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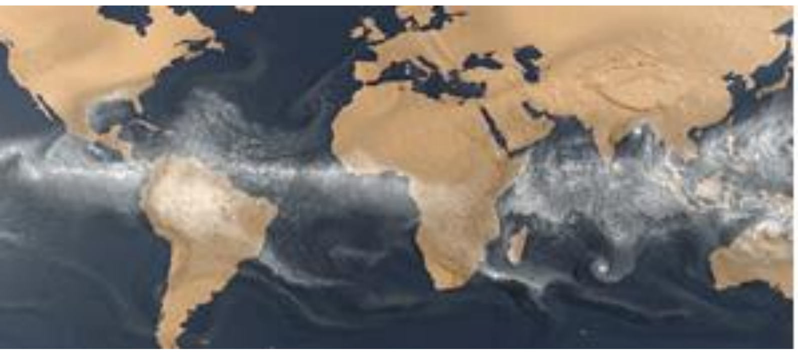

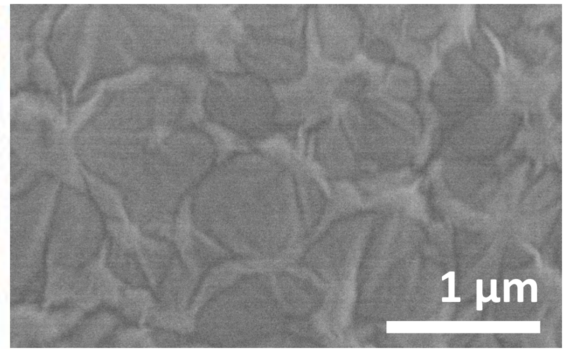

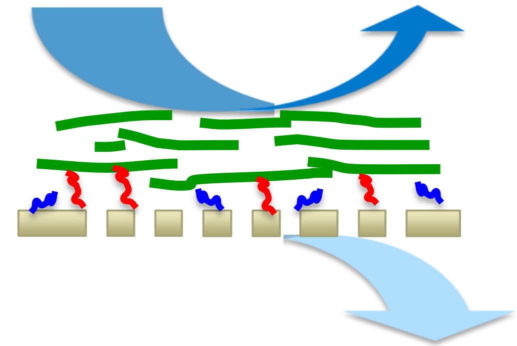

Cross-flow desalination of cooling tower water with graphene oxide/polymer membranes

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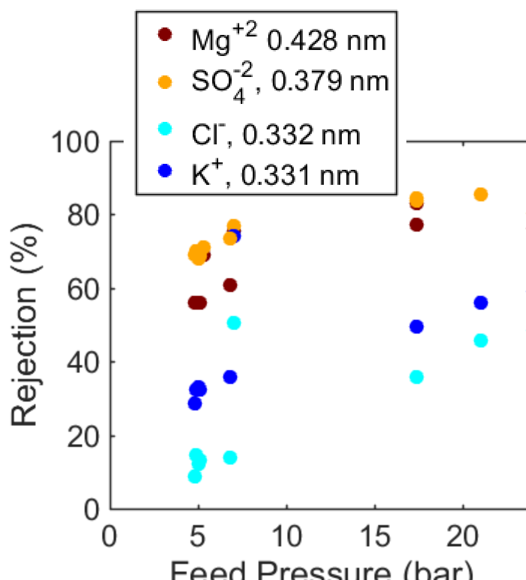
U.S. DEPARTMENT OF ENERGY NNSA National Nuclear Security Administration

Supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

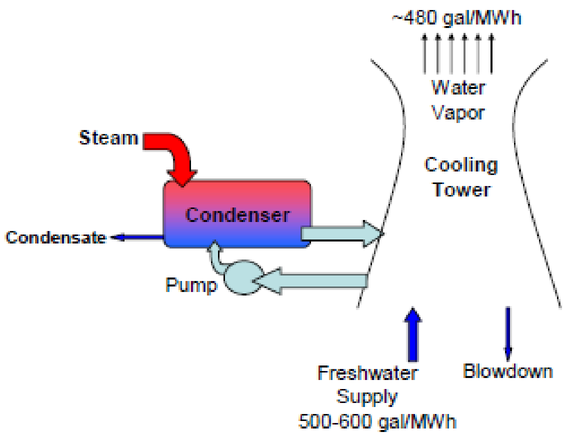
Outline

- **Introduction to graphene oxide/polymer membranes**
- **Pressure-dependent ion rejection**
- **Current work: Structure-property-performance relationship**
- **Rejection of emerging contaminants of concern**



Desalination is critical for energy resiliency

Power plants



Water challenges: Energy use, permeance

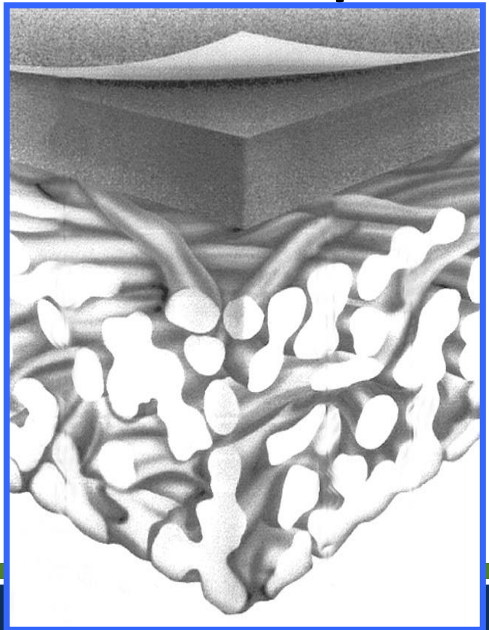
- Keep divalent ion loads <100 mg/L
- Minimize biofouling with low-level chlorination

Goals

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

Thermoelectric utilities rely on thin-film composite reverse osmosis membranes

- permeance ~ 3 LMH/bar
- rejection > 98%
- degraded by >0.1 mg/L free chlorine



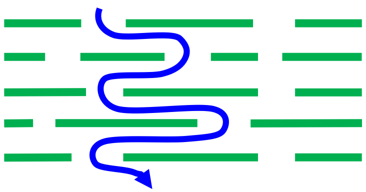
Thin (100-200 nm) Polyamide Layer

Polysulfone Support (micro-porous)

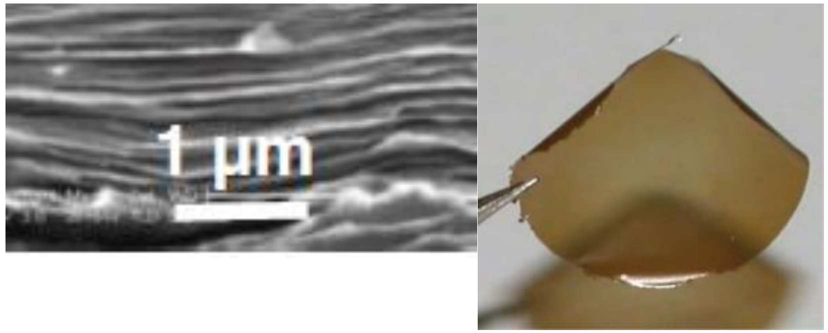
Fabric Support (meso-porous)

Water permeates through the thin slits defined by the laminar nanosheets

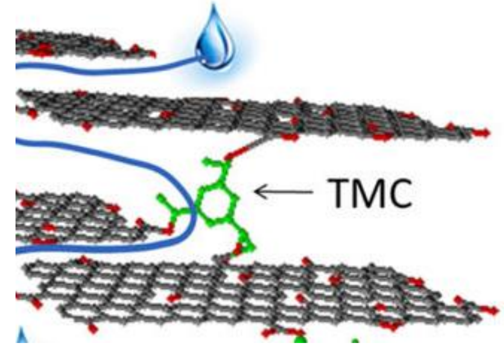
Permeation around GO sheets in laminar GO membranes



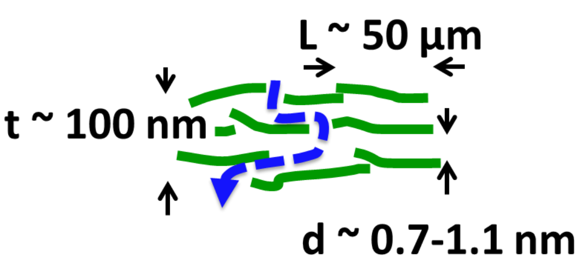
[1]

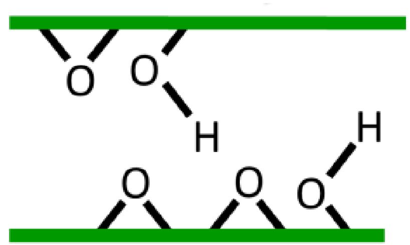


[2]



Oxygen moiety nanopillars define thin-slit permeation pathway



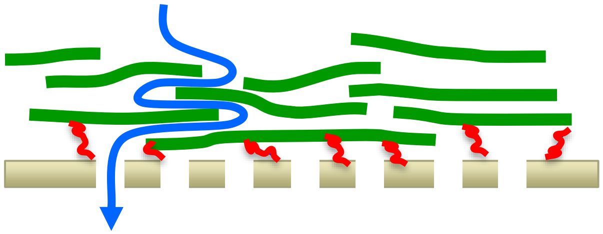


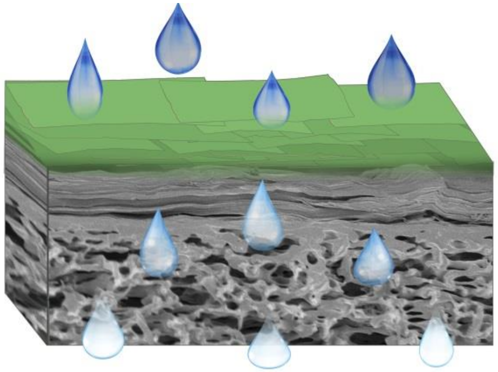
Thin-slit permeation pathway defined by oxygen moiety "nanopillars"

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

Sandia's GO/polymer membranes comprise three key layers

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





~2" x 4" membrane

How do these membranes perform in challenging water chemistries?

How do we optimize the laminar GO structure for maximum flow, rejection, and durability?

Automated cross-flow system allows for month-long desalination tests

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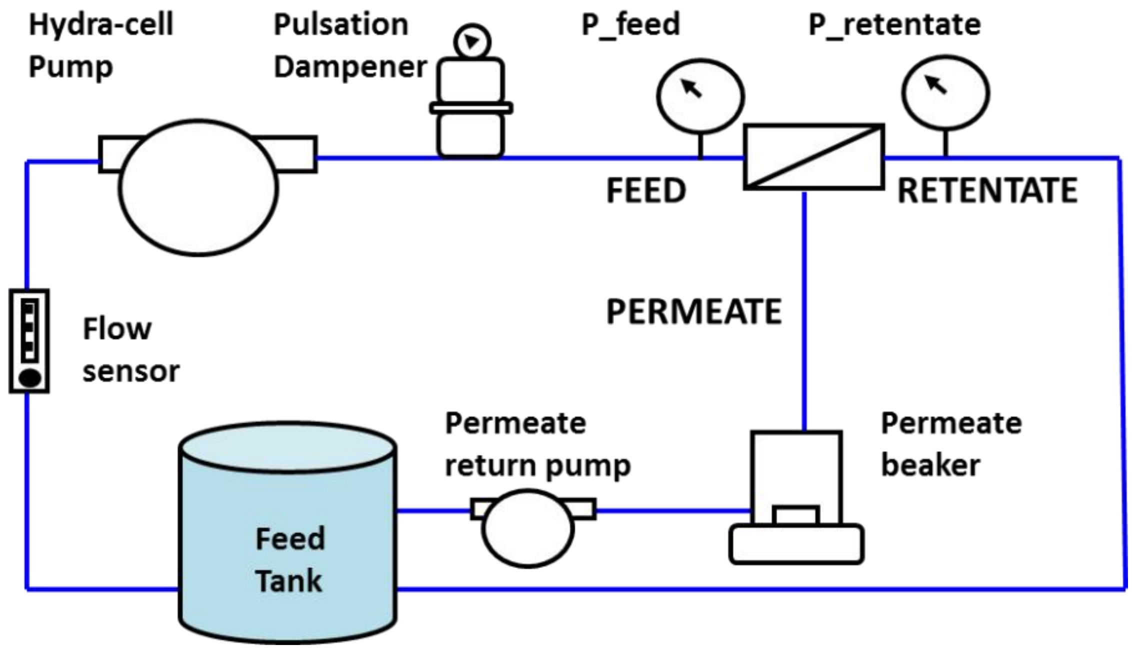


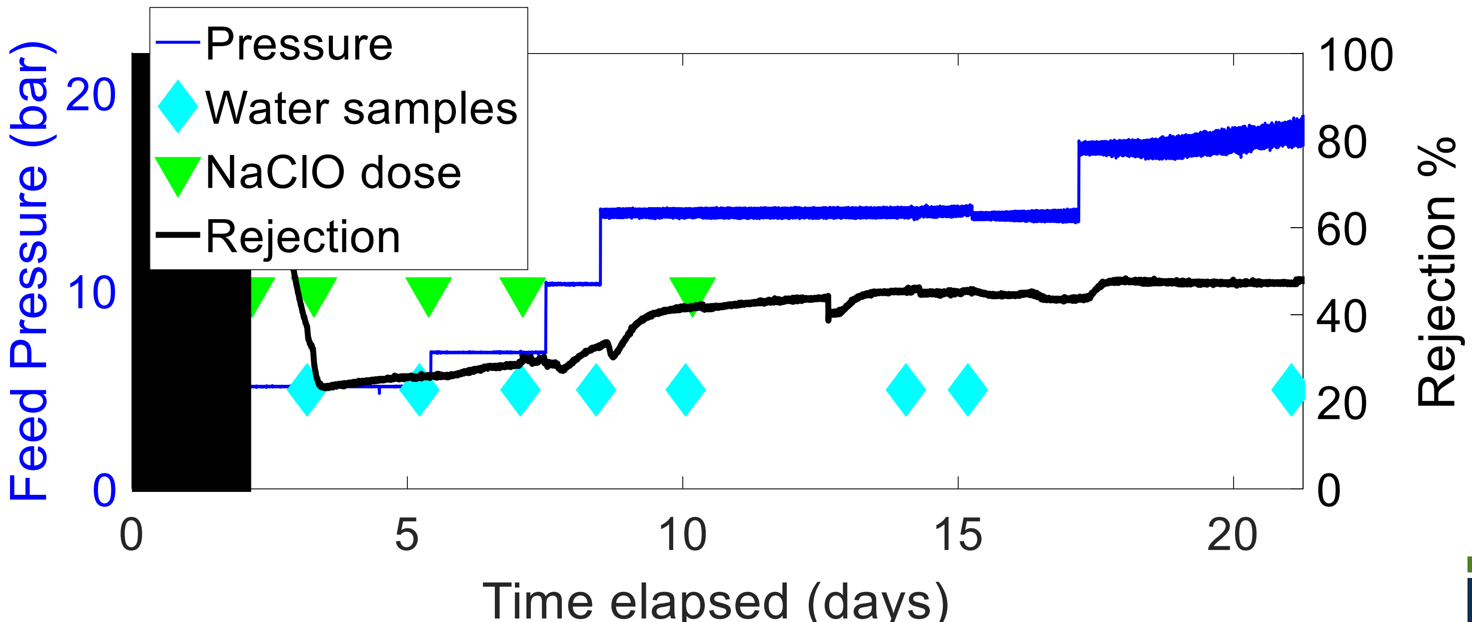
Control
- Feed tank water salinity
- Driving pressure

Monitor
- Conductivity, feed & permeate
- Permeate flow

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

Desalinate cooling tower water

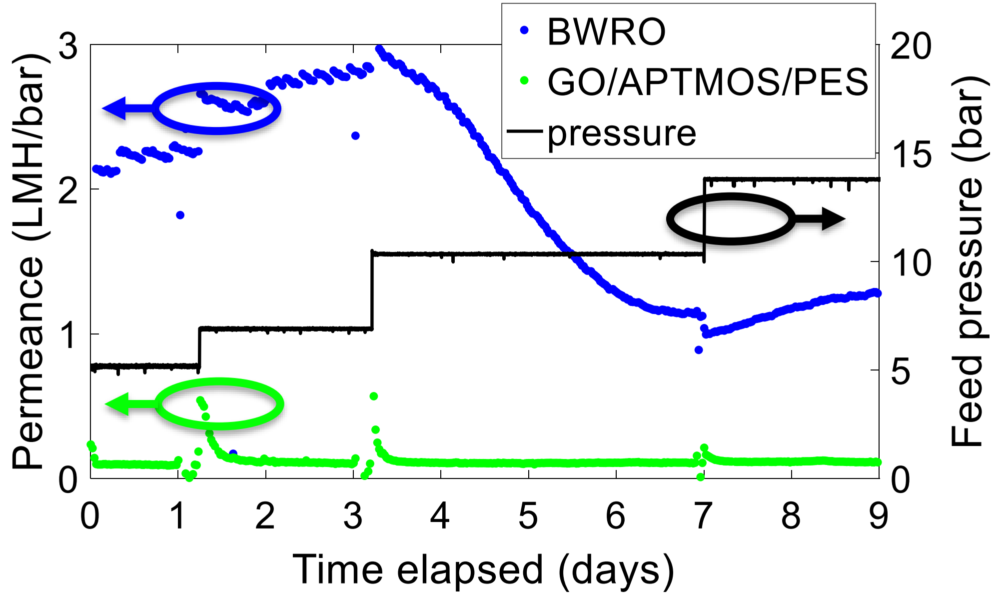
APS power plant	Feed cond. (µS/cm)	Pressure (psi)	Chlorine dose (ppm)	Duration (days)	Key finding
Redhawk	1000 – 10,000	100-200	1 (single dose)	28	Minimal biofouling and scaling of GO/polymer membrane
W. Phoenix, autoclaved	4000	100-400	1-3 (repeated)	30	Divalent ion rejection saturates at ~250 psi
Ocotillo	6000	75-250	0.5 (repeated)	17	Ion rejection doesn't scale with GO thickness



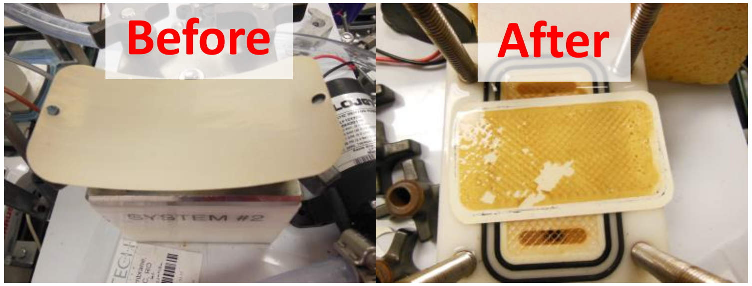
GO/polymer resists inorganic scaling and biofilm growth

Challenged commercial brackish water RO (BWRO) and GO/polymer membrane with W. Phoenix cooling tower blowdown.

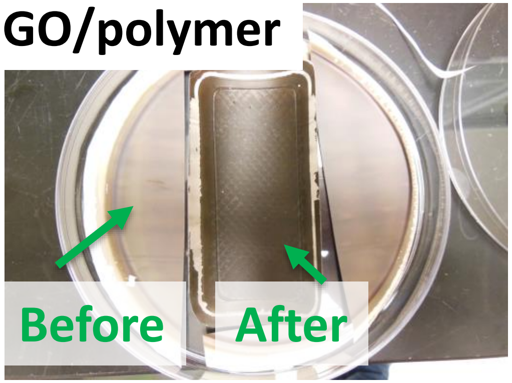
- **Pre-treatment**: Pre-filtered through a 0.2-µm filter to remove suspended solids
- Clean-in-place: **None needed**



Dow BWRO membrane



GO/polymer



After 1 month, BWRO membrane permeance dropped 10x to 0.3 LMH/bar. GO/polymer permeance is stable at 0.1 LMH/bar.

Current work: Investigating the membrane structure-property performance relationship

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Durability

- GO/PES tolerant to repeated 1-3 mg/L chlorine doses
- Minimal biofouling observed after month-long desalination tests

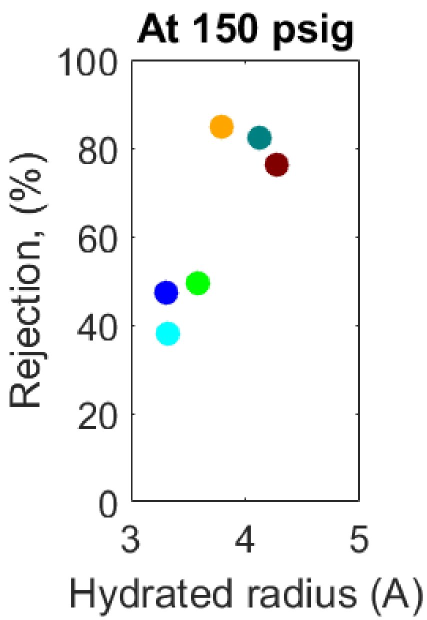
Rejection

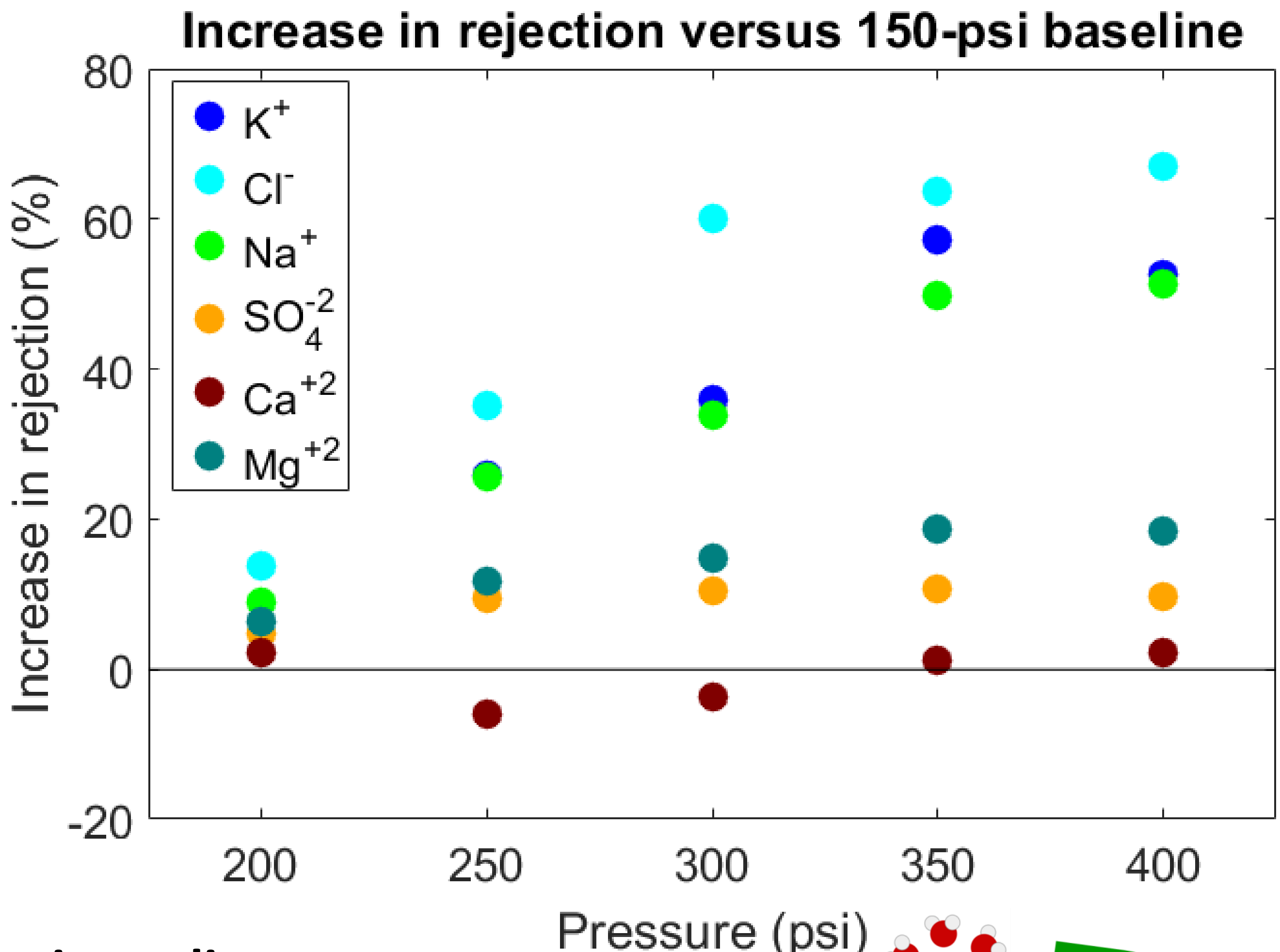
- >98% for brackish water RO (BWRO) membranes
- GO/PES have 70-90% rejection for divalent ions in cross-flow measurements

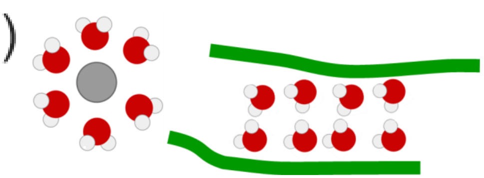
Permeance = flux/pressure:

- Commercial BWRO membranes have permeance ~ 3 LMH/bar
- GO/PES have permeance ~0.1-0.2 LMH/bar

Divalent ion rejection saturates at ~250 psi







Feed water is W. Phoenix cooling tower water.
Chlorine doses were 1-3 mg/L.

GO/polymer membranes robust in cross-flow test conditions

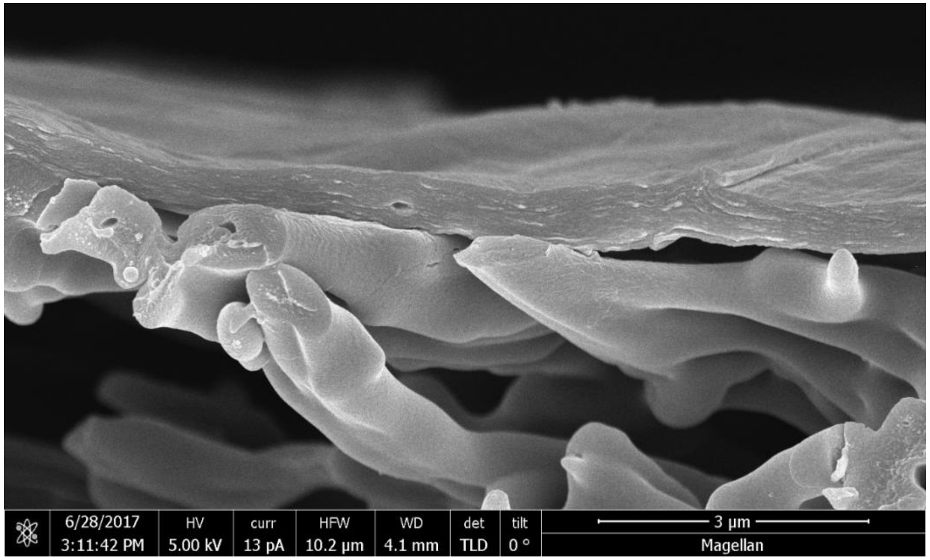
Reference	GO thickness	Permeance (LMH/bar)	Pressure (bar)	Rejection	Test conditions	TRL
BWRO, brackish water RO	Polymer membranes	3	30	99% for 10 mM $MgSO_4$	Cross-flow	**9**
Our work	**500-700 nm**	**0.1-0.2**	**5-25**	**80-95% for 10-100 mM SO_4^{2-}**	**Cross-flow**	**3-4**
Hu 2013	5-50 nm	80-280	0.34	10-20% for 20 mM NaCl; 30-45% for 10 mM Na_2SO_4	Dead end	1
Joshi 2014	1 µm	~10	25	K^+, Mg^{2+} permeate at 2 mol/h m^2	Osmotic	2
Xia 2015	10s of nm	27	0.4	12% DOC removal (~1000 Da)	Dead-end	1
Abraham 2017	100 µm	0.5 – 1.0	15	97% for NaCl	Osmotic; Evap.	1

Dow BW30 FILMTEC membrane spec sheet.
M. Hu and B. Mi, *Environ. Sci & Tech., 47,* 3715-3723, (2013).
R. Joshi *et al. Science.* 343, 752-754 (2014).
S. Xia *et al. Desalination* 371, 378-387 (2015).
J. Abraham *et al. Nature Nano* DOI:10.1038 (2017).

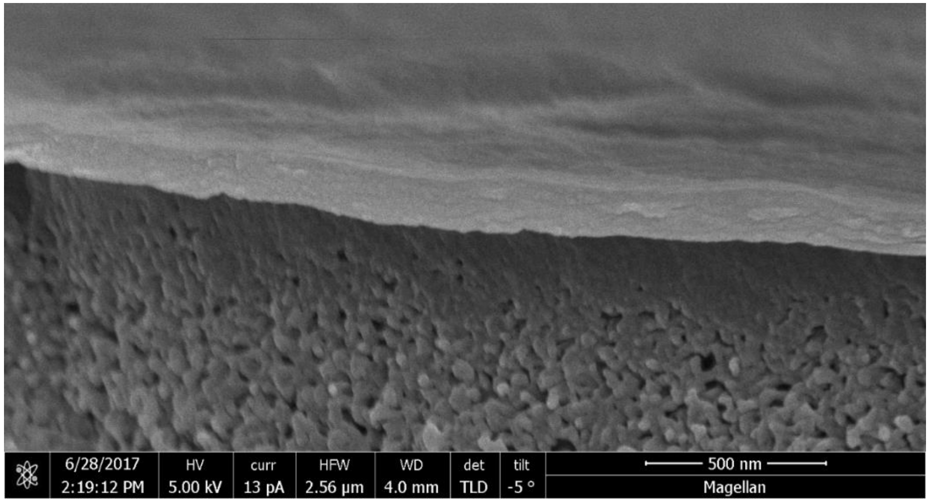
TRLs assigned by test condition and feasibility of scale-up.

Increase permeance with thinner GO layers

GO thickness ~520 nm



GO thickness ~110 nm



For GO layers ~500—700 nm,
P = 0.1—0.2 LMH/bar
(*n* = 9 membranes)

For GO layers ~50—120 nm,
P = 0.3—1.1 LMH/bar
(*n* = 3 membranes)

Rejection of emerging contaminates of concern (CECs) at low pressure

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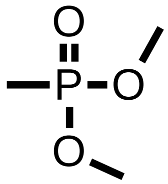
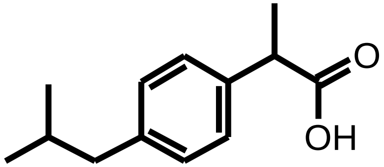
	Feed conc. (ppm)	Permeate conc. (ppm)	Rejection at 100 psi (%)	Feed conc. (ppm)	Permeate conc. (ppm)	Rejection at 300 psi (%)
DMMP	96	7.0	**92.7%**	102.4	5.5	**94.6%**
Ibuprofen	10.6	93 ppb	**99.1%**	10.4	111 ppb	**98.9%**
Chlorate	68.5	18.5	**72.9%**	70.6	9.7	**86.2%**
Nitrate	50.0	3.3	**93.5%**	49.1	nd	**100%**
Phosphate	76.3	3.9	**94.8%**	71.2	2.2	**96.9%**
Sulfate	352.9	6.6	**98.1%**	365.1	4.9	**98.7%**

DMMP



dimethyl methyl phosponate,
a chemical weapon and pesticide surrogate

Ibuprofen



- Chlorate is on EPA contaminate candidate list (CCL-4)
- Phosphates, nitrates from agriculture run-off

Est. 60-nm thick GO layers; permeance = 0.4 LMH/bar

Conclusions

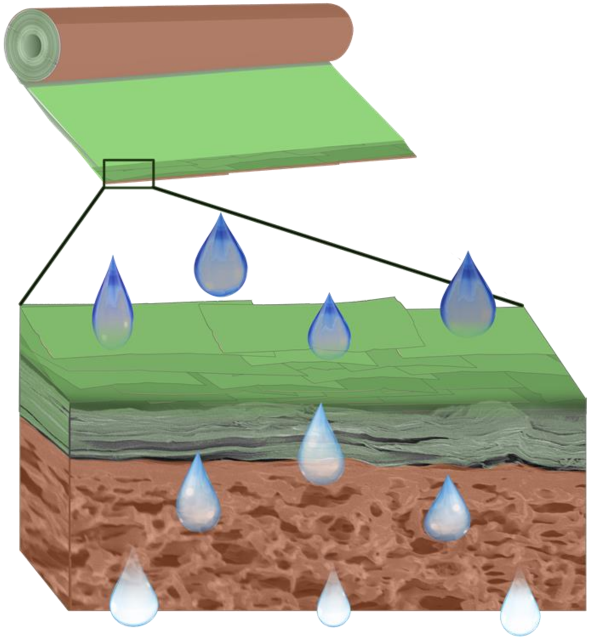
GO/PES membranes are robust enough to withstand cross-flow desalination operating conditions in month-long tests.

Recycling cooling tower water

- Demonstrated tolerance to 1-3 ppm bleach
- Constant permeance indicates minimal membrane scaling

CEC rejection

- >94% rejection of DMMP and ibuprofen
- Permeance increases with decreasing laminar GO thickness



Acknowledgements

Current research team: Michael Hibbs, Curt Mowry, Adam Pimentel, Trey Pinon, Craig Stewart, Mary Louise Gucik, and Kevin Zavadil

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

Funding

Polaris project with EPRI
Richard Breckenridge, program manager