SAND2014-20445C

Switchable Anti-biofouling Coatings

December 15, 2014

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Marine Hydrokinetic Technologies (MHK)

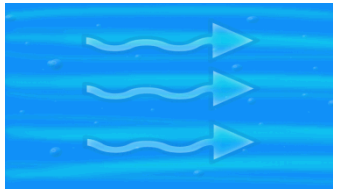
- Engineered turbines and buoys harvest energy from tides and currents

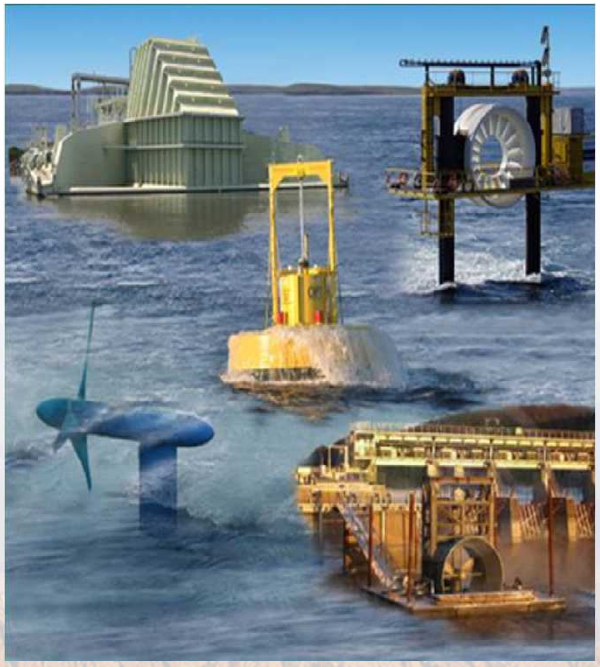
- Verdent RITE East River Project: 10 yr license for 30 Grid connected turbines

- Verdent Power: One turbine can power 20 to 30 homes (CBS News, 8/7/2013)

Wave

Tidal/Current





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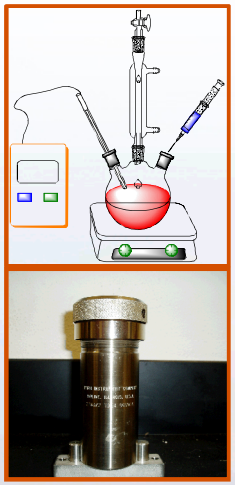
MHK Advanced Materials Program

Challenges: (1) environmental degradation (e.g., corrosion, biofouling, mineral fouling, sediment fouling/erosion, cavitation, etc.); (2) component materials reliability; (3) environmental impact (toxicity).

Impact: development cycle, component selection, performance, reliability, O&M, cost.

Program Approach: **Industrial Guidance** **Technology Transfer** **Novel Materials & Coatings**

Novel Coatings Synthesis

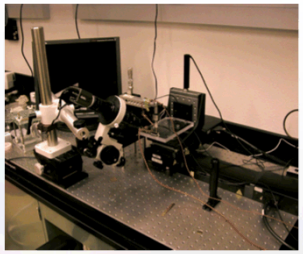


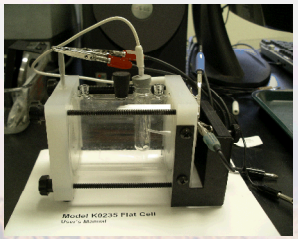
SNL, BYU

Biofouling Testing

SNL, NDSU

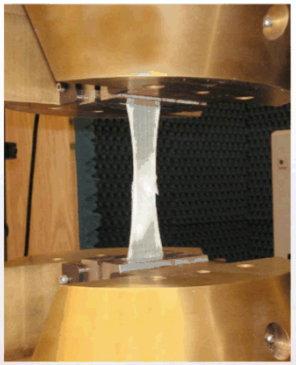
Corrosion/Reliability Testing





SNL

Composite Fabrication & Performance Testing



SNL, MSU

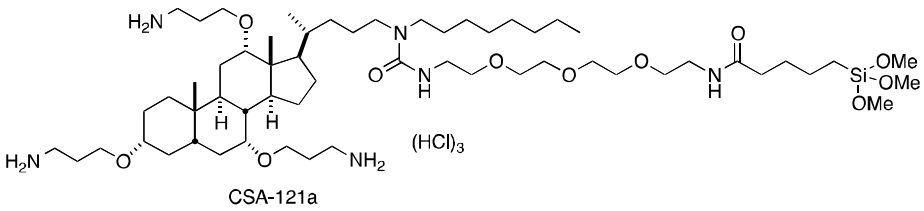
Environmental Monitoring

ORNL

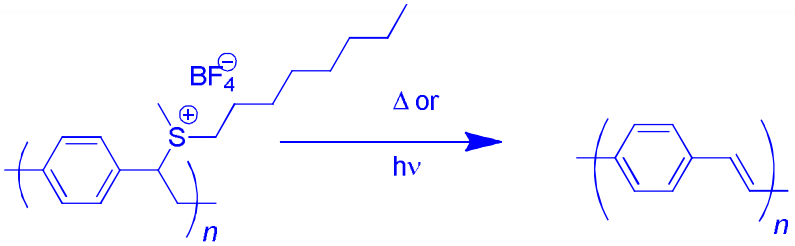
BYU MONTANA STATE UNIVERSITY OAK RIDGE National Laboratory Sandia National Laboratories

Coatings & Materials– R&D Examples

Synthesis of Antifouling & Anticorrosion Coatings



Ceragenins (P. Savage)



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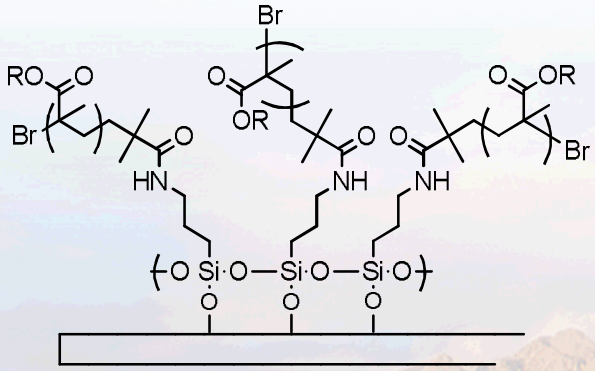
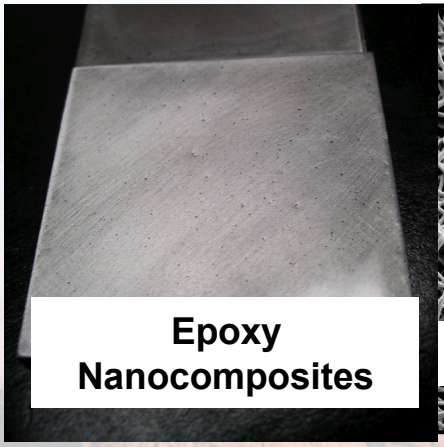
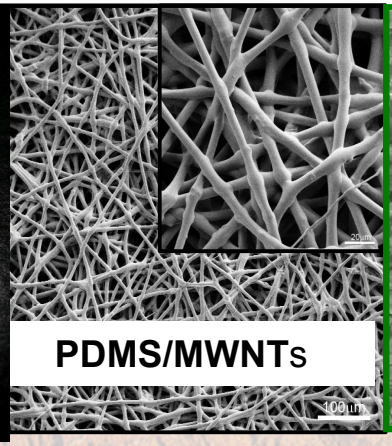
Polysulfonium (S. Dirk)[1]

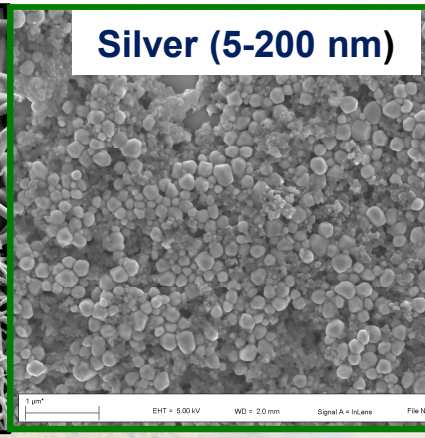
Zwitterionic (M. Hibbs)



Nanobased Coatings (BAHS & Dirk)



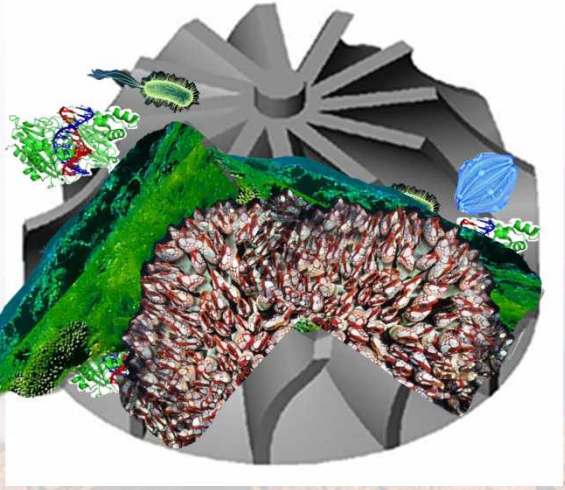




Sandia National Laboratories

Biofouling and MHK Technologies

- Fast accumulation of micro and macro organisms
  - Conditioning film, bacteria and singe cell diatoms, biofilms, algae, barnacles
- Increases weight, hydrodynamic friction and corrosion
- Reduces efficiency of MHK technologies



ocean.si.edu

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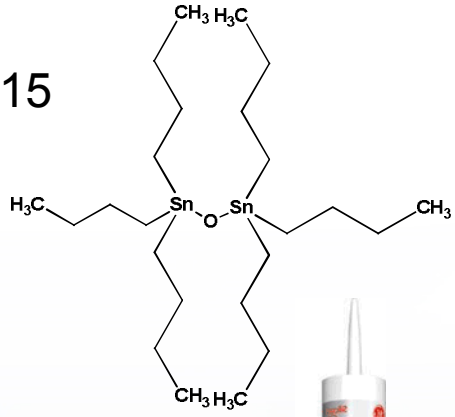
Anti-biofouling Coatings Overview

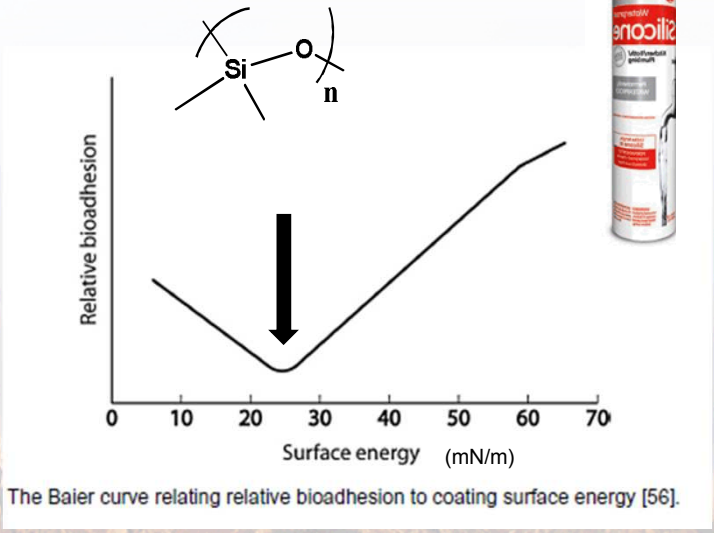
- Biofouling a problem for centuries
  - Coatings used to prevent/delay biofouling
  - US market for antibiofouling to reach $978.7 million by 2015

- Traditional Commercial Coatings - Biocides
  - Leachable Cuprous Oxide
  - Mercury and lead
  - Tributyltin (TBT)
  - Environmental concerns

- Next Generation of Coatings – low toxicity

- Polysiloxanes
  - Ideal surface energy prevents adhesion, easy release
  - Water resistant
  - Intersleek 700 and 900





The Baier curve relating relative bioadhesion to coating surface energy [56].

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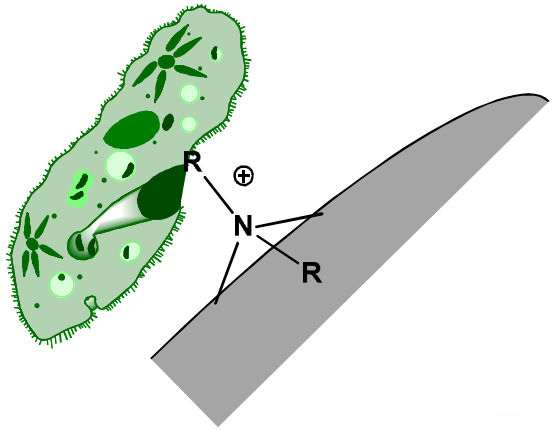
A Better Coating

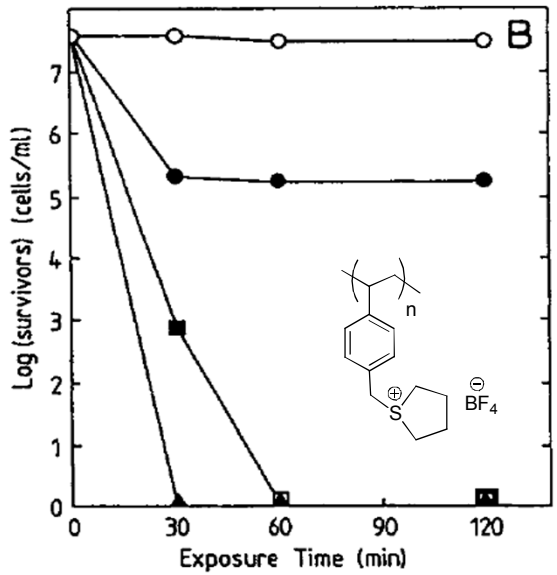
How can we build a better coating?

- Environmentally friendly– does not leach
- Antifouling –prevents microbial attachment
- Fouling release – Easy removal
- Switchable



Antimicrobial Salts in Coatings

- Sulfonium
- Quaternary Ammonium
  - Low Toxicity
  - Antimicrobial
  - Good leaving groups



(○) blank, (▲) 340 μM, (■) 34 μM; (●) 3.4 μM,

A. Kanazawa et. al, J. Polym. Sci. Part A: Polym. Chem. Vol. 31 (1993)

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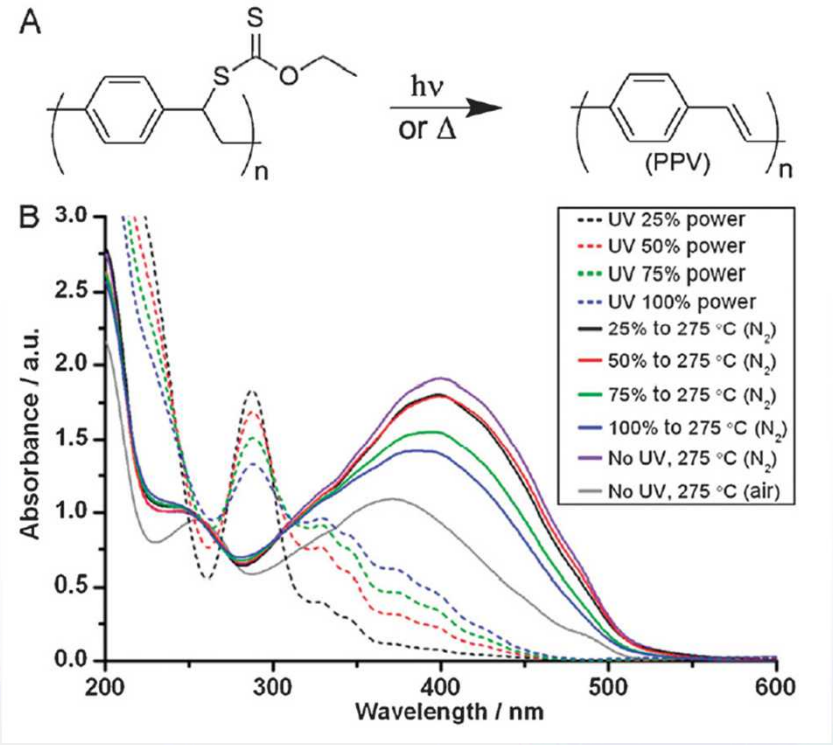
Switchable Chemistry

Previous work by our group:

Elimination of xanthate group results in p-phenylene vinylene (PPV)

- Thermally and photochemically switchable
- Elimination of xanthate group leads to a structural change and potentially a change in surface energy



R.S. Johnson et. al., *Chem. Commun.* **2011;** R.S. Johnson et. al., *Adv. Mater.* **2010**

K+

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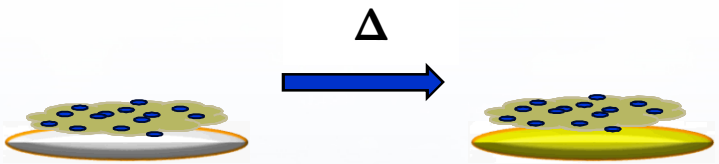
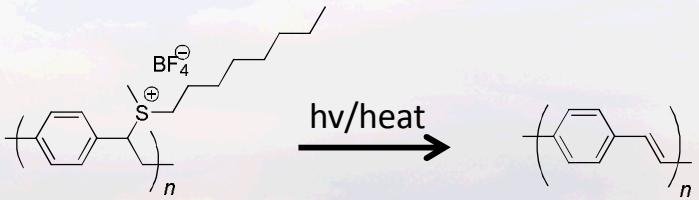
Proposed Mechanism

Polymeric salts act as a biocide and leaving group

- Salt and alkyl side chain acts as a biocide
- Heat conjugates material
- Accumulation removed by water shear force





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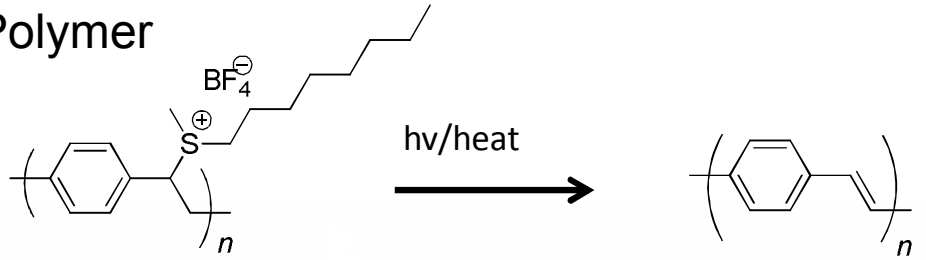
Three Versions of Salt Polymers Synthesized

Sulfonium Polyphenylene Vinylene Polymer



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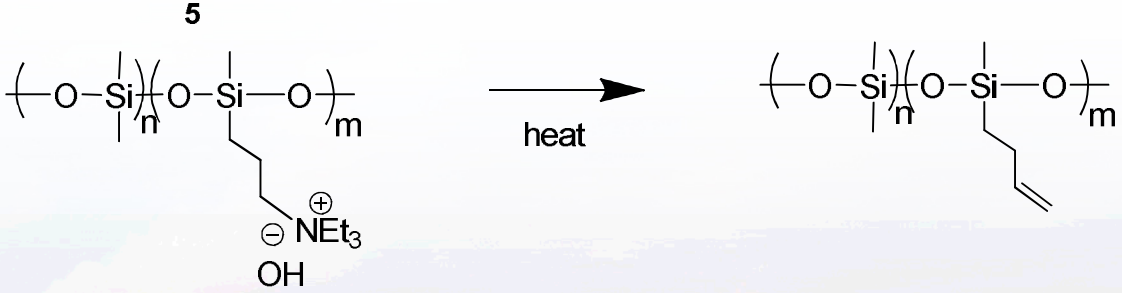
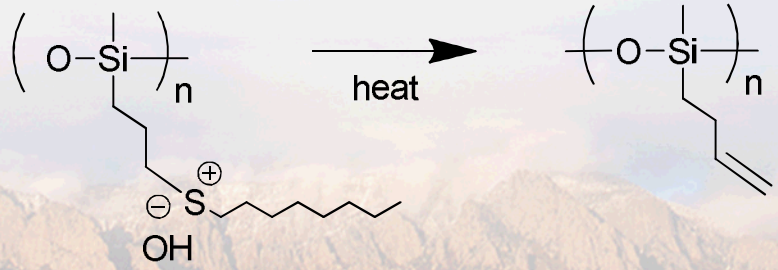
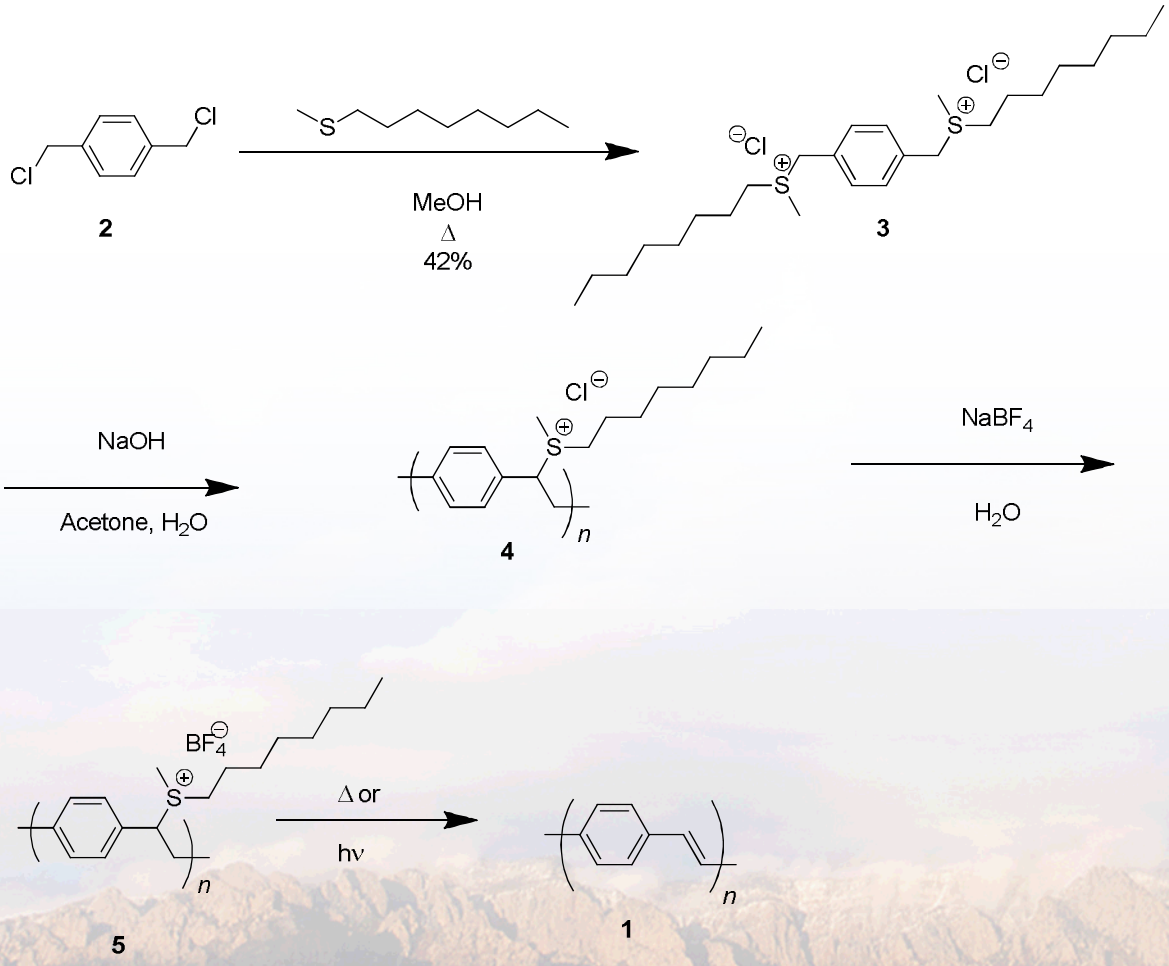
Ammonium Silane Polymer and Copolymer



Sulfonium Silane Polymer



Initial Sulfonium Polymer Synthesis



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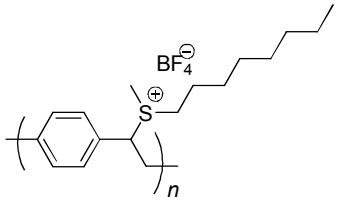
Evaluation Sulfonium Polymer Antibacterial Activity



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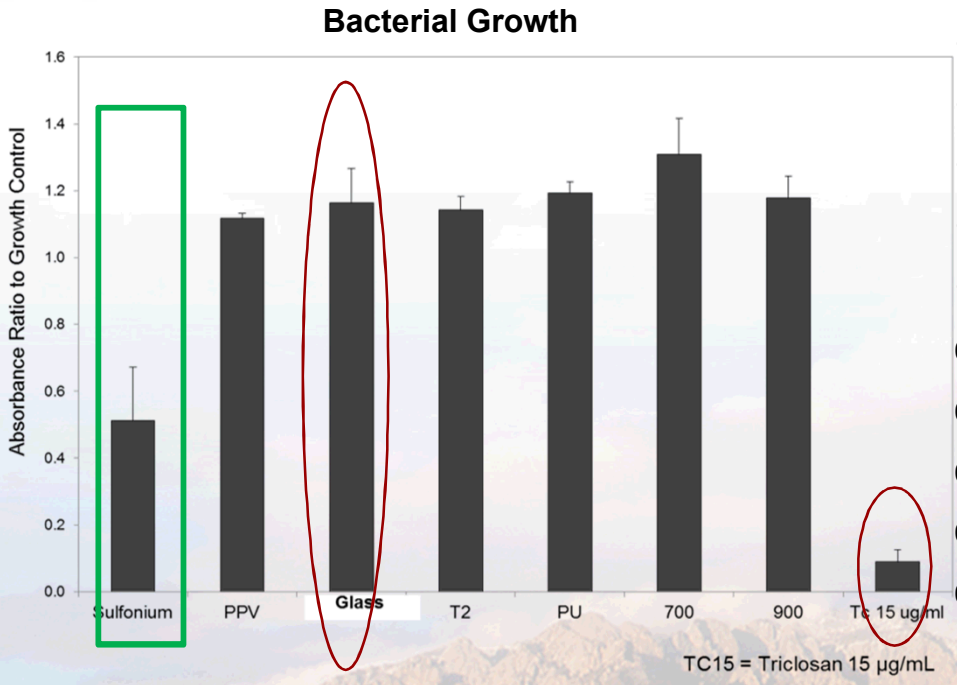
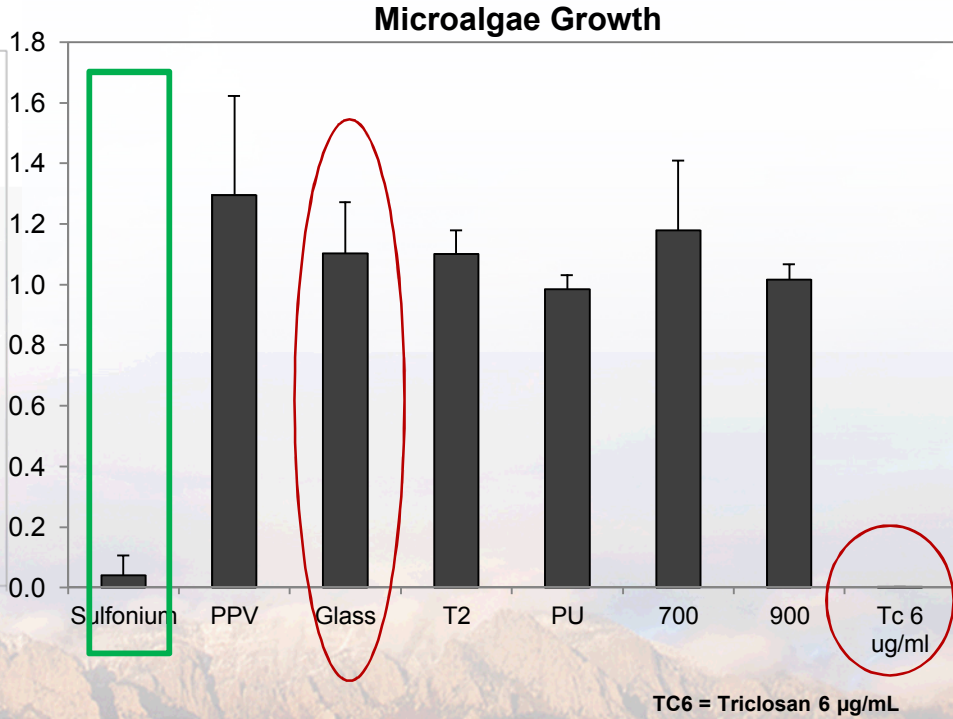
Results:

- Effective antimicrobial for bacterial and microalgae
- Water soluble





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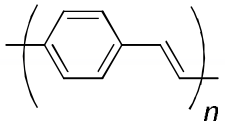
Evaluation of PPV Fouling Release



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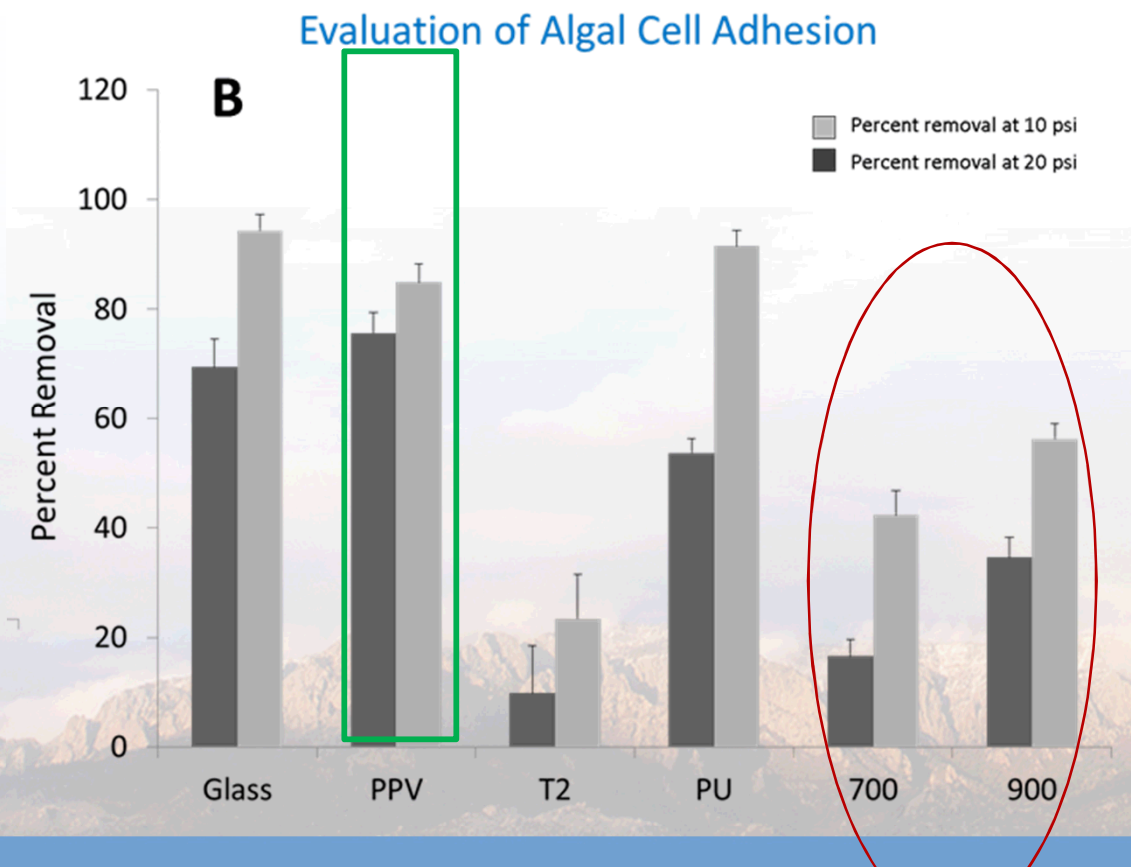
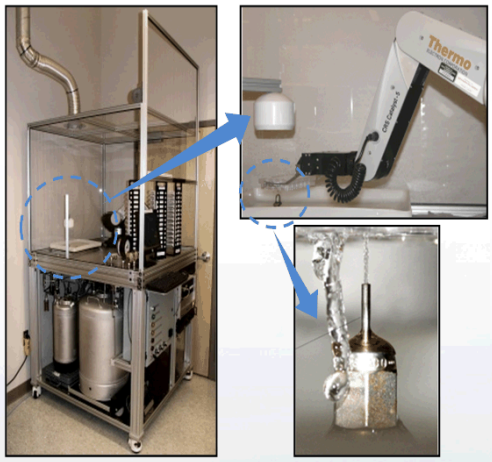
Results:

- More fouling removed with fouling release coating than with current commercial coatings



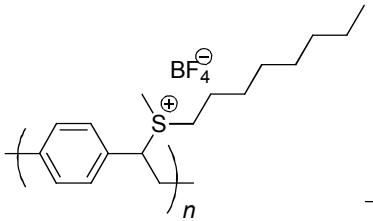


Water Jet Treatments

Summary of Polyphenylene Coatings

Achieved:

- Good antimicrobial activity
- Great fouling release activity
- One way switchable



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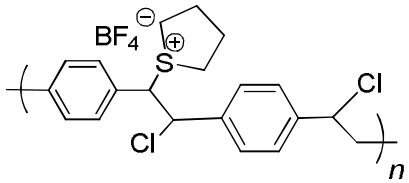
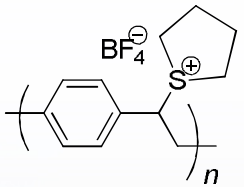


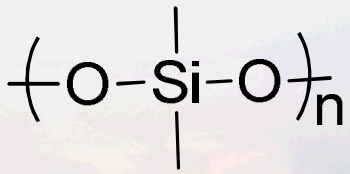
However:

- Reduction in water solubility through co-polymerization, led to reduced solvent solubility



Next approach:

- Siloxane backbone polymer
- Retain switchable properties



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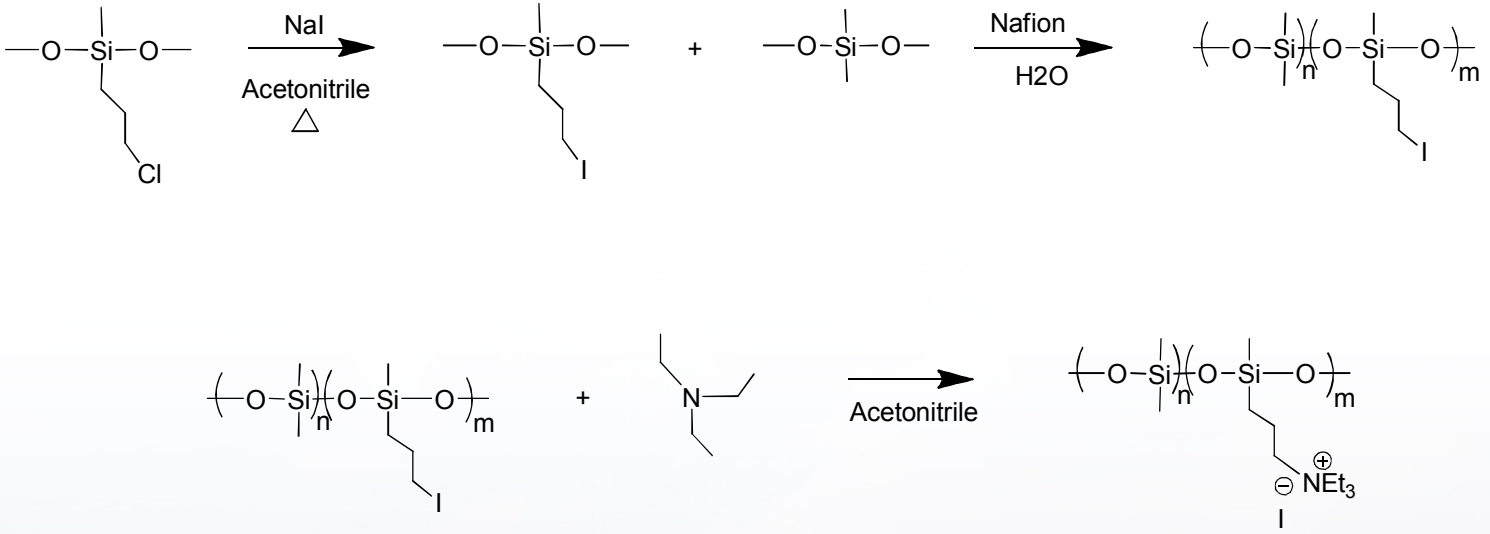
Ammonium Silane Polymer and Copolymer



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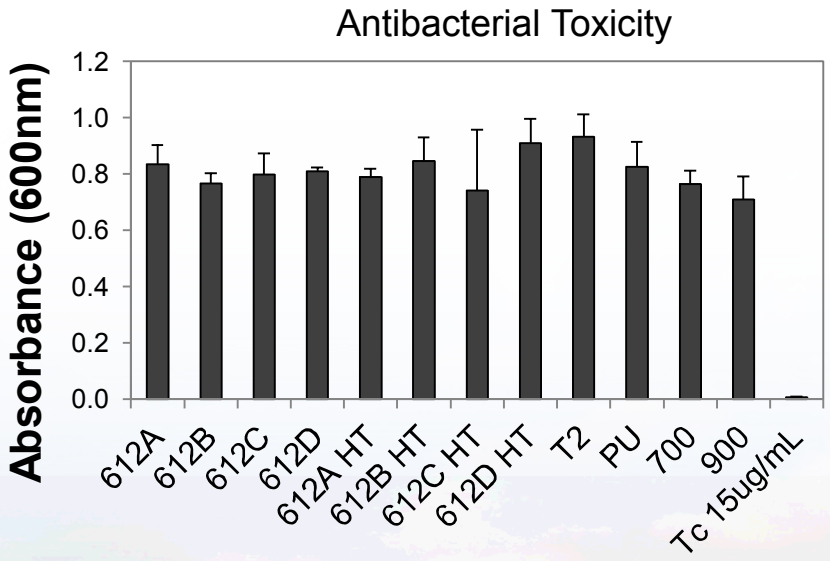
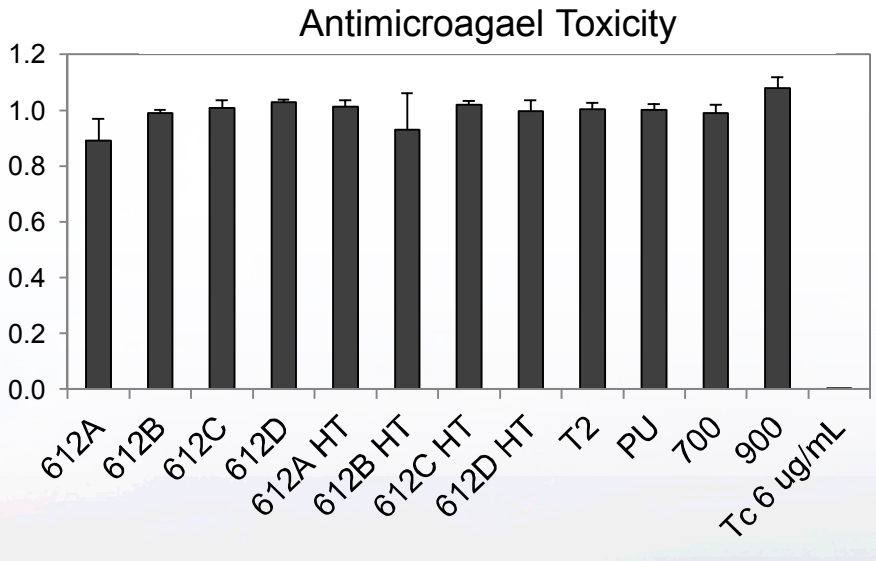
Leachate Tests Indicated No Water Solubility





Tc = Triclosan

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National Nuclear Security Administration

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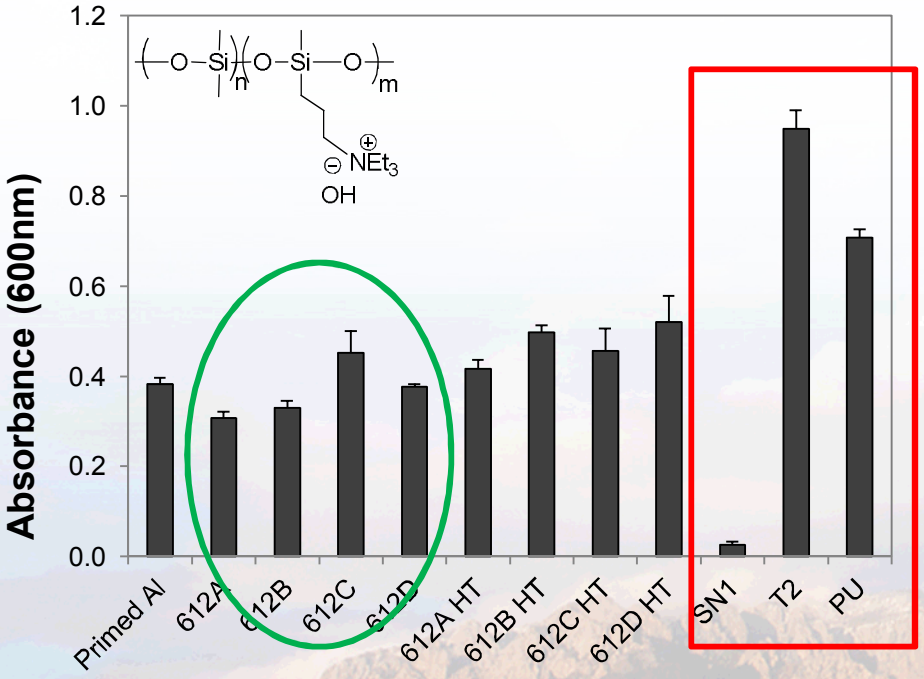
Effect of Coatings on Biofilm Growth
(Before Switching)

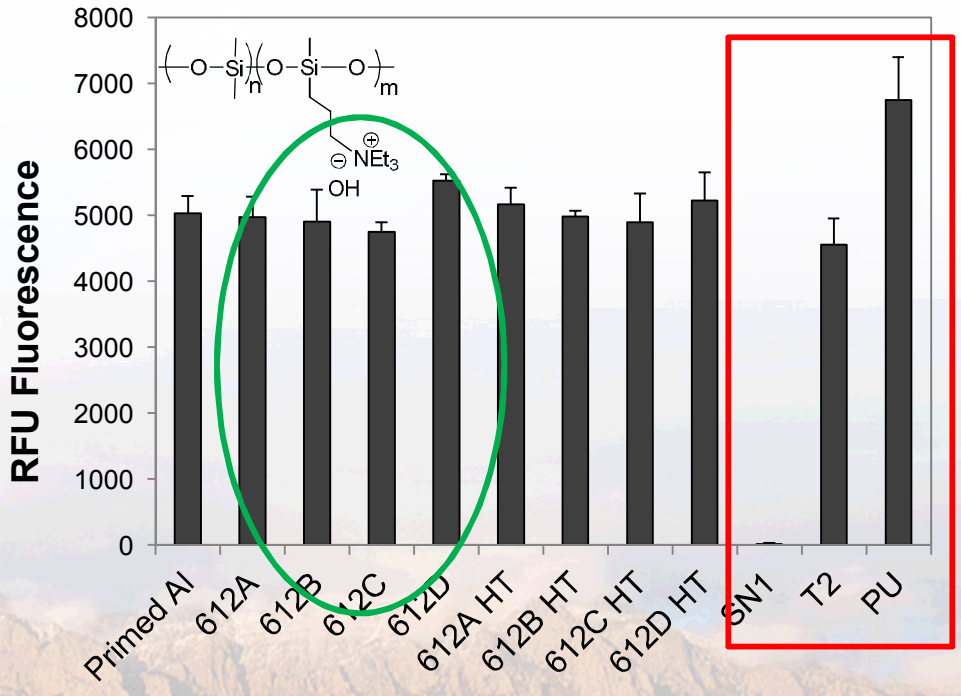
*Fair established bacterial biofilm reduction

*No established microalgae biofilm reduction

Evaluation of Bacterial Biofilm Growth



Evaluation of Microalgae Biofilm Growth



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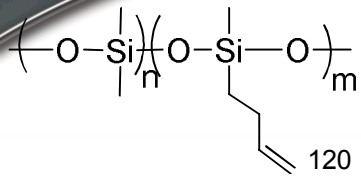
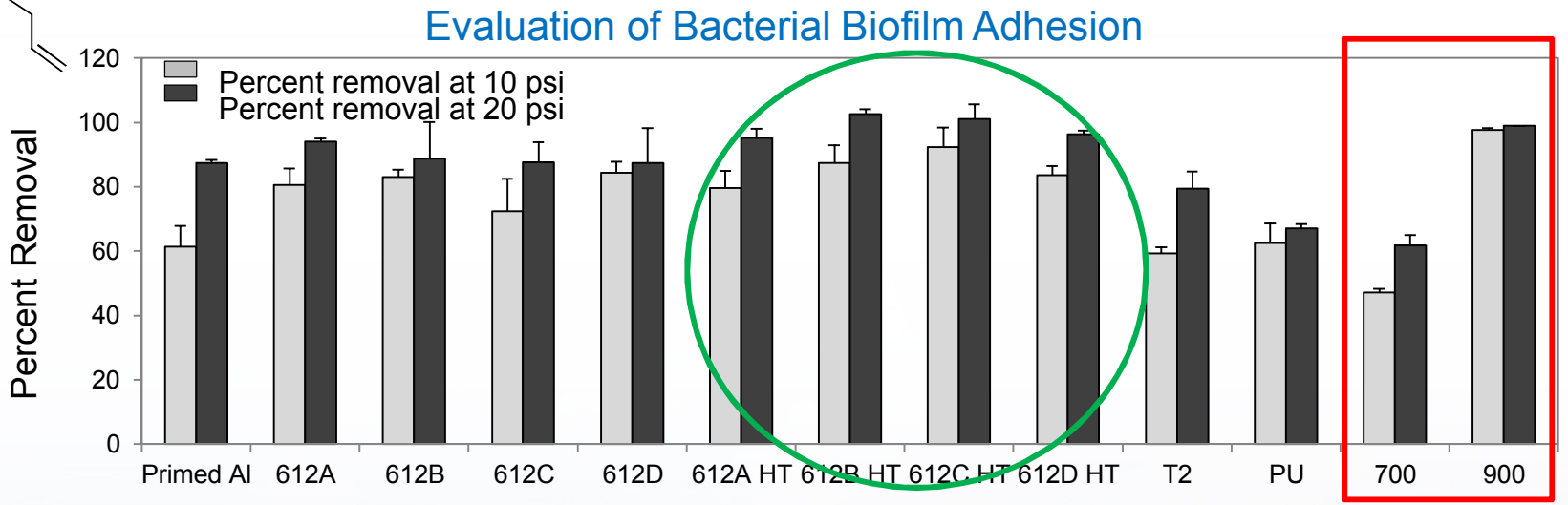
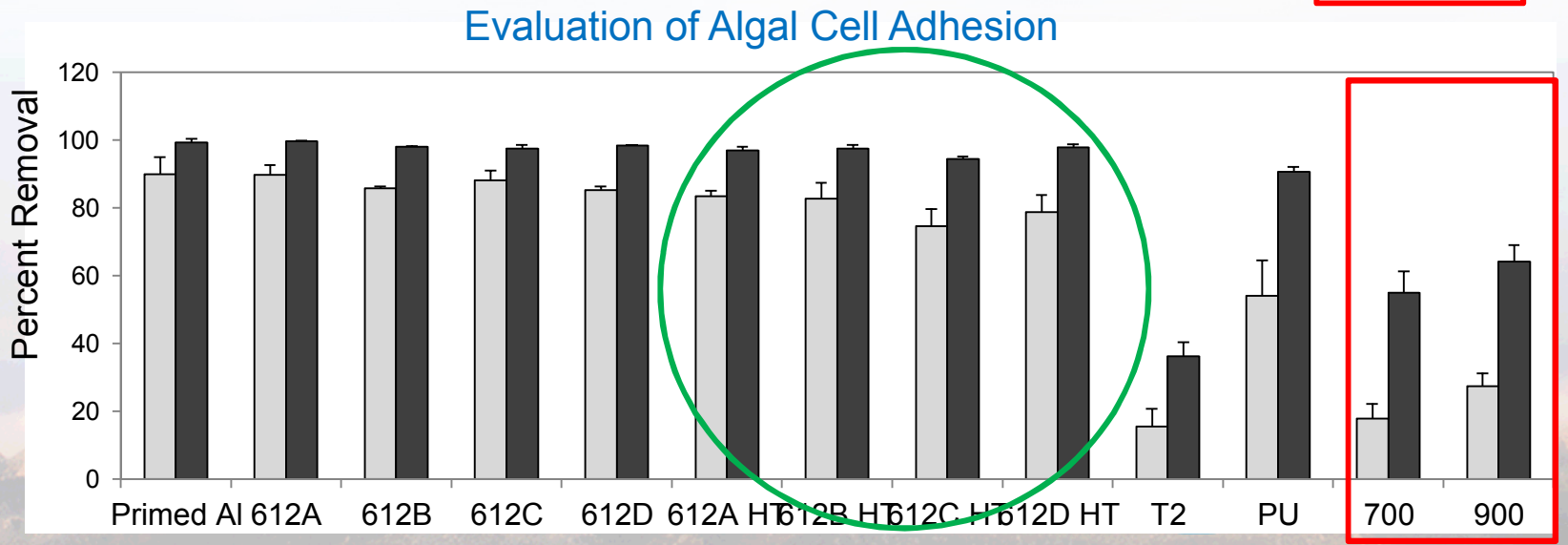
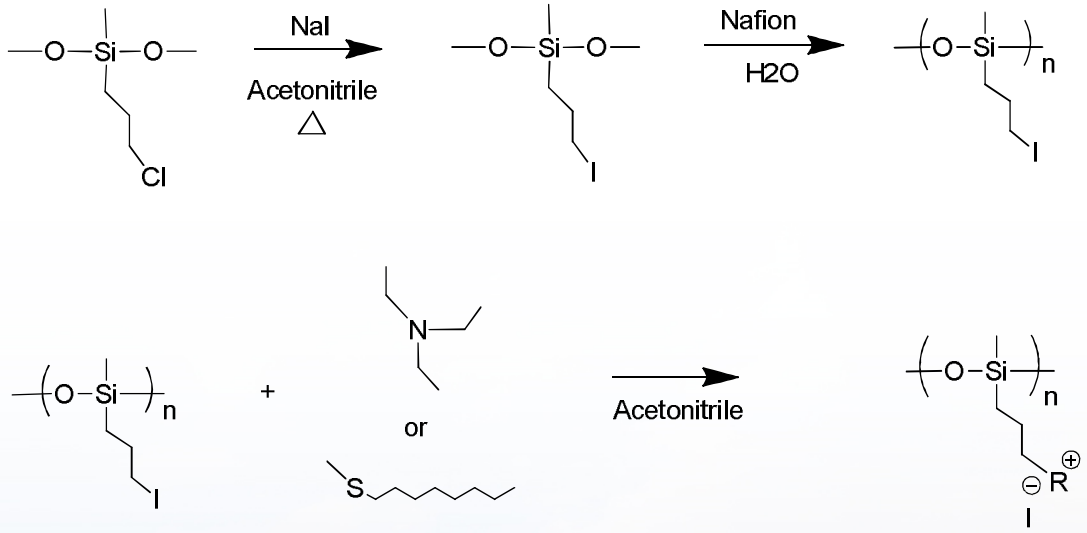
Effect on Fouling Release
(After Switching)

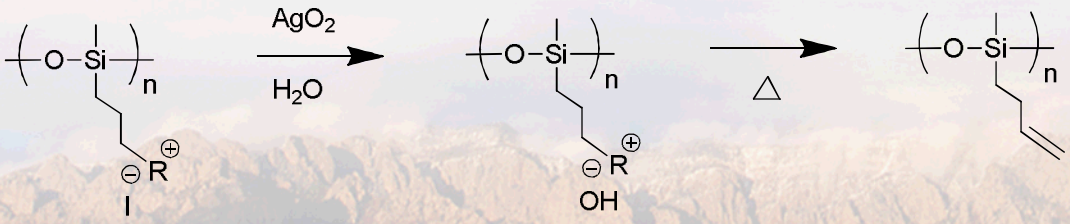






Ammonium and Sulfonium Silane Polymers





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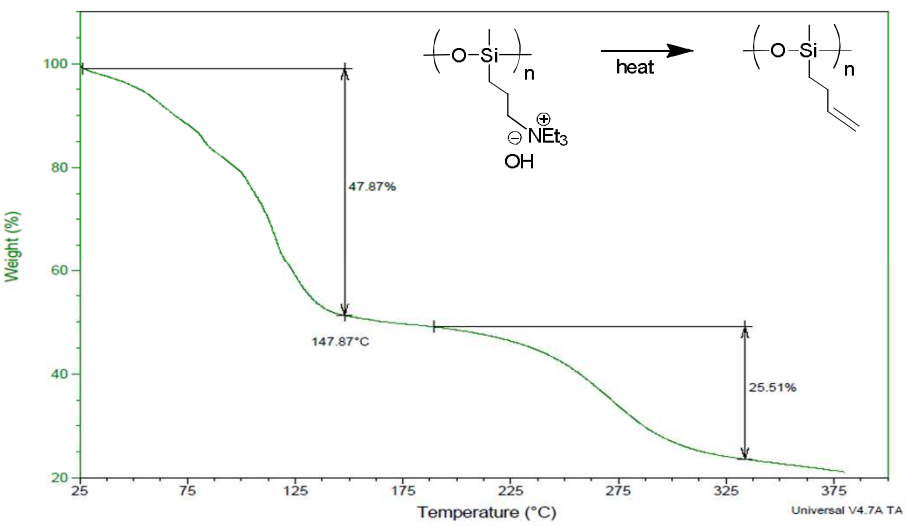
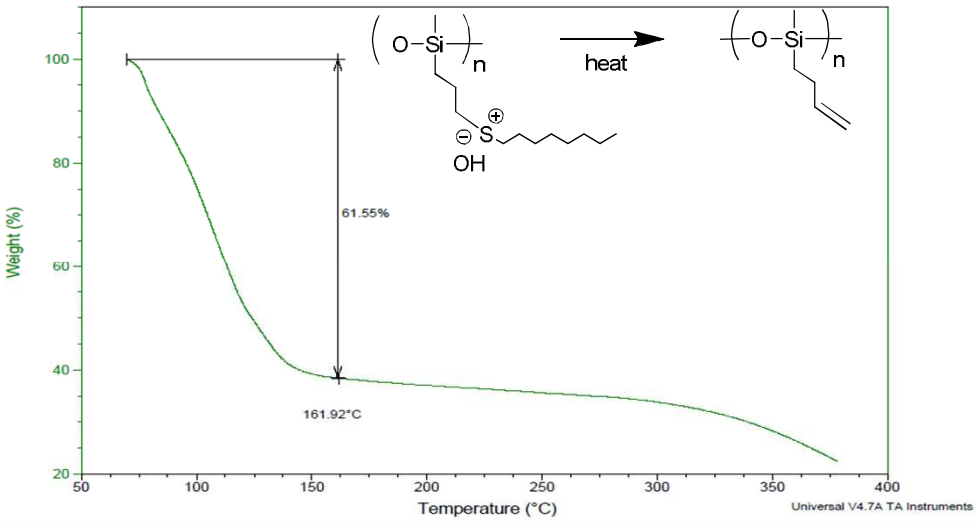
Polymer Characterization (XPS, TGA, IR)

Ammonium-silane



Sulfonium-silane



XPS Analysis - Atomic Concentration [%]

Coating	C	N	O	S	Si	Salt/Si	Heat Treated Salt/Si
Ammonium	70	5	16	0	8	0.625	0.333
Sulfonium	69	1	15	7	9	0.778	0.384

Silane polymers analyzed by XPS, then heat treated for 30 minutes at 150° degrees and analyzed for salt loss

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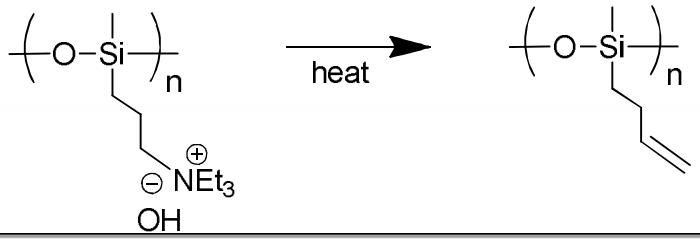
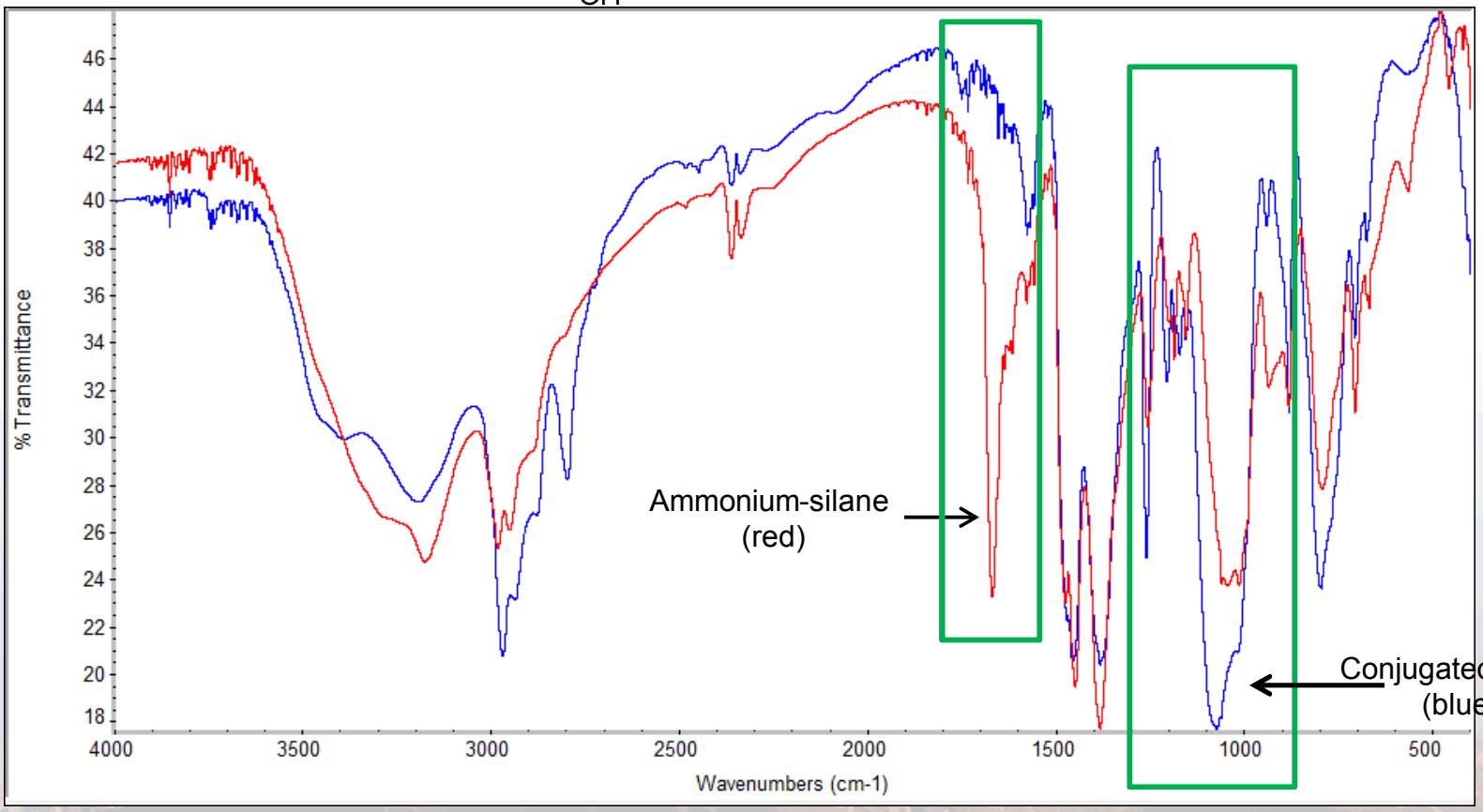
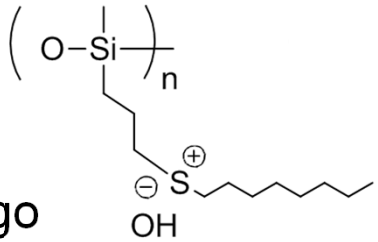
Infrared Spectroscopy





Coating Incorporated with Epoxy and Paint

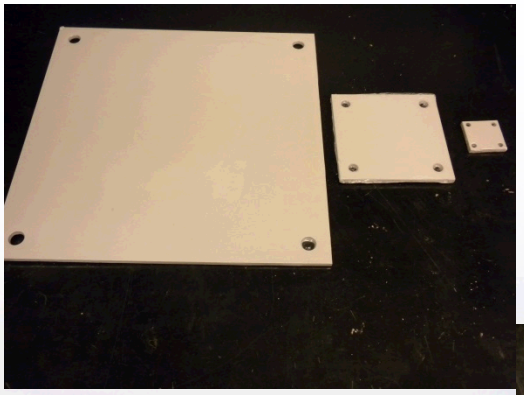
Incorporate the Sulfonium-Silane polymer in Epon 8021

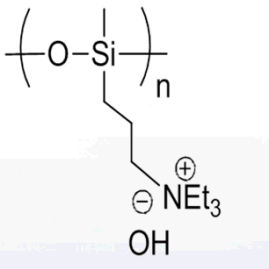


Incorporate the Ammonium-Silane polymer in Intersleek 970 Paint

Brush incorporated coatings onto primed aluminum panels to undergo testing:

PNNL Open Water Testing
- Up to 90 days exposure
- Fouling accumulation
- 1”, 3”, 6” panel coupons





NDSU Testing
- Short-term testing
- Fouling accumulation
- Fouling release

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- Place holder for new data being delivered at the end of this week showing results for coating when incorporated with epoxies and paints

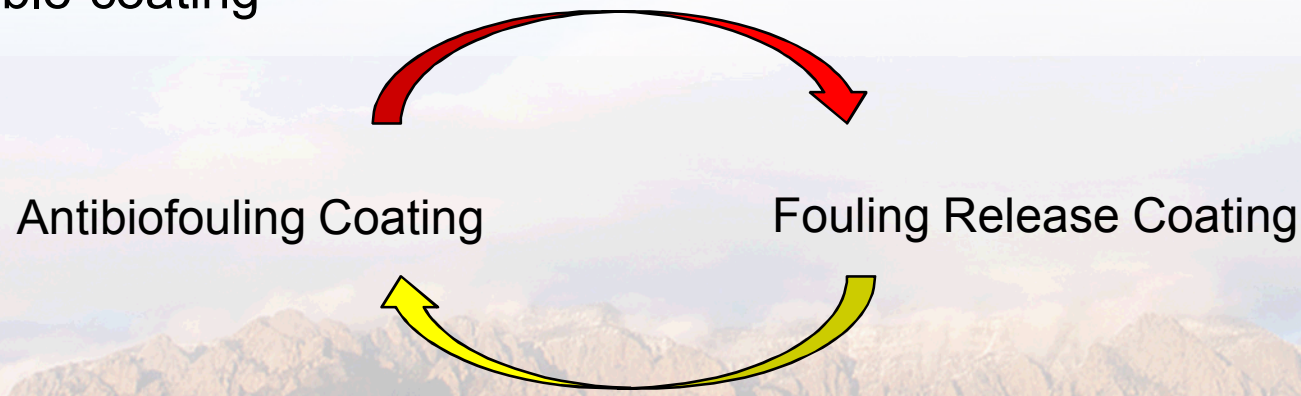
Summary of Silicon based Coating

- Silicone-based coatings synthesized performed as well, or better, than current commercial fouling release coatings

- Incorporated with epoxy and paint to increase longetivity

Currently undergoing open water testing an Pacific Northwest National Labs

*Ultimate goal is to synthesize an effective antifouling reversible, switchable coating



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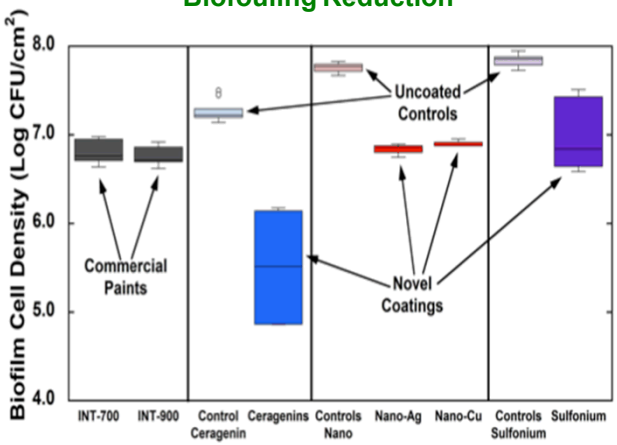
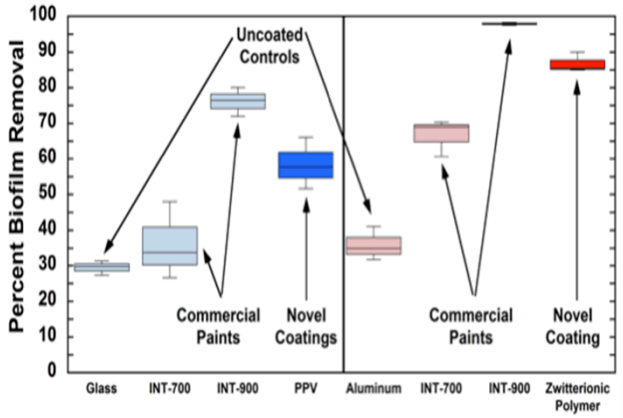
Advanced Material Program

Novel Antifouling Coatings Development: Show Significant Statistical Reduction in Biofouling

(A) **Biofouling Reduction**



(B) **Foul Release**

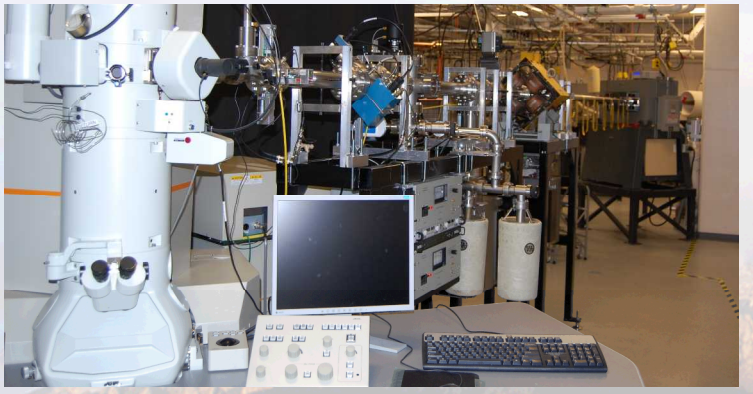


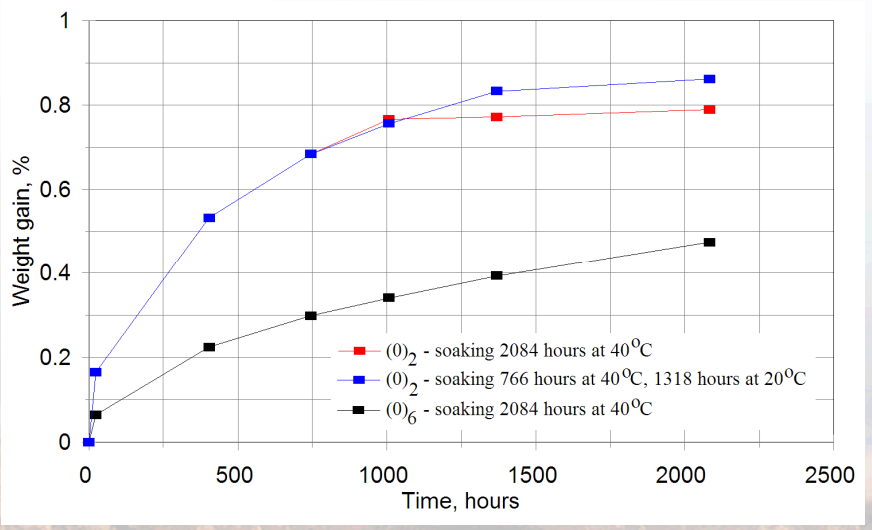
TOXIC

Performance Testing wind-based composites for MHK technology

Transfer & Diffusion Modeling

Understanding Corrosion & Biofouling Processes at the Nano to Micron scale with In situ TEM





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Thank You!

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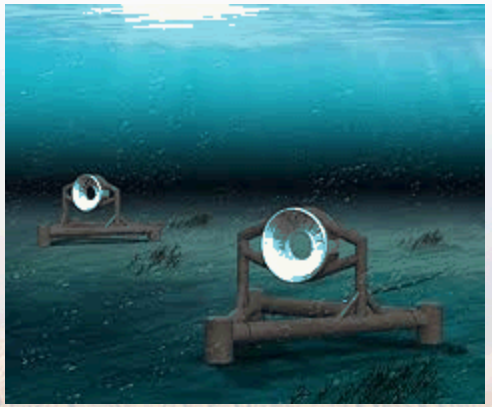

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NNSA National Nuclear Security Administration

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