

### **RISKC**Learning

Nanotechnology – Applications and Implications for Superfund



Scientific Excellence Research Relevance

February 13, 2007 Session 2: "Nanotechnology - Metal Remediation" Dr. Mason Tomson, Rice University Dr. Shas Mattigod, Pacific **Northwest National Laboratory** 



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## **Contaminant Removal and Water Reuse: Research Opportunities with Nanotechnology**

# Arsenic Adsorption on Nanoscale Magnetite

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### Overview of Arsenic

- · Widely distributed in earth's crust
- In water by dissolution of ores/minerals
- Concentrated in areas by erosion
- Human Activities sources
  - Residue from alloys and treatments
  - Burning of fossil fuels
- Largest threat to humans
  - Inorganic As(III) and As(V)
  - In drinking water

3



These are the most general and important "first" points to know about Arsenic. The particularly important point, highlighted in green, is that it is As(III) that is the largest threat to humans.

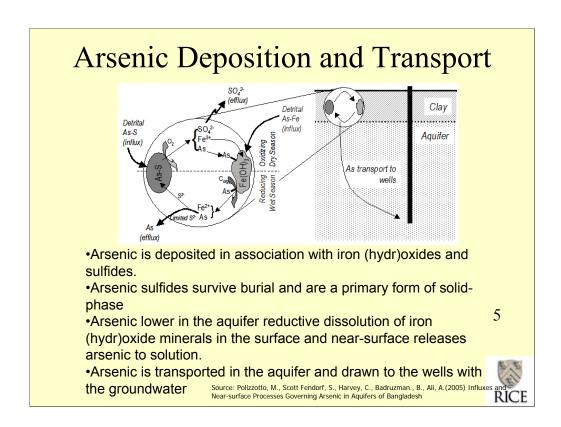
## Arsenic Mobility Profile

- Arsenates-As(V)
  - Usually occurs as ions: H<sub>2</sub>AsO<sub>4</sub>- and HAsO<sub>4</sub><sup>2</sup>-
    - · predominates in aerobic soils
- Arsenites As(III)
  - Occurs as H<sub>3</sub>AsO<sub>3</sub> (pH below 9.2)
  - Exists in slightly reduced soils
  - Larger concern than As(V) because of
    - · higher toxicity
    - greater mobility
- Arsenic in water
  - rather than solubility equilibrium controlling the mobility of arsenic, it is usually controlled by redox conditions, pH, biological activity, and adsorption/desorption reactions.
- Arsenic immobilization through ionic adsorption can be controlled within normal oxidizing Eh/pH conditions to varying degrees

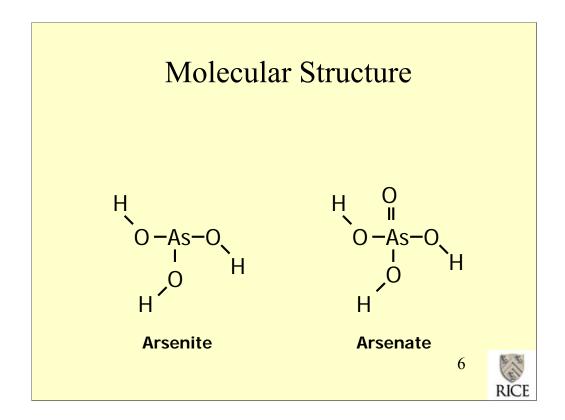
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Redox conditions, pH, biological activity and specific chemical reaction are keys to distribution – NOT A GENERAL SOLUBILITY BALANCE!

The last statement is a "soft" way of saying "without normal oxidizing and acid conditions, we have a problem!"



This is how arsenic is deposited and gets into a aquifer.



For the scientifically and chemically oriented audience members!

### Where Does Arsenic Come From?

- Natural sources of arsenic (contained in 250 naturallyoccurring minerals)
  - Minerals (particularly sulfides)
  - Oxides (particularly metals)
  - Volcanic-derived sediment
  - Can affect large areas, such as extensive aquifers
- Significant human activity sources
  - mineral extraction and processing
  - glass manufacturing
  - wood preserving
  - pesticide production and application
  - waste pile leaching
  - and coal/oil production and processing
  - Extent/occurrence is usually over a limited area



7

The picture is a sample of arsenic sulfide.

Important points to emphasize are that:

- •Aquifers are "vessels" that can, potentially, extend a contamination problem over a wide area.
- •Human activity sources of arsenic, though potentially and actually life-threatening, usually create contamination zones that are <u>limited</u>, relative to natural sources.

### **Arsenic Redox Reaction**

• 
$$H_3AsO_4 + 2H^+ + 2e^- \rightarrow H_3AsO_3 + H_2O$$
Arsenate – As(V)
Arsenite – As(III)

- The key is that arsenic is "locked away" in iron oxyhydroxides when there is plenty of oxygen present. The oxidized form, arsenate, dominates. When the oxygen level is low, "reducing environment", arsenate converts to arsenite.
- When arsenite is exposed to oxygen, it oxidizes, but the rate in air is only a few percent in one week. (Clifford, D., Ceber, L., Chow, S. (1983)

8



A reducing environment can create and preserve arsenite. When we withdraw it from that environment, as in withdrawing water from a well, it can take a long time for a significant portion of the arsenite to oxidize and become "safer"!

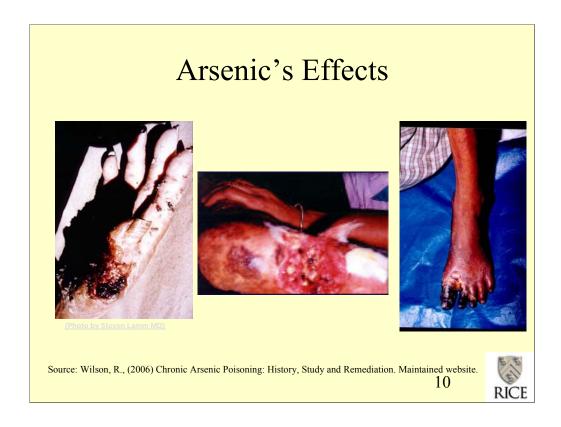
## Perspective on Long Term Exposure Drinking Water - Health Impact

- Cancer of the skin, lungs, urinary bladder, kidney
- Skin changes: pigmentation changes & thickening
- Increased risks of lung/bladder cancer and of arsenic-associated skin lesions have been observed at arsenic concentrations less than 0.05 mg/L (50 ppb)
- No universal definition of the disease (combination of harmful symptoms/maladies) caused by arsenic.
   This complicates assessment of the breadth of arsenic's effect on the health in any population.

9



This is the result of arsenic ingestion – including inhalation impact on the lungs. (I don't have a specific reference for the 50 ppb statement, but it is stated in at least one place in USGS or WHO publications. JWC)



Plenty more on the referenced website!

## Scope of the Problem!



- "The life-time risk of **dying from cancer** by drinking one liter of water per day containing an arsenic concentration of 50 μg/L could be as high as **1 in 100.**" (NRDC, 2001)
- "The theoretical lifetime excess risk for bladder and lung cancer combined is estimated to be approximately 1 in 1000 at 3 micrograms per liter."
- "According to some estimates, arsenic in drinking-water will cause 200,000 -- 270,000 deaths from cancer in Bangladesh alone (NRC, 1998; Smith, et al, 2000).

11



#### This is how the

Contamination

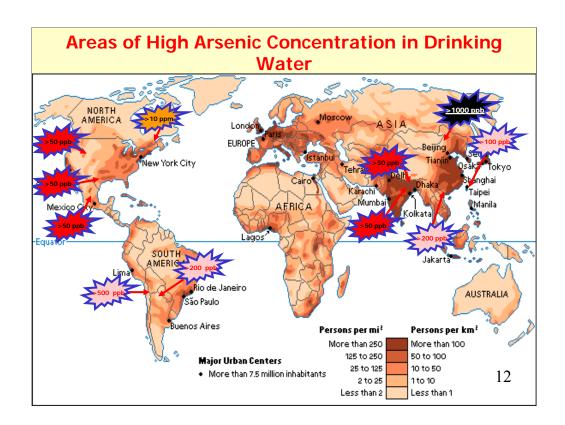
Location and Level of contamination

Population

Health

and Life and Death

come together!



The values shown are far from the highest recordings in these areas, but they are presented to provide a "sampled picture" of how arsenic contamination is spread throughout the world. (The next slide – if used – is a table showing the ranges of concentrations encountered in some of these areas.)

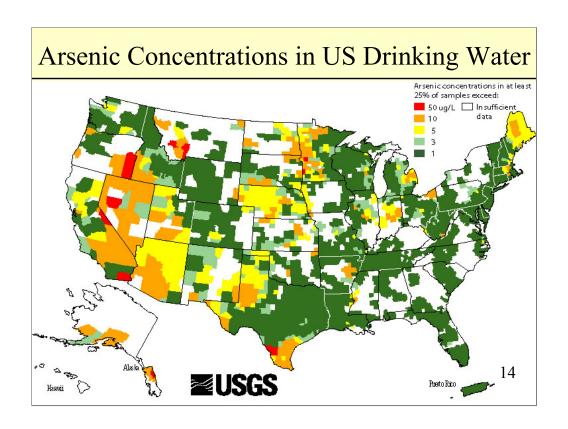
## International Arsenic Contamination Sites

Location	Conc. As (ppb).
Taiwan: Southwest Coast	100–1810
Taiwan: Putai	470–897
Chinese Inner Mongolia (Hetao Plain)	50–1080
Bangladesh: Ganges Delta	10–2040
Bangladesh: Pabna (North District)	50–14,000
India: West Bengal	50-3400
Vietnam: Hanoi and Red River Valley	1–3050

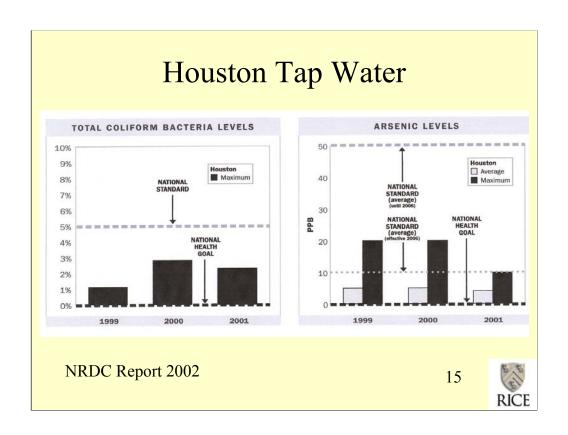
Note: Table adapted from Joanna Shaofen Wang and Chien M. Wai, U.Of Idaho. J. Chem. Ed.,vol. 8, n.2, p.209 Feb., 2004



Clearly, the values on the previous slide (which showed 100 ppb in Taiwan, > 200 ppb in Bangladesh and >1,000 in China) were not maximum values! In fact the next slide shows haw bad the problem is in one area in Bangladesh.)



Here is map of the sampled concentrations of arsenic in the water in the United States. Recently (January 2006), the USA has imposed a standard of <10 ppb (<10 mg/L) concentration in drinking water in the Country. This change from the previous 50 ppb has intensified the search for improved processes for reducing the amount of arsenic in drinking water – **on top of** the demands caused by much more hazardous concentrations in other areas of the world.



## Perspective: Contamination Levels

- According to some estimates, arsenic in drinking-water will cause 200,000

   270,000 deaths from cancer in Bangladesh alone (NRC, 1998; Smith, et al, 2000).
- Seven of 16 districts of West Bengal (India) have been reported to have ground water arsenic concentrations above 0.05 mg/L; total population is over 34 million (1996); estimated that the **population using arsenic-rich water is more than 1 million (above 0.05 mg/L) and 1.3 million (above 0.01 mg/L)** (Chowdhury et al,1997).
- According to a British Geological Survey study in 1998 on shallow tubewells in 61 of the 64 districts in Bangladesh, 46% of the samples were above 0.010 mg/L and 27% were above 0.050 mg/L. It was estimated that the number of people exposed to arsenic concentrations above 0.05 mg/l was 28-35 million and the number exposed to more than 0.01 mg/l (10μg/L) is 46-57 million (BGS 2000).
- EPA estimated that some **13 million of the population of USA**, mostly in the western states, are exposed to arsenic in drinking- water at 0.01 mg/L, although concentrations appear to be typically much lower than those encountered in areas such as Bangladesh and West Bengal. (USEPA 2001)

Source" World Health Organization (United Nations) Fact Sheet No. 210 (rev. May, 2001)



This is an "encapsulation of information" that briefly gives glimpse of the extent of the contamination and potential health impact of arsenic contamination.

# Drinking Water "Recommendations" & "Standards"

#### • World Health Organization Recommendations

<u>Year</u>	<u>Concentrat</u>	<u>ion</u>
1958	0.20 mg/L	(200 ppb)
1963	0.05 mg/L	(50 ppb)
1993	0.01 mg/L	(10 ppb)

#### United States

- 50 ppb was set by Public Health Dept. in 1942
- EPA adopted this standard in 1975 as "interim" regulation
- IN 1986 Congress converted this "interim" to a National Regulation and requested EPA review and set new standards.
- 50 ppb (0.050 mg/L) prior to January, 2006
- 10 ppb, currently



## New Jersey proposes toughest arsenic standard worldwide

The state of New Jersey has proposed an arsenic standard for drinking water that, if adopted, would be twice as stringent as the U.S. EPA standard and World Health Organization guideline of 10 parts per billion (ppb). The 5-ppb standard is based on recommendations from the New Jersey Drinking Water Quality Institute (NJDWQI), which found that a 10-ppb level wouldn't meet the level of protection required by state

doesn't permit. For example, it is far more expensive to reduce arsenic levels in states such as New Mexico than in New Jersey, explained Bradley Campbell, commissioner of the state's Department of Environmental Protection (DEP), in a policy directive.

Environmentalists and water purveyors, both of which are represented on NJDWQI committees, say they support the New Jersey standard. Many in the state say that

ES&T March 15, 2004



18

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### Effects of New Standard

- Max. Levels reduced from 50 μg/L to 10 μg/L
- 13 million people in areas of higher standard (West, Midwest, N. England)
- Annual Estimated Reductions:

	Cases	Deaths	
Bladder Cancer	19-31	5-8	
Lung Cancer	19-25	16-22	
Diabetes	?	?	19
Heart Disease	?	?	

Source: Environmental Protection Agency (US) (Jan. 2001) Technical Fact Sheet EPA 815-F-00-016



Here is the Environmental Protection Agency's assessment of the <u>annual</u> impact of reducing the levels of arsenic in drinking water in the United States

# Annual Estimated Cost of Raising Arsenic Standard: <50ppb to <10ppb

EPA estimates the total national annualized costs of treatment, monitoring, reporting, recordkeeping, and administration for this rule to be approximately \$181 million (using 1999 dollars at a three percent discount rate.

#### In millions of dollars

Treatment	\$ 177*
	*(3% Discount Rate, \$millions)
Monitoring	2.7
State Costs	1.0
Total	\$ 181

20



Source: Environmental Protection Agency (US) (Jan. 2001) Technical Fact Sheet EPA 815-F-00-016

Note that this is the annual cost.

# Motivation for Our Work with Nanotechnology

- A need for a cost-effective and highperformance technology to remove arsenic from drinking water
  - Reduce arsenic to less than  $10\mu g/L$  in less than a minute
- The mechanism of arsenic removal by iron oxides



## **Current Technologies**

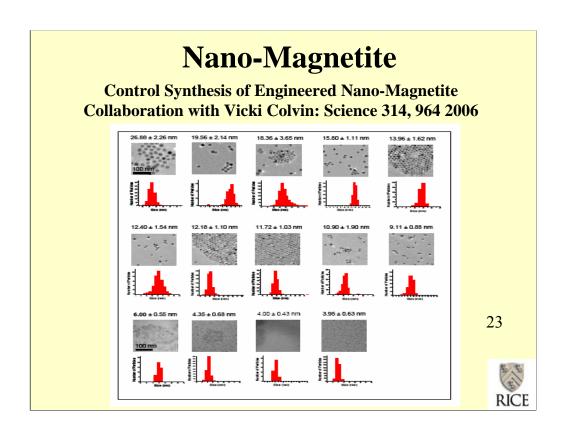
• US EPA As standard level: 10µg/L

Technology	Disadvantages
Ion exchange	No As(III) removal Interference from SO <sub>4</sub> <sup>2</sup> -& TDS
Membrane methods	Expensive
Coagulations with iron salts	Solid-liquid separation

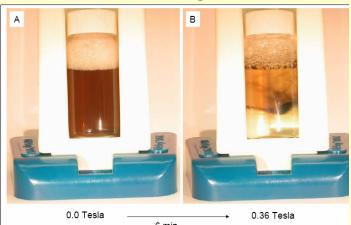
22

http://www.unu.edu/env/Arsenic/Han.pdf (accessed October 16, 2006)





# Magnetic Properties of Nano-magnetite

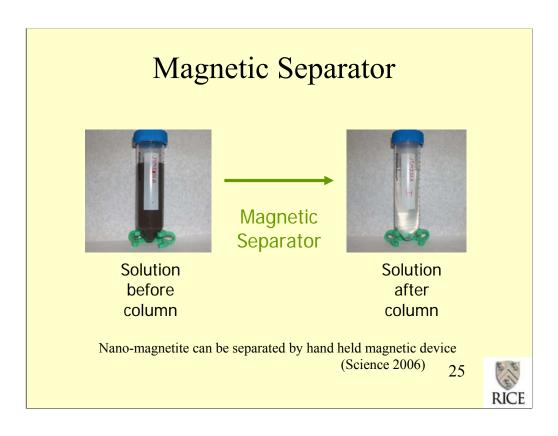


 $\begin{tabular}{lll} Magnetite nanocrystals $< 40 \ nm$: Single domain magnet \\ Size dependent magnetic properties: ferromagnetic (>20 \ nm) \\ & paramagnetic (6-20 \ nm) \\ \end{tabular}$ 

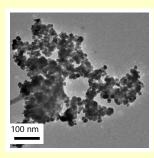
(Science 2006)

24

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## Magnetite Nanoparticles



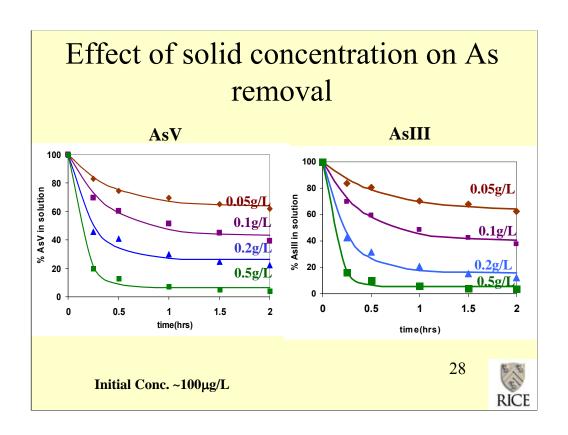
- Mean particle diameter: 20nm
- Surface area:  $60\text{m}^2/\text{g}$



## Experimental Set-up: Vessel Apparatus

- Temperature controlled
- Overhead agitator/stirrer
- 3 connectors by 3-way valves
  - Sampling
  - Ar gas
  - Solution injection/gas purging
- Anoxic/ Oxic conditions





## Modified Rate Equation

$$[As]_{t} = \frac{[As]_{0}}{1 + (q_{max} * b) * r_{sw}} + ([As]_{0} - \frac{[As]_{0}}{1 + (q_{max} * b) * r_{sw}}) * e^{k_{m} * SSA * r_{sw} * t}$$

[As]<sub>t</sub>: As concentration at time, t (s)

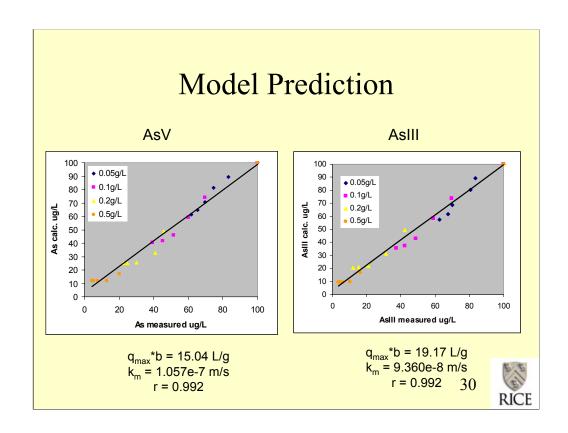
[As]<sub>0</sub>: As concentration at time = 0,  $(\mu g/L)$ 

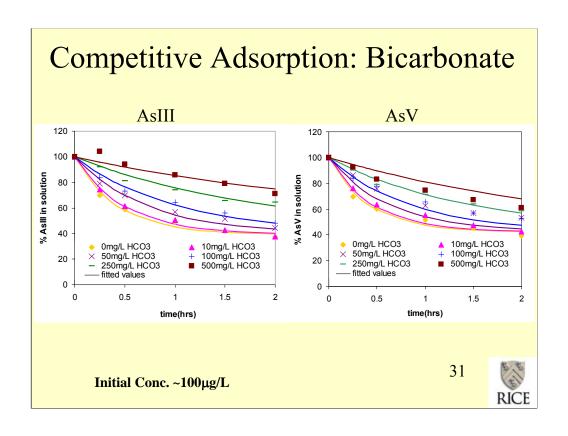
 $q_{max}$  \*b: Langmuir isotherm (L/g)  $r_{sw}$ : solid to solution ratio (g/L or g/m<sup>3</sup>)

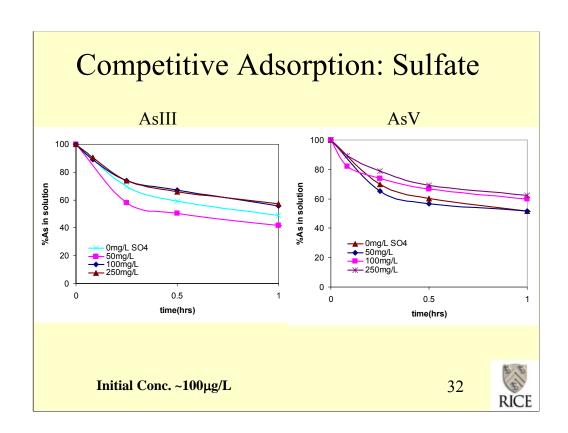
SSA: specific surface area (m<sup>2</sup>/g)

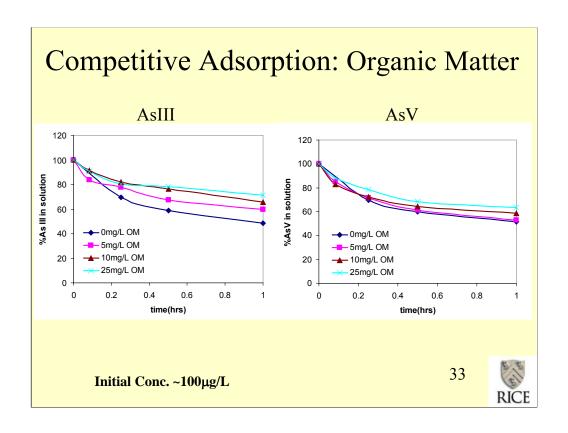
t: time (s)

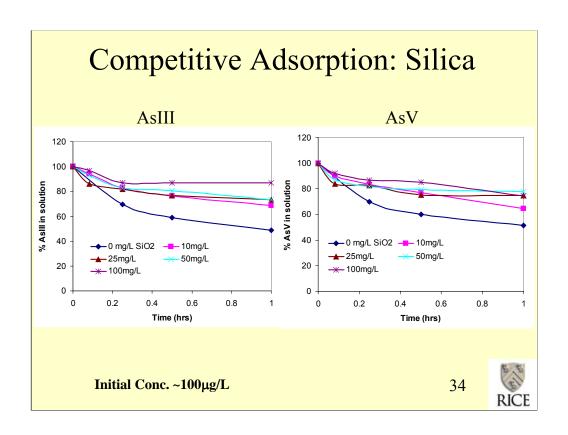


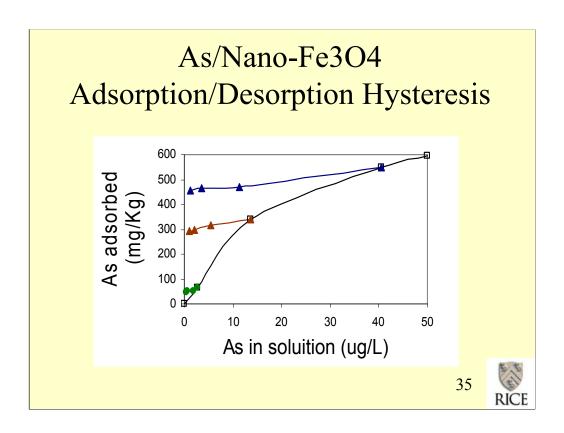












## Field Test – Brownsville, TX

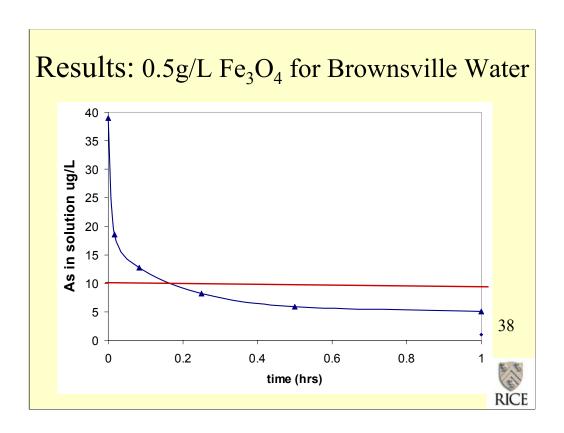
 Arsenic-contaminated water from Southmost Regional Authority Desalination Plant Brownsville,TX in August, 2006: Wells #8 and 12 (Brackish water: ~ 5mS/cm)

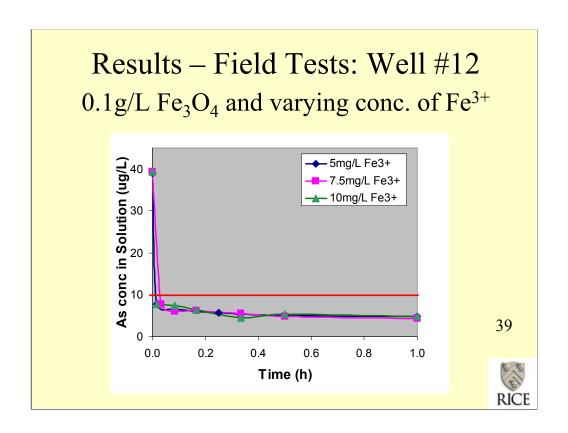


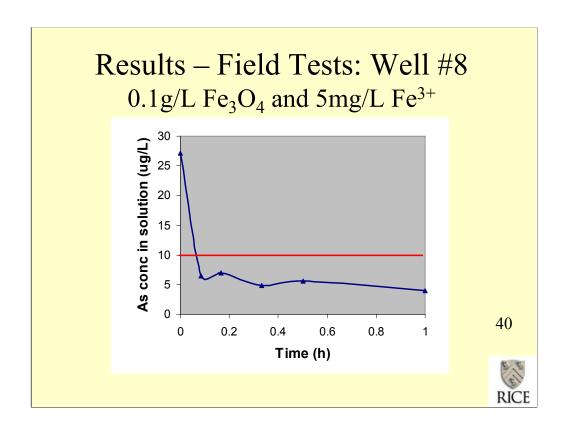
# Characterization of Brownsville Wells

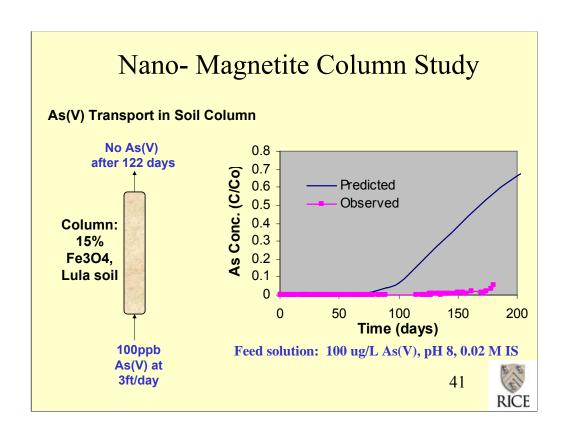
	Well #8	Well #12
Initial As (µg/L)	27.2	39.0
рН	7.32	7.39
Alkalinity	335	464.6
$(mg/L as HCO_3^-)$		
SO <sub>4</sub> <sup>2-</sup> (mg/L)	1165	1192.5
Silica	41.4	36.4
(mg/L as SiO <sub>2</sub> )		
PO <sub>4</sub> <sup>3-</sup> (mg/L)	0.23	0.16

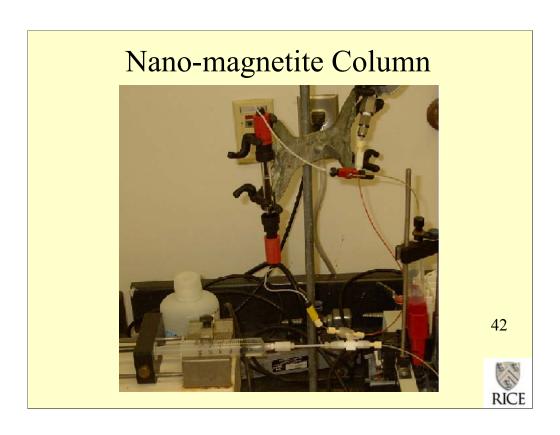
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Material	Sorbent (kg)/ month	1 gram treats L water	Waste to dispose of kg (1 yr) <sup>3</sup>	Backwash Frequency (day)	Efficiency <sup>1</sup>
Alumina + Metal Oxide	0.24	3.8	2.883	14	0.003
Activated Neutralized Red Mud [As(III)]	360.7	0.002	4328.13	Periodic	(0.003) est.
Ion Exchange	No R	emoval of Toxi	c As(III) <sup>3</sup>	~ 3	0.014
Nano- magnetite	0.09	10	1.1	0	(7.5 to 75) <sup>2</sup> est.
2g 11.7 nm M		l gal	> Amenable	nces	tic separat

Lets start with some applications.

As you know, Mason and Vicki are working to develop a novel approach to remove arsenic from drinking water using magnetite nanoparticles that are not only superior sorbents with minimal bleed-off potential, but are also amenable for magnetic separation.

This could therefore result in a cost-effective treatment system that could be used at the household-level to alleviate arsenic poisoning in many areas of the world that. Clorox who makes Britta filters has shown a lot of interest.

## Conclusions

- Sulfate, organic matter, silica, bicarbonate have intermediate to large effect on adsorption
- Ca, Mg, K, Trace Metals have little to insignificant effect on adsorption
- Arsenic concentration < 10μg/L in a minute by adding iron salts and magnetite nanoparticles
- Successful field test
- Inhibition of arsenic removal and iron oxide formation in the presence of citrate 44

# Acknowledgement

 Funding of this project is from the Center for Biological and Environmental Nanotechnology (CBEN) at Rice University, NSF, and EPA STAR nanotechnology grant

45







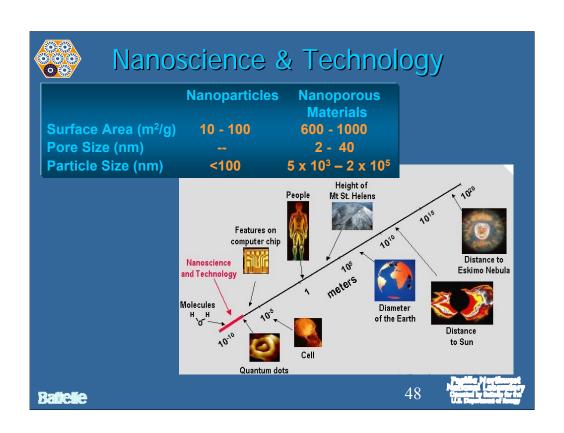
### **Functionalized Ceramic Nanoporous Sorbents**

- 1. Introduction
- 2. Nanoporous Sorbents
  Substrate Synthesis
  Monolayer Functionalization process (SAMMS)
  Host design for molecular recognition
- 3. Performance SAMMS (Self Assembled Monolayers on Mesoporous Supports) thiol SAMMS Cu-EDA SAMMS HOPO SAMMS
- 4. Treatment costs & waste form stability
- 5. Potential Applications & Commercialization

**Battelle** 

47







## Why Nanoporous Sorbents?

### **Technology Need**

ppb - ppt treatment levels

### Large surface area - controlled pore size

Dense packed functionality
High contaminant loading
Enhanced adsorption kinetics

#### Particle size: 5 – 120 μm

Silt and sand size material (non toxic) Easier to fabricate engineered forms (vs nanoparticles)

#### Silica based substrate

Inexpensive to produce Environmentally compatible & stable

49



