HOLISTIC SOLUTIONS TO MANAGING AND REDUCING PFAS IN WASTEWATER

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RAMBOLL

2019 LOUISIANA SECTION ANNUAL CONFERENCE
TOPICS

- Overview
- Source Identification & Control
- Sampling and Analysis
- Treatment Technology Effectiveness
- Residual Management
- Case Studies
  - Technology Review
  - Effects of Advanced Treatment
  - AFFF Spill Sludge Management
PFAS – AT A GLANCE

- Human-made substances
- Do not hydrolyze, photolyze or biodegrade under typical environmental conditions and are extremely persistent in the environment
- C-F bond is one of the strongest chemical bonds
- Found in soil, air and groundwater at sites around the world
- Toxicity, mobility and bioaccumulation potential pose potential adverse effects for the environment and human health

- Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA) have been detected globally in the tissues of fish, bird and marine mammals
PFAS SOURCES

Processes
- Fluoropolymer coatings
- Plastics/polymers
- Teflon™, Stainmaster® carpets, Scotchgard™ Gore-Tex®
- Aqueous film forming foams (AFFF)
- Mist suppressants in metal plating operations
- Photolithography (semiconductors)
- Photography and film products

Product uses
- Food wrappers/paper, fast food containers, microwave popcorn bags, pizza boxes
- Non-stick cookware
- Water-resistant textiles, carpets, clothing, leather
- Ski and snowboard waxes
- Adhesives, paints, sealants
- Aviation hydraulic fluids
- Cleaning products
- Shampoo, dental floss, cosmetics
INTRODUCTION: REGULATORY STATUS

• Regulations for non-drinking water and residuals are state to state
• Drinking water has EPA current health advisory limit (70 ng/L)
  • Some state advisories lower
• EPA approved analytical method for drinking water
  • Anticipate EPA draft for surface water end of 2019
  • Anticipate EPA draft for wastewater and soil end of 2020
• No clear industrial standards

ITRC maintains database of state and country specific updates
Last updated 9/18
PFAS - USA REGULATORY PERSPECTIVE

1990s
USEPA receives information on PFOS and PFOA blood levels in general population

2002
USEPA SNUR restricts reintroduction into the market for PFOS based products.

2004
PFAS found to have contaminated drinking water supplies in Minnesota

2006
USEPA 2010/2015 PFOA Stewardship program – 95% reduction of PFOS, PFOA precursors and homologues by 2010, 100% by 2015

2007
USEPA SNUR broadened the scope to include 183 chemicals within PFAS class

2009
USEPA established drinking water health advisories of 200 ng/L (ppt) for PFOS and 400 ng/L for PFOA

2013
USEPA initiates requirement for public drinking water supply monitoring of 6 unregulated perfluorinated compounds

2016
USEPA revises drinking water health advisory to 70 ng/L for PFOS, 70 ng/L for PFOA and 70 ng/L combined PFOA and PFOS

2018
State specific proposed drinking water standards and effluent discharge limitations are being developed

2019
USEPA issues draft interim recommendations for screening levels. PFAS action plan including development of Maximum Contaminant Levels (MCL) for PFOS and PFOA

Michigan has issued extremely low water quality standards. Depending upon receiving stream, PFOS limit is 11 to 12 ng/L
REGULATIONS AND CONCERNS ARE WORLD-WIDE

New law (EU) 2017/1000 to be implemented from July 4, 2020/2023 – under REACH eliminating PFOS
SOURCE IDENTIFICATION & CONTROL

• Source identification and control are crucial to managing PFAS discharges

• Process Wastewater
  • Review Material Data Sheets and Chemical Abstract Service (CAS) numbers for all PFAS related compounds
  • Groundwater or well water used as makeup water

• PFAS use in facility (non-process)
  • AFFF

• Many times, facilities identify PFAS use and overlook other possible contributors
  • Stormwater Runoff
    • Soil contamination
  • Potable water
  • Sanitary discharge
SAMPLING AND ANALYSIS

• Three published methods (USA) for analyzing PFAS:
  • USEPA Method 537.1 – Drinking water only
  • ASTM D7979 – Non-Drinking Water/Sludges
  • ASTM D7968 – Soils

• “Modified Method 537” is used for non-drinking water, sludges, and soils
  ➢ Exact laboratory method can be proprietary » care must be taken when comparing results obtained from different laboratories to establish baseline criteria

• Method Detection Limits (MDLs) for water ranges from 0.25-1.0 ng/L

• Reliability Limits (RLs) or method reporting limit of 2-5 ng/L
  ➢ Combined MDL for a range of site specific PFAS could exceed proposed discharge limit

• Prevent false positives
  ➢ Everyday maintenance items such as Teflon tape and Pipe Thread Compound can introduce small positive test results
SAMPLING AND ANALYSIS FOR PFAS

SAMPLING DO

HDPE

SAMPLING DON’T

LDPE

CONFIDENTIAL SETTLEMENT COMMUNICATIONS
# DEMONSTRATED TREATMENT TECHNOLOGIES OVERVIEW

<table>
<thead>
<tr>
<th>Treatment Technology</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granular Activated Carbon (GAC)</td>
<td>• Demonstrated PFAS removal, efficiency 80 to &gt;99%, depending upon species and medium matrix&lt;br&gt;• The isotherms are very steep at low concentrations: there is a limited number of adsorption sites with very favorable adsorption energies resulting in high doses&lt;br&gt;• Minimum of two stage systems typically required&lt;br&gt;  - Three stage in many applications&lt;br&gt;• Slightly better capacity at lower pH values&lt;br&gt;• Requires reactivation at very high temperatures or disposal of spent carbon&lt;br&gt;• Typically considered for drinking water treatment and wastewater treatment (both municipal and industrial)</td>
</tr>
<tr>
<td>Polymeric Resin Adsorption</td>
<td>• PFAS removals can be as high as 95 to &gt;99%&lt;br&gt;• Extended contact times typically required&lt;br&gt;• Requires resin regeneration and regenerant treatment or spent resin disposal and destruction&lt;br&gt;• Typically considered for industrial wastewater and leachate treatment</td>
</tr>
</tbody>
</table>
# Demonstrated Treatment Technologies Overview

<table>
<thead>
<tr>
<th>Treatment Technology</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>Membrane Filtration</td>
<td>- Removals dependent on “compound size”</td>
</tr>
<tr>
<td></td>
<td>- Reverse Osmosis removes nearly all PFAS</td>
</tr>
<tr>
<td></td>
<td>- Nanofiltration</td>
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<tr>
<td></td>
<td>- Ultrafiltration</td>
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<tr>
<td></td>
<td>- Produces a concentrate that requires additional treatment</td>
</tr>
<tr>
<td></td>
<td>- Considered for industrial and municipal treatment, particularly reuse</td>
</tr>
<tr>
<td></td>
<td>applications</td>
</tr>
<tr>
<td>Advanced Oxidation Process</td>
<td>- Can remove all PFAS, depending upon process</td>
</tr>
<tr>
<td>(AOP)</td>
<td>- Typically requires high energy</td>
</tr>
<tr>
<td></td>
<td>- Primarily considered for high strength industrial wastewater treatment</td>
</tr>
<tr>
<td>Compounds</td>
<td>RO</td>
</tr>
<tr>
<td>-----------------------------------</td>
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</tr>
<tr>
<td>PFBS Perfluorobutane Sulfonic Acid</td>
<td>Removal &gt;90%</td>
</tr>
<tr>
<td>PFOA Perfluorobutanoic Acid</td>
<td>Removal &gt;90%</td>
</tr>
<tr>
<td>PFPGA Perfluoropentanoic Acid</td>
<td>Removal &gt;90%</td>
</tr>
<tr>
<td>PFHxA Perfluorohexanoic Acid</td>
<td>Removal &gt;90%</td>
</tr>
<tr>
<td>PFHxS Perfluorohexane Sulfonic Acid</td>
<td>Removal &gt;90%</td>
</tr>
<tr>
<td>PFPoPFOA (GenX) Perfluoro-2-propoxypropanoic acid</td>
<td>Limited data on treatment</td>
</tr>
<tr>
<td>PFPoDA Perfluoroheptanoic Acid</td>
<td>Removal &gt;90%</td>
</tr>
<tr>
<td>NaDONA (GenX) Sodium dodecafluoro-3H-4,8-dioxanonanoate</td>
<td>Limited data on treatment</td>
</tr>
<tr>
<td>PFOS Perfluorooctane Sulfonic Acid</td>
<td>Removal &gt;90%</td>
</tr>
<tr>
<td>PFOA Perfluorooctanoic Acid</td>
<td>Removal &gt;90%</td>
</tr>
<tr>
<td>PFNA Perfluorononanoic Acid</td>
<td>Removal &gt;90%</td>
</tr>
<tr>
<td>PFDS Perfluorodecanic acid</td>
<td>Removal &gt;90%</td>
</tr>
<tr>
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<td>Removal &gt;90%</td>
</tr>
<tr>
<td>PFDA (also listed as PFUnA)</td>
<td>Limited data on treatment</td>
</tr>
<tr>
<td>N-MeFOSAA 2-(n-Methylperfluorooctanesulfonamido) acetic acid</td>
<td>Limited data on treatment</td>
</tr>
<tr>
<td>N-EtFOSAA 2-(n-Ethylperfluorooctanesulfonamido) acetic acid</td>
<td>Limited data on treatment</td>
</tr>
<tr>
<td>PFDoDA Perfluorododecanoic acid</td>
<td>Limited data on treatment</td>
</tr>
<tr>
<td>PFTDA Perfluorotridecanoic Acid</td>
<td>Limited data on treatment</td>
</tr>
<tr>
<td>PFTrDA Perfluorotridecanoic Acid</td>
<td>Limited data on treatment</td>
</tr>
<tr>
<td>PFAdA perfluoro-n-hexadecanoic acid</td>
<td>Limited data on treatment</td>
</tr>
<tr>
<td>PFODA Perfluorooctadecanoic acid</td>
<td>Limited data on treatment</td>
</tr>
</tbody>
</table>
RESIDUAL MANAGEMENT

• Residual management of PFAS material is often neglected when addressing primary direct discharge concerns

• Facilities must understand the complete loading to the treatment system
  ➢ Biological sludge management

• Third party disposal facilities have begun regulating PFAS
  ➢ No state or federal guidelines
  ➢ Adds significant effort and cost to a facility
# CASE STUDY
ONE OF THE FIRST TREATMENT TECHNOLOGY EVALUATIONS/INSTALLATIONS

<table>
<thead>
<tr>
<th>TREATMENT TECHNOLOGY</th>
<th>PERCENT REMOVAL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SULFONATED FC's</td>
</tr>
<tr>
<td>AOP Examples</td>
<td></td>
</tr>
<tr>
<td>Ozone</td>
<td>0</td>
</tr>
<tr>
<td>Ozone + H₂O₂</td>
<td>0 to 60</td>
</tr>
<tr>
<td>Super Critical CO₂ Extraction</td>
<td>20 to 98</td>
</tr>
<tr>
<td>Super Critical Water Oxidation</td>
<td>100</td>
</tr>
<tr>
<td>Adsorption Examples</td>
<td></td>
</tr>
<tr>
<td>Activated Carbon with pH Adjustmen</td>
<td>100</td>
</tr>
<tr>
<td>XAD Resins</td>
<td>up to 100 for specific compounds</td>
</tr>
<tr>
<td>Spun Glass Fiber Filters</td>
<td>0</td>
</tr>
<tr>
<td>Membrane Filtration</td>
<td></td>
</tr>
<tr>
<td>Ultra Filtration</td>
<td>30 to 80</td>
</tr>
<tr>
<td>Nano Filtration</td>
<td>70 to 90</td>
</tr>
<tr>
<td>Reverse Osmosis</td>
<td>100</td>
</tr>
</tbody>
</table>
Conclusions

- GAC most effective to meet target discharge requirements
- One of the largest industrial GAC treatment systems in the US
  - 26 vessels, lead/lag configuration, each containing 9,700 kg GAC
  - Capacity to treat over 13,700 m³/d
  - Provided effective treatment below regulated levels
- Facility has since expanded treatment capacity
  - 6 more vessels
CASE STUDY
EFFECT OF ADVANCED TREATMENT

Background

• New underground treatment plant in Mikkeli, Finland

• Membrane Bioreactor Reactor (MBR)

• Tertiary treatment required to meet discharge objective

Objectives

• Nutrient and micro pollutant removal requirements:
  • Total P < 0.2 mg/L
  • Environmental Quality Standard (EQS) for PFOS of <0. 65 ng/L

• Start-up 2020
CASE STUDY
EFFECT OF ADVANCED TREATMENT

- 1.5 year pilot test
- PFOS increase in both conventional and MBR treatment
- >70% increase of PFOA in MBR process whereas conventional activated sludge process increased PFOA only about 40%
- Final design includes GAC and Reverse Osmosis as tertiary treatment
CASE STUDY
AFFF SPILL SLUDGE MANAGEMENT

Background

- Faulty valve released up to 1,000 gallons of AFFF to primary containment
- Heavy rains resulted in overflow from primary containment to local POTW
- POTW was notified and diverted a portion of the contaminated flow into aerobic digesters
- The local sludge residuals management company notified the POTW that they would not accept any sludge for land application containing measurable levels of PFOS or PFOA.
- The Industrial Facility agreed to manage and pay for the POTW sludge disposal to a regulated landfill until PFOS and PFOA levels abated

Challenges

- No previous monitoring for PFAS at POTW (influent, effluent, or sludge)
- No previous monitoring for background PFAS at Industrial Facility
- No POTW industrial pretreatment monitoring program for PFAS
- No PFAS regulatory limits or requirements regarding POTW sludge management
- Industrial facility and POTW located in a state with:
  - Well-publicized history of PFAS contamination
  - On-going public relations problem concerning land-application of sludges
### CASE STUDY
#### AFFF SPILL SLUDGE MANAGEMENT

<table>
<thead>
<tr>
<th></th>
<th>Volume (MG)</th>
<th>Avg. TSS (mg/L)</th>
<th>Lb. TSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anoxic Basins</td>
<td>0.5</td>
<td>5000</td>
<td>20850</td>
</tr>
<tr>
<td>Aeration Basins</td>
<td>1.5</td>
<td>5000</td>
<td>62550</td>
</tr>
<tr>
<td><strong>Aerobic Solids Inventory (lbs)</strong></td>
<td></td>
<td></td>
<td><strong>83400</strong></td>
</tr>
<tr>
<td>Effluent TSS</td>
<td></td>
<td>3</td>
<td>Flow MGD</td>
</tr>
<tr>
<td>WAS to Digestion</td>
<td>8500</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td><strong>Total Solids Leaving Activated Sludge (Lb/Day)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Activated Sludge SRT (Days)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Aerobic Digestion</td>
<td>1.5</td>
<td>8500</td>
<td>106335</td>
</tr>
<tr>
<td><strong>Digested Sludge to Disposal (Tons/day)</strong></td>
<td></td>
<td></td>
<td>13</td>
</tr>
<tr>
<td><strong>Average Sludge Cake Solids (%)</strong></td>
<td></td>
<td></td>
<td><strong>20%</strong></td>
</tr>
<tr>
<td><strong>Dry Sludge to Disposal (Lb/Day)</strong></td>
<td></td>
<td></td>
<td>5200</td>
</tr>
<tr>
<td><strong>Digestion SRT (Days)</strong></td>
<td></td>
<td></td>
<td>20.4</td>
</tr>
<tr>
<td><strong>Total SRT (Activated Sludge + Digestion [Days])</strong></td>
<td></td>
<td></td>
<td><strong>32.1</strong></td>
</tr>
</tbody>
</table>

A minimum of 3 sludge ages or 96-100 days to remove contaminated solids
CASE STUDY
AFFF SPILL SLUDGE MANAGEMENT

Pulse Input for completely mixed reactor:

\[ C = C_0 e^{-\frac{t}{SRT}} \]

Where:

- \( C \): Concentration at Time (t, days)
- \( C_0 \): Initial Concentration
- \( SRT \): Solids Retention Time (days)

Solids PFOA and PFOS Concentrations
CONCLUSIONS

• PFAS discharge management is fast becoming one of today’s most pressing environmental challenges

• Rapidly changing regulatory landscape along with a lack of final analytical methods combine to present many challenges for understanding, managing, and reducing PFAS discharge

• Managing PFAS discharge is complicated

Everything regarding PFAS is changing fast! Staying informed of recent developments regarding regulations, testing, and treatment is an absolute must when planning and implementing PFAS management solutions.
REFERENCES


EPA, “Drinking Water Treatability Database.”


Michigan Department of Environmental Quality (MDEQ), “Perfluoroalkyl And Polyfluoroalkyl Substances (PFAS) Minimum Laboratory Analyte List”

