CHAPTER II

FUNDAMENTAL KNOWLEDGE

The self-sustaining discharge of electrons in a non-uniform electric field between a thin wire and a coaxial cylinder is called a corona discharge. This name is descriptive of the glowing light effects found when the applied voltage is several kilovolts. High vacuum is not always required and corona discharge can be generated at or near atmospheric pressure. The gas pressure needs not be low for the discharge to occur, but at low gas pressure the corona is not visible. The luminous part of the discharge is usually restricted to a region close to the wire surface, which may be positive or negative with respect to the cylinder. One distinguishes between positive and negative coronas by the applied positive or negative voltage of the central electrode.

Coronas are by no means only artificially produced. It is the natural phenomenon of the glow or corona surrounding the sun but is only visible during a total solar eclipse. In addition, nature produces them between and within electrically charged clouds. A theory on cloud electrification attributes this process to the corona on and around ice particles in the clouds. According to this theory, corona is not only the effect but also the cause of the appearance of charged clouds and therefore of lightning and thunderstorms.

In a corona discharge reactor, there are three regions in the void space between the anode and cathode as shown in **Figure 2.1**. In the high electron energy region, free electrons are emitted from the cathode surface and rapidly accelerated. Surrounding gas molecules will be ionized after collision with these free electrons and negative ions are produced. In the transient region, the electron energy is just enough to dissociate gas molecules to produce neutral radicals. In the vast region of low-energy electrons, electrons are prone to be captured after collision with gas molecules. Cluster formation and electron attachment reaction generally take place in this region.

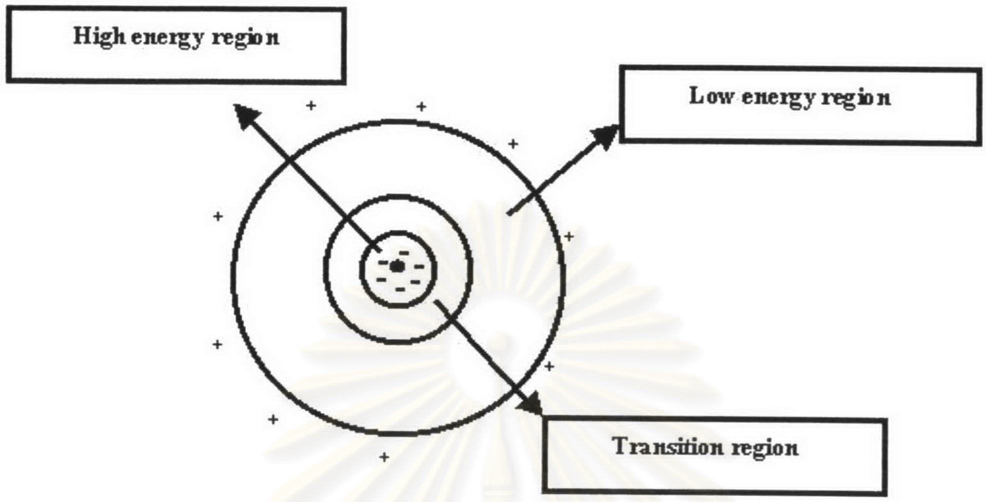

Figure 2.1 The regions of corona discharge reactor

2.1 Electron attachment reaction

When low-energy electrons collide with electronegative gas molecules, some electrons are captured by the gas molecules, and negative ions are formed. This phenomenon is called "electron attachment" (Massey, 1976). Electron attachment depends on the electron energy level, the structure of the gas molecule, and its electron affinity. There is a huge difference between the electron attachment probability of the gas molecules and that of the carrier gas. This high selectivity is reflected in the production of negative ions (Caledonia, 1975 and Massey, 1976, 1979). Therefore, electronegative impurities of very dilute concentration become negative ions by electron attachment, and they can effectively be separated from the neutral gas (for example, N_2) in an electric field.

In the case of excessively high-energy electron colliding with a gas molecule, the molecule would not only be negatively ionized but may be dissociated or be positively ionized due to the loss of one electron from the molecule itself. In contrast, if an electron whose energy is too low reaches the molecular orbital, the electron can not be captured by the molecule. It is necessary to take into account the moderate (appropriate) range of electron energy when the attachment probability is to be enhanced. A great deal of effort has been devoted to generate or utilize electrons with a variety of energy range via quite a number of gas-discharge devices. However, the appropriate range of electron energy contributing exclusively to electron attachment generated by such devices has not been clarified because of the limitation of measurement devices and/or techniques.

At the exact moment when an electron is captured by a gas molecule, the molecule would be placed at an excited state. To become stable, the molecule must release the excess energy in quanta, for example, by collision with another electron, by collision with another gas molecule, by being decomposed, or by radiation. Various processes for the electron attachment reaction have been reported (Moruzzi and Phelps, 1966) as shown by Eqs. (2.1), (2.2), and (2.3). A mixture of an electron-attaching gas, AB, and an appropriate third body, M, is considered in these processes.

Dissociative attachment: $$e + AB \rightarrow A^- + B \qquad (2.1)$$

Three-body attachment: $$e + AB + M \rightarrow AB^- + M \qquad (2.2)$$

Radiative attachment: $$e + AB \rightarrow AB^- + h\nu \qquad (2.3)$$

Since the electron attachment probability of the gas molecule is also dependent upon its electron affinity, it is reasonable to expect that a molecule that contains one or more atoms with high electron affinity would have high probability of electron attachment. For example, in a comparison between SF_6 and N_2, the electron affinities of S, F, and N are 200 kJ/mol, 333 kJ/mol, and –26 kJ/mol, respectively. So it is not surprising that the probability of electron attachment for

SF_6 molecule is reportedly 10^{11} times that of N_2 molecule (Hickman and Fox, 1956). This huge difference in the electron attachment probability among various kinds of gas molecules results in high selectivity in the formation of the corresponding negative ions. Therefore, even a specific gas component whose concentration is extremely low can effectively be separated from the main (neutral) gas in an electric field by utilizing the electron attachment reaction. Also one can expect the method based on electron attachment to be one of the most efficient methods of gas purification.

Since most malodorous components in the crematory emission are highly electronegative gaseous components, electron attachment seems to be one highly effective way to remove them in an electric field. With further advancement of the technology and the use of multi-stage reactor, it is reasonable to aim at the simultaneous removal of both gaseous pollutants and fine particles since the basic principle of corona discharge and subsequent deposition on the anode is similar to that of an Electrostatic Precipitator (ESP) (White, 1960; Oglesby and Nichols, 1978; Ogawa, 1984). This is however beyond the scope of this work.

2.2 Principle of gas purification

Figure 2.2 illustrates the principle of gas purification by the removal of an impurity, AB, from an inert gas in a cylindrical corona-discharge reactor (Tamon et al., 1995). The corona discharge is employed here because it is an efficient method to supply a large number of low-energy electrons to the gas stream. The cathode is a wire stretched along the axis of the reactor and the outer cylinder acts as grounded anode. High DC voltage (-5~ -15kV) is applied to the cathode to induce corona discharge in the reactor. Electrons generated at the cathode drift to the anode along the applied electric field. During their drift to the anode, a portion of them collides with the gas molecules. Negative ions, A^-, are thus selectively produced by electron attachment and they likewise drift to the anode as the electrons do.

In an ideal case, the number of electrons generated in the reactor is sufficient for all gaseous impurities to hitch up with the electrons and all negative ions thus generated are able to completely deposit on the anode surface. In other words, the outlet gas is devoid of unwanted impurities and complete removal is achieved. In reality, upon their arrival at the anode, certain kind of negative ions might simply discard their charges without depositing on its surface. In this case these gaseous impurities can not be separated using the simple deposition-type reactor. In any case, it is most desirable to capture most of the negative ions arriving at the anode surface. The idea of how to remove negative ions at the anode will be described later.

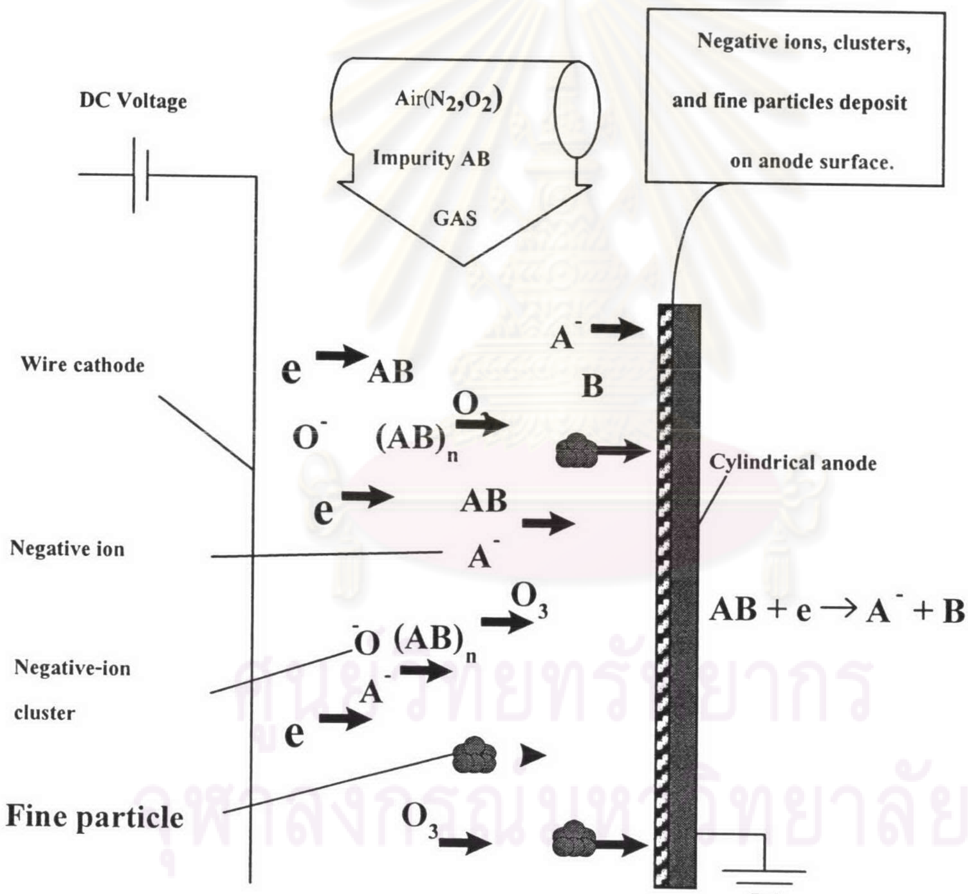

Figure 2.2 Principle of gas purification

Besides the above - mentioned removal mechanism associated with electron attachment reaction in the corona-discharge reactor, it is believed that other removal mechanisms may simultaneously contribute to the removal efficiency. When single negative ions are produced in the reactor, they may possibly interact with other adjacent gas molecules via their electrostatic forces and negative - ion clusters may be formed. Each cluster then contains multiple gas molecules targeted for removal. When the clusters drift to the anode and manage to deposit there, the removal efficiency is greatly enhanced.

Another possible mechanism contributing to the removal efficiency is the so-called radical reaction. When dissociative electron attachment also takes place in the reactor, not only negative ions but also reactive radicals are produced. In particular, the radicals may readily be produced in the immediate vicinity of the cathode surface where high electric field strength exists. It is logical to assume that the removal efficiency would be enhanced by radical reaction, which, however, often results in the generation of reaction by-products.

The reaction of targeted gas molecules with O_3 is frequently mentioned. Ozonation reaction usually takes place when oxygen coexists in the gas stream. High-energy electrons close to the cathode surface collide with O_2 molecules to dissociatively produce O^- radicals. O^- Radicals can next react with O_2 molecules to produce O_3, which is reactive with various kinds of gases. Hence, ozonation reaction is expected to contribute to the oxidative destruction of a number of gaseous impurities in the gas stream, thus improving the removal efficiency while yielding by-products.

2.3 Types of reactor

As mentioned in section 2.2, in some cases certain kind of negative ions produced by electron attachment would drift towards but do not easily adhere to the anode surface. Thus they end up as uncaptured negatively charged or uncharged impurities at the outlet of the conventional deposition-type reactor, and cause a decrease in their removal efficiency. It is therefore essential to find out how to effectively remove such negative ions at the anode. This has motivated Tamon et al. to propose three types of reactor, as shown in **Figure 2.3**

2.3.1 Deposition-type reactor

Some negative ions readily adhere to the anode surface of the reactor after releasing their negative charges there. In this case they may form solid particles or react with the metallic anode. The solid particles form a thin deposition layer on the anode surface. Thus, the so-called deposition-type or (simple) reactor is adequate for the removal of these negative ions. Periodic cleaning of the anode surface or its replacement is often necessary to maintain high removal efficiency.

2.3.2 Sweep-out-type reactor

In some uncommon cases certain negative ions do not easily deposit on the anode surface but change back to the original uncharged molecules after releasing electrons at the anode surface. In such cases, the deposition-type reactor is not suitable because the original molecules of the gas impurities are not removed but diffuse back to the main gas stream. To solve this problem, the sweep-out-type reactor, which uses a porous pipe wall made of sintered metal as anode is recommended. A small portion of the carrier gas around the anode surface is swept out by suction through this pipe to restrict backward diffusion of the concentrated electronegative impurities so that the removal efficiency would be kept high. The swept-out stream with a much higher concentration of the gas impurities can then be treated using a suitable conventional method.

2.3.3 Wetted-wall reactor

Another option to remove negative ions at the anode surface is the wetted-wall reactor. Negative ions reaching the anode of the reactor can be absorbed into a down-flowing liquid film on the vertical anode surface. This absorption of the ions improves the removal efficiency. The most important advantage is the self-cleaning of the anode, which makes it suitable even for dirty gas streams containing both dust and gaseous pollutants. The major drawback is the need for a liquid (mostly water) treatment and recycles system. Anyway, the corona-discharge reactor to be investigated in this work will be limited to the deposition type because it is easier to construct and operate, and is applicable as a first step of the fundamental study in a laboratory.

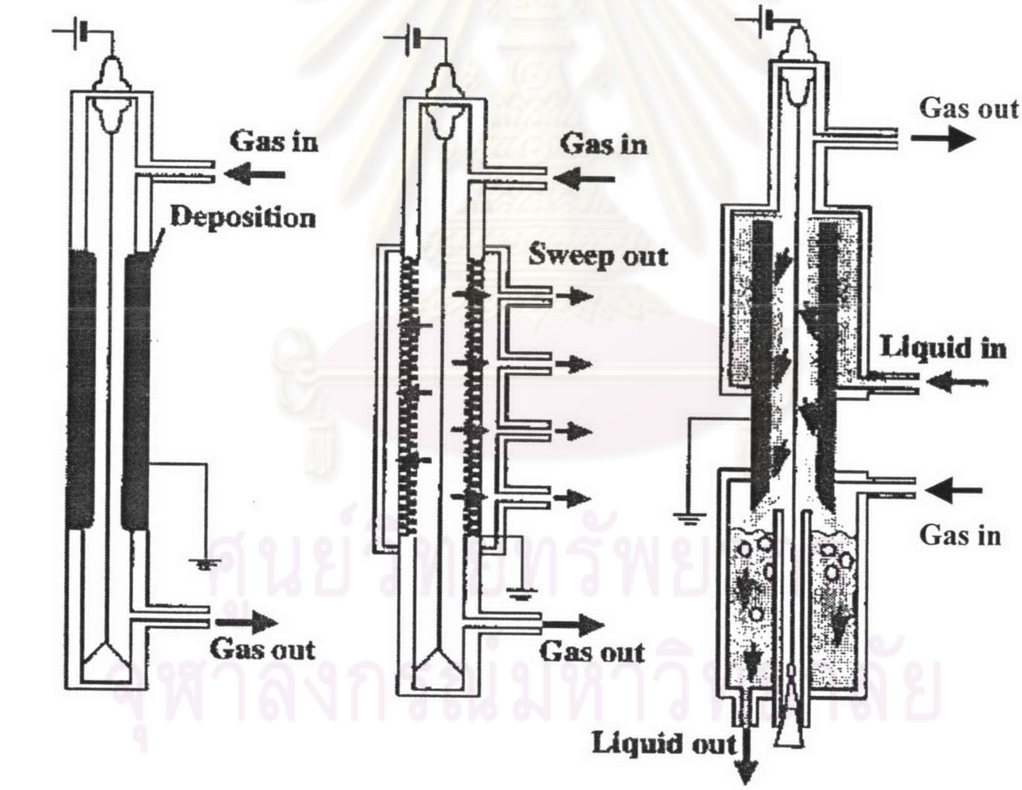

Figure 2.3 Types of corona-discharge reactor

2.4 Effect of coexisting oxygen (ozone effect)

When O_2 is present in a gas mixture, it usually reacts with discharged electrons. Electron attachment on O_2 has been reported in the literature (Morruzzi and Phelps, 1966; Massay, 1976; Rapp and Briglia, 1976; Chantry and Schulz, 1967).

$$O_2 + e^- \longrightarrow O_2^- \qquad (2.4.)$$

$$O_2 + e^- \longrightarrow O + O^- \qquad (2.5)$$

Moruzzi and Phelps (1966) reported that the reaction in **Eq. (2.4)** occurs in the low electron energy range ($E/p < 1.5$ V.m^{-1}.Pa). In contrast, the reaction in **Eq. (2.5)** occurs in the higher electron energy range. Also in the corona-discharge reactor, the closer the electrons are to the cathode wire, the higher their energy level. When an O_2 molecule collides with a high-energy electron near the cathode wire in the corona-discharge reactor, production of O^- is expected as in **Eq. (2.5)**. Next O_3 is produced from the reaction of O^- with O_2 (Loiseau et al., 1994; Hadj-Zaine et al., 1992).

In short, some ozone (O_3) is produced. Since O_3 is very reactive, the ozonation reaction is used in some commercial devices for deodorization and sterilization. The same ozonation reaction is expected to contribute to the removal of gas impurities in the present corona discharge reactor.

2.5 Effect of negative-ion cluster

If a negative ion induces the formation of a cluster of multiple gas molecules, the removal efficiency of the impurities will be improved. This effect is significant because one negative ion and several gas molecules constitute a cluster that drifts to the anode and deposits on it.

2.6 Effect of temperature

The influence of gas or reactor temperature on the relationship between the voltage and the current has been confirmed (Sano et al., 1997). As expected, the higher the temperature, the lower the required voltage becomes. Reportedly, several factors may be considered as the reason for the temperature dependency of the voltage-current relationship. They are (1) the positive change in the frequency of the thermal electron emission from the cathode surface to initiate the corona discharge; (2) the positive change in the propagation rate of free electrons in the high electric field region around the wire cathode; (3) the positive change in the ionization rate of the gas molecules; (4) the positive change in the mobility of the ions.

As for the temperature effect on the dissociative electron attachment of O_2, it was reported that the dissociative electron attachment rate increased when the temperature increased. Thus it is logical to consider that the formation of clusters is inhibited by temperature elevation because the ion clusters are thought to be less stable at high temperature condition.