SAND2016-5870C

Exceptional service in the national interest

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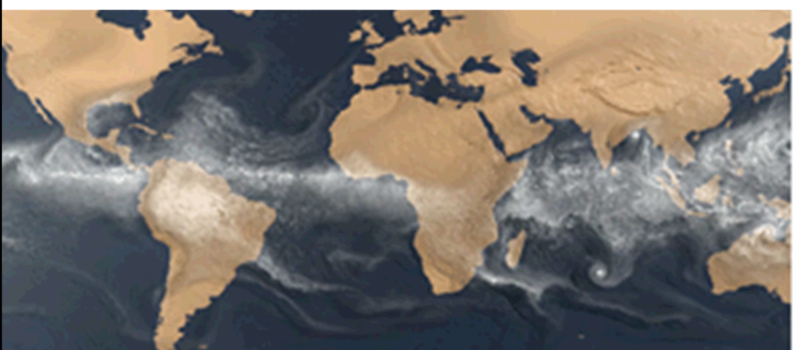

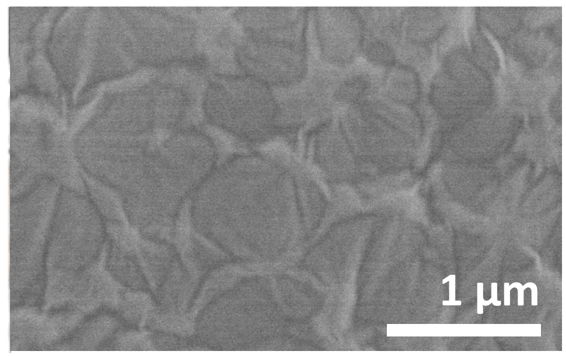

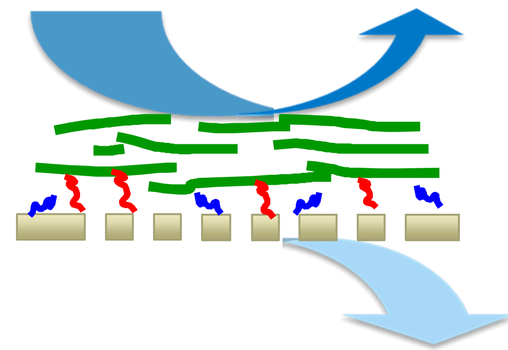

GO desalination membranes

Laura Biedermann, lbieder@sandia.gov

Michael Hibbs, Mike Hightower, Curt Mowry, Trey Pinon, Craig Stewart and Kevin Zavadil

U.S. DEPARTMENT OF ENERGY   NNSA National Nuclear Security Administration

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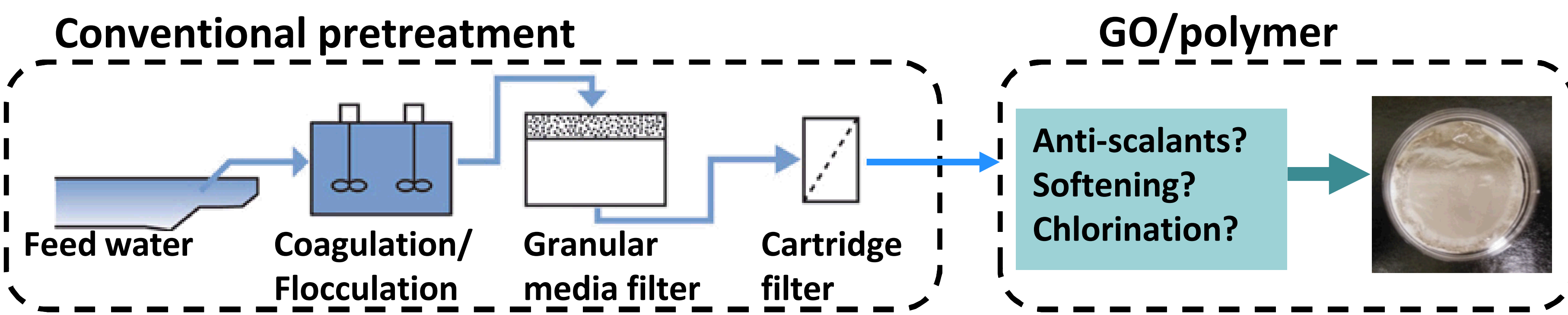
Outline

Sandia's interest in desalination technologies

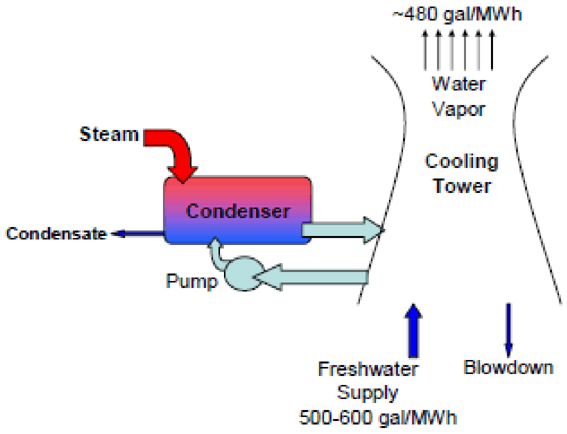

Design and performance of GO/polymer composite membranes

- Robust and scalable membrane assembly
- Pressure-dependent rejection with simple salt solutions
- Minimal fouling when recycling Redhawk cooling water



Desalination is critical for energy security

Power plants



Water challenges: Energy use, permeance

- Keep divalent ion loads <100 mg/L
- Minimize biofouling with low-level chlorination

Goals

- Increase cooling water cycles of concentration
- Diversify water supplies (brackish, waste water,…)

Hydraulic fracturing

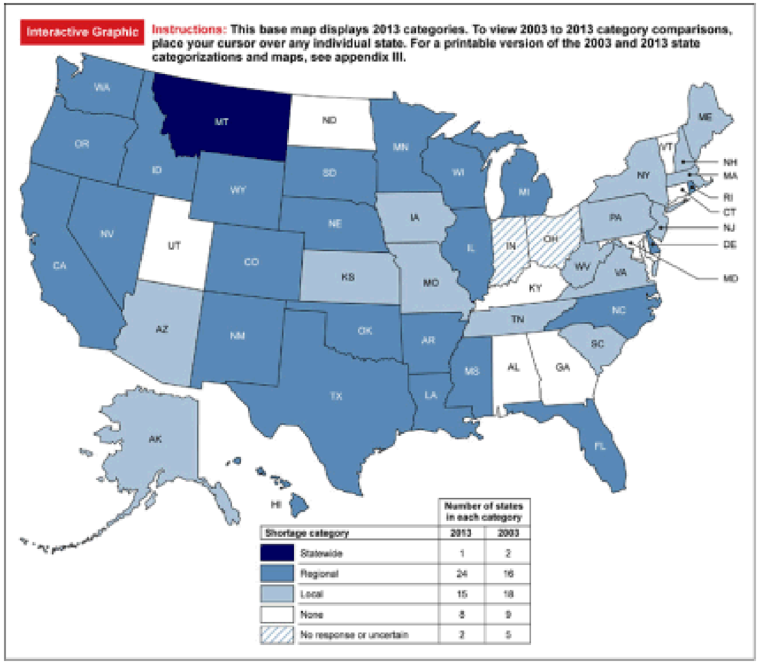
Water challenges: Energy use, recovery, robustness

- Diverse water chemistries: TDS 1000-400,000 mg/L, oil up to 2 g/L, biocides, foaming agents

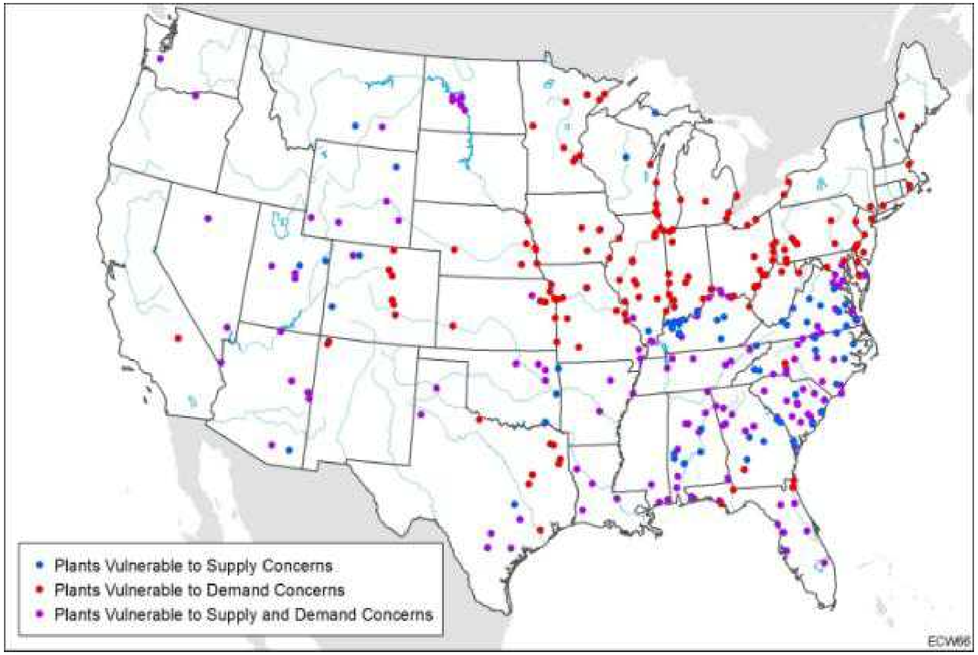
Goals

- High recovery to reduce environmental/disposal cost
- Recycle produced water for productive reuse

Water Stress Impacts on U.S. Electric Power



Sources: GAO analysis of state water managers' responses to GAO survey; Map Resources (map).



2013 State Water Stress

Coal Power Plants Vulnerable to Water Supply Stress and Water Competition

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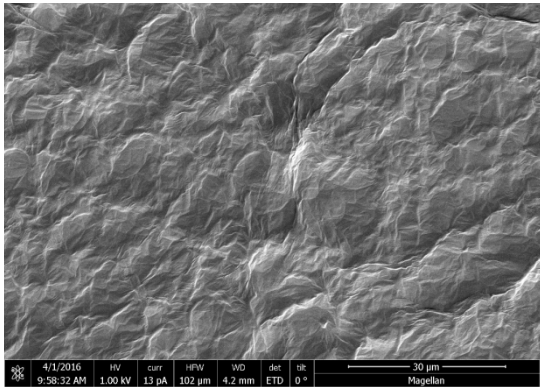
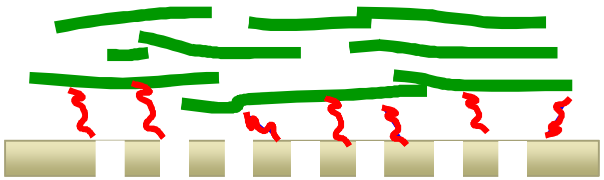




Next steps to improve performance

Conclusions

Graphene and graphene-oxide are related robust nanosheet materials

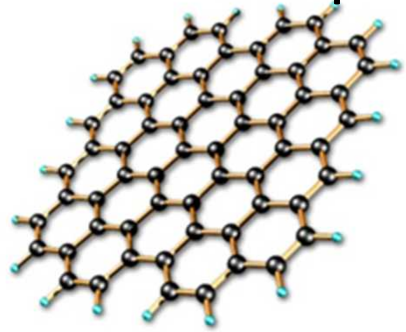
Natural graphite

Mechanical exfoliation

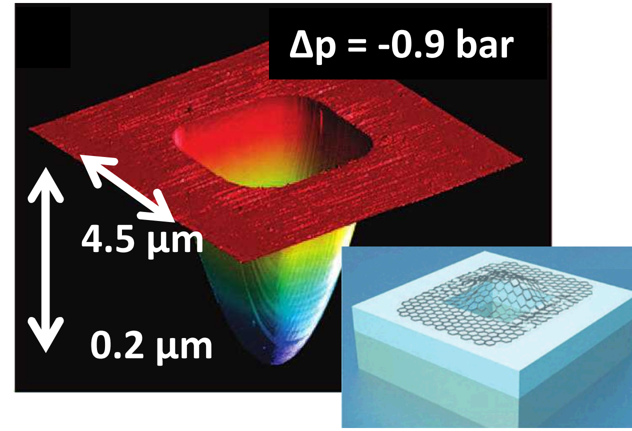
Chemical oxidation

Graphene

Hexagonal carbon network forms the basal plane

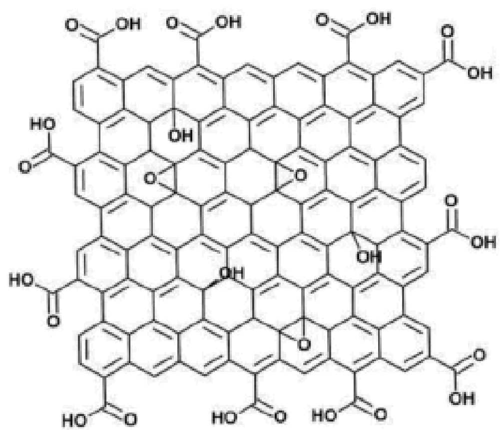


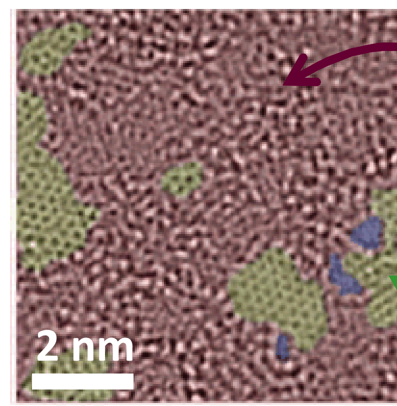
A pristine graphene membrane is impervious to gasses



Graphene Oxide (GO)

oxygen functional groups decorate the basal plane





oxidized domains

graphitic domains

Two proposed structures for graphene-based desalination membranes

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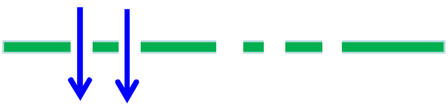
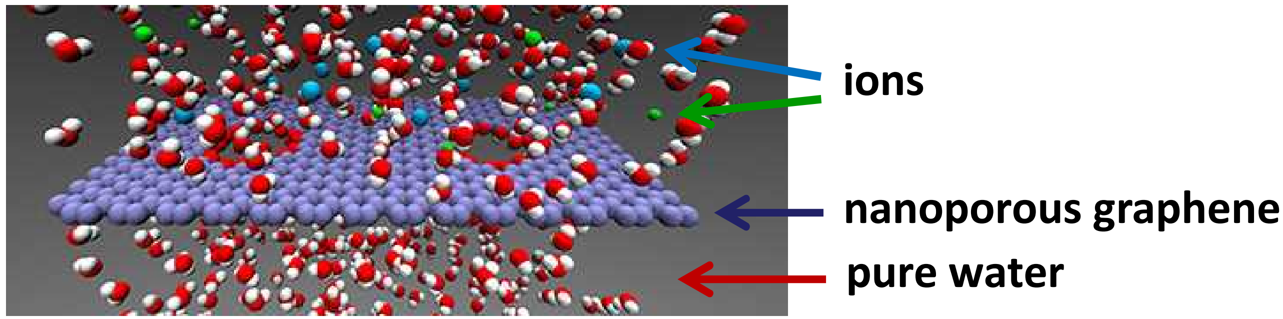
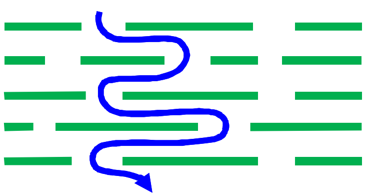
Permeation through nanoporous monolayer graphene



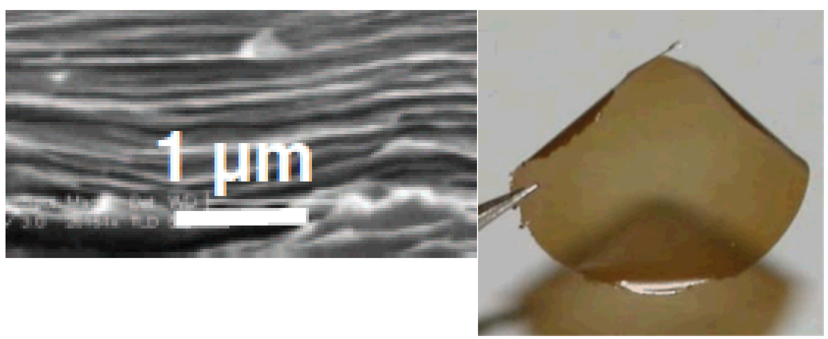
[1]



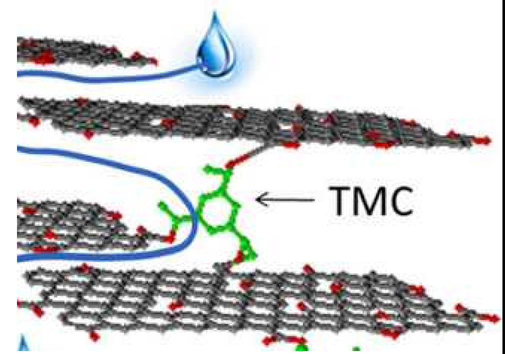
Permeation around GO sheets in laminar GO membranes



[2]



[3]

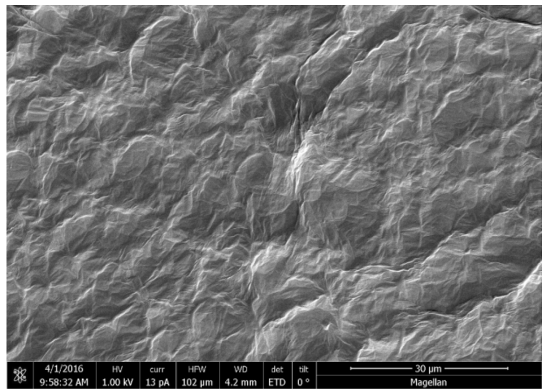


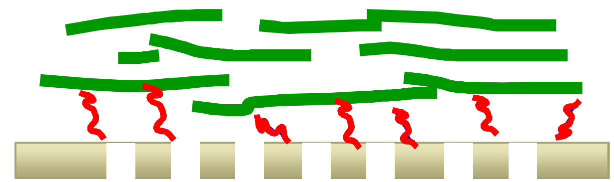
Theory and experiment suggest that nanosheet-based desalination membranes will have 10x-100x flux of current technologies, revolutionizing low-energy water production and recycling.

[1] Lockheed Martin Perforene membrane, [2] R. Nair *et al.*, *Science* 335 (2012), [3] M. Hu and B. Mi, *Environ. Sci & Tech.* 47 (2013)

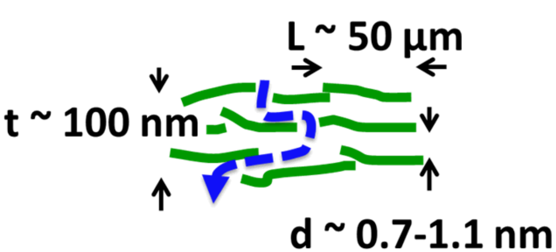
Our GO membranes comprise three key layers

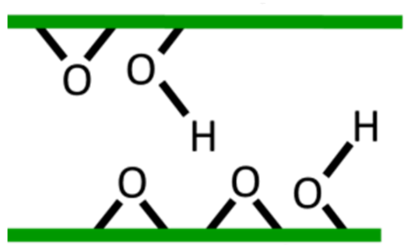
Laminar graphene oxide, covalent linker molecules and porous polymer support provide ion rejection, membrane integrity, and mechanical durability





Intrinsic nanoscale properties of laminar GO drive water permeation and are optimum for desalination





Thin-slit permeation pathway defined by oxygen moiety "nanopillars"

Photo courtesy R. Montoya; SEM courtesy D. Grant

Vacuum-filtration directed assembly of GO on polymer membrane supports

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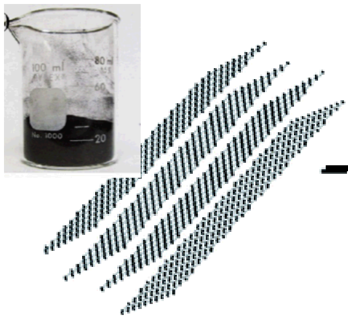
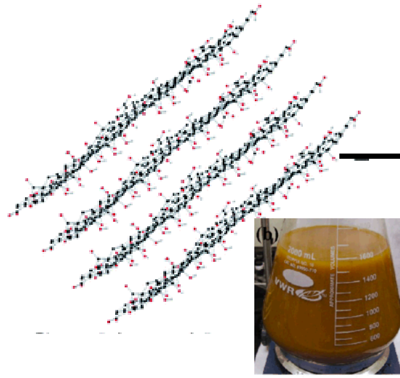
graphite



Oxidation

HPO_4, H_2SO_4, $KMnO_4$

graphite oxide



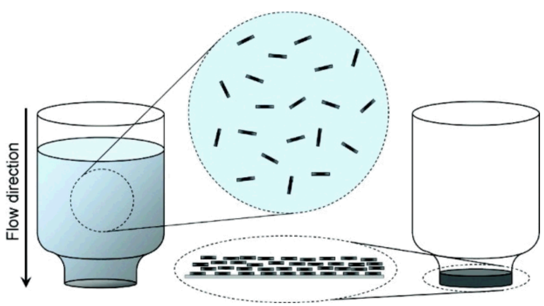
Exfoliation

1 M HCl wash

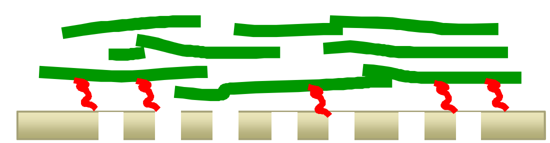
graphene oxide

Material cost: \$0.10/m² for a 100-monolayer GO membrane

GO sheets are re-dispersed in a dilute filtration suspension and vacuum-filtered onto a porous polymer membrane



functionalized polyester (PET) or polyethersulfone (PES)



Scale-up to larger membrane sizes requires appropriate polymer support membrane

GO/polyester membranes had promising permeance and rejection …

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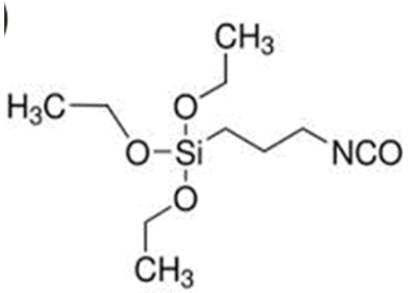
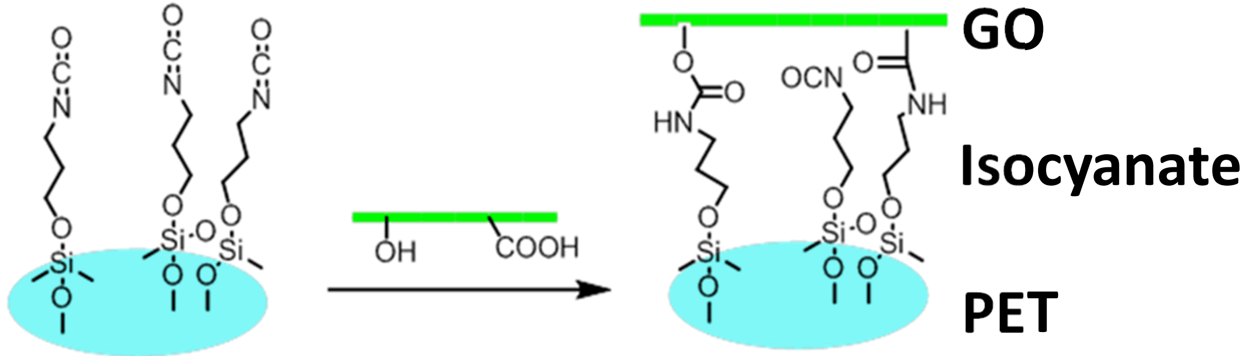
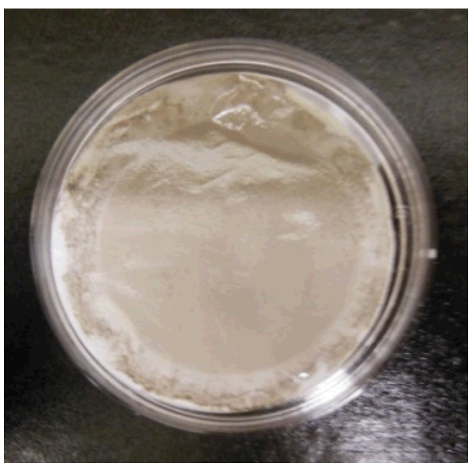


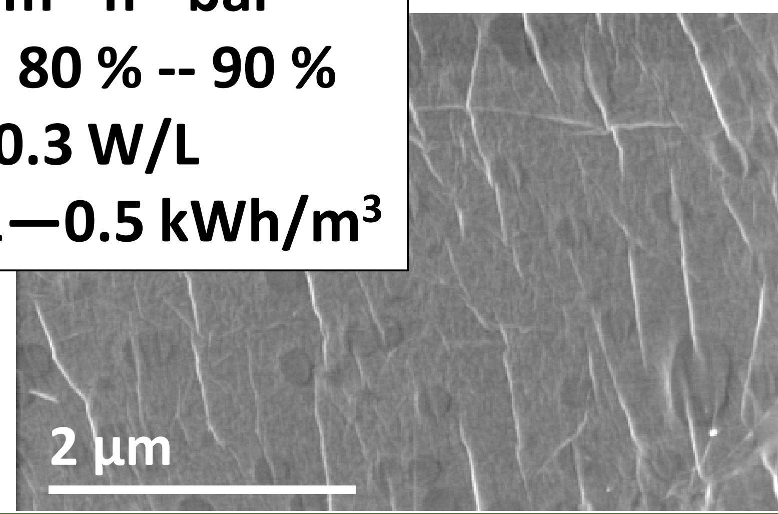


GO/Isocyanate/PET



47-mm polyester support w/ isocyanate linkers

Permeance: 0.5 -- 2 L m^{-2} h^{-1} bar^{-1}
Sulfate ion rejection: 80 % -- 90 %
Power needed: 0.2—0.3 W/L
Minimum energy: 0.1—0.5 kWh/m^3



… brittle polyester membranes could not be scaled to larger 2” x 4” cross-flow test size

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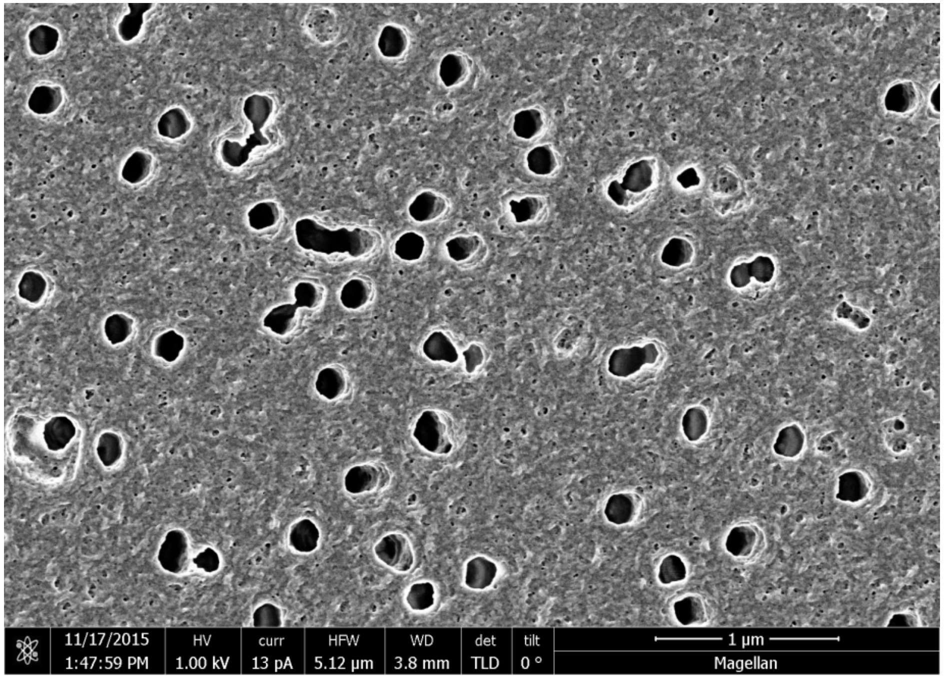
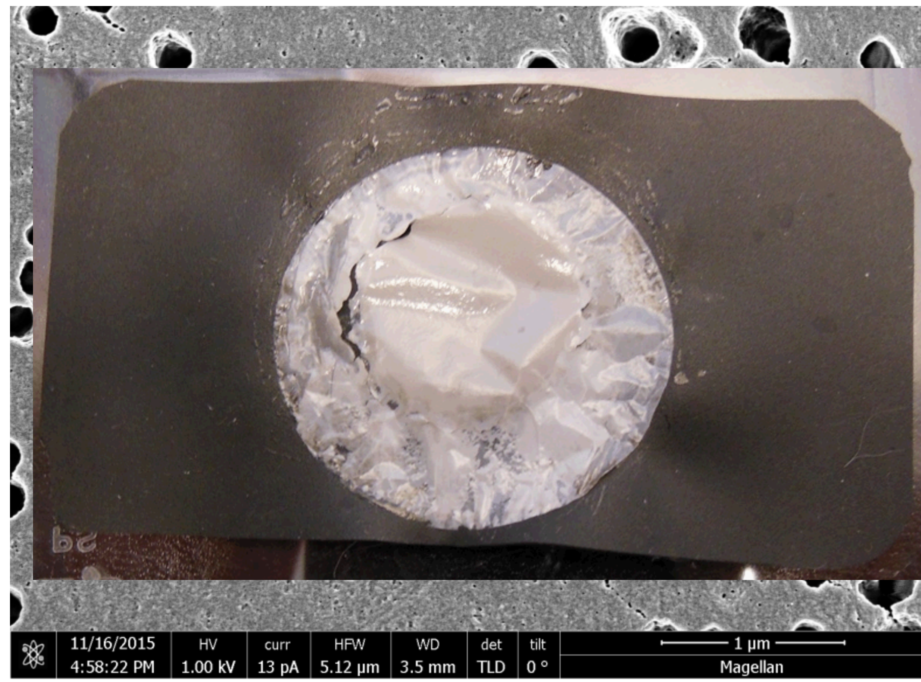


← Pristine PETE

Following 10-min UV-ozone exposure →

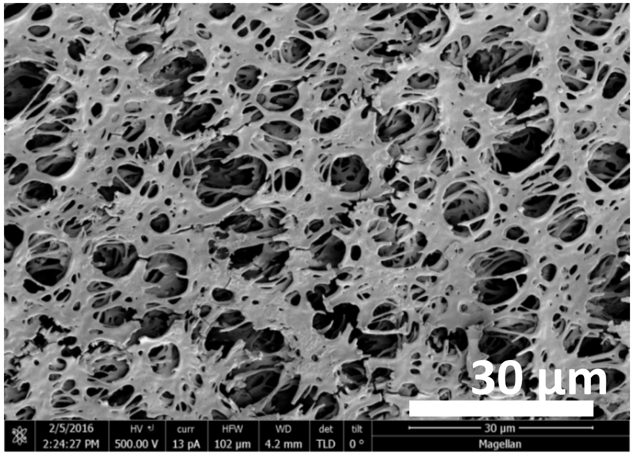


SEMs show cracks connecting pores of UV-ozone treated polyester membranes

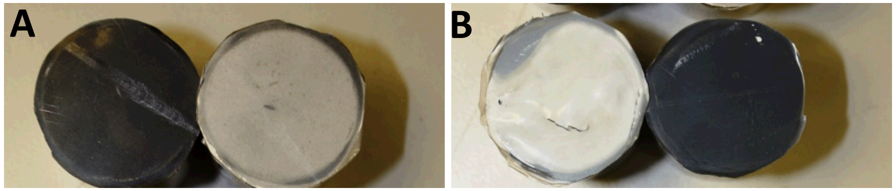
Robust polyethersulfone (PES) membranes can withstand strains ~20 % before fracture

Membrane	Thickness	Treated Toughness
PETE	10 µm	$28 \pm 7 \times 10^4$ J/m^3
PES	120 µm	$80 \pm 24 \times 10^4$ J/m^3

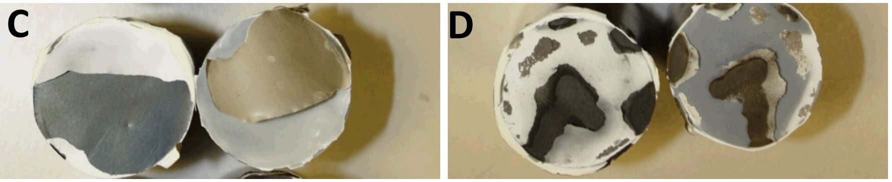
PES following 10-min UV-ozone exposure →



Tensile-pull tests demonstrate cross-linking molecule minimizes GO delamination



GO/PES, without covalent linker



GO/PES, with covalent linker

A: Failure at GO/PES interface

B: Failure at GO/epoxy interface

C, D: Failure predominately within PES membrane

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Sandia National Laboratories

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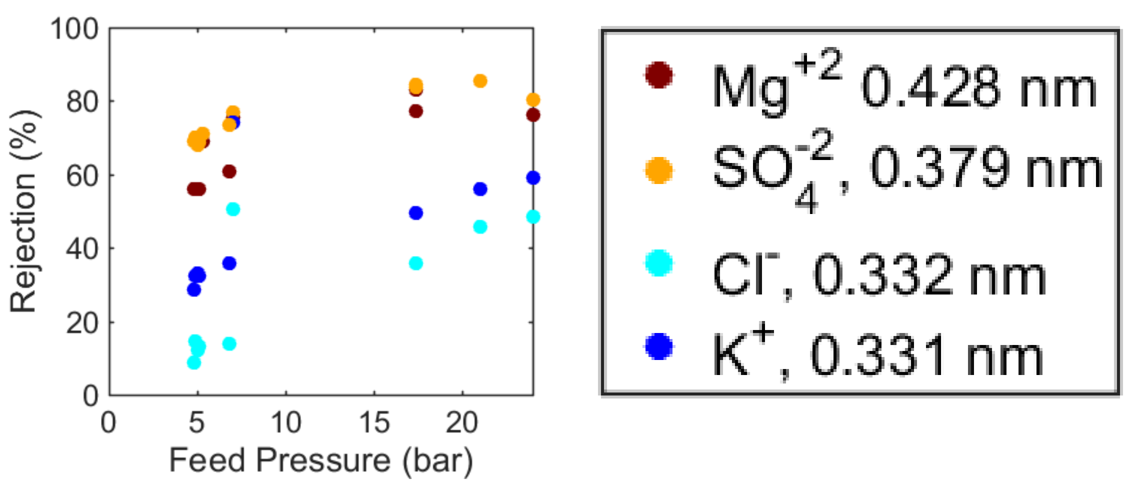
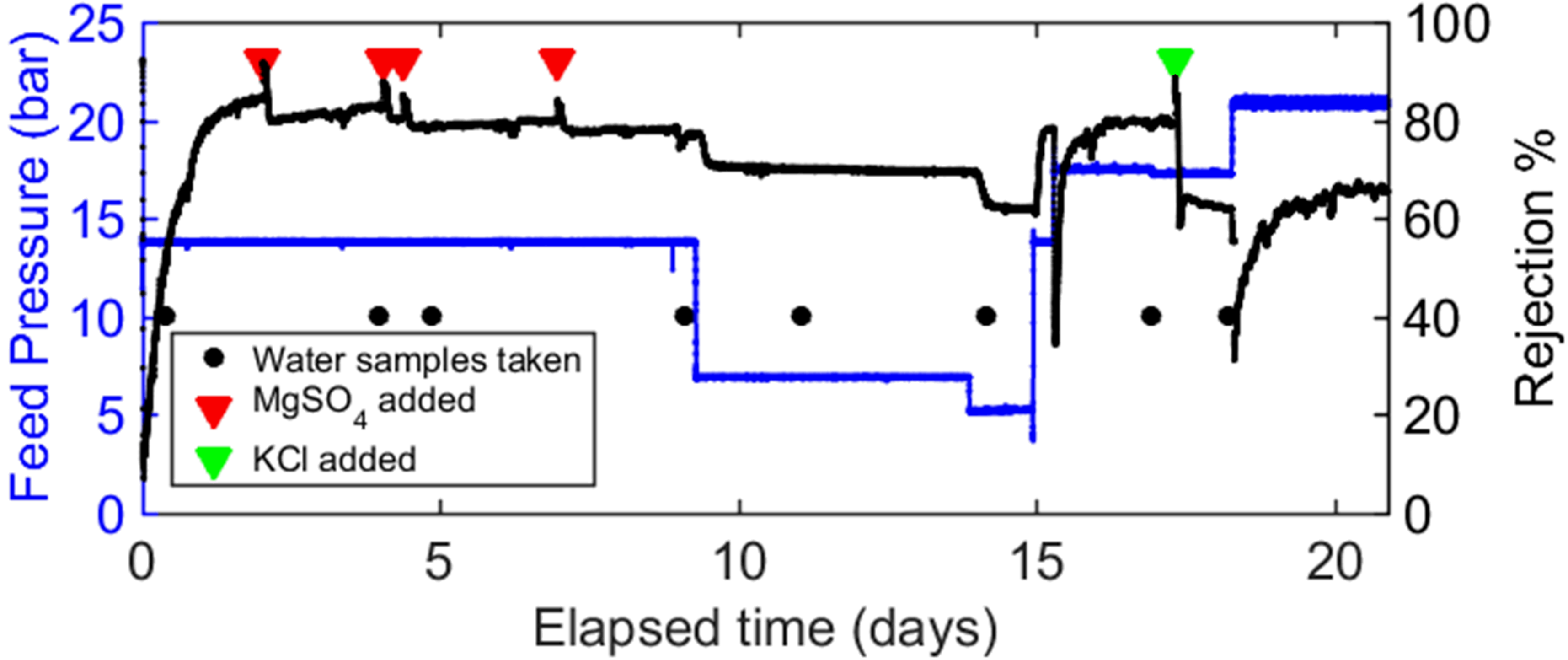
- → **Pressure-dependent rejection with simple salt solutions**
- **Minimal fouling when recycling Redhawk cooling water**



Next steps to improve performance

Conclusions

Membranes show stable performance during month-long permeation tests



Control

- Feed tank water salinity
- Driving pressure

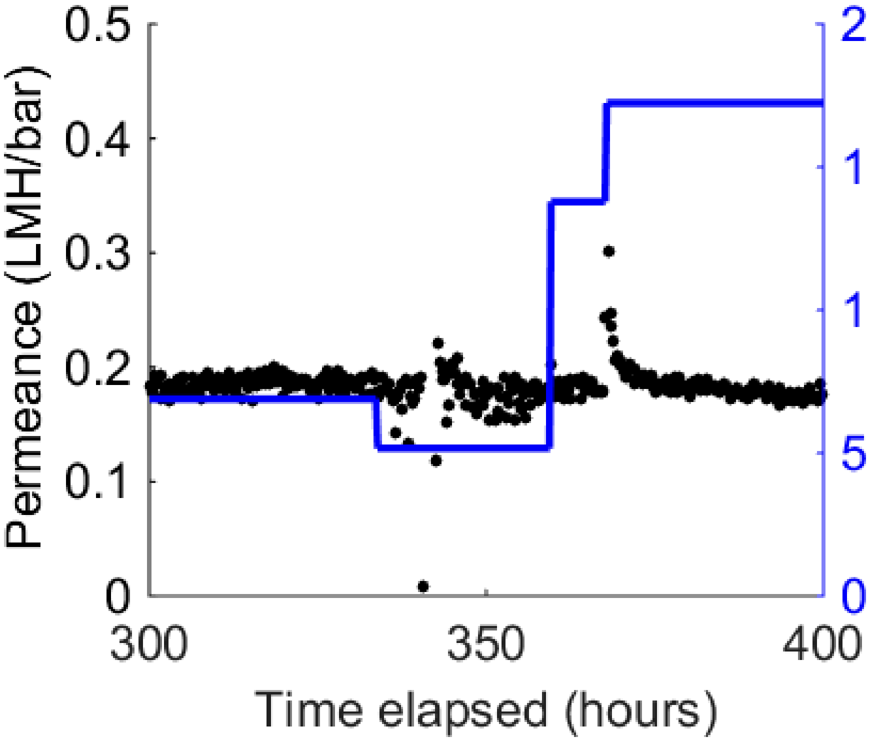
Monitor

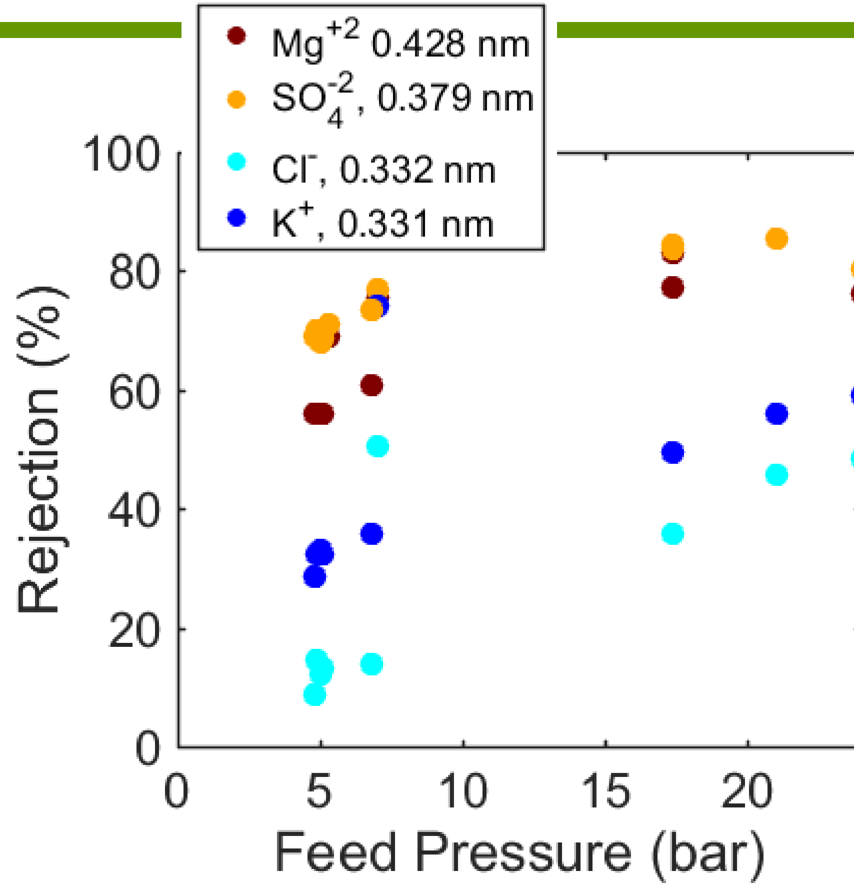
- Conductivity, feed & permeate
- Permeate flow

Calculate

- Rejection (%)
- Permeance (LMH/bar)

Extended cross-flow permeation tests show pressure-dependent rejection





Permeance is independent of feed salinity (0-10 ppm $MgSO_4$)
Rejection increases with driving pressure and increasing hydrated-ion radii

Hydrated radii: B. Conway and E. Ayranci, *J. Soln. Chem.* 28, 163-192 (1999)

Maximum achievable rejection, > 90%, determined by electrochemical impedance spectroscopy (EIS)

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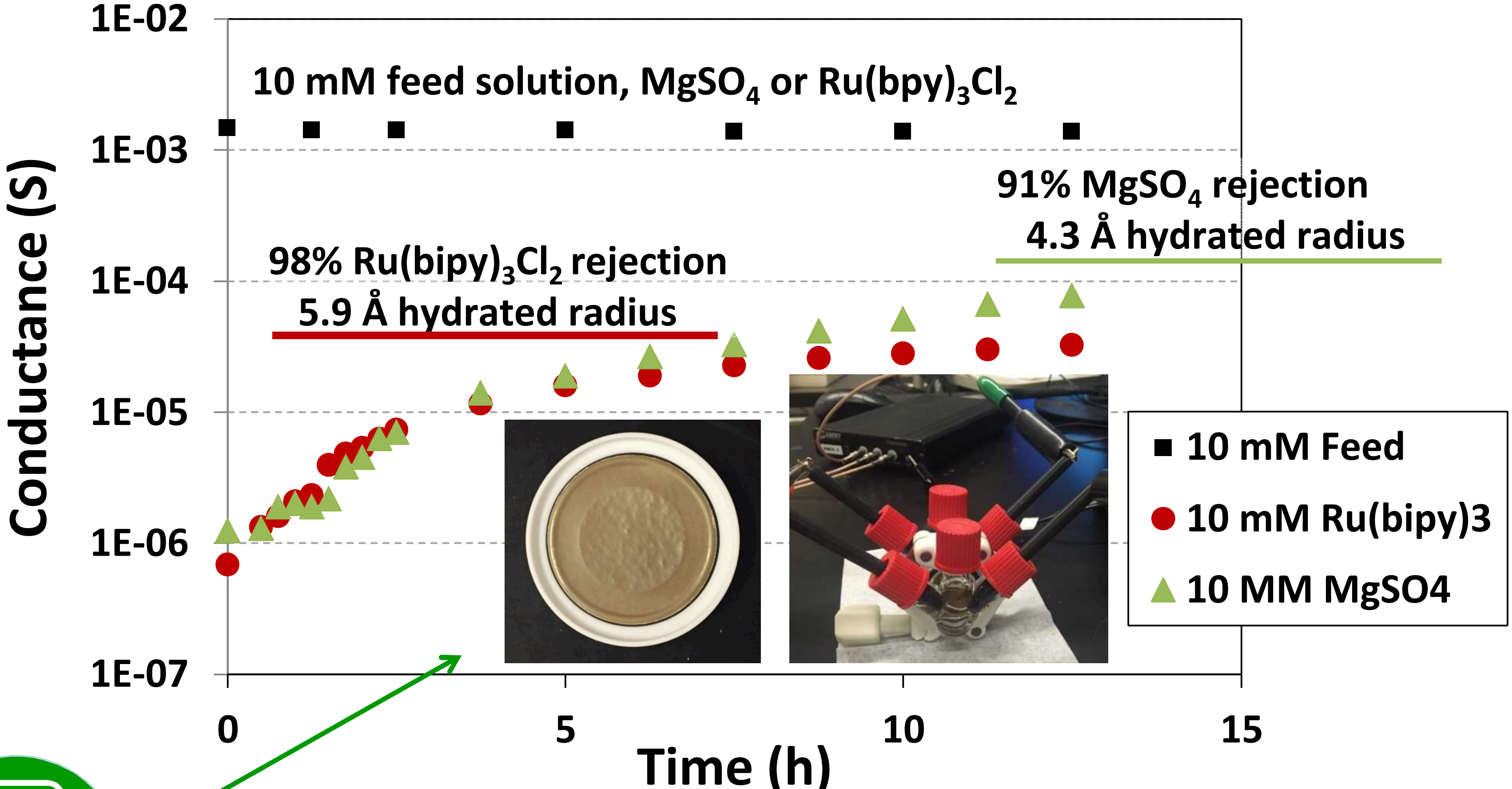

- EIS and cross-flow permeation tests are conducted on the same parent membrane
- 70-80% $MgSO_4$ cross-flow rejection for the same membrane

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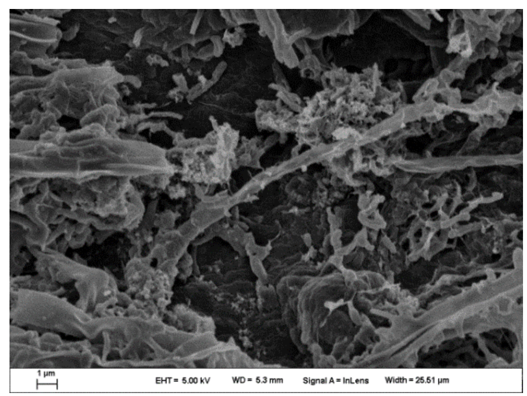


P. megasperma mold

Next steps to improve performance

Conclusions

Redhawk Cooling tower water

Sandia National Laboratories

Applied Specialties, Inc.

33555 Pin Oak Parkway
Avon Lake, OH 44012
440-933-9442

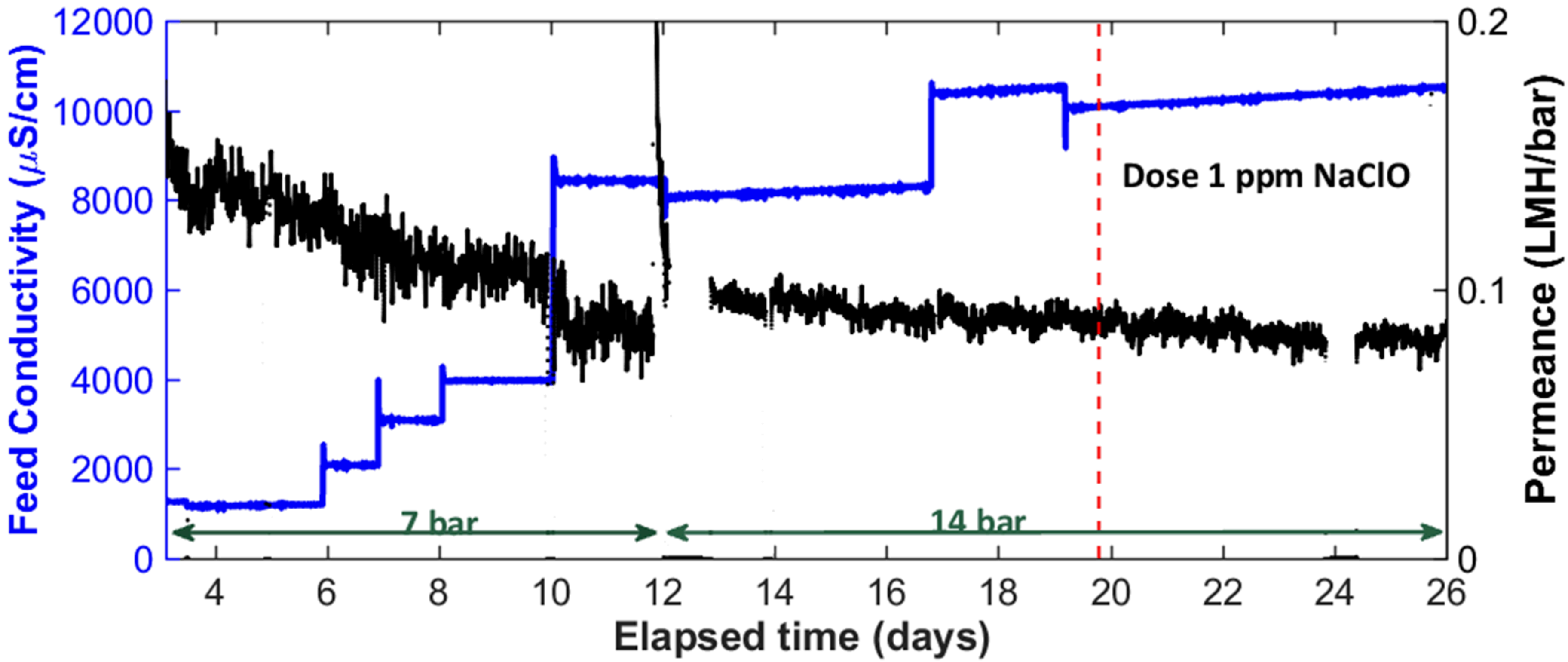
Client/Location:	APS Redhawk	Date Sampled:	2/16/16
Sample Name:	2 CT	Date Received:	2/23/16
Sample Number:	160223-Y	Analysis Date:	2/24/16

Procedure	Result*	Reporting Limit	Method
pH	6.69	0.100	D-1293
Alkalinity "P" (as CaCO3)	---	2.000	D-1067-B
Alkalinity, Total (as CaCO3)	120.0	2.000	D-1067-B
Conductivity	23,430	1.000	D-1125-A
Calcium Hardness (as CaCO3)	1,405	2.397	Calc
Total Hardness (as CaCO3)	1,988	3.297	Calc
Silica	116.9	9.574	Calc
Fluoride	---	2.400	EPA 300.0
Chloride	8,247	2.400	EPA 300.0
Nitrite	---	1.200	EPA 300.0
Bromide	---	2.400	EPA 300.0
Nitrate	292.0	1.200	EPA 300.0
Sulfate	7,633	9.600	EPA 300.0
Phospate	---	6.000	EPA 300.0

** Results reported as mg/L unless otherwise stated*

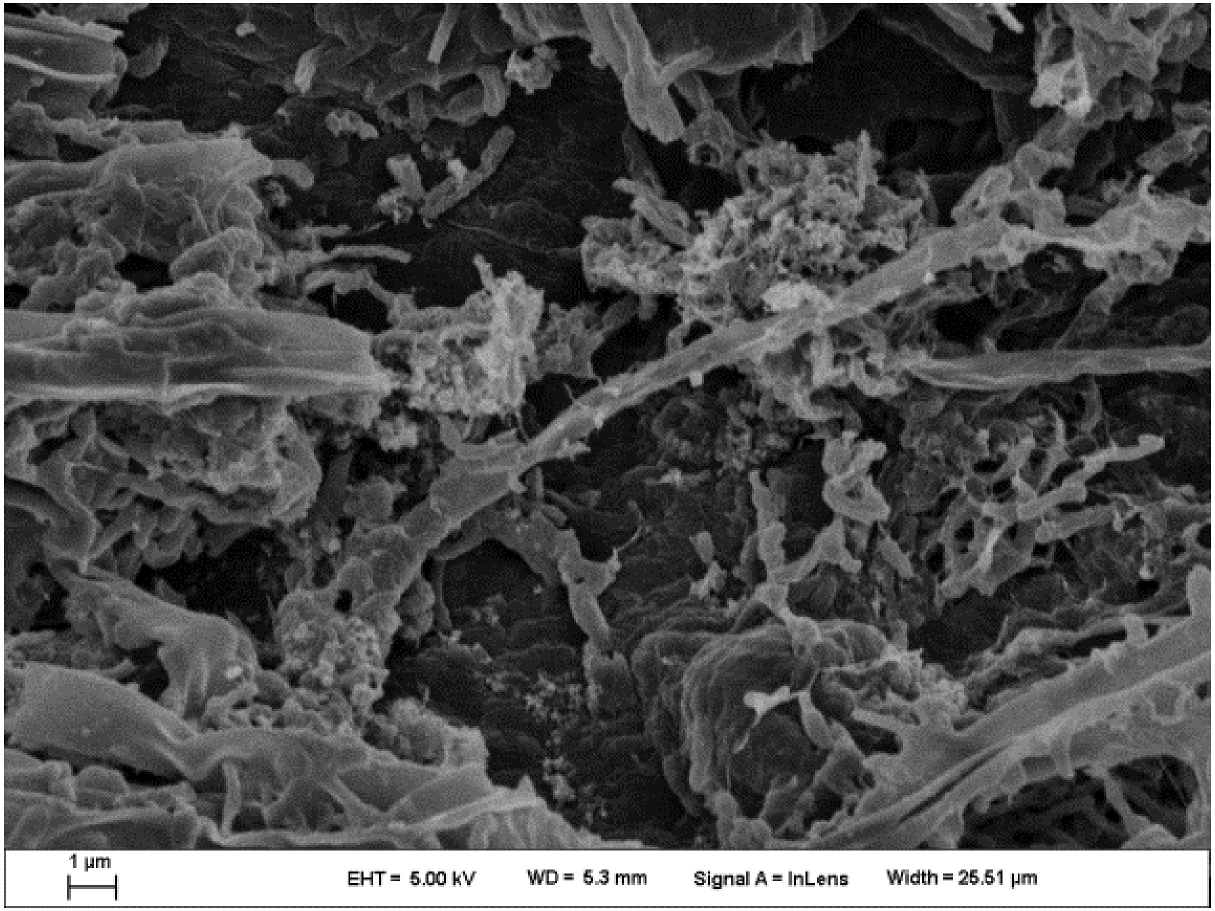
Analyst: TM

Recycled Redhawk water through a GO/PES membrane in a month-long scaling test



Rejection remained constant following feed tank dose to 1 ppm NaClO
Permeation stabilized at 0.1 LMH/bar

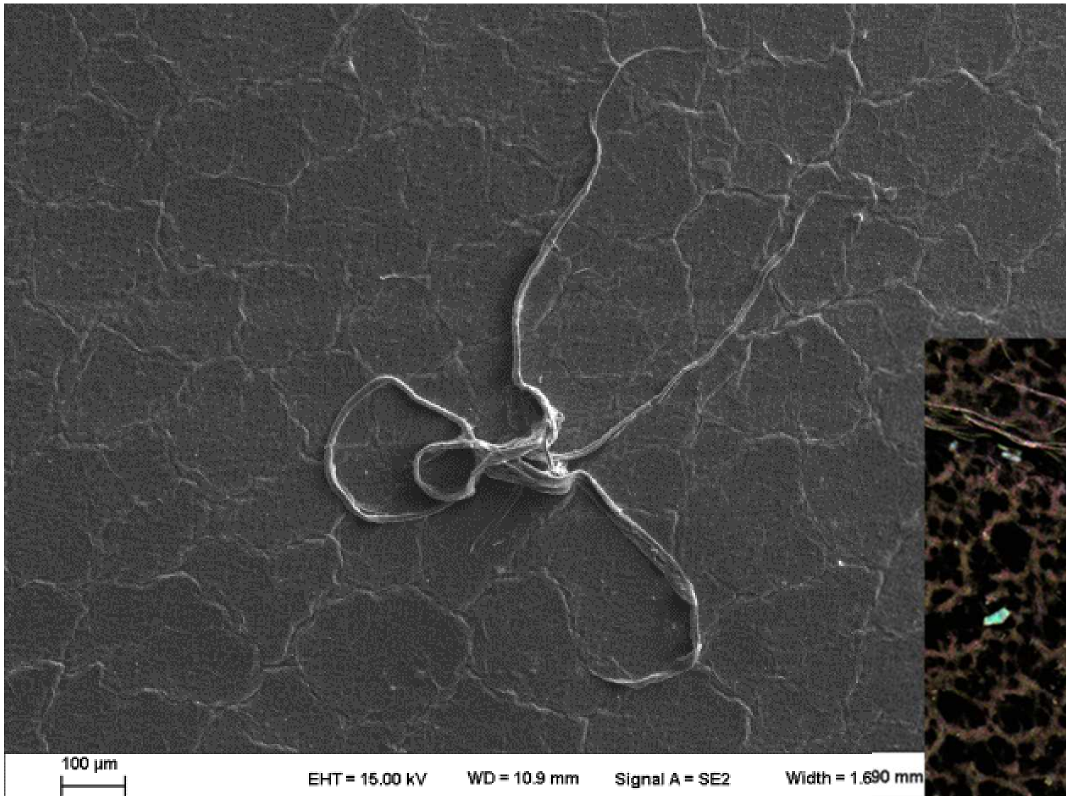
Extensive mold growth on PVC tubing during month-long filtration of cooling tower water



Phytophthora sp. grew extensively on the PVC tubing and in the polymer feed water tank

Minimal biofouling and scaling observed on GO

A rare spore on the GO membrane



Alumina silicate crystal on the GO membrane

Antimicrobial activity of GO previously reported, see X. Huang *et al., ACS Appl. Mater. Interfaces* 8, 14334-14338 (2016)

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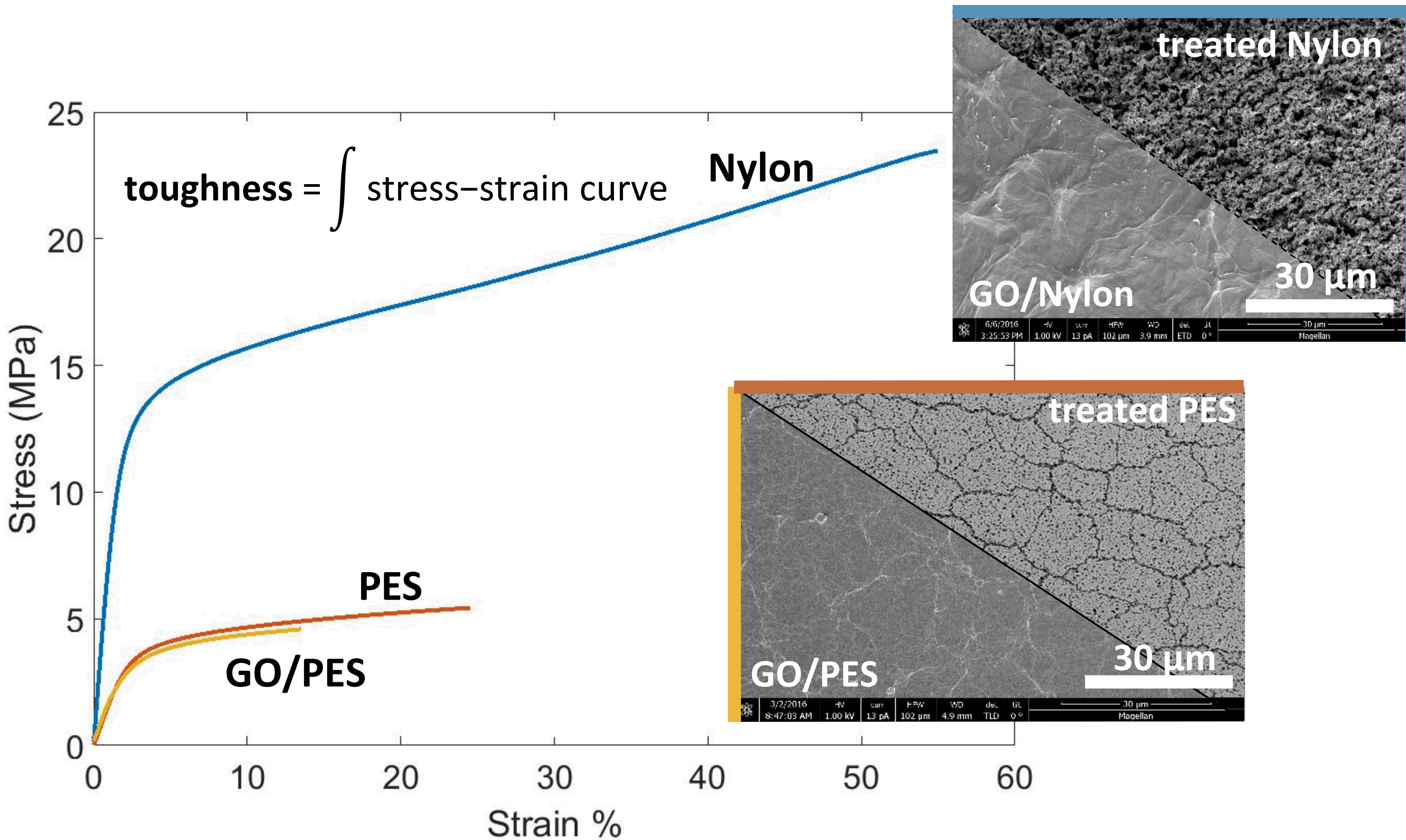
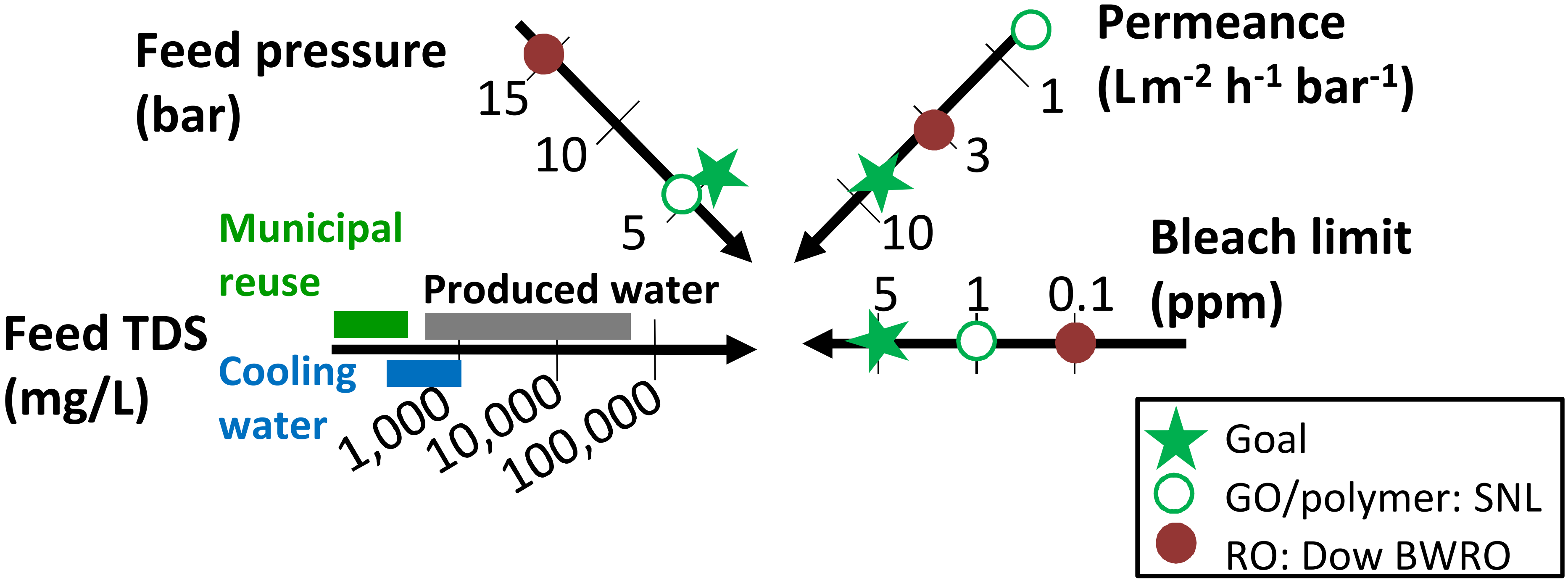
Conclusions

Increase flux by assembling GO on a high-porosity Nylon membrane



Stress-strain measurements show Nylon membranes are tougher than PES

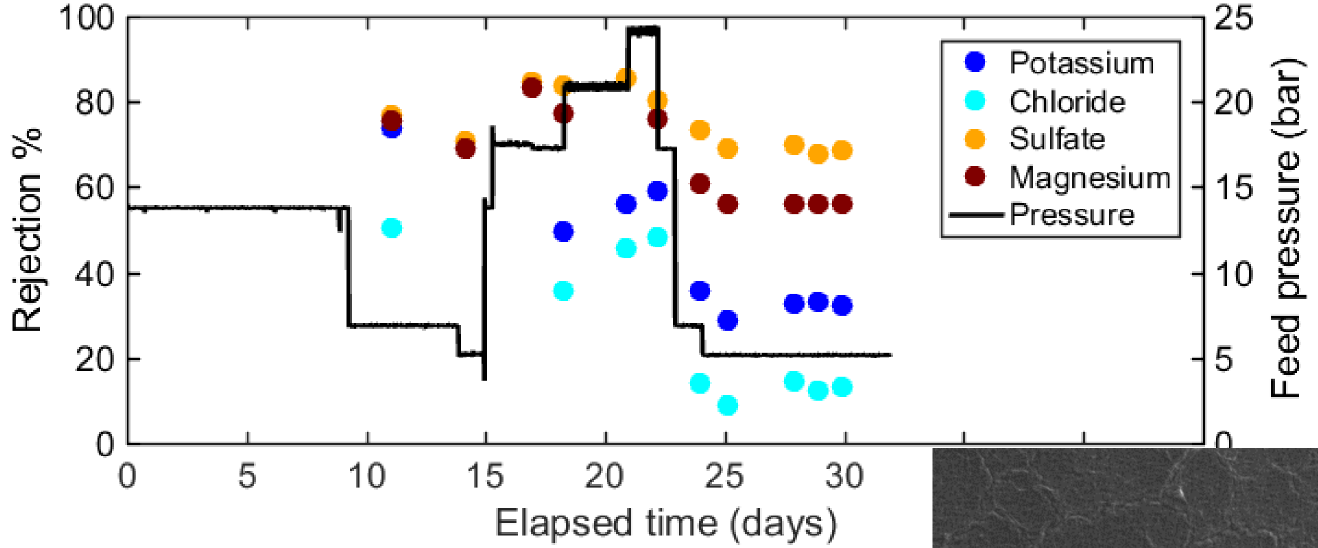
Operational considerations drive GO/polymer membrane design



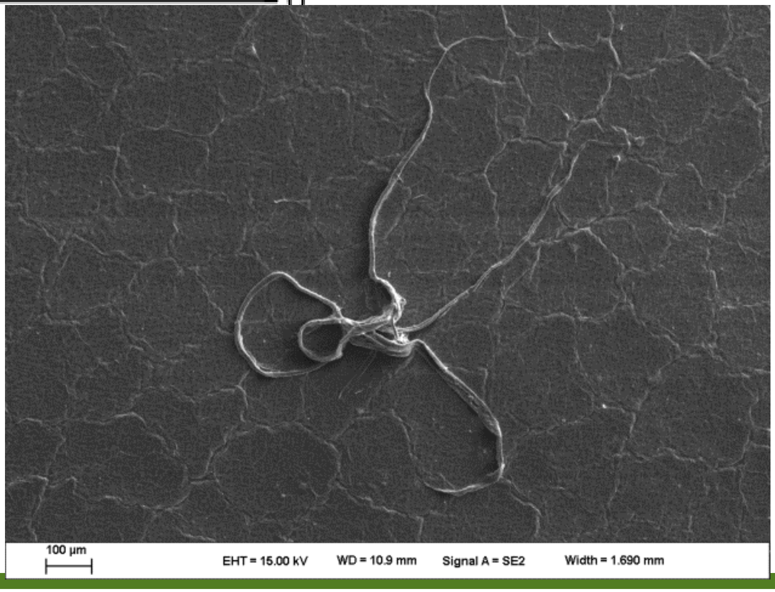
To increase permeance and lifetime (durability), we are now fabricating GO membranes on Nylon supports. Nylon has twice the toughness of PES, greater porosity, and is broadly chemically tolerant.

Conclusions

Month-long test shows ion rejection scales with pressure



Natural anti-microbial properties of GO inhibit biofouling



Acknowledgements

Current research team: Michael Hibbs, Mike Hightower, Curt Mowry, Trey Pinon, Craig Stewart and Kevin Zavadil

Additional collaborators: Amy Allen, Dick Grant, and Lonnie Haden

Funding

EPRI | ELECTRIC POWER RESEARCH INSTITUTE

Seedling CRADA project with EPRI
Richard Breckenridge, program manager

Laboratory Directed Research & Development

Lagniappe

Ideal properties of nanoscale-enabled desalination membranes

Sandia National Laboratories

Physical properties

- Pore diameter < 1 nm
- High pore density
- Chlorine-tolerant
- Resistant to biofouling and sulfate scaling
- Bottom-up manufacturability

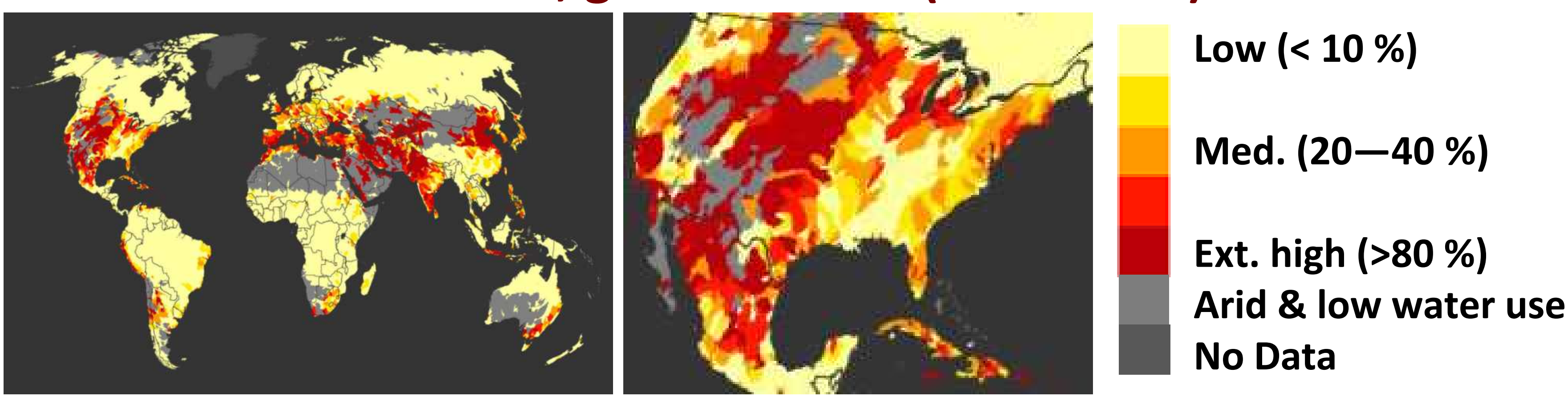
	Desired Performance	**Reverse Osmosis**
Salt rejection	> 95 %	99.0 % (min)
Permeance	> 10 LMH/bar	2.9 LMH/bar
Energy use	< 0.1 W/L	
Chlorine tolerance	1-5 ppm	< 0.1 ppm

DOW FILMTEC BW30-400 membrane used for RO comparisons, msdssearch.dow.com

DOE: Six Strategic Pillars to Address the Water-Energy Nexus

1. Optimize freshwater efficiency of energy production, electricity generation, & end use technologies
2. Optimize energy efficiency of water management, treatment, distribution, & end use technologies
3. Enhance the reliability and resilience of energy and water technologies
4. Increase safe and productive use of nontraditional water sources through improved technology
5. Promote responsible energy operations w.r.t water quality, ecosystem, and seismic impacts
6. Exploit productive synergies among water and energy system technologies

Baseline Water Stress, global and US (1950-2010)



Nanoscale graphene oxide (GO) structure enables low energy desalination

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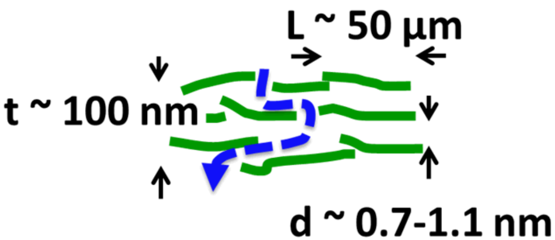
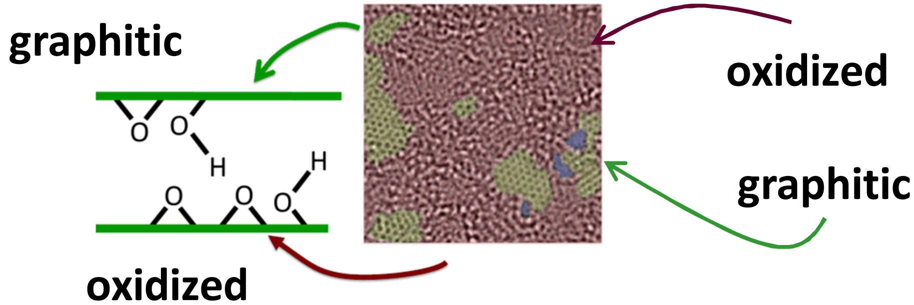
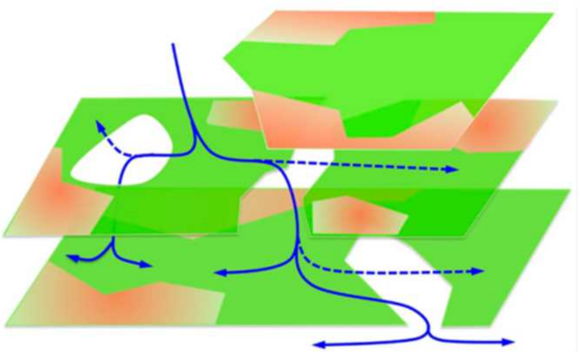
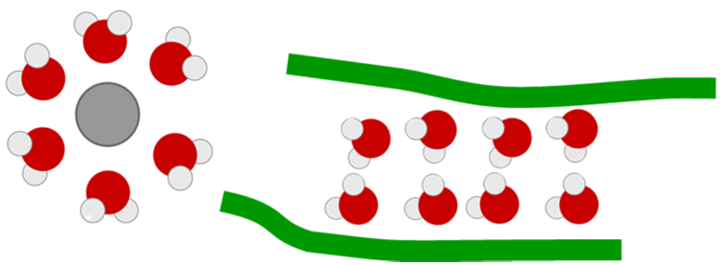
Thin-slit permeation pathway defined by oxygen moiety "nanopillars"





Intrinsic nanoscale properties of laminar GO drive water permeation and are optimum for desalination

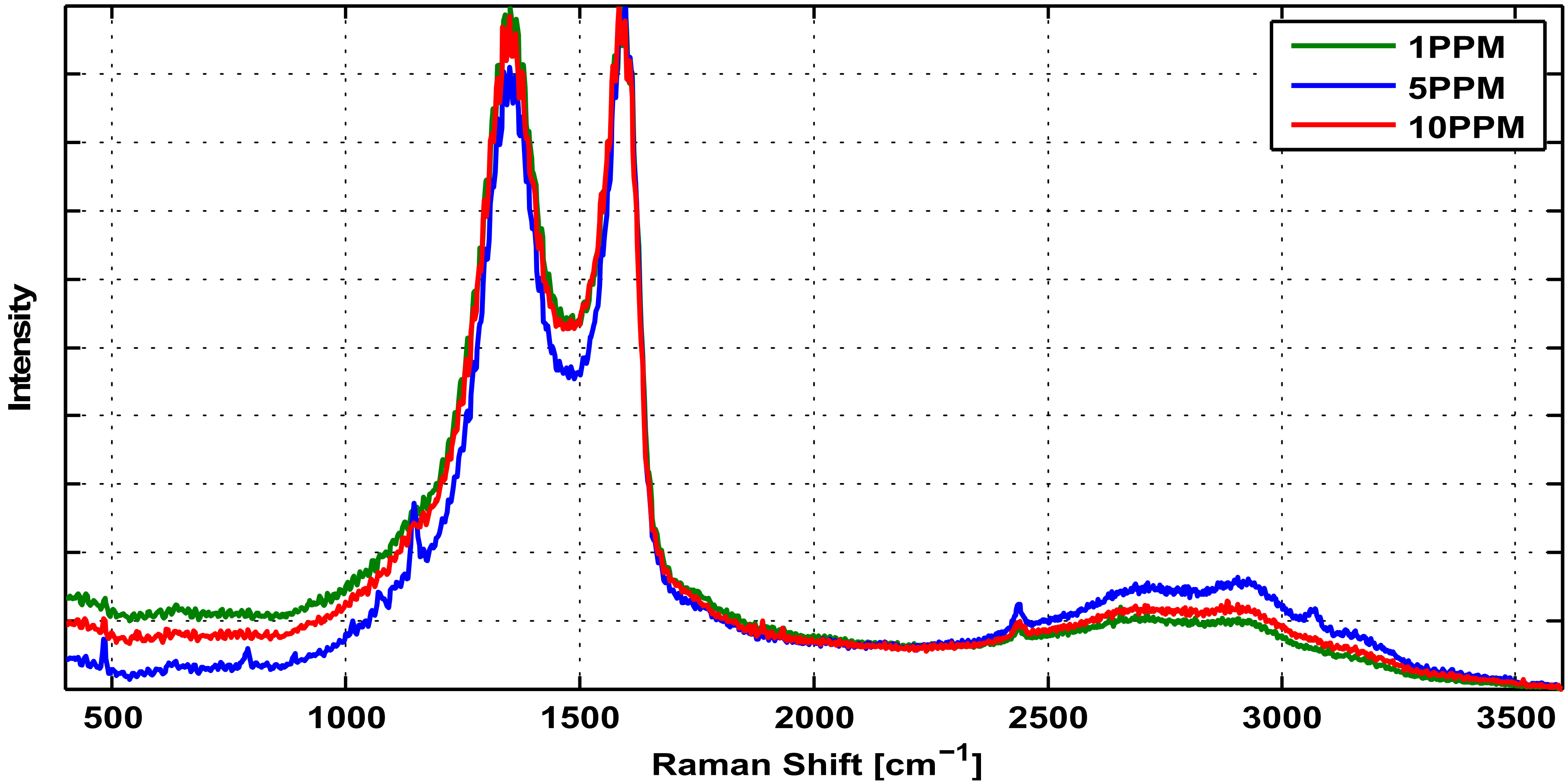




→ **Low-energy flow: Water flux is driven by strong interactions with the GO sheets, not by external pumps.**

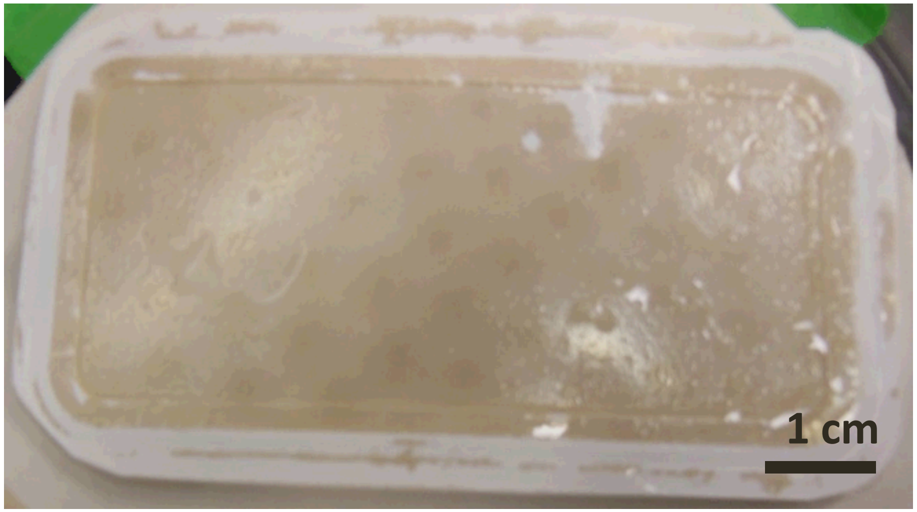
[1] R. Nair *et al., Science* 335, 442-444 (2012)
[2] D. Boukhvalov *et al., Nano Lett.* 13, 3930-3935 (2013)

GO structure is robust to 1-ppm, **one month** free chlorine exposure

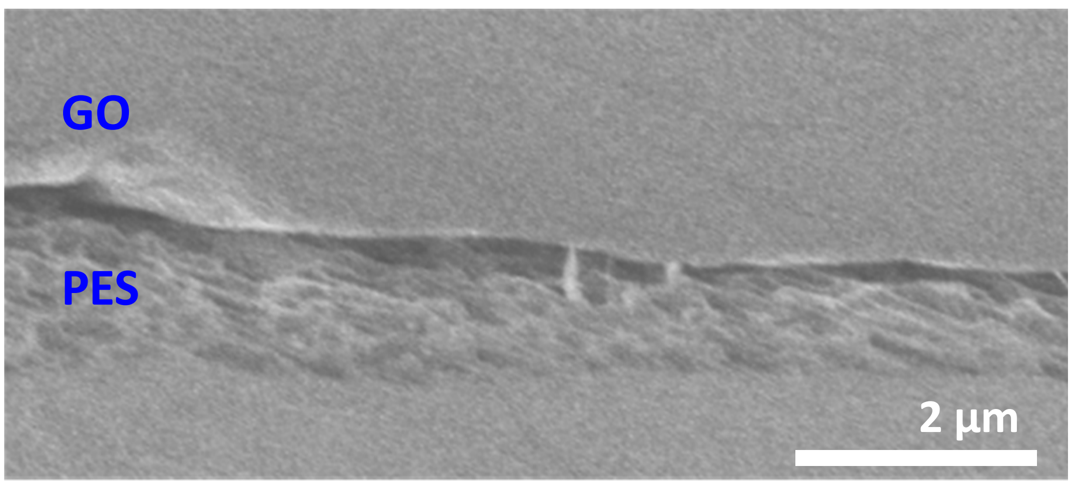


Low-levels of chlorination (~1—10 ppm) will minimize biofouling in greywater recycling

GO/PES: Delamination during cross-flow permeation limits ion rejection



Delamination following 1 ½ -day permeation test at 14 bar and 8-hour exposure to 60-ppm bleach.



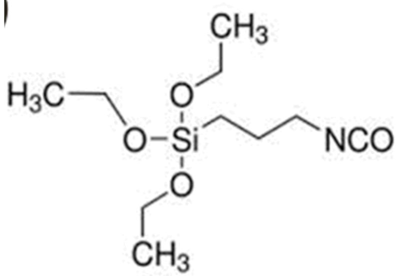
Representative delamination at the GO/PES interface.

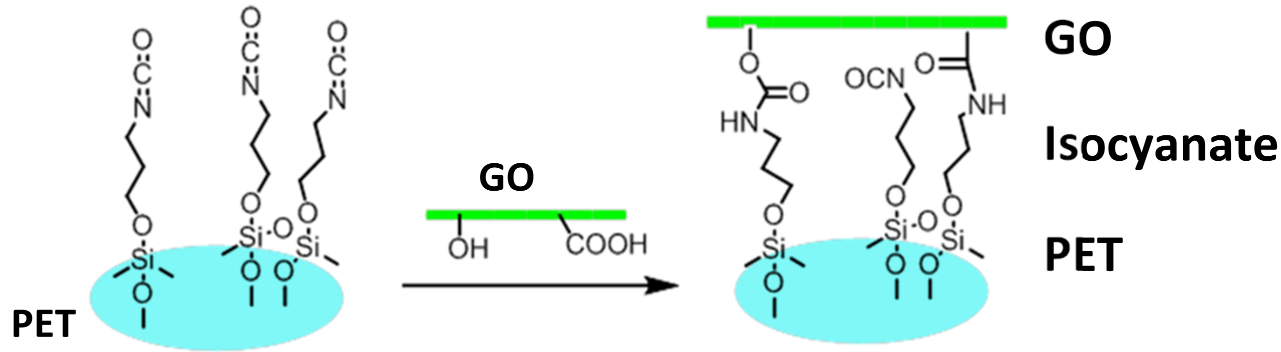
Will covalently binding GO to PES prevent delamination of the laminar GO?

Covalent linking isocyanate agents prevent delamination of the laminar GO

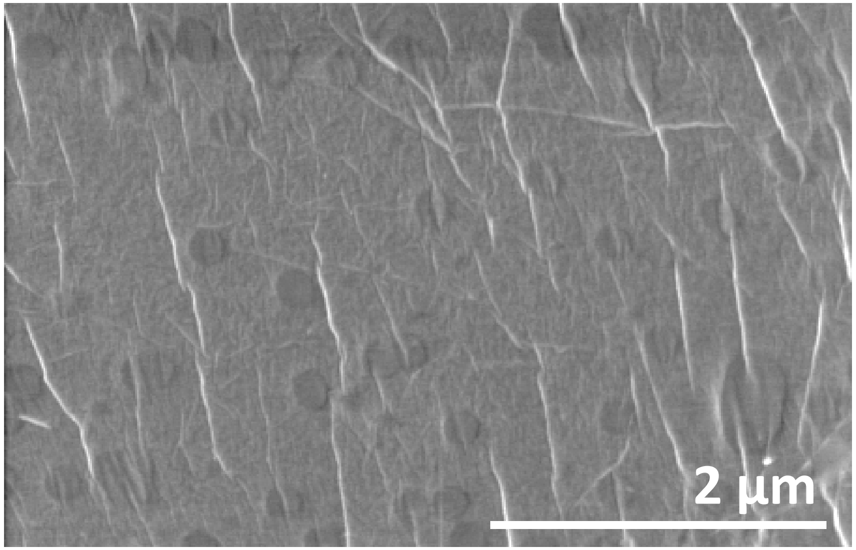
Sandia National Laboratories

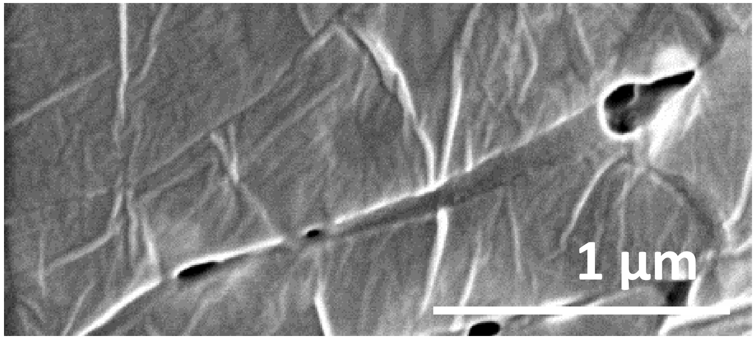
Isocyanate





GO/Isocyanate/PET, following permeation tests





**Effective isocyanate binding,
even over fractured polyester (PET)**