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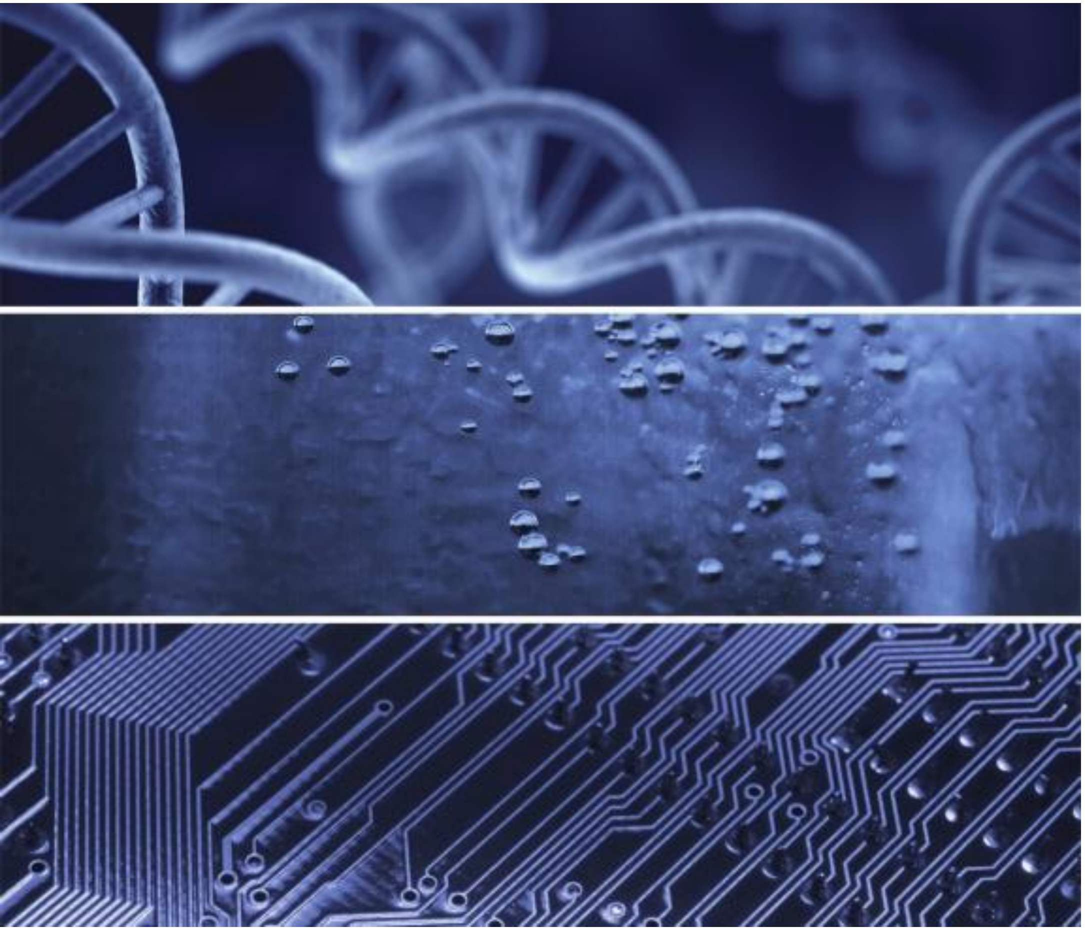

Advanced Contamination Control using Novel Polyarylsulfone Membrane Technology

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Archita Sengupta, *Intel Corporation*
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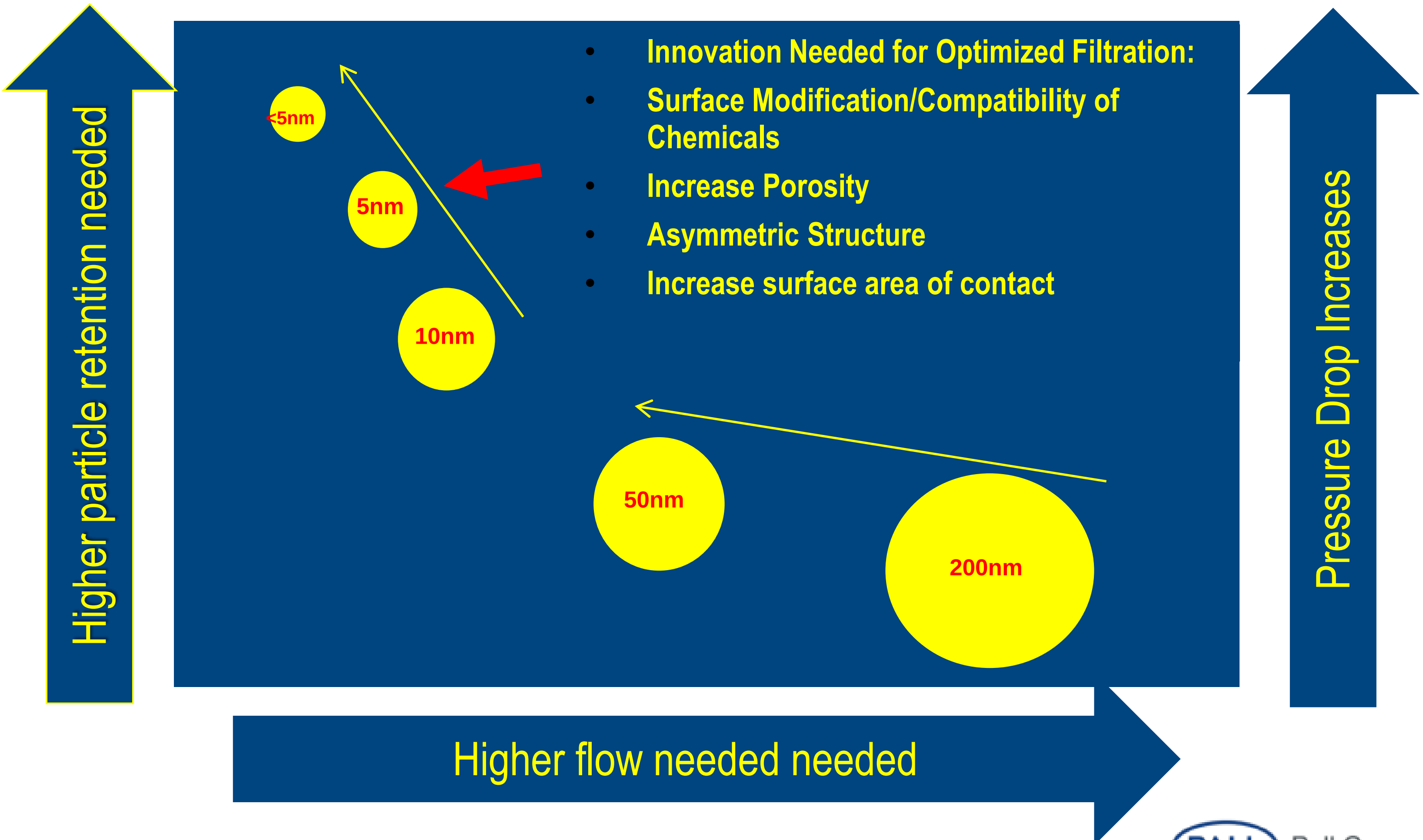
Outline

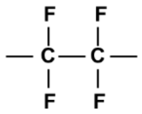
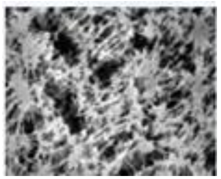
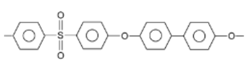
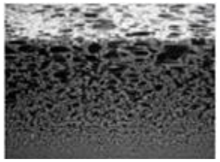
- Background
- Development of Evaluation Program
- Test Program and Results
- Supporting Fab Application Results
- Assessment of Results and Conclusions
- Next Steps
- Acknowledgments

Background: Rationale for Study

- Filtration must keep up with “Paradigm Shift” in Defect Tolerance for Next generation Technology Nodes
- Customized Filtration is needed to Aggressive Chemistry/Processes
- Innovation needed for <=5nm Metals/Particles/Organics/NVR removal for next generation need



Core Membrane Properties: PTFE and HAPAS

PTFE vs HAPS comparison		
	PROS	**CONS**
$(CF_2 - CF_2)_n$  **PTFE (PFOA free)** 	**Chemically most inert**	**High unit cost**
	High Temperature Resistance (185°C)	**Most expensive surface modification**
	High Purity	**High temperature aggressive service requires special package design**
	Primary retention by surface size exclusion	**Minimal depth capture, surface loading only**
	Long term stability	**Typically low flux rates**
	Available semi-phobic	**Completely to semi-phobic**
	Aggressive chemistry application	**Disposability an isue in some countries**
$[O\text{-}Ø\text{-}C(CH_3)_2\text{-}Ø\text{-}O\text{-}Ø\text{-}SO_2\text{-}Ø]_n$  **HAPAS Highly Asymmetric Polyarylsulfone** 	**Good chemical resistance in aqueous chemistries pH 1 -14**	**Limited solvent and conc acid, oxidizer resistance**
	Dual retention mechanisms: mechanical sieve final filter with integral tortuous path prefilter	**Packaging material may limit thermal or long term chemical resistance**
	Highest flux rate	
	Better Cost of Ownership as alternative for non-aggressive chemistry	
	High surface energy w/o surface modification – helps wetting of medium	
	Good temperature resistance (90°C)	
	High dirt holding capacity	

- The present study was undertaken to explore the suitability of a filter employing **highly asymmetric polyarylsulfone** ("HAPAS") medium with other components of high density polyethylene (HDPE) in a variety of aggressive acids, bases, and blends
    - The 5 nm rated Pall Ultipleat® SP DR product was the model chosen for evaluation

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Considering HAPAS vs. PTFE for Critical Filtration

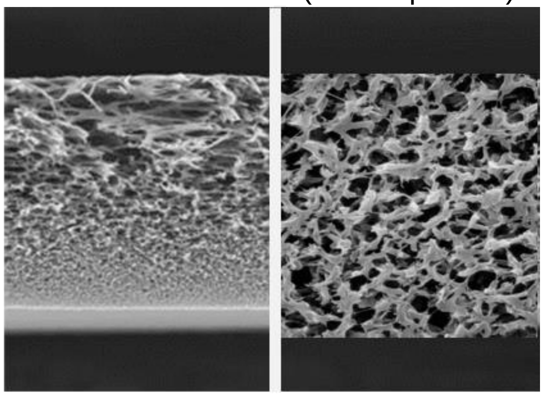
- The results show that a next-generation filter containing HAPAS medium has applicability in a wide variety of dilute and aggressive chemicals
  - But how does it compare to an all-perfluoropolymeric filter? The table below considers various characteristics:

Property	HAPAS	PTFE
Finest available rating	2 nm	5 nm
Flow, psid/GPM-10" equiv.	0.7	0.75 - 1.0
Unit Cost	X	3X - 7X
Compatibility	Acceptable for a wide range of chemicals, up to 70ºC	Acceptable across most chemicals, up to 185ºC

- **The Ultipleat SP DR product employing HAPAS medium provides a suitable alternative on the basis of several characteristics**

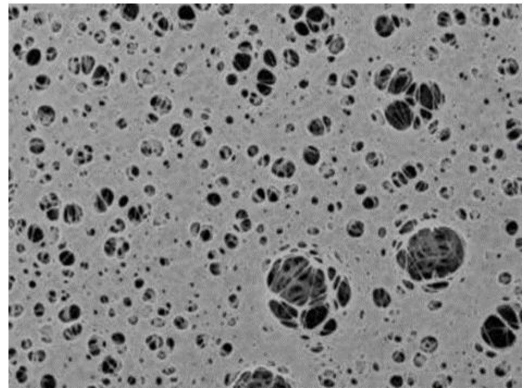
Advantages of Highly Asymmetric Polyarylsulfone ("HAPAS") Filtration Medium

Asymmetric | Isotropic (for comparison)

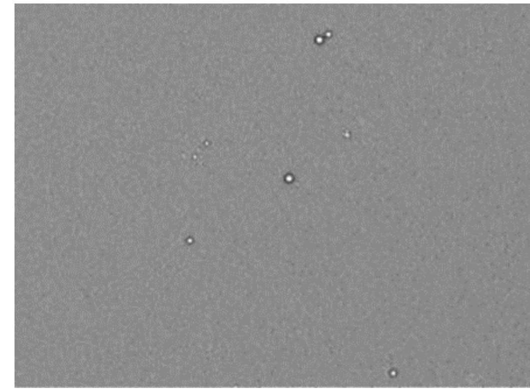


Cross-section – upstream at top

Medium available as fine as 2 nm (5 nm shown)

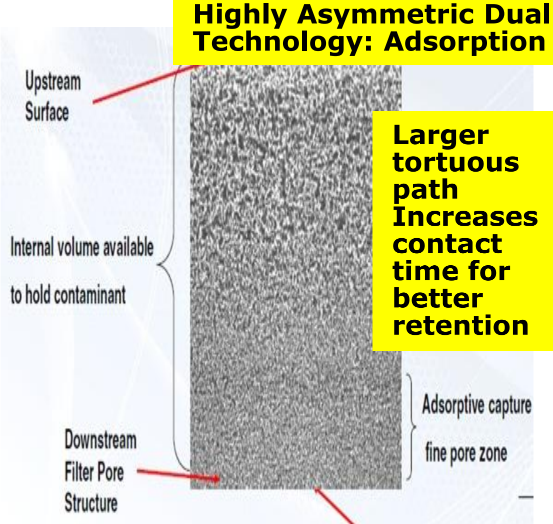


Large pore face – upstream



Fine pore face – downstream

Highly Asymmetric Dual Retention Technology: Adsorption and Sieving



Larger tortuous path Increases contact time for better retention

Depth filtration with in-built pre-filter Narrow pore distribution at final layer capture particles by size exclusion

- Longer on-stream life: Higher Voids Volume for greater dirt holding capacity
- Highly asymmetric structure: Improved pressure drop characteristics compared to isotropic membranes
- While provided in prewet fashion: possesses relatively high critical wetting surface tension
  - Diminishes dewetting potential in aqueous application
- Superior Flow Rates w/ lower pressure drops
  - High bath turnover rate for rapid particle removal

Planned Program of Study

1. Identify suitable chemistries and conditions to use
2. Develop testing program for flat sheet materials
3. Conduct soaks with periodic sample removal for evaluation
4. Assess flat sheet data to better define device testing
5. Develop test program for devices
6. Conduct soaks or flow tests with periodic sample removal for evaluation
7. Testing in actual application environment with collection of performance data
8. Assess and interpret all data to develop conclusions on compatibility

Targeting Candidate Chemistries and Conditions to Use

Chemical / Chemistry	Reason for Interest	Conditions
Hydrogen Peroxide (H_2O_2)	Occurs widely in cleaning, etching, and stripping chemistries	5% - 30%, room temperature (R.T.)
Tetramethylammonium hydroxide (“TMAH”)	Widely used in cleaning, etching, and PR developer chemistries	2% - 25%, R.T.
Hydrofluoric Acid (HF)	Widely used in cleaning and etching, sometimes at high conc.	49%, R.T.
Isopropanol (“IPA”)	Frequent use in drying; model of organic content	100%, R.T and 70°C
SC1, SC2 (ammonia or HCl + H_2O_2 + H_2O)	Aggressive blends, often used at elevated temperatures	SC1: 1:1:5; SC2: 1:5:10, R.T. (sheet), 60°C (device)
Hydrochloric Acid (HCl)	Strong acid model; used in blends	10% - 37%, R.T.
DI Water	Cleaning agent	100%, 70°C
Proprietary Blends	Used for BEOL cleaning / stripping; indicator for organics	Specialized

Suitable Test Methods for Flat Sheet Materials

- Samples of HAPAS medium were produced in coupon and disk forms; samples of HDPE support material were produced as coupons

- Collections of disks and coupons were immersed in various chemicals selected
  - Sealed in vessel and subjected to elevated temperature, where applicable

- Samples removed periodically and subjected to physical and chemical testing
  - Tensile measurements of coupons via Dynamic Mechanical Analyzer (“DMA”)
  - Flow rate measurement, using water, at defined ΔP, for disks
  - FTIR spectra of coupons obtained

- Where applicable and suitable, HAPAS medium exhibiting retention of other properties subjected to 5 nm gold nanoparticle (“GNP”) retention testing
  - Generally restricted to fresh HAPAS and longer duration soaks

Summary of Tensile, Flow, and IR Spectroscopic Test Results For Flat Sheet Materials—Three Month Exposure

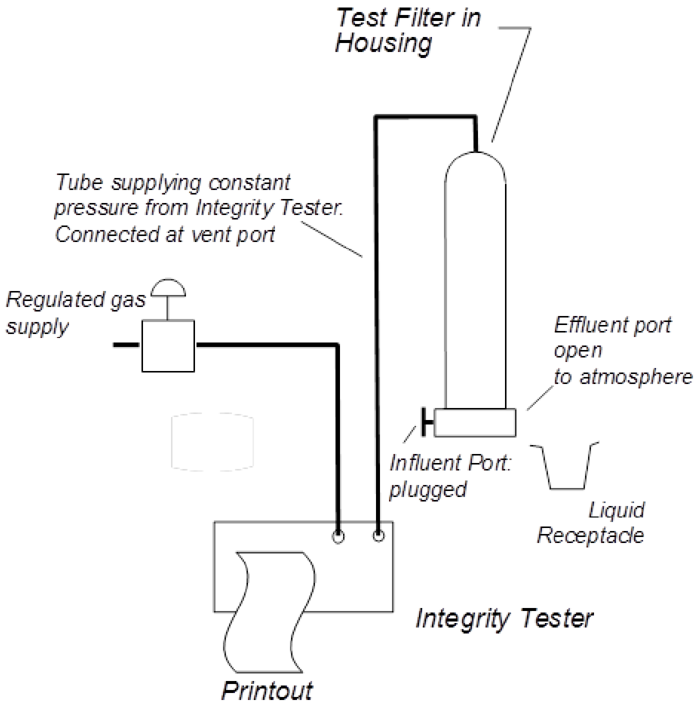
Media 5 nm HAPAS							S/D layer	
Chemical	Conc	temp	Water flow	Retention (LRV at 5 nm)	Mechanical Property (DMA)	Chemical Composition (FTIR)	Mechanical Property (DMA)	Chemical Composition (FTIR)
HCl	37%	20C	↔	↓	↔	↔	↔	↔
	20%		↔		↔	↔	↔	↔
	10%		↔	↔	↔	↔	↔	↔
H2O2	30%	20C	↑↑	↓↓	↔	↔	↔	↔
	20%		↑↑	↓↓	↔	↔	↔	↔
	10%		↑↑	↓↓	↔	↔	↔	↔
	5%		↑↑	↓↓	↔	↔	↔	↔
SC1	*	20C	↔	↔	↔	↔	↔	↔
*NH_4OH:H_2O_2:H20 – 1:1:5								
SC2	†	20C	↔	↔	↔	↔	↔	↔
†HCl:H_2O_2:H20 – 1:5:10								
IPA	100%	20C	↔	↔	↔	↔	↔	↔
IPA	100%	70C	↑	↓	↓	↔	↓	↔
HF	49%	20C	↔	↓	↔	↔	↔	↔
TMAH	25%	20C	↔	↔	↔	↔	↔	↔
	10%		↔	↔	↓	↔	↔	↔
	2%		↔	↔	↔	↔	↔	↔

↓↓ ↑↑	significant change	↓ ↑	slight change	↔	no significant change

Results suggest compatibility with most chemicals used

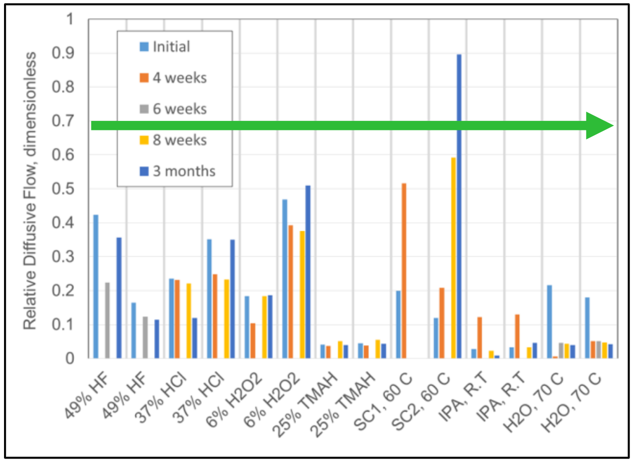
Assessment of Flat Sheet Results and Continuing on to Device Testing

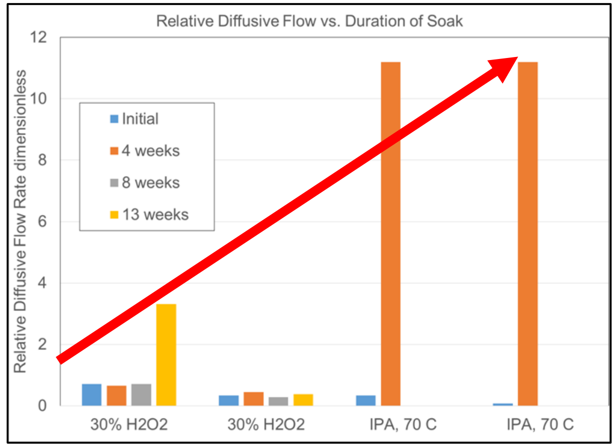
- The decision made to soak actual filters in the most concentrated version of chemical
  - Including 30% H_2O_2, essentially as a negative control
- Expansion of program to test in (1:1:5) SC1 and (1:5:10) SC2 at 60ºC with flow
- Evaluation plan:
  - Collect baseline data on filters
    - Non-destructive integrity test
    - ΔP vs. flow rate (using water)
    - Rinse test in water for particles
  - Soak filters for periods up to 3 months with periodic repeat of tests
  - Post-soak check of robustness via pulsation testing in water

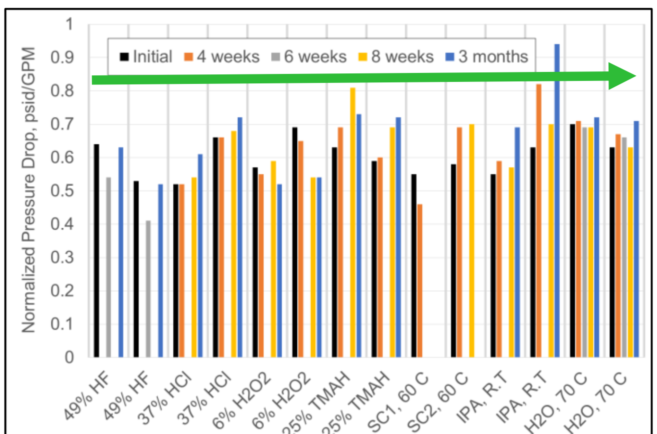


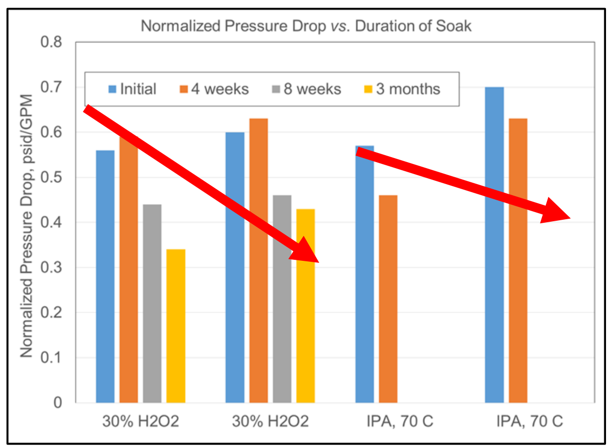
Schematic of Integrity Test Set-up

Integrity Test and Pressure Drop *vs.* Flow Rate with Respect to Time for Target Chemicals









Diffusive flow and pressure drop testing revealed the following:

- For most chemicals, parameter changes within acceptable limits
  - Suggests ***compatibility*** over soak time used
- **30% H_2O_2** sample shows integrity loss at 3 mo, and major drop in ΔP at 8 wk.
  - Some affect—***limited compatibility***
- Loss of integrity and ΔP drop at 4 wk for **70ºC IPA**
  - This suggests ***incompatibility***

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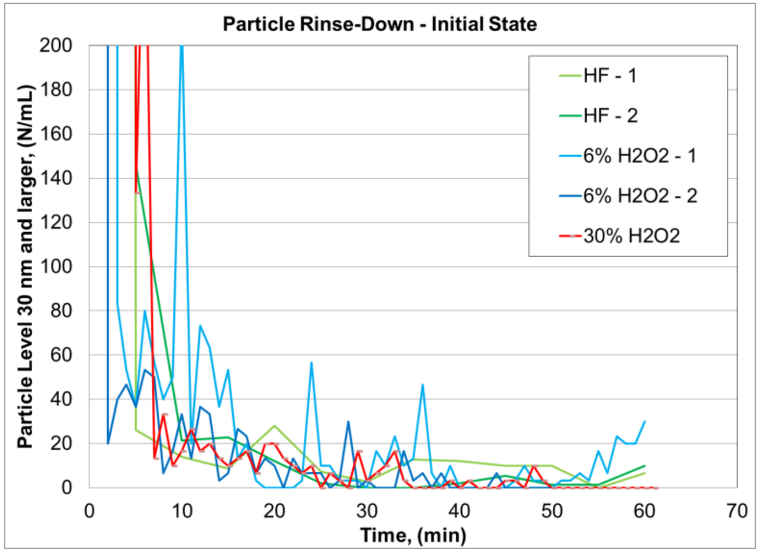
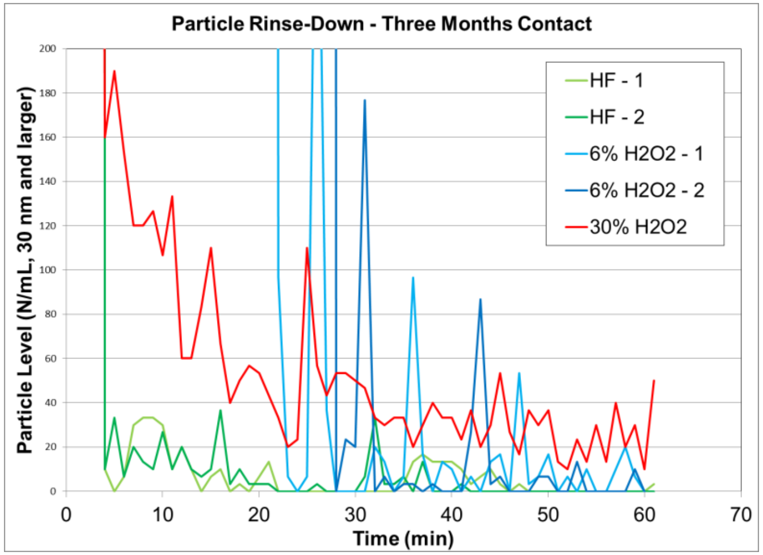
Comparative Initial and Post-Contact "Rinse-in" Results in DIW for Selected Cases

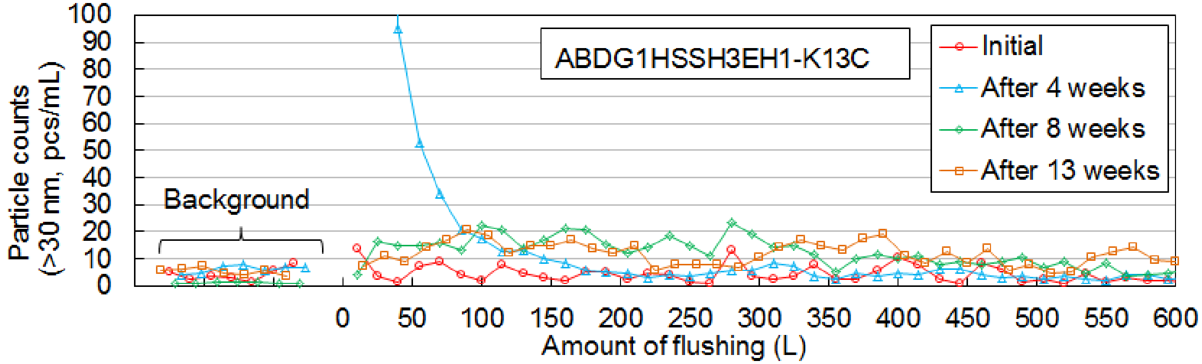


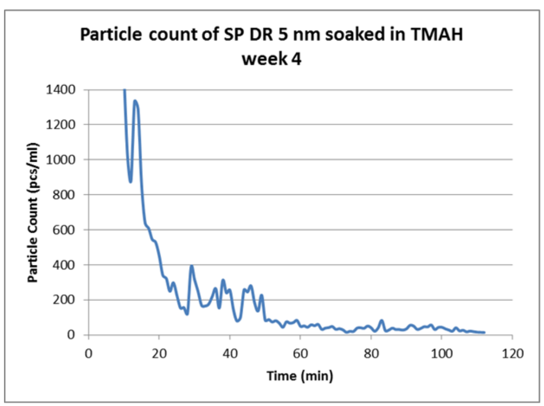


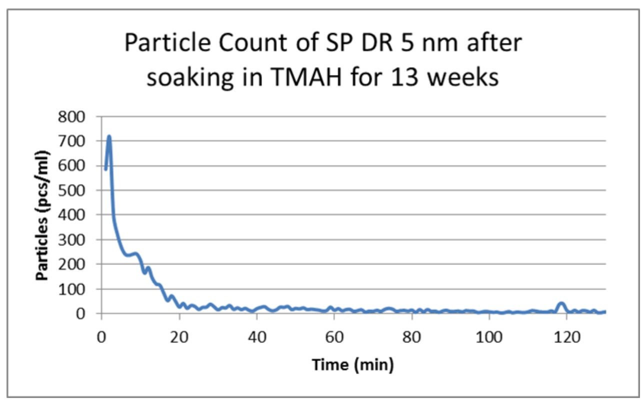
Particle rinse tests in water pre- and post-soak can be used to evaluate potential changes resulting from contact:

- Filters soaked in 49% HF and 6% H_2O_2 recover background levels
  - **Suggests minimal effect from long-term contact, and compatibility with these chemicals**
- By comparison, filter soaked in 30% H_2O_2 exhibits relatively high level after 60 minute rinse
  - **Suggests limited compatibility**

Comparative Initial and Post-Contact “Rinse-in” Results in DIW for Selected Cases, *cont.*



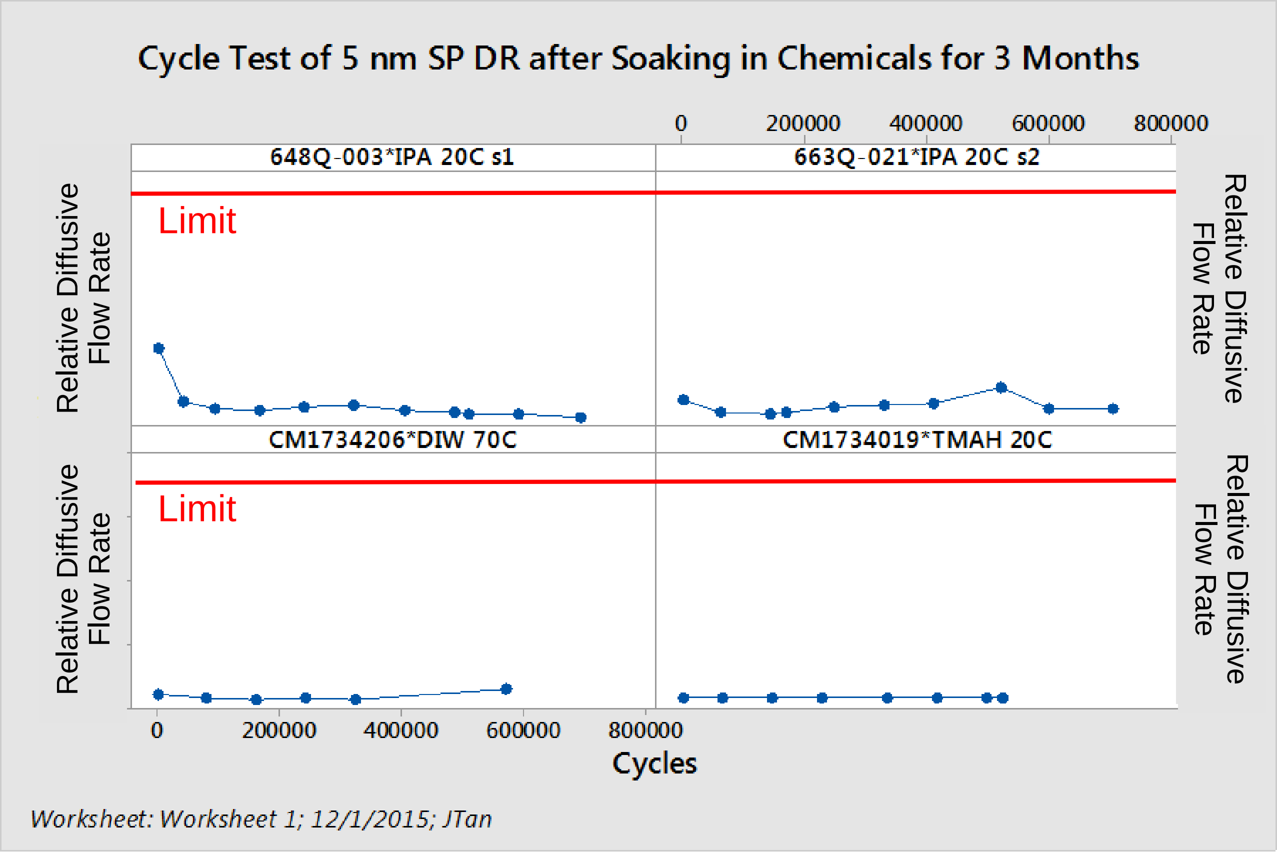




- Filter contacted with flowing **SC2** (1:5:10) at 60ºC exhibits **minimal change in transient particles over time**
- Filter soaked in **TMAH** appears to **achieve low particle level *quicker* after longer soak duration**

Results confirm absence of degradation of the filter in these chemistries and confirm compatibility

Durability Tests on IPA (20ºC) and TMAH Soaked Filters



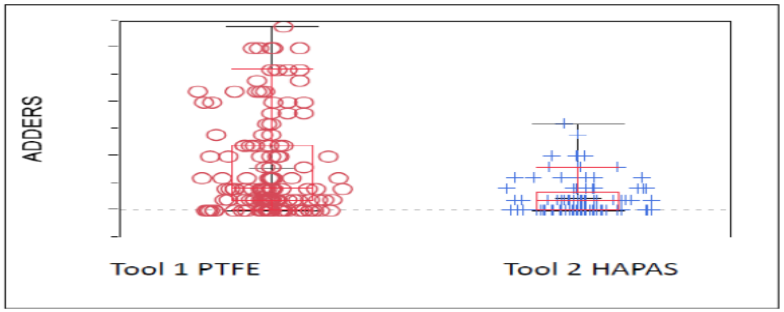
This test provides supplemental information on post-soak filter behavior by subjecting them to additional, cyclic stress

- ***Stressed filters show no loss of integrity even after over 500k cycles, further confirming compatibility in R.T. IPA and 25% TMAH***

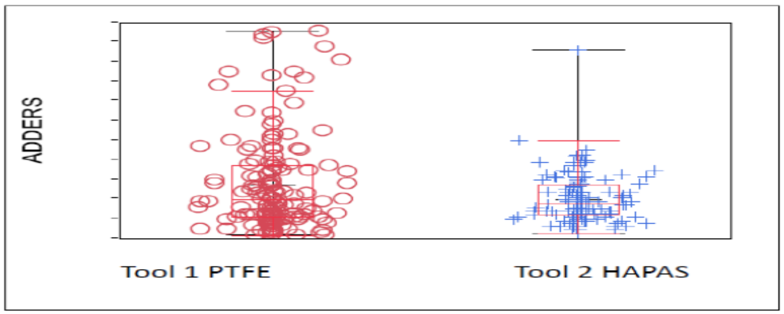
Side by Side Comparison of PTFE vs HAPAS performance

First 30 days Defect monitor data at IDM Advance technology Node WE tools

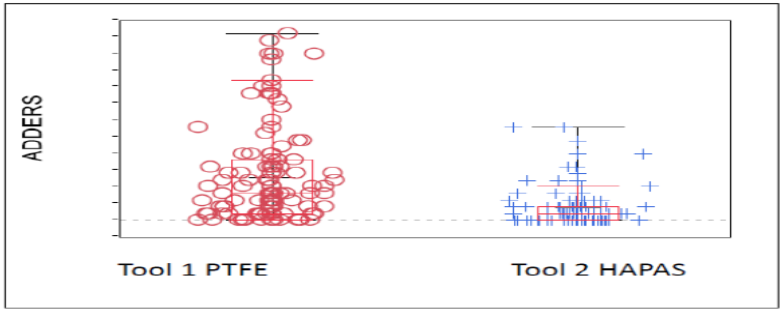
TOTAL_ADDERS: Chemistry A:
PTFE vs HAPAS



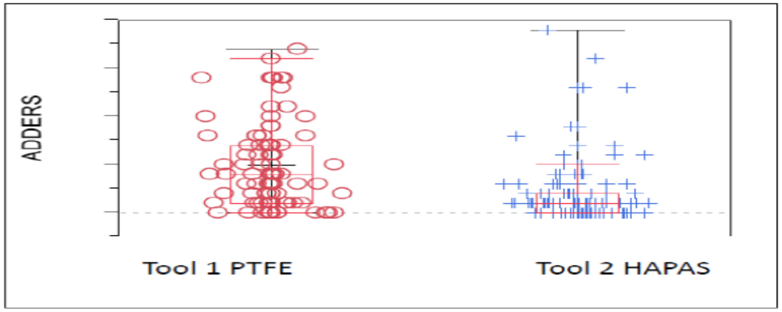
TOTAL_ADDERS: Chemistry B:
PTFE vs HAPAS



TOTAL_ADDERS: Chemistry C:
PTFE vs HAPAS



TOTAL_ADDERS: Chemistry D:
PTFE vs HAPAS



Data Reference: Ryan Mackiewicz, Intel Corporation.

Assessment of Results and Conclusions

- Test program was effective in showing differences in behavior of both components and complete filters tested in various chemicals
  - Flat sheet tests were useful for guiding device testing
- Test Results show that the Ultipleat SP DR product with HAPAS medium can be applied in a variety of WEC chemicals, including concentrated versions of TMAH, HF, and HCl, dilute H_2O_2, and IPA at room temperature, and SC1 and SC2 at 60ºC
  - The product exhibited incompatibility with 30% H_2O_2, and with IPA at 70ºC
- Lab test results are supplemented by real time field qualification data on advanced technology node tools showing value of employing the HAPAS product in actual WEC application .

Overall, we find that a filter product containing HAPAS medium indeed provides a very useful technically viable and lower cost-of-ownership alternative to all-perfluoropolymeric filters for a wide range of applications

Next Steps

- Expansion of program to broader array of specialty chemicals and conditions
  - Especially to include more blends, including organics
  - Extension to higher temperatures
- “Fine-tuning” of testing
  - Exploration of additional evaluation methodologies
  - Shorter duration-increased interval testing for certain chemicals
- Incorporation of more flow-based tests

Acknowledgements

- PALL: Thank you so much to Ibrahim Mohamed-Ali, Mai Nguyen, Kei Lau, and Pauline Adejo of the Port Washington team, Virgil Briggs, Mike Gofkowski, Shawn Hubbard, Yi Wang, Valerie Pritchard, John Tomancik, and Dick Stoyell of the Cortland team, and Shusaku Daikoku, Mitsutoshi Nakagawa, Tomoyuki Takakura, and Shuichi Tsuzuki of the Tsukuba team for all the extensive lab work and additional assistance provided during the project
- Intel: Thank you so much to Ryan Mackiewicz And Ameya Bapat for providing field data

Thank you for listening! ☺