Use of Extraction Modeling to Predict Contamination Levels in Ultrapure Water Systems

Gary Van Schooneveld[1], Quynh Le[2], Bob McIntosh[3], Slava Libman[4]

[1]CT Associates, Inc., 7121 Shady Oak Road, Eden Prairie, MN 55344
[2]Balazs™ NanoAnalysis, 46409 Landing Pkwy, Fremont, CA 94538
[3]Enviro-Energy Solutions, 13023 NE Highway 99, Vancouver, WA 98686
[4]FTD Solutions, 4755 Forge Road, Colorado Springs, CO 80907

Background

- Management of ionic, metallic, organic and particle contamination in ultrapure water is critical to ensure high product yield in the semiconductor manufacturing process.
- Acceptable levels and limits of these and other contaminants continue to be reduced due to reduced feature dimensions and increasingly complex 3D structure.
- The International Roadmap for Devices and Systems (IRDS) provides guidance and criteria to these and other requirements as it anticipates the future needs of the industry.
- SEMI specifications are being developed and revised to aid the industry in meeting these new requirements.
- This presentation will focus on the test work done in support of the alignment of SEMI F57, Specification for Polymer Materials and Components Used in Ultrapure Water and Liquid Chemical Distribution Systems and SEMI F63, Guide for Ultrapure Water Used in Semiconductor Processing.

Objectives

- Establish an extraction database using pipe and tubing materials from multiple manufacturers and material suppliers.
  - PVDF pipe (2 manufacturers, 2 raw materials)
  - PFA tubing (3 manufacturers, 2 raw materials)
- Develop an extraction model for predicting contamination levels in room temperature and hot UPW systems.
- Align SEMI F57 extraction requirements with SEMI F63 using extraction model and the measured PVDF and PFA extraction performance data.

Acknowledgements

- This effort was a highly collaborative effort.
- Participating companies:
  - Multiple pipe, tubing and material suppliers:

PVDF	Agru	Arkema	Georg Fischer	Solvay	
PFA	Chemours	Daikin	Entegris	Parker	St Gobain

  - Laboratories: Air Liquide Balazs and Solvay Laboratory Services
  - Modeling and analysis – CT Associates

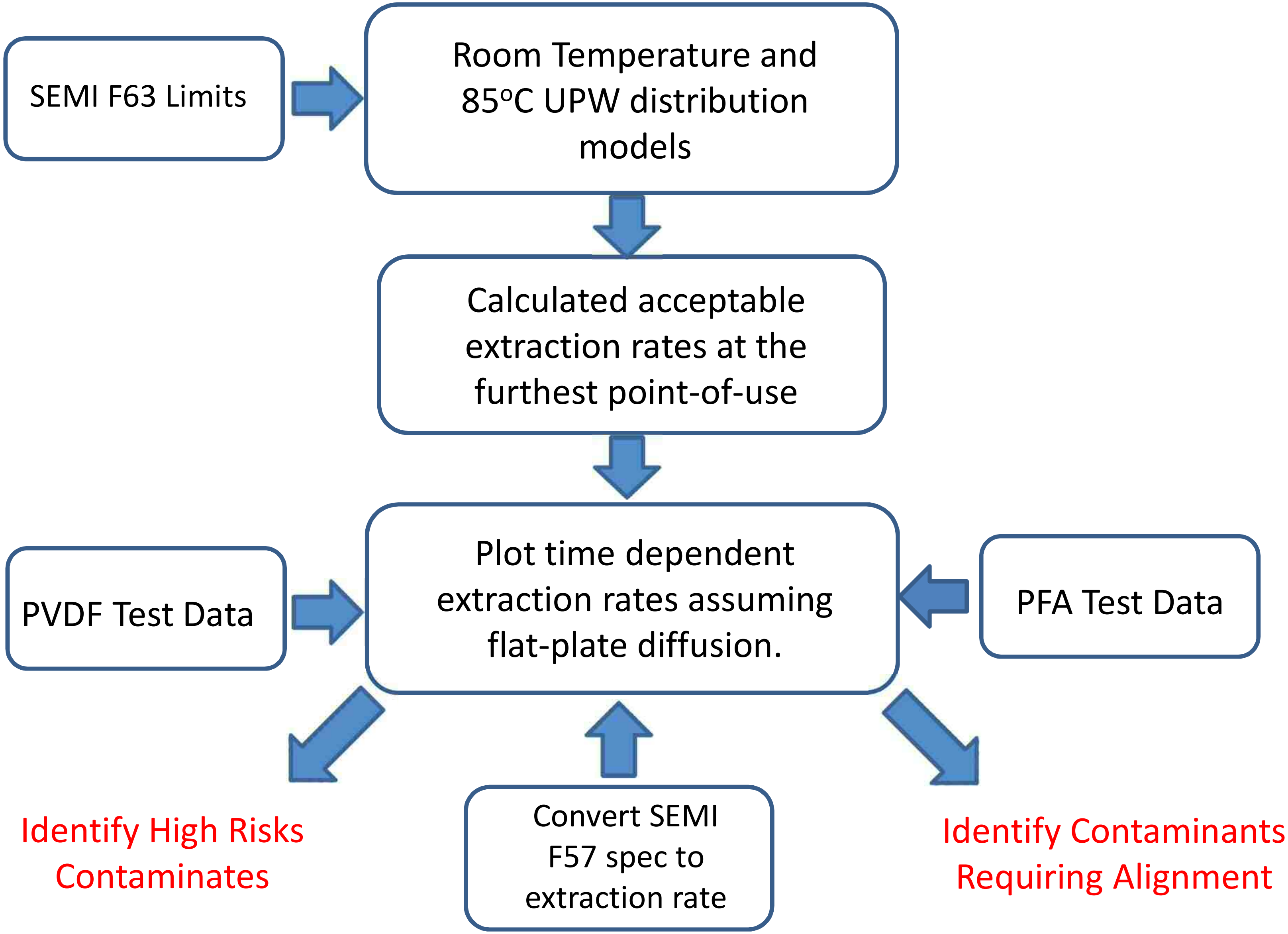
Experimental Plan

	PVDF pipe		PFA tubing	
Week	Hot (85°C)	RT	Hot (85°C)	RT
1	X	X	X	X
2	X	X	X	X
3				
4				
5	X	X	X	X
6				
7				
8		X		
9				
10		X (85°C)		

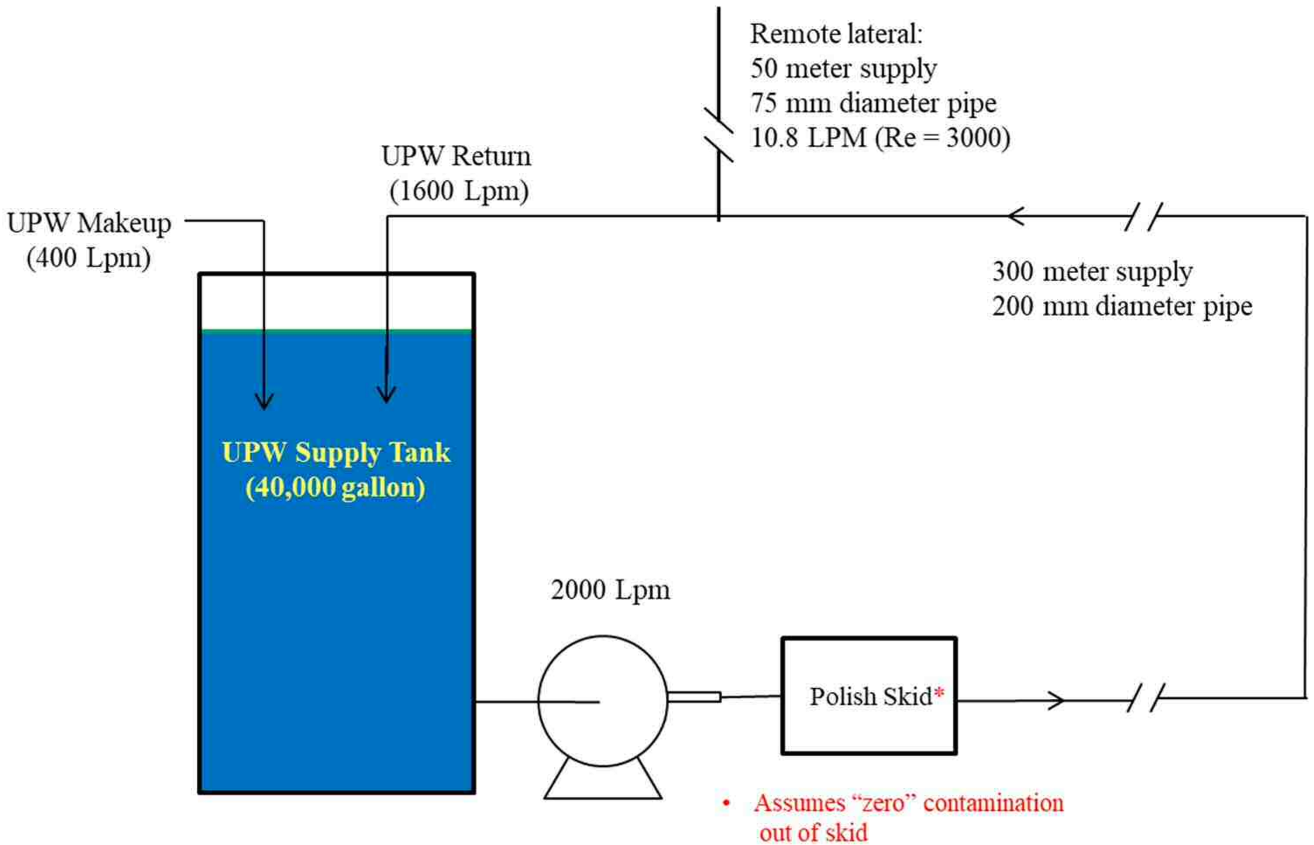
- Prepare all samples per SEMI F40, “Practice For Preparing Liquid Chemical Distribution Components for Chemical Testing.”
- Use full immersion for PVDF pipe samples (3.2cm OD x 0.24cm wall x 7.0cm long)*
- Use inside surface extraction for PFA (3/8” tubing ¼ " ID x 25 ft length)
- Contaminant extraction measured:
  - Trace metals – For RT, ICP-MS, Thermo Finnigan High Resolution ICP-MS, For 85° C, ICP-MS, Perkin Elmer Nexion ICP-MS
  - Anion - Ion Chromatography. Thermo Fisher Dionex ICS 5000
  - Total Organic Carbon - Siever 5310C TOC Analyzer)

* Solvay tested both inside only and full immersion

Analysis Methodology



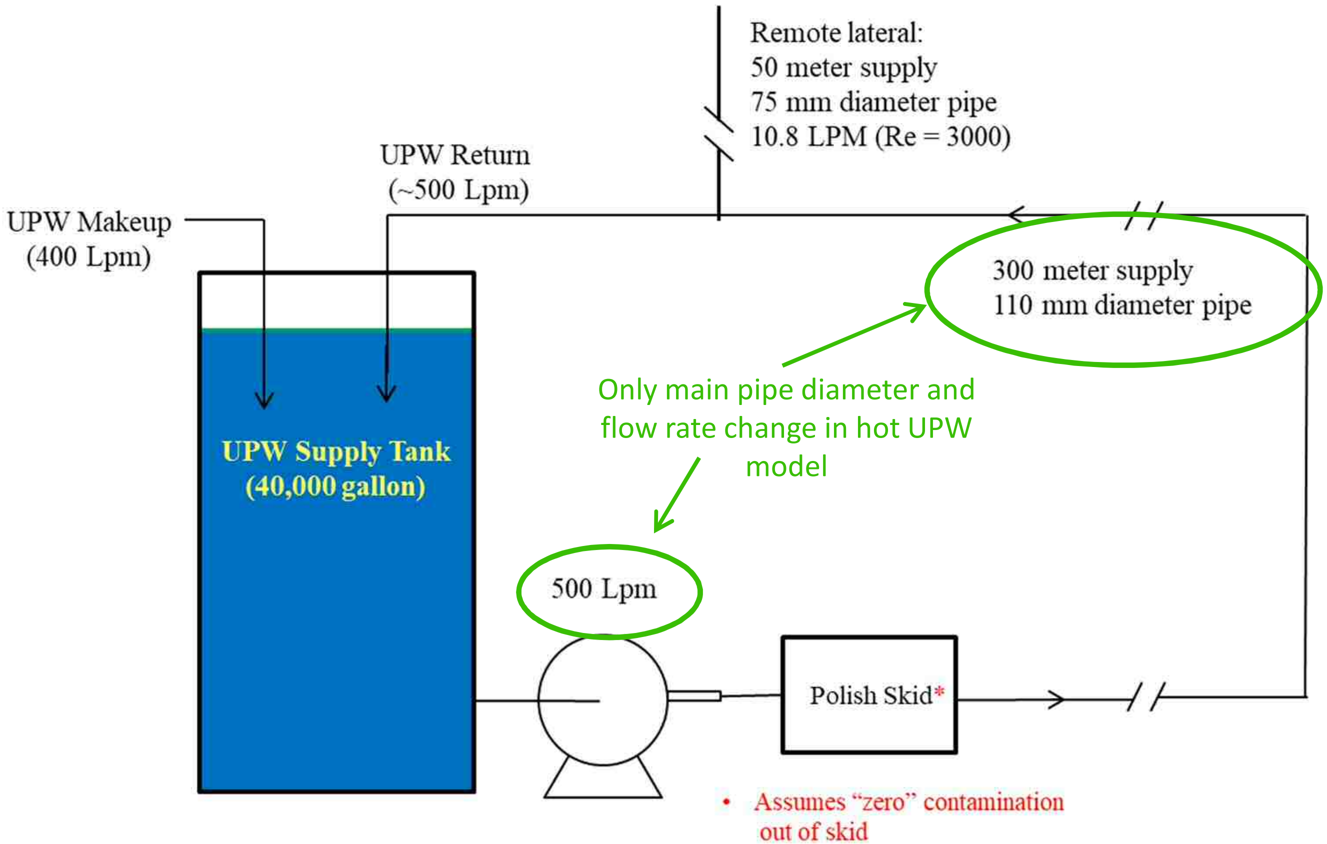
Room Temperature UPW Distribution Model



Contamination Mass Balance: In – Out (Usage + Return) + Makeup – Consumption = 0

Δ Concentration = Pipe Length (m) x Pi x Diameter (m) x Extraction rate (mg/m^2/Day) / Flow Rate (Liters/Day)

Hot UPW Distribution Model

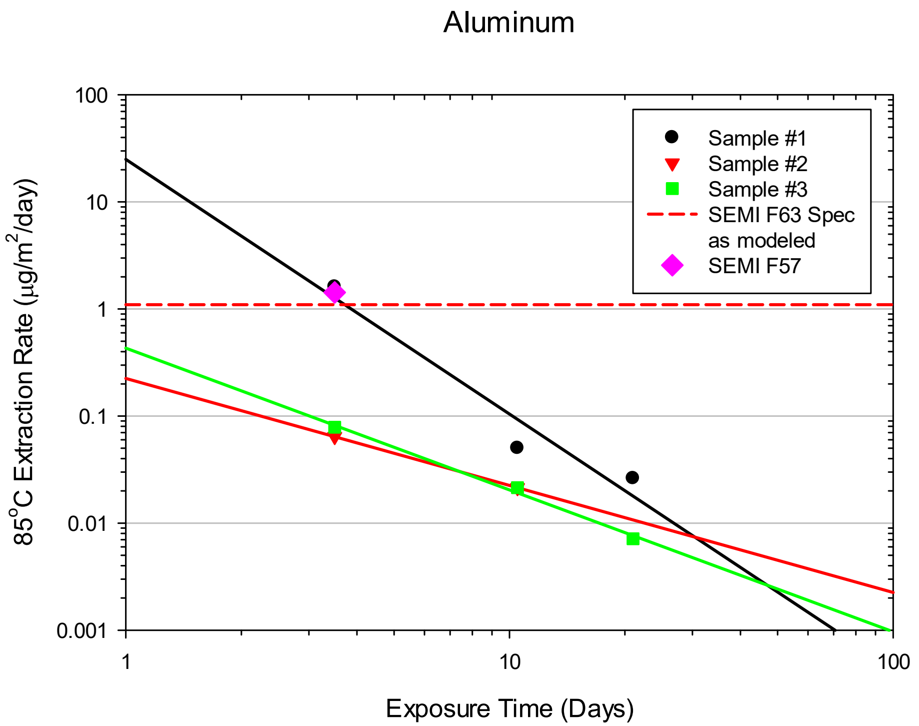


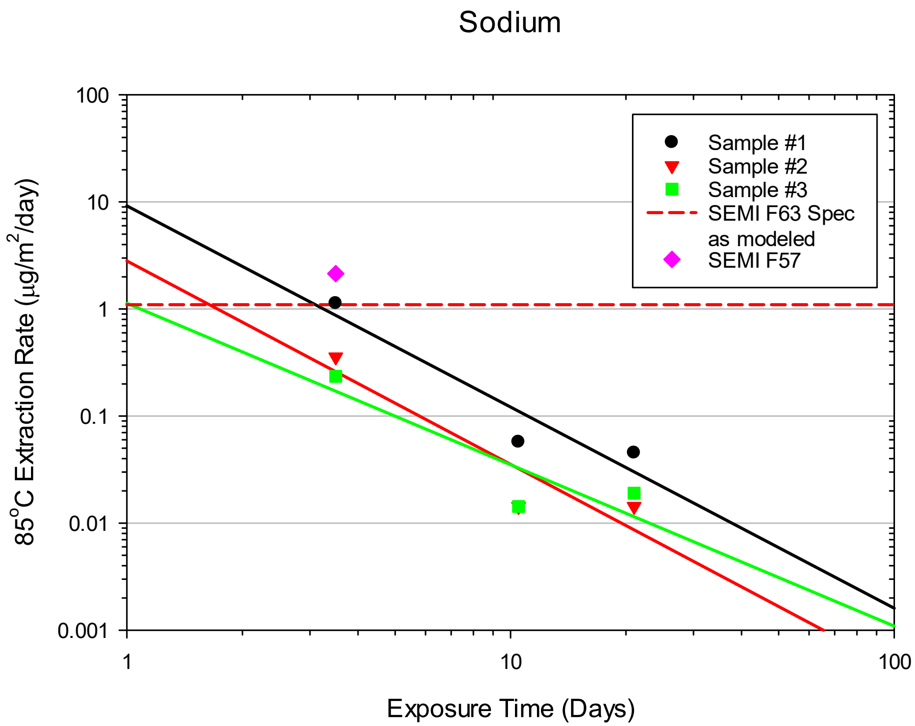
Contamination Mass Balance: In – Out (Usage + Return) + Makeup – Consumption = 0

Δ Concentration = Pipe Length (m) x Pi x Diameter (m) x Extraction rate (mg/m^2/Day) / Flow Rate (Liters/Day)

Test Results

PVDF at 85^{o}C UPW





Examples of extraction results with good alignment between SEMI F57, SEMI F63 and material performance

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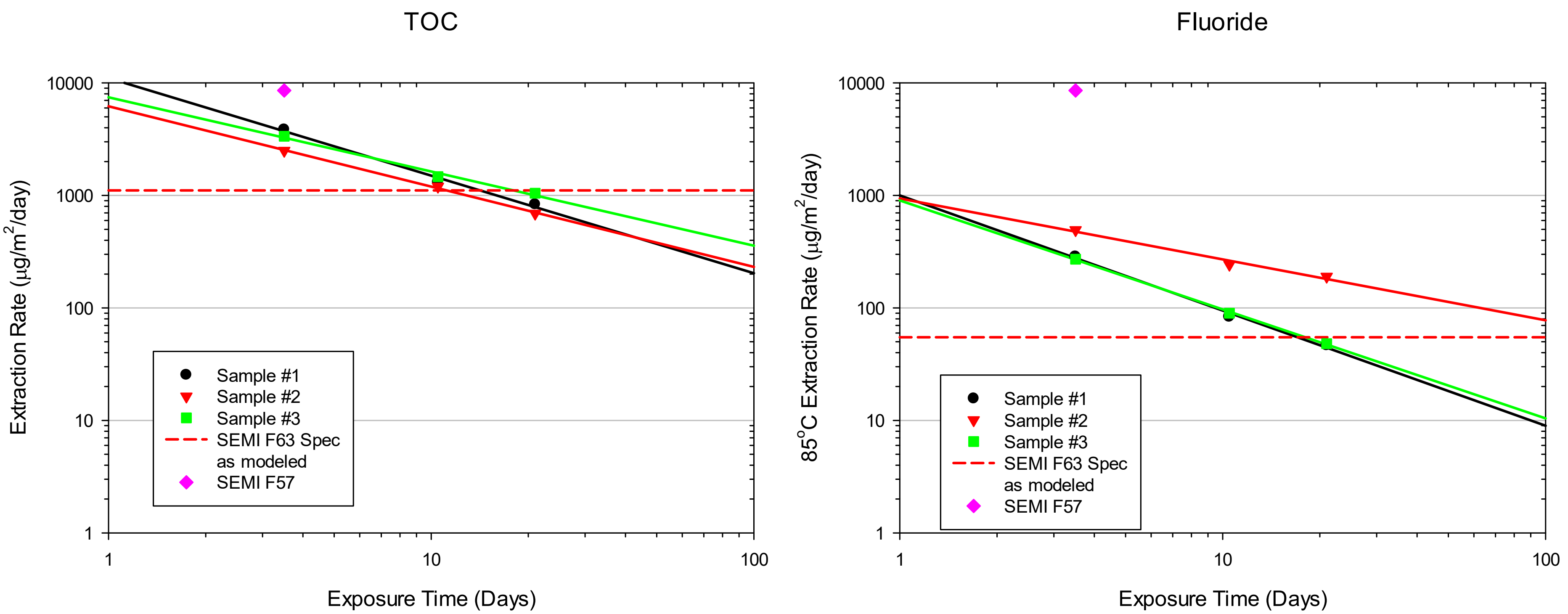
PVDF at 85°C UPW



Examples of extraction results without alignment between SEMI F57, SEMI F63 and material performance

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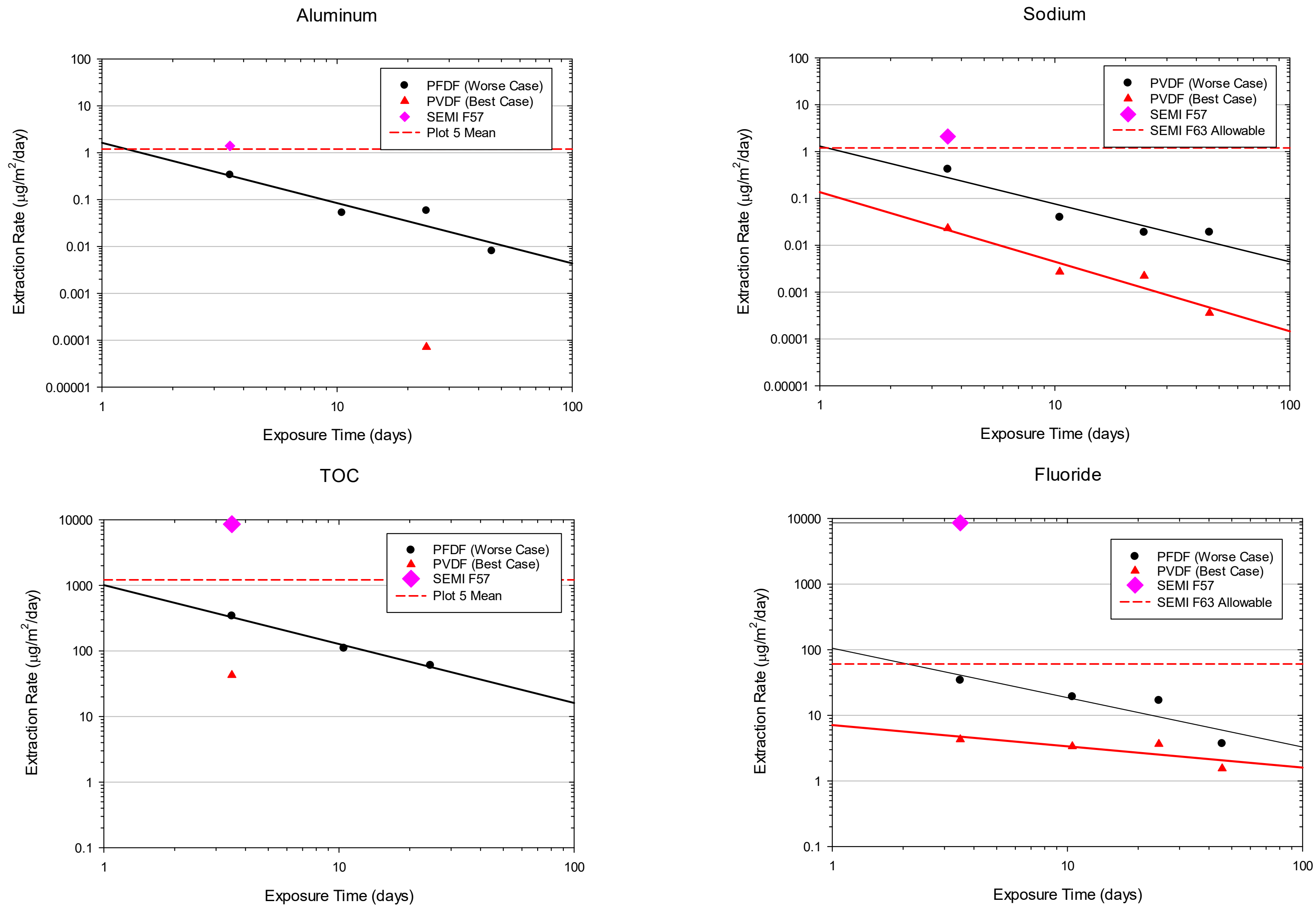
PVDF in Ambient UPW



Contributed contamination, based on all PVDF materials tested at room temperature, are predicted to be lower than the guidelines established in the current version of SEMI F63.

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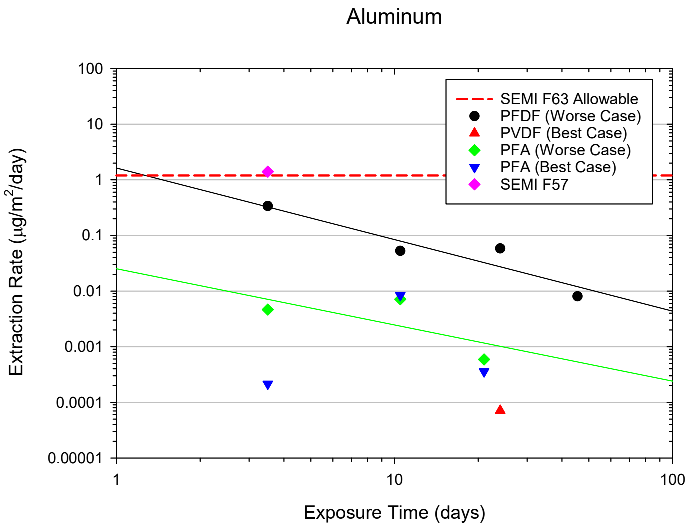
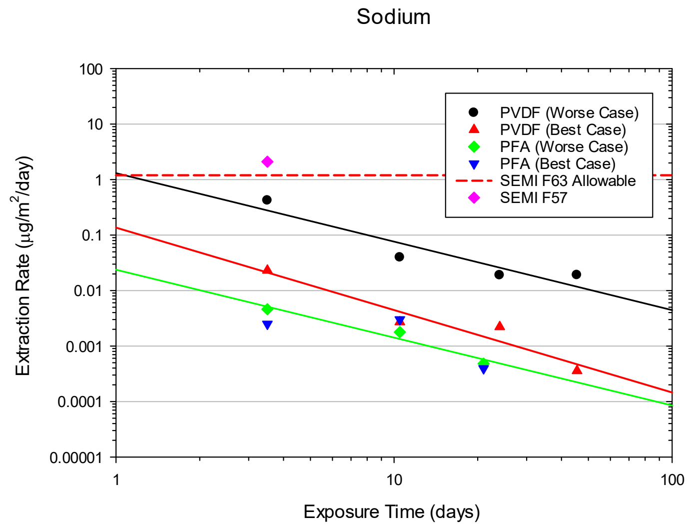
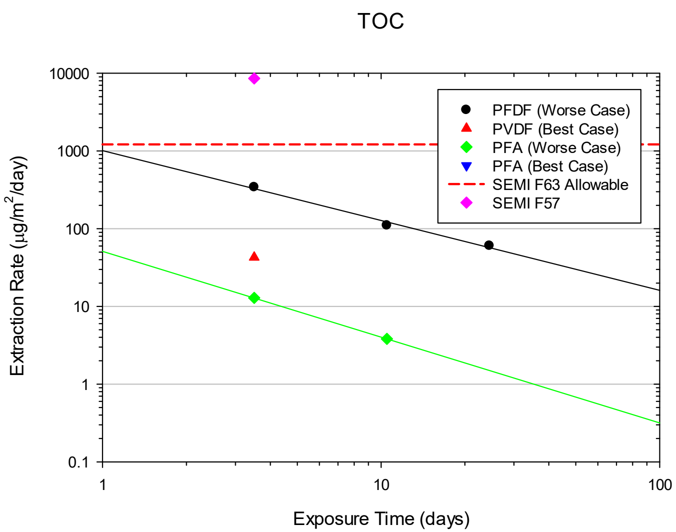
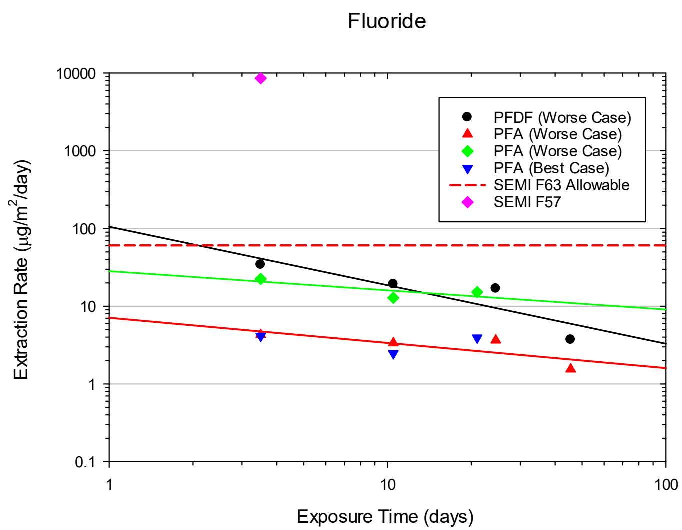
PFA at Room Temperature









PFA consistently had lower extraction rates at RT than PFDF for all measured contaminates except boron which was slightly higher but well below the specifications.

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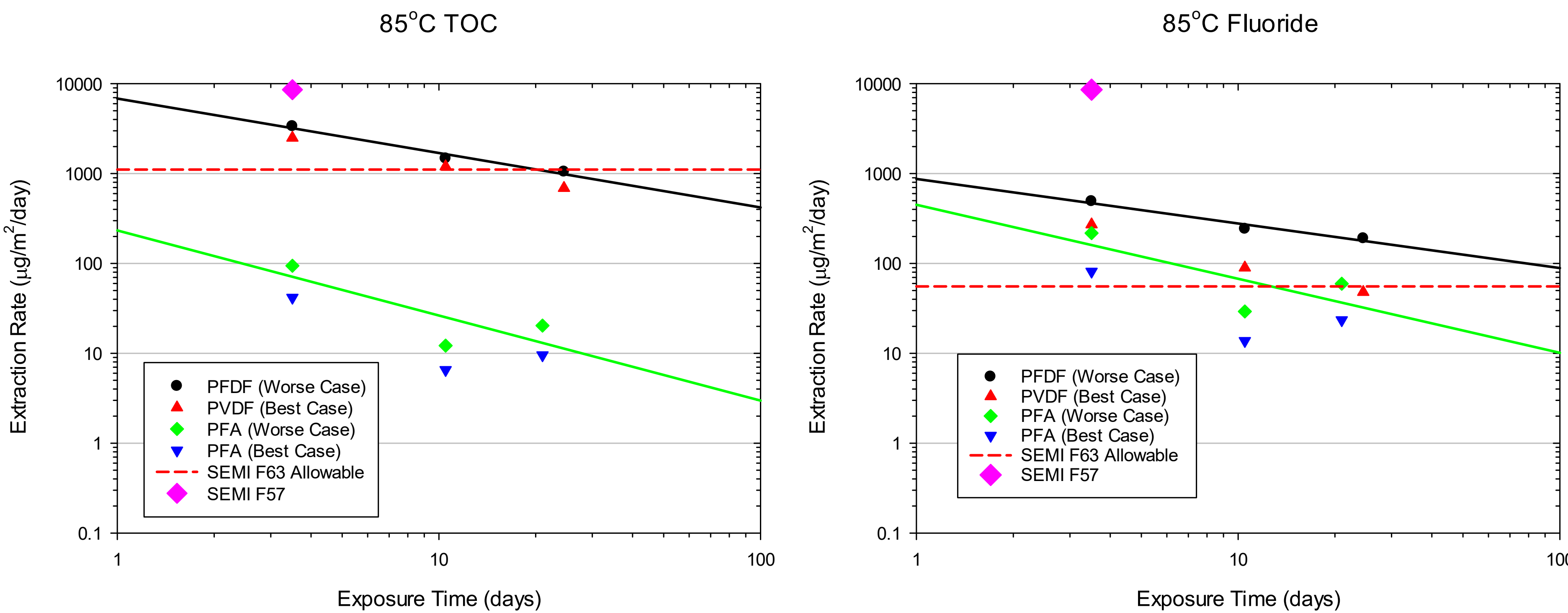
PFA vs PVDF at 85°C



- PFA consistently had lower extraction rates at 85°C than PFDF for all measured contaminates except nitrite which was slightly higher but well below the specifications.

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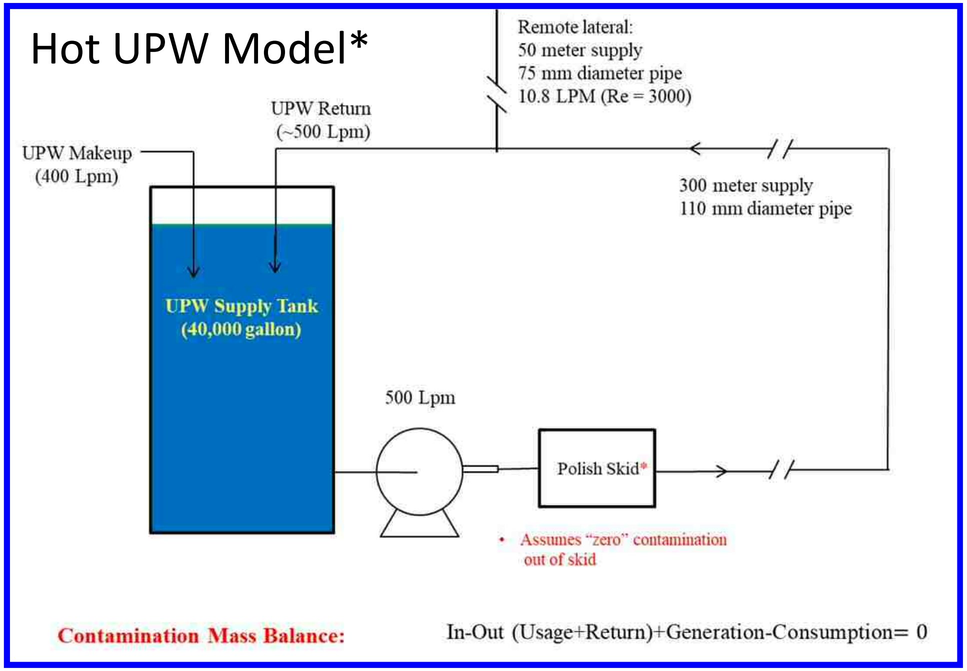
SEMI F57/SEMI F63 Alignment – Hot UPW

SEMI F63 Limits		F63 Limits Based on Extraction Model	SEMI F57 Rqrts as Extraction Rate
Constituent	limit (ppt)	Extraction Rate Allowable (µg/meter^2/day)	Extraction Rate Allowable (µg/meter^2/day)
Ions			
Ammonium	<50	55.5	-
Bromide	<50	55.5	14
Chloride	<50	55.5	429
Fluoride	<50	55.5	8,571
Nitrate	<50	55.5	14
Nitrite	<50	55.5	14
Phosphate	<20	22.2	43
Sulfate	<50	55.5	43
Metals			
Aluminum	<1	1.1	1.4
Antimony	<10	11.1	-
Arsenic	<10	11.1	-
Barium	<10	11.1	2.1
Boron	<50	55.5	4.3
Cadmium	<10	11.1	
Calcium	<1	1.1	2.9
Chromium	<1	1.1	0.1
Copper	<1	1.1	2.1
Iron	<1	1.1	0.7
Lead	<10	11.1	0.1
Lithium	<1	1.1	0.3
Magnesium	<1	1.1	0.7
Manganese	<10	11.1	0.7
Nickel	<10	11.1	0.1
Potassium	<1	1.1	2.1
Sodium	<1	1.1	2.1
Strontium			0.1
Tin	<10	11.1	-
Titanium	<1	1.1	-
Vanadium	<10	11.1	-
Zinc	<1	1.1	1.4
On-line TOC (ppt)	<1000	1,109	8,571

Hot UPW Model*



*Hot UPW model is slightly more challenging than the ambient model and is being used in the alignment analysis.

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SEMI F57/SEMI F63 Alignment – Hot UPW

SEMI F63 Limits		F63 Limits Based on Extraction Model	SEMI F57 Rqrts as Extraction Rate
Constituent	limit (ppt)	Extraction Rate Allowable (µg/meter^2/day)	Extraction Rate Allowable (µg/meter^2/day)
Ions			
Ammonium	<50	55.5	-
Bromide	<50	55.5	14
Chloride	<50	55.5	429
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Phosphate	<20	22.2	43
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Nickel	<10	11.1	0.1
Potassium	<1	1.1	2.1
Sodium	<1	1.1	2.1
Strontium			0.1
Tin	<10	11.1	-
Titanium	<1	1.1	-
Vanadium	<10	11.1	-
Zinc	<1	1.1	1.4
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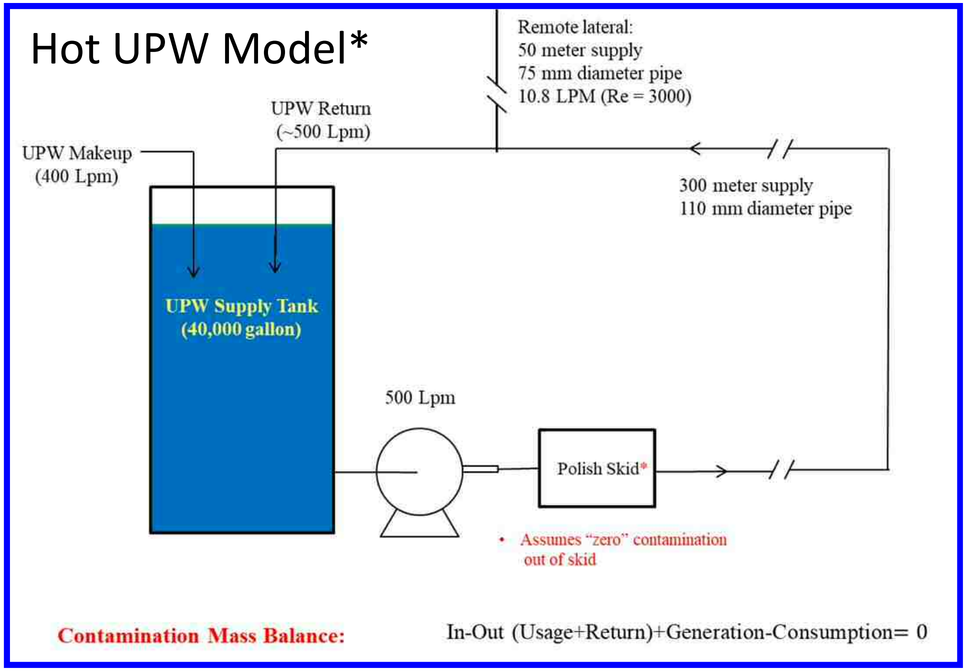

No alignment required, materials are compliant
No SEMI F57 Spec
No SEMI F63 Limit
Alignment required, materials are compliant
Alignment required, materials may be non-compliant

*Hot UPW model is slightly more challenging than ambient models and is being used in the alignment analysis.

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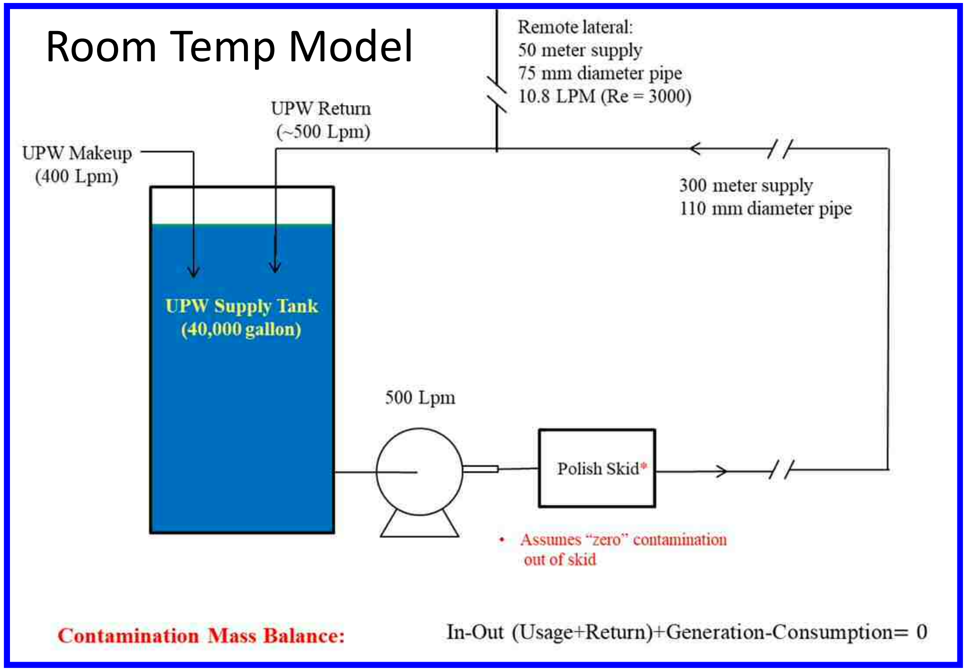
SEMI F57/SEMI F63 Alignment – RT UPW

SEMI F63 Limits		F63 Limits Based on Extraction Model	SEMI F57 Rqrts as Extraction Rate
Constituent	limit (ppt)	Extraction Rate Allowable (µg/meter^2/day)	Extraction Rate Allowable (µg/meter^2/day)
Ions			
Ammonium	<50	55.5	-
Bromide	<50	55.5	14
Chloride	<50	55.5	429
Fluoride	<50	55.5	8,571
Nitrate	<50	55.5	14
Nitrite	<50	55.5	14
Phosphate	<20	22.2	43
Sulfate	<50	55.5	43
Metals			
Aluminum	<1	1.1	1.4
Antimony	<10	11.1	-
Arsenic	<10	11.1	-
Barium	<10	11.1	2.1
Boron	<50	55.5	4.3
Cadmium	<10	11.1	
Calcium	<1	1.1	2.9
Chromium	<1	1.1	0.1
Copper	<1	1.1	2.1
Iron	<1	1.1	0.7
Lead	<10	11.1	0.1
Lithium	<1	1.1	0.3
Magnesium	<1	1.1	0.7
Manganese	<10	11.1	0.7
Nickel	<10	11.1	0.1
Potassium	<1	1.1	2.1
Sodium	<1	1.1	2.1
Strontium			0.1
Tin	<10	11.1	-
Titanium	<1	1.1	-
Vanadium	<10	11.1	-
Zinc	<1	1.1	1.4
On-line TOC (ppt)	<1000	1,109	8,571



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Observations and Summary

- Experimental data and modeling predicts that the current PVDF and PFA tubing and piping materials will contribute levels of trace metal, ionic and TOC contamination that are lower than the limits established in SEMI F63 at room temperature.
- PFA consistently had lower extraction rates at RT and 85^{o}C than PFDF for all measured contaminates except boron at RT and nitrite at 85^{o}C.
- At 85^{o}C, all the PVDF materials initially had a higher level of TOC and fluoride extraction than recommended by SEMI F63.
- At 85oC, all the PFA material initially had higher level of fluoride extraction than recommended by SEMI F63.
- Within 60 days of exposure, all material tested at 85^{o}C (except one for TOC) had a level of TOC and fluoride extraction below that recommended by SEMI F63.

Thank you for your attention!