Upstream Environmental Technology Project, EP13
Project Review 2/25/04, Houston, Texas

Lawrence Livermore National Laboratory and Shell Oil Company
Joint Project

Hydrophobic Membranes for Removal of Organic Impurities in Production Water

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Objective and Goal

- **Objective** is to remove contaminant organic compounds from drilling and production waters
- **Target** is oil production platforms
- **Approach** is through hydrophobic aerogel technology
- **Result** is water clean enough to be released into the environment
- **Goal** is to have a process developed ready for commercialization within three years

Benefits of New Technology

Production water is an environmentally sensitive issue

- Over 210 million barrels/day of production water
- 3 times the world oil production
- 50% is re-injected, 50% discharged
- Much discharged water requires treatment
  - Metals
  - Free oil
  - Dissolved organics
- Treatment cost ~ $0.6/bbl or more
- Dissolved organics are particularly elusive to treat

New treatment technology is desirable to lower costs

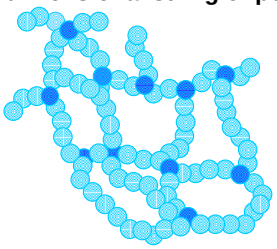
Existing Technologies

- Free oil
  - Centrifuge
  - Hydrocyclones
  - Membranes
  - Coalescers
- Dissolved Organics
  - Gas stripping
  - Biotreatment
  - Solvent extraction
  - Adsorption
  - Oxidation, wet air, UV
  - Membranes

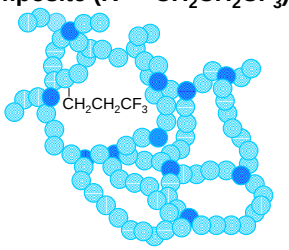
New treatment technology is desirable to better remove dissolved organics

Aerogels are Proposed Materials for Treatment

Unmodified aerogel
Three dimensional string of pearls



Hydrophobic aerogel composite (R = $-CH_2CH_2CF_3$)

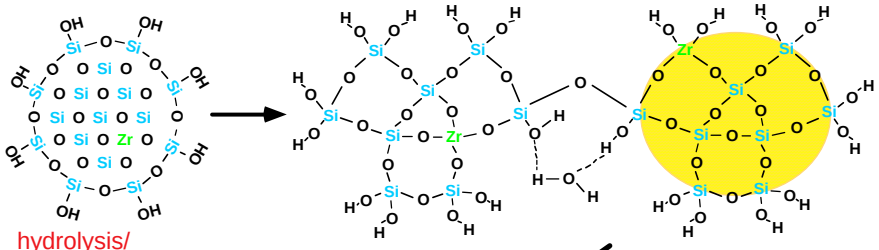


Open foam like structures with high surface areas (100s m^2/g), low densities (0.2 g/cc) and high porosity (90^+%)

Incorporation of R group can vary the chemical properties of the aerogel (hydrophobic)

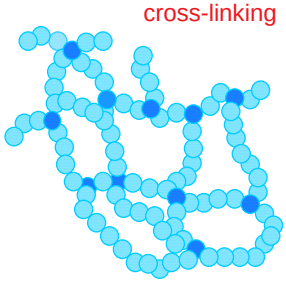
Exceptional properties of chemically modified aerogels may enable an inexpensive means for the large-scale removal of contaminants from aqueous solutions

Aerogel Formation Reactions



hydrolysis/
condensation

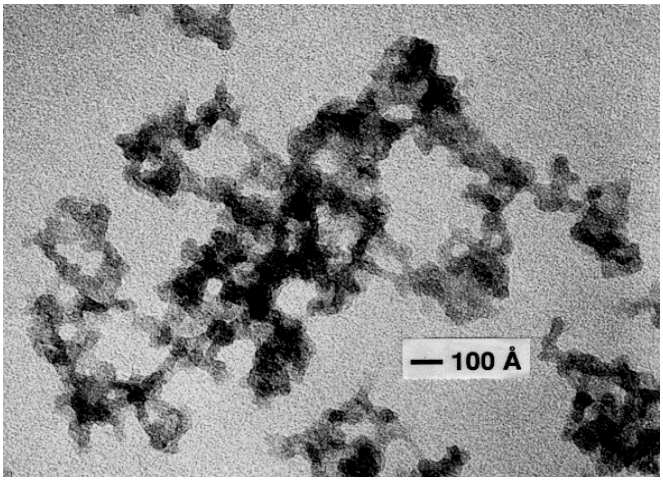
cross-linking



three dimensional array

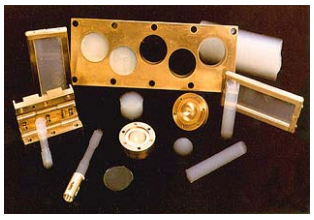
Wet from solvent ⇒ sol-gel
Supercritically dried ⇒ aerogel

TEM of Vanadia-Silica Aerogel



TEM = transmission electron micrograph

Commercial Applications of Aerogels

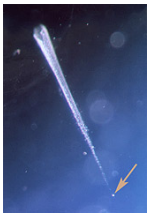


Aerogels can be cast into many shapes

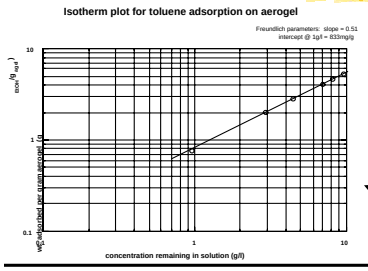
Materials
- Thermal and acoustic insulation
- Capacitive de-ionization for water purification
- Light weight lenses and mirrors
- Transparent window insulation
- Energy storage devices
- Chemical detection

First cosmic particle trapped by aerogel

Space exploration
- Insulation for Mars Lander and Sojourner Rover
- Capture medium for cosmic particles on shuttles
- Particle capture on EURECA satellite
- Particle capture on the STARDUST comet mission



Removal of Solvents and Oil from Water



Aerogel out performs carbon in adsorbing organic contaminants from water

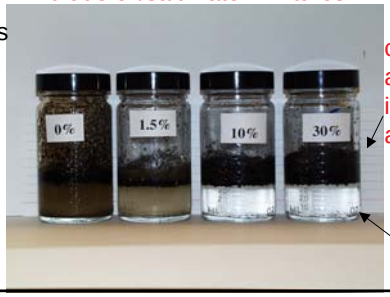
- 32 x better for adsorbing toluene
- 42 x better for adsorbing ethanol
- 131 x better for adsorbing Cl-benzene
- 69 x better for adsorbing TCE

Freundlich isotherm experiment for toluene

Aerogel removes crude oil from oil spills

- adsorbs up to 230 x its own weight
- can be used as a membrane for continuous oil removal
- can be used as coating material for potential cost effective operation

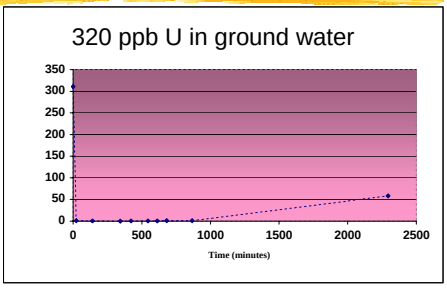
crude oil/salt water mixtures



crude oil adsorbed into aerogel

clear water

Removal of Uranium from Ground Water



Demonstration operation at Site 300

- Site 300 is a remote explosives testing facility for LLNL
- Several areas are contaminated with uranium which is getting in the ground water
- No cost effective method has been approved for the uranium removal
- Modified hydrophobic aerogel/granulated activated carbon composite was tested
- Results indicate complete success

Composite aerogel technology is moving towards commercialization

Technical Approach

- **Use chemically modified aerogels to absorb and separate organics from production water**
  - **Developing modified aerogels to target primarily dissolved organics (hydrophobic)**
  - **Developing optimum deployment method (powder, granular, membrane)**
- **Design integrated process with aerogel for deployment in remote locations (off shore production)**
  - **Pilot plant testing**
  - **Aerogel synthesis scale-up**
  - **Process design**

Aerogels have potential advantages over existing technologies

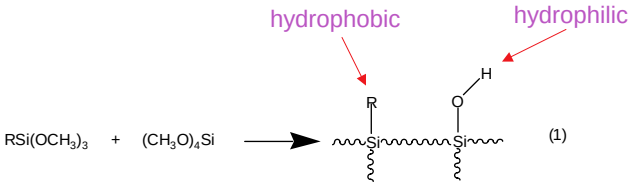
Technical issues that need to be addressed

- **Adsorption capacity of aerogels for target compounds**
  - **Intrinsic kinetics for powdered aerogel**
  - **Interferences due to ions and salts**
  - **Effect of form of application**
- **Recycle or reuse of aerogel**
  - **Regeneration if column use**
  - **Stability if membrane use**
- **Adsorption capacity for real samples**
  - **Performance dependant on composition of production water**
  - **Performance under extreme conditions**
- **Scale-up issues**
  - **Production of aerogels**
  - **Pilot plant testing**

Why Aerogels?

- Great structural properties for absorbing
  - High surface area
  - High porosity
- Can be made hydrophobic, I.e. reject water
  - Important for separation, particularly in low concentrations
  - Important for aerogel stability
- Can contain hydrophobic and hydrophilic sites
  - Hydroxyl surface groups give hydrophilic properties
  - $CH_2CH_2CF_3$ groups give hydrophobic properties
- Can be synthesized with other attractive properties
  - Proven to absorb metals (U, Cr, As, Au)
  - Proven for incorporation of other R groups

Surface Structure of Aerogels



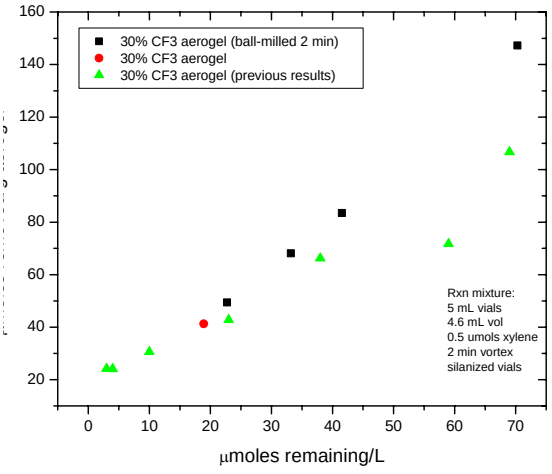
Hydrophobicity is dependent upon $CH_2CH_2CF_3$/OH ratio
$CH_2CH_2CF_3$/OH ratio depends upon formulation

Formulation (mole ratio)	Si with OH/Si with R
0.02 ($Si_{51}O_{103.5}C_3H_4F_3$)	50/1
0.13 ($Si_{8.7}O_{16.9}C_3H_4F_3$)	8/1
0.35 ($Si_{3.9}O_{7.2}C_3H_4F_3$)	3/1
0.53 ($Si_{2.9}O_{5.3}C_3H_4F_3$)	2/1
1.0 ($Si_2O_{3.5}C_3H_4F_3$)	1/1

Target Compounds in Production Water

Compound	Max Conc	MW	Sol w	Log K_{ow}
Benzene	10 mg/L	78	1800 mg/L	2.1
Toluene	10 mg/L	92	500 mg/L	2.7
Ethylbenzene	10 mg/L	106	200 mg/L	3.2
Xylene	10 mg/L	106	180 mg/L	3.2
Napthalene	1 mg/L	128	30 mg/L	3.3
Phenanthrene	100 ug/L	178	1 mg/L	4.5
Phenol	10 mg/L	94	8300 mg/L	1.5
Formic Acid	600 mg/L	46	misc	-0.54
Acetic Acid	700 mg/L	60	misc	-0.17
Propanoic Acid	50 mg/L	74	~370,000 mg/L	0.33
Butanoic Acid	10 mg/L	88	~100,000 mg/L	0.79
Pentanoic Acid	10 mg/L	102	~10,000 mg/L	1.4
Hexanoic Acid	10 mg/L	116	~5000 mg/L	1.9
Heptanoic Acid	10 mg/L	130	~1000 mg/L	2.4
Octanoic Acid	10 mg/L	144	<1000 mg/L	3.1
Nonanoic Acid	10 mg/L	158	<1000 mg/L	3.4

$CF_3CH_2CH_2$ modified aerogel as an absorbing material—xylene in water



Xylene absorption from water

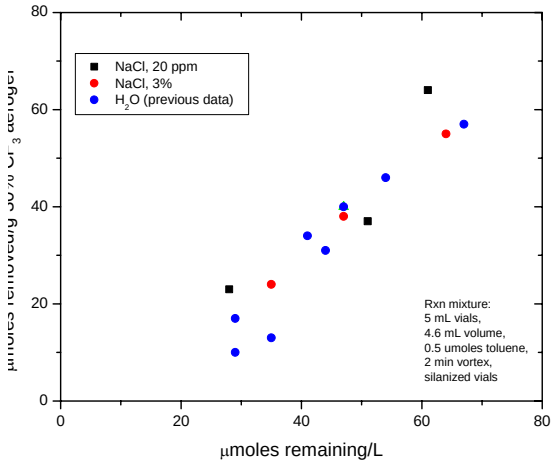
Batch Experiment

CF_3-hydrophobic aerogel is the absorbant

Compares different preparation of aerogels of the same formulation

Diffusion limits are not apparent in absorption

$CF_3CH_2CH_2$ modified aerogel as an absorbing material—toluene from NaCl in water



Toluene absorption from water and salt water

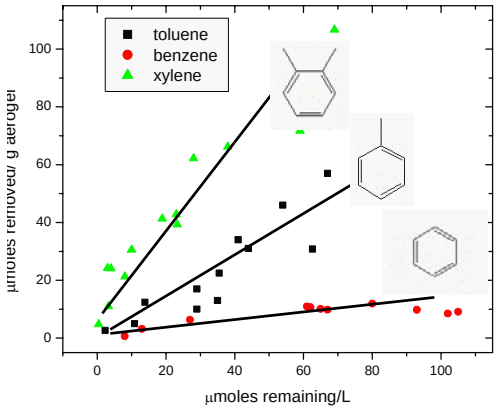
Batch Experiment

CF_3-hydrophobic aerogel is the absorbant

Compares absorption from water to absorption from salt water

NaCl has little or no effect on absorption
Ions may possibly not interfer with performance

$CF_3CH_2CH_2$ modified aerogel as an absorbing material—BTX from water



BTX absorption from water

Batch experiments

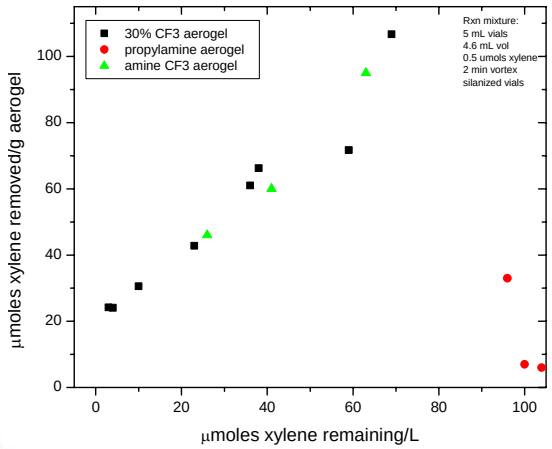
CF_3-hydrophobic aerogel is the absorbant

UV-vis single component analysis

Compound	Max Conc	MW	Sol w	Log Kow
Benzene	10 mg/L	78	1800 mg/L	2.1
Toluene	10 mg/L	92	500 mg/L	2.7
Ethylbenzene	10 mg/L	106	200 mg/L	3.2
Xylene	10 mg/L	106	180 mg/L	3.2

Absorbance appears to follow Log K_{ow}

Xylene Absorption by Modified Aerogels



Xylene absorption from water

Batch Experiment

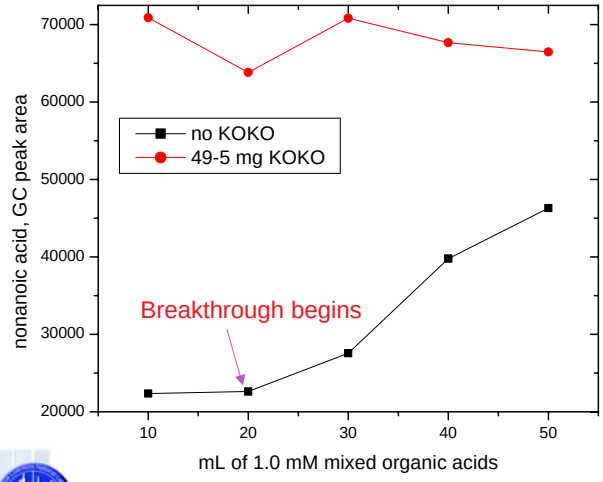
CF_3-Hydrophobic aerogel
NH_2-Hydrophilic aerogel
Combination aerogel (through synthesis) are absorbants

UV-vis detection single component analysis

CF_3-Hydrophobic works; NH_2-Hydrophilic does not work
Components do not appear to interfere

Nonanoic Acid Absorption by Carbon

Adsorption of nonanoic acid by 0.5 x 0.5 cm KOKO column

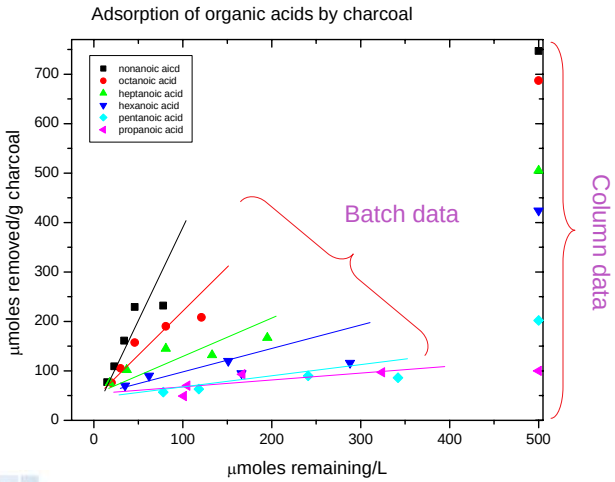


Nonanoic acid absorption from water

Column Experiment

Granulated Activated Carbon is absorbant

Organic Acids Removal by Carbon



Organic acids absorption from water

Granulated Activated carbon is absorbant

Compares batch data with column data

Batch and column data appear to agree for carbon

Deliverables

- **1st year**
  - **Production methods of aerogels (powdered, granular, and membrane)**
  - **Intrinsic adsorption kinetics and capacities for powdered aerogels**
  - **Measurements on surrogate and real production waters**
- **2nd year**
  - **Column testing of granular and composite aerogels (adsorption capacities)**
  - **Testing of membrane forms of aerogels**
  - **Selection of form for scale-up**
- **3rd year**
  - **Synthesis of materials for pilot plant testing**
  - **Pilot plant testing**
  - **Transfer aerogel synthesis technology to aerogel production company**
  - **Design full scale treatment facility**

Deliverables as of 2/25/04

Proposed Deliverable: Synthesis of hydrophobic aerogels for testing

Progress: Synthesized several different hydrophobic and hydrophilic aerogels

- **30%, 10%, and 1.5 % by weight formulation propyl-CF_3 hydrophobic aerogel, hot methanol extraction and CO_2 extraction**
- **30 wt % ethyl-NH_2 hydrophilic aerogel CO_2 extraction**
- **heptadecafluoro hydrophobic aerogel CO_2 extraction**

Proposed Deliverable: Measurement of powdered hydrophobic aerogel adsorption properties with surrogate solutions

Progress: Measured absorption parameters for aerogels on selected surrogate solutions

- **30% propyl-CF_3 hydrophobic aerogel,**
- **ethyl-NH_2 hydrophilic aerogel**
- **granulated activated carbon**

Surrogate Solution: benzene, toluene, xylene, phenols, and naphthenic acids

Deliverables as of 2/25/04 Continued

Proposed Deliverable: Determination of intrinsic absorption kinetics of aerogels for surrogate water solutions

Progress: Measured kinetic parameters for absorption for 30% propyl-CF_3 hydrophobic aerogel were under selected conditions

- **Higher concentrations of targets, indicate the adsorption kinetics are relatively fast**
- **Lower concentrations, the statistical scatter in the data was sufficient that good kinetic parameters could not be obtained**

Proposed Deliverable: Selection of production water for testing

Progress: Selected several types of production water in concert with Industrial Sponsor based on our targets of interest

- **Production waters were selected based on typical compositions of interest as well as specific interests of the Industrial Sponsor**

Deliverables as of 2/25/04 Continued 2

Proposed Deliverable: Obtaining production water for testing (special handling required)

Progress: Obtaining production waters with full analysis provided by Industrial Sponsor

- **Wyoming and Gulf of Mexico coming first**
- **North Sea production water will be available when we are ready to test them**

Proposed Deliverable: Measurement of adsorption properties of aerogels with production water (not yet time for milestone)

Progress: Adapted analytical methods, UV-vis and purge and trap GC-MS, and LC-MS techniques, to analyze complex mixtures, necessary for analysis of production water treatments

Proposed Deliverable: Comparison of capacities and kinetics of surrogate solutions and selected production water (not yet time for milestone)

Progress: Constructed and developed column testing procedures for carbon and revised batch testing procedures

Changes in Milestones and Deliverables

Proposed Deliverable 1st year: Determine intrinsic adsorption kinetics of aerogels for surrogate water solutions

Proposed Deliverable 1st year: Measure of adsorption properties of aerogels with production water

Proposed Deliverable 1st year: Compare capacities and kinetics of aerogels for surrogate solutions and selected production water

Deliverables have been postponed because the batch testing method under the current experimental design is being modified. This is being reconfigured and the effort will commence within 2 months, and will extend into the second year

Proposed Deliverable 2nd year: Test absorption properties of aerogels for surrogate solutions and production water by column method

Deliverable has been started this first year due to problems with batch testing. Constructed and tested column system with activated carbon. Testing will commence when synthesis of larger batch of 30% propyl-CF_3 hydrophobic aerogel is completed.

Summary and Conclusions

- Successfully produced several different types of aerogels for testing
- Batch testing indicated
  - Hydrophobic aerogels show affinities toward BTEX type compounds
  - Phenol and carboxylic acids are not removed with hydrophobic aerogels
  - More materials development necessary
  - Batch testing method has materials contact problems
- Column testing indicated
  - system ready to go based on carbon results
  - Multicomponent analytical methods refined and usable

Budget

3 year program with cost sharing LLNL/Shell
LLNL contribution from DOE, Shell contribution in-kind and/or funds in

Fiscal Year May to April

Year	LLNL	Shell
First	$240K (0.75 FTE)	in-kind (0.3 FTE)
Second	$240K (0.75 FTE)	in-kind, funds in
Third	$175K (0.5 FTE)	in-kind, funds in

LLNL breakdown - 80% personnel, 20% materials and miscellaneous

Research Team

- **Hydrophobic Aerogels for Removal of Organic Impurities in Aqueous Phase by Adam H. Love, M. Leslie Carman, Paul R. Coronado and John G. Reynolds presented at 13th Symposium on Separation Science in Energy Applications, Gatlinburg, TN in October 2003.**
- **Engineering surface functional groups on silica aerogel for enhanced cleanup of organics from produced water by Adam H. Love, M. Leslie Hanna and John G. Reynolds, Manuscript submitted for publication in Nov 2003 to *Separation Science and Technology*.**

Planned activities for Shell and LLNL

3 year program cost sharing LLNL/Shell
LLNL contribution from DOE, Shell contribution in-kind and/or funds in

- **Testing of aerogel for removal of selected organic contaminants representative of typical waste stream**
- **Testing with potential performance inhibitors (scaling compounds, emulsions etc.)**
- **Optimize aerogel composition for best contaminant removal activity**
- **Determine resilience to wear and tear of optimum formulation**
- **Determine optimum method of deployment (single piece membrane, granular, powder, coating) for process**
- **Scale up of aerogel production**
- **Pilot-plant scale-up of process**
- **Full process scale-up**

Laboratory work performed at LLNL
pilot plant and full scale work performed at Shell

Deliverables and Milestones 1st Year

Labor: 0.75 LLNL FTE, $240K; 0.3 I Partner FTE, in-kind Supplies: $25K

- **Synthesis of hydrophobic aerogels for testing—03 Mo**
- **Measurement of powdered hydrophobic aerogel adsorption properties with surrogate solutions—06 Mo**
- **Selection of production water for testing—06 Mo**
- **Determination of intrinsic adsorption kinetics for surrogate water solutions—08 Mo**
- **Obtaining production water preserved (special handling) for testing—09 Mo**
- **Measurement of adsorption properties with production water—11 Mo**
- **Comparison of capacities and kinetics of surrogate solutions and selected production water—12 Mo**

Deliverables and Milestones 2nd Year

Labor: 0.75 LLNL FTE, $240K; 0.3 I-Partner FTE, in-kind; Supplies: $25K

- **Synthesis of granular hydrophobic aerogels for column testing—14 Mo**
- **Column testing of surrogate solutions—17 Mo**
- **Determination of column kinetics and adsorption capacities for surrogate solutions—18 Mo**
- **Measurement of column adsorption properties with production water—19 Mo**
- **Determination of column adsorption properties with production water—20 Mo**
- **Measurement of column adsorption properties with alternate production water—21 Mo**
- **Determination of column adsorption properties with production water—21 Mo**
- **Synthesis of membrane form hydrophobic aerogels for testing—23 Mo**
- **esting of effectiveness of selected membrane designs for eparations—24 Mo**

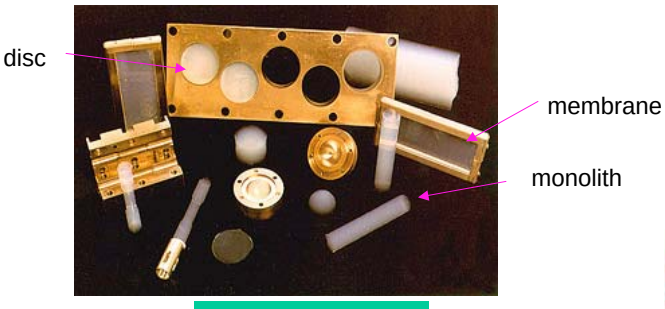
Deliverables and Milestones 3rd Year

Labor: 0.5 LLNL FTE, $175K; 0.3 I-Partner FTE, in-kind and funds in Supplies: $25K

- **Synthesis of granular hydrophobic aerogels for pilot-plant testing—26 Mo**
- **Scale-up design of column or membrane separation pilot plant—26 Mo**
- **Construction of separation pilot plant for field testing—28 Mo**
- **Pilot plant level field testing of hydrophobic aerogels—32 Mo**
- **Develop aerogel synthesis with outside company—34 Mo**
- **Design plans for potential full-scale aerogel-based water treatment facility for off shore use—36 Mo**

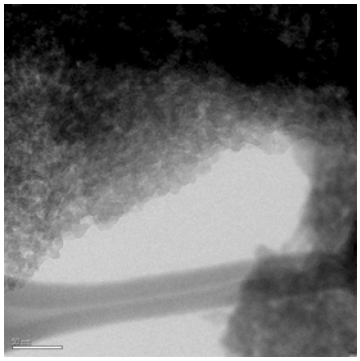
Aerogels

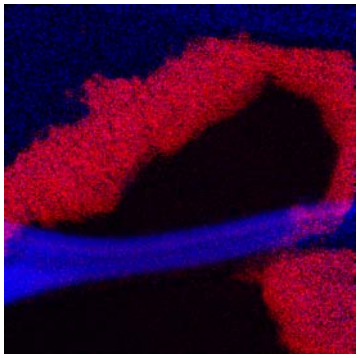
- **Aerogels are sol-gel materials supercritically dried**
  - **High surface areas (500 to over 1000 m^2/g)**
  - **High porosity (90^+%)**
  - **Low density (0.1 to 0.3 g/cc)**
  - **Can be made as monoliths, membranes, and coatings**
- **Aerogels can also be chemically modified**
  - **Fluorinated to be hydrophobic**
  - **Functionalized to bind selectively**



Cast silica aerogels

TEMs of composite show typical aerogel microstructure



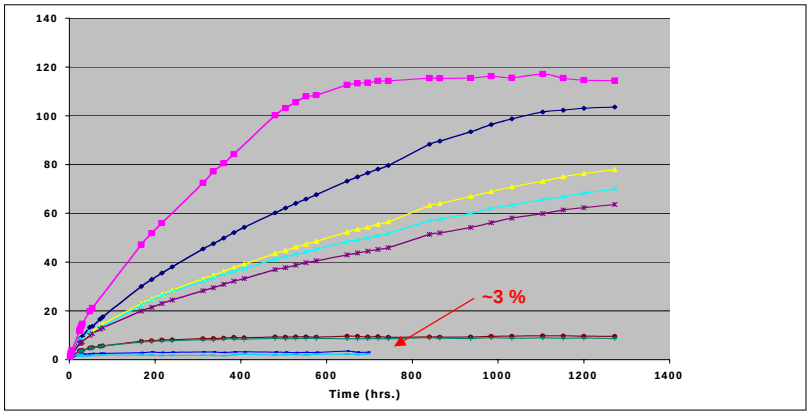


Silicon - Red
Carbon - Blue

- Elemental mapping shows composite homogeneity
  - Fluorine is assumed to be uniformly dispersed on some of the carbons

Hydrophobic/Hydrophilic Nature of CF_3-Aerogels

Samples exposed to water-saturated air atmosphere at 20°C



Increasing concentration of $CF_3(CH_2)_2$- decreases H_2O adsorption

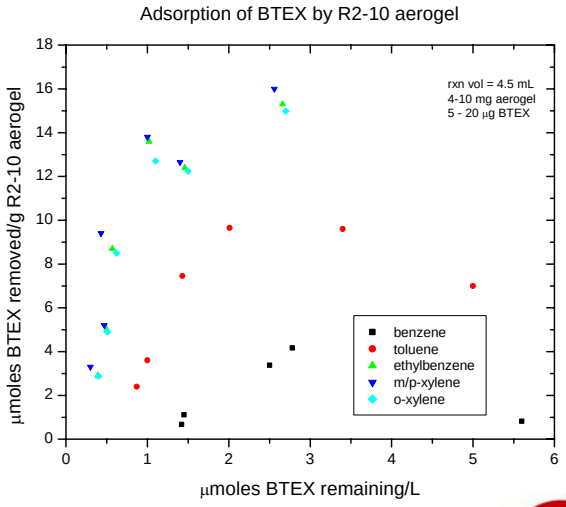
Other Modifications to Aerogels

- **Hydrophilic** **R = $CH_2CH_2NH_2$**
  Should attract hydrophilic organics
- **Phosphorus group** **R = $CH_2CH_2P(O)(OC_2H_5)_2$**
  Should attract polar type compounds
- **Thiol group** **R = $CH_2CH_2CH_2SH$**
  Should attract polar type compounds
- **Aromatic** **R = C_6H_5**
  Should attract aromatic type compounds
- **Hydrophobic** **R = $CH_2CH_2(CF_2)_7CF_3$**
  Should be superhydrophobic

BTEX Absorption by Modified Aerogels

Batch experiments
Absorption by
hydrophobic aerogel

Detection by purge
and trap GC/MS
allows detection of
multiple components



Techniques developed for more efficient analysis