Non-equilibrium Plasma Applications for Water Purification Supporting Human Spaceflight and Terrestrial Point-of-Use

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THE BUSINESS CASE FOR TECHNOLOGY INNOVATION FOR WATER

Clean and safe water is essential for public health and healthy ecosystems, for the nation’s economic well-being, and for the welfare of our families and communities.

Water use in the United States: For example in 2005 almost 330 billion gallons of freshwater was withdrawn for use: (EPA numbers)

29.4 billion gallons per day were withdrawn for domestic use.
19.2 billion gallons per day were withdrawn for industrial and mining use.
138.8 billion gallons per day were withdrawn for use in farming (including agricultural and horticultural irrigation, livestock, and aquaculture).
142 billion gallons per day were withdrawn to produce energy in thermoelectric power plants

Many aspects of the U.S. economy depend on large supplies of water:
In 2012, the total revenue for the domestic U.S. water and wastewater industry was $139 billion.
In 2011, 44 million anglers spent $48 billion to fish in U.S. waters.
In 2007, irrigated crops accounted for 55 percent of the total value of U.S. crops.
In 1999, the beverage industry used 12 billion gallons of water to produce $58 billion worth of products…..

Hydraulic Fracking ?....Oil-spill cleanup?...

Further EPA numbers
Water, uses of water resources, and the services to provide clean water play a significant role in economies around the world. Value of the global water market—control and cleanup of water—is estimated at $500 billion per year.
Plasma-Based Water Treatment Technology Addresses NASA mission needs as well Terrestrial Clean Water Availability in a Variety of Venues

- **Water resource use/reuse** on ISS (87%), and long-duration missions (Mars)
  - Alternative to filtration and bio-reactor approaches
  - Simplified implementation

- **Environment** (“Green”) Protection of the Great Lakes, ship ballast water, chicken/hog farms (pH)
  - Pre-treatment of contaminants before emission into harbors, rivers and streams
  - Textile dyes, VOCs, invasive microbes

- **Point-of-use** water treatment for all countries, and Military base camps
  - Straightforward integration in areas without significant water treatment infrastructure

Plasma treatment leads to decomposition of organic compounds in water and destruction of viruses, yeast, bacteria, e-coli, and other microorganisms.
WATER PURIFICATION BY HV NANOSECOND PLASMA

• Hardware
  – Stainless steel “Faraday Cage” chamber
  – High voltage (100KV, 2-5 ns pulse modulator,
  – 100KHz repetition frequency
  – Non-thermal/Non-equilibrium Plasma
  – Supports the study of fast ionization waves

Non-Equilibrium Plasma Lab -- Interaction of non-thermal plasmas with dielectric liquids (hydrocarbon fuels, water, etc). Fuel activation for reduced ignition delay and reduced emissions.
Water Purification by Non-Thermal Plasma Treatment
Discharge Evolution/Species Evolution

- Pulsed Repetitive High-Voltage Nanosecond non-equilibrium, non-thermal plasma discharge produces the following dominant highly-reactive species: H2O2, OH, O, O3, N2, e, etc. In addition the discharge produces extremely high E-fields, UV radiation, and shockwaves.

- Discharge undergoes series of transitions with increasing voltage (~10 kHz): Corona-to avalanche-to streamer--- Streamer is associated with high chemical reactivity

<table>
<thead>
<tr>
<th>Oxidizing Species</th>
<th>Relative Oxidation Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHLORINE</td>
<td>1.00</td>
</tr>
<tr>
<td>HYPOCHLOROUS ACID</td>
<td>1.10</td>
</tr>
<tr>
<td>HYDROGEN PEROXIDE</td>
<td>1.31</td>
</tr>
<tr>
<td>OZONE</td>
<td>1.52</td>
</tr>
<tr>
<td>ATOMIC OXYGEN</td>
<td>1.78</td>
</tr>
<tr>
<td>HYDROXYL RADICAL</td>
<td>2.05</td>
</tr>
</tbody>
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Glow/Avalanche with microdischarges Voltage= 10 kV
Streamers and microdischarge Voltage= 17 kV
Decomposition Efficiency

- Decomposition efficiency is defined as mass decomposed per kW*Hr
- At early times decomposition efficiency is high
  - Considerably higher than glow discharge or pulsed corona methods

Methylene Blue, simulated textile mill waste water was rapidly decolorized during plasma application
AN EMERGING THREAT IN LAKE ERIE AND OHIO RIVERS: CYANOBACTERIA

New and advanced water treatment methods need to be developed to extract or destroy the emerging threats: Microcystin, Anatoxin – A. Microcystins are a group of hepatoxins (toxins that affect the liver).

In August 2014, the city of Toledo, Ohio, issued a three-day advisory telling 500,000 people in the area not to drink the tap water. The reason? A large algae bloom in Lake Erie – the city's source of water – had produced unsafe levels of the toxin microcystin, which, when swallowed, can cause nausea, fever and, ultimately, liver damage.

Microcystin is difficult to remove via conventional means (not by boiling)
-- Requires advanced filtration or advanced oxidation for removal (ozone, reverse osmosis, ultra filtration)

UMichigan: Samples of the most common microcystin (MC-LR) were treated with underwater DBD plasma jet. Successful removal of microcystin in water using low temperature atmospheric plasma was achieved!
Plasma generated advanced oxidation processes decompose toxins not addressed by conventional treatment methods

<table>
<thead>
<tr>
<th>Toxin</th>
<th>Purpose</th>
<th>Human Toxicology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halogenated hydrocarbons</td>
<td>Industrial solvents</td>
<td>Possible birth defects; suppression of central nervous system</td>
</tr>
<tr>
<td>Aromatic compounds (e.g. benzene, toluene)</td>
<td>Chemical intermediate for synthesis of plastics and polymers</td>
<td>Known carcinogen (e.g. leukemia)</td>
</tr>
<tr>
<td>Pentachlorophenol (PCP)</td>
<td>Electrical insulating oils</td>
<td>Cancer causing; disrupts hormones</td>
</tr>
<tr>
<td>Pesticides</td>
<td>Agriculture</td>
<td>Linked to birth defects, nervous system damage, lymphoma, and cancer</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>Health care</td>
<td>Can lead to antibiotic resistant microbes; affect human hormonal balance</td>
</tr>
<tr>
<td>Cyanide</td>
<td>Mining, industrial chemical processing</td>
<td>Poison; disrupts cellular respiration</td>
</tr>
</tbody>
</table>

$\text{CH}_3\text{OH} + \cdot \text{OH} \rightarrow \cdot \text{CH}_2\text{OH} \rightarrow \text{H} - \text{C} - \text{H} \rightarrow \text{H} - \text{C} - \text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$

$\cdot \text{OH}/\text{O}_2 \rightarrow \cdot \text{OH}/\text{O}_2 \rightarrow \cdot \text{OH}/\text{O}_2$

OH driven decomposition of methanol
Unique Features and Advantages of the High-Voltage Nanosecond Pulsed Plasma Process

• This discharge produces several highly reactive species. They include the production of chemically active substances, including ozone, hydrogen peroxide, hydroxyl and superoxide free radicals, UV radiation generated by the discharge itself, and acoustic and shock waves.
  – These components are strong oxidizers-Advanced oxidation processes(AOP)!

• Environmentally friendly. No use of externally-introduced chemicals (e.g. Chlorine) that may lead to production of carcinogens or mutagenic products during the disinfection process.

• As effective as ozonization, chlorination, and UV radiation.

• The plasma generated is non-thermal and is, therefore, unlikely to affect the nutritional and other properties of water and foods, such as milk, in the killing of contaminant micro-organisms. The system developed may be used for pasteurization of liquid products.

• Effective in microbial killing and low cost. Destruction of microrganisms –Ecoli, Crystosporidium (Milwaukee, 1993), on contaminated surfaces, water and food.

• Excellent potential for rapid degradation/treatment of pollutants in industrial and domestic wastewater, and ship ballast. Other possibilities include cell-lysing, scale prevention in chillers, removal of metals in small quantities, etc

• Reactor Design: Variation of discharge duty cycle and amplitude controls radical production and reaction rates

• The US has the potential to realize the benefits of advanced water and wastewater strategies on a national scale. Achieving this will require engaging engineering, financial, and political leadership to crystallize an actionable national water agenda.

Happily, this is happening now!!
BACKUP SLIDES
Recycle/Reuse of onboard water is the only practical option to supporting long duration human spaceflight missions
- e.g. en route to Mars or distant asteroids

In situ resource utilization will be important for surface expeditionary crews and future far-point outposts
- Extraction of water is key to survival

Whether recycling system water or extracting from extraterrestrial body, source water must be purified
- Organic contaminants, bacteria and viral particles of known and unknown origin must be removed

Product water quality considerations
- Toxicity
- Color
- Test
- Smell

Advanced technologies needed to address the water purity problem
- Terrestrial spinoffs will improve purification methods here on Earth
Some Current and Developing Technologies to Clean Water

- **Filtration**
- **Chemical Treatment**
- **UV Treatment**
- **Plasmas as a source of AOP**

- Through the interaction of plasmas with liquid water, a plasma can be a source of multiple advanced oxidation agents and pathways:
  - $\cdot OH$, Ozone, UV, excited nitrogen species
  - Supercritical water
  - Ultrasound and shockwaves
- Plasma-water interaction can be achieved directly via so-called liquid streamers or indirectly by either plasma interaction with surface of liquid or via plasma production in bubbles.

- Direct exposure to liquid:
- Direct radiolysis production in liquid
- Gas phase plasma is more energy efficient
- Liquid surface forms reaction interface

- Inlet and outlet diagrams showing UV rays and disinfection chamber.