

Measurement and Modeling of TOC and Fluorine Ion Extraction from Polymeric Piping in Hot Ultrapure Water

Gary Van Schooneveld¹, Peter Maenke¹, Jikku Thomas², Bob McIntosh³

¹CT Associates, Inc., 7121 Shady Oak Road, Eden Prairie, MN 55344

²Entegris Inc., 129 Concord Rd, Billerica, MA 01821

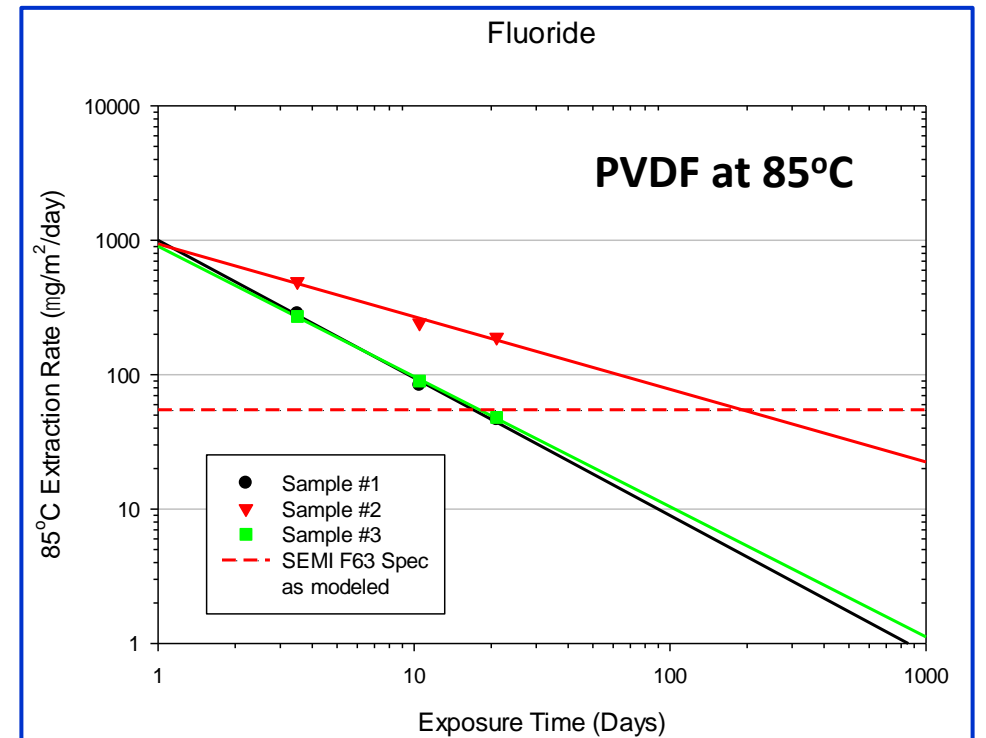
³Enviro-Energy Solutions, 13023 NE Highway 99, Vancouver, WA 98686

Presentation Outline

- Problem Statement
- Technical Objectives and Approach
- Test Apparatus and Metrology
- Extraction Results and Projections
- Contamination Identification
- Key Takeaways

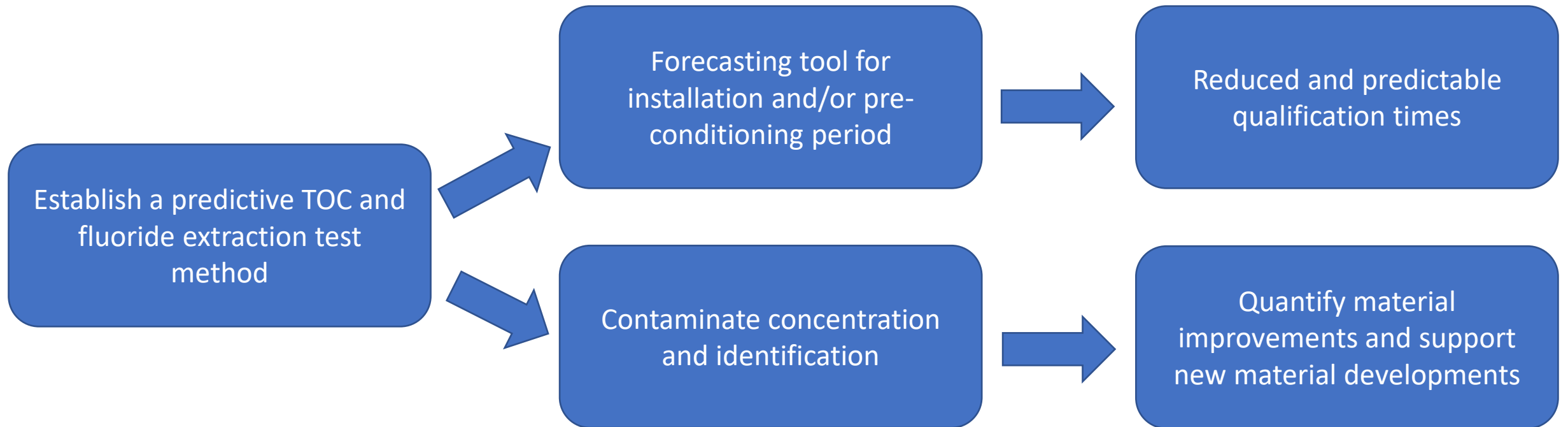
Problem Statement

- “Time to qualification” is becoming increasingly critical.
 - Some hot UPW systems can take up to 6 months to meet “quality”.
- Long-term chip reliability is becoming a significant performance driver.
 - Leached organics are potential source of particle precursors and organic films.
 - Elevated fluoride contamination may contribute to reliability reduction.



Van Schooneveld, et al, “Use of Extraction Modeling to Predict Contamination Levels in Ultrapure Water Systems”, Ultrapure Micro 2018 Austin, Texas

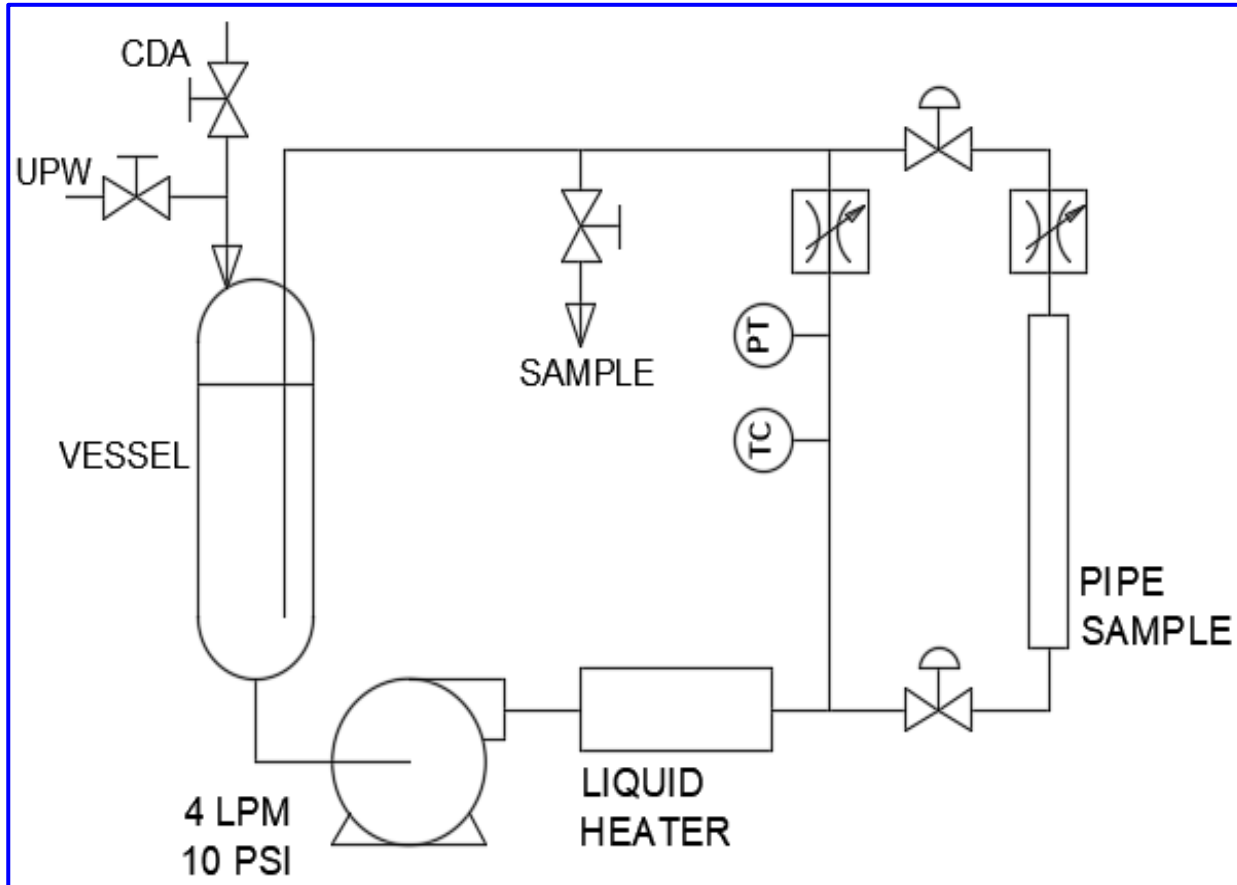
Technical Objectives



Technical Approach

1. Construct and qualify an 85°C closed loop UPW system.
2. Demonstrate the of repeatability of the method using PVDF piping.
3. Assess the validity of a diffusion-limited extraction model for forecasting long-term extraction rates.
4. Utilize next-generation analysis tools for TOC contaminate identification and quantification.

Extraction Apparatus

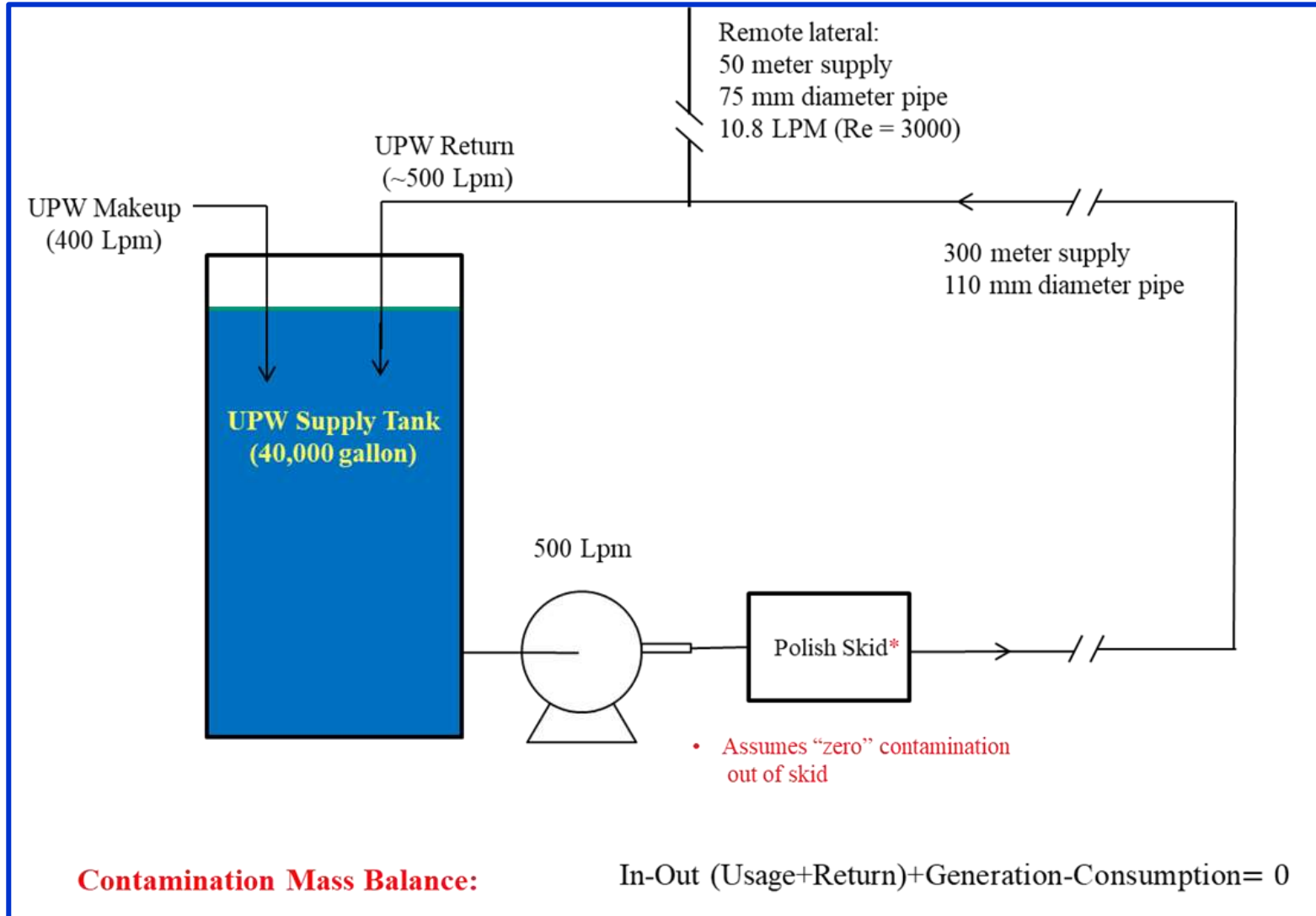


- All PFA construction (except for quartz heater)
- 90-day preconditioning period with continuous UPW feed and bleed.
- All test fluid required for the test as present at the start of the test.

Three long-term extraction tests were performed in 85°C UPW:

- 30-day test system spool
- 90-day extraction of PVDF pipe
- 60-day extraction of PVDF pipe

Hot UPW Distribution Model



Hot UPW distribution model developed by the 2018 SEMI F57 Task Force.

Metrology Utilized:

- In-line Metrology:

- TOC - Sievers 500RL TOC Monitor
- Particle and Particle Precursors - Kanomax FMT Model 9010 Scanning Threshold Particle Counter

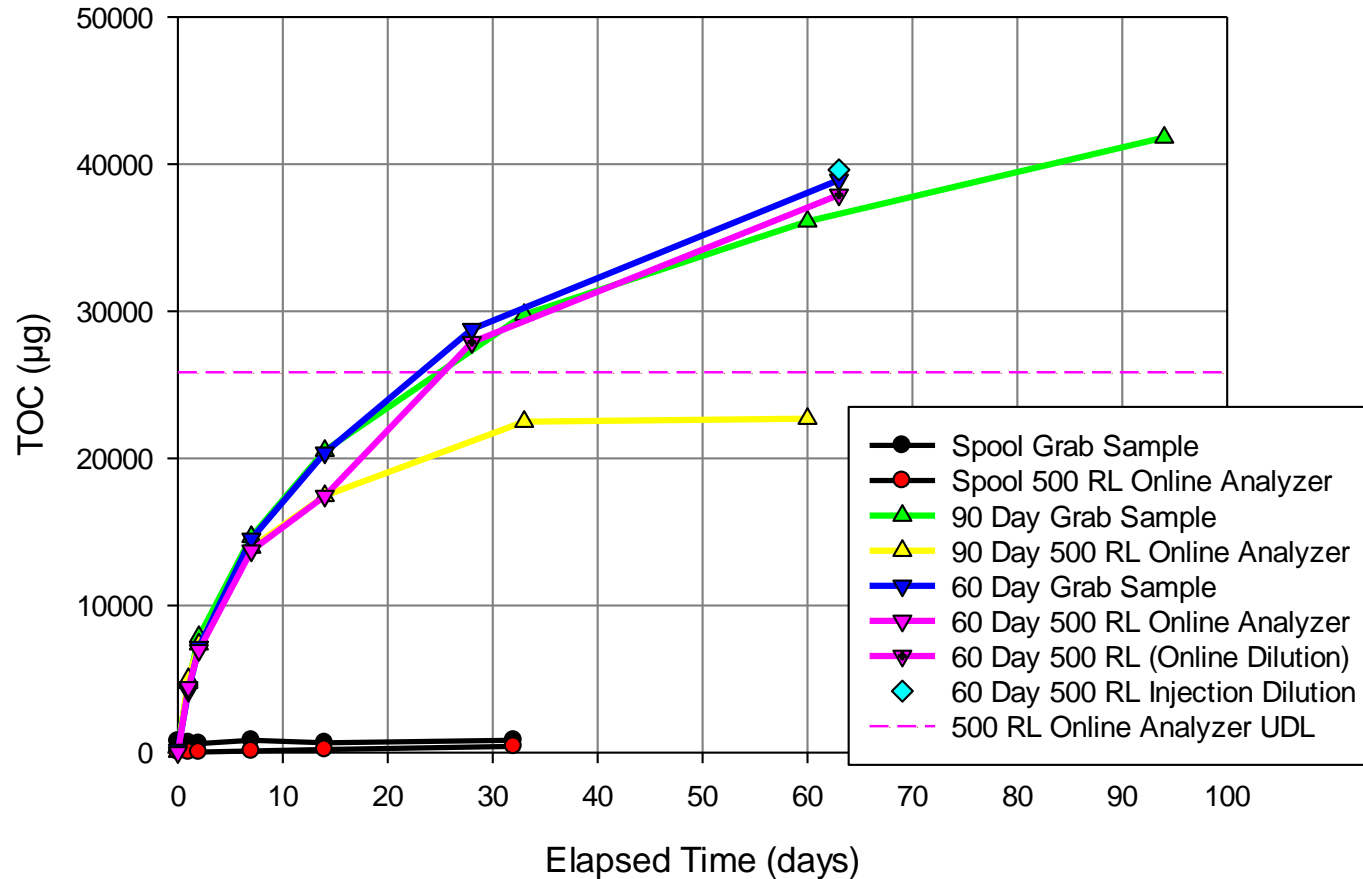
- Grab Samples:

- TOC - Balazs
- TOC Speciation – Balazs
- Fluorine - Balazs
- Kanomax STPC and CTA Liquid Nanoparticle Sizer (LNS)
- Particle and particle precursor morphology and composition – Focus Aerosol Deposition (FAD)

Test Results

TOC Extraction Results

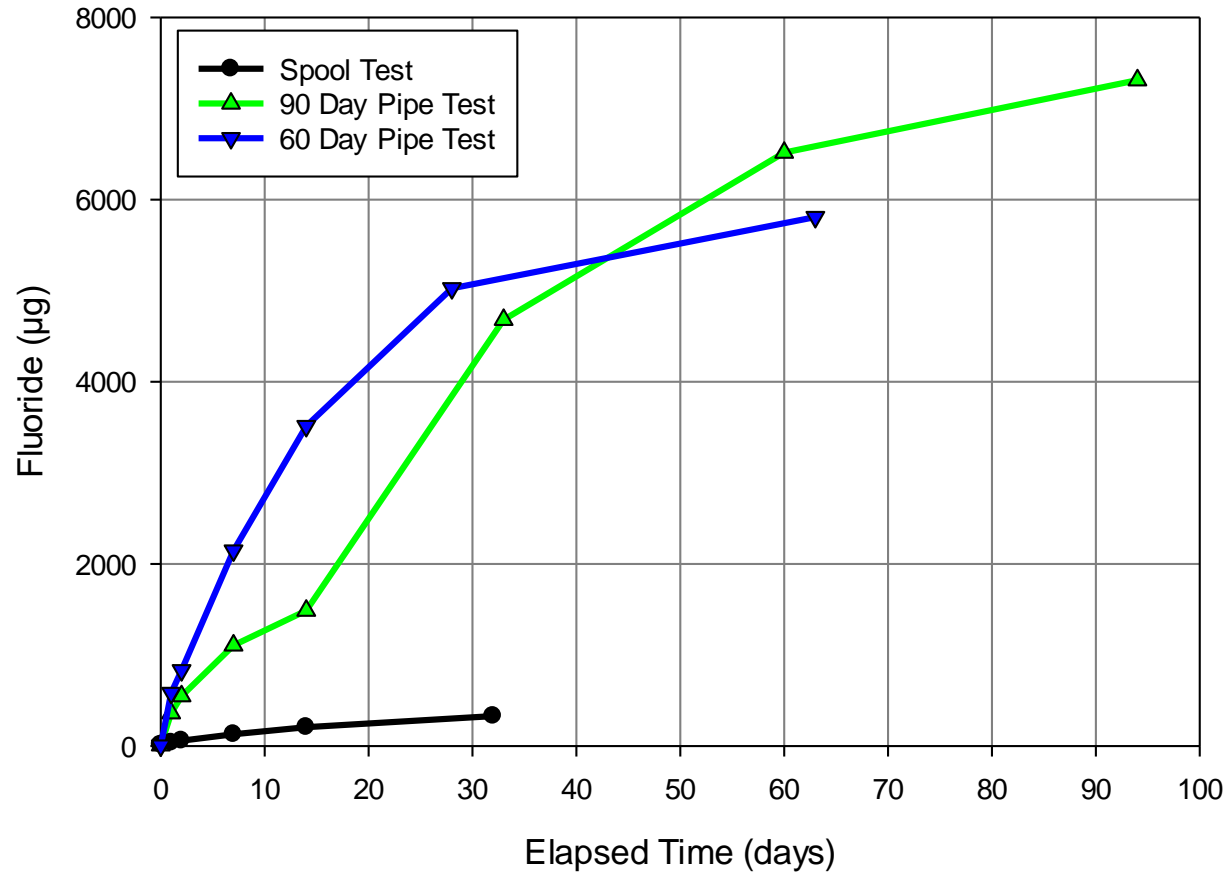
TOC Mass Extracted



- Contaminate concentrations are converted to mass extracted.
- Online dilution required for TOC measurement due to upper limit of TOC monitor.
- Excellent correlation between online TOC measurements and grab sample measurements.
- Excellent repeatability.
- Very strong signal to noise .

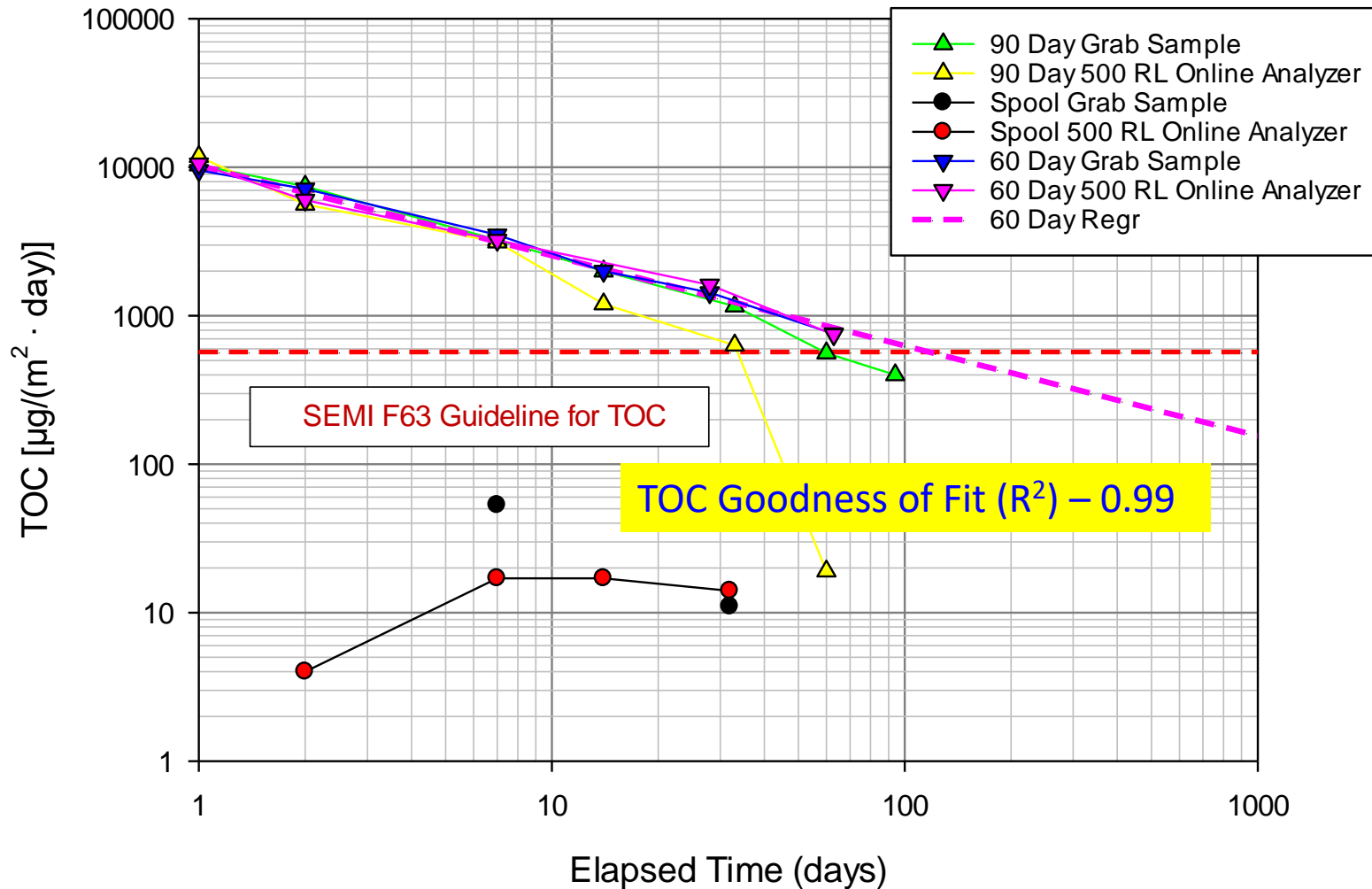
Fluoride Extraction Results

Fluoride Mass Extracted



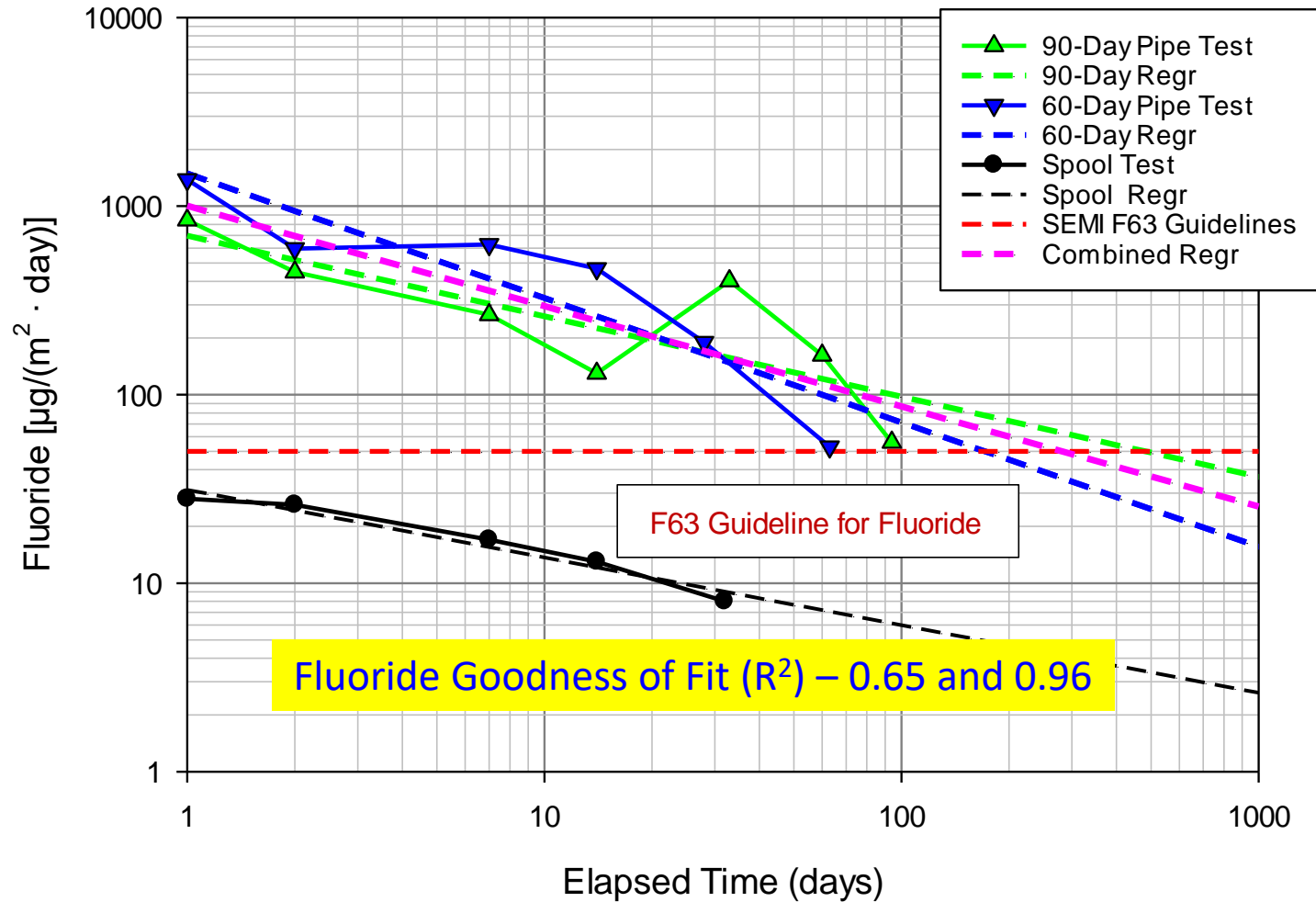
- Contaminate concentrations are converted to mass extracted.
- Fluoride results were not as repeatable as the TOC results.
- Strong signal to noise.

Extraction Rate Analysis - TOC



- Excellent log-log linearity validates the use of a diffusion-limited extraction model for TOC.
- Projected time to qualification:
 - 60-day projection – 117 days
 - 28-day projection – 149 days
 - 14-day projection – 132 days
 - 7-day projection – 166 days
- 30-day test period appears to be adequate to project TOC qualification time.

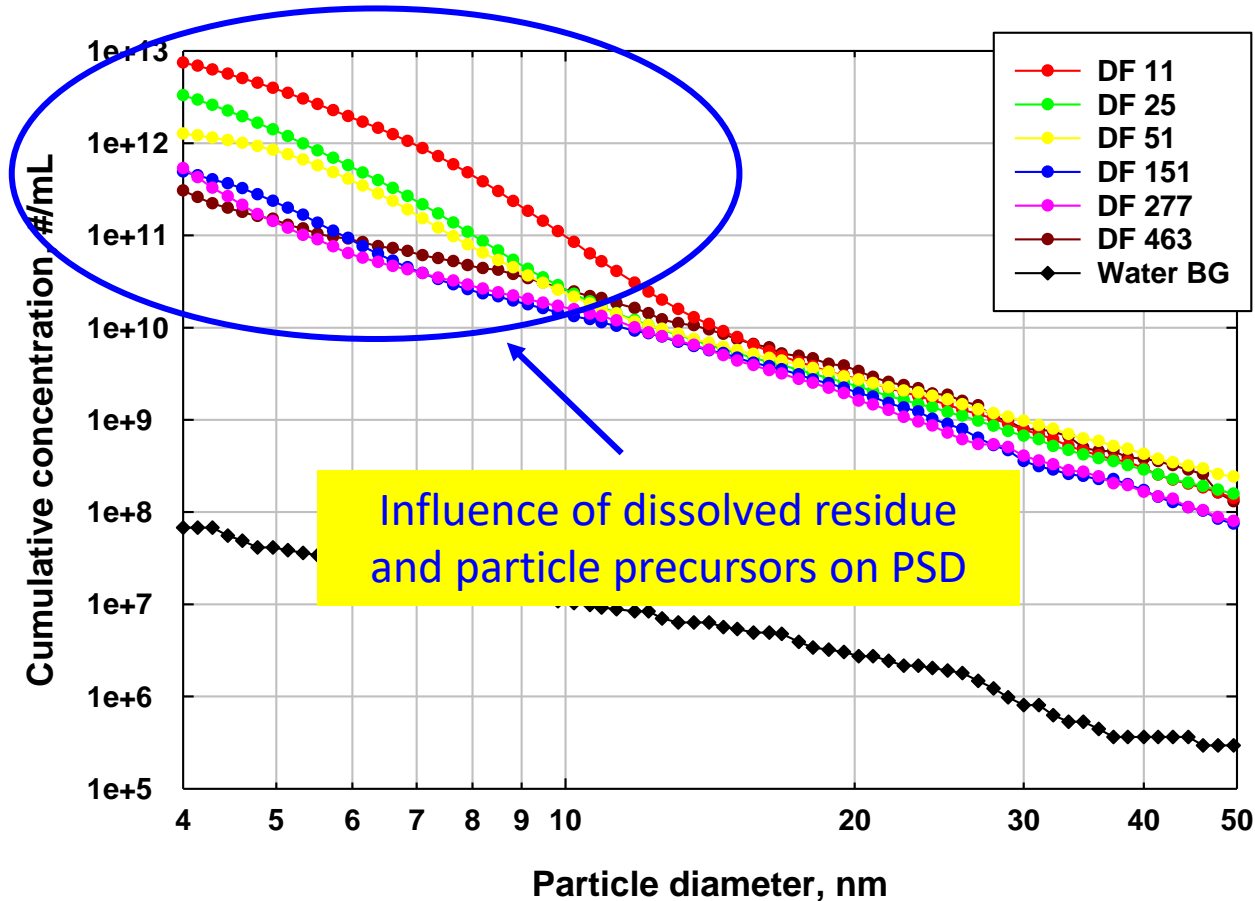
Extraction Rate Analysis - Fluoride



- Projected time to – 170 to 450 days (275 days combined)
- Variability in the fluoride data needs to be reduced to improve accuracy of projection.
 - Batch preparation of bottles
 - Analyze all samples as batch

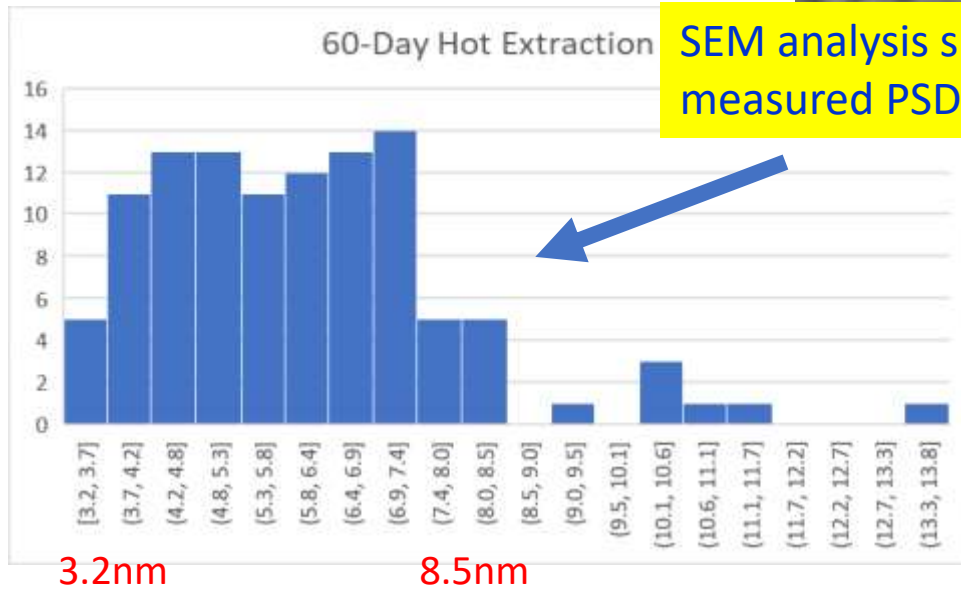
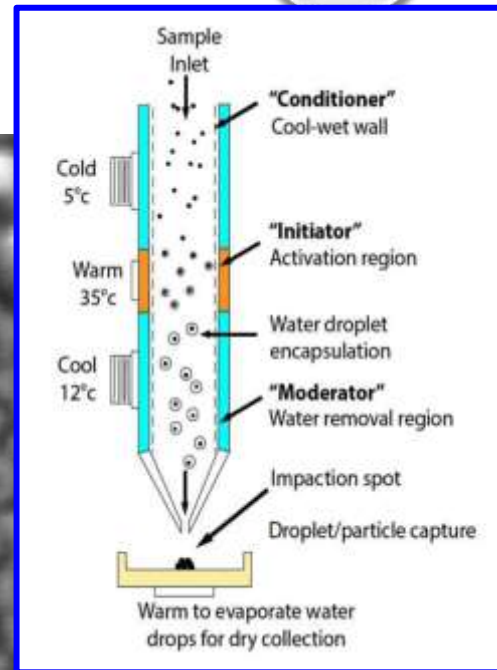
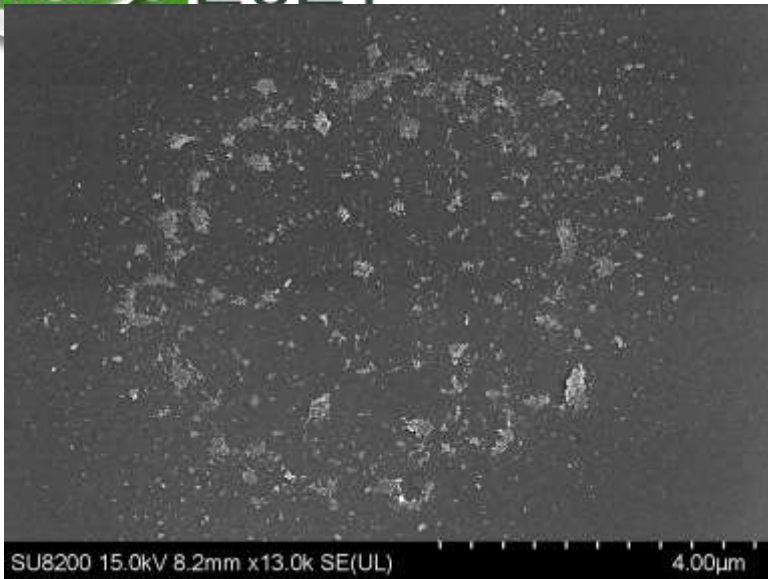
Contaminate Identification

Hot UPW Particle and Particle Precursor Extract Size Distribution via LNS

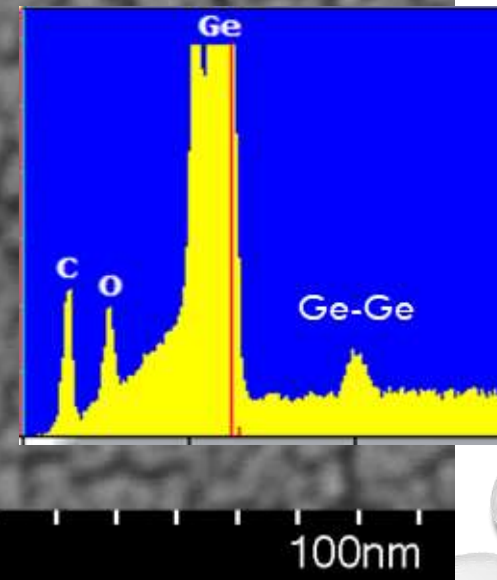


- Particle size distribution, when normalized for dilution, provides insight to the proportion of dissolved matter and particle precursor to native particles.
- A significant portion of the contamination extracted appeared to be native particles smaller than 10 nm.

SEM/EDX via FAD Collection



SEM analysis supports LNS measured PSD



Key Takeaways

- The hot UPW extraction test method presented provides a valuable tool for suppliers and end-users to compare and predict “Time to Qualification” of polymeric piping particularly for TOC and fluoride extracts.
- Concentration of contaminants over time provides the opportunity to identify specific contributors and guide material improvement and new material development.
- LNS and FAD analysis of the extractant revealed a significant quantity of sub-10 nm particles and particle precursors.
- A 30-day test period appears appropriate now with 14 days possible with additional data.
- Additional work is required to reduce variability of the fluoride extraction results.

Thank you for your attention!

Contributors:

- Peter Maenke – CT Associates, Inc (peter.maenke@ctassociatesinc.com)
- Jikku Thomas – Entegris, Inc. (jikku.thomas@entegris.com)
- Bob McIntosh – Enviro-Energy Solutions (bob@enviro-e.com)