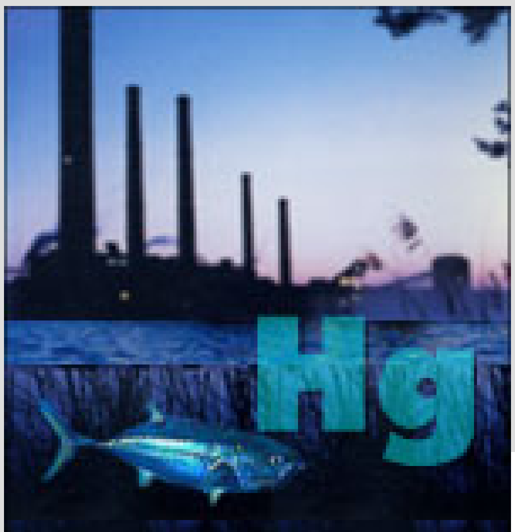
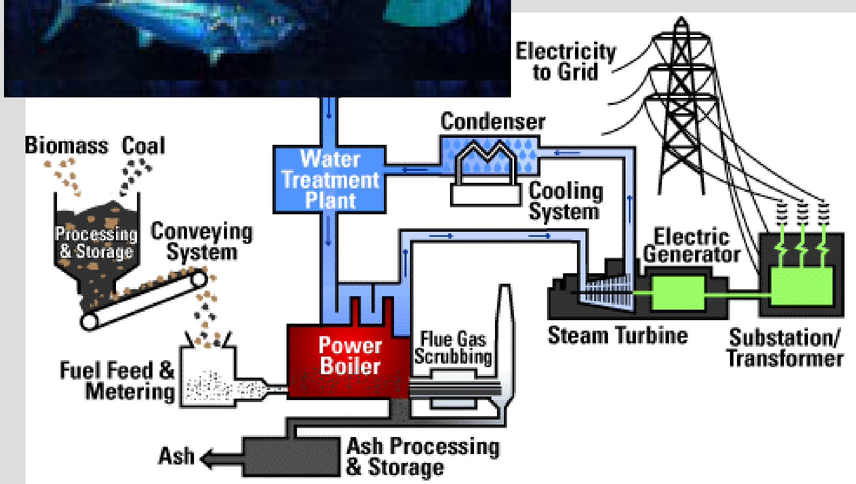
Heavy Metal Sequestration Using Functional Nanoporous Materials





Glen E. Fryxell, Shas V. Mattigod,
Kent Parker, Richard Skaggs

US EPA Workshop on Nanotechnology for Site Remediation

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October 20-21, 2005

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Mercury Emissions

EPA's Clean Air Mercury Rule (CAMR) (3/15/05)
Current estimated power plant emissions range from 43 to 52 tons Hg/year (48) (158 tons anthropogenic Hg/year total)

Two options:
1) Install MACT and reduce emissions nationwide by 14 tons (29%) by 2008
2) Or, by 2010, reduce this to 38 tons Hg/year (co-benefit, "CAIR"), and by 2018, reduce this to 15 tons Hg/year

Current air pollution control devices can capture some Hg, but this varies widely depending on a number of variables

Current baseline estimates: $50,000-$70,000 per pound Hg removed ($4.3B to $6.7B)

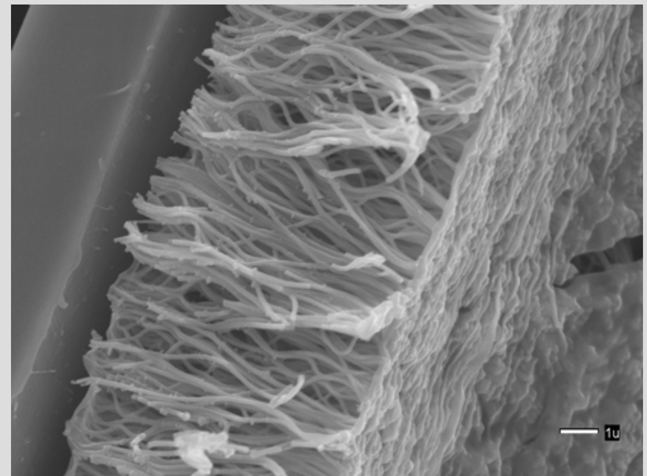
Near-term goal: 50-70% Hg capture, at 25-50% reduction in cost

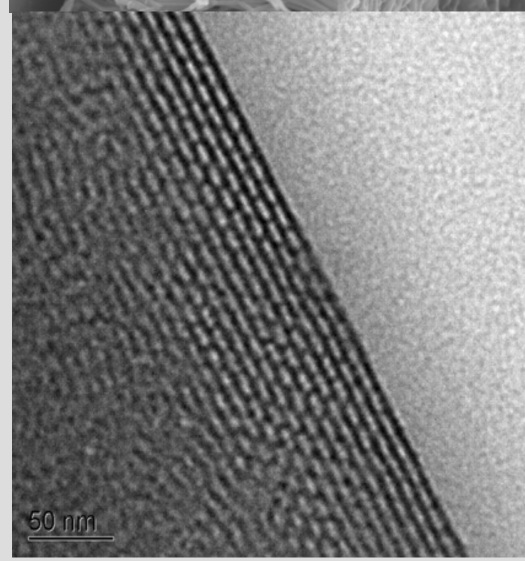
Longer-term goal: 90+% capture by 2010

Advantages of nanomaterials for heavy metal sequestration

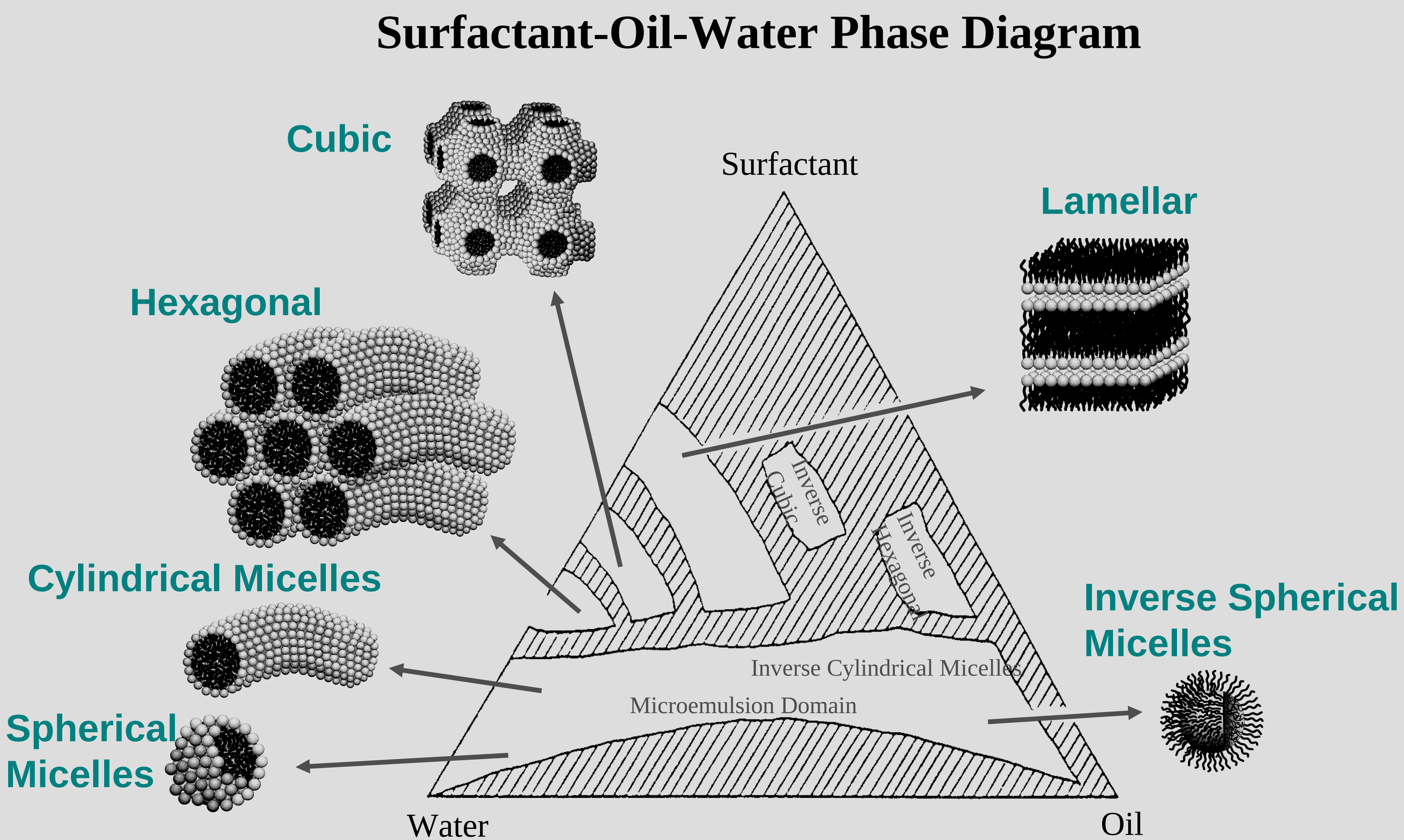
Nanomaterials provide:

- High surface area (capacity)
- Well defined structure
- High reactivity
- Easy dispersability
- Readily tailored for application in different environments
- Chemistry/materials developed for remediation processes are readily tailored to sensing/detection

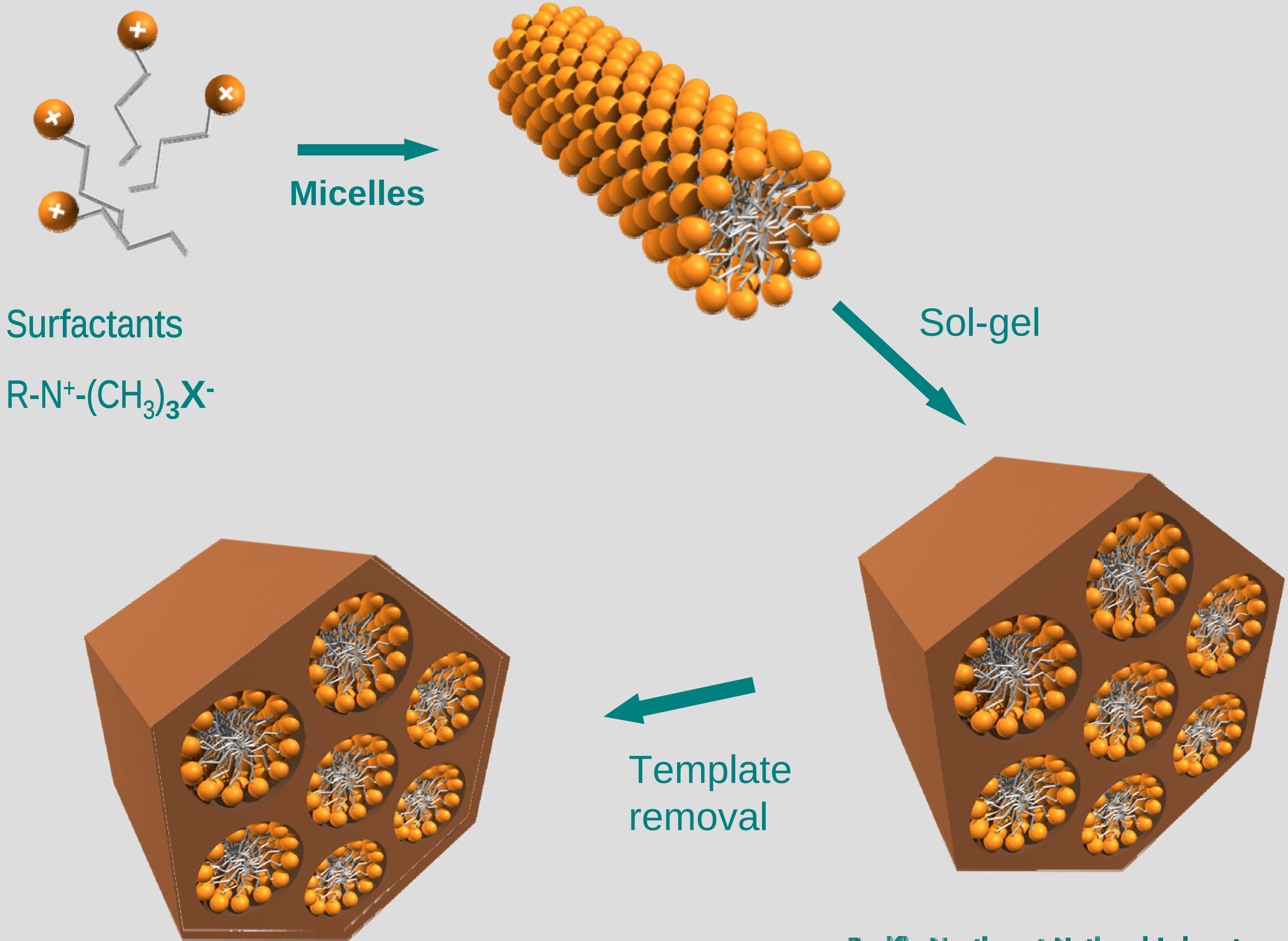


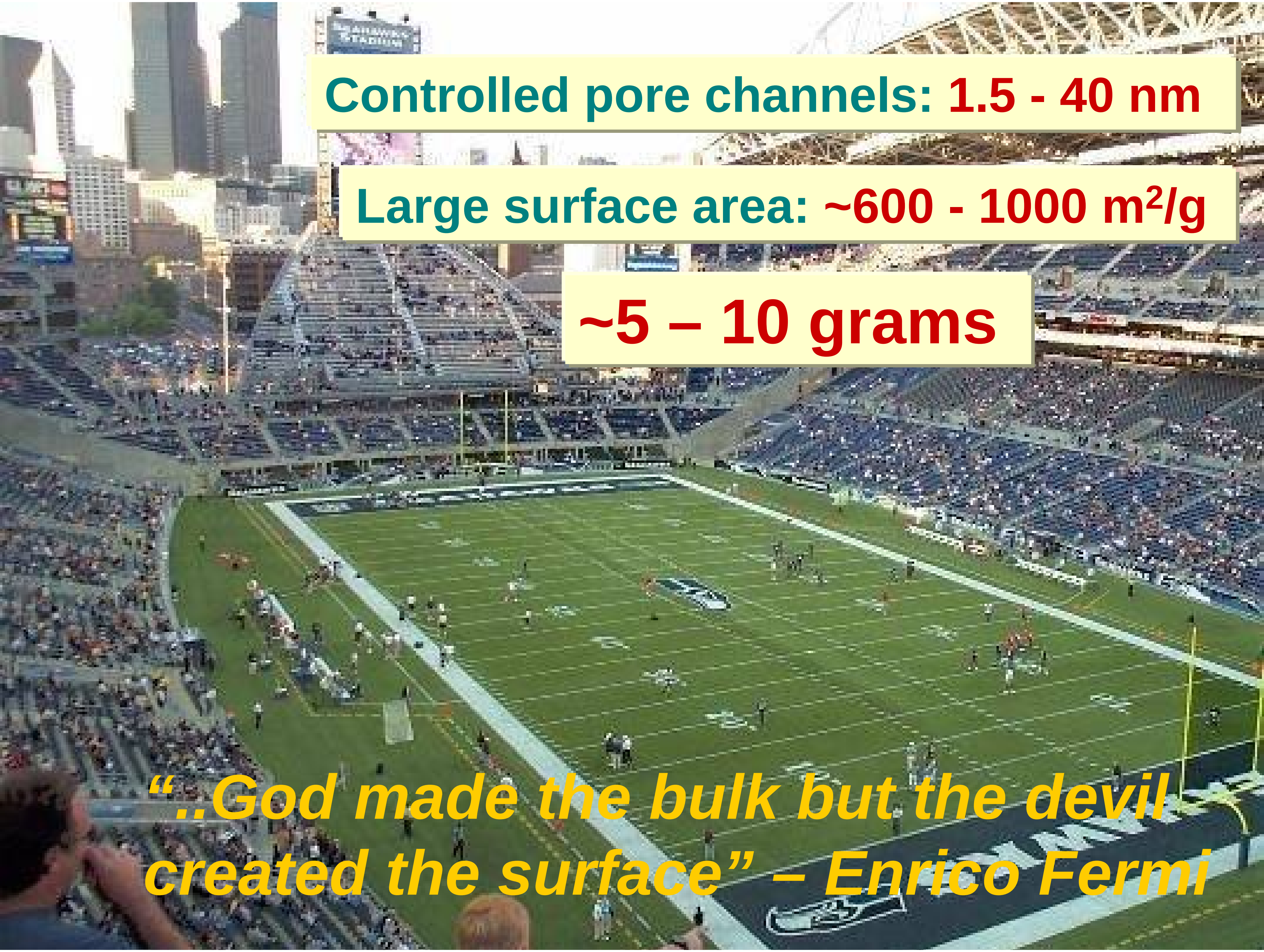


Micelles as macromolecular templates



Nanoporous Ceramic Substrates





Controlled pore channels: 1.5 - 40 nm

Large surface area: ~600 - 1000 m^2/g

~5 – 10 grams

"..God made the bulk but the devil created the surface" – Enrico Fermi

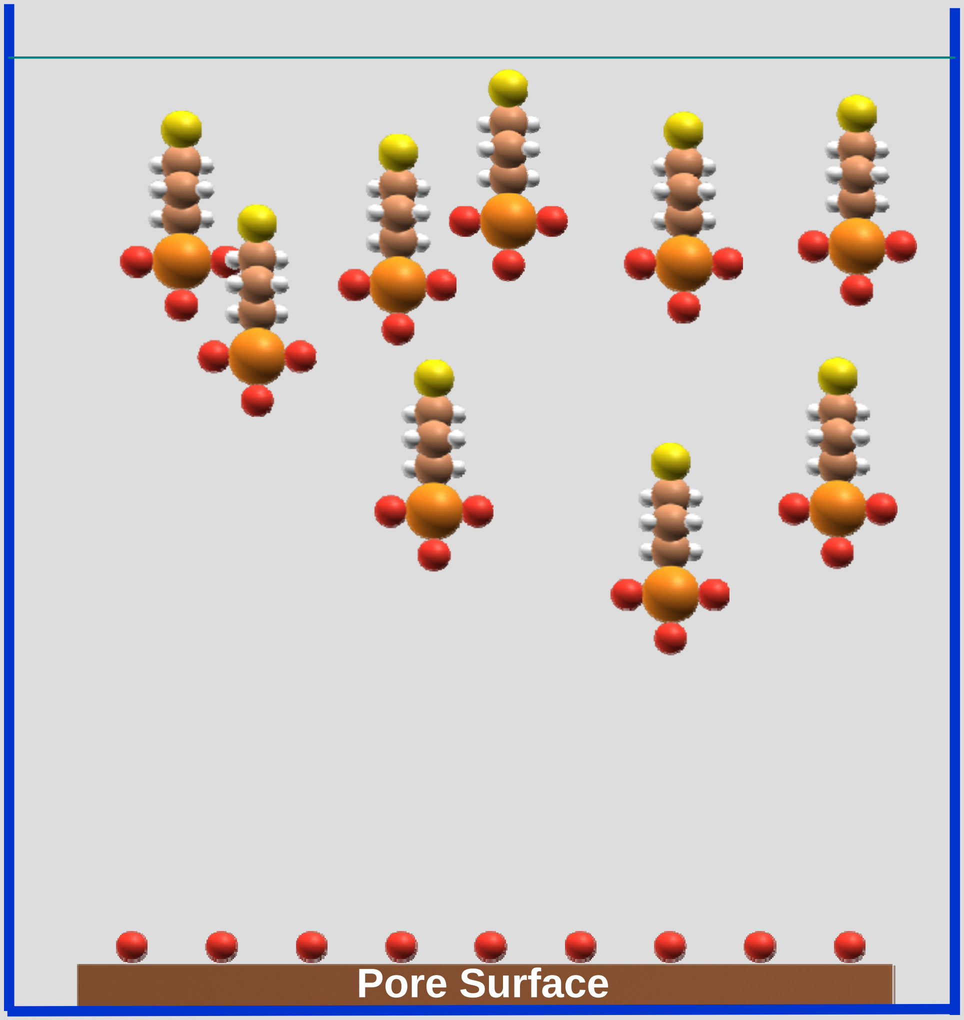
So the way that we get the surface chemistry we need is….

Molecular self-assembly

Self-assembly driven by Van der Waals interactions between chains, as well as the interaction between the headgroup and the surface.

Monolayer Advantages

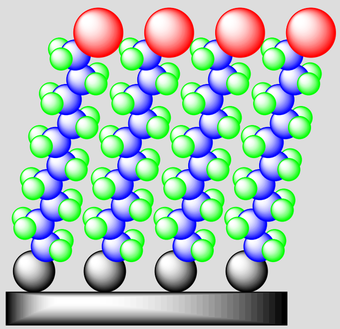
- Well-established silanation chemistry
- Stabilized surface
- Highest possible ligand density
- Easily tunable chemistry



"Designing Surface Chemistry in Mesoporous Silica" in "Adsorption on Silica Surfaces"; pp. 665-687, Marcel-Dekker, **2000**.

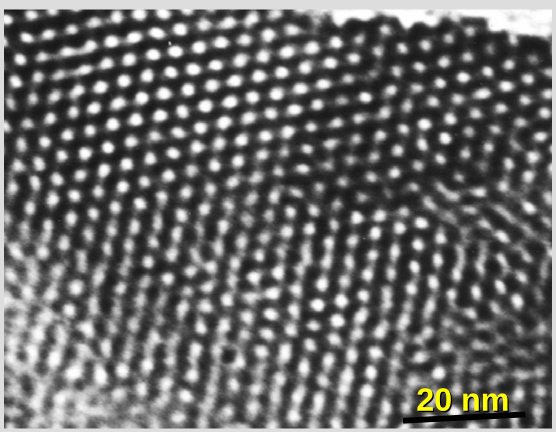
SAMMS: Self-Assembled Monolayers on Mesoporous Supports

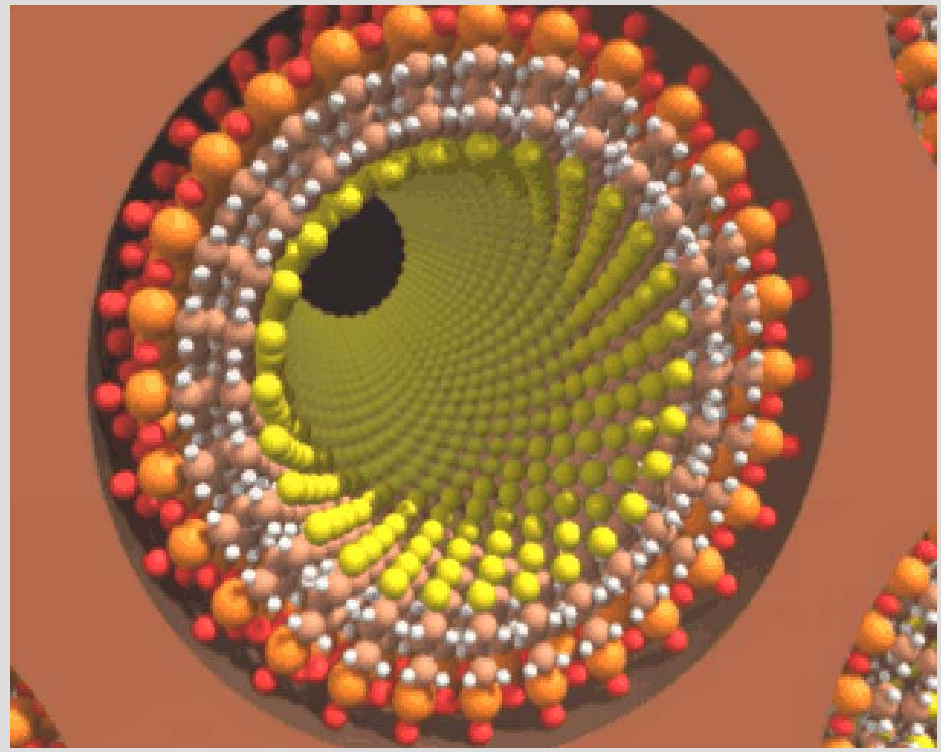
A. Self-assembled monolayers



+

B. Ordered mesoporous oxide





First reported in:

Science 1997, *276*, 923-926.

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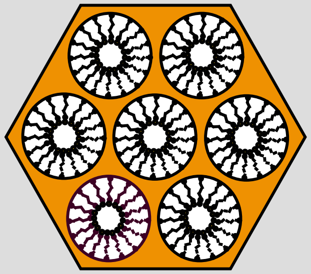
SAMMS in a Nutshell

- Extremely high surface area = high capacity
- Rigid, open pore structure provides for fast sorption kinetics
- Chemical specificity dictated by monolayer interface, easily modified for new target species
- Proximity effects allow multiple ligand/cation interactions
- Sequestration can be driven either by metal/ligand affinity or by adduct insolubility
- Good chemical and thermal stability
- Easily regenerated/recycled



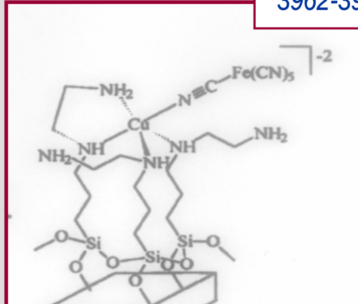
"Environmental and Sensing Applications of Molecular Self-Assembly"

in "Encyclopedia of Nanoscience and Nanotechnology";

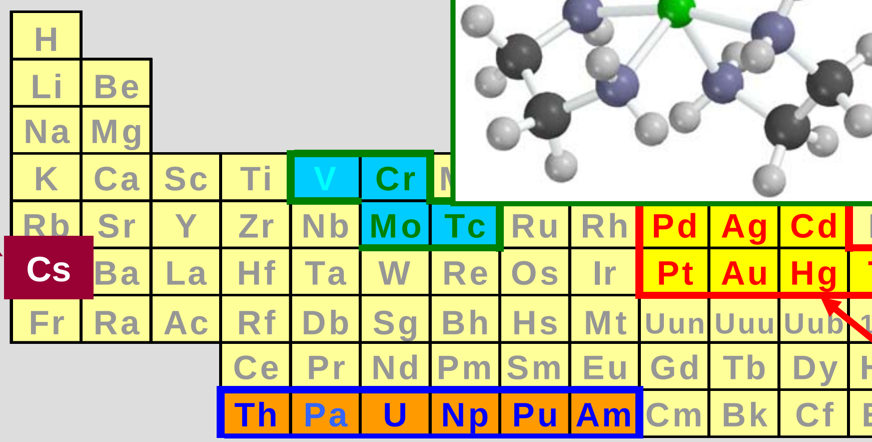
Dekker, **2004,** pp. 1135-1145.

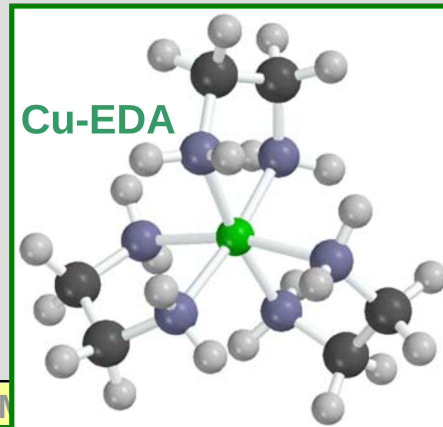
Tailoring SAMMS interfacial chemistry to the periodic table

Env. Sci. & Tech. 2001, 35, 3962-3966.



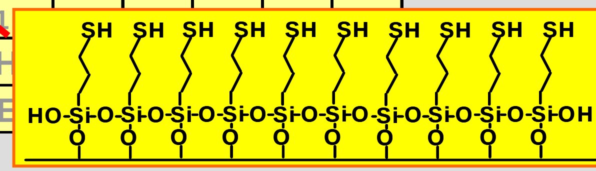
Cu-FC-EDA





Chemistry of Materials 1999, 11, 2148-2154
J. Physical. Chem. B. 2001, 105, 6337-6346.
J. Synchrotron Radiation, 2001, 8, 922-924

Radiochimica Act 2003, 91, 539-545



Thiol

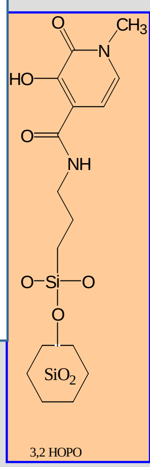
Science, 1997, 276, 923-926.
J. Synchrotron Radiation, 1999, 6, 633-635
Sep. Sci. & Technol. 1999, 3411, 2329-2345
Mat. Tech. Adv. Perf. Mat. 1999, 14, 183-193
Surf. Sci. & Catalysis, 2000, 105, 729-738.

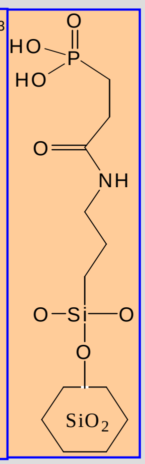
Env. Sci. & Tech. 2005, 39, 1324-1331 .

Env. Sci. & Tech. 2005, 39, 1332-1337 .

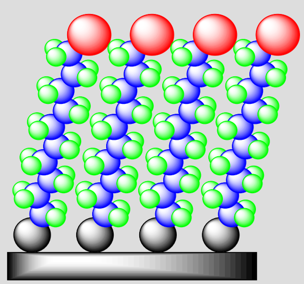
J. Materials Chemistry 2004, *14*, 3356-3363

Chem. Comm. 2002, 1374-1375.





HOPO Prop-Phos



….all by varying the monolayer ligand field.

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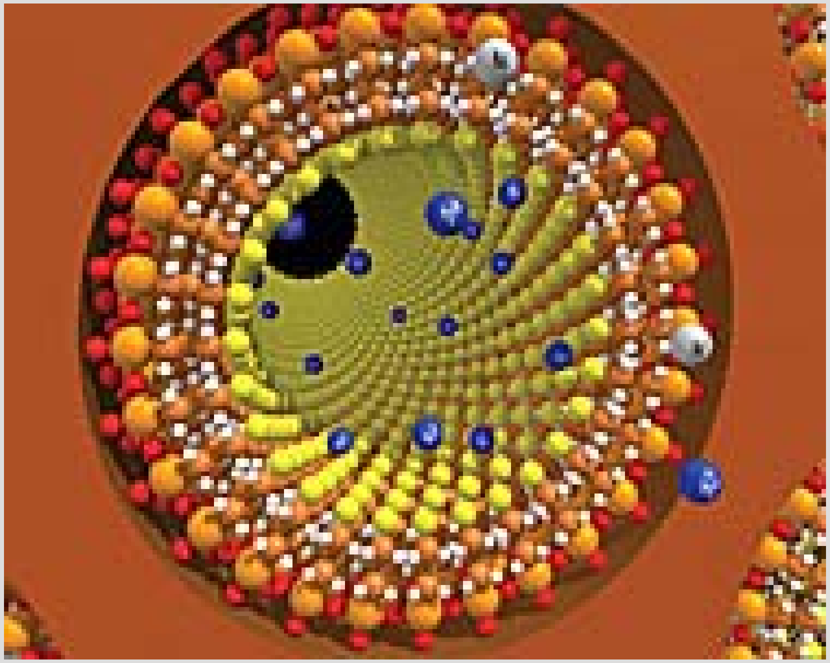
Thiol-SAMMS overview

- Extensive literature precedent for using thiols to bind “soft” heavy metals (e.g. Hg, Cd, Au, etc.).
- Silane loading density can be tailored to 4, 5 or 6 silanes/nm^2 depending on the synthetic methodology employed.
- This loading density allows Thiol-SAMMS to absorb as much as 2/3 of its own weight in Hg.



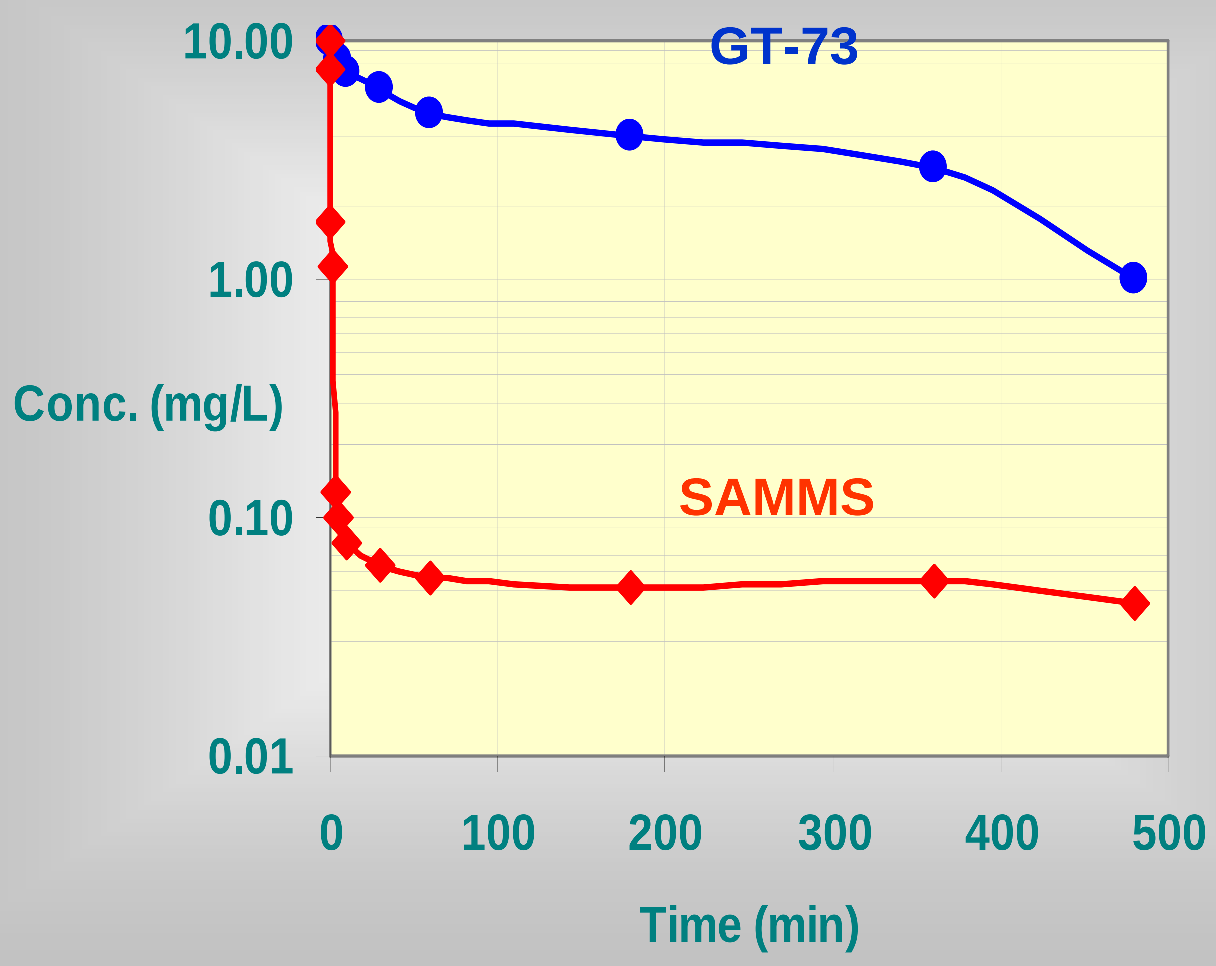
Mercaptopropyl siloxane monolayer lining the pore surface of mesoporous silica. The mercury (shown in blue) binds to the sulfur atoms (sulfur atoms are shown in yellow).

TECHNOLOGY NEWS AND TRENDS

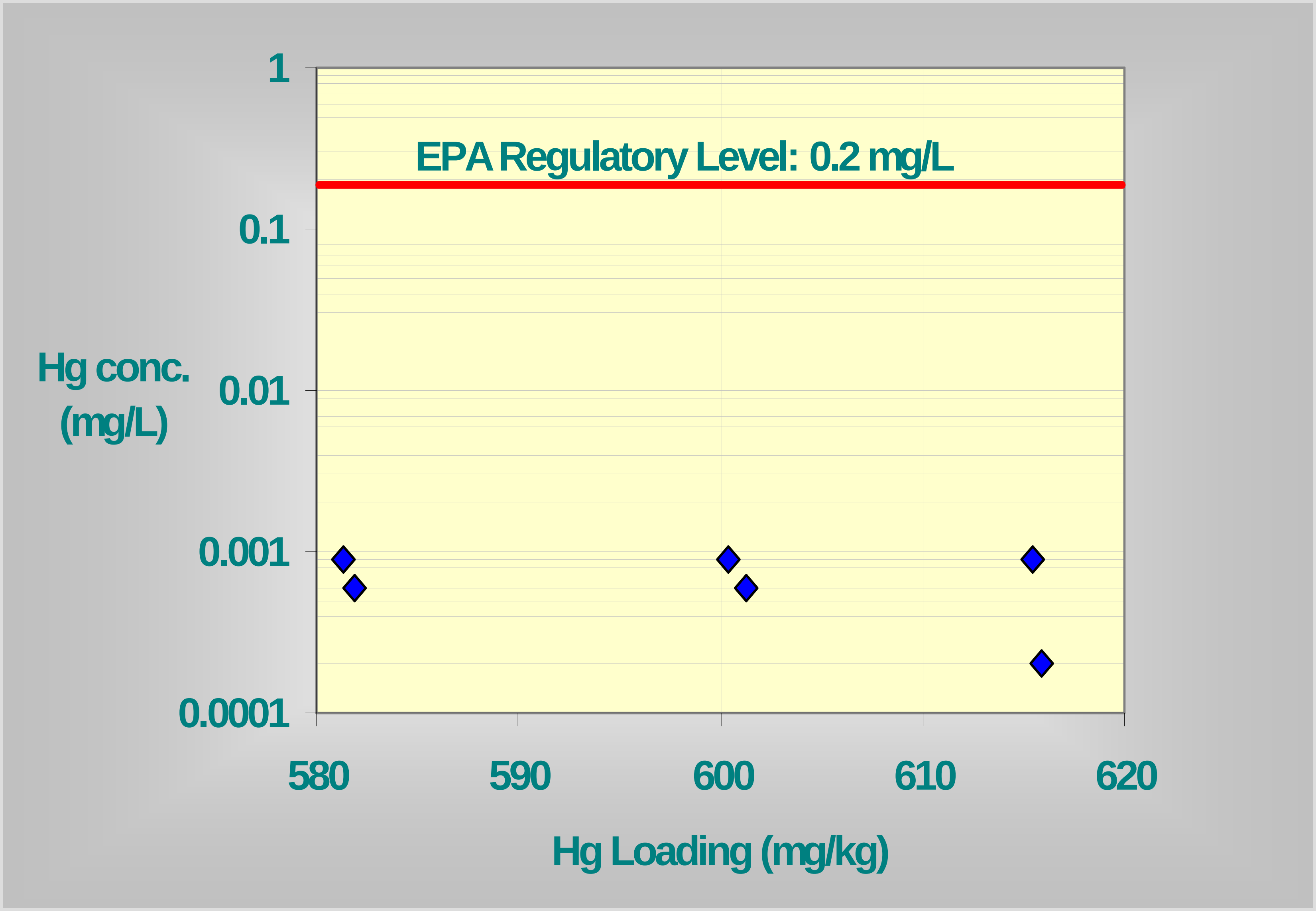
(Sept. 2005 issue)

http://www.cluin.org/products/newsltrs/tnandt/view.cfm?issue=0905.cfm#5

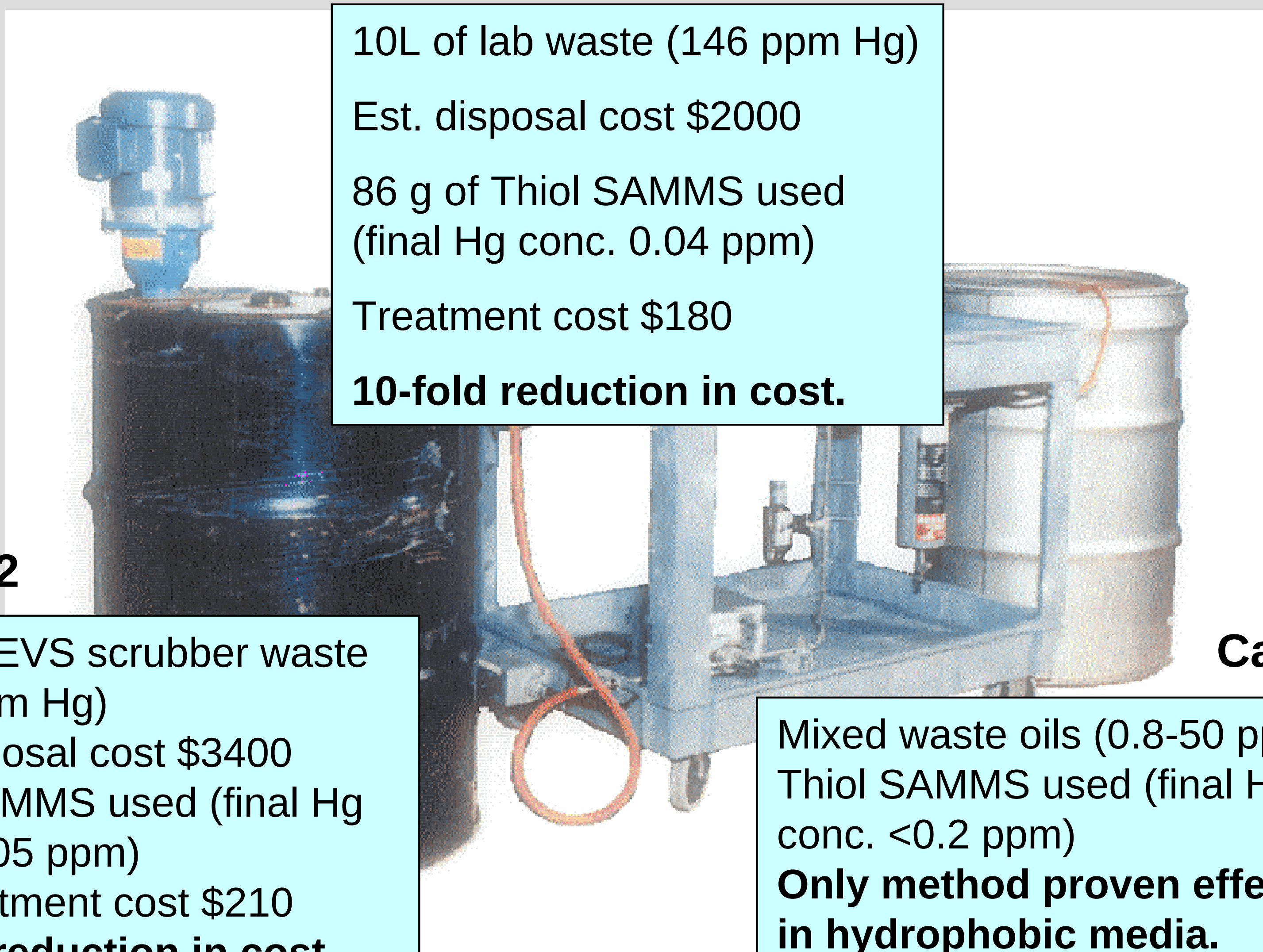
Mercury Adsorption Kinetics: Thiol SAMMS



TCLP Data for Hg-loaded thiol-SAMMS



Actual Hg waste clean-up



Case #1

10L of lab waste (146 ppm Hg)

Est. disposal cost $2000

86 g of Thiol SAMMS used (final Hg conc. 0.04 ppm)

Treatment cost $180

10-fold reduction in cost.

Case #2

200L of EVS scrubber waste (4.64 ppm Hg)
Est. disposal cost $3400
Thiol SAMMS used (final Hg conc. 0.05 ppm)
Est. treatment cost $210
15-fold reduction in cost.

Case #3

Mixed waste oils (0.8-50 ppm Hg)
Thiol SAMMS used (final Hg conc. <0.2 ppm)
Only method proven effective in hydrophobic media.

Ref: Klasson et al. 1999, 2000 ORNL

Preliminary Material Lifetime Cost Comparison

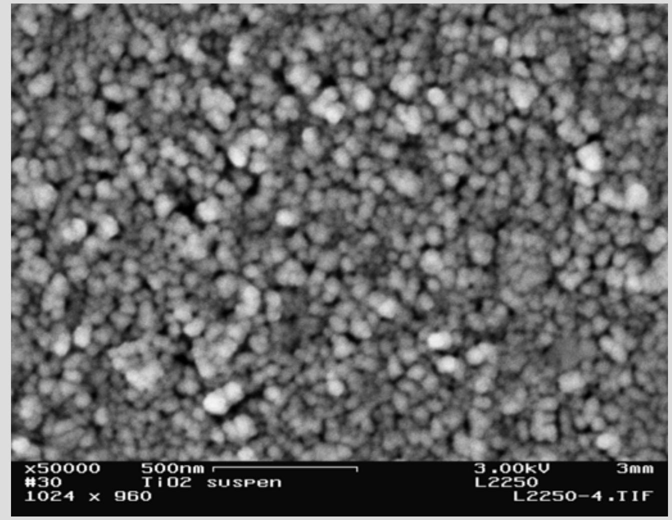
Basis	SAMMS	Resin	Act. C
Material Cost ($/kg)	110	40	2
Hg Loading (g/kg)	6	0.5	0.002
Substrate (kg)	167	2000	500,000
Material cost to remove ~1 kg Hg	$18,370	$80,000	$1,000,000
Waste Disposal Cost @ $60/cft	$771	$6,349	$2,380,952
Total Treatment Cost ~5.4Mgal	$19,141	$86,349	$3,380,952

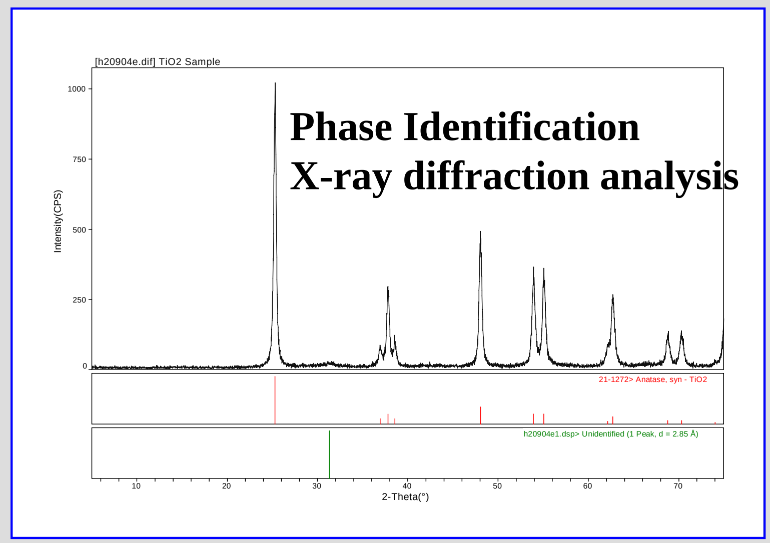
Waste Stream Hg Conc: 10 ppm

Variations on the SAMMS theme: Functionalized TiO_2 Nanoparticles

TiNano40™ Characteristics

Surface Area (BET)	51.2 m2/g
Particle Density	3.88 g/cm3
Particle Size	40 – 60 nm
TiO2	99.8%
Impurities	
0.2%	
(ZrO2, SiO2,	
Cl, P2O5, ZnO)	
Crystalline Phase	Anatase

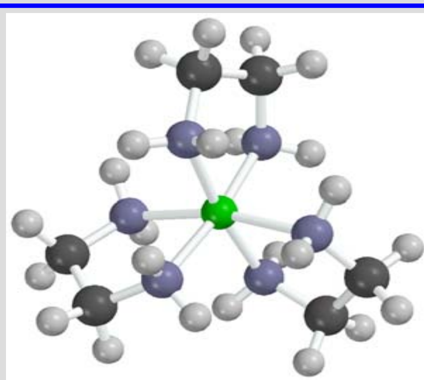


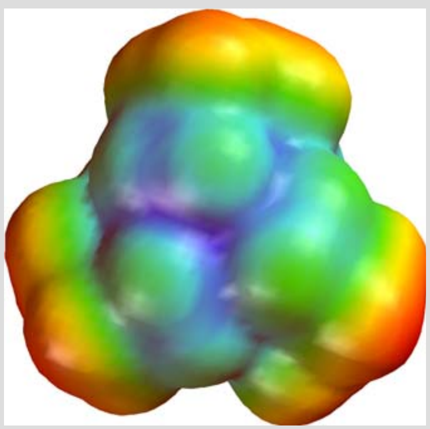


Env. Sci. & Technol. 2005 (in press).

Functionalization

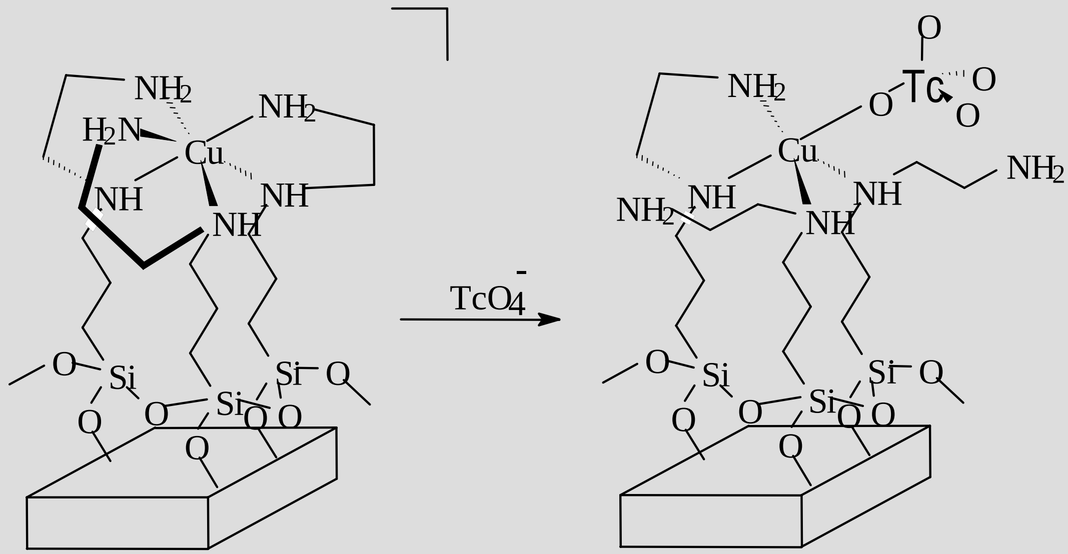
Cu (II) EDA Functionality for bonding tetrahedral anions (e.g. arsenate, chromate)





Chem. Mater. 1999, 11, 2148-2154.

Binding mechanism

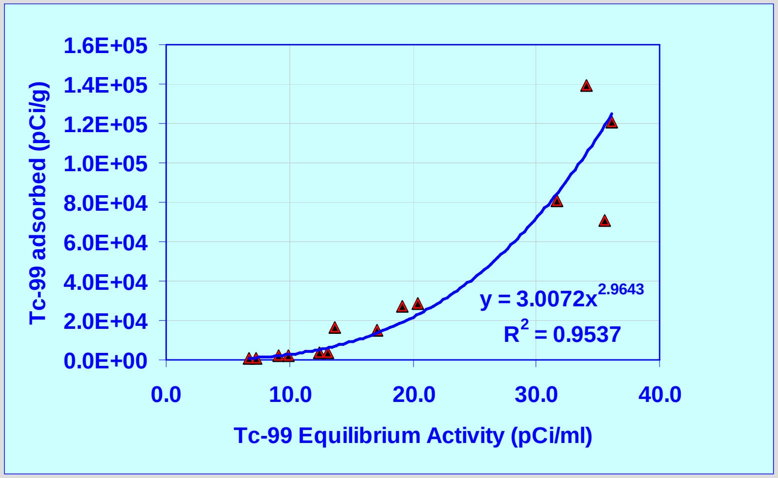


J. Physical. Chem. B. 2001, 105, 6337-6346.

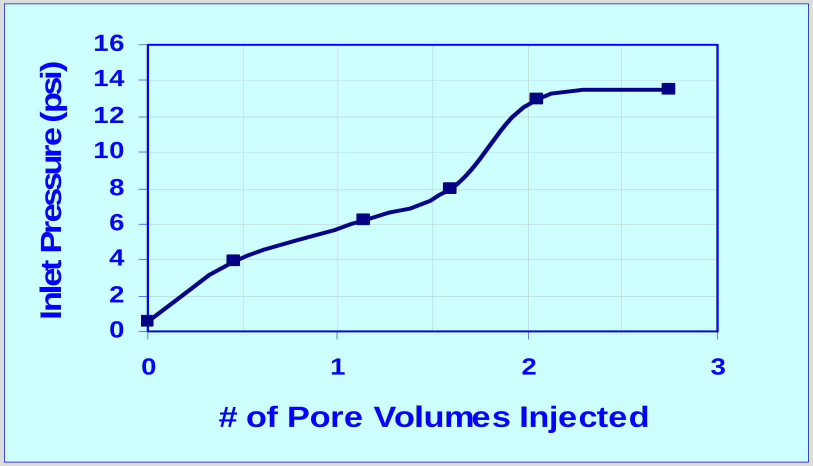
Env. Sci. & Technol. 2005, 39, 7306-7310.

Performance

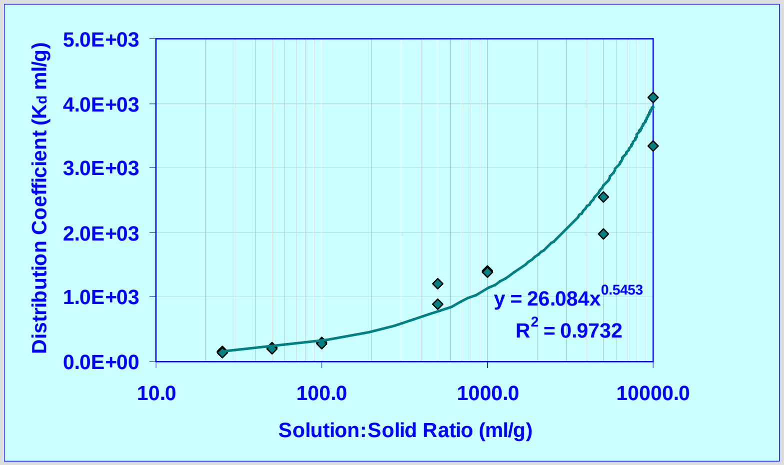
Loading



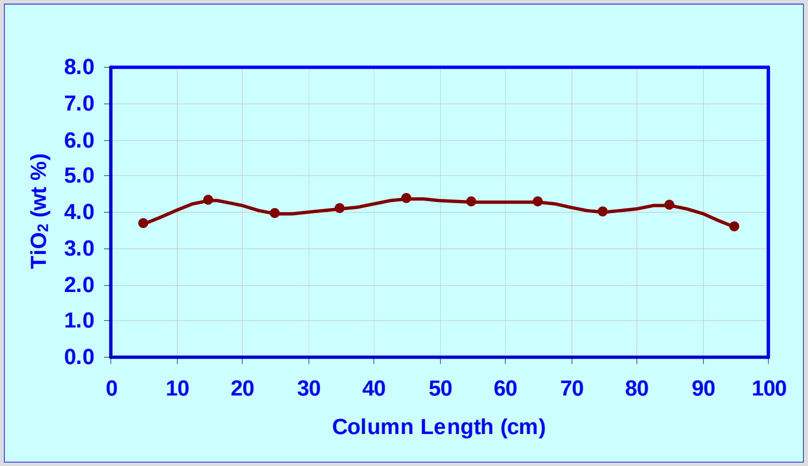
Back pressure



Distribution coefficient



Distribution in soil column



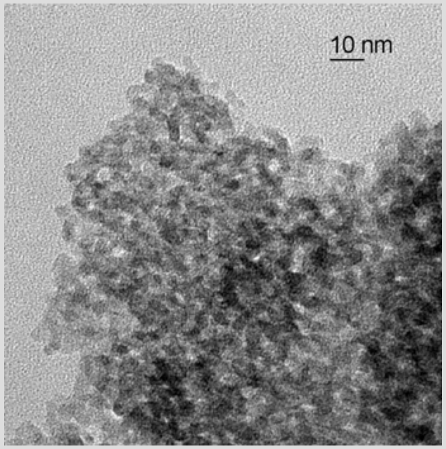
30 mesh sand test matrix

Tc-99 Adsorption Experiments

Maximum Tc-99 loading: ~1.3 x 105 pCi/g.

Tc-99 Kd: 1.5 x 102 – 4.0 x 103 ml/g.

Variations on the SAMMS theme: Promising new materials….



Mesoporous metal phosphates – actinides, pertechnetate, chromate, etc.

<u>**Capture the strengths of SAMMS**</u>:

High surface area

High functional density

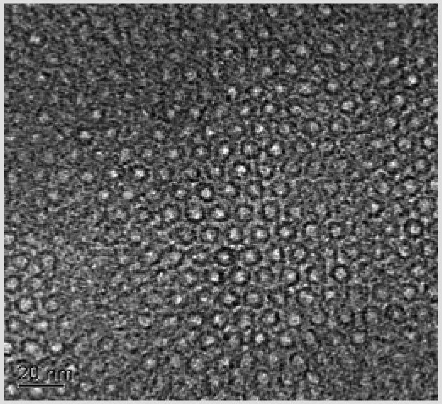
Rigid open pores structure

High affinity

….and use this an opportunity to:

Make the backbone inherently functional

Tailor materials for harsh environments



Functional mesoporous carbons – heavy metals

Conclusions

- SAMMS is a very effective method for separation and stabilization of environmentally problematic species
- High surface area and dense monolayer coating creates high sorbent capacity
- Rigid open pore structure allows for facile diffusion into the pores, hence rapid sorption kinetics.
- Specificity is dictated by the monolayer interface, and is easily tailored for a wide variety of heavy metals and radionuclides
- New classes of functional nanomaterials that also capture these strengths are on the horizon.