Abiotic Treatment Technologies for In-Site Remediation of Persistent Perfluoroalkyl Acids

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US Military big user of AFFFs, which are a primary source of PFAAs and likely present at > 550 sites.

Additional, many other military sites due to use/releases of AFFFs to extinguish hydrocarbon fires or industrial activities, etc.

PFAAs are persistent, bioaccumulative, and relatively mobile.

Provisional health advisory levels are well below what is expected at military sites.

Currently, no viable in-situ technology has been successfully demonstrated for the entire suite of PFASs, particularly linear PFOS, or PFAA precursors.

*Moody and Field, 1999; Moody et al., 2003; Schultz et al., 2004
PFASs in Aqueous Film Forming Foams (AFFFs)  
(Place & Field, EST, 2012)

Electrofluorination-based fluorinated surfactants

Telomer-based fluorinated surfactants

Perfluorosulfonic acids  
PFSAs (PFOS $pK_a < 0$)

Perfluorocarboxylic acids  
PFCAs (PFOA $pK_a < 4$)

Terminal microbial end products

$\Sigma = \text{PFAAs} = \text{perfluoro alkyl acids}$
Initial Approach: Chemical Oxidative Treatment

- **Fenton’s Reagent**
  - Thermodynamic studies indicate not effective
  - PFOS not degraded with an aggressive treatment.

- **Ultraviolet reactions**
  - Successful for only PFOA
  - Conditions not applicable in situ

- **Permanganate**
  - Some success with PFOS at ≥ 65 °C & low pH *(Liu et al, 2012)*

- **Sonolysis**
  - Good results for PFOA and PFOS
  - Not applicable for in situ

- **Persulfate**
  - UV and heat activation established successful for PFOA *(Hori et al., 2005; Lee et al, 2012; Liu et al., 2013)*

*Choice of activation mode dependent on effectiveness and efficiency for a given environment, e.g., in-situ versus ex-situ.*
Heat-activated Persulfate for 3 Representative PFASs

**Experimental Variables**

- Temperature (20 ~ 60 °C)
- Unbuffered pH
- Persulfate (Na$_2$S$_2$O$_8$) Conc. (0 ~ 20,000 mg/L, 84.00 mM)
- PFACs conc. (50 ~ 2,500 µg/L, 0.12 µM ~ 6 µM)
- Fuel co-contaminants (BTEXs up to 1,000 µg/L)
- Aquifer
Varying Temperature

\[ [\text{Na}_2\text{S}_2\text{O}_8] = 10,000 \text{ mg/L} \]

Varying \([\text{Na}_2\text{S}_2\text{O}_8] \), \( T = 50 \degree \text{C} \)

- Removal rate ↑ with ↑ temperature and ↑ \([\text{Na}_2\text{S}_2\text{O}_8]\)
- Linear Arrhenius Plots (right graph)
- Unbuffered pH (pH decreases with reaction)
- Same for PFCA range tested: 50 ~ 2,500 \( \mu \text{g/L} \) (0.12 \( \mu \text{M} \) ~ 6 \( \mu \text{M} \))
Heat (50 °C) - Activated Persulfate
[Na$_2$S$_2$O$_8$] – 10,000 mg/L, 50 °C

~100 µg/L M) (0.241 µM) PFOA

- PFOA and 6:2 FTS unzipped to smaller PFCAs
- Eventually complete abiotic mineralization (F$^-$ and CO$_2$)
- Co-contaminants (@ 1000 mg/L) - PFAS degradation NOT affected
- PFOS unaltered at 90 C with 60.5 mM Na$_2$S$_2$O$_8$ as well as at 90 C with 84 mM Na$_2$S$_2$O$_8$
- PFOA & PFOS will coexist in groundwater, thus technologies that can remediate both are needed
High PFOS concentration (0.2 mM PFOS = 3.4 mM Fluoride)

High persulfate concentration and no controls presented

Hydrothermal (HT) – high temperature and pressure

Method Development

Approach for successful exploration requires:

- Accurately quantify target parent PFAS (and isomers)
  - High extraction efficiencies of all phases
  - Reliable chromatographic separation and detection
- Accurately quantify fluoride and sulfonate metabolites
  - Above background noise
  - Optimize nanocomposite synthesis to minimize background
  - Minimize analytical matrix effects
  - High extraction efficiencies and appropriate analytical methods
- Identify organic metabolites and quantify if possible
  - TOF, MS/MS probing of aqueous and extractants
  - Headspace sampling (requires airtight reaction vessel)

Analytical methods are treatment technique dependent
Reductive Approaches: Literature

- **UV (254 nm) photolysis- generated aquated electrons ($e_{aq}^-$) from iodide ($E_0 = -2.9$ V) (Park et al., 2009)**
  - PFOS degraded faster than PFOA (under argon atmosphere)
  - Not applicable for in situ

- **Vitamin B$_{12}$ (Ochoa-Herrera et al., 2008)**
  - Successful for only branched PFOS isomers, but not linear chain

- **Boron Doped Diamond Electrode (Carter and Ferrell, 2008)**
  - Some success for PFOS
  - Very expensive
  - Not applicable for in-situ

- **Zero Valent Iron (ZVI) ($E_0 = -0.447$ V) (Hori et al., 2005; 2008)**
  - Degraded PFOS at high T & high pressure (→ near supercritical)

- **Electrochemical (Schaefer et al., 2015, J Hax. Materials)**

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Theoretical and experimental evidence: PFOS is amenable to reduction. Need: Enhance reactivity and delivery.
Our Current Research Questions

- What **extent** of reductive transformation especially of linear PFOS can be achieved with the primary reductive techniques proposed?

- What are the **intermediates** of PFCAs and PFSAs defluorination using the proposed reductive techniques?

- How is reductive transformation affected by various **solution parameters** (pH, electrolyte composition, redox potential) and co-contaminants likely to be associated with AFFF-contaminated groundwater at military sites?

- How does the presence of **porous media** affect defluorination potential and reductant reactivity?

- How amenable are intermediates to other remediation processes (**treatment train potential**)?
Reductive Approaches Probed to Date

- **Metals**
  - nZVI – *not successful by itself*
  - nZVI/Pd as a function of % Pd, initial pH, temperature
  - nZVI/Pd/Al
  - nZVI/Ni with GO or GAC
  - Mg/Pd

- **Enhanced delivery**
  - Fe$_3$O$_4$ composites
  - Deposit reactive metals within clay layers
  - Organo-bentonite

- **Vitamin B12 with**
  - Ti-citrate
  - Cu
  - n-ZVI
  - n-ZVI/Pd
Expected Inorganic Metabolites

\[
\text{F}^- + \text{SO}_3^{2-} + \rightarrow \text{per/poly-fluoroalkanes} + \text{Poly-fluoroalkyl sulfonates}
\]

- Any sulfite generated expected to rapidly convert to sulfate:

Consistent with Literature: Sulfite oxidation rate = 0.009 /h (Shizuo Tsunogai, 1971)

SO\(_3\) (at 0 h) no intentional exposure to O\(_2\)

SO\(_3\) (after 20 h) after exposure to O\(_2\)
PFOS Isomers in Technical Grade PFOS & Formulations

Linear 65-75%

4-PFOS

1-PFOS

5-PFOS

2-PFOS

6-PFOS

3-PFOS

dm-PFOS
Isomer Separation and Response Optimization

- Standard analyses – all isomers elute in one peak
- Ascentis F5 allows for isomer separation
- Selexion allows for enhanced response to each isomer
Why nZVI Systems?

- ZVI is a potent reductant \( (E_0 = -0.447 \text{ eV}) \)
- Nano-sized ZVI (nZVI) - high surface area (40~60 \( \text{m}^2/\text{g} \))
- Cost-effective (low installation and operation cost)
- Low environmental impact and low toxicity
- nZVI can be doped with a catalyst such as Pd, Pt, Cu, Ni and Ag to improve the reactivity.
- Successful for dehalogenation of chlorinated alkenes, alkanes, and PCBs

\[ \text{Mechanisms of contaminants (e.g. chlorinated solvent) removal} \]

- a) Direct electron transfer
- b) Hydro-defluorination onto the catalyst surface
- c) Hydro-defluorination onto the nZVI surface

Gunawardana et al, 2011
Effect of %Pd and Mass of Bimetal

- For Pd/Fe ≥ 0.043, no significant difference on PFOS removal.

- \([\text{PFOS}]_o = 1,570 \ \mu\text{g/L}\)
- No pH adjustment
- Initial pH = 5.57
- Final pH after reaction: \(→ 6.53, 6.45, 4.99, 6.26\)
- \(T= 22^\circ \text{C for 6 d}\)

![Bar chart showing PFOS removal % for different Pd/nZVI wt/wt ratios]

- Pd/nZVI wt/wt ratio
- For Pd/Fe ≥ 0.043, no significant difference on PFOS removal.
Effect of Initial pH with Pd/nZVI

- Acidic and basic initial pH had highest and similar PFOS removal.
- Removal lowest at near neutral pH condition.

- [PFOS]₀ = 1,570 µg/L
- 1% Pd/0.2 g nZVI
- pH adjusted with HCl or NaOH
- T= 22 °C for 6 d
Temperature Effect with Pd(1%)/nZVI (0.2 g)

Role of temperature not clear

~ 0.4 mol F⁻ generated per mole PFOS lost
~ 0.3 mol SO₄²⁻ per mole PFOS lost
pH Effect with Pd/Fe/Al Trimetal

- Initial high pH slowed/reduced PFOS removal likely due to Al(OH)₄⁻ formation
- Reaction appeared complete by 24 h

- [PFOS]₀ = 880 µg/L
- 1% Pd/0.5g of Fe/Al
- pH adjusted with HCl/NaOH
- Base added at 0, 24, and 48 h
- T= 22 °C
- Reacted for 6 d
Ni-nZVI

Method

- Ni content over Fe\(^0\) was 1.8 wt%.
- Batch experiments were carried out in triplicates for:
  ✓ Ni/Fe
  ✓ Ni/Fe-Graphene (NiFe-GO)
  ✓ Ni/Fe-Activated Carbon (NiFe-AC)
- 0.2 gr was added to each replicate and matrix. Both were mixed for 3 days.
- A blank containing 10 mL of PFOS (2 ppm) was carrying out together with all the samples.
- 4 extractions using ethyl acetate.

- pH shifts during reaction:

<table>
<thead>
<tr>
<th>ID</th>
<th>NiFe</th>
<th>NiFe-GO</th>
<th>NiFe-AC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix Day 0</td>
<td>7.21</td>
<td>7.71</td>
<td>7.70</td>
</tr>
<tr>
<td>Matrix Day 3</td>
<td>8.62</td>
<td>8.90</td>
<td>8.65</td>
</tr>
<tr>
<td>Day 0</td>
<td>7.39</td>
<td>7.17</td>
<td>7.95</td>
</tr>
<tr>
<td>Day 3</td>
<td>10.18</td>
<td>10.61</td>
<td>10.28</td>
</tr>
</tbody>
</table>
• 51% to 57% PFOS not recovered so assume ‘transformed’
• Four extractions was found sufficient for PFOS from nZVI particles
• Apparent higher loss for Ni-nZVI on activated carbon may be extraction efficiency issue – now using 5 extractions
• More associated with NiFe-AC particles (~85%).

• Significant differences were observed on NiFe-AC compared to NiFe (P < 0.0001) and NiFe-GO (P < 0.0001).
Isomer-specific Removal

**L-PFOS**

- NiFe: 40% ± 2%
- NiFe-GO: 38% ± 2%
- NiFe-AC: 50% ± 2%

**Branched PFOS**

- NiFe: 75% ± 3%
- NiFe-GO: 50% ± 3%
- NiFe-AC: 50% ± 3%

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*Percent Removal for Isomer-specific Removal of Branched PFOS with NiFe, NiFe-GO, and NiFe-AC.*
Why Vitamin $B_{12}$ Systems?

- Vitamin $B_{12}$ (cyanocobalamin) is produced by anaerobic bacteria contains a corrin ring that coordinates a cobalt atom.
- Cobalt center of V-$B_{12}$ can exist in 3 oxidation states ($B_{12a}$, $B_{12r}$, $B_{12s}$).
- Electrons transferred from reduced metal (Ti exemplified below but also assessed with other metals) to the contaminant.

Some degradation of branched PFOS, not linear PFOS.
70 C, pH=9
(Ochoa et al., 2008)

Reduced Ti (III) Citrate

2e$^-$

Oxidized Ti (IV) Citrate

2e$^-$

$B_{12a}$

$B_{12r}$

$B_{12s}$

Unknown intermediates + Fluoride

Most nucleophilic
Vitamin B12 (0.4 mM) + n-ZVI (0.2 g)

- Similar PFOS removal in both systems
- Inorganic metabolite production varies
- Organic metabolites also appear different
Effect of Temperature and Initial pH for B$_{12}$+ Ti System

- Heat enhanced only PFOA removal
- At T=70 °C, PFOS removal increased with increase in initial pH

At 22 °C,
- pH not adjusted
- [PFOA]$_o$ = 609 µg/L
- [PFOS]$_o$ = 358 µg/L
- [B$_{12}$] = 0.5 mM
- [Ti-citrate] = 35 mM
- Unadjusted pH
- T= 22 or 70 °C for 5 d

At 70 °C,
- pH not adjusted
- [PFOA]$_o$ = 4,655 µg/L
- [PFOS]$_o$ = 358 µg/L
- [B$_{12}$] = 0.5 mM
- [Ti-citrate] = 45 mM
- pH adjusted with NaOH
- T= 70 °C for 5 d
Effect of Cu°, Pd° or Fe° in B<sub>12</sub> - Ti system

[PFOS]<sub>0</sub> = 4,655 µg/L, T = 70 °C, Reaction = 5 d

- Addition of Fe° (as an electron donor) to B<sub>12</sub>+Ti system did not enhance PFOS removal.
- Addition of Cu° or Pd° (as a catalyst) to B<sub>12</sub>-Ti-citrate system decreased PFOS removal.
- In Ti-system, high Cl<sup>-</sup> concentration interfered with F<sup>-</sup> quantitation.
- B<sub>12</sub>+Fe system, F<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were detected indicating partial reduction.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>[pH]&lt;sub&gt;0&lt;/sub&gt;</th>
<th>[pH]&lt;sub&gt;f&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>B12-Fe</td>
<td>10.41</td>
<td>8.03</td>
</tr>
<tr>
<td>B12-Pd/Fe</td>
<td>10.41</td>
<td>7.61</td>
</tr>
<tr>
<td>B12-Ti-Cu</td>
<td>9.54</td>
<td>6.86</td>
</tr>
<tr>
<td>B12-Ti-Fe</td>
<td>9.54</td>
<td>9.23</td>
</tr>
<tr>
<td>B12-Ti</td>
<td>9.54</td>
<td>6.03</td>
</tr>
</tbody>
</table>

10-14 mol F<sup>-</sup> generated per mole PFOS lost
~ 0.7 mol SO<sub>4</sub><sup>2-</sup> per mole PFOS lost
Effect of Temp. in B$_{12}$ (0.4 mM) + nZVI (0.2 g) System

- PFOS removal increased with temperature.
- At 70 °C, PFOS removal continued to increase from 5 to 21 days.
- Most degraded PFOS is branch-PFOS.
- PFOS removal in only Vitamin B12 (no metals to enhance electron shuttle) unexpected.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>[pH]$_o$</th>
<th>[pH]$_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>22 °C at 21 d</td>
<td>10.51</td>
<td>9.89</td>
</tr>
<tr>
<td>70 °C at 21 d</td>
<td>10.51</td>
<td>6.67</td>
</tr>
<tr>
<td>70 °C at 5 d</td>
<td>10.41</td>
<td>8.03</td>
</tr>
<tr>
<td>B12-PFOS (no Fe)</td>
<td>10.51</td>
<td>9.14 (22 °C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.52 (70 °C)</td>
</tr>
</tbody>
</table>

PFOS isomers Chromatographs in B$_{12}$-Fe at 70 °C (in Aqueous phase) → Stock, D-14, and D-21
Isomer-Specific Peak Comparison for B12-nZVI

**L-PFOS**

- **22C**
- **70C**

**6-PFOS**

- **22C**
- **70C**

**5-PFOS**

- **22C**
- **70C**

**3&4-PFOS**

- **22C**
- **70C**

**Other isomers**

- **22C**
- **70C**
Organic Metabolites

- LC/MS-ESI/TOF (and GC/MS Orbitrap forthcoming)
- Several metabolites produced not in controls
- Expect some perfluoroalkyl alkane/alkenes
- Currently using a mass defect approach to identify metabolite

Example: Peaks in Ni/nZVI Treatment Systems:

- Positive Mode
  - 4 similar peaks observed in all systems
  - One additional peak in graphene oxide (GO) system

- Negative Mode
  - 1 peak observed in all
  - Peak was different in activated carbon (AC) system
Many combinations have been used in field applications

- ZVI-type treatment zone coupled to natural or enhanced anaerobic treatment zone
- ISCO treatment zone coupled to enhanced or natural aerobic degradation
- Aerobic degradation treatment zone coupled to an anaerobic abiotic (ZVI) or bioremediation (biowall) treatment zone

One treatment can ‘soften’ a compound to be amenable to natural anaerobic or aerobic degradation and/or to a subsequent chemical treatment.

At many of the sites where PFASs exist, redox conditions may already be depleted in $O_2$ (redox range -100 to -250 mV) due to degradation of fuel and other easily biodegradable contaminants.

Order and placement of treatment train for PFASs depends on proximity to source and contaminants present – precursor oxidation will lead to increased concentration of PFAAs.

NRC (2013); IRTC (2011)
Current Use of Reductive Technologies in the Field

- Used for Cl-methanes, ethanes, and ethenes, chlorinated phenols, PCBs, hexachlorocyclohexanes, munitions, metals, nitrates, perchlorate
- Permeable Reactive Barriers (PRBs)
- Reductions in the target zone of typically 50 to 90 percent
  - Treatment Trains
  - In-situ Injection

<table>
<thead>
<tr>
<th>Barrier Media</th>
<th>Superfund</th>
<th>Industrial</th>
<th>US Gov.</th>
<th>International</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZVI</td>
<td>5</td>
<td>36</td>
<td>26</td>
<td>16</td>
<td>83</td>
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<tr>
<td>Non-Fe reactive materials</td>
<td>1</td>
<td>6</td>
<td>1</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>Bio-barrier</td>
<td>0</td>
<td>6</td>
<td>5</td>
<td>4</td>
<td>15</td>
</tr>
<tr>
<td>Combo/Sequenced (* ZVI)</td>
<td>0</td>
<td>4</td>
<td>2</td>
<td>0</td>
<td>6 (5*)</td>
</tr>
</tbody>
</table>

- Enhancing ZVI-based techniques
  - Nano-ZVI (nZVI) - *pilot & full-scale tests with nZVI1 shows 50-90% conc. reduction*
  - Surface coated/encapsulated nZVI-type particles (enhanced for in-situ injection)
  - Carbon/ZVI, C-rich organic/iron combinations (PRBs)
  - Emulsified ZVI, ZVI-clays, organophilic-ZVI clays (PRBs, in-situ injection)

NRC (2013); IRTC (2011)
Take Home Messages

- No magic bullet!
- PFOS is the big challenge - more about steric hindrances
- Reductive approaches showing some promise for ‘softening’ PFOS (partial transformation)
- Linear PFOS remains the primary challenge – energetically the most stable and ~75% of what is in the environment
- Many published studies lack sufficient recovery efficiencies and background issues
- **We are not ready for any field-scale attempts for in-situ remediation due to**
  - Increasing PFAAs due to aerobic transformation of precursors – increased mobility
  - Unknown metabolites
  - Toxicity potential unknown or unclear for metabolites
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Drs. Marc Mills & Kavitha Dasu*
  U.S. EPA, NRMRL
  Fate/remediation expertise; * PFAS fate/ analytical expertise (with PI)

Dr. Hongtao Yu
  Jackson State University
  Chemistry/biochemistry; NSF-funded NMR Center
Our challenge

Beneficial Technologies

Environmental Stewardship

Quality of Life