A MODEL OF OZONE GENERATION IN POSITIVE POLARITY ELECTROSTATIC PRECIPITATORS

by

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NOMENCLATURE

$[O_3]$	Quantity of ozone generated by volume
$\underline{a}$	wire radius
pphm	parts per hundred million
E_o	onset electric field for the corona kV/cm (kilo-volts/centimeter)
m	roughness factor 1.0 for smooth wires <1.0 for rough wires
δ	relative density of air
T	temperature in degrees Kelvin
P	pressure
E_{avg}	average electric field in the corona (kV/cm)
Δa	width of the corona (ionizing sheath)
V_o	onset voltage for the corona
b	radius of the charging cylinder
Q	energy dissipated in the ionizing sheath per unit of time
E	error mean square
I	corona current mA (milliamps)
$\underline{a}^*$	effective radius
E_s	electric field at the surface kV
Q*	air flow L/sec

INTRODUCTION

Electrostatic precipitation has become commonplace: in industry, wherever stack effluents must be reduced; in office buildings, where the removal of fine particulate matter reduces the soiling of furnishings; and in living quarters, where the air must be cleaned of air-borne allergens.

Electrostatic precipitation is considered one of the most efficient mechanisms for removing particulate matter from the air. It is based on the principle that charged particles can be collected in an electric field.

Electrostatic precipitators have been used to clean stack effluents since 1908 [1], but their application to occupied spaces was delayed because they produced excessive amounts of ozone, a health hazard. Stack-cleaning precipitators use a negative polarity charging section to charge the particles. In 1937 Penney [2] introduced the positive polarity charging section as a means of reducing ozone generation, even though it was less efficient for occupied space applications.

Although positive polarity electrostatic precipitators have become commonplace, very little has been published analyzing or quantifying ozone production. The design of precipitators to limit ozone production has been done qualitatively.

It is desirable to maximize collection efficiency of electrostatic precipitators for occupied spaces while minimizing ozone generation. Therefore it would be advantageous to be able to predict both quantities from known, easily measured parameters. The measured and calculated efficiencies of electrostatic precipitators have been extensively covered in the literature [3,4].

It is the purpose of this study, therefore, to contribute to the understanding of ozone production in the positive polarity charging section.

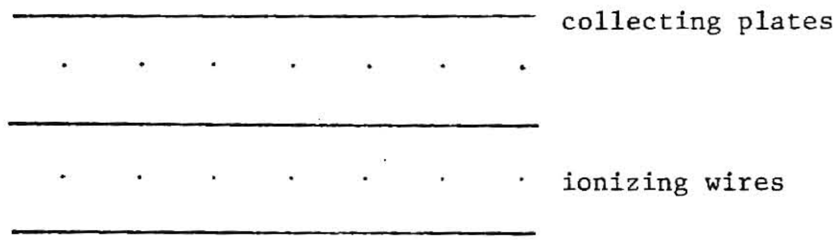
ELECTROSTATIC PRECIPITATION

Electrostatic precipitators can be catagorized into two types: (1) negative polarity precipitators and (2) positive polarity precipitators. The polarity refers to that of the fine wire.

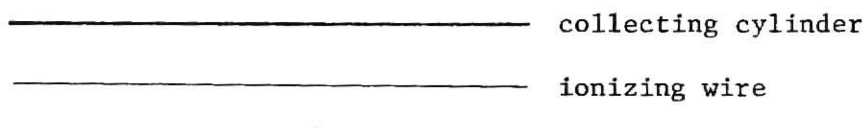
In the negative polarity precipitator, most of the particulate matter receives a negative charge from ions produced in a negative corona (corona will be defined in "Corona Formation") about a fine wire. The charged particles are usually collected in the same chamber where the charging occurs. Schematic drawings of two single stage precipitators are presented in Figure 1a. In positive polarity electrostatic precipitators, most of the particulate matter receives a positive charge from ions produced in a positive corona about a fine wire. The collection of positively charged particulate matter occurs in a separate collection chamber that immediately follows the charging section, as depicted in Figure 1b.

It should be noted that the voltages involved in the two types of precipitators differ significantly. In negative polarity precipitators, the charging section may vary from 30,000 to 100,000 volts. The voltage is limited in both cases to prevent "spark-over" in the section. Olgesby [5,p.3] discusses the difference in "spark-over" voltage:

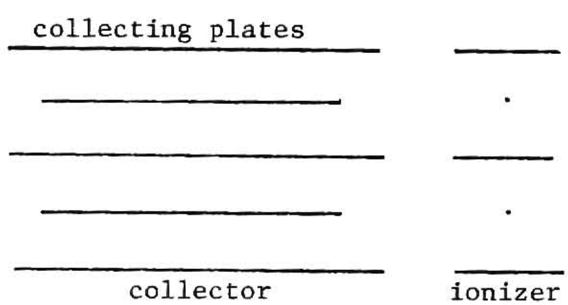
"It is postulated that a spark or arc breakdown in the interelectrode space occurs by formation of a streamer originating at the positive electrode surface. In the positive corona, the origin of the streamer would be at the surface of the discharge wire, and hence in a high field region. In the negative corona, the positive



(a) Single-stage, wire-and-plate type



Single-stage, wire-in-tube type



(b) Two-stage, wire-and-plate type

Figure 1. Schematic diagrams of single-stage and two-stage electrostatic precipitator.

electrode is the collection plate and the field near this surface is considerably less than in the discharge electrode; hence a higher voltage would be required for spark propogation."

Although most of the current literature on electrostatic precipitators is written primarily on negative polarity electrostatic precipitators, much of the analysis is applicable to both types. For background purposes, a brief review of electrostatic precipitation theory is presented here.

Corona Formation

A corona is an ionizing zone created when a non-uniform electric field exceeds the breakdown potential of air about some electrode, and the electric field then decreases below the breakdown potential of air before reaching the other electrode. If the electric field did not decrease below the breakdown potential, there would be "spark-over" between the electrodes. Because of the significant differences in the positive and negative corona (besides their appearance), each will be discussed separately. Positive corona has a bluish glow that extends uniformly the length of the wire, while negative corona emits localized reddish tufts at points along the wire.

Positive Corona

Cosmic rays and other types of radiation produce free electrons in the atmosphere [6,p.202]. When a positive potential is applied to a fine wire, as in the case of positive polarity electrostatic precipitation, the free electrons will be accelerated towards the wire.

Free electrons will collide with gas molecules in their path and produce many types of collisions [7]. Slow electrons might be captured by gas molecules to produce negative molecular ions. Some electrons may dissociate gas molecules into two atoms, one neutral, the other ionized. Electrons in molecules may also be raised to higher energy levels. When these electrons fall back to their natural state, they emit quanta of energy in the visible and ultraviolet range [5,p.202]. In other types of collisions, a stable molecular ion and an electron may be the products.

Where a collision occurs forming an electron-positive ion pair, two electrons will then be available to produce more collisions, and the positive ion proceeds to the grounded electrode. As electrons liberate other electrons, electron "avalanches" are produced. The resultant ionic current consists of the electrons proceeding to the positive wire and positive ions proceeding towards the grounded (negative) electrode.

Electrons reaching the wire are prevented from neutralizing the positive charges on the wire by "the continuously supplied current from a high-voltage power supply" [7,p.2]. As such, the wire is an electron accepter (sink).

White [3,p.85] felt that ultraviolet light quanta radiated from the visible glow region are "the most probably source of primary electrons required to maintain the positive corona," because they "have ample energy to ionize gas molecules with lower ionization potentials." This ionization must occur near the visible corona glow, "because most gases are quite opaque to the short wavelength radiation of the ultraviolet region."

The onset electric field, E_o, at the wire surface has been established empirically for both types of corona formation by Peek [3,p.85] for smooth round wire:

$$E_o = m(30\delta + 9\sqrt{1/\delta \underline{a}})\ \text{kV/cm} \qquad (1)$$

where m = roughness factor

δ = density of air

$\underline{a}$ = radius of wire

The relative air density, δ, is computed as follows:

$$\delta = \frac{T_o}{T} \times \frac{P}{P_o} \qquad (2)$$

where T_o = 298°K

T = actual air temperature

P_o = 760 mn Hg

P = actual pressure

The onset voltage [3,p.92] is then:

$$V_o = \underline{a}\, E_o \ln\left(\frac{b}{\underline{a}}\right) \qquad (3)$$

where b = the radius of the charging cylinder for the wire-in-cylinder geometry.

Negative Corona

Negative corona differs from positive corona in that the wire is no longer an accepter of electrons, but a source of electrons. To free electrons from the negatively charged wire, naturally occurring gas ions, of which there are about $1000/cm^3$ [8,p.340], must be accelerated to a high enough energy level that they will liberate electrons upon impact with the wire.

The liberated electrons will produce electron-positive ion pairs as in the positive corona in the high electric field immediately surrounding the wire. Positive ions thereby produced will be accelerated towards the negatively charged wire and will liberate more electrons from the wire. Electrons may also be liberated from the wire by quanta of energy emitted in the visible corona by the photoelectric effect [3,p.85].

The electrons freed will slow to speeds less than that needed for ionization as they move away from the wire. As they come into contact with gas molecules, these free electrons, not having the energy to ionize the molecule, will instead attach themselves and create negatively charged ions. These negative ions will then migrate to the grounded (positive) electrode.

Particle Charging

Electric field lines will concentrate about particles. The concentration will be the greatest for conducting particles, and will diminish for dielectric particles with increasing dielectric constant [3,p.131].

Following the electric field lines, the ions produced in the corona will collide with the particles, and attach themselves by the "mirror image" phenomenon (where an ion of given charge will produce a mirror (opposite) charge on the surface of the particle.

Field charging, as described above, predominates for particles larger than 0.5μ diameter, but diffusion charging is more important for particles less than 0.2μ diameter. In diffusion charging, the random motion of the smaller particles (due to thermal energy or collisions with gas molecules) brings the particles into contact with the ions.

In the intermediate range, 0.2 to 0.5μ diameter, both processes are important [3,p.128].

Only a finite amount of charge can be collected on particles. The three most important factors limiting particle charge magnitude are: (1) the size of the particle; (2) the length of time the particle is in the charging zone; and (3) the concentration of ions in the charging zone. Saturation charge, the amount of charge a particle can hold is largest for large particles, is only asymptotically approached for a particle, because ions on the surface of the particle begin to repel other ions from approaching the particle. High concentrations of ions, large corona current, are necessary to approach saturation charge while limiting charging time. Typical charging time would be a few tenths of a second.

Charged particles are removed from the air flow by Coulomb attraction to an oppositely charged plate. They have migration velocities normal to the plate proportional to their charge and the collection field strength. When particles reach the plate they adhere both to the charged surfaces and particles previously deposited there, forming a highly adhesive deposit [9,p.46].

<u>OZONE</u>

The health hazards of exposure to ozone have been known for many years, but typical of the 1916 reaction to the potential hazards was that of Vosmaer [10,p.166]:

"...it is highly to be regretted that unfair and illogical experiments have led some people to the wronge conclusion that ozone is a dangerous gas. Almost any substance is a poison when taken in a dose that is a hundred times too strong."

In the early 1900's, ozone was known for its ability to purify water and air, and as Vosmaer [10,p.172] points out, was thought to have immense therapeutic possibilities:

"It is highly probable that ozone administered in the right dose and in the right way, will have a beneficial effect on the course of certain diseases, such as phthisis, chlorasis, obesity, and probable many others. There is no reason why it should not..."

In 1963, the deodorizing abilities of ozone were still recognized, but as Summer [11,p.191] points out, there was serious doubt as to its therapeutic value.

"A word of warning must be added. Trade literature somtimes seems to emphasize "certain" benefits the occupants of a room supplied with ozonized air are supposed to enjoy. Such benefits range from 'revitalization' to 'improving the oxygen content of air'... it is an essential requirement that at no time should be more ozone produced than is required for destroying the smell."

Health Hazard

An appreciation of the necessity to minimize ozone production in residential precipitators is contingent upon an understanding of its health effects.

Ozone is a pale bluish gas [12,p.98], with a pungent (sharp, irritation) odor. Ozone is detecable to the senses at a threshold of two to five parts per hundred million by volume (pphm). It is an allotrope of oxygen and has a molecular formula of O_3.

Ozone occurs naturally in the atmosphere, resulting from such natural phenomena as lightning. There is also widespread man-made ozone production by such common things as high power lines. It is produced commercially for sterilizing air, purifying water and for use as a bleaching agent.

There is also a naturally occurring layer of ozone at 60,000 to 85,000 feet that is highly beneficial to man. This ozone layer absorb ultraviolet radiation and thus shields the earth from much of its damaging effects [13,p.39]. We will not be concerned, though, with this ozone layer as a part of this study.

The symptoms associated with exposure to ozone are many and can last long beyond the exposure period. Eye, nasal and throat irritation are early symptoms. Chest cramps, frontal headache, vertigo, fatique, cough, stupefaction and continuous body pain have also been attributed to exposure to ozone [15].

Irritation to the nose and throat begins to occur at about five pphm and a person may receive a headache from exposure to 100 pphm for a period of thirty minutes [14,p.358].

A literature survey showed the lethal dosage to vary from 500 to 2000 pphm. In industrial environment, welders exposed to 900 pphm for 3 to 14 days suffered severe chest pains, cough, and dyspnea (difficulty in breathing) for as long as nine months after the onset of the symptoms [15].

The long-term health effects of ozone have been a controversial subject. Consumer Bulletin Annual for 1968 "warned against possible health hazards caused by exposure to ozone generated by electronic air cleaners" [15]. These possible health hazards are cited by those who feel that continuous exposure to ozone at any level can be harmful. The rationale is as follows:

"So far... no tests on radiomimetic effects of ozone have been conducted at levels below 0.1 p.p.m. (10 pphm).

Those who accept the cumulative argument maintain that tests at lower levels are desirable but unnecessary."

'The effect is cumulative: eventually, the organism will be in trouble. To say that there is a concentration so low that it will have no effect is impossible. It (ozone) will kill bacteria, and it can eventually affect something larger.' - Soskind [15]".

On the other side of the issue there are a few medical papers that "suggest that exposure to small amounts of ozone may be beneficial" [15]. Even an increase in mental acuity is suggested in some cases.

The Division of Occupational Health, Bureau of Medicine and Surgery United States Navy has established a limit of 2.0 pphm on nuclear submarines [15]. In this case, it should be noted, that the sailors are exposed continuously, 24 hours a day, for intervals of 60 days or more.

Although at this time it's only speculation, there is some possibility that history may prove that Vosmaer was more right than wrong. Fresh mountain air, considered by many to be a kind of "therapeutic first aid" because of its crisp clean smell, may well owe that fragrance to the ozone produced in its forests [16].

Professional organizations have felt obligated to set maximum allowable concentrations for toxic gases. In 1954, the American Conference of Governmental Industrial Hygienists (ACGIH) [13,p.41] established a value of 10 pphm of air by volume "as the maximum average atmospheric concentration of ozone to which workers may be exposed for an 8-hour working day without injury to health." The World Health Organization (WHO) [14,p.358] established, in 1973, industrial limits for an 8-hour exposure of 100-200 ug/m^3 (5 to 10 pphm) ozone.

Some plants appear to be more susceptable to damage from ozone. Concentrations of only 6 pphm for short spans to 3 to 4 hours have damaged alpha and white pine [14,p.322].

The Food and Dry Administration, Division of the U.S. Department of Health, Education and Welfare [17,p.27] has proposed a maximum concentration of 5.0 pphm of ozone in occupied spaces such as homes and hospitals where people may be exposed continuously for periods of up to 24 hours a day.

Ozone Formation

In 1970, Versagi [15] discussed the ozone problem associated with electrostatic precipitators. After researching the literature, Versagi presented what was known about ozone and what was feared about it. In an editorial summary he stated, "The weight of available medical evidence is on the side of caution."

Since Castle [18,p.491] assumes that ozone is produced in the ionizing sheath immediately surrounding the corona producing wire, an accurate account of ozone production would necessitate an understanding of the molecular ion chemistry evolving in the corona. Unfortunately, such an analysis has not been reported in the literature, and the derivation of such an analysis is considerably beyond the scope of this study.

For the purposes of this study, a stoichiometric approach to the production of ozone will be attempted. The energy balance is:

$$3\ O_2 \rightarrow 2\ O_3 \qquad 68\ \text{kcal./mole} \qquad (4)$$

The amount of energy, therefore, required to produce one ozone molecule is 1.5 eV.

PREVIOUS CONTRIBUTIONS

Electrostatic precipitators deteriorate with usage and time. Particularly undesirable are corrosion and nicking of the ionizing wire's surface. It has long been known that anomalies on the surface of the ionizing wire cause sharp increases in ozone production. A satisfactory explanation of this increase in ozone production due to the anomalies, though, is not to be found in the literature.

As an introduction to the problem of ozone generation in these specific cases, a review of previous contributions in the field of positive polarity ozone production will be presented, followed by an evaluation of the "nicked wire" phenomenon.

Smooth Corona Wire

White [1] tracing the history of electrostatic precipitation through the mid 1950's, credited Cottrell with producing the first full scale commercial electrostatic precipitator around 1908. Cottrell's precipitator was a single stage unit with charging and collection occurring in the same unit. At that time negative polarity in the charging section was recognized as being superior to positive polarity because higher voltages and larger currents, and consequently greater collection efficiency, could be maintained. But the large size of the precipitator made it impractical for many applications.

By the mid-1930's, the two-stage positive polarity electrostatic precipitator, where charging was carried out in the first stage followed by collection in a separate stage, had been developed. Penney [2] stated that this configuration would be applicable to many situations where the electrostatic precipitators of his day were not. He outlined the limitations of Cottrell type electrostatic precipitators as:

1. D.C. Voltages of from 30,000 to 100,000 and appreciable current are required.
2. The space required is large both for the precipitator proper as well as the high-voltage transformer and rectifier.
3. The corona discharge of the conventional precipitator generates so much ozone that the cleaned air, although free of dust, is too irritating to the nose and throat to be used for ventilation.
4. First cost and maintenance are both high as compared to other types of cleaning equipment.

In this design, Penney utilized positive polarity in the charging section as the solution to the high voltage requirements of negative polarity precipitators. Since positive polarity charging units run from 6,000 to 12,000 volts at a few milliamps of current, (higher voltages will cause "spark-over") this negates not only the problem of the size of the large transformers and rectifiers, but also the initial cost. Positive polarity also produces less ozone than negative.

The two stage approach had a charging section with a non-uniform ionizing electric field, followed by a uniform collecting field. The non-uniform field in the charging section was needed to produce ions, while the uniform field in the collecting section was desirable to limit ionization and avoid "spark-over."

To demonstrate that adequate efficiencies could be attained by positive polarity charging units, Penney [2,p.163] produced 99.5% number efficiency with a dust of ground silica rock, of unknown size distribution. A number efficiency is a comparison of the number of particles per unit volume entering the precipitator with the number per unit volume leaving.

Quantitative analysis of ozone production in electrostatic precipitation was limited to general statements for many years. An example is given by Penney in his discussion of abnormal coronas [19,p.321]. He pointed out that when a "flare" (glow) extended beyond the normal positive corona glow, "the ozone generation may be many times that of the normal discharge."

Some of the earliest quantitative analysis was performed by White and Cole [30,p.241] in 1960. They concluded that ozone generation "was closely proportional to corona current and inversely proportional to gas flow rate for a constant corona wire diameter." But unfortunately only experimental work supporting the latter conclusion was presented.

Lagarias [20,p.272] later that same year stated that "positive operation produces roughly 1/7 as much ozone as negative operation." The reasoning for the lower ozone generation, Lagarias felt, was that "ozone is formed by high energy electron bombardment of oxygen molecules. By operating at positive polarity, positive ions predominate in all regions except immediately adjacent to the discharge electrode." He also went on to state that the smaller diameter corona wires allow "lower operating voltages to be used which help reduce ozone formation." Lagarias, though, neither provided supporting data nor cited any references to support his generalizations.

Sutton, et al. [17] performed studies of the concentrations of ozone in residential structures. They found that typical residential electrostatic precipitators produce between 5 x 10^{-6} and 20 x 10^{-6} ft^3 O_3/min. (5 to 20 ppm/min.) [17].

Probably the most significant contribution, to date, in the field of ozone generation in the positive corona has come from Castle, et al. In an early paper, Castle [18,p.489] lists the qualitative design criteria that have been established over the years "to minimize the formation of ozone...:

1. use of positive polarity corona rather than negative,
2. use of a two-stage design where the charging and collection functions are separated,
3. use of smooth, round corona wire of the smallest possible diameter compatible with mechanical strength,
4. use of the lowest possible corona current compatible with satisfactory collection efficiency,
5. use of the maximum air flow rate compatible with satisfactory collection efficiency,
6. elimination of any stray discharges such as may occur due to end effects, sharp points, or edges, etc."

With the support of limited data, Castle [18,p.491] goes on to make two important assumptions "regarding ozone formation:

1. since the ionized sheath represents the most chemically active region in the discharge, it is assumed that the ozone production takes place entirely within the ionized sheath;

2. because of the existance of the most energetic electrons immediately adjacent to the wire surface and the probable function of this surface as a catalytic reaction site, it is further assumed that most of the ozone is formed very close to, or even at the surface of the wire."

Castle postulates that ozone production should be a function of the voltage drop across the ionizing sheath for a given corona current and air flow. The voltage drop is the product of the average electric field in the ionizing sheath and the width of the ionizing sheath.

Castle, working with Awad, has also studied ozone generation with a heated corona wire [22] and the effect of nicked wires on ozone production [23,p.376]. Their work with heated wires confirms the finding of Sutton, et al., [17,p.30] that there will be significant ozone reduction when the air is heated. The nicked wire studies will receive more extensive analysis later in this report.

The "Nicked Wire" Phenomenon

When a corona wire is "nicked" the ozone generation is increased dramatically. But the increase, although very real and well documented, is almost a paradox.

One could define a nick as a macroscopic deformation on an otherwise "smooth, round" wire surface. Macroscopic means that they are visible to the naked eye. The deformation is usually an indent into the wire's surface, but the important aspect is the formation of some kind of an edge. These edges, as will be shown later, seem to be the source of increased ozone generation.

An edge has a very large curvature (small radius), though, which then seems to lead to the paradox. It is desirable to have a wire of the smallest radius, commensurate with mechanical strength, to reduce ozone production. In the limiting case of the edge, though, more ozone is generated.

As was stated earlier, the electric field at the surface of the wire at the corona onset, E_o, decreases as the roughness of the wire surface increases. The roughness of the wire will depend on the number and type of nicks, and other surface anomalies.

It is difficult to generate and interpret "nicked wire" data. First, a procedure to uniformly and reproducibly "nick" the wires is needed. If the nicks are only qualitative, quantitative analysis of the data is questionable.

Awad and Castle [23,p.376] performed a "nicked wire" experiment, the results of which are given in Fig. 2. Studying the ozone production past 0.15 mA, note that the production apparently rises to a peak for an intermediate number of nicks and then falls off with more nicks. The results, though, are not in accordance with common observation. Ozone production does not rise to a certain level and then fall off as a function of surface deformation. The data are not totally inexplainable, though and will be covered in detail later in this thesis.

Corrosion is another important type of deformation that leads to increased ozone production. Oxidation of the wire's surface is the most common type of corrosion. In many respects, corrosion is a type of nicking phenomenon that produces sharp edges. Instead of being macroscopic, though, it is microscopic.

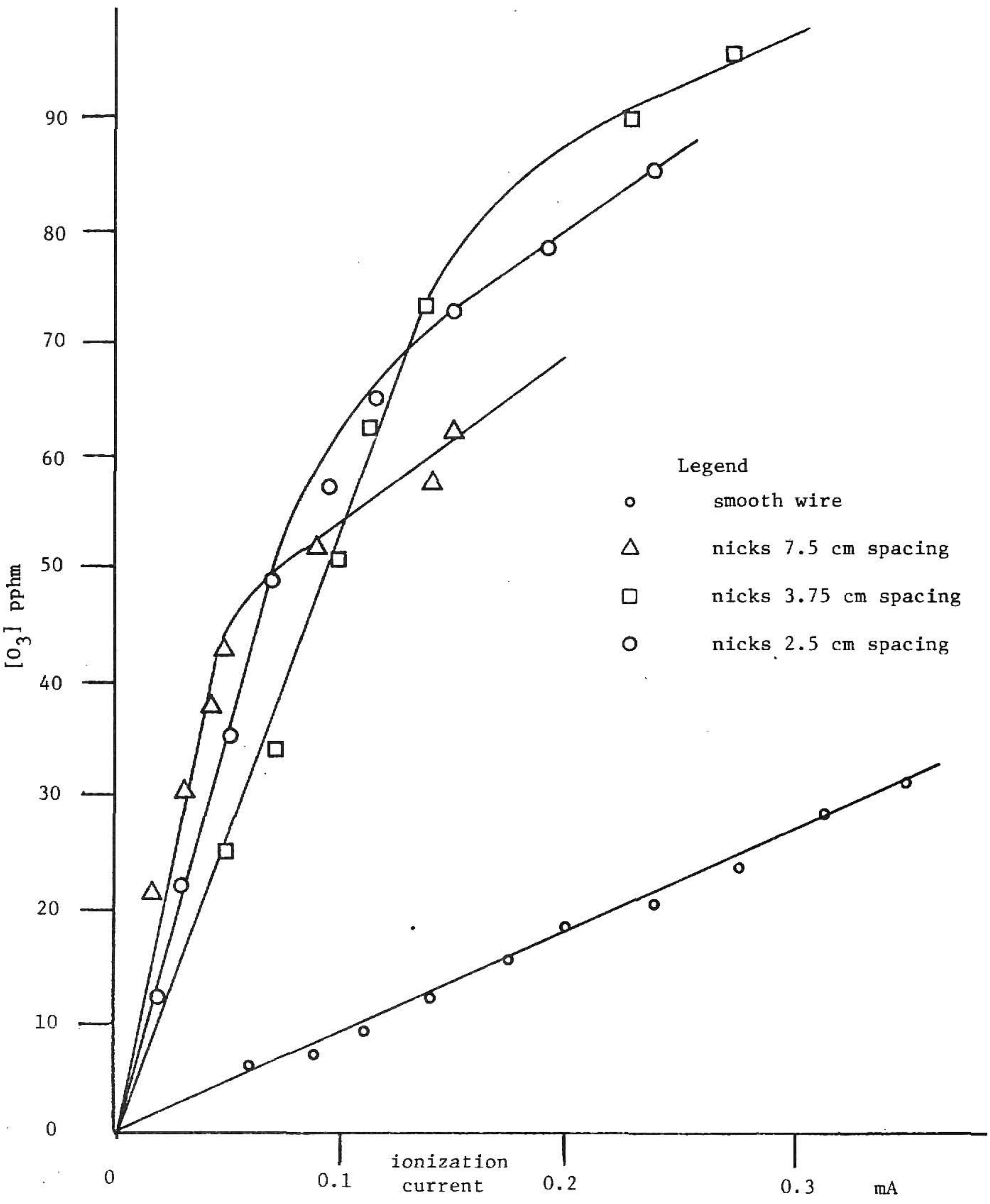


Figure 2. Ozone-Current Characteristics under Positive Corona with Variable Surface Nicks.

"Most oxidation theories have assumed that the reaction production is present on the metal surface as a plane parallel, compact film. This is, in fact, not a valid assumption in many cases as has been shown experimentally by optical and electron microscope studies. Bardolle and Benard in 1952 showed that...discrete oxide particles, called nuclei, were formed on large grained iron specimens... Similar observations have since been made on iron...copper... nickel...cadmium...copper and silver... [24,p.355]."

Castle [25,p.186] did some work on ozone production as a function of time. Reproduced in Fig. 3 are his results for platinum and stainless steel wires. It was noted that the ozone production in the case of stainless steel wire did seem to increase from the formation of the oxide.

Castle [18,p.494] attributes the increase in ozone generation to an increase in the "effective surface area of the wire." Since Castle does not define "effective surface area" in the paper, it is not possible to evaluate his conclusion.

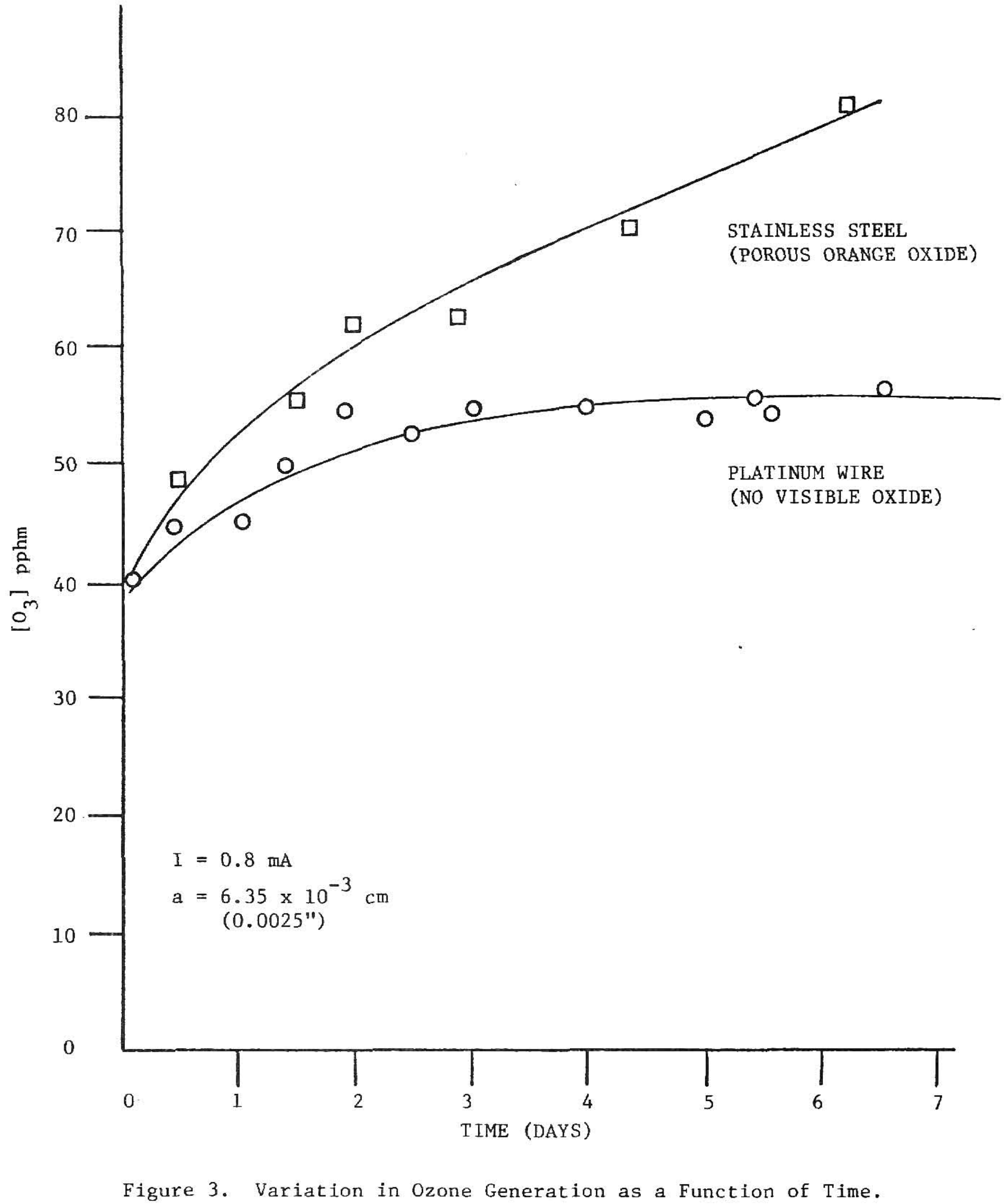


Figure 3. Variation in Ozone Generation as a Function of Time.

CRITIQUE OF OZONE GENERATION PARAMETERS

Before one can evaluate the "exception to the rule," one must first have an understanding of the "rule". No serious study of the "nicked wire" phenomenon is possible without a firm background of ozone generation resulting from the smooth wire. For this purpose an evaluation of ozone parameters in the smooth wire is presented here.

In determining which parameters best account for the ozone production, it would be desirable that the parameters be applicable over a wide range of sizes, and not be material dependent. This is especially critical because the calculations for corona onset electric field and voltage are not material dependent. Thus, to be able to utilize previous studies, and develop a simple model which would be applicable over the widest range of variables, the best parameters would be neither size nor material dependent.

"Accepted" Parameters

Some parameters of ozone production have become fairly well established over the years. These parameters will be discussed and the rationale behind them will be evaluated.

Corona Current

White and Cole [20,p.241] concluded that ozone generation "was closely proportional to corona current." Castle [25,p.169] presented data to confirm this conclusion. Castle then went on to establish a new parameter, $[O_3]/I$ (ozone production per unit corona current). This parameter was calculated by taking the slope from the ozone production versus corona current graph for constant wire diameters.

Because the production of ozone is the result of ionic reactions, it would be reasonable to expect the amount of ozone produced to be linearly proportional to the amount of ionic activity in the ionizing sheath. Since corona current is related to ionic activity, it would be logical that the amount of ozone produced would be linearly proportional to the amount of corona current.

Corona current and voltage in electrostatic precipitators have been studied extensively, and it has been shown that corona current is a non-linear function of the voltage [3,p.104]. Ozone generation could be attributed to either current or to voltage. The choice of current seems more logical because ozone generation is linearly proportional to the corona current.

Unfortunately, it is not practical to limit ozone production by limiting corona current, because high corona currents are needed to establish high efficiencies in the electrostatic precipitator.

Air Flow

White and Cole [20,p.241] were also the first to establish that ozone production (in pphm) was "inversely proportional to gas flow rate." Castle [25,p.172] acknowledges White and Cole's work and presents data that merely confirms their work.

This means that the total amount of ozone produced is independent of the air flow. The air flow merely serves as a dilution medium for the ozone that is produced. Since reducing the air flow does not reduce the ozone production, it can be concluded, therefore, that the amount of oxygen is not the limiting factor in ozone production in the presence of an adequate oxygen supply.

Castle's Original Work

Castle [18,p.490] presents theoretical bases that ozone production should be a function of the average electric field, E_{avg}, in the ionizing sheath and of the width of the ionizing sheat, Δa:

$$[O_3] = f(E_{avg} \times \Delta a) \qquad (5)$$

The average electric field and sheath width are calculated as follows:

$$E_{avg} = (E_o + 30)/2 \quad \text{kV/cm} \qquad (6)$$

where E_o = onset electric field, kV/cm

$$\Delta a = 0.3\,\sqrt{\underline{a}}\ \text{cm} \qquad (7)$$

where $\underline{a}$ = radius of the wire

The onset electric field for the corona, as was shown earlier, is a function of the wire size:

$$E_o = m(30\delta + 9\sqrt{1/\delta \underline{a}}) \quad \text{kV/cm} \qquad (1)$$

This would be the field strength at the surface of the wire. We can assume the field strength at the outer edge of the ionizing sheath to be the breakdown potential of air, 30 kV/cm [26,p.257]. Combining Eqns. (1) and (6), the average electric field, for standard temperature and pressure (δ=1) and smooth wire (m=1) would therefore be a function of wire size:

$$E_{avg} = 30 + 4.5\sqrt{1/\underline{a}} \quad \text{kV/cm} \qquad (8)$$

Since Eqn. (7) established the width as a function of wire size [26,p.258], the following product is a function of wire size:

$$E_{avg} \times \Delta a = 9\sqrt{\underline{a}} + 1.35 \text{ kV} \tag{9}$$

Castle [18,p.490] recognized this quantity as the "voltage drop across the (ionizing) sheath," and gave the physical significance of the parameter as follows:

> Experience with oxonizers (sic) has shown that the amount of oxone (sic) produced per unit time is a direct function of the amount of electrical power which is dissipated in the discharge. It is reasonable to expect that a similar relationship should exist in a corona discharge...

As derived from Castle [18,p.491]:

$$[O_3] = f(E_{avg} \times \Delta a)\ I/Q^* \quad \text{pphm} \tag{10}$$

where Q^* = air flow

The voltage drop across the ionizing sheath parameter has the very interesting characteristic that it is basically independent of the voltage. This means that after the onset of corona, the voltage drop across the ionizing sheath is independent of the voltage in the charging section. Initially, this voltage drop is a function of the voltage in the charging section because the corona onset voltage is a function of the corona onset electric field; as in the wire-in-cylinder configuration:

$$V_o = \underline{a} \times E_o \ln (b/\underline{a}) \tag{3}$$

Loeb [27,p.43] explains why the voltage drop across the ionizing section does not change with increased voltage in the charging section:

Another pecularity of an ionic space charge stabilized current is that, as potential increases, ion production and concentration increases. This rapidly absorbs the increase in potential, so that the potential drop across the ionizing zone remains constant.

Paraphrasing Loeb, an increase in potential in the charging section would produce an increase in ionic activity in the ionizing sheath. This increase in ionic activity would manifest itself as an increase in corona current [27,p.46]. We have already seen that ozone production is linearly proportional to corona current.

Since this voltage drop across the ionizing sheath decreases with smaller wire sizes, and smaller wires do produce less ozone: the theory does seem to explain why ozone production is less. When Castle [18,p.492] evaluated his data, though, he did not use the theoretically sound "voltage drop" across the ionizing sheath; instead he uses $E_{avg} \times \underline{a}$, as the best correlation with his data without justifying the parameter.

Castle [18], at that time, was concerning himself with only a half dozen copper wires, all less than 16 mil (0.016 inch) diameter. Presented in Figure 4 is ozone production per unit current as a function of $E_{avg} \times \Delta a$ for his data. In Table 1, the correlation coefficients and error mean squares, are presented for the original data as a function of various parameters. Note that all three possible parameters have correlation coefficients in excess of 0.995, and that the smallest error belongs to $E_{avg} \times \Delta a$. Why Castle then chose to use the parameter, $E_{avg} \times \underline{a}$, is not really clear.

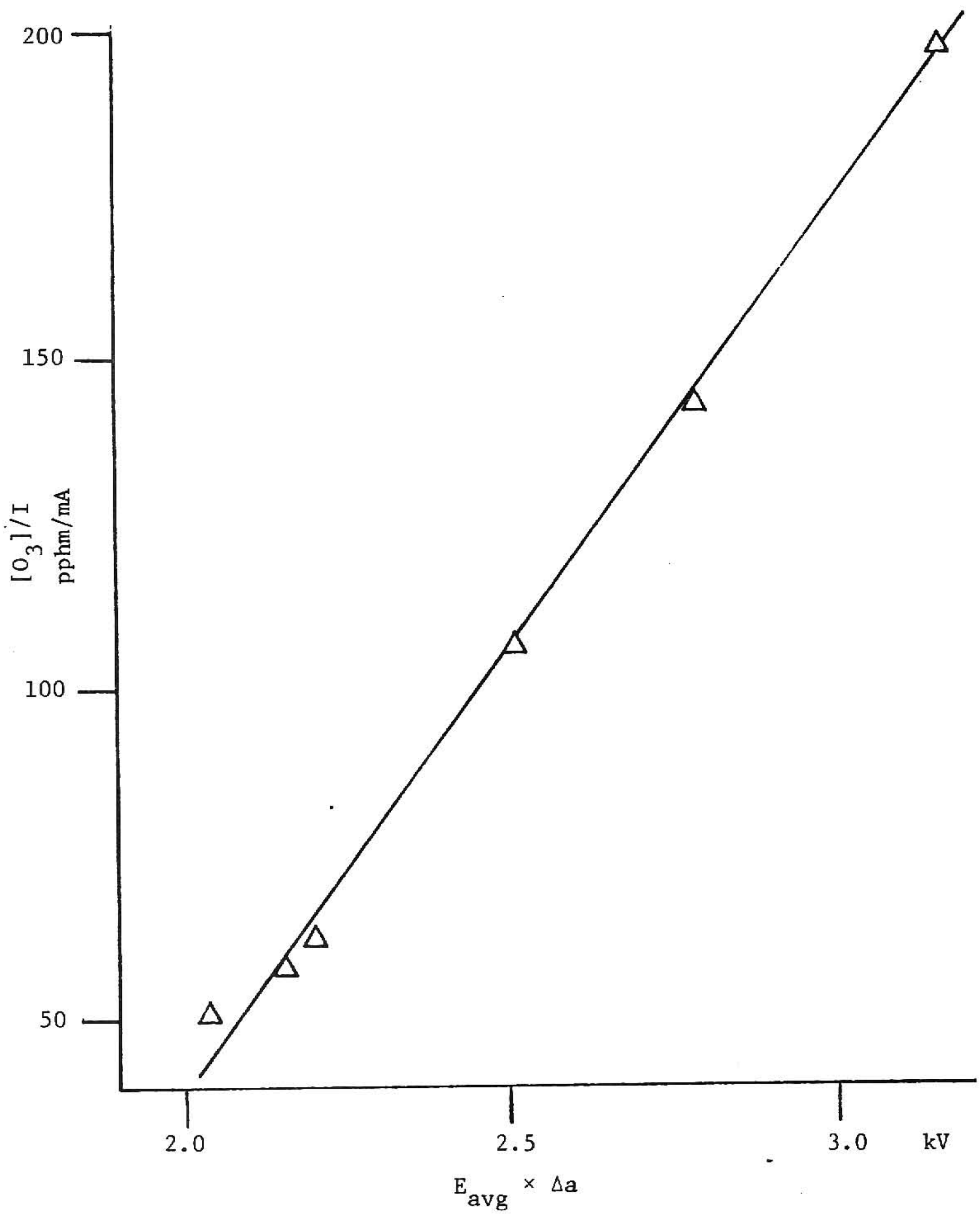


Figure 4. $E_{avg} \times \Delta a$ versus $[O_3]/I$ for Original Data.

Table 1: Correlation Coefficients and Error Mean Square

(a) Original Data

Parameters	Correlation Coefficients	Error Mean Square
$E_{avg} \times \underline{a}$	.9981	3.919
$E_{avg} \times \Delta a$	.9991	2.656
$\underline{a}$	.9951	6.235

(b) Compiled Data

Parameters	Correlation Coefficients	Error Mean Square
$E_{avg} \times \underline{a}$	.9850	15.44
$E_{avg} \times \Delta a$	.9710	21.16
$\underline{a}$	.9860	14.91

The inclusion of a (radius of the wire) as a parameter is reasonable. Castle [18,p.491], himself, points out that "ozone is formed very close to, or even at the surface of the wire." Castle attributes the increased ozone production from a wire with a surface oxide coating to the increase in effective surface area of the wire. The correlating parameter would be some constant times the radius. Such constants are superfluous for correlation purposes, though, so the inclusion of the constant is not important.

Compiled Data

To evaluate the parameters over the widest range of variables, a compilation of Castle's [18] and Awad-Castle's [22,23] data for many materials and a large range of wire sizes is presented in Table 2. Also present are the values of various parameters which were a function of radius (Table 2). In Figure 5, this data is presented as a function of $E_{avg} \times \Delta a$, and in Table 1 the correlation coefficients and error mean square are presented for the compiled data as a function of various parameters. Note the high correlation coefficients again, and the almost equal error terms for $E_{avg} \times a$ and a, itself.

Statistical Test

After studying the figures, it might be concluded that the wire radius was as good a parameter as any tested. In order to judge the validity of that observation, statistical tests were run on the compiled data against $E_{avg} \times a$, $E_{avg} \times \Delta a$, and a plus several more. Included as

Table 2: Compiled Data

Material	Radius (cm)	$[O_3]/I$ (pphm/mA)	$E_{avg} \times \underline{a}$ kV/cm	$E_{avg} \times \Delta a$ kV/cm
Copper [18]	.00635	51	.549	2.066
(Castle)	.008	58	.642	2.152
	.0089	62	.692	2.199
	.0165	106	1.073	2.504
	.0254	142	1.479	2.784
	.0406	196	2.125	3.161
Aluminum [22]	.0102	68.3	.761	2.26
Carbon Steel	.0318	178	1.755	2.95
Tin to Copper	.0318	191	1.755	2.95
Chromel A	.0318	183	1.755	2.95
Tungsten	.0318	198	1.755	2.95
Copper	.0337	213	1.837	3.00
Nichrome	.0362	168	1.944	3.07
Bronze	.0432	213	2.233	3.23
Stainless Steel	.0572	286	2.791	3.50
Stainless Steel	.0751	390	3.485	3.81
Copper [18]	.00463	32.2	.445	1.962
(Burgess)	.00635	52.1	.551	2.068
	.0089	65.3	.691	2.199
	.0165	108.9	1.059	2.497
	.0406	171.6	2.122	3.164
Platinum [18]	.0038	41.5	.391	1.905
Platinum	.0055	48.7	.499	2.018
Stainless Steel	.00625	48.3	.543	2.061
Tungsten	.00625	48.3	.543	2.061
Aluminum [23]	.0102	70.9	.761	2.26
Chromel A	.0315	173.4	1.744	2.95

△ [18] Copper, Castle

o [22]

□ [18] Copper, Burgress

O [18] Non-Copper

◇ [23]

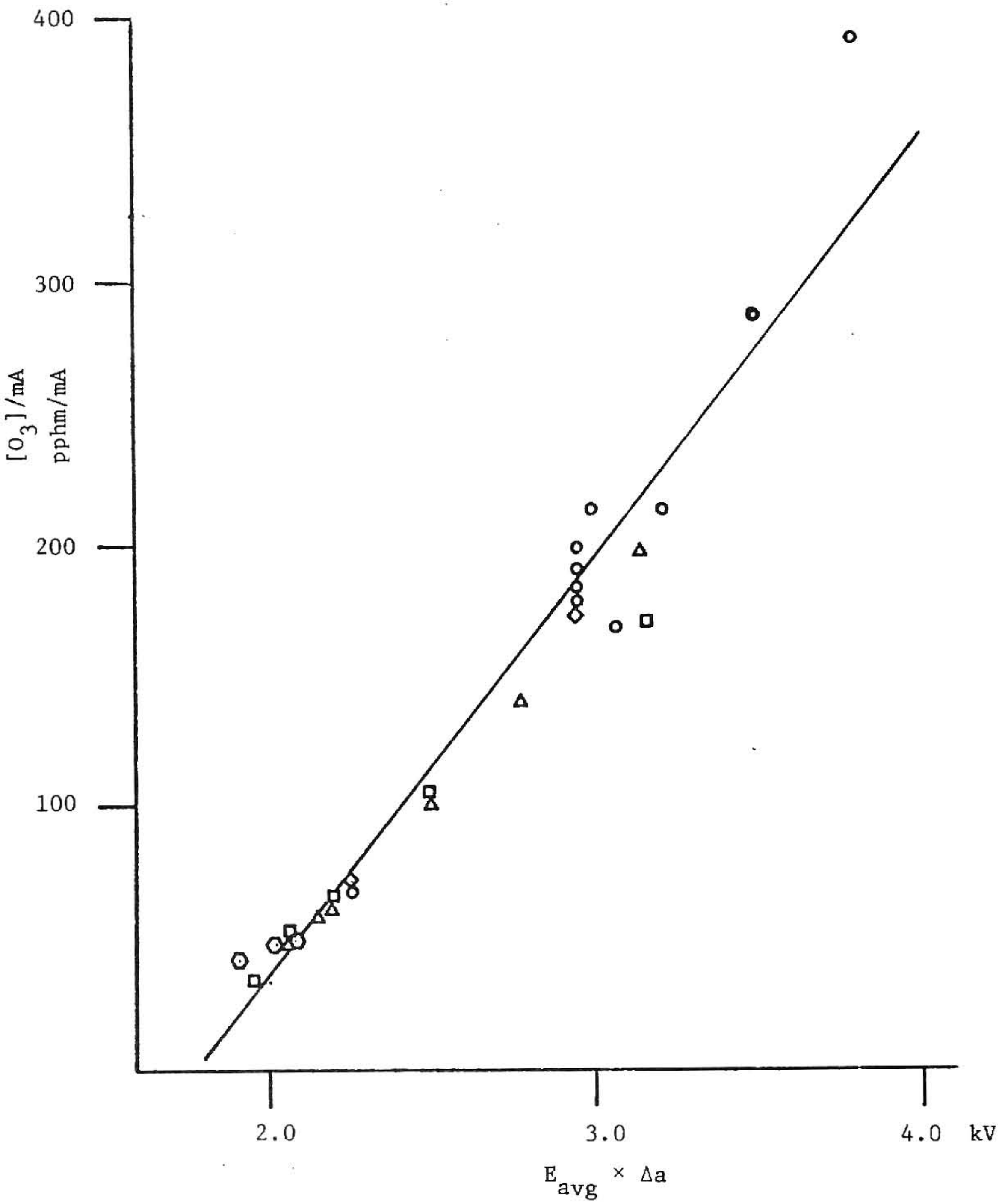


Figure 5. $E_{avg} \times \Delta a$ versus $[O_3]/I$ for Compiled Data.

other plausable parameters were: the average electric field, E_{avg}; the onset voltage, V_o; the onset electric field times the radius, $E_o \times \underline{a}$; and a power of the radius, $\underline{a}^{3/4}$. The justification for including these parameters will be given later.

The statistical test employed was a step-wise deletion regression analysis. A multilinear model was created first using all of the parameters, and then parameters which were determined not to have made a significant contribution to the model were eliminated. Presented in Table 3 is the correlation matrix for the parameters that were evaluated.

Unfortunately, the results of the stepwise deletion regression analysis were in conclusive. That is, the procedure was not able to single out any one parameter as being the best to explain the data. The correlations between the parameters, because they were all a function of $\underline{a}$, were too high (Table 3) and resulted in critical rounding errors that prevented a proper analysis of the data. From a different viewpoint, though, it was also proven that no one parameter was statistically better than any other parameter in correlating with the $[O_3]/I$.

Evaluation of Applying Parameters to Anomalies

Since no one parameter is more significant, statistically, another possibility for evaluating the meaningfulness of each parameter is to analyze their application to anomalies.

In this section, physical meaning will be attributed to each of the parameters that were considered in the step-wise delection analysis. The parameter will then be evaluated as if it were the only parameter

Table 3. Correlation Matrix

$\underline{a}$	1	1.0000							
E_{avg}	2	-0.8789	1.0000						
V_o	4	0.9822	-0.9251	1.0000					
$E_{avg} \times \underline{a}$	5	0.9982	-0.9045	0.9885	1.0000				
$E_{avg} \times \Delta a$	6	0.9836	-0.9470	0.9907	0.9926	1.0000			
$E_o \times a$	7	0.9960	-0.9163	0.9904	0.9995	0.9958	1.0000		
$\underline{a}^{3/4}$	8	0.9958	-0.9161	0.9906	0.9995	0.9959	1.0000	1.0000	
$[O_3]/I$	3	0.9860	-0.8769	0.9736	0.9850	0.9721	0.9831	0.9829	1.0000
	No.	1	2	4	5	6	7	8	3

1 radius, $\underline{a}$

2 Average Electric Field, E_{avg}

4 Onset Voltage, V_o

5 Average Electric Field times radius, $E_{avg} \times \underline{a}$

6 Average Electric Field times Sheath width, $E_{avg} \times \Delta\underline{a}$

7 Onset Electric Field times radius, $E_o \times \underline{a}$

8 Power of radius, $\underline{a}^{3/4}$

3 Ozone production, $[O_3]/I$

affecting $[O_3]/I$ from anomalies. Those parameters which cannot reasonably account for the increased ozone production will then be eliminated. Hopefully, we will then be left with the most important parameter(s) of ozone production.

Surface Area. If one believes surface area as a function of the wire radius $\underline{a}$ is the most important parameter, then the increase in ozone should be proportional to the increase in surface area. This implies that ozone production depends on the amount of surface area available as a reaction site. This follows from one of Castle's [18,p.491] assumptions about ozone formation: "the probable function of this (wire's) surface as a catalytic reaction site."

If only the amount of surface available as a reaction site is important, then the value of the electric field at the surface is not important. In other words, as long as there was a corona, the electric field at the wire's surface would exceed the breakdown potential of air, and the only parameter limiting ozone generation would be the surface area. Working with wires of two different radii, 0.0406 cm and 0.00635 cm, Castle [25,p.181] wound the smaller wire around the larger with a pitch of perhaps two centimeters. Presented in Table 4 are the results of his experiment.

Table 4

Configuration	$[O_3]/I$
(a) One 0.00635 cm wire	51 pphm/mA
(b) One 0.0406 cm wire	196 pphm/mA
(c) (a) wound around (b)	800 pphm/mA

Configuration (c) represents an anomaly on the surface of the large wire that increased the surface area by 16 percent, and the ozone production far exceeded that which could be expected by the increased surface area. Also note that configuration (c) produced ozone far in excess of the sum of the two individual wires.

If surface area is the only important parameter, there are no alternatives (such as electric field, etc.) to explain this discrepancy. Since the surface area does not in itself adequately account for this discrepancy, then the disproportionate increase in ozone production has to be the result of another phenomenon.

Average and Onset Electric Fields, E_{avg} & E_o. Average electric field, E_{avg}, is probably one of the more interesting possible parameters: it is negatively correlated with ozone generation. That is, $[O_3]/I$ increases while E_{avg} decreases. This follows because E_{avg} decreases with increasing radius (Eqn. (11)), while it has been seen that $[O_3]/I$ increases as the radius increases for the smooth wire.

$$E_{avg} = m(30\delta + 4.5\sqrt{1/\underline{a}\delta}) \quad \text{kV/cm} \tag{11}$$

Assuming the average electric field to be the most important parameter, increased $[O_3]/I$ with anomalies on the surface can be explained. Irregularities will cause the roughness factor, m, to decrease. As m decreases, E_{avg} decreases, and because of the negative correlation an increase in ozone production would be expected. Experimental evidence shows that anomalies do produce more ozone (Table 4.)

If the average electric field is the only important parameter, then ozone production in the ionizing sheath is independent of the sheath width. E_{avg}, though, is only meaningful in terms of the sheath width, because it is the average electric field in the sheath. E_{avg} is a function of the onset electric field at the surface of the wire which, because it is not dependent on the sheath width, may be a better parameter.

If the electric field at the surface of the wire is the only important parameter, then ozone production is not limited by the amount of wire surface available as a reaction site, but only limited by the field at the wire. When there are anomalies on the surface of the wire, E_o decreases as the roughness factor decreases and ozone production increases. This parameter, therefore, also correlates negatively with ozone production resulting from anomalies on the wire's surface.

Awad and Castle [23,p.380] provide information on the decrease in the electric field in their "nicked wire" experiment. For the case of the fewest nicks, 7.5 cm apart, (Fig. 2), the onset voltage decreased from 12 kV to 11.5 kV. From Eqns. (1) and (3) it can be seen that the only difference between the two onset voltages could have been in the onset electric field at the surface of the wire; and the only variable that was not held constant was the roughness factor. While there was only a four percent reduction in the onset electric field for the nicked wire from that for the smooth wire, the ozone production at 0.1 mA was six times as much. Considering two stainless steel wires in the same size range, 0.0572 and 0.0571, (Table 2) as the nicked wire, E_o for the larger wire was 7 percent less than E_o for the smaller wire, but the ozone production was only 1.4 times as much.

<u>Onset Electric Field Times the Radius, $E_o \times \underline{a}$.</u> Having first considered the cases of surface area, and onset electric field by themselves, it is also possible to combine the two to form a third parameter, $E_o \times \underline{a}$. If this is then the only important parameter, ozone production is a function both of the onset electric field strength at the surface of the wire and the surface area available to act as a reaction site.

The parameter of $E_o \times \underline{a}$ can be rejected with the same argument that rejected E_o. $E_o \times \underline{a}$ decreased for the nicked wire [23,p.380] from the value for the smooth wire, because the onset voltage decreased while ozone production increased. In the case of the stainless steel wire (Table 2), $E_o \times \underline{a}$ increased and ozone production increased. Because of this contradiction, this is not the best parameter.

The electric field at the surface of the wire, though, varies due to the anomalies, even though the potential of the surface must be at a constant value. Possibly a new parameter, E_s, the electric field at any point, might be more meaningful. The computation of $E_s \times \underline{a}$ is very complex because E_s varies over the surface of the wire as will be discussed in the section on electric fields about anomalies.

<u>Average Electric Field Times the Sheath Width, $E_{avg} \times \Delta a$.</u> The computation of $E_{avg} \times \Delta a$ becomes very complex also when trying to consider the non-uniform electric field strength at the surface, E_s. For this reason, both $E_s \times \underline{a}$ and $E_{avg} \times \Delta a$ will be discussed later in this thesis after an evaluation of the electric field about anomalies is made. (A detailed discussion of $E_{avg} \times \underline{a}$ was given in "Castle's Original Work").

Onset Voltage, V_o. For many years voltage was thought to be the important parameter in ozone generation [3,p.24]. This follows from the onset voltage:

$$V_o = \underline{a} \times E_o \times \ln b/\underline{a} \qquad (3)$$

As the wire radius decreases, the onset voltage then decreases; and as a consequence ozone generation decreases. The onset voltage also decreases when the surface of the wire is nicked, but the parameter no longer correlates with ozone generation. This follows from the same evaluation as $E_o \times \underline{a}$.

Power of Wire Radius, $a^{3/4}$. The last parameter to be analyzed is a power of the radius, $\underline{a}^{3/4}$. Its conclusion is purely empirical. When correlated with Castle's original six copper wires, it gives an error very close to the error from $E_{avg} \times \Delta a$. Since the parameter had no physical significance originally, none will be rationalized.

Average Electric Field Times the Radius, $E_{avg} \times \underline{a}$. Of the first three parameters that were discussed with regard to Castle's original six copper wires, only the average electric field times the radius has yet to be evaluated. Although Castle uses $E_{avg} \times \underline{a}$ for his original six copper wires, he never attributes any physical significance to the parameter.

It is the opinion of the author that Castle used $E_{avg} \times \underline{a}$ as an approximation of $E_{avg} \times \Delta a$. In future works Castle only referred to the latter parameter [23,p.374]. His ignoring $E_{avg} \times \Delta a$ leads the author to believe that he concluded it had no physical significance.

Best Parameters

In the process of evaluating the seven ozone generation parameters that were correlated by the Step-Wise Deletion Analysis only one, $E_{avg} \times \Delta a$, remains, and one other $E_x \times \underline{a}$, established that might possibly explain ozone generation for both the smooth wire and the nicked wire conditions. These two parameters, $E_{avg} \times \Delta a$ and $E_s \times \underline{a}$, will be evaluated in the following chapter.

With regard to air flow, ozone production (in pphm) should still be inversely proportional to the air flow since air flow merely dilutes the ozone concentration.

With regard to corona current, ozone production will not necessarily be linearly proportional to the corona current (Fig. 2). This phenomenon of non-linearity will also be discussed in the following chapter.

MODEL OF OZONE GENERATION

The model presented proposes to account for the increased ozone generation that is found when anomalies occur on the surface of the charging wire. The rationale behind the model and the verification will be discussed in detail.

Statement of the Model

> Increased ozone production, $[O_3]/I$, from wires with surface anomalies can be attributed to excess energy (above that which is needed to maintain the corona), which is dissipated in localized zones about the anomalies. This excess energy is a function of the localized, high-electric fields formed at and about the anomalies.

The model, in itself, is not intended to be a new theory of ozone generation in the positive polarity electrostatic precipitator. Awad and Castle [23,p.376] discussed "the localized field enhancement caused by the nicks." Castle [25,p.183] discussing results of spiralling the small wire around the larger one (Table 4), concluded that "surface discontinuities [in the positive corona] adversely affect the ozone generation; presumably by creating local regions conducive to ozone formation having above average electric field strengths."

Although the model does not claim to be a new theory, an extensive analysis of this or any similar model has not appeared in the literature.

The Unstable Ozone Production in Positive Corona

Ozone production in the case of the smooth wire is unstable since any anomaly will increase ozone production. Experiments with negative polarity have aided in understanding the instability of the positive corona. In the negative polarity, ionization is visibly localized at various points along the wire (tufts). These tufts will "dance" along the wire unless they encounter a deformation. If the wire is nicked, the turfts will affix themselves to the nicks.

Awad and Castle [23,p.376] investigated nicked wires with negative polarity. As expected they found that they could increase the number of tufts on the wire by increasing the number of nicks. Surprisingly, as they increased the number of nicks, ozone generation decreased for the same current.

Apparently, the strength of the electric field at each deformation decreased because more localized ionizing zones were available to produce the same amount of ionization current. Thus, a larger percentage of the energy dissipated went to maintaining the corona with the weaker electric fields.

It will be shown, that for the positive polarity case, any anomaly of the surface will increase the average electric field at that point. If the local electric field is increased, it then follows [25,p.183] that the ozone generation will have to increase, even though the average electric field in the corona may decrease. From Eqn. (11), recall that the average electric field will decrease as the roughness factor decreases.

We will define the voltage drop about an anomaly to be the potential drop across an imaginary sheath width, Δa, for the anomaly. This imaginary Δa will be the distance, normal to the surface of the wire, between the surface of the anomaly and that distance at which the electric field due to the anomaly, alone decreases to 30 kV/cm. This is an imaginary sheath width because there is no real sheath for the anomaly on the surface of the wire. It would be a real sheath width if the anomaly were maintaining a corona independent of the wire.

Ozone production from a voltage drop due to an anomaly cannot be obtained from Fig. 5, in the same manner as the voltage drop about the wire. Energy dissipated as a result of the voltage drop about the anomaly is more than that required to maintain the corona, because the corona is being maintained essentially by the large wire.

For a smooth wire, energy dissipation is stable and occurs uniformly across the entire wire, most of the energy being required to maintain the corona as will be shown in Table 5. Where surface anomalies are present, localized, enhanced (additive) electric fields are formed resulting in excess energy above that which is needed to maintain the corona.

This excessive energy must be shown to be adequate to explain the increased ozone production for the model to be meaningful. Quantitative analysis, though, is limited by the difficulty in evaluating the electric field at the deformation and by the lack of knowledge of the molecular ion chemistry of the corona.

Electric Fields About Anomalies

As was discussed, the onset electric field E_s on the surface of the wire will be lowered due to the anomaly (but not necessarily at the anomaly). This follows because E_o is a function of the roughness of the wire. Since any anomaly will only increase the roughness of the wire, there will be a decrease in E_o with the advent of an anomaly. This decrease, though, will not necessarily be as great at the anomaly itself.

Any time that an anomaly appears on the surface of a conductor, there will be a buildup of charges at that anomaly, and the result will be a localized, high-electric field about the anomaly [28]. Furthermore, the strength of the electric field will be a function of the inverse of the radius. That is, the smaller the radius of the anomaly, the larger will be the electric field about the anomaly.

The field, of course, cannot go to infinity as Mittra [29,p.4] points out because the amount of energy that can be stored "in any finite neighborhood of the edge must be finite." This variation in electric field charge about the surface of the wire does not affect the potential of the wire, which must be constant over the entire surface of the wire.

Choice of Best Parameter

Since it was shown in the previous section that ozone generation correlated both with $E_s \times \underline{a}$ and $E_{avg} \times \Delta a$ for the smooth wire case, these parameters will be evaluated in terms of the increased electric fields caused by anomalies.

Either parameter could account for the increase in ozone production due to the high electric fields about anomalies. A decision must be made whether the electric field at the surface of the resulting localized average electric field across the corona is more significant. This depends on whether the ozone production really occurs at the surface or in the ionizing zone. The true parameter can only be determined, though, by a study of the molecular ionic chemistry.

Because Castle [18] recognized $E_{avg} \times \Delta a$ as the voltage drop across the corona while there is no apparent parallel significance to $E_s \times \underline{a}$, $E_{avg} \times \Delta a$ seems to be the most promising at this time. If Castle's [18,p.491] assumption of the surface area as a reaction site, is proved true the evaluation of $E_s \times \underline{a}$ may be more meaningful.

Verifications of the Model

The parameter $E_{avg} \times \Delta a$ will be used to account for the production of ozone in three different types of anomalies: (1) the small wire wound around a larger wire; (2) wires of equal size twisted to form one wire; and (3) the nicked wire. It will be shown that the model is also applicable to corrosion.

Case (1): Small Wire Wound Around a Larger Wire

The combination of the two wires will form a unique wire. The irregularities, where the surfaces of the two wires come in contact with each other, can be compared to scratches extended the length of the wire. As such, they would be considered very serious anomalies and would significantly lower the electric field needed at the surface of the wire for corona onset. As was stated earlier, the roughness factor, which accounts for this reduction of corona onset, runs from 0.6 to 0.9. Because of the extensiveness of this irregularity, the lower limit, 0.6, would probably be a fair approximation. If one then multiplies the resulting voltage drop in the ionizing sheath by the corona current, the product is the energy dissipated in the ionizing sheath, Q, per unit time.

$$(E_{avg} \times \Delta a) \times I = Q \quad \text{joules/sec} \tag{13}$$

It was shown earlier that the energy needed to form one ozone molecule is 1.5 eV (Eqn. (4)). If all the energy in the ionizing sheath were spent in the production could be calculated from the total energy dissipated.

As an example, utilizing the two wires from Castle [18], 0.00635 cm and 0.0406 cm, the total amount of energy dissipated for an arbitrary corona current can be determined. Since it is known that any deformation increases ozone production [18,p.489], then the theoretical lower limit of potential ozone production should be made assuming smooth wires. These calculations are presented in Table 5.

When comparing potential with actual ozone production, it can be seen (Table 5) that the ozone reaction consumes only a small part of the total energy dissipated. Most of the remaining energy must be spent maintaining the corona, the source of ions for particle charting.

The case of a small wire wound around a larger wire, represents a well-defined anomaly, having an electric field that is well-behaved in comparison to the singularity found at a sharp edge. With the assumptions of the model and a few approximations it should be possible to determine if the electric fields formed about the anomalies are large enough to account for the increased ozone generation.

Table 5: Potential Ozone Production, Smooth Wire

Let air flow = 2.36 L/sec
= 0.105 mole of air/sec

Let current = 0.4 mA

Radius =	0.00635 cm	0.0406 cm
E_{avg} =	86.47 kV/cm	52.33 kV/cm
a =	0.0239 cm	0.0604 cm
Q =	0.8264 joule/sec	1.264 joule/sec
	5.158×10^{18} eV/sec	7.89×10^{18} eV/sec
O_3 =	3.44×10^{18} O_3 molecules/sec	5.264×10^{18} O_3 molecules/sec
	5.71×10^{-6} mole O_3/sec	8.73×10^{-6} O_3 mole O_3/sec
$[O_3]$ =	5.44×10^{-5} O_3 by volume	8.31×10^{-5} O_3 by volume
	5440 pphm O_3	8314 pphm O_3
Measured $[O_3]$ =	51 pphm	196 pphm

Let us now calculate an "effective radius", $\underline{a}^*$, for the combined wires from the total cross sectional area of both wires:

$$\underline{a}^* = [(0.00635)^2 + (0.0406)^2]^{1/2} \quad (14)$$
$$= 0.0411 \text{ cm}$$

Using Eqns. (1) and (6), the onset electric field and the average electric field for standard temperatures, assuming a roughness factor of 0.6, will be:

$$E_o = 0.6(30 + 9.0\sqrt{1/0.0411}) = 44.6 \text{ kV/cm} \quad (15)$$

$$E_{avg} = \frac{44.6 + 30}{2} = 37.3 \quad (16)$$

The width of the sheath, since the electric field decreases linearly away from the surface, can be calculated from Cobine [26,p.257]:

$$\Delta a = \underline{a} \times E_o/30$$

$$\Delta a = 0.0411 \times 44.6/30 \text{ cm} \quad (17)$$
$$= 0.0611 \text{ cm}$$

The voltage drop across the ionizing sheath will then be:

$$E_{avg} \times \Delta a = 37.3 \times 0.0611 \text{ kV} \quad (18)$$
$$= 2.28 \text{ kV}$$

The *ozone production* due to the new wire, of radius $\underline{a}^*$, which can then be determined from Fig. 5, should be 75 pphm/mA. If we use 0.4mA (as in Table 5)

$$[O_3]/\text{air} = 0.4\text{mA} \times 75 \text{ pphm/mA} = 30 \text{ pphm}$$

attributable to the new wire.

It was stated earlier that the ozone generation from the combined wires was 800 pphm/mA (Table 4). At 0.4 mA

$$[O_3]/\text{air} = 0.4\text{mA} \times 800 \text{ pphm/mA} = 320 \text{ pphm}$$

attributable to the combined wires. This means that there is a net ozone production of

$$320 - 30 = 290 \text{ pphm}$$

to be accounted for.

In order to compute the ozone production that might possibly be attributable to the small wire, some assumptions about the field at the surface of the small wire must be made. Since this electric field at the surface of an anomaly has been shown to be a function of the radius of the anomaly and in fact reaches a singularity for an edge, the electric field at the surface of the small wire, the anomaly, would also be dependent on its radius. As an approximation to the electric field at the surface of the small wire, E_o that would be calculated for the small wire (as if it were isolated) will be used. Since no anomalies exist on the small wire, the roughness factor will equal one (1).

For estimating purposes, the added voltage drop for the enhanced field will be the voltage drop for the ionizing sheath of the small wire as if it were isolated.

Since electric fields add vectorally, it can be assumed that only that component of the electric field of the anomaly normal to the large wire will be available to enhance the electric field. This means ignoring any possible contributions from the bottom of the small wire and only considering 78 percent of the top half. Seventy-eight percent is the average value of the electric field normal to the large wire.

The increased potential in the enhanced field will then be a fraction of 2.066 kV (Table 2):

$$0.5 \times 0.78 \times 2.066 = 0.806 \text{ kV} \qquad (19)$$

Since the small wire accounts for 14 percent of the surface area of the new wire, it can be safely assumed that at least 14 percent of the ionic current will pass within the enhanced field. From Eqn. (13), the energy dissipated to the enhanced electric field would then be:

$$0.14 \times 0.4 \text{ mA} \times 0.806 \text{ kV} = 0.045 \text{ joules/sec} \qquad (20)$$

Since ozone production will be proportional to the energy dissipated [18,p.491], ozone production can be calculated using Table 3:

$$0.045/0.8264 \times 5440 = 302 \text{ pphm} \qquad (21)$$

The potential production of 302 pphm may appear to be too close to the required value of 290 pphm needed to demonstrate that the model does work. After closer analysis of the assumptions that were made, it becomes obvious that the potential ozone production should be much higher. The field strength at the anomaly is probably a lot higher; and the amount of current passing through the enhanced field would be significantly greater because of the intense ionic activity originating there. If the electric field about the small wire is larger, then the amount of energy dissipated will be greater and the energy needed to produce 290 pphm [O_3] will only be some fraction of the total energy dissipated about the anomaly.

Provided in Fig. 6 is a rough sketch of what the electric field looks like about the anomaly. Note that the equipotential lines from a steep gradient at the anomaly.

If all the energy went to producing ozone, there would be barely enough ozone produced (302 pphm) to account for the amount of ozone that the model attributes to the anomaly (290 pphm).

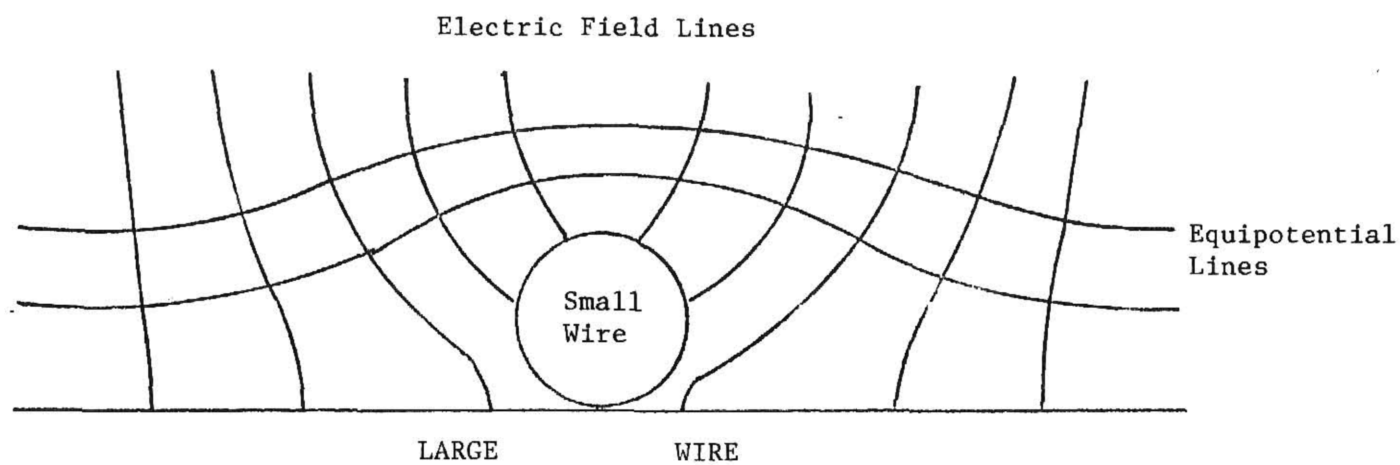

Electric Field Lines
Equipotential Lines
Small Wire
LARGE
WIRE

Figure 6.

Case (2): Wires of Equal Size

In evaluating the model it is also very important to analyze what happens in the limit where the two wires are of equal size. Castle [25,p.181] again provides data on such a case. In this instance, the size of the wires are such that the electric field of each will disrupt the electric field of the other. Thus, both wires must be involved in sustaining the corona. As seen in Table 6, the two twisted wires do not produce the large increase in ozone production that occurred when the wires were of different sizes (Table 4)

Table 6

[26,p.181]

radius = 0.0089 cm

Configuration	$[O_3]/I$
Single wire	59 pphm/mA
Two twisted wires	69 pphm/mA
Three twisted wires	80 pphm/mA
Four twisted wires	86 pphm/mA

This data, though, still shows the additive effect of the electric fields.

Figure 7 shows an analysis similar to that used in Case (1) can be applied to the various configurations. The effective radius, a*, for the various configurations can be determined from the cross sectional areas, and the onset electric field at the surface of the wire can be approximated.

Since wires are conductors, charges will reside on the surface. Therefore, the free area inside the three and four wire configurations will be assumed to be part of the wire.

Castle [25,p.182] states that the voltage-current characteristics for the four wire case were almost identical to a wire having a radius calculated from the cross sectional area. Therefore, E_o must not have been lower or the onset electric voltage would have been lower. Consequently, a roughness factor of one (1) can be assumed for the various configurations. A roughness factor of one (1) would not have been a good approximation for the case in which one wire was much larger than the other because the latter case was a better parallel of ozone production from an anomaly.

Presented in Table 7 are the calculations of a possible voltage drop across the ionizing sheath for each configuration. From this value the expected ozone generation can be determined from Figure 5.

Since the one (1) wire configuration was one of Castle's [18] original six data points, the difference between the expected and the measured ozone concentration is just the fluctuation of data points about the "best fit" line. The other deviations, though, appear to be actual reductions in ozone concentration.

Concerning the electric field about the configurations, Castle [25,p.182] points out that the surface electric field will be reduced in the irregularity as compared to the surface field strength of a surface which is not exposed to the surface of another wire. This reduction of the electric field in the space around the irregularity will result from two phenomena: (1) the reduction of the field at

$\underline{a}$ = 0.0089 cm copper wire

O_3/I = parts per hundred million of ozone by volume per milliamp of current

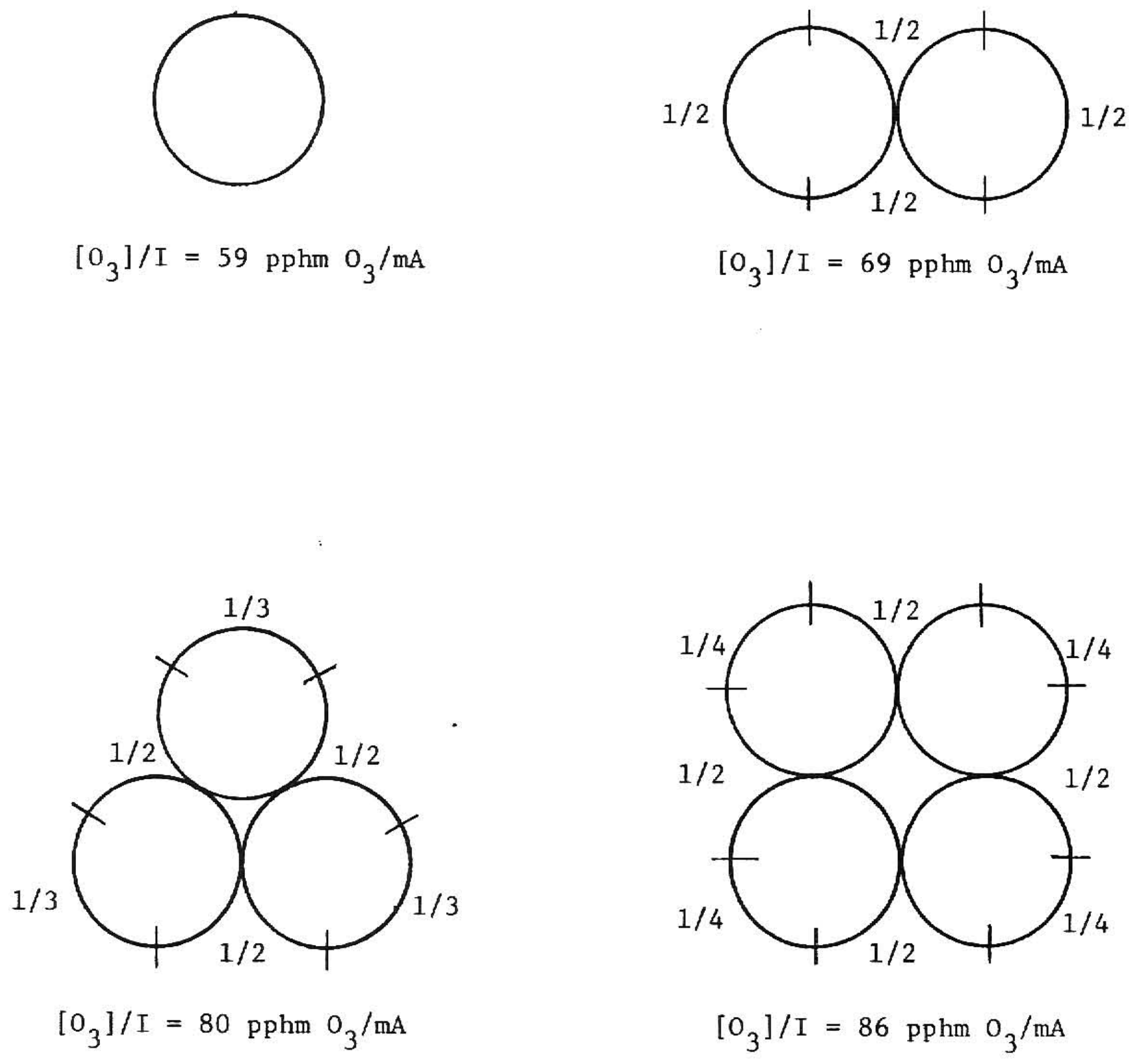


Figure 7. Diagram of Multiwire Configurations.

Table 7

Configuration	1 wire	2 wires	3 wires	4 wires
Cross Section Area ($x10^{-4}$ cm)	2.488	4.976	7.597	10.63
Effective Radius <u>a</u>* (cm)	0.0089	0.0126	0.0156	0.0184
E_o (kV/cm)	125.4	110.2	102.1	96.3
E_{avg} (kV/cm)	77.7	70.1	66.0	63.2
$\Delta a = 0.3\sqrt{r}$	0.0283	0.0337	0.0375	0.0407
$E_{avg} \times \Delta a$ (kV)	2.199	2.361	2.473	2.572
Expected $[O_3]/I$	65	88	103	117
Measured $[O_3]/I$	59	69	80	86
Difference in $[O_3]/I$	6	19	23	31
Number of Irregularities	0	2	3	4
Ozone decreases per irregularity		9.5	7.67	7.75

the surface of the wire due to the presence of the other wire, and (2) the vectorial addition of the fields at the surface of each wire.

In each irregularity one-fourth of the surface area of any wire will be exposed to one-fourth of the surface area of another wire regardless of the number of wires (Fig. 7). To apply the model, the electric field strength at the surface may be approximated with the effective radius $\underline{a}^*$. Since the onset electric field decreases with increasing radius, it can be expected that the net electric field in the irregularity will decrease with increasing number of wires.

According to the model, a net decrease in the electric field in the irregularity should produce less ozone. The three and four wire configurations show this decrease in ozone production per irregularity, because the ozone decrease per irregularity (Table 5) is greater for the four wire configurations than for the three wire configurations. The difference in the ozone decrease per irregularity, which is by no means a proof of any kind, agrees with the small difference between the calculated electric fields at the surface of each wire.

The reason that the two wire configuration did not increase ozone production in the irregularity (to be compatable with the three and four wire configurations) can be attributed to the poor assumption made about its effective radius. The three and four wire configurations presented more meaningful effective radii because their radii did not go to zero at the irregularity. Possibly then a smaller effective radius for the two wire configuration could have somehow accounted for the collapse of the radius at the irregularities. Since a smaller effective radius would result in a smaller average electric field (Eqn. (8)) and sheath width (Eqn. (7)), there would have been less ozone produced due to the decrease in the voltage drop. This decrease in ozone production for the two wire configuration might have then brought the ozone decrease per irregularity into proper perspective with the other wire configurations.

When Castle [25,p.182] examined the data, he noted that the ozone production for the various multiwire configurations was less than that for a round wire with the same effective radius. He attributed the reduction to the decrease in active surface area, which was a result of the electric field reduction at the irregularity.

A proper field analysis, considering electric fields and equipotential lines, is not really important to the model in Case (1) or in Case (2) because the analysis is basically stoichiometrical. Thus, the value of the electric field at every point in the corona is not important as long as the amount of energy dissipated can be approximated. If the molecular ion chemistry of ozone production in the positive corona had been reported in the literature, then perhaps a proper field analysis could have been utilized to analyze ozone production due to anomalies and irregularities.

Case (3): The Nicked Wire

The last case to be discussed is Awad and Castle's [23,p.376] experiment on the nicked positive polarity wire (Fig. 2).

Awad and Castle claimed that their data showed that ozone production from the nicked wire eventually leveled off to the same $[O_3]/I$ slope as for the smooth wire. The observation seems faulty, though, because it is possible to draw parallel lines through the data above 0.150 mA as is done in Fig. 8. In the two extreme cases that are not parallel to smooth wire line, the results of the low and the high number of nicks were already drawn essentially parallel to each other but not to the smooth wire data (Fig. 2).

If all the lines are parallel, the apparent ozone production of the intermediate data is then reduced. The difference between the top lines (Fig. 8) at the lower end is only a little over five percent. Castle [25,p.74] states that the accuracy of the ozone measuring instrument "was estimated at 5 percent." So it is at the least doubtful that the two lines represent significant differences.

It is the opinion of the author that ozone production increased sharply with the initial nicks, but additional nicks followed a pattern of "diminishing returns." Additional nicks produced more ozone, but the amount was within the error limits of the ozone measuring equipment.

This opinion might not seem to apply to the data below 0.050 mA (Fig. 2). Here the ozone production decreases for the intermediate number of nicks, but rises again for the most number of nicks. The conditions that lead to the phenomenon, though, were not normal positive corona conditions. Awad and Castle [23,p.376] describe the condition:

> *"...a reduction in the positive corona onset is due to the localized field enhancement caused by the nicks. Therefore, the positive corona with the presence of the nicks starts with localized discharge at these nicks and has the same visual appearance as the tufts of the negative corona...once the nick-free part of this nicked wire starts to form the uniform sheath...[O_3] starts to decrease also.*

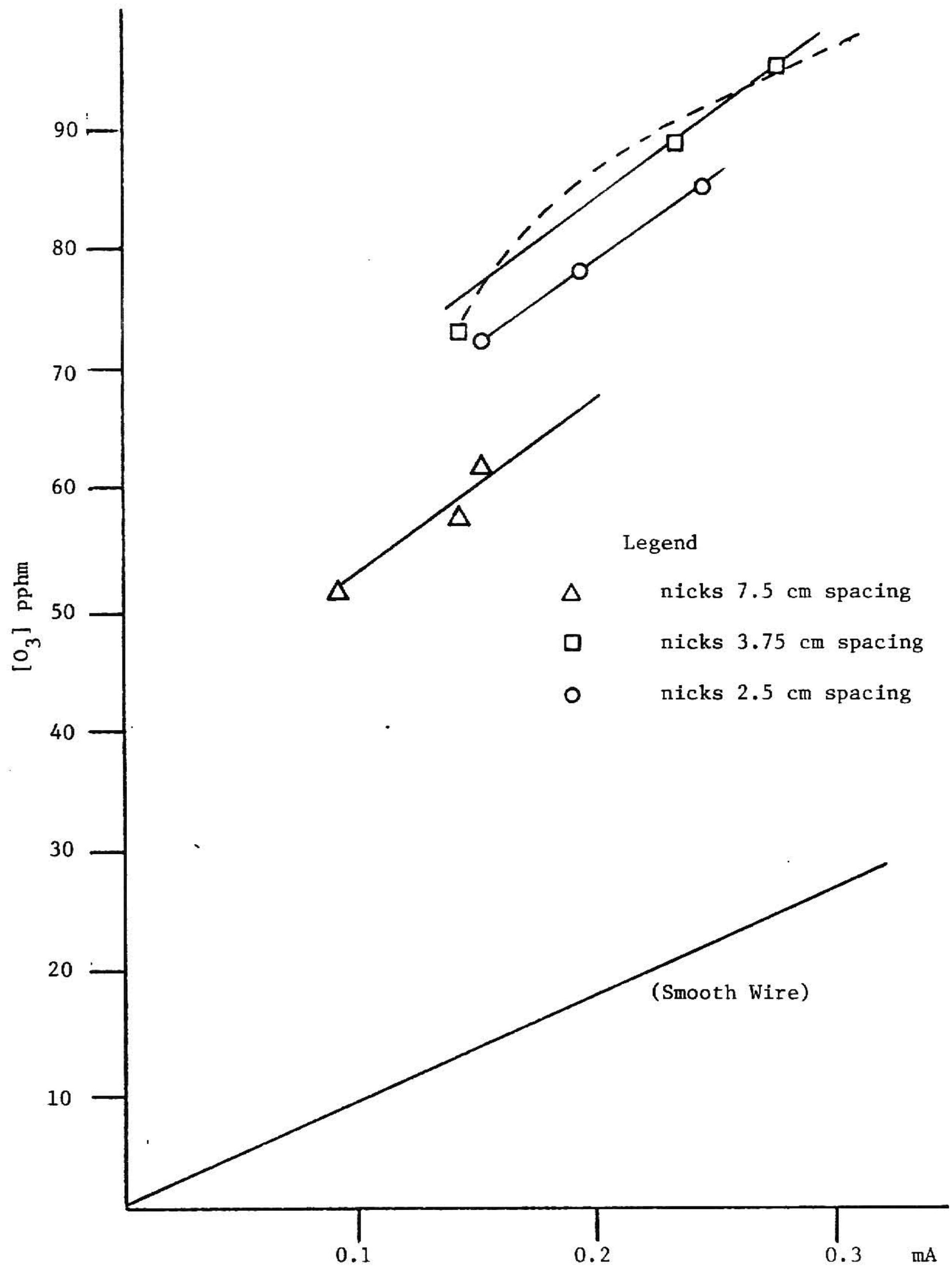


Figure 8. Ozone-Current Characteristics Above 0.15 mA.

It was demonstrated earlier why the ozone production for the negative polarity case decreased with the increasing number of nicks (because the strength of the field at each nick is decreased). Since the positive polarity appeared visually similar to the negative polarity, there is evidence that the positive polarity is behaving in a similar manner in the low current region. The fact that the production might also be linear in this region follows from Loeb [27,p.43], who has shown that the voltage drop which maintains the corona must remain constant.

Therefore, it follows that the ozone production in the intermediate case should decrease (Fig. 2), but the increase for the wire with the most number of nicks does not follow. The fact that this trend does not follow the negative polarity case may be the result of the problems involved in reproducing uniform nicks.

As the current is increased the electric field and the resulting voltage drop at the nicks decrease as the ionizing sheath progresses over the length of the wire. From earlier discussions, it follows that the ozone production should not continue to rise linearly because the enhanced electric fields and the resulting excess energy at the nicks is decreasing. When the corona finally stabilizes over the entire wire, the voltage drop at each point on the wire will become fixed and the ozone production will again be linear with current.

There appears to be no basis for the belief that the ozone production in the higher current region should produce parallel slopes for the various number of nicks (Fig. 8). There is reason to believe that the lines must diverge if they are not parallel. If the lines converged, they would then cross and ozone production would not be a function of the number of anomalies. This contradicts that which has been observed.

It can also be shown that these lines should not be parallel to the line for the smooth wire (Fig. 2) and must, in fact, diverge from the line for the smooth wire. If one of the nicked lines were parallel to the smooth wire line, then the ozone (in pphm) produced at the nicks would reach a constant and would not increase with an increase in current. Additional ozone production would only result from the activity about the nick-free part of the wire.

Since increased ionic activity has been shown to increase ozone production, then ozone production in the enhanced fields about the nicks should increase if the ionic activity increases. If the ionic activity about the nick were to level off at some point, then a greater proportion of the ionic current would have to be produced by the nick-free part of the wire. From stoichiometric considerations, an increase in the amount of energy needed for corona current would necessitate a decrease in the amount of energy available to produce ozone. Since such a reduction is not noted (ozone production remains linear to current), ionic activity at the nicks cannot level off at some point.

Applicability

The meaningfulness of the model lies in its ability to account for ozone generation in all cases. The three cases presented in this chapter demonstrated that the model is reasonable and applies over a wide range of deformations.

Corrosion, another important type of deformation, was not analyzed. Evaluation of the effect of corrosion on ozone production, though, cannot be quantitative, because of the problems involved in quantifying the "nuclei" that are the corrosion. Application of the model to corrosion must then be accomplished by reasoning.

It is the opinion of the author that the application of the model to the problem of corrosion is merely a scaling consideration. The nuclei will form small enhanced electric fields about themselves, and the cumulative effect of all of the nuclei will produce significant increases in ozone production.

The model does seem reasonable in accounting for the increase in ozone production from various anomalies.

SUMMARY AND CONCLUSIONS

Ozone production from a positive corona about a fine wire has been studied with special consideration given to the non-ideal case, where anomalies on the surface of the fine wire increased ozone production. A model has been presented that accounts for the increased ozone production due to the anomalies.

The model utilizes a stoichiometrical approach to ozone production and attributes the increased ozone production about anomalies to excess energy in the localized zones about the anomalies. The excess energy is a function of localized, high-electric fields about the anomalies.

Various anomalies (small wire spiralled around the large wire, and the nicked wire) have been discussed, and the model has been demonstrated to account for the increased ozone production in these cases. From the anomalies discussed, the model might be extended to cover corrosion.

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A MODEL OF OZONE GENERATION IN POSITIVE
POLARITY ELECTROSTATIC PRECIPITATORS

by

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AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Mechanical Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1975

ABSTRACT

The production of ozone from the positive polarity electrostatic dust precipitator makes it a potential health hazard. There is a need, therefore, to better understand the cause of production of ozone in the precipitator.

Presented in this thesis is a plausible model of ozone generation in the positive corona formed about a fine wire in the charging section of an electrostatic precipitator. Special consideration is given to the non-uniform positive corona resulting from deformation of the surface of the fine wire.

The model, which utilizes a stoichiometrical approach to the production of ozone, relates ozone production to the amount of energy available in the ionizing sheath (corona). In the case of deformations of the fine wire's surface, excessive energy at the deformation above that which is needed to maintain the corona is available to increase ozone production.

To demonstrate the applicability of the model, which is derived from previous contributions in the field, the model is utilized to account for the ozone production from fine wires with various types of surface deformations.