Non-Thermal Plasma Techniques for
Abatement of Volatile Organic Compounds and Nitrogen Oxides

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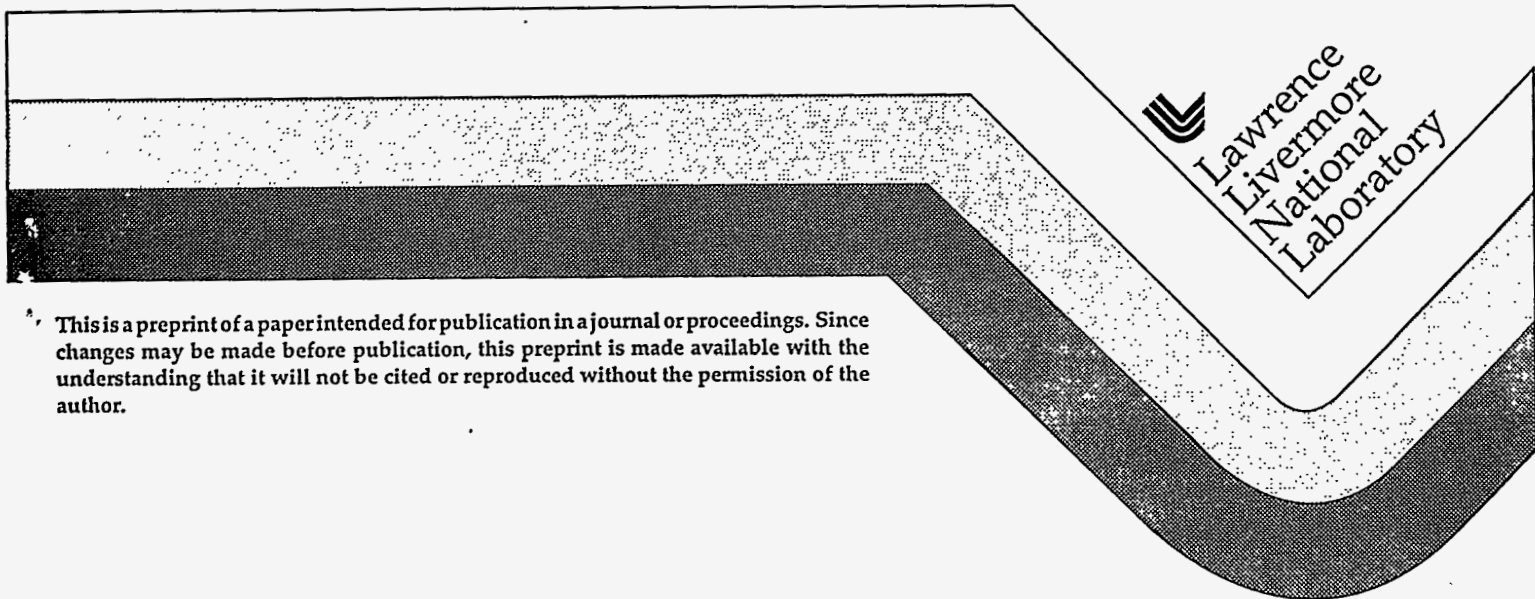G. E. Vogtlin
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NON-THERMAL PLASMA TECHNIQUES FOR ABATEMENT OF VOLATILE ORGANIC COMPOUNDS AND NITROGEN OXIDES

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ABSTRACT

Non-thermal plasma processing is an emerging technology for the abatement of volatile organic compounds (VOCs) and nitrogen oxides (NO_x) in atmospheric-pressure air streams. Either electrical discharge or electron beam methods can produce these plasmas. Each of these methods can be implemented in many ways. There are many types of electrical discharge reactors, the variants depending on the electrode configuration and electrical power supply (pulsed, AC or DC). Two of the more extensively investigated types of discharge reactors are based on the pulsed corona and dielectric-barrier discharge. Recently, compact low-energy (<200 keV) electron accelerators have been developed to meet the requirements of industrial applications such as crosslinking of polymer materials, curing of solvent-free coatings, and drying of printing inks. Special materials have also been developed to make the window thin and rugged. Some of these compact electron beam sources are already commercially available and could be utilized for many pollution control applications.

In this paper we will present a comparative assessment of various non-thermal plasma reactors. The thrust of our work has been two-fold: (1) to understand the scalability of various non-thermal plasma reactors by focusing on the energy efficiency of the electron and chemical kinetics, and (2) to identify the byproducts to ensure that the effluent gases from the processor are either benign or much easier and less expensive to dispose of compared to the original pollutants. We will present experimental results using a compact electron beam reactor and various types of electrical discharge reactors. We have used these reactors to study the removal of NO_x and a wide variety of VOCs. We have studied the effects of background gas composition and gas temperature on the decomposition chemistry. For all of the VOCs investigated, electron beam processing is remarkably more energy efficient than any type of discharge processing. For carbon tetrachloride in dry air, e-beam processing is up to sixty times more energy efficient than discharge processing. We have also found that e-beam processing is about six times more energy efficient than discharge processing in dissociating molecular nitrogen, which is required for the subsequent chemical reduction of NO to N_2 and O_2.

INTRODUCTION

Cost effective technologies for disposal of nitrogen oxides (NO_x) and volatile organic compounds (VOCs) are being sought by government and by industry, and there is a need for reliable data concerning the decomposition mechanisms and kinetics associated with these compounds. Non-thermal plasma processing is an emerging technology for the abatement of NO_x and VOCs in atmospheric-pressure gas streams. Either electron beam irradiation or electrical discharge methods can produce these plasmas. The basic principle that these techniques have in common is to produce a plasma in which a majority of the electrical energy goes into the production of energetic electrons, rather than into gas heating. Through electron-impact dissociation and ionization of the background gas molecules, the energetic electrons produce free radicals and additional electrons which, in turn, oxidize or reduce the pollutant molecules. The potential of electron beam and electrical discharge methods has been demonstrated for the abatement of NO_x and many kinds of VOCs [1].

To apply non-thermal plasma processing to pollution control, the electrical energy consumption and byproduct formation need to be addressed. The thrust of our work has been to understand the scalability of the non-thermal plasma technique by focusing on the energy efficiency of the process and identifying the byproducts.

There are many types of non-thermal plama reactors that are being investigated for pollution control applications. Whatever the type of reactor, the plasma can induce four basic types of reactions with the pollutant molecules, as shown in Fig. 1. For stationary applications, it may be sufficient to oxidize NO to NO_2; the latter is then further oxidized by OH radicals to nitric acid. Some form of scrubbing is required to collect the final products. For mobile engine applications, it is very important to make a distinction between NO removal by chemical oxidation and NO removal by chemical reduction. To avoid the need for scrubbing of process products, the desired method of NO removal is by chemical reduction; i.e. the conversion of NO to the benign products N_2 and O_2. For typical exhaust gases without additives, the only species that the plasma can produce to implement NO reduction is the N atom. For some VOCs such as carbon tetrachloride, the electrons play a key role in the direct decomposition of the VOC molecules.

The electron mean energy in a plasma reactor is very important because it determines the types of radicals produced in the plasma and the input electrical energy required to produce those radicals. Fig. 2 shows the dissipation of the input electrical power in a dry air discharge. Note that at low electron mean energies (< 5 eV) a large fraction of the input electrical energy is consumed in the vibrational excitation of N_2. Electron mean energies around 5 eV are optimum for the electron-impact dissociation of O_2, which is important for the production of O radicals. These oxidizing radicals play a key role in the initial decomposition of some types of VOCs. To implement the chemical reduction of NO to benign molecules such as N_2 and O_2, the important reducing species is the N atom, which is produced through the electron-impact dissociation of N_2. High electron mean energies are required to efficiently implement the dissociation of N_2. For VOCs that take advantage of electron-induced or ion-induced decomposition, high electron mean energies are also required to efficiently implement the ionization of the background gas.

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- ***Oxidation***

$$e + O_2 \Rightarrow e + O(^3P) + O(^1D)$$
$$O(^3P) + NO + M \Rightarrow NO_2 + M$$
$$O(^1D) + H_2O \Rightarrow OH + OH$$
$$OH + NO_2 \Rightarrow HNO_3$$

- ***Reduction***

$$e + N_2 \Rightarrow e + N + N$$
$$N + NO \Rightarrow N_2 + O$$

- ***Electron-induced decomposition***

$$e + N_2 \Rightarrow e + e + N_2^+$$
$$e + O_2 \Rightarrow e + e + O_2^+$$
$$e + CCl_4 \Rightarrow CCl_3 + Cl^-$$

- ***Ion-induced decomposition***

$$N_2^+ + CH_3OH \Rightarrow CH_3^+ + OH + N_2$$

Fig. 1. The plasma can induce four basic types of reactions with the pollutant molecules.
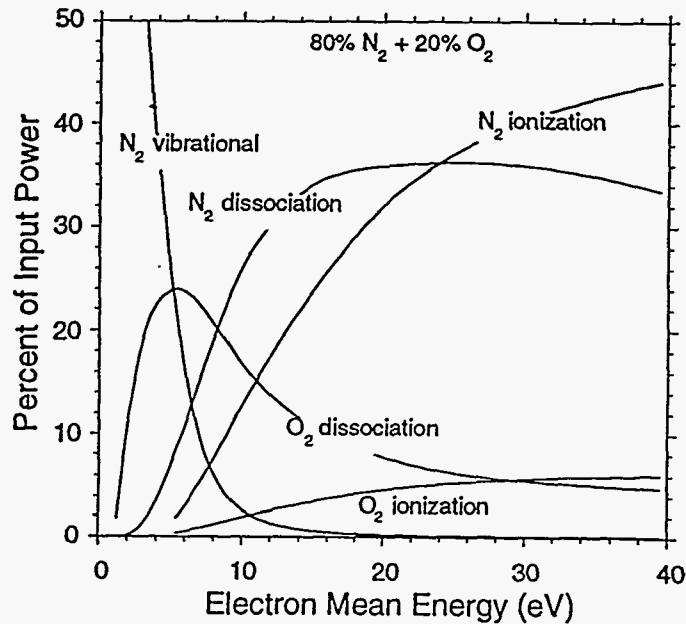

Fig. 2. Power dissipation in a dry air discharge, showing the percent of input power consumed in the electron-impact processes leading to vibrational excitation, dissociation and ionization of N_2 and O_2.

Much of our work has been devoted to the characterization of the electron mean energy in the plasma. In terms of the electron energy distribution produced in the plasma, we believe there are basically only two types of non-thermal atmospheric-pressure plasma reactors: electrical discharge reactors and electron beam reactors. Electrical discharge techniques can be implemented in many ways, depending on the electrode configuration and electrical power supply (pulsed, AC or DC). Two of the more extensively investigated types of electrical discharge reactors are the pulsed corona and the dielectric-barrier discharge, shown in Fig. 3. In the pulsed corona method, the reactor is driven by very short pulses of high voltage, thus creating short-lived discharge plasmas that consist of energetic electrons, which in turn produce the radicals responsible for the decomposition of the undesirable molecules. In a dielectric barrier discharge reactor, one or both of the electrodes are covered with a thin dielectric layer, such as glass or alumina. Dielectric-barrier discharge reactors, also referred to as silent discharge reactors, are now routinely used to produce commercial quantities of ozone. Whereas in the pulsed corona method the transient behavior of the plasma is controlled by the applied voltage pulse, the plasma that takes place in a dielectric-barrier discharge self-extinguishes when charge build-up on the dielectric layer reduces the local electric field.

Electrical Discharge Reactors

Pulsed Corona

gas flow

discharge arrested by removing drive field

Dielectric Barrier

AC

gas flow

DIELECTRIC

discharge arrested by charging of dielectric

Electron Beam Reactor

Electron Gun

Accelerator/ Scanner
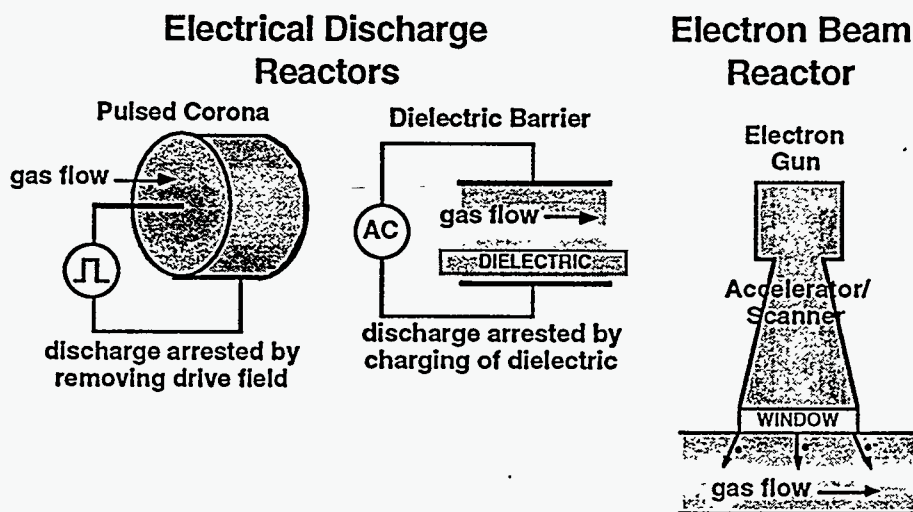
WINDOW

gas flow

Fig. 3. There are basically two types of non-thermal atmospheric-pressure plasma reactors: electrical discharge reactors and electron beam reactors.

For most electrical discharge reactors our results suggest that the attainable electron mean energy is rather limited and cannot be significantly enhanced by changing the electrode configuration or voltage pulse parameters. This has driven our efforts to improve the efficiency of the non-thermal plasma process by using a compact electron beam source. In this paper we present data on non-thermal plasma processing of NO_x and various VOCs using a pulsed corona reactor, a dielectric-barrier discharge reactor, and an electron beam reactor.

TEST FACILITY

All of our experiments were performed in a flow-through configuration. To characterize the energy consumption of the process for each VOC, the composition of the effluent gas was recorded as a function of the input energy density. The input energy density, Joules per standard liter, is the ratio of the power (deposited into the gas) to gas flow rate at standard conditions (25°C and 1 atm). The amount of NO_x or VOC was quantified using a chemiluminescent NO_x meter, an FTIR analyzer and a gas chromatograph/mass spectrometer.

Our electron beam reactor used a cylindrical electron gun designed to deliver a cylindrically symmetric electron beam that is projected radially inward through a 5 cm wide annular window into a 17 cm diameter flow duct. An electron beam of 125 keV energy was introduced into the reaction chamber through a 0.7 mil thick titanium window. The electron beam current was produced from a low-pressure helium plasma in an annular vacuum chamber surrounding the flow duct.

Our pulsed corona reactor is a 1.5 mm diameter wire in a 60 mm diameter metal tube 300 mm long. The power supply is a magnetic pulse compression system capable of delivering up to 15-35 kV output into 100 ns FWHM pulses at repetition rates from 15 Hz to 1.5 kHz. The power input to the processor was varied by changing either the pulse energy or pulse repetition frequency. For the same energy density input, either method produced almost identical results. The gas mixtures were set with mass flow controllers. The gas and processor temperatures can be maintained at a temperature that can be controlled from 25°C to 300°C.

We wanted to see if there are significant fundamental differences in the performance of various discharge reactors. We therefore investigated whether it is possible to improve the processing efficiency by taking advantage of transient high electric fields during the formation of the streamer plasma. To do this, the voltage pulse should be very fast-rising, but with a pulse length short enough so that most of the radical production occurs only during streamer propagation. One way of achieving this condition is by combining the fast-rising, strongly non-uniform applied electric field of a corona reactor with the self-extinguishing microdischarge pulses of a dielectric-barrier discharge reactor. We therefore used a reactor that is a form of hybrid between a pulsed corona reactor and a dielectric-barrier discahrge reactor. The reactor consisted of a wire (1.5 mm diameter) in a 300 mm long dielectric (alumina) tube with inner and outer diameters of 28 mm and 35 mm, respectively. The middle 150 mm of the dielectric tube has aluminum foil coating the outside to form the outer electrode.

RESULTS

The application of electron beam irradiation for NO_x removal in power plant flue gases has been investigated since the early 1970's in both laboratory- and pilot-scale experiments [2-5]. Electrical discharge methods are relatively new entrants in the field of flue gas cleanup [6-8].

There are basically two types of reactions responsible for the depletion of NO by non-thermal plasmas: oxidation and reduction (see Figure 1). In power plant flue gas

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treatment applications, the purpose of the plasma is to oxidize NO. The plasma produces OH radicals that play the major role in the simultaneous oxidation of NO and SO_2 to their respective acids. The presence of SO_2 lowers the power requirement of the oxidation process by recycling the OH radicals (see Figure 4). The presence of O radicals provide additional oxidation of NO to NO_2; the latter is then further oxidized by OH radicals to nitric acid. The desired products, in the form of ammonium salts, are then obtained by mixing ammonia with the formed acids. Some form of scrubbing is required to collect the final products.
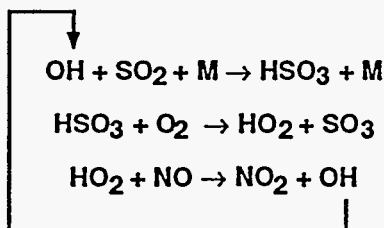
$$OH + SO_2 + M \rightarrow HSO_3 + M$$
$$HSO_3 + O_2 \rightarrow HO_2 + SO_3$$
$$HO_2 + NO \rightarrow NO_2 + OH$$

Fig. 4. In flue gas treatment by non-thermal plasmas, the OH radical plays a key role in the simultaneous oxidation of NO and SO_2. The presence of SO_2 serves to lower the energy cost for oxidation of NO by converting OH to HO_2; the OH radical is then reproduced when NO is oxidized by HO_2.

Recently there has been a growing interest in the application of non-thermal plasmas to the removal of NO_x from engine exhaust gases [9]. For mobile engine applications, it is very important to make a distinction between NO removal by chemical oxidation and NO removal by chemical reduction. To avoid the need for scrubbing of process products, the desired method of NO removal is by chemical reduction; i.e. the conversion of NO to the benign products N_2 and O_2. For typical exhaust gases without additives, the only species that the plasma can produce to implement NO reduction is the N atom. The term "NO reduction" refers strictly to the reaction

$$N + NO => N_2 + O.$$
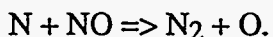
The plasma produces N atoms through electron-impact dissociation of N_2 in the exhaust gas:

$$e + N_2 => e + N + N.$$
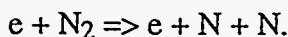
The development of a technology for the chemical reduction of NO_x in oxygen-rich environments would represent a breakthrough in the transportation industry. The implication of such a technology is far reaching for mobile sources since it will allow fuel-efficient, lean-burn gasoline and diesel engines to be developed that decrease CO_2 greenhouse gas emissions yet still permit the reduction of harmful NO_x, carbon monoxide and hydrocarbons. Although such a technology exists for stationary combustion sources, a more feasible, cost-effective and environmentally sound approach for mobile sources does not exist.

Fig. 5 shows a comparison between electron beam, pulsed corona and dielectric-barrier discharge processing of 100 ppm of NO in N_2. The concentration of NO is presented as a function of the input energy density deposited into the gas. In the $NO-N_2$

mixture the removal of NO is dominated by the reduction reaction N + NO => N_2 + O. These experiments therefore provide a good measure of the electron-impact dissociation rate of N_2. Fig. 5 shows that the energy consumption for NO reduction by electron beam processing is six times less than that of pulsed corona or dielectric-barrier discharge processing. The energy density required to reduce NO is around 20 Joules/liter and 120 Joules/liter by electron beam and electrical discharge processing, respectively. These experiments provide a good measure of the specific energy consumption for electron-impact dissociation of N_2. The specific energy consumption obtained by electron beam processing represents the minimum energy cost for N_2 dissociation that can be achieved in any type of atmospheric-pressure non-thermal plasma reactor [10, 11].
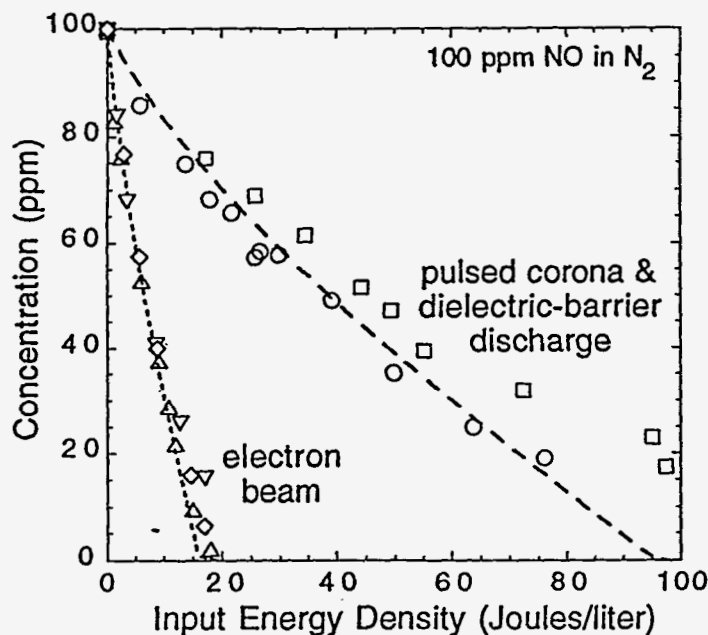

Fig. 5. Electron beam, pulsed corona and dielectric-barrier discharge processing of 100 ppm NO in N_2.

VOCs are emitted from manufacturing the multitude of consumer products used very day. In most manufacturing processes, either for the raw materials, intermediates, or the finished product, VOC-containing materials are present as chemicals, solvents, release agents, coatings, and decomposition products that eventually must be disposed. In such manufacturing, there is usually a gaseous effluent that contains low concentrations of organics and is vented into the atmosphere. Chlorinated VOCs are some of the most common solvents used, and are now found in hazardous concentrations at many industrial and government installations. The electron beam method has been applied to the removal of trichloroethylene [1, 12-13], carbon tetrachloride [14- 16] and other types of volatile hydrocarbons from industrial off-gases [17]. Some of the electrical discharge reactors that have been investigated for VOC abatement include the pulsed corona [18-20], ferroelectric

packed bed [19-20] dielectric-barrier discharge [21-27], surface discharge [28-29], gliding arc [30-31] and microwave [32].

Fig. 6 shows a comparison between electron beam, pulsed corona and dielectric-barrier discharge processing of 100 ppm of carbon tetrachloride (CCl_4) in dry air (20% O_2 80% N_2) at 25°C. The rate limiting step in the decomposition of CCl_4 is determined by the dissociative attachment of CCl_4 to the thermalized electrons in the created plasma: $e + CCl_4 => Cl^- + CCl_3$. During the creation of the plasma, electron-ion pairs are produced through primary electron-impact ionization of the bulk molecules, such as $e + N_2 => e + N_2^+$ and $e + O_2 => e + O_2^+$, and the corresponding dissociative ionization processes for N_2 and O_2. An analysis of the rates of the reactions discussed above suggests that the energy consumption for CCl_4 removal is determined by the energy consumption for creating electron-ion pairs. Fig. 6 shows that the energy consumption for CCl_4 decomposition by electron beam processing is around sixty times less than that of pulsed corona processing. The energy density required to decompose CCl_4 by 90% is around 20 Joules/liter and 1270 Joules/liter by electron beam and electrical discharge processing, respectively. This result demonstrates that for VOCs requiring copious amounts of electrons for decomposition, electron beam processing is much more energy efficient than electrical discharge processing.

The main products in the plasma processing of CCl_4 in air are Cl_2, $COCl_2$ and HCl. These products can be easily removed from the gas stream; e.g. they dissolve and/or dissociate in aqueous solutions and combine with $NaHCO_3$ in a scrubber solution to form NaCl.
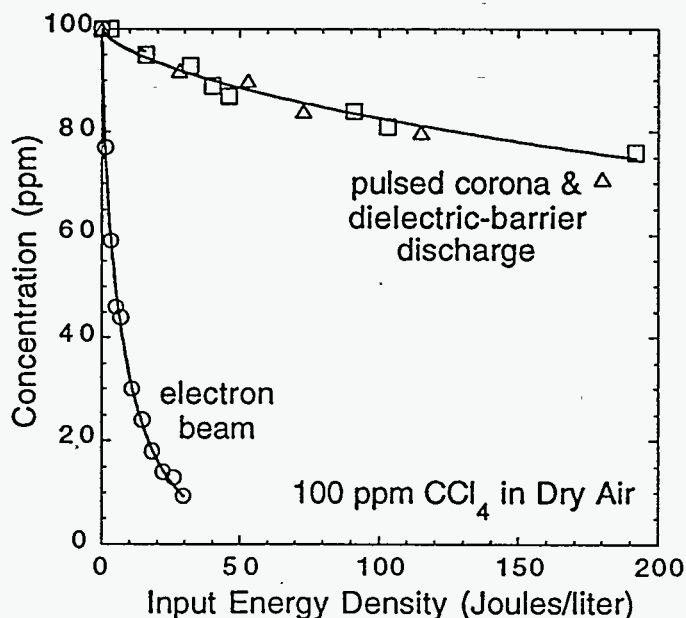

Fig. 6. Electron beam, pulsed corona and dielectric-barrier discharge processing of 100 ppm of carbon tetrachloride in dry air.

Fig. 7 compares electron beam and pulsed corona processing of 100 ppm trichloroethylene (TCE or C_2HCl_3) in dry air at 25°C. Compared to the other VOCs investigated, TCE is easy to decompose and the energy consumption is low in either electron beam or pulsed corona processing. Although the energy efficiency for electron beam processing of TCE is also higher than pulsed corona processing, the difference in processing efficiencies is not as dramatic as that for CCl_4. Our byproduct measurements and material balance analysis point to significant amounts of dichloroacetyl chloride (DCAC), phosgene, and hydrochloric acid in addition to smaller amounts of CO and CO_2 in the effluent. The high efficiency in decomposing TCE has been explained on the basis of a chain reaction propagated by Cl. The energy density required to decompose TCE by 90% is around 6 Joules/liter and 38 Joules/liter by electron beam and pulsed corona processing, respectively.
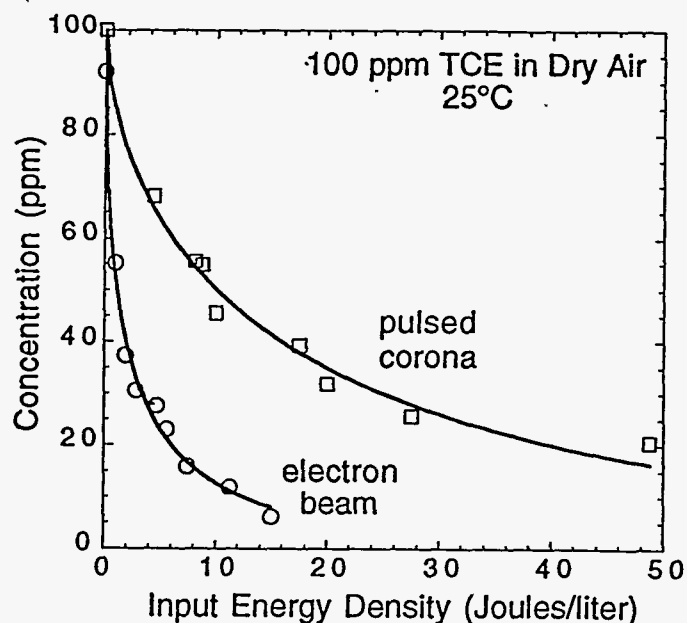

Fig. 7. Electron beam and pulsed corona processing of 100 ppm of trichloroethylene in dry air.

In discharge processing, the rate coefficients for electron-impact dissociation and ionization reactions strongly depend on the electron mean energy in the discharge plasma. In pulsed corona and dielectric-barrier discharge reactors, the non-thermal plasma is produced through the formation of statistically distributed microdischarges known as streamers. The electrons dissociate and ionize the background gas molecules within nanoseconds in the narrow channel formed by each microdischarge. The electron energy distribution in the plasma is complicated because the electric field is strongly non-uniform (e.g. because of strong space-charge field effects) and time dependent. During the microdischarge formation phase, the electron number rises drastically. Due to field strength

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enhancement in the ionization wave, the highest electron energies occur during this phase. The mean electron energy reaches values of more than 10 eV - suitable for large dissociation and ionization of the gas. However, since this is a highly transient phase, and since the ionization wave covers only small parts of the gap at the same time, this phase seems to be less important in producing most of the active radicals. Most of the species responsible for the chemical processing are generated in the microdischarge channels already established during the main current flow. In each microdischarge column, the electrons acquire a drift velocity, v_d, and an average energy corresponding to an effective E/n, i.e., the value of the electric field E divided by the total gas density n. The efficiency for a particular electron-impact process can be expressed in terms of the G-value (number of dissociation reactions per 100 eV of input energy) defined as

$$G\text{-value} = 100 \, k \, / \, (v_d \, E/n)$$

where k is the rate coefficient (cm^3/molec-s). The rate coefficient k represents the number of reactions in a unit volume per unit time. The quantity $v_d \, E/n$ represents the amount of energy expended by the electrons in a unit volume per unit time. In Fig. 8 the calculated G-values for various electron-impact dissociation and ionization processes in dry air are shown as functions of the electron mean energy in the discharge plasma [16, 33].
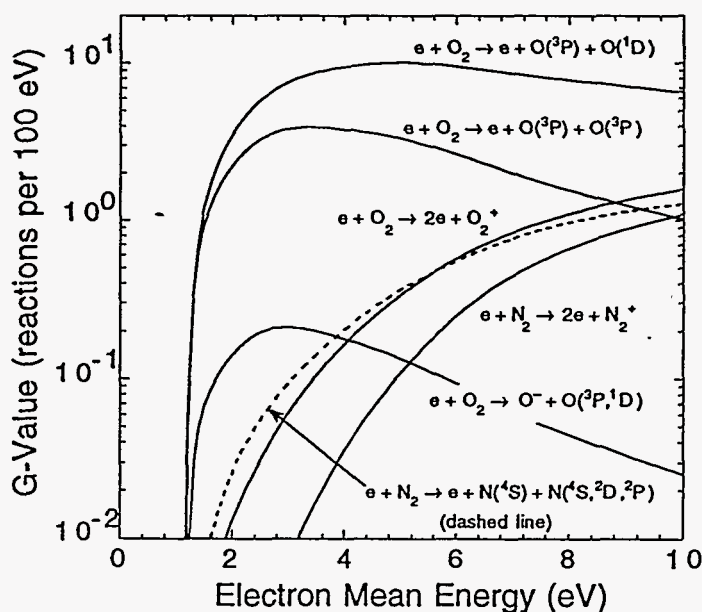

Fig. 8. Calculated G-values (number of reactions per 100 eV of input energy) for dissociation and ionization processes in dry air, shown as functions of the electron mean energy in a discharge plasma.

Under most conditions encountered in pulsed corona or dielectric-barrier discharge processing, the effective E/n is close to the value for breakdown (Paschen field) [33-34]. Fig. 9 shows the breakdown values for the reduced field strength, E/n, as a function of the

electrode gap spacing for an atmospheric pressure discharge. Note that for typical electrode gap spacings used in the implementation of pulsed corona or dielectric-barrier discharge reactors, the breakdown E/n is limited to values between 100 and 300 x 10^{-17} V-cm^2. For air-like mixtures, the effective E/n is around 150 x 10^{-17} V-cm^2, which corresponds to an electron mean energy of about 4 eV. The corresponding average electron energies are shown in Fig. 10. There are two ways of increasing the electron mean energy: (1) use very narrow gap spacings (100 microns or less) to increase the breakdown E/n for the same applied voltage, or (2) use very fast rising voltage pulses (10 nanoseconds or less risetime) to increase the breakdown E/n for typical gap spacings. We have investigated both methods. In the first case we used a parallel-plate dielectric-barrier discharge reactor with a gap spacing of 50 microns. With such a narrow gap we have been able to increase the electron mean energy to around 10 eV, as verified by experiments using simple mixtures of NO or NO$_2$ in N$_2$. In the case of very fast rising voltage pulses, the breakdown E/n could increase to about twice the normal breakdown E/n, i.e. around 300 x 10^{-17} V-cm^2, which corresponds to an electron mean energy of around 7 eV. A reasonable upper limit for the effective E/n is 400 x 10^{-17} V-cm^2 for an extremely fast rising voltage pulse; this condition corresponds to an electron mean energy of about 9 eV.
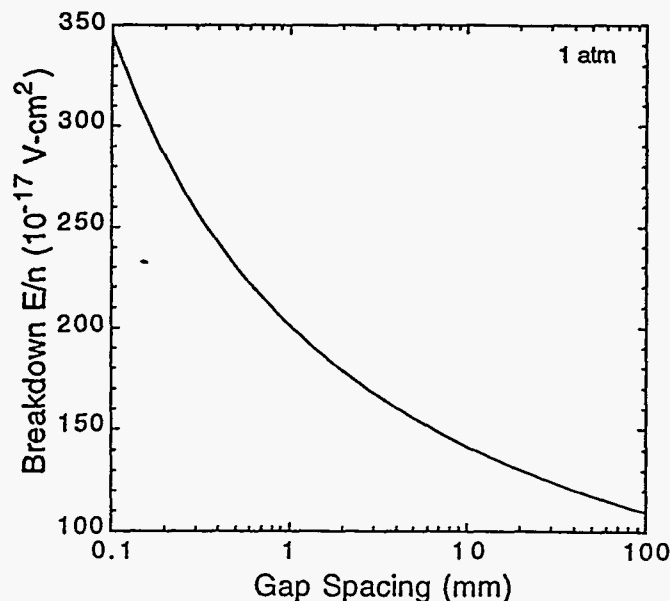

Fig. 9. Breakdown values for the reduced field strength, E/n, as a function of the electrode gap spacing for an atmospheric pressure discharge. E is the electric field and n is the total gas density.

For the discharge reactor conditions used in most of our experiments we have verified that the effective electron mean energy is around 4 eV. Table 1 shows a comparison of the calculated G-values for dissociation processes in dry air using an electron beam and a discharge reactor. Discharge plasma conditions are optimum for the dissociation of O$_2$. Table 2 shows a comparison of the calculated G-values for ionization

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processes in dry air using an electron beam and a discharge reactor. Note from Tables 1 and 2 that the production of N atoms and electron-ion pairs is much higher in an electron beam reactor compared to that in a discharge reactor. As shown in Fig. 11, electron beam reactors are also more efficient in producing OH radicals.
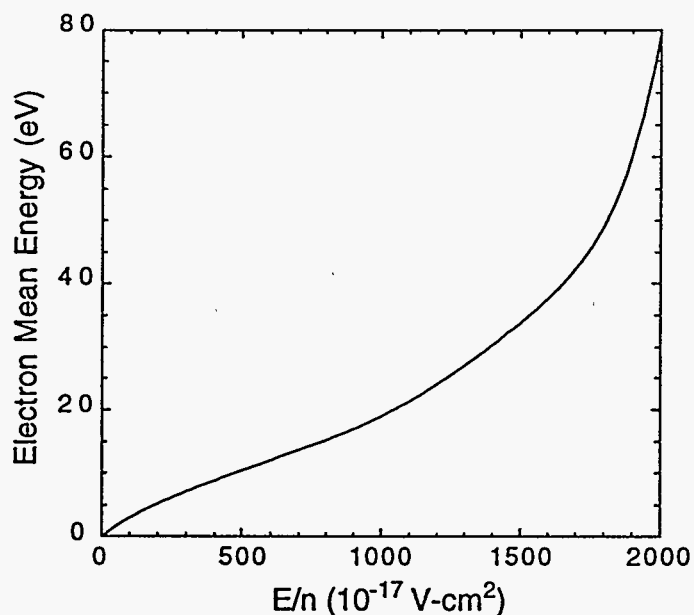

Fig. 10. Average kinetic energy of the electrons in air as a function of the reduced field strength, E/n. The E/n experienced by the plasma in electrical discharge reactors is typically less than 300×10^{-17} V-cm^2. The average electron kinetic energy is thus limited to values less than 10 eV.

Table 1. Calculated G-values (number of reactions per 100 eV of input energy) for dissociation processes in dry air using an electron beam and an electrical discharge reactor.

REACTION	Electron Beam	Discharge
$e + N_2 \rightarrow e + N(^4S) + N(^4S,^2D,^2P)$	1.2	0.17
$e + O_2 \rightarrow e + O(^3P) + O(^3P)$	1.3	4.0
$e + O_2 \rightarrow e + O(^3P) + O(^1D)$	2.65	10.0
$e + O_2 \rightarrow O^- + O(^3P, ^1D)$	0.11	0.19

Table 2. Calculated G-values (number of reactions per 100 eV of input energy) for ionization processes in dry air using an electron beam and an electrical discharge reactor.

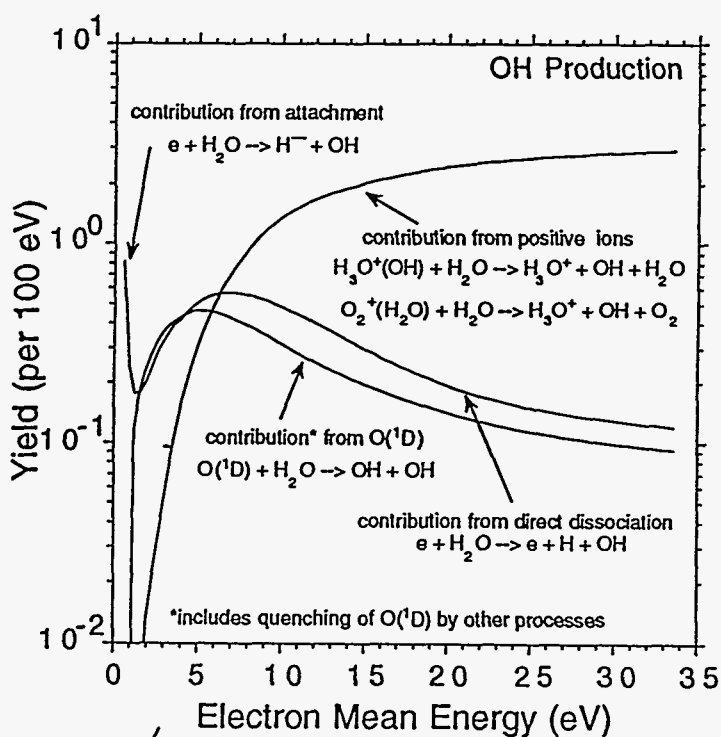| REACTION	Electron Beam	Discharge
$e + N_2 \rightarrow 2e + N(^4S, {}^2D) + N^+$	0.69	$< 10^{-6}$
$e + N_2 \rightarrow 2e + N_2^+$	2.27	0.044
$e + O_2 \rightarrow 2e + O_2^+$	2.07	0.17
$e + O_2 \rightarrow 2e + O(^1D) + O^+$	1.23	0.0016

Fig. 11. Contributions of various processes to the production of OH as a function of the electron mean energy in the plasma for a gas mixture of 5% O_2, 10% H_2O, 15% CO_2 and 70% N_2. In electron beam processing, the OH radicals come mainly from the positive ions reacting with H_2O.

CONCLUSIONS

There are basically two types of non-thermal plasma reactors: electrical discharge reactors and electron beam reactors. Electrical discharge reactors can be implemented using pulsed, AC or DC power supplies. For most electrical discharge reactors our results suggest that the attainable electron mean energy is rather limited. This has driven our efforts

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to improve the efficiency of the non-thermal plasma process by using a compact electron beam source. Recently, compact low-energy (<200 keV) electron accelerators have been developed to meet the requirements of industrial applications such as crosslinking of polymer materials, curing of solvent-free coatings, and drying of printing inks. Special materials have also been developed to make the window thin and rugged. Some of these compact electron beam sources are already commercially available and could be utilized for many pollution control applications.

We have compared the basic energy requirements for electron beam and electrical discharge processing of NO_x and a wide variety of VOCs. Because of their low electron mean energies, electrical discharge reactors are most suitable only for processes requiring O radicals. For ozone synthesis, electrical discharge reactors are definitely more efficient. For processes requiring copious amounts of N atoms, OH radicals, electrons or ions, the use of electron beam reactors is generally the best way to minimize the electrical energy consumption. For all the VOCs we have investigated, we found that electron beam processing is more energy efficient than electrical discharge processing. We believe most VOCs are more efficiently decomposed by electron-induced or ion-induced decomposition reactions. Electron beam reactrors are much more efficient in producing electron-ion pairs. For VOCs such as carbon tetrachloride that require copious amounts of electrons for its decomposition, electron beam processing is remarkably more energy efficient.

ACKNOWLEDGMENTS

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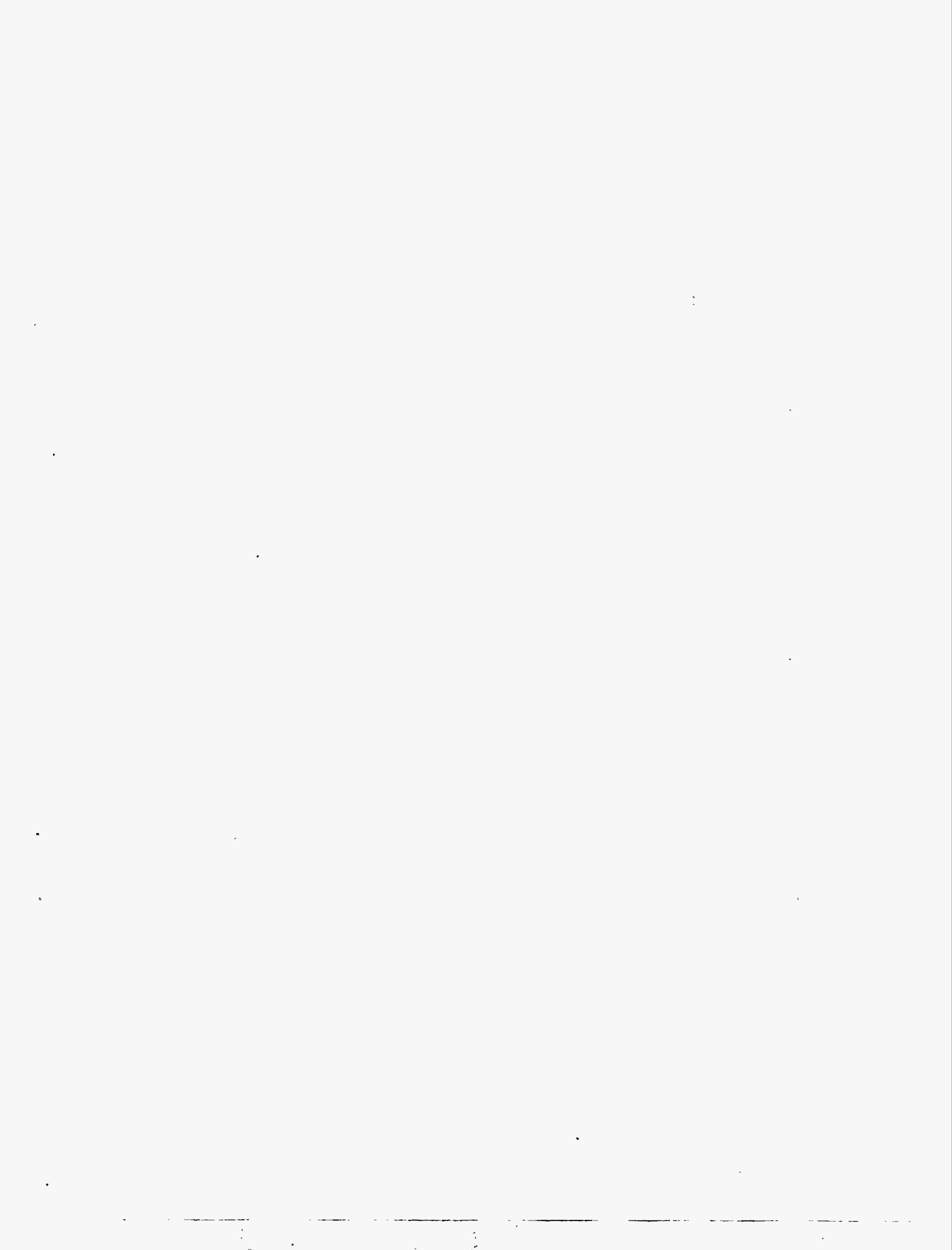
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