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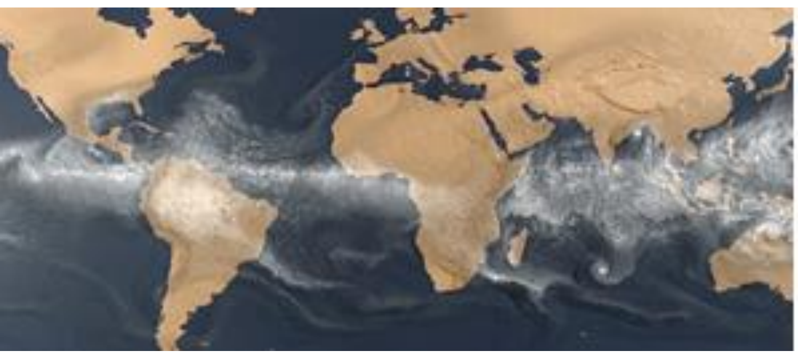

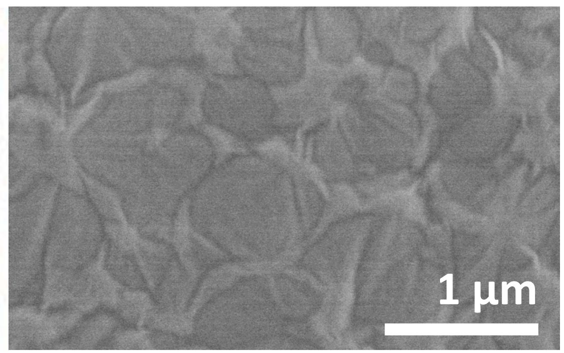

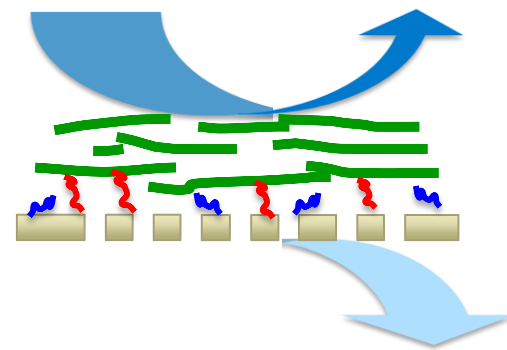

GO desalination membranes

Laura Biedermann, lbieder@sandia.gov

Susan Altman, Michael Hibbs, Curt Mowry, and Kevin Zavadil

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Outline

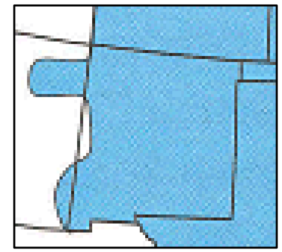
Sandia National Laboratories

Sandia's interest in desalination membranes

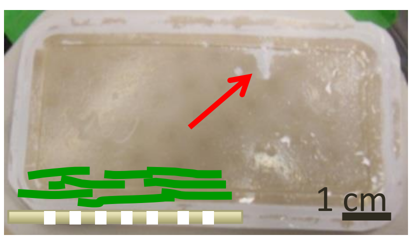
Produced water

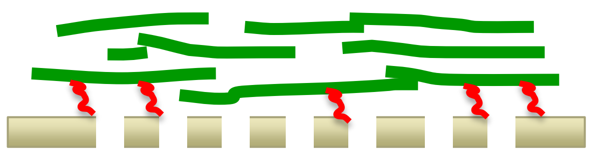
DOE NE, EPRI

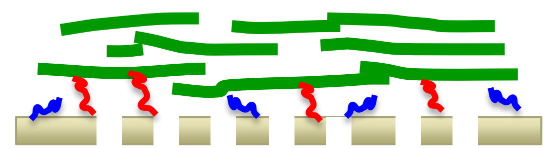
NM brackish aquifers



Design and performance of GO/polymer composite membranes







Challenges ahead

Conclusions

Chemically robust desalination membranes are required for complex water streams

Evaporation pond for produced water

US Army: 3000 gallon water bladder in Pakistan

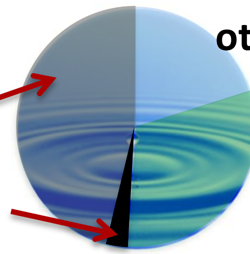
Images courtesy netl.doe.gov and darpa.gov

Desalination of brackish water would increase resiliency of wet-cooled power plants

US freshwater withdraws:

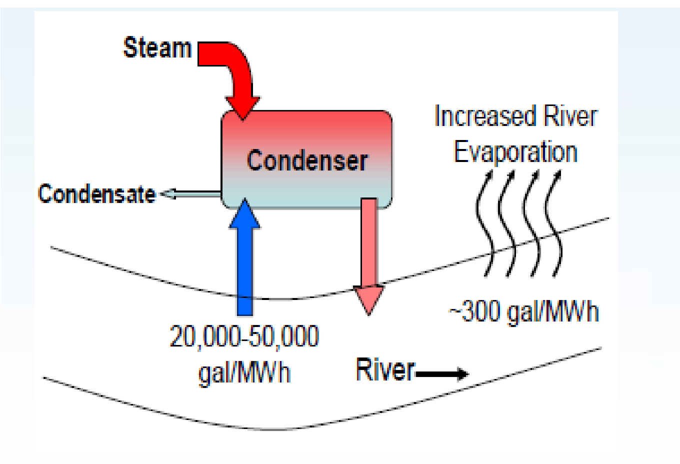
Thermal power plants:

- Water returned to the environment
- Evaporated water (3%)



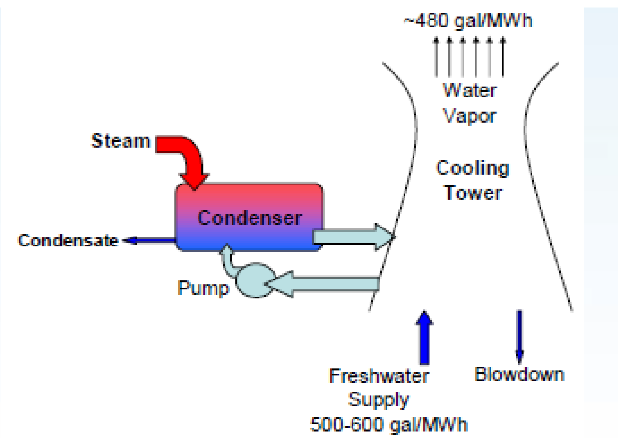
Once-through Cooling

Impact: 20,000 – 50,000 gal/MWh



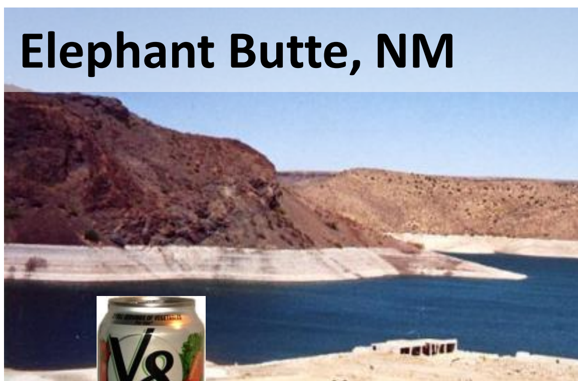
Closed-Loop (Evaporative) Cooling

Impact: 500-600 gal/MWh

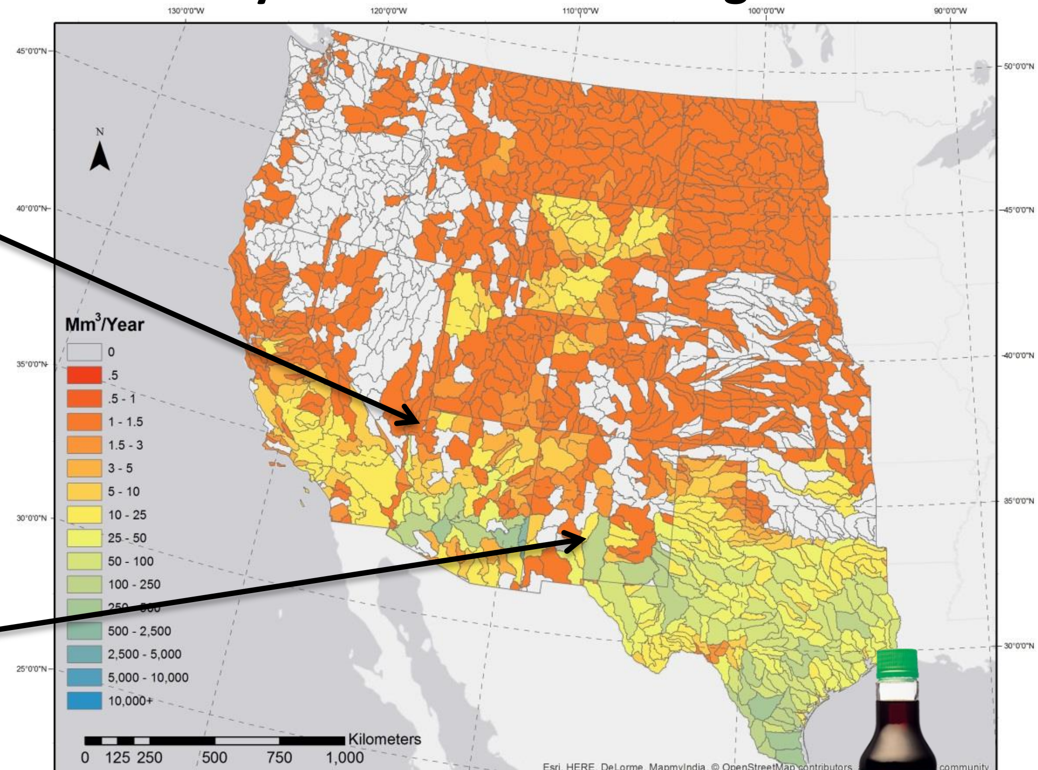


Slide courtesy Mike Hightower

Brackish water is abundant in the US



Availability of shallow brackish groundwater



brackish | **sea water**

1000—10000 ppm | **35,000 ppm**

Ideal properties of nanoscale-enabled desalination membranes

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	5 ppm	< 0.1 ppm

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

Graphene and graphene-oxide are related robust nanosheet materials

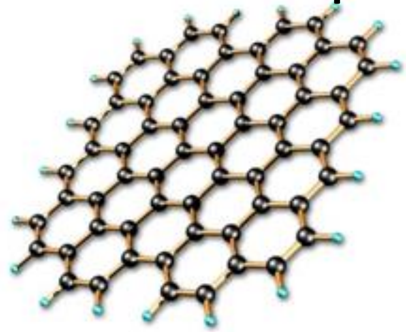
Natural graphite

Mechanical exfoliation

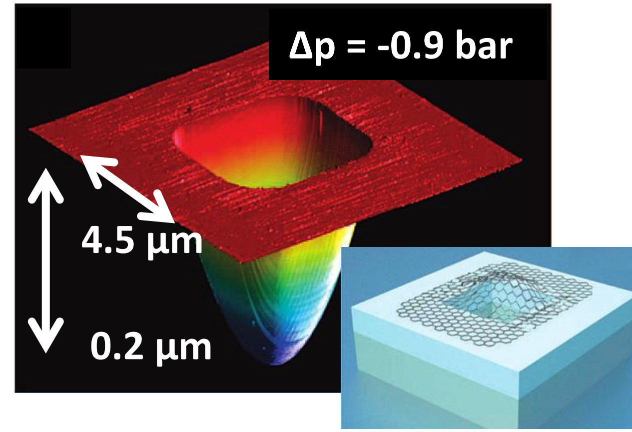
Chemical oxidation

Graphene

Hexagonal carbon network forms the basal plane

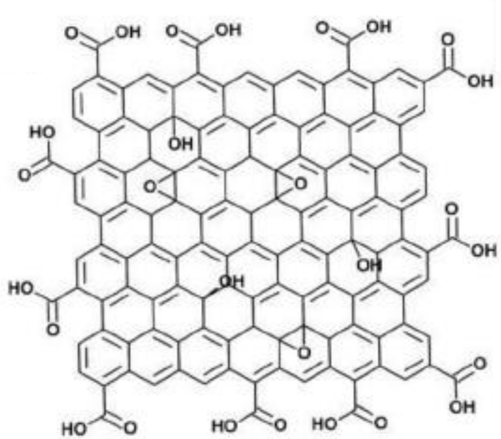


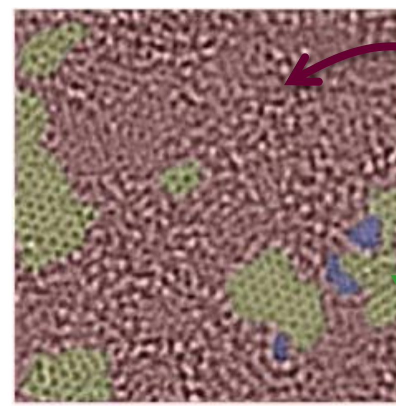
A pristine graphene membrane is impervious to gasses



Graphene Oxide (GO)

oxygen functional groups decorate the basal plane





oxidized domains

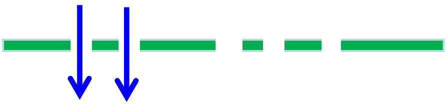
graphitic domains

G. Eda and M. Chhowalla, *Adv. Mater*. 2010

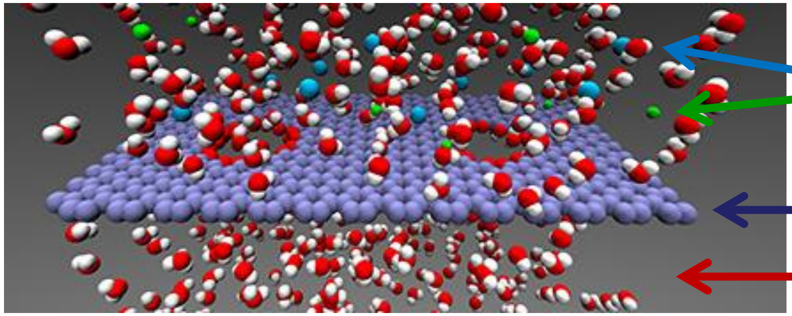
J. Bunch *et al.*, *Nano Lett* 8 (2008).

Two proposed structures for graphene-based desalination membranes

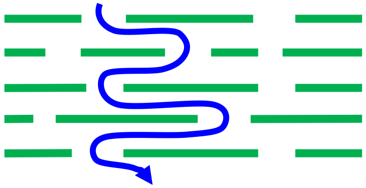
Permeation through nanoporous monolayer graphene



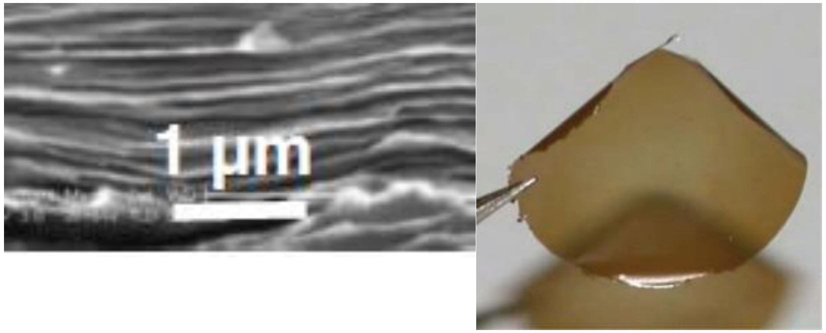
[1]



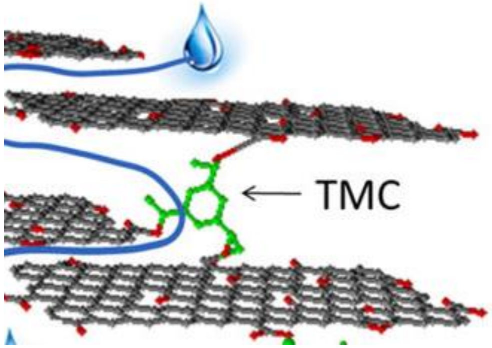
Permeation around GO sheets in laminar GO membranes



[2]



[3]

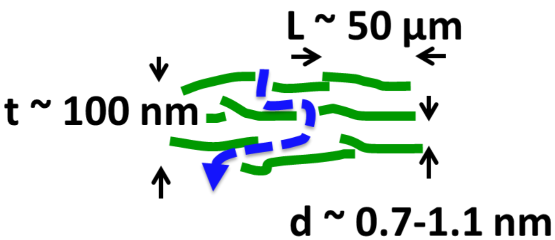


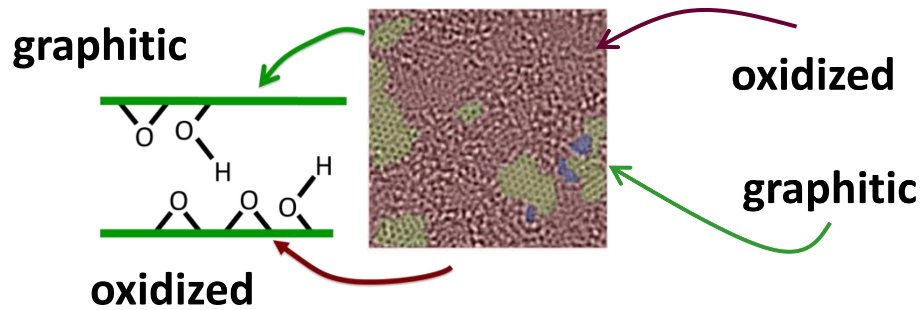
Theory and experiment suggest that nanosheet-based desalination membranes will have 10x-100x flux of current technologies, revolutionizing low-energy water production and recycling.

[1] Lockheed Martin Perforene membrane; [2] R. Nair *et al., Science* 335, 442-444 (2012); [3] B. Mi *et al.*

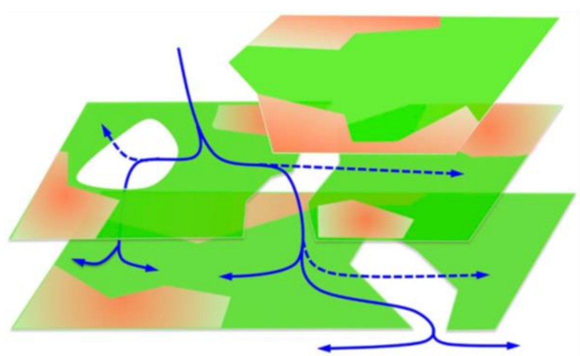
Nanoscale graphene oxide (GO) structure enables low energy desalination

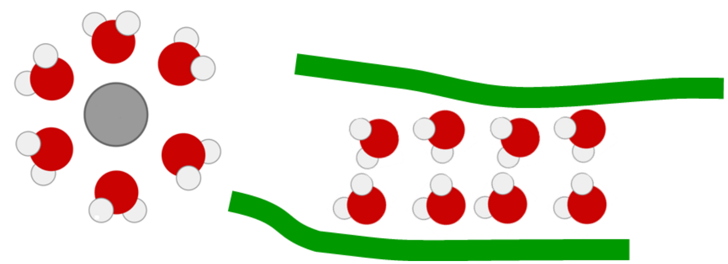
Thin-slit permeation pathway defined by oxygen moiety "nanopillars"





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)

Vacuum-filtration directed assembly of GO on polymer membrane supports

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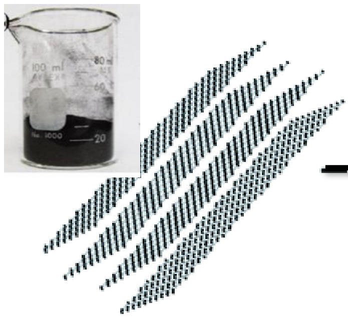
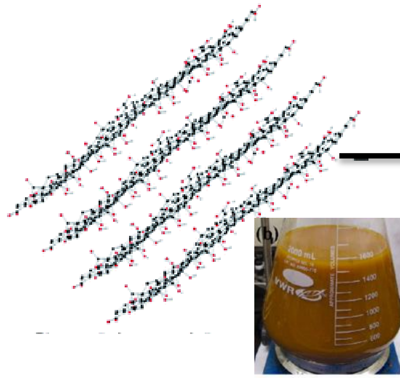
graphite | **graphite oxide** | **graphene oxide**



Oxidation →

HPO_4, H_2SO_4, $KMnO_4$

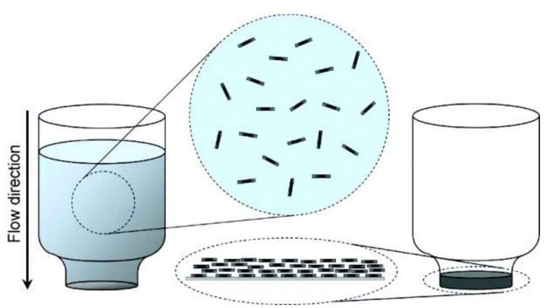


Exfoliation →

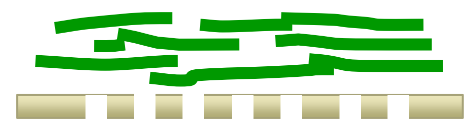
1 M HCl wash

Material cost: \$0.10/m^2 for a 100-monolayer GO membrane

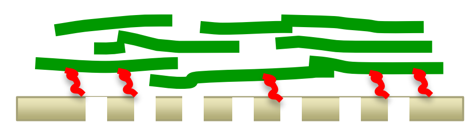
GO sheets are re-dispersed in a dilute filtration suspension and vacuum-filtered onto a porous polymer membrane



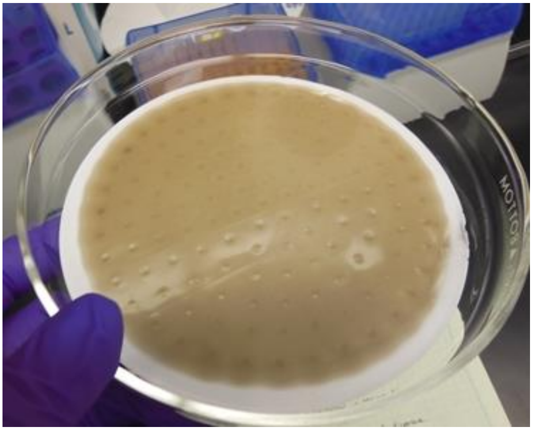
polyethersulfone (PES)



functionalized polyester (PET)



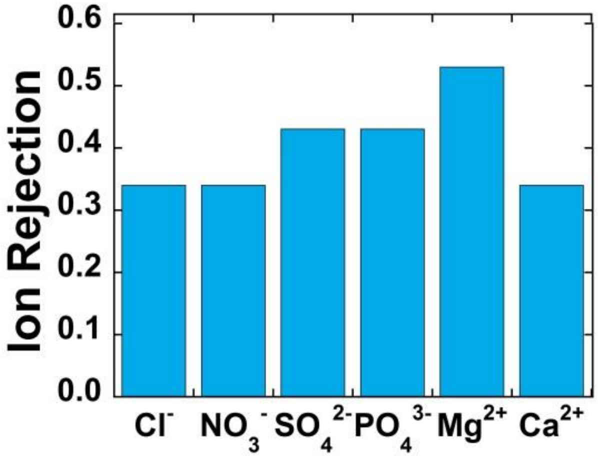
GO/PES membrane: Moderate ion rejection following 60-100 ppm bleach exposure



~100 GO monolayers on a polyethersulfone (PES) membrane, 124-mm diameter

Dead-end filtration (post-bleach)

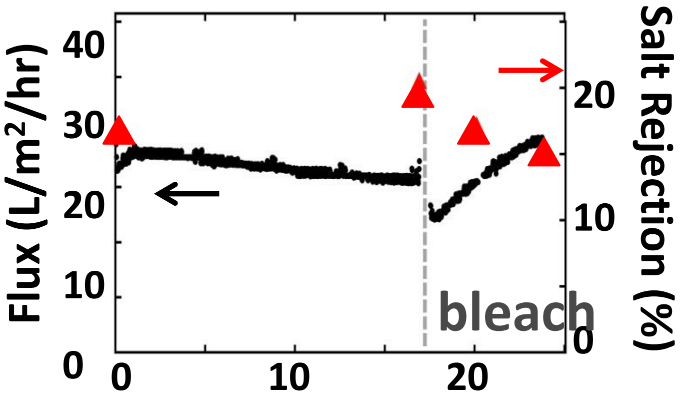
Flux ~10 L m^{-2} h^{-1} at 1 bar



Following 100 ppm, 30 min bleach

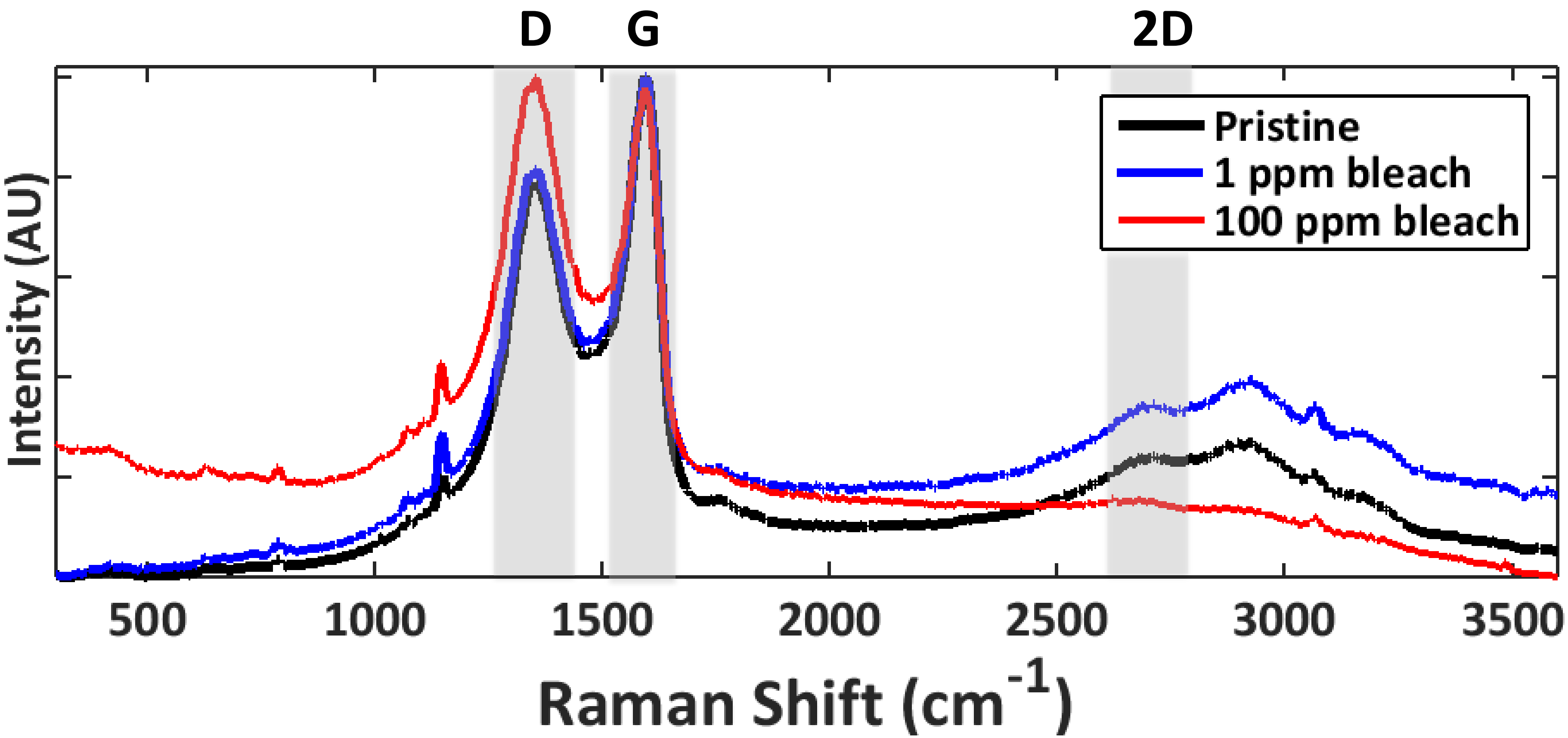
Cross-flow filtration

Flux ~25 L m^{-2} h^{-1} at 14 bar



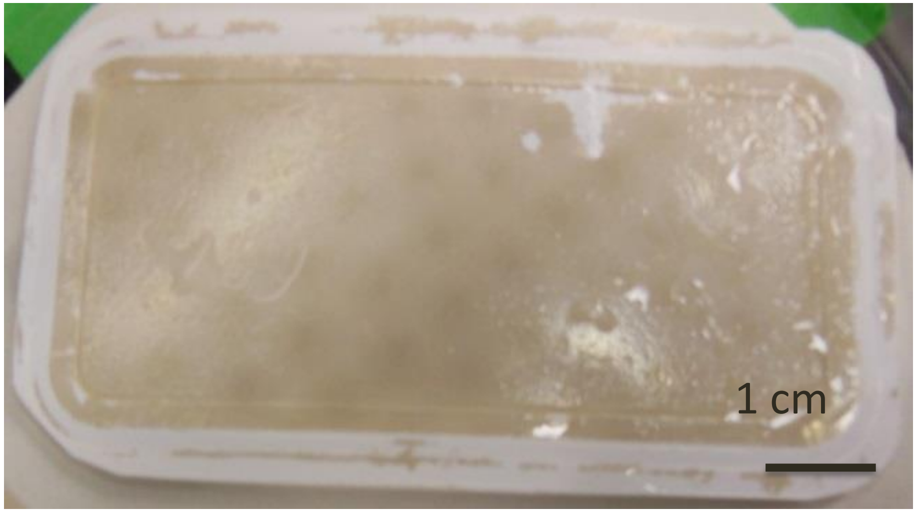
1200 ppm $MgSO_4$; 60 ppm bleach

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

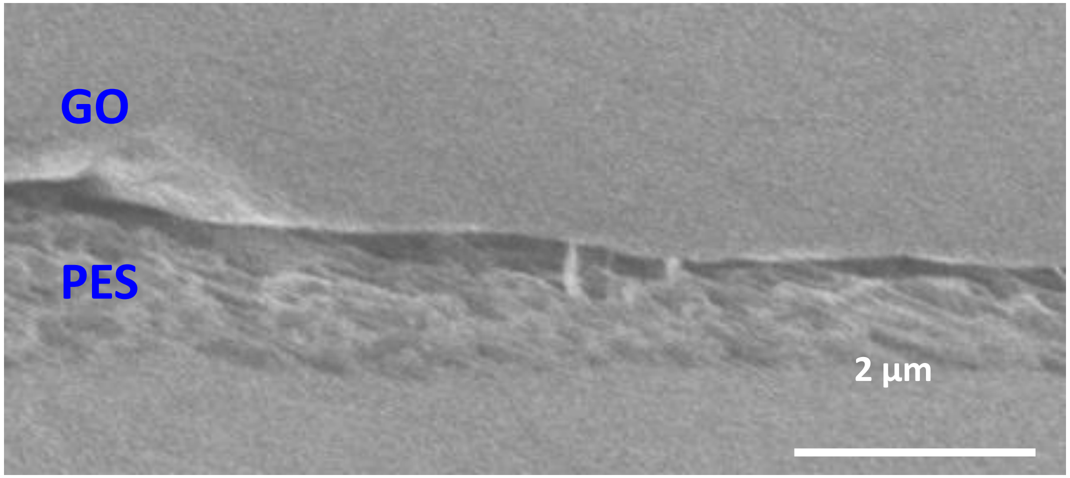


Low-levels of chlorination (~1—5 ppm) will minimize biofouling in greywater recycling

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



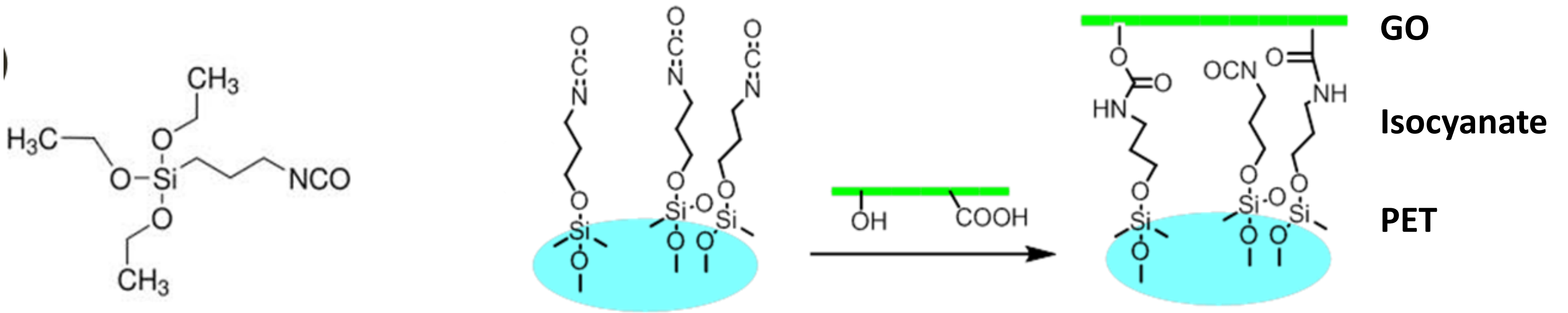
Delamination following 1 ½ -day permeation test at 14 bar and 8-hour exposure to 60-ppm bleach.



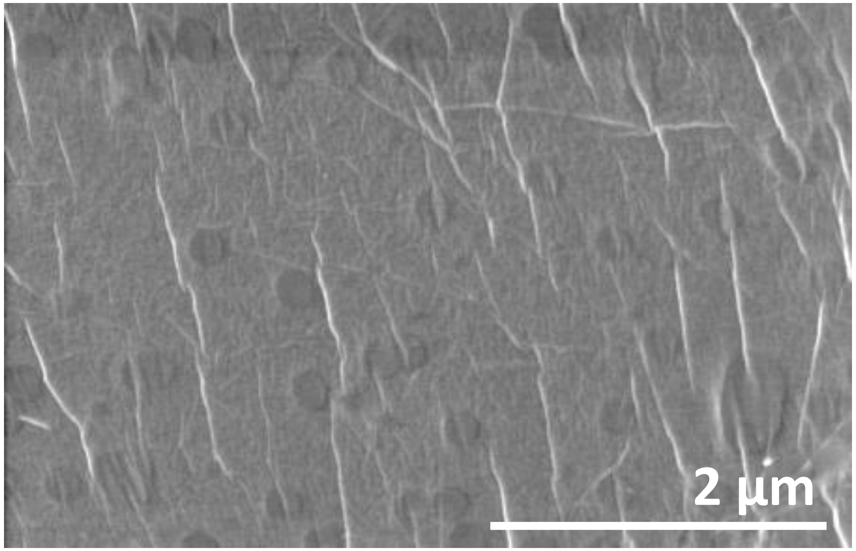
Representative delamination at the GO/PES interface.

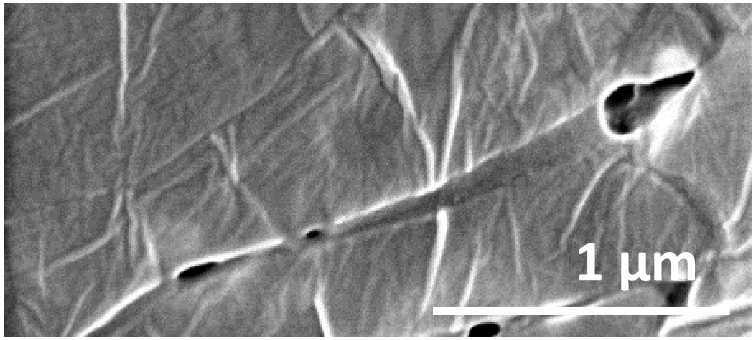
Will covalently binding GO to PES prevent delamination of the laminar GO?

Covalent linking isocyanate agents prevent delamination of the laminar GO



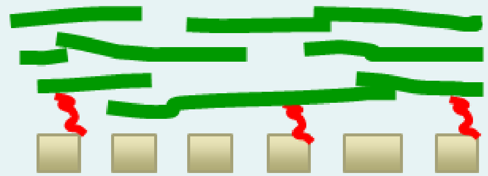
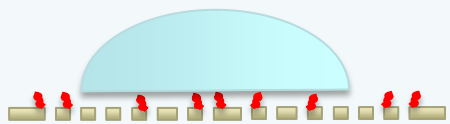
GO/Isocyanate/PET, following permeation tests





Effective isocyanate binding, even over fractured PET

Hydrophilic polymeric membrane interfaces required for high flux GO membranes

	Isocyanate only
Functional groups	
Contact angle	45° 
Permeance ($L\ m^{-2}\ h^{-1}\ bar^{-1}$)	0.5
Power needed (W/L)	0.3
Sulfate ion rejection	80 %

Dead-end permeation tests

Challenges ahead for GO-based desalination membranes

Increase hydrophilicity of GO/PET interface
Optimize GO/PET separation distance

Determine rejection of monovalent salts

Resistance to biofouling and scaling is unknown

Scale-up to spiral-wound membrane elements

C. Yeh *et al, Nature Chem* 2015 (DOI:10.1038/NCHEM.2145)

Conclusions

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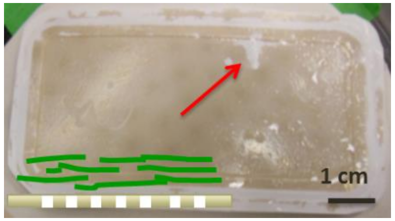
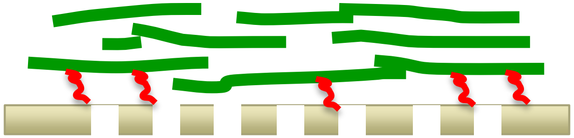
No cross-linker molecules



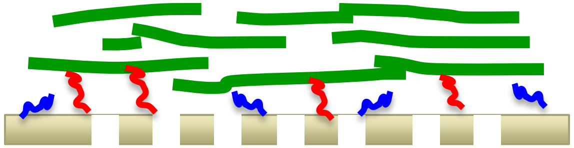
1.8 L m^{-2} h^{-1} bar^{-1}
Sulfate ion rejection: 15-20 %

Slightly hydrophilic



0.5 L m^{-2} h^{-1} bar^{-1}
Sulfate ion rejection: 80 %

More hydrophilic



2.1 L m^{-2} h^{-1} bar^{-1}
Sulfate ion rejection: 90 %

- **Covalent linking of the laminar GO to the polymer support is required for stability in cross-flow permeation**
- **Increasing the hydrophilicity of the GO/PET interface improves flux**
- **GO sheets are tolerant to 1 ppm chlorine, but degraded by 100 ppm chlorine**
- **Improved understanding of GO as a membrane material**

Acknowledgements

Sandia National Laboratories

Research team: Susan Altman, Michael Hibbs, Curt Mowry, and Kevin Zavadil

Additional collaborators: Thomas Beechem and Katharine Harrison

Funding:

Laboratory Directed Research & Development

NMSBA
Los Alamos National Laboratory
Sandia National Laboratories

New Mexico Small Business Administration (NMSBA) collaboration with WEN Engineering

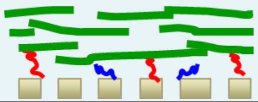
Laura Biedermann, lbieder@sandia.gov

Lagniappe

Predicted performance metrics

Metric	Target (GO)	Current (GO)	Commercial RO (Dow FilmTec)	Path forward
Permeance (energy)	>10 L m^{-2} h^{-1} bar^{-1}	0.5-2 L m^{-2} h^{-1} bar^{-1}	0.7-2.9 L m^{-2} h^{-1} bar^{-1}	Increase interface hydrophilicity and polymer porosity
Flux				
Driving pressure	< 2 bar	3 bar	11.5 bar (brackish) 55 bar (sea water)	Increase interface hydrophilicity and polymer porosity
Chlorine tolerance (lifetime)	5 ppm; >10^5 ppm-hours	> 1 ppm; >= 600 ppm-hr	<0.1 ppm	Accelerated lifetime tests for chlorine exposure
Salt rejection (efficiency)	> 95%, divalent > 90 %, monovalent	80—90 % for SO_4	> 99% for NaCl, ideally ~90—95 %, in field	Increase membrane uniformity
Recovery (efficiency)	> 80 %	Not yet tested	25—50 %	Depends on max TDS
Duration between cleaning	3 months	Not yet tested	30 days Lifetime, 2-5 years	
Biofouling resistance				
Silicate fouling resistance				

Next step: Increasing flux by tuning interface hydrophilicity and substrate porosity

Functional groups	Isocyanate only 	Isocyanate and PEG 
Contact angle	45°	40°
Permeance (L m^{-2} h^{-1} bar^{-1})	0.5	2.1
Sulfate ion rejection	80 %	90 %

Increase hydrophilicity of polymer support with silane-based functional groups

Isocyanate functional groups ( ) covalently bind the laminar GO to the polymeric support.

Adding non-binding hydrophilic polyethlyene glycol (PEG,) increases permeance and ion rejection.

Increase interface hydrophilicity

- Synthesize novel covalent linker molecule with a hydrophilic polyethlyene glycol backbone and isocyanate and trimethoxy silyl end groups to bind to the GO and polymer, respectively

Increase substrate porosity from current 200-nm pore size

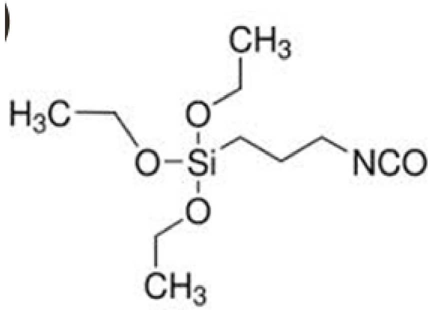
- Determine maximum porosity that supports self-assembly of laminar GO membranes

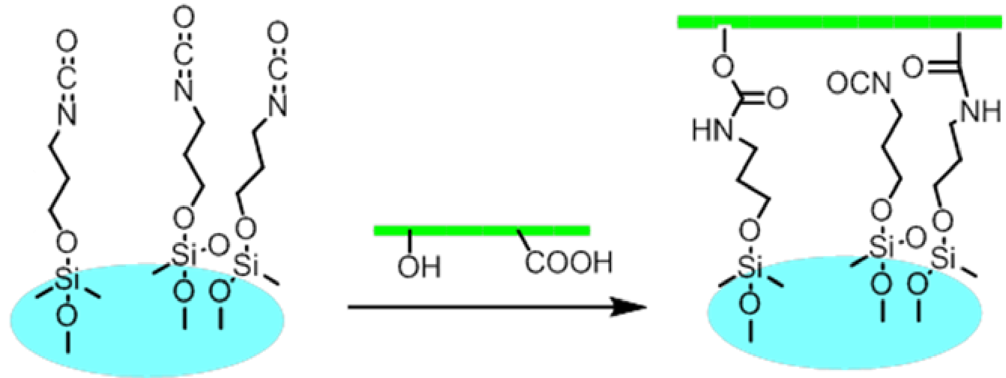
Determine maximum total dissolved salts (TDS), which impacts recovery

- Conduct cross-flow permeation measurements with increasing salinity of feed water

Flux through permeable GO membranes on porous polymeric supports is dominated by the interface chemistry and surface energetics

Isocyanate covalent binding chemistry





(3-isocyanatopropyl)triethoxysilane forms a polysiloxane coating via silanization of the polymeric support at hydroxyl groups. The isocyanate forms urethane or amide bonds with the GO when it reacts with hydroxyl or carboxyl groups, respectively.

To increase the hydrophilicity of the functionalized PETE membranes, additional membranes were prepared with a mixture of isocyanate and 2-[methoxy(polyethyleneoxy)$_{6\text{-}9}$ propyl]-trimethoxysilane (PEG). Weight percentages of the siloxane agents were held at 5—6% in toluene. Three weight ratios of isocyanate:PEG were used (5:1, 1:1, and 1:5). As with the membranes treated with only isocyanate, the isocyanate:PEG membranes were rinsed in toluene. In this report, functionalized GO membranes refers generically to GO/APTMS/PETE, GO/Isocyanate/PETE, and GO/Isocyanate:PEG/PETE membrane samples

USGS: A coal-fired thermoelectric power plant