ABSTRACT

Environmental Applications of Plasma Physics:
Aerosolized Nanoparticle Decontamination using an Inductively Heated Plasma Device

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Materials with sizes on the nanometer scale are highly desired for their unique size-dependent properties that prove beneficial in industrial and consumer processes. However, the increased use of nanomaterials could lead to an increased risk of exposure to materials that are detrimental to human health. The link between inhalation of nano-scale particles and diseases of the lungs are of particular concern. In an effort to reduce the risk of exposure to aerosolized nanometer sized particles, a new method is recommended to remove nanoparticles from the air using plasma. It is proposed that the test system subject SiO_2 nanoparticles to plasma treatment in an inductively heated plasma generator to study the effectiveness and efficiency of plasma as an aerosolized nanoparticle decontamination mechanism. The treatment system is a multi-step process involving the generation and characterization of nanoparticles and plasma treatment, followed by the collection and disposal or distribution of remaining particles.

Environmental Applications of Plasma Physics and
Aerosolized Nanoparticle Decontamination using Inductively Heated Plasma

by

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A Thesis

Approved by the Department of Physics

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Submitted to the Graduate Faculty of
Baylor University in Partial Fulfillment of the
Requirements for the Degree
of

Master of Science

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May 2018

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CHAPTER ONE

Introduction

Introduction to Particulate Matter

Advancements in industrialization and urbanization have caused an unfortunate byproduct: air pollution. Perceived as a modern-day curse, air pollution is broadly defined as the emission of harmful substances to the atmosphere[1]. Over time, high rates of air pollution emissions lead to poor air quality in the surrounding area, which can lead to negative health effects for the people breathing that air. The American Lung Association's 2017 State of the Air Report declared "nearly four in ten people live in an area where the air is unhealthy[2]." Unhealthy air, in this context, is defined as air with an Air Quality Index (AQI) value over 100[3]. One of the largest contributing factors to poor quality of air in the United States, and across the world, is particulate matter pollution. Air can be contaminated with a variety of substances, but fine and ultrafine particulates are of particular concern due to their complicated composition, high concentration, and small size. Inhaled ultrafine particulates have been linked to diseases such as dementia, angina, and inflammation of the respiratory tract [4,5,6]. The most notable health effects of inhaled ultrafine particulates appear in the lungs and respiratory system[7,8].

Air Quality

Air quality measures the condition of air at a particular place and time in terms of ambient air pollution[9]. Air quality is in constant flux. Time of day, topography and weather conditions can impact the immediate air quality in a particular area[10]. While certain conditions affecting air quality are intrinsic, or beyond human control, many human activities are causing a rapid decrease in worldwide air quality[11]. Common daily activities like driving cars and heating buildings release byproducts into the air that become harmful to humans and the environment[12].

Nitrogen dioxide, sulfur dioxide, ozone, and particulate levels are all considered in the assessment of air quality[13]. Figure 1 shows satellite-derived maps of the concentration levels of total ozone over the South Pole, nitrogen dioxide concentrations worldwide, and fine particulate matter worldwide. Figure 1A shows that the concentration of ozone is relatively low over the poles, indicated by purple and blue colors, and increases towards the equator. Figure 1B indicates worldwide levels of nitrogen dioxide in the atmosphere. High concentrations are visible over parts of the United States, China, and Europe. Figure 1C represents the levels of fine particulate matter in the atmosphere. Sand, a natural fine particulate, is mainly responsible for the high concentrations over Northern Africa[14]. High particulate concentrations in other areas, like in the area around Beijing, China, are believed to be related to human activities that release particulates into the environment. Higher concentration areas are seen in regions that are densely populated where human activities produce larger amounts of pollutants than in less dense regions.

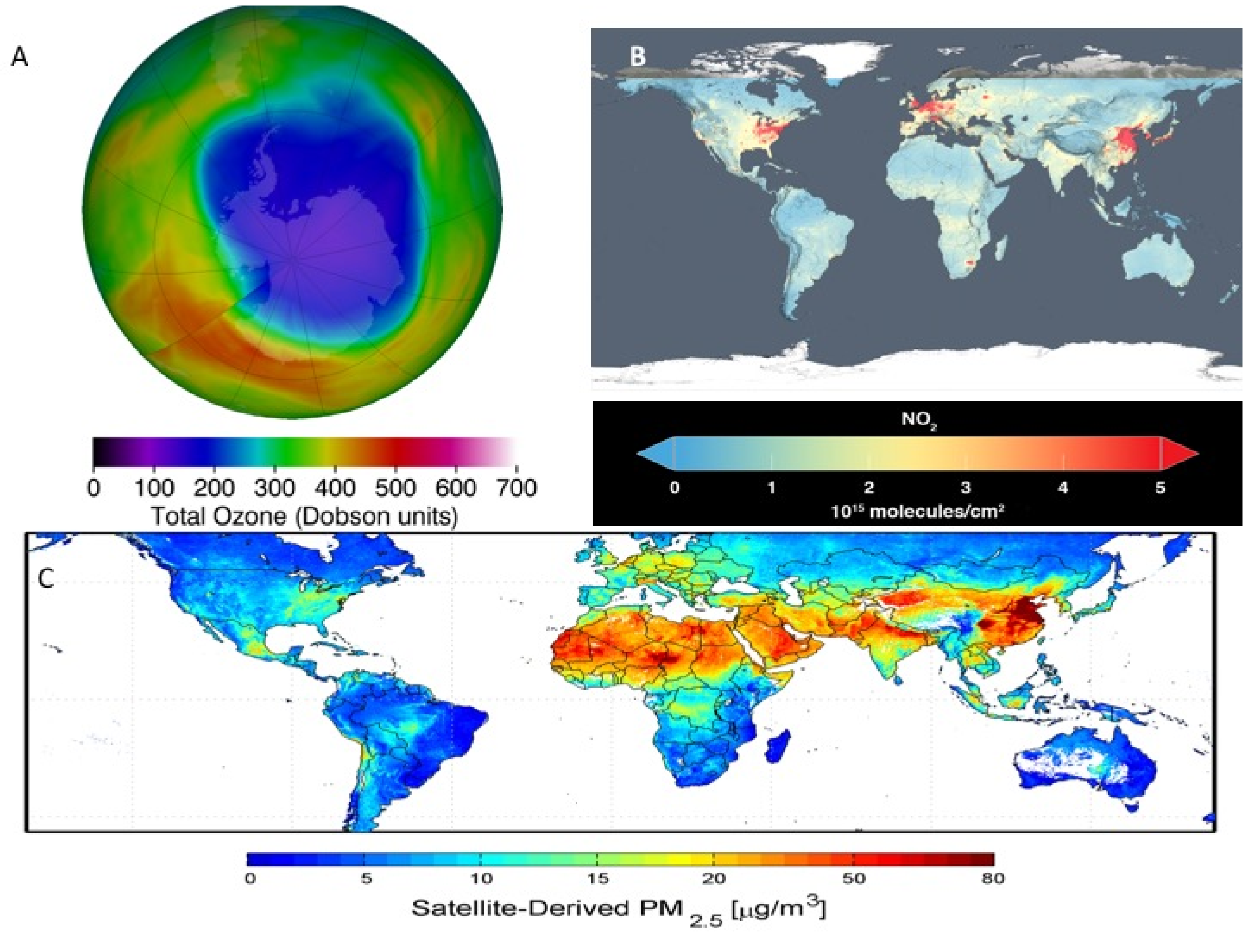

Figure 1: Levels of air pollutants in the atmosphere. A) Ozone B) Nitrogen Dioxide C) Fine Particulate Matter. Images courtesy of NASA.

Particulate Matter Pollution

One of the leading causes of the decline in global air quality is particulate matter pollution, which can refer to both microscopic solid particles and liquid droplets suspended in the air [11,15]. Particulate matter pollution is a complex mixture containing particles of varying shapes and sizes that when inhaled can have detrimental health effects on the lungs and heart[11]. Particulates can vary in size from small nanometer-sized aerosols up to micrometer-sized grit like dust, dirt, soot, and smoke.

There are several ways to categorize pollutants. Particulate matter pollution is most often categorized by size or by source. Visible (particles greater than10 micrometers) and respirable (particles less than 10 micrometers) particulates are the broadest size groups[16]. Respirable particulates can be further divided into coarse and fine particles. Coarse inhalable particles are particles with diameter between 2.5 micrometers and 10 micrometers[12]. Figure 2 represents the size categorization of air pollutants[16]. Dust, pollen, and mold are considered coarse inhalable particles. Fine inhalable particles have diameters smaller than 2.5 micrometers[11]. Combustion particles, organic compounds, and aerosolized metals are examples of fine inhalable particles. Coarse inhalable particles and fine inhalable particles are the main subgroups of particulates considered for regulation of air pollution due to their significant health impacts, but another category of particulates, ultrafine, also exists. Ultrafine particles have diameters less than 100 nanometers[17]. The main source of ultrafine particulate matter worldwide is vehicle combustion.

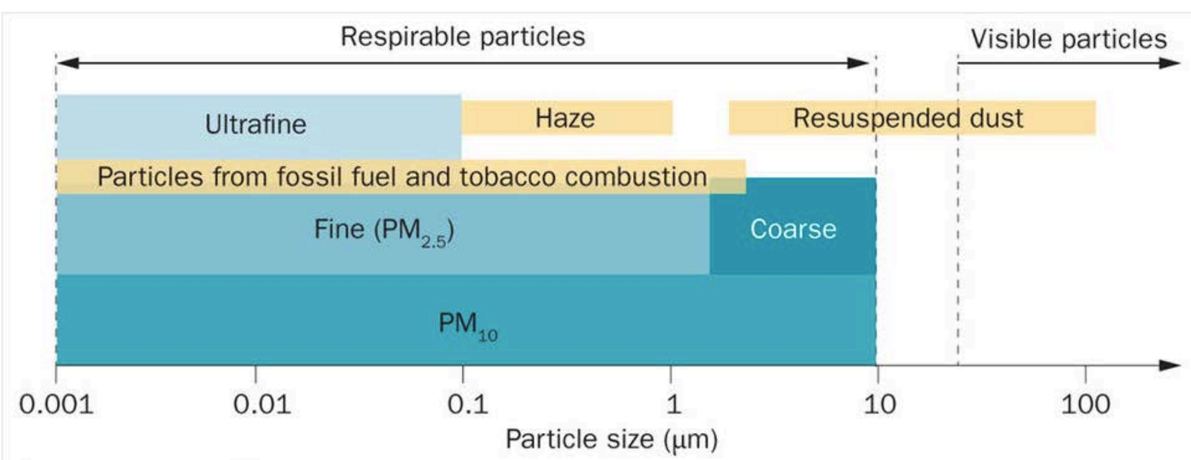

Figure 2: Size categorization of air pollutants. Reprinted by permission from Springer Customer Service Centre GbmH: Springer Nature, Nature Reviews Cardiology, (Environmental factors in cardiovascular disease, K. Cosselman), (2015).

Figure 3 illustrates the size ranges of aerosolized particulates[11]. To remain suspended in the air, particulates must be very small. Even in comparison to the width of a single strand of hair, particulates are tiny: on average five coarse particles can fill the diameter of a single strand and another four fine particles can span the diameter of a single coarse particle.

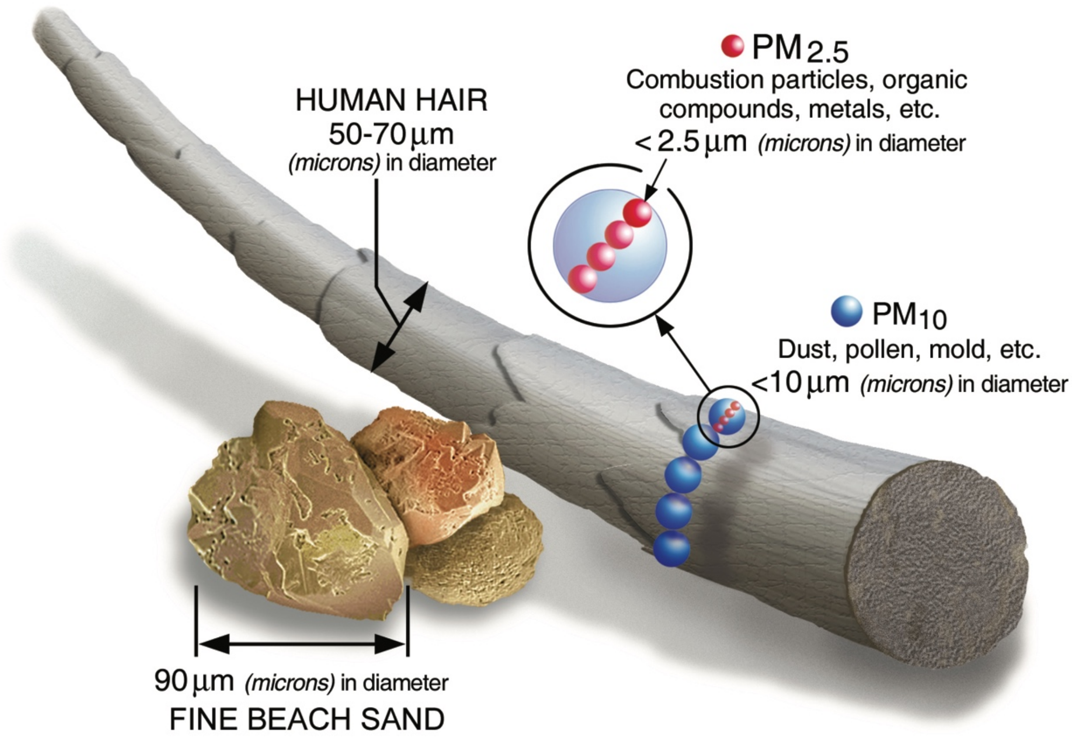

Figure 3: Typical particle sizes of a grain of sand, a strand of hair, and fine and coarse particulates. Image courtesy of the EPA.

Particulates can also be categorized based on whether they are formed through natural processes or are man-made. Some natural sources of particulate matter pollution are dust, pollen, sea spray aerosols, and particulate matter emitted from volcanic eruptions and seismic activity[12]. Natural sources of particulate matter contribute to air pollution and can have negative effects on human health and the environment, but most of the particulate pollution that damages human health and the environment comes from human-made sources and the resulting chemical reactions. These types of particles can be emitted directly from the source, and are known as primary emissions, or can be formed in the atmosphere through reactions between gaseous emissions and other compounds in the air and thus are called secondary emissions.

The main sources of primary emissions are combustion, construction, demolition, industry, and agriculture. Combustion of coal, oil, and wood all contribute to particulate matter pollution[12]. Burning coal for heat and energy releases carbon monoxide and other particulate matter into the air. Oil combustion fuels vehicles, which emit exhaust fumes into the atmosphere. Wood combustion is also used for heat and generating power and increases the amount of soot in the air. Construction not only uses vehicles that contribute to pollution from exhaust emissions, but also releases cement dust particles into the air. Demolition releases dust particles into the atmosphere which can be carried long distances by the wind. The manufacturing processes used industrially release toxic fumes. Agriculture uses large diesel vehicles that contribute to exhaust fumes. Pesticides and chemicals are also released into the air during agricultural processes[15]. Each source contributes directly to the overall particulate pollution in the air. Table 1 summarizes the different ways to categorize air pollutants[18].

Table 1: Classification of Air Pollutants

Size	Source	Way of Reaching the Atmosphere	Space Scale	Physical State	Chemical Composition
Visible (> 40 μm)	Combustion	Primary	Indoor	Solid	Sulfur-containing
Coarse (< 10 μm)	Construction	Secondary	Regional	Liquid	Nitrogen-containing
Fine (< 2.5 μm)	Demolition		Global	Gaseous	Carbon-containing
Ultrafine (< 0.1 μm)	Agriculture				Halogen-containing
	Industry				Metallic
	Natural				Radioactive

Most pollutants are only emitted into air, water, or soil, but over time, cycle through to impact other areas. Combustions particles, vehicle exhaust fumes, and dust from construction and mining are released directly into the air while the main soil pollutants come from sewage sludge and fertilizers. Water pollution typically comes from waste runoff. Figure 4 represents the cyclic process that occurs between the air, water, and soil. All three aspects are connected to one another, so pollution of one can impact any or all of the others. Pollutants emitted into the air are particularly harmful as they can be transferred to both water and soil through deposition. Pollutants can evaporate from water into the air or percolate through the surrounding soil. Pollutants on and in soils can be picked up by wind to contaminate air. Leaching is the process through which contaminated soils can pollute water. As water comes into contact with contaminated soil, the pollutants can dissolve into the water or be carried away if the water is moving. Any polluted source has the potential to transfer pollutants to living beings. Humans and other living things can then take in pollutants through inhalation, ingestion, or direct contact with polluted sources.

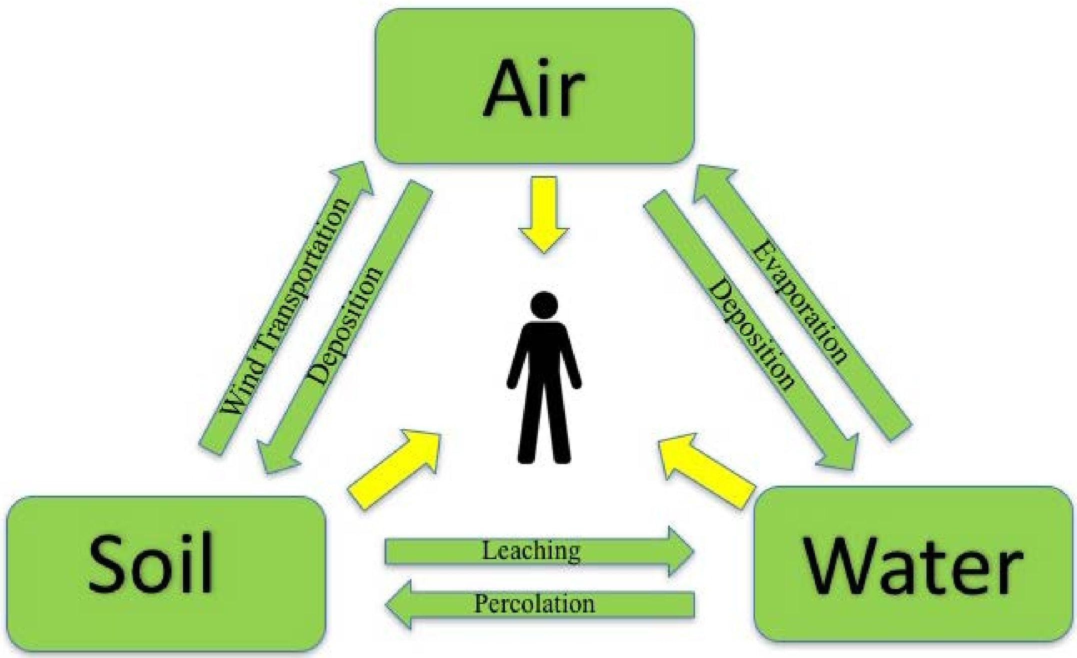

Figure 4: Mechanisms by which particulate matter pollution enters the environment. Particulate matter circulates through the environment between air, water and soil. Humans take on particulate matter by ingesting contaminated food or water, inhalation particulate matter from the air, or by contact with a source containing particulate matter.

While primary pollutants are emitted directly into the air from a source, secondary pollutants are formed when primary pollutants react in the atmosphere[19]. Secondary pollutants form by the processes of nucleation, coagulation, and condensation as shown in Figure 5. The emitted particulate matter reacts with chemicals in the atmosphere to form new particles in a process called nucleation, as these new particles become the nuclei for the formation of larger particles. Once the nuclei are formed, particles begin to coagulate on the nuclei, combining to form larger particles. Coagulation is most effective when many small particles are in close contact. These particles collide and stick together until they form a particle with a surface area large enough for condensation to occur. As the surface area increases, gas and vapor molecules begin to condense on surface of the particle further increasing its size. Coagulation and condensation are only efficient modes of growth for small particles as other forces begin to take over when the particles reach the micrometer size. Sulfates and nitrates are the most common secondary pollutants[11].

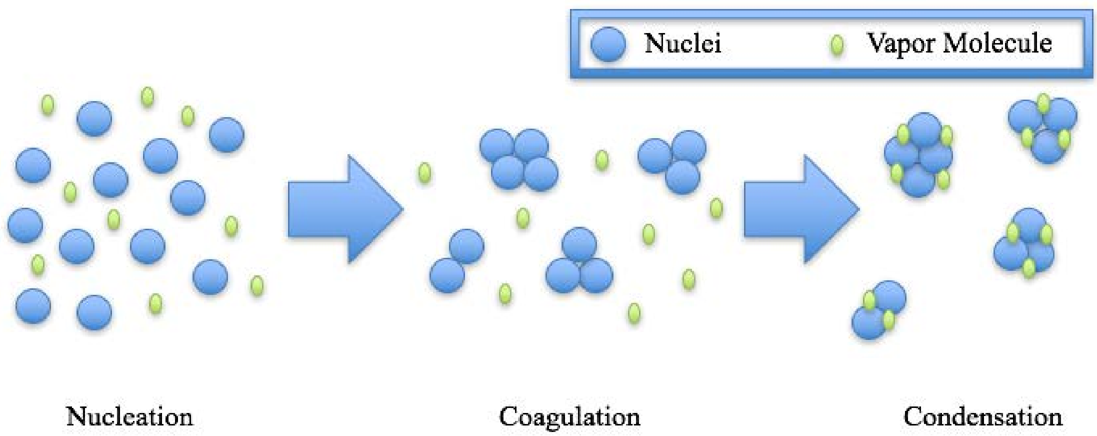

Figure 5: Secondary emission formation process. Particulate matter reacts with particles in the air to form nuclei. The nuclei coagulate together forming particles with larger surface areas that allow for condensation of gas and vapor molecules to further the growth of the particle.

Effects of Particulate Matter on the Body

Inhalation of fine particulate matter (particles with diameters smaller than 2.5 micrometers) causes the greatest health risk to humans[11,12,13]. Long-term exposure to particulate matter pollution has been linked to premature death, heart attacks, irregular heartbeat, asthma, decreased lung function, and increased respiratory symptoms[12]. Even short-term exposure has been shown to cause irritation to the eyes and throat[6]. Particulate matter pollution is especially harmful to sensitive populations like children, the elderly, and pregnant women[12]. High exposure levels in pregnant women have been linked to premature delivery and birth defects in the baby[15]. According to the World Health Organization, exposure to particulates has been linked to 25% of lung cancer deaths, 8% of chronic obstructive pulmonary disease (COPD) deaths, and 15% of ischemic heart diseases including angina, myocardial infarction, and sudden heart death[20].

The body's defense mechanisms can filter out larger particles more easily than smaller ones, which are able to pass through some of the body's defense systems and cause damage[12]. Certain organs are better able to protect against small particles. The skin, for instance, is not easily penetrated by fine particulate matter while the lung's defensive barriers are more permeable to fine particulates[21]. Inhaled particulate matter interacts with the air-blood barrier structure that controls gas exchange in the lungs. This barrier is thin and provides a relatively high chance for fine particulate matter to pass through the barrier and enter other parts of the body[22]. Studies comparing exposure to particulates and hospital admission rates for respiratory and cardiovascular diseases found high correlation rates between admissions and areas with high fine particulate matter pollution, while no statistical correlation was found between admissions and coarse particulate matter pollution[23,24].

While diseases associated with fine particulate matter are most prevalent in the lungs and heart, ultrafine particulate matter in the brain has been linked to an increased risk for certain conditions. For example, ultrafine magnetite particles, which enter the air through combustion processes in vehicles, have been linked to Alzheimer's, dementia, and epilepsy[4]. The electrochemical reactivity of magnetite is believed to be a key link to these conditions. Figure 6 shows major organs of the body and the specific conditions of each organ that are linked to exposure to fine and ultrafine particulate matter.

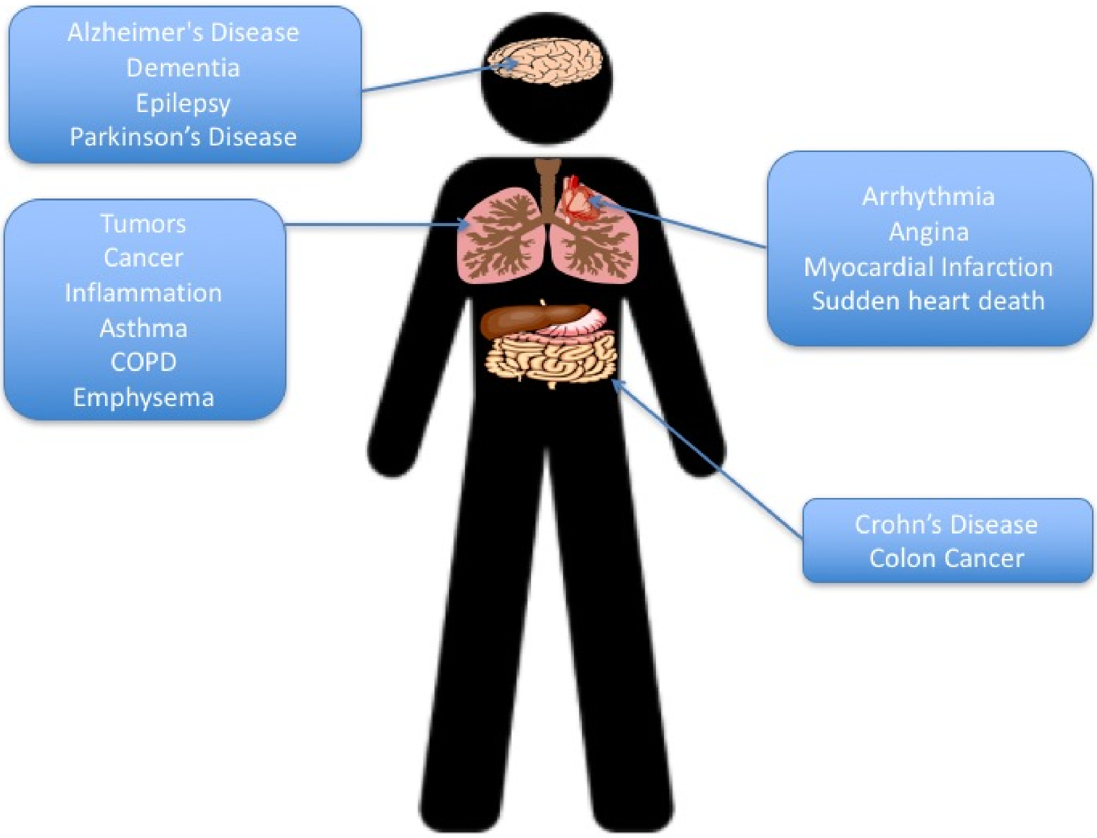

Figure 6: Diseases and conditions linked to inhalation of fine and ultrafine particulate matter pollution. The major organs affected are the brain, lungs, heart, and intestinal tract.

Epidemics

Poor air quality is linked to a wide variety of diseases, but a few of these diseases have gotten to the point of being classified as epidemics. The prevalence of asthma and COPD has increased recently, especially in developed countries. Since genetic changes in a population require thousands of years of adaptations, the increase in cases of asthma and COPD are likely environmental[7].

Asthma is a chronic disease of the lungs characterized by wheezing, coughing, and chest tightness[25]. Certain components of air pollution mix with natural allergens in the air to worsen the symptoms of asthma. The small particulates in air pollution can interact with pollen and other plant-derived allergens that are able to reach peripheral airways and induce asthma symptoms in sensitive subjects. Once in the airways, particulate pollution has an inflammatory effect allowing for easier penetration of natural allergens into cell membranes[7].

The prevalence of asthma (Figure 7) has increased in industrialized countries. The number of reported adults with asthma in the United States went from 20 million in 2001 to 25 million in 2009[26]. Worldwide, nearly 300 million people suffer from asthma symptoms, a number that is expected to increase by more than 100 million by the year 2025[26]. Nearly 1 in 250 deaths worldwide are linked to asthma[27]. Environmental factors are believed to be a reason for the increase, as small-scale studies have shown there is a positive correlation between fine particulate matter pollution and emergency room emissions for asthma symptoms[28,29].

COPD, characterized by progressive airflow limitation to the lungs, is one of the leading causes of death worldwide. While smoking is a known major cause of COPD, one study analyzing COPD cases by country shows that individuals who have never smoked make up between 14-30% of cases, indicating that other environmental factors are also important risk factors[30]. Out of all the lung conditions, COPD is most highly correlated with outdoor air pollution[31]. The repetitive action of inhaling polluted air leads to the chronic inflammation associated with COPD. A major source of pollutants responsible for inflammation and COPD is combustion of fossil fuels[31]. Figure 8 shows the number and distribution of deaths associated with COPD for the year 2010[8]. Comparing with the global distribution of fine particulate matter pollution (Figure 1C), there are noticeable correlations. High levels of fine particulate matter exist in eastern Asia, particularly China and Northern India. This region is also where the some of the highest mortality rates are shown in Figure 8. Regions displaying more moderate levels of fine particulate matter pollution exhibit lower COPD mortality rates.

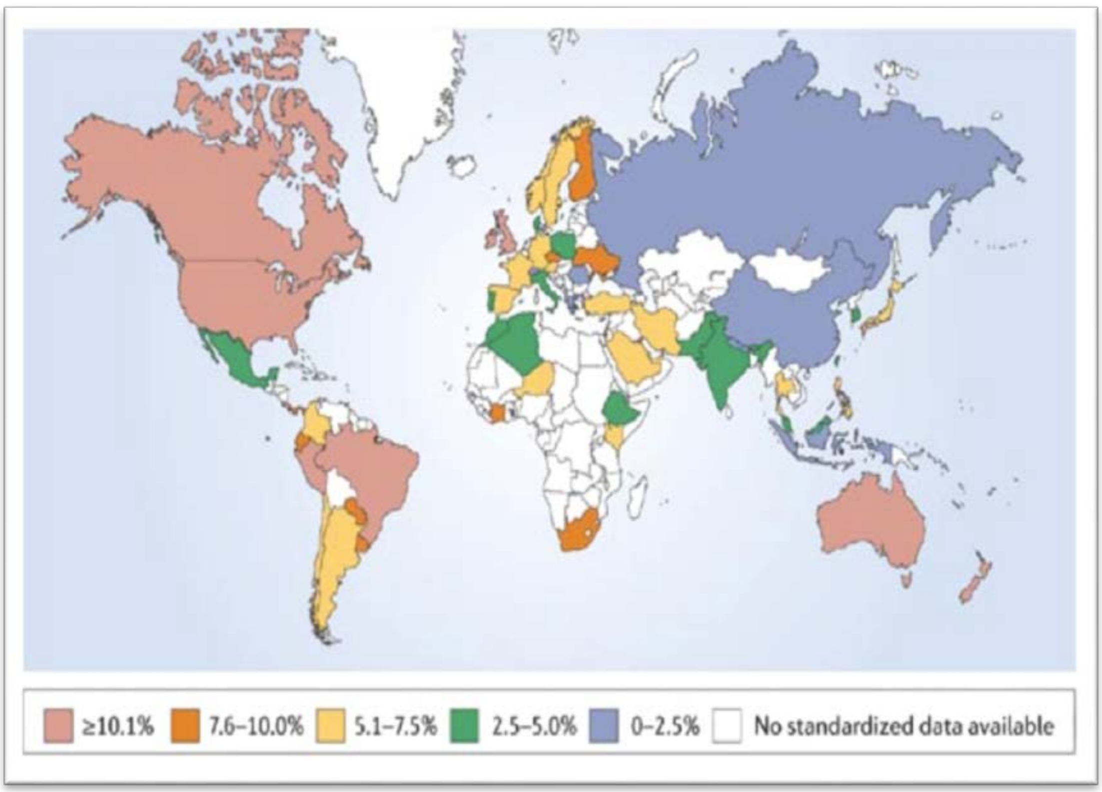

Figure 7: Worldwide prevalence of asthma. Percentile ranges represent the percent of individuals with asthma per country. Reprinted by permission from Springer Nature: Springer Nature, Nature Reviews Immunology, The increase in the prevalence of asthma and allergy: food for thought, Graham Devereaux, 2006.

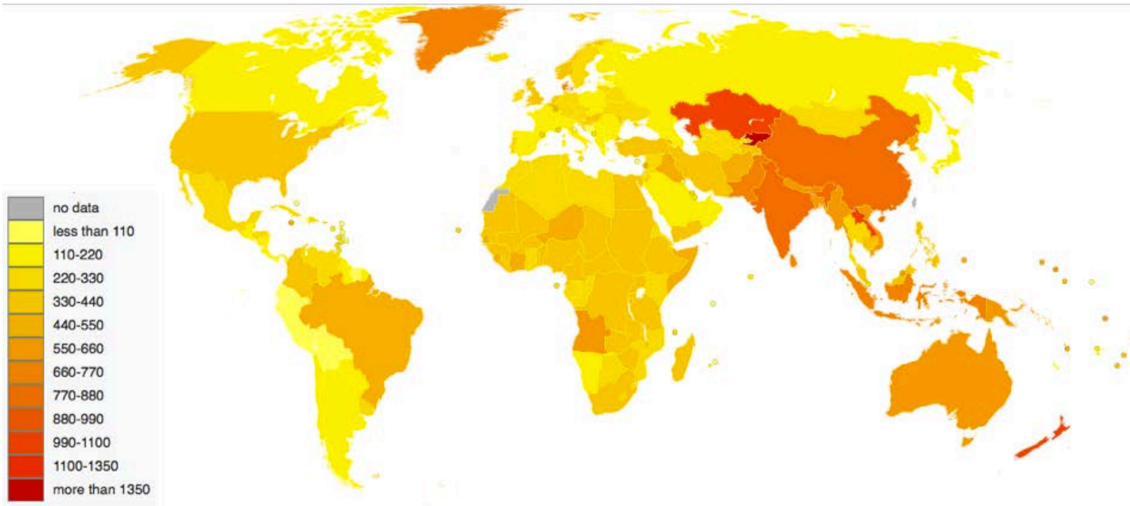

Figure 8: COPD deaths per 100,000 people by country in the year 2010. Figure courtesy of Lokal_Profil, CC BY-SA 2.5, https://commons.wikimedia.org/w/index.php?curid=8443664.

Nanoparticles in Society

Nanoparticles are microscopic particles with at least one dimension less than 100 nm[32]. Because of the overlapping size classification, nanoparticles are a subgroup of the ultrafine particulates classification[33]. For the context of this paper, the term nanoparticle will refer to engineered nanoparticles intentionally produced by man while ultrafine particle or nanoparticulate will refer to nano-scaled particles created by natural processes[34]. A comparison of ultrafine particles and nanoparticles is shown in Figure 9[33].

Nanoparticles are highly desired for their size dependent qualities such as creating stronger, lighter, cleaner, and more durable surfaces. These characteristics make research and development of nanoparticle applications desirable for manufacturing, medical and environmental technologies, and cosmetics.

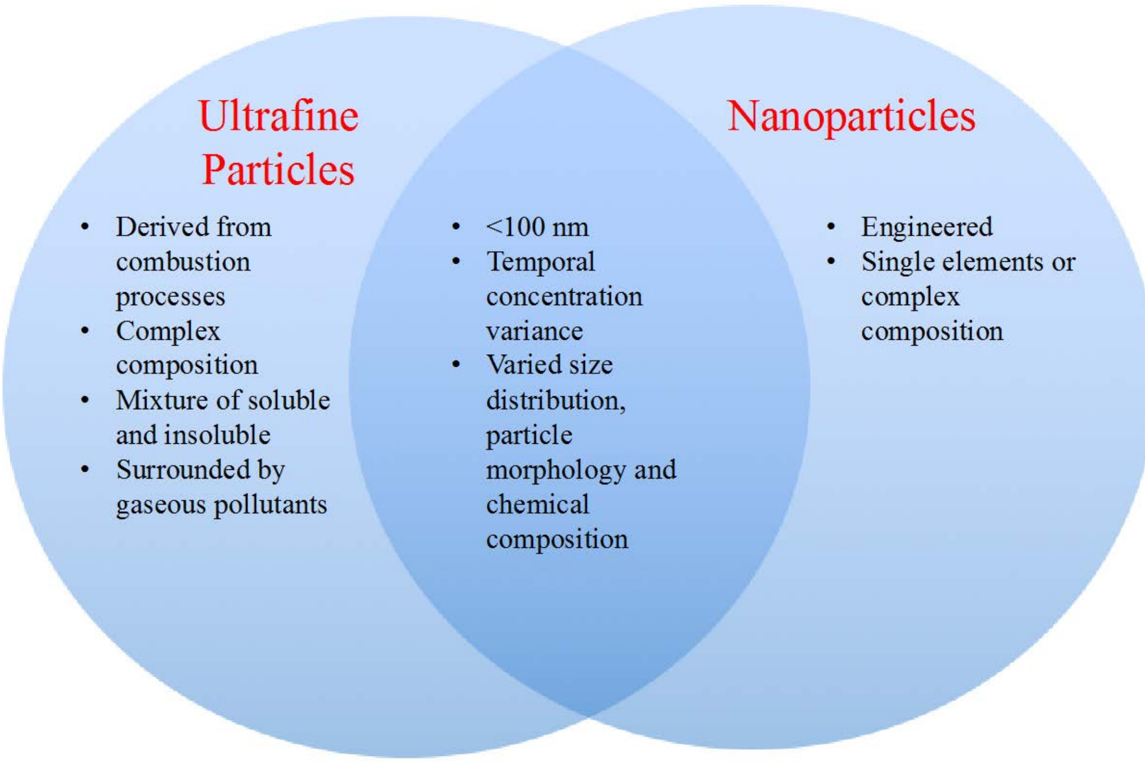

Figure 9: Comparison of the physiochemical properties of ultrafine particles and nanoparticles

Nanoparticles are being incorporated into many consumer products. Currently, nanoparticles are used for enhancing clothing, sunscreen, cosmetics, food packaging, dietary supplements, and other everyday items. Research is being conducted to incorporate nanoparticles into the fields of renewable energy, computers, communication, pollution control, agriculture, and medicine. Table 2 lists of some of the most commonly produced nanoparticles, their field of use, and their use[35].

Table 2: Common Nanoparticles and Their Uses

Nanoparticle	Field	Use
Polymeric micelle	Medical	Drug delivery to tumors
Iron oxide	Medical	Breakup bacterial clusters
Cerium oxide	Medical	Antioxidant
Silicon carbide	Manufacturing	Production of strong, lightweight material
Nickel	Medical	Wound healing
Silicate	Manufacturing	Protective barriers and films
Zinc oxide	Manufacturing	Industrial coatings
Silver	Cosmetics	Anti-bacterial, odor resistance
Copper tungsten oxide	Environmental	Break down oil
Iron	Environmental	Remove groundwater pollutants
Carbon	Manufacturing	Fuel cells
Silicon	Manufacturing	Lithium-ion batteries
Gold	Medical	Drug delivery to tumors
Zinc oxide	Cosmetics	Reduce UV exposure to skin

The research and implementation of nanoparticles is a rapidly growing field[33]. At the same time, ultrafine particles, under which nanoparticles are classified, pose a greater risk to human health due to their small size and ability to bypass the body's defense mechanisms. In light of this, the effects of nanoparticles on the body are also being investigated. Humans can come into contact through a variety of ways both in an occupational setting and through the use of consumer products.

In the United States alone, an estimated two million people work with nanoparticles[36]. Though there is potential for any individual to be exposed to nanoparticles, the individuals working with nanoparticles are most at risk for the harmful effects extended nanoparticle exposure can cause. Individuals working in an environment that could lead to exposure to nanoparticles are protected through the Occupational

Safety and Health Administration (OSHA). OSHA classifies nanoparticles as a threat when inhaled due to their ability to be deposited in the respiratory tract, which can lead to inflammation in the lungs and damage to cells and tissue[37]. Nanoparticles are also listed as a possible carcinogen[38]. Nanoparticles are able to penetrate cell membranes and damage the cell structure and function. Outside of internal bodily risk imposed on workers by nanoparticles, there is also a greater risk of fire and explosion due to the chemical catalysts and combustibility of nanomaterials. Currently, OSHA only recommends standards for carbon nanofibers and titanium dioxide. OSHA advises minimizing exposure through a number of specified best practices such as engineering controls, personal protective equipment, and medical screening of workers[39].

Consumer health is also of concern as the use of nanoparticles increases[40]. There are currently very few regulations governing the use and reporting of nanoparticles in a product.

Environmental Remediation using Plasma

The scientific community has begun looking into ways to use the technological advances to improve human health and the environment. Plasma, or ionized gas, is being studied for its many uses in environmental remediation and medical applications due to its wide range of temperatures and lack of required catalysts. Current environmental applications of plasma involve decontamination of microorganisms from surface materials, water, and air. Not only does plasma have high decontamination efficiency and economic benefits, plasma processing typically does not yield hazardous byproducts and requires fewer chemical additives than conventional remediation methods[41, 42]. The successful application of plasma for fine particle decontamination in water and on surfaces makes it a good candidate for decontamination of nanoparticles from the air.

One potential device that could fill these needs is an inductively heated plasma generator (IPG), such as Baylor University's IPG6[43]. This device has the ability to generate plasma with the necessary energy to generate the decontamination reactions in a confined environment. An IPG is an advantageous way to generate plasma because it does not use an electrode, allowing for a larger variety of gases, including chemically reactive gases, to be used for generation. IPGs also allow larger volumes of gases to be studied at higher powers for longer time periods compared to other methods of plasma generation[44]. This paper will present the current applications of plasma technology for environmental remediation and human health while describing the theory behind the plasma and nanoparticle systems in an effort to design an effective mechanism of nanoparticle contamination remediation using an inductively heated plasma generator. Chapter II will cover the basic plasma and nanoparticle theory that impacts the plasma nanoparticle decontamination processes. Chapter III will discuss current environmental applications of plasma. Chapter IV will set up the parameters for using an IPG for decontamination of aerosolized nanoparticles.

CHAPTER TWO

Theory

Plasma

There are four states of matter: solids, liquids, gases, and plasma[45]. The density of the materials determines the main structural differences between the states. Figure 10 shows common examples of each state of matter; phase changes occur as energy is added to the system. For solids, particles are tightly packed, unable to move freely, and occupy a definite volume. Liquids do not have the definite arrangement of particles like solids, but the particles are still tightly packed and occupy a definite volume. Gases have large particle spacing and can occupy an indefinite volume[45].

Gases become plasmas when energy is introduced to the system allowing electrons to break free from the nucleus[46]. Plasma consists of positively charged ions, electrons, and neutrals like atoms, molecules, and radicals[47]. Common examples of plasma shown in Figure 11 include the Northern Lights, fluorescent lights, lightning, and stars.

The free-flowing electrons characteristic of plasma give the state its unique properties. The presence of the free charge carriers allows plasma to react to electromagnetic fields and conduct electrical current[47] so that plasma can be accelerated, contained, and heated by the proper configuration of electric and magnetic fields[44]. The separation of ions and electrons produce electric fields while the motion of the ions and electrons generate magnetic fields[48].

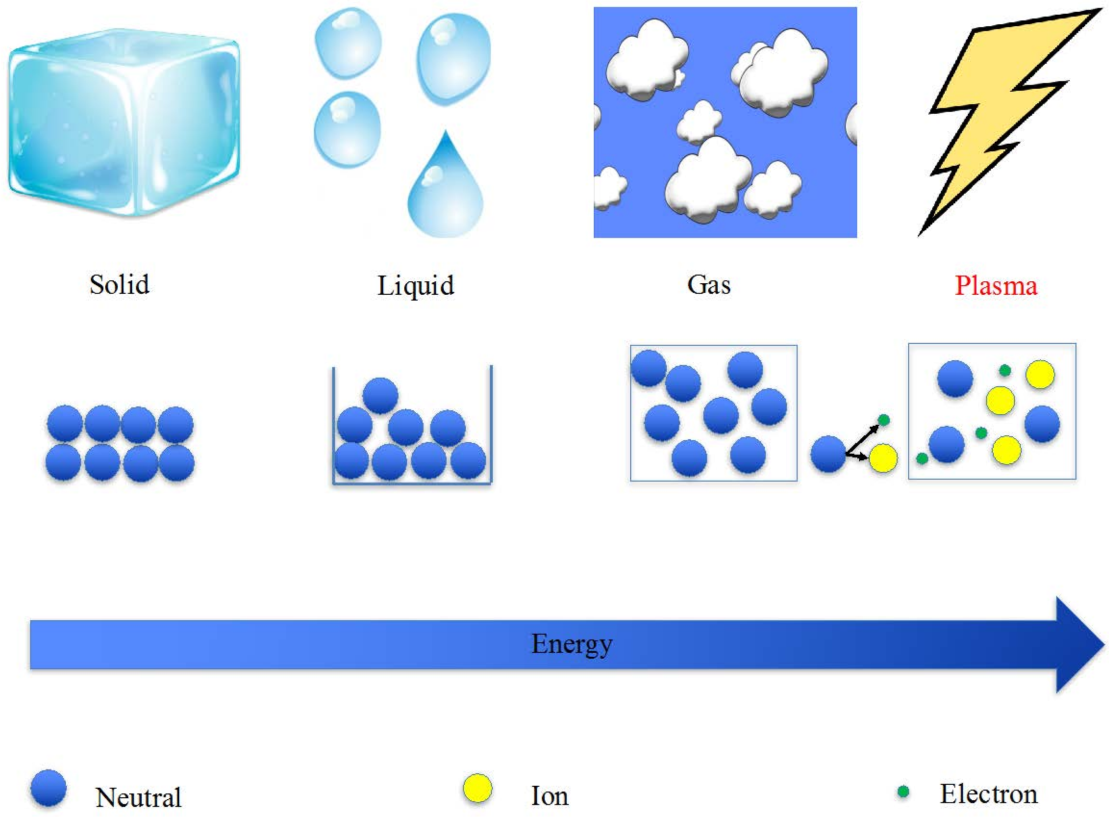

Figure 10: Physical states of matter and their molecular composition

While a generalized definition of plasma could apply to almost any ionized gas, there are two restrictions an ionized gas must meet to be truly considered plasma. The first requirement is that of balanced charges or quasi-neutrality. The second requirement involves a natural shielding effect of charged particles, which is characterized by the Debye length[49]. The degree of ionization, number densities of the plasma species, and temperature impact the quasi-neutrality and shielding conditions.

Figure 11: Common examples of plasma: a) The Northern Lights b) A neon sign c) Lightning d) The Sun. Images courtesy of NASA.

Number Density

Since plasma consists of electrons and various ions, it is necessary to define the number density for each individual species[50]. The number density is the number of a particular type of particle present in the plasma per cubic meter[51]. Plasma is characterized by not just one type of particle's number density, but by the number densities of each individual species[50]. The number density of particle type, *s*, is given by

$$\int_{-\infty}^{\infty} f_s(\mathbf{v})\mathrm{d}v_x dv_y dv_z = n_s \qquad (1)$$

where $f_s(\mathbf{v})$ is the distribution function

$$f_s(\mathbf{v}) = n_s \left(\frac{m_s}{2\pi\kappa T_s}\right)^{3/2} e^{-\frac{m_s v^2}{2\kappa T_s}} \qquad (2)$$

in which v is the velocity, m_s is the mass of the particles, κ is Boltzmann's constant, and T_s is the temperature.

Degree of Ionization

Ionization, the gain or loss of an electron from an atom, is a necessary condition for plasma to exist[52]. Gases begin exhibiting characteristics of plasma, like electrical conductivity and response to magnetic fields, when even just one percent of the particles are ionized [53]. Ionization degree, η_i, describes the ratio of ionized particles to all particles, including neutrals, and is a function of the number density of the neutral gas particles (n_a) and the number densities of all charged gas particles (n_z)

$$\eta_i = \frac{\sum_z n_z}{n_a + \sum_z n_z}. \quad (3)$$

where z is the charge number of a positive ion.

For the typical case, $\eta_i << 1$ (a partially ionized plasma ranging from $10^{-5} < \eta_i < 10^{-3}$)[47]. Gas tube discharges and neon lights are examples of partially (or weakly) ionized plasma. Fully ionized plasma has an ionization degree close to one (100% ionization)[54]. The interplanetary medium and stellar interiors are typically fully ionized plasma.

Quasi-Neutrality

One of the defining characteristics of a plasma is the condition of quasi-neutrality. The number density of the ions as a whole is approximately equal to the number density of the electrons, a condition referred to as quasi-neutrality [47], which can be expressed mathematically as

$$n_e \approx \sum_z Z n_z \quad (4)$$

where Z is the charge number of a positive ion and n_z is the number density of z-times charged ions[47]. Local regions of positive and negative charges may exist in the plasma, but throughout a large volume, the number density of the electrons and ions are nearly the same[49].

Temperature

Another important plasma characteristic is the temperature of the ions and electrons, which is proportional to the average kinetic energy of the particles[50]. A hot, or thermal, plasma has a uniform temperature wherein the ions and electrons have the same kinetic energy[55]. In general, thermal plasma is fully ionized and approaches local thermodynamic equilibrium, requiring a detailed balance between each plasma process and its reverse process. Plasmas in thermodynamic equilibrium are characterized by their high temperature, pressure and number densities[56].

For a plasma to be in thermodynamic equilibrium, certain conditions must be met. The first condition is that the temperature of all species must be equal[50]. To be in thermodynamic equilibrium, the population of excited states obeys a Boltzmann distribution, which gives the probability of a given particle within a species to have a certain energy based on that species' temperature. For a constant temperature, the velocity distribution of each species (Equation 2) in the plasma is Maxwellian[56]. This distribution function indicates the speed a particle species in the plasma will most likely have for a given temperature.

For plasma to be in thermodynamic equilibrium, the plasma volume needs to be large enough that the central region is homogeneous and not subject to boundary conditions[57]. This ideal situation can be hard to create or maintain, and deviations from equilibrium often occur in plasma. As long as the plasma can still be considered in equilibrium in a small region, the local thermodynamic equilibrium allows for the same treatment in that region as plasma in thermodynamic equilibrium[56].

The ions and neutrals in a cold, or non-thermal, plasma have a lower temperature than the electrons. The differing masses of electrons and ions allows for this state to occur. The rate of energy transfer between different particle species is slower than the rate of energy change between particles of the same species. Transferring energy between ions and electrons is much slower than transferring between ions or between electrons. When the plasma is heated, substantial temperature differences between the species will develop[50].

Plasma can also fall into an intermediate category: translational plasma. Generally, hot plasmas are in equilibrium, and cold plasmas are not in equilibrium. It is possible, however, for a hot plasma to not be in an equilibrium state. Plasma gas temperatures can reach as high as 10^3 K without achieving equilibrium. This situation is considered a translational plasma because it marks the transition into thermal plasma and can take on characteristics of both hot and cold plasma[18].

Plasma Regimes

Plasma can exist across of broad range of number densities and temperatures. Plasma can exist as a cold plasma with low number density to a hot plasma with high number density and various mixtures in between. Plasma can be classified into different regimes depending on the particular combination of temperature and number density. The typical plasma regimes are classical plasmas and quantum plasmas. Classical plasmas have low number densities and high temperatures and can be studied using the principles of classical mechanics principles while quantum plasmas generally have higher number densities and lower temperatures and obey quantum mechanics principles. The divide between the two regimes is known as the quantum degeneracy line[58]. Figure 12 shows the range of conditions in which plasma can exist [59]. The red line indicates the quantum degeneracy line. Classical plasmas are above and to the left of the red line while plasmas below and to the right of the red line exhibit quantum mechanical properties[49]. Neon signs, lightning, and solar cores fall in the classical regimes while strongly coupled plasmas and the core of Jupiter fall into the quantum regime.

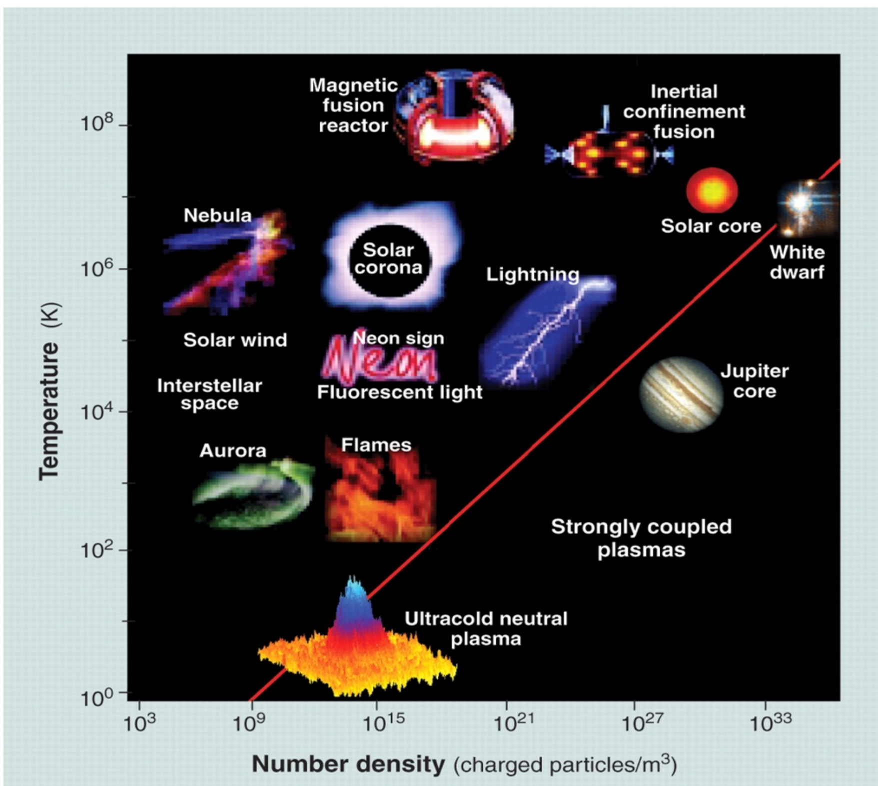

Figure 12: Range of temperature and number densities of plasma Reprinted by permission from Springer Nature: Springer Nature. Astrophysics and Space Sciences. Advances in Numerical Modeling of Astrophysical and Space Plasmas, Anthony L. Peratt. 1997.

Debye Shielding

A second fundamental characteristic of plasma is that the charged particles within the system rearrange themselves to cancel out electric fields within the plasma. For example, consider a positive test charge placed in a homogenous plasma. Positive charges attract electrons and repel ions. As the electrons gather, their presence in the region creates an area with a net negative charge. The receding ions lead to positive charges becoming clustered in another region. The clustering of positive and negative charge produces polarity in the plasma. The polarization of the plasma, and associated redistribution of charges, acts as a shield preventing particles at a great enough distance from feeling the effects of the positive charge[49]. The Debye length determines the distance over which the shielding takes place. At a distance of one Debye length, the potential due to the test charge is reduced by a factor of 1/e. Since plasmas are a three-dimensional medium, the effect forms of sphere around the particle with the radius being the Debye length.

The Debye length, and thus the size of the spherical shielding effect, is determined by the density and temperature of the particles [49]. The electron Debye length of a given plasma is determined by the temperature of the electrons (T_e) and electron number density (n_e). The Debye length can be determined by considering a test charge embedded in a uniform plasma and finding the electrostatic potential (Φ) using Poisson's equation,

$$\nabla^2\Phi = -\frac{\rho_q}{\epsilon_0} = -\frac{e}{\epsilon_0}(n_0 - n_e) \tag{5}$$

where ρ_q is the charge density, ϵ_0 is the permittivity of free space, e is the electric charge, and n_0 is the number density of the ions and electrons far from the test charge[50].

Following the derivation presented in Gurnett and Bhattacharjee, a solution for the potential is found assuming that Φ=0 at infinity and the electrons have a Maxwellian distribution[50]. The general principles of kinetic theory provide the velocity distribution function for the electrons as

$$f_e(v) = n_0 \left(\frac{m_e}{2\pi\kappa T_e}\right)^{3/2} \mathrm{e}^{-\frac{\left(\frac{1}{2}m_e v^2 + q\Phi\right)}{\kappa T_e}} \tag{6}$$

where q=-*e*. This equation, which is similar to the Maxwellian distribution of Equation 2, has an extra factor of exp[-qΦ/kT]. This factor comes from statistical mechanics, as the total energy, both the kinetic and potential energies, need to be included. The distribution function (Equation 5) is integrated over velocity space to find the electron density

$$n_e = n_0 e^{\frac{e\Phi}{\kappa T_e}}. \tag{7}$$

Substituting Equation 6 into Equation 4 gives the non-linear differential equation

$$\nabla^2\Phi = -\frac{n_0 e}{\epsilon_0}\left(1 - e^{\frac{e\Phi}{\kappa T_e}}\right) \tag{8}$$

which can be solved analytically using a Taylor series expansion keeping only the first-order terms to obtain

$$\nabla^2\Phi = \frac{n_0 e^2}{\epsilon_0 \kappa T_e}\Phi. \tag{9}$$

The electrostatic potential can be assumed to be symmetric due to the isotropic nature of plasma. This assumption allows Equation 8 to simplify to

$$\frac{\partial^2}{\partial r^2}(r\Phi) - \frac{n_0 e^2}{\epsilon_0 \kappa T_e}(r\Phi) = 0 \tag{10}$$

which has the general solution

$$\Phi = \frac{A}{r} e^{-\frac{r}{\lambda_D}} \tag{11}$$

where A is a constant and r is the radial distance from the origin if the test charge was placed at zero. The factor λ_D is the Debye length, and is given by

$$\lambda_D^2 = \frac{\epsilon_0 \kappa T_e}{n_0 e^2}. \tag{12}$$

The constant A can be determined by requiring the potential to reduce to the Coulomb potential as the radius goes to zero. Ionized gases are considered plasmas if the dimensions are significantly greater than the Debye length.

Plasma Sheaths

For plasma to be in thermal equilibrium, the ions and electrons must have the same average kinetic energy. Because of the mass difference between ions and electrons, electrons must have much greater velocities to maintain the same average kinetic energy as the ions. Electrons can have velocities several orders of magnitude greater than ions[60].

When an object of finite size is placed in a plasma at thermal equilibrium, the faster moving electrons are more likely to collide and stick to the object than the slower moving ions. This allows the object to acquire a negative net charge. As the object becomes negatively charged, other local electrons are repelled and nearby ions begin to be attracted. Eventually, the electron current collected by the object will reach a balance with the incident ion current, and the system will reach an equilibrium state. The plasma surrounding the negatively charged object exhibits a higher ion density, thus producing an electrically polarized region. This polarized region is called a plasma sheath[50]. The electrostatic potential of the plasma sheath decays exponentially with the characteristic length scale determined by the Debye length. The electrostatic potential can be determined by equating the incident electron and ion currents. By equating the incident electron and ion currents, the electrostatic potential is approximated to be[50]

$$V = -\frac{\kappa T_e}{2e}\left[\ln\left(\frac{m_i}{m_e}\right) + \ln\left(\frac{T_e}{T_i}\right)\right]. \tag{13}$$

Plasma Frequency

The time scale associated with oscillations of particles within a plasma is an important parameter which determines the frequency of the plasma. The plasma frequency sets the lower cutoff for the frequencies of electromagnetic radiation that can pass through a plasma[49]. Oscillations occur when energy, often in the form of a beam of electrons, displaces the electrons in the plasma along the path of the energy. Regions of positive and negative charge are created as the electrons move away from the ions, which can be considered stationary on timescales which are short compared to the ion oscillation frequency. The displacement of electrons in a plasma produces an electric field due to the charge separation. The created charge imbalance creates an electric field, which can be calculated using Gauss's Law:

$$E = \frac{n_0 e}{\epsilon_0} \Delta x \tag{14}$$

where Δx is the displacement of the electrons. The electrons respond to the restoring force by moving back toward the original position, but momentum causes the electrons to overshoot the original position. The restoring force once again tries to bring the electrons back to the original position. The inertia of the electrons and the restoring force continue acting on the system leading to harmonic motion of the electrons, such that the equation of motion can be written in the form of Hooke's Law[49]:

$$F = -k\Delta x = qE \tag{15}$$

where k is the effective spring constant. Rewriting in the form

$$\frac{d^2 \Delta x}{dt^2} + \omega^2 \Delta x = 0 \tag{16}$$

where ω is the frequency, and substituting in the expression for the electric field given in Equation 14, this gives

$$\frac{d^2\Delta x}{dt^2} + \left(\frac{n_0 e^2}{\epsilon_0 m_e}\right)\Delta x = 0. \tag{17}$$

From comparison of Equation 16 and Equation 17, the electron plasma frequency (ω_{pe}) is seen to be

$$\omega_{pe}^2 = \frac{n_0 e^2}{\epsilon_0 m_e}. \tag{18}$$

The electron plasma frequency is determined by the number density of the electrons. The greater the electron number density, the greater the charge imbalance to provide the restoring force. Larger charge imbalances, and thus larger forces, lead to higher frequencies. The plasma period is inversely proportional to the plasma frequency[61]. Figure 13 illustrates the harmonic motion of the electrons during plasma oscillation.

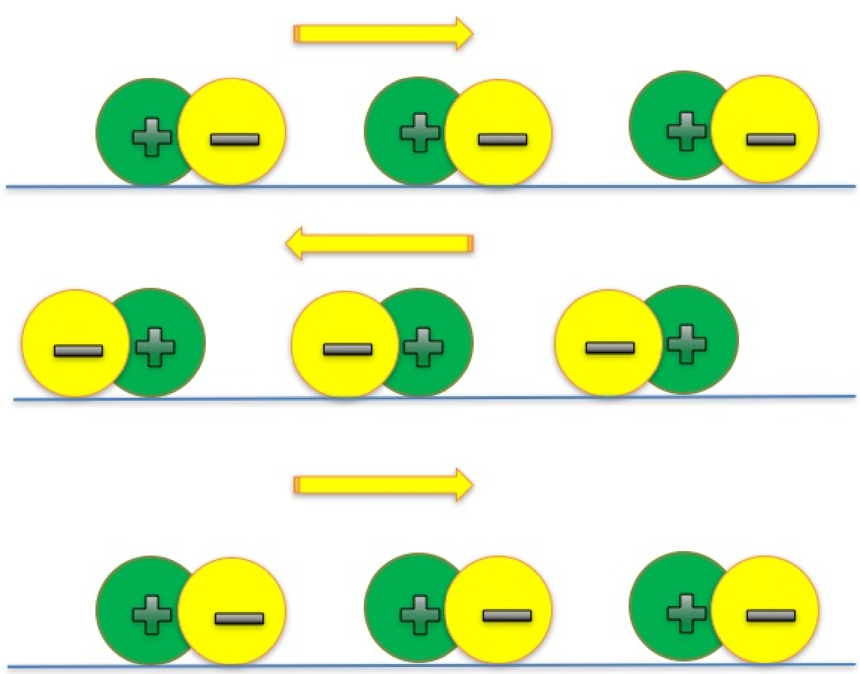

Figure 13: Harmonic oscillation of electrons during plasma oscillation.

Nanoparticles

Nanoparticle Characteristics

Nanoparticles are microscopic particles with at least one dimension less than 100 nanometers. Generally, nanoparticles are considered more toxic than larger particles of the same composition. Characterizing nanoparticles can be tedious as there are many different ways nanoparticles impact systems. From a health perspective, the relevant characteristics are the size, the shape, and the composition of the particle.

Size of the particle is a key characteristic which determines the impact of nanoparticles on the body. There are three classifications of nanoparticle sizes: one-dimensional, two-dimensional, and three-dimensional. One-dimensional particles have only one dimension in the nanometer scale while the other dimensions can be larger. Examples of one-dimensional particles are thin films and surface coatings. Two-dimensional particles have two of three dimensions in the nanometer range and include nanostructured films attached to a substrate. Finally, free nanoparticles are considered three-dimensional nanoparticles since all dimensions are nanoscaled[62].

Nanoparticles have a greater surface area to volume ratio than particles of the same material at a larger size, which allows nanoparticles to be more reactive than the larger particles. Because of the relatively large surface area, more of the chemical the particle is made of lies on the surface. The exposure to a greater amount of a chemical per particle, combined with typically high concentrations of nanoparticles, causes nanoparticles to be considered more toxic than larger particles of the same composition.

The size of the particle is important because it is the key factor that determines how deep into the body a particle can travel. Nanoparticles are able to pass through the body's defense systems to reach the lungs, blood and other major organs. The larger nanoparticles will deposit in the respiratory tract, generally causing irritation to the eyes, nose, and throat. The smaller nanoparticles pass through the two defense layers the lungs have to clear pollutants, depositing in the deepest part of the lungs. Once deposited on the surface layer of the lung, the particles mix with the aqueous boundary layer of the lung. The particles are able to pass through the layer and enter the bloodstream where they are further transported throughout the body[63]. Only very small particles are able to penetrate cell membranes.

Another important characteristic from a health perspective is chemical composition. Carbon-based and metal-based nanoparticles are the two divisions for chemical composition groups[64]. Carbon-based nanomaterials are some of the most attractive and widely used nanomaterials[65], exhibiting the desirable qualities of high strength to size ratio, excellent resistance to corrosion, and electrical and thermal conductivity and stability[66]. Carbon nanotubes, nanowires, and fullerenes are common examples of carbon-based nanoparticles[67]. The most common method for this type of nanoparticle to get into the air is through diesel exhaust[66]. Carbon-based nanoparticles exhibit size-dependent cytotoxicity and are highly linked to inflammation and diseases of the lungs[65].

Metal-based nanoparticles are commonly composed of metal oxides. Copper, gold, zinc, iron, titanium, and silver are metals that are common on the nanoscale range. The elemental composition of the metallic particle plays a major role in the effect on the body. For instance, gold is considered relatively safe and has even been used as a catalyst in cancer treatments[68]. On the other hand, many metallic nanoparticles exhibit cytotoxic and genotoxic effects. Aluminum has been linked to disorders of the brain, copper to impairment of the liver, kidneys, and spleen, and silver has been linked to damage to all four of these organs[65]. Table 3 lists some of the most common nanoparticles that are linked to negative impacts on the body as well as the generating source of the nanoparticles and how the nanoparticles enter the body.

While each type of particle can have negative impacts on human health, a combination of metallic and carbon-based nanoparticles can be even more detrimental. Combining metallic and carbon-based nanoparticles can increase the reactivity of the nanoparticle. The combination of metallic nanoparticles with carbon nanoparticles has been shown to increase the oxidative stress, increasing harmful free radicals in cells. Metallic iron is able to potentiate the effect of carbon black nanoparticles specifically[66].

Different shapes, or morphologies, of nanoparticles serve different purposes with health effects likely due to the shape of nanoparticles. Controlling the shape is key to using nanoparticles in emerging scientific and medical applications. The main shape characteristics are flatness, sphericity, and aspect ratio, the ratio of width to height.

Nanotubes and nanowires have high aspect ratios while spherical particles have low aspect ratios[69]. Aspect ratio is key to determining respirability and inflammation potential [66]. Low-aspect ratio nanospheres and short nanorods can cause some inflammation in the lungs with long-term exposure, but high aspect ratio nanorods and nanotubes are associated with significant inflammation[70].

Table 3: Common Nanoparticles and Their Impact on the Body

Nanoparticle	Source	Mechanism	Impacted Body Part
Magnetite	Combustion	Inhalation	Brain
Aluminum Oxide	Industry	Inhalation Contact	Brain
Gold	Industry	Inhalation	Lungs Liver
Copper Oxide	Industry	Ingestion	Liver Kidneys
Silver	Industry	Inhalation Contact	Lungs Spleen Kidneys Liver Brain
Zinc Oxide	Industry	Inhalation Contact	DNA
Iron Oxide	Industry	Inhalation	Liver Spleen Lungs Brain
Titanium Oxide	Industry	Contact	DNA Lungs Immune System Liver Kidneys Spleen
Carbon-based	Combustion	Inhalation	Lungs
Silica	Natural	Inhalation	Liver

Nanomaterial Trends

Nanomaterials exhibit significantly different physical and chemical properties than corresponding bulk material. Due to the large surface area to volume ratio of nanoparticles, the energy associated with the atoms of nanomaterials are different than corresponding materials composed of larger size particles. This leads to size dependent trends in the thermodynamic properties of nanomaterials[71]. Two important size dependent trends are those of the specific heat and cohesive energy of a nanomaterial.

The specific heat is the amount of heat required to raise the temperature of a unit mass of a substance by one degree[72]. Specific heat is believed to vary inversely with particle size due to the high atomic thermal vibration energies of surface atoms. Surface atoms on nanomaterials have larger vibration amplitudes than corresponding bulk materials, resulting in higher energies[71]. Because of this trend of increasing specific heat, as particle size decreases more heat must be added to the system to raise the substance by one degree.

The cohesive energy, the energy required to divide a crystal into individual atoms, is also dependent on size[71]. Cohesive energy is gained by arranging atoms in a crystalline state as opposed to a gaseous state[73]. This is an important quantity because it accounts for the strength of metallic bonds. Cohesive energy increases with increasing particle size. This trend is seen until particle sizes reach 100 nm, at which point the cohesive energy approaches the constant bulk value. For metallic particles, this effect means that as the particle size decreases, the bonds will break more easily, and thus the melting point will decrease.

Particle Charging

The interaction between plasma and nanoparticles relies heavily on the effects of particle charging. The charge of particles in a plasma depends on isolation. A single particle in a plasma is isolated, but as more particles enter the plasma, the proximity of one particle to another affects the particle charge. The proximity is important to charging when $\Delta/\lambda_D \sim 1$, where Δ is the average interparticle spacing, and λ_D is the Debye length. In general, particles cannot be considered isolated, and the effects of close proximity must be accounted for.

The electron and ion currents to the particle are needed to determine particle charge. The electron current (I_e) is given by

$$I_e = -4\pi a^2 e n_e \sqrt{\frac{kT_e}{m_e}} exp\left(\frac{eV_s}{kT_e}\right) \tag{19}$$

where a is the radius of the particle, T_e is the electron temperature, n_e is the electron density, m_e is the electron mass, and V_s is the particle potential. The ion current (I_i) is defined as

$$I_i = 4\pi a^2 e n_i \sqrt{\frac{kT_i}{m_i}} \left(1 - \frac{eV_s}{kT_i}\right) \tag{20}$$

where T_i is the ion temperature, n_i is the ion density, and m_i is the ion mass. The particle potential is determined by the floating grain potential where the net current to the particle is zero, $I_e + I_i = 0$. The particle potential can be solved for by setting the electron current equal to the ion current to obtain

$$n_e \sqrt{\frac{T_e}{T_i}} \sqrt{\frac{m_i}{m_e}} e^{eV_s/kT_e} + n_i \left(1 - \frac{eV_s}{kT_i}\right) = 0. \tag{21}$$

This equation can be solved for the particle potential, V_s, and then be used to calculate the particle charge Q[74].

$$Q = eZ = 4\pi\epsilon_0 a V_s. \quad (22)$$

Nanofabrication and Plasma Processing

Interactions between plasma and nanoparticles can result in two outcomes: creation or destruction of nanoparticles. The conditions for nanofabrication using plasma are generally considered safer for human health and the environment because the reactions are performed in a confined, controlled environment that prevents toxic fume exposure. Some of the benefits of plasma nanofabrication over conventional methods are illustrated in Figure 14[36]. Being able to choose a wide variety of gases to generate the plasma is another advantage of this method since it allows more precise control over the reactions that generate the nanoparticles.

Plasma can bring about the destruction of nanoparticles through two main processes. The first process is gasification, which involves the conversion of toxic substances into nontoxic byproducts. Etching, the material removal of surfaces by plasma processes, is the second process through which plasma can break down particles[75]. While these two processes are well established on the micro-scale, plasma gasification and plasma etching are proving to be valuable tools for sterilization of unwanted nanoparticles as well.

Nanofabrication using Plasma

The diversity of energetic species (ion, electrons, atoms, excited molecules, and charged particles) present in plasma provide an advantage for plasma nanofabrication processes over conventional thermal vapor processing[36]. The energetic particles interact with each other as well as the surface material to begin the nanofabrication process at lower temperatures than neutral gases. Plasma nanofabrication has higher nanoparticle production rates than conventional methods over a shorter period of time[76].

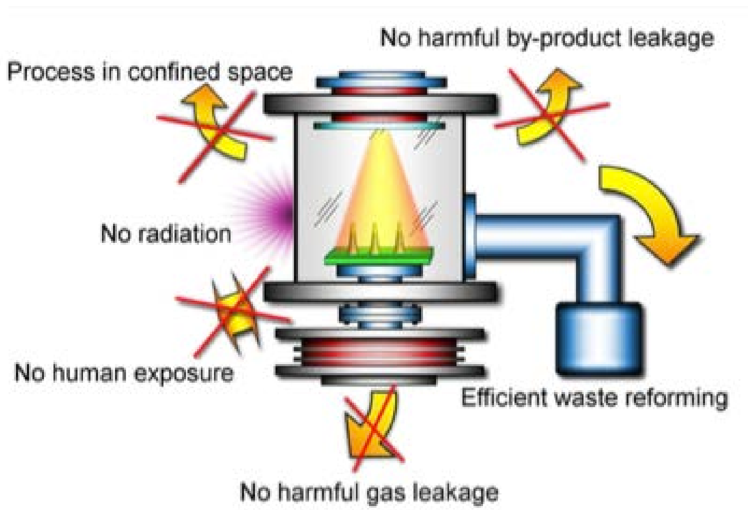

Figure 14: Benefits of plasma nanofabrication over convention methods include lack of human exposure to radiation, harmful gas leakage, and harmful by-product leakage. Reprinted by permission from IOP Publishing: Institute of Physics and the Physical Society, Journal of Physics D: Applied Physics, Plasma nanofabrication and nanomaterials safety, Z J Han, 2011.

Plasma nanofabrication can essentially be considered a one-step process[36]. While many steps take place to form the nanoparticles, after supplying the energy to produce the plasma, the process begins naturally and no more human involvement is needed until the end. The process begins when the plasma vaporizes a precursor material. The vapor then gets transported to a cooler area of the plasma further from the plasma generation site. Quenching, or rapid cooling, of the vapor causes supersaturation, which directly results in the rapid production rate and high particle production numbers associated with this process[77]. At this stage, nanoparticles form from the vapor through a combination of three methods: homogeneous nucleation, heterogeneous condensation, and coagulation, a process illustrated in Figure 13. Homogeneous nucleation occurs randomly, but leads to uniform nuclei formation throughout the medium. Heterogeneous condensation occurs when the nuclei is completely surrounded by supercooled vapor. In this case, nucleation typically occurs at areas where there is an inconsistency such as surface or temperature boundaries[78]. Figure 15 demonstrates this process for nanofabrication using thermal plasma[77].

After nucleation, nanoparticles continue to grow by coagulation. Coagulation occurs through aggregation and deposition processes. As more nuclei are generated in the medium, the nuclei begin to collide and stick together forming rough aggregates. These aggregates continue to grow in this manner until they reach a diameter around 50 nm. After this point, surface deposition on individual particles becomes the main growth mechanism. As deposition on the particles increases, the aggregate as a whole starts to become smooth[79].

Plasma Processing of Nanoparticles

Plasma nanofabrication is gaining interest for its safer nanoparticle production techniques, but plasma can also be used as a remediation tool for unwanted nanoparticles in the air. Plasma can treat nanoparticle pollution in two ways. Nanoparticles can either be converted into safer byproducts or destroyed.

Nanoparticles are converted into safer byproducts through the process of gasification, sometimes referred to as plasma pyrolysis. This process is beneficial because it produces lower levels of air emissions and slag leachate (waste contaminated water) into the environment. Gasification is a non-incineration thermal process that takes place in an oxygen-starved environment combined with high temperature to break down wastes into simple molecules[80].

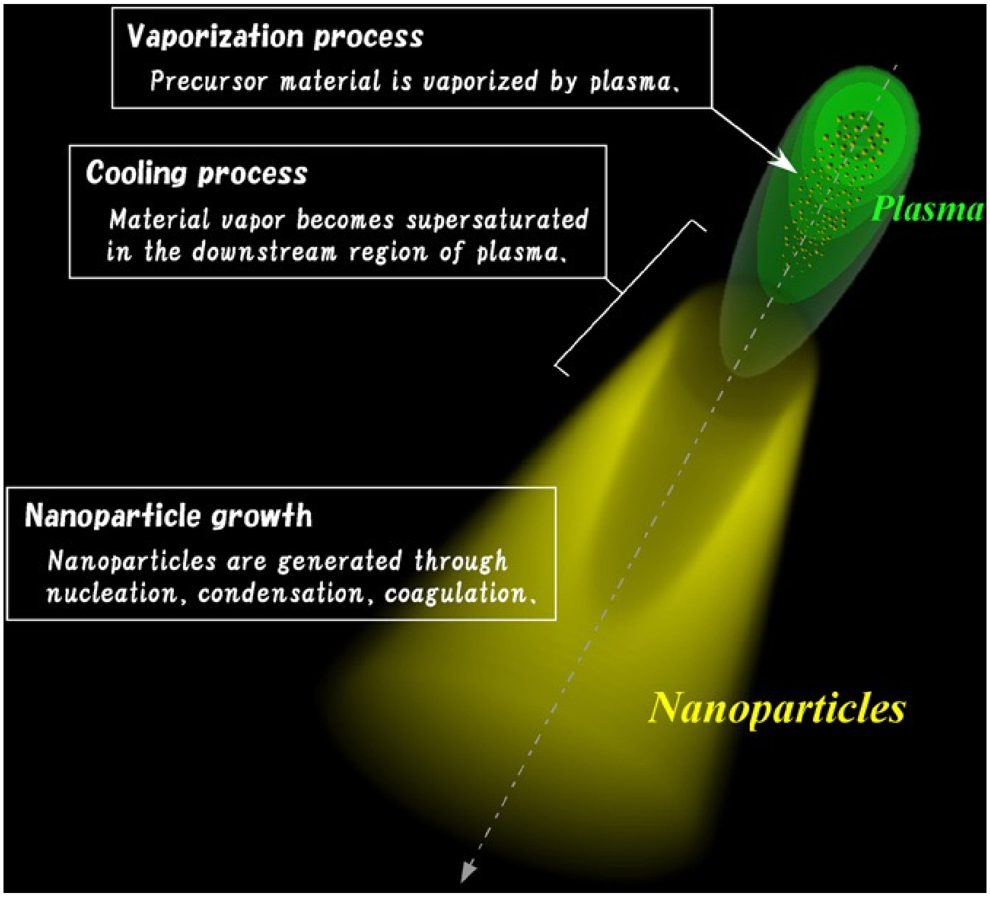

Figure 15: Nanofabrication process using thermal plasma Reprinted by permission from IOP Publishing: Institute of Physics and the Physical Society, Journal of Physics D: Applied Physics, Thermal plasmas for nanofabrication, Masaya Shigeta, 2011.

Gasification converts matter into a synthesis (combustible) gas and inert slag (waste water). The process begins by feeding waste into an arc plasma furnace from the top. The waste then falls onto molten slag where the gasification process happens[80]. Inside the furnace, the waste is heated, melted and vaporized. The extreme conditions inside the furnace allow for molecular dissociation to occur. As the molecular bonds are broken apart, molecules are broken down into individual atoms in the gas phase[81]. This process, and a typical device used for gasification, are shown in Figure 16[80].

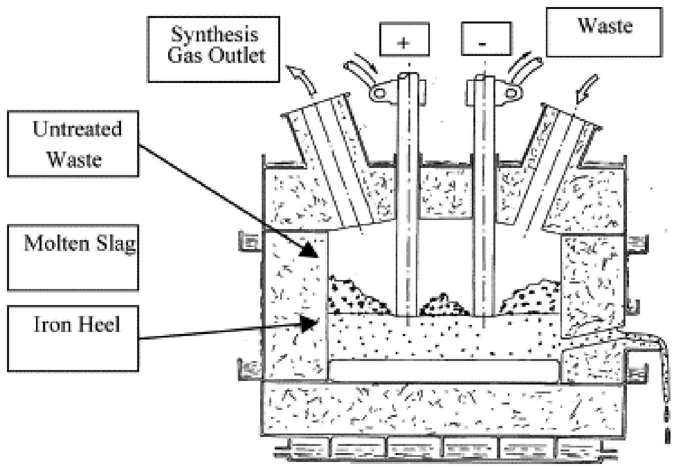

Figure 16: Plasma gasification process. Reprinted by permission from Elsevier: Elsevier, Journal of Hazardous Materials, Demonstration plasma gasification/vitrification system for effective hazardous waste treatment, K. Moustakas, 2005.

This process works for large masses of solid organic matter as well as nanotubes and nanoparticles. Nanotubes and nanoparticles experience rapid results. For nanotubes, gasification first strips off the outer layer of the tip of the tube. Then, as the outer layer is being gasified, the tip of the inner layer is attacked. Finally, the inner tube is completely gasified and the entire tube is decomposed into individual atoms. Nanoparticles are stripped in a similar manner, but require less time for treatment since there aren’t as many layers to remove compared to the nanotubes. Treatment times of 5-10 seconds have been shown to be long enough to completely gasify nanoparticles[82].

The sterilization process by which plasma destroys particles is known as etching, the process by which material is removed from a surface. Etching can take place through wet or dry processes. Wet etching involves placing substrates (reaction surfaces) in a reactive solution that leads to the chemical reactions that remove the material leading to products that are soluble and can be carried away by the solution. On the other hand, plasma etching is a type of dry etching process where the substrate is placed in a reactive gas resulting in volatile products that are carried away by a gas stream. Given enough time and energy, the plasma etching process can break nanoparticles down into completely oxidized, indistinguishable particles.

The general plasma etching process begins by generating the etchant species and diffusing the etchant onto the substrate. Plasma is then applied to the system. The ions and electrons adhere to the surface creating a thin film. The film is highly reactive and causes surface damage to the etchant. Increased temperature causes further reaction to occur until the etchant is broken down into byproducts. These byproducts are then released from the surface through ion collisions and diffused as a bulk gas[83].

For nanoparticles, plasma etching removes the surface lipid layer and any defect states first. With continued application, plasma etching will crack the surface of the nanoparticle. These cracks continue to grow until the core of the particle becomes indistinguishable from the shell interface due to the depth and width of the cracks. At this point, the nanoparticle is considered destroyed[84].

The time the treatment is applied has varying effects that can be beneficial for different applications. A plasma etching treatment of one minute is long enough to remove any layers of surface defects without altering the structure or morphology of the nanoparticle. After a five-minute treatment, cracks will appear, but the particle will still remain intact. Nanoparticle destruction occurs after a ten-minute treatment[84].

CHAPTER THREE

Applications of Plasma for Environmental Remediation

Current Particulate Matter Pollution Control Methods

Industrialization doesn't come without a cost. Technological advancements continue to increase the standard of living, but an improvement in one aspect of life can at times have a negative impact in another area. Most negative impacts from industrialization come through pollution. The Philosophy of Pollution Prevention involves either modifying the manufacturing and generation processes by increasing efficiency or using different raw material or recovering and reusing material to produce less waste[18]. However, emitting fewer pollutants into the air is not always an easy task. Because of this, different mechanisms have been established to clean up the air after pollutants have entered the environment. Three common devices for particulate matter pollution control are gravitational setting chambers, cyclonic control devices, and fabric filters[85].

Gravitational settling chambers work best for larger particle sizes in a gas stream. These rectangular chambers slow the velocity of the polluted gas to allow time for gravity to cause particles to settle to the bottom of the chamber for removal at a later time. This process is effective for particles greater than 50 μm[85].

Instead of relying on the gravitational force for particle separation, cyclonic control devices utilize a centrifugal force to separate particulate matter from gas. The applied centrifugal force can be many times greater than the gravitational force, which allows for smaller particulates to be separated from the gas. These devices work by injecting a polluted gas into a rotating chamber. As the gas begins to spin, the centrifugal force throws the higher density particulates to the outside of the chamber where they stick to the device walls. The gas exits the chamber at the top while the particulates slide down the walls to be collected at the bottom. Because the centrifugal force increases with particle diameter, the efficiency of cyclonic control devices increases with increasing particle sizes. Cyclonic control devices are most effective for coarse particulates and have little effect for fine and ultrafine particulates[85].

Fabric filters are currently one of the best pollution control devices for smaller particle sizes. Fabric filters require a polluted gas to pass through a series of fabric. The fabric traps particulate matter while allowing gas to pass through. The particulate matter trapped by the fabric remains on the surface of the fabric as a layer of thin dust. As more particulates are trapped, the dust building on the surface creates a thicker barrier for particulates to pass, effectively allowing for higher trapping efficiencies. Fabric filters are effective for particles greater than 0.5 μm[85].

Potential for Plasma Applications

While current air pollution control devices are highly effective for coarse and some fine particulates, there is a lack of technology that effectively removes ultrafine particulates. A new device is still needed that removes ultrafine particulates while also reducing exposure to humans. Current devices use trapping methods that allow particulates to collect for later removal. During this removal process, humans can be exposed to the pollutants that were removed from the air.

Plasma technology provides options to fit both these needs. Plasma technology offers the potential to remove ultrafine particulates from the air while also allowing the process to occur in a contained area that prevents leakage and human exposure. Plasma also offers a number of different options that allow for adaptability to the nature and source of the pollutant. Microwave plasmas, dielectric barrier discharges, hollow cathode discharges, electron beams, and hybrid methods of generating plasma have been studied for their ability to improve environmental conditions such as purification of air and water and sterilization of medical equipment.

Plasma Technologies

Thermal plasma (hot and nearly fully ionized), non-thermal plasma (cold with only a small fraction of molecules ionized), and translational plasma (a hot non-thermal plasma that marks the transition into the thermal temperature ranges) can be used for environmental purposes. There are many plasma technologies falling under each category that can be used for environmental remediation as shown in Figure 17[18]. Dielectric barrier discharges and microwave driven plasma, two of the most commonly used devices in environmental remediation, are in the non-thermal and translational ranges, while microwave driven plasmas and inductively heated plasmas fall into the translational and thermal ranges. These systems and some of their applications are described below.

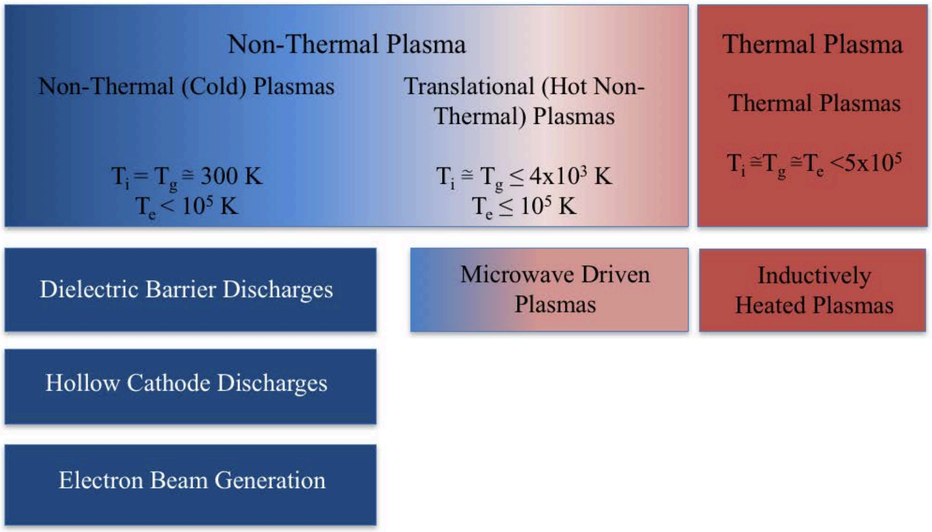

Figure 17: Classification of plasma technologies by plasma species. T_i is the temperature of the ions. T_g is the temperature of the gas. T_e is the temperature of the electrons. Plasma technologies fall into three categories: Non-thermal, translational, and thermal. Figure based on data from M. Shigeta and A.B. Murphy, J. Phys. Appl. Phys. **44**, 174025 (2011).

Dielectric Barrier Discharges

Dielectric barrier discharges (DBDs) are one of the most commonly used devices for environmental applications and are characterized by the presence of an electrical insulator, or dielectric, in the discharge space between electrodes [86]. DBDs generate non-thermal plasmas at atmospheric pressure[87]. The wide variety of planar and cylindrical geometries available to generate the discharges allows for construction of compact systems with small gas streams. A standard set up for a planar DBD device in which a voltage is applied to the top electrode and the bottom electrode is grounded is shown in Figure 17. The gas flows in the area between the electrodes and the discharges occur in this same area. Figure 17(a) shows a planar DBD with a dielectric material covering one electrode while Figure 18(b) shows a dielectric material covering both electrodes[88].

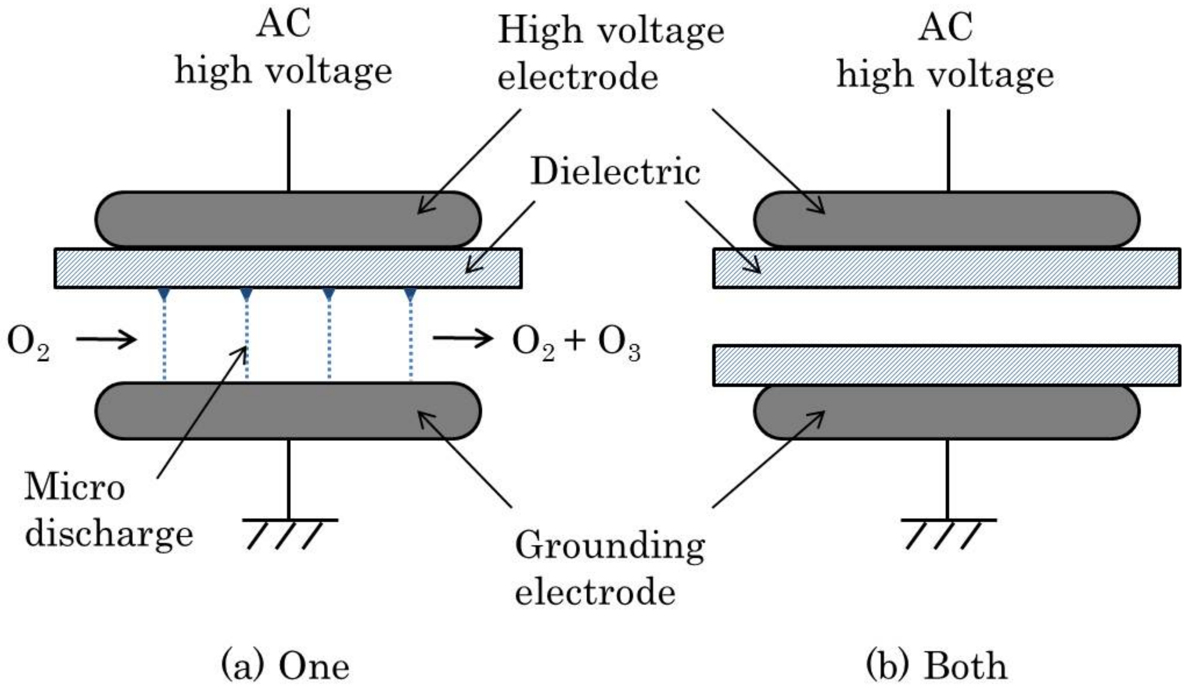

Figure 18: A typical planar dielectric barrier discharge device constructed with (a) one dielectric and (b) two dielectrics Reprinted by permission from INTECH: Takao Matsumoto, Douyan Wang, Takao Namihira and Hidenori Akiyama (2012). Non-Thermal Plasma Technic for Air Pollution Control, Air Pollution - A Comprehensive Perspective, Dr. Budi Haryanto (Ed.), InTech, DOI: 10.5772/50419. Available from: https://www.intechopen.com/books/air-pollution-a-comprehensive-perspective/non-thermal-plasma-technic-for-air-pollution-control.

To generate the discharges, a voltage is applied to the metal electrodes to generate strong electric fields[89]. When the electric field is sufficiently strong, breakdown of the gas between the electrodes will occur as a large number of microdischarges. The gas between the microdischarges remains unionized and absorbs the energy dissipated by the microdischarges[90]. The discharges dissociate the ions from the electrons. The ions initiate the chemical reactions that result in the destruction of the pollutants[89]. Ions remove pollutants from the air through magnetic attraction. When the ions attach to the pollutants, the pollutants become too heavy to drift in the air and become grounded on a surface[91].

DBDs provide the advantages of non-thermal plasma and atmospheric pressure operation making them an ideal technology for many environmental applications such as gas treatment, surface sterilization, and ozone generation[90]. Non-thermal plasma is advantageous because it can remove toxic molecules at room temperature without using too much energy to heat the background gas. Most of the discharge energy goes to producing energetic electrons without heating the electrons[88]. Thus, the plasma energy is mainly applied to electron impact dissociation and ionization of the background gas to produce free radicals, which decompose toxic molecules[88].

The materials of both the electrodes and the dielectrics can be altered in DBD devices to fit varying environmental needs. Pollutant removal rates are impacted by the chemical properties of the electrode material. Stainless steel electrodes, which provide an inactive surface, have proven useful in removing contaminants from water while copper electrodes have uses in medical and environmental settings[92,42,93]. Stainless steel is desired for its passivity whereas copper, which can react with anions and participate in the reaction processes, is beneficial due to its high catalytic activity[94]. Glass, quartz, and ceramic materials are commonly used dielectrics[89].

Hollow Cathode Discharges

Hollow cathode discharge (HCD) devices get their name from the unique hollow structure of the cathode used to generate the discharges. The benefit of the HCD comes from the hollow cathode effect in which the current density increases as the cathode separation distance decreases[95]. This allows for electrical conduction at lower voltages than when using a comparable flat cathode. HCD devices can be constructed using equipotential parallel plates or cylindrical geometries. Variations of a cylindrical HCD device are shown in Figure 19. Figure 19(a) demonstrates a geometry where the cathode forms a hole while Figure 19(b) illustrates a cathode forming a cavity. A hole has the entire width of the top open while a cavity is partially closed off by the upper portion of the HCD. As shown in figure 19(c), a plate geometry can be formed by removing the bottom plate and the cylindrical portion of the cathode from the configuration shown in Figure 19(b)[96].

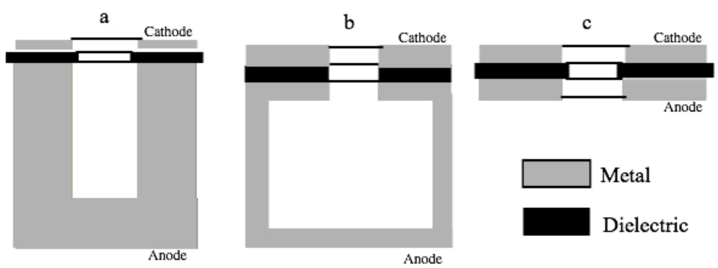

Figure 19: Hollow cathode discharge geometries: (a) cathode forming a hole (b) cathode forming a cavity (c) parallel plate Adapted with permission from IOP: American Institute of Physics, Plasma Sources Science and Technology, High pressure hollow cathode discharges, Karl Schoenbach, 1997.

When the pressure is sufficient, around atmospheric levels at small cathode separation distances, the mean free path of ionization (the average distance traveled by a moving particle between collisions) will be on the order of the radius of the hole in the cathode[96]. This will allow the electrons to gain enough energy to begin oscillating between the potentials in a pendulum motion[95]. The pendulum motion generates secondary electrons and leads to the formation of a sheath. Above a certain power threshold, the sheath will begin to break down as the electrons begin discharging their energy causing plasma arcs[95]. HCDs produce non-thermal atmospheric pressure plasma that is useful for converting hazardous gases. Nitrogen oxide conversion has been particularly successful with HCDs, achieving results of up to 100% conversion of NO_x in nitrogen[97].

Electron Beam Generation

Another way to generate plasma is to use electron beams produced by electron accelerator units[98]. The electron beam generation method can be more efficient than conventional methods, while also being easily scalable to various treatment areas[99]. Conventional methods for creating a plasma rely on directly heating the electrons in a gas by applying an external electric field. Ionization in this manner can lead to a significant loss of input power. By passing a beam of energized electrons through a gas, ionization of the gas occurs first, followed then by dissociation and excitation of atoms and molecules.

A typical design of an electron beam generation system is shown in Figure 20[100]. The process for generating plasma by electron beams begins by heating a hollow cathode. An electron beam is generated in a high vacuum chamber with an electron gun. The electron beam is injected into the heated hollow cathode[101]. The electrons are then accelerated through the grounded anode to set the shape of the beam[99]. The beam is accelerated into a vacuum then transits to the gas stream. The electron energy is transferred to the gas where the fast electrons interact with the gas species creating ions and radicals. The free radicals attack organic compounds leading to decomposition of pollutants[98]. Electron beam generated plasmas are particularly useful at removing SO_2, NO_x, and VOCs from the air[98].

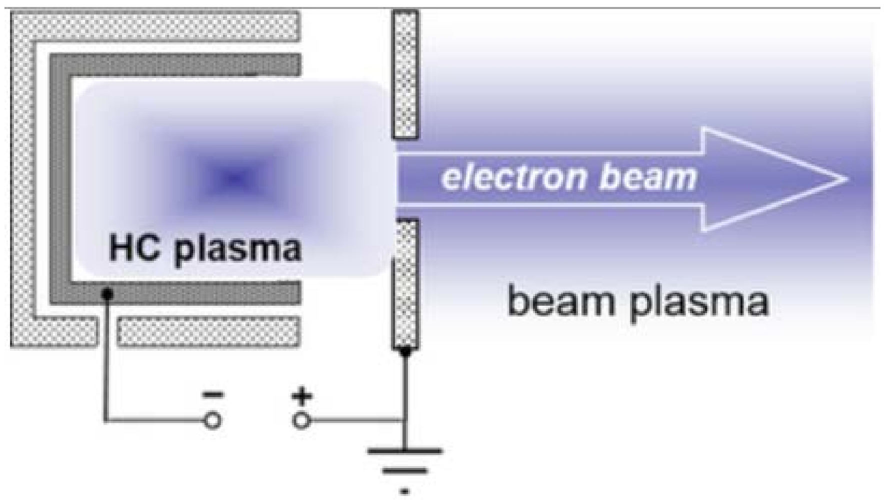

Figure 20: Electron beam generation mechanism using a hollow cathode source Reprinted by permission from Electrochemical Society: Electrochemical Society, ECS journal of solid state science and technology, Electron Beam Generated Plasmas for Ultra Low Te Processing, S.G. Walton, 2015.

Microwave Driven Plasma

Microwave driven plasma (MDP) generates plasma discharges through application of electromagnetic waves in the microwave frequency (frequencies between 300 MHz and 300 GHz)[102]. With gas temperatures up to 4000 K, this type of non-equilibrium translational plasma is hot enough to decompose organic molecules[103]. MDP devices use a non-electrode method of generating the plasma that is advantageous since it allows for a wider range of powers (up to 6 kW) and gas flow rates (hundreds of L/min) than many electrode-based devices[103].

A typical MDP generating device consists of three main parts: the microwave generator, the microwave supply and measuring system, and the gas supply[103]. The microwave power supply is generally provided by a magnetron connected to the discharge generator. The magnetron produces the microwaves that are focused by a cable onto a torch. Plasma is ignited by a piece of copper wire and sustained by a carrier gas flowing through the torch[104].

MDPs are particularly useful for environmental applications because the high temperature associated with the translational plasma allows for a breakdown of stable pollutants. MDPs have been shown to be particularly useful for hydrocarbons and chlorofluorocarbons that are known to deplete the atmosphere's ozone layer. Decomposition efficiencies for chlorine- and fluorine-based volatile organic compounds ranged from 61-100% for power supplies between 200-400 W using a nitrogen gas plasma[105].

Hybrids

Non-thermal plasma is a valuable tool for removing many pollutants from the air, but for certain pollutants the removal efficiency is low. In the case of low removal efficiency, hybrid plasmas can be used to enhance efficiency. Hybrid plasmas use enhancements, like catalysts and chemical injections, to aid in pollutant breakdown.

A catalyst increases the rate of a chemical reaction without being permanently changed[106]. Catalysts can be placed either directly in the plasma or downstream from the plasma as shown in Figure 21. For catalysts directly in the plasma, radiation and active species in the plasma increase catalyst activation while catalysts downstream from the plasma zone allow for independent control of each element. For both situations, the catalyst prevents loss of radicals in gas phase reactions by absorbing radicals from the plasma. Catalysts also trap small particles on their surface thus increasing retention time and allowing for greater decomposition. Plasma and catalysts work well for deodorizing air and filtering out biodegradable compounds[18].

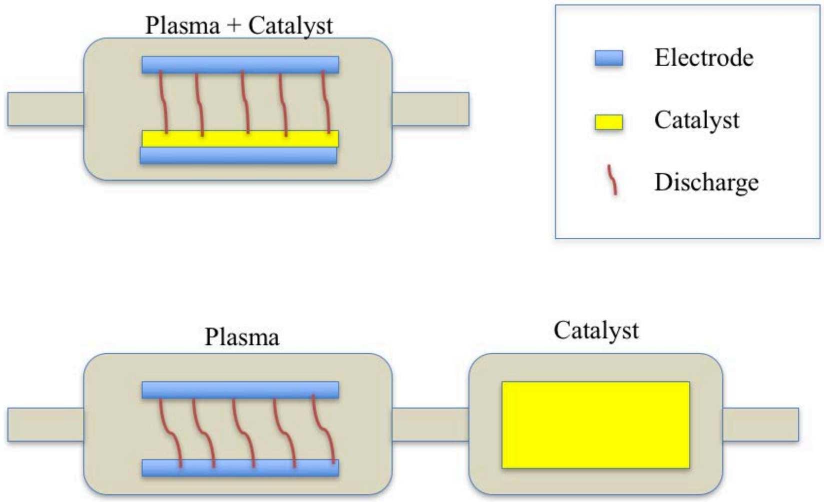

Figure 21: Plasma-catalyst systems with catalyst directly in plasma and downstream from plasma zone. Figure based on image from M. Shigeta and A.B. Murphy, J. Phys. Appl. Phys. **44**, 174025 (2011).

Injection methods are able to enhance removal efficiency while also preventing damage to the surfaces of a plasma generating device. A plasma wet scrubber is a common example of enhancing reactions by injecting substances into plasma. For a typical wet scrubber, water is injected into a DBD. This allows for plasma to be generated in a mixed environment containing a dielectric, air, and water. The discharge produced in this mixed environment behaves like a partial discharge in a void where the discharge does not fully bridge the gap between the electrodes [107]. The process works by oxidizing then neutralizing a pollutant before it is scrubbed out by the device [18].

Environmental Applications of Plasma Technology

Pollution control has widely become a goal of many nations around the world. Regulations in Europe and the United States call for tightening of exhaust emission standards, calling for cutting of current levels by 25% in the next decade [108]. While lowering emissions will reduce environmentally linked health issues, pollutants currently exist and new pollutants will continue to be emitted. Establishing reliable, efficient, and budget friendly environmental remediation tools goes along with regulations for environmental health. Many researchers are beginning to explore how to develop the opportunities for environmental remediation provided by the field of plasma science. The following applications are just a few examples of current plasma technologies being explored for the treatment of surfaces, water, and air for the benefit of human and environmental health.

Applications for Surface Treatment

Plasma treatment of surfaces covers a broad spectrum of contaminants and contamination surfaces. Plasma devices have largely been studied for surface decontamination effects in the medical field, where it has been shown that plasma applications are effective in reducing surface contamination from microbial contaminants in a hospital environment[109]. Non-thermal plasma (NTP) is useful in the medical field due to its low temperature, which allows for treatment of living tissue in addition to the treatment of inorganic medical devices. Altering the plasma generation device allows the treatment of different surface types and sizes. DBDs are most effective at treating large surface, such as areas while corona discharges (discharges generated between bare metal electrodes without a dielectric barrier) work best for small spot treatment. Coronas work best for smaller areas since the discharges appear at sharp electrode geometries like points and edges unlike DBDs which discharge across the entire plane of the electrode.

Atmospheric pressure plasma jets provided the best results for complex geometries with narrow cavities like the tube of a catheter[109].

Plasma can also be used as a surface treatment method for human tissue. When applied directly to the skin, NTP acts as a disinfectant to sterilize tissue, aid in would healing, and enhance blood coagulation[110].

The medical field faces a strong need for technology to combat hospital induced (nosocomial) infections and antibiotic-resistant bacteria. The best method for reducing the threat to patients from infection and bacteria while in the hospital is through sterilizing hospital equipment, staff, and visitors. This process can be tedious and expensive for medical equipment, require multiple scrubbing sessions for surgeons and hospital staff, and, at times, be nearly impossible to enact for hospital visitors. Plasma sterilization techniques are desirable for medical applications because it works at the atomic level and can reach all surfaces in complex equipment while also being applicable to live tissue.

One device being studied for medical applications of surface sterilization is the sandwich electrode [92]. The design allows for biocompatible, low-temperature plasma to be generated for *in vivo* applications. The plasma dispenser utilizing a sandwich electrode discharge device, illustrated in Figure 22, is a modified dielectric barrier discharge device. The design consists of two electrodes spaced close together (approximately 4 mm separation). The device is named for the effect of the two electrodes surrounding (sandwiching) a Teflon plate. The Teflon plate sits on top of a copper sheet electrode. A stainless-steel wire mesh electrode is placed directly on top of the Teflon plate. A sandwich electrode device is included on the top and bottom of the dispenser with the wire mesh electrodes facing each other. The mechanism for producing the plasma is the same as in a DBD, but due to the geometry of the mesh, the plasma is only produced in the squares between the wire mesh. The bacteria is placed in the plasma treatment zone between the two sandwich electrode devices. The plasma chemistry reactions result in reactive oxygen species and reactive nitrogen species which are used to kill surface bacteria.

Applications for Water Purification

Water purification is an area of interest as water scarcity becomes a growing concern. Many areas around the world lack access to clean drinking water. Only three percent of the Earth's water is freshwater and of that a large portion is trapped in glaciers or otherwise unfit to drink[111]. Water pollution, or the presence of substances that modify the water in a negative fashion, is a leading cause of unfit drinking water[112]. Water pollutants include organic and inorganic material. Organic matter includes VOCs and decaying plant and wildlife material[111]. A wide variety of human activities contribute to the amount of inorganic pollutants in water. Pollutants enter the water through industrial waste, sewage, chemical runoff, and marine dumping[113].

Plasma generated through dielectric barrier discharge (DBD) devices has been found to be an effective method for removing impurities from water. The microdischarges produced by DBD devices produce ultraviolet radiation in the germicidal wavelength (200-280nm) that effectively treats impure water[114]. The DBDs used for water treatment follow similar structural designs, but achieve different results by varying operation parameters, discharge environment, and electrode material. Higher voltages applied at lower frequencies have exhibited the most efficient removal rates for bacteria[115]. This effect is thought to occur since it is assumed cell membranes respond more to short pulses of electric fields as opposed to constant electric fields. Varying the electrode material allows for the reactive properties of that material to be utilized. The discharge environment refers to the generation of plasma in air or directly in water[42]. Each provides advantages and creates different reaction pathways depending on the contact area of the plasma with water.

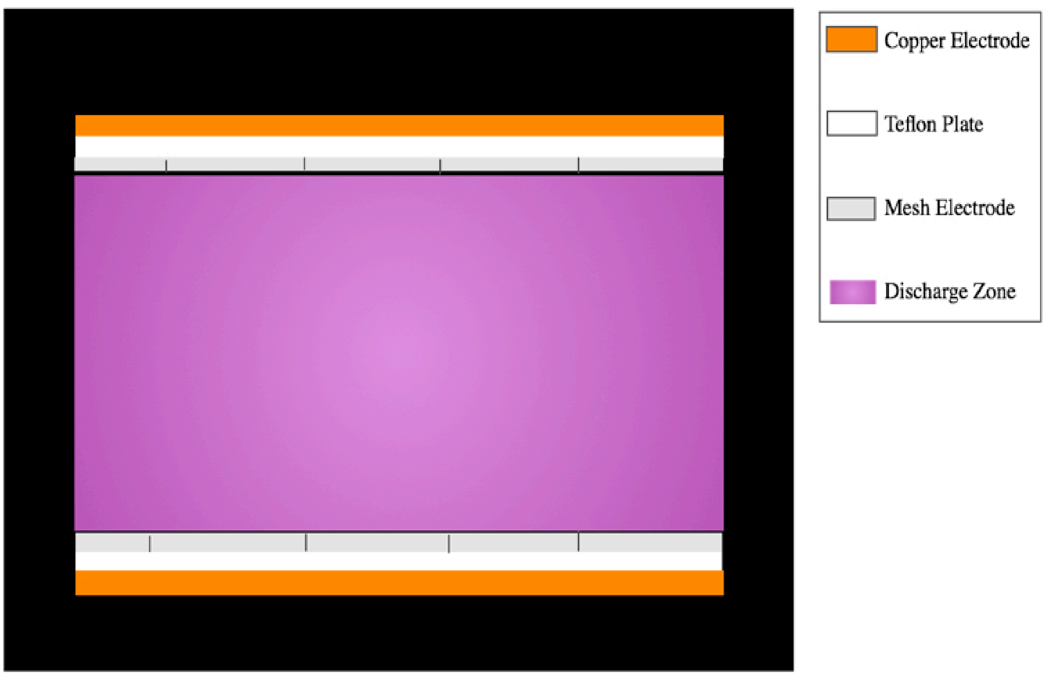

Figure 22: Plasma dispenser utilizing a sandwich electrode discharge device. The dispenser consists of two sandwich electrodes made of a copper electrode, a Teflon plate, and a wish mesh electrode encapsulated within a container. The plasma discharges between the two sandwich electrodes. Bacteria can be treated inside the discharge zone. Based on image from G.E. Morfill, T. Shimizu, B. Steffes, and H.-U. Schmidt, New J. Phys. **11**, 115019 (2009).

The treatment of *Escherichia coli (E. coli)* provides an example of how different variations of the DBD design can impact water treatment. *E. coli* is a species of bacteria that can live in water and cause significant illness if ingested by humans[116]. Copper and silver are two commonly used electrode materials that have been tested for treatment of *E. coli* contaminated water. Copper, selected for its catalytic activity, combined with stainless-steel and quartz generate plasma activated water (PAW). The DBD consists of a quartz dielectric sandwiched between a powered copper electrode and a grounded stainless-steel electrode. The plasma generated in air adjacent to the contaminated water creates acidic solutions that kill *E. coli* bacteria. PAW yields sustained antibacterial effects that can last for up to a week[93]. Another method to treat *E. coli* in water involves the use of plasma generated directly in the water. A powered silver electrode combined with a grounded stainless-steel electrode generates microdischarges directly in the water. This allows the plasma discharges allows for electroporation of the cell walls. This opening of cell wall pores allows silver nanoparticles released into the solution during the discharges to enter the cells. The antibacterial effect of silver aids in the bacterial efficacy[117].

A downside to using plasma for water treatment is that the technology development is slow because there are no general principles to guide the design of a reactor. In an effort to address this, a study was conducted to identify and characterize the design parameters that influence water treatment efficiency to improve the feasibility of a widely available plasma reactor[118]. This study used pulsed electrical discharge plasma formed directly in or above the contaminated water to treat chemical and biological pollutants. Pulsed electrical discharge plasma was used because it does not yield hazardous byproducts and required little to no chemical additives while offering a broad range of treatment methods.

The design consisted of a high voltage power supply for plasma generation, a glass vessel fitted with an airtight cap, and a point-to-plate electrode configuration. Rhodamine B in water was the test species. Nine different reactor types (Figure 23) were studied to determine an optimal reactor design. The reactors tested discharges in liquid (Figure 23(a)) and gas (Figure 23(b)), as well as contact oriented reactors (Figure 23(c-e)), and bubbling reactors (Figure 23(f-i)). The study found discharges in gas were more effective than liquid because gas discharges produced broader, longer, more numerous channels or conductive plasma pathways. These effects increased the plasma liquid contact area, leading to higher removal efficiencies. Reactors that used bubbling were also found to be more effective since they also increased plasma liquid contact area.

Applications for Air Purification

Aerosolized particulates have been linked to many illnesses, making the need for better air pollution control methods even more important. Non-thermal plasmas (NTPs) can act to purify air through electron beam discharges, pulsed streamer discharges, or electrical discharges. For air purification, pulsed streamer discharges have the ability to deodorize air in houses, cars and factories. When a catalyst is supplied, plasma can clean air indoors and remove volatile organic compounds from factory air [119]. NTP techniques are desirable for air purification techniques because they are energy efficient, provide flexibility with chemical reactions, and can treat multiple toxic molecules at once [88].

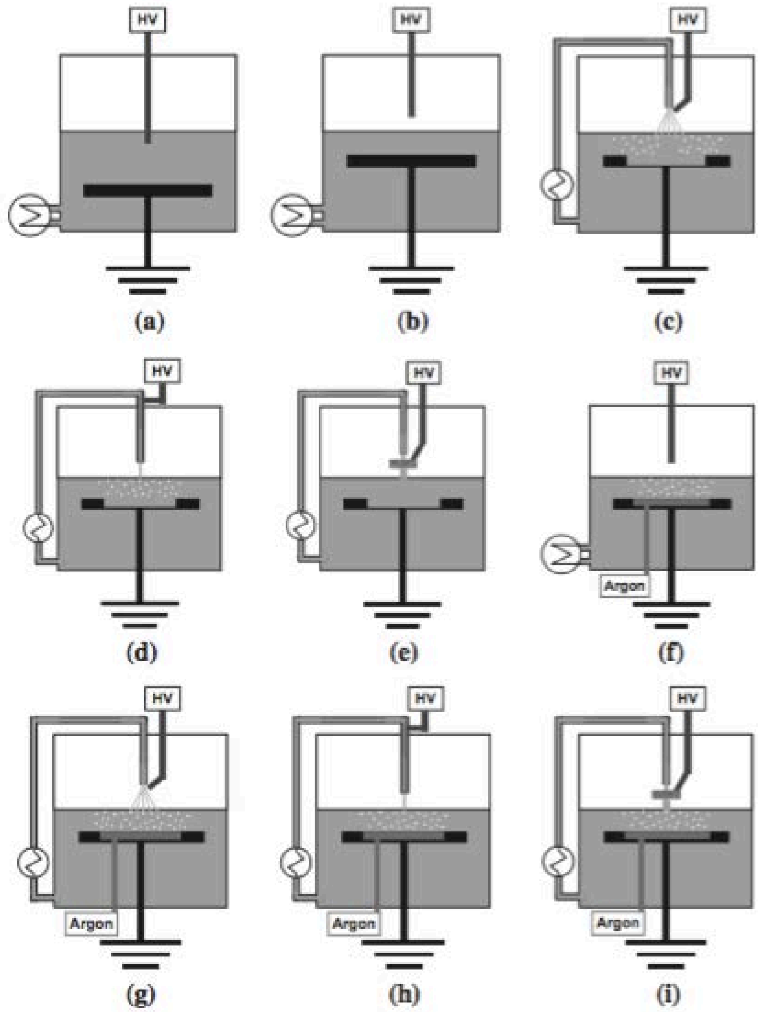

Figure 23: Plasma-based water treatment reactor designs: (a) point-plate with discharge in liquid, (b) point-plate with discharge in gas, (c) turbulent jet, (d) laminar jet, (e) reticulated vitreous carbon high voltage (RVC HV), (f) point-plate with discharge in gas with bubbling, (g) turbulent jet with bubbling, (h) laminar jet with bubbling, and (i) RVC HV with bubbling. Reprinted by permission from Elsevier: Elsevier, Chemical Engineering Journal, Plasma-based water treatment: Conception and application of a new general principle for reactor design, Gunnar Stratton, 2015.

One device that has been found particularly useful in cleaning air contaminated with exhaust fumes from power plants, municipal-waste incinerators, and combustion boilers is the electron beam dry scrubber (EBDS) [88]. The dry process is beneficial since it does not require expensive catalysts to remove pollutants. The EBDS operates in the same manner as electron beam generated plasma in which electrons are accelerated by a high voltage in a vacuum region then injected into a gas processing chamber through a foil window as shown in Figure 24 [88]. The electron energy is used for dissociation and ionization of the background gas. Ionization generates a shower of electrons which produce large volumes of plasma.

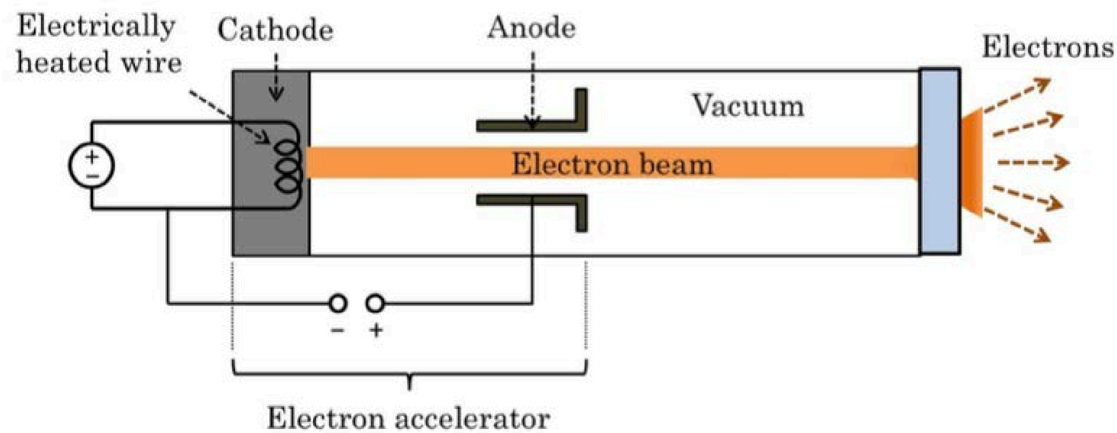

Figure 24: Electron beam generator used for the electron beam dry scrubber. Reprinted by permission from INTECH: Takao Matsumoto, Douyan Wang, Takao Namihira and Hidenori Akiyama (2012). Non-Thermal Plasma Technic for Air Pollution Control, Air Pollution - A Comprehensive Perspective, Dr. Budi Haryanto (Ed.), InTech, DOI: 10.5772/50419. Available from: https://www.intechopen.com/books/air-pollution-a-comprehensive-perspective/non-thermal-plasma-technic-for-air-pollution-control.

The EBDS is capable of removing nitrogen oxides (NO_x), sulfur oxides (SO_x), and volatile organic compounds (VOCs). The treatment process for combustion flue gases is demonstrated in Figure 25[88]. The process begins when oxidative radicals (O, OH, and HO_2) are produced by electron beam irradiation into O_2 gas. The radicals oxidize the nitrogen oxides and sulfur oxides into HNO_3 and H_2SO_4 which can be converted into the byproducts ammonium nitrate and ammonium sulfate. These byproducts are collected by an electrostatic precipitator where they can be collected and either disposed of or sold for fertilizer. The EBDS process exhibited 95% removal efficiency for SO_2 and 80% removal efficiency for NO_x.

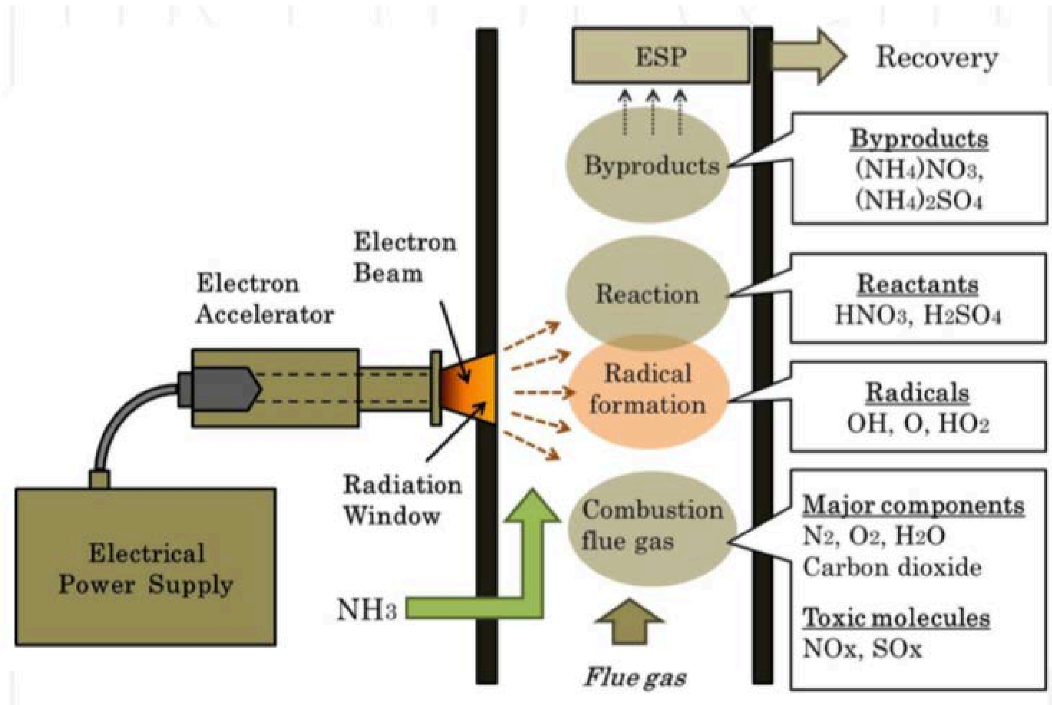

Figure 25: Combustion flue gas treatment process using an electron beam dry scrubber. Reprinted by permission from INTECH: Takao Matsumoto, Douyan Wang, Takao Namihira and Hidenori Akiyama (2012). Non-Thermal Plasma Technic for Air Pollution Control, Air Pollution - A Comprehensive Perspective, Dr. Budi Haryanto (Ed.), InTech, DOI: 10.5772/50419. Available from: https://www.intechopen.com/books/air-pollution-a-comprehensive-perspective/non-thermal-plasma-technic-for-air-pollution-control.

Need in Future Plasma Applications

The wide array of uses of plasma for the improvement of human health and the environment is evident, but there is still a gap in the field. Most devices currently in use and being studied operate to eliminate contaminants on the micrometer scale. The growing use of nanoparticles in industry and consumer products will also need to be met by remediation techniques. Plasma applications offer a nanoparticle pollution solution. Research has already been conducted showing the efficiency of plasma at removal of nano-size titanium dioxide in aqueous solution [120]. However, the greatest risk to humans from nanoparticles come through inhalation. This risk presents the need for an effective method for protecting both workers and consumers from the exposure to nanoparticle contaminants in the air. Plasma technology offers the potential to remove nanometer sized particulates from the air to reduce the risk of exposure through inhalation.

CHAPTER FOUR

Experimental Design for Ultrafine Particulate Remediation using an Inductively Heated Plasma Generator

Benefits of Plasma in Air Pollution Control

Nanotechnology is quickly becoming a key factor for technological and economic growth around the world[121]. Increasing demand for nanotechnology will require an equal demand for technology to counteract the potential negative health effects linked to nanoparticulate inhalation. Plasma technology offers a broad range of environmental applications [(119,88,122,123,124,120,42,118)] and has the potential to be an effective and efficient aerosolized nanoparticulate pollution control method.

Ambient air contains a mix of pollutants such as particulate matter, greenhouse gases, volatile organic compounds (VOCs), and bacteria [123]. Traditional air pollution control devices require complex integrated systems to clean the air. Each part of the system only tackles one type of pollutant. Typically, a pollution control system would need separate devices for particulate matter, VOCs and bacteria. Plasma is beneficial over these traditional systems because it is capable of treating multiple types of pollutants at once[123].

The versatility of plasma goes beyond the type of pollutant it can treat. Generally, there are three methods of approaching pollution control technology: diluting waste to acceptable levels then releasing it back into the environment, converting waste to harmless byproducts then releasing it back into the environment, and converting waste to reusable products [123]. Plasma can be used in two of these approaches to reduce air pollution. Plasma oxidation-catalyst reactions convert pollutants to harmless gaseous byproducts while oxidation chemistry that occurs when plasma is mixed with additives can convert pollutants to reusable byproducts[122].

Plasma Treatment Process for Air Pollution

The plasma treatment process for air pollution consists of four stages: nanoparticle generation, plasma treatment, separation and collection of byproducts, and disposal or distribution. The four stages, beginning with ambient air contaminated with particulate matter and ending with treated air in which particulate matter has been removed, is outlined in Figure 26. The first stage of the process involves the generation of nanoparticles for testing purposes. Nanoparticle generation allows for the production of well-characterized, monodispersed, aerosolized nanoparticles at relatively high concentrations [125]. In a real-world application, this stage could be omitted and replaced with natural air that is known to contain contaminants. In a test situation, however, it is necessary to know the particle type and concentration to verify the effectiveness of the treatment.

After generation, the aerosolized nanoparticles will be transported into the plasma zone for treatment. The plasma treatment zone acts as the disinfectant area for contamination. Plasma acts as an effective pollution control device for particulate matter across a broad range of sizes. Plasma's extreme conditions allow for molecular dissociation to occur causing molecular bonds to break apart. Molecules can be broken down into individual atoms and elemental components in the gas phase [81]. The treatment time and temperature are the key variables in this stage. Longer treatment times result in higher removal efficiencies of particles as a whole, while shorter treatment times can be effective in removing surface contaminants from individual particles [82]. Temperature is a more complex variable though, as the optimal temperature for maximum removal efficiency varies by pollutant type. For example, SO_2 removal rates are higher at lower temperatures (164 -170°F vs 175 – 185 °F) while NO_x experience higher removal rates at higher temperatures (165 °F vs 185 °F) [126].

After plasma treatment, byproducts and any remaining particles will need to be separated from the air and collected. This step can also contain a quality assurance and quality control (QA/QC) step. The QA/QC process will ensure the plasma treatment is effective at removing contaminants and that the air is safe to release back into the environment. The final step is to release the treated air back into the environment and properly dispose of or continue treatment of any hazardous byproducts until they are no longer a danger.

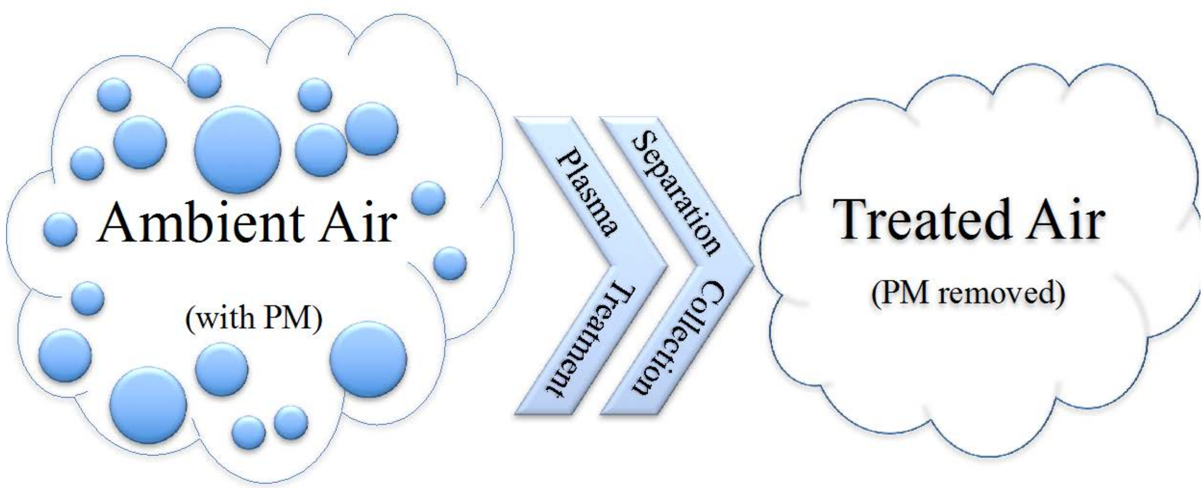

Figure 26: The plasma treatment process for air pollution is a four-step process. Step one involves the identification of particulate matter in the air (natural or man-made). In step two the contaminated air is sent into a plasma treatment zone where plasma is applied to the air to break down contaminants. After plasma treatment, the next step is to separate out and collect any remaining particulates before finally releasing the treated air with the particulate matter removed out of the system.

Parts of the Plasma Treatment System

Each step in the plasma treatment system is fulfilled by a specific piece of equipment. An aerosolized nanoparticle reactor generates well-characterized nanoparticles for testing the effectiveness of the plasma treatment process. An inductively heated plasma generator (IPG) acts as the source of plasma and provides the region for air treatment to occur. An electrostatic precipitator acts as the collection device. Electrostatic precipitators can both separate particulates from the surrounding air and collect the particulates to prevent further mixing. The final stage requires two pieces of equipment. For treated air that is to be released back into the surrounding environment, a gas release valve that is only opened after full treatment is required. A byproduct reformer is needed to collect any byproducts for proper disposal or further treatment to ensure safety. Figure 27 lays out the process of the plasma treatment system.

The Nanoparticle Generator

To study the effects of plasma treatment on ultrafine particulates, engineered nanoparticles will need to be introduced to the system upstream of the plasma zone. The nanoparticle generator needs to be capable of stable, long-term synthesis of nanoparticles to provide consistency during the plasma treatment process. One current device offering the consistency and stability needed to test the effects of plasma on nanoparticles is a silica (SiO_2) nanoparticle reactor, such as that used by Ostraat and Sayes for occupational health and safety studies [125,127]. This device is capable of stable, long-term synthesis of amorphous SiO_2 aerosolized nanoparticles with diameters ranging from 10-70 nm at concentrations of $10^4 – 10^7$ particles/cm^3. Silica is a good test particle because it is the most abundant mineral in the Earth's crust [128]. Common forms of silica include sand and quartz, and it is used in glass manufacturing. Silica nanoparticles are commonly used as additives to strengthen composites and as drug delivery systems in biomedical applications [129]. The nanoparticle generation process requires synthesis of nanoparticles followed by a series of characterization methods.

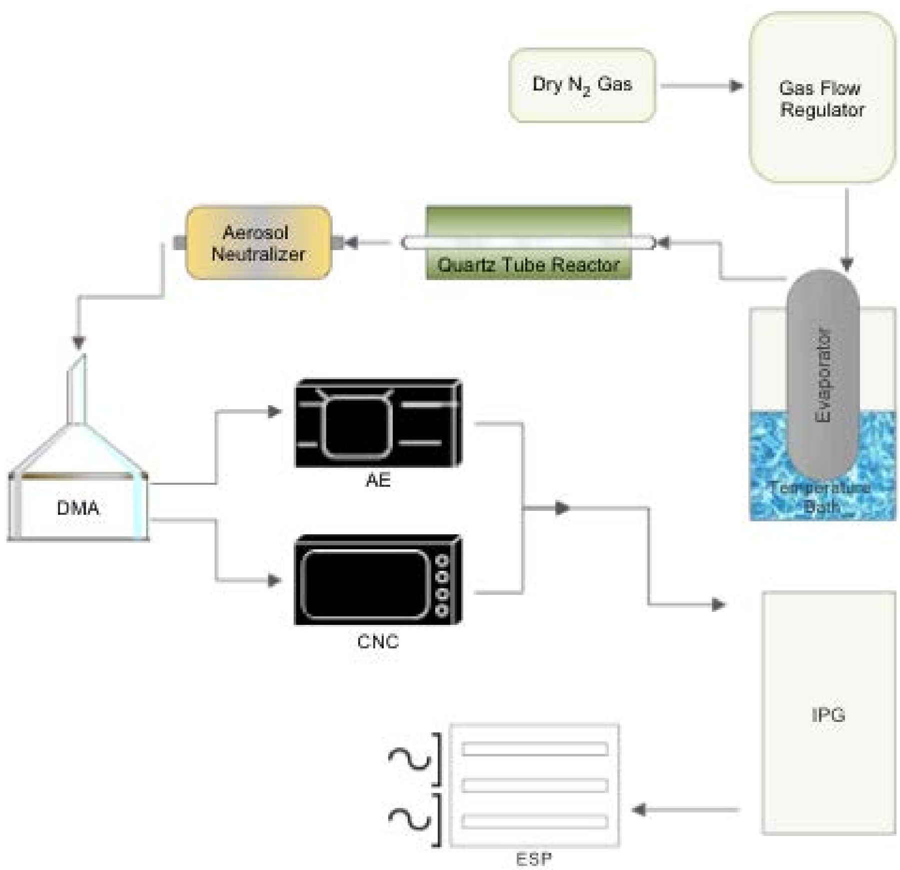

Figure 27: Summary of plasma treatment process for air pollution. To simulate a contaminated environment in a controlled setting, nanoparticles will be generated and characterized by an aerosol nanoparticle reactor before passing into the plasma treatment zone. After plasma treatment by an inductively heated plasma generator, the air will pass through an electrostatic trap to separate air from any remaining contaminants. Treated air can be released back into the environment through a gas release valve or recycled for continued plasma generation while byproducts need to be collected in a waste reformer for further treatment or proper disposal.

Synthesis of nanoparticles begins by separating particle-free N_2 gas into two controlled flows of gas. One flow (Q_{pr}) is sent through a precursor material of tetraethylorthosilicate (TEOS) while the other flow (Q_{dil}) bypasses the precursor. The TEOS precursor is contained in an evaporator in a controlled temperature bath as shown in Figure 28 [127]. As Q_{pr} flows through the evaporator, it draws some of the TEOS from the surface and transports that TEOS out of the evaporator. After leaving the evaporator, Q_{pr} and Q_{dil} recombine and mix together again before entering a quartz tube reactor and furnace. In the furnace, TEOS undergoes thermal decomposition. At temperatures as low as 750 °C, homogenous nucleation will begin to occur and SiO_2 aerosol nanoparticles form [127].

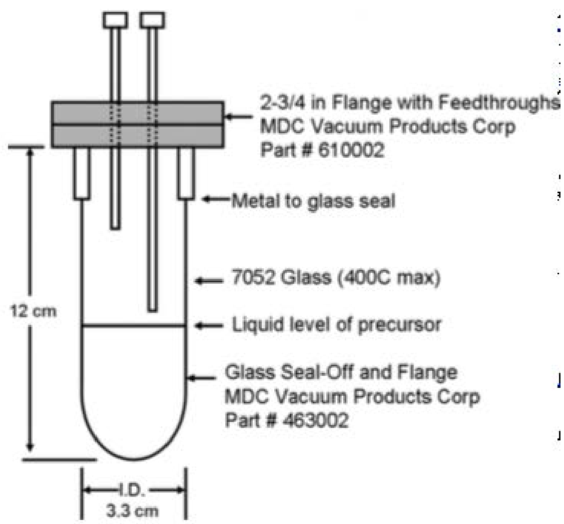

Figure 28: The TEOS precursor is contained in a glass evaporator sealed to allow the gas in and out. Reprinted by permission from Taylor and Francis: Taylor and Francis, Journal of Occupational and Environmental Hygiene, SiO2 Aerosol Nanoparticle Reactor for Occupational Health and Safety Studies, Michele L. Ostraat, 2008.

After synthesis, the aerosolized nanoparticles go through a series of characterization devices to determine their properties. The first characterization process is for size classification. As the SiO_2 aerosol nanoparticles exit the furnace, they cool and then enter a krypton (Kr-85) aerosol neutralizer (TSI Aerosol Neutralizer Model 3077) to bring the particles to a well-known charge distribution before determining the size distribution of the generated nanoparticles[130]. Aerosolized particles distributed by nebulization are typically electrostatically charged. High charge levels can increase loss of particles to the walls of the characterization devices so the charge needs to be neutralized to best maintain the generated particles. The Kr-85 aerosol neutralizer is a radioactive aerosol neutralizer that contains inert Kr-85 gas sealed inside a stainless-steel tube shielded by a metal outer housing. The aerosolized particles pass through the space between the tube and the housing. The device ionizes the surrounding atmosphere into positive and negative ions. Highly charged particles in the aerosol discharge by capturing oppositely polarized ions. The aerosol reaches a steady-state Boltzmann charge distribution of negative and positive charges before exiting the neutralizer [131]. The generated nanoparticles flow from the aerosol neutralizer into a differential mobility analyzer (DMA) (TSI Differential Mobility Analyzer Model 3081) where particles are classified based on the electrical mobility to determine size [127]. A DMA is capable of measuring size distribution of particles from 1 nm – 1 μm using differential mobility analysis [132]. The electrical mobility of a particle relates to its ability to traverse an electric field and is defined as the ratio of the constant limiting velocity of a charged particle in an electric field to the magnitude of the electric field:

$$\mu = \frac{q}{k_b T} D \tag{5}$$

where μ is the electrical mobility (m^2/Vs), q is the electrical charge of a particle (C), k_b is the Boltzmann constant, T is the gas temperature, and D is the diffusion coefficient

(m^2/s)[133]. Electrical mobility depends both on particle size and electrical charge: smaller particle size and/or higher particle charge result in higher electrical mobility. DMAs classify particle size by allowing particles to drift through a generated electric field[132]. A series of voltage range steps is applied to the particles in the electric field. At a certain voltage range, particles will match the position of the outlet gap of the DMA and pass through the device. Particles that pass at a given voltage range are classified as a particular size[130].

Once the size of the nanoparticles is determined by the DMA, the particles flow into two devices for further characterization. Nanoparticles are detected with either a condensation nucleus counter (CNC) (TSI Condensation Particle Counter Model 3756) or an aerosol electrometer (AE) (TSI Aerosol Electrometer Model 3068B). CNCs are useful for detecting low particle concentrations while AEs are useful for detecting high particle concentrations. Both detectors are used in case the concentration of particles exceeds the limit of either detector [127]. CNCs count aerosol particles passed out of the DMA by exposing particles to a saturated vapor fluid and allowing condensation to occur as the particles supersaturate the vapor fluid [134]. The incoming particles are enlarged by vapor condensation to a detectable size as the aerosol passes through a heated saturator. The heat allows alcohol vapor to condense on the particles and grow into droplets which are then detected with a laser beam. Particle number is then estimated by scattered laser light [130]. Aerosol Electrometers (AEs) measure the net charge of generated aerosols and calculate the particle number concentration. AEs use a filter to collect charged particles. An electrometer measures the electrical current trapped in the filter. The particle number concentration is calculated using with the operational calculation equation

$$N = \frac{I}{en_{pq_e}} \quad (6)$$

where N is the total number concentration, e is the elementary unit of charge ($1.602\text{x}10^{-29}$ C), n_p is the number of charges per particle, q_e is the flow rate in cm^3/sec, and I is the electrical current in Amperes[135]. The entire process from synthesis to characterization is demonstrated in Figure 29[125].

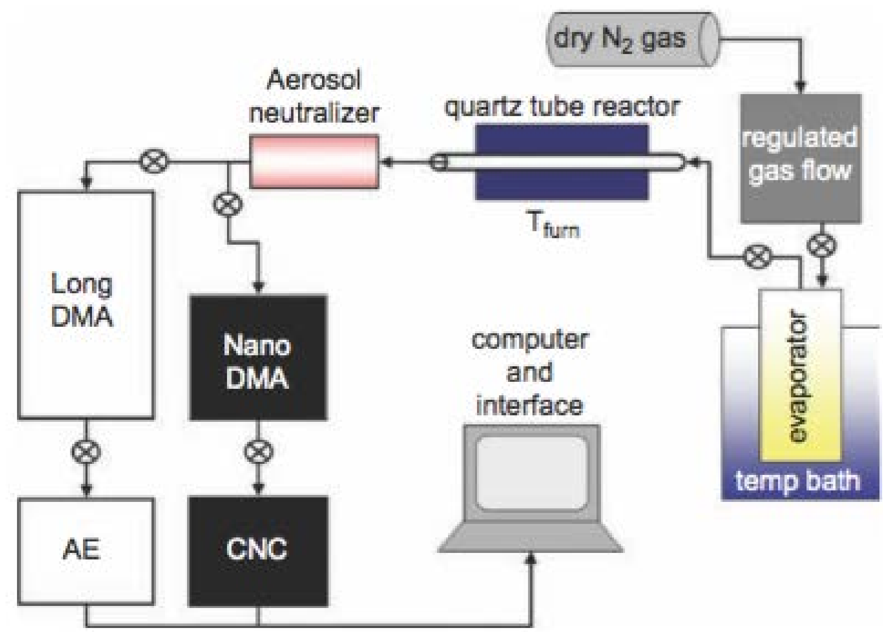

Figure 29: Diagram of the aerosol nanoparticle reactor and characterization instruments. SiO_2 nanoparticles are generated by passing a dry N_2 gas flow through an evaporator containing TEOS. The gas flow entrains some TEOS from the evaporator into a quartz tube reactor and furnace where nucleation will lead to the formation of SiO_2 nanoparticles. The NPs go through a series of instruments to determine particle size, concentration, and particle number size distribution. Reprinted by permission from Taylor and Francis: Taylor and Francis, Inhalation Toxicology, Changing the dose metric for inhalation toxicity studies: Short-term study in rats with engineered aerosolized amorphous silica nanoparticles, Christie M. Sayes, 2010.

The Inductively Heated Plasma Generator

After synthesis and characterization, the aerosol nanoparticles are ready for plasma treatment. An inductively heated plasma generator (IPG) can be used to supply plasma and the plasma treatment zone. IPGs couple power inductively into plasma through electromagnetic induction that produces electric currents to supply the energy for plasma generation [136].

IPGs consist of a discharge tube surrounded by an induction coil[137]. Plasma generation begins by injecting a gas into the tube. A high frequency alternating current is then applied to the coil surrounding the tube to produce a series of axial and azimuthal electric and magnetic fields [138]. The current flowing in the wire produces a strong, oscillating axial magnetic field. The oscillating magnetic field generates a ring current inside the tube in the opposite direction to the current in the coil. The current inside the tube generates another magnetic field opposite to the magnetic field generated by the current in the wire. This series causes the electrons in the injected gas to accelerate. When the kinetic energy of the electrons becomes greater than the ionization energy of the gas, the electrons become unbound, ionizing the gas and producing plasma [138]. The continued application of current to the wire drives the system, allowing for the production of more free electrons that will continue to collide with atoms sparking a chain reaction to maintain the plasma. The free electrons and atoms increase the electrical conductivity of the plasma, allowing the electrical field inside the tube to heat the plasma [44].

The IPG6-B is a miniaturized inductively heated plasma generator that could fulfill the needs of the plasma source for the plasma treatment process[43,139,140]. The IPG6-B utilizes a copper induction coil and a quartz discharge tube 40 mm in diameter [44,43]. The operational parameters of the IPG6-B include a maximum power supply of 15 kW at a 13.56 MHz frequency with pressures as low as 2 Pa and gas mass flow rates less than 0.5 g/s. Possible injection gases are air, argon, hydrogen, helium, oxygen, and carbon dioxide[43]. The IPG6-B feature a side arm diffusion tube at a right angle to the main flow tube to allow for the diffusion of reactants into the chamber.

The Electrostatic Precipitator

After passing through the plasma treatment zone, the aerosol flow containing the decomposed particulates will pass into an electrostatic precipitator (ESP) to remove the aerosolized decomposition byproducts. ESPs are designed to remove suspended particulates from flowing gas using the force of an induced electrostatic charge to impede the particles from passing through the device [141]. These devices are advantageous because energy is applied only to the particulate matter being collected, allowing for more efficient energy consumption.

The general principle for an ESP uses a row of wires followed by a stack of plates as shown in Figure 30[142]. A negative voltage is applied between the wires and the plates. This voltage causes particles to become ionized as the air flows through the wire region. An electrostatic force between the plates causes the ionized particles to be diverted toward the grounded plates. Particles then build up on the collection plate and can be removed from the system[142].

This type of two-stage ESP with charging of particles taking place separately before collection has exhibited removal efficiencies between 77-99% for ultrafine particulates and nanoparticles [143]. One particularly effective ESP design for particulates less than one micrometer is the electric air cleaner system [144]. This system uses an ESP with three sections as seen in Figure 31. The first section is the ionizer consisting of a series of discharge wires and electrically grounded collecting plates. The second section is the collector consisting of discharge plates and grounded plates. The discharge plates are wrapped in a film of dielectric material to create an electric barrier and prevent sparking. The final section is a carbon filter. The electric air cleaner system works on the same principle as the general ESP, but the addition of the collection zone allows small particles that could potentially pass through the filter to be contained. The electrostatic force between the plates in the collector zone diverts light particles onto the collector plates while heavier ones pass through the zone to be deposited on the carbon filter [144].

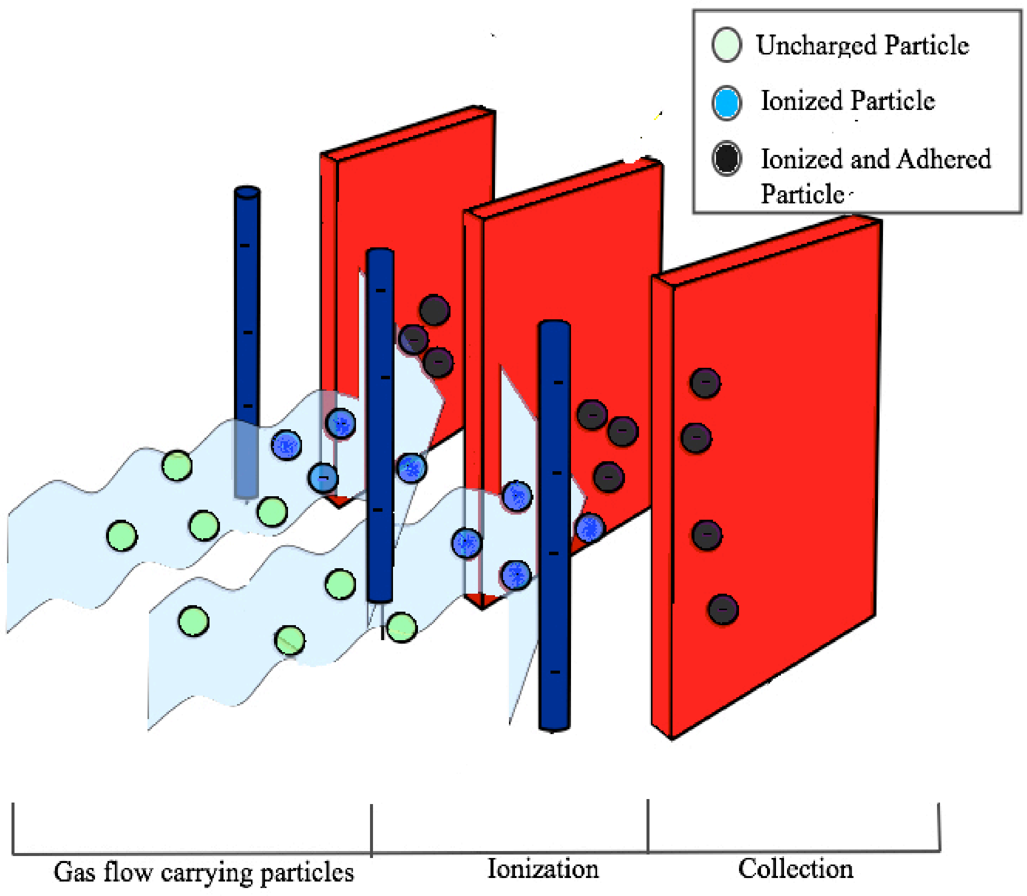

Figure 30: Electrostatic precipitator diagram. ESPs remove particles from air by charging the particles in the ionization zone and attracting the particles to the collection plates in the collection zone. Adapted from E. Mason, 2012.

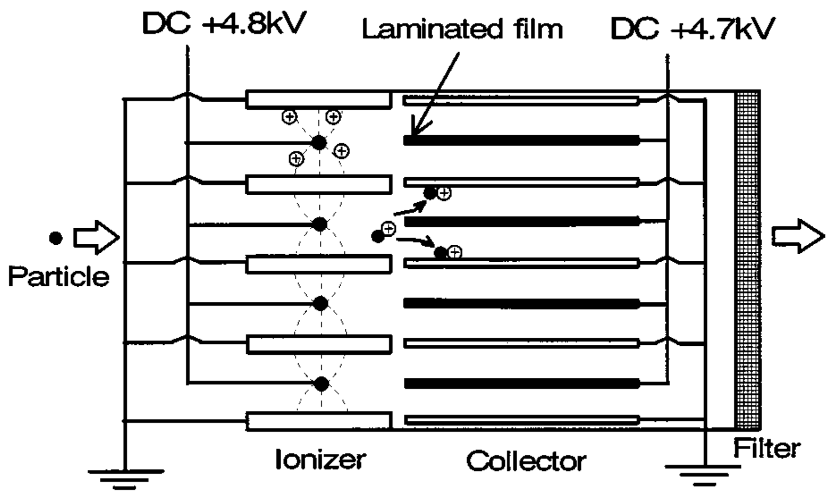

Figure 31: Diagram of a two-stage ESP. Three sections are used to ionize particles in gas before collection. The first section, the ionizer, charges particles. The ionized particles are diverted to the filter by an electrostatic force between the plates in the collector zone. Reprinted by permission from IEEE: M. Okubo, T. Yamamoto, T. Kuroki, and H. Fukumoto, IEEE Trans. Ind. Appl. **37**, 1505 (2001). ©2001 IEEE.

The use of plasma in the treatment phase provides an advantage in the collection stage as well. Plasma treatment will not only decompose particles, but will also charge the particles due to the collection of ions and electrons from the plasma. Since the particles will gain charge during the treatment process, the additional ionization step in the ESP isn't required. The ESP could be adapted from a traditional two-stage device into an effective one stage ESP. For this adaptation, the charging and collecting would still occur separately, but the charging would not occur in the ESP. The plasma treatment phase operates as the source of ionization in place of the row of wires in the proposed ESP design.

The Release Valve and Byproduct Reformer

The final stage of the plasma treatment process is the release of treated air back into the environment. A one-way release valve is required to keep outside air from flowing back into the system while still allowing the treated air to leave.

After the treated air has left the system, there are still particulates adhered to the collection plates of the ESP. A byproduct reformer system can be constructed to remove these left behind particulates in an environmentally friendly manner. Leftover particulates are removed from the plates by mechanical rappers that vibrate the plates and shake the particulates loose. The particulates then fall to a collection area below the ESP. A conveyor belt carries the particulates away from the system for proper disposal or recycling [145]. Particulates trapped in the ESP collection zone can be recycled and further treated through multiple rounds of the plasma treatment process until the particulates are either completely decomposed by the plasma or no longer considered a hazardous substance.

Possible Adaptations

The goal of using plasma to remove ultrafine particulates and engineered nanoparticle contaminants from air to be released back to the environment could be fulfilled utilizing the plasma treatment system as described, but further adaptations could be applied for expand the usability of the system. Adaptations could provide for testing the removal efficiency of various nanoparticles by altering the dry gas and precursor material used in the nanoparticle generator. In addition to SiO_2, zinc oxide and nanosilver are some of the most commonly engineered nanoparticles. When added to consumer products, these nanoparticles can increase desired properties, but some studies have also linked the nanoparticles to an increase in the production of free radicals which can accumulate in tissue and damage DNA [146]. These nanoparticles could be generated using a modified nanoparticle generation method adjusted to suit gas and precursor material.

For instance, nanosilver can be generated by passing an argon gas flow over a piece of bulk silver in place of the evaporator [147]. Zinc oxide nanoparticles can be generated by passing an oxygen and argon gas mixture over liquid zinc droplets [148]. Ideally, multiple types of particles would be tested individually, then in combination with other particle types to simulate and study the removal efficiencies in ambient air.

The system is designed on the idea of producing better air quality for breathing, but it could be adapted for consumer nanoparticle uses as well. In some cases, nanoparticles may be desired for a specific purpose, but can collect surface contaminants during storage of transportation. By aerosolizing the contaminated nanoparticles and passing them through the system, a shorter treatment time could allow for just the removal of the surface contaminants without causing any defect to the nanoparticle itself [82]. The nanoparticle could then be collected in the ESP and returned to its original purpose without the surface contaminants. In this system, the air is not necessarily treated for release as air to breath, so it could be recycled back through the system and used to continue the plasma generation for further engineered nanoparticle surface decontamination.

CHAPTER FIVE

Conclusions

Air quality impacts quality of life. Depending on the exposure time-scale, exposure to poor air quality can result in short-term effects, such as coughing, or long-term effects, such as cardiovascular disease[149]. A key factor in the decline of air quality is the increase of air pollutants from human activities[150]. While air pollutants cover any substance that could be harmful if inhaled in high enough concentration, particulate matter pollution, specifically fine particulate matter, poses particular threats to human health. Fine particulate matter has been linked to many diseases with the most notable effects appearing in the lungs.

The health impacts of particulates on the nanometer scale are becoming increasingly important as the use of nanotechnology advances. The particulates fall under the ultrafine particulate category, but their impact on the body is still debated and needs further study. In the meantime, while the effects of these particulates are still uncertain, the close link of nanoparticulates to their larger fine particulate counterparts, and the known risks of exposure to them, generates the desire to reduce exposure to ultrafine particulates as well as fine particulates. Air filters are one of the more popular air pollution control mechanisms, but the small size of nanoparticulates allows for the possibility of passing through traditional air filters. Because of this, new technology and devices are needed to reduce the exposure to ultrafine particulates.

One potential field that could answer the growing need of ultrafine particulate pollution remediation is plasma physics. Plasma is ionized gas, or a collection of charged particles whose dynamics are governed by electromagnetic forces[49]. Plasma is currently being applied for decontamination of medical surfaces and water. Successful decontamination of larger, coarse particulate matter in flue gases has occurred using plasma treatment. The successful plasma decontamination techniques in other environmental applications makes it a good candidate for ultrafine particulate pollution remediation.

Inductively heated plasma offers a mechanism for nanoparticle decontamination. Inductively heated plasma is generated by electromagnetic induction which produces electric currents to supply the energy for plasma coupling. Inductively heated plasma breaks down molecules through the gasification process. This process uses the extreme heat of the plasma to break apart chemical bonds of molecules, thus converting them into a synthesis gas.

The design for a system utilizing inductively heated plasma to breakdown nanoparticulates into their basic elements is presented. The process involves generating and characterizing nanoparticles to use for testing removal efficiencies of the plasma treatment. After the nanoparticles are generated and characterized, they will enter an inductively heated plasma generator (IPG), specifically Baylor’s IPG6-B. The IPG generates the plasma in an air environment to activate the chemical reactions that break down nanoparticles into their elemental components. After plasma treatment, the elemental components are captured in an electrostatic precipitator. The electrostatic precipitator uses the charge on the particulates induced during the plasma treatment to divert them to the collection plates. This allows for collection and proper disposal of any unwanted particulates that remain.

The suggested aerosolized nanoparticle decontamination system using an inductively heated plasma generator utilizes the concepts of plasma physics to improve environmental health. Plasma treatment is beneficial because it provides decontamination of potentially toxic substances in a confined space without exposing humans to byproduct or gas leakage or harmful radiation. Inductively heated plasma provides a potential solution to the risk posed by nanoparticulates as the use of nanotechnology increases.

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