Sulfur and nitrogen are emitted to the atmosphere during the combustion of coal and other fossil fuels principally as the gases sulfur dioxide (SO₂) and nitric oxide (NO). In uncontrolled systems, approximately 90% of the sulfur in the fuel is converted to SO₂ and 5% to SO₃. The balance is emitted in flyash or collected in the bottom slag. (1) Coal combustion accounts for about 60% of the man-made sulfur oxide emissions (2,3), which represent 1/3 of the total global sulfur emissions to the atmosphere, viz. 300 x 10⁶ tons SO₂/yr. (3) Nitrogen oxide emissions during fossil fuel combustion result from high temperature reaction of atmospheric nitrogen and oxygen, as well as partial combustion of nitrogenous compounds in the fuel. Important factors that affect NO production include: Flame and furnace temperature, residence time of combustion gases, rate of cooling, and presence of excess air. (1) Coal combustion accounts for 20% of the man-made NO emissions, which represent 1/10 of the 500 x 10⁶ tons/yr produced by natural sources. (4)

The atmospheric transport, conversion, and fate of sulfur dioxide and nitric oxide is quite complex. While qualitative descriptions of some conversion and deposition mechanisms are available, quantitative estimates of the importance of each mechanism remain crude.

Sulfur dioxide emitted into the atmosphere is advected and dispersed by the general air flow and smaller scale turbulence. Direct adsorption may occur on vegetation and soil surfaces (5). SO₂ may also be "washed out" in precipitation (6). However, it is generally believed that most SO₂ is chemically converted to sulfuric acid or a particulate, sulfate before removal from the atmosphere.

In the presence of sunlight, SO₂ may be oxidized in a three body reaction by photochemically produced monatomic oxygen. (7) Rapid hydration would follow to form a sulfuric acid mist. The presence of ammonia may buffer the reaction and increase production of sulfates. (8)

\[
\begin{align*}
SO_2 + O + M & \rightarrow SO_3 + M \\
SO_3 + H_2O & \rightarrow H_2SO_4 \\
H_2SO_4 \cdot nH_2O + NH_3 & \rightarrow NH_4^+ , SO_4^{2-} , nH_2O
\end{align*}
\]

Other investigators (9, 10, 11) have recently proposed SO₂ reaction with either OH or HO₂ as an important homogeneous gas-phase conversion mechanism.

\[
\begin{align*}
HO_2 + SO_2 & \rightarrow SO_3 + OH \\
OH + SO_2 + M & \rightarrow HSO_3 + M
\end{align*}
\]
This mechanism has been purportedly demonstrated in laboratory experiments (11), but remains to be verified under actual field conditions. The development of a remote monitoring instrument for OH (9) should provide more information on its relative significance.

Direct photo-oxidation of SO$_2$ is considered to be negligible. (12)

Heterogenous reactions on solid or liquid surfaces represent a second important class of SO$_2$ oxidation mechanism. The presence of heavy metal ions, such as iron or manganese have been observed to catalyze the conversion of SO$_2$ to acid sulfates. (13) Oxidation rates are highly dependent on temperature and relative humidity.

Catalytic oxidation may also occur on dry surfaces. Novakor, et al. (14) have demonstrated catalytic formation of sulfate on carbon soot in the laboratory and have identified several sulfur compounds on the surface of carbon particulates collected in urban atmospheres.

Sulfur compounds emitted during combustion and converted to sulfates are ultimately removed from the atmosphere by dry deposition and precipitation. Although the removal rates are not well quantified, the atmospheric residence time is estimated to range between one and seven days. (3) Long range transport of sulfates may therefore extend to hundreds of kilometers from the SO$_2$ source. (15, 16, 17,18)

"Ballpark" estimates of net SO$_2$ to sulfate conversion rates for several mechanisms are listed below.
### Table 1

SO$_2$ to SO$_4$ Conversion Rates

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>SO$_2$ Consumption Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct photo-oxidation</td>
<td>0.5 %/hr</td>
</tr>
<tr>
<td>Indirect photo-oxidation</td>
<td>1-3 %/hr</td>
</tr>
<tr>
<td>Air oxidation in liquid droplets</td>
<td>1-20 %/hr</td>
</tr>
<tr>
<td>Catalyzed oxidation in liquid droplets</td>
<td>1-20 %/hr</td>
</tr>
<tr>
<td>Catalyzed oxidation on dry surface</td>
<td>1-13 %/hr</td>
</tr>
</tbody>
</table>

Observed SO$_2$ consumption in a coal-fired power plant plume
- 70% relative humidity
- 100% relative humidity

(Table adapted from 19, 20)
Nitrogen compounds are emitted during fossil fuel combustion principally as NO. Oxidation to NO₂ occurs very rapidly, however. Equilibrium valence of NO and NO₂ are determined by the following reactions:

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]  \hspace{1cm} (6)  
\[ \text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} \]  \hspace{1cm} (7)

The NO/NO+NO₂ ratio is approximately 0.5 during daylight and 0.1 at night. (9)

NO may undergo a series of complex chain reactions (typically 100 times slower than the NO - NO₂ reaction) with olefinic hydrocarbons and hydroxyl radicals to form nitrate compounds. A typical sequence might be:

\[ \text{O}_3 + \text{HC} \rightarrow \text{RO}_2 \]  \hspace{1cm} (8)  
\[ \text{RO}_2 \cdot + \text{NO} \rightarrow \text{NO}_2 + \text{R} \cdot \]  \hspace{1cm} (9)  
\[ \text{R} - \text{CH} \rightarrow \text{R} - \text{C} \cdot + \text{R} - \text{C} - \text{O} - \text{O} \cdot \]  \hspace{1cm} (10)  
\[ \text{NO}_2 \rightarrow \text{R} - \text{C} - \text{O} - \text{O} - \text{NO}_2 \]  \hspace{1cm} (11)

Measurements of nitrate ions in rain (21) suggest that NO₂ is transformed to nitrates in precipitation. However, the direct reaction

\[ \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 \]  \hspace{1cm} (11)

has not been shown to be significant in the atmosphere. (4) Two other mechanisms have been suggested recently (9) for nitrous and nitric acid formation during daylight:

\[ \text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M} \]  \hspace{1cm} (12)  
\[ \text{NO}_2 + \text{HO}_2 \rightarrow \text{HNO}_2 + \text{O}_2 \]  \hspace{1cm} (13)

Both mechanisms remain to be verified by field measurements of hydroxyls.

Heterogeneous surface catalysis of NO and NH₃ on carbon soot has been proposed by Chang and Novakov (22). In laboratory experiments they have generated volatile ammonium salts at ambient temperatures and reduced nitrogen compounds at elevated temperatures, in qualitative agreement with field observation at urban California sites.
Little information is available on the consumption rate of \( \text{NO}_2 \) by the mechanisms described. However, Robinson and Robbins have estimated the residence time of \( \text{NO}_2 \) to be three days, based on the total atmospheric nitrogen cycle. (23)

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