Regenerable Ion Exchange Treatment with Hydrothermal Alkaline Treatment (HALT): Full Spectrum PFAS Capture and Destruction

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ECT2 Montrose Environmental Group

Aquagga

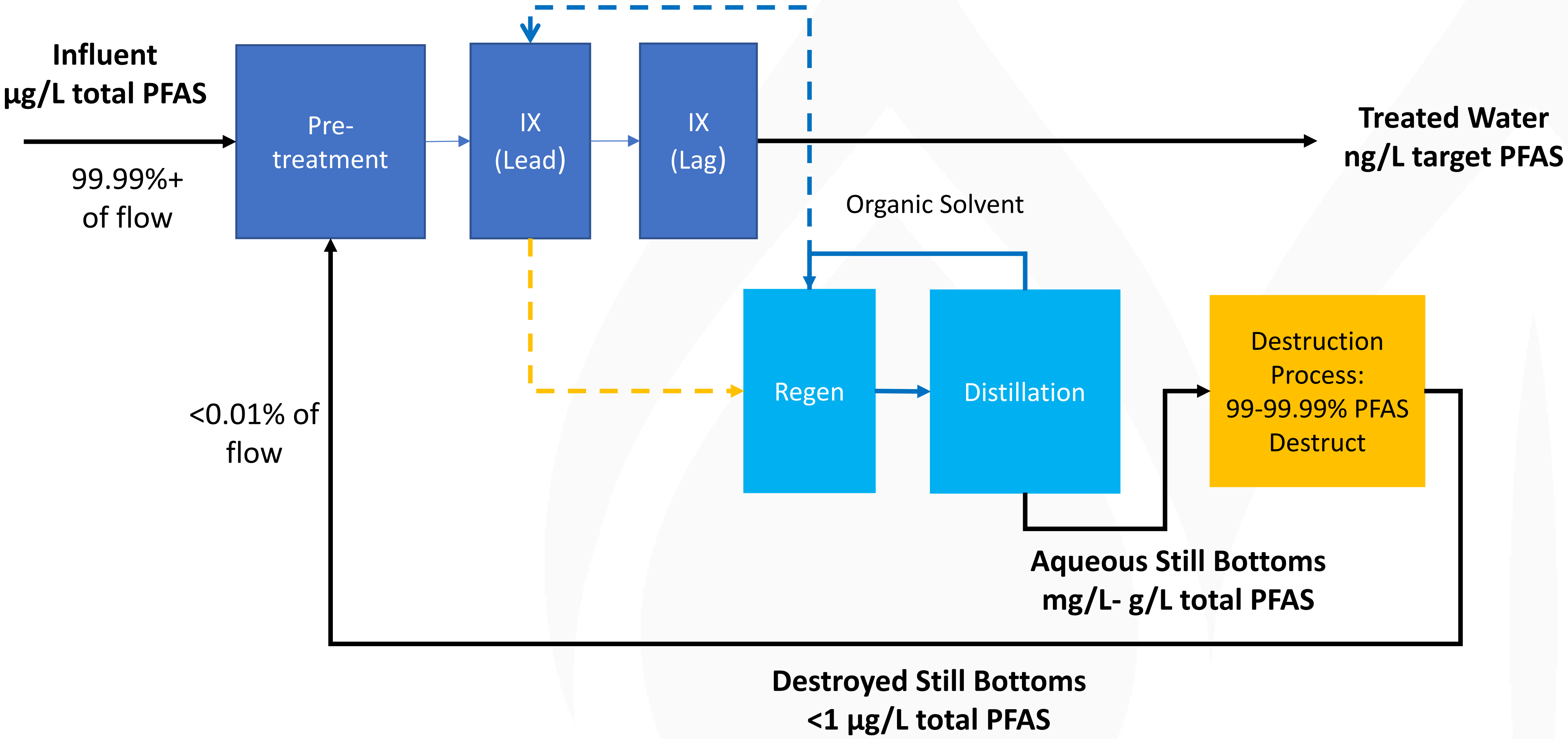
Acknowledgments

- Hunter Anderson at AFCEC
- Aquagga Collaborators (Brian Pinkard, Gus Millevolte, Conrad Austin)
- ECT2 Colleagues (Steve Woodard, Mike Nickelsen, John Berry, Dave Kempisty, Jess Haxon, Cameron McClellan, J Esteves)

Key Messages

- Regen IX is a good fit for high conc PFAS influent and/or short chain PFAS removal
- Regen IX creates a PFAS concentrate (“still bottoms”) amenable to destruction
- Hydrothermal alkaline treatment (HALT) is robust in the still bottoms matrix
- Full spectrum PFAS destruction with mineralization observed with HALT
- HALT conditions can be optimized to 99.9%+ destruction efficiency
- Regen IX and HALT can be paired to create a closed loop treatment process

Regen IX Process with Destruction Incorporated



Still Bottoms: End product of the regen IX process

Relevant Characteristics:

- 2%+ NaCl
- ~0.1 to 5 g/L total PFAS
- Color
- Inorganic ions (nitrate, sulfate)
- Neutral to basic pH
- Trace solvent

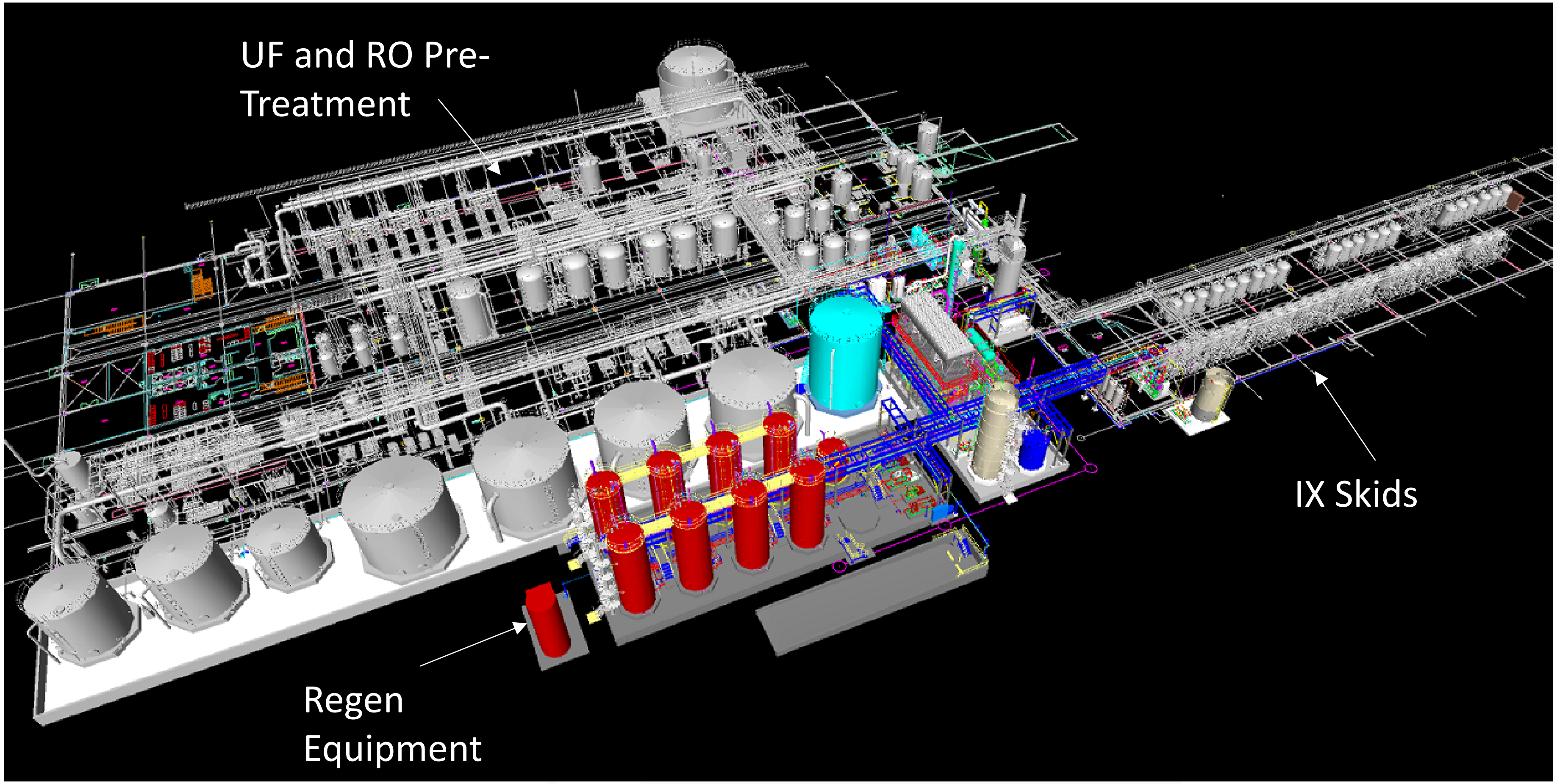
ECT2 Full Scale Regen IX System Images

Complete System Aerial in Australia

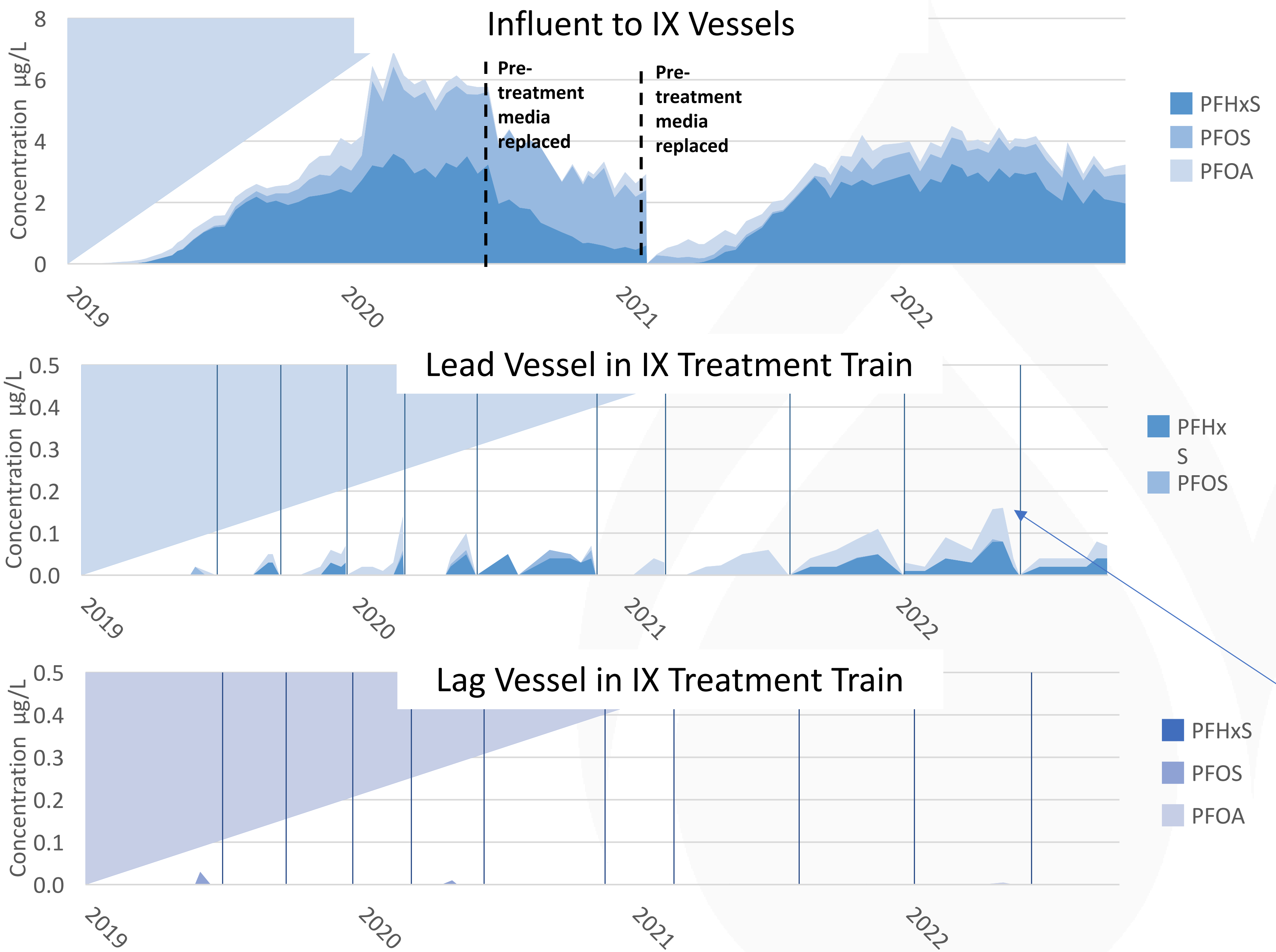
Resin Vessels

Distillation Equipment

Overview of an 8000 gpm Regen IX Plant Designed for Industrial Client



Continuous Regen IX Performance Over Four Years of Operation



Across 4 years of regeneration cycles, the IX resin continues to achieve PFAS treatment objectives with no degradation in performance

Vertical lines indicate resin regeneration in lead vessel (triggered by exceedance of 70 ppt PFOS + PFHxS in lead vessel effluent); vessels rotated following regen

Fate of Still Bottoms

- At most ECT2 regen IX systems, still bottoms are Superloaded onto mixed media
    - Overall concentration factors of 1 million + ($V_{water\ treated}$/ $V_{Disposed\ Superloader\ media}$)
    - Superloader media lasts years without replenishment
- Still bottoms are also a prime candidate for PFAS destruction
    - Low volume - 10,000x+ concentration factor ($V_{water\ treated}$/ $V_{Still\ Bottoms}$)
    - High concentration (mg/l to g/l total PFAS)

Superloader vessels for a 200 gpm system

Still Bottoms can be Superloaded onto media or destroyed with a process such as HALT

Hydrothermal Alkaline Treatment (HALT)

- Developed at Colorado School of Mines; offered commercially by Aquagga
- Barely subcritical treatment - high pressure, high temperature, high pH (350°C, >20.7 MPa, pH>14)
- Destruction reaction with PFAS is driven by a nucleophilic reaction with hydroxide; thermal degradation also occurs
- Residence times ~ minutes
- pH adjustment occurs at end of reaction

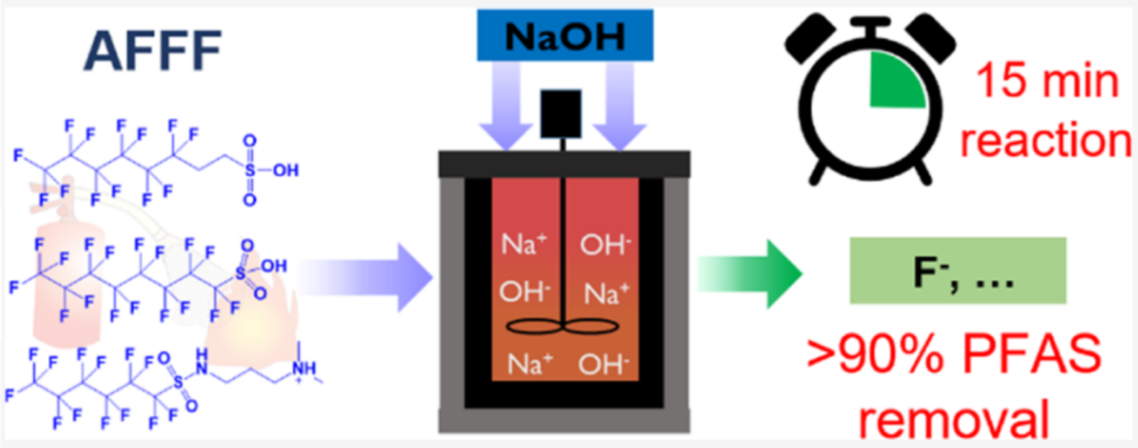


Image from Hao et al 2021

Aquagga HALT Test Plan

- ECT2 collected still bottoms from a US DoD site in Spring 2023
- Multiple additional PFAS spiked at 25 mg/l
  - Another subset was additionally spiked with additional salts to simulate RO-treatment and desorption of common anions
- Aquagga conducted testing in two phases in the 1 gph pilot unit:
  - Compared treatment of RO-still bottoms to typical still bottoms
  - Optimized for NaOH concentration
  - Optimized for temperature

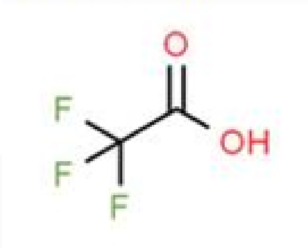
Salt, mg/L	Still Bottoms	RO Still Bottoms
NaCl	27,000	60,000
Na_2SO_4	4,800	6,000
$NaNO_3$	8,000	20,000

Testing Goals: Optimize Still Bottoms Treatment with HALT + Close F Mass Balance

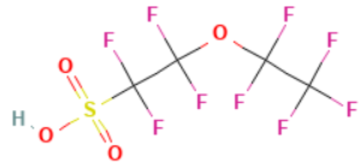
Aquagga HALT Test Plan

- Untreated and treated samples analyzed at Enthalpy Analytical for:
    - 533 PFAS analyte list
    - Polar PFAS analyte list
    - Fluoride
    - Adsorbable organofluorine (AOF) – EPA Method 1621
    - Gas phase: FTIR (at ECT2 R&D lab)

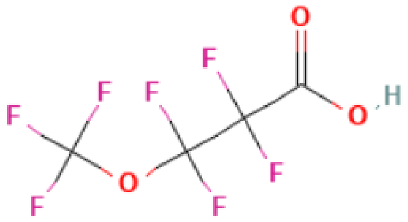
TFA



PFEESA



PFMoPrA



Testing Goals: Optimize Still Bottoms Treatment with HALT + Close F Mass Balance

Percentage Destruction by Analyte

	Initial Concentration After PFAS Additions (ppb)	Test 1.1	Test 1.2	Test 1.3	Test 1.4	Test 2.1	Test 2.2	Test 2.3	Test 2.4
		Level 3 NaOH Design Temp; Very high salt	Level 4 NaOH Design Temp; Very high salt	Level 3 NaOH Design Temp	Level 4 NaOH Design Temp	Level 2 NaOH Design Temp + 25	Level 5 NaOH Design Temp + 25	Level 2 NaOH Design Temp + 35	Level 1 NaOH Design Temp + 35
TFA	26,400	99.51%	99.50%	99.326%	99.605%	99.884%	99.871%	99.878%	99.664%
PFPrA	16,200	99.90%	99.89%	99.980%	99.940%	99.810%	99.790%	99.801%	99.826%
PFBA	34,000	99.99%	99.98%	99.990%	99.985%	99.998%	99.998%	99.998%	99.998%
PFPeA	4,870	99.96%	99.96%	99.970%	99.954%	99.990%	99.989%	99.989%	99.991%
PFHxA	14,700	99.98%	99.98%	99.983%	99.974%	99.996%	99.996%	99.996%	99.996%
PFHpA	2,910	99.91%	99.91%	99.926%	99.913%	99.979%	99.977%	99.978%	99.981%
PFOA	35,100	99.95%	99.99%	99.961%	99.961%	99.999%	99.999%	99.999%	99.999%
TFMS	22,200	85.20%	85.69%	96.531%	97.100%	97.865%	99.489%	99.793%	99.819%
PFBS	30,400	92.10%	95.13%	95.249%	95.023%	98.744%	99.783%	99.978%	99.901%
PFPeS	1,340	91.24%	95.91%	95.225%	94.111%	98.972%	99.807%	99.963%	99.887%
PFHxS	38,000	--	94.63%	92.107%	80.424%	99.201%	99.774%	99.962%	99.736%
PFOS	12,200	--	97.47%	75.056%	72.239%	99.843%	99.793%	99.865%	99.247%
6:2 FTS	28,900	98.95%	98.90%	98.972%	98.424%	99.987%	99.997%	99.997%	99.997%
HFPO-DA	37,400	99.99%	99.99%	99.993%	99.990%	100.000%	99.999%	99.999%	100.000 %
PFMOPrA	33,300	99.99%	99.99%	99.989%	99.986%	99.998%	99.998%	99.998%	99.998%
PFEESA	35,400	84.27%	90.89%	90.963%	89.503%	98.726%	99.523%	99.938%	99.776%
AOF	121,260	--	--	--	--	98.542%	99.843%	99.843%	99.843%

Blue cells were non-detect in treated solutions and represent minimum percentage destruction

99% to 99.99% Destruction Across All PFAS Under Optimized Conditions

Percentage Destruction by Analyte

	Initial Concentration (ppb)	Test 1.1 Level 3 NaOH Design Temp; Very high salt	Test 1.2 Level 4 NaOH Design Temp; Very high salt	Test 1.3 Level 3 NaOH Design Temp	Test 1.4 Level 4 NaOH Design Temp	Test 2.1 Level 2 NaOH Design Temp + 25	Test 2.2 Level 5 NaOH Design Temp + 25	Test 2.3 Level 2 NaOH Design Temp + 35	Test 2.4 Level 1 NaOH Design Temp + 35
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PFCAs, Fluorotelomers, and perfluoroalkyl carboxylic ethers completely destroyed under all test conditions

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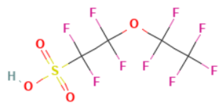
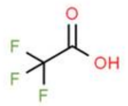


PFSA destruction percentages were largely independent of chain length

Perfluoroalkyl ether sulfonate had similar recalcitrance as PFSAs

Percentage Destruction by Analyte



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Excellent destruction of ultrashort PFAS, including TFA and TFMS

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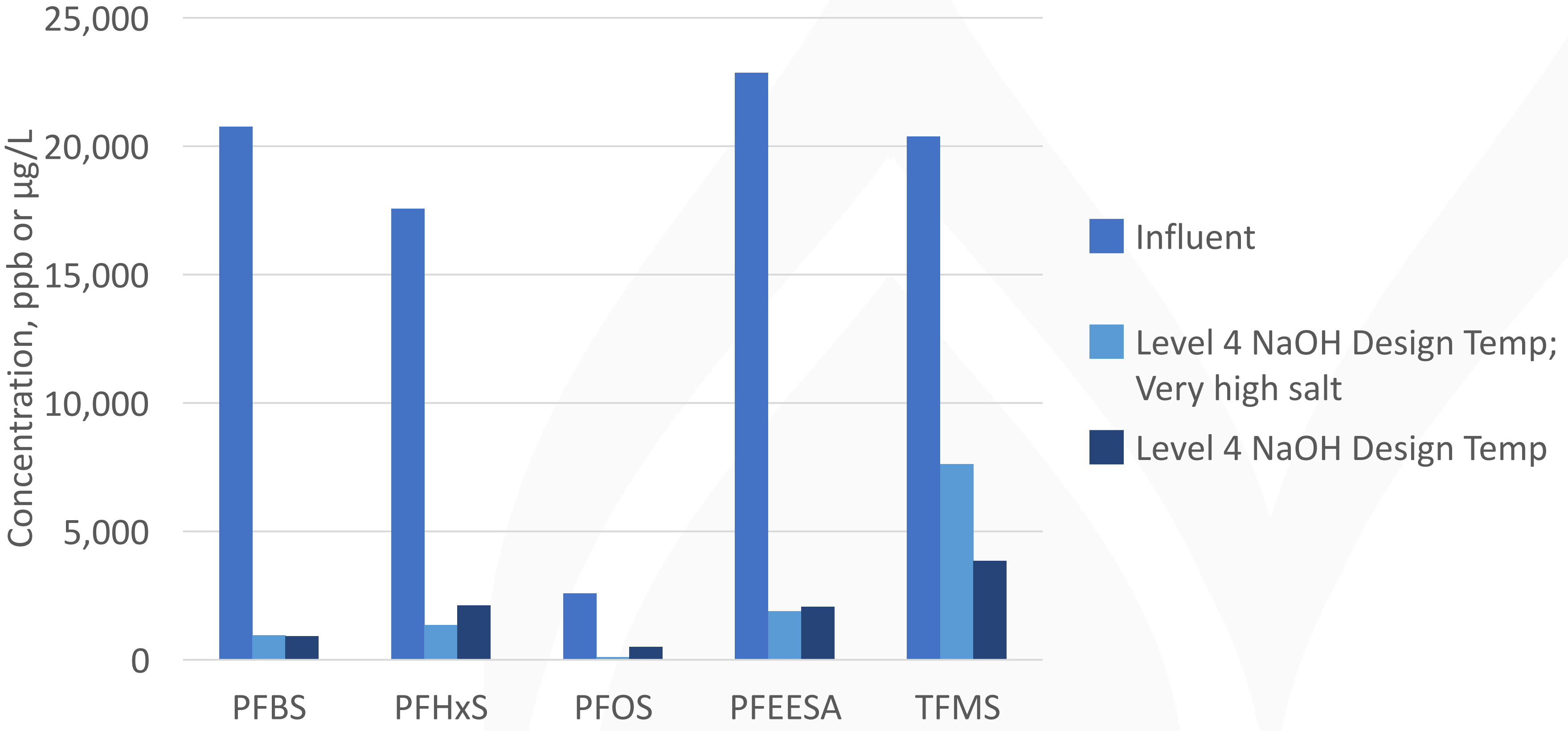
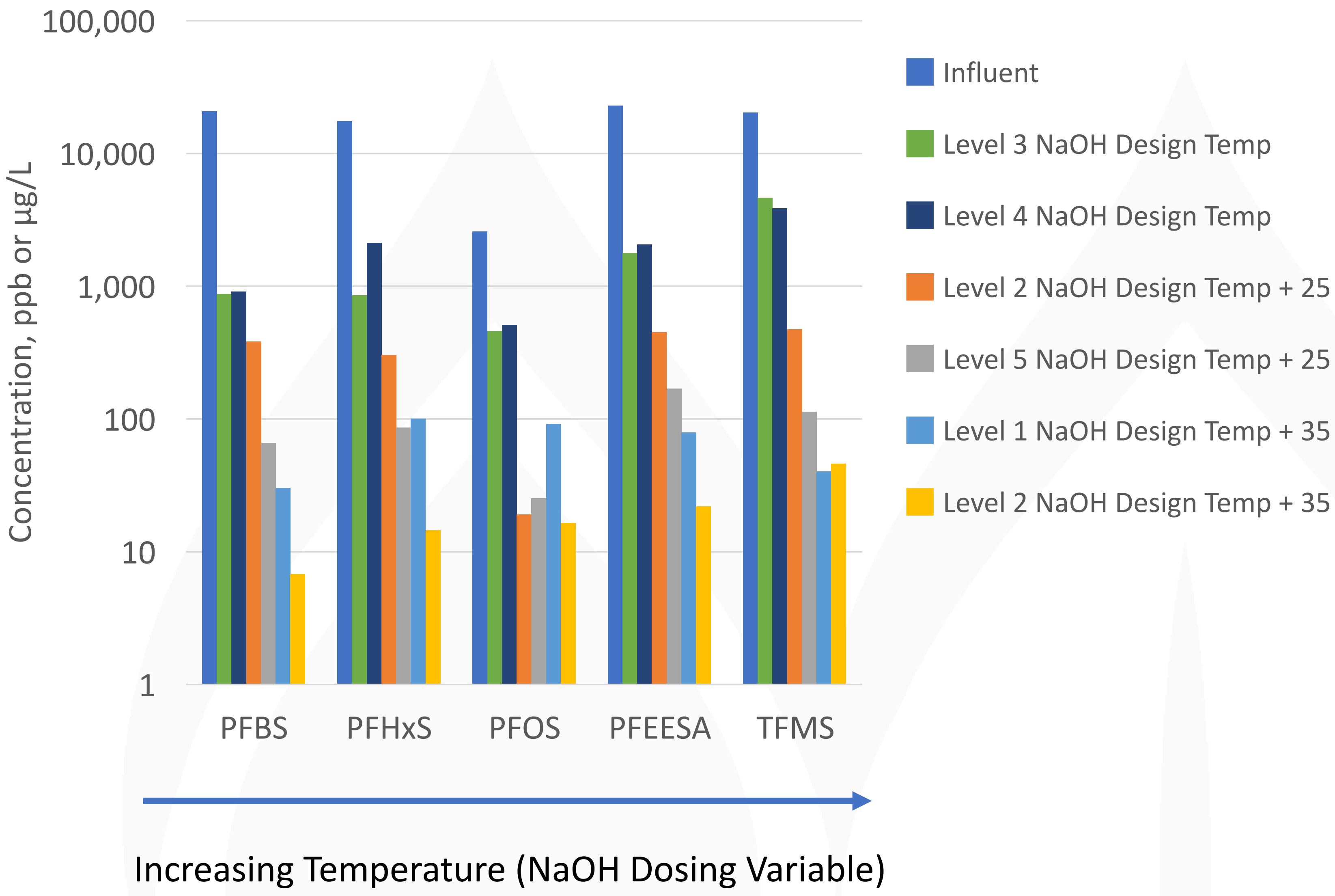
99.8%+ destruction of AOF – line of evidence for mineralization

HALT Testing: RO-Concentrated Still Bottoms vs Regular Still Bottoms



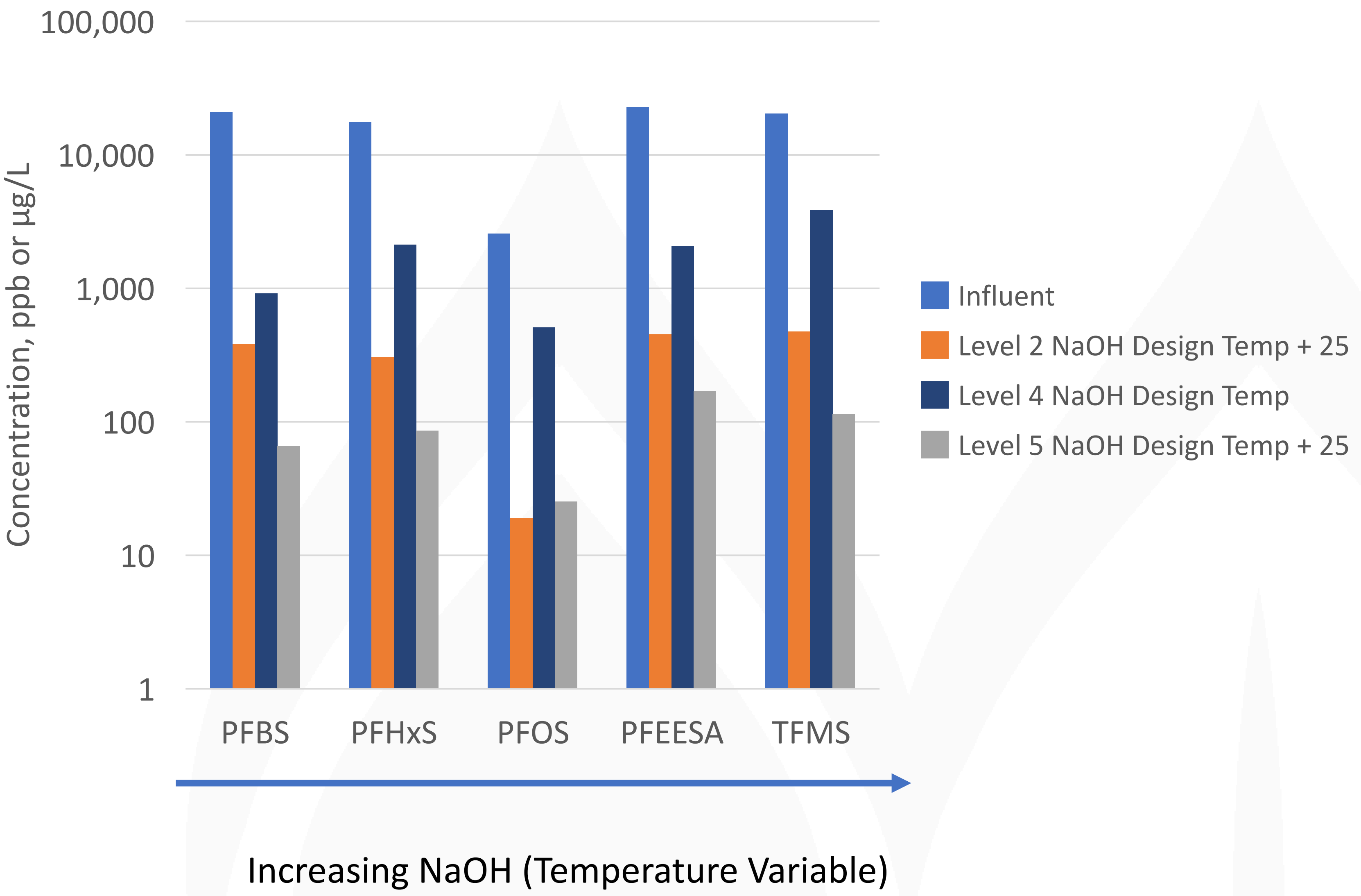
Simulated RO-Concentrated Still Bottoms Matrix Did Not Adversely impact HALT

Variation in Recalcitrant Compounds in Treated Effluent



Increasing Design Temperature by 25 - 35 C Increased Destruction 90-99%

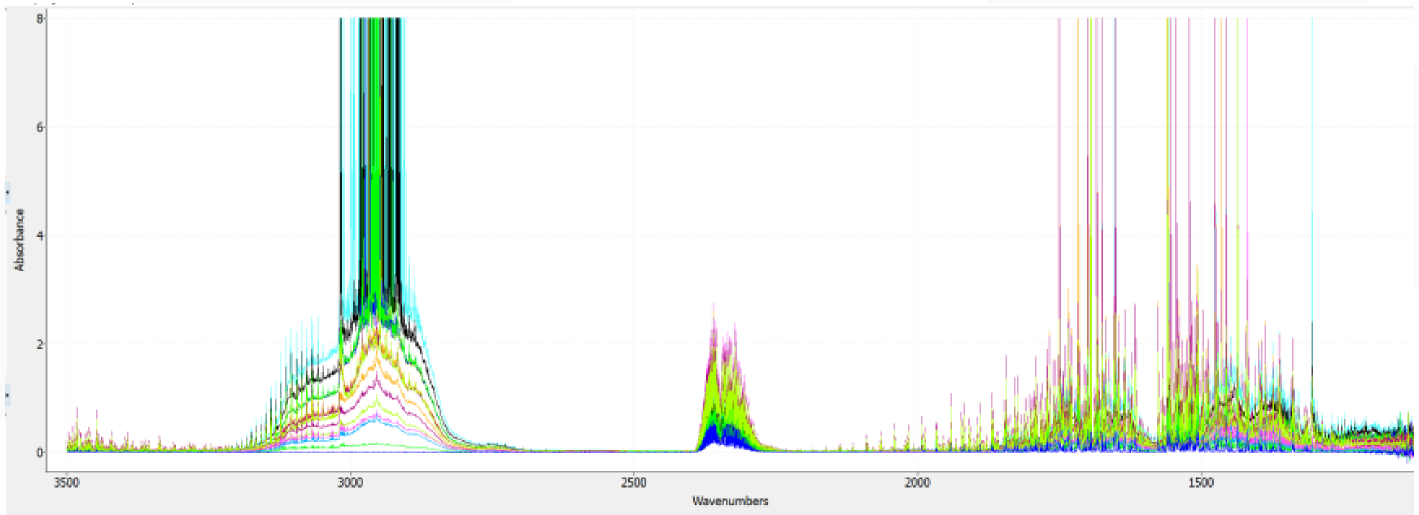
Variation in Recalcitrant Compounds in Treated Effluent



Increasing NaOH Dosage Was Less Impactful than Increasing Temperature

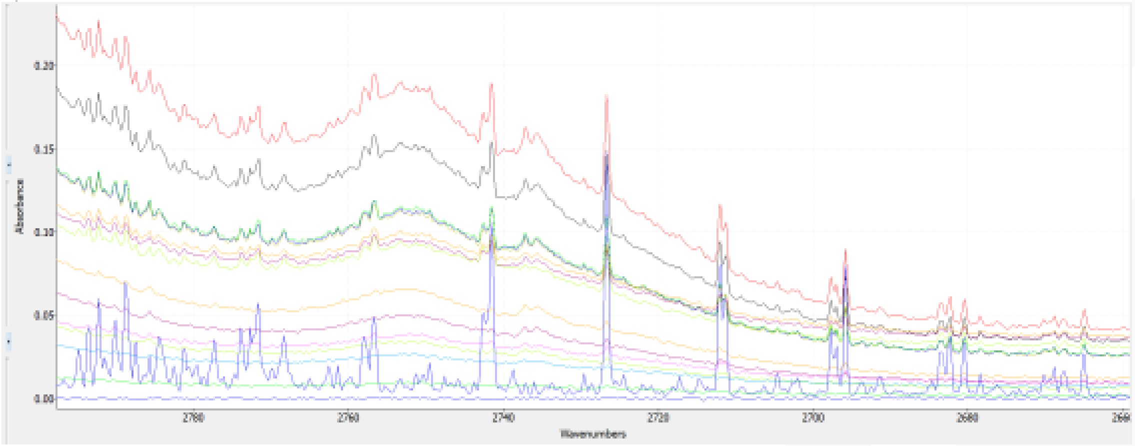
Qualitative FTIR Analysis of Offgas

- Three samples were analyzed by a Thermoelectrically cooled Fourier Transform Infrared Spectroscopy (FTIR)
- All three had similar spectra
- FTIR reference spectra used to evaluate the presence/ absence of various potential byproducts

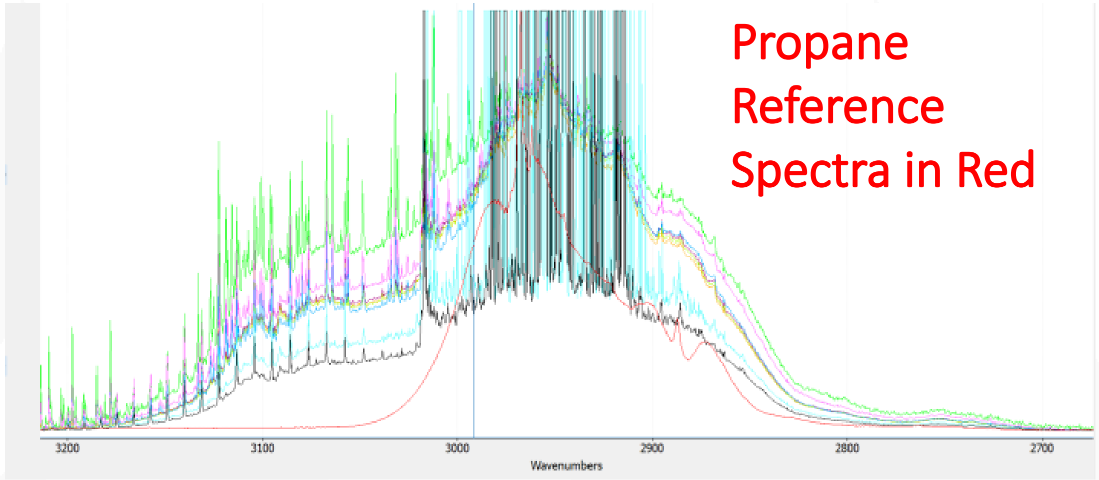


FTIR Analysis of Gas Effluent – Presence of Alkanes

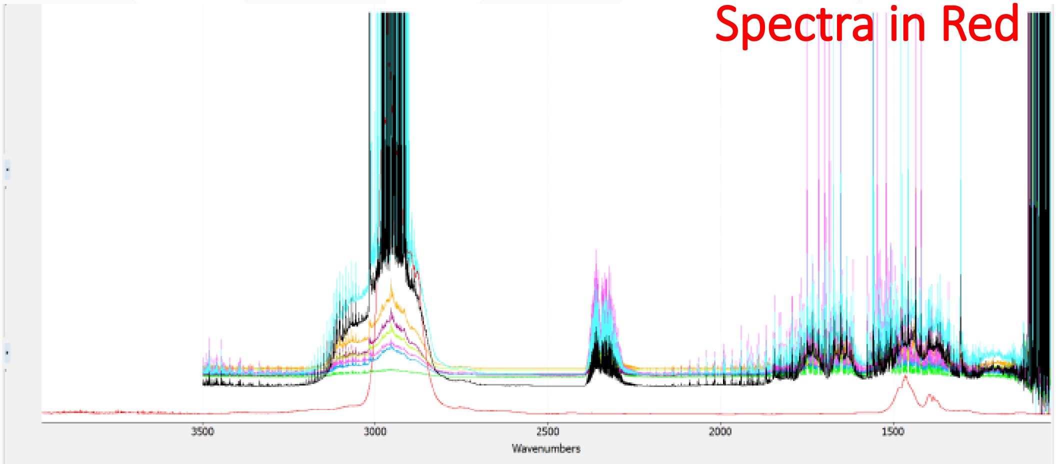
Methane Reference Spectra in Purple



Propane Reference Spectra in Red



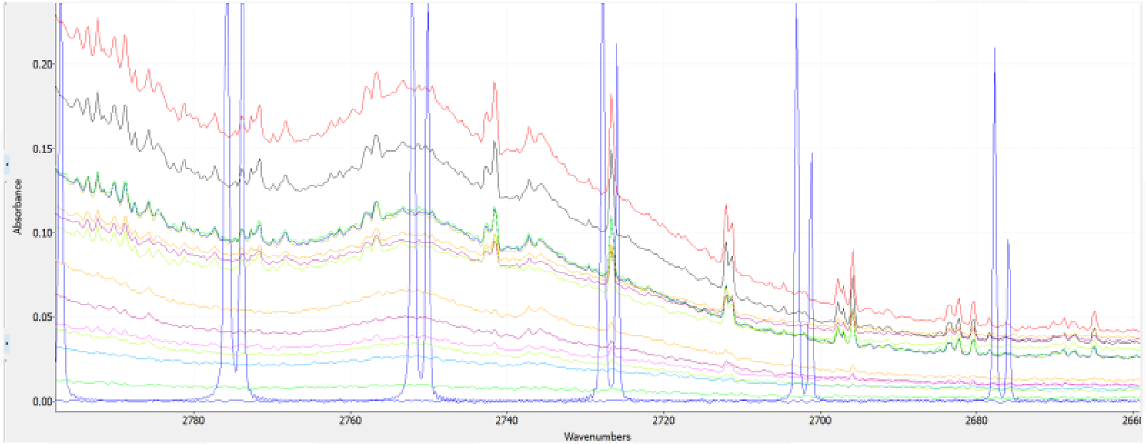
Butane Reference Spectra in Red



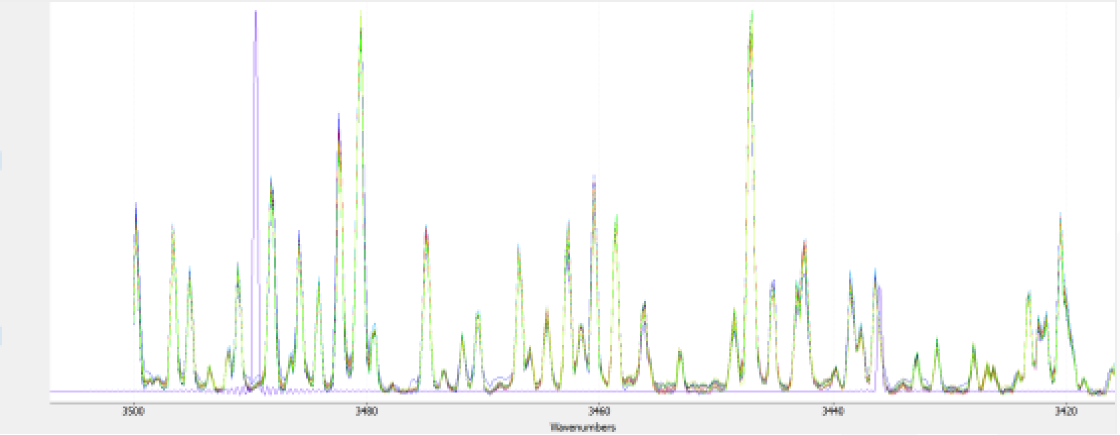
Significant reference spectra overlap indicates presence of methane, propane, butane

FTIR Analysis of Gas Effluent – Lack of HF, HCl, and CF_4

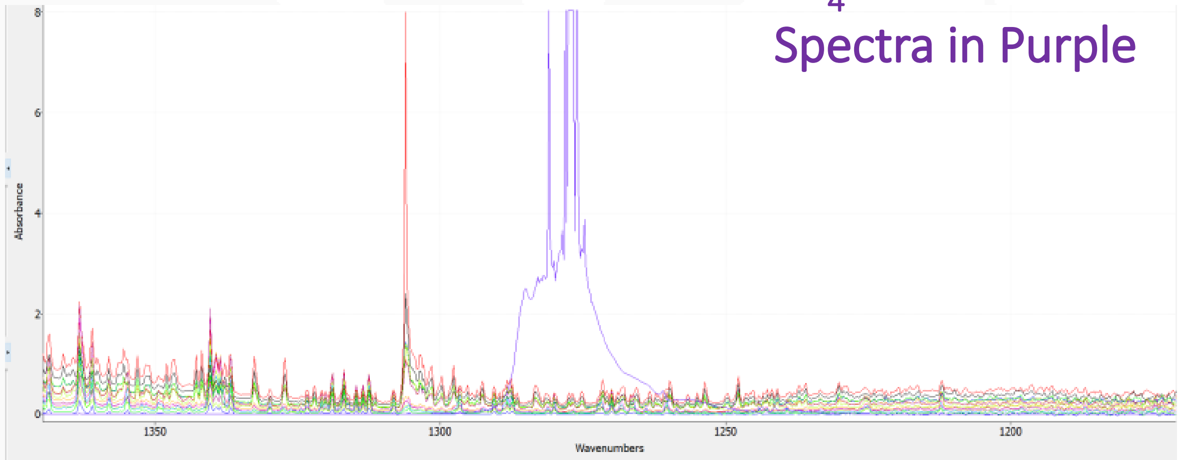
HCl Reference Spectra in Purple



HF Reference Spectra in Purple

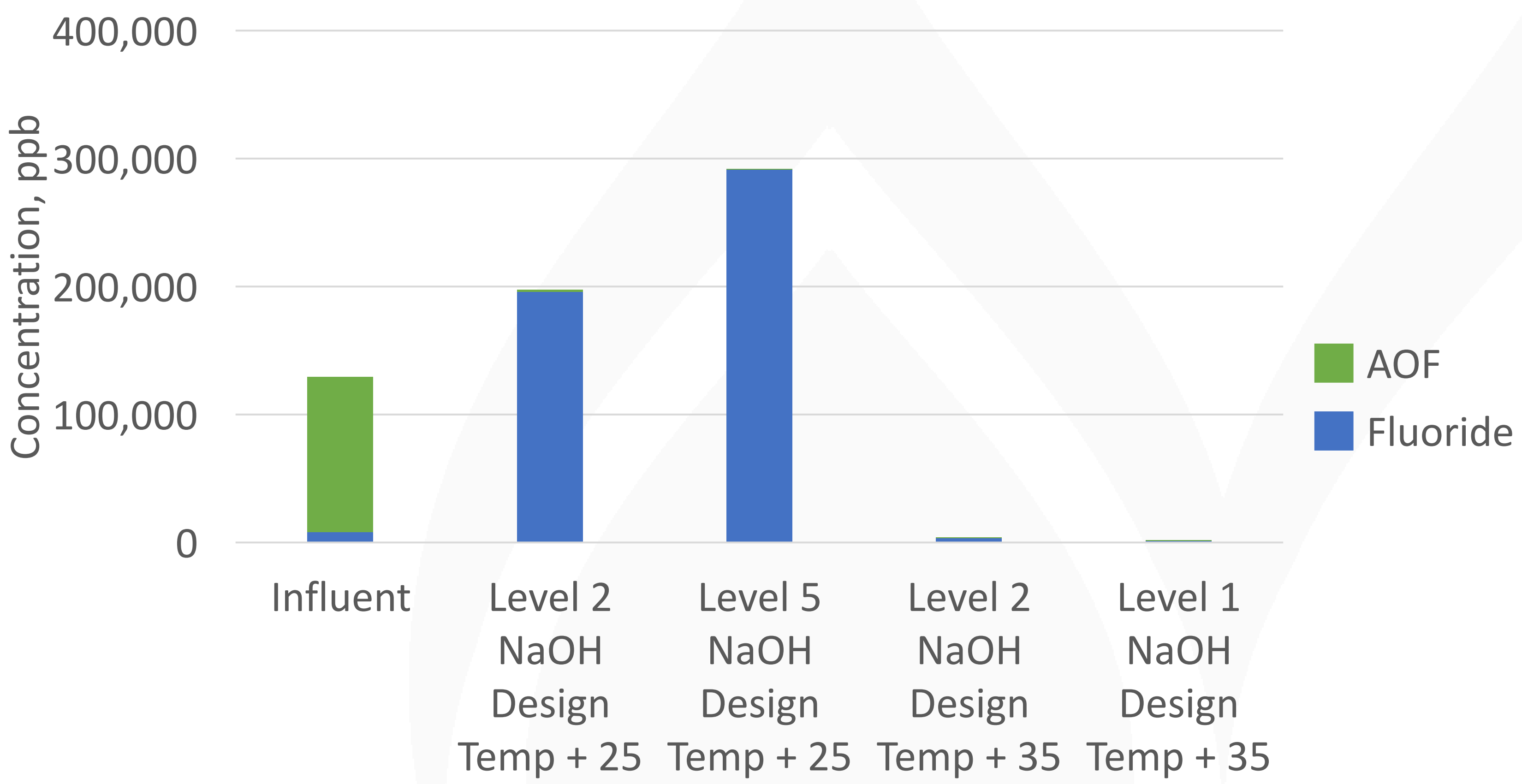


CF_4 Reference Spectra in Purple



Lack of reference spectra overlap indicates lack of HCl, HF, and CF_4

Fluorine Mass Balance



Best Fluorine Mass Balance Observed at Design Temp + 25 C

Strong Evidence for PFAS Mineralization Using HALT on Still Bottoms

- Disappearance of All Target PFAS
- Disappearance of Ultrashort PFAS
- Disappearance of Total Organofluorine
- No Fluorinated Gas Phase Products Identified
- ~35% to > 100% Recovery as Fluoride

Key Messages

- Regen IX is a good fit for high conc PFAS influent and/or short chain PFAS removal
- Regen IX creates a PFAS concentrate (“still bottoms”) amenable to destruction
- Hydrothermal alkaline treatment (HALT) is robust in the still bottoms matrix
- Full spectrum PFAS destruction with mineralization observed with HALT
- HALT conditions can be optimized to 99.9%+ destruction efficiency
- Regen IX and HALT can be paired to create a closed loop treatment process