Rapid Removal of PFAS from Investigation Derived Waste (IDW) in a Pilot-scale Plasma Reactor

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Team Members

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• Stephen Richardson, GSI Environmental
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Background

- Historical use of aqueous film forming foams containing PFAS for firefighting and training activities at DoD sites, commercial airports and industrial facilities.
- Potential for groundwater contamination at up to 600 sites.
- PFOA/PFOS concentrations measured in groundwater at multiple locations are often several orders of magnitude higher than federal drinking water health advisories.
- PFAS are difficult to remove using traditional treatment approaches.
- PFAS are very recalcitrant because of the stability of the C-F bond.
Plasma-based Water Treatment

**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.

Electrical discharge plasma formed *directly in* or *above* water makes use of OH radicals to oxidize and aqueous electrons to chemically reduce organic and inorganic compounds.

https://www.nature.com/articles/srep40379

Pictures courtesy of Plasma Research Laboratory, Clarkson University
Plasma Formation

Circuit diagram for a pulsed power supply

Plasma in argon gas contacting water

S\textsubscript{l} = liquid solute  \quad S\textsubscript{g} = gas solute
Plasma PFAS Treatment

Bench-scale Degradation of PFOA and PFOS in the Enhanced Contact Plasma Reactor

PFOA and PFOS Degradation: Liquid- and Gas-phase Byproducts

> 98% of PFOA at the interface protrudes out into the plasma
Liquid Byproducts - PFOA

PFAA byproducts

Non-PFAA byproducts

Liquid Byproducts - PFOS

**PFAA byproducts**

85% of the theoretical sulfate that could be produced from the oxidation of sulfur present in 8.3 mg/L of PFOS.

**Non-PFAA byproducts**


F in organic byproducts < 2% of initial F (PFOS)

85% of the theoretical sulfate that could be produced from the oxidation of sulfur present in 8.3 mg/L of PFOS
Gaseous Byproducts


F in cyclic fluoroalkanes ~1% of initial F
Fluorine Mass Balance

PFOA
- Liquid byproducts – 74%
- Gas-phase byproducts – 2.5%
- Sorption – 22%

PFOS
- Liquid byproducts – 57%
- Gas-phase byproducts – 1%
- Sorption – 38%

Plasma PFAS Treatment

HV

Argon

0.5-2 GPM

Plasma reactor rack with closed doors (two plasma reactors are inside)

Power supply rack that houses the main components of the plasma-generating electrical network
Two rotating spark gaps used to generate plasma.

First plasma reactor

Second plasma reactor
Measurement of power in the plasma reactors

External power supplies
Video of one of the plasma reactors in operation
Degradation profiles of combined 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.
Field Demonstration of the Scaled-up Plasma Reactor

- Field demonstration was performed September 16-27, 2019 at former Fire Training Area 2, Wright-Patterson AFB
- Designed as a mobile unit for treatment of stored IDW purge water or other sources of PFAS-impacted water
Plasma Side of the Trailer

Diagram showing:
- Reactors
- Recycle tank
- Influent tank
- Effluent tank
Field Demonstration - Water Composition

- PFAS-impacted water was pumped from two monitoring wells, FTA2-MW02B (Well B) and FTA2-MW02C (Well C)

- PFOA and PFOS concentrations:

<table>
<thead>
<tr>
<th>Well</th>
<th>PFOA (ppt)</th>
<th>PFOS (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTA2-MW02B</td>
<td>185</td>
<td>1100</td>
</tr>
<tr>
<td>FTA2-MW02C</td>
<td>416</td>
<td>3944</td>
</tr>
</tbody>
</table>

~350 gallons of PFAS-impacted groundwater were treated at various reactor operating conditions (flowrates, no. of recycle events*)

- Well B conditions: 0.3 GPM, 0.6 GPM and 0.9 GPM per reactor treated for 8 cycles, 8 cycles and 10 cycles respectively.
- Well C conditions: 0.3 GPM and 1.1 GPM per reactor treated for 8 cycles each.

*One cycle (18 gal of water) is defined as a single pass through the reactor from the influent tank.
Trailer Performance Results: Well B at 0.9 GPM* for 10 Cycles

**PFOA+PFOS (ng/L)**

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>Final</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1750</td>
<td>BDL</td>
</tr>
<tr>
<td>Final</td>
<td>BDL</td>
<td>BDL</td>
</tr>
</tbody>
</table>

*Initial and final concentrations for PFOA+PFOS.

**6:2FTS (ng/L)**

<table>
<thead>
<tr>
<th></th>
<th>6:2FTS</th>
<th>8:2 FTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1052</td>
<td>96</td>
</tr>
<tr>
<td>Final</td>
<td>BDL</td>
<td>BDL</td>
</tr>
</tbody>
</table>

*Initial and final concentrations for 6:2FTS and 8:2 FTS.

*Higher number of cycles needed at lower flowrates due to the presence of precursors

BDL=Below Detection Limit (< 9 ng/L)
## Trailer Performance Results: Well B at 0.9 GPM for 10 Cycles

<table>
<thead>
<tr>
<th></th>
<th>PFHxS (ng/L)</th>
<th>PFNA (ng/L)</th>
<th>PFNS (ng/L)</th>
<th>PFOA (ng/L)</th>
<th>PFOS (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial</strong></td>
<td>1160</td>
<td>72</td>
<td>20</td>
<td>208</td>
<td>1504</td>
</tr>
<tr>
<td><strong>Final</strong></td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>PFBA (ng/L)</th>
<th>PFBS (ng/L)</th>
<th>PFHpA (ng/L)</th>
<th>PFHxA (ng/L)</th>
<th>PFPeA (ng/L)</th>
<th>PFPeS (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial</strong></td>
<td>140</td>
<td>488</td>
<td>288</td>
<td>640</td>
<td>476</td>
<td>268</td>
</tr>
<tr>
<td><strong>Final</strong></td>
<td>102</td>
<td>93</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
</tbody>
</table>

![Concentration vs Cycle Graph](image1)

![Concentration vs Cycle Graph](image2)
Trailer Performance Results: Well C at 1.1 GPM for 8 Cycles

Initial | Final | PFOA+PFOS
|---|---|---|
| 4640 | 8.64 | (ng/L)
| 2550 | BDL | 6:2 FTS
| 550 | BDL | 8:2 FTS

0 1 2 3 4 5 6 7 8

Concentration (ng/L)

0 500 1000 1500 2000 2500 3000

Cycle

0 1 2 3 4 5 6 7 8

Concentration (ng/L)

0 500 1000 1500 2000 2500 3000
Trailer Performance Results: Well C at 1.1 GPM for 8 Cycles

<table>
<thead>
<tr>
<th></th>
<th>PFHPS (ng/L)</th>
<th>PFHxS (ng/L)</th>
<th>PFNA (ng/L)</th>
<th>PFNS (ng/L)</th>
<th>PFOA (ng/L)</th>
<th>PFOS (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>156</td>
<td>1952</td>
<td>192</td>
<td>28</td>
<td>408</td>
<td>4232</td>
</tr>
<tr>
<td>Final</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>8.64</td>
<td>BDL</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>PFBA (ng/L)</th>
<th>PFBS (ng/L)</th>
<th>PFHpA (ng/L)</th>
<th>PFHxA (ng/L)</th>
<th>PFPeA (ng/L)</th>
<th>PFPeS (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>232</td>
<td>636</td>
<td>436</td>
<td>1068</td>
<td>772</td>
<td>416</td>
</tr>
<tr>
<td>Final</td>
<td>412</td>
<td>134</td>
<td>BDL</td>
<td>14</td>
<td>11</td>
<td>BDL</td>
</tr>
</tbody>
</table>

#TheECSummit
Removal of Short-chained PFAS with the Addition of a Surfactant

Cationic surfactants (CTAB) electrostatically and hydrophobically interact/associate with short-chained PFAS and transport them to the plasma-liquid interface.

In the CTAB addition experiments (0.9 GPM for 4 cycles) the CTAB concentration was increased to 0.04 mM before each cycle.
## Trailer Performance Results: Energy Use

Energy requirements and calculated costs for reducing the initial PFOA+PFOS concentration to below 70 ng/L (argon and recycling costs included)

<table>
<thead>
<tr>
<th>Test</th>
<th>Energy required (KWh)</th>
<th>Total Cost</th>
<th>Cost/cycle</th>
<th>Cost/gallon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Test B</td>
<td></td>
</tr>
<tr>
<td>0.3 gpm</td>
<td>4 (4 cycles)</td>
<td>$0.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6 gpm</td>
<td>1 (1 cycle)</td>
<td>$0.12</td>
<td>$0.12/cycle</td>
<td>$0.0067/gal</td>
</tr>
<tr>
<td>0.9 gpm</td>
<td>1 (1 cycle)</td>
<td>$0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Test C</td>
<td></td>
</tr>
<tr>
<td>0.3 gpm</td>
<td>3 (3 cycles)</td>
<td>$0.36</td>
<td>$0.12/cycle</td>
<td>$0.0067/gal</td>
</tr>
<tr>
<td>1.1 gpm</td>
<td>2 (2 cycles)</td>
<td>$0.24</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Summary

- Plasma-based water treatment is an effective technology for the treatment of various sources PFAS-impacted water.
- Co-contaminants have no effect on the PFAS treatment efficiency.
- Higher volumetric flowrates reduce the treatment time.
- The treatment is capable of reducing PFOA+PFOS to < 70 ng/L in ~ 2 cycles (4 minutes of treatment).
- Long term treatment of PFOA and PFOS results in the formation of a range of liquid byproducts and minor concentrations of cyclic gas-phase byproducts.
- The technology is highly scalable and is more efficient than leading alternative destructive processes for treatment of PFAS-contaminated water.
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