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# Plasma Applications for Environmental Protection

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***Abstract-Plasmas (both thermal and non-thermal) are known to be utilized for various environmental applications. These applications mostly include fields of air pollutant treatment, wastewater and drinking water decontamination, and thermal disposal of solid waste. The non-thermal plasmas used for environmental applications are mainly high-pressure discharges, such as DBDs, pulsed corona discharges, microwave plasmas, electron beams and dielectric packed bed reactors. An increasing number of investigations are devoted to the decomposition of nitrogen and sulphur oxides in flue gases, and of volatile organic compounds (VOC) emitted from various industrial processes. Many hazardous organic compounds are readily attacked by excited species, free radicals, electrons, ions and/or UV photons generated in DBDs. Moreover, investigations are going on to use dielectric barrier discharges (DBDs) for the generation of H2 and elemental sulphur from H2S and for the conversion of the greenhouse gases CO2 and CH4 to liquid fuels. The thermal plasmas mostly used for this purpose include several kinds of arcs.***

***Index Terms-Corona Discharge, Dielectric Barrier Discharge, Ozonation***

## I. INTRODUCTION

Plasma is the fourth state of matter. It differs from solids, liquids and gases in so far as its atoms are divided into free-floating 'negative' electrons and 'positive' ions (an atom which has lost its electron/s).

Fig1. Showing Plasma, the Fourth Matter

It is sometimes referred to as an ionized gas. Students are generally taught about only three states of matter, and when Plasma does get a mention, little importance is assigned. Not only should plasma be added to the list, but the order should be reversed to put it in first place. The reasons for this will become clear. The term Plasma was borrowed from blood plasma in order to describe its almost life-like and self-organising properties. Plasma sometimes emits light when under the excitation of electrical and magnetic fields. Plasma is almost everywhere. At least ninety-nine percent of the known universe is, in fact, matter in its plasma state! The surface of the sun is plasma; not hot gas, which is quite a different thing.

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Plasma in space consists entirely of ions and electrons, and is thus very energetic or 'hot'. Only when cooled does it form the matter to which we are familiar here on Earth: solids, liquids, and gases. Because plasma remains electrically charged in space, it is influenced more by electromagnetic forces than gravity. In fact space, once considered mostly empty, has been found to be alive with plasma. Vast flows of charged particles have been discovered spanning hundreds-of-thousands of light years across interstellar space. The most familiar examples of electrical plasmas here on earth are neon signs and lighting, television screens, and electrical arc welding machines. Fire and Lightning are also forms of Plasma.

## II. TREATMENT OF AIR POLLUTANTS

The emissions of SOx, NOx, and VOC by various industrial and agricultural processes is an important source of air pollution and therefore a problem for human health and the environment in general.

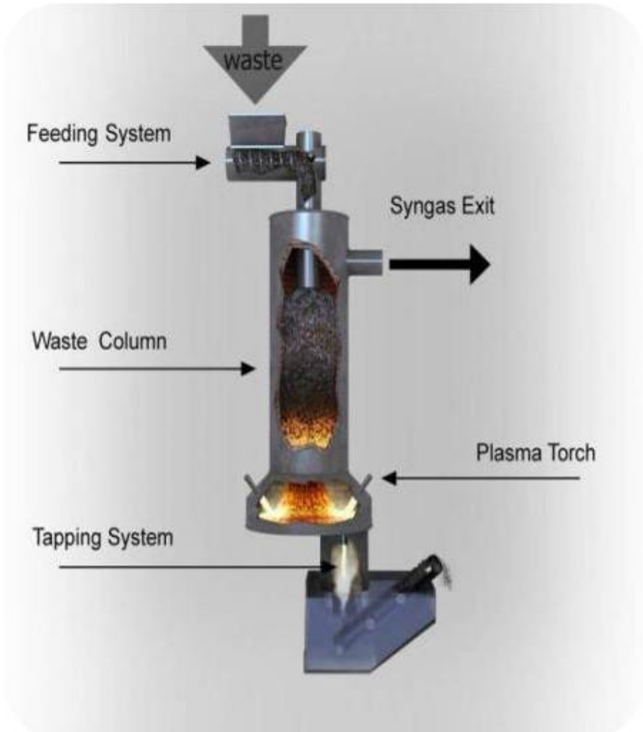


Fig3. Showing How the Waste Material Is Processed in the Chamber

There is a wide range of applications of plasma processes for the treatment of these pollutants. In this report, they are classified based on the types of plasmas (mostly NTP) applied.

## III. CONVENTIONAL NTP REACTORS

There is a variety of types of NTP reactors, such as DC corona discharge, pulsed corona discharge, dielectric barrier discharge, surface discharge, ferroelectric pellet packed-bed reactor, microwave, plasma jet, and gliding arc. These are further subdivided by the type of power supply (pulse, DC,



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DC+pulse, AC, AC+DC, RF, microwave etc.), the presence of a dielectric barrier or catalyst, geometry (cylinder, plate) and mode of discharge, etc. The classification of electrical discharges itself is also quite complicated as it depends on polarity, voltage level, and gas composition. The chemical potential of each discharge mode also differs enormously from one discharge to another. Three types of plasma treatment methods have been used as follows:

a. Remote plasma methods: The radicals were generated by a high pressure discharge plasma reactor and injected into the gas streams.

b. Indirect plasma/radiation methods: High and low pressure gas discharge lamps were used to generate ultraviolet UV with and without photo catalysts for treatments of waste gases. Electron beam and high energy gamma irradiation are also in this category.

c. Direct plasma methods: Pulsed, AC or DC corona discharges were generated in polluted gas and treating flue gas directly by electron, ion and radical chemical processes.


Fig2. Showing Purification of Air

The polluted air/gas mixture is usually rather complex and requires integrated pollution control systems to remove aimed pollutants. One advantage of plasma technology is the simplification of these integrated systems. For example, an advanced in-door air cleaning system requires PM control-devices (filters or ESP), bacteria control devices (UV lamps or injecting chemicals), odours and VOC control devices (UV photo catalysts - normally need different wavelength UV lamp, catalysts, adsorbents for each chemical species). However, a non-thermal plasma method based on pulsed corona can be acting as combined ESP, UV source and chemical decomposition reactor to reduce volume or in some cases even avoiding catalysts, adsorbents or injection chemicals for the treatment of mixed VOC and odours. The conventional NTP reactors that are mostly employed in air/gas treatment operations include dielectric-barrier discharge (DBD), surface discharge (SD), pulsed corona discharge and dielectric pellet packed-bed reactor. Dielectric barrier discharge (DBD) has at least one dielectric material between the electrodes. The materials commonly used for the dielectric barrier include glass, quartz, mica, epoxy mixtures and alumina. The discharge characteristics in DBD are highly dependent on the gas composition, type of dielectric material and operating conditions of voltage and frequency. In air-like mixtures at atmospheric pressure, the dominant discharge mode is the short-lived filaments referred to as micro discharge or streamer. When inert gases are present, the glow-mode discharge become dominant and is called atmospheric pressure glow discharge (APGD).

The above mentioned technology is traditionally most suitable for oxidation processes, due to the nature of high plasma density and moderate electron temperature devices. Hence, an application to replace oxidation catalyst for automobiles and intermediate oxidation of VOC was investigated. Since the device requires narrow gap distances between two electrodes, only small to medium gas flow rate (10–102 Nm3/h) flue gas treatments can be achieved. The modification of electrode surfaces and the optimization of AC waveform shapes were investigated. Surface discharge (SD) is very similar to DBD as it also uses a dielectric barrier. An alumina ceramic-based SD reactor was developed for the decomposition of volatile organic compounds (VOC) and chlorofluorocarbons (CFCs), sterilization and the generation of ozone. The high-purity alumina ceramic (purity higher than 92 %) has very good electrical, mechanical, thermal and chemical properties. A high frequency AC voltage of 10 kV and 10 kHz was applied between the corona electrodes and the induction electrodes, which are separated by about 0.5 mm by the inner ceramic layer. Under normal operating conditions the SD reactor produces a very high ozone concentration (5 000–15 000 ppmv in air, 5–10 % in oxygen), resulting in a very high efficiency of ozone generation (i.e. up to 900 g-O3/kWh in air). This result can be ascribed to the presence of a free-gas zone, where ozone can be accumulated without being destroyed by the discharge. A pulsed corona discharge is energized with a pulse power supply with a fast voltage rise time of several tens of nanoseconds and voltage rise time of above 500V/ns. The use of pulse power was first introduced in an electrostatic precipitator to enhance the removal efficiency by optimizing the peak voltage and current distribution. The reactors used for pulsed corona discharge are of two types: either with or without a dielectric barrier. The discharge mode in pulsed corona discharge is usually the streamer mode, where the ionization zone is spread over the entire gap. Therefore, the electrode gaps can be set at around 10 cm or more, which is highly favourable for large-scale applications and reducing the pressure drop. A positive polarity is usually adopted because the propagation of the streamer is more prominent and rapid than with a negative polarity. One of the distinctive characteristics of the pulsed corona discharge is the use of a short-duration pulse voltage. Due to the short duration of the applied voltage, the energy dissipation by ions can be minimized, resulting in the enhancement of energy efficiency. Several pilot-scale studies have used a similar electrode configuration (wire-plate) to that of ESP. The pulsed corona reactor/power supply design requires an applied voltage pulse front faster than ion frequency, hence only electrons can follow electric field change and ions almost are not moving as background gas molecules. Then, an applied voltage fall off rapidly to prevent an occurrence of spark discharge. Since only streamer corona occurs in discharge, this device is categorized as high plasma density and medium electron temperature device. However, this device only can handle medium gas flow rates (10–102 Nm3/h), since the fast rising pulse only can be achieved with small capacitance between electrodes. The pulsed power approaches overcome this limitation through the fast rising current values, since an induced electric field can be generated by the fast rise current. Due to the plasma parameters, the pulsed corona and power devices are suitable for Cl-based VOC and acid gas treatments. Ferroelectric pellet packed-bed reactors were investigated



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for VOC's decomposition, odour removal, and CO2 reduction. The most widely used ferroelectric material is barium titanate (BaTiO3), which has a dielectric constant of 2 000–10 000. Other perovskite-type ferroelectric materials, such as Mg2TiO4, CaTiO3, SrTiO3 and PbTiO3, have also been used. When the ferroelectric materials are exposed to an external electric field a spontaneous polarization occurs in the direction of the electric field, resulting in a high electric field at the contact points of the pellets. Electrical discharges, sometimes referred to as partial discharge, take place in the vicinity of the pellets' contact points. Although the use of pellets is disadvantageous in terms of pressure drop, the pellets lead to a uniform distribution of gas flow and discharge in the reactor. Ferroelectric pellet packed-bed reactors can easily be modified to incorporate a catalyst. Ferroelectric pellets and catalysts reduce the amounts of unwanted by-products, such as NOx and ozone. This combined system was also found to be effective in the decomposition of ammonia. For the practical use and the optimal design of NTP reactors, it is necessary to understand not only the physical properties but also the differences in the energy efficiency. It is still controversial whether NTP reactors have the same performance regardless of their type and driving power supply.

## IV. HYBRID NTP/WET PROCESS SYSTEMS

Plasma followed by adsorption/chemical reaction. The basic idea of this type of hybrid process is the removal of reaction intermediates or final products from the gas phase by adsorption and/or chemical reaction. For example, a two-stage combined process of NTP with a wet scrubber containing a sodium sulphite (Na2SO3) solution for the removal of NOx and SO2 was developed. In this system the roles of the plasma and the wet scrubber are the partial oxidation of NO to NO2 and the reduction of NO2 to N2 (using the Na2SO3 solution), respectively. Gas-phase NTP can enhance liquid-phase chemical reactions. It has been found that a pulsed corona discharge in the gas phase greatly enhances the liquid-phase oxidation of absorbed sulphite (HSO3–) to sulphate (SO42–). A comparative test using methanol solutions as OH radical scavenger demonstrated that the OH radical plays an important role in the liquid-phase oxidation. In recent years, gas-phase NTP over the surface of water has received a great deal of attention for application as a wastewater treatment. Electrical discharge over a liquid surface can also modify the mass-transfer characteristics. The corona discharge greatly enhanced the absorption of various gases (SO2, NH3, H2S, Cl2, CO2) due to the decrease in gas-phase mass-transfer resistance. In recent work by Lee et al. a similar trend was reported for SO2 absorption into deionised water. The mechanism of this type of heterogeneous reaction is still unknown and needs further extensive studies in the future. Plasma-Enhanced (Assisted) Catalysis (PEC). Recently the combination of NTP and a catalyst has gathered attention as a way of increasing energy efficiency and optimizing the by-product distribution. This combination can be either single stage or two stage. In the two-stage system, the catalyst bed is usually placed downstream from the NTP reactors. This two-stage system is referred to as a PEC system. One of the distinctive advantages of the PEC system is that it can combine the optimum conditions of the NTP and the catalyst, which are usually quite different from each other. For example, the optimal temperature for the catalyst is usually higher than that for the NTP. In the PEC system the NTP and catalyst have different roles. NTP has two important roles in the PEC: partial conversion of the reactant and the formation of ozone. The partial oxidation of the reactant is important for NOx removal. Since many NOx removal catalysts have higher activity toward NO2 than NO, the conversion of NO to NO2 drastically enhances the removal efficiency of NOx. Furthermore, the optimum temperature window of the catalytic reaction can also be lowered with this process. Reducing agents (NH3 and hydrocarbons) are added at the inlet of the catalyst bed to reduce NO2 to N2. Because of the similarity in the catalytic reactions, this type of NOx removal method is also referred to as a plasma-enhanced selective catalytic reduction (PESCR). In the decomposition of VOC, ozone produced in the NTP reactor enhances the decomposition of VOC over the subsequent catalyst bed. In this case, ozone can be produced either directly in the flue gas stream or indirectly in a separate flow with air (or oxygen). To some extent, the PEC combines the established aspects of each process, and rapid progress in both academic study and industrial application is expected. Plasma Driven Catalysis (PDC). In the PDC process, catalysts are placed directly in the NTP reactor. These catalysts are activated by NTP in the low-temperature region, where thermal catalysis does not occur. The shape of the catalyst is either honeycomb, foam or pellet. In contrast to the PEC system, all reactions of gas-phase, surface and their interaction take place simultaneously. The gases are introduced into the reaction zone through the contact materials for heat-transfer purposes. The catalysts may include alumina, zirconium silicate, cobalt oxide, thorium oxide, activated carbon, molecular sieves, silica gel, etc. The advantage of this type of configuration is the presence of very active species close to the catalyst.

## V. TREATMENT OF POLLUTED WATERS

There is a continuing need for the development of effective, cheap and environmentally friendly processes for the disinfection and degradation of organic pollutants from water. Ozonation processes are now replacing conventional chlorination processes because ozone is a stronger oxidizing agent and a more effective disinfectant without any side effects. However, the fact that the cost of ozonation processes is usually higher than chlorination processes is their main disadvantage.


Fig4. Depicting Purification of Polluted Water

Therefore, water treatment by direct electrical discharges may provide a means to utilize these species in addition to ozone. Pulsed corona discharge, DPD and contact glow discharge electrolysis techniques are being studied for the purpose of cleaning water. The units based on electrical discharges in water or close to the water level are being



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tested at industrial-scale water treatment plants. In the area of water purification, ozone synthesis is an industrially accepted application of electrical discharges. Ozone is required in huge quantities for drinking water and wastewater treatment. The major advantages of the ozonation process over conventional chlorination processes for water treatment are:

a .There is no need to store and handle toxic chemicals

b. By-products of ozonation do not have any known adverse effects on health or the environment

c. Ozone is a stronger and faster-acting oxidizer

d. Ozone can safely destroy a broader range of organic contaminants

e. Ozone helps in removal of colour, odour and suspended solid materials

f. Ozone is far more efficient in killing bacteria, viruses, spores and cysts

If the reactor is designed so that the electrical discharges take place in close proximately to the water surface, i.e. just above the water level, some of created radicals may get into water and destroy the pollutants. In this way, the water treatment unit becomes simpler as there will be no need for a separate electrical discharge reactor for ozone synthesis and tubing to carry ozone enriched air/oxygen. Electrical discharges in aerated water are also possible. Most of the produced radicals are among the strongest oxidizing agents. Therefore, instead of ex-situ electrical discharges for ozone production, the in-situ electrical discharges in water may provide a means to utilize most of these chemically active species for water cleaning. Furthermore, the intense electric fields necessary for electrical discharges are also lethal to several kinds of microorganisms found in water and show a synergistic lethal effect when combined with conventional disinfectants such as O3 and H2O2.

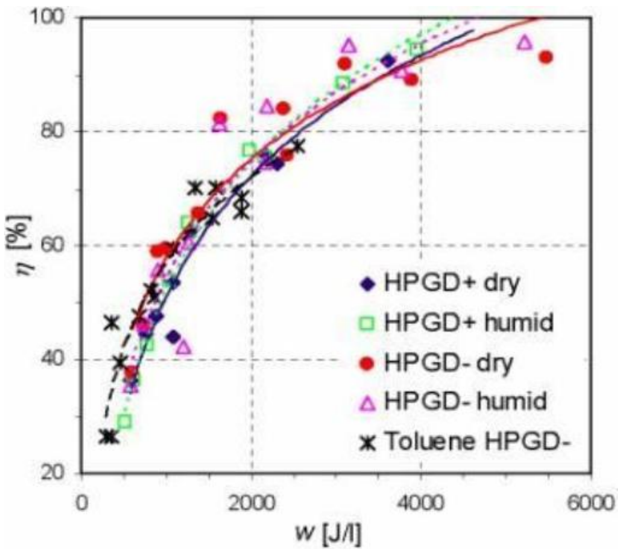


Fig5. Curve Showing the Effect of High Pressure Glow Discharge (Hpgd) Under Various at Atmospheric Conditions

The electrical discharges in water may also produce ultraviolet (UV) radiation and shock waves, which help in the destruction of pollutants. For these reasons direct electrical discharges in water are clearly the best next-generation technologies for water treatment they are environment friendly and may prove to be far more effective than conventional oxidants and disinfectants. Techniques of direct electrical discharges in water and the electrical discharges in close proximity to the water surface are being rapidly developed and tested on the industrial scale for water and wastewater treatments. On the other hand, direct electrical discharges in water need much higher electric fields and more complicated power sources. In the case of water purification the three following types of electrical discharges are often reported:

a. Contact glow discharge electrolysis,

b.Dielectric barrier discharges (also called silent discharges),

c. Pulsed corona discharges.

In contact glow discharge electrolysis a continuous DC voltage of around 0.5 kV is applied to a thin wire anode in contact with the water surface while the cathode is dipped in water and isolated from anode through porous glass. A sheath of vapour forms around the anode through which current flows as a glow discharge. Charged species in the plasma (present in the discharge gap or sheath of vapour around the anode) are accelerated due to the steep potential gradient and enter the liquid phase with an energy that may be as high as 100 eV. In the case of contact glow discharges almost all the species in the discharge zone. In silent discharges and pulsed corona discharges, like described below, only free electrons gain high energy and the rest of the heavier charges and neutrals remain close to room temperature and the plasma generated in this way is called a cold plasma or a non-equilibrium plasma. In a dielectric barrier discharge reactor the electrical discharges take place between electrodes where at least one of the electrodes is covered with a thin layer of dielectric material, such as glass or quartz. In the case of the water treatment application of dielectric barrier discharge reactors, a layer of water around one of the electrodes acts as a dielectric. Usually an AC voltage of around 15 kV is applied across the electrodes. In both cases of contact glow discharge electrolysis and dielectric barrier discharge reactors the electrical discharges take place in the gas phase in close proximity to the water surface. They require an intense electric field for electrical discharge to take place in water. Such a high electric field is possible by applying high-voltage pulses of 15–100 kV, usually of positive polarity with a sharp rise time (a few nanoseconds) and short duration (nano to microseconds) in a pulsed corona discharge reactor. Furthermore, the pulsed corona discharges are effective disinfectants and they can also take place in the gas phase in close proximity to the water surface. This is why most of the studies on water treatment are carried out using pulsed corona discharge reactors and the available industrial scale units are also based on this technique. A pulsed corona discharge reactor requires a pulse generator and a reactor. The pulse generator is commonly based on the discharge of a capacitor on a low-inductance circuit through a spark gap switch. The reactor is comprised of metallic electrodes and fittings made of some insulating materials. The electrodes are usually in a needle–plate arrangement where a needle is connected to the high-voltage terminal and the plate is earthed. The needle is covered with an insulator, for example Teflon, and only its tip is exposed, so that an intense electric field may develop at the needle tip.



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## VI. SOLID WASTE TREATMENT

The treatment of solid waste by plasma is usually associated with thermal utilization of waste. Among those, gasification technique is rather well researched and applied in industrial scale.

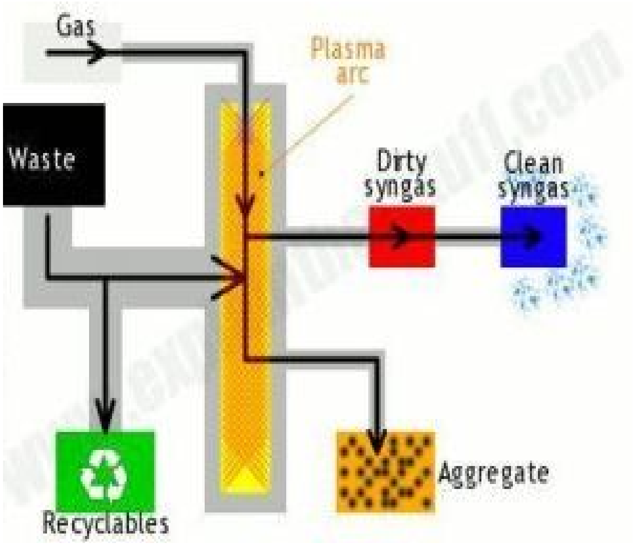


Fig6. Solid Waste Treatment Using Plasma Arc

Plasma gasification has been in use since the late 1800s in the metal industry, expanding into the chemical industry in the 1900s. Today, plasma gasification technology is again expanding to diversify feed stocks. Plasma torches heated up to 20,000°C gasify feedstock. The by-products include steam, electricity, syngas and rock wool. Very little is remaining of the feedstock once gasified. Gasification is not incineration; in plasma gasification the waste input is pyrolysed by the high temperature into its constituent elements: H2, O2, C, N2 etc. The converter conditions are controlled so that prior to exit, the elements reform into the desired syngas that is rich in CO and H2. The materials that cannot be converted into syngas, such as metal, glass, rock and concrete are vitrified to produce an inert slag. The slag is 1/250 of the volume of the processed solid waste. Plasma arc gasification is a waste treatment technology that uses high electrical energy and high temperature created by an electrical arc gasifier. This arc breaks down waste primarily into elemental gas and solid waste (slag), in a device called a plasma converter. The process has been intended to be a net generator of electricity, depending upon composition input wastes, and to reduce the volumes of waste to being sent to landfill sites. Four types of gasifier processes are currently available for commercial use: counter-current fixed bed, co-current fixed bed, fluidized bed and entrained flow. New technology considered is the high temperature conversion of waste reactors. Since waste treatment technologies are not an object of PlasTEP project, they are not reviewed here in detail.

## VII. CONCLUSION

Thermal plasmas offer some unique advantages for the destruction of hazardous wastes compared to classical combustion. The high energy density and temperatures associated with thermal plasmas and the corresponding fast reaction times offer the potential of large throughputs in a small reactor. Finally, thermal plasmas can easily be integrated into a manufacturing process which generates hazardous wastes, thus permitting the destruction of the wastes at the source.

## VIII. ACKNOWLEDGEMENT

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