Evolution of Industrial Ozone Generation

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Abstract

A vast selection of different ozone generator designs is commercially available on today’s market. In large-scale applications, the ground electrode is designed as gas/water tube heat exchanger, which is filled with tubular high-voltage electrodes on the gas processing side. Available constructions differ in diameter, length and arrangement of the tubular electrodes, type and support of the dielectric material and in the character of the applied microdischarges. Narrowest tolerances of the discharge gap and dielectric layer guarantee a uniformly distributed filamentary DBD plasma pattern along the ozone generator tube and therefore a homogeneously feed gas processing.

Goal of the presented work is to explore the benefits from an inhomogeneous feed gas processing. A finite element model is utilized to simulate an inhomogeneous power induction along the ozone generator tube. The simulation yields the local power density, the local gas temperature gradient and a relative DBD packing density. Combined with experimental data, a sufficient set of information can be obtained to infer a strong correlation between electrode arrangement and generator characteristics. Therefore, several arrangements, evenly distributed within a given space, were designed, simulated, manufactured and tested on a representative scale.

An arrangement with pronounced power induction at the generator inlet manifests several advantages over homogeneous plasma processing arrangements. The degree of filamentation turns out to be decisive, indicating a new potential through plasma tailoring.
Increased robustness and substantial savings in electrical consumption were obtained on an industrial scale with more than one hundred square meters of active DBD area.

Key Words

Ozone; power induction, generation efficiency, causality, discharge filament, DBD plasma, nitrogen admixture, dinitro-pentoxide, optimization.

Introduction

A variety of factors influence the design of an ozone generator. Low power consumption, robustness of operation and minimum maintenance requirements are of highest importance, especially in large-scale industrial or municipal applications. At the smaller scale, ease of use and the lowest cost per unit, turn out to be of higher interest than power efficiency. Thus, different technologies and manufacturing processes compete at various scales, leading to a wide spectrum of technical solutions.

The nature of available ozone generator technology has recently been reviewed by U. Kogelschatz (2005). The so-called dielectric barrier discharge (= DBD) is used in almost all possible regimes of gaseous breakdown to enrich ozone within an oxygen carrying feed gas. In a pin, wire or mesh to plate arrangements many discharge types such as corona or streamer-corona (Becker et al. 2005) may be utilized. The typical operation with adjacent plates or concentric cylinders relies on Townsend-like to streamer discharges, which might be used in a continuous mode to produce a pronounced filamentary discharge pattern or, in a pulsed mode, to produce a homogenous discharge pattern.

Efficiency numbers, g/kWh, found in literature, are widely scattered, since they were obtained for different regimes of ozone concentrations, cooling conditions and scales of production. In industrial or municipal large-scale applications, ozone concentrations ranging from 9 to 14 weight percent in an almost pure oxygen carrying feed gas, at production capacities ranging from 20 to several hundred kilograms of ozone per hour, have to be provided to the customer. Cooling water temperatures around 30°C are found at most sites in the USA or in Asia. Lang et al. (2005) reported the optimum electrode arrangement for such operating conditions, which was obtained from a broad range of measurement campaigns. In this work, the evolution of ozone generation technology is addressed by investigating the causality between electrode arrangement and ozone generator properties and efficiency. To accomplish this task, the following approach was chosen:

1. Creation of a finite-element model, which simulates the power induction along the discharge gap, taking into account the local background condition.
2. Calibration of free model parameters with measured data.
3. Selection of several electrode arrangements, well distributed in the design-parameter space.
4. Manufacturing, testing and simulation of the selected electrode arrangements.
5. Investigation of the causality.
6. Optimization of the electrode arrangement and subsequent validation of the postulated causality.

The model parameters are forced to include implicit information about the investigated causality. A direct interpretation of phenomena becomes possible in the case of few and significant model parameters.

For the sake of completeness, other approaches for the investigation of causality have to be mentioned. Eliasson et al. (1986) and Pitchford et al. (2005) followed a bottom-up strategy and implemented a computational model, which was used to simulate the transients in the ozone synthesis of a single discharge and the build-up of higher ozone concentrations through the DBD plasma processing. Due to the nature of bottom-up approaches, such models would reproduce phenomena as far as included in the code and ignore unknown higher order effects. The strength lies in the ability to explain phenomena, while it may be of limited help for process optimization purposes.

**Materials and Methods**

**Numerical Simulation of Power Induction**

The electrical power induced into n slices of a concentric cylindrical DBD electrode arrangement can be calculated by the extended Manley formula (Manley, T.C. 1943, Kogelschatz et al. 1982):

\[
P = \alpha \cdot 4f \sum_{i=1}^{n} C_{D,i} \frac{1}{1+\beta_i} U_{\text{min},i} (U_{\text{peak}} - U_{\text{min},i}) \quad [\text{kW}]
\]

where

\[
i \quad : \quad \text{i}^{\text{th}} \text{ slice}
\]
\[
n \quad : \quad \text{amount of slices per cylinder} \quad [\text{]}
\]
\[
U_{\text{peak}} \quad : \quad \text{peak voltage} \quad [\text{V}]
\]
\[
U_{\text{min},i} \quad : \quad \text{minimum voltage i}^{\text{th}} \text{ slice} \quad [\text{V}]
\]
\[
f \quad : \quad \text{frequency} \quad [\text{Hz}]
\]
\[
C_{D,i} \quad : \quad \text{capacitance of dielectrics i}^{\text{th}} \text{ slice} \quad [\text{F}]
\]
\[
\alpha \quad : \quad \text{adjustable parameter} \quad [0, \infty]
\]
\[
\beta_i \quad : \quad C_{G,i}/C_{D,i} \quad [\text{]}
\]

The so-called \(\alpha\)-effect parameter was introduced by Kogelschatz et al. (1982) to account for partial activation of the available discharge area at lowest electrical loads, especially with the presence of mechanical tolerances in a realistic electrode arrangement. In a more general approach the \(\alpha\)-parameter is utilized as adjustable parameter to match the measurement data. This can be justified by a comparison of two electrode arrangements, which are operated at identical plasma conditions, i.e. power density, outlet ozone concentration, average cooling water temperature, cooling water temperature gradient and average gas pressure. Both arrangements
have an identical discharge gap but differ in the thickness of the dielectric layer. The following results are obtained in such a case:

- The degree of filamentation increases with increasing thickness of the dielectric layer (Hirth et al. 1981).
- After the adjustment of Cd, β, Upeak and Umin in [1] (with n=1) the α-parameter turns out to increase with increasing thickness of the dielectric layer. Nota bene: This effect exceeds deviations in efficiency.

Hence, the interpretation of α as packing density of the spatial distribution of filamentary microdischarges seems to be reasonable and consistent with its original interpretation.

The spatial resolution of locally induced power is then achieved by a finite element approach. The electrode arrangement is sliced into n pieces or n equal volumes respectively, which need to account for the local discharge gap size, local dielectric capacitance and the local Umin. The estimate of the local Umin is not obvious; it was done as follows:

- Local breakdown voltage:
  An increase of 100 Volts per weight percent of ozone was determined experimentally.
- Ozone build-up profile:
  The build-up profile can be enveloped by a linear and an exponential curve. Thus, a third order regression is selected to fit two third of the outlet ozone concentration at one third of total applied power.
- Local Umin:
  60 percent of the local breakdown voltage. Corresponding measurements (charge vs. voltage Lissajous plot) indicate even smaller values.
- Local gas pressure:
  A linear decrease from inlet to outlet was assumed.
- Local gas temperature:
  The total gas temperature increase of usually 5°C was split into the fraction of locally dissipated power.

Several iterations are required to adjust α in equation [2], in order to equalize the simulated induced power to the measured power. The complimentary information about the measured power must be retrieved from measured data or regression data models (Montgomery, D.C. 2001), expressed as a function of typical conditions in the plasma (ozone concentration, power density, average pressure, average cooling water temperature and frequency). For this work, the following regression models were determined for each electrode arrangement:

- power efficiency
- rms-voltage
- rms-current
- power factor
- pressure loss
The finite element simulation is calibrated with real measurement data, which is a prerequisite to project the intrinsic properties of the investigated plasma physics into estimated model parameters. The gained information includes:

- Distribution of locally induced power.
- Profile of gas temperature increase.
- Determination of the average filament packing density of the electrode arrangement, which is going to be paired with qualitative and quantitative properties of corresponding measurement results.

**Definition of Efficiency**

Efficiency, as utilized in this work, is defined according to equation [2]:

\[
\eta = \frac{0.82}{E_s} \cdot 100 \quad [\%]
\]

where

\[
\begin{align*}
\eta & : \text{power efficiency} \quad [\%] \\
0.82 & : \text{binding energy} \quad \text{O}_2 \rightarrow \text{O}_3 \quad [\text{kWh/kg}] \\
E_s & : \text{specific energy consumption} \quad [\text{kWh/kg}]
\end{align*}
\]

Figure 1 shows an example of an ozone concentration vs. efficiency curve. The so-called single-pulse efficiency is obtained at zero ozone concentration. Due to increasing loss-terms, a nonlinear increase of \(E_s\) is observed as the ozone concentration increases. The classical ozone generator has a limit concentration, which is related to a trade-off between ozone destruction and formation and to a poisoned state by NO\(_x\)-related plasma chemistry in air.

![Figure 1](image)

**Figure 1:** Example of a curve of efficiency vs. ozone concentration; efficiency is defined according to equation [2].
Selection and Specification of Electrode Arrangements

In order to focus the investigation on the most promising electrode arrangement geometry, advanced methods of nonlinear regression analysis were utilized to mine a database containing several thousand sets of steady-state measurement results. A so-called Takagi-Sugeno Fuzzy regression model (Babuska, R. 1998) succeeded and indicated the potential of a cone-shaped discharge arrangement, as shown in Figure 2 (Vezzù, G. 2005).

![Figure 2: Projection of the multidimensional regression model: power efficiency [%] vs. ozone concentration [wt%] and discharge gap [mm].](image)

This result reflects and validates also the work presented by Lang et al. (2005), where, for operation in oxygen at ozone concentrations around 12 weight percent, an optimum discharge gap of around 0.3mm was arrived at.

The causality between power induction and efficiency was detected by investigating several power induction patterns:

1. Power linearly increasing from the inlet to the outlet
2. Power linearly decreasing from the inlet to the outlet
3. Power inhomogeneously distributed

A selection of tested and manufactured electrode arrangements is shown in Table 1, including information about the size of the discharging gap and the capacitance of the dielectric. Each position represents a tubular, enamel-coated electrode of approx. 0.5m length and 0.056m diameter, which is inserted into a stainless steel
The four electrodes are connected in series, which makes them act as one electrode or one system.

**Table 1.** Selection of electrode arrangements. Every arrangement consists of 4 electrodes of approx. 0.5m length and approx. 0.056m diameter. The size of the discharge gap and capacitance of the dielectric is specified for all four positions (1: inlet, 4: outlet).

<table>
<thead>
<tr>
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</thead>
<tbody>
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<td>0.38</td>
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</tr>
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<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
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<td>9.0</td>
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<td>12.0</td>
</tr>
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</table>

The reference arrangement consists of four identical electrodes, which leads to an almost homogeneous power induction pattern. On the market, the reference arrangement is known as AT98. It’s a classical representative of a homogeneous feed gas processing ozone generator, which is still being used for oxygen-fed plants and high concentrations. Arrangements B to G are designed to yield an inhomogeneous power induction pattern. They are representatives of a novel type of ozone generator with inhomogeneous feed gas processing, which is expected to yield substantial advantages over the classical products.

**Test Rig and Measurement Devices**

The utilized test rig falls under the ISO 9000 quality regulations of Ozonia Ltd. (Vezzù, G 2006) and contains the following main components:

- 450kVA power supply with special transformer
- 7-tubes generator with 4 electrodes per tube
- Mass flow controllers for oxygen, nitrogen and other gases
- Back-pressure control loop with pressure controller
- UV/V spectrometer with special cuvette for ozone measurement
- IR spectrometer for measurement of NOx and other side products
- Gas and cooling water temperature sensors at the generator in- and outlet
- Gas pressure sensors at the generator in- and outlet
- HV- and current probes connected to a 3-phase power meter
- Ciller with cooling water mass flow controller
- Oscilloscope for Upeak/Umin determination

For the sake of highest reproducibility of results, regular control measurements, with known electrode arrangements, were performed.
Results and Discussion

Simulation of Local Induced Power

Table 2 combines the information about investigated electrode arrangements (from Table 1) with parameters of operation and results of the simulation.

Table 2: The electrode arrangements, completed with information about electrode design parameters, settings and results of the numerical simulation (1: inlet, 4: outlet). Fractions of locally applied power are represented by the parameter $f_{q_1..4}$.

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<tr>
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<td>5479</td>
<td>5479</td>
<td>5479</td>
<td>5229</td>
<td>5130</td>
<td>5140</td>
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<tr>
<td>$\alpha$</td>
<td>0.97</td>
<td>0.84</td>
<td>0.94</td>
<td>0.92</td>
<td>1.14</td>
<td>1.25</td>
<td>1.21</td>
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<td>0.038</td>
<td>0.038</td>
<td>0.035</td>
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<td>0.036</td>
<td>0.036</td>
<td>0.036</td>
<td>0.035</td>
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<td>0.032</td>
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<tr>
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<td>0.034</td>
<td>0.034</td>
<td>0.034</td>
<td>0.032</td>
<td>0.032</td>
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</tr>
<tr>
<td>$\text{gap}_4$ [mm]</td>
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<td>0.032</td>
<td>0.032</td>
<td>0.032</td>
<td>0.032</td>
<td>0.032</td>
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<tr>
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<tr>
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<td>9.6</td>
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<td>9.31</td>
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<td>0.215</td>
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<td>3.26</td>
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<tr>
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<td>24.5%</td>
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<td>26.3%</td>
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<tr>
<td>$f_{q_3}$</td>
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<td>25.5%</td>
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<tr>
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<td>16.3%</td>
<td>26.7%</td>
<td>22.4%</td>
<td>20.5%</td>
<td>21.7%</td>
<td>21.1%</td>
</tr>
</tbody>
</table>

A comparison of the various arrangements reveals the following:

- $U_{peak}$ varies with the size of the average discharge gap, obtained from the regression data models.
- The average packing density $\alpha$ varies with the electrode arrangement. Values larger than 1 indicate an increased packing density compared to the reference arrangement used for the calibration of the model. The absolute value is influenced by $U_{min}$, which was kept at a constant 60 percent of the local breakdown voltage.
- Arrangement F has the highest $\alpha$ value and the lowest average capacitance $C_{d_1..4}$. 
Arrangement G has the highest discontinuity in the local power density.

Arrangement B has the highest variation of the gap to dielectric capacitance ratio $\beta_{1..4}$, the local power density $q_{1..4}$ and the fraction of applied power $f_{q_{1..4}}$.

Arrangement C is the only arrangement with an increasing fraction of applied power from the inlet to the outlet.

The power induction pattern is found to be sensitive to changes of the design parameters displayed in Table 1. The highest local power induction is almost double the lowest local power induction. The estimate of the achievable resolution of locally induced power is a value around 1 percent on the absolute scale.

**Causality between Power Induction and Efficiency**

Figure 3 is a graphical illustration of the simulated power induction patterns as summarized in Table 2. The complementary information about power efficiency, relative to the reference electrode arrangement, is added to the axis with the arrangements letters. The following comments can be made:

- Arrangement B is found to be too aggressive. A long-term operation is not possible, as the generator starts to pulse itself.
- Arrangement C is the only electrode arrangement with an increasing power induction pattern, but turns out to be less efficient than the reference arrangement.
- Arrangements D to G show a gradually increasing fraction of applied power at the generator inlet. An optimum seems to exist and this optimum is a power induction pattern close to arrangement F.

A higher resolution of the finite-element simulation reveals even more detailed information. Figure 4 illustrates a simulation of arrangement F with 100 slices (see [1]), which yields the following insights:

- The progress of the local power density is discontinuous. A high power density is applied at low ozone concentrations.
- The temperature profile indicates a favorable increased gradient at lower ozone concentration.
- The high average filamentary discharge packing density of arrangement F is obviously due to the long section of smooth power induction.

The phenomenology is completed with the observation of burn-in velocity. Burn-in is related to the build-up of a metallic oxides layer on the surface of the electrodes and of the stainless steel tubes. Arrangement F is found to accomplish burn-in almost 50 times faster than the reference arrangement, which confirms a significantly increased surface contacting.
**Figure 3:** Graphical illustration of simulated power induction patterns. Each pattern is paired with information about the efficiency relative to the reference electrode arrangement.

**Figure 4:** Finite element simulation ($n = 100$) of an ozone generator tube assembled with four electrodes connected in series according to arrangement F. The temperature curve is valid for cooling water cross-flow.
Three major hypotheses have to be considered:

- The observed efficiency increase is due to the favorable temperature gradient at low ozone concentrations, achieved by a specific power induction pattern.
- The observed efficiency increase is due to the balance and degree of discharge filamentation at low and high ozone concentrations.
- The observed efficiency increase is due to a combination of both.

The decreased efficiency of arrangement G disproves the first hypothesis as the dominating effect. The balance and degree of discharge filamentation is obviously a substantial part of the obtained efficiency increase.

**Formation and Characteristics of By-Products**

The most prominent by-product of an oxygen-fed ozone generator is dinitro pentoxide (= \(N_2O_5\)), which originates from a required nitrogen blending at ozone concentrations higher than eight weight percent (Lang et al. 2005). The phenomenon is related to open metallic surfaces in the discharging area as shown by Pontiga et al. (2004), while it does not seem to affect ozone synthesis in the plasma (Pitchford et al. 2005). Apart, only laughing gas (=\(N_2O\)) was found to coexist.

The determination of the amount of formed \(NO_x\) was done with an infrared spectroscop, which is equipped with a 10cm stainless steel gas cell, CaF\(_2\) windows and sensors for gas temperature and gas pressure compensation (Kogelschatz et al. 1987). The following results were obtained:

- The amount of formed \(NO_x\) scales linearly with the amount of nitrogen admixture
- Determining factor in the \(NO_x\) formation is the ozone concentration. Apart from that, only a weak influence of the cooling water temperature was found.
- \(N_2O_5\) formation is a non-linear function of the ozone concentration. A second order regression formula is needed to fit the data.
- \(N_2O\) seems to be a linear function of ozone concentration.

The dependence of \(N_2O_5\) and \(N_2O\) formation from ozone concentration, at 3 wt% of nitrogen admixture, is shown in Figure 5. The measurements were repeated for several electrode arrangements with different discharging gap geometries. A comparison of the 0.4mm and the 0.32mm gap curves indicates a marginal decrease in \(NO_x\) production with smaller discharging gaps. This is confirmed by the curve for the variable gap with an arrangement similar to arrangement F.

\(N_2O_5\) is observed to deposit as crystalline substance on slightly cooled surfaces. The inclusion of metallic ions leads to a brownish color of the deposit, which liquefies immediately in the presence of moisture. Thus, a humidity trap was installed to observe and compare the dirt formation potential (= deposition of \(N_2O_5\)) of various electrode arrangements. The results are summarized in Table 3.
The amount and physical properties of formed N$_2$O$_5$ molecules or clusters affect the dirt deposition potential and can be influenced by the design of the electrode arrangement. The configuration 1:3 was found to stay absolutely clean even under exacerbated conditions. The degree of filamentation in the high-load and in the low-load regions seems to shift the final size of N$_2$O$_5$ clusters to a regime no longer governed by diffusion (Vezzù, G. 1999). It is interesting to note the increased efficiency for the 1:5 case with the lowest local temperature gradient. This supports the hypothesis of degree and balance of discharge filamentation as the dominating effect and cause of the achieved efficiency increase.
Characteristics of an Optimized Electrode Arrangement

An electrode arrangement may be optimized according to the needs of the application and/or to the conditions of operation. A comprehensive optimum includes both aspects:

− The discharge filaments are tailored to increase the power efficiency
− The power induction pattern is adjusted to maximize robustness at all conditions of operation

The application of these criteria leads to an ozone generator with amazing properties, as illustrated in Figure 6. The classical shape of an efficiency curve is represented by the dashed line with a pronounced limiting concentration. The measured data fits the classical curve shape in the low ozone region only. An almost linear trend is evident in the high ozone region, which deviates from a zero and first order kinetics as suggested by Hirth et al. (1983). As a matter of fact, an efficient and robust system is exclusively obtained from the optimized discharge arrangement.

The prove of concept was done on large-scale, in a so-called Duplex vessel, with a total active area of 112.7 square meters and a production capacity of approx. 60 kilograms per hour at 10 weight percent of ozone concentration. An ozone concentration of approx. 16 weight percent (see monitor picture in Figure 7) was achieved and could be held without any problems, even at increased cooling water temperatures and at high power densities.

Figure 8: Ozone concentration vs. efficiency at constant power density, cooling water temperature, pressure and frequency. The classical curve fits only in the low ozone region. The high ozone region reveals a linear trend.
Conclusions

Plasma Tailoring

A tailored degree of filamentation at low and high ozone concentrations benefits the ozone generation process in terms of:

– reduced power consumption
– increased range of applicable ozone concentrations
– neutralization/conditioning of detrimental by-products

Figure 7 illustrates the conceptual design needed for the application of such inhomogeneous feed gas processing. This type of arrangement was manufactured and successfully operated on the large-scale.

The physics of ozone synthesis in a DBD plasma may be summarized as follows:

– Highly filamented DBD discharges are best-suited to the production of ozone concentrations in the range of 6 to 14 wt%.
– The preferred characteristic of the microdischarges is Townsend-like, at reduced electric fields E/n, around 190Townsend.
– Smaller than 0.3mm discharging gaps require thick dielectric layer to maintain a good filamentation at reasonable efficiency.
– The formation of by-products, such as N₂O₅, depends on the nitrogen admixture and the ozone concentration. It is almost independent from the design of the electrode arrangement.
– N₂O₅ is needed to protect metallic surfaces in the discharging gap.
Detrimental side-effects, induced by N\textsubscript{2}O\textsubscript{5}, can be avoided by a proper design of the electrode arrangement. The phenomenon is related to the diffusion rates of formed N\textsubscript{2}O\textsubscript{5} clusters.

**Scale of Ozone Production and Applicable Technical Solutions**

The technology presented in this work is best-suited for large ozone production capacities of up to several hundred kilograms per hour, at concentrations between 6 to 14 weight percent. Corresponding electrode designs have a length of up to 3 meters and are bundled to obtain several hundred square meters of active DBD area.

The desired precision will determine the choice among the competing materials and manufacturing technologies (as shown in Table 1). The challenge imposed by such requirements directly affects manufacturing in terms of:

- Precision and tolerances of dielectric tubes, plates or coated layers
- Compatibility of the dielectric component with the metallic electrode

Components may be utilized as they are available on the market, with standard tolerances. At increased levels of precision, only a few approaches succeeded in the past:

- Coating of precise metallic tubes or plates
- One-sided metallization of high-precision ceramic plates

Eventually, it is a question of cost per total active DBD area. The capacity of a plate ozone generator is scaled through the adjustment of the total amount of plates. The cost of the unit scales accordingly, which is a linear function of the number of plates. Tubular arrangements are designed as gas/water tube heat exchanger. The cost per unit of active area manifests a regression towards larger vessel volumes and becomes significantly cheaper at large-scale. The trade-off was found to be in the range between 1 to 10 kilograms per hour, which promotes the tubular arrangement on the basis of a heat-exchanger vessel for applications with middle and high ozone demands.

**References**


