PLASMA FOR WATER TREATMENT

Miroslaw Dors
8.30 – 11.00

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The Szewalski Institute of Fluid-Flow Machinery
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Outline

• Plasma technologies for water cleaning
  – Plasma sources for water treatment
    • Types of electrical discharges used for water treatment
      – Discharges in gas
      – Discharges in water (electrohydraulic discharges)
    • Reactors
    • Diagnostics
  – Physics of electrohydraulic discharges

• Plasma processes in water cleaning technologies
  – Plasma processes and plasma-induced processes in destruction of organic compounds and microorganisms
    • Chemical reactions
    • Biocidal effects
    • Comparison to other water treatment technologies

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Plasma technologies for water cleaning

Different approach

Remote → Ozone

Indirect → UV, electron beam

Direct → Electrical discharges in water

Plasma injection → Electrical discharges above water

Plasma technologies for water treatment - Remote

Ozonation – fully commercialized method

- Ozone is generated in a Dielectric Barrier Discharge
- Absorption of ozone in water
- Used in drinking water plants
- Ballast water management

NK-O3 Blue Ballast System, USA/Korea

Plasma technologies for water treatment - Indirect

UV sources

- LP mercury vapor lamps
- Low-pressure high-output (LPHO) mercury vapor lamps
- MP mercury vapor lamps
- Electrode-less mercury vapor lamps
- Metal halide lamps
- Xenon lamps (pulsed UV)
- Eximer lamps
- UV lasers
- Light emitting diodes (LEDs)

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Efficiency means electrical to germicidal UV conversion

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Plasma technologies for water treatment - Indirect

UV irradiation - disadvantages

- Mackey et al. (2004)
- Linden et al. (2004)
- Chang et al. (1985)
Plasma technologies for water treatment - Indirect

UV irradiation – reactors and systems

ST110P system by SEN Lights Co., Japan

WEDECO UV Systems, USA

Plasma technologies for water treatment - Indirect

Electron beam

Thermal electron emission from filaments in vacuum then accelerated by a high electric field. Then through Ti or BN thin film by tunnel effects.


few cm depth water flow
Electrical discharges used for water treatment
Discharges in gas phase with liquid electrode – Plasma injection

- DC, AC or pulsed corona

- needle-to-plate
- hollow needle-to-plate
- mesh-to-plate
- multiple needle-to-plate
- wire-to-cylinder (water layer on the inner wall; pulsed corona only)
- wire-to-plate (pulsed corona only)
Electrical discharges used for water treatment

Discharges in gas phase with liquid electrode – pulsed corona

Wire-to-plate

Wire-to-cylinder

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Electrical discharges used for water treatment

Gliding Arc

Gas (air, O₂, N₂) flow: 10-12 L/min. AC supply: 250 W, 100 mA. Water: 400 mL for 5 min, pH=5.4, 40 μS/cm.
Electrical discharges used for water treatment

Direct liquid phase discharges – “electrohydraulic discharges”

- needle-to-plate
- hollow needle-to-plate (gas injected into water) (pulsed corona, pulsed spark discharge)
- pinhole (pulsed corona)
- needle-to-needle (pulsed arc discharge)

The reason why the breakdown mechanism in liquids is more complicated than solids and gases is evident:

- Liquids are much denser in comparison with gases and do not exhibit the long range order as in most solids.
- Additionally, the purity of the liquid, such as dissolved gases which form micro-bubbles in the liquid, plays a significant role in the breakdown process.

\[
V \geq \sqrt{\frac{DC_p \rho T_0^2}{\sigma_0 E_a}} \cdot \frac{L}{R_0}
\]

- \(V\) – breakdown voltage
- \(D\) – thermal diffusivity of water (ca. 1.5e-7 m²/s)
- \(C_p \rho\) – specific heat per unit volume
- \(T_0\) – temperature
- \(\sigma_0\) – water conductivity
- \(E_a\) – Arrhenius activation energy for the water conductivity
- \(L\) – breakdown channel length
- \(R_0\) – breakdown channel radius
Electrical discharges used for water treatment

Direct liquid phase discharges – pulsed corona and spark

- Inception voltage increases with protrusion length
- Discharge type changes when decreasing distance
- Streamer propagation velocity: 30 000 m/s (2 orders slower than in air)


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NEEDLE-PLATE REACTOR for DISCHARGE in WATER

Electrical field \( E \sim U/r_c \)

\( r_c \) – radius curvature of needle electrode

\( E_{\text{min}} = 1 \text{ MV/cm for } U=20 \text{ kV and } r_c<200 \mu \text{m} \)

Courtesy of Dr. P. Lukes. IPP, Prague
Electrical discharges used for water treatment

General physical properties

- A typical order of magnitude of the local electrical breakdown field of water is $1 \text{ MVcm}^{-1}$ (in the case of microsecond pulsed breakdown), which is more than 30 times the breakdown electrical field of atmospheric pressure air.

- For large pulse widths (i.e. several microseconds to dc), especially in high conductive water solutions, the process of breakdown is preceded by vapour formation due to heating by the pre-breakdown current in the liquid.

Historically, two principal schools:

- The first favours an electron multiplication theory in the liquid - In the past, it was often believed that a current multiplication mechanism such as the development of electron avalanches in gas discharges to initiate breakdown. It is interesting to note that electron avalanches have been observed in cyclohexane. Even more direct correlation between these avalanches and the consequent formation of vapour bubbles in the liquid has been demonstrated. However, electron avalanche processes in bulkwater are nearly negligible due to the usual small high electrical field region near the metal electrode and the large scattering cross sections which make it almost impossible for the electrons to gain sufficient kinetic energy for impact ionization. Additionally, free electrons are generally absent in water because even if they are present, they are quickly solvated within 1 ps time scales. Hence, the probability of free electrons in the bulk water is negligible, although one must be careful not to generalize ideas for different liquids and not to exclude electron avalanche processes without a good motivation.
The second school favours a **bubble mechanism breakdown theory** or more generally a phase change mechanism breakdown theory - a general acceptance is growing that pre-existing bubbles and field enhancement effects in the near electrode region are involved even for nanoseconds voltage pulse widths. Bubbles can pre-exist due to dissolved gases or can be generated by local heating (energy injection from the electrode by pre-breakdown currents) and cavitation.
Electrical discharges used for water treatment

Direct liquid phase discharges – pulsed corona and spark

Corona discharge

Spark discharge

Electrical discharges used for water treatment

Direct liquid phase discharges – pulsed corona – gas production

Vertical cross-section wide
Electrical discharges used for water treatment

Direct liquid phase discharges – pulsed corona – gas production

Electrical breakdown is generally defined as the moment when a conductive plasma channel forms an electrical connection between the two metal electrodes inside the liquid. This leads to the formation of a spark or arc. A time lag between application of the high voltage and breakdown is always observed.

This time lag consists of three successive steps:
• initiation phase or streamer inception,
• streamer propagation phase,
• spark and arc phase.
Electrical discharges used for water treatment
Streamer propagation mechanisms

Different streamer modes are observed depending on polarity of the powered electrode and the pulse width and amplitude of the applied voltage pulse.

- At first a bushlike hemispherical primary streamer (PS) can be observed showing 100–200 filaments.
- Then, a fast secondary streamer (SS) appears above a certain threshold voltage (which depends on the geometry of the setup) and can be considerably longer.

Electrical discharges used for water treatment
Discharges in liquid phase (needle-to-plate)
Pulsed corona discharge development

Events from pre-breakdown to post-discharge in pulsed corona in water
(distilled water, needle-plate, gap 40 mm, voltage 23 kV, pulse duration 10 us, current 5 A)

S. Kanazawa, Y. Ichihashi, S. Watanabe, S. Akamine, R. Ichiki, T. Ohkubo, T. Sato, M. Kocik, J. Mizeraczyk
IJ Plasma Environm. Sci. Techn., 2012)
Electrical discharges used for water treatment

Streamer propagation mechanisms

1. **Primary streamer (subsonic streamer):**
   - low electron density,
   - low temperature,
   - low pressure.
   - its propagation mechanism: series of current pulses and electron avalanches in successive vapour bubbles,
   - appear at low amplitude voltage pulses often filling a hemisphere with a size of a few hundred micrometres (at least for positive streamers) or have a bush-like shape (negative streamers have many short side branches and are shorter in length than positive streamers. Bubble production during the discharge is also much lower for negative voltages than for positive ones under the same conditions).
   - propagation velocity of $100 \text{ms}^{-1}$ to a few km s$^{-1}$

2. **Secondary streamer:**
   - high electron density,
   - high temperature,
   - high pressure,
   - its propagation mechanism: field induced dissociation and ionization of molecules in the bulk liquid,
   - propagation velocity in the range 10–100 km s$^{-1}$. 
Electrical discharges used for water treatment

Streamers propagation – current waveform

Zoom on the current waveform, (0) beginning of the applied voltage pulse, (1) initiation (or pre-initiation) current due to conductivity of water ~300 mA here, (2) current ramp of the plasma primary positive streamer ~50 mA, (3) current increase of the secondary positive streamer ~1 A, (4) reilluminations (7 μS cm⁻¹, 40 kV)


Current waveform in distilled water, (0) stray displacement current, (1) pre-initiation current due to water conductivity, (3) large pulse of the secondary positive mode followed by (4) reillumination spikes with decaying amplitude (4 cm gap, 40 kV)

Current waveform in 500 $\mu S \ cm^{-1}$ water, there are no reillumination spikes, (1) initiation current, (3) propagation, (4) decay; there is a large current even when the discharge has stopped propagating and just decays according to the voltage pulse decay (4 cm gap, 40 kV).


Electrical discharges used for water treatment

Direct liquid phase discharges – pulsed corona – conductivity

- In the pulsed corona the current is mostly transferred by ions.
- In water of high conductivity:
  - large current
  - faster compensation of space charge
  - streamer length shortening
  - higher power density in the channel
  - higher plasma temperature, UV and acoustic waves
Electrical discharges used for water treatment

Direct liquid phase discharges – pulsed corona – conductivity

1 μS/cm

200 μS/cm

600 μS/cm

FWHM = 36 μs (voltage pulse)

FWHM = 1.2 μs (voltage pulse)

FWHM = 0.8 μs (voltage pulse)

Effect of the solution conductivity on temporal evolution of the integral light emission from the discharge (U = 21 kV).
Hydrogen Balmer lines are responsible for the typical magenta or blue–red colour.

*P. Sunka, Plasma Sources Sci. Technol. 8 (1999) 258–265*

Role of ceramics: increasing the electrical field strength on the anode wire surface due to the redistribution of the field inside the interelectrode space during the prebreakdown stage, thus generating a larger number of discharge channels per pulse.

*P. Lukes, IEEE Trans. on Plasma Sci., 36 (4) 2008*
Electrical discharges used for water treatment

Direct liquid phase discharges – pulsed corona – wire-to-plate

A. Abou-Ghazala, IEEE Trans. on Plasma Sci., 30 (4) 2002

Electrical discharges used for water treatment

Direct liquid phase discharges with gas bubbles – pulsed corona

A.A. Joshi, J. Hazardous Mat., 41, 1995, 3-30
Electrical discharges used for water treatment

Direct liquid phase discharges with gas bubbles – pulsed corona


(a) w/o discharge  (b) 5-10 ns  (c) 15-20 ns  (d) 55-60 ns  (e) 150-155 ns  (f) 300-305 ns  (g) still photograph

I. Oxygen bubbles and discharge images

100–200 μS/cm

Electrical discharges used for water treatment

Direct liquid phase discharges with gas bubbles – RF discharge


quartz rod
quartz tube
outlet for water and bubbles
230°
25mm
80mm
inner electrode
outer electrode
13.56MHz
Ar gas water

imaginary cross sections of the discharge chamber and bubble
imaginary cross sections of the inner electrode
quartz tube
quartz rod
bubble
a widerange of gap distances
inner electrode
plasma in a bubble
outer electrode

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Electrical discharges used for water treatment

Direct liquid phase discharges with gas bubbles – microwave discharge

(a) Experimental setup

(b) bubble control plate


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Electrical discharges used for water treatment

Direct liquid phase discharges – pulsed arc

- In the pulsed corona the current is mostly transferred by electrons
- High current heats a small volume of plasma (quasi-thermal plasma)


Development of arc

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Electrical discharges used for water treatment

Direct liquid phase discharges – pulsed arc, pulsed spark, pulsed corona

Applied Voltage Effect at d = 0.3 mm

Courtesy of Prof. J.S. Chang
Electrical discharges used for water treatment

Direct liquid phase discharges – pulsed arc, pulsed spark, pulsed corona

Applied Voltage Effect at \( d = 5 \text{ mm} \)

150 V - corona

175 V - spark

200 V - arc

Courtesy of Prof. J.S. Chang

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Electrical discharges used for water treatment

Direct liquid phase discharges – pulsed arc – UV radiation

UV-A – 315-400 nm

UV-B – 280-315 nm

Courtesy of Prof. J.S. Chang

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Electrical discharges used for water treatment

Direct liquid phase discharges – pulsed arc – pressure wave

\[ \text{Ps} \quad \text{– shockwave} \]
\[ \text{Pe} \quad \text{– reflection wave} \]


Electrical discharges used for water treatment

Direct liquid phase discharges with gas bubbles – pulsed arc

1 – Quartz cylinder
2 – Al top and bottom
3 – Copper electrodes
4 – Quartz gas tubes
5 – Arc discharge
6 – Liquid
7 – Drain hole
8, 9 – Sampling tubes

Electrical discharges used for water treatment

Diaphragm discharge in water

Experimental conditions:

- High voltage: 1-3 kV
- Discharge current: 90-250 mA
- Input power: 90-300 W
- Solution: water + electrolyte (+ dye)
- Optimal solution conductivity: 100-1000 μS·cm⁻¹

Courtesy of Dr. P. Lukes

Electrical discharges used for water treatment

Hybrid reactors – combined discharges

Separate charging by two HV sources

Hybrid-series

Charging by one HV source

Hybrid-parallel
Electrical discharges used for water treatment

Hybrid-Series Gas-Liquid Electrical Discharge Reactor

Simultaneous formation of discharge in water and in the gas above water surface (gap~5 mm)

**HV:** DC pulsed power supply (positive polarity $U = 0-100$ kV, $C = 2 \text{nF}, f = 60 \text{ Hz}$)

**Liquid phase point electrode:** tungsten sharpened wire (curvature radius $\sim 100 \mu\text{m}$)

**Gas phase planar electrode:** Reticulated vitreous carbon (RVC) disk

**Summary**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pulsed corona</th>
<th>Pulsed arc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Repetition rate</td>
<td>$10^2-10^3$ Hz</td>
<td>$10^{-2}-10^{-3}$ Hz</td>
</tr>
<tr>
<td>Voltage pulse</td>
<td>$10-10^3$ kV</td>
<td>$1-10$ kV</td>
</tr>
<tr>
<td>Current pulse</td>
<td>$10^{-2}$ A</td>
<td>$10^3-10^4$ A</td>
</tr>
<tr>
<td>Voltage pulse rise time</td>
<td>$10^{-7}-10^{-9}$ s</td>
<td>$10^{-5}-10^{-6}$ s</td>
</tr>
<tr>
<td>Gap of cm</td>
<td>≈ 1 J</td>
<td>≈ 1 kJ</td>
</tr>
<tr>
<td>Electric field at electrode</td>
<td>$100-10 000$ kV/cm</td>
<td>$0.1 -10$ kV/cm</td>
</tr>
<tr>
<td>Current transfer</td>
<td>Ions</td>
<td>Electrons</td>
</tr>
</tbody>
</table>

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Electrical discharges used for water treatment

Summary

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<tr>
<th>Parameter</th>
<th>Pulsed corona</th>
<th>Pulsed arc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma nature</td>
<td>Non-thermal</td>
<td>Quasi-thermal</td>
</tr>
<tr>
<td>Shockwave</td>
<td>Week-moderate</td>
<td>Strong</td>
</tr>
<tr>
<td>UV</td>
<td>Week-moderate (conductivity dependence)</td>
<td>Strong</td>
</tr>
<tr>
<td>Heat production</td>
<td>Week</td>
<td>Strong</td>
</tr>
<tr>
<td>Conductivity influence</td>
<td>Strong</td>
<td>Week</td>
</tr>
<tr>
<td>Electrode erosion</td>
<td>Week</td>
<td>Strong</td>
</tr>
</tbody>
</table>

Plasma technologies for water treatment - Remote

Ozone reactions

\[ O_3 + OH^- \rightarrow O_3^- + OH^* \]
\[ O_3^- \rightarrow O^{**-} + O_2 \]
\[ O^{**-} + H_2O \Leftrightarrow HO^* + HO^- \]

Oxidation potential
Chemical processes induced in water

Removal of organic compounds – Electron beam

Project of a commercial plant (Austria), 1993:

- 20 kW accelerator (500 keV)
- with ozone (1kg/h)
- treating 108 m³/h of groundwater forming 3 mm layer in the reactor

- perchloroethylene (PCE): 61 µg/L => 1 µg/L
- using 200 J/L and ozone ≥ 6 mg/L

P. Gehringer, H. Eschweiler (2001)
Chemical processes induced in water

Processes induced by gas discharge to water surface

Formation of ozone and its dissolution in water
\[ \text{O}^3\text{P} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \]

Vaporization of water surface => formation of water vapor

Formation of OH radicals from ozone dissolved in water
\[ \text{O}_3 + \text{OH}^- \rightarrow \text{O}_3^- + \text{OH}^* \]
\[ \text{O}_3^- \rightarrow \text{O}^* + \text{O}_2 \]
\[ \text{O}^* + \text{H}_2\text{O} \Leftrightarrow \text{HO}^* + \text{HO}^- \]

Formation of OH radicals via electron impact dissociation of H_2O in vapor
\[ e^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+ + e^- \]

Formation of OH radicals via reaction of excited O atoms with H_2O in vapor
\[ \text{O}^{(1}\text{D}) + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{OH}^- \]

 Courtesy of Dr. P. Lukes

Chemical processes induced in water

Oxidative species from secondary reactions - diagnostics

- \[ \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2 \]
- \[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \]
- \[ \text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2 \]
- \[ \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \]
- \[ \text{HO}_2 + \text{H} \rightarrow \text{H}_2\text{O}_2 \]

- Direct measurements of produced long-lived chemical active species
  - simultaneous production of ozone decrease in the gas and H_2O_2 production in water

- Indirect measurements of short lived species (e.g. OH radicals) through chemical changes of model organic compounds in water
  - phenol and substituted phenols
Chemical processes induced in water
Diagnostics

- HPLC (High Performance Liquid Chromatography) - for organic compounds measurements,

- UV-VIS spectrometry - analysis in UV range and visible range of light for diagnostics of inorganic compounds, like O$_3$, H$_2$O$_2$ and OH radicals:
  - O$_3$ – iodometric method: O$_3$ + 2KJ + H$_2$O $\rightarrow$ J$_2$ + 2KOH + O$_2$ (give pink complex with N,N-dimethyl-p-phenylenediamine), $\lambda$=515 nm; or reaction with Indigo dye, $\lambda$=600 nm
  - H$_2$O$_2$ – reaction with titanyl ions: Ti$^{4+}$ + H$_2$O$_2$ + 2 H$_2$O $\rightarrow$ TiO$_2$.H$_2$O$_2$ + 4 H$^+$ (give yellow complex), $\lambda$=407 nm

- TOC analysis - which Total Organic Carbon analysis - for the measurement of the sum of organic compounds:
  - mineralization and measurement of produced CO$_2$ (e.g. IR measurement)

- Microbiological analysis – different for specific microorganisms.

Chemical processes induced in water
Diagnostics – OH radicals

- in plasma -> Optical Emission Spectroscopy (OES), $\lambda$=309 nm

- in water -> fluorescence:
  - with terephthalate, $\lambda$=426 nm (excitation at $\lambda$=312 nm)
  - with coumarin 3-carboxylic acid (CCA), $\lambda$=450 nm (excitation at $\lambda$=396 nm)
  - with benzoate, $\lambda$=350 nm (excitation at $\lambda$=300 nm)
  - with phenoxazinone, $\lambda$=585 nm (excitation at $\lambda$=570 nm)
  - with indoxyl-β-glucuronide (IBG)
Chemical processes induced in water

Gas phase discharge - oxidation reactions

\[ \text{O}_3 \Rightarrow \text{OH} \Rightarrow \text{Phenol} \]

**Diagram:**
- \( \text{O}_3 \) gaseous (ppm) vs. Processing time (min)
- \( \text{O}_3 \) aqueous (mM) vs. Processing time (min)

**Data:**
- \( \text{H}_2\text{O} \) vs. \( \text{H}_2\text{O} + \text{Phenol} \)

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Chemical processes induced in water

Oxidation reactions in water

**Diagram:**
- \( \text{H}_2\text{O}_2 \) (mM) vs. Processing time (min)
- Concentration (mM) vs. Processing time (min)

**Consumption of \( \text{OH} \):**
- Leads to decreased production of \( \text{H}_2\text{O}_2 \)

**Phenol:**
- Dihydroxyphenols (Catechol, Hydroquinone, Resorcinol)
- Organic acids

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**References:**

Chemical processes induced in water

Oxidation reactions – OH attack on Phenol ring

\[
\text{OH} \cdot \xrightarrow{\text{OH}^-} \text{HO}_2^- \xrightarrow{\text{O}_2} \text{HO}_2 \cdot \xrightarrow{\text{HCHD} \cdot} \text{Ring opened products}
\]

Chemical processes induced in water

Oxidation reactions – O₃ attack on Phenol ring

\[
\text{H}_2\text{O} \xrightarrow{\text{O}_2} \text{HO}_2 \cdot \xrightarrow{\text{HCHD} \cdot} \text{muconaldehyde} \quad \text{cis,cis-muconic acid}
\]

Courtesy of Dr. P. Lukes
Chemical processes induced in water

Hybrid gas-liquid discharge – influence of gas

Initial conditions: pH=3.6, $\sigma=100 \, \mu S/cm$


Chemical processes induced in water

Hybrid gas-liquid discharge – influence of gas

Argon atmosphere

- catechol
- hydroquinone
- 1,4-benzoquinone
- maleic acid

Oxygen atmosphere

- catechol
- hydroquinone
- 1,4-benzoquinone
- cis,cis-muconic acid
- cis,trans-muconic acid
- maleic acid

Courtesy of Dr. P. Lukes

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Chemical processes induced in water
Hybrid gas-liquid discharge – influence of pH

Hybrid-O\textsubscript{2} atmosphere

Hybrid-Ar atmosphere


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Chemical processes induced in water
Hybrid gas-liquid discharge – influence of pH

\[ \text{OH} \xrightleftharpoons{\text{OH}^-} \text{O}^- \]

\[ \text{pK} = 9.89 \]

\[ \text{O}^- + \text{O}_3 \rightarrow k_{\text{O}_3} = 1.3 \times 10^3 \text{ M}^{-1} \text{s}^{-1} \]

\[ \text{O}^- + \text{O}_3 \rightarrow k_{\text{O}_3} = 1.4 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \]

Courtesy of Dr. P. Lukes
Chemical processes induced in water

Hybrid gas-liquid discharge – additional source of OH

Peroxone $\text{O}_3/\text{H}_2\text{O}_2$ process

$$2 \text{O}_3 + \text{H}_2\text{O}_2 \rightarrow \text{pH} > 5 \rightarrow 2 \text{OH}^\cdot + 3 \text{O}_2$$

Production of additional OH radicals through decomposition of ozone by $\text{H}_2\text{O}_2$ at high pH

Courtesy of Dr. P. Lukes

Chemical processes induced in water

Liquid phase discharge – no O$_3$

Scheme 1. Chemical reactions in the discharge channel.

$\text{H}_2\text{O} + \text{M} \rightarrow \text{H} + \text{OH} + \text{M}.$
$\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}.$
$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2.$
$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}.$
$\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}.$
Chemical processes induced in water

Liquid phase discharge – no O₃

- OH as the only oxidative species
- dependence on the conductivity

\[
\frac{d[H_2O_2]}{dt} = \text{production (zero-order reaction)} - \text{decomposition (photolysis - thermolysis)}
\]

M. Dors, Int. J. Plasma Env. Sci. Techn., 1 (2007) 76-81,

Chemical processes induced in water

Liquid phase discharge – Phenol oxidation

Enhancement by Fenton reaction:

\[
Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH
\]

M. Dors, Int. J. Plasma Env. Sci. Techn., 1 (2007) 76-81,
Chemical processes induced in water

Removal of organic compounds – Pulsed Arc Electrohydraulic Discharge

Reduction of TOC in Sludge-Water (d = 0.5mm, V = 1-2.2kV)

![Graph showing TOC concentration over PAED treatment time for different water samples.](Image)

TOC concentration (mg/L) vs. PAED treatment time (min).

- Sludge-water
- Pond surface water
- Pond bottom water with 33g/L sediment
- Pond bottom water with 100g/L sediment

Courtesy of Prof. J.S. Chang

Chemical processes induced in water

Removal of organic compounds – Pulsed Arc Electrohydraulic Discharge

Generations of gaseous by-products (CO, CO₂, CₓHᵧ, SO₂ and H₂S) (sludge-water, Initial TOC = 120mg/L)

- [CO]
- [CO₂]
- [CₓHᵧ]
- [SO₂]
- [H₂S]

Accumulated CO, CO₂, and CₓHᵧ (mg/L) vs. treatment time (min).

Accumulated SO₂ and H₂S (mg/L) vs. treatment time (min).

d = 0.5mm, V = 1kV

Courtesy of Prof. J.S. Chang
Removal of organic compounds – Pulsed Arc Electrohydraulic Discharge

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Change in Water Quality (Dissolved Oxygen)

Dissolved oxygen concentration (mg/L)

PAED treatment time (min)

Pond water
Pond water with 33g/L sediment

Change in Water Quality (pH)

pH

PAED treatment time (min)

Pondwater
Pondwater with 33g/L sediment
Pondwater with 100g/L sediment

Courtesy of Prof. J.S. Chang
Chemical processes induced in water
Removal of organic compounds – Pulsed Arc Electrohydraulic Discharge

Organic compounds decomposition

- phenols
- trichloroethylene
- polychlorinated biphenyl
- perchloroethylene
- pentachlorophenol
- acetophenone
- organic dyes (such as methylene blue)
- aniline
- anthraquinone
- monochlorophenols
- methyl tert-butyl ether (MTBE)
- benzene
- toluene
- ethyl benzene (BTEX)
- 2,4,6-trinitrotoluene
- 4-chlorophenol
- 3,4-dichloroaniline

Change in Water Quality (Conductivity)

PAED treatment time (min)

Conductivity (mS/m)

- Pond water
- Pond water with 33g/L sediment
- Pond water with 100g/L sediment
- Sludge-water

Courtesy of Prof. J.S. Chang
**Biocidal effects**

Disinfection mechanisms – UV irradiation

- 240 to 280 nm - damaging nucleic acids of microorganisms

![UV irradiation diagram](image)

(Tchobanoglous, 1997)

**HOWEVER,**

Under certain conditions, some organisms are capable of repairing damaged DNA and reverting back to an active state in which reproduction is again possible – “Dark repair mechanisms”

---

**Biocidal effects**

UV irradiation – requirements for disinfection

<table>
<thead>
<tr>
<th>Surface Water Treatment Rules – Minimum Treatment Requirements¹</th>
<th>Giardia</th>
<th>Virus</th>
<th>Cryptosporidium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regulation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>US EPA Long Term 2 Enhanced Surface Water Treatment Rule</td>
<td>3-log removal (99.9%)</td>
<td>4-log removal (99.99%)</td>
<td>2.5-log additional treatment for filtered systems</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3-log additional treatment for unfiltered systems</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>UV Dose Requirements (mJ/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target pathogens</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Cryptosporidium</td>
</tr>
<tr>
<td>Giardia</td>
</tr>
<tr>
<td>Virus</td>
</tr>
</tbody>
</table>

most viruses can be easily inactivated with chlorine so UV disinfection for virus inactivation may not be necessary
Biocidal effect of electrohydraulic discharges

<table>
<thead>
<tr>
<th>Spark/Arc</th>
<th>Corona</th>
<th>Ozonation</th>
<th>Fenton</th>
<th>Peroxone</th>
</tr>
</thead>
<tbody>
<tr>
<td>• OH, HO_2, H_2O_2&lt;br&gt;• UV irradiation&lt;br&gt;• shock wave&lt;br&gt;• heat</td>
<td>• OH, HO_2, H_2O_2, O_3&lt;br&gt;• UV irradiation</td>
<td>• O_3&lt;br&gt;• OH</td>
<td>• OH</td>
<td>• OH&lt;br&gt;• O_3</td>
</tr>
</tbody>
</table>

\[ \text{O}_3 + \text{OH}^\cdot \rightarrow \text{O}_3^\cdot + \text{OH}^+ \]

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^+ + \text{OH}^- \]

\[ 2 \text{O}_3 + \text{H}_2\text{O}_2 \rightarrow 2 \text{OH}^+ + 3 \text{O}_2 \]

Combined plasmachemical inactivation of bacteria in water

Inactivation mechanisms is complex – both chemical and physical effects play role

![Graph showing energy input vs. survival ratio](image)

* Courtesy of Dr. P. Lukes
Biocidal effect of electrohydraulic discharges
River water disinfection - number of microorganisms

Microorganisms grown in 22°C

Microorganisms grown in 36°C


Prof. Mirosław Dors, mdors@imp.gda.pl

Biocidal effect of electrohydraulic discharges
River water disinfection - number of microorganisms

E. coli
Total coli


Prof. Mirosław Dors, mdors@imp.gda.pl
Biocidal effect of electrohydraulic discharges

Disinfection mechanisms – O₃ and OH action

➢ Bacteria
  • destruction of bacterial membrane through alteration of:
    - glycoproteins or glycolipids (Scott and Lesher, 1963)
    - certain amino acids such as tryptophan (Goldstein and McDonagh, 1975)
  • disruption of enzymatic activity of bacteria by acting on the sulfhydryl groups of certain enzymes (Giese and Christensen, 1954)
  • affection of both purines and pyrimidines in nucleic acids (Scott and Lesher, 1963)

➢ Virus
  • modification of the viral capsid sites that the virion uses to fix on the cell surfaces. High concentrations of ozone dissociate the capsid completely (Cronholm et al., 1976 and Riesser et al., 1976)

➢ Protozoa
  • modifications in the oocyst structure ...

Biocidal effect of electrohydraulic discharges

Principal known disinfection byproducts

➢ Aldehydes
  • Formaldehyde
  • Acetaldehyde
  • Glyoxal
  • Methyl glyoxal

➢ Acids
  • Oxalic acid
  • Succinic acid
  • Formic Acic
  • Acetic acid

➢ Aldo- and Ketoacids
  • Pyruvic acid
Biocidal effect of electrohydraulic discharges

Pulsed Arc Electrohydraulic Discharge

\[ E. \text{coli inactivation} \]

\[ \begin{align*}
V &= 4 \text{kV} \\
\text{PAED}: 5 \text{ sec/pulse, 100 pulse} &= 9\text{ min} \\
\text{Accumulative energy for 100 pulses for high conductivity water} &= 2.8 \text{ kWh/m3} \\
\text{Accumulative energy for 100, 300, 400, 500 pulses for low conductivity water} &= 6.3, 19, 25.3 \text{ and } 31.6 \text{ kWh/m3}
\end{align*} \]

\[ \text{Courtesy of Prof. J.S. Chang} \]

Prof. Mirosław Dors, mdors@imp.gda.pl

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Biocidal effect of electrohydraulic discharges

Pulsed Arc Electrohydraulic Discharge

\[ \text{Bacillus subtilis inactivation} \]

\[ \begin{align*}
V &= 4 \text{kV} \\
\text{PAED}: 5 \text{ sec/pulse, 100 pulse} &= 9\text{ min} \\
\text{Accumulative energy for 100 pulses for high conductivity water} &= 2.8 \text{ kWh/m3} \\
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\end{align*} \]

\[ \text{Courtesy of Prof. J.S. Chang} \]

Prof. Mirosław Dors, mdors@imp.gda.pl
Biocidal effect of electrohydraulic discharges
Pulsed arc in the sea water – removal of algae and mussels

Before

After

Courtesy of Prof. J.S. Chang

Biocidal effect of electrohydraulic discharges
Pulsed Arc Electrohydraulic Discharge

Mortality of Zooplankton (Lake Ballast Water, 30 animals/L, V=2.3kV, d =0.5mm)

Time after PAED treatment (hrs)

Mortality (%) 120

100

80

60

40

20

0

Lake Ballast Water 1 with 10 minutes treatment
Lake Ballast Water 1 with 2 pulsed treatment
Lake Ballast water 1 for control
Lake Ballast Water 2 with 10 minutes treatment

1mm

Courtesy of Prof. J.S. Chang
Biocidal effect of electrohydraulic discharges

Pulsed arc in the sea water – disinfection, pilot station

Regional Municipality of Waterloo’s Mannheim
Drinking Water Treatment Plant, Canada – Pulsed arc discharge in water
- 50 L/s
- *E. coli*
- *B. subtilis*
- Natural Organic Matter
- MTBE

---

**Comparison to other water treatment technologies**

Table 5. Comparison of water purification processes

<table>
<thead>
<tr>
<th>Physical</th>
<th>Chemical</th>
<th>Mechanical</th>
<th>Biological</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV-C</td>
<td>ClO₂</td>
<td>O₂ / H₂O₂</td>
<td>Sand/gravel</td>
</tr>
</tbody>
</table>

- Strength against micro-organisms
- Oxidation power
- Removal of inorganic pollutants
- Removal of algae
- Destruction of urine components (NH₃)
- Destruction of phenols

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>No modification of flavour, no bacteria resistant to it, relatively simple, cheap</td>
<td>No oxidation or lasting effect; control difficult; efficiency dependent on amount of water pollution etc.</td>
<td>Drinking water for biological swimming pools; aquariums; cooling water; water supply; spa water; brewery water; laboratory water</td>
</tr>
<tr>
<td>Simple process easily controlled lasting effect germicidal action in associated piping</td>
<td>CH₃NH₂ gives an unpleasant smell; bacteria become partially resistant; allergic reactions possible; check of pH value necessary; exact dosage of chlorine necessary</td>
<td>Drinking water; swimming pools</td>
</tr>
</tbody>
</table>

---

*Courtesy of Prof. J.S. Chang*
# Comparison to other water treatment technologies

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Optical</th>
<th>Radiolysis</th>
<th>Gas Discharges</th>
<th>Electrohydraulic Discharges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone</td>
<td>Cl/ClO₂</td>
<td>UV-C</td>
<td>UV-Photocatalyst</td>
<td>E-beam</td>
</tr>
<tr>
<td>Micro-organisms</td>
<td>♦</td>
<td>O</td>
<td>♦</td>
<td>Δ</td>
</tr>
<tr>
<td>Oxidation Power</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>Algae Destruction</td>
<td>Δ</td>
<td>X</td>
<td>O</td>
<td>X</td>
</tr>
<tr>
<td>Urine Components Destruction</td>
<td>♦</td>
<td>O</td>
<td>X</td>
<td>O</td>
</tr>
<tr>
<td>VOCs Destruction</td>
<td>O</td>
<td>X</td>
<td>X</td>
<td>O</td>
</tr>
<tr>
<td>Removal of Inorganics</td>
<td>Δ</td>
<td>X</td>
<td>X</td>
<td>Δ</td>
</tr>
</tbody>
</table>

*Courtesy of Prof. J.S. Chang*

## Summary

**Energy efficiency of plasma in water cleaning**

<table>
<thead>
<tr>
<th>Relative energy efficiency</th>
<th>0.07: OGE</th>
<th>1: PCD in water, PCD in air 0.9mm above water, CGDE, AC-GlidArc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.7: DD</td>
<td>AC-GlidArc AC gliding arc discharges, Ar argon, Co initial concentration of dye in treat-water, CGDE contact glow discharge electrolysis, DD diaphragm discharges, GDE glow discharge electrolysis, G50 energy yield at 50% conversion, HS-PCD hybrid-series pulsed corona discharges, MWD microwave discharges, DBD dielectric barrier discharges, DC direct current, O₂ oxygen, O₃ ozone, PCD pulsed corona discharges, RDF radio-frequency discharges, RT refers to the number of row from which values of ‘REEr’ and ‘G50r’ are taken to calculate ‘REE’, REE relative energy efficiency, SD spark discharges, SSD streamer and spark discharges, UV ultraviolet radiations</td>
</tr>
<tr>
<td>100</td>
<td>1: PCD in water, PCD in air 0.9mm above water, CGDE, AC-GlidArc.</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>0.07: OGE</td>
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</tr>
<tr>
<td>2000</td>
<td>1: PCD in water, PCD in air 0.9mm above water, CGDE, AC-GlidArc.</td>
<td></td>
</tr>
</tbody>
</table>

*Prof. Mirosław Dors, mdors@imp.gda.pl*
Drinking water treatment plant

Can plasma substitute several conventional methods?
**Alien marine invasive species**

- **Comb Jelly**
- **Mnemiopsis**
- **Northern Pacific Seastar**
- **European Zebra Mussel**
- **Green Algae**
- **Round Goby**
- **European Shore Crab**

**Biological invasions of the world water ecosystem**

*Mnemiopsis* species invading the Caspian Sea
(introduced from ship ballast water)
75% of the zooplankton was depleted
Collapse of entire fisheries
Depletion of sturgeon

Crabs invading water ecosystem
Biological invasions of the world water ecosystem

Huge blooms of toxic algea contaminate shellfish causing thousands of deaths

Once the species has invaded, nothing can be done about it
The introduction of invasive marine species into new environments by ship ballast water is one of the four greatest threats to the oceans (Global Environment Facility (GEF)).

- 85 thousand vessels are transferring 10 billion tons of ballast water per year.
- About 110 million plankton specimens are carried in 1 m$^3$ of ballast water.
- At least 7,000 different species per day are being carried in ship ballast tanks around the world.

Courtesy of Prof. M. Bai, DMU, China

Ballast water management

**Mechanical and chemical treatment**

Diagram of Ballast Water Management System

- During water intake:
  - Plankton (living), Multi-Sand Bacteria (one portion)
  - Delantrol drain
  - Chemical feed unit

- During water discharge:
  - Clean sea water exceeding emissions standards
  - Filtration unit

**Ozone treatment**

- Air compressor
- $O_2$ enrichment
- $O_3$ generator
- Ballast tank

Ballast Water Management System
Kuraray Co., Ltd, 2009 http://www.kuraray.co.jp

NK-O3 Blue Ballast System
USA/Korea

Huge equipment, $O_3$ – high-energy consumption, dosage 10 mg/L
Other applications
As a source of seismic waves – sea bed mapping

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• An W, Baumung K and Bluhm H 2007 Underwater streamer propagation analyzed from detailed measurements of pressure release J. Appl. Phys. 101 053302


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