



Nanotechnology and Nuclear : One Case Study

Rice University

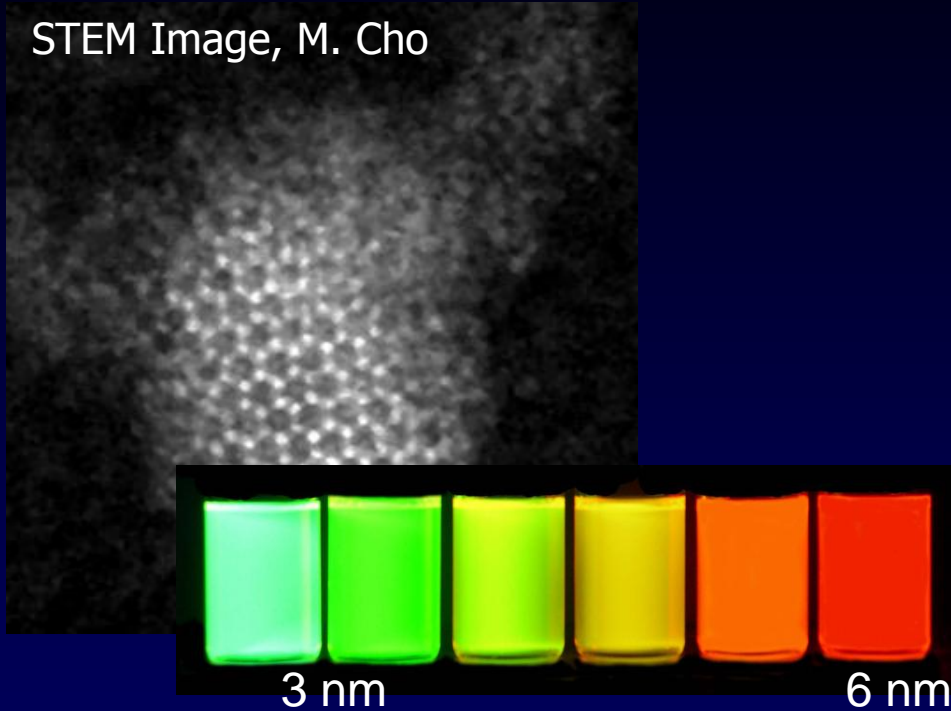
Professor Vicki Colvin

Pitzer-Schlumberger Chair of Chemistry

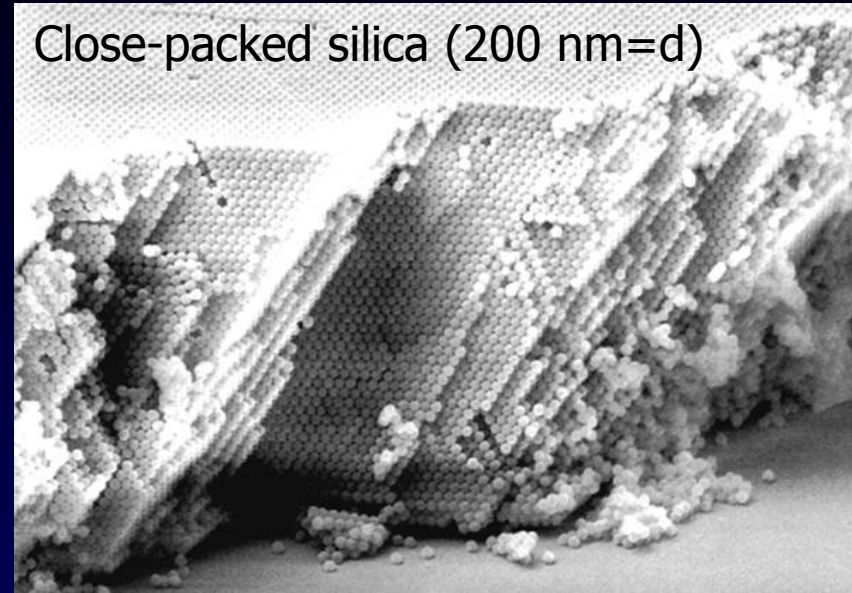
<http://www.rice.edu>

Features of Nanoparticles: The Hammer

STEM Image, M. Cho



Close-packed silica (200 nm=d)



- They are very, very small
- Their properties are size-dependent
- They can assemble into larger structures

The Needle in the Haystack: The Nail

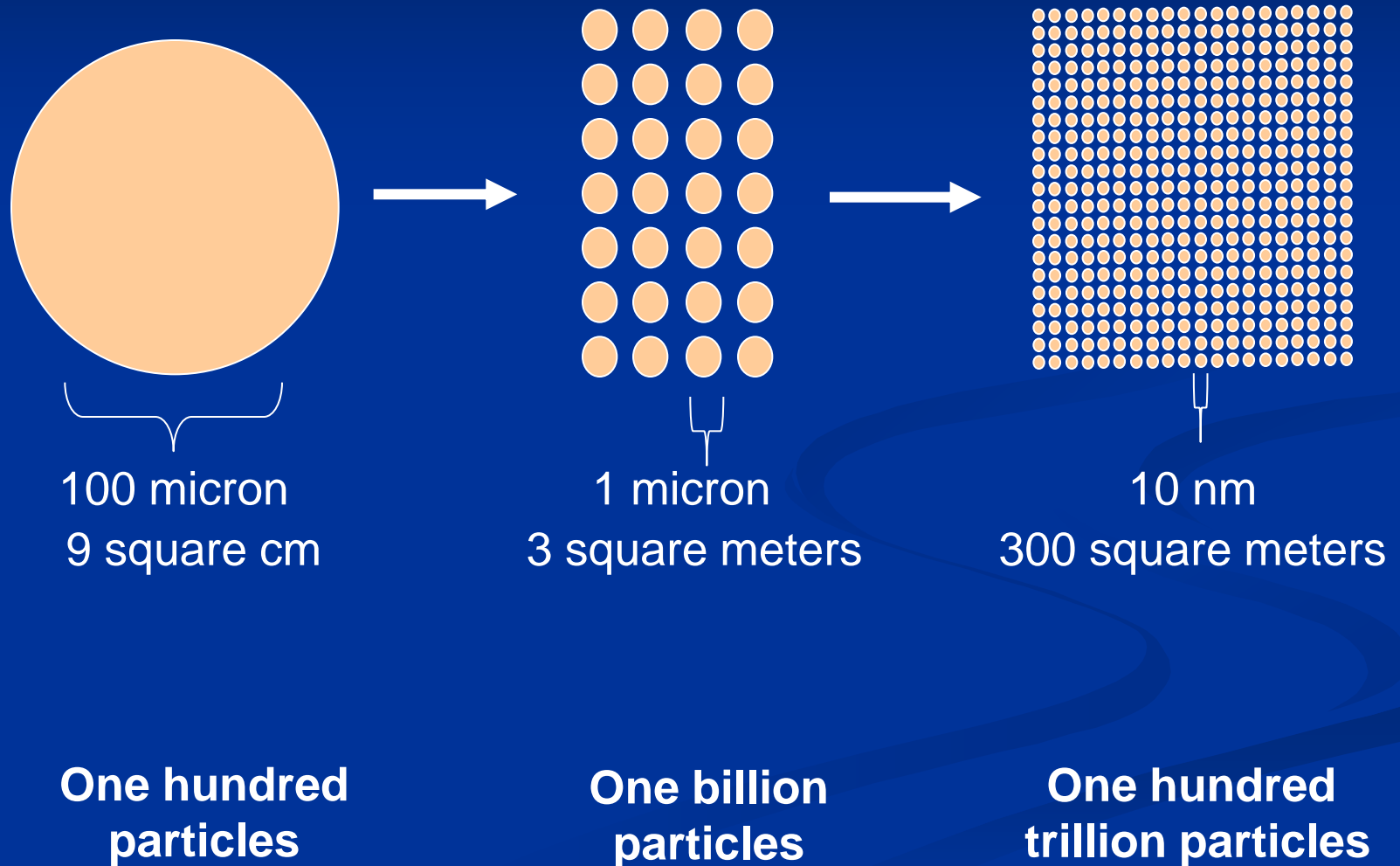


Can we concentrate Uranium from soils so that it can be analyzed and reclaimed?

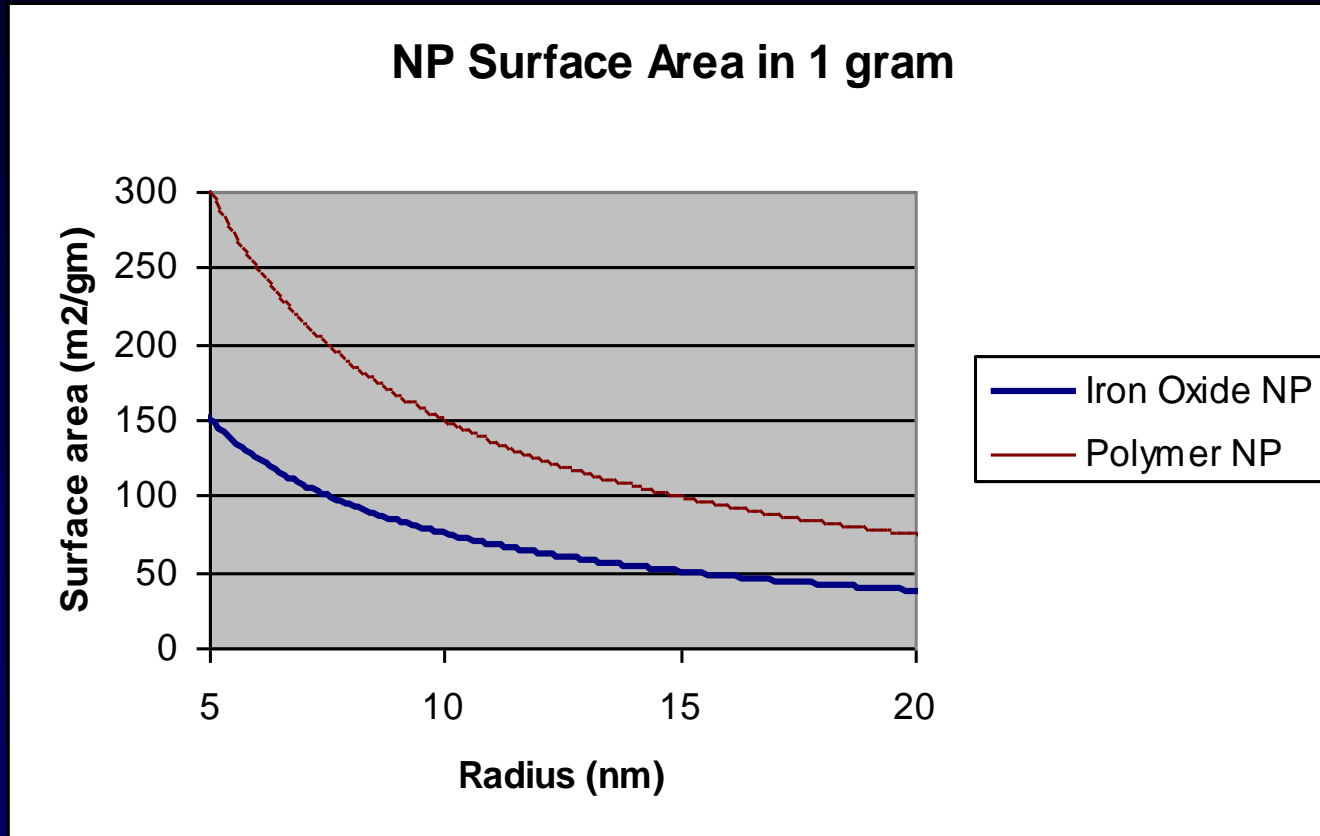


Dr. John Fortner

Small stuff, huge surface



Nanoparticles: Super Small

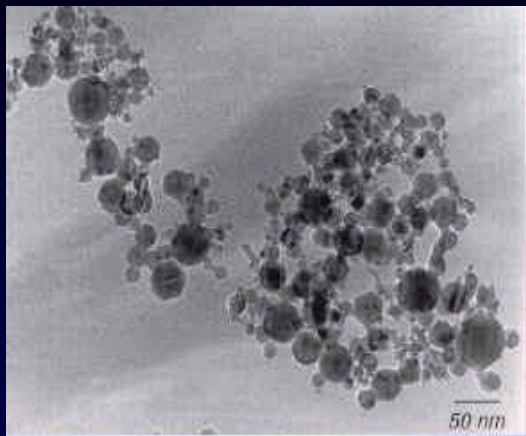


Surface area in 1 gram $\sim 4 \pi r^2 / (4/3 \pi r^3 \cdot \text{density})$

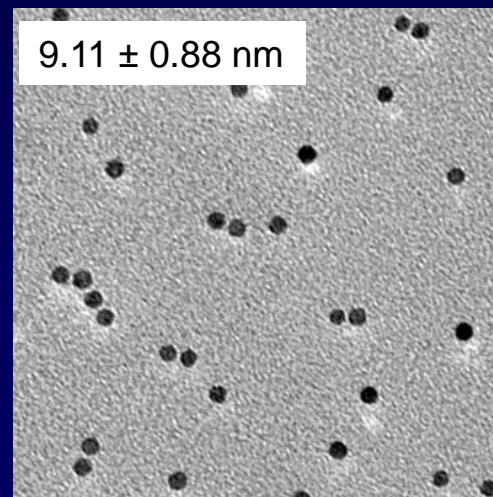
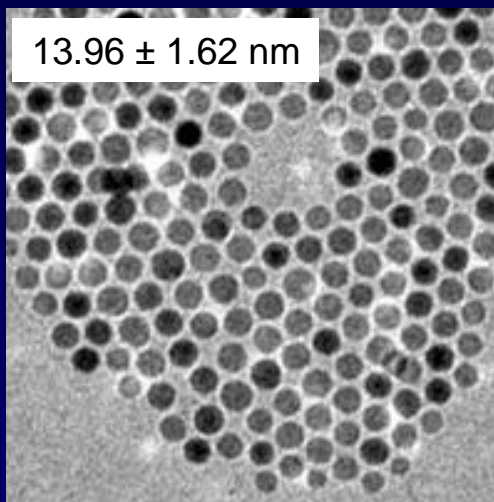
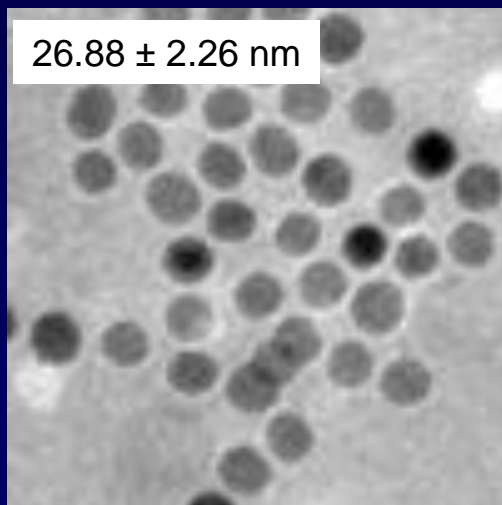
With that much surface: surface matters

Commercial nano-oxides have problems

- Agglomerated → poor magnetic separation
- Larger nanoparticles → lower sorption
- Bad size distribution → no optimization



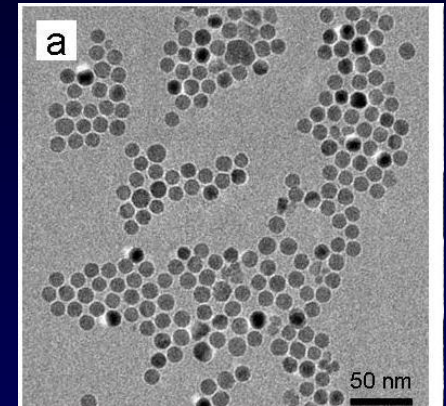
From Kemico, avg size 20 nm



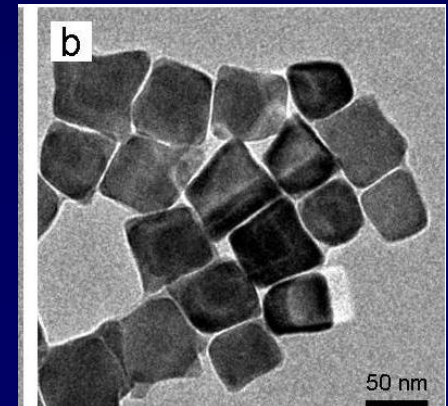
W. Yu, V. L. Colvin, Chem. Comm. (2004)

High Technology through Low Tech Manufacturing

Precursor	Surfactant	Solvent
FeOOH (Iron Oxo Hydrate)	Oleic acid ((9Z)-octadec-9-enoic acid)	ODE (1-octadecene)

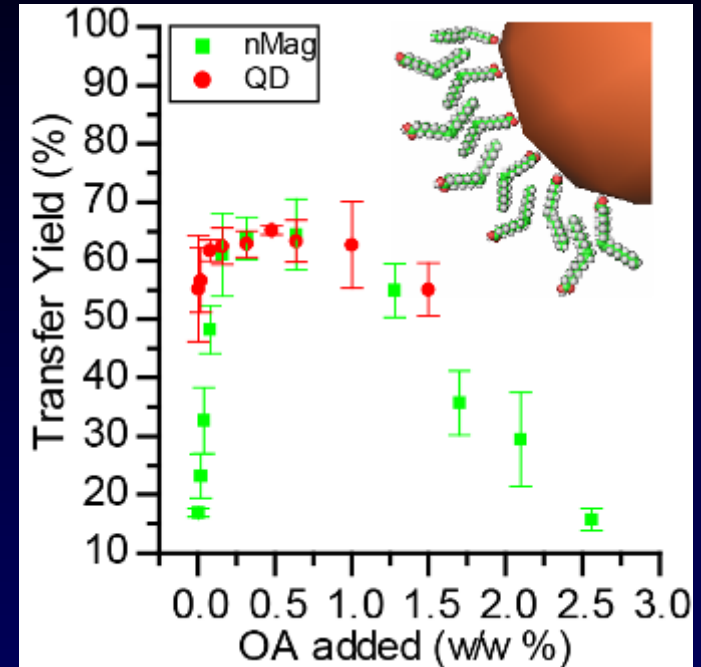


Diesel Oil Diluents



Surface Stabilization of Materials

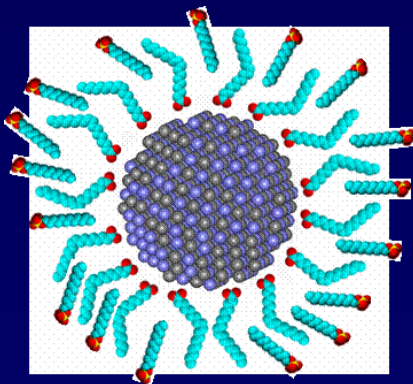
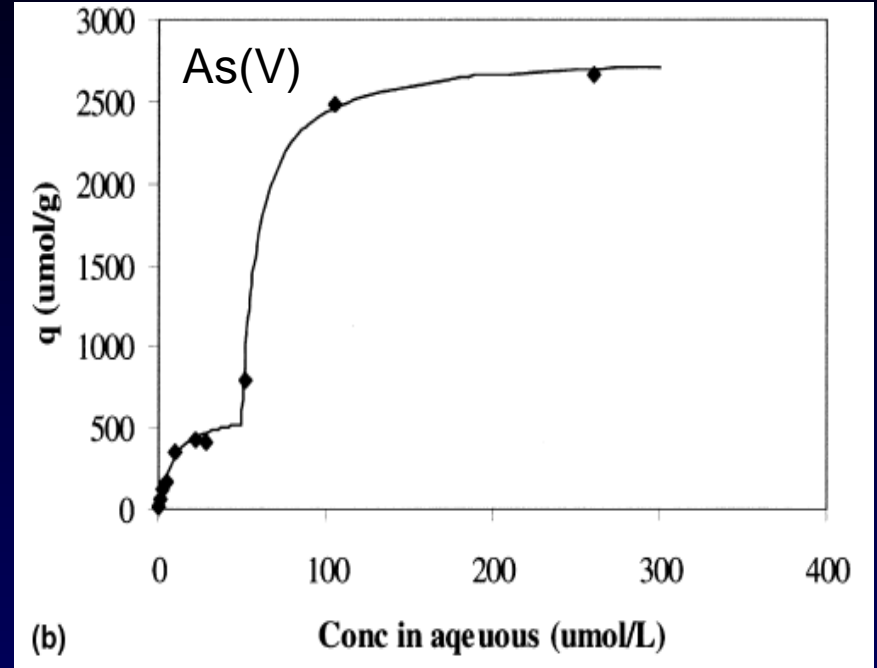
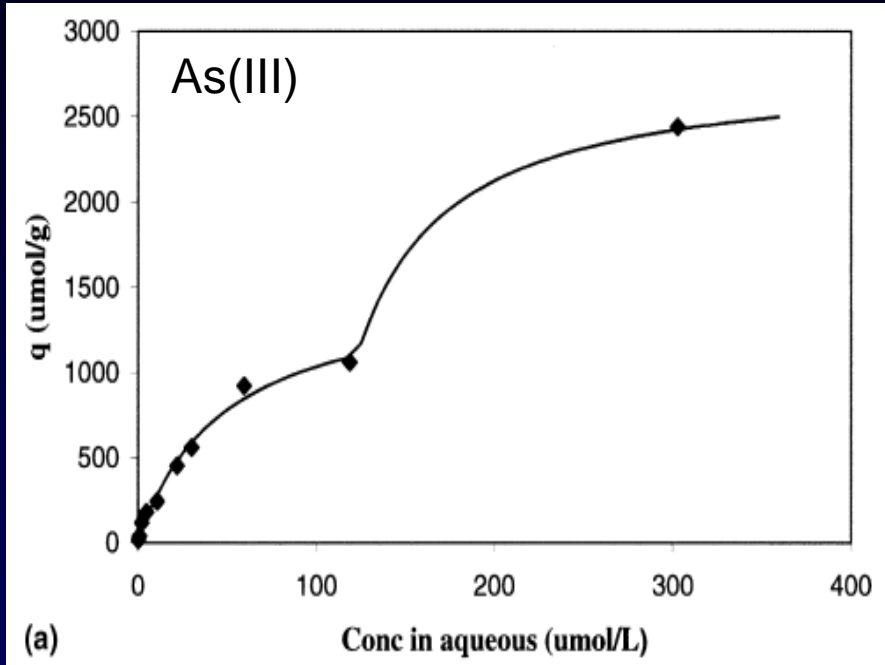
J. T. Mayo and Arjun Prakash



Oleic Acid Bilayer Stabilization

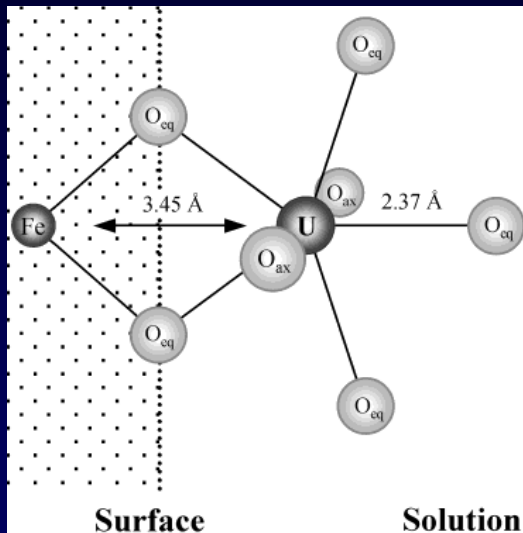
- Fatty acid bilayers – stable suspensions, strong
- Available detergents work well – colloidally stable, weak
- Both options maintain magnetic properties

Nano-Iron Oxide: Huge Capacities for Arsenic



- 10 nm Magnetite can sorb arsenic
- Sorption capacities (\blacktriangle) of 12% (w/w)
- 1 gm of sorbent could treat 2000 L of water
- Must be highly crystalline and non-hydrated

Iron Oxide and Uranium: Strong Interaction



Missana, T., U. Maffiotte, and M. Garcia-Gutierrez, *Surface reactions kinetics between nanocrystalline magnetite and uranyl*. *Journal of Colloid and Interface Science*, 2003. 261(1): p. 154-160.

Missana, T., M. Garcia-Gutierrez, and V. Fernandez, *Uranium(VI) sorption on colloidal magnetite under anoxic environment: Experimental study and surface complexation modelling*. *Geochimica Et Cosmochimica Acta*, 2003. 67(14): p. 2543-2550.

T.B. Scott, G.C. Allen, P.J. Heard and M.G. Randell, *Reduction of U(VI) to U(IV) on the surface of magnetite*. *Geochimica et Cosmochimica Acta*, 2005.

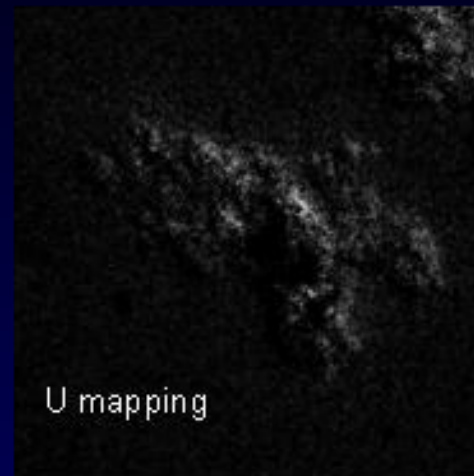
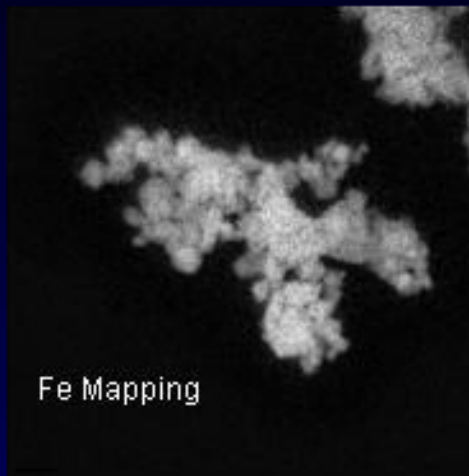
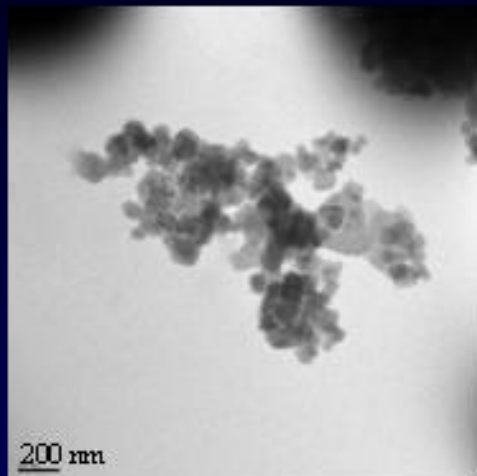
S. El Aamrania, J. Giménez, M. Roviraa, F. Secob, M. Grivé, J. Brunoc, L. Duroc and J. de Pablo, *A spectroscopic study of uranium(VI) interaction with magnetite*. *Applied Surface Science*, 2007

Waite, T. D.; Davis, J. A.; Payne, T. E.; Waychunas, G. A.; Xu, N. Uranium(VI) adsorption to ferrihydrites Application of a surface complexation model. *Geochim. Cosmochim. Acta* 1994

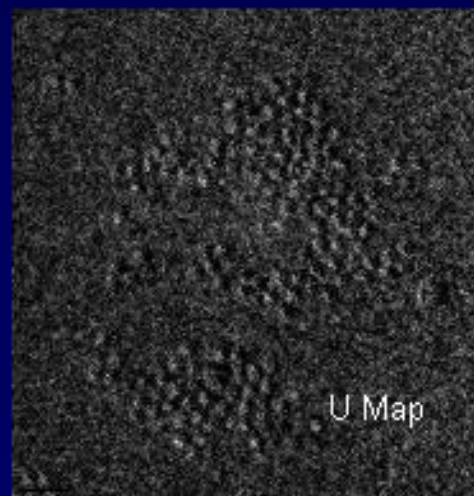
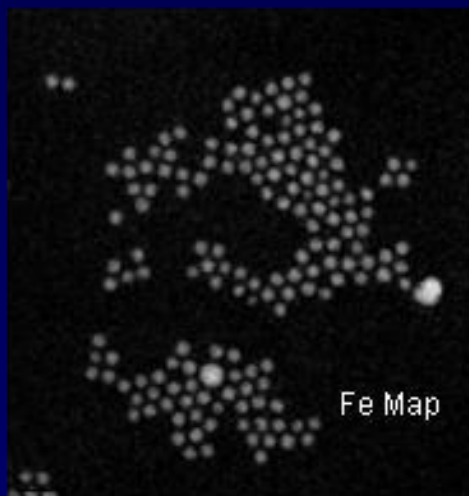
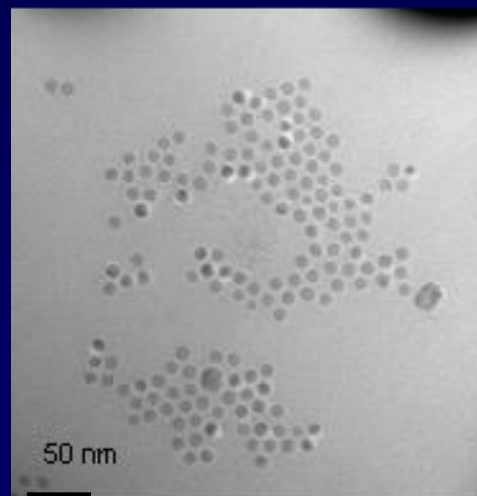
Catalano, J. G.; Brown, G. E., Jr. Analysis of uranyl-bearing phases by EXAFS spectroscopy: Interferences, multiple scattering, accuracy of structural parameters, and spectral differences. *Am. Mineral.* 2004.

Surface Chemistry Consistent with Iron-Uranyl Complex

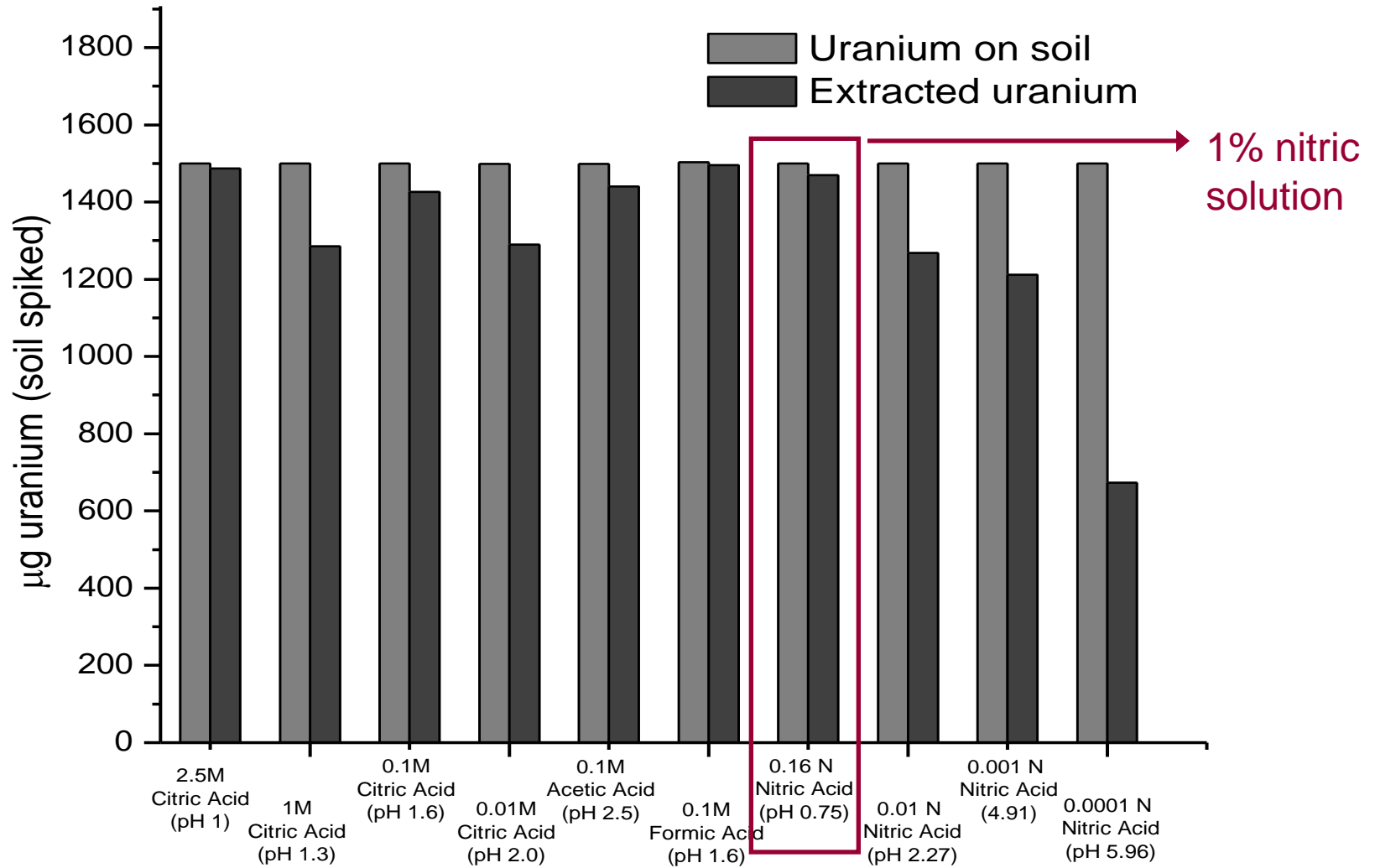
Commercial nMAG



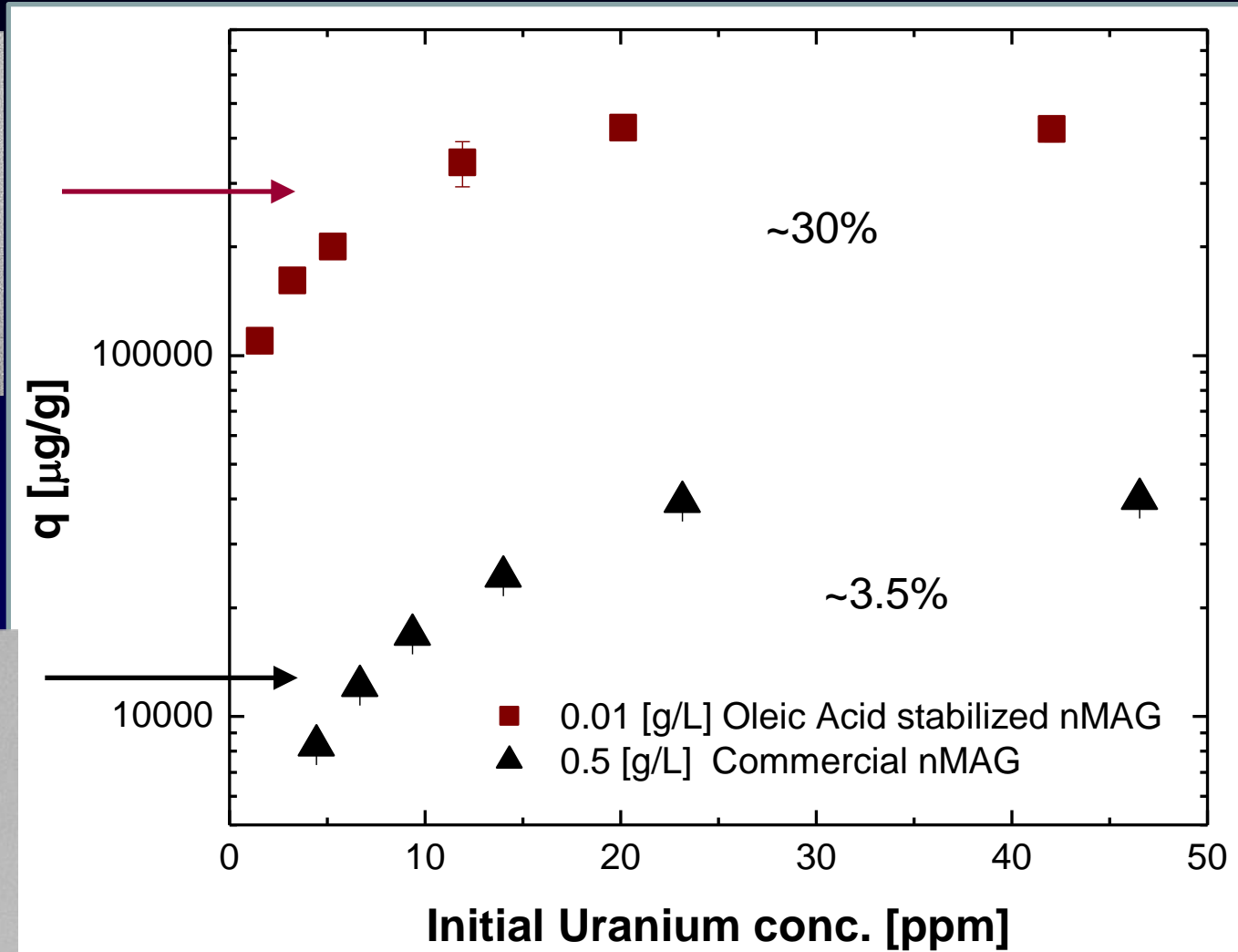
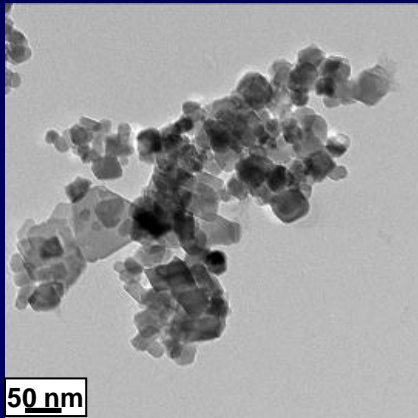
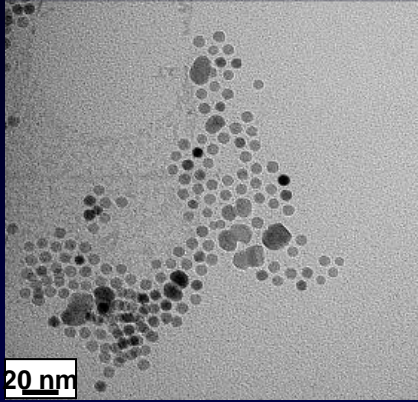
Oleic acid stabilized nMAG



Iron Oxide: Also Ideal for Uranium Species



Theoretical Sorption Capacities: 30 w/w %



pH 5, DI Water, 12 hrs

Aqueous nMAG-Uranyl Sorption: Totals

Variable Water Sources

0.05 [g/L] nMAG

Source	Initial U conc.	U Recovery
Brays Bayou	7.45 [ppb]	75.1±5.0%
Ground (well) Water	4.92 [ppb]	86.3±20.0%
Millipore	4.83 [ppb]	99.3±0.1%

From Soil (Sandy) Extractions

nMAG conc.	Initial U conc.	U Recovery
0.05 [g/L]	35.1 [ppb]	99.1±0.2%
0.3 [g/L]	33.4 [ppm]	100.4±0.3%



nMAG conc.	Initial U conc.	Max. Sorption
0.005 [g/L]	45.9 [ppb]	3.40±0.90 [mg/g]
0.05 [g/L]	58.8 [ppm]	292±14 [mg/g]

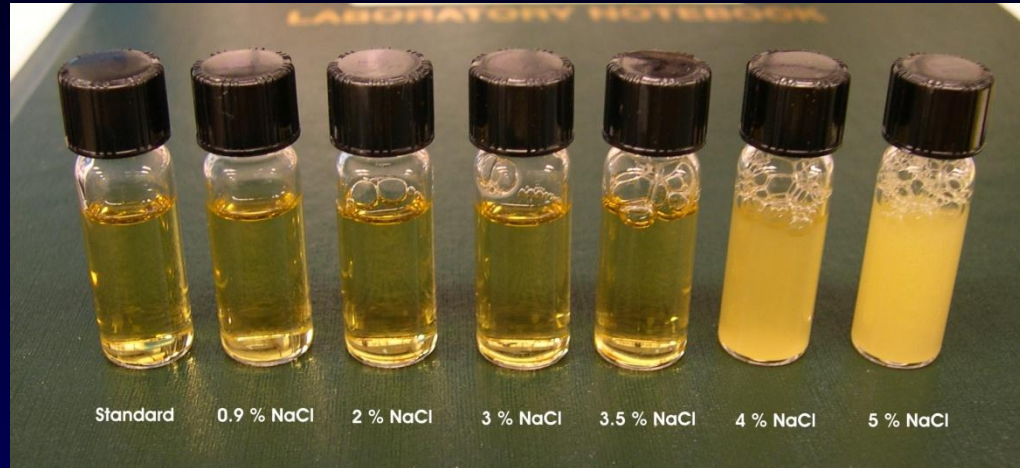
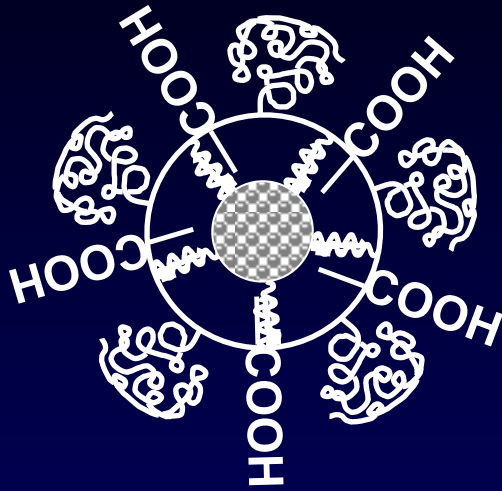
Analysis

Reclamation



Removing Nanoscale Magnetite: Difficult!

Dr. Cafer Yavuz and J. T. Mayo



Iron oxide nanocrystals, in water, variable NaCl

Filtration is energy and capital intensive

Pressure goes as radius squared

Not viable for rural communities

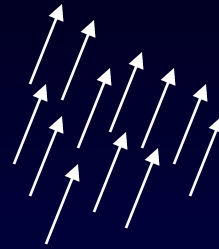


Asian tribune.com

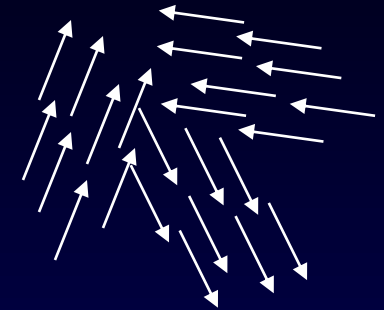
Nanoparticles: Size Changes Properties



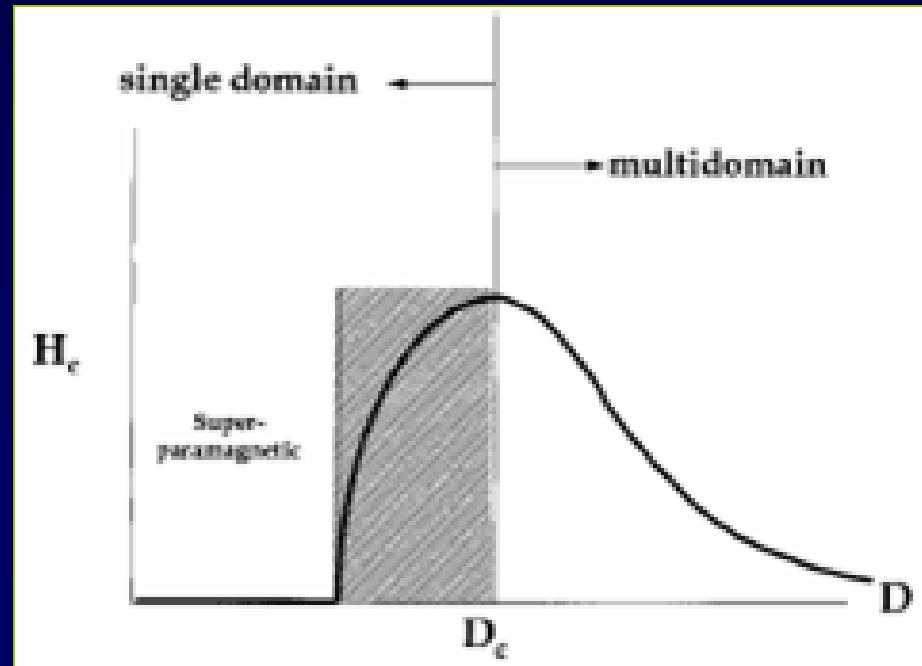
Small cluster: Supraparamagnetic
Easy to magnetize



Larger cluster: Single Domain
Magnetization can shift



Bulk solid: Permanent magnet
Small magnetization



A Surprising Observation

*Nanocrystals
interact with
very, very low
magnetic fields*

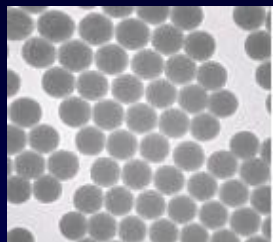
$$F_m = \mu_0 \chi V_p H \nabla H$$

↓
*Much larger in
nanocrystalline
magnetite*

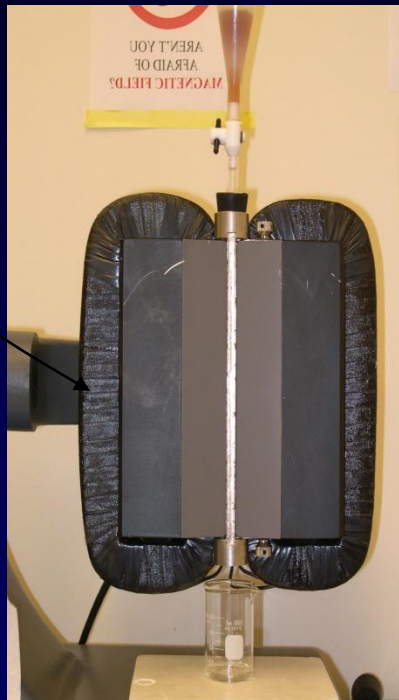


Method to remove magnetic materials

1 Tesla Electromagnets
Narrow bore columns

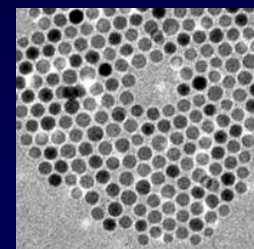
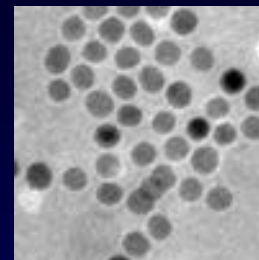
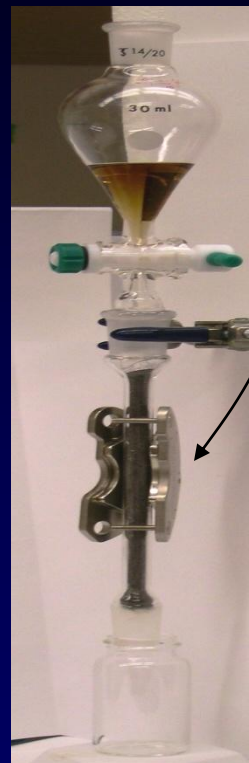


1 gram = .1 m²



Old way

100 mTesla
Hard drive magnet



1 gram = 50 m²

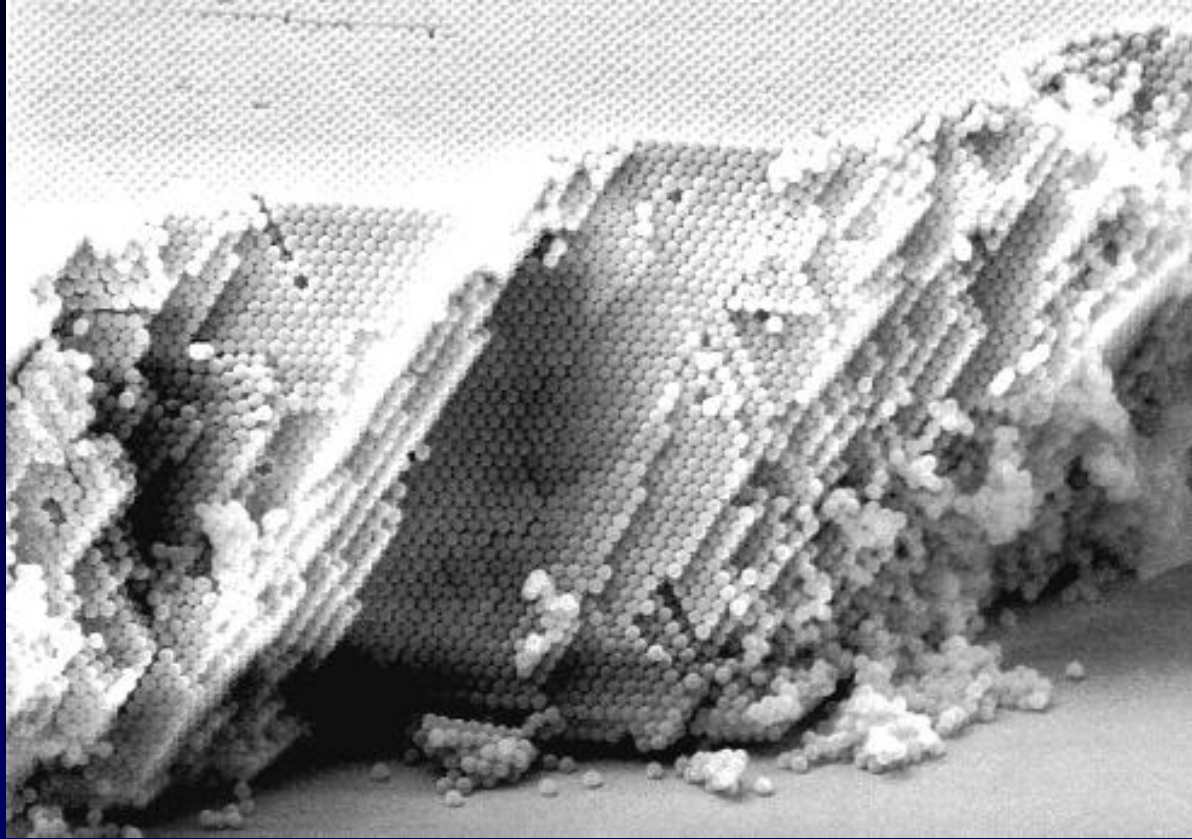
New way

nMAG Separation: Fast and Low Tech

Material	Separation	Percent nMAG Removal
Commercial	20 nm Filter	99.9%
Igepal® CO-630	20 nm Filter	99.6%
Oleic Acid	20 nm Filter	98.9%
Commercial	Magnetic	99.9%
Igepal® CO-630	Magnetic	95.3%
Oleic Acid	Magnetic	93.3%



Nanoparticles: Assembly Properties

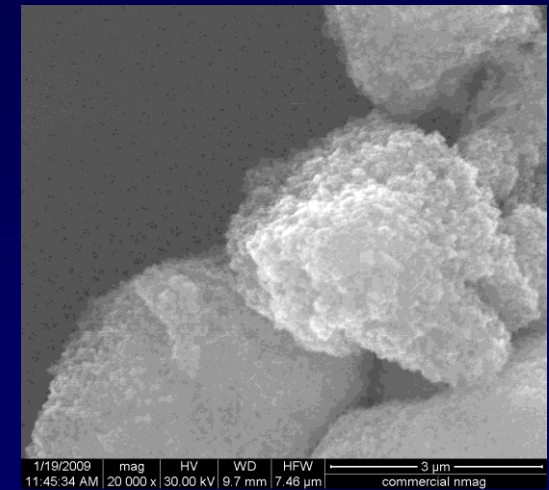
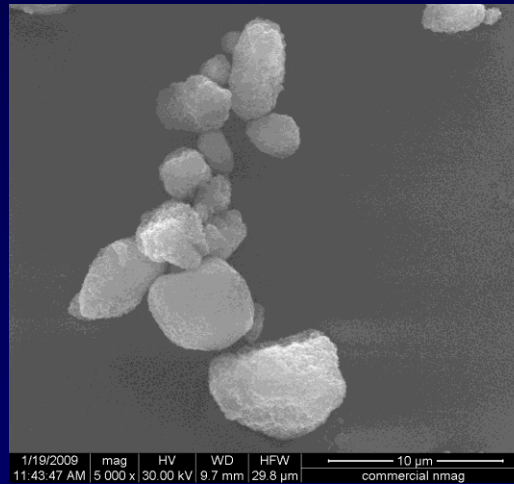
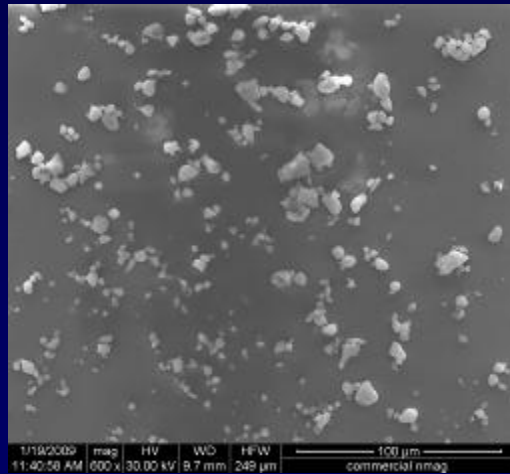


Nanoparticles (200 nm diameter silica, above) will form dense films when diameters are *uniform*

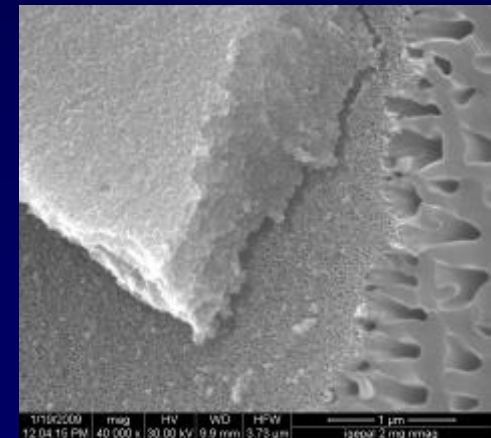
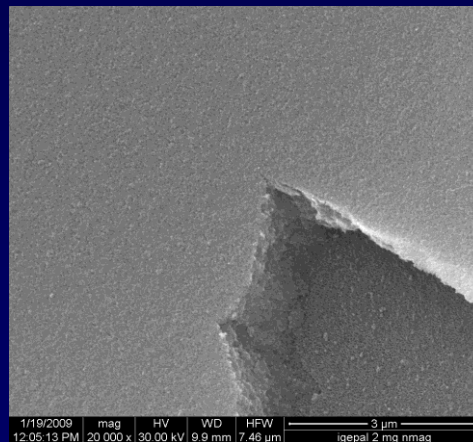
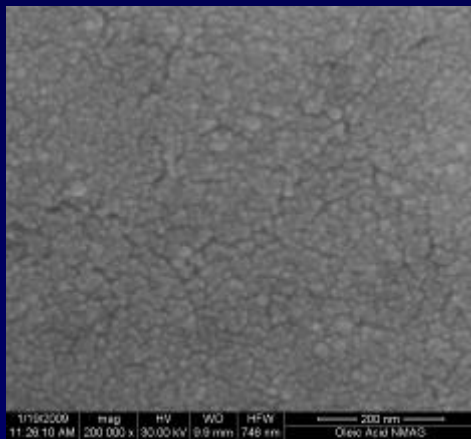
Uranium on commercial nano-oxides: no counting



Penetration depth of alpha particles < 1 micron, only surface is counted

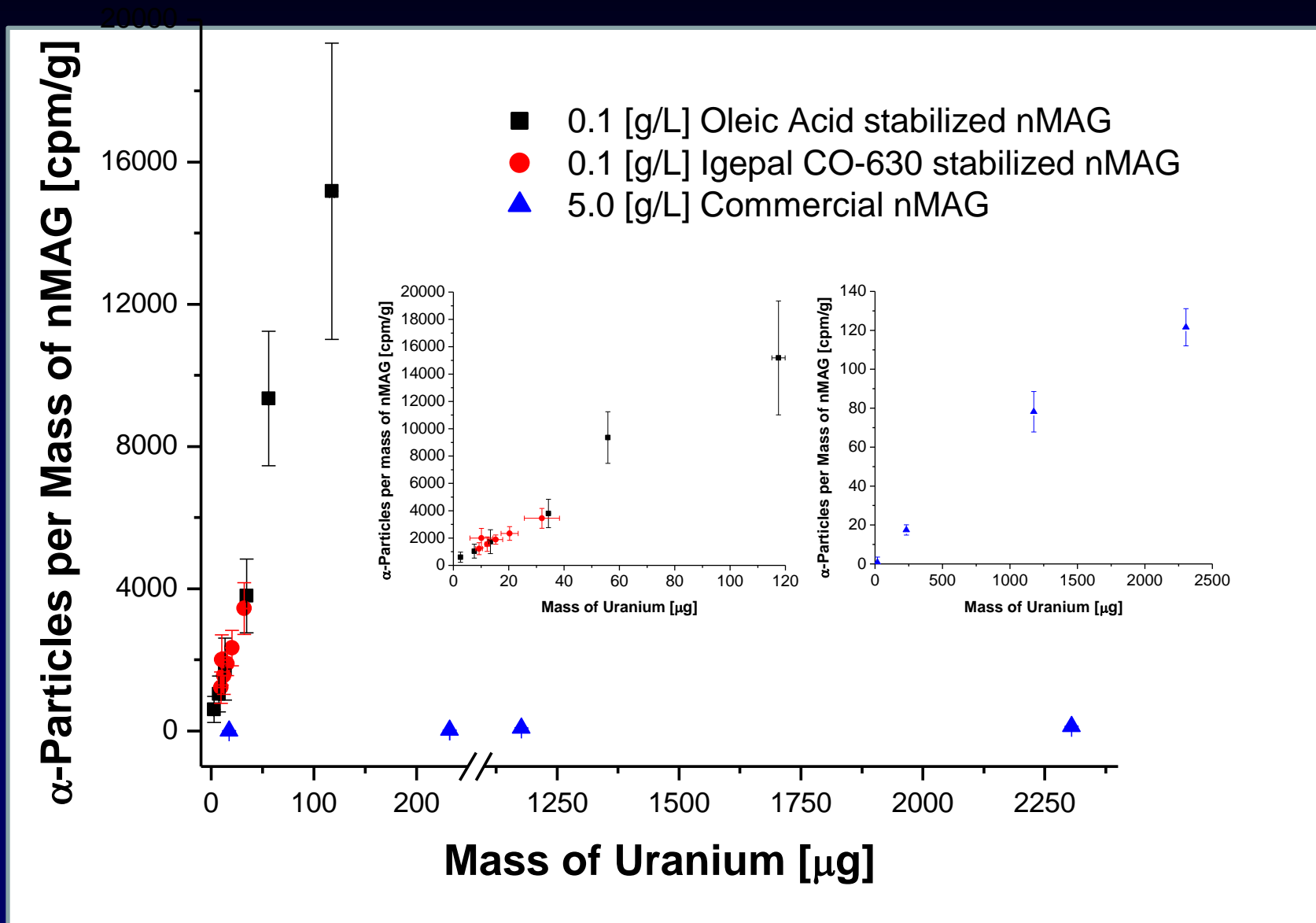


Unless nanoparticles are uniform: well packed

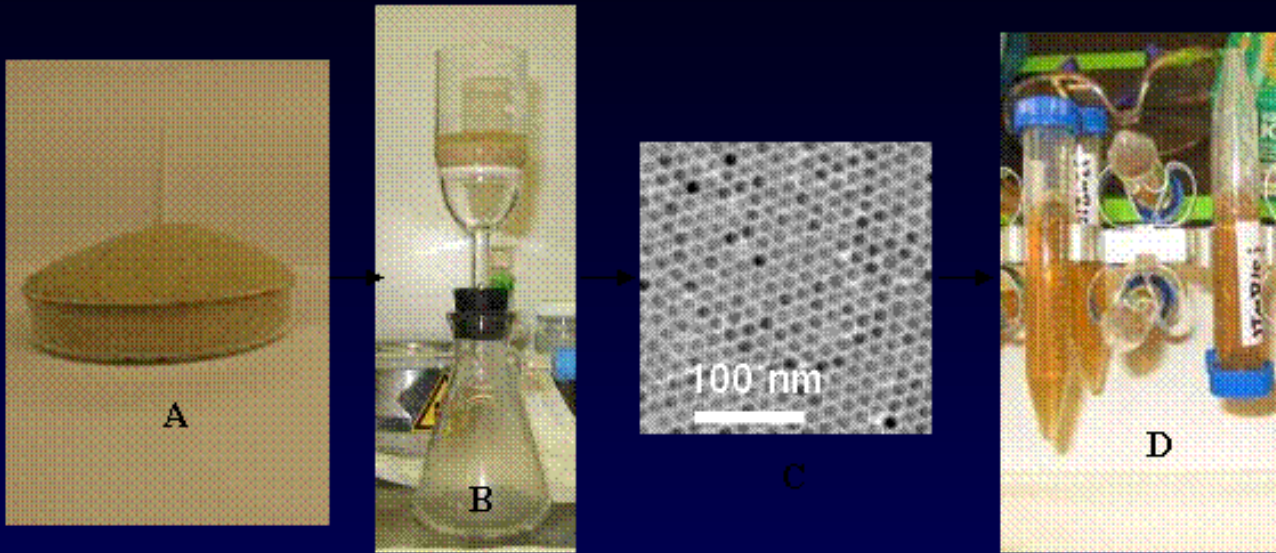


Film of nanoscale magnetite (11.92 nm) stabilized in water with oleic acid bilayer.

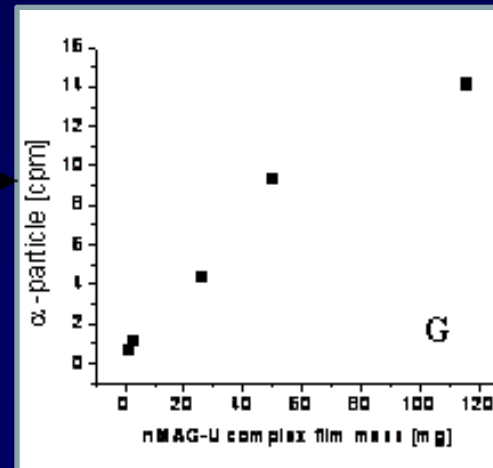
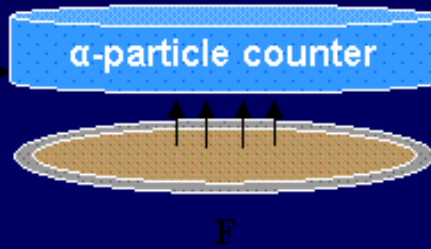
Ppb level detection in Concentrates



Ultratrace detection with handheld detector



= x 5



= x >10,000

The Needle in the Haystack and Beyond



For analysis nanoparticles offer ideal platforms for radionuclides

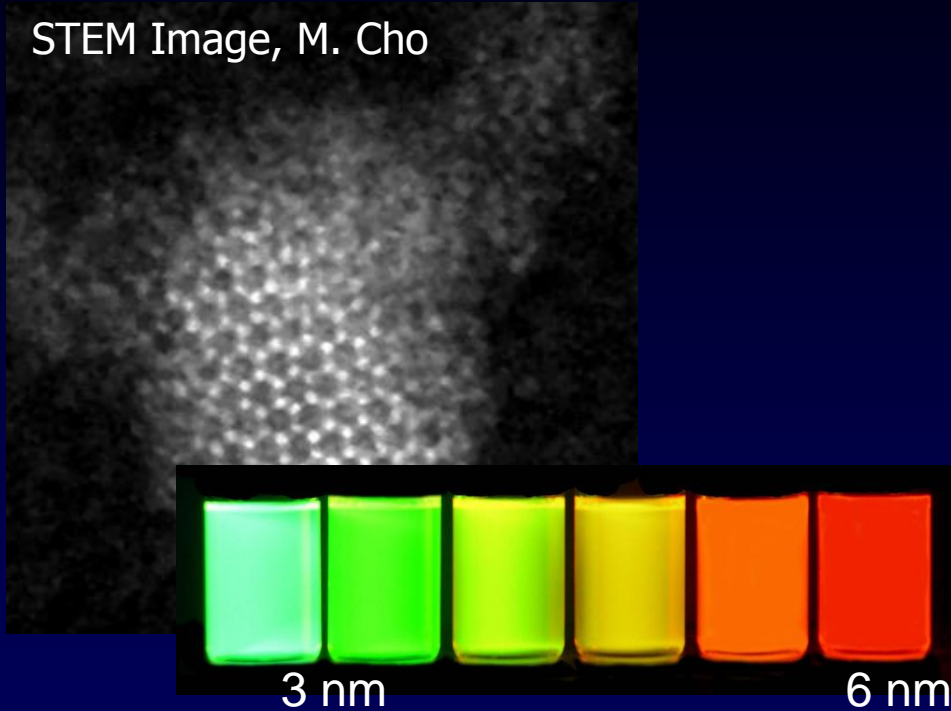
- *Surfaces for other radionuclides*
- *Fast, efficient and simple detection*

For reclamation may also offer similar advantages except

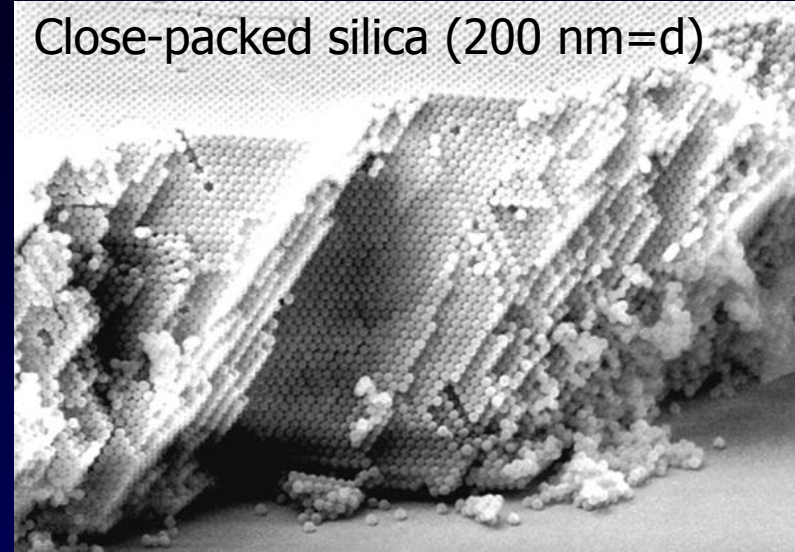
- *Interfering ions in local water*
- *Efficiency of reconcentration*

The Hammer and Nail Together

STEM Image, M. Cho



Close-packed silica (200 nm=d)



- They are very, very small: 30 w/w% sorption
- Their properties are size-dependent: facile magnetic removal
- They can assemble into larger structures: uniform thin films for alpha counting

Other Possible Nails

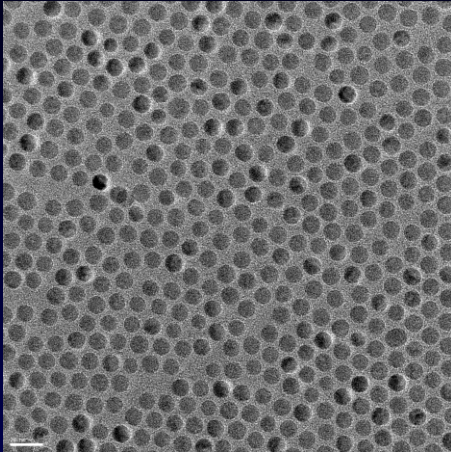
- Ultrafine and uniform uranium oxide nanocrystals for safe fuels: improve thermal conductivity – find the 'optimal size'
- Nanoscale dopants for steel to improve radiation resistance: nanoparticles can stop crack propagation
- Improved thermal conductivity and mechanical strength in nanoscale composites

END

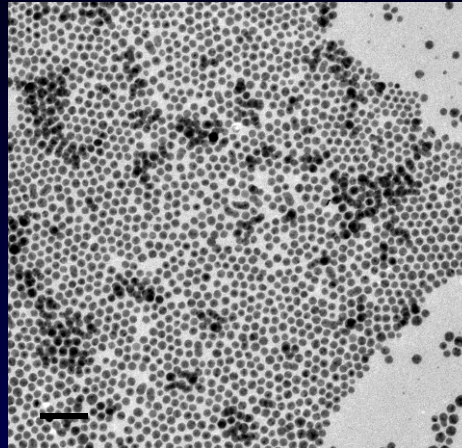


'Nano'X: High Surface Area & Tunable Properties

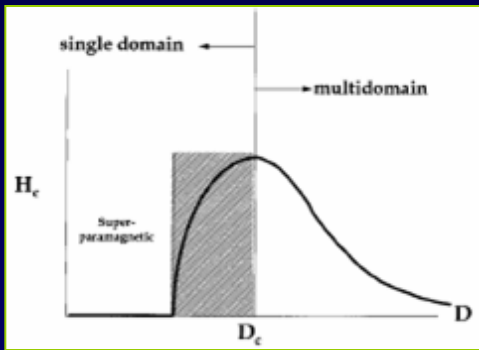
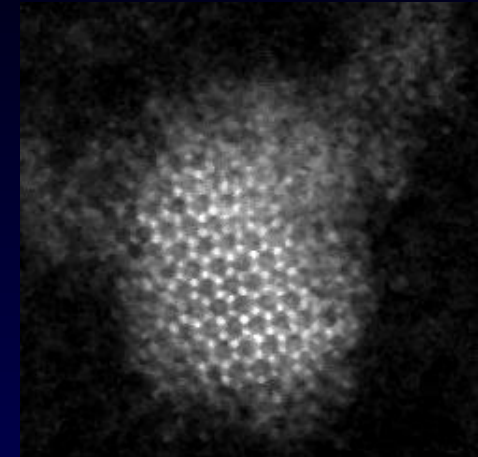
Iron Oxide (~10 nm)



Silver (~ 10 nm)

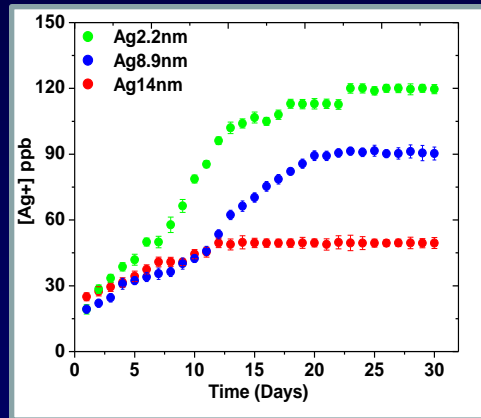


CdSe (8 nm)



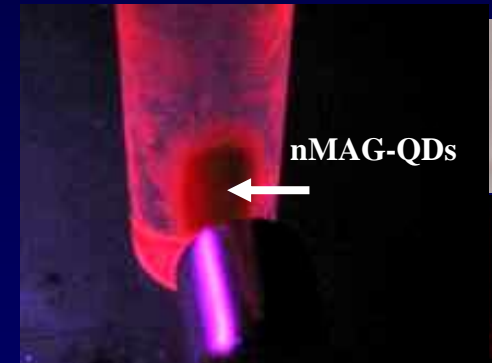
**Size-dependent
Magnetism**

Arjun Prakash and
Seung Soo Lee



**Size-Dependent
Reactivity**

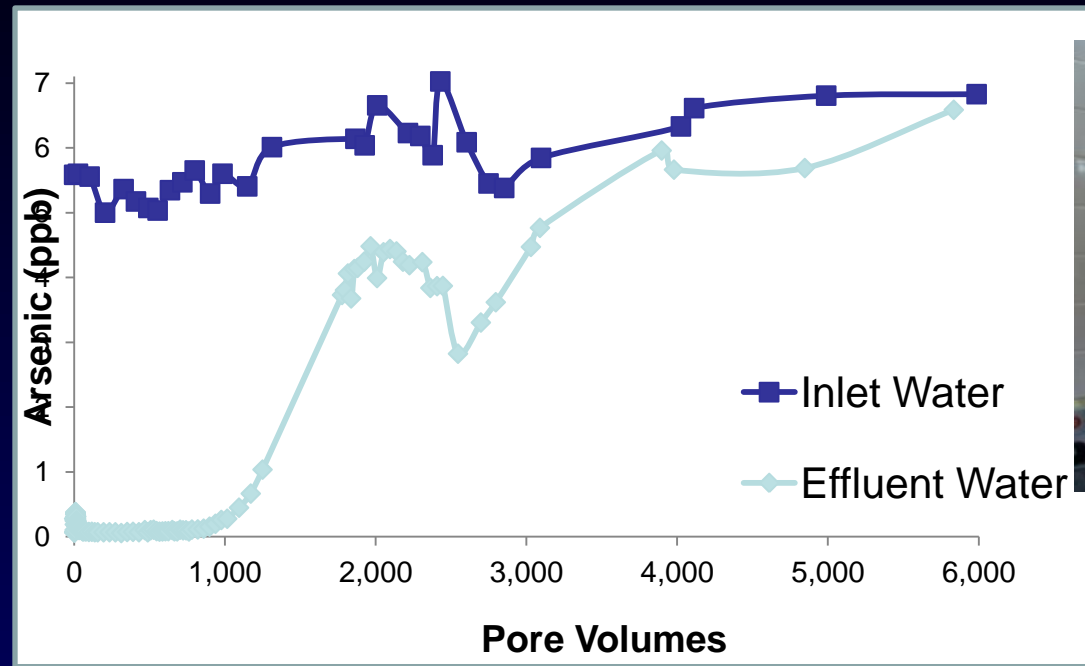
Hema Puppala



**Size-Dependent
Emission**

MinJung Cho

Field Tests: Arsenic Removal Well #4



Scaling-up materials and processes for the field – yes, you still need chemists

Arsenic problem in groundwater wells, limit the city's water supply

Working at remote field sites (above) for in-line filters

\\ First pass – Pipes, fittings, garden sand (Home Depot) plus nanoMagnetite

About Uranium

(Fun)

44,000 tons mined 2008

^{235}U is the only naturally occurring fissile isotope

All three major U isotopes are alpha (α) emitters

^{239}Pu produced from ^{238}U by neutron capture

Occurrence of Natural Uranium

Blood	Up to 0.5 ppb
Bone	0.2 – 70 ppb
Tissue	1 – 3 ppb
Total in Body	0.01 – 0.4 mg
Earth's Crust*	2 ppm
Soils	0.7 – 11 ppm
Sea Water	3 ppb

*48th most abundant element

Natural Abundance

Half-life

	Natural Abundance	Half-life
Uranium-238	99.3%	4.5×10^9 years
Uranium-235	0.7%	0.7×10^9 years
Uranium-234	0.005%	0.245×10^6 years

Uranium Oxides:

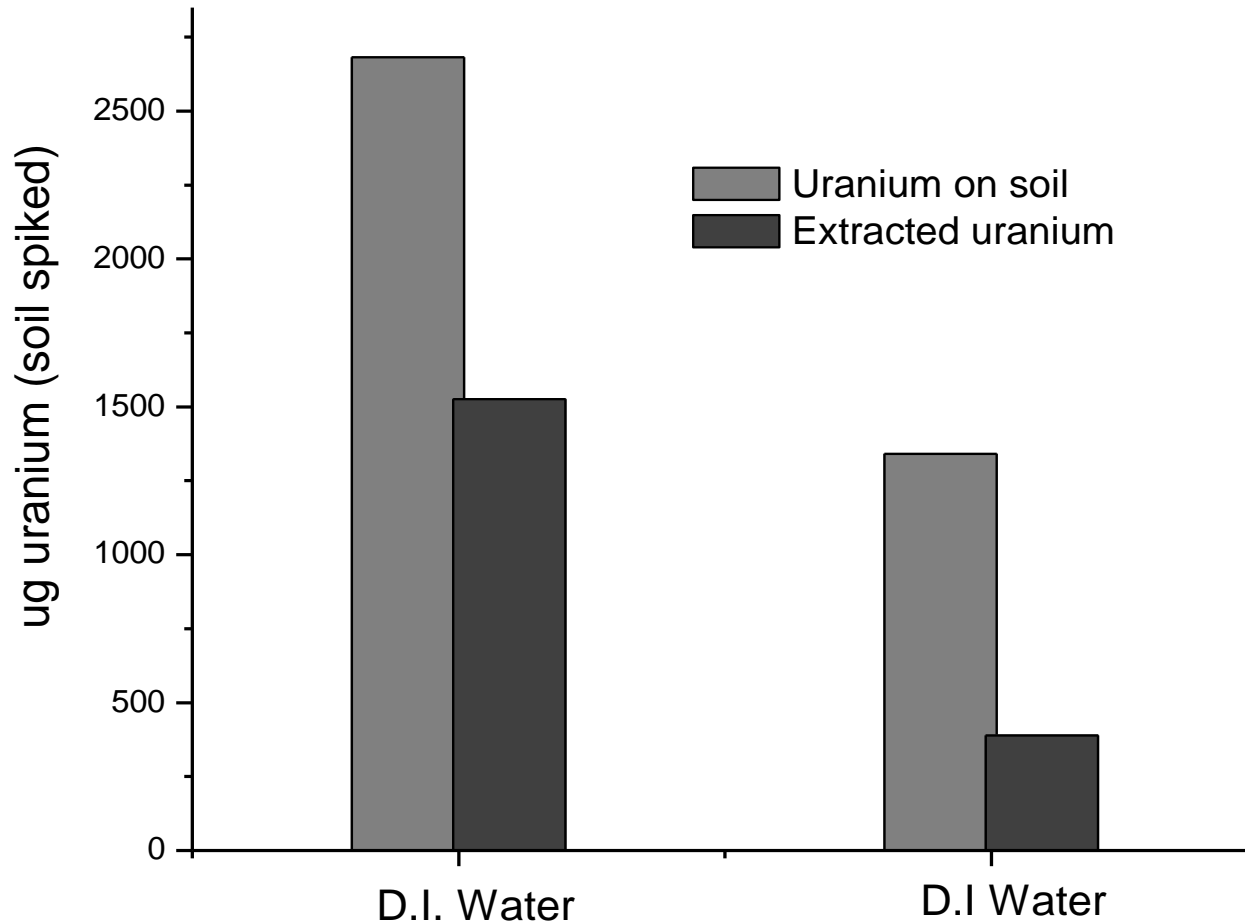
Uranyl (UO_2^{+2})

Uranite (U_3O_8)

Pitchblende (UO_2)

Also U_2O_3 , and UO_3

Environmental Matrices: Uranyl Soil (Sand) Extractions



Washed sea sand with uranium spiked as dissolved uranyl nitrate stock

EXTRA SLIDES

Rice Research: Integrative and Interdisciplinary

Wiess School of Natural Sciences

Biochemistry & Cell Biology

Chemistry

Ecology &
Evolutionary Biology

Earth Science

Mathematics

Physics & Astronomy

Central Institutes

Nanotechnology

Computation

Applied Physics

Biomedical

Energy

Brown School of Engineering

Bioengineering

Chemical and Biomolecular Eng.

Civil & Environmental Eng.

Computational & Applied
Mathematics

Computer Science

Electrical & Computer Eng.

Mech. E and Materials Science

Statistics

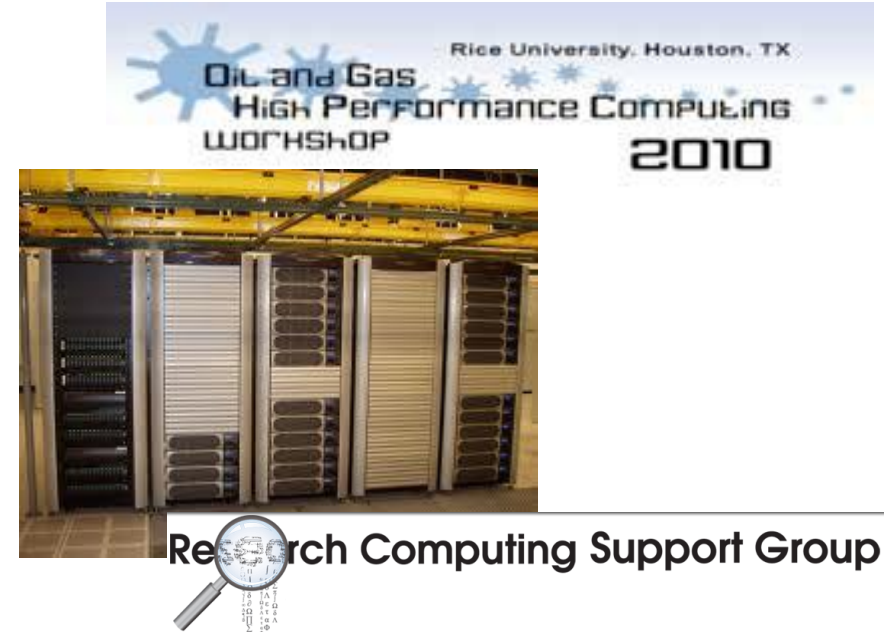
Rice: First Mover in High Performance Computing



Ken Kennedy

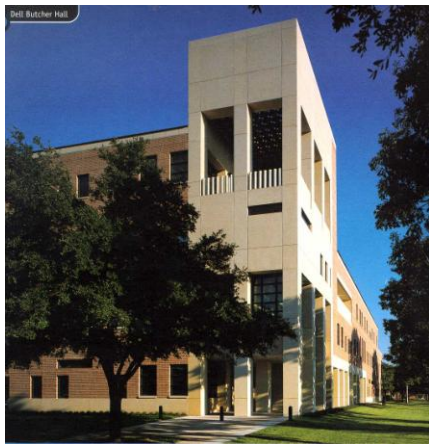


Duncan Hall: Computing

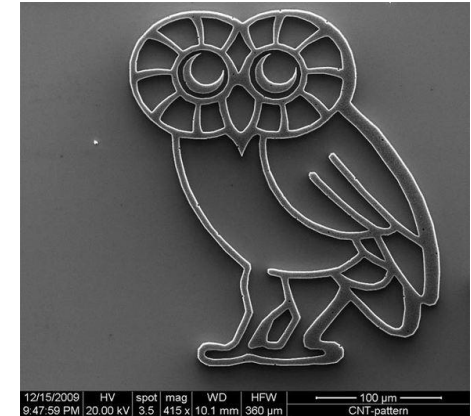
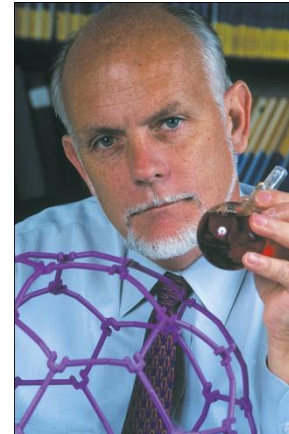
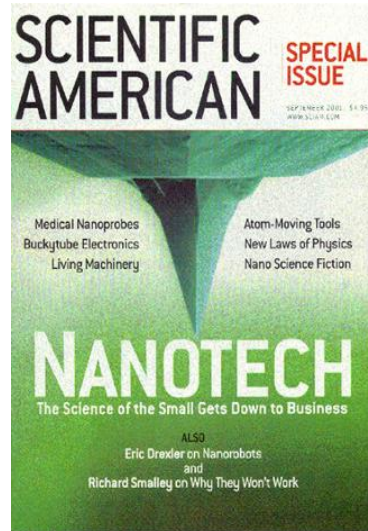


- Ken Kennedy Institute for High Performance Computing
 - One of the first Science and Technology Centers funded by U.S. NSF: 1989
 - Duncan Hall built (1998) and significant faculty hires in HPC
 - National academy members in digital signal processing, parallel computing
 - Current emphasis: visualization, data mining and applications in oil and gas

Rice: A First Mover in Nanotechnology



Dell Butcher Hall

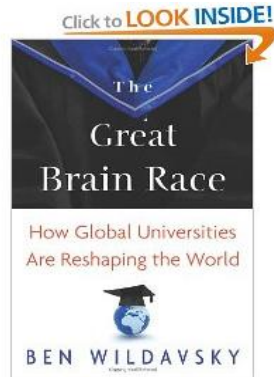


Richard Smalley Institute for Nanotechnology

- Ranked among top five nanotechnology programs in the world³
- The first university-sponsored nanotechnology effort (1994!)
- 2 Nobel prizes awarded in 1996 for discovery of C_{60}
- Houses one of NSF's national nanotechnology centers: CBEN
- More than 20 nanotechnology faculty, center of gravity is materials



Challenges for Research Universities



(A) The globalization of higher education:

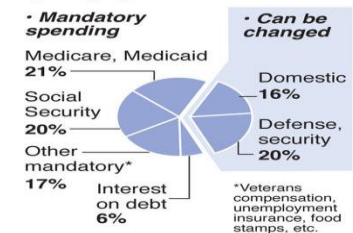
- Growing importance of global rankings and presence
- Our students hired by global, not national, companies
- Competition now global, fewer net research 1 universities

(B) Decrease in federal funding for research

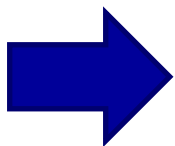
- NSF, NIH, DOE: best case -2%, worst case -10%
- Professors writing more grants – success rates 1 in 10
- For Rice, 5% of operating budget from overhead

Where to cut the federal budget?

Most spending is mandatory. Cuts can be made on only 36 percent unless the law is changed. Fiscal year 2010 spending of \$3.5 trillion by category:



Source: Bipartisan Policy Center's Restoring America's Future report
Graphic: Judy Treible
© 2011 MCT



Rice Must Seek Unconventional Approaches to Supporting Research and Related Programs

<http://www.rice.edu>

The Future of Research at Rice

What are interdisciplinary grand challenges that:

- (A) Truly define the greatest problems of our time
- (B) Are of great interest to a large number of faculty
- (C) Leverage our historical investments in nano, bio, and computing
- (D) Reflect our geographic location and community interests



Energy and the
Environment

Biology and
Biomedicine

Rice University - Texas Medical Center

*Rice is part of the world's largest medical complex:
New Bioscience and Biomedical Research Initiative*



Rice University – Energy Capital

Marathon oil, ConocoPhillips, Chevron, Baker Hughes, Shell
BP (US Headquarters), Halliburton, Schlumberger, Exxon Mobil

A photograph of the Rice University campus in Houston, Texas. The foreground is filled with lush green trees. In the middle ground, several university buildings are visible, including a prominent brick building with a red roof and a tall, modern brick building. In the background, the Houston skyline is visible, featuring several skyscrapers under a clear sky.

Rice University

Drill-Down to Specifics: Workshops

What are interdisciplinary grand challenges that:

(A) Truly define the greatest problems of our time

(B) Are of great interest to a large number of faculty

(C) Leverage our historical investments in nano, bio, and computing

(D) Reflect our geographic location and community interests

*Energy and the
Environment*

*Biology and
Biomedicine*

Technology and Science
for Greener Carbon

Quantitative
Medicine

Energy Transitions and
Energy Culture

Physical and Systems
Biology



Energy at Rice : *The E-squared Initiative*

Results of a working group, Fall 2010

Faculty workshops fall 2011 and spring 2012

Top Ten Problems for Mankind (Smalley)



An Insight: The Blue Elephant Slide

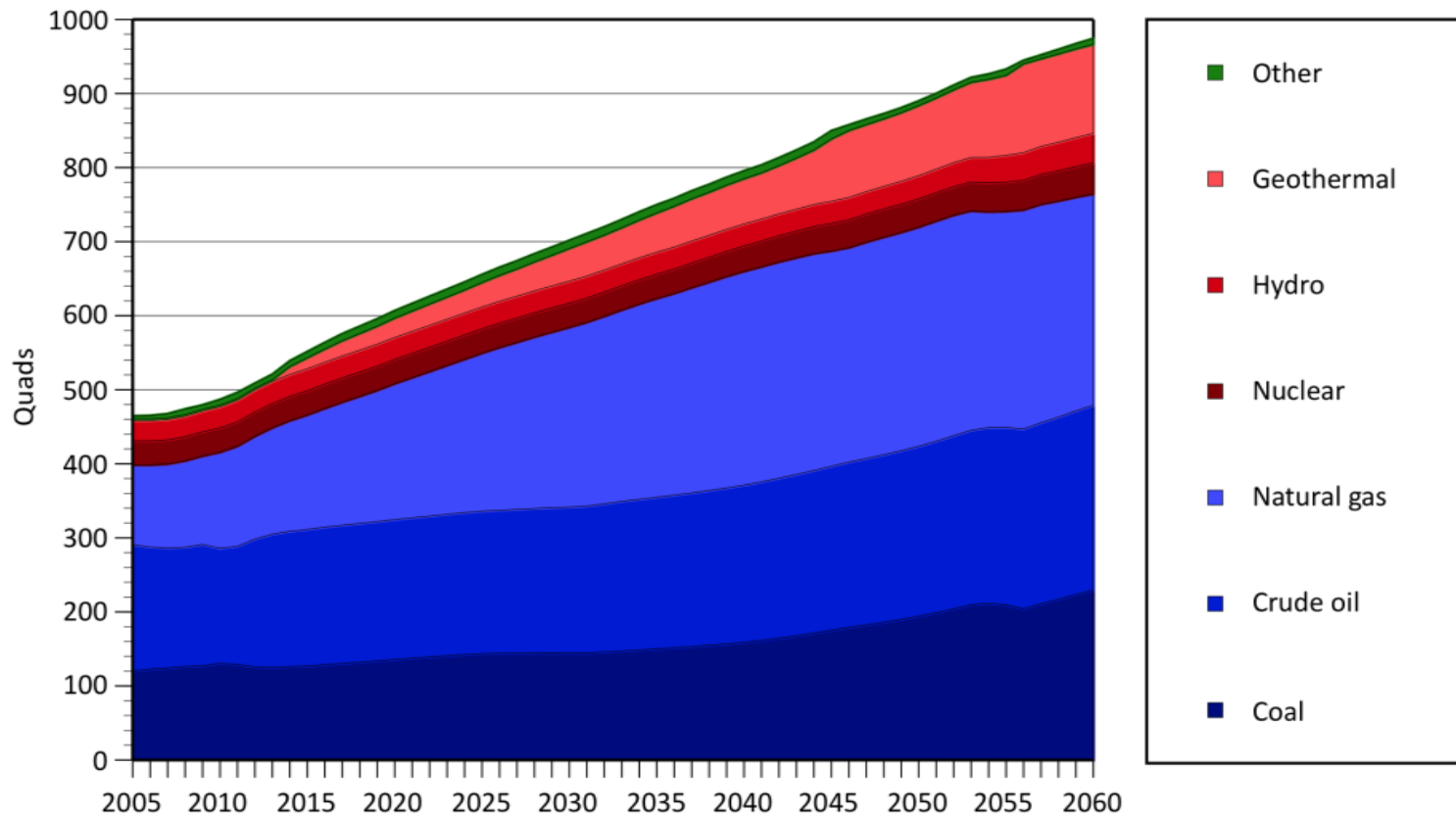
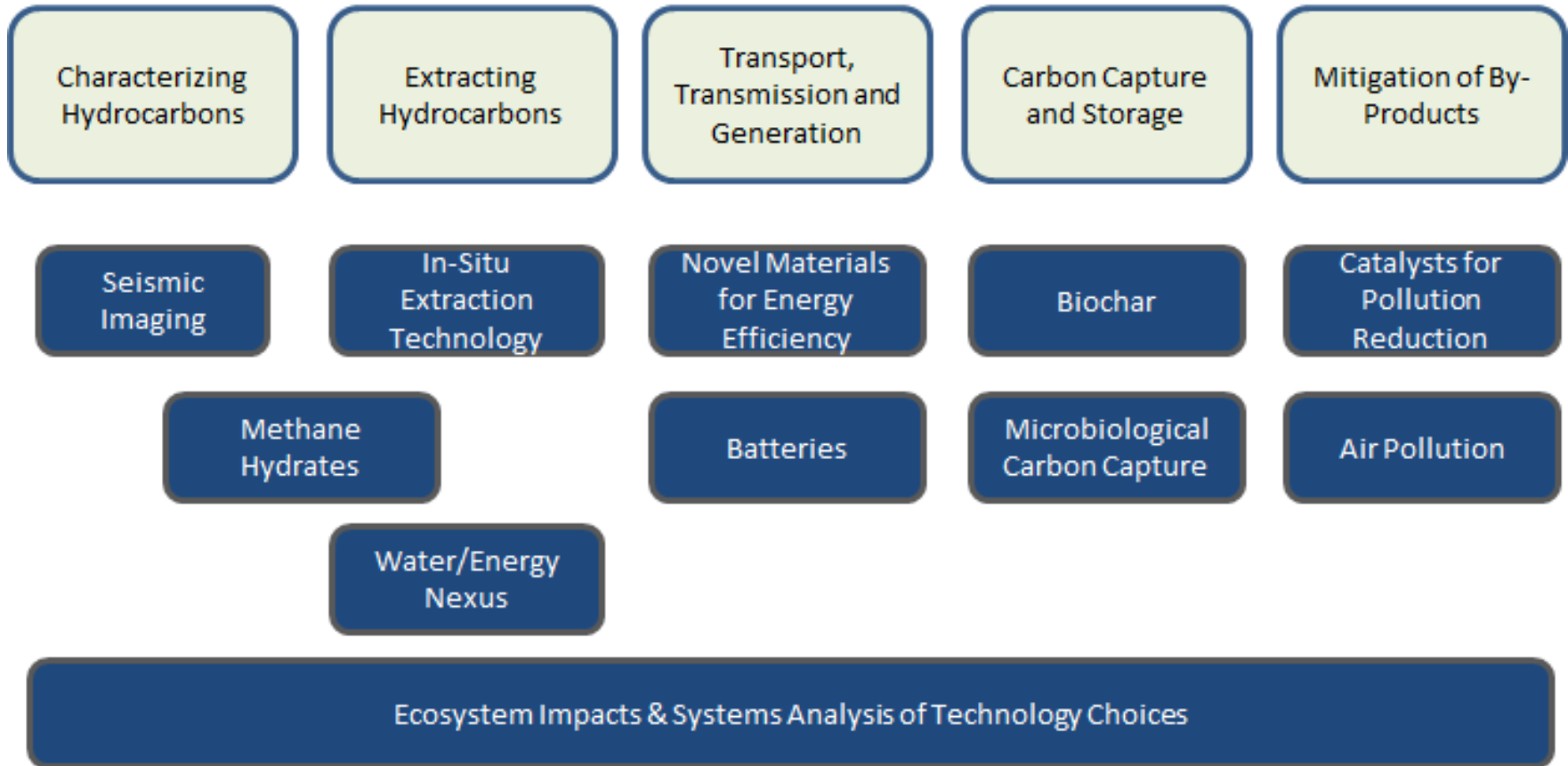


Figure 1. The projected diversity of the global energy supply assuming existing policies. Even the most extreme assumptions only moderately change the anticipated contribution of renewable sources to global energy supply for many decades. (from Peter Hartley Rice Economics)

Greener Carbon: Central to E-squared I

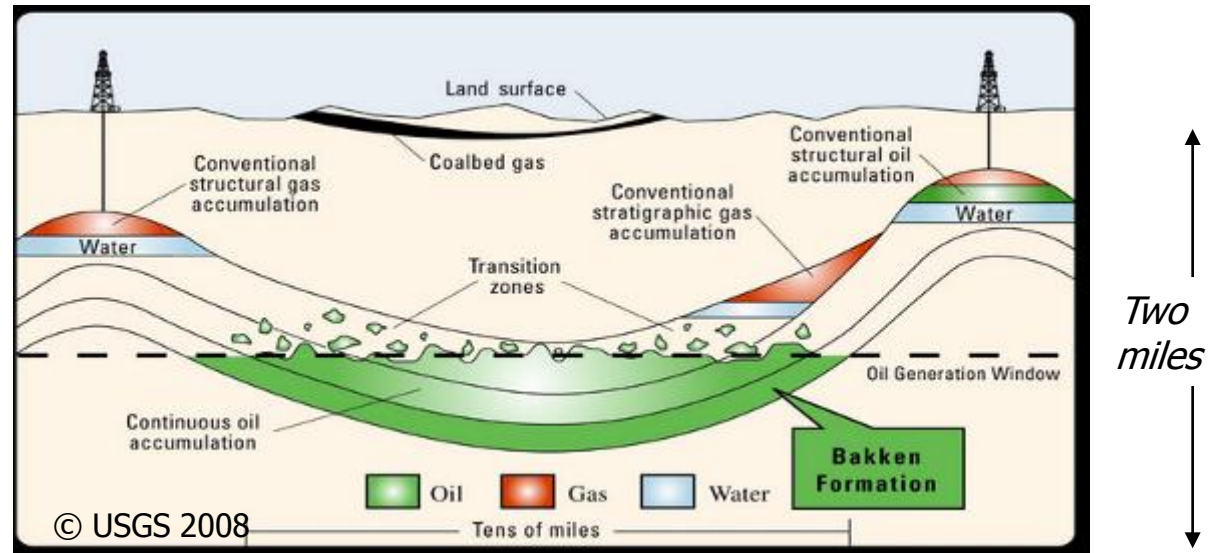
Greener Carbon Science and Technology



Nanotechnology: In-situ and reservoir imaging

Improve information about reservoirs using engineered nanostructures

- Enhanced nanotracers
- Near borehole sensing
- Contrast for remote sensing
- Self-propelled reporters ...



Challenge 1: Can nanoparticles fully sample a reservoir? e.g. how can we engineer mobility?

Challenge 2: What is the scheme for detecting nanoparticles in the subsurface?

Advanced Seismic: Both Computation and Collection

Two images ideally that I could explain briefly :>

- Rice geophysics ranked #12 in country
- Inverse problem consortium
- New NSF grants in imaging and visualization, matched by Chevron

Flow Assurance and Chemical EOR

Two images ideally that I could explain briefly :>

- Awards and recognition of Hirasaki ?
- Brine consoritum and xxx consortium
- Increased energy support particulary in heavy oil and unconventional resources

Water Treatment and Management

Two images ideally that I could explain briefly :>

- Nano-enabled water treatment funded through major federal center
- Other bullet?

Responsible Development of Shale Gas: Nascent

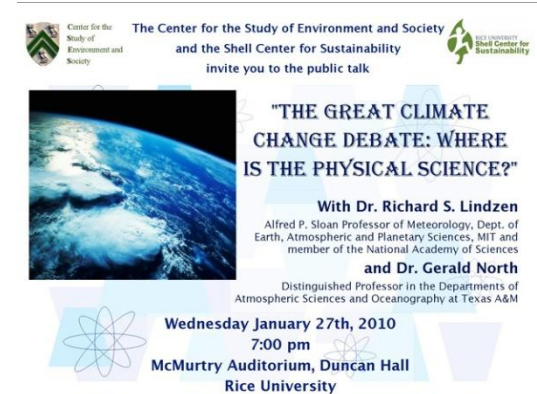
- Active policy research in shale gas in Baker Institute
- Very controversial topic, technically complex
- Many opportunities for new technical capabilities



Center for the Responsible Development of Unconventional Hydrocarbons: An Honest Broker



ICON INTERNATIONAL COUNCIL
ON NANOTECHNOLOGY
A partnership for nanotechnology stewardship and sustainability



- Rice has strong history as an 'honest broker' in controversial and technically complex public debates
- Rice's physical location in a large urban center, near major oil and gas companies, make it an instant leader
- Relevant topic for companies: Anthropology and sociology of working productively in complex and alien cultures

Towards Greener Carbon:

A program of the e-squared initiative



Center for Greener Carbon: a program
of the E-squared initiative

- Bullets to be drawn by what I get on the other slides

Energy at Rice: Now

Faculty workshop follow-up in November 2011

- Still a “Green Carbon” Emphasis, but Broader
- Identification of best use for institutional funds (e.g. seed monies)
- Over 70 faculty participated (high interest)

Success stories in early corporate interactions (6 months)

- Master agreement with Baker Hughes in late November
- Brazil partnership with BG group company
- Ongoing relationship development with many others

Workshop in late March: Planning the E2I Rice Initiative

- Business plan (how to pay for \$1 million in general infrastructure)
- Operations plan (how the organization will operate)
- Governance plan (how it will be governed)



Rice University: Future Strategy and BP



Energy research



Biomedical research



Global Partnerships

Why Rice University?

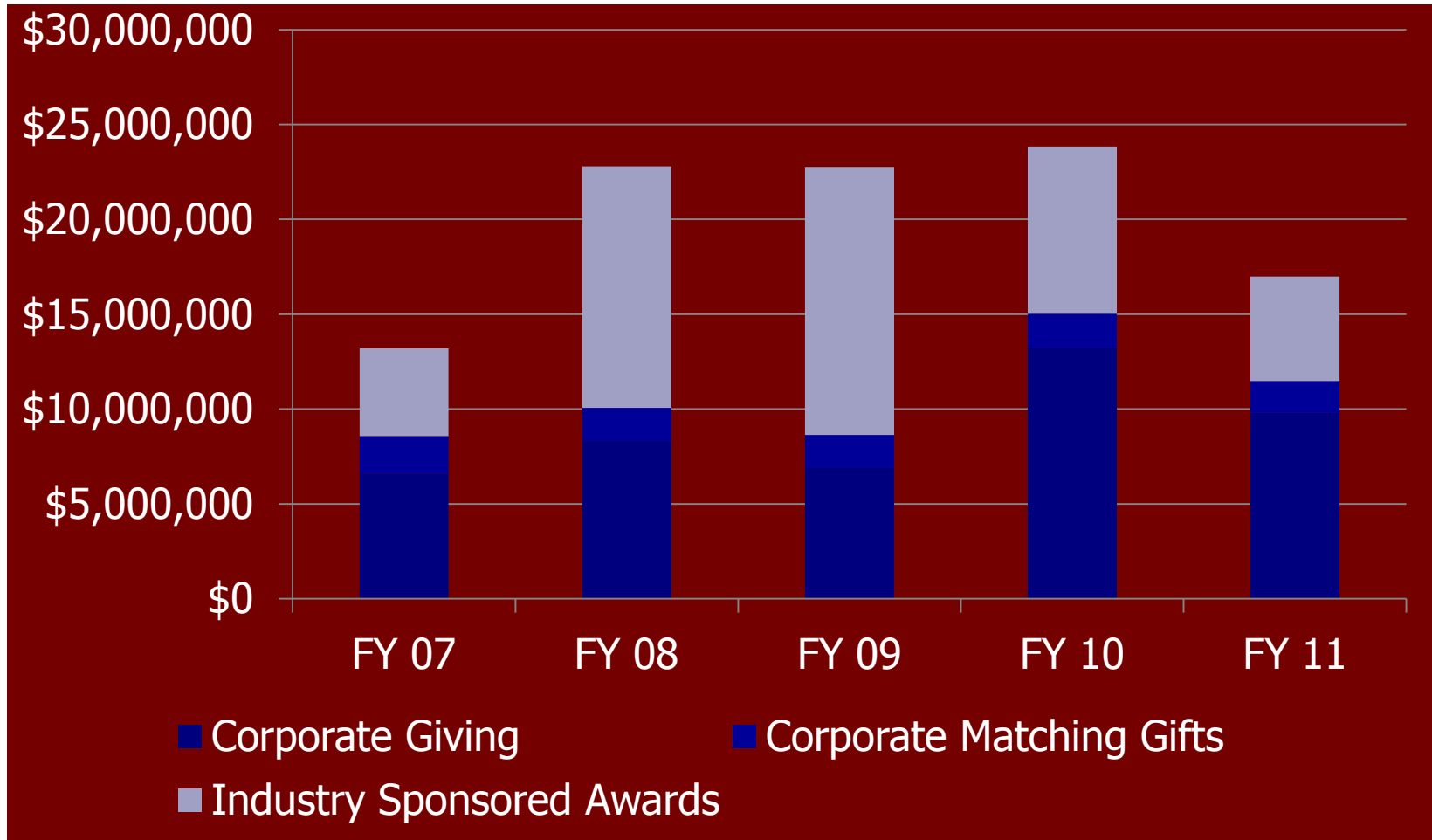
***A shared interest in making energy
production and transmission
sustainable.***



Rice University: The agenda for the day

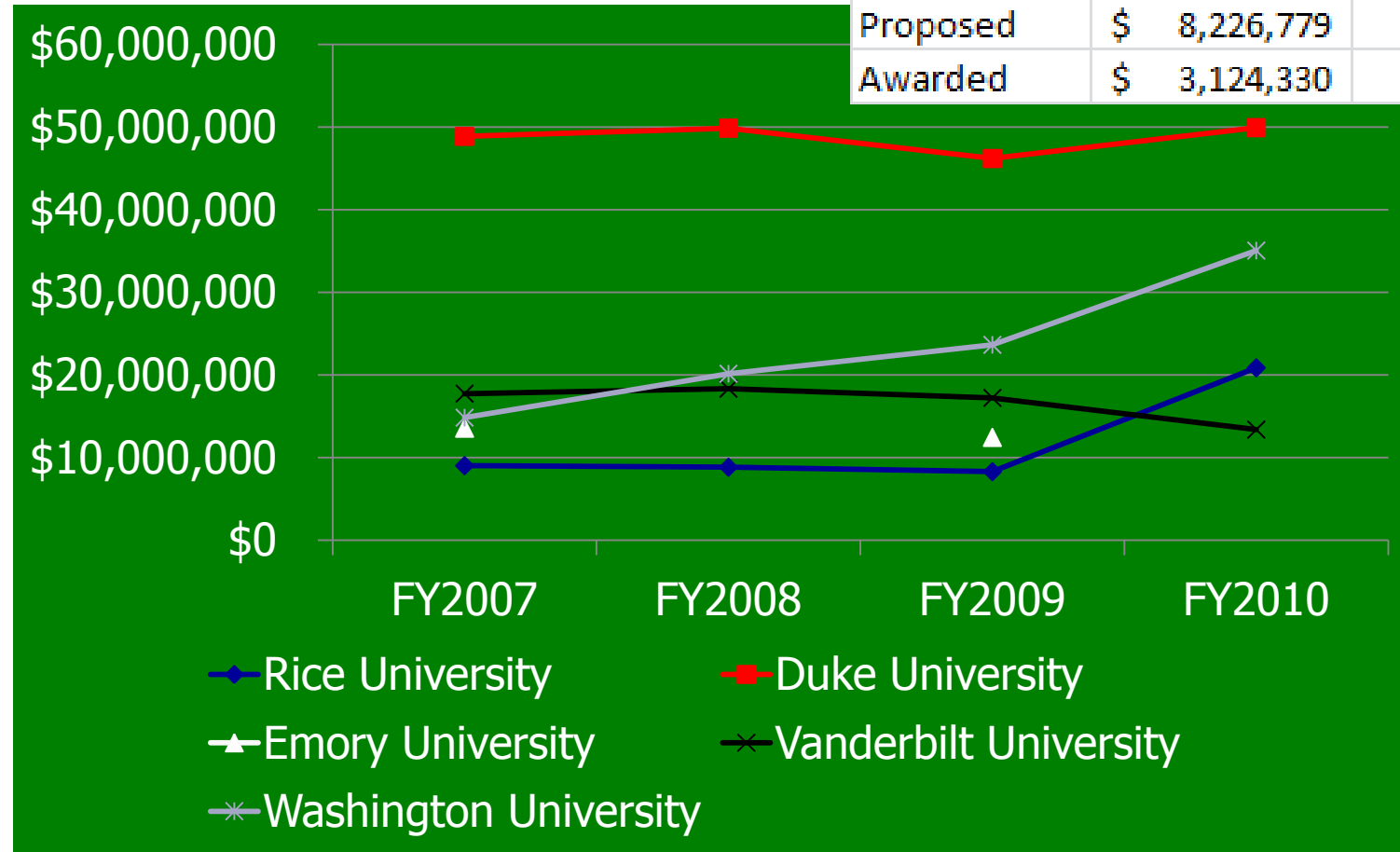
Please reproduce a mini-version of the agenda here

Rice's Existing Industrial Support



Rice: Real Opportunity for Growth

Total* Corporate Giving FY2007-FY2010



FY2011 Industry Proposals and New Awards

Proposed	\$ 8,226,779	75	
Awarded	\$ 3,124,330	40	

*Includes cash, in-kind, and matching gifts; Source: Council for Aid to Education

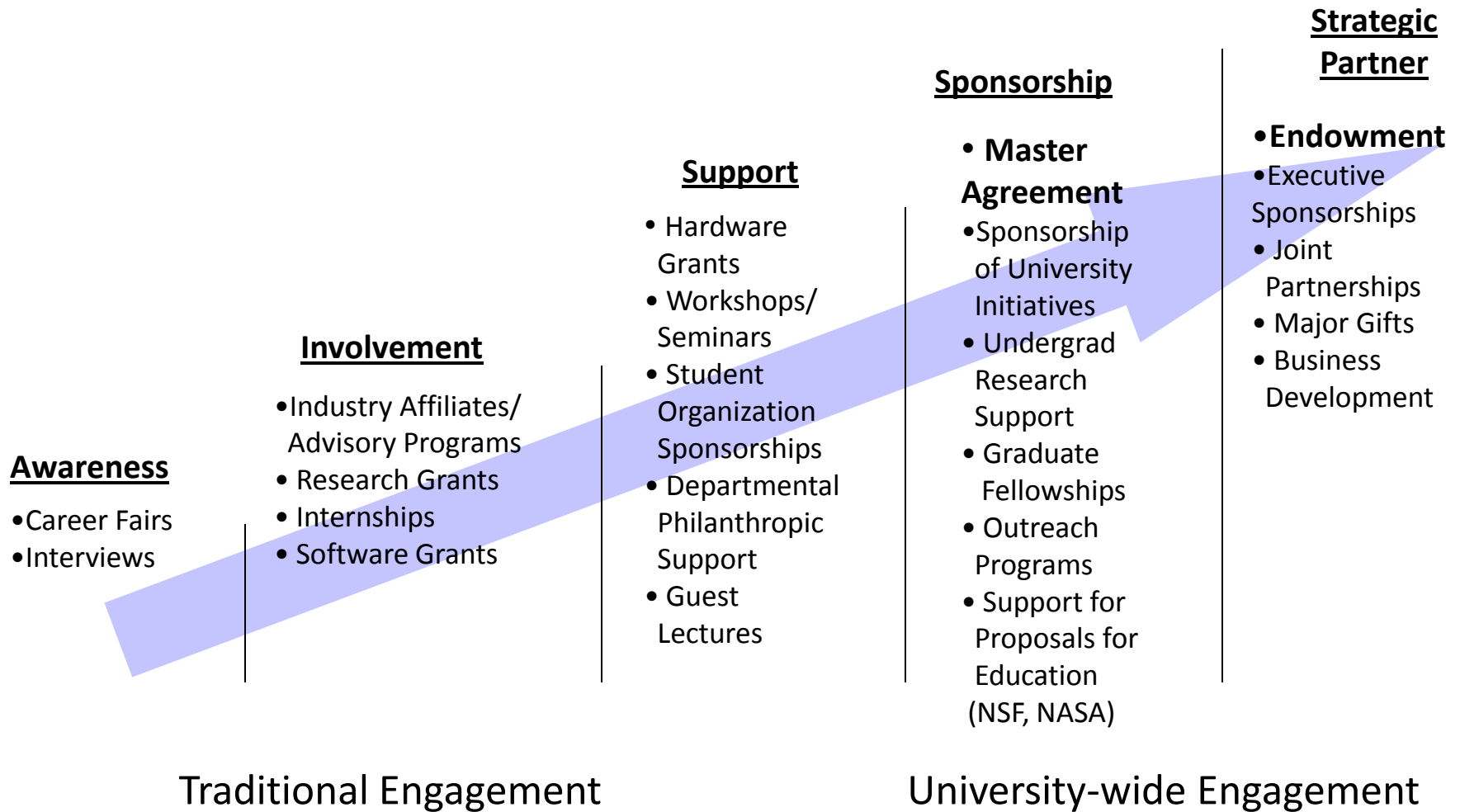
Our Strategy for Corporate Relations

Mission: To structure corporate interactions around “master agreements” that link to multiple areas on campus

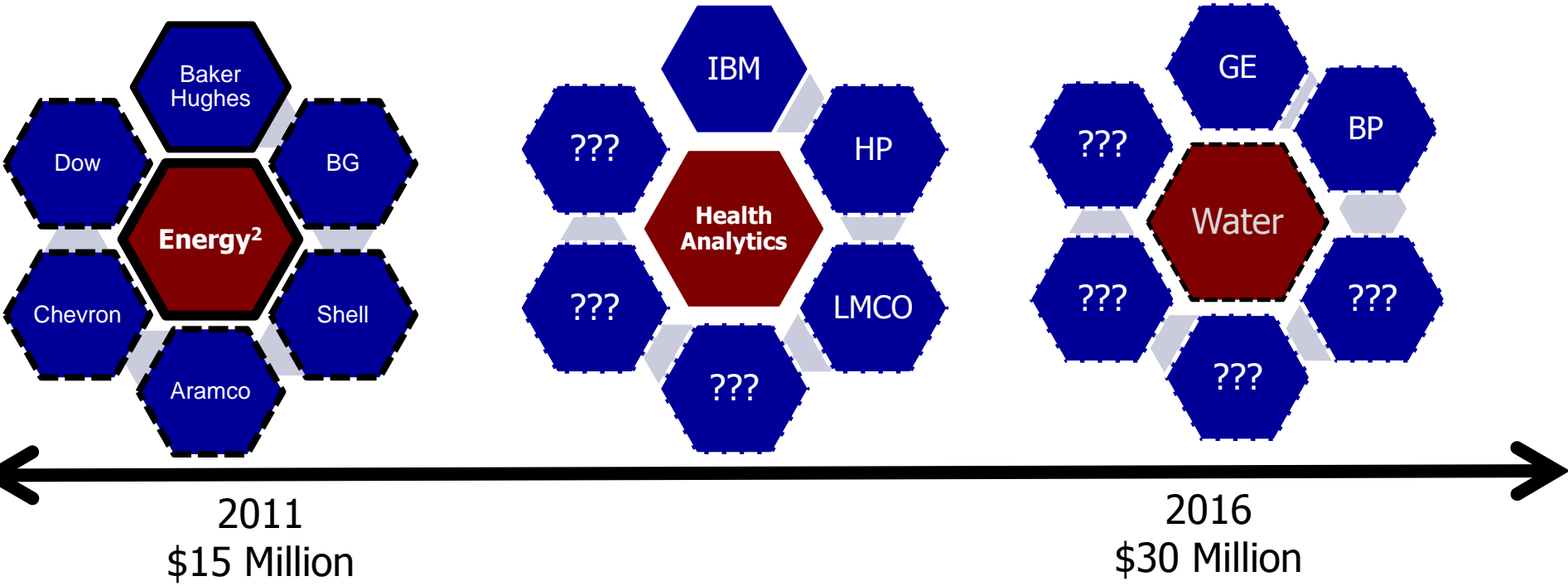
We do this by:

- Corporate Council: 3Rs
- “Tiger Teams” to translate interest into commitment
- Data Sharing: Campus Connector; Newsletters
- Swifter negotiations on industry agreements
- Reorganization of Center for Career Development

Master Agreements: A Stepping Stone



Corporate Engagement: 5 Yr. Vision



- Thematic clusters: nurture cross-company relationships to add value
- Master agreements that integrate programs across campus
- University administration that is efficient and responsive to partners
- Tangible rewards for divisional collaboration in corporate relations

Barriers to Corporate Engagement

Barrier	Response or counterbalance
Little faculty interest in corporate research	Let faculty drive thematic areas
	Offer faculty workshops, seed funding
	Declining federal budget will force interest
Internal mistrust of centralized strategy	Demonstrated success (e.g. Baker Hughes)
	Corporate Council and Newsletters
	Internal MOU for sharing targets
Access to key corporate decision-makers	Engage Rice trustees
61	Increase awareness (e.g. workshops, seminars) 7/13/2012
Rice's size: few alumni, narrower research	Identify thematic areas (e.g. don't try to do it all)

Corporate Engagement with Universities: *A Time of Great Change*

- No longer *ad hoc* : must link to a long-term strategy
- Collaboration and global efforts are now desired
- Industry wants relationships, not just transactions
- Opportunity for innovation in these partnerships

Existing and Targeted Master Agreement Partners

- Baker Hughes*
- Lockheed*
- Anadarko
- Aramco Services/Saudi Aramco
- BG
- BP
- Chevron
- ConocoPhillips
- Dow
- ExxonMobil
- GE
- Halliburton
- IBM
- Intel
- Kinder Morgan
- Marathon
- Schlumberger
- Shell
- Statoil
- Total
-

Key strategic questions

- What level of engagement is appropriate for Rice?
- Why Rice?
- How can Rice best communicate what it has to offer to companies?
- What kind of deals is Rice willing to offer?
- How can Rice organize itself internally to best support effective corporate engagement?
- What risks need analysis?
- How do we measure performance?

Challenges and Opportunities

Strengths

- Excellent faculty working in areas of corporate interest
- Top tier students
- Prestigious institution
- Neutral convener
- Marriage of Technical and Policy Expertise

Weaknesses

- No consistent track record
- Small recruiting pool
- Key faculty may get overcommitted
- Varied and competing points of contact
- Barriers to internal collaboration

Corporate Engagement

Opportunities

- Increasing international ties
- Location in Houston (energy, bio, medical, Fortune 500)
- Strong ties to government, industry, and community leaders

Threats

- Increasing competition as federal funding decreases
- Move towards in-kind versus cash contributions
- Established energy institutes



The Value Proposition

For Companies

- Talent acquisition
- Research tied to business solutions
- Business opportunities
- Employee/Executive Training
- Consultants
- New Technologies
- Positive PR
- Neutral convener

For Rice

- Funds to support projects, programs, research, events
- Real-world problems
- Internship and career opportunities
- Licensees
- In-kind donations
- Access to specialized facilities
- Clients for Professional Masters and Exec Ed Programs

Case Study: Baker Hughes

Collaboration Areas

- Sponsored Research
- Undergraduate Student Design
- Baker Institute
- Visiting Scholars Program
- Professional Development
- International Graduate Fellowship Program
- Internships

Agreement Enhancements

- Discount on indirect costs
- Allowance of days for reviews of publication
- Arbitration for dispute resolution
- Allowance of days for Intellectual Property review

Rice University – Energy Capital

Marathon oil, ConocoPhillips, Chevron, Baker Hughes, Shell
BP (US Headquarters), Halliburton, Schlumberger, Exxon Mobil

A photograph showing the Rice University campus in the foreground, with a dense line of green trees. In the background, the Houston skyline is visible under a hazy sky. Several prominent skyscrapers are visible, including the Texas Tower. A tall stadium light pole stands on the left side of the frame. The text 'Rice University' is overlaid in white at the bottom center.

Rice University

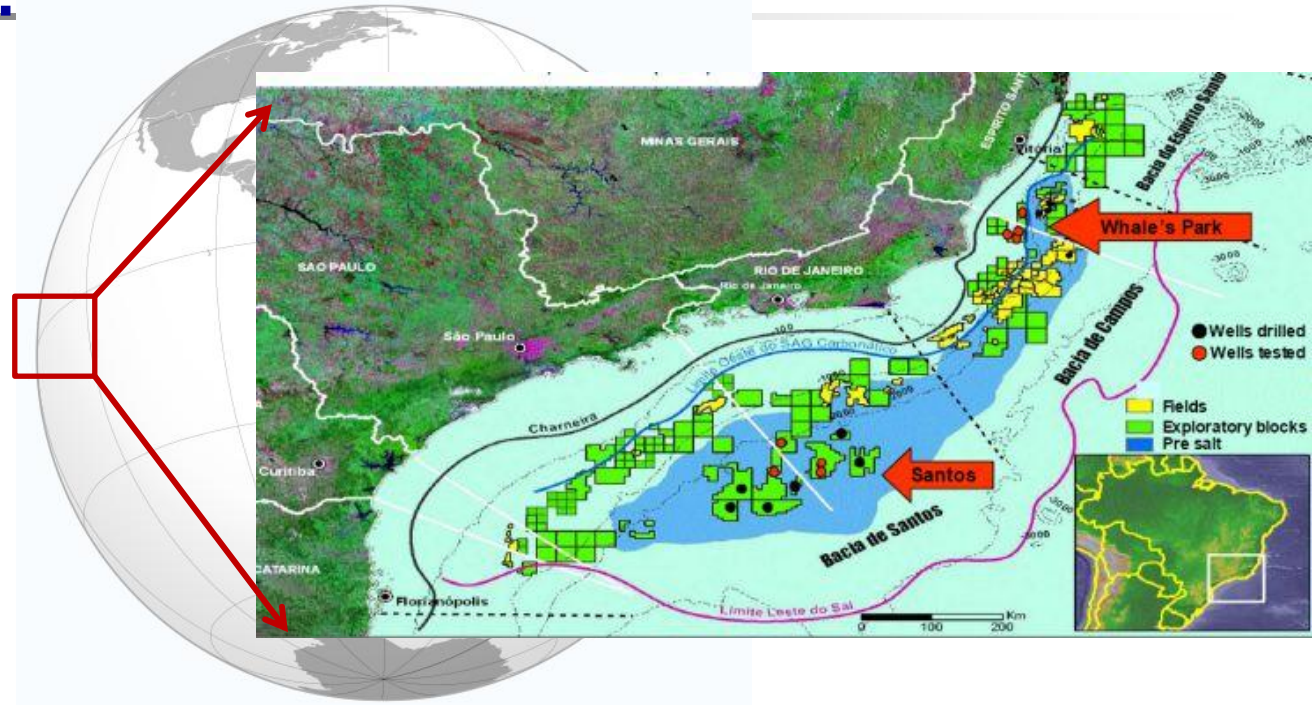
New Research Initiatives at Rice

- Energy research – cross-disciplinary studies of energy transitions and the sustainable and innovative use of hydrocarbons
- Biomedical research – develop nanomedicine and quantitative biology as tools for detecting and curing disease
- International partnerships – orient campus programs towards natural partners in China, Brazil and Mexico



In Brazil, Rice finds a natural intersection of our international and energy research strategies

Why Brazil?



- 9th largest economy, one of the fastest growing in the world
- Energy industry has increasing interest in Brazil (pre-salt)

Rice has a first mover advantage in Brazil among U.S. un

Support Programs with Government \$\$



*The 'research obligation':
1% of all off-shore profits
must return to higher
education in Brazil*

- Focus Rice-Brazilian University research collaborations in energy
- Make these collaborations appealing to the Brazilian government
 - Focus on researcher exchange (Dilma's "Science without borders" program)
 - Find ways to get industry matching funds into government exchanges
 - Emphasize entrepreneurship and the innovation culture
- Plan for growth: the obligation will increase substantially in 10 years



Towards Academic Supercenters: Transnational and Thematic

RICE

BG Group

- Tuition for graduate students
- Bench fees for researchers

CNPq

- Stipends for researchers
- Travel and medical fee



May offer
small direct
support to US
hosts



**Rice
University**



**UFS
C**

BG Group

- Research support on campus
- Travel funds for activities
- Support for visiting faculty



<http://www.rice.edu>

A Specific Program: UFSC-Rice



We are putting in a proposal to a O&G company (BG), and the Brazilian national science foundation (CNPq) which will bring ~\$1.5 million in annual support plus a steady supply of Brazilian researchers to Rice.



Brazilian graduate students supported by CNPq and their Rice costs by BG. UFSC pays for our students to exchange.



Brazilian post-docs supported by CNPq and their Rice costs by BG. UFSC pays for our post-docs to exchange.



Brazilian faculty have mini-sabbaticals at Rice and one Rice faculty per year spends 8 weeks at UFSC.

Value of Strong Rice-Brazil Programs

- (1) The next generation of energy leaders in a vital emerging economy will have deep connections to Rice
- (2) Non-traditional funding for faculty research in interdisciplinary areas such as energy and water
- (3) Programs in Brazil provide a persuasive answer to the question 'Why Rice?' for potential industry partners

Our Brazil strategy uses international exchange and collaboration to grow our research enterprise

The Needle in the Haystack Problem



Can we concentrate Uranium from soils so that it can be analyzed and reclaimed?



Dr. John Fortner