentration whereas the deposition rate on alkaline cotton (E) levelled off at approx. 2 ng·s⁻¹·g⁻¹.

![SO2 deposition rate after 5 minutes on acid lignin-free copy paper and archive paper exposed to different concentrations of SO2 at 50% RH.](image)

Figure 17 The SO2 deposition rate after 5 minutes on acid lignin-free copy paper and archive paper exposed to different concentrations of SO2 at 50% RH.

The deposition rate of SO2 at steady state is probably controlled by the rate of conversion of the adsorbed SO2. Where acid wood-free (A) paper was concerned, the probable step, as proposed earlier, was oxidation of SO2(ads) to SO4²⁻ in the aqueous phase. At low contents of catalysts and oxidants, the reaction between dissolved O2 and S(IV) is negligible and thus "independent" of concentration of SO2 and, as a consequence of the slow removal of S(IV)(ads), the deposition rate of SO2 dropped to nearly zero.

The deposition rate of SO2 on alkaline cotton (E) paper was highly related to the sulfation of calcite. Somewhat surprisingly, we found that the seven-fold increase of concentration had no effect on the uptake of SO2 at a steady state, which implies that the rate-determining step is chemical in nature.

4.3 The effect of nitrogen dioxide on the deposition of sulfur dioxide

The addition of NO2 at 50% RH had no effect on the SO2 deposition on any of the exposed paper grades. The deposition velocities at steady state were unaltered compared to the corresponding runs in an SO2 environment.

On addition of NO2 at 85% RH, the rate of SO2 uptake was significantly enhanced on all papers, except for the alkaline CTMP. Simultaneously with the SO2 measurements, the NO2 concentration was monitored. The NO2 con-
centration was the same irrespective of whether \( \text{SO}_2 \) was present or not, i.e. there was no \( \text{NO}_2 \) consumption that corresponded to the increased deposition of \( \text{SO}_2 \). No detectable \( \text{NO}(g) \) was formed. The results indicated that \( \text{NO}_2 \) took part only as a catalyst. If so, this is in agreement with earlier observations on several materials where the catalytic action of \( \text{NO}_2 \) has been demonstrated (Johansson et al. 1988; Svensson, Johansson 1993).

The most interesting result in high humidity was achieved on acid wood-free. A four-fold increase in the deposition velocity of \( \text{SO}_2 \) in high humidity was noted when \( \text{NO}_2 \) was added. The increase in the \( \text{SO}_2 \) deposition rate was probably due to an increase in the oxidation of adsorbed four-valent sulfur on the surface. The enhancement of oxidation of \( \text{S}(\text{IV}) \) on an "unprotected" paper with no alkali reserve will probably result in an accelerated accumulation of sulfuric acid which then promotes the hydrolysis of cellulose, eqs. (1) and (2).

The strong synergetic effect on the \( \text{SO}_2 \) deposition when the alkaline papers were exposed to \( \text{SO}_2 \) plus \( \text{NO}_2 \) at high humidity may be explained by the high \( \text{CaCO}_3 \) content. The catalytic effect of \( \text{NO}_2 \) on the oxidation of four-valent sulfur adsorbed on a calcite surface has been reported by Johansson et al. (1988). The presence of \( \text{NO}_2 \) promotes the forming of gypsum, \( \text{CaSO}_4 \cdot 2\text{H}_{2}\text{O} \) according to eqs. (4) and (5), and thus allows a greater pick-up rate of \( \text{SO}_2 \) on the paper. As this strongly synergetic effect was not seen below 85% RH, the presence of water seems to be crucial for the \( \text{SO}_2/\text{NO}_2 \) interaction on paper.

The addition of \( \text{NO}_2 \) had no effect on the rate of deposition of \( \text{SO}_2 \) on alkaline \( \text{CTMP} \), indicating that the limiting deposition velocity on this paper was already reached in an environment of \( \text{SO}_2 \) alone \( (v_d = 1.1 \text{ mm/s}) \).

**Alkaline cotton** paper behaved unexpectedly, as the rate of \( \text{SO}_2 \) deposition decreased with time in the presence of \( \text{NO}_2 \) in spite of the excess amount of \( \text{CaCO}_3 \) present. At steady state, the deposition velocity was barely half that for the alkaline wood-free and alkaline \( \text{CTMP} \) papers. The \( \text{CaCO}_3 \) in both alkaline cotton and alkaline wood-free originated from chalk, and for that reason we expected the same behaviour in the \( \text{SO}_2 + \text{NO}_2 \) environment for both papers. Whether or not this lower deposition rate compared with that on the alkaline wood-free is a disadvantage for the ageing stability is a matter of discussion. If it is assumed that all the adsorbed \( \text{SO}_2 \) reacts with \( \text{CaCO}_3 \), the alkaline filler in alkaline cotton will last longer than that in the other two papers and thus prolong its permanence. However, an alternative explanation of the low deposition rate on the alkaline cotton could be that the calcite particles were partially shielded from reacting with \( \text{SO}_2 \), for example through the formation of a film of dry-strength resin over their surface.

Since humidity seemed to play a significant role in the \( \text{SO}_2/\text{NO}_2 \) interaction on paper, the higher rate of oxidation of \( \text{SO}_2 \) due to the presence of \( \text{NO}_2 \) may be avoided by keeping the humidity as low as possible.
4.4 The effect of ozone on the deposition of sulfur dioxide

The uptake of SO₂ by paper was significantly increased by the presence of O₃ (Table 7). Ozone is an efficient oxidizing agent and we believe that it accelerated the deposition rate of SO₂ by oxidation of the four-valent sulfur bound to the paper surface according to:

\[
\text{SO}_2^{\text{ads}} + \text{O}_3(g) + \text{H}_2\text{O(ads)} \rightarrow \text{SO}_4^{2-}(\text{ads}) + \text{O}_2(g) + 2\text{H}^+(\text{ads})
\]  

(6)

The deposition velocity of SO₂ on acid wood-free was three times higher in the presence of O₃ at 50% relative humidity. The effect was even more dramatic at 85% RH as the deposition rate of SO₂ was seven times higher in the presence of 200 ppb O₃.

The consistently high rate of deposition of SO₂ on alkaline CTMP suggests other reactions besides the sulfation of calcite in this paper, e.g. sulfonation of lignin. The higher rate of deposition of SO₂ in 50% RH in the presence of O₃ supported this suggestion of parallel reactions in paper. A deposition rate after 20 hours comparable to that in the alkaline wood-free would be expected if the adsorbed SO₂ had reacted solely with calcite.

The reaction of SO₂ with alkaline wood-free and in some measurements with the alkaline cotton was consistent with what has been demonstrated on sulfation of calcite. The higher SO₂ deposition rate on alkaline wood-free and alkaline cotton may again be assigned to the presence of calcite. The adsorbed four-valent sulfur on the paper was either oxidized directly to its six-valent state or reacted with water and calcite to form gypsum via calcium sulfite, eqs. (4) and (5). The synergetic effect of ozone is favoured by a higher humidity (Mangio 1991).

These results, especially for acid wood-free, clearly demonstrate the negative influence of O₃ on the permanence of so-called unprotected papers such as rosin-sized and containing groundwood. We believe that ozone plays a significant role for the air-pollutant-related deterioration processes of paper. The results indicate the importance of regulation of humidity and control of air pollutants besides SO₂ in the air supply to archives and libraries.

4.5 The consumption of alkali reserve due to the uptake of sulfur dioxide

It was established early that the presence of CaCO₃ favours ageing stability (Jarrell et al. 1936). If a few per cent of CaCO₃ are present, paper is regarded as permanent (ISO 9706:1994). Under controlled conditions, this is probably in agreement with reality. However, one should bear in mind that under severe conditions, the alkalinity of the filler may rapidly be consumed. Figure 18 presents a rough estimate of the durability of the buffer in the alkaline wood-free calculated from the steady-state deposition rate of SO₂ under ambient conditions. This rough estimate describes the relative importance of the relative humidity, the catalytic effect of NO₂ and the oxidizing effect of O₃ on the uptake of SO₂ in an alkaline paper. However, it should be noted that paper sheets are rarely exposed freely but are stacked in boxes or bound volumes.
Figure 18  The estimated durability of CaCO₃ filler in the alkaline lignin-free copy paper in different polluted environments. The concentrations are: SO₂ = 107 ppb, NO₂ = 350 ppb, O₃ = 230 ppb.

5  CONCLUSIONS

The main conclusions from the present study of how air pollutants are deposited on and attack paper materials may be stated as follows:

• Investigated papers showed a good stability towards SO₂ alone.
• The addition of NO₂ increased the pick-up of SO₂ at high relative humidities.
• The addition of O₃ also increased the pick-up of SO₂ at intermediate humidities.
• The acid environment due to conversion of adsorbed SO₂ to SO₃²⁻ or SO₄²⁻ is probably the main cause of degradation of paper by pollution with SO₂.
• The capacity of an alkaline buffer for neutralising acid pollutants in paper probably depends upon the paper manufacturing process and on the origin of the filler.
• The relative humidity in repositories should be kept as low as possible in order to minimise the interaction of air pollutants in paper.
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