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<td>Author(s)</td>
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<td>Citation</td>
<td>IEEE Transactions on Dielectrics and Electrical Insulation, 7(5): 646-653</td>
</tr>
<tr>
<td>Issue date</td>
<td>2000-10</td>
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<tr>
<td>Type</td>
<td>Journal Article</td>
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<td>URL</td>
<td><a href="http://hdl.handle.net/2298/16072">http://hdl.handle.net/2298/16072</a></td>
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Streamer Discharges in Liquids and their Applications

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ABSTRACT
Industrial applications using pulsed power technologies have been developed in many fields. One of them is the treatment of exhaust gas by using uniformly produced streamer discharges. Streamer discharges in liquid also generate extremely high electric fields at the tip of streamers, as well as high energy electrons, ozone, other chemically active species, ultraviolet rays and shock waves. All of these may be utilized to sterilize microorganism and to decompose molecules and materials. Large-volume streamer discharges in water have been produced in order to realize industrial applications. A wire to plane electrode configuration has been used. The discharge in water shows similar optical radiation to that in an atmospheric gas as provided by evidence from still photographs. The influence of polarity, conductivity, electrode geometry and hydrostatic pressure on the streamers in liquid, the mechanism of streamer discharges and possible industrial applications of streamers in liquids, are discussed in the present work.

1 INTRODUCTION
Industrial applications of pulsed power technology have been developing rapidly in many fields, such as the treatment of exhaust gases such as nitrogen oxides, sulfur oxides and dioxin; the sterilization of microorganism; the removal of biological wastes; the fragmentation of rocks; the recycling of concrete and electric appliances; and the surface treatment of material [1-8]. The application of electric fields with a short pulse width allows direct interaction with biological cells without heating the tissues [1, 9, 10].

Pulsed power may be used to produce nonthermal plasmas in atmospheric pressure gases that generate a high electric field at the tips of streamer discharges and produce high energy electrons, free radicals, ultraviolet rays and ozone [2, 3, 11-13]. These manifestations of streamer discharges have been used in the treatment of exhaust gases, removal of volatile and toxic compounds such as dioxin, and the sterilization of microorganisms.

The breakdown phenomena in liquids have been studied for a long time, in particular its relation to electrical insulation [14-17]. Large volume streamer discharges can be produced not only in atmospheric pressure gases but also in liquids using the most recent development in pulsed power technology [14, 18, 20]. These streamer discharges in liquids are able to produce a high electric field, high energy electrons, ozone, chemically active species, ultraviolet rays and shock waves, which readily sterilize microorganisms and decompose molecules and materials.

Pulsed electric field treatment has been used for cleaning of water containing organic chemical impurities and in water-air mixtures (aerosol) [20]. The streamer discharge in water has a thermal nature, and the streamers are gas discharges in thin vapor bubbles, which occur in water [14, 21]. Although streamer discharges in liquids and in aerosols generally have similar features, the streamers in liquids are denser than those in aerosols. The large volume streamer discharges have large commercial applications, such as the treatment of sludge water, the dissociation of toxic chemicals like dioxin, the cleaning of contaminated water, the sterilization of milk and juices and others.

First of all the method to produce large volume streamer discharges is described in this review. It is very important to make streamers over a large volume of the liquid for commercialization of these systems. Then, after describing the influence of polarity, conductivity, electrode geometry and pressure on the streamers, the mechanism of streamer discharges and their applications are summarized.

2 CHARACTERISTICS OF STREAMER DISCHARGES

2.1 PRODUCTION OF LARGE VOLUME STREAMER DISCHARGES

A small-volume streamer discharge has been produced by using a point to plane electrode [22-25]. As stated already, the production of large volume streamer discharges is important in order to realize their industrial applications.
Figure 1. Cross section of the reactor to produce a large volume streamer discharge.

Figure 1 shows a cross section of a reactor to produce a large volume streamer discharge [14,18]. It consists of a HV cable input, a water inlet and outlet, a plastic vessel with an acrylic window for optical measurements and an electrode system. The inner electrode has a disk shape, radius 1 cm, and thickness 1 mm, is made of stainless steel, and is attached to the HV cable. The outer, grounded, electrode is made of stainless steel and has a variable inner diameter (40 to 88 mm).

Positive HV pulses are obtained from a Marx generator with a variable number of stages. The stage capacitance and the charging voltage are 0.22 µF and 40 kV, respectively. The number of stages can be varied from 3 to 12, providing a peak output voltage in the range of 120 to 480 kV with nearly constant current in a short circuit load.

Figure 2. Time-integrated photograph of the discharge at Marx output voltage of 200 kV in distilled water.

In order to achieve a large volume streamer discharge, it must be equally distributed azimuthally in space between electrodes, and have a length close to the electrode gap separation. Figure 2 shows the time-integrated photograph of the discharge at a Marx output voltage of 200 kV in distilled water with a resistivity of 10⁴ Ω m. A uniform streamer discharge with a volume of ~ 200 to 300 cm³ is obtained between the electrodes. ~ 20 arc channels are observed with streamers. Framing photographs taken with Imac0n-790™ (Hadland Photonics Ltd.) are shown in Figure 3. The frame gate and the interframe times are 20 and 100 ns, respectively. The streamer discharges expand uniformly. The streamers shown in Figure 2 are ultrahigh-speed luminous positive tertiary streamer (PTS) or third mode [26], which usually have a filamentary structure and can be obtained in highly overstressed gaps and fast rise time voltage pulses [15]. Figure 4 shows the voltage and current waveforms in distilled water (a) and tap water (b) with 39 mm electrode separation.

The uniformity of the streamer discharge is dependent on water conductivity, electrode separation and applied voltage. Examples of uniform and nonuniform discharges are summarized in Table 1. The streamer pattern radius showing the final radius of the streamer cloud was measured on the open shutter photographs. This radius corresponds to the maximum streamer length before an arc discharge occurs. After arcing, the streamers do not propagate anymore. The good uniformity means that the streamer discharges have a radius >90% of the electrode separation. The poor uniformity corresponds to a streamer pattern radius <70% of the interelectrode distance. The uniformity of
The streamer discharge improves with decreasing applied voltage, increasing electrode separation, and increasing water conductivity.

![Wire electrode Plane electrode](image)

**Figure 5.** Time-integrated photograph of discharges in tap water under a thin wire to plane electrode configuration.

The volume of the streamer discharges was greatly increased by using a thin wire electrode placed in parallel with a plane electrode. Figure 5 shows a time-integrated photograph of discharges in tap water, which were produced by 9 stages of the Marx bank. The diameter of the thin wire was 1 mm, and the electrode separation and the length of plane electrode were 45 and 150 mm, respectively. The thin wire electrode was positive. The number of streamers per unit length increased with the intensity of the electric field on the surface of the thin wire electrode. Crossed electrodes, i.e., a thin wire electrode in parallel with four plane electrodes and a thin wire electrode surrounded by a spiral or a mesh electrode, are necessary in order to get large volume streamer discharges.

### 2.2 POLARITY EFFECTS ON STREAMERS

Polarity effects on the structure and the velocity of streamers were summarized in [15, 26]. Figure 6 shows schematic structures of positive (a) and negative (b) streamers for a point to plane electrode [26]. In the case of a positive point electrode, the 1st anode mode with a velocity of \(2 \times 10^2\) m/s appears, and then a bushy streamer, defined as the 2nd anode mode, propagates with a velocity of \(4 \times 10^3\) m/s. Finally, the 3rd anode mode becomes dominant. In saturated n-hexane and cyclohexane, the shapes of the streamer are only bush-type for a negative point, but both bush-type and tree-type are observed for the positive electrode. In unsaturated 1-hexane, there is only bush-type for a negative point and tree-type for the positive electrode. In benzene, there are both bush-type and tree-type streamers for the negative point, but only a radial-type for the positive electrode [30].

Although a typical example is shown in Figure 6, these structures may change with the applied voltage waveform. Also, the electrode configuration [15], the hydrostatic pressure [27-29], the characteristics of the liquid [30-32] and additives [33, 34] have large effects on the structure of streamers. If we apply a negative pulsed voltage with a fast risetime to a point-plane electrode, the second cathode mode disappears. The same suppression has been observed in hexane and toluene when the pressure is increased \(> 10\) MPa [26]. In the case of a positive pulsed voltage, the 3rd anode mode becomes dominant [18]. In saturated n-hexane and cyclohexane, the shapes of the streamer are only bush-type and tree-type for the positive electrode. In benzene, there are both bush-type and tree-type streamers for the negative point, but only a radial-type for the positive electrode [30].

The polarity effect in insulating oil was summarized by Beroual et al. [15]. The positive streamer can be classified in three consecutive stages: the 1st anode mode (positive primary streamer), the 2nd anode mode (positive secondary streamer), and the 3rd anode mode (tertiary streamer). The primary positive streamer with a velocity of \(2 \times 10^2\) m/s has an umbrella-like structure and reaches near the opposite electrode. At a higher applied voltage, the 2nd anode mode with a velocity of \(3.2 \times 10^3\) m/s appears in the form of bright stems with a tip ionization zone in the shape of brush-type structures [3]. Further higher applied voltage causes a short 1st anode mode growth, an earlier 2nd anode mode inception, and an ultra-high-speed 3rd anode mode with a velocity >10^5 m/s. The 3rd anode mode is less branched and often filamentary. The structure of negative streamers in insulating oil appears to change depending on the applied electric field. The structures of the 1st cathode mode (negative primary streamer) changes from the shape of a leafless treetop to a compact bushy structure with many branches as the applied voltage increases. At very high fields, the streamer shape changes again. Only one branch bridges the gap with a velocity that can exceed 10^5 m/s. For larger gaps (>40 mm), a secondary stage could be detected.

The disk to circular electrode shown in Figure 1 produced multiple positive streamers. Figure 7 shows the dependence of the streamer length of the 3rd anode mode (tertiary streamers) on time for various applied voltages in distilled water. The streamer expansion velocity...
Figure 7. Dependence of the streamer length of the 3rd anode mode (tertiary streamers) on time for various applied voltages in distilled water.

Figure 8. Dependence of the breakdown time lag on the breakdown voltage in distilled water, 0.001 and 0.01 M sodium chloride solutions.

is independent of the voltage pulse amplitude for a fast rising pulsed voltage and is \( \approx 3 \times 10^4 \) m/s. The number of major visible positive streamers increases with increasing applied voltage [14,18]. The number of negative streamers is much less than that of the positive streamers.

### 2.3 INFLUENCE OF LIQUID CONDUCTIVITY

Electronic conduction processes in dielectric liquids have been studied for many years [35-41]. The voltage and current waveforms for both distilled and tap water are shown in Figure 4. Although the prebreakdown current in distilled water, just before the rapid voltage drop corresponding to breakdown, is significantly less than that in tap water, the time lag to breakdown is almost similar in both experiments. The framing photographs of the streamer discharge in distilled water taken with the image converter camera are shown in Figure 3. The voltage applied to the inner positive electrode is 200 kV. A number of major filamentary self-luminous streamers propagate between the electrodes with almost constant velocity of \( 3 \times 10^4 \) m/s, which is calculated from the increase of streamer pattern radius with time. The streamer velocity is similar for both distilled and tap water despite the 2.5 order of magnitude difference in their conductivities.

The dielectric breakdown in water has been investigated by changing the conductivity and using high amplitude electric fields of sub microsecond duration [21]. Figure 8 shows the dependence of the breakdown time lag on the breakdown voltage in distilled water, and 0.001 and 0.01 M (molar) sodium chloride solutions. The influence of conductivity on discharges is small, and therefore bulk heating via ionic current contributes little to the initiation of the breakdown process.

### 2.4 EFFECTS OF ELECTRODE GEOMETRY

The characteristics of streamers depend on the electric field. The electric field \( E \) on the surface of the wire in a wire to plane electrode is expressed by the following equation [42]

\[
E = \frac{2\sqrt{h^2 - R^2} V}{(2hR - 2R^2) \ln \left( \frac{h + \sqrt{h^2 - R^2}}{R} \right)}
\]

where \( h \), \( R \), and \( V \) are the distance between the center of the wire electrode and the plane electrode, the radius of wire, and applied voltage to the wire, respectively. For example, in the case of the 5 cm gap separation and 50 \( \mu \)m wire electrode, the electric field on the surface of the wire is enhanced by \( \sim 240 \times \) the average field.

This enhancement factor is determined by the electrode geometry, and is one of the important factors to initiate the streamer and to shape the streamer structure. The electrode geometry is also one of the important factors to determine whether streamer remains single or spreads into multiple forms.

### 2.5 INFLUENCE OF HYDROSTATIC PRESSURE

The hydrostatic pressure has a large effect on the structure and the velocity of streamers. The streamer volume and the number of streamer branches decrease with increasing hydrostatic pressure. These phenomena are shown clearly in Figure 9 [15]. These photographs are taken for negative streamers in cyclohexane, and changing pressure. The number and amplitude of current and light pulses and the average streamer velocity are reduced. Consequently, there is a decrease in the number and amplitude of microdischarges which contribute to the propagation of streamers [15]. A further increase in the pressure causes the disappearance of the streamer, and the corresponding current and light pulses [16]. Therefore the breakdown strength of liquids increases with increasing hydrostatic pressure. These phenomena have been investigated on a microsecond time scale [43-45]. The influence of pressure decreases as the pulse duration is reduced to the sub-microsecond time scale [27].

A short pulse with 3 ns risetime and 100 ns duration was used to investigate the breakdown in water. Gap separations from 0.4 to 2.1 mm were used, and the pressure was changed from atmospheric to 40 MPa. The time lag to breakdown has been found to increase with increasing pressure. Figure 10 shows the propagation velocity of the ionizing front in distilled water as a function of pressure [21]. The gap separation is
The time lag to water breakdown, using 100 ns pulse voltage, has been found to increase with increasing pressure. These experiments indicate that the bubble mechanism is a contributing factor to the sub-microsecond discharge formation in water [21]. The time to form these bubbles was 3 to 13 ns, depending on field and pressure. The field emission currents from asperities [57], which can provide the necessary heating and free electrons, were considered as the most probable agent contributing to bubble nucleation.

The streamer is increasing in length with time. Taking the measured velocity of a streamer \( v \), the rate of increase of the water mass \( dm/dt \) (in kg/s) involved in the streamer propagation process is:

\[
\frac{dm}{dt} = \pi r^2 \rho_w
\]

where \( r \) and \( \rho \) are the radius of the streamer tip and the density of water. The radius of the streamer tip is assumed to be constant during the streamer propagation process, according to the literature data [58].

In the case of multiple streamers shown in Figure 2, the calculated power of a single streamer is multiplied by the total number of visible streamers of \( \sim 50 \) and the total power \( P_t \) for 50 streamers becomes \( 10.85 \text{ MW} \). This power is in good agreement with the power calculated from the discharge current and voltage.

The influence of small concentrations of electronic scavenger additives on the shape and velocity of negative streamers [31, 59] and the spectroscopic analysis of the light emitted by streamers [32] indicate that electronic processes are present also. With regards to the positive streamers, the electronic scavenger additives have negligible effect on the shape and velocity. It is thought that both gaseous and electronic processes occur simultaneously in the prebreakdown phase, even if one of them is dominant in one case and the second in another [16].

4 APPLICATION OF STREAMER DISCHARGES

4.1 PRODUCTION OF CHEMICAL REACTANTS

Several methods, such as oxidation using ozone and high-energy electron irradiation, have been tried for the treatment of pollutants in liquids. Recently, another method using streamer discharges in liquid was considered [60-62]. The streamer discharges in liquid produced by pulsed HV generate reactants such as OH, H, HO\(_2\), H\(_2\)O\(_2\), O\(_2\), O, O\(_3\) and O\(_3\). These reactants treat organic compounds by oxidation. Especially, the OH and O radicals and O\(_3\) are known to play an important role in oxidative purification of water and in degrading organic compounds [24, 63].

Figure 11 shows a typical example of the emission spectra of radicals from a pulsed streamer discharge in distilled water [64, 65]. Several peaks were observed. The peaks were identified as follows: at 282 nm (\( A^2\Sigma^+ \rightarrow X^2\Pi \)) and at 309 nm (\( A^2\Sigma^+ \rightarrow X^2\Pi \)) are from OH radicals. Peaks in the visible region are \( H_\alpha \) (656.5 nm), \( H_\beta \) (486.1 nm) and \( H_\gamma \) (434.0 nm), respectively [64, 65]. Peaks at 777.1 nm (\( 3p^3P \rightarrow 3s^2 \)) and 844.6 nm (\( 3p^3P \rightarrow 3s^2 \)) are from the emission lines of atomic oxygen.
Figure 11. Typical emission spectra of radicals from a pulsed streamer discharge in distilled water.

### 4.2 REACTION MECHANISMS

The O radical reacts directly with pollutants in water by oxidation. In addition, the O radical reacts with liquid to produce the OH radical by the following reaction

\[ O + H_2O \rightarrow 2OH \]  

(4)

Also, the OH radicals are produced by the reaction with hydrogen peroxide as follows

\[ O + H_2O_2 \rightarrow OH + HO_2 \]  

(5)

The OH radicals oxidize organic compounds directly. The primary oxidation products are oxidized to form secondary products, and finally it is expected that carbon dioxide is formed.

Ozone can react with organic compounds directly, and also decomposes into other radicals, which react with the organic compounds. Water decomposition by ozone produces many transient oxidizing species such as OH, HO₂, O₃, O₂, O₃⁻, O₂⁻ [64]. These oxidizing species destroy organic compounds effectively.

### 4.3 REMOVALS OF PHENOL AND TRICHLOROETHYLENE

The initial reaction rate constants for the formation of hydroxyl radicals, hydrogen peroxide and aqueous electrons produced by pulsed streamer discharges were described by Joshi et al. [66]. The degradation of phenol in aqueous solution was studied by Sharma et al. [60] using a pulsed streamer discharge. It was observed that a variety of waste water contaminants could be destroyed using this reactor. The transient and final byproducts of phenol treated by a pulsed streamer discharge were studied by Sato et al. [25].

The experimental apparatus for the treatment of phenol with a pulsed streamer discharge is shown in Figure 12(a) [25]. A point-to-plane geometry electrode system was used with a separation distance of 21 mm. The electrodes are a sharp platinum point and a 20 mm diameter stainless steel disk. A rotating double spark-gap switch was used to generate a HV pulse. Typical oscillograms of the pulse voltage and current are shown in Figure 12(b). The liquid was circulated with a peristaltic pump and was cooled through a coiled-pipe heat exchanger to ambient temperature. The liquid circulation rate was adjusted from 20 to 200 ml/min. The concentration of the phenol and byproducts in the solution were measured by using gas chromatography and high-performance liquid chromatography. The liquid chromatography ultraviolet detector was set at a wavelength of 754 nm. Carbon dioxide was measured by absorption in barium hydroxide followed by back titration with standardized HCl.

![Figure 12](image-url)  

Phenol removal with increasing residence time.

Phenol with an initial concentration of 50 ppm was removed by pulsed streamer discharges. The phenol removal increased with increasing residence time, as shown in Figure 13 [25]. The intermediate main byproducts were hydroquinone, pyrocatechol and 1,4-benzoquinone. The phenol and intermediate products were removed completely after increasing the residence time. The hydrogen peroxide and carbon dioxide are considered the candidates for final byproducts.

Trichloroethylene is a toxic substance. It was difficult to remove it by common water treatment techniques. The pulsed streamer discharge is an effective candidate to remove it. Trichloroethylene with an initial concentration of 100 ppm was reduced by 90% using pulsed streamer discharges [64].
4.4 OTHER POSSIBLE APPLICATIONS

Large volume streamer discharges can be produced in liquids, and generate extremely high electric fields [67], high energy electrons, ozone, chemically active species, ultraviolet rays and shock waves [68], which sterilize microorganisms and decompose molecules and materials. Possible applications of large volume discharges are as follows: (a) sewage treatment, (b) water treatment, (c) ozone water production, (d) treatment of dioxin, (e) treatment of volatile organic compounds, (f) sterilization of food, (g) deodorization and (h) free radical sources.

5 CONCLUSIONS

A large volume streamer discharge in water was produced by using a wire to plane electrode configuration. A Marx bank was used to supply the pulsed HV of 120 to 480 kV between two electrodes. The streamer discharges in water generate extremely high electric fields at the tips of the streamers, high-energy electrons, ozone, chemically active species, ultraviolet rays and shock waves. An increase in the streamer discharge volume is important in order to realize industrial applications, such as the sterilization of microorganisms and the decomposition of molecules. The influence of polarity, conductivity, electrode geometry and pressure on liquid streamers, the mechanism of streamer discharges, and the applications of streamers have been discussed and summarized.

REFERENCES


