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Was können Plasmen im Wasser besser?

Wirkmechanismen von Entladungsplasmen in Trink- und Abwässern

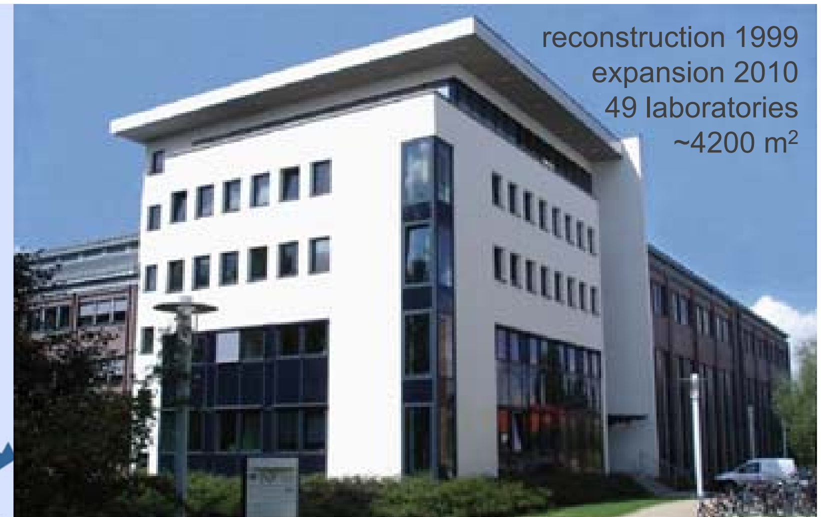
Innovationsforum „Plasma plus Umwelt“
Rostock-Warnemünde, 22.-23. März 2012

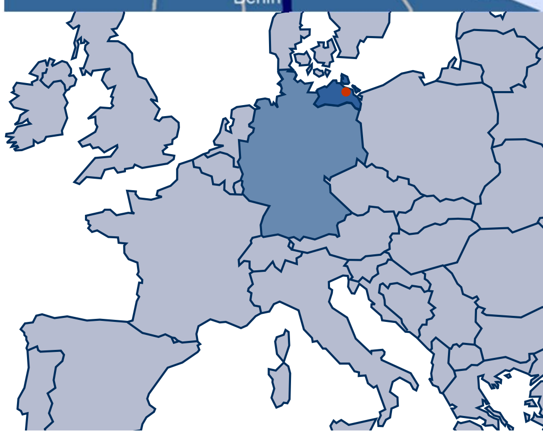
INP Greifswald

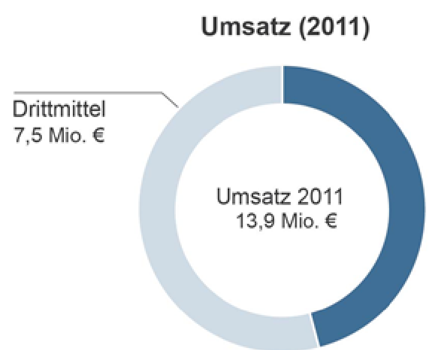
Leibniz Gemeinschaft

VON DER IDEE BIS ZUM PROTOTYP

INP Greifswald in Numbers







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Research Divisions

& OBERFLÄCHEN MATERIALIEN

& UMWELT ENERGIE

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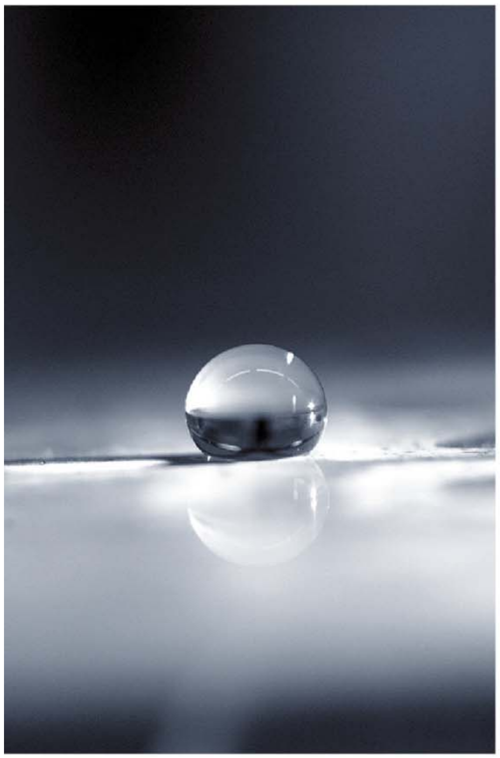
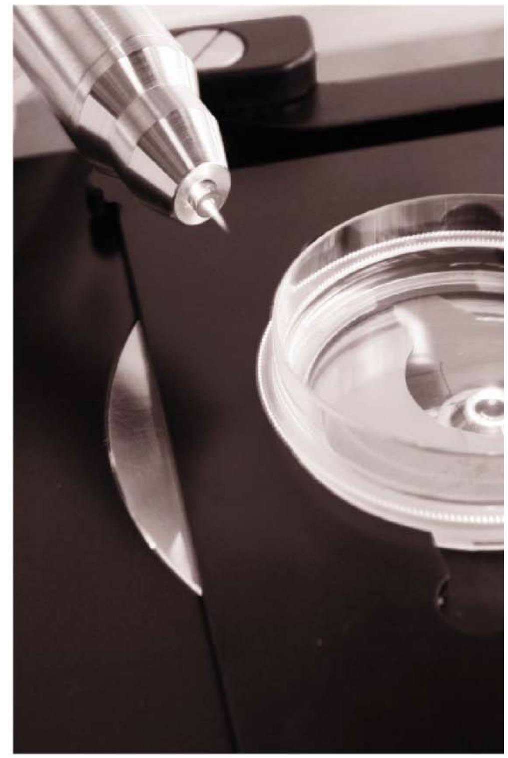
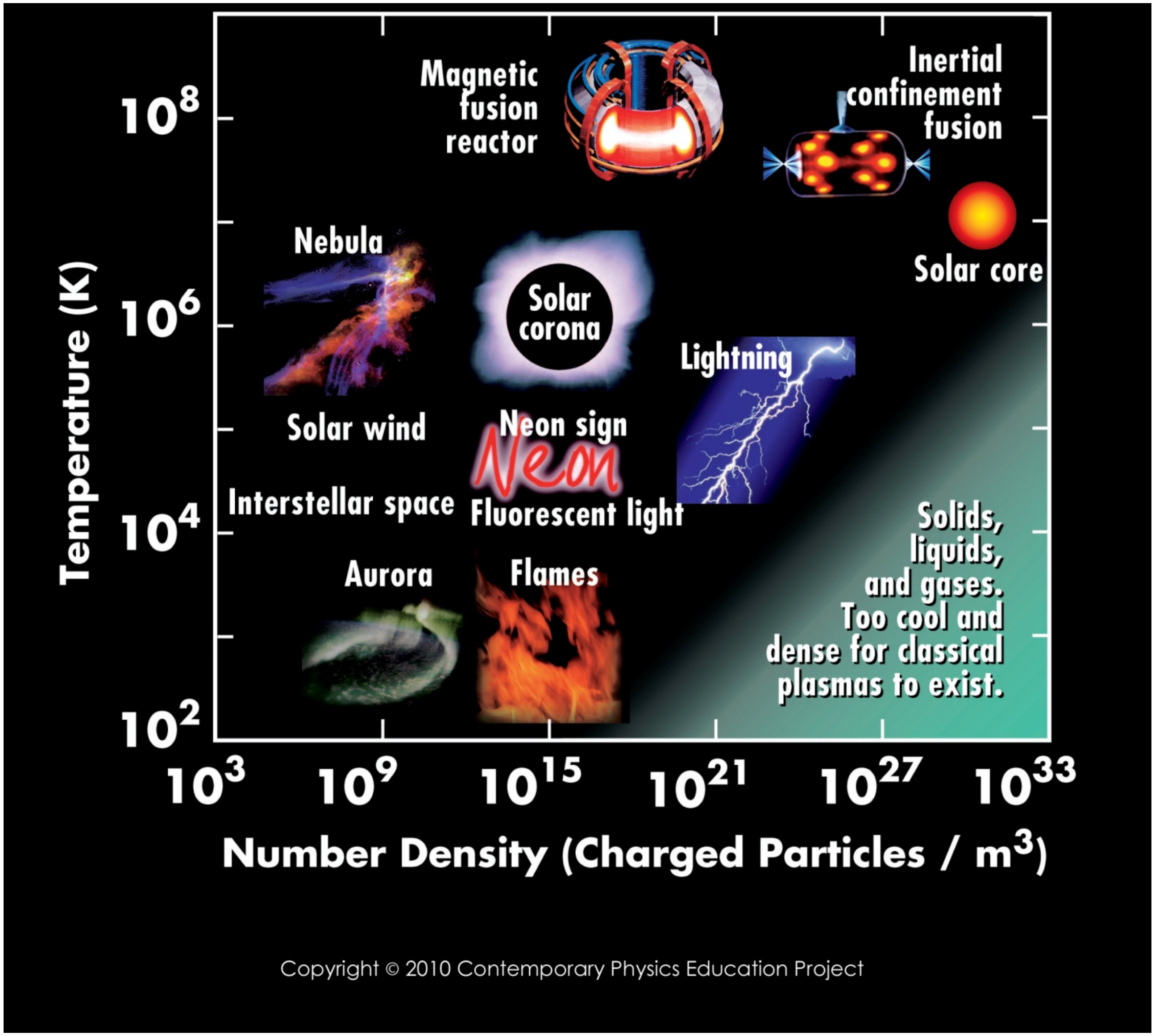


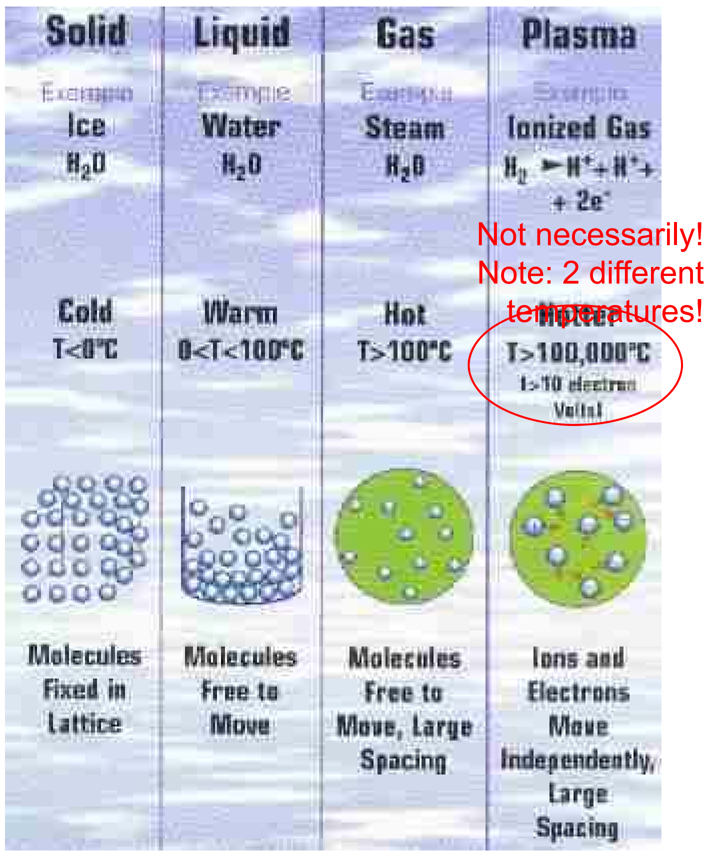


“Our World is Plasma”

Plasma – "The 4th State of Matter"



Plasma – “The 4th State of Matter”



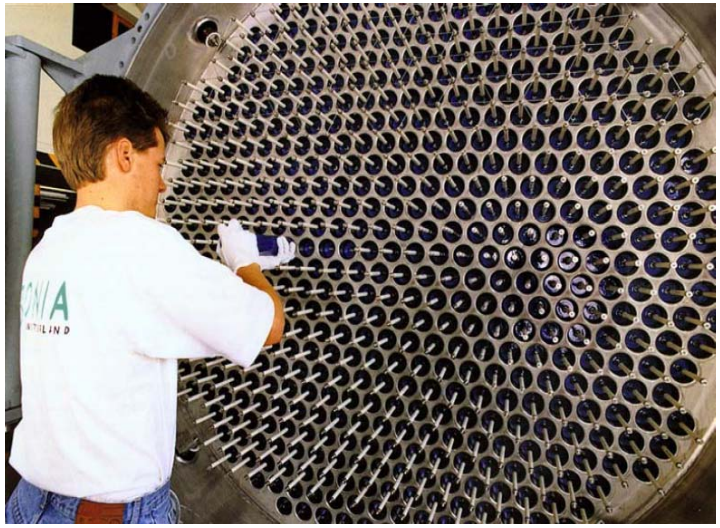
www.yksd.com/distanceedcourses/Courses/PhysicalScience/Lessons/ThirdQuarter/Chapter09/09-02.html

Energy provided leads to the controlled loss of the cohesion of matter, associated with the break of molecular bonds, and ionization of molecules and atoms. (In technical used plasmas the energy is provided by electrical means.)

The result is a **highly reactive** gaseous phase, which is characterized by the density of constituents (electrons, ions, excited molecules and atoms) and their respective energy, i.e. temperature.

A **Non-thermal plasma** is characterized by a hot electron gas of several thousand degrees moving in between cold, i.e. close to room temperature, heavier particles. (Accordingly are reaction kinetics primarily determined by electrons.)

Ozonation of Water

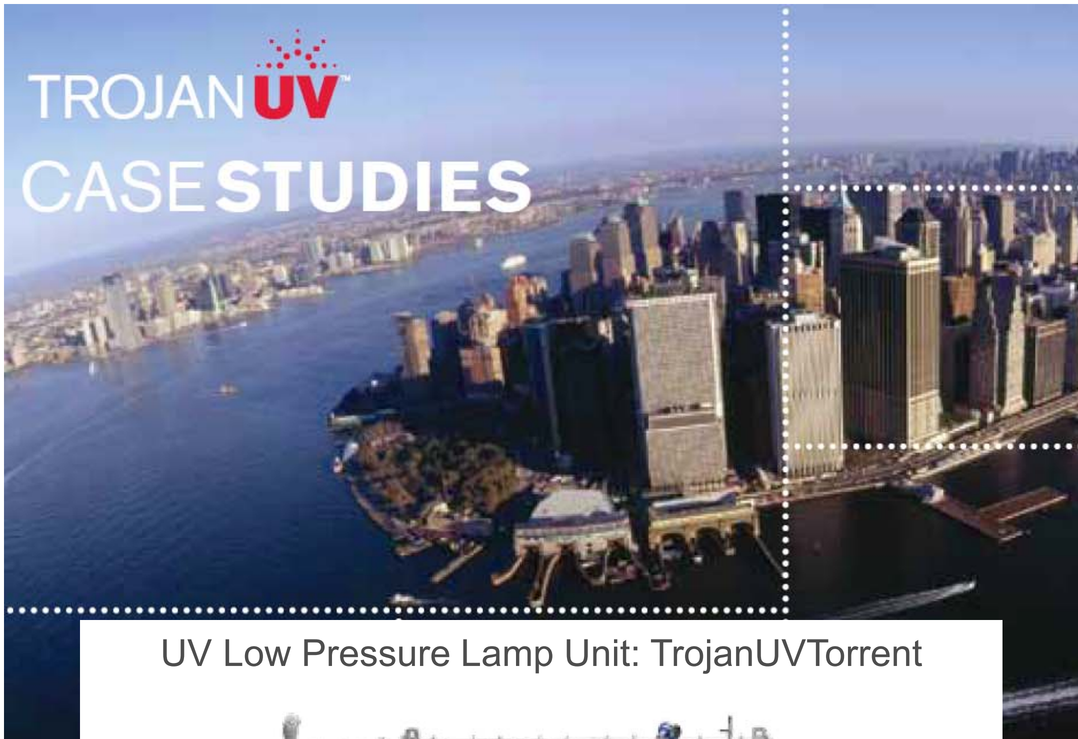


Ozonation is the oldest plasma based technology for the treatment of water (Werner von Siemens 1857).

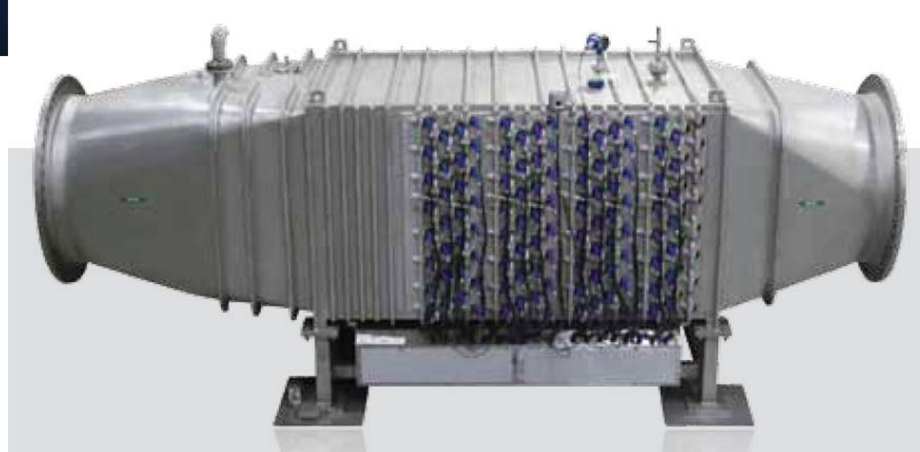
Ozone-Generator
(Ozonia AG, Zürich)

Ozonation Facility
(Wasserwerk Rostock, installed 1995)

UV-Treatment of Trinking Water



UV Low Pressure Lamp Unit: TrojanUVTorrent



THE TROJAN SOLUTION

When completed in 2012, NYC will operate the largest drinking water UV installation in the world – the Catskill/Delaware UV Facility – with a capacity to treat 2.24 billion gallons per day (BGD). Combined, the Catskill/Delaware and Croton water plants will supply residents of NYC with over 2.8 BGD of high quality drinking water.

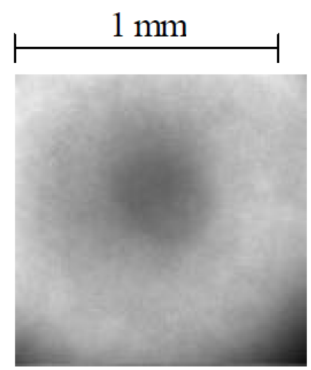
SYSTEM DESIGN PARAMETERS

- CATSKILL/DELAWARE UV SYSTEM PEAK FLOW CAPACITY: 2.24 billion gallons per day
- CROTON UV SYSTEM PEAK FLOW CAPACITY: 600 million gallons per day
- TOTAL FLOW: >2.8 billion gallons per day
- DISINFECTION REQUIREMENT: Minimum dose of 40 mJ/cm^2
- TARGET REDUCTION OF CRYPTOSPORIDIUM: 3-log
- NUMBER OF UV UNITS: 56 Units (Catskill/Delaware), 20 Units (Croton)

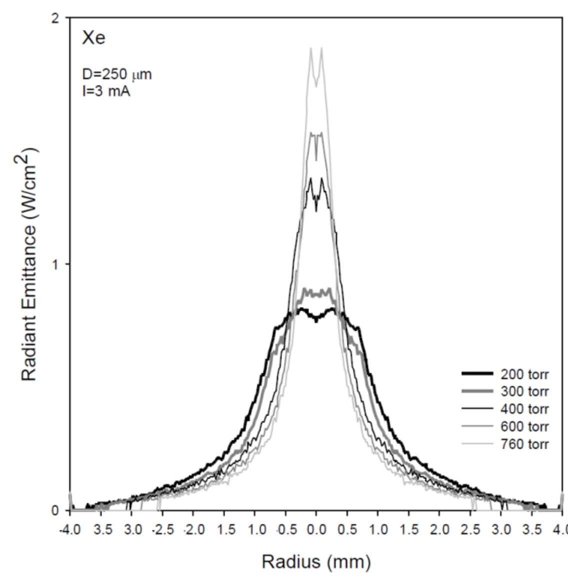
UV-Treatment of Water

UV Low Pressure Lamp Unit: TrojanUV

Microhollow Cathode Discharges
as uv (excimer) lamps of high emittance

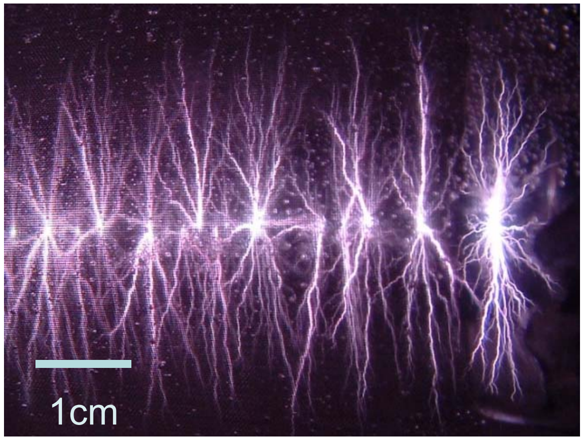


Xenon-Emission (175 nm)



Plasmas with Water: Examples

Pulsed Corona in Water

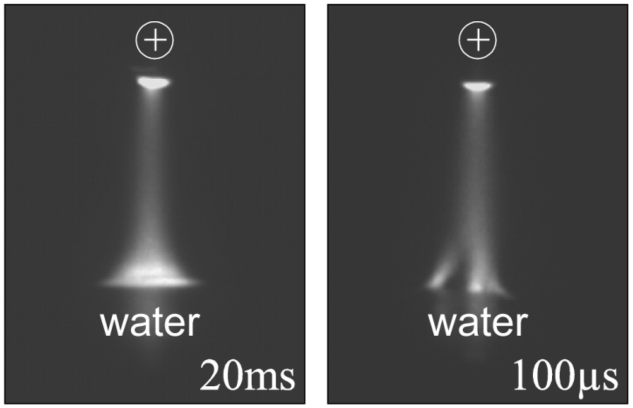


Plasma Jet Expelled into Water

Arc Discharge in Water

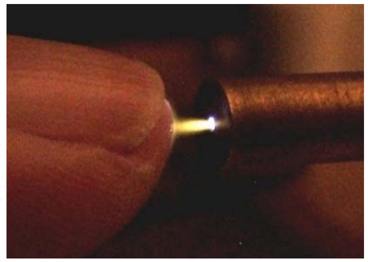
www.eng.tau.ac.il/research/laboratories/ed
p_lab/photogal_files/photogal.htm

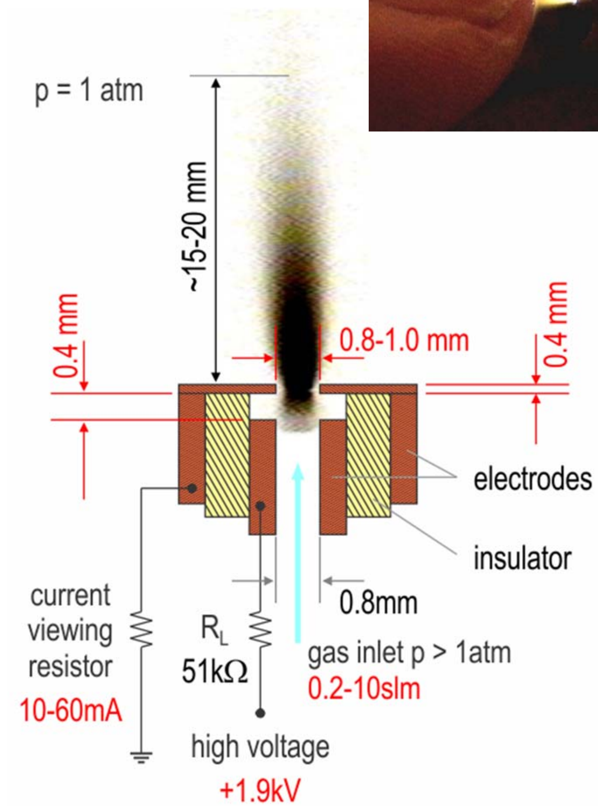
Glow Discharge on Water Surface



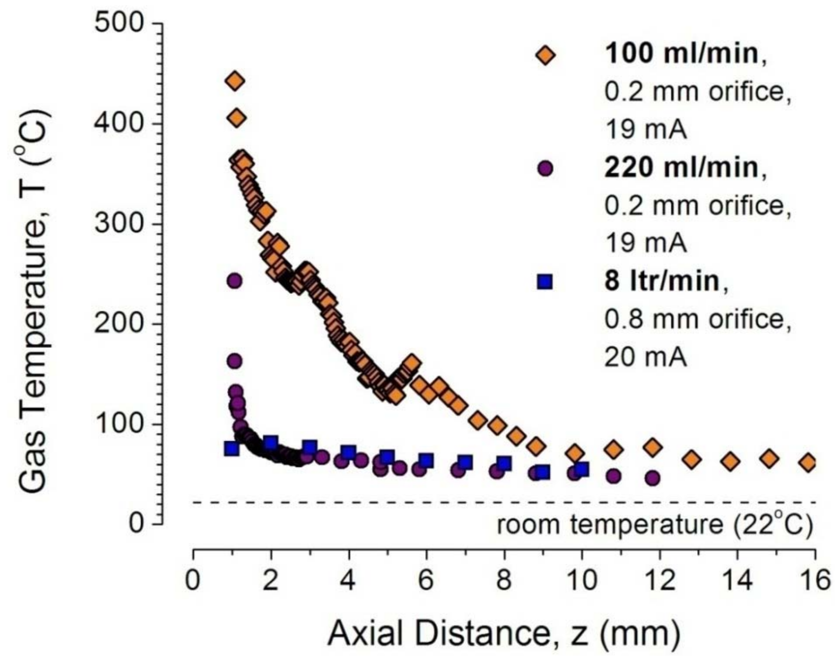
P. Bruggeman et al., J. Phys. D: Appl. Phys. 41 (2008) 215201.

Atmospheric Pressure Air Plasma Jet



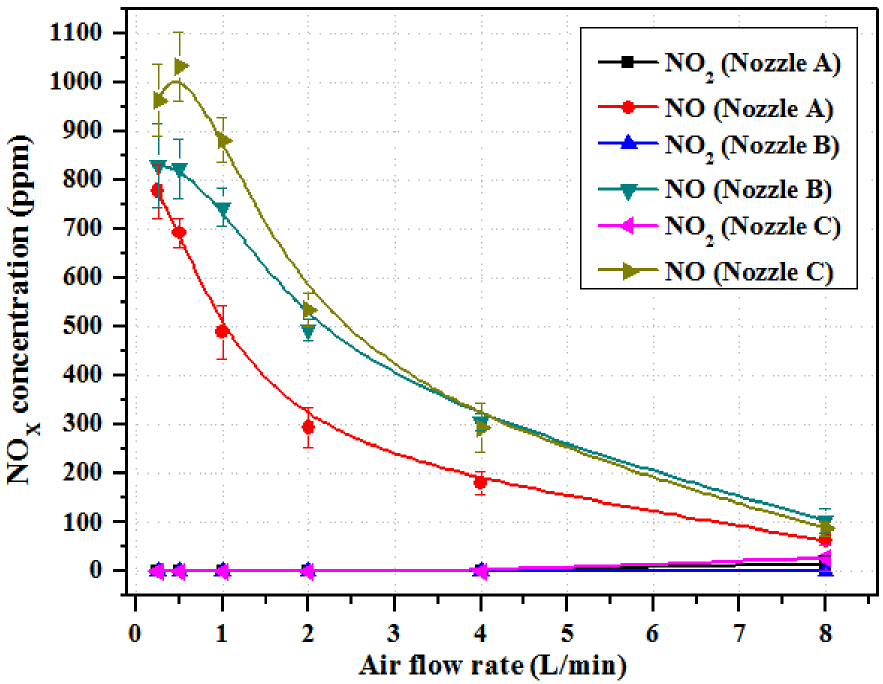


- operated with any gas or gas mixture
- adjustable afterglow temperature (and chemistry)

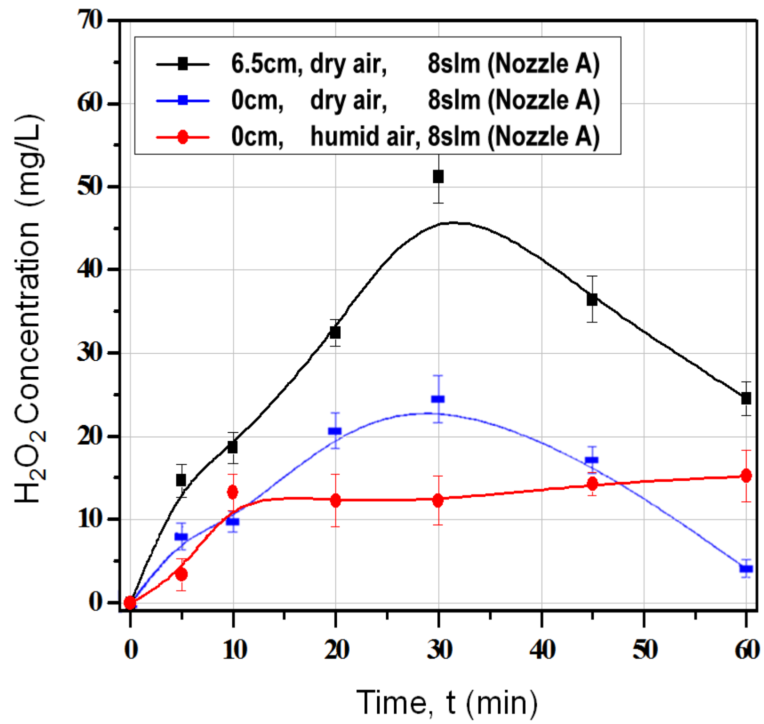


Atmospheric Pressure Air Plasma Jet

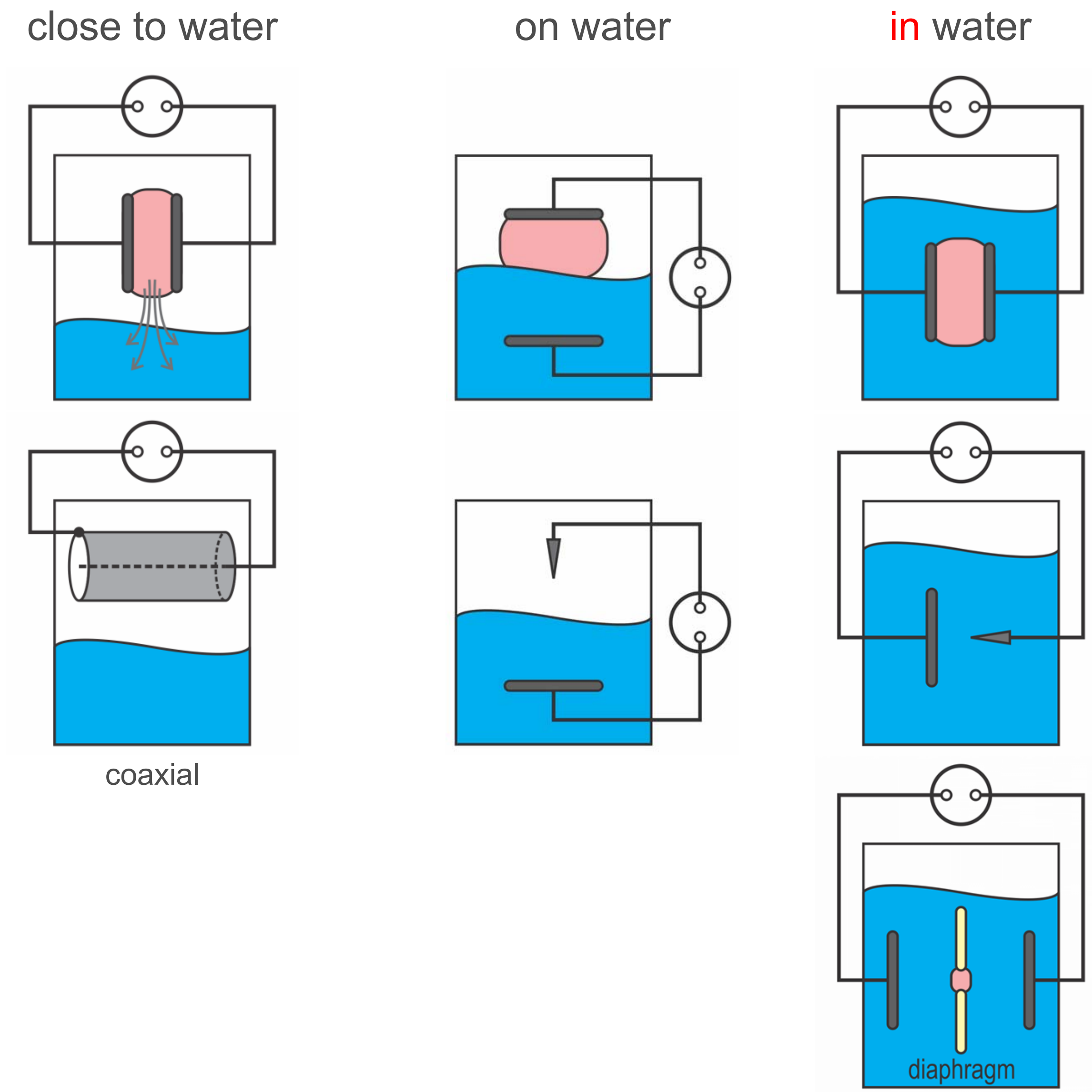
NO_x Concentration Depending on Flow Rate and Nozzle Geometry



H_2O_2 Concentration in Water Depending on Ambient Conditions



Plasmas with Water: Generation



Plasmas in Water: Processes

Strong electric fields are applied to generate

- pulsed arc discharges (energy: ~1J/pulse, operating frequency: 10-1000Hz); or
- pulsed corona discharges (energy: ~1kJ/pulse, operating freq.: 0.001-1Hz).

Physical processes:

- bubble formation;
- possible development of supercritical fluid conditions;
- localized regions of high temperature and pressure;
- formation of shock and acoustic waves;
- emission of uv light.

Chemical processes:

- generation of hydrogen peroxide (H_2O_2);
- molecular oxygen and hydrogen;
- hydroxyl (OH) and hydroperoxyl (HO_2);
- ozone (O3) and other radicals.

All Reaction Mechanisms can be utilized simultaneously against chemical and biological contaminations!

Plasmas in Water: Demonstrated Applications

- degradation of organic compounds including phenols, trichloroethylene, polychlorinated biphenol, perchloroethylene, pentachlorophenol, acetophenone, organic dyes (methylene blue), aniline, anthraquinone, monochlorophenols, methyl *tert*-butyl ether, benzene, toluene, ethyl benzene, 2,4,6-trinitrotoluene, 4-chlorophenol, 3,4-dichloroaniline;
- oxidation of inorganic ions including iodides, bromides, sulfides, manganese (Mn^{2+}), chromium (Cr^{2+}), arsenic (As^{3+});
- Combinations of activated carbon with ozone treatment and hydrogen peroxide led to possibilities of synergistic catalytic reactions and continuous carbon regeneration

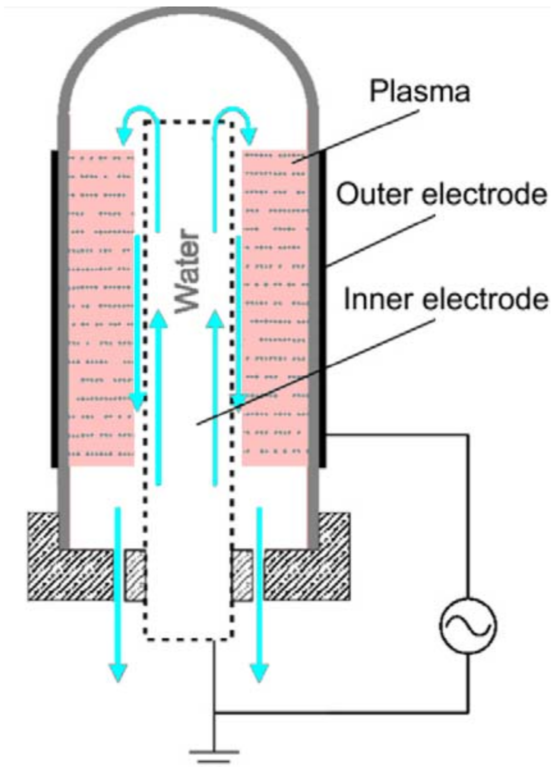
  (catalysts, including TiO_2, alumina, and zeolites have also been investigated);
- chemical synthesis of a range of organic compounds, hydrocarbons, polymers, nanomaterials;

- inactivation and destruction of viruses, yeasts and bacteria, including *E.coli*, *S.aureus, P.aeruginosa*

  (Note: effect on microorganisms associated with strong electric field);
- prevention of biofilms on cooling and drinking water pipes.

Removal of Arsenic from Ground Water

Comparison of pre-treatment with ozone and plasma



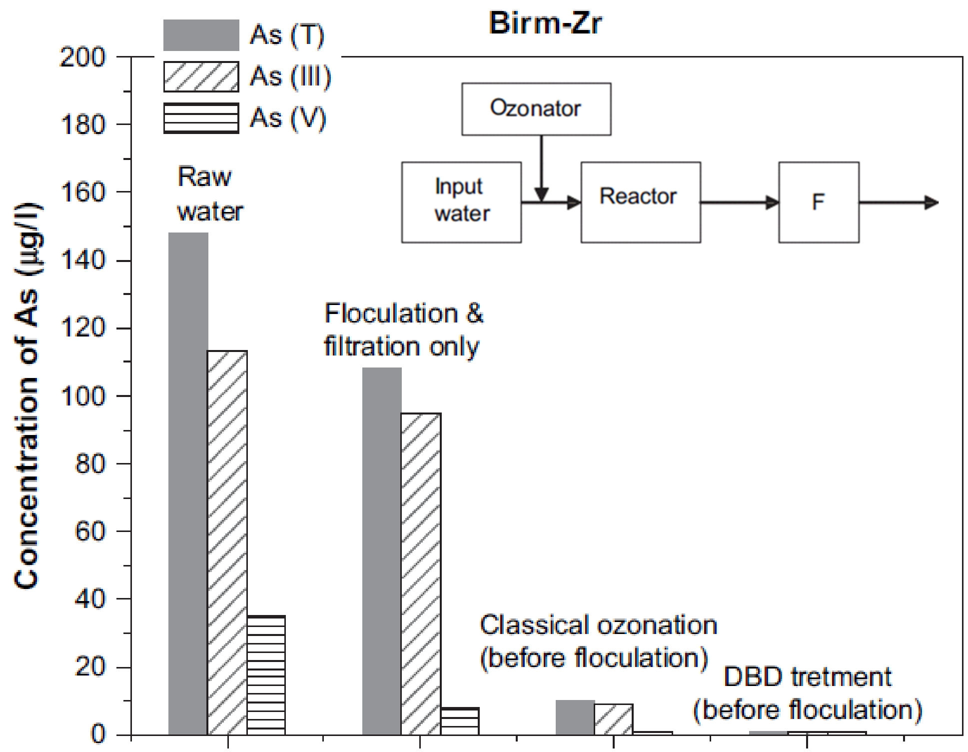


Fig. 4. Arsenic treatments with Birm® sorption.

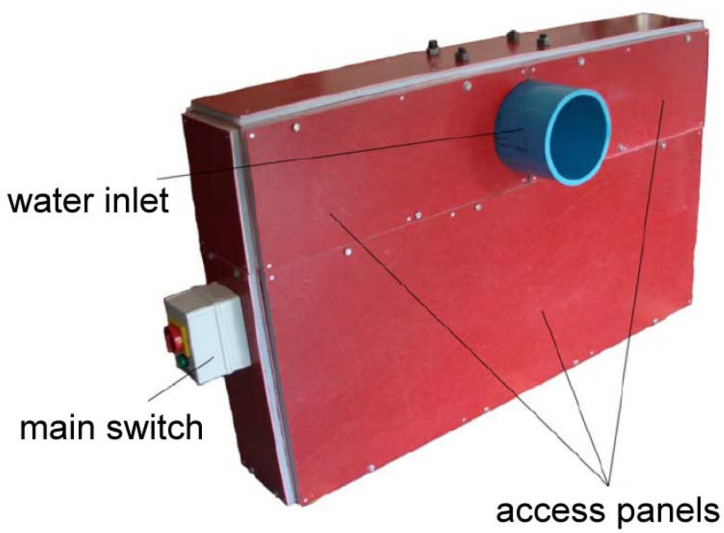
Dragan Manojlovic et al., Vacuum 83 (2009) 142.

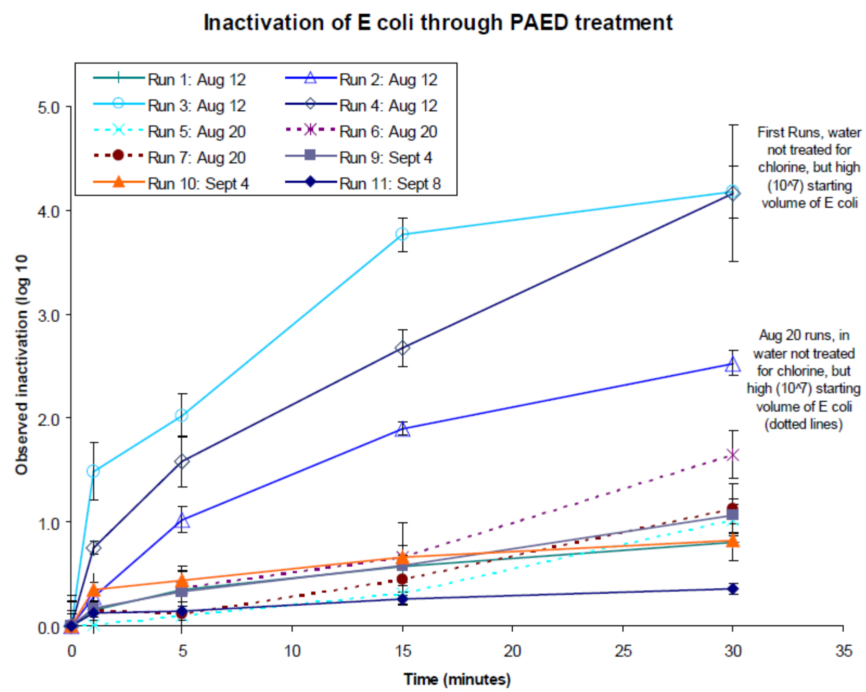
Pulsed Arc Electrohydraulic Discharge Device

Pulsed Arc Electrohydraulic Discharge (PAED) Device

(Pulsed Arc Discharge)

Boyd Technologies, LLC, South Lee MA, 2009

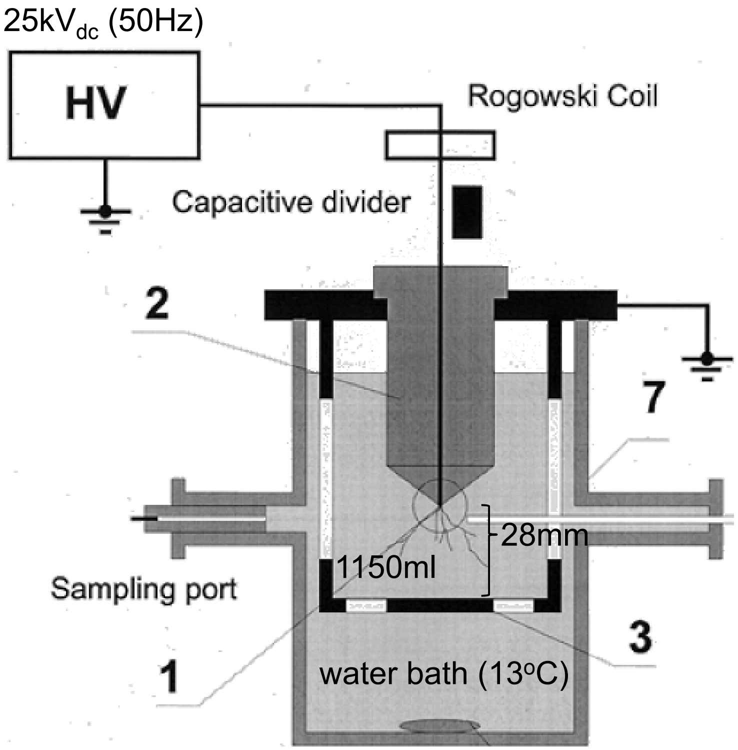


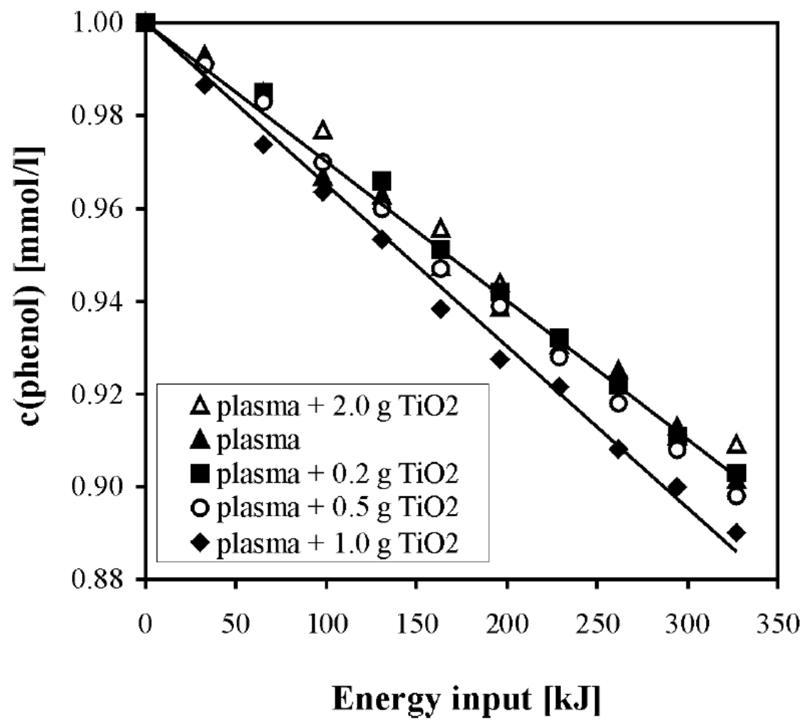


M. Walker et al., Feasability Assessment Boyd Technologies, LLC (2009).

Plasma Enhanced TiO_2 Photocatalysis

Degradation of phenol by underwater pulsed corona discharge in combination with TiO_2 photocatalysis





P. Lukes et al., Res. Chem. Intermed. 31 (2005) 285.

Plasma Enhanced Adsorption

Degradation of methylene blue and phenol by underwater pulsed corona discharge in combination with (catalytic) adsorbents

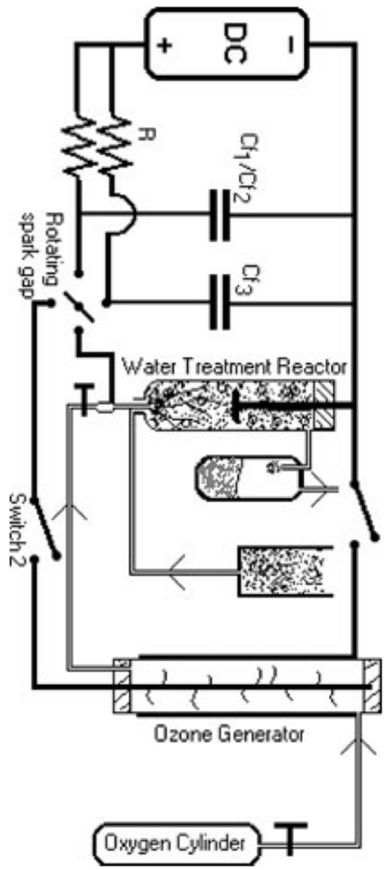


Table 2. Characteristics of treated phenol solution at a flow rate of 3.3 ml min^{-1}.

Condition	Treated solution: Concentration (mg $litre^{-1}$)	Energy efficiency (10^{-9} mol J^{-1})	pH	Conductivity ($\mu S\ cm^{-1}$)
No treatment	25	—	6.1	20
PCDs	21	1.1	5.3	58
PCDs + ozone	9	4.3	4.0	30
PCDs + silica gel	8	4.5	4.2	27
PCDs + ozone + silica gel	3.5	5.7	3.7	55

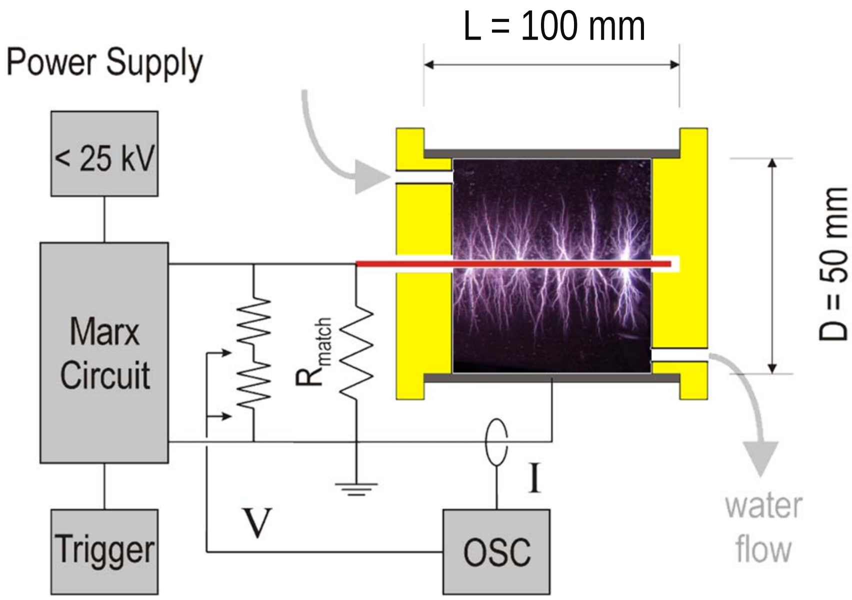
Table 3. Characteristics of treated methylene blue solution at a flow rate of 10 ml min^{-1}.

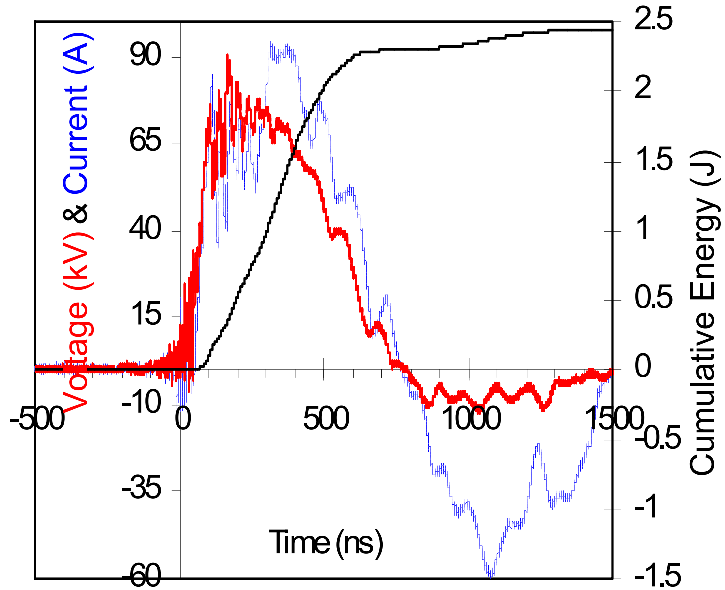
Condition	Treated solution: Concentration (mg $litre^{-1}$)	Energy efficiency (10^{-9} mol J^{-1})	pH	Conductivity ($\mu S\ cm^{-1}$)
No treatment	13.25	—	9	16.4
PCDs	10.4	0.58	5	19
PCDs + ozone	3.3	2.0	7.2	20
PCDs + ozone + silica gel	0.1	2.7	5.5	22

M.A. Malik, Plasma Sources Sci. Technol. 12 (2003) S26.

Tailored Electrical Discharges in Water

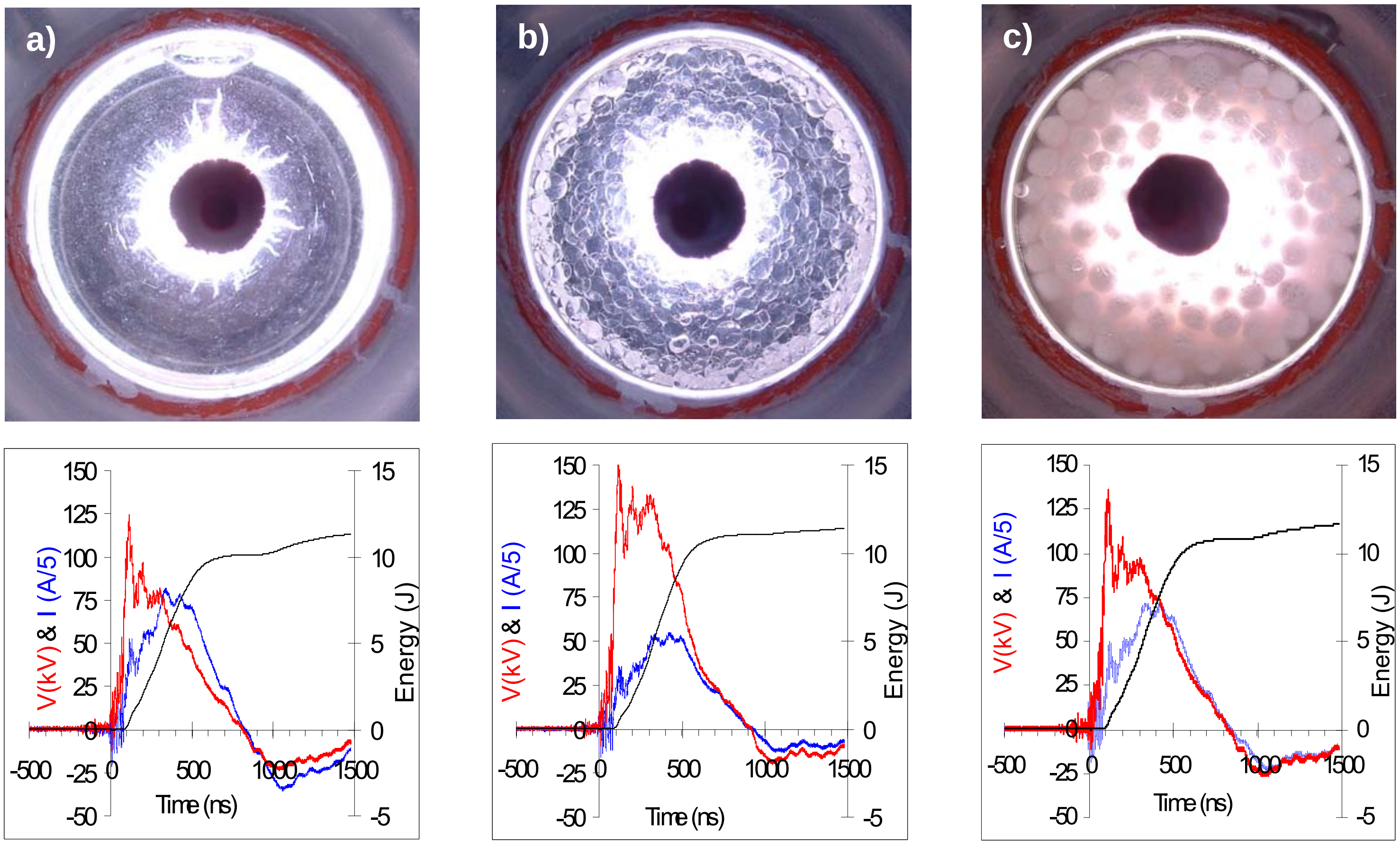
By shortening the duration of the applied electric high voltage pulse are dissipation losses reduced and efficiency and efficacy of pulsed discharges in water enhanced.





M.A. Malik, Y. Minamitani, S. Xiao, J. F. Kolb, K.H. Schoenbach, “Streamers in Water Filled Wire-Cylinder and Packed-Bed Reactors,” IEEE Trans. Plasma Sci. 32 (2005) 490.

Tailored Electrical Discharges in Water



no packing　　silica gel　　alpha-alumina

M.A. Malik, Y. Minamitani, S. Xiao, J. F. Kolb, K.H. Schoenbach, “Streamers in Water Filled Wire-Cylinder and Packed-Bed Reactors,” IEEE Trans. Plasma Sci. 32 (2005) 490.

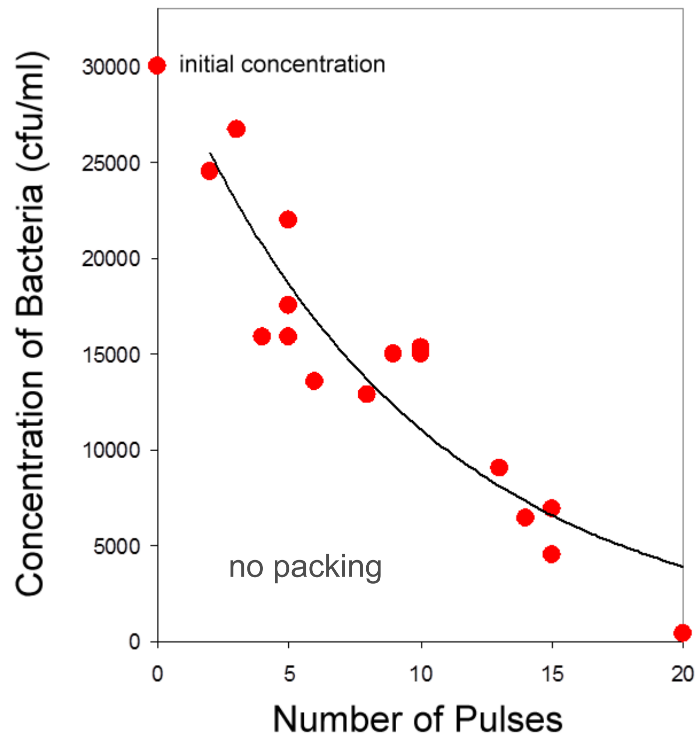
Tailored Electrical Discharges in Water

Decomposition of Methylene Blue

	concentration (mg/ltr)	pH	conductivity (µS/cm)
no treatment	13.25	9	16.5
PCD	3.0	4.7	24
PCD + α-alumina	1.1	6	36
PCD + γ-alumina	0.47	9	116
PCD + silica gel	not detectable	3.9	60

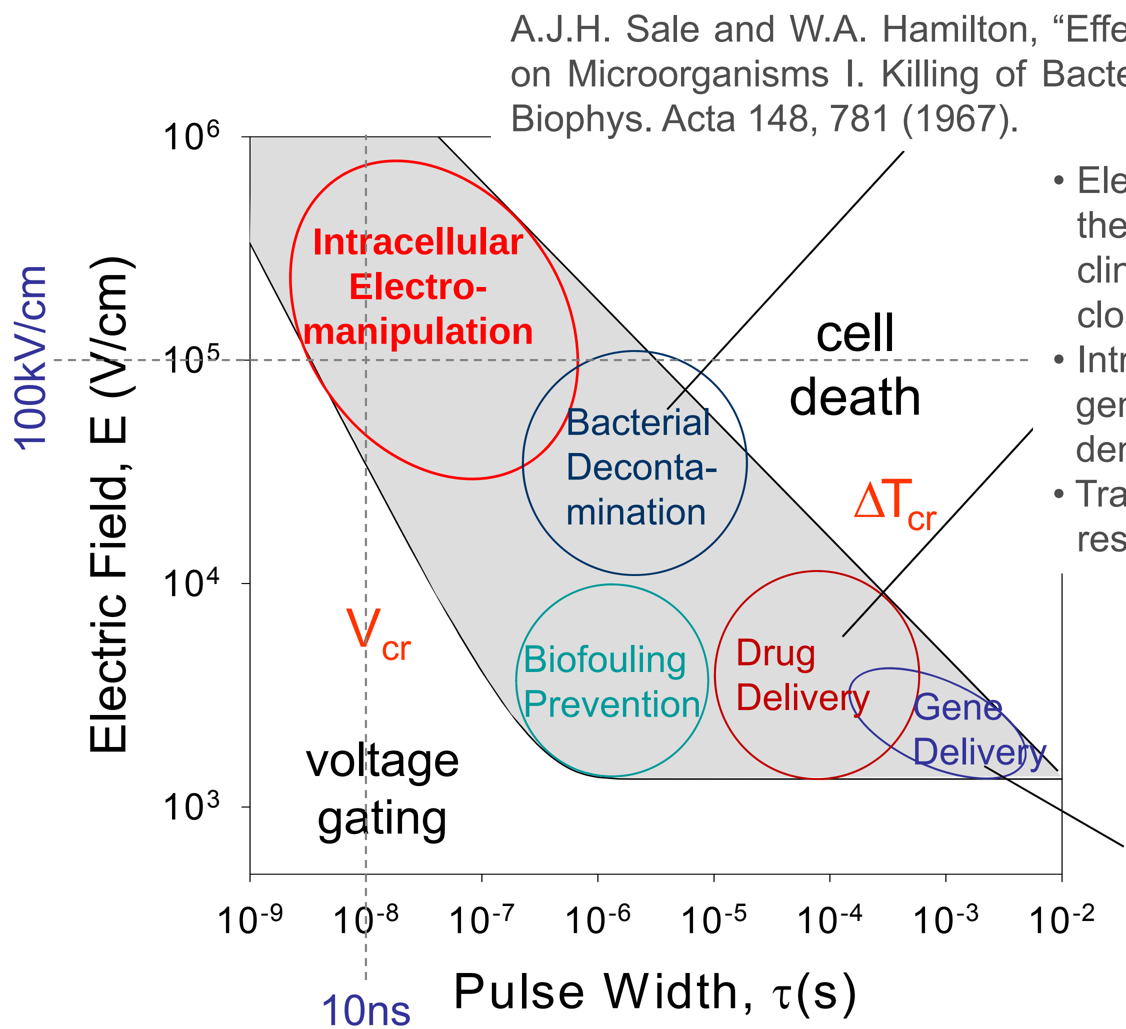
PCD: Pulsed Corona Discharge
Flow Rate: 3.3 ltr/min
Pulse Repetition Rate: 0.1 Hz

E.coli Decontamination



M.A. Malik, Y. Minamitani, S. Xiao, J. F. Kolb, K.H. Schoenbach, “Streamers in Water Filled Wire-Cylinder and Packed-Bed Reactors,” IEEE Trans. Plasma Sci. 32 (2005) 490.

Pulsed Electric Field Effects on Cells



- Electroporative delivery of chemo-therapeutic drugs into tumor cells clinical studies underway close to market introduction
- Intravascular delivery of drugs and genes with catheters successfully demonstrated
- Transdermal drug delivery research state

Gene therapy delivery of DNA by electro-poration into a variety of tis-sues has been demonstrated

Treatment of Turbid Water

Pulsed Electric Field Treatment (80kV/cm, 1µs, 10Hz)
for Bacterial Reduction in Hospital Wastwater

Table 1 Reduction efficiency of the pulsed electric field treatment of clinical wastewater spiked with *Pseudomonas aeruginosa* depending on the energies used

	P. aeruginosa (strain 1095)		*P. aeruginosa* (strain 1071)	
Energy value (J ml^{-1})	CFU ml^{-1}	Decimal order of magnitude reduction	CFU ml^{-1}	Decimal order of magnitude reduction
0	3×10^5		1×10^6	
84	2×10^3	2·2	1×10^3	3·0
117	4×10^2	2·9	1×10^3	3·0
137	1×10^3	2·5	2×10^3	2·7
146	1×10^2	3·5	2×10^2	3·7
162	0	5·5	20	4·7
190	0	5·5	20	4·7

A. Rieder et al., Journal of Applied Microbiology 105 (2008) 2035.

Summary

- Electrical discharge plasmas can be integrated in almost any geometry.
- Pulsed discharges in water are simultaneously highly effective against chemical and biological contaminants.
- Discharge parameters can be opitimized for applications (e.g. short electric pulses).
- Pulsed discharges and pulsed electric fields are effective in turbid water.
- Plasmas in water can increase catalytic efficiencies.

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