Electrohydraulic Discharge and Nonthermal Plasma for Water Treatment

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The application of strong electric fields in water and organic liquids has been studied for several years, because of its importance in electrical transmission processes and its practical applications in biology, chemistry, and electrochemistry. More recently, liquid-phase electrical discharge reactors have been investigated, and are being developed, for many environmental applications, including drinking water and wastewater treatment, as well as, potentially, for environmentally benign chemical processes. This paper reviews the current status of research on the application of high-voltage electrical discharges for promoting chemical reactions in the aqueous phase, with particular emphasis on applications to water cleaning.

1. Introduction

The application of strong electric fields in water and organic liquids has been studied for many years, because of its importance in electrical transmission processes and its practical applications in biology, chemistry, and electrochemistry. More recently, liquid-phase electrical discharge reactors have been investigated, and are being developed, for several environmental applications, including drinking water and wastewater treatment, as well as potentially for environmentally benign chemical processes. Generally, strong electric fields applied to water (electrohydraulic discharge) initiate both chemical and physical processes. Two of the basic types of electrohydraulic discharge differ primarily by the amount of energy deposited in the system. The corona or corona-like system uses discharges of ∼1 J/pulse, whereas the pulsed arc discharge uses energy of ∼1 kJ/pulse and larger. The characteristics of these two different electrohydraulic discharge systems are summarized in Table 1. Note that processes have been developed that fall within the range determined by these two limits, and future work is necessary to fully identify the quantitative changes in the formation of reactive species and the degradation of contaminants with discharge operation between these two limits.

Table 1. Characteristics of Different Electrohydraulic Discharges[a]

	Value	
parameter	pulsed corona	pulsed arc
operating frequency	10^2−10^3 Hz	10^{-2}−10^{-3} Hz
current (peak)	10−10^2 A	10^3−10^4 A
voltage (peak)	10^4−10^6 V	10^3−10^4 V
voltage rise	10^{-7}−10^{-9} s	10^{-5}−10^{-6} s
pressure wave generation	weak to moderate	strong
UV generation	weak to moderate	strong

[a] Data taken from Chang et al.[1]

The pulsed corona system[2,3] operates at 10^2−10^3 Hz and the peak current is <100 A, with voltage rise times on the order of 1 ns. A streamer-like corona is generated in water, relatively weak shock waves are formed, a moderate amount of bubbles is observed, weak-to-moderate ultraviolet (UV) radiation (at high solution conductivity) is formed, and this system forms radicals and reactive species in the narrow region near the corona discharge electrodes. The pulsed arc system[4] operates at 10^{-2}−10^{-3} Hz, and the peak current is >1 kA with a microsecond order voltage rise. An arc channel generates strong shock waves within the cavitation zone, and the gas inside the bubbles is ionized (plasma bubbles).[5] Transient supercritical water conditions are also formed. The strong UV emission and high radical density are observed to be only short-lived in the cavitation zone. The corona discharge is more sensitive to the solution conductivity than the pulsed arc.

To apply high-voltage electrical discharges to alleviate environmental problems, it is necessary to consider the types of chemical reactions initiated by the discharge and the effects of the physical processes (e.g., shock waves, cavitation, light emissions) on the promotion of desirable chemical reactions. A large variety of reactor and electrode configurations have been studied for both fundamental understanding and practical

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applications. AC, DC, and pulsed electric fields have been applied in conditions where the electrodes have been fully immersed in the liquid phase, where one electrode has been placed in an adjacent gas phase, and/or where arcing across the electrodes may occur. Capacitor discharges in liquids with energies up to 25 kJ/pulse have also been studied in the pulsed arc systems.

High-voltage electrical discharges directly in water (electrohydraulic discharge) or in the gas phase above the water (nonthermal plasma) have been demonstrated to produce hydrogen peroxide,[6-11] molecular oxygen and hydrogen,[12,13] and hydroxyl, hydroperoxyl, hydrogen, oxygen, and other radicals[9,10,14-18] and, with the addition of air or oxygen at the high voltage electrode, ozone.[14,19-24] In addition, depending upon the solution conductivity and the magnitude of the discharge energy, shock waves and UV light may also be formed.[2,25,26] These reactive species and physical conditions, in turn, have been shown to rapidly and efficiently degrade many organic compounds, including phenols,[9,27-35] trichloroethylene,[36] polychlorinated biphenyl,[37] perchloroethylene and pentachlorophenol,[36,38,39] acetophenone,[40] organic dyes (such as methylene blue),[41] aniline,[42] anthraquinone,[14,43] monochlorophenols,[31] methyl *tert*-butyl ether (MTBE),[44] benzene, toluene, ethyl benzene (BTEX),[45] and 2,4,6-trinitrotoluene, 4-chlorophenol, and 3,4-dichloroaniline.[26,46-48] In addition, the oxidation of several inorganic ions in water has been studied with various electrical discharge processes.[49-52]

Electrical discharge and the related application of pulsed electric fields (below discharge conditions) in water have also led to the destruction and inactivation of viruses, yeast, and bacteria[7,53-68] and to the dislodgment of mussels and removal and prevention of biofilms on cooling and drinking water pipes.[69-72]

Potential exists for applications of high-voltage electrical discharge processes to the field of green chemistry through the use, in the chemical synthesis, of a range of organic compounds,[73-78] hydrocarbons,[79] polymers,[80-83] and nanomaterials.[84-91] Other applications of high-energy capacitor discharges, pulsed arcs, in water include simulation of underwater explosions,[92] metal forming,[93] rock fragmentation,[93] shock wave lithotripsy,[93-96] and such biomedical engineering applications as surgery and skin treatment.[97-99]

Physical processes resulting from high electric fields include bubble formation,[7,100-107] the reduction of the size of bubbles formed when gas flows through hollow needle high-voltage electrodes,[20,105,107,108] the possible development of supercritical fluid conditions, the production of localized regions of high temperature and pressure, and the formation of shock and acoustic waves.[2,25,94,109-111] Emissions of UV light have also been reported.[1,28,112-114]

Both physical and chemical factors may be important in promoting desirable chemical reactions. Waste components can either be directly degraded by the discharge (e.g., pyrolysis reactions, photolysis reactions, direct electron impact collisions) or they can be degraded indirectly through reactions with one or more of the primary and secondary molecular, ionic, or radical species produced by the discharge. The relative importance of these direct and in-direct mechanisms will be strongly dependent on the intensity of the energy input to the system as well as on the composition of the reacting environment.

Direct chemical means for degrading organic compounds using ozone,[115] hydrogen peroxide,[116-119] and combinations of these species[120-123] have been utilized for many years. Ozone has been studied for over 100 years and is generally synthesized in a gas-phase plasma discharge[124-126] and bubbled into the liquid.[115,127] This process generally suffers from restrictions due to interphase mass transfer resistance. The Fenton's reaction, the catalytic decomposition of hydrogen peroxide into hydroxyl radicals by metal ions[118,128] and the corresponding photo-Fenton reaction where UV light initiates the peroxide decomposition[119,129-131] have been utilized for water treatment. Photochemical methods including photolysis, photocatalysis,[132] and UV/ozone/hydrogen peroxide (Peroxone) have been the subject of much recent interest.[133-135] Ultrasound,[136-141] microwave plasma discharges,[142,143] thermal plasma processes,[144-146] supercritical oxidation,[147-149] catalytic oxidation,[150-152] thermal oxidation (thermal incineration), and direct electrochemical[153-155] reactions have been studied. To evaluate the potential of electrical discharge processes for water pollution treatment, it is necessary to compare them to these other advanced oxidation technologies.

Removal by adsorption onto activated carbon is often used for relatively dilute waste streams.[156] This method also requires regeneration of the carbon and disposal of the organic compounds removed from the activated carbon. Some more-recent efforts have focused on combining electrical discharge processes or other advanced oxidation technologies (AOTs) with activated carbon[157,158] or biological treatment.[159-161] This latter combination capitalizes on the ability of the electrical discharge processes to break biologically recalcitrant bonds and uses the relatively less-expensive biological processes for the more readily biodegradable components of the waste. Combinations of activated carbon with ozone treatment,[162,163] hydrogen peroxide,[164] electrical discharges,[165,166] electron beams,[167] or wet air oxidation[168,169] lead to the possibilities of synergistic catalytic reactions and continuous carbon regeneration. Further work with the combination of other catalysts[170] including TiO_2,[34] alumina,[170] and zeolites[171] has been conducted.

In summary, the potential advantages of electrical discharge process (e.g., electrical discharges in water, in air above water, and simultaneously in water and gas) include the following:

(1) Direct in situ production of multiple types of highly reactive chemical species, including molecules and radicals, thereby eliminating the need for externally supplied sources of hydrogen peroxide, ozone, and other highly reactive compounds;

(2) Enhancement and facilitation of gas phase reactions through (a) quenching of gas phase reaction products by transfer into the liquid and (b) reactions of species formed in the liquid phase and subsequently transferred to the gas;

(3) Enhancement and facilitation of liquid-phase reactions through (a) absorption of reactive species from the gas and (b) transfer of volatile liquid-phase reaction products into the gas phase;

(4) Simultaneous facilitation and enhancement of gas- and liquid-phase reactions;

(5) Control of relative amounts of reactive species through the adjustment of applied electric fields and gas/liquid flow rates;

(6) Enhancement of gas/liquid mass-transfer rates through (a) electrohydrodynamic flow at the gas/liquid interface and (b) reduction of bubble size when gas is injected through the high-voltage discharge electrode;

(7) Production of UV light, shock waves, and putative supercritical conditions localized in the nonhomogeneous discharge channel of the discharge, and;

(8) Catalytic effects in the case of combined pulsed electrical discharge and various additive particles such as activated carbon, zeolites, photocatalysts, transition metals, and other heterogeneous catalysts, including those coated on the electrodes.

The design and analysis of electrical discharge reactors for promoting liquid reactions are very complex problems, because of the wide range of closely coupled physical and chemical factors involved. Furthermore, these physical and chemical processes are closely linked to such reactor features as electrode geometry, electrode materials, presence of gas and liquid phases, and solution conductivity and composition. The present state of knowledge of all of these physical and chemical factors is not sufficient for predictive and accurate reactor design and analysis, however, significant advances have been made.

The general issues and questions regarding the role of electrical discharge processes for water treatment include the following:

(1) Do electrical discharge processes in the liquid phase lead to fundamentally different reaction mechanisms and breakdown pathways than those of other AOTs? Is the basic chemistry of the degradation of organic chemical species (or inorganic chemical species transformations) by these processes the same as that in the other AOTs?

(2) Can the analysis of the electrical discharge processes be conducted as a two-step process: the formation of reactive species by fast physical (or physical/chemical) processes and subsequent relatively slower chemical degradation reactions?

(3) Do electrical discharge reactors have significant advantages over other AOTs with regard to energy of primary reactant production (or primary waste degradation), interphase mass transfer of reactants, reactor control and stability, selectivity, reactor size, and contact time−capital costs versus operating costs, and simplicity or complexity of use?

(4) Where do the electrical discharge processes fit in? Are some specific types of wastes more suited for treatment by electrical discharge processes? Are there alternative means to utilize electrical discharge processes in combination with other AOTs or conventional methods?

(5) What are the basic reactor design issues that are specific to electrical discharge processes in the liquid phase?

Answers to the aforementioned questions are current subjects for study. The present review will seek to place these questions and issues within the framework of what is known about electrical discharge processes in water treatment.

2. Types of Electrohydraulic Discharge and Nonthermal Plasma for Water Treatment

2.1. Electrode Geometry and Phase Distribution. A wide variety of different types of liquid phase and liquid/gas phase electrical discharges have been studied. Figure 1 illustrates the basic types of electrode and reactor geometry that have been considered. In the cases where both high-voltage and ground electrodes are placed directly in the liquid phase, point-to-plane geometry has most typically been studied for pulsed discharges (see Figure 1A). However, experiments with plane-to-plane electrodes separated by surfaces with small pinholes have also been conducted (see Figure 1F) with pulsed discharges. DC discharges at lower applied voltages have been used with hollow tubular high-voltage electrodes and a bar-type ground. For pulsed arc systems, point-to-point electrode systems (Figure 1H) have been used. Research on the aforementioned types of reactors has been obtained from the electrical engineering and physics literature, where an understanding of the electrical breakdown conditions in dielectric fluids was of primary interest.[172] Typically, high-voltage (on the order of kilovolts, kV) but short-width pulses have been applied to the fluid in these situations. More recently, thin disk electrodes (see Figure 1G) and a wire cylinder geometry[9,173,174] have been developed (see Figure 1I) for liquid-phase systems. DC discharges with multiple-pin electrodes and gas injection have also been utilized.[67] Another well-studied electrode configuration is where the high-voltage electrodes (single or multiple points or plane (Figure 1C, D, and E)) are placed in the gas phase above the liquid surface. Application of AC or DC fields in this system leads to the glow discharge process that has arisen from research on electrolysis.[6,10] DC discharges over the water surface,[175,176] AC discharges with flat plates over water surfaces,[177] AC barrier discharges over water,[178] AC discharges with multiple points over water surfaces,[179] and pulsed discharges from wire electrodes over water surfaces[180] have been studied. DC discharges have also been produced through two water layers separated by an air gap, whereby the water layer serves as liquid nonmetallic electrodes.[181] Pulsed corona, spark, arc, and DC discharges can also be formed when the high voltage is placed in the gas phase above the liquid surface with the ground immersed in the liquid.[29,175,179,182−184] Applications of the pulsed corona discharge above the water surface with various electrode configurations (Figure 1C, D, E), the AC gliding arc (Figure 1J, K, and L), and even the injection of water droplets into the gas-phase discharge[185] have been used to treat water-phase and, less commonly, gas-phase pollutants.

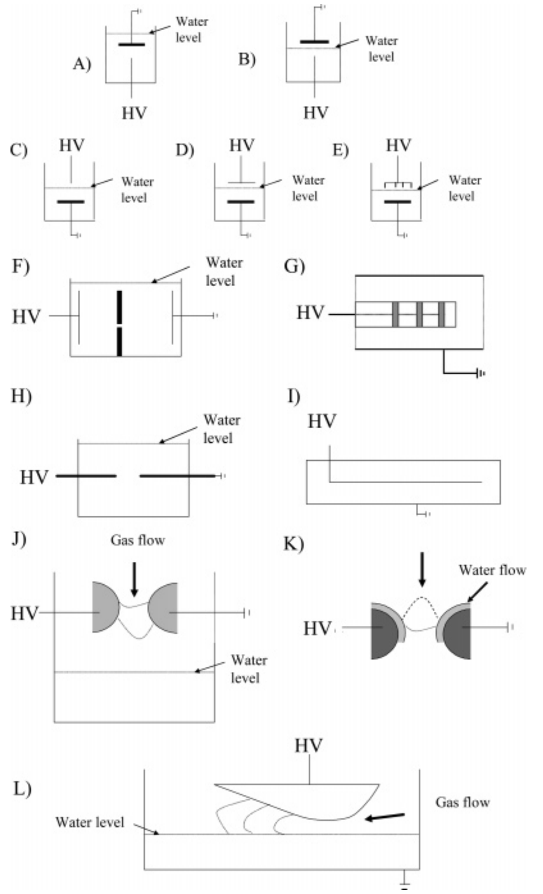


Figure 1. Schematic of reactor and electrode configurations: (A) point-to-plane liquid-phase corona reactor; (B) point-to-plane with air gap liquid-phase corona reactor; (C) single point-to-plane glow discharge reactor; (D) plane-to-plane glow discharge reactor; (E) multiple point-to-plane glow discharge reactor; (F) pinhole reactor; (G) ring electrode reactor; (H) point-to-point arc reactor; (I) wire-cylinder reactor; (J) gas-phase gliding arc over water surface; (K) gliding arc with water film; and (L) gliding arc to water surface.

Many types of gas−liquid discharge reactors have been proposed. One configuration involves the production of ozone in a separate gas-phase dielectric barrier reactor, using air or oxygen as the feed, followed by the injection of the gas into the liquid phase through hollow electrodes.[186,187] The small cloudy bubbles that are formed lead to efficient ozone mass transfer into the liquid. This electric field enhancement of gas/liquid mass transfer through reduction of bubble size[104,188] may be very applicable to water-treatment processes. In the second configuration, it is possible to bubble oxygen or air through the hollow electrode needles at high potential, whereby the ozone formed can directly transfer into the liquid.[189] DC corona with oxygen flowing through the high-voltage hollow needle electrode has been shown to be effective at degrading phenol and Methylene Blue.[190] Reaction rate constants for the formation of hydrogen peroxide, aqueous electrons, and hydroxyl radicals were determined to increase with applied voltage and that the major reactive species formed are hydroxyl radical, atomic hydrogen, and ozone.

Recent work has demonstrated the utility of placing the ground in the gas above the liquid−gas interface with the high-voltage electrode immersed in the liquid (Figure 1B) and placing one high-voltage electrode in the gas phase, one in the liquid phase, and a ground in the liquid phase between the two high-voltage electrodes.[21,191] The wetted wall or falling film reactor uses a gas-phase discharge in contact with a liquid falling over the ground.[192,193] In other approaches to enhancing the contact between the gas and liquid-phase reactors, the utilization of electrical discharges in foams[194−197] and in water with high concentrations of bubbling gases[198] have been investigated. Three-phase gas−liquid−solid packed-bed reactors have also been studied.[199]

In summary, the reactor types to be considered in this review are as follows: (i) pulsed corona (corona-like)−electrohydraulic discharge (PCED) reactors, (ii) pulsed spark−electrohydraulic discharge (PSED) reactors, (iii) glow discharge water treatment (GDWT) reactors, (iv) gas-phase pulsed corona discharge water treatment (GPPC) reactors, (v) pulsed arc electrohydraulic discharge (PAED) reactors, (vi) hybrid gas−liquid electrical discharge (HGLED) reactors, and (vii) pulsed power electrohydraulic discharge (PPED) reactors. Pulsed corona, or “corona-like”, discharges in water are formed using pulsed power supplies and produce “streamer-like” channels within the liquid phase. These reactors typically operate at a few joules per pulse and the streamer channels do not propagate across the entire electrode gap. Pulse spark discharges can be formed in systems similar to those of liquid pulsed corona discharges; however, the spark arises when the high current filamentous channel bridges the electrode gap. Glow discharge systems typically utilize DC power supplies, and, with the high voltage in the gas, a glow (nonthermal plasma) is formed above the water surface. Gas-phase pulsed corona discharge (also, nonthermal plasma) can be produced in reactors similar to those of the glow discharge. (Note that many studies have been reported on gas-phase plasma and nonthermal plasma.[200−202]) Pulsed arc discharges typically use large energy ($\gg$1 kJ per pulse) capacitor discharges directly in the water. Hybrid reactors utilize discharges in both the liquid and gas (sometimes bubble) phases. Pulsed corona electrical discharge utilizes a fast-rising voltage, but pulsed power electrohydraulic discharge also utilizes a fast-rising current.[203]

2.2. Pulsed Corona−Electrohydraulic Discharge (PCED) and Pulsed Spark Electrohydraulic Discharge (PSED) Reactors. Clements et al.[14] conducted an extensive analysis of both the chemical and physical factors that occur in pulsed (“pulsed streamer corona” or “corona-like”) electrical discharges (on the order of 1 J/pulse) in water with both electrodes immersed (see Figure 1A) with and without the combination of various gases bubbled through the high-voltage electrode. Using electrical discharges in point-to-plane geometry, emissions spectroscopy was used to show the production of significant quantities of hydrogen radicals in the liquid phase and, by chemical means, the formation of ozone when air or oxygen was bubbled through a hollow electrode needle immersed in the water. They also reported anthraquinone dye bleaching with this setup. This study demonstrated the importance of the solution conductivity on streamer length and discharge structure. Joshi et al.[8] measured the rates of formation of hydrogen peroxide (by direct chemical measurements) and hydroxyl radicals (by indirect chemical methods) in a pulsed corona discharge reactor with point-to-plane geometry similar to that used by Clements et al.[14] Recent experiments with other hydroxyl radical probes have provided more-accurate measures of hydroxyl radical formation rates and, using different chemical probes, have assessed hydroxyl radicals generated in the discharge zone.[18] Sato and co-workers[7,15,16] and Sunka et al.[9] confirmed the existence of hydroxyl radicals, as well as demonstrated the existence of other hydrogen and oxygen radicals by emissions spectroscopy, and both studies measured hydrogen peroxide by chemical methods in similar point-to-plane pulsed electrical discharge reactors.

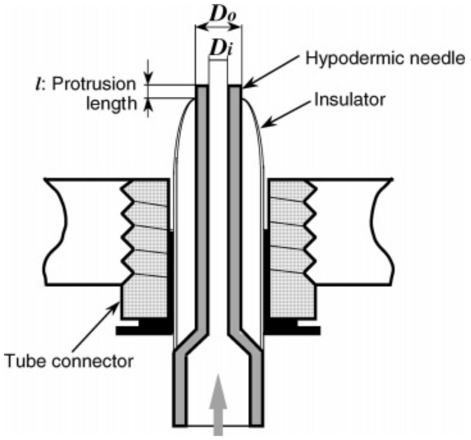


Figure 2. Schematic of point electrode with insulation for liquid-phase high-voltage discharge. Adpated from refs 204 and 409.

Several investigators have used the point-to-plane electrode system for underwater pulsed discharge experiments. To produce a pulsed discharge in water, it is necessary to have a high-intensity electric field at the tip of the electrode. Typical fields on the order of 10^7-10^9 V/m (see refs 2 and 109) are required to initiate discharges in water. A point electrode tip with appropriate insulation makes it possible to form a concentrated electric field. The discharge pattern and electric current across the electrode gap in water is dependent on the length of the needle electrode protruding from the surface of the insulating material. A small protrusion from the insulator surface (e.g., $\leq$1 mm) leads to the formation of better discharge in water, compared to larger protrusion values (e.g., 1 mm to 2 mm). This is due to the fact that the electric field concentrates near the electrode edge or interface between the metal and the insulator. Therefore, proper insulation at the electrode is the most important requirement for generating a high-intensity electric field in liquid water, because water is much more conductive than air. Figure 2 shows a schematic of the high-voltage electrode used in such studies.[16,101,204] In contrast, it is relatively easy to produce a corona discharge in the air or gas phase, because the air surrounding the needle is a very good insulator.

One of the major problems of the point-to-plane geometry used in these pulsed corona reactors is that the very large electric field at the high-voltage electrode (up to 10^9 V/m (refs 2 and 9)) necessary to produce the discharge causes extensive wear on the electrode.[205,206] As the radius of curvature increases at the tip, the field decreases and the discharge reaches a condition where it cannot be sustained any longer. To overcome this limitation, Sunka and co-workers.[9,173] have developed ceramic-coated metal electrodes that can be used in a wide variety of geometrical configurations, including wire cylinder or planar (Figure 1I) systems. In these studies, metallic electrodes were coated with a thin layer of porous ceramic. These electrodes were prepared by thermal plasma spraying and have porosity of 3%−5%. The role of the ceramic layer is to concentrate the pre-discharge current in small open pores, thus increasing the electric field on the electrode surface to a value of $E \approx U/d_c$, where U is the applied voltage and d_c is the thickness of the layer. These composite electrodes have been used in reactors with planar and coaxial electrode geometry. Many discharge channels, distributed almost homogeneously on the electrode surface, have been generated at applied voltages of 20−30 kV. Discharge with the composite electrode corresponds to a limiting case of the diaphragm discharge (see Figure 1F) in which the perforated dielectric sheet is placed adjacent to the electrode. In a coaxial reactor, the composite ceramic electrode has been operated for 15 h at an average power of 100 W with no observable deterioration. Silicated ceramic (Almandine) have been used in these experiments, but layers with other chemical composition can be prepared using the thermal spraying technology. The composite electrodes can be made in various forms and dimensions, enabling the construction of reactors that can operate at an average power in the kilowatt range. (Note that most electrode configurations, including the needle electrodes and the ceramic-coated electrodes, lead to release of the metals into solution; the metal particles can have significant effects on the chemical reactions in the bulk solution.[207] Measures should be taken to either reduce the negative effects or, in some cases, capitalize on the positive effects.)

Anpilov et al.[208] used a dielectric coating on a metal electrode plate where small open channels through the dielectric coating allow gas to flow into the region of the water discharge. This configuration is analogous to that discussed previously by Sunka[9] with the addition of the gas supply channel. The gas bubbles in the region of the discharge in ref 208 facilitate the plasma formation and may affect the formation of UV light and hydrogen peroxide.

Kurahashi et al.[209] measured the formation of hydrogen peroxide and hydroxyl radicals in water from a pulsed discharge with a DC bias, utilizing point-to-plane geometry with small oxygen bubbles formed by electrolysis. In a fundamental study of the discharge formation, they showed a single O_2 bubble forming within a glass tube containing the high-voltage electrode and water solution. After the gas forced the liquid out of the tube at 5 kV, the discharge formed and emissions spectroscopy showed radical formation.

Another electrode configuration used in liquid-phase corona discharge uses the "pin hole" geometry (also called diaphragm discharge (see Figure 1F); this is very similar to a capillary discharge[210]). In this system, the planar high-voltage and ground electrodes are separated by an insulating plate with small holes.[211−213] The pre-discharge current is concentrated in the small hole and leads to strong thermal effects, causing bubble formation and breakdown. Pulsed corona discharge occurs at the pinhole because of the very high electric field in the pinhole. Typically, metal-plate-type electrodes are placed on opposite sides of an insulating plate (with the pinholes) made from materials such as Bakelite, poly(vinyl chloride), or ceramics. The streamer length varies with the electrical conductivity of the water solution, the flow rate of the water through the pinhole, and the voltage polarity of the applied pulse. For the case of a discharge with a magnitude of 25 kV and frequency of 50 Hz, using a 6 nF pulse forming capacitor, the streamer length varied over a range of 0−10 mm at the negative side.[211,214] The streamer length was <5 mm at the positive side. In the case of the point-to-plane electrode configuration with an intervening pinhole, the pinhole acts as a point electrode. Therefore, the streamer length on the negative side of the pinhole (the same as applying positive pulse to the point electrode) is larger than that on the other side of the pinhole. When the flow rate through the pinhole is increased, the length of the streamers on both sides decreases. This decrease of streamers could be due to the flow washing out tiny bubbles or ions from the pinhole. Through measurements of the attenuation of X-rays through a diaphragm discharge, Sokolov determined the rate of expansion of the plasma region[212] to be in the range of 300−50 m/s over a time period of 5−40 μs. Yamada et al.[214] demonstrated phenol degradation in a reactor configuration for a variety of "pin hole" sizes from 0.1 mm to 1.0 mm. Because this electrode system produces, during the pre-discharge phase, strongly inhomogeneous electric fields with structures similar to those in point-to-plane geometry, the generation of plasmas with similar parameters is to be expected. The energy efficiencies for phenol degradation and dye decolorization in a reactor with a single pinhole are the same as those in the case of a point-to-plane electrode system. It may be possible to improve the reactor operation by modifying such design parameters as, for example, using multiple pinholes.[214−217] However, care should be taken in using multiple pinholes, because it is very difficult to discharge simultaneously at each pinhole, and to do so, very large applied voltages may be required.

Lisitsyn et al.[218] have developed a liquid-phase pulsed electrical discharge reactor with disk-shaped electrodes placed in a ring-to-cylinder configuration (see Figure 1G). This system may overcome some of the problems associated with point-to-plane geometry, including increasing the volume of the plasma discharge active region and reducing the problems of needle tip wear. These factors are important for industrial applications where scaleup is critical, and it is clear that the point-to-plane electrode system would be difficult to scale up. In the ring-to-cylinder electrode system, the ring electrode(s) is(are) insulated up to the very edge. The ring electrode is placed coaxially at the center of an outer cylinder grounded electrode. A streamer, a spark with a streamer, or a spark discharge can be formed from the edge of the ring electrode and can propagate to the outer ground cylinder electrode. As in the point-to-plane geometry, the protrusion length of the ring electrode from the insulator surface affects the initiation voltage of the steamer discharge. The most effective conditions for phenol degradation occurred in the case of a protrusion length of 0.5 mm from the insulator surface. The phenol degradation rate is approximately the same as that in the case of a point-to-plane system; however, the ring-to-cylinder type is considered to be suitable for scaling up the reactor through stacking multiple rings in series down the reactor, therefore leading to a larger plasma region.[219,220]

2.3. Glow Discharge Water Treatment (GDWT) and Gas-Phase Pulsed Corona Discharge Water Treatment (GPPC) Reactors. Another major electrode configuration that has been studied arises from the research on glow discharge electrolysis.

The early work on this topic is summarized by Hickling.[6,10,221,222] Davies and Hickling[6] performed an extensive study of glow discharge electrolysis, where a DC voltage of up to 1.5 kV was applied to a planar electrode suspended above the water surface (see Figure 1D). They studied the influence of gas type and pressure, electrolyte composition, and electrode materials on the formation of hydrogen peroxide in the liquid phase. Hickling and Linacre[221] showed that this electrode system leads to the oxidation of ferrous salts, and they conjectured that the ionization and dissociation of water molecules in the gas phase above the liquid surface dominate over electrolytic processes in the water. They suggested that the bombardment of the liquid surface by ions produced in the gas leads to similar chemical processes in the liquid that occur in radiation chemistry.

The synthesis and degradation of many organic compounds, including a range of amino acids, have been studied in glow discharge electrolysis and the related contact glow discharge electrolysis, whereby both electrodes are submerged in the liquid phase.[30,74−78,221,223−227] These studies have developed from the pioneering work of Miller,[73] involving the problem of the chemical origin of life under conditions simulating the early atmosphere of the Earth. Miller used both gas-phase silent discharges and high-frequency AC spark discharges in contact with water surfaces to demonstrate that more-complex bio-organic compounds, including many amino acids, could be produced by nonbiological means. More-recent aspects of amino acid synthesis have been conducted by Morvova.[228,229] This work may also be of interest for future work using electrical discharge processes for the synthesis of various chemical species, which is of great interest in the field of “green chemistry”.

Point-to-plane DC corona discharge with the high voltage above the water surface (with the gas gap containing air) leads to the formation of nitrates and nitrites[50] and to increases in the acidity[230,231] in the liquid phase. It was postulated that NO and NO_2 are formed in the gas phase from the nitrogen in the air and that reactions with water, hydroxyl radicals, and other oxidants in the liquid phase lead to nitrate and nitrite formation. The formation of these various species in the gas above the water, as well as pH changes in the water, may lead to important effects on the chemistry of the reactions in the liquid phase.

Pulsed corona discharge in the gas phase above the water surface has also been used to treat the *gas*-phase contaminants. The *wet-type* nonthermal plasma reactors (see Figure 1C, E) have been used to remove nitrogen oxides[232,233] and sulfur dioxide,[192,234] CF_4,[235] and acetaldehyde[193] from the gas phase. Reaction products from the gas (such as nitrates, sulfates, and HF) are readily absorbed into the liquid phase. It is also possible that liquid-phase reactions contribute to the removal of the gas-phase contaminants; however, further research is necessary to elucidate the mechanisms for these systems.

Other studies with electrode configurations with the high-voltage electrode (DC, AC, or pulsed) in the gas phase and the ground either in the water or on the water surface (see Figure 1C and E) include the following: those of Goheen et al.[41] with various organic dyes; Sharma et al.[41] with Methylene Blue and carbon tetrachloride; Josephson and Sharma[36] with perchloroethylene (PCE) and pentachlorophenol (PCP); Sharma et al.[38] with PCP; Hoeben et al.[29,236−238] with phenol and atrazine; Tezuka and co-workers[30,42,50,239,240] with phenols, chlorophenols, benzoic acid, and aniline; Piskarev with $KMnO_4$, KCN, and orange aniline dye;[182,183] and Sano with phenol, acetic acid, and Rhodamine B dye.[175] Robinson et al.[241,242] studied the generation of ozone by AC fields with parallel-plate geometry with the high-voltage electrode in the gas phase and the ground electrode in the water. Pulsed discharges of nanosecond duration over a water surface have also been shown to generate full-spectrum UV radiation with a maximum in the range of 200−300 nm and lead to the extensive destruction of bacteria.[114]

Piskarev and co-workers[182−184] have shown for corona, spark, and arc discharges with high-voltage electrodes over the water surface and ground electrodes in the water that ozone is formed in the gas and hydrogen peroxide is formed in the liquid. Recently, it has been shown that placing the high-voltage electrode (for pulsed corona) in the aqueous phase and the ground in the gas phase leads to the simultaneous formation of larger quantities of hydrogen peroxide in the liquid phase and ozone in the gas phase (see Figure 1B).[21,191] The reactions of ozone, hydrogen peroxide, and other radicals in such cases may lead to very effective degradation of organic compounds. As mentioned previously, high-voltage electrodes submerged in water lead to hydrogen peroxide formation; however, when hollow-needle high-voltage electrodes are immersed in water and gas is bubbled through them, ozone is formed, but hydrogen peroxide formation is suppressed.[243] The simultaneous gas/liquid discharge when an air gap is used leads to the production of both ozone and hydrogen peroxide; however, note that the presence of humid air is known to decrease the efficiency of ozone generation in gas-phase plasma.[244,245]

One approach that has been suggested to overcome the limitations of metal electrode wear is to form a discharge between two liquid layers separated by a gas gap, whereby the liquid layers serve as nonmetallic electrodes.[181] A gas-phase plasma is formed in the region between the two liquid layers that flow over ceramic chutes with metal electrodes implanted in the ceramic. It was suggested that the discharge properties can be controlled through variation of the liquid conductivity and electrolyte concentration, and that this configuration has promise for treating polluted gases.

Another type of reactor utilizes knife-edge electrodes in the gliding arc configuration (see Figure 1J, K, L). In the gliding arc, usually an AC discharge is formed between two thin electrodes with a gas flowing through the gap between the electrodes. The gas stabilizes the system by sweeping the arc from its inception in the upstream electrode region to the other side of the electrode region, where the arc dissipates. Arcs are constantly forming and reforming in the system and the gas flow prevents excessive wear and heating of the electrodes. This type of system has been extensively studied for gas-phase treatment,[246−251] and studies have been conducted for liquid-phase treatment[252−258] and sterilization.[259] In treating the liquid phase, the arc can be formed over the liquid surface (Figure 1J), the liquid surface can be used as the ground electrode (Figure 1L), a water film can flow over the electrode surface (Figure 1K), or water can be sprayed through the plasma zone.[256,257] The formation of hydroxyl radicals and other reactive species in the gliding arc configuration (Figure 1J) were determined to be similar to those in humid gas-phase pulsed corona discharge.[49]

2.4. Pulsed Arc Electrohydraulic Discharge (PAED) and Pulsed Power Electrohydraulic Discharge (PPED) Reactors.

The degradation of various organic compounds has been studied in very large capacitor arc discharge processes (in terms of kJ/pulse) for applications to toxic chemical destruction in waste treatment by Hoffmann.[25] Chang and co-workers[1,4,69] developed and evaluated a pulsed arc system with point-to-point electrodes (see Figure 1H) for the removal of zebra mussels from the intake pipes of water-treatment facilities. Basic aspects of the discharge of high-energy capacitors in water include large UV light emissions from exploding wires,[112,113,260] shock wave formation,[261] and large amounts of thermal energy and hydrogen gas emissions. Lee determined that a discharge of 10 kJ/g in an aluminum powder water slurry led to the release of large amounts of thermal energy and hydrogen gas (95% of the total).[262] In an alternative approach, Parker[263] used high-current AC systems to produce thermal processes for the pyrolysis and gasification of hazardous liquid wastes.

3. Physics of Electrohydraulic Discharge

Electrical discharges in water can be classified into partial electrical discharges, where the discharge current flows from one electrode; however, it does not reach the counter electrode, and arc or spark discharge. In the partial discharge, the current is transferred by ions (corona-like, pinhole, atmospheric glow discharge electrolysis). The electric fields for initiation of such discharges are on the order of 10^8 V/m. Such discharges are of relatively low current, creating in water high electric fields and forming some nonthermal plasma. It is evident that, in such situations, the solution conductivity has an important role in parameters of the generated plasmas. The discharge current is transferred by slow ions. Higher conductivity (a higher concentration of ions) results in a larger discharge current and, on the other hand, a shortening of the streamer length (faster compensation of the space charge electric fields on the head of the streamer). This results in a higher power density in the channel (a higher power dissipated in a smaller volume) resulting in an increase in the plasma density, a higher plasma temperature (higher UV radiation) and the generation of acoustic waves.

Spark and arc discharges are quite different from the “partial” discharges. The current between electrodes is transferred here by electrons. Because of the relatively high breakdown electric field of water, a small interelectrode gap is necessary and the discharge current heats a small volume of plasma, which results in the generation of almost thermal plasma (the temperatures of the electron and the heavy particles are almost equal, as known from measurements on a water-stabilized plasma torch). The spark and arc discharges differ only in their durations. In the initial phase of the spark, the discharge channel is not heated enough and its resistance is high (of the order of 10 Ω). However, after some hundreds of nanoseconds, the current decreases to sub-ohm values (measured in association with the spark gap shock wave generator), and after some microseconds, the electric field in the spark channel is very low and it does not differ from the arc. Temperatures of the spark and arc discharges plasmas should be $>$10 000 K and high-power UV radiation is produced. Also, the OH band was measured in the spectrum. In the case of fast sparks, strong shock waves also are generated. With the present state of the art, it is impossible to match the impedance of the power supply to the sparks, which is the reason people use exploding wires in such experiments to match the condenser bank to the discharge (to have a longer channel with a higher resistance).

3.1. Streamer Formation in Water. The investigation of *gas-phase* discharges has led to very detailed one- and two-dimensional streamer propagation models, coupled with ionization and chemical processes that occur in the streamers.[264−269] For the liquid phase, models have been developed for pulse radiolysis and a detailed understanding is available on the structure of high-energy deposition in the liquid phase from electron beams and other sources.[270−273] However, the understanding of the *liquid-phase* high-voltage electrical discharge is much less developed, because of less detailed knowledge of the ionization and collision events that are occurring in water. With respect to understanding the differences between gas discharges and liquid discharges, it is necessary to consider both density and conductivity differences. The substantially higher density of liquids leads to much higher collision frequency and lower mobility of charges, and the much higher electrical conductivity of liquids, specifically water, lead to a large concentrations of ions.[2] The ions, which are present in the liquid at a concentration of $>10^{19}$ cm^{-3} for 200 μS/cm, strongly alter propagation of the streamer by compensating the space charge electric field on the streamer head.

Experiments on liquid-phase pulsed electrical discharges have provided some information on the rates of streamer propagation[274−280] and other characteristics of the nonhomogeneous nature of the water breakdown. Streamer lengths are generally on the order of centimeters, and channel widths are on the order of 10−20 μm.[274,281] The velocity of propagation, which is on the order of 10^7 cm/s, has been measured by high-speed laser Schlieren photography of electrical discharges in hexane,[275−278] other hydrocarbons,[282] and water.[279,280] Streamer velocities in liquid nitrogen measured with a high-speed shadow graph optical system were 10^5 cm/s and 10^4 cm/s for positive and negative polarity, respectively.[283] Estimates based on interelectrode gap distance and lag time before breakdown in water give similar values of 10^6 cm/s.[281] Interferometric methods have been used to study shock wave formation.[274] Analysis of the nanosecond time-scale transient development of electrical resistance in sparks forming in organic liquids promises to provide an increased understanding of the propagation of dielectric discharge in liquids.[284,285]

Leipold et al.[286] measured the pre-breakdown discharge in a point-to-plane discharge with micrometer-scale spatial resolution and a 10-ns time resolution. For the case where the plate was the cathode, local heating near the anode needle was shown to lead to gas formation and the production of 10-μm-diameter microbubbles. They suggested that the discharge then propagates through the gas bubbles.

Generation of H, O, and OH radicals in the pulsed corona discharge in water have been proven by emission optical spectroscopy in the visible and UV range.[7,9,14,16] Electron density of $>10^{18}$ cm^{-3} in the discharge ($\sigma = 0.2$ mS/cm) has been determined from the Hα spectral line profile, and O lines can be used for estimation of mean electron energy (electron “temperature”). Comparing the measured fine structure of the OH spectral band with the computed structure, a rotational temperature of $>$2000 K of the OH radicals has been estimated.[287] All discharge parameters vary with the water conductivity. An increase in water conductivity results in higher discharge current, the generation of shorter channels with a higher electron density (faster compensation of the space charge electric field on the streamer head), and a higher power radiated in the UV range. At water conductivities of $>$1 mS/cm, strong acoustic (pressure) waves are generated, indicating heating of solution. However, it is not currently possible to describe processes occurring in the streamer corona discharge generated in the liquid phase quantitatively.

Some aspects of liquid-phase corona discharge can be established through detailed consideration of sample experiments with point-to-plane geometry.[14] For example, in a pulsed corona system with an electrode gap distance of 45 mm, the streamer-type discharge occurs. The streamers form at the needle tips and propagate toward the ground electrode; however, in the pulsed corona system, the streamers do not reach the ground electrode. When a positive polarity pulse voltage is applied to

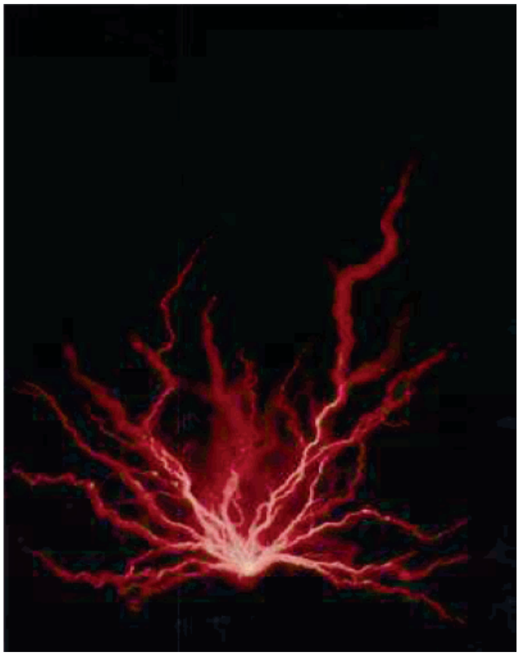


Figure 3. Photograph of streamers in liquid-phase pulsed corona discharge; time exposure is used to show the multiple discharge channels. (Reprinted from ref 410, with permission from the Japan Society of Applied Physics.)

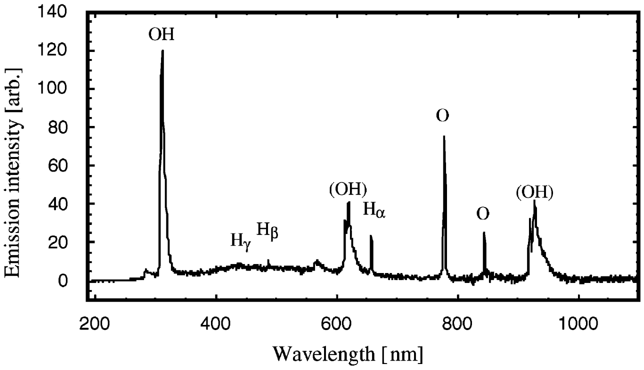


Figure 4. Emission spectra from pulsed streamer discharge. (Reprinted from ref 16, with permission from Elsevier.)

the point electrode in deionized water, many short streamers are formed whereby in each streamer a small white region is surrounded by a thin magenta-colored layer. A large number of small bubbles are also formed near the electrode. The magenta streamer becomes very long and filamentary, and the color changes from magenta to blue-red with increasing pulse voltage (Figure 3). From the emission spectrum of the pulsed streamer corona discharge in distilled water, OH, H, and O radicals are detected, as shown in Figure 4. Other materials, including iron from the stainless steel hypodermic needle and platinum from the platinum electrodes, are detected in the emissions spectra. The voltage polarity has a large effect on the OH radical emission intensity. The OH radical is generated at a higher rate in the case of applying positive polarity to the point electrode than that for the case of applying negative polarity. When a negative polarity pulse is applied to the point electrode, a magenta streamer is also obtained. The magenta streamer has many short branches and has a shorter length than that of the positive. Small bubble formation is also observed for the negative polarity case.

When oxygen gas is bubbled into the plasma region through the needle electrode, OH radical densities for both pulse polarities increase as the oxygen flow rate increases, until leveling off at a flow rate of ~50 mL/min.[14] The O radical density increases as the oxygen flow rate increases more rapidly than the OH radical at a low flow rate. The dependence of the O radical density on the oxygen flow rate is basically the same as that of the OH radical, except for the case of low flow rate when positive polarity pulse is applied. In the case of bubbling inert gases such as argon, the radical density increases more rapidly than with oxygen at the same flow rate. In argon, the H atom emission intensity is the strongest, but in oxygen, the H emission is much lower. In the case of helium, a similar phenomenon is observed. The emission intensity changes with changing liquid conductivity. The OH radical intensity is weak when the conductivity is low (ca. 1 μS/cm). As the conductivity is increased, the streamer channel length, as well as the OH intensity, increases. The intensity reaches a maximum at a conductivity of 10−80 μS/cm. When the conductivity is increased further, the OH intensity again weakens.

The two general classes of theories for liquid-phase high-voltage electrical discharges are (i) the electrical theories and (ii) the theory of thermal bubble formation.[172,279,280,288−295] (Other theories have been proposed; see Gallagher[172] for a review of these models in the literature up to 1975, Sharbaugh et al.[296] for reviews to 1978, Jones and Kunhardt[288,297] for review of research up to 1995, and Bernoual for review concentrating on organic liquids up to 1998.[298]) These theories are directed mainly toward describing the breakdown mechanisms in the liquid. In the thermal theory, it is hypothesized that the heat generated by the electric field produces bubbles, and that electric fields propagate through the bubbles in a manner similar to that in the gas phase. Kuskova[109,291,299] proposed a model based on field-assisted thermal dissociation as the first stage in breakdown, and solved the equations of electrodynamics (material balances on electrons, protons, hydroxyl ions, and positive ions coupled to Poisson's equation and a thermal energy balance with a Joule source) to simulate the electric field propagation through the liquid. Jones and Kunhardt[288−290,297] considered the effects of pressure and solution conductivity on breakdown in water and found that higher pressure, but not increasing conductivity, increased the time lag for the start of breakdown. They developed a model where breakdown begins in the low-density regions of the liquid, i.e., bubbles formed by heating of the fluid by field-emission currents. Utilizing the solution of the acoustic wave equation near a high-voltage electrode, Korobeinikov and Yanshin[109] concluded that electrical discharges are not initiated by bubbles formed by cavitation caused by electrostriction, because the bubbles have a lifetime that is too small (10^{-8} s) for free electrons to form.

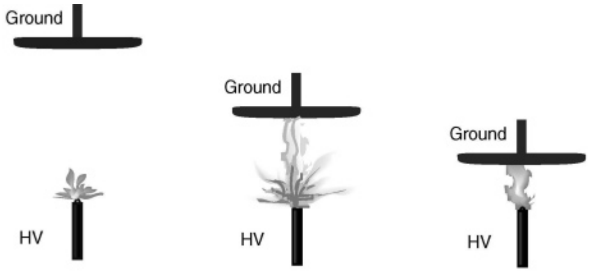
A thermodynamic model was developed to account for 13 components in a NaCl water solution at high temperature and high pressure for a 160-J pulse plasma discharge.[300] This model predicts temperatures in the range of 5000−9000 K, pressures initially at 5000−10 000 atm dropping to 200−300 atm, and ion densities in the range of 10^{17}−10^{20} cm^{-3}.[300]

In recent studies, Lisitsyn et al.[281] have argued that streamers propagate because of water vaporization at the streamer tip. The power measured from the current and voltage waveforms compared closely to the power required to vaporize the liquid contained within the volume of the streamer channels. The measured resistance of the streamer discharge was determined to be much lower than that of the free water. This result, coupled with the fact that the streamer velocities in deionized and tap water were equivalent, was taken as evidence for the major role of ionization in the liquid on the pre-breakdown current. Proton mobility in the vapor phase (but not the liquid phase) is sufficient to account for the velocity of streamer propagation. Further study of discharge in organic liquids by light emissions measurements and gas chromatography of reaction products suggest that, in fast filamentary streamers, ionization dominates, and in slow brush-like streamers, vaporization is dominant.[301]

In summary, no published model explains all the experimental results that occur in high-voltage pulsed electric discharges in water (see also section 3.3 for models of arc formation in water and applicability to the lower-energy discharges considered here). The model of Jones and Kunhardt[289] assumes that the breakdown starts at the cathode, which contradicts the general observation used in the design of water pulse forming lines, that the breakdown electric field is two times higher for negative polarity than for positive polarity. The pure thermal bubble mechanism (i.e., heating water for evaporation) applies only in very high conductivity solutions of several mS/cm and perhaps in the high-energy arc discharge. The concentration of ions in high conductivity solutions is only 2 orders of magnitude lower than that of the water molecules, and the effect of friction of ions and water molecules should be taken into account. Generally, there is a large difference between discharges in deionized or distilled water and high conductivity water. In distilled water, the relaxation time (ϵ/σ) is on the order of 10 μs and in water with a conductivity of 0.2−2 mS/cm, it is much shorter. Future work is needed to develop a comprehensive theory of high-voltage electrical discharges in water. (It can be noted in passing that dimensional analysis has been applied to the analysis of water corona discharge to circumvent the lack of detailed physical models.[302])

The structures of discharge channels formed in the dielectric breakdown of gases, liquids, and at the gas/liquid interface have also been studied as a stochastic processes using fractal models[303−309] and Monte Carlo simulations of fractal-type breakdown.[305,306] These models provide simulations of the branch or treelike structures that form in breakdown processes. The fractal dimension of multichannel streamer development over a water surface was determined through experiment to be 1.8.[310] The higher value of 1.8, in comparison to that for discharge over a solid dielectric (1.7), is attributed to the solution conductivity, leading to high space filling of the discharge over the water surface. (To fill a two-dimensional surface, the fractal dimension would be 2.) Measurements of fractal dimension and simulations of fractal structures of discharges in gases, liquid, and at the gas/liquid interface can provide insight on the nature of the geometrical structure of the discharge and discharge propagation. However, these studies have not provided connections of the fractal properties to the other physical/chemical processes that are occurring in these discharges.

3.2. Spark Formation in Water. Sparks can form in water either with or without the simultaneous formation of streamers (see Figure 5). Smaller gap spacing can be used in a point-to-plane reactor in the latter case with simultaneous spark and streamer formation than in the case when only streamers are formed. In the combined system, the magenta-colored streamers were formed near the high-voltage needle tip and they extended to the ground electrode in a manner similar to the case of the streamer discharge alone. Generally, the streamers propagate to the ground electrode via the action of the high-intensity electric field between the point-to-plane electrodes (on the streamer head). Near the ground electrode, the streamer color changes to white as the streamer propagates toward the ground electrode. The state of the discharge changes from the streamer mode to the spark mode after the streamer contacts the ground electrode. The time for formation of the spark is dependent on the electrode gap distance. At a small electrode gap distance of ∼5 mm, the spark discharge occurred at a very short time, following the increase in the voltage pulse. A bright white-colored discharge was observed with a popping sound when a 6−10 nF pulse forming capacitor was used.



(a) streamer discharge (electrode gap 30 mm)

(b) spark with streamer discharge (electrode gap 15 mm)

(c) spark discharge (electrode gap 7 mm)

Figure 5. Schematic of point-to-plane discharge: (a) streamer discharge, (b) spark with streamer, and (c) spark discharge. (Reprinted from ref 312, with permission from Elsevier.)

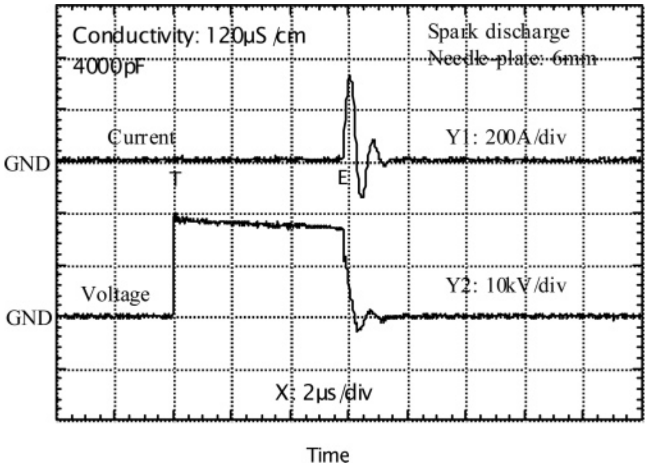


Figure 6. Variation of voltage and current for the spark discharge with needle−plate electrodes in water. (Reprinted from ref 15, with permission from Elsevier.)

As shown in Figure 6, a streamer discharge current on the order of several amperes is recorded after a short time delay (in the figure, this current is not shown, because of a large ordinate scale). The current increases as the discharge channels are formed. Thereafter, the discharge current increases very rapidly and reaches a maximum of 320 A. Because the energy source is a storage capacitor, the current decreased after reaching the maximum value.[15]

The time delay between the increase in the voltage pulse and the formation of the spark discharge is dependent on the capacitance of the storage capacitor and the conductivity of the aqueous solution. The delay time increases as the applied pulse voltage decreases and the distance between electrodes increases. The emissions intensity of the spark discharge reaches a maximum at wavelengths of 400−500 nm. Emissions peaks that result from OH, H, and O radicals, as well as a strong broadband, are observed. The light pulse from the spark discharge includes a broad spectrum of “white light” containing wavelengths from 200 nm in the UV range to 1000 nm in the near-infrared (NIR) range. The spectral distribution is similar to that of sunlight.

Oscillograms of both the light emitted at 309 nm (OH radical emission) and the electrical input power are shown in Figure 7. Most of the electrical energy is delivered to the spark discharge

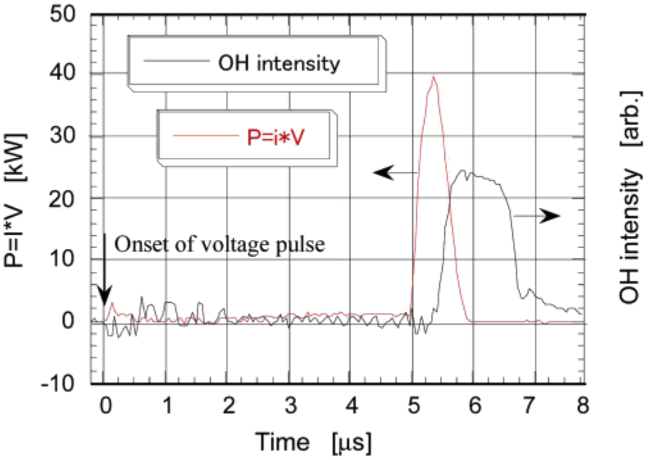


Figure 7. Oscillograms of light emissions at 309 nm (OH radical emission) and the electrical input power for spark discharge in water. (Reprinted from ref 312, with permission from Elsevier.)

in <1 μs, and the peak power reaches several thousands of kilowatts (with an 8-nF storage capacitor). The 309-nm light is emitted slightly after the spark current initiates and continues longer than the electric power. The spark energies are dissipated relatively slowly as the spark channel expands and as the temperature decreases.[15,311]

The concentration of hydrogen peroxide increases as the input energy increases. In the case of the streamer discharge, the hydrogen peroxide concentration increases linearly as the input energy increases, indicating zero-order kinetics. However, for the spark discharge, the hydrogen peroxide concentration increases more rapidly at lower input energies.[31] For all input energies, the concentration of hydrogen peroxide produced by the spark discharge is much higher than that of the streamer discharge. The spark with a streamer has been determined to be better than the streamer alone in the destruction of phenol.[312]

3.3. Arc Formation in Water. In the higher-current and higher-energy pulsed arc systems, the mechanism of arc formation may more likely follow the thermal mechanism previously mentioned. In this theory, when an applied voltage pulse is high enough and the power supply is capable of allowing large current flow, the temperature of the water will rise through Joule heating ($\sim I^2Rt$, where I is the current and R is the resistance of water). This heating leads to water vaporization. The vaporized water molecules will be ionized, and, subsequently, the arc channels will be formed. Parts of the metal electrodes will also be vaporized, and these species will contribute to the formation of thermal plasma. Hence, the applied voltage falls off when the pulsed current is initiated, as shown in Figure 8.[1] Figure 9 shows the corresponding power waveform.[1] The plasma temperature in spark and arc channels are normally a few thousand and twenty thousand degrees Celsius, respectively, and the plasma density is at least as high as 10^{17} cm^{-3}. In spark and corona discharges, the electron temperature is greater than the gas or ion temperature ($T_e > T_g$), and in the arc, $T_e = T_g$. Significant amounts of UV emission and radical atoms will be formed in these arc channels.[1]

Because of the large pulse energy injected into the water in a very short time period (ca. 1 μs), pressure waves will be formed. The pressure wave is due to the fast heating of the channel. Figure 10 shows the pressure (oscillations) corresponding to the pulsed arc for Figures 8 and 9.[1]

A high-energy (25 kJ) capacitive discharge reactor has been used to produce arcs in water. For example, a system consisting of two electrodes submerged in a 4-L reaction vessel to which a 135 mF capacitor bank is discharged across the spark gap has been operated.[26,46,48] A 300-ns-rise-time semiconductor switch was used to trigger the discharge and was capable of generating a 20 ms pulse with a total energy of 25 kJ and a peak power of 1 GW. Under normal experimental conditions, measurements of the voltage across the electrodes can be as high as 5 kV with peak currents of 90 kA (5 kV and 90 kA give 450 MW). The system is electrically analogous to an underdamped LRC circuit with a period of 50 ms.

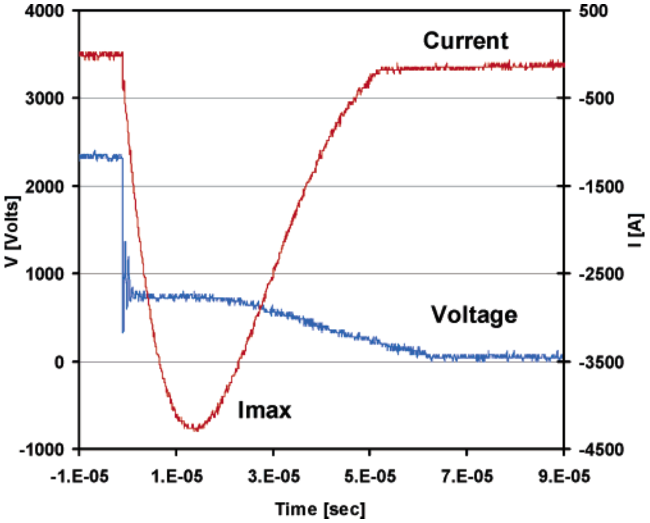


Figure 8. Voltage and current pulses for an electrohydraulic pulsed arc discharge in water. (Taken from ref 1, with permission from J. S. Chang, Copyright 2002.)

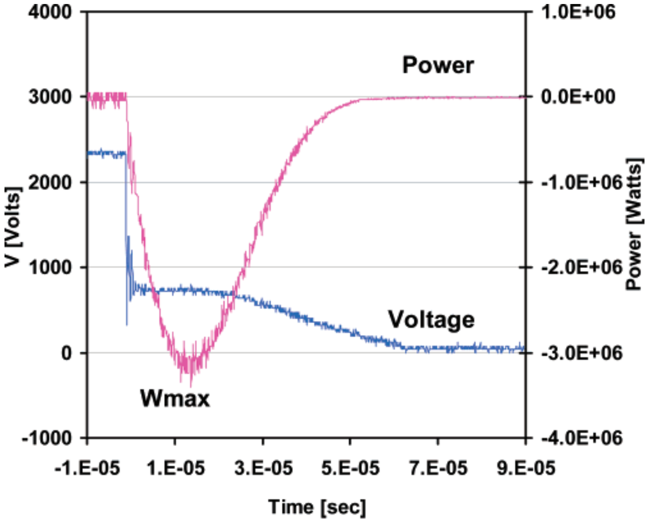


Figure 9. Power pulses for an electrohydraulic pulsed arc discharge in water (corresponding to the same discharge as given in Figure 8). (Taken from ref 1, with permission from J. S. Chang, Copyright 2002.)

Because the energy input is much higher than in the corona and spark systems discussed previously, the rapid thermal heating and bubble formation may have a much larger role in the discharge propagation. Therefore, it is likely that, following the rapid discharge of the capacitor bank in this system, a fraction of the current leaks into the spark gap and heats the water surrounding the electrodes, thus forming gas bubbles. These bubbles may enable the formation of a plasma channel across the liquid medium. The plasma arc channel may reach temperatures in the range of 14 000−50 000 K, and it functions as a blackbody radiation source with a maximum emittance in the vacuum ultraviolet (VUV) spectrum ($\lambda = 75-185$ nm). The plasma channel consists of a highly ionized, high-pressure and

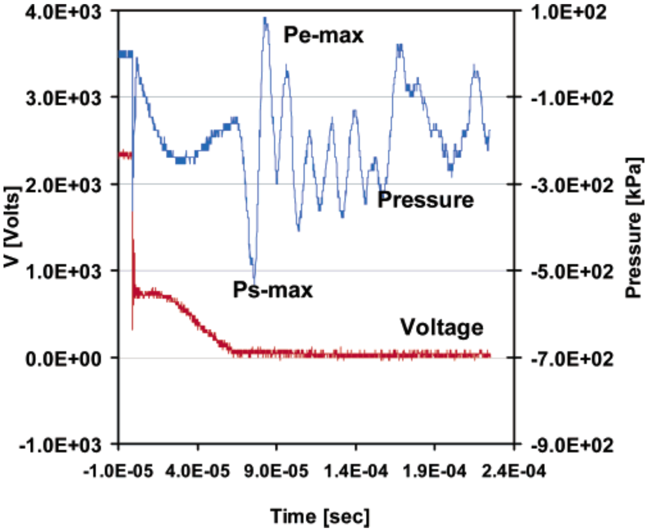


Figure 10. Pressure waves for an electrohydraulic pulsed arc discharge in water (corresponding to the same discharge as given in Figure 8). (Taken from ref 1, with permission from J. S. Chang, Copyright 2002.)

high-temperature fluid. Once formed, the plasma channel has a tendency to expand. The mechanical inertia of the surrounding water resists this expansion resulting in the development of very high pressures. (The pressure amplitude is dependent on the ratio of the heating rate (roughly the time derivative of the dissipated power) to the speed of sound minus the speed of expansion.) The energy stored in the plasma channel is slowly dissipated (slow relative to the plasma formation process) as thermal radiation and mechanical work. At the detonation front, the high-pressure buildup in the plasma is transmitted into the water interface and an intense compression wave (shock wave) is formed that travels ahead of the expanding gas bubble at a speed several times faster than the speed of sound only at very high pressure. (At 6 kbar, the speed of sound is only 1.56 times higher than at the normal pressure.) Pressure jumps across the shock can be as high as ∼5−20 kbar. When the shock wave reaches a free surface, the stress-free condition at the interface instantly transforms the compression wave into a tension (or rarefaction) wave and it is reflected back into the liquid medium (simultaneously with pushing the water into air). This rarefaction wave induces cavitation as it travels back through the water. The shock waves, rarefaction waves, and gas bubble expansion sustain a highly turbulent mixing environment until all pressures are equalized.

Further details on the structure of high-energy (kJ per pulse) discharge in high-conductivity (mS/cm) water were determined via the emissions spectroscopy of sodium vapor and shadow graph photography. These methods demonstrated the existence of a narrow transition vapor layer (0.025 mm) between the plasma region and the water.[313] Approximately 10% of the energy of the discharge dissipated in this transition layer, and the authors[313] argue that propagation of the discharge channel within the liquid is strongly influenced by thermal effects and phase transition. (However, because the thermal conductivity of the transition layer is rather small, evaporation of the water by UV radiation seems more likely.)

Several models have been developed to describe electrohydraulic discharge in water, with particular emphasis on determination of the pressure, bubble radius, and plasma temperature evolution with the discharge time.[314−316] Kratel's model[314] is based on the formation of a plasma channel between two point electrodes, and it was used to determine the current, temperature, channel radius, and particle density, utilizing the conservation of mass, energy, momentum, and charge. The plasma pressure, internal energy, and conductivity were subsequently determined as functions of time from these quantities. Simulations were performed over a range of parameters, giving reasonable agreement with experimental data. For a 1.8 kJ pulse, the results gave a peak temperature of 4×10^4 K, a channel radius of 3 mm at 8 μs, and peak particle densities of 10^{21} cm^{-3}. For short times, the predicted pressure deviated from the model. In an analogous model, including the equation of motion of a spherical bubble and mass and energy balances, Lu et al.[315] determined the pressure, temperature, and electron density for a 1-J pulse to be 5×10^3 atm, 5×10^4 K, and 4×10^{26} m^{-3}, respectively. Simulations of the same model with 1-kJ pulses compared very well with the experimental data, with respect to changes in the bubble radius with time.[317] The model also shows, for a 200-J pulse, that an ambient pressure of 1−100 atm reduces the bubble size but does not affect the plasma temperature.[318] The fact that the model works reasonably well over such a large range of energy pulses is very encouraging; however, further experiments and tests are necessary over a broader range of conditions.

3.4. Physical Disruption of Biological Cells and Macromolecules. Pulsed electric fields under conditions where electrical discharges do not form have been studied as a means for cell disruption in biochemistry, biology, medicine, drug delivery,[319] and food purification.[320] Although this review is primarily concerned with the conditions leading to the formation of electrical discharges, it is important to consider the mechanisms of cell disruption in pulsed electric fields to evaluate the possible mechanisms involved in biological applications of electrical discharges in water. Electrical breakdown or disruption of biological membranes in a pulsed electric field (PEF) is well-known and can be explained by the principle of electromechanical compression.[319,321] This phenomenon causes the formation of transmembrane pores, and the size or number of these pores can be varied according to the conditions of the applied electric field. If the total area of induced pores is small in relation to the total surface area of the membrane, the pores are able to reseal, mainly as the result of diffusion of lipid molecules and rearrangement of the proteins (reversible disruption). On the other hand, at very high fields, a very large number of pores may be formed, or the diameters of individual pores may enlarge as a result of secondary processes. In these cases, a limit is reached where the ratio of total pore area to total membrane area is so unfavorable that the membrane is no longer able to repair these perturbations. Irreversible disruption will then occur. Based on these phenomena, various applications of PEF have been investigated in the fields of biotechnology and water treatment. When the disruption of a biological membrane is reversible, electroporation[319,322−324] or electrofusion[321,325,326] are possible, and irreversible disruption is applicable to the pulsed sterilization technique.[54,57,327−329]

Several studies have investigated the effects of electrical pulses on living cells. Sale and Hamilton[54] found that rectangular pulses of up to 25 kV/cm for 2−20 μs destroyed bacteria even when the products of electrolysis were excluded from the cell by encapsulation of the cells within gels. They suggested that the effect of the electric field was to cause irreversible destruction of the membrane. Subsequently, a large amount of research has been reported in the biology literature on the topic of electroporation.[319] Virus inactivation in pulsed high-voltage electric fields has been studied by Mizuno et al.,[56] where they showed that the DNA and RNA of a virus were damaged when using fields of 30 kV/cm. The effect of PEF on chromosomal DNA, plasmid DNA, and RNA was studied, and the decomposition of these nucleic acid molecules was observed, although plasmid DNA was relatively stable against PEF.[330] Bacteria and yeast have also been inactivated by pulsed electric fields.[7,54,55,59−61,63]

The Russian literature contains extensive work on the application of water discharges for microorganism destruction.[331] Bogomaz et al.[331] summarized the action of high-voltage pulsed electrical discharge in water to include (i) local action arising from chemical reactions near the plasma and (ii) nonlocal action due to shock wave and UV radiation. They found that the conditions for shock wave formation are pulses with energies of 1−10 kJ with pulse lengths of 1−10 μs. An initial concentration of 10^9 cm^{-3} *Escherichia coli* cells led to 5-orders-of-magnitude destruction with ∼3 J/cm^3.

Pulse energies of 1 kJ with 40 kV and 0.1−40 Hz were studied for bacteria destruction and electrode wear in point-to-point geometry. It was observed that, at 10 J/mL, ∼100% of the bacteria was destroyed and mechanical destruction could not account for the sterilization effect. In several other studies, pulsed corona discharges were also determined to be superior to PEFs in deactivating microorganisms.[64,332] The presence of gas bubbles dispersed in a liquid lead to a liquid-phase plasma discharge that was more effective than the PEF without the gas bubbles in destroying *E. coli, Staphylococcus aureus, Staphylococcus enteritidis*, and *Bacillus cereus*.[65] Sato et al.[7,57] considered yeast inactivation using pulsed corona discharge and found that the addition of OH radical scavengers did not lead to changes in the survival rate. However, it is known that hydrogen peroxide is a strong sterilization agent.[333] These results suggest that the roles of chemical and physical processes on microorganism destruction in electric discharges are not clearly understood. Moreover, most studies on electrical discharges in water involved bacteria that is suspended in solution (sessile), and studies that compare the removal of sessile and planctonic (attached) bacteria are needed.

For other applications, it has been observed that some intracellular proteins may be selectively released through the pores induced by PEF treatment, because the size of these pore areas can be controlled according to the electric condition of PEF treatment. The releasing profiles of intracellular enzymes from *Saccharomyces cerevisiae* using PEF were studied, and the release of invertase and alcohol dehydrogenase can be controlled by controlling the electric condition.[334] Ohshima et al.[335] demonstrated the selective release of gene product from recombinant *E. coli* using PEF, and they suggested that this technique is a powerful tool for the efficient recovery of the target protein from the cell.

Recently, the effect of PEF on protein or enzyme activity has been studied. Inactivation of milk alkaline protease,[336] lipase,[58] and papain[337] by high-voltage PEF (30−50 kV/cm) has been demonstrated. On the other hand, Ohshima et al.[338] reported that enzyme activities were enhanced by PEF treatment when the PEF amplitude was 10−15 kV/cm. They also demonstrated the refolding of denatured peroxidase and prevention of peroxidase denaturation using PEF.

The effects of UV radiation and shock wave generated by high-energy electrohydraulic arc discharge reactors on bacteria have been studied in the context of drinking water treatment[339,340] and food science and protection.[341−343] The high-energy electrohydraulic arc discharge process can be an effective technique for water disinfection for the following reasons. The arc discharge leads to the generation of hot, localized plasmas that strongly emit high-intensity UV light, produce shock waves, and generate hydroxyl radicals during water photodissociation. UV light in the range of 200−400 nm is mutagenic to cells,[344] shock waves are known to mechanically rupture cell membranes,[96] and hydroxyl radicals lead to oxidative cell damage.

In summary, high-voltage PEFs induce interesting phenomena in such biomaterials as cell membranes, nucleic acids, and proteins. These results suggest that the PEF techniques have potential for application to biotechnology as well as to wastewater treatment. An understanding of the mechanisms of the effects of PEF on biomaterials may help in understanding the mechanisms of electrical discharges on biomaterials. Several studies suggest that pulse corona discharges in water are superior to PEFs in regard to deactivating microorganisms and that high-energy electrohydraulic discharges can destroy many organisms. The roles of chemical species such as hydrogen peroxide and physical factors such as UV light and shock waves may be more important under electrical discharge conditions. However, with the exception of cell membrane disruption by PEFs, the detailed mechanisms of many of these phenomena, including the pulse corona discharge and the electrohydraulic discharge, are not fully known.

3.5. Formation of Ultraviolet Light in the Liquid Phase. One key question, still not fully answered, in the research on liquid-phase pulsed corona electrical discharge is: to what extent does the electrical discharge do more than produce the reactive species of hydrogen peroxide, ozone, and hydroxyl radicals? This will, of course, be dependent on the magnitude of the energy discharged into the liquid. For example, Sato et al.[28] determined that ∼15% of the phenol degradation can be attributed to UV light produced by the discharge under joule-per-pulse conditions. Lukes and co-workers[31,345] reported increasing levels of UV light formation as the solution conductivity increased. In the studies of Lukes, UV light was measured through incorporation of chemical actinometry using UV transparent cells immersed within the liquid phase. Discharges over water surfaces have also been shown to produce UV light.[114] Furthermore, thermal effects, UV radiation, and shock waves generated by the discharge may be important in highly conductive liquids. Additional quantitative estimates and modeling of these effects are needed to address these issues fully.

In the case of kJ pulses in the pulsed arc discharge reactor, the plasma channel formed during an electrohydraulic discharge can reach temperatures of 14 000−50 000 K. The channel thus functions as a blackbody radiation source with a maximum emittance in the VUV region of the spectrum ($\lambda = 75-185$ nm (ref 112)), as determined from model calculations. The VUV light emitted from the hot plasma is absorbed by the water layer immediately surrounding the plasma channel,[346] and the UV light with $\lambda > 184$ nm penetrates into the bulk of the solution. In principle, all wavelengths of <200 nm are absorbed by water. The stepwise multiphoton absorption at UV light intensities $>10^6$ W/cm^2 generated by picosecond and nanosecond laser irradiation is known to produce nonlinear photoprocesses in nucleic acids.[47,347,348] Experiments have shown that electrohydraulic arc discharge reaches intensities as high as 3×10^6 W/cm^2, which leads into the multiphotonic photochemistry regime. These factors clearly will have an effect on chemical reactions and, especially, the destruction of microorganisms.

3.6. Shock Wave Formation. During the formation of the plasma channel (1−2 ms) in a pulsed arc electrohydraulic discharge reactor, an intense 5−20 kbar or 10−20 MPa shock wave is generated due to the rapidly expanding plasma channel.[349] The resulting shock wave can induce pyrolytic and free-radical reactions indirectly via electrohydraulic cavitation.[350] The pressure shock wave is followed by a rarefaction wave that

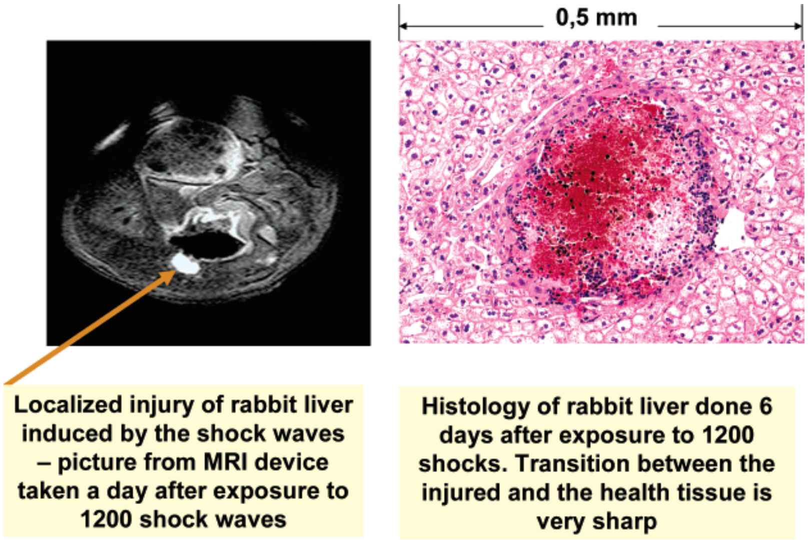


Figure 11. (A) Localized injury of rabbit liver induced by the shock waves; the picture shows a magnetic resonance image (MRI) taken a day after exposure to 1200 shock waves. (B) Histology of rabbit liver 6 days after exposure to 1200 shocks; the contrast between the injured tissue and the healthy tissue is very sharp.

produces cavitations. The collapsing cavitations create strong secondary shocks with very short duration (~60 ns that sometimes result in sonolumeniscence (excitation of light spikes)), and these shocks can interact with structures on the size of cells. Figure 11 shows the highly localized action of the shocks on a rabbit liver (the transitional layer is of the order of 5−10 cell dimensions.

3.7. Discharge over Water Surface. Various types of discharges over water surfaces have been studied experimentally. Several studies have focused on the formation of UV light above the water surface. Although these discharges have many features in common with gas-phase discharge, the interactions with the water surface may affect the physical aspects of the discharge, as well as the chemical processes occurring in the liquid. For example, in the case of a barrier-type discharge over the water surface, it has been found by chemical actinometry that intense shortwave (<190 nm) and soft (190−430 nm) UV light are produced and reaches the liquid phase.[351] In this case, the discharge is not in direct contact with the liquid surface. In the case of corona or spark discharge directly over the water surface where the streamer channel propagates along the surface of the water, the water conductivity has an important role in the nature of the discharge channel propagation, the channel length and current are directly related, and UV light is also produced.[352−355]

4. Chemical Reactions in Electrohydraulic Water Treatment

Chemical reactions induced by electrical discharges in water are dependent on several factors. For example, the aqueous solution composition can affect the reactions through the presence of electrolytes and radical quenchers. Conductivity affects the electrical discharge in water, leading to lower rates of formation of active species, but higher rates of formation of UV light.[31,356,357] The nature of the liquid-phase electrode can also affect the reactions in the liquid. Although direct electrochemical reactions may not be important, ions and particles released into solution from the electrode can affect solution chemistry. Furthermore, in gas−liquid discharge environments, the nature of the gas phase (typically air, oxygen, nitrogen, or argon) will affect the formation of gas-phase species, which, in turn, will transfer into the liquid. The liquid may also evaporate and affect gas-phase reactions. It is also important to note that electrical discharge reactions in liquid and gas−liquid systems can lead to post-discharge reactions that may be due to the longer-lived radicals and reactive species formed in the discharge.[358]

4.1. Plasma Chemistry at the Gas/Liquid Interface. Direct measurements of the chemical reactions occurring at the gas/liquid interface have not been reported; however, research on glow discharge and contact glow discharge electrolysis provides some information about the chemical processes that may be occurring at the interface. In certain electrode configurations where the high-voltage and ground electrodes are placed in different phases, discharge along the surface of the interface can be observed. For example, when the high-voltage needle electrode is placed in the water phase and the ground electrode is in the gas above the water surface, "gaslike" streamers are observed to propagate along the surface of the interface.

In addition, studies of glow discharge electrolysis imply that ions, radicals, and neutral species produced in the gas phase may transfer into the liquid phase through action of the electric field.[10,359−362] It is suggested in this work that H_2O^+ that is formed in the gas phase bombards the surface of the gas/liquid interface under the influence of the large electric field driving force, and it then subsequently reacts with liquid H_2O to form hydroxyl radicals.[10,359] The hydroxyl radicals can recombine to form hydrogen peroxide and, generally, the radicals participate in radiolytic reactions. It was suggested that the average energy of the positive gaseous ions entering the liquid phase is >100 eV.[360] Sengupta et al.[359] measured the yield of hydroxyl radicals in contact glow discharge electrolysis using radical quenchers. They found that, for a range of voltages and electrolyte compositions, the yields of H_2 and H_2O_2 per mole of electrons were >0.5, which is the limit imposed by Faraday's law. It was postulated that this high yield was due to several factors. For example, a reaction zone may be formed where liquid water is dissociated into H_2 and O_2 and where H_2O_2 is formed. They also suggested that gas-phase water can be dissociated into H_2 and O_2 in a gas-phase plasma region adjacent to the anode. Joule heating near the electrode, leading to vaporization of the solvent and hydrodynamic instability, may lead to the transition from normal electrolysis to the formation of the contact glow discharge.[363] In a related study of contact glow discharge electrolysis, Tezuka[13] measured the formation of hydrogen peroxide in the liquid phase and hydrogen and oxygen evolution in the gas phase above the liquid surface. At low voltage and current, hydrogen and hydrogen peroxide yields were approximately stoichiometric. However, hydrogen and hydrogen peroxide increased with different rates as the voltage and current increased. Oxygen formation was unaffected by the current, while it decreased with increasing voltage. In the case of the contact glow discharge electrolysis, it is necessary to know the detailed electrode configuration. When the needle and its insulation are immersed in water, the discharge burns in water vapor and the current is limited by the solution conductivity. This situation is very similar to an "arclike" phase of the corona discharge.

Lecuiller et al.[361] found that, in a point-to-plane corona discharge in oxygen gas above a water surface, the negative ions O_3^- and O_2^- were formed. These species respectively lead to the formation of OH and HO_2 in the liquid phase by two separate pathways that involve either (O_3^-, CO_3^-) or (O_4^-, CO_4^-, $N_2O_2^-$, O_2^-). Goldman et al.[364] utilized a system with a grid electrode placed between the high-voltage needle and the water surface (the ground) and a suction tube placed adjacent to the needle electrode. Using the suction to remove neutral species or the grid to remove charged species, they found that the *combination* of ions and neutrals formed in the gas discharge were responsible for pH changes in the liquid solution. Thus, activated neutral species had an important role in the pH decrease.

Gas-phase pulsed corona over water for the degradation of phenol in aqueous solution has been extensively studied.[29,175,237,238,365−367] Laser-induced fluorescence spectroscopy was used for in situ diagnostic measurement of phenol and intermediate products. This methodology has the advantage (over conventional liquid chromatography) of providing high spatial and temporal (10−100 ns) resolution. However, the technique suffers from difficulties in the determination of absolute concentrations of chemical species. It was determined that phenol removal was most rapid when the gas-phase atmosphere above the water surface was oxygen and that hydroxyl radical reactions as well as ozone reactions lead to the degradation processes. Different degradation byproducts were formed from phenol, depending on the whether the gas was oxygen or argon.

The formation of ozone in the gas phase and hydrogen peroxide in the liquid phase was measured for several types of corona discharge reactors with gas/liquid interfaces.[21] It was found that the formation of hydrogen peroxide in the liquid phase was independent of the presence of the gas-phase discharge for two types of hybrid gas−liquid reactors and for a reference reactor without a gas-phase discharge. All three reactors had a high-voltage electrode in the liquid phase. However, the hybrid parallel reactor had a high-voltage electrode in the gas with a ground electrode at the interface, the hybrid series reactor had a ground electrode placed just above the water surface in the gas phase, and the reference reactor had a ground electrode in the water. The parallel reactor produced higher levels of ozone than the series reactor. The parallel reactor was determined to be superior for the degradation of nitrobenzene,[368] whereas the series reactor was superior for the degradation of phenol. More detailed studies of phenol and substituted phenol have been conducted in the series reactor configuration,[32,33] showing electrophilic attack by hydroxyl radicals and ozone on phenol as the major mechanisms for degradation under argon and oxygen atmospheres, respectively. Electrophilic substitution was proven by the correlation of reactivity with the Hammett substituent constants.

Table 2. Typical Reaction Rate Constants for Liquid-Phase Electrical Discharge Reactors[a]

reaction	reaction rate constant	reference source(s)
radical formation		
$H_2O \rightarrow H + OH$	10^{-8}−10^{-10} M s^{-1}	8, 18
radical−molecule reaction		
OH + organic → products	10^{9}−10^{10} M^{-1} s^{-1}	127
photochemical reactions (natural water)		
$^1O_2$ + organic → products	(pH-dependent) 10^{6}−10^{8} M^{-1} s^{-1}	375
electron−molecule		
$e_{aq}^- + H_2O_2 \rightarrow OH + OH^-$	10^{10} M^{-1} s^{-1}	380
Fenton's reaction		
$Fe^{2+} + H_2O_2 \rightarrow OH + OH^- + Fe^{3+}$	10^{2} M^{-1} s^{-1}	118
ozone−molecule		
O_3 + organic → products	(pH-dependent) 10^{-2}−10^{4} M^{-1} s^{-1}	127
aqueous electron reactions		
e_{aq}^- + chloroform → products	10^{10} M^{-1} s^{-1}	270
e_{aq}^- + benzene → products	$<10^{7}$ M^{-1} s^{-1}	270

[a] From radiation chemistry and other sources.

The effect of the gas-phase discharge on reactions in the liquid for other types of electrical discharge processes has not been studied in detail. No fundamental studies have been conducted to analyze the chemical reactions that may occur at the gas/liquid interface in pulsed corona discharge, and this is a very important area for future work, because the hybrid gas−liquid discharge system seems to be very promising.

It is important to note that a range of studies have been conducted to determine the effects of gas discharges above polymer and other solid surfaces,[369−374] and these studies have lead to interesting results concerning the formation of nodules and water layers on the solid surfaces, as well as the oxidation of the surface, formation of nitrates in the water layers, and the possible incorporation of nitrogen within the matrix of the solid.

4.2. Bulk Liquid-Phase Chemistry. Initial models of the bulk phase corona-induced chemical reactions for direct pulsed electrical discharge in water were reported by Joshi et al.[8] and Grymonpre et al.[166,356] In those studies, it was assumed that the pulsed corona discharge leads to the formation of hydrogen peroxide, hydroxyl radicals, and aqueous electrons. Recent studies have improved on the basic corona-initiated reactions through the measurement of molecular hydrogen, hydrogen peroxide, and oxygen in the stoichiometric ratios of 4:2:1.[12] The other major species produced by the corona reactor were assumed to be the same as those formed in radiation processes such as electron beam radiation and pulse radiolysis in water. Some of these species participate in the radical propagation and termination reactions (for an extensive set of reactions, see ref 243). The oxidation reactions for the organic compounds—in this case, phenol—and its primary oxidation products were assumed to follow the kinetics of liquid-phase hydroxyl radical attack, where hydroxyl radicals were primarily formed through Fenton reactions from hydrogen peroxide. The kinetic constants for most of these reactions were obtained from the radiation and oxidation chemistry literature.[271,273]

Sample reaction rate constants for liquid-phase reactions are given in Table 2. Note that liquid-phase reactions with organic compounds can be highly pH-dependent, whereas, generally, direct reactions with hydroxyl radicals are usually very fast and not highly specific, in comparison to reactions with ozone. UV reactions lead to the formation of hydroxyl radicals, oxygen radicals (e.g., $^1O_2$), and peroxyl radicals and the rates of formation of these species are highly dependent on the UV flux and absorption in the liquid phase.[375]

Phenol is a good, representative, small aromatic compound, because phenol oxidation has been extensively studied in many systems. These systems include supercritical water oxidation,[376] ultrasonication,[138] ozonation,[115] UV photolysis, and pulsed streamer corona.[27] In most of these studies, the oxidation of phenol was achieved through reaction with hydroxyl radicals, although phenol can also react at a slower rate by direct reactions with ozone. Hydroxyl radicals electrophillically attack phenol to form the primary products catechol, resorcinol, and hydroquinone. Other hydroxyl radicals then react with the primary products to produce mucconic and fumuric acids, as well as other organic acids. These organic acids are then oxidized to form the smaller organic acids such as oxalic and formic acids. The final end products of the hydroxyl radical oxidation of phenol are carbon dioxide and water.

Grymonpre and co-workers[165,356] and Lukes and co-workers[31,345] measured the rate of formation of hydrogen peroxide as functions of solution conductivity and applied voltage for pulsed corona discharge with both electrodes submerged in the aqueous phase. The rate of formation was observed to decrease with increasing solution conductivity and to increase with applied voltage. For the range of parameters studied, it was determined that corona-induced hydrogen peroxide formation coupled to known radiation chemistry[271] and Fenton's chemistry[377,378] could be used to describe the behavior of phenol degradation under a wide variety of initial iron and phenol concentrations[356] for relatively low-conductivity solutions. In addition, the model was able to predict the pH change during the course of the experiments accurately. However, note that the model requires further work to predict the pH for non-Fenton conditions accurately. Full sensitivity analysis[379] was also conducted and indicated the importance of hydrogen peroxide direct formation and degradation. For higher-conductivity solutions, it is necessary to further develop the model to include UV formation and additional hydrogen peroxide decomposition mechanisms. Further considerations of conductivity changes during the course of the experimental runs is also necessary.

4.3. Chemical Effects in Pulsed Arc Systems. Experiments with exploding wires have shown that large-energy electrohydraulic arc discharges induce extreme electromagnetic and mechanical conditions in the bulk solutions outside of the plasma channel region. These conditions may affect both chemical reactions and the inactivation of microorganisms in solution.[92,260,349,381] For example, recent work has demonstrated the destruction of such organic compounds as atrazine[382] and methyl *tert*-butyl ether (MTBE)[383] by pulsed arc systems. As in the other electrical discharge reactors, the simultaneous occurrence of multiple processes makes the chemistry and physics quite complicated. In an attempt to differentiate between the various physicochemical processes, they can be grouped into localized and extended effects. The oxidative degradation processes that occur within the plasma channel and within the immediate vicinity of the plasma channel can be defined as local processes. These include pyrolysis within the high-temperature plasma, oxidation due to direct and indirect VUV photolysis, and supercritical water oxidation. Mechanical damage resulting from shock waves and UV radiation in the bulk aqueous solution is an extended effect. In the context of biological disinfection, the localized effects lead to zero-order kinetics. In the electrohydraulic arc discharge process, chemical degradation can occur within the plasma channel directly due to pyrolysis and free-radical reactions. However, the small volume of the plasma channel (1−3 mL) limits the amount of solution that can be directly exposed to high-temperature pyrolytic processes.

As the plasma channel cools over 1−3 ms, thermal energy is transferred to the surrounding water, resulting in the formation of a steam bubble.[92] Within the steam bubble, the temperatures and pressures are high enough for the formation of transient supercritical water.[381] However, the overall bulk liquid temperatures after 50 discharges is <35 °C, confirming that most of the chemical and bactericidal effects are due to other nonthermal mechanisms.

To understand the effects of high-voltage discharge on microorganism deactivation, it is useful to consider the effects of UV light on the nucleic acids. In low-intensity, UV irradiation of nucleic acids, for example, absorption to the first excited singlet and triplet states (S1 and T1, respectively) leads to the formation of C5−C6 cyclobutyl dimers between neighboring pyridines, weakening and distorting DNA strands, ultimately blocking DNA replication. Nonconventional high-lying quasi-Rydberg SN and TN state photochemical processes in thymine can occur with high-intensity UV irradiation because of two photon absorption mechanisms that lead to the formation of DNA-base radicals, ejection of a hydrated electron, or direct ionization.[384−386] Oxidative damage incurred by the subsequent reactions between these highly energetic moieties and the cellular material produces DNA single- and double-strand breaks.[347,387−389] The inactivation process displays kinetics similar to disinfection by pulsed radiolysis and ionizing radiation,[390] and additional pathways of action have been verified, i.e., the formation of single- and double-strand DNA breaks (ssb and dsb, respectively), interstrand cross-linking, and protection by the cytoplasm.[387,389,391]

Pulsed electrohydraulic discharge has been shown to reduce the concentration of NH_4OH substantially and lead to significant pH changes.[1] Because of the intensive energy input, the formation of UV light and shock waves, and the generation of various radicals such as hydroxyl, this type of process is likely to contribute to the degradation of various organic compounds through many different pathways.

4.4. Fundamental Effects of High Electric Fields on Chemical Reactions. The effects of an arbitrary spherical potential on chemical reactions were first studied by Debye,[392,393] who extended the classical diffusion model of Smoluchowski.[394] Onsager considered the solution of the Smoluchowski equation with an electric field.[395,396] More recently, Hong and Noolandi[397] have extended this work by solving the time-dependent Smoluchowski equation with electric field terms, including either Coulombic attraction or repulsion. This analysis is important for recombination, neutralization, and scavenging events that occur in the liquid phase through theoretical expressions describing diffusion-controlled reaction rates with superimposed drift.[393]

In the case of high-voltage electric fields, Kuskova[292] developed a theory based on the original work of Frohlich[398] and Zener[399] for the electrical breakdown of ionic crystals. Kuskova[292] determined that the reaction rate constant in highly polar liquids followed the relation

$$k(E) = K(0)\exp\left(\frac{2\sqrt{e^3E/\epsilon}}{kT}\right) \tag{1}$$

where E is the electric field, k the Boltzmann's constant, ϵ the dielectric permittivity, and T the absolute temperature. Joshi et al.[8] used this expression to consider the effects of the electric field on reactions in the liquid-phase corona reactor; however, only a narrow range of electric fields was studied.

The field of electrocatalysis[400] generally refers to electrode oxidation in liquid media. It has been shown that hydrogen will react on a platinum graphite electrode in an aqueous KOH solution. A 1−2 V potential on the electrode increased the reaction rate 500%, and it was inferred that hydroxide ions act as promoters.[400] Electrocatalytic effects have not been studied within the context of high-voltage electrical discharge processes; however, at low voltage, TiO_2 photocatalysts can be activated using relatively low-voltage sources in water.[401] Furthermore, it is interesting to note that the electric field effects and the chemical reactions of electrical discharges in water have been suggested to be similar to those that occur in sonochemistry, although further work on this matter is necessary.[137]

5. Conclusions

Electrical discharge reactors are currently under intensive investigation for the treatment of contaminants in wastewater, as well as many other applications. Systems with a wide range of electrode and reactor configurations have been tested in the laboratory to assess the efficiency of these processes. The major reactive species, including hydroxyl radicals, ozone, and hydrogen peroxide, and reactive conditions such as ultraviolet (UV) light and shock waves have been identified by chemical and physical methods for many of these specific processes. However, quantitative information is not available for all systems, and the role of other reactive species must be carefully evaluated. Much information from gas-phase nonthermal plasma systems, radiation chemistry, and other advanced oxidation methods can be used to interpret chemical reactions in the liquid-phase systems; however, the physical processes for streamer formation and electric field propagation in the liquid state are poorly understood. Kinetic models of the major chemical reactions with full sensitivity analysis of only few specific systems have been developed. Further model analysis requires complete sensitivity analysis coupled with flux analysis to determine key pathways for important processes. Full testing of the models requires independent evaluation of model parameters and true predictions of experimental results.

For low concentrations of organic and inorganic contaminants dissolved in the water, lower-energy corona and glow discharge processes may be useful, as indicated by some of the bench studies. For high concentrations of organic compounds in the liquid phase, larger energy-arc- and pulsed-arc-type processes may be more effective. Hybrid gas−liquid systems may be especially useful for degrading gas- and liquid-phase pollutants simultaneously. Further work at both the laboratory scale and the pilot scale is necessary to fully evaluate the potential of these types of processes for water pollution control. It is vitally important to develop data for the comparison of the various processes under similar conditions of contaminant concentration, solution pH, and conductivity, as well as residence time and energy density.

The emphasis of this review has been on the basic chemical and physical aspects of water treatment with high-voltage electrical discharges. Several factors not covered in this review which are important for the eventual practical application involve such issues as the close coupling of the power supply and circuit network with the reactor and integration of the electrical discharge process with other treatment operations. The analysis and development of semiconductor switches for high-voltage, high-power applications are very important for pulsed discharge processes and are currently the subjects of investigation and development.[94,332,402−407] Coupling advanced oxidation processes with other processes such as biological treatment has been suggested as a cost-effective means to utilize the advanced oxidation method.[160,161,408] In such cases, the advanced oxidation method can degrade the target organic into byproducts that can easily be decomposed by other, less-energy-intensive, processes, such as biological treatment.

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