

PFAS – the “Forever Chemicals”: Destructive Treatment Technologies



Clarkson™

WALLACE H. COULTER
SCHOOL OF ENGINEERING

PFAS TREATMENT CHALLENGES

Several unique properties for environmental contaminants

- Strong C-F bond
- Low volatility
- Charged (high solubility)

EVALUATING DESTRUCTIVE TREATMENT TECHNOLOGIES

- Reactor conditions required
- Effectiveness
 - Chain-length dependence
 - Byproducts produced
 - Effluent treatment required
- Is there a compound specific concentration range (initial and final)
- Ability to scale-up
- Cost

For many technologies some of these are not fully known.

Lots of Advanced Oxidation Processes (AOPs) have been tried.

Most with limited success.

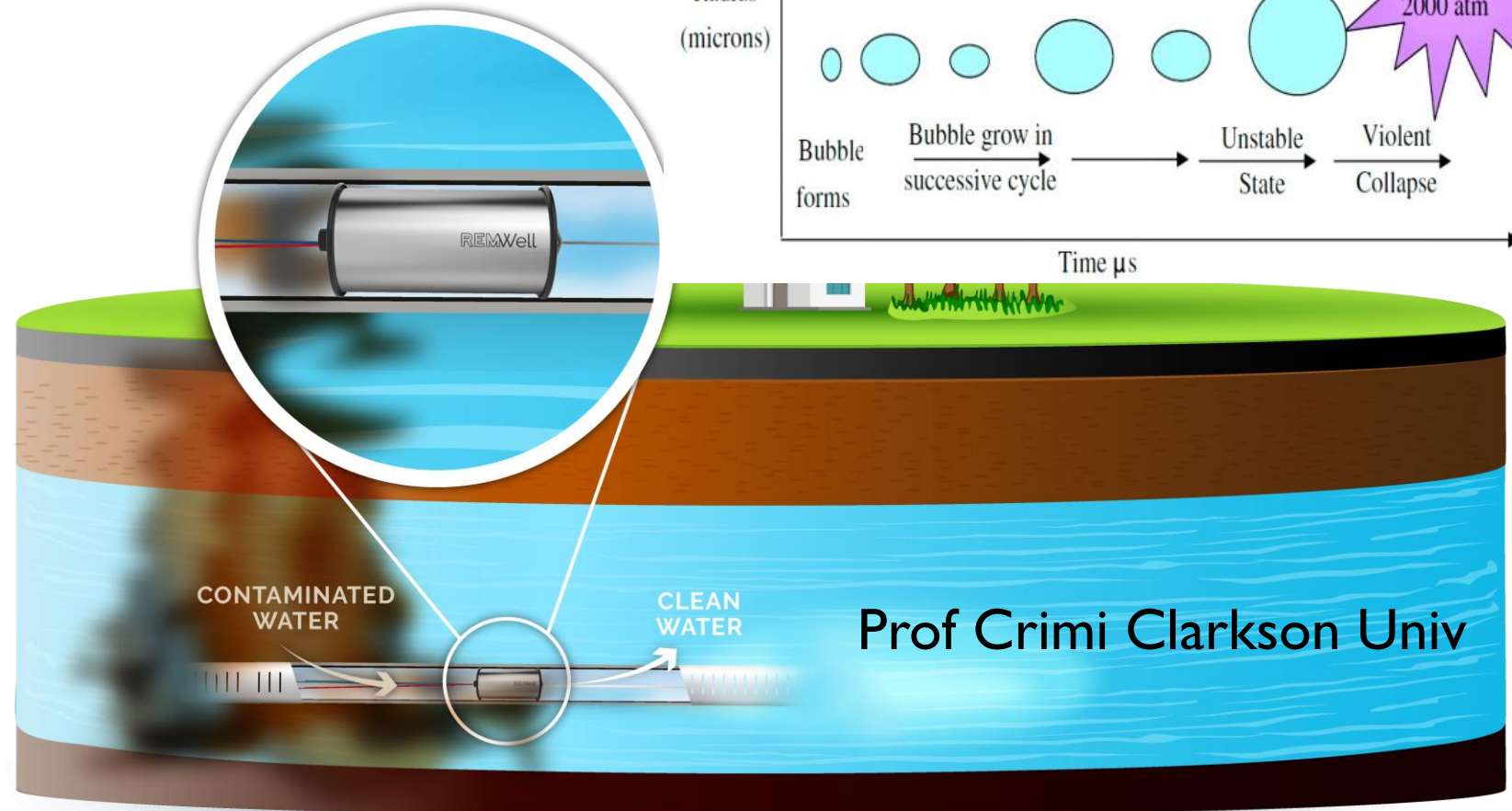
Need new approaches.

Oxidation Approach	Intermediates and Byproducts
Persulfate	F ⁻ , PFPrA, PFHpA, PFHxA, PFPA PFPeA , PFBA,TFA
Permanganate	F ⁻ , SO ₄ ²⁻
UV-Fenton	F ⁻ , Formic acid, PFPrA, PFHpA, PFHeA, PFPeA , PFBA
Fe(III)	F ⁻ , PFPrA, PFHpA, PFHeA, PFPeA
Ferrates	No observed F ⁻
Fe(III) and Oxalate	F ⁻ , PFPrA , PFBA, PFPeA, PFHxA, PFHpA
Plasma	F ⁻ , TFA PFPrA , PFBA, PFPeA, PFHxA, PFHpA, PFBS
UV-Pb-modified TiO ₂	PFHpA , PFHeA, PFPrA, TFA PFPeA, PFBA
Sonolysis	PFHpA, PFHxA, PFPA, TFA and F ⁻ ,PFHpS, PFHxS, PFOA
Photocatalysis with Inidium oxide	F ⁻ ,PFHpA , PFHeA, PFPrA, PFPeA, PFBA
TiO ₂ photocatalysis	PFHpA, PFHpA, PFPeA, PFBA
Environmental photolysis	PFBA, PFBS, PFOA
Electrochemical oxidation	F ⁻ , TFA, PFPA, PFBA, PFPeA, PFHxA, PFHpA
Photolysis with persulfate	F ⁻ ,CO ₂ , SO ₄ ²⁻ PFBA, PFPeA, PFHxA, PFHpA
Microwave hydrothermal decomp.	F ⁻ ,CO ₂ , PFBA, PFPeA, PFHxA, PFHpA, PFHeA

SONOLYSIS – IN SITU TREATMENT

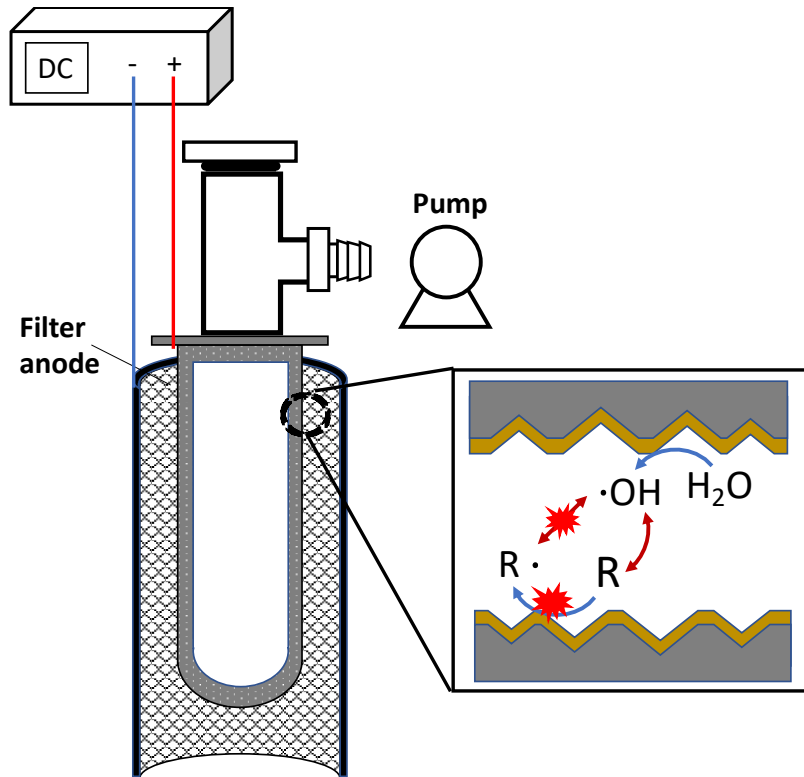
- In situ sonolytic reactor for treatment of PFAS
- Undergoing field trials

Not scalable for larger flowrates



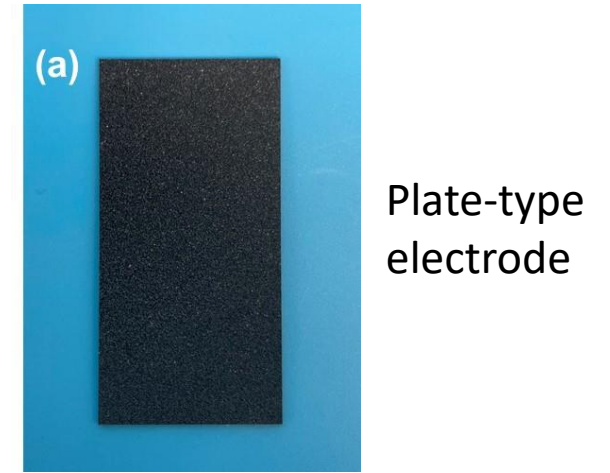
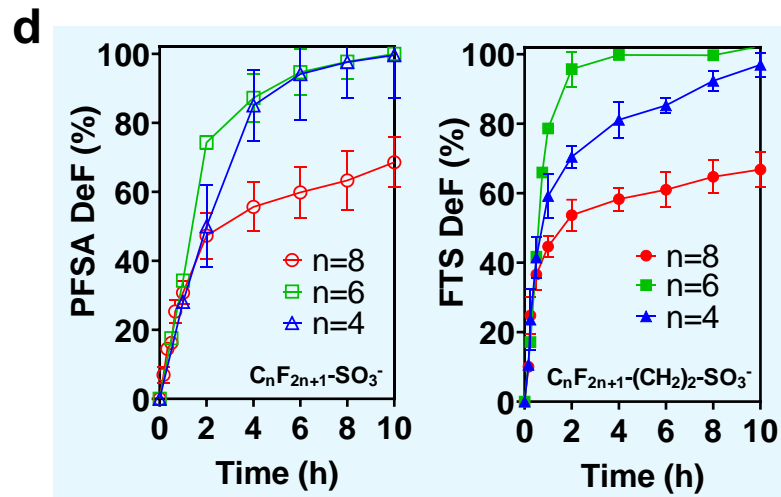
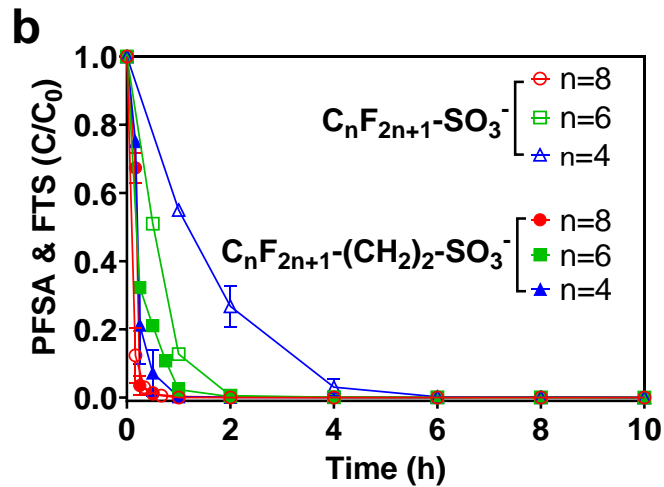
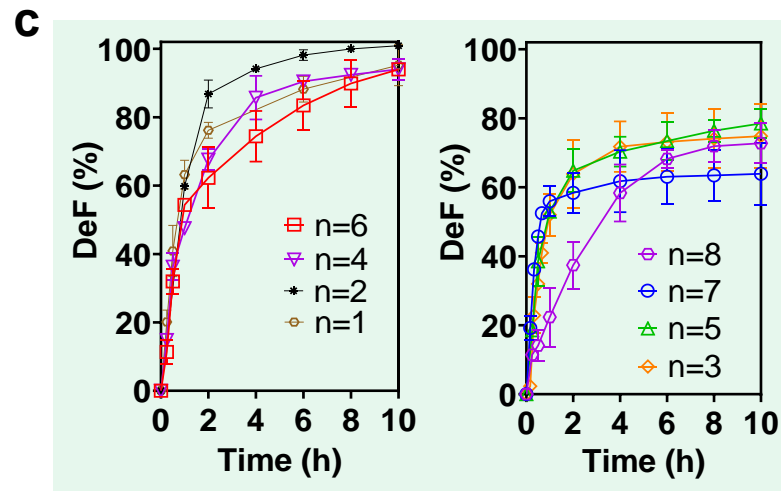
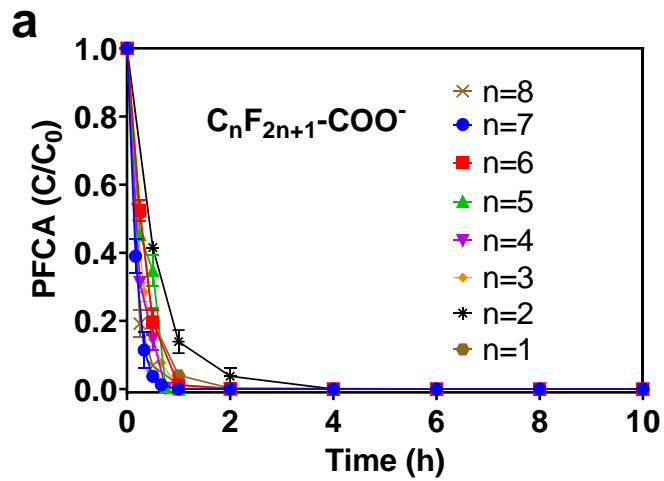
One start-up commercializing this technology

ELECTROCHEMICAL OXIDATION



Production of hydroxyl radicals using electricity





750 mL reactor volume

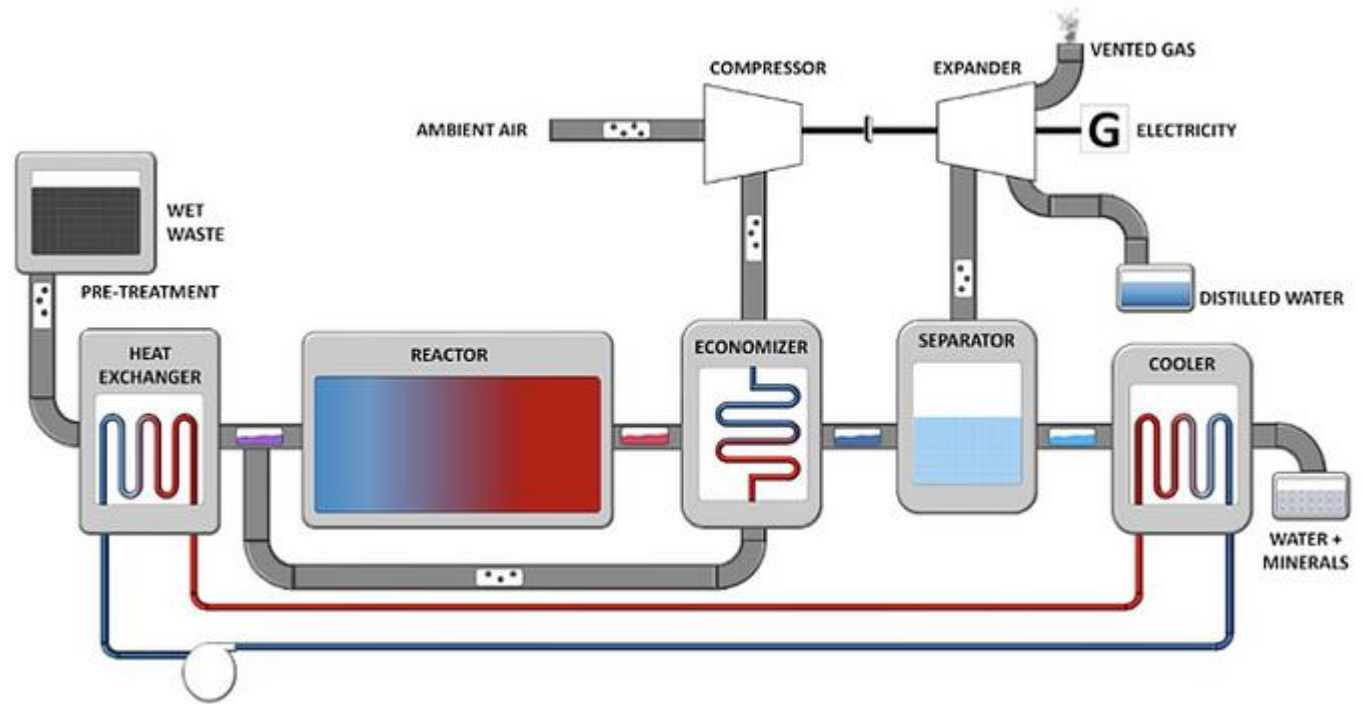
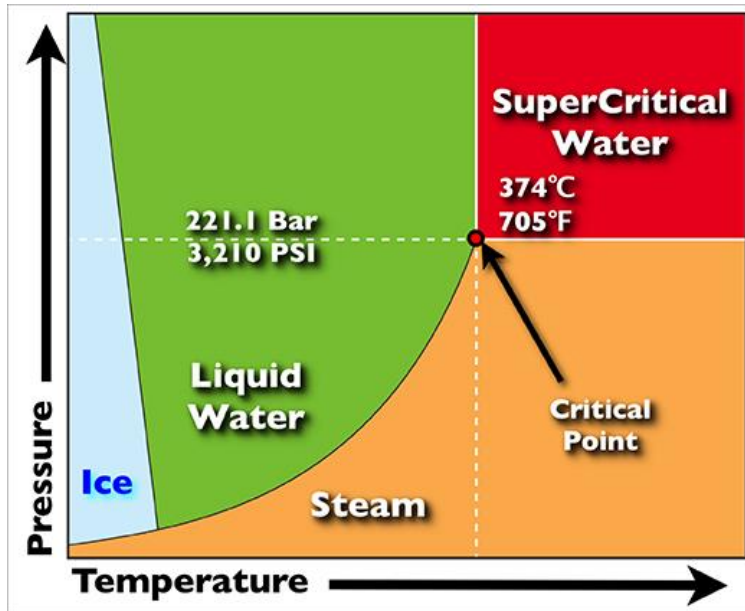


Flow-cell electrode

(Manuscript under review)

High defluorination efficiency, challenges with scale-up since surface contact is required, energy intensive, potentially toxic byproducts produced

SUPERCRITICAL WATER OXIDATION



Good removal, independent of chain length, susceptible to corrosion particularly if salts are present, pH adjustment and control needed, energy and infrastructure intensive

Several companies involved in commercializing this technology

HYDROTHERMAL ALKALINE TREATMENT (HALT)

Requires alkaline amendment (typically sodium hydroxide [NaOH] to pH >14), high-pressure (~25 MPa) and high-temperature (~350 °C)

Chain length independent, few byproducts

Scale-up unknown

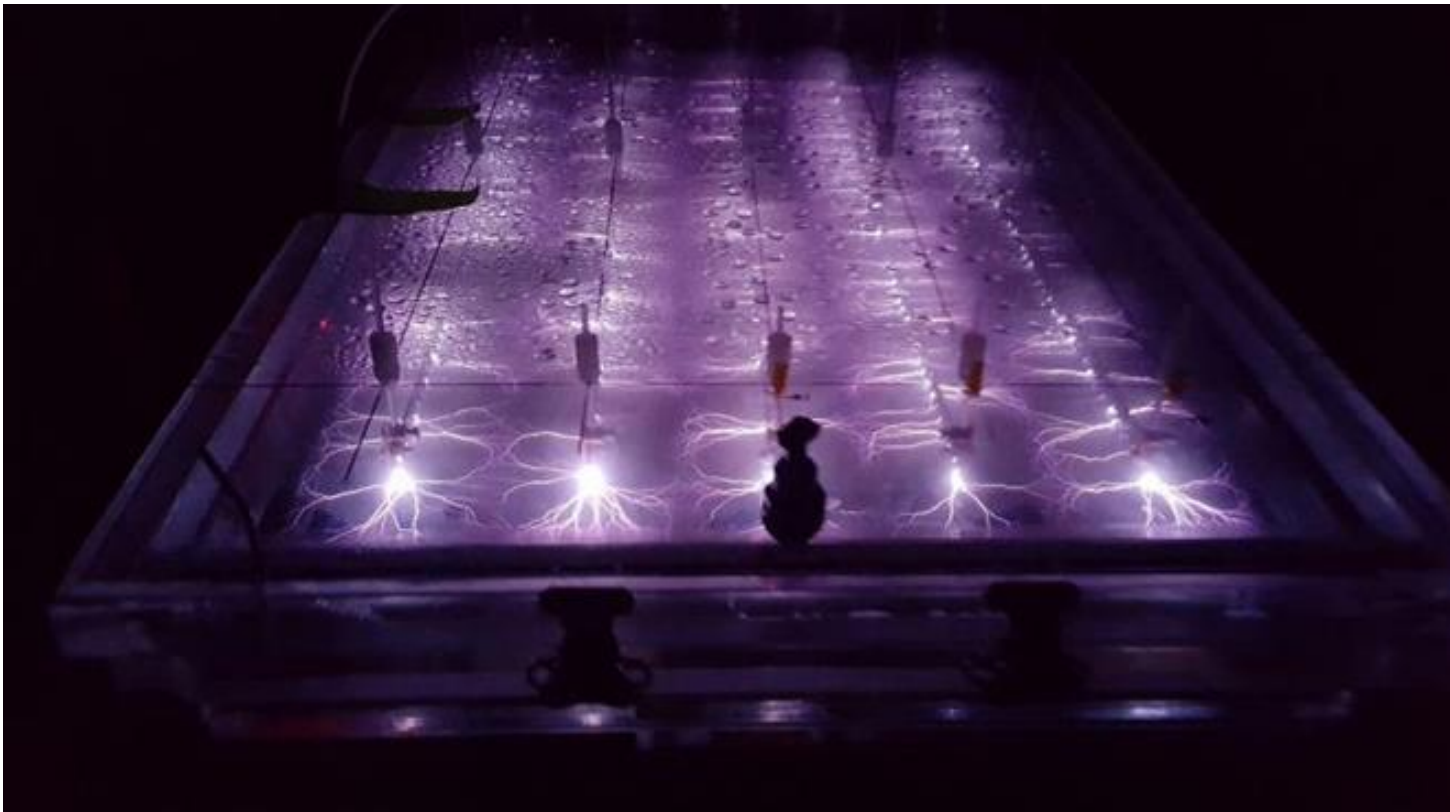
High pH effluent

Energy intensive

One start-up commercializing this technology



ENHANCED CONTACT PLASMA FOR PFAS DESTRUCTION



Professors Mededovic Thagard
and Holsen

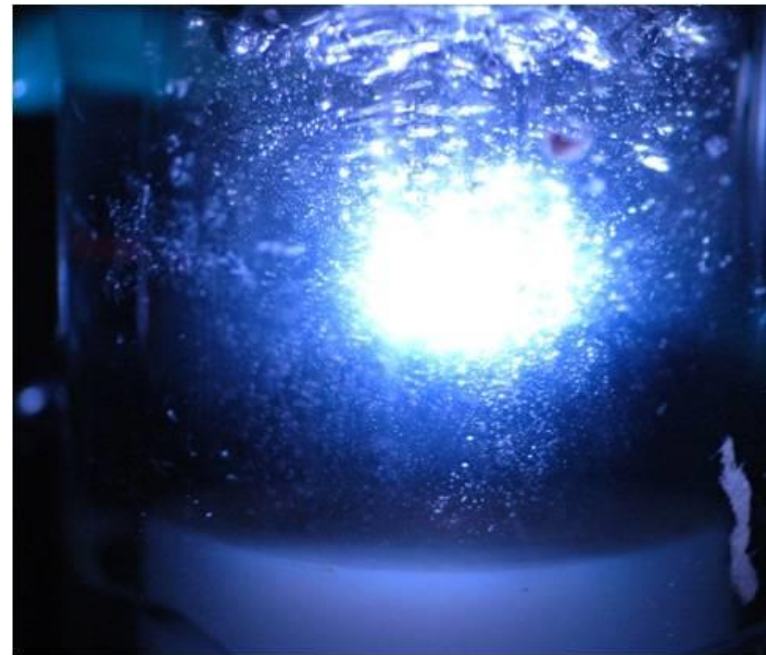
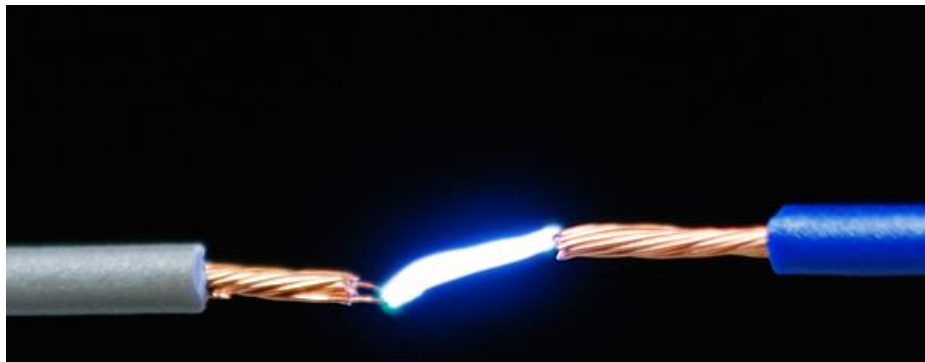
Start-up company DMAX Plasma
Inc



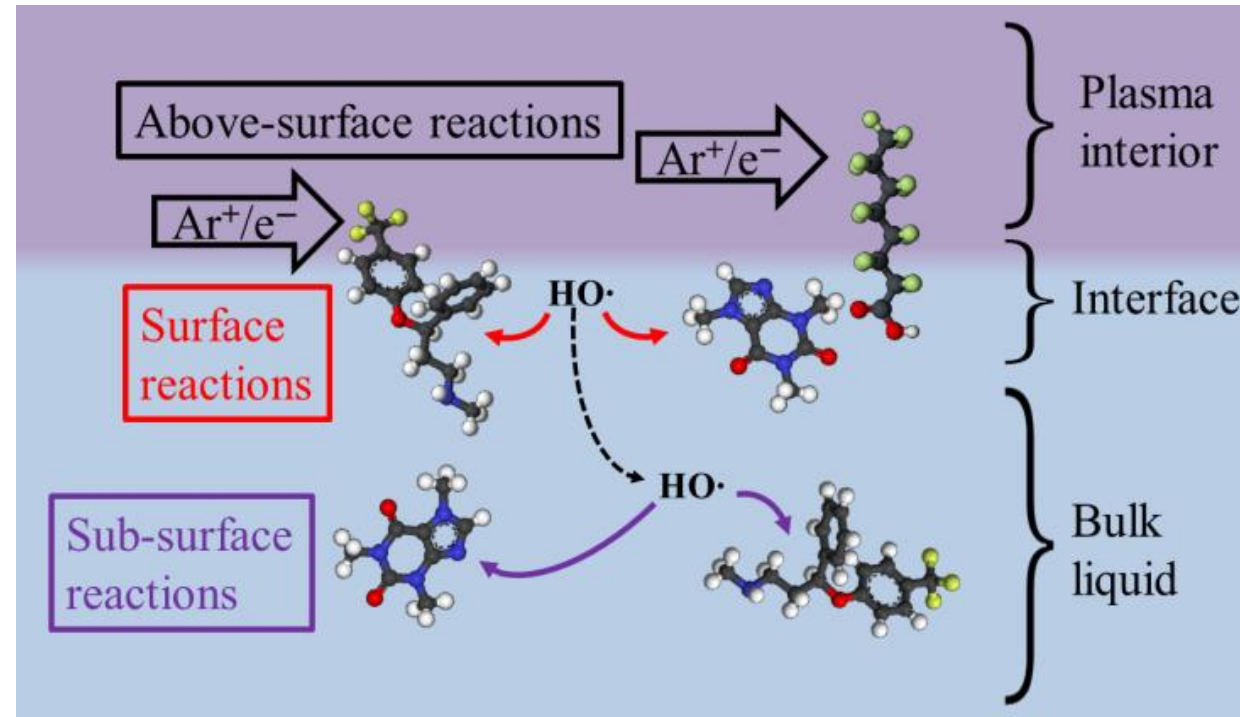
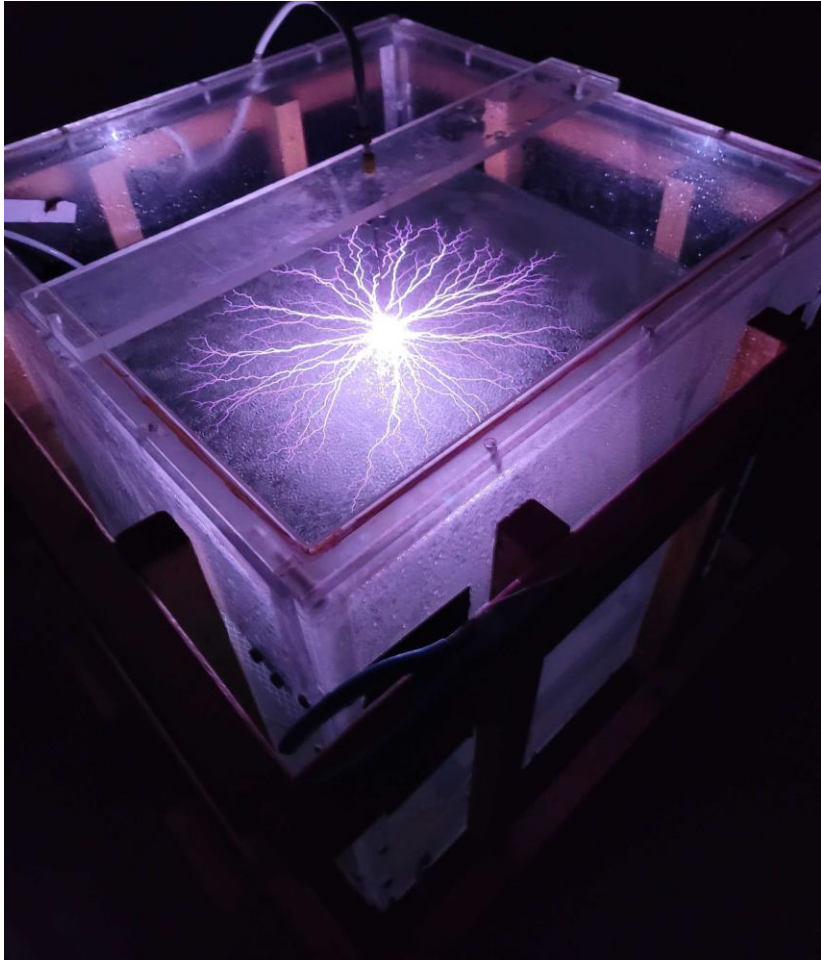
Video of one of the plasma reactors in operation

PLASMA

- Plasma is an ionized gas consisting of a quasi-neutral mixture of neutral species, positive ions, negative ions, and electrons.
- Plasmas are created by applying a potential difference between two metal electrodes. One of the electrodes can be immersed in a liquid.
- Plasma-based water treatment uses electricity to convert water into a mixture of highly reactive species (i.e., plasma) that rapidly and non-selectively degrade recalcitrant organic contaminants.



GAS-LIQUID REACTORS: THE BEST PERFORMING PLASMA TREATMENT SYSTEMS

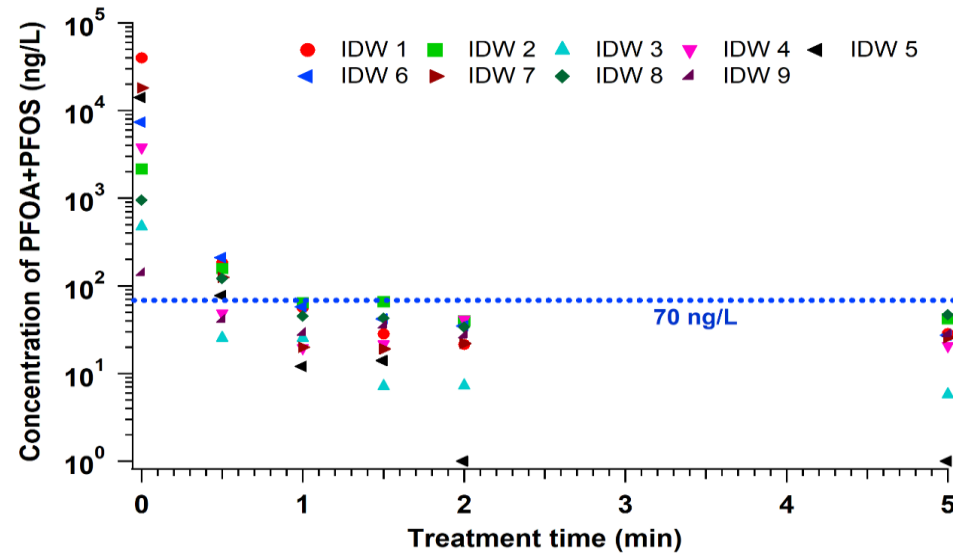


- Argon gas bubbles bring the PFAS to the gas-water interface near to where the plasma is generated (argon is recycled).
- Reductive species like solvated electrons and argon radicals play a key role in PFAS destruction (breaking the C-F bond).

BATCH REACTOR PERFORMANCE: REMOVAL OF PFAS FROM INVESTIGATION-DERIVED WASTE (IDW)



PFOA and PFOS concentrations in investigation derived waste (IDW) obtained from 9 different Air Force site investigations. Treatment volume is 4 L. No pre-treatment.



AFCEC funded
project partnered
with GSI
Environmental

Removal of PFOA+PFOS to < 70 ng/L in 2 minutes

Several successful field trials treating 1000's of gallons each

Short-chain removal slow – can be improved with the addition of a surfactant

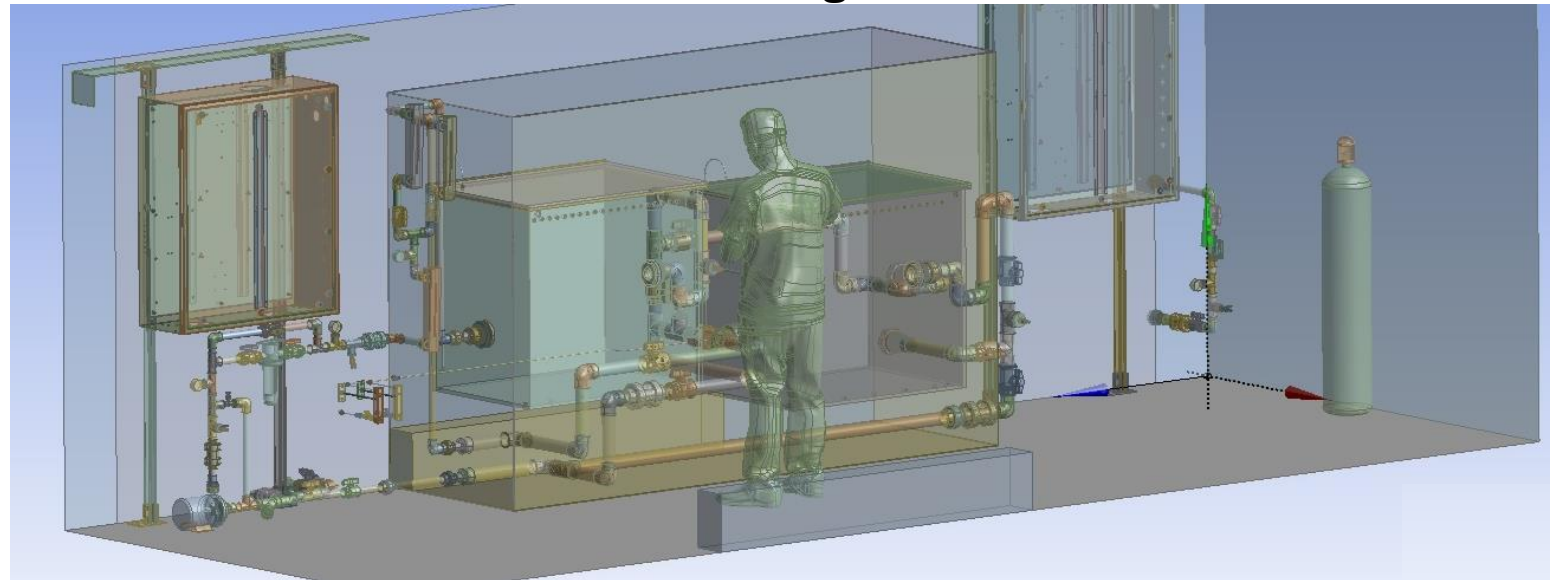
Energy costs low – fractions of a penny/gallon

DMAX PLASMA ECo-PR_e™

- ✓ ONLY field proven PFAS “Degradation and Destruction” solution
- ✓ Cost Effective – Low Energy & Operating Expense
- ✓ High Scalable Throughput
- ✓ Treat Any PFAS mix, Anywhere (mobile available)
- ✓ No Hazardous By-Products
- ✓ Safe & Durable Operation



DMAX Plasma 4th generation mobile treatment trailer





Newest trailer with
automated
controls

Treating
membrane
concentrate at
Wright Patterson
Air Force Base this
week

QUESTIONS ABOUT DESTRUCTIVE TECHNOLOGIES

- Can you verify destruction with fluoride recovery? Are the compounds truly destroyed?
- What intermediates or byproducts may form?
- What impact do precursors have on mass balance?
- What is the energy cost?
- What are the implementation challenges?