Florida State University
• Founded 1851, Enrollment 44,000
• Ranked 18 of US Public Research Universities (USNWR)

Florida A & M University
• Founded 1887, Enrollment 10,000
• Public HBCU in Florida

FAMU-FSU College of Engineering
• Founded 1982
• Shared by FSU and FAMU

Chemical and Biomedical Engineering
• Enrollment: 500 undergraduates, 50 graduates
• 18 tenure track faculty members

National High Magnetic Field Lab
General Department Research Areas
- Department of Chemical and Biomedical Engineering -

• Biomedical Engineering
  • Imaging (NMR, MRI) - Grant, Li, Holmes, Mohammadigoushki
  • Cellular and Tissue Engineering – Grant, Li, Holmes
  • Biomaterials - Ali, Guan, Holmes, Ramakrishnan

• Materials
  • Polymers - Alamo, Arnett, Chung, Hallinan, Ricarte
  • Complex Fluids - Mohammadigoushki, Ramakrishnan
  • Electronic Materials - Siegrist
  • Nano - Materials – Ali, Grant, Guan, Hallinan, Kalu, Ramakrishnan, Siegrist

• Chemical Engineering
  • Catalysis – Chung
  • Chemical Reaction Engineering – Locke
  • Energy storage – batteries – Hallinan, Kalu
Hydroxyl Radicals in Gas-Liquid Water Plasma Reactors

Professor Bruce R. Locke
Florida State University
Department of Chemical and Biomedical Engineering
Tallahassee, FL

Funding
National Science Foundation CBET – 1236225, 1702166
Czech Fulbright Commission, Florida State University
Contacting Plasma with Liquid Water

Underwater

Electrical discharge underwater (pulsed, RF, microwave)
- $10^{-3}$ to 1 J/pulse (also ns to $\mu$s pulses possible)
- up to kJ/pulse - electrohydraulic discharge, arc formation, exploding wire
- breakdown underwater: 1 MV/cm

Gas-liquid Interface (AC, DC, or pulsed)

Discharge in gas
- plasma in gas
- gas phase breakdown
- plasma touches water surface
- liquid properties can be important (conductivity)

Gliding arc  Planar  Bubbles  Films

Combined gas/liquid  Scaled prototypes  Water spray
Applications of Plasma with Liquid Water

• Water pollution treatment
  • Wide range of organic and some inorganic compounds – emerging contaminants – perfluorinated species, antibiotics, personal care products

• Air pollution treatment (wet plasma – water sprays and films)
  • Nitrogen and sulfur oxides, volatile organic compounds (VOCs)

• Disinfection and biomedical
  • Bacteria, yeast, viruses
  • Biomedical – wound healing, cancer treatment

• Chemical synthesis
  • Partial oxidation – alcohols, aldehydes…
  • Nanoparticle synthesis
  • Polymer coatings
  • Plasma activated water for agriculture uses – nitrates/nitrites, seed germination…

Many reviews on this subject published in last 10 years: Akiyama, Malik, Locke, Sunka, Sato, Bruggeman, Lukes, Thagard, Weltmann, Brandenburg,…..

Complexities of Gas-Liquid Water Plasma Chemistry

**PLASMA GAS PHASE CHEMISTRY**

- Chemistry strongly dependent on gas composition (air, N₂, O₂, Ar, He)
- Not all factors equally important or occur in all types of gas-liquid plasma

**LIQUID PHASE CHEMISTRY**

Key Chemical Species from Electrical Discharge with Water

Electron dissociation
\[ \text{H}_2\text{O} + e^- \rightarrow \text{H} + \cdot\text{OH} + e^- \]

Thermal dissociation
\[ \text{H}_2\text{O} + \text{M} \rightarrow \text{H} + \cdot\text{OH} + \text{M} \]

Possible Products and active species

Molecules: (stable)
- \text{H}_2, \text{O}_2, \text{H}_2\text{O}_2, (\text{O}_3)

Radicals and atoms: (short life)
- \text{O}, \cdot\text{H}, \cdot\text{OH}, \text{HO}_2

Ions:
- \text{H}^+, (\text{H}_3\text{O}^+), \text{O}^+
- \text{H}^-, \text{O}^-, \text{O}_2^-, \cdot\text{OH}^-
- e_{\text{aq}}^-

Standard oxidation potentials
- \cdot\text{OH} = 2.80 \text{ V}
- \text{O} = 2.42 \text{ V}
- \text{O}_3 = 2.07 \text{ V}
- \text{H}_2\text{O}_2 = 1.77 \text{ V}
- \cdot\text{HO}_2 = 1.7 \text{ V}

Disinfection, chemical destruction
Stable molecular carrier for \text{OH} radicals

May be important for reduction reactions
**Hydroxyl Radical Generation from Water**

![Hydroxyl Radical](image)

- **Thermodynamic limit**
  
  \[ \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \cdot\text{H} \]

- **UV light**
  
  \[ \text{H}_2\text{O} + h\nu \rightarrow \cdot\text{OH} + \cdot\text{H} \]

  (120 to 190 nm, depends on quantum yields and lamp efficiencies)

- **Radiation**
  
  \[ \text{H}_2\text{O} + e^- \rightarrow \cdot\text{OH} + \cdot\text{H} + e^- \]

  (electron beams, gamma radiation)

- **Plasma**
  
  \[ \text{H}_2\text{O} + e^- \rightarrow \cdot\text{OH} + \cdot\text{H} + e^- \]

  Subject of this talk

**Yields** (molecules/100 eV)

<table>
<thead>
<tr>
<th></th>
<th>Liquid</th>
<th>Gas with Vapor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermodynamic</td>
<td>2 to 3</td>
<td>5 to 6</td>
</tr>
<tr>
<td>UV light</td>
<td>2 to 4</td>
<td>7 to 9</td>
</tr>
<tr>
<td>Radiation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* -note: yields estimated from literature where data was obtained under wide range of different operating conditions and measurement methods
Note on Importance of Hydroxyl Radical
- Gas Phase -

- Provides insight into oxygen and water chemistry in interstellar space: $10^4$-$10^6$ cm$^{-3}$ (low temperature and density)

- Earth atmosphere:
  - Formed in stratosphere by UV: $10^6$ cm$^{-3}$
  - Cleans nitrogen oxides, organics from troposphere, 0.01 to 1 s

- Indoor air – similar chemistry as in atmosphere
  - Clean air: $10^4$ to $10^5$ cm$^{-3}$
  - Photolysis of HONO: $10^6$ cm$^{-3}$
  - With air cleaners: $10^7$ to $10^8$ cm$^{-3}$

- Combustion – main reactant: $10^{14}$ to $10^{16}$ cm$^{-3}$, high temperature and pressure (1 to 5% of species)

- Gas phase plasma reactors (with water vapor): $10^{13}$-$10^{15}$ cm$^{-3}$, atmospheric pressure and temperature
Note on Importance of Hydroxyl Radical
- Liquid Phase -

• Close coupling of ∙OH with H₂O₂ in the liquid phase
• Natural water:
  • UV photolysis of nitrate, dissolved organic matter
    • H₂O₂: 50-1000 nM
  • Natural seawater – ∙OH: 10⁻⁹ to 10⁻⁶ nM
  • Acid mine water – ∙OH: 10⁻⁵ to 10⁻³ nM
• Found in biology
  • Cells: H₂O₂ 1 to 10 nM
• Advanced oxidation technologies (∙OH based processes)
  • O₃, O₃/H₂O₂, O₃/H₂O₂/UV, Fenton(H₂O₂/Fe)
  • ∙OH: 10⁻⁴ to 10⁻¹ nM (quasi steady-state due to very high reactivity)
• Plasma contacting liquid water
  • ∙OH: 10⁻¹ nM (quasi steady-state due to very high reactivity)
### Reaction Rate Constants
(Second order M$^{-1}$s$^{-1}$, Tarr (2003))

<table>
<thead>
<tr>
<th></th>
<th>·OH</th>
<th>O$_3$</th>
<th>pH</th>
<th>$e_{aq}^-$</th>
<th>·H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>7.8x10$^9$</td>
<td>2</td>
<td>2-3</td>
<td>9.0x10$^6$</td>
<td>9.1x10$^8$</td>
</tr>
<tr>
<td>Phenol</td>
<td>6.6x10$^9$</td>
<td>1300</td>
<td>2</td>
<td>2.0x10$^7$</td>
<td>1.7x10$^9$</td>
</tr>
<tr>
<td>Chlorophenol</td>
<td>12x10$^9$</td>
<td>1600</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formic acid</td>
<td>0.13x10$^9$</td>
<td>5</td>
<td>2-4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>4x10$^9$</td>
<td>17</td>
<td>2</td>
<td>1.9x10$^9$</td>
<td></td>
</tr>
</tbody>
</table>

- ·OH reactions near diffusion limits 10$^{10}$ M$^{-1}$s$^{-1}$ in liquids
- Competing (reduction) reactions with ·H and $e_{aq}^-$ (depends upon species)
- O$_3$ can be important if [O$_3$] $>>$ [·OH] (ozone solubility range 10$^{-5}$ to 10$^{-3}$ M)
- Rate(·OH)/Rate(O$_3$) = 1 (chlorophenol); = 100 (others) (for max O$_3$)
Idealized Reaction Pathways (with H$_2$O only)

$\text{H}_2\text{O} \rightarrow \text{H} \cdot + \cdot \text{OH}$

(Primary yield - radiation chemistry)

$\cdot \text{OH} + \cdot \text{OH} \rightarrow \text{H}_2\text{O}_2$

$\cdot \text{H} + \cdot \text{H} \rightarrow \text{H}_2$

$\cdots \rightarrow \text{O}_2$

Molecular products (stable)
$\text{H}_2$, $\text{O}_2$, $\text{H}_2\text{O}_2$
(Ideal quenching - Fridman)

Desired reactions in/near plasma (very fast reactions)
$\cdot \text{OH} + \text{organic} \rightarrow \text{products}$

Undesired reactions in/near plasma
$\cdot \text{OH}$ quenching...
$\text{H} \cdot + \cdot \text{OH} \rightarrow \text{H}_2\text{O}$
(Absolute quenching - Fridman)

Used outside of plasma
$\text{H}_2\text{O}_2$ – in liquid
$\text{H}_2$ and $\text{O}_2$ – in gas
Underwater Discharge

Discharge Reactions

\[ \text{H}_2\text{O} + e^- \rightarrow \cdot \text{H} + \cdot \text{OH} + e^- \]
\[ \text{H}_2\text{O} + \text{M} \rightarrow \cdot \text{H} + \cdot \text{OH} + \text{M} \]

Recombination Reactions

\[ \cdot \text{OH} + \cdot \text{OH} \rightarrow \text{H}_2\text{O}_2 \]
\[ \cdot \text{O} + \cdot \text{O} \rightarrow \text{O}_2 \]
\[ \cdot \text{H} + \cdot \text{H} \rightarrow \text{H}_2 \]
\[ \cdot \text{H} + \text{O}_2 \rightarrow \text{HO}_2\cdot \]
\[ \text{HO}_2\cdot \leftrightarrow \cdot \text{O}_2 + \cdot \text{H}^+ \]

Overall (Bulk) Reaction

(Experimental Observations)

\[ 6\text{H}_2\text{O} \rightarrow 4\text{H}_2 + 2\text{H}_2\text{O}_2 + \text{O}_2 \]


Discharge Reactions


Overall (Bulk) Reaction

(Experimental Observations)

\[ 6\text{H}_2\text{O} \rightarrow 4\text{H}_2 + 2\text{H}_2\text{O}_2 + \text{O}_2 \]

• Geometrical patterns of energy deposition from high energy electrons
• Chemical probes used to determine primary yields – products formed in the chemical core
• Note: O and O₂ not typically found in underwater radiation reactions
• Non-homogeneous energy deposition, fast time scales
• Kinetics in spur leads to homogeneous kinetics at 10⁻⁷ s
Discharges at Gas-Liquid Interface

- Plasma propagates in gas phase along the gas/liquid interface
- Requires lower electric field to generate plasma than inside water
- More efficient generation of plasma

Flow system useful to control gas, liquid, and plasma contacting, fluid residence times, and to measure gas and liquid products and reactants.
Flowing Film Plasma Reactor System

Water pump

Stainless steel inlet capillary
0.25 mm ID

Quartz reactor body

Optical emissions Spectrometer (w/ optical fiber)

Plasma discharge region

Stainless steel outlet capillary
1 mm ID

Mixing zone

Pressure regulator

Gases

Eagle Harbor Nanopulser

Rogowski coil

Nanopulser

HV -

HV probe

HV pulse generator stage

R_s

R_p

R_s

Gas samples:
FTIR (on-line)
GC, GC/MS, NMR

Gas phase

Gas flow meter

Liquid phase

Liquid samples:
GC, GC/MS, NMR, UV spectroscopy

Bubble flow meter

Liquid samples:
GC, GC/MS, NMR, UV spectroscopy
High Speed Imaging

Gas flow region
Liquid film flow region
Gas-liquid interface / Plasma discharge region

4 mm
3 mm

Flow direction

*4,000 fps

Deionzed water with argon carrier.

*1/60 sec. shutter speed

*1/12,000 sec. shutter speed

*1/12,000 sec. shutter speed
Connecting Physical and Chemical Processes

**Input waveform properties**
- Peak voltage
- Frequency
- Pulse width and shape
- Rise time

**Discharge waveform properties**
- Breakdown voltage
- Peak current
- Total current
- Energy per pulse

**Reactors configuration**
- Electrode gap distance
- Nozzle size
- Reactor volume, shape
- Liquid flow rate
- Gas flow rate

**Feed species**
- Gas composition
- Liquid composition
  - pH, conductivity

**Plasma properties**
- Plasma gas temperature
- Electron density
- Electron energy (distribution)
- Size (diameter, volume) plasma channel

**Chemical species formation**
- ·OH, H₂O₂, etc. - reaction and production rates
- ·OH, H₂O₂, etc. - energy yield

**Transport Processes**
- Hydrodynamics
  - Gas volume
  - Liquid volume
  - Residence times, mixing patterns
- Mass and energy transport processes

**Chemical species formation**
- ·OH, H₂O₂, etc. - reaction and production rates
- ·OH, H₂O₂, etc. - energy yield
Reactor Characterization

- Geometrical Properties (Wandell et al., 2018)
  - Volumes of liquids and gases
  - Interfacial area (gas-liquid and plasma-liquid)
  - Residence times of liquids and gases
    - 100-250 ms (liquid), 2–5 ms (gas); nozzle size dependent

- Hydrodynamics (Wandell et al., 2018)
  - Roles of nozzle size, gas and liquid flows
  - Flow patterns and regimes (annular flow)
  - Pressure in reactor (choked flow) higher pressure forces liquid to form film on walls
  - No evidence of plasma discharge affecting hydrodynamics

- Mass and energy transfer (Hsieh et al., 2016)
  - Liquid and gas (film theory)
  - Liquid and plasma
Electrical and Plasma Properties

• Waveforms
  • Ignition coil (microsecond pulser)
  • Nanopulsers

• Plasma properties
  • Plasma gas temperature
  • Electron density
  • Electron energy
  • Plasma volume

• Effects of reactor conditions (Wang et al. 2018, 2019)
  • Effects of carrier gas composition
  • Effects of gas and liquid flows
  • Effect of pulse properties
  • Effects of solution conductivity
## Power Supplies - Nanopulsers

1) **Airity Technologies (custom)**

- Frequency: 1 kHz
- Voltage: 3.8 kV peak
- Rise time: 140 ns
- Energy: 80 to 140 μJ/pulse
- Power: 0.13 W
- Argon

**Graphs:**
- Voltage and current over time
- Instantaneous power over time

**Frequency Ranges:**
- to > 60 kHz

---

2) **Eagle Harbor Technologies (commercial)**

- Frequency: 2 kHz
- Voltage: 5.5 kV peak
- Rise time: 20 ns
- Energy: 150 μJ/pulse
- Power: 0.30 W
- Argon

**Graphs:**
- Voltage and current over time
- Instantaneous power over time

**Frequency Range:**
- to 10 kHz

**Pulse width range:**
- 20 to 260 ns
Power Supplies – Microsecond Pulsers

3) Ignition Coil Based (Professor Radu Burlica – Iasi, Romania)

- High efficiency ignition coil
  - Audi
- DC power supply
  - input voltage (12 V)
  - BK Precision 1740B
- Frequency generator
  - 500 Hz, 40% duty cycle
  - BK Precision 4010A

- Characteristics:
  - Inexpensive, small
  - Microsecond pulses
  - Robust
  - Limited control, Waveforms noisy
  - Restricted range of liquid conductivities (500 μS/cm)

500 Hz pulse, argon with deionized water

Yellow = voltage
Red = power
Blue = current (~ 200 μs)
Temperature Measurement Methods

- Example: (Eagle Harbor nanopulser)
  - Power setting: 12kV 20ns 2kHz
  - Water flow rate: 2 ml/min
  - Helium

Trace \( \text{N}_2 \) added
\( \text{N}_2 \) (C-B)
Specair fitting

Two temperature fitting
Boltzmann plot of OH (A-X)
Program from Dr. Jan Vorec
(Masaryk University)

(Wang, Wandell, Locke, 2018)
Plasma Gas Temperature Results
(Eagle Harbor nanopulser)

- Method of measurement, N₂ or OH, gives similar results.
- Helium significantly cooler than argon.
- Temperature independent of discharge power.

(Wang, Wandell, Locke, 2018)
Electron Density Measurement
(Eagle Harbor nanopulser)

$H_\alpha$ fitting: example, 18 kV, 20 ns, 2 kHz

(Wang, Wandell, Locke, 2018)
Electron Density Results
(Eagle Harbor nanopulser)

- Electron density in helium 1 order of magnitude lower than in argon.
- Electron density in helium relatively more sensitive to discharge power.
- Discharge power varied by changing voltage.

(Wang, Wandell, Locke, 2018)
Time Resolved Electron Density
(Eagle Harbor nanopulser)

(20 kV, 1 kHz, and 20ns, DI water liquid flow rate 2 mL/min)

- Note time decay of electron density longer than current/voltage pulse in argon.

(Wang, PhD dissertation, 2018)
Influence of Liquid Conductivity
(Eagle Harbor nanopulser)

- Plasma properties relatively unaffected by large changes in liquid conductivity. (Discharges effectively in near seawater, (seawater = 50 mS/cm), conductivity.)
- Unique for EH nano-pulser (not found with microsecond pulser), fast rise time.
- Some effects of conductivity above 36 mS/cm seen for argon, but not helium.

(Wang et al., 2019)
Chemical Processes Analyzed
- role of hydroxyl radicals -

• A simple model of hydroxyl radical formation (Wang et al., 2018)
• Hydroxyl radical formation from probes (ignition coil, nanopulser)
  • Methylene Blue (non-volatile, liquid phase) (Hsieh et al., 2016)
  • Ethanol probe (volatile, liquid phase) (Hsieh et al., 2017)
  • Carbon dioxide probe (gas phase) (Hsieh et al., 2017)
  • Effect of frequency (EH and Airity nanopulsers)
• Hydrogen peroxide formation (EH nanopulser)
  • Effects of flow and carrier gas (Wang et al., 2018a)
  • Effects of solution conductivity (Wang et al., 2018b)
  • Effect of pulse properties (Wandell et al., 2018)
• Hydrocarbon partial oxidation (Bresch et al., 2015, PCPP)
• Dioxane oxidation with plasma + bioreactor (Yiong et al., 2019)
• Nitrogen oxide formation (Wandell et al., 2019; Bulusu et al. 2019)
  • Hydroxyl radicals with gas phase probes (NO and CO)
  • Gas phase NO/NO₂ measurements, liquid phase NO₂⁻, NO₃⁻
Reaction Model Based upon Fast Quenching in Film

Cross section of plasma channel

\[ l = (2D_it_p)^{1/2} \]
\[ = 1 \text{ \mu m} \]

Plasma core

Plasma film

Hydrogen peroxide mass balance in film: neglect diffusion and spatial variation in film

\[ \frac{dC_{H2O2}}{dt} = k_f C_{OH}^2 - k_d C_{H2O2} \]

\[ C_{OH} = C_{OH}^0 e^{-bt} \]

Decreasing with pulse

\[ k_d = k_d' e^{-bt} \]

Production Rate

\[ P_{H2O2} = C_{H2O2} (t_p) V_{film} f \]

\[ V_{film} = L \pi \left( R_p^2 - (R_p - l)^2 \right) \]

Hydrogen peroxide mass balance in film: neglect diffusion and spatial variation in film

\[ C_{OH} = \text{concentration of } \cdot \text{OH in core} \]
### Reaction Model Based upon Fast Quenching

Reactions: $(k_f$ and $k_d')$

- $H_2O_2$ formation from $\cdot OH$ in film
- $H_2O_2$ degradation by $\cdot OH$, $\cdot H$, $O$, $e^-$
- rapid quenching of $\cdot OH$ in film

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate coefficient $k$</th>
<th>$k$ in helium at 358 K</th>
<th>$k$ in argon at 600 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$OH + OH + Ar \rightarrow H_2O_2 + Ar$</td>
<td>$6.9 \times 10^{-43}(T_g/300)^{-0.8}$</td>
<td>3.96×10^{-43}</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>$OH + OH + He \rightarrow H_2O_2 + He$</td>
<td>$3.7 \times 10^{-43}(T_g/300)^{-0.8}$</td>
<td>3.21×10^{-43}</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$H + H_2O_2 \rightarrow HO_2 + H_2$</td>
<td>$2.81 \times 10^{-18} \exp(-1890/T_g)$</td>
<td>1.17×10^{-19}</td>
<td>8.70×10^{-19}</td>
</tr>
<tr>
<td>4</td>
<td>$H + H_2O_2 \rightarrow H_2O + OH$</td>
<td>$1.69 \times 10^{-17} \exp(-1780/T_g)$</td>
<td>1.43×10^{-20}</td>
<td>1.20×10^{-19}</td>
</tr>
<tr>
<td>5</td>
<td>$O + H_2O_2 \rightarrow HO_2 + OH$</td>
<td>$1.4 \times 10^{-18} \exp(-2000/T_g)$</td>
<td>5.25×10^{-21}</td>
<td>4.99×10^{-20}</td>
</tr>
<tr>
<td>6</td>
<td>$OH + H_2O_2 \rightarrow H_2O + HO_2$</td>
<td>$2.91 \times 10^{-18} \exp(-160/T_g)$</td>
<td>1.86×10^{-18}</td>
<td>2.23×10^{-18}</td>
</tr>
<tr>
<td>7</td>
<td>$e + H_2O_2 \rightarrow H_2O + O^-$</td>
<td>$1.57 \times 10^{-16} T_e^{-0.55}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>$e + H_2O_2 \rightarrow OH + OH^-$</td>
<td>$2.7 \times 10^{-16} T_e^{-0.5}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>$e + H_2O_2 \rightarrow 2OH + e$</td>
<td>$1 \times 10^{-9}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>$e + H_2O_2 \rightarrow H + HO_2 + e$</td>
<td>$1 \times 10^{-9}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Model ·OH Predictions

- Smaller size argon plasma has higher ·OH concentration in core during pulse.
- Slight increase in ·OH with discharge power for both gases.
- Data on H₂O₂ used to determine ·OH in plasma using model.
- \(<\text{OH}>= 4\times10^{14} \text{ cm}^{-3}\) in argon and \(2\times10^{14} \text{ cm}^{-3}\) in helium (time averaged in pulse)
- For comparison in combustion – \(10^{14}\) to \(10^{16} \text{ cm}^{-3}\)

(Wang, Wandell, Locke, 2018)
Other Model Results

H₂O₂ model data comparison

Calculated H₂O₂ degradation rates

Relative H₂O₂ degradation rates by electrons and ·OH

- More H₂O₂ degradation in argon
- Argon – higher rates with electrons
- Helium – higher rates with ·OH
- Degradation strongly affects net formation of H₂O₂
- Role of liquid water is to sequester H₂O₂ and suppress degradation in plasma

(Wang et al., 2018)
Effects of Frequency on Hydroxyl Radical
(data for input to model, Airity Nanopulser)

\[ \text{H}_2\text{O}_2 \]

(energy per pulse ranges from 80 to 140 mJ/pulse)

H\(_2\)O\(_2\) data: V. Babicky, M. Clupek, V. Jirasek, P. Lukes

- Airity power supply, 2 mL/min, 0.25 mm inlet nozzle, 70 V delivered
- Energy per pulse ranges from 80 to 140 mJ/pulse
- H\(_2\)O\(_2\) data: V. Babicky, M. Clupek, V. Jirasek, P. Lukes
Effects of Frequency on Hydroxyl Radical
(model results compared with \cdot\text{OH} from OES)

- Variation in \cdot\text{OH} with frequency correlated with electron density variation.
- \cdot\text{OH} measurements with time and space in progress (Vorac & Dvorak – Masaryk U.).

Airity power supply, 2 mL/min, 0.25 mm inlet nozzle, 70V delivered
Molecular Hydrogen Production

- In Helium
  \[ H_2:O_2 = 3.4 \]

- under water
  \[ H_2:O_2 = 4 \]

(Airity power supply, S. Bresch, IPP)

- Trend for \( H_2 \) formation similar to those for \( \cdot \text{OH} \); \( H_2 \) may rapidly escape plasma region.
- \( H_2O_2 \) levels off at high frequency, likely due to degradation reactions.
- Formation of \( O_2 \) demonstrated from water in argon and helium carrier gases.
Influence of Liquid Conductivity: $\text{H}_2\text{O}_2$
(Eagle Harbor nanopulser)

- Relatively small changes in $\text{H}_2\text{O}_2$ formation with large changes in liquid conductivity for nanopulser.
- Large range of operation possible with nanosecond pulser but not microsecond power supply.
Liquid phase ·OH Scavenger
(Methylene Blue – a water soluble organic dye)

<table>
<thead>
<tr>
<th>OH• production rate</th>
<th>(mol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂ from dl H₂O</td>
<td>2.40 ± 0.25 x 10⁻⁷</td>
</tr>
<tr>
<td>H₂O₂ from 0.1 mM MB</td>
<td>2.57 ± 0.12 x 10⁻⁷</td>
</tr>
<tr>
<td>MB decoloration</td>
<td>2.30 ± 0.13 x 10⁻⁹</td>
</tr>
<tr>
<td>MB mineralization</td>
<td>1.38 ± 0.67 x 10⁻⁸</td>
</tr>
</tbody>
</table>

- Complete MB decoloration has little effect on ·OH (H₂O₂) production.
- MB complete degradation requires 57 moles of ·OH.
Hydroxyl Radicals in Liquid Phase

• Based upon non-volatile organic dye decoloration in liquid
• Ignition coil data with argon carrier gas. (Hsieh, 2015)

\[
\ln \left( \frac{[MB]}{[MB]_0} \right) = -tk[OH]_{pss}
\]

\[ [OH]_{pss} = 1.2 \text{ to } 4.3 \times 10^{-10} \text{ M} \]

• For comparison - Advanced Oxidation Technologies
  – ·OH: \(10^{-4}\) to \(10^{-1}\) nM (quasi steady-state due to very high reactivity)
·OH reacts in the liquid phase (near interface) with MB
MB does not affect H₂O₂ formation (in plasma zone)
Some ·OH is able to go from plasma to liquid interface to degrade MB
• Overall 2 moles of ·OH to convert ethanol to acetaldehyde.
• Number of ·OH independent of specific pathway.
• Measure reaction product of acetaldehyde.
• Underestimate due to further oxidation of acetaldehyde.
·OH Production Rate from Ethanol

·OH + ·OH → H₂O₂
C₂H₆O + 2·OH → C₂H₄O + 2H₂O

- H₂O₂ completely depleted by ethanol.
- Acetaldehyde accounts for same amount of ·OH as H₂O₂.
- H₂O₂ likely formed in plasma zone near plasma-liquid interface.
• Major product acetaldehyde, primarily collected in the gas phase.
• Ethanol can deplete H$_2$O$_2$ by competing fully for ·OH.
• Ethanol can transfer into the plasma zone (unlike MB which stays in liquid).
**OH Radicals from Carbon Monoxide**

(Gas phase reactions and probe)

\[
\text{CO} + \text{OH}^\bullet \rightarrow \text{CO}_2 + \text{H}^\bullet
\]

- Significant gas phase ·OH that does not form \(\text{H}_2\text{O}_2\).
- ·OH available for reactions with gaseous species as well as liquid.
- Requires high CO to affect \(\text{H}_2\text{O}_2\).
• CO may be reacting with ·OH that goes to form other species like H₂O.
• Large amounts of CO needed to affect H₂O₂ production. Supports idea that most H₂O₂ is formed in plasma zone near liquid interface.
Hydroxyl Radical Generation from Water

- Thermodynamic limit
  (from $\Delta H_r$)
  $$\text{H}_2\text{O} \rightarrow \cdot\text{OH} + \cdot\text{H}$$
  Yields* (molecules/100 eV)
  20

- UV light
  $$\text{H}_2\text{O} + h\nu \rightarrow \cdot\text{OH} + \cdot\text{H}$$
  (120 to 190 nm, depends on quantum yields and lamp efficiencies)
  Yields* (in liquid) 2 to 3
  (in gas with vapor) 5 to 6

- Radiation
  $$\text{H}_2\text{O} + e^- \rightarrow \cdot\text{OH} + \cdot\text{H} + e^-$$
  (electron beams, gamma radiation)
  Yields* (in liquid) 2 to 4
  (in gas with vapor) 7 to 9

- Plasma
  $$\text{H}_2\text{O} + e^- \rightarrow \cdot\text{OH} + \cdot\text{H} + e^-$$
  Underwater: (Sahni and Locke, 2006)
  10^{-2} (primary) 2x10^{-1} (w/ H_2O_2)
  Yields* (exp, probes, ignition coil) 2 to 5
  (exp, probes, nanopulser) 3 to 7
  (model, H_2O_2, nanopulser) 2 to 4

- Advanced Oxidation Processes
  (O_3, O_3/UV, H_2O_2/O_3, H_2O_2/UV, H_2O_2/Fenton)
  2 to 8 (in liquid)
Hexane Oxidation
(Ignition coil, gas phase reactant)

Experiments and modeling show products due to $\cdot$OH and $\cdot$H reactions

- Hexane fed as gas – dilute amount to prevent polymerization.
- Products in liquid and gas
- Quantum chemical calculations using Gaussian 03

(Bresch et al., 2015)
Initial Reaction Steps

- Although both \( \cdot \text{OH} \) and \( \cdot \text{H} \) reactions possible
- \( \cdot \text{OH} \) reactions generally more likely based upon \( \Delta G \) (and products – see next slide)

(Bresch et al., 2015)
Colored boxes – products observed (NMR, GCMS)

- OH products observed

(Bresch et al., PCPP, 2015)
Example Application

- Partial degradation of 1,4 dioxane by plasma
  - 1, 4 dioxane highly water soluble, non-volatile
  - Emerging groundwater contaminant found in combination with chlorinated contaminants
- Mineralization in bioreactor after plasma reactor
- Seeking to improve overall efficiency by reducing overall energy cost by combining plasma for initial degradation with bioreactor for complete mineralization of products from plasma.

(Xiong et al., 2019)
Plasma/Bioreactor Treatment Performance

- Optimum HRT in plasma reactor occurs when majority of dioxane is converted to intermediates in plasma reactor, but organic products remain.
- Plasma degrades 1,4-dioxane; bioreactor degrades remaining products.
- Plasma/bioreactor utilizes 5 times less power than plasma alone and bioreactor is about 5 times faster than without plasma.
- Bioreactor alone can only partially remove 1,4-dioxane and organic carbon.
Dioxane Plasma Degradation Pathway
(liquid phase, ·OH based)

(boxed products detected By GC/MS and NMR)

Products from 1, 4 dioxane suggest oxidation by ·OH.
Formation of Nitrogen Oxides in Ar/N₂

Liquid Phase Results

- Increasing N₂
  - NO₃⁻ saturates and NO₂⁻ continues to increase gradually w/ N₂
  - Limitation of ·OH supply likely
- Increasing N₂ in argon up to 3% reduces H₂O₂ about 25%.
  - Note ·OH is still present to form H₂O₂, but H₂O₂ not largely suppressed by high N₂ (like CO probe shown previously).
Gas Phase CO as ·OH Scavenger in Ar/N₂

- Increasing CO:
  - Does not affect NO formation
  - Lowers NO₂, H₂O₂, NO₂⁻, and NO₃⁻
- Reactions: CO + ·OH → CO₂ + ·H
  - ·OH + ·OH → O + H₂O (more likely source of O for NO formation)
  - NO + ·OH → HNO₂ (decreased due to CO quenching ·OH)
  - NO₂ + ·OH → HNO₃ (decreased due to CO quenching ·OH)
Hydroxyl Radicals in Ar/N₂ Plasma

CO scavenging ·OH

• Significantly more ·OH in CO reactions than in total H₂O₂ and NOₓ.
• Implies room for improvement in plasma oxidation reactions
• ·OH energy yield 6.7 eV/100 molecules provides information on “primary” formation of ·OH
Hydroxyl Radicals in Ar/N₂ Plasma

NO scavenging of ∙OH

**Experimental data suggests ∙OH controls formation of HNO₂, HNO₃ and atomic oxygen**

HNO₂ and HNO₃ production limited by back reactions with increase in inlet NO
Summary of Nitrogen Species Reaction Pathways

Gas Phase

\[ \text{Ar/NO} \]

Plasma zone

\[ e^- \]

\[ \text{•OH + H•} \]

\[ \text{•OH+•OH} \rightarrow \text{H}_2\text{O+O} \]

\[ \text{NO+O} \rightarrow \text{NO}_2 \]

\[ \text{•OH+•OH} \rightarrow \text{H}_2\text{O}_2 \]

\[ \text{NO+•OH} \rightarrow \text{HNO}_2 \]

\[ \text{NO}_2+•\text{OH} \rightarrow \text{HNO}_3 \]

Liquid phase

\[ \text{H}_2\text{O} \]

\[ \text{H}_2\text{O}_2 \]

\[ \text{HNO}_2 \]

\[ \text{HNO}_3 \]

Flow direction

Degradation

\[ \text{H}_2\text{O}_2+e^- \rightarrow \text{•OH+•OH+e^-} \]

\[ \text{HNO}_2+•\text{OH} \rightarrow \text{H}_2\text{O+NO}_2 \]

\[ \text{HNO}_3+•\text{OH} \rightarrow \text{H}_2\text{O+NO}_3 \]

\[ \text{NO}_3+•\text{OH} \rightarrow \text{HO}_2+\text{NO}_2 \]
Conclusions

• Gas-liquid reactor utilized here characterized with respect to
  • Geometry of gas and liquid volumes and interface
  • Hydrodynamic flow patterns, pressure, and mass transfer characteristics
  • Effects of power supply type (microsecond vs nanopulser)
  • Plasma gas temperature, electron density, and electron energy
  • Effects of solution conductivity, pulse frequency, power supply type
    • Nanopulser (fast rise) operates to near seawater conductivity without large drop in $\text{H}_2\text{O}_2$.
    • Formation of hydroxyl radicals, hydrogen peroxide, oxidation products of several organic compounds including liquid phase, gas phase, and volatile compounds

• Relatively high efficiency for ·OH formation demonstrated
  • ·OH (primary) energy yields comparable to all other AOPs
  • ·OH reactions/reaction products found in both gas phase and liquid phase
  • ·OH reactions
    • Reactions of many organic compounds in the liquid and gas phases
    • Control formation of nitrogen oxides, particularly formation of acids
    • Control formation of hydrogen peroxide
    • Degradation reactions (reverse and others) can reduce efficiencies
Recent Collaborators

Dr. Kevin Hsieh (ChE PhD 2015)
Dr. Stefan Bresch (Chem PhD 2015)
Robert Wandell (ChE PhD 2016)
Huihui Wang (ChE PhD 2018)
Yi Xiong (CEE PhD candidate)
Radha Bulusu (ChE PhD candidate)

Prof. Igor Alabugin (Chem/Biochem)
Prof. Youneng Tang (Civil Envir. Engr.)
Prof. Radu Burlica (Iasi University)
Kosuke Tachibana (PhD, Tokyo Inst. Tech. Oita University)
Dr. Jan Voráč (Masaryk University)

- Undergraduates
  - Basiel Makled
  - Parastou (Mandy) Shahzeidi
  - David Reece
  - Rachel Gallan
  - Qiao Zhang (BS/MS)

- Others
  - Eagle Harbor Technologies
  - Patrick Breslend, FSU
  - Dr. Pavel Dvorak, Masaryk Univ.

- Institute of Plasma Physics, Prague
  - Dr. P. Lukes, Dr. V. Jirasek
  - Dr. V. Babicky, Dr. M. Clupek
  - Dr. M. Simek
Thank you for your interest.
Hydroxyl Radicals in N₂/Ar Plasma

- Significantly more \( \cdot \text{OH} \) in CO reactions than in total \( \text{H}_2\text{O}_2 \) and \( \text{NO}_x \).
- Implies room for improvement in plasma oxidation reactions
- \( \cdot \text{OH} \) energy yield 6.7 eV/100 molecules provides information on “primary” formation of \( \cdot \text{OH} \)
Water Plasma (electron) Interactions

Molecules  $e^- + H_2O \rightarrow e^-, O, H, OH$

Clusters  $e^- + H_2O_{liq}$

Aerosols  $e^- + H_2O_{liq}$

Surfaces  $e^- + H_2O_{liq}$

Electron interaction with one water molecule.

Electrons interact with groups of water molecules.

Plasma/gas continuous phase.
Water Plasma (electron) Interactions

Bubbles

$\text{H}_2\text{O}_{\text{liq}}$

Vapor bubble

Thermal or Injected bubble

Liquid is continuous phase

Plasma Channels

$\text{H}_2\text{O}_{\text{liq}}$

$e^{-}$

Increasing photographic time exposure

Fine bubbles formed
Treatability Ranges
(adapted from Tarr, 2003)

Non thermal plasma

Thermal plasma

Chemical oxygen demand (COD) g/l

10^{-2}  10^{-1}  1  10^{1}  10^{2}  10^{3}

- ADVANCED OXIDATION
- BIOLOGICAL OXIDATION
- SUPERCritical OXIDATION
- INCINERATION
Predicted generation of ·OH by various AOPs

<table>
<thead>
<tr>
<th>Process</th>
<th>O₃</th>
<th>H₂O₂</th>
<th>UV</th>
<th>O₃</th>
<th>UV</th>
<th>H₂O₂</th>
<th>OH yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/kWh</td>
<td>g/kWh</td>
<td>eV/photon</td>
<td>mole O₃/mole OH</td>
<td>mole photon/mole OH</td>
<td>mole H₂O₂/mole OH</td>
<td>molecules/100 eV</td>
</tr>
<tr>
<td>O₃</td>
<td>50</td>
<td></td>
<td></td>
<td>1.5</td>
<td></td>
<td></td>
<td>1.9</td>
</tr>
<tr>
<td>O₃</td>
<td>100</td>
<td></td>
<td></td>
<td>1.5</td>
<td></td>
<td></td>
<td>3.7</td>
</tr>
<tr>
<td>O₃/UV</td>
<td>50</td>
<td>1</td>
<td></td>
<td>1.5</td>
<td>0.5</td>
<td></td>
<td>1.8</td>
</tr>
<tr>
<td>O₃/UV</td>
<td>50</td>
<td>6</td>
<td></td>
<td>1.5</td>
<td>0.5</td>
<td></td>
<td>1.8</td>
</tr>
<tr>
<td>O₃/UV</td>
<td>100</td>
<td>1</td>
<td></td>
<td>1.5</td>
<td>0.5</td>
<td></td>
<td>3.6</td>
</tr>
<tr>
<td>O₃/UV</td>
<td>100</td>
<td>6</td>
<td></td>
<td>1.5</td>
<td>0.5</td>
<td></td>
<td>3.3</td>
</tr>
<tr>
<td>O₃/H₂O₂</td>
<td>50</td>
<td>50</td>
<td>1</td>
<td></td>
<td></td>
<td>0.5</td>
<td>2.1</td>
</tr>
<tr>
<td>O₃/H₂O₂</td>
<td>100</td>
<td>50</td>
<td>1</td>
<td></td>
<td></td>
<td>0.5</td>
<td>3.3</td>
</tr>
<tr>
<td>H₂O₂/UV</td>
<td>50</td>
<td>1</td>
<td></td>
<td></td>
<td>0.5</td>
<td>0.5</td>
<td>7.6</td>
</tr>
<tr>
<td>H₂O₂/UV</td>
<td>50</td>
<td>6</td>
<td></td>
<td></td>
<td>0.5</td>
<td>0.5</td>
<td>6.4</td>
</tr>
<tr>
<td>H₂O₂ Fenton</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td></td>
<td>3.9</td>
</tr>
<tr>
<td>H₂O₂ Fenton</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td></td>
<td>7.9</td>
</tr>
</tbody>
</table>

- Stoichiometry taken from Glaze, 1987
- Does not account for low O₃ solubility and mass transfer
- Idealized view due to solution (pH, scavengers, etc.) conditions
# Hydroxyl Radicals from AOPs

<table>
<thead>
<tr>
<th>Process</th>
<th>Overall reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_3$</td>
<td>Molecular: $O_3$ + reactant $\rightarrow$ product</td>
</tr>
<tr>
<td></td>
<td>Radical: $O_3$ ... $\rightarrow$ ·OH</td>
</tr>
<tr>
<td>H$_2$O$_2$ - Fenton</td>
<td>$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + \cdot OH + OH^{-}$</td>
</tr>
<tr>
<td>O$_3$/H$_2$O$_2$</td>
<td>$H_2O_2 + 2O_3 \rightarrow 2 \cdot OH + 3O_2$</td>
</tr>
<tr>
<td>UV</td>
<td>Reactant + h$\nu$ $\rightarrow$ products</td>
</tr>
<tr>
<td>O$_3$/UV</td>
<td>$O_3$+H$_2$O + h$\nu$ $\rightarrow$ 2 ·OH + O$_2$</td>
</tr>
<tr>
<td>UV/H$_2$O$_2$</td>
<td>$H_2O_2 + h\nu \rightarrow 2 \cdot OH$</td>
</tr>
<tr>
<td>O$_3$/UV/H$_2$O$_2$</td>
<td>$2O_3 + H_2O_2 + h\nu \rightarrow 2 OH + 3 O_2$</td>
</tr>
</tbody>
</table>

Key species: input – O$_3$, H$_2$O$_2$, UV  major reactant - ·OH
Ozone Reactions in Water

1) $\text{O}_3 + \text{reactant} \rightarrow \text{products}$

2) $\text{O}_3 \rightarrow \cdot\text{OH}$
   (net 1.5 moles $\text{O}_3$ to 1 mole $\cdot\text{OH}$)

$\cdot\text{OH} + \text{reactant} \rightarrow \text{products}$

Limitations
- Ozone solubility in water
- Mass transfer
- Solution properties, e.g. scavengers

(Staehlin and Hoigne, 1985)
UV and Chemical Pathways

Ozone + UV

\[ \text{O}_3 + \text{H}_2\text{O} + \text{hv} \rightarrow 2 \cdot \text{OH} + \text{O}_2 \]

(Peyton/Glaze 1988)

H$_2$O$_2$ + UV

\[ \text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \cdot \text{OH} \]

(Peyton 1990)
Scaled-up Prototype
Oxygen Addition

- Oxygen addition leads to significant ozone formation in the gas phase.
- Oxygen addition only slightly decreases H$_2$O$_2$ formation.
- Oxygen addition has no effect on MB decoloration in liquid.
  - Suggests ozone transfer to liquid and reactions is liquid slow.
# Dye Removal

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Energy Yield g/kWh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulsed discharge in water</td>
<td>0.08 to 0.2</td>
</tr>
<tr>
<td>DC discharges in air over water film</td>
<td>4.9</td>
</tr>
<tr>
<td>Plasma jet discharge with argon</td>
<td>0.4</td>
</tr>
<tr>
<td>PCD in water with O$_2$ bubbling</td>
<td>0.59</td>
</tr>
<tr>
<td><strong>Water film reactor with argon (this work)</strong></td>
<td><strong>2.3 to 4.0</strong></td>
</tr>
<tr>
<td>Laminar jet with bubbling (Thagard)</td>
<td>11.4</td>
</tr>
<tr>
<td>Water spray in PDBD with O$_2$</td>
<td>45</td>
</tr>
<tr>
<td>UV/H$_2$O$_2$</td>
<td>0.1</td>
</tr>
<tr>
<td>Ultrasound</td>
<td>0.2</td>
</tr>
<tr>
<td>Photocatalysis</td>
<td>0.2</td>
</tr>
<tr>
<td>Ozonation</td>
<td>0.3</td>
</tr>
</tbody>
</table>

**Figure:**

- **Total Organic Carbon Removal:**
  - 0.5 mM RhB
  - 0.1 mM MB

**Graph:**

- TOC Removal % vs Liquid Flow Rate (mL/min)
Key issues

• Can we control the chemical reactions by changing the input conditions?
  • How affect efficiency and selectivity?

• Do the input pulse parameters affect plasma properties such as electron density, electron temperature, and plasma temperature?

• Do these plasma properties affect chemistry?

• What is the role of liquid water?
  • Source of reactants: from liquid to plasma
    • $\text{H}_2\text{O}$: ·$\text{OH}$ oxidant, $\text{H}$ reductant
  • Interface and transport of mass and energy
    • Second phase improves plasma, thermal, and chemical quenching and increases gradients at phase boundary
    • Magnitudes of the gradients in temperature and concentration at interface
    • How do gradients affect chemical reactions?
    • Which reactive species transfer between plasma and liquid?
  • Collects products: from plasma to liquid
    • $\text{H}_2\text{O}_2$, alcohols, aldehydes,...
Summary

- Organic compounds in gas phase: hexane, CO, ethanol
- Organic compounds in the liquid phase: MB, ethanol
Electrical Circuit Model for Conductivity Effects
(Eagle Harbor nanopulser)

$R_p(t) \approx \frac{l}{Ae\mu_e N_e(t)}$

$R_p, R_w, R_{1,2,3,4}$: Resistance of plasma, water film, and resistors in the circuit
$C_p$: Capacitance of reactor
$A$: Cross-section area of plasma channel
$e$: Elementary charge
$\mu_e$: Mobility of electron
$N_e$: Electron density
$l$: Electrode gap
$L$: Inductance of wire

- $N_e(t)$ – assumed to follow current pulse.

(Wang et al., 2019)
Simulating Discharge Voltage and Current
(Eagle Harbor nanopulser)

(Power Supply: 20 kV, 2kHz, 50ns; DI water 1mL/min; Argon)
Liquid Conductivity and Breakdown Voltage
(Eagle Harbor nanopulser)

- Power Supply: 20 kV, 2kHz, 50ns; 40 mS/cm, 1mL/min; Argon
- Breakdown voltage drops with liquid conductivity

(Wang et al., 2019)
Influence of Applied Voltage on Breakdown

Conditions/Assumptions:
- 40mS/cm KCl solution
- Carrier gas: Argon
- Electron density was assumed unchanged with applied voltage
- Two applied voltages with different pulse rise time were used

- Longer rise times lead to lower breakdown voltages.
- Ignition coil power supply rise time 4 µs insufficient to generate discharge at high conductivity.
- Eagle Harbor power supply rise time 20 ns works very well.