It is evident from the previous chapters that particulate matter and gaseous oxides are prominent pollutants emitted through the stacks of the industrial plants which are considered for the present investigations. Some selected processes usually employed to combat these pollutants are highlighted in this chapter. The available techniques can be classified in two categories, i.e. those applicable to source control methods and used in removing the pollutants from the fuel prior to the combustion. These methods are also referred as 'top of the pipe' techniques others are in which pollutants are controlled after emission from the source. These are called 'end of the pipe' techniques. In the present study we have considered the case of post generation control or end of the pipe technologies. The emphasis is laid on controlling the emission of particulate matter and acidic pollutants (NOx and SOx). The most prevalent technique for the particulate control is the Electro Static Precipitator (ESP) and the advanced techniques for simultaneous removal of acidic pollutants are Electron-Beam Irradiation (EBR) and Pulsed Corona Discharge (PCD). A brief description of these processes is given in the following sections. Further details are reported in the subsequent chapters of the thesis.

### 3.1 Electrostatic Precipitator

An electrostatic precipitator is a particle control device that uses electrical forces to move the particles out of the flowing gas stream onto collector plates. The ESP's action consists of three essential functions:

- the suspended particles are given an electrical charge,
- the charged particles are subjected to electric field to migrate them towards the collecting plates and
- the collected particles are removed to a receptacle with as little loss as possible.
Some salient features and parameters influencing the ESP performance are as follows:

3.1.1. Electric Field

The electric field is provided between a metallic wire (known as discharge electrode) and the plate (collecting electrode) with the help of D.C. voltage source. Fig. 3.1 and Fig. 3.2 gives a schematic diagram of the (a) tubular and (b) parallel plate ESPs and Fig. 3.3 gives overall view. The negative terminal of potential source is connected to the discharge electrode to generate negative corona, while the collecting plate is grounded. The field variation is high enough to ionize the gas surrounding the wire. The potential applied to the discharge electrode may be of the order of 10 kV to 70 kV. The magnitude of the field near the wire varies nearly inversely as the wire diameter. The typical values of discharge electrode wire diameter is of few millimeters (4mm to 12 mm).

The high density field around the wire creates corona discharge. The field strength at which the corona begins is that [1] which accelerates the stray electrons to sufficient energies to cause ionizing collisions in the gaseous species present. Peek [1] has shown semi-empirically that the onset of corona in air occurs at an electric field strength $E$ defined by

$$E_c = 3 \times 10^6 m \left( \delta + 3.0 \sqrt{\frac{\delta}{a}} \right)$$

where

- $a$ is the radius of corona wire
- $m$ is the wire roughness factor,
- $\delta$ is the relative air density = $T/T_0 \cdot P/P_0$
- $p$ is pressure of the air
- $T$ is temperature of the air
- $T_0$ is 298 degree K

values of $m$ in practice range from about 0.5 to 0.9, the corresponding voltage is given by
Fig. 3.1 Schematic diagram of a parallel-plate precipitator

Fig. 3.1 Schematic diagram of a wire and pipe precipitator
Fig. 3.2 Simplified wire-plate schematic diagram of an ESP
Fig. 3.3 Cutaway view of a modern ESP showing various parts (courtesy of the Institute of clean Air companies).
\[ V_c = 3\times10^6 \text{ am} \left( \delta + 3.0 \right) \left( \frac{\delta}{a} \right) \left( \varepsilon_n \frac{b}{a} \right) \]

\( b = \text{cylinder radius}. \)

By using a confound mapping technique Cooperman [2,3] was able to transform the common geometry consisting of a wire positioned midway between parallel plates into a wire parallel to a single plate.

Electric field variation with the wire diameter is shown in Fig. 3.4. Electric field vs, radius of wire

3.1.2. Corona Generation

Gases found in the effluents of industrial processes are neutral molecules mainly the oxides of carbon, nitrogen, hydrogen, sulphur and molecular nitrogen and oxygen. The gas discharge requires a source of initiating electrons and a sufficient number of sustaining electrons to maintain the avalanche process. Initiating electrons are provided by the ionization of a small percentage of the gas molecules by naturally occurring radiation. It has been estimated that approximately 20 ion-electron pairs per cubic centimeter per second are produced by this means, which is a sufficient number to initiate the corona process. The already present positive ion and electron are acted upon by the field. Electrons near the wire will be accelerated to high velocities acquiring sufficient energy to release additional electrons on impact with neutral gas molecules, further creating additional positive ions and free electrons. Each of the additional electrons is accelerated to cause further impact ionization. the process is repeated many times so that large number of electrons and positive ions are generated. It gives an avalanche as shown in Fig. 3.5.

This repeated splitting of gas molecules give rise to a glow around the discharge electrode which look like a Crown (hence the name Corona) [4]. If the discharge electrode (wire) is negative (negative corona), electrons from the corona region move towards the grounded electrode and positive ions move towards the discharge electrode, for reversed polarity (positive Corona), the movement is exchanged.
Fig. 3.4 Relationship between electric field at the Corona wire surface and wire size. 
(Source: ref. [33])
Fig. 3.5 Illustration of the corona generation process.
### 3.1.3. Electric Current

Beyond the Corona glow region the electric field rapidly diminishes so that the electron velocities can no longer cause ionization and the electron would migrate towards the collection surface. If no electro-negative gases were present in the inter electrode space, the electron would migrate towards collecting surface at large velocities and the resultant current would be high and spark over can occur when the voltage is increased beyond the corona on set voltage. But in practice it does not happen so soon because all industrial effluents contain large quantities of electronegative gases such as oxygen, and carbon dioxide. the greater the electronegativity, the greater the probability of capture of electrons. The captive rate also depends on concentration of the gas [5].

Few electrons emitted from the corona process will penetrate a considerable distance into the inter electrode region. This conduction by free electrons leads to an increase in the effective mobility of the gas stream. The current flow would therefore be greater than if all of the electrons were attached at the edge of the corona region, hence the concentration of the ion forming gas can alter the current voltage relationship. At the surface of the corona the current is carried almost by positive ions while it is due solely by negative charges in the quiescent zone away from the wire.

The conditions necessary for the maintenance of a stable negative corona include a copious source of electrons near the discharge electrode and an effective space charge in the passive zone between the electrodes. In the absence of a sufficient limiting space charge, the avalanche process would grow until sparking occur.

The effect of gas pressure and temperature on Corona starting potential has been experimentally determined by shale [6] and it is found that the decreased pressure or increased temperature and field increase the current which results in spark over at reduced voltages. In positive corona the same effect would not occur, since the current carriers are positive ions. Electrons from the avalanche process are attached to the corona wire and donot travel to collecting electrode. Hence positive corona should have more favorable voltage current.
relationship in higher temperature region [7]. The current voltage relationship also depends on the effective mobility of charge carriers which in turn depends on the nature of the gas present.

3.1.4. Sparkover and Back Corona

High electrical resistivity of the collected dust layer can result in either of two conditions that limit the corona current which results in reduced particle charging and second the force with which the dust is held on collecting surface is increased. For high resistivity dusts, sparkover will occur at current densities low enough than of a low or intermediate dust resistivity. For high resistivity dust, electrical break down of the dust layer will occur at very low current densities resulting in back corona or reverse ionization. Sparkover can also occur with clean electrodes due to electrical breakdown of the gases in the inter electrode space. However breakdown of the gases in the dust layer can occur at conditions much lower than those required for breakdown of the gases in the inter-electrode space. Both the wire diameter and spacing alter electric field and hence determine the conditions for spark initiation and propagation [8].

If the dust layer resistivity is low the spark can occur at low voltage due to large current. The accelerating electric field is low which results in low migration velocity and reduced efficiency. While high resistivity can result in large voltage drops and high electric field within the dust layer itself. The field can be large enough for currents normally encountered in precipitator practice. This field exceeds the breakdown strength of the dust (for majority of industrial dusts breakdown occurs in the range from 10 to 20 kv/cm). For high resistivity dust, the voltage drop across and the electric field in the dust layer can be very large even at low current densities, and breakdown can occur at voltages lower than those required to propagate a spark across the interelectrode space. If this occurs, a condition of back corona develops and the voltage current curves of the precipitator depart from normal curves.

The significance of a back corona condition is that the breakdown releases positive ions (for a negative corona precipitator) and these ions are propelled into the interelectrode space. These positive ions impinge on negatively charged particles thus reduce the charging of particles and reduce the efficiency. Several factors can modify sparkover and back corona conditions such
as thickness of dust layer, character of dust layer. Generally current densities of the order of $2 \times 10^{-9}$ amp/cm$^2$ are found for a resistivity in the range of $1-5 \times 10^{11}$ ohm-cm.

At high temperatures, current conduction is primarily governed by composition of dust and relatively independent of the nature of the flue gases. The conduction is called volume conduction. The volume resistivity decreases with temperature. At lower temperatures conduction is termed as surface conduction and depends on gas composition, as well as on dust composition.

3.1.5. Particle charging

The particulate must be charged by the electric field to impart a driving force towards the collection electrode. This force is proportional to the field and charge on the particle.

Particle charging normally takes place in the region between corona and collecting electrode. The particles are charged by the negative ions and electrons in this region in case of negative corona and by positive ions in case of positive corona.

There are two mechanisms responsible for the charging of particles referred as field charging and diffusion charging. Field charging is the dominant mechanism for particles with a radius greater than about $0.5 \mu$m while diffusion charging becomes dominant in case of particles less than $0.2 \mu$m is diameter.

Field charging is due to collisions between the ions and particles suspended in the gas stream due to ordered motion of ions under the influence of electric field, while diffusion charging takes place due to random thermal motion of the particles and ions. If these ions are retained by the dust, the particles become charged. Field charging depends on the electric field, physical dimensions and dielectric constant of the particles [9,10,4]. If the effect of electric field is taken into consideration the charging equations for diffusion charging can't be solved in closed form but must be solved in an iterative fashion. Arendt and Kallman and then White and recently by Liu and Yeh and Smith and McDonald have given the analysis of this mechanism [11,4,12,13]. The most definitive experimental work as charging was that of Hewitt[14] and this
work is generally the basis for comparison with theoretical relationships.

The charge on a particle as function of time is given by the equation [31,32].

\[
q(t) = 12 \frac{k}{k+2} \pi \varepsilon_0 a^2 E_0 \frac{t}{t + \psi} = q_0 \frac{1}{1 + \frac{\psi}{t}}
\]

(3.3)

where \( q(t) \) - field charge at time \( t \)

- \( k \) = dielectric constant of the dust
- \( \varepsilon_0 \) = permittivity of free space
- \( a \) = particle radius
- \( E_0 \) = electric field
- \( \psi = 4\varepsilon_0 N_0 e b \)
- \( e \) = electronic charge
- \( b \) = mobility of ions
- \( N_0 \) = ion concentration

For diffusion charging, the charge \( q(t) \) is given by [33]

\[
q(t) = \frac{akt}{e} \ell_n \left[ 1 + \frac{\pi a VN_0 e^2 t}{kT} \right]
\]

(3.4)

where

- \( T \) = temperature in Kelvin
- \( V \) = potential

It is apparent that no saturation charge exists for diffusion charging process. This is due to the reason that the range of thermal velocities does not have an upper boundary limit, though the limit for diffusion charging may reach when the electric field at the surface of the particle is sufficient to emit an electron by field emission, this situation is never encountered in practice.
For combined charging the charge is given by [33] the relation

$$\frac{dq}{dt} = \frac{q_s}{\psi} (1 - \frac{q}{q_s})^2 + a^2 eN_0 \sqrt{\frac{8kT\pi}{m}} \exp \left(-\frac{qe}{akT}\right) \quad (3.5)$$

This equation is a nonlinear differential equation with no analytic solution. Approximate solutions are obtained by the use of iterative integration methods.

Theoretical treatment of particle charging by both processes is given in the work of Smith and McDonald [13]

3.1.6. Fluid Dynamics

If we consider the motion of dust particle under the influence of various forces such as inertial force, electric forces and viscous force, the motion can be given by the equation of the form

$$\frac{dw}{dt} \frac{6\pi \mu a w}{m} = \frac{qE}{m} \quad (3.6)$$

\(w\) = particle velocity towards the collection electrode
\(a\) = particle radius
\(q\) = charge an particle
\(E\) = electric field
\(m\) = mass of particle
\(\mu\) = viscosity of the gaseous stream

solving for \(w\) gives

$$\omega = \frac{qE}{6\pi \mu a} \left[1 - \exp \left(-\frac{6\pi \mu at}{m}\right)\right] \quad (3.7)$$

The \(m/6\pi \mu a\) denotes the time constant \(\psi\) of the motion. The velocity \(w\) reduces its terminal value within five time constants.
For particle of unit density at atmospheric pressure in air $\psi$ comes out to be $= 1.23 \times 10^7 a^2$, $a$ is in meters.

Residence time for dust in a precipitator typically ranges from 2 to 5 seconds. Thus for particles up to about $50\mu m$ in diameter, the acceleration time is short compared to the residence time in the collector. The larger particles ($50\mu m$ and above) are generally collected entirely and the residence time for smaller particles is long compared to the acceleration time. The approximate value of particle velocity becomes

$$\omega = q E_p / 6\pi \mu a$$

which is the expression for particle migration velocity encountered in all practical practices.

For field charging, the migration velocity becomes

$$w = 12 \frac{k}{k+2} \pi \epsilon_o a^2 E_o \frac{1}{1 + \frac{\psi}{E}} \frac{E_p}{6\pi \mu a}$$

(3.8)

For particles of high dielectric constant $k/k+2 \approx 1$ and $\psi/t$ approaches zero, the steady state migration velocity for field charging becomes

$$w = \frac{2\epsilon_o E_o E_p a}{\mu}$$

$E_o$ = uniform external field
$E_p$ = field near particle

For smaller particles the velocity goes on increasing hence acceleration time more than residence time and their collection remains incomplete.
Optimum performance of precipitators requires well balanced flow distribution through the precipitator zones and a lower level of turbulence. The disturbed flow of gases affects the collection efficiency by changing the migration velocity, residence time, increased sneakage and increased re-enterainment.

3.1.7. Particle Collection

In all practical precipitators the gas flow is turbulent and the motion of a dust particle will be the result of turbulence and migration velocity. Deutsch [15] derived equation for dust collection efficiency theoretically and White [5] derived an identical expression based on the probability of collection for a single particle. Both derivations lead to collection efficiency equation of the form

\[ \eta = 1 - \exp \left( \frac{-A}{V_g} w \right) \]  \hspace{1cm} (3.9)

\( \eta \) = collection efficiency  
\( A \) = collecting surface area  
\( V_g \) = gas flow rate  
\( w \) = particle migration velocity

The equation has been verified experimentally.

The development of above equation assumes several simplifying assumptions as:

i) Particles are immediately charged  
iit)
ii) Gas velocity does not affect migration velocity  
iii) Particle moves with terminal velocity  
iv) Mutual repulsion of particles is neglected  
v) Effect of collisions is neglected  
vi) No disturbing effects such as reunion, reentrainment, uneven gas flow or back corona  
vii) Particles are of single size.
3.1.8. Modification of Deutsch Equation

Many practical considerations modify the original simplified collection efficiency equation such as

Reenterainment: Reenterainment can occur as a result of impact of particle being precipitated onto dust surface. Particles can dislodge the already collected due to inertial force of larger particles. Reentrainment can also occur during rapping.

Sneakage: Some of the dust laden gas can by-pass the electrified region through hoppers and above the field plates.

Charging time: In case of high current density and moderate resistivity the charging time is of the order of milliseconds and this does not affect the collection much. However charging time can be appreciable if current density is kept low to prevent excessive sparking or back corona [16]. In such cases dust can travel considerable distance before acquiring saturation charge.

Particle size and concentration: The field is modified by the space charge. In the inlet region of precipitator space charge is large, current is reduced (due to reduced mobility of dust particles), as particulates are removed, greater part of current is due to ions and electrons so current is larger. Particle size directly influences migration velocity. It is established that the migration velocity reaches a minimum in the region around 0.2 to 0.5μm and increases for particle sizes above and below this range.

Several investigators have attempted to modify the Deutsch equation to take into account the practical situations. Cooperman [17] states that Deutsch equation neglects the role of diffusional forces in the precipitator in addition to the linear diffusion, a difference in particle concentration would result in a back diffusion if the particle concentration at collection surface is larger than that within the central section.
He suggests an equation of the form

$$\eta = 1 - \exp \left\{ -\frac{6}{\alpha} \left( 1 - \frac{1}{2\alpha^2} \right) \frac{L}{6} \right\}$$

(3.10)

$$\delta = (1-f) \frac{b \omega}{2D_1}$$

$$\alpha = \frac{bV}{2D_1}$$

b = half width of the precipitator duct (comparable to radius)

f = ratio of particle transport away from the collecting electrode to the migration velocity

w = electrical migration velocity (theoretical)

$$D_1 = \text{particle diffusion coefficient in direction of gas flow}$$

$$V = \text{man gas transport velocity}$$

After some manipulation

$$\frac{\delta}{\alpha} = (1-f) \frac{w}{v} \quad \text{and} \quad \frac{L}{b} = \frac{L}{b} \cdot \frac{h}{h} = \frac{A_c}{A_d}$$

$$h = \text{height of collection electrode}$$

$$A_c = \text{collection electrode area}$$

$$A_d = \text{cross section of the duct}$$

thus $$\frac{\delta}{\alpha} \cdot \frac{L}{b} = (1-f) \frac{w}{v} \cdot \frac{A_c}{A_d} = (1-f) \frac{W}{V_g} \cdot \frac{A_c}{V_g}$$

$$V_g = \text{volume flow of gas}$$

so

$$\eta = 1 - \exp[-(1-f)(1 - \frac{1}{2\alpha^2}) \frac{A_c w}{V_g}]$$

(3.11)

The factor (1-f) modifies w and (1-1/2\alpha^2) modifies the volume flow rate
Figure 3.7: Variation of dust resistivity with temperature for varying moisture. Source Ref. [33].
Fig. 3.8 Variation of dust resistivity with temperature with varying sulphur source ref. (33)
Fig. 3.9 Relation between specific collection area and collection efficiency at different migration velocity. Source ref. [33]
If reentrainment velocity \((w_r)\) and electrical migrate velocity \(W_e\) is postulated then the factor \(1-f = \frac{w_r}{w_e}\) and

\[
\eta = 1 - \exp \left[ -\frac{w_e - w_r}{w_e} \left(1 - \frac{1}{2\alpha^2} \right) \frac{A}{\nu_g} W_e \right]
\]

\(w_e - w_r = w_n\) (net particle velocity towards collection electrode and finally

\[
\eta = 1 - \exp \left[ -\left(1 - \frac{1}{2\alpha^2} \right) \frac{w_n A}{\nu_g} \right]
\]

\((3.12)\)

3.1.9. Overall Efficiency of ESP

These modifications to the convenient Deutsch equation in part explains the difference between the performance of a precipitator and mathematical predictions. They are in general less desirable than a systems model approach in that they involve corrections applied to empirical equations rather than the development of theoretical relationship in the system model. The important factors influencing the precipitator efficiency are gas flow distribution as optimum performance requires uniform flow distribution and low level of turbulence. The performance depends strongly on physical and chemical properties of gas and particles treated. The composition, temperature and pressure of the gas govern the basic corona characteristics, while particle size, particle concentration and electric resistivity of the ash affect both corona and particle collecting properties. Resistivity depends primarily on ash composition, gas temperature, water vapour and SO₃ in flue gas. Variation of resistivity with temperature with flue gas having different % of moisture and SO₃ and collection efficiency with collection area with different migration velocity are shown in figures (1) Resistivity vs temperature for different %age moisture and SO₃ (ii)Efficiency vs. collection area at different migration velocities. (iii) Efficiency vs particle diameter at different current density. The resistivity change with temperature and moisture are shown in Fig.5.7, 5.8 and 5.9.
3.1.10. Pulsed ESP

With high dust resistivity, say $>10^{10}$ ohm-cm, a voltage drop across the dust layer can result in breakdown within the dust layer, causing collected dust to re-enter into the drift region i.e. back Corona generation takes place. Recently the performance of ESP's has been much improved by the use of high voltage (HV) pulses which are superimposed on a DC bias voltage [18,19]. The HV pulses are used for the ion production while particle charging, particle migration and dust layer formation are assured by the DC bias voltage which can be kept below the ionization threshold. Back Corona is avoided, the average current is very low and energy consumption is reduced. The use of HV pulses offer a flexibility which allows for optimum conditions even in case of variable gas flow and variable dust size. Collection efficiencies over 99% are achieved by using HV pulse widths in the range of 50 ms to 1ms.

3.2 Flue Gas Desulphurization

Many methods are in use for reducing $\text{SO}_2$ effluent from thermal power plants. The methods include the sulphur reduction from the fuel, in which the sulphur content of the coal and oil can be reduced by mineral beneficitation and chemical processing. Limestone injection is one of the methods investigated for possible applications to $\text{SO}_2$ control. Limestone is added to the fuel to react with the sulphur oxides formed in the combustion process. Fluidised bed combustion is accomplished by burning the coal in the bed of limestone that is maintained in a fluid state by the combustion air and gases.

At present, the predominant approach to control $\text{SO}_2$ is directed to scrubbing the flue gas prior to discharge into the stack. Desulphurization can be done by wet, dry or alkali scrubbing [20]. More recently the Japanese Company MITSUBISHI HEAVY INDUSTRIES LTD. has devised a compact desulphurization system. The process subsystems are shown schematically in the fig. 2.2 (FGD fig.)
3.2.1 Wet Process and its Limitations

In this process the flue gas is scrubbed with a slurry that contains lime (CaO) and limestone (CaCO₃) as well as the salts CaSO₃ 2H₂O and CaSO₄ 2H₂O (gypsum). The SO₂ in the gas reacts with the slurry to form additional CaSO₃ and CaSO₄ salts which are recycled with the addition of fresh lime or limestone. The chemical reactions are thought to be

\[
\begin{align*}
\text{CaO} + \text{H}_2\text{O} &= \text{Ca(OH)}_2 \\
\text{Ca(OH)}_2 + \text{CO}_2 &= \text{CaCO}_3 + \text{H}_2\text{O} \\
\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 &= \text{Ca(HCO}_3)_2 \\
\text{Ca(HCO}_3)_2 + \text{SO}_2 + \text{H}_2\text{O} &= \text{CaSO}_3 \cdot 2\text{H}_2\text{O} + 2\text{CO}_2 \\
\text{CaSO}_3 \cdot 2\text{H}_2\text{O} + \frac{1}{2} \text{O}_2 &= \text{CaSO}_4 \cdot 2\text{H}_2\text{O}
\end{align*}
\]

One technique employs a spray tower after the particulate removal system where it flows in counter to the limestone slurry spray. The sprayed limestone slurry collects in the bottom of the tower and is recirculated back to the spray tower by a pump. The bled slurry is sent to a dewatering system.

Advantages of the process are good efficiencies, good reliability and low flue gas energy requirements. It is also capable of removing the residual particulates. The main limitation of the process is the build up of scale in the spray tower and the possibility of plugging. Other disadvantages are the relating of the flue gas a larger gas pressure drop requiring higher power requirement than dry FGD system and difficult sludge disposal.

3.2.2 Dry Flue Gas Desulphurization System

The dry FGD system utilizes an aqueous slurry of lime (CaO), to capture flue gas SO₂ by forming CaSO₃ and CaSO₄ in spray absorbers. The slurry is atomised usually by centrifugal atomizer into a fine spray that promotes the chemical absorption of SO₂ and small spray particles are quickly dried by the hot flue gases which are carried along with the desulphurised gas stream. The reaction particulates as well as those carried by the flue gases (fly ash) are removed mainly by fabric filter before the gas is drawn to the stack. The main advantage of dry process is the easy disposal of the waste material. The SO₂ removal efficiency of this process is less than that of wet process.
3.2.3. Single Alkali Scrubbing

Solutions of NaOH, Na₂SO₃ or ammonia are excellent absorbers of SO₂. The advantage of alkali scrubbing is that it avoids the scaling and plugging problems. Ammonia scrubbing has the advantage that the scrubber product, (NH₄)₂ SO₄ can be used as fertilizer, the disadvantage is that the process produces trouble-some fumes.

A well developed sodium scrubber is the Wellman Lord SO₂ recovery process. The process utilizes a water solution of sodium sulphite (Na₂SO₃) for scrubbing. Alkali scrubbing the flue gas is first pretreated by cooling and removal of particulates and then SO₂ is scrubbed.

\[ \text{SO}_2 + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} = 2\text{NaHSO}_3 \]

The NaHSO₃ is sent to forced circulation evaporator crystalliser via a surge tank. Through the application of low pressure steam, such as from a turbine exhaust the sulphite is regenerated in the form of slurry.

\[ 2\text{NaHSO}_3 \rightarrow \text{Na}_2\text{SO}_4 \uparrow \text{SO}_2 \uparrow + \text{H}_2\text{O} \]

The product SO₂ may be utilised to produce liquid SO₂ or sulphuric acid or elemental sulphur. The process is called Claus process. This process is based on addition of H₂S.

\[ \text{SO}_2 + 2\text{H}_2\text{S} \rightarrow 3\text{S} + 2\text{H}_2\text{O} \]

Another practical method is use in magnesite cycling method, in which the SO₂ gas is absorbed in a scrubber sprayed with a suspension of magnesium hydroxide in water. The magnesium sulphite so formed is dried and roasted producing SO₂ and magnesium oxide.
3.3 Advanced Process for Combined Removal of SO₂ and NOₓ

The technologies for the simultaneous removal of SOₓ and NOₓ are based on electron beam technology (EBT) and pulsed corona discharge (PCD).

3.3.1. Electron Beam Technology

This technology is basically a flue gas treatment (FGT) system for removal of both NOₓ and SOₓ. The process flow diagram is shown in Fig 3.6. High energy electrons (300-800 kev) from the beam excite the flue gas molecules producing an abundance of reactive ions and free ions. These radicals oxidise NO₂ and SO₂ to higher levels particularly acid forming molecules which are readily neutralised by the alkalinity in the lime or fly ash. Another process employs NH₃ injection, gas cooling and humidification of the flue gas prior to electron beam subjection. Solid reaction products (NH₄)₂SO₄ and NH₄NO₃) are potentially useful fertilizers but may be contaminated by metals from fly ash.

The oxidation of NO, NO₂ and SO₂ in an e-beam or pulsed corona reactor is in principle comparable to oxidation of these gases in the atmosphere. In atmospheric chemistry the OH radical, formed by photo dissociation of water plays a key role in the transformation of NOₓ and SO₂ to nitric and sulphuric acids. Even ammonia is present in the atmosphere. Many reactions with NO, NO₂, SO₂, NH₃, O₃ and OH radicals in humid atmosphere have been investigated by Seinfeld [21].

The possible main reactions applicable to electron beam technology given by Tokunaga and Suzuki [22] and Alekseev et al [23], are as under:

a) Formation of primary ions, radicals and excited states:

- ionisation \( e^{-} + N_2 \rightarrow N_2^{+} + 2e^{-} \)
- Charge transfer \( N_2^{+} + O_2 \rightarrow N_2 + O_2^{+} \)
- Cluster formation \( O_2^{+} + nH_2O \rightarrow O_2^{+}(H_2O)_n \)
- dissociation \( e^{-} + N_2 \rightarrow 2N + e^{-} \)
- dissociative attachment \( e^{-} + H_2O \rightarrow OH + H \)
- dissociative ionisation \( e^{-} + H_2O \rightarrow OH^{-} + H^{+} + e^{-} \)
- electronic excitation \( e^{-} + N_2 \rightarrow N_2^{+} + e^{-} \)
Fig. 3.6 Process flow diagram of electron beam technology.
B) Formation of secondary radicals and radical loss:

\[ \text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH} \]

\[ \text{H}_2\text{O}^+ + e^- \rightarrow \text{OH} + \text{H} \]

\[ \text{N}_2^+ + \text{OH} + \text{H} \]

\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad \text{M is third body} \]

\[ \text{O} + \text{OH} \rightarrow \text{H} + \text{O}_2 \]

\[ \text{H} + \text{O}_2 \rightarrow \text{HO}_2 \]

\[ \text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \]

\[ \text{O}_3 + \text{O} \rightarrow 2\text{O}_2 \]

\[ \text{NH}_3 + \text{OH} \rightarrow \text{NH}_2 + \text{H}_2\text{O} \]

\[ \text{NH}_2 + \text{O} \rightarrow \text{NH} + \text{OH} \]

c) \text{No}_x\text{ oxidation}:

\[ \text{NO} + \text{OH} + \text{M} \rightarrow \text{HNO}_2 + \text{M} \]

\[ \text{NO} + \text{H}_2\text{O} \rightarrow \text{NO}_2 + \text{OH} \]

\[ \text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M} \]

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]

59
NO + N → N₂ + O

NO + NH₂ → N₂ + H₂O

NO₂ + O → NO + O₂

NO₂ + OH + M → HNO₃ + M

d) SO₂ Oxidation:

SO₂ + OH + M → HSO₃ + M

HSO₃ + O₂ → SO₃ + H₂O₂

SO₃ + H₂O → H₂SO₄

e) Salt Formation

NH₃ + HNO₃ → NH₄NO₃

NH₃ + H₂SO₄ → NH₄HSO₄

NH₃ + NH₄HSO₄ → (NH₄)₂SO₄

3.3.2. Pulsed Corona Discharge

In case of pulsed corona the intense electric field at the streamer head are responsible for generation of active radicals which can convert NOₓ and SO₂ into their respective acids which can be removed by addition of NH₃ or H₂O by another ESP.
The acidic oxides laden gases are allowed to flow through a pulsed plasma reactor. Energetic electrons created by intense electric field ranging between 100-1000 kV/cm at the streamer head produces O, OH and HO₂ radicals. Since the fast rising voltage pulse (~μs) produces streamers (discharge in the form of small lines occurring just before the electron avalanche takes place), the radicals can appear within microseconds.

Many types of discharges are in the use for the creation of non thermal plasmas. Other discharges besides the pulsed corona are the barrier or silent discharge which are often used for Ozone generation and also for removal of SO₂ and NOx [24,25]

3.3.3. Streamer Formation

The weakly luminous and narrow discharge channels that are observed preceding the much brighter arc discharges in both uniform and non-uniform fields are called streamers.

Streamer formation and propagation have been explained by Raether and Meek [26] mainly on the basis of field distortion by space charge. The head of the electron avalanche and the positive ions which are left behind the avalanche form a sort of dipole. The dipole field modify the external field. The ADS (Anode Directed Streamer) is in fact a "Modified" electron avalanche. When a strong space charge field and initial electrons are present at the Cathode side of the initial electron avalanche, a CDS (Cathode Directed Streamer) can be formed. The CDS propagates as a result of secondary avalanches. The CDS propagates in a direction opposite to the electron drift velocity while ADS propagates in direction of electron drift.

Meek's streamer criterion is

\[
\alpha'x = 22.7 + \eta_n(x) 
\]

\(\alpha' = \text{net ionisation coefficient.}\)

For electrode gap; in the range 0.01-0.1 meter, Meek's criterion reduces to \(\alpha'x=18-20\) close to Raether's empirical criterion \(\alpha'\approx20\).
Meek's criterion may be inaccurate because it is based on a rough estimation of the space charge field which can significantly influence the avalanche development before a streamer is formed. Usually, the Raether-Meek criterion for streamer formation is written as

\[ \alpha'x = 18-20, \; Ne = e^{\alpha'x \cdot 10^8} \; Ne = \text{ion density} \]

At fixed \( E_d/n \), the diffusion radius at the moment of the avalanche to streamer transition decreases with increasing gas density \( n \) as

\[
\frac{r_D}{n} = \frac{1}{n} \sqrt{\frac{4\alpha'/\alpha}{\alpha'/\alpha n} \cdot \frac{D_f/\mu e}{E_d/n}} = \frac{1}{n} \tag{3.14}
\]

The space change field \( E_s = \frac{q_d e^{\alpha'x}}{4\pi\varepsilon_0 r^2} \)

The reduced space change field \( \frac{E_s}{n} \approx \frac{1}{n r_D^2} \sim n \)

3.3.4. Streamers in Pulsed Corona

The discharge structure of pulsed positive corona has been investigated by Nasser. The main results have been obtained with sub microsecond HV pulses applied to point plate gaps in ambient air have been published in Nasser's book [27]. The streamers were made visible by means of the Lichtenberg technique (photographing the streamers) The streamers are observed in form of branches from a spot as shown in fig. 5.10. The positive streamers (CDS) have more branching than negative streamers (ADS).

To start negative streamers a higher pulsed voltage is required and the existence region for negative streamer is smaller than positive streamers.
Fig. 3.10 Litchenberg Figures
The difference between DC and pulsed corona is that in a Corona discharge operated with short-scale-microsecond HV pulses and moderate repetition rate (<1KH) the drift of ions is strongly limited when compared to DC Coronas. On the other hand, if the repetition rate of a pulsed corona discharge is high, the space charge effects resulting from ion drift can have a similar influence as in DC corona. A higher repetition rate will increase the average ion density and the ion collection efficiency will be higher by increasing the duty cycle (the ratio of pulse width and the period between pulses), exactly as in electrostatic precipitators.

It is possible to extend the Raether-Meek criterion for streamer formation to non-uniform fields. The product $\alpha'x$ is replaced by the ionization integral

$$N_e(r) = \exp \left[ \int_{r_0}^{r} \alpha'(r')dr' \right] = 10^8$$

(3.15)

where $r_0$ is the position of the initial electron that start the avalanche. With low repetition rate, the voltage required for steamer formation can be calculated with this integral. The minimum voltage required for streamer inception $V_{i,\text{min}}$ can be determined by recalculating $N_e(r)$ with $r = r_{\text{critical}}$ for stepwise increasing voltage levels until the condition $N_e(r) = 10^8$ is satisfied.

The influence of the gas composition on the electron transport coefficient can be seen by solving the Boltzman equation. For the description of electron- molecule kinetics it is assumed that the macroscopic properties of electrons are independent on space and time variables and sole function of $E/n$. This assumption is referred as local equilibrium. The electron energy distribution function (which is the key variable in the solution of the Boltzmann equation) depends almost completely on collisions of electrons with the neutral background gas. The Boltzman calculation requires a reliable and complete set of cross-sections for momentum transfer, excitation, attachment and ionization in the gases N$_2$, O$_2$, CO$_2$ and H$_2$O. These input parameters can be varied so as to obtain the best possible agreement between measured and calculated streamer properties. Measurable streamer discharge properties, which serve as comparison with model predictions, are (a) the streamer induced current in the external circuit, (b) streamer inception
3.3.5. Solution of the Boltzmann equation

The dynamics of an assembly of electrons can usually be characterised by an electron distribution function \( F(r,w,t) \). The time evolution of this function is described by the Boltzmann equation:

\[
\frac{\partial F}{\partial t} + w \nabla_r F + a \nabla_w F = C(F)
\]  

(3.16)

where \( w \) is the electron velocity vector and \( a (= q_eE/m_e) \) the acceleration vector. The collision operator \( C \) represents the gain and loss of electrons in the velocity space element \( dwdr \) due to both elastic collisions (momentum exchange) and inelastic collisions (excitation, ionization etc.)

The solution is approached by using the simplification of local equilibrium \( F(r,w,t) = n_e(r,t) . f(w) \), usually the electron velocity distribution function is expanded into a series of Legendre polynomials \( P_k \).

\[
f(w) = f_0(w) + \sum_{k=1}^{\infty} f_k(w)P_k(\cos\theta)
\]  

(3.17)

\( \theta \) is scattering angle of electron with respect to fixed direction.

The velocity distribution function \( f_0(w) \) is related to energy distribution function \( f_\omega(\omega) \) by

\[
\frac{\sqrt{\varepsilon}}{\omega} f_\omega(\omega) \, d\varepsilon = 4\pi \omega^2 f_\omega(\omega) dw
\]

The energy distribution function is normalized by

\[
\int_{\varepsilon_\text{low}}^{\varepsilon_\text{high}} f_\omega(\varepsilon) \, d\varepsilon = 1
\]  

(3.18)
From the electron energy distribution function, the electron transport coefficients $w_e$ and $D_T$ (diffusion radius) can be calculated as [28]

$$w_e = \frac{e}{3n} \sqrt{\frac{2}{m_e}} \int_0^\infty \frac{\xi}{\sigma_m(\xi)} \frac{df_o}{d\xi} d\xi$$  \hspace{1cm} (3.19)

$$D_T = \frac{1}{3n} \sqrt{\frac{2}{m_e}} \int_0^\infty \frac{\xi}{\sigma_m(\xi)} f_o(\xi) d\xi$$  \hspace{1cm} (3.20)

$\sigma_m(\xi) = \text{effective momentum transfer cross-section including both types of collisions}$

Kinetic rate coefficients can be calculated as:

$$k_i = \sqrt{\frac{2}{m_e}} \int_0^\infty \sqrt{\xi} \sigma_i(\xi) f_o(\xi) d\xi$$ \hspace{1cm} (3.21)

where $\sigma_i$ are cross sections for ionization, attachment, dissociation and excitation.

Pulsed Corona and e-beam deNO$_x$ and deSO$_2$ processes have much in common. Both processes are initiated by electrons producing ions and radicals which transform the pollutants into acids. However, differences also exist between the two processes. In particular the properties of electrons (spatial and energy distribution) are very different. In the streamer corona discharge, electrons are produced in these discharge channels while in e-beam irradiated gas, the spatial distribution of electrons is rather uniform. In streamer corona discharge the average energy of electrons is about 10 ev whereas this range for e-beam is 300-800 kev.

Advantages of pulsed corona deNO$_x$ deSO$_x$ process, when compared to a combination of selective catalytic reduction for deNO$_x$ and the wet limestone gypsum process for deSO$_x$ are
- NO\textsubscript{x} and SO\textsubscript{2} are removed simultaneously in a single reactor with low capital cost.
- it is dry method, no waste water management is required
- electrode structure is similar to those used in conventional ESPs.
- the pressure drop in the reactor is small compared to catalytic converters for deNO\textsubscript{x}.
- reheating of flue gas before release in atmosphere is not needed.
- the by-products are useful.

### 3.3.6. Chemical Equilibrium for SO\textsubscript{2} and NO\textsubscript{x}

The initial NO concentration has a significant influence on the percentage of NO that can be oxidised. At an energy density of $1\mu$rad [\((10\text{kJ/kg} \div 2.8\text{wh/Nm}^3)\)] an initial NO concentration of 100 ppm is almost completely oxidised while for an initial concentration of 500 ppm only $\approx 70\%$ is oxidised. The increase of water vapors decreases both NO and NO\textsubscript{2} concentrations, it may be due to the reason that OH radicals react with NO and NO\textsubscript{2} to form HNO\textsubscript{2} and HNO\textsubscript{3}.

The presence of water vapors to be essential for SO\textsubscript{2} removal. Even at high irradiation doses of N\textsubscript{2}-O\textsubscript{2}-SO\textsubscript{2} mixtures almost no decrease of the SO\textsubscript{2} concentration is measured. A remarkable result is the improved NO\textsubscript{x} removal efficiency with SO\textsubscript{2} addition. At an energy density of 2Mrad, without SO\textsubscript{2}, an initial NO concentration of 235 ppm decreases to 50 ppm while about 150 ppm NO\textsubscript{2} is formed, thus only 35 ppm NO\textsubscript{x} is removed. When 1050 ppm SO\textsubscript{2} is added, the NO concentration decreases to 40 ppm and the NO\textsubscript{2} concentration decreases to 125 ppm, thus about 70 ppm NO\textsubscript{x} is removed.

The addition of NH\textsubscript{3} improves the removal of both SO\textsubscript{2} and NO\textsubscript{x}. The reaction rate increases with temperature. NO\textsubscript{x} is never completely removed, even with high stoichiometric NH\textsubscript{3} addition and with high relative water vapour concentration. Hence the presence of the radicals NO\textsubscript{x} and SO\textsubscript{2} influence each other and some equilibrium is set up.

### 3.3.7. Removal of Salts Obtained from SO\textsubscript{2} and NO\textsubscript{x}

The simultaneous removal of NO\textsubscript{x} and SO\textsubscript{2} from flue gas of coal-fired electrical power plants has been investigated by the Italian National electricity board ENEL [29,30]. The pulsed
corona deNO$_x$ deSO$_2$ process is connected down stream to DC negative ESP. The solid particles formed in the process are ammonium nitrate and ammonium sulphate. Practically all particles possess a diameter in the range of 0.1-1µm that is suitable for efficient removal in an ESP or by bag filter.

These advanced processes will find increasing use in the time to come once their commercial viability is established on a large scale. The ESP technology for particulate control is extensively used the world over in diverse industries where particulate matter is suspended in the flue gas exhausting to the atmosphere. Case studies for some typical industries where the particulate control technologies are in use will be discussed in the subsequent chapters of this thesis.
REFERENCE


