



Advanced Oxidation/Reduction for PFAS in Co-Contaminated Groundwater

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Agenda

- Background
- Treatment Technologies
- Advanced Oxidation
- Bench-Scale Case Studies
- Proposed Bench-Scale Study
- Summary



Courtesy of APTwater, LLC

Background

- Prevalence
 - Over 3,000 PFAS compounds have been on the market
- Chemistry
 - Hydrophobic and oleophobic
 - Stable, recalcitrant
 - Carbon-Fluorine bond is strong
 - Persistent in environment
 - Half life > 40 years (USEPA)
 - Many are soluble and highly mobile
- Potential Risk
 - PFOA and PFOS identified in groundwater/potable water
 - USEPA Lifetime Health Advisory = 70 ng/L
 - Other proposed state levels range from 8 to 70 ng/L for PFAS

Perfluorooctane sulfonate (PFOS)

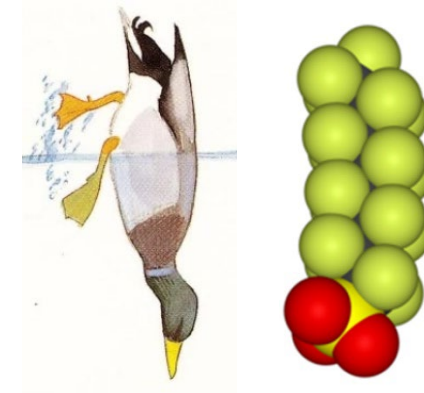


Perfluorooctane carboxylate (PFOA)



Courtesy of ITRC

Hydrophobic



Hydrophilic

Linear Versus Branched Isomers

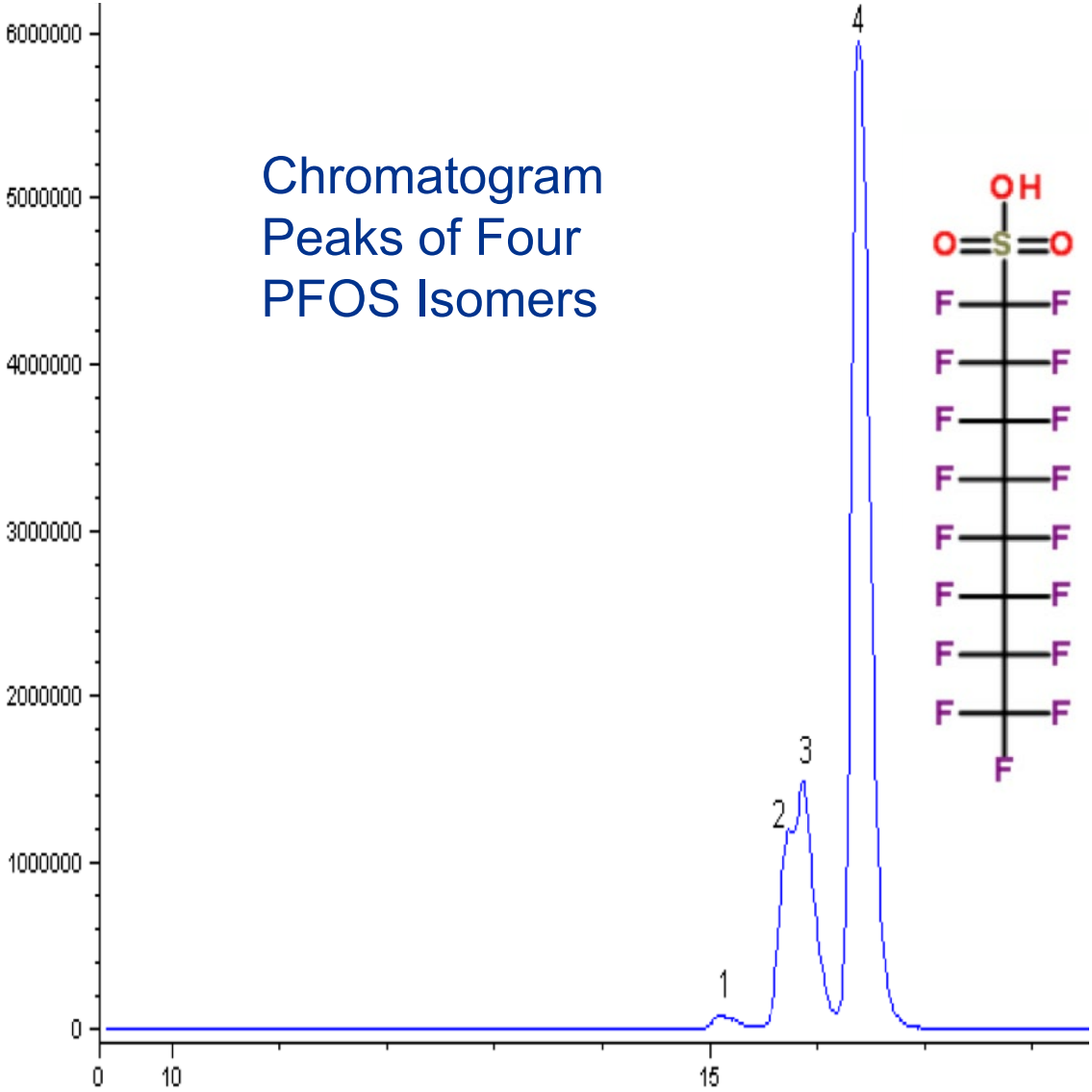
PFOS Isomers: Both $C_8F_{17}SO_3^-$



PFOS linear isomer



PFOS branched isomer



Chromatogram Peaks of Four PFOS Isomers

PFAS Treatment Technologies

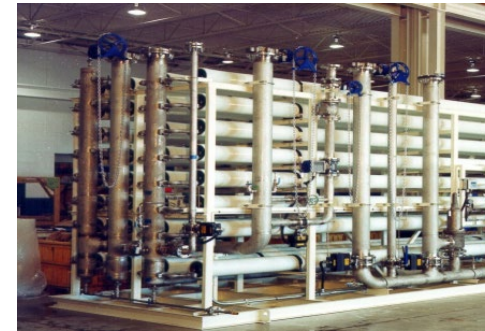
- ITRC Defined Three Categories:
 - **Field Implemented Technologies** – Multiple, well documented, full-scale demonstrations
 - **Limited Application Technologies** – Limited implementations, or not documented in peer-reviewed literature
 - **Developing Technologies** – Researched at the laboratory or bench scale, not yet field-tested



Field Implemented Technologies

■ Water

- Adsorption
 - Granular Activated Carbon
 - Ion Exchange
- Reverse Osmosis
- Precipitation/flocculation
 - Pretreatment of high concentrations



CH2M, 2017

Limited Application Technologies

■ In Situ Sorption

- Colloidal activated carbon with a biopolymer; PolyDADMAC
- Two documented PFAS application case studies so far

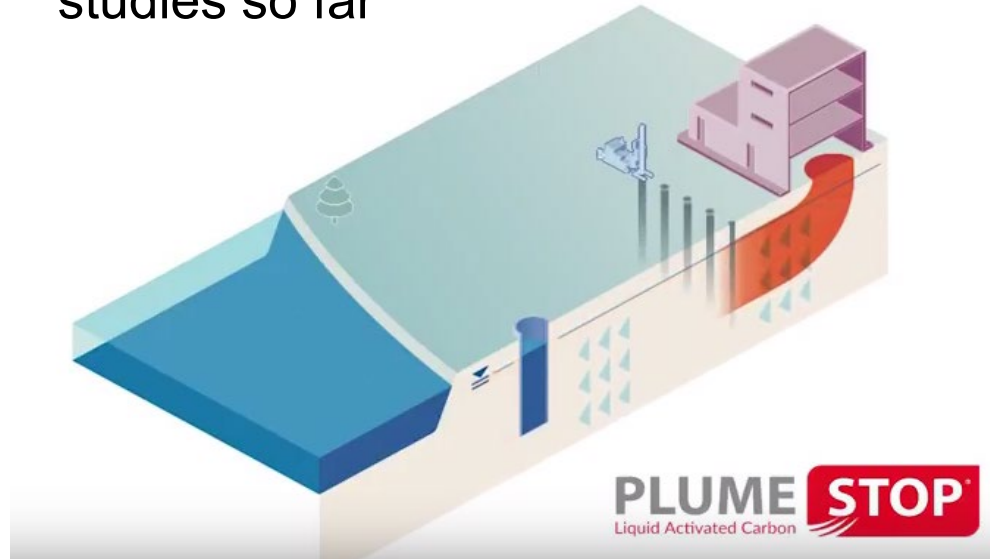


Illustration courtesy of Regenesys, Inc.

■ Foam Fractionation

- Uses air and proprietary concentrating/drying of foam

■ Ozofractionation

- Uses ozone to separate PFAS from water
- Multiple stage process concentrates in steps

Developing Technologies

- Alkaline Ozone/Perozone
- Electrochemical Oxidation
- Electrochemical Coagulation
- Zero-Valent Iron
- UV + Sulfite
- Vitamin B12 with titanium citrate
- Sonolysis
- Non-Thermal Plasma

Developing Technologies

- **Alkaline Ozone/Perozone**

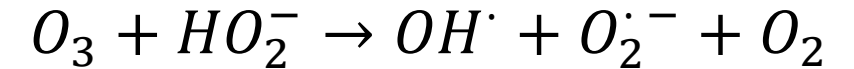
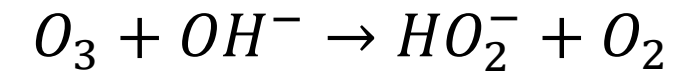
- Electrochemical Oxidation
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- Zero-Valent Iron

- UV + Sulfite
- Vitamin B12 with titanium citrate
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- Non-Thermal Plasma

Redox Manipulation (Oxidation / Reduction)

- Many oxidants have been tested:
 - Ozone, hydrogen peroxide, iron or heat activated sodium persulfate
 - Most require high doses, high temperature, catalysts
- “Conventional” Advanced Oxidation (Ozone, UV/H₂O₂) has limited effectiveness
 - Oxidation can mineralize PFOA and carboxylic acids; not as effective for PFOS and sulfonic acids
- Production of reducing radicals (superoxide, hydroperoxide, solvated electrons) enhances oxidation

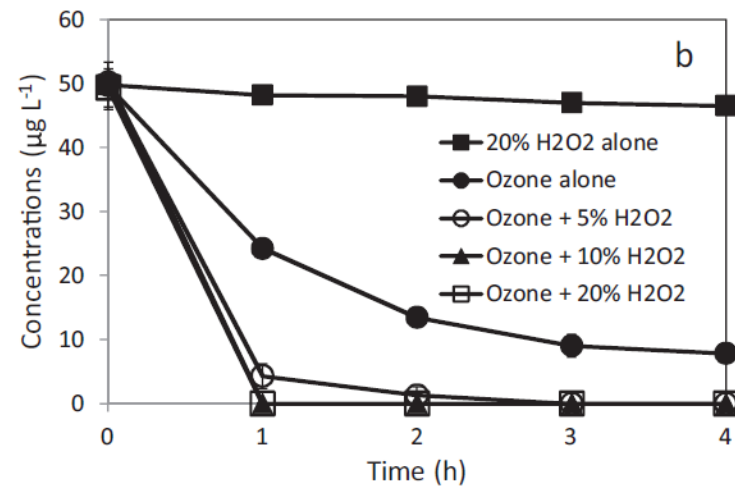
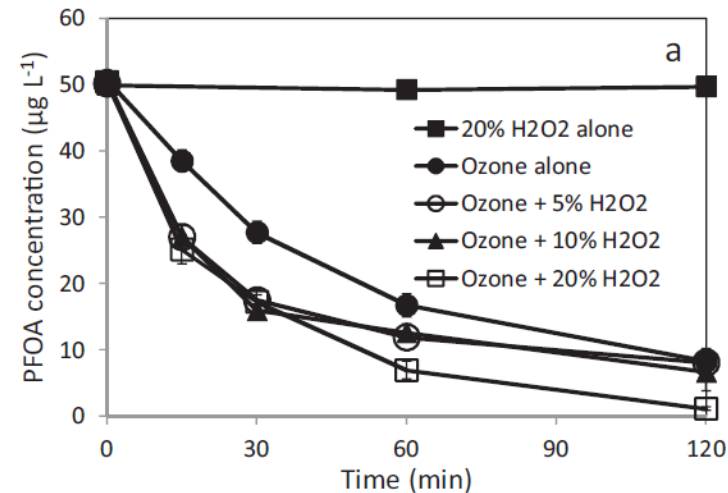
Alkaline Advanced Oxidation



- Generates both radicals
 - Hydroxyl (OH[•])
 - Superoxide (O₂^{•-})
- Accelerated by
 - High pH
 - Addition of H₂O₂

Alkaline Perozone Bench-Test

- Academic work published in 2012 by Lin et. al. (Journal of Hazardous Materials)
- Uses perozone (hydrogen peroxide + ozone) at unconventional pH values (pH 11)
- Ozone pretreatment and addition of hydrogen peroxide
- Indicates removal of PFOS > PFOA



(a) PFOA; (b) PFOS

Lin, A. et.al., 2012, J Haz Mat

Alkaline Ozone Bench-Test

- Bench-scale study conducted by Piper Environmental
- Amended with ozone only, under pressure with continual injection and recirculation
- Two conditions were evaluated
 - Test 1: Neutral pH (7 – 8)
 - Test 2: Alkaline pH (11 – 12)



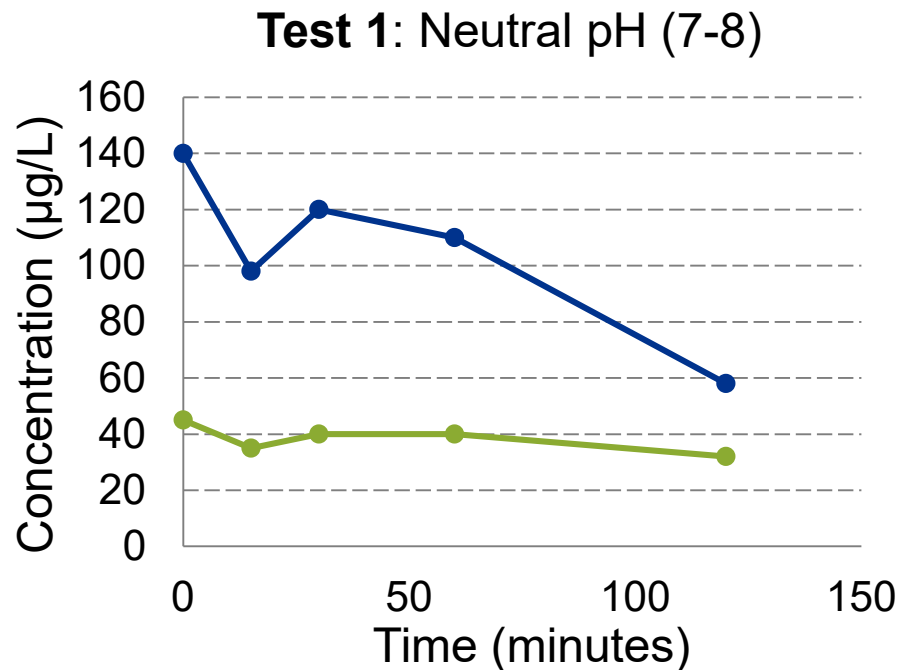
Courtesy of Piper Environmental Group Inc.

Alkaline Ozone Bench-Test Results

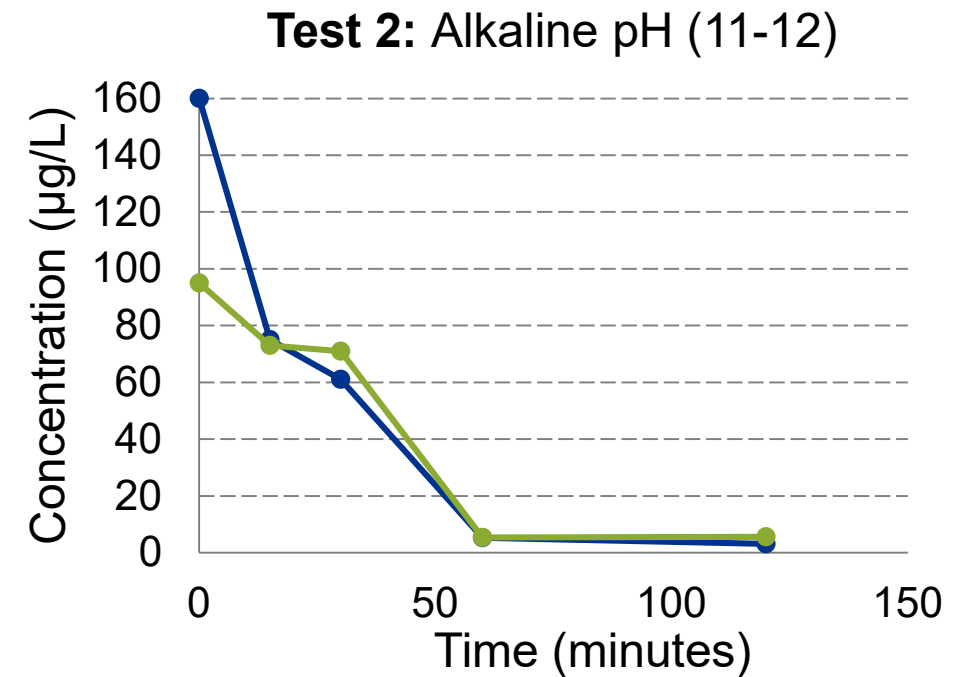
Data corroborates results observed during 2012 Lin Study

- Significant reduction of PFOS and PFOA when activated with NaOH, forming the hydroxyl radical (OH•)

Courtesy of Piper Environmental Group

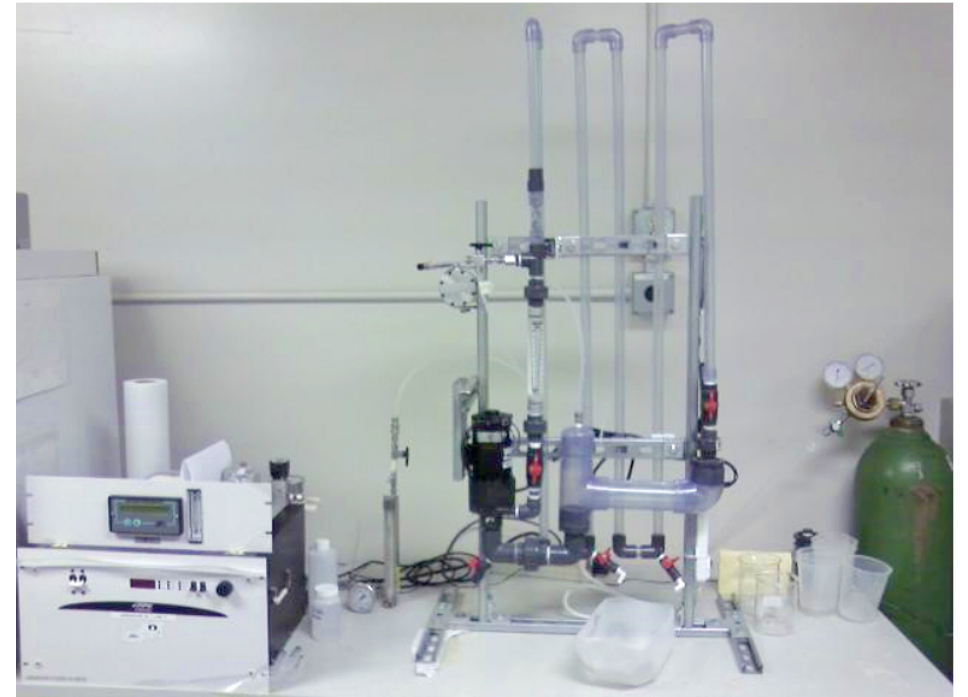


● PFOS
● PFOA



Proposed Bench-Scale – Overview

- Testing is being conducted in coordination with APTwater, LLC using their using their HiPOx bench-scale reactor
 - Evaluate groundwater from two sites
 - Site 1: Co-contaminants PFOA/PFAS and CVOCs
 - Site 2: Co-contaminants PFOA/PFAS/FTS with petroleum hydrocarbons
 - Baseline sampling conducted immediately prior to testing to account for losses
 - Control samples (no treatment) to compare to baseline results
 - Equipment blanks using certified PFAS-free DI water to assess for potential cross-contamination



Courtesy of APTwater, LLC

Proposed Bench-Scale – Experimental Design

- Build on previous work with more complete first-step screening
 - Use both ozone and perozone
 - Evaluating single versus dual pH steps
 - Various hydrogen peroxide to ozone molar ratios
- Groundwater Optimizing Tests
- Groundwater and Soil Optimization Tests

Initial Test	Ozone Dose (mg/L)	Pre-Treatment pH	H ₂ O ₂ :O ₃ Mole Ratio	Final pH
1	2,000	natural	0	natural
2	2,000	natural	0	11
3	2,000	natural	0.50	natural
4	2,000	natural	0.25	11
5	2,000	natural	0.50	11
6	15% of 2,000	natural	0	11
	85% of 2,000	11		
7	15% of 2,000	natural	0.25	11
	85% of 2,000	11		
8	15% of 2,000	natural	0.50	11
	85% of 2,000	11		

Proposed Bench-Scale – Data Collection

Parameter	Justification
PFAS Compounds	<ul style="list-style-type: none"> • PFOS, PFOA, PFBS, NEtFOSAA, NMeFOSAA, PFDA, PFDoA, PFHpA, PFHxS, PFHxA, PFNA, PFTA, PFTTrDA, PFUnA, 4:2FTS, 6:2FTS, 8:2FTS • Post-treatment will be compared to baseline and controls • Laboratory to report branched and linear isomers
Co-Contaminants	Site 1: Chlorinated ethenes; Site 2: Petroleum hydrocarbons
pH	Asses whether target pH values are met for each test scenario
ORP	Monitor progress of oxidation
Temperature	Monitor temperature changes over course of oxidation reaction
O ₃ / H ₂ O ₂ Residual	Assess percent consumed to quantify required quench chemical
Alkalinity, Turbidity, TOC, COD, Total and Dissolved Metals (Al, Co, Cu, Fe, Mg, Mn, Ni, Zn)	Potential scavenger of oxidation chemicals (ozone/peroxide) and could be a limiting factor for reactivity and overall performance. Data will be used to help determine total oxidant dosage required.

Summary

- PFAS compounds are recalcitrant and difficult to treat in situ
- The prevalence, chemistry, and potential risks of PFAS compounds necessitate attention to developing in situ remediation strategies
- Recent studies indicate alkaline ozonation/perozone is a promising technology for treatment of PFAS-impacted groundwater
- Bench-testing is currently underway that will build on previous studies to assess advanced alkaline oxidation as a proposed in situ remedy
- Objective is to identify the most promising advanced alkaline oxidation bench-scale treatments for evaluation in a field-scale pilot study
 - Commercially available, field scalable equipment demonstrated for other contaminants

Thank you!

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