Meeting the New Drinking Water Standard for Arsenic:

Occurrence, Implications and New Technological Solutions for Treatment

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

Objectives of Talk

- Provide arsenic overview at different scales
    - Bird's eye view -> molecular view
- Illustrate how water quality policy draws on different views
  - Controversy over basis of new Arsenic MCL
  - Occurrence, toxicity, cost
  - Unintended consequences of new MCL
- Describe work at Sandia National Laboratories to reduce treatment cost
  - Describe basic principles of treatment methods
  - Pilot tests of new adsorptive media
  - Rapid testing techniques
- Discuss what this all means in the real world
  - Helping communities deal with the new Arsenic Standard

‘The King of Poison and the Poison of Kings’

- Skin Cancer, Skin lesions
- Bladder Cancer
- Lung Cancer
- Cardiovascular Disease
- Blackfoot Disease

These are result of exposure to relatively high doses over extended period of time.

Other effects of concern include diabetes, cancers of liver and kidney, birth defects, developmental problems

Mass poisoning by arsenic - the premier global public health problem?

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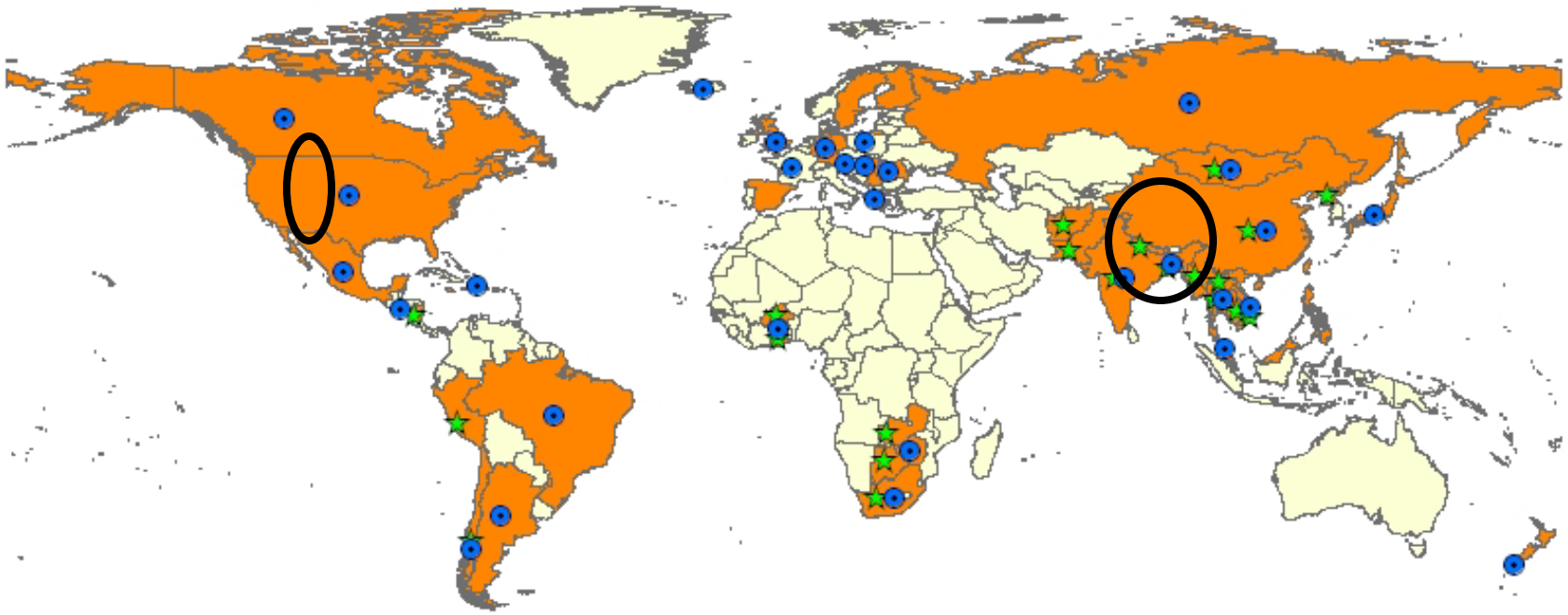
Global Map of Countries with Arsenic in Drinking Water

(from Aquifers, Mining Operations or Geothermal Waters)



★ 21 Countries Affected by Arsenic Identified by UNICEF (Ali,M., 2005)

● 30 Countries Affected by Arsenic Identified by Smedley (Smedley, 2004)

(Murcott, S. 2005)

(Map by Zheng Gong, MIT '08)

Source of The Arsenic Contamination

Arsenic is associated with the alluvial sediments

High carbon content in the alluvial deposits creates an anaerobic environment which enhances the release of arsenic.

Promotion of Tube Wells

To decrease infant mortality due to water born diseases from untreated surface water.

High arsenic levels were found in many of the tubewells.

Resultant chronic arsenic poisoning is a public health problem in regions of Nepal, West Bengal India, and Bangladesh in South Asia.

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Natural Arsenic Contamination in Asia

NEPAL

Teri Lands: Subtropical belt of flat alluvial land where 11 million people live

200 thousand tube wells provide potable water

8% > 50 ppb Arsenic (MCL)

29%> 10 ppb Arsenic (WHO MCL)

BANGLADESH

Except for the Hill Tracts the whole country is affected

~ 10 million tube wells

27% > 50ppb Arsenic(MCL)

46% > 10ppb Arsenic (WHO MCL)

(Khandakar, 2003)

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Table 3. Bangladesh: Estimated Health Impact of Arsenic Contamination of Tubewells

Impact on health/ type of illness	Males	Females	Combined
Cancer cases:			
Fatal cancers/year	3,809	2,718	6,528
Nonfatal cancers/year	1,071	1,024	2,095
Total cancer fatalities accumulated over 50 years	**190,450**	**135,900**	**326,400**
Arsenicosis cases[a]:			
Keratoses	277,759	74,473	352,233
Hyperpigmentation	654,718	316,511	971,230
Cough	21,823	68,887	90,712
Chest sounds	144,831	67,025	211,858
Breathlessness	93,247	176,874	270,122
Weakness	132,927	240,176	373,104
Glucosuria	67,887	63,551	131,439
High blood pressure	94,396	88,366	182,762
Total arsenicosis cases in each year	**1,487,588**	**1,095,863**	**2,583,460**

Deaths/year

Cases/year

[a] *Figures indicate average number of cases occurring in each year (not number of new cases).*
Source: Maddison, Luque, and Pearce 2004, p. 32.

Source: World Bank. Towards a More Effective Operational Response. Vol 1. Policy Report, 2005 p. 28

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Table 1. Summary of the Distribution, Nature, and Scale of Documented Arsenic Problems (>50 µg L^{-1}) in Aquifers in South and East Asia

Location	Areal extent (km^2)	Population at risk[a]	Arsenic range (µg L^{-1})
Alluvial/deltaic/ lacustrine plains			
Bangladesh	150,000	35,000,000	<1-2,300
China (Inner Mongolia, Xinjiang, Shanxi)	68,000	5,600,000	40-4,400
India (West Bengal)	23,000	5,000,000	<10-3,200
Nepal	30,000	550,000	<10-200
Taiwan (China)	6,000	(?) 10,000[b]	10-1,800
Vietnam	1,000	10,000,000[c]	1-3,100
Myanmar	(?) 3,000	3,400,000	-
Cambodia	(?) <1,000	320,000[d]	-
Pakistan	-	-	-

- Not available.
[a] Estimated to be drinking water with arsenic >50 µg L^{-1}. From Smedley 2003 and data sources therein.
[b] Before mitigation.
[c] United Nations Children's Fund (UNICEF) estimate.
[d] Maximum.
Source: World Bank Regional Operational Responses to Arsenic Workshop in Nepal, 26-27 April 2004.

60 million at risk in Asia (estimate)

Source: World Bank. Towards a More Effective Operational Response. Vol 1. Policy Report, 2005 p. 26

The Public Health Trade-off

Table 4. Estimated Annual Deaths from Diarrheal Disease of Children under Five

Country	Region	Annual total mortality of children under the age of five[a]	Low estimate (15% of child mortality under 5 years due to diarrhoea)	High estimate (30% of child mortality under 5 years due to diarrhoea)
Bangladesh	South Asia	323,000	48,450	96,900
Cambodia	East Asia	65,000	9,750	19,500
China	East Asia	735,000	110,250	220,500
India	South Asia	2,346,000	351,900	703,800
Lao PDR	East Asia	20,000	3,000	6,000
Myanmar	South Asia	129,000	19,350	38,700
Nepal	South Asia	74,000	11,100	22,200
Pakistan	South Asia	579,000	86,850	173,700
Vietnam	East Asia	64,000	9,600	19,200
South Asia total		3,451,000	517,650	1,035,300
East Asia total		884,000	132,600	265,200
Total		4,335,000	650,250	1,300,500

[a] Data from UNICEF website.

Source: World Bank. Towards a More Effective Operational Response. Vol 1. Policy Report, 2005 p. 29

Water Quality Policy in the United States
Development of Arsenic MCL

- **Recent reduction of drinking water Maximum Concentration Level (MCL) for arsenic from 50 ppb to 10 ppb was intended to reduce incidence of bladder cancer and other cancers in US.**
- **Arsenic MCL reflects consideration of:**
  - **Toxicity**
  - **Occurrence**
  - **Cost of Compliance**
- **Policy reflects tradeoffs among competing goals, set in a background of uncertainties in data, models, and poorly understood social and cultural issues.**

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Questions about the New Arsenic Standard in the US – 2001.

Debate was bitter at times

NRDC Denounces EPA's Proposal to Withdraw New Arsenic-in-Tap-Water Standard; Group Says Move is Unwarranted and Illegal -- and Vows to Sue

WASHINGTON (March 20, 2001) -
The Bush administration's announcement today to withdraw the new arsenic-in-tap-water standard is a craven capitulation to the mining industry and other corporate interests at the expense of the health of millions of Americans, said NRDC (Natural Resources Defense Council).

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Is arsenic toxic at expected levels of exposure?

Toxicity and Carcinogenicity

- As(III) bonds with sulfhydryl groups in cysteine
  - Can inhibit activity of >200 proteins
- Arsenic generate reactive oxygen species/free radicals
  - Reactive oxygen species (ROS) cause damage to proteins and lipids
  - ROS generation by metals is associated with DNA damage (strand breakage, cross-links, hydroxylation)
  - Alters DNA repair and methylation pattern
- Chromosomal damage
- Methylated forms (MMA, DMA) now seen as toxic and directly carcinogenetic

Uncertainties in Models for Arsenic Toxicity

- **In Vivo Animal Models**
  - **Strength is ability to manipulate system and control exposures**
  - **Some weaknesses include:**
    - **Dramatic differences in arsenic metabolism, excretion and toxicity profile between species**
    - **Animals have not proven to be a good model for arsenic carcinogenicity**
- **In Vitro Models (cells)**
  - **Strength is ability to test mechanisms, manipulate and control exposures, human cells available**
  - **Some weaknesses include**:
    - **Cells out of tissue and organ context**
    - **Normal cells difficult to obtain and maintain**
    - **Difficult to determine whether responses are meaningful to human exposures**

Epidemiologic Studies at Low Exposures are Ambiguous

- **Studies prior to 2001 Standard**
  - **Some studies carried out in populations in Taiwan, South America show elevated bladder cancer risks. ("relative risk" = 5 –11).**
  - **As concentrations were generally above 50 μg/L.**
  - **Results of studies of US and European populations at lower As concentrations show no increased risk or are ambiguous.**

- **Post-2001 studies**
  - **Results: *do not* suggest that chronic exposures to arsenic at low levels (50 – 100 μg/L) lead to increased mortality risk for bladder or lung cancer for the majority of populations studied.**
  - **Some studies suggest interaction between smoking and exposure to arsenic ***may*** lead to increased risk for bladder and lung cancers;**
  - **Smokers may experience a higher risk at levels below 100 μg/L**
  - **Elevated incidence in New Mexico (>10 ppb) reported recently**
  - **Potential role of arsenic in endrocrine disruption**

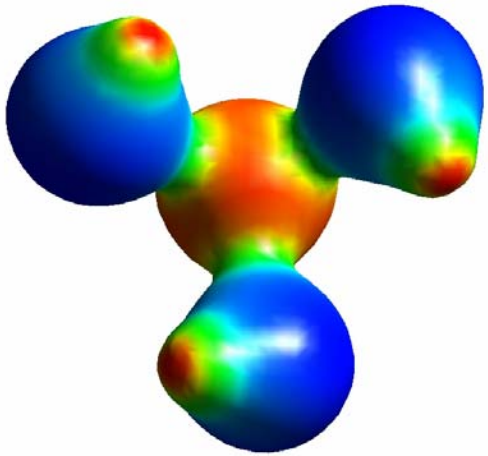
Is exposure to arsenic likely?

What controls distribution and behavior of arsenic in the environment?

Volcanic Sources of Arsenic

- **Strongly enriched in volcanic gases compared to magma**
  - **sublimation of As_2O_3 (193°C) and As_2S_5 (500° C)**
  - **enrichment factor = 1000 - 1000000**
- **Abundant in silicic volcanics**
  - **derived volcaniclastic sediments**
  - **associated hydrothermal systems**
    - **As is a pathfinder elements in prospecting for hydrothermal gold deposits**

Arsenic Speciation Controls Behavior in Aquatic Environments

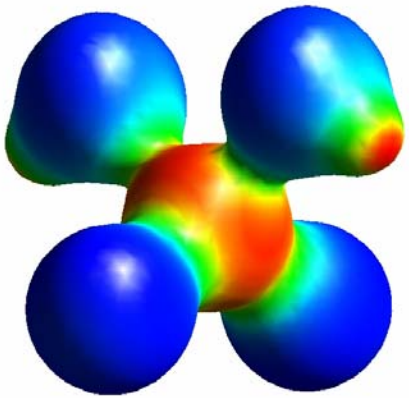


H_3AsO_3

Inorganic arsenic in groundwater usually exists as a combination of neutral As^{III} (arsenite) and anionic As^{V} (arsenate).

Arsenite is believed to be more toxic than arsenate.

$H_2AsO_4^-$



As^{V} is adsorbed more than As^{III} by metal oxides at near-neutral pH because of coulombic attraction.

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Increase of Arsenic in Natural Waters

- **Reductive dissolution of iron oxides**
  - **co-release of adsorbed and structural As**
- **Reductive desorption of As(V)**
  - **strongly sorbed As(V) -> weakly sorbed As(III)**
- **Competitive desorption**
  - **phosphate, bicarbonate, silicate, dissolved organics**
- **pH changes**
  - **increased pH leads to As(V) desorption**

Same principles important in design of treatment technology.

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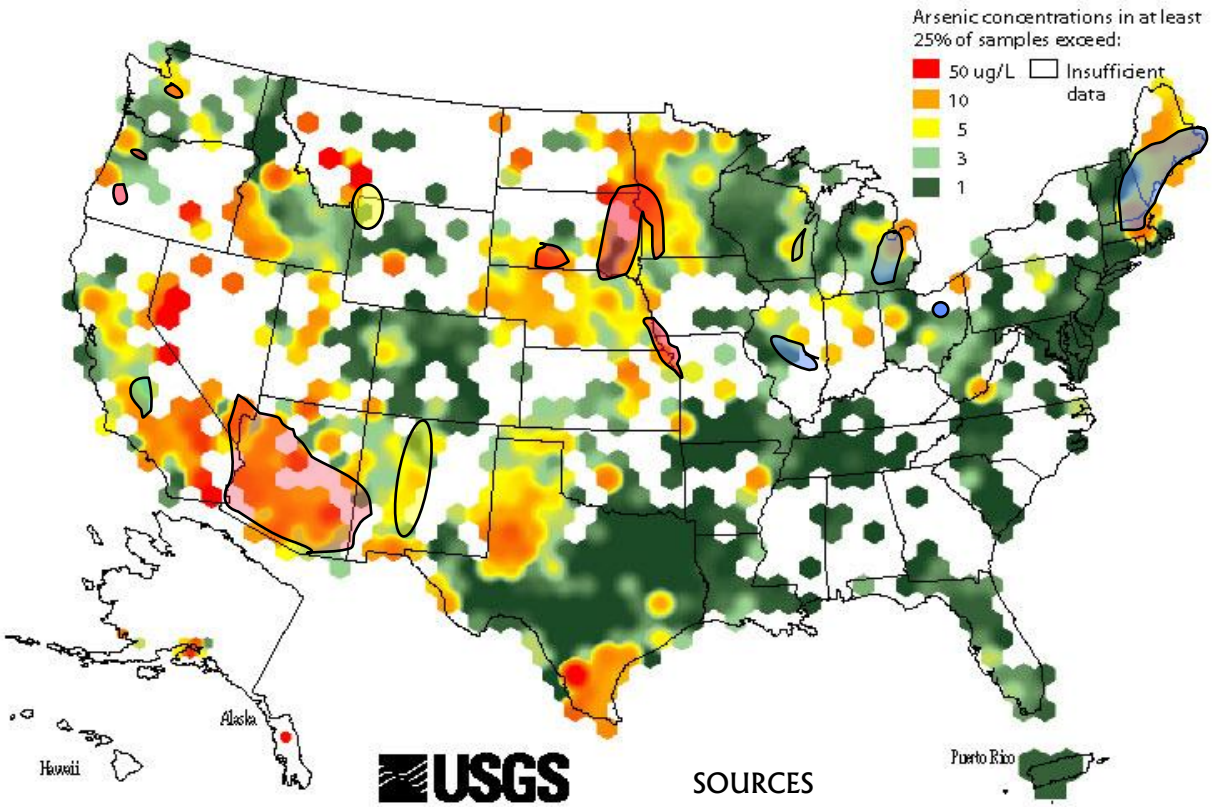
Arsenic Occurrences and Sources in the U.S.



Adapted from Welch et al. (2000) and Ryker (2001).

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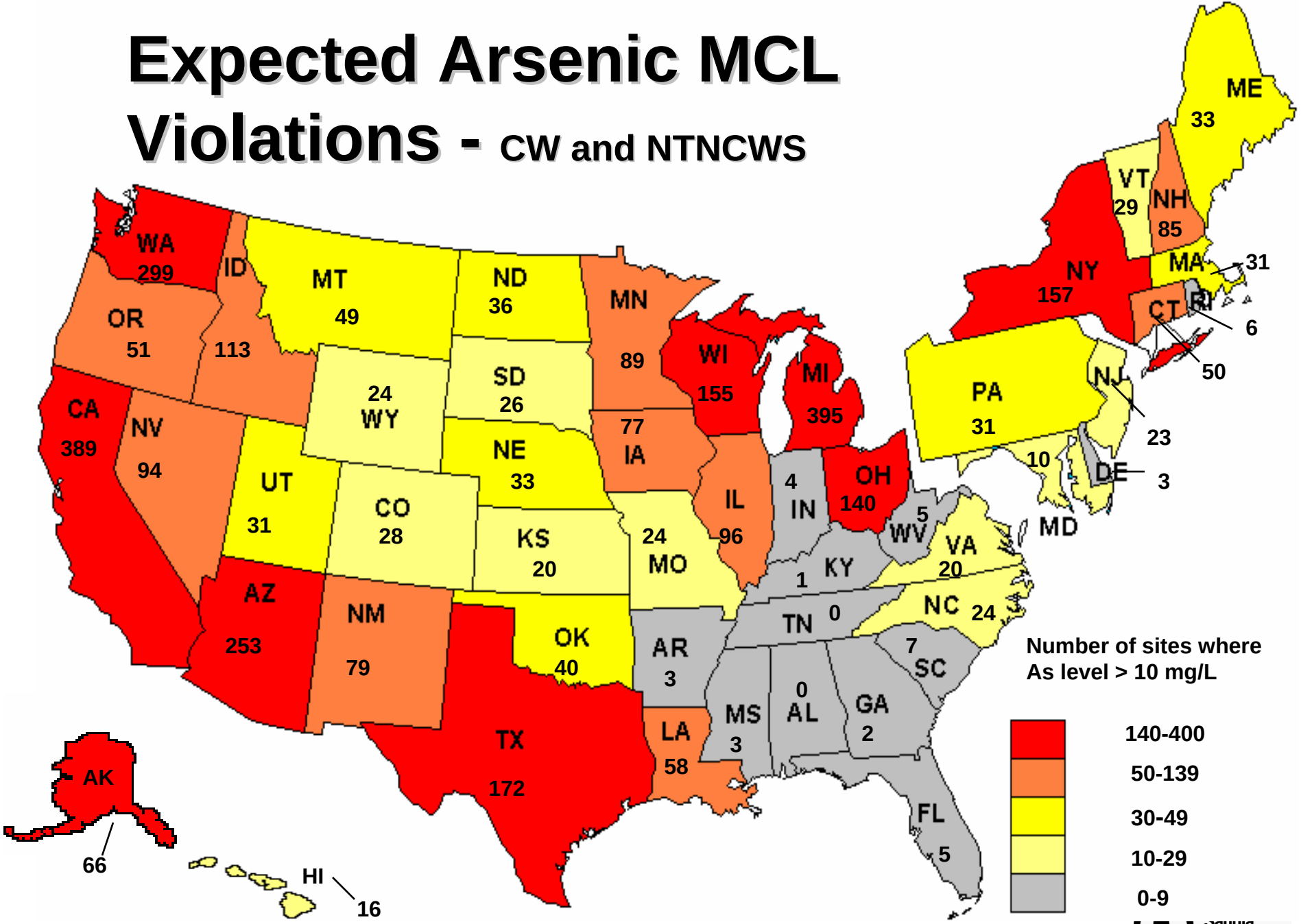
Expected Arsenic MCL Violations - CW and NTNCWS



Source: USEPA (2000b)

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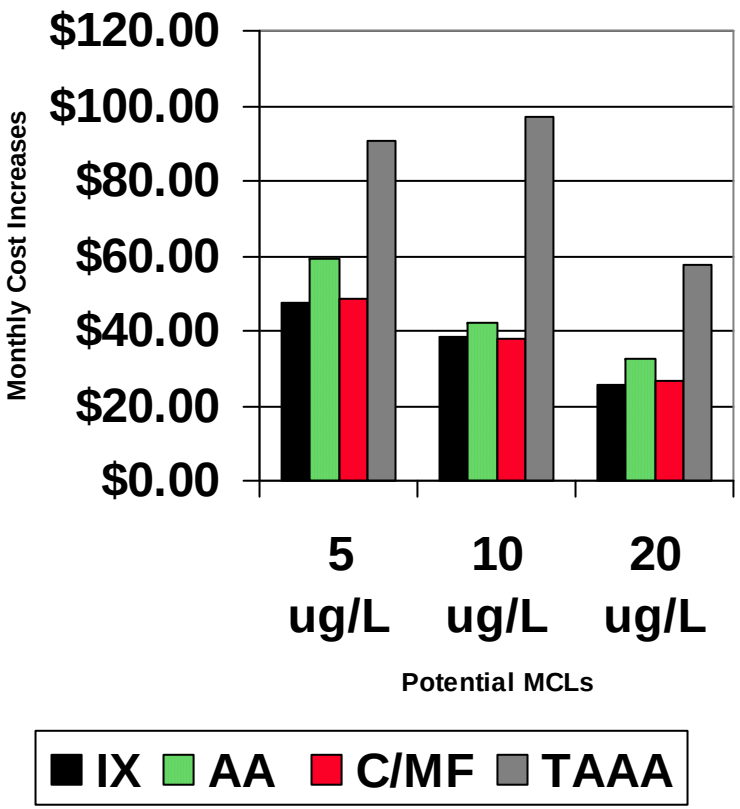
What will it cost to comply with the new standard?

Will the cost cause undue hardship?

General Treatment Choices

- **Reverse Osmosis**
  - Removes almost all solutes by forcing water through membrane with tiny pores
  - Leads to 30 –50% water loss; brine is waste
- **Precipitation/filtration processes**
  - Production of adsobent floc by addition of chemicals
  - Floc and adsorbed As removed by filtration with various materials
  - Sludge discharged into sanitary sewer
  - Best for large systems
  - Ex. - Coagulation/microfiltration
- **Sorption treatment processes**
  - Granular or fibrous material adsorbs arsenic
  - Regeneration or throw-away residuals
  - May create new waste
  - Good for small systems
  - Ex. - Ion exchange or activated alumina

Monthly Cost Increase in Cost of Water with EPA Best Available Technologies



- At 5 μg/L: $47 - $59/month in large systems; $91/month in small systems
- At 10 μg/L: $38 - $42/month in large systems; $91/month in small systems
- At 20 μg/L: $25 - $32/month in large systems; $57/month in small systems

- (Bitner, 2001)

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Unintended Consequences of new MCL for Arsenic

- The health effects from income redistribution may have adverse health consequences.
  - $90/month additional cost for rural NM household
- Injury risks from water treatment may exceed the benefits.
  - Based on traffic accident statistics and distance from chemical supply sources for treatment
  - Results depend on assumed dose-response model and treatment technology
- Rural water utilities may cease to operate.
- Rural residents may switch from a public supply to a unregulated private well.

Summary: Arsenic in the United States

- **Recent reduction of drinking water Maximum Concentration Level (MCL) for arsenic from 50 ppb to 10 ppb was intended to reduce incidence of bladder cancer and other cancers in US.**
- **Estimated national annual costs of implementing 10 ppb MCL range from $165M to $605M to save 7 – 33 lives.**
  - **$5M – $23.9M /life saved**
  - **$1.3M – $6.6M/ year of life saved**
  - **About 1 life/500,000 exposed persons per year**
- **New MCL is controversial due to high costs and uncertain health benefits.**

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Reducing Treatment Costs: Arsenic Water Technology Partnership

- **Congressional Appropriation - $13M FY03 – FY06**
- **DOE- funded peer-reviewed, cost-shared research program to develop and demonstrate innovative technologies for removal and disposal of arsenic from drinking water**
- **Partner Roles**
  - **Bench-Scale Studies (AwwaRF)**
  - **Demonstration Studies (Sandia)**
  - **Economic Analysis/Outreach (WERC)**
- **Focus on small systems**
  - **40% of resources directed to rural and Native American utility needs**
  - **Minimize costs - capital, operating, maintenance**
  - **Minimize residual quantities & disposal costs**

Can advances in water treatment technology significantly reduce costs?

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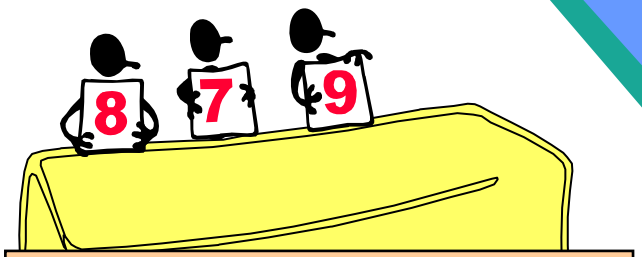
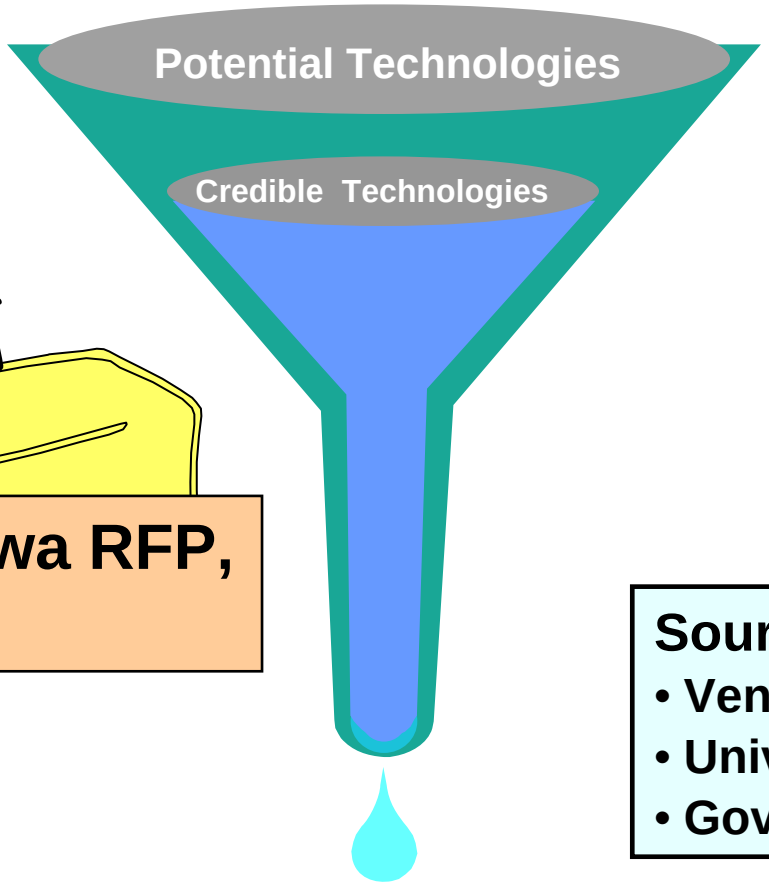
AWTP Technology Screening Process



Forum, Awwa RFP, WERC



- Innovation
- Performance
- Cost
- Complexity
- Maturity

Sources of new technologies
- Vendors
- Universities
- Government labs

Suggested Pilot Technologies

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General Treatment Innovations

- **Sorption treatment processes**
  - Regenerable, higher capacity and selectivity
  - More stable residuals
  - 'Tougher' sorbents
  - Coatings on inexpensive materials (industrial waste, natural materials)
- **Precipitation/filtration processes**
  - Enhanced coagulation with Fe compounds or polyelectrolytes
  - Improved filtration with nanocomposite materials
  - Recycle systems to minimize chemical addition

2003, 2004, 2005 Vendor Forums led to recommendation of innovative technologies for initial pilots and others for additional bench-scale studies

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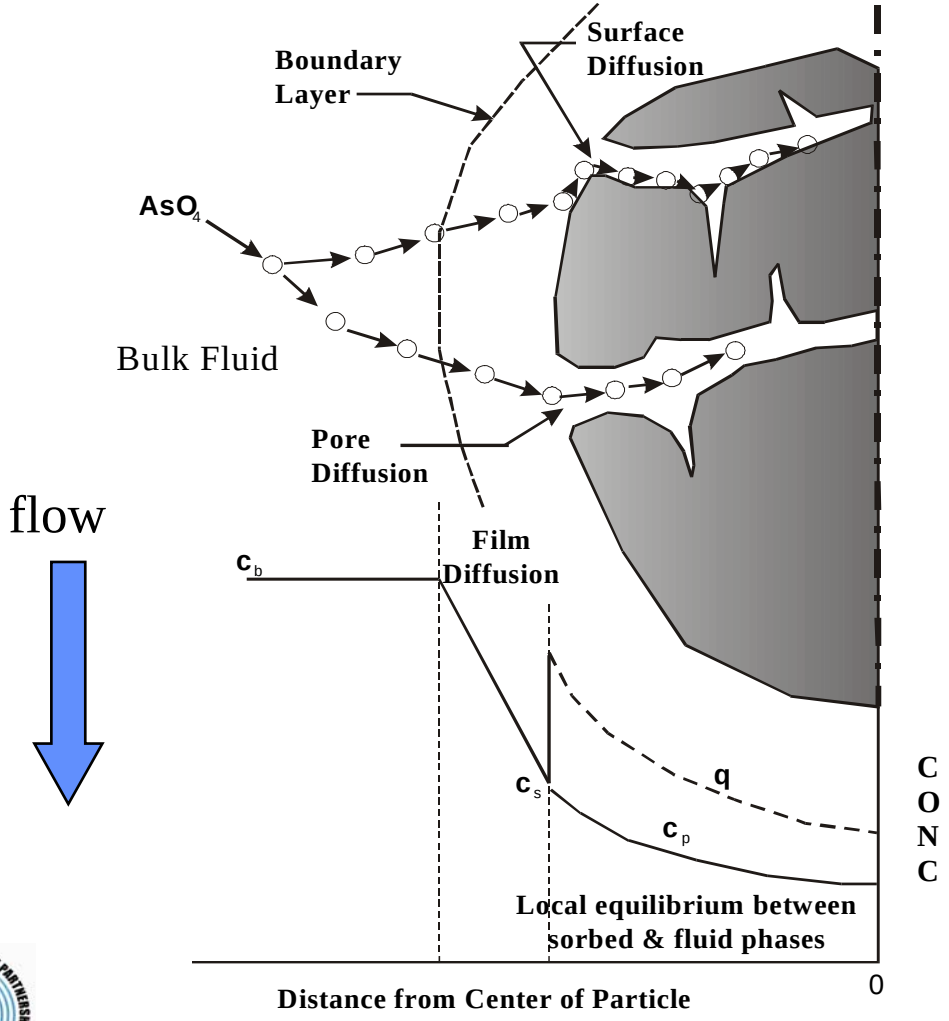
Performance of Adsorptive Media



Controlling factors

- Sorption equilibria
- Intraparticle diffusion rates
- Uniform flow

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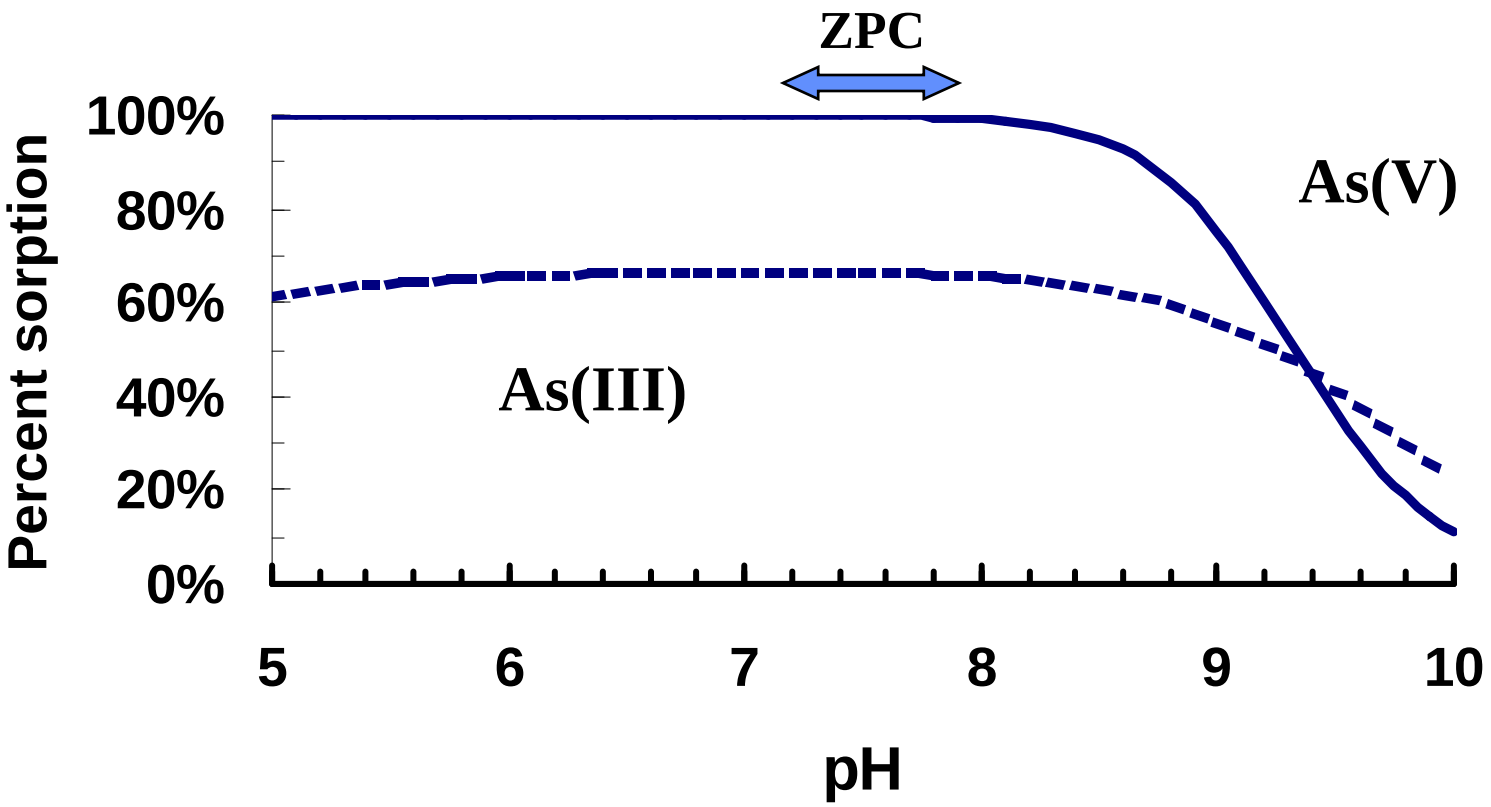
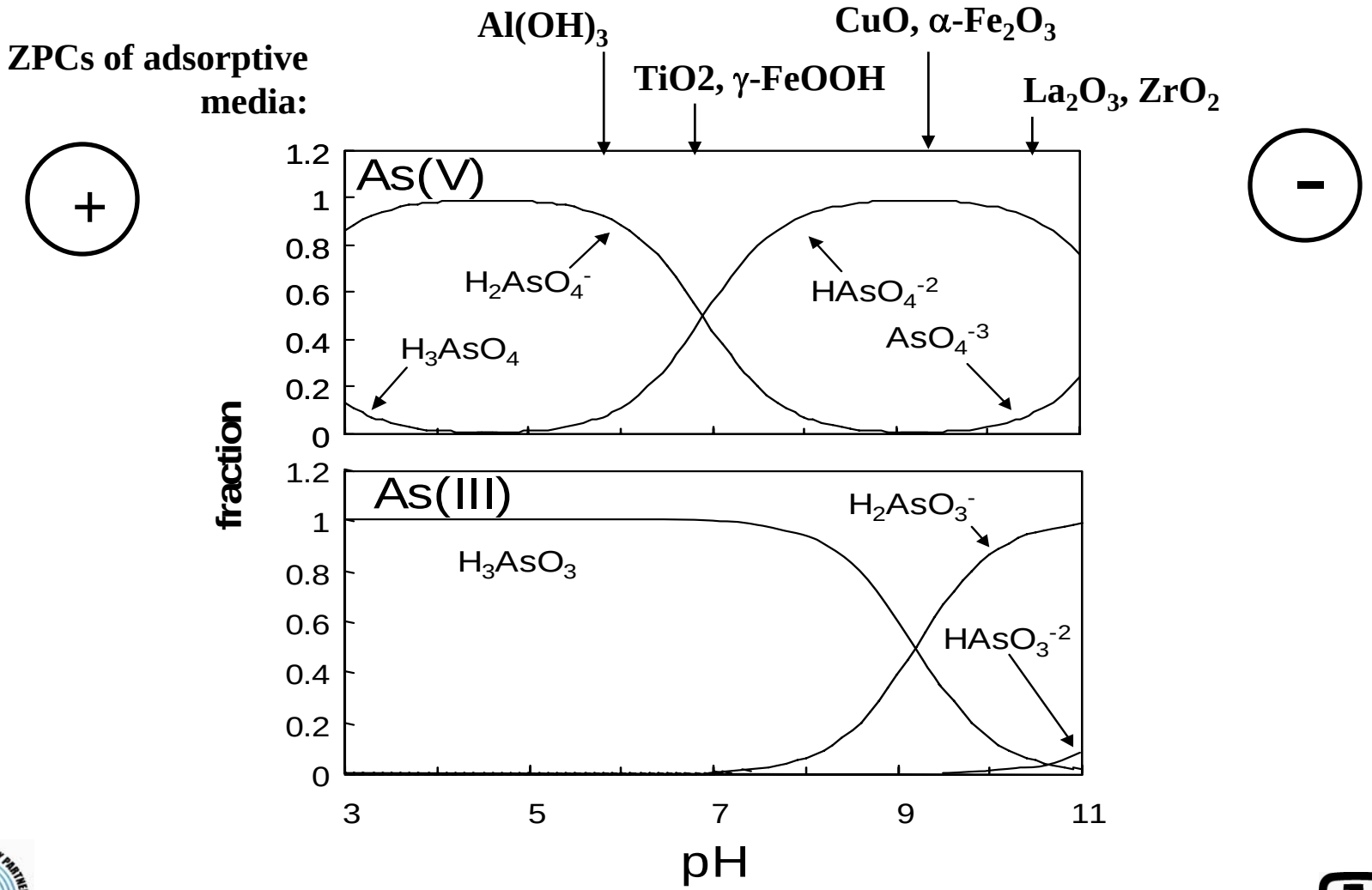
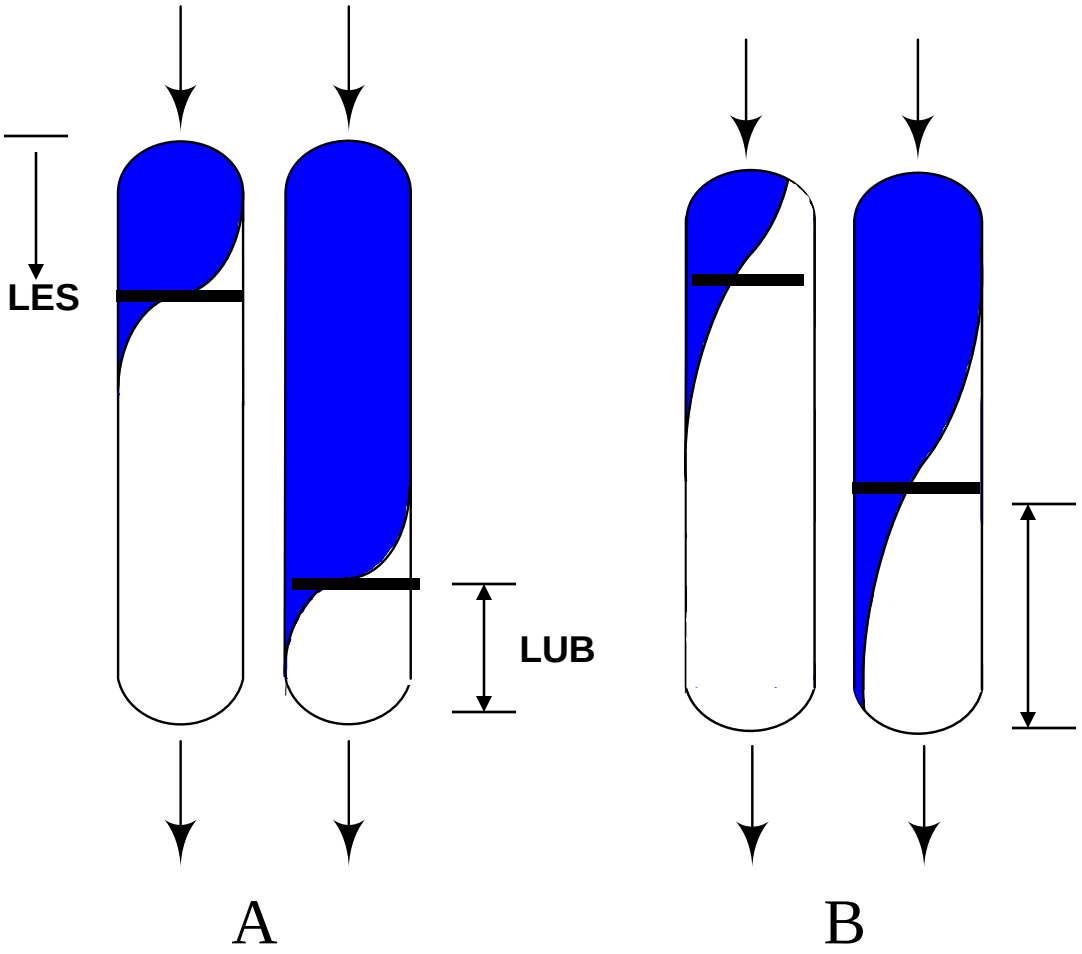
pH and Sorption by adsorptive media
Example: $Fe(OH)_3$

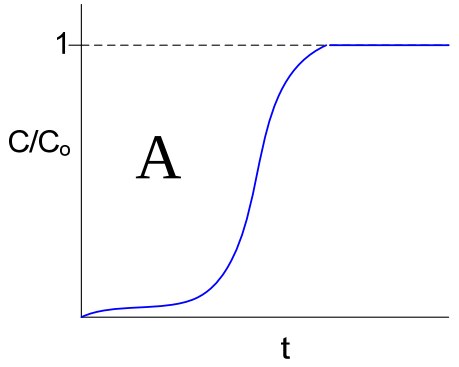


pH and Speciation

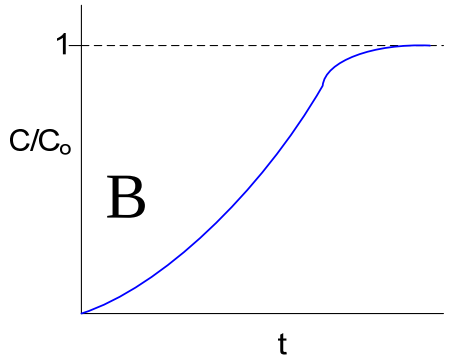


Sorption isn't the whole story: Shape of mass transfer zone determines capacity





Later breakthrough



Earlier breakthrough

LES = Length of Equilibrium Bed LUB = Length of Unused Bed

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Sorption Treatment Innovations

- **Fe, Ti, Cu, Zr or mixed metal oxides in granules formed by chemical precipitation or nanoparticle agglomeration. (e.g. AdEdge, Kemiron, Argonide, Graver)**
- **Coating granular activated carbon (GAC), strong base anion exchangers resin or polymeric ligand exchangers with nanoparticulate metal oxides. (e.g. Purolite, Resintech, Auburn University, Arizona State)**
- **Coating inexpensive natural media or waste products with metal oxides or other functional groups. (e.g. ADA, Virotec, Lawrence Berkeley Labs)**
- **Increased surface area and chemical selectivity based on fibrous or gel substrates coated by metal oxides or materials with sulfhydryl functional groups. (e.g. NMSU, Weber State, Drexel University)**

Sandia Pilot Test Concepts

- **Side-by-side demonstrations of technologies tested by AwwaRF bench-scale program, WERC design contest, University programs, or commercial technologies vetted through Vendor Forums**
  - **Test duration: 3 – 9 months; longer, if multiple pilots at same site**
  - **Test size: 0.3 – 10 gpm**
  - **Different technology classes: adsorptive media, Coagulation/Filtration, *membranes, electrochemical***
- **Cooperative effort between Sandia, Technology Owner and Site Owner**
- **Test Protocols developed with help from NSF International, academia, industry during 2004-2005**

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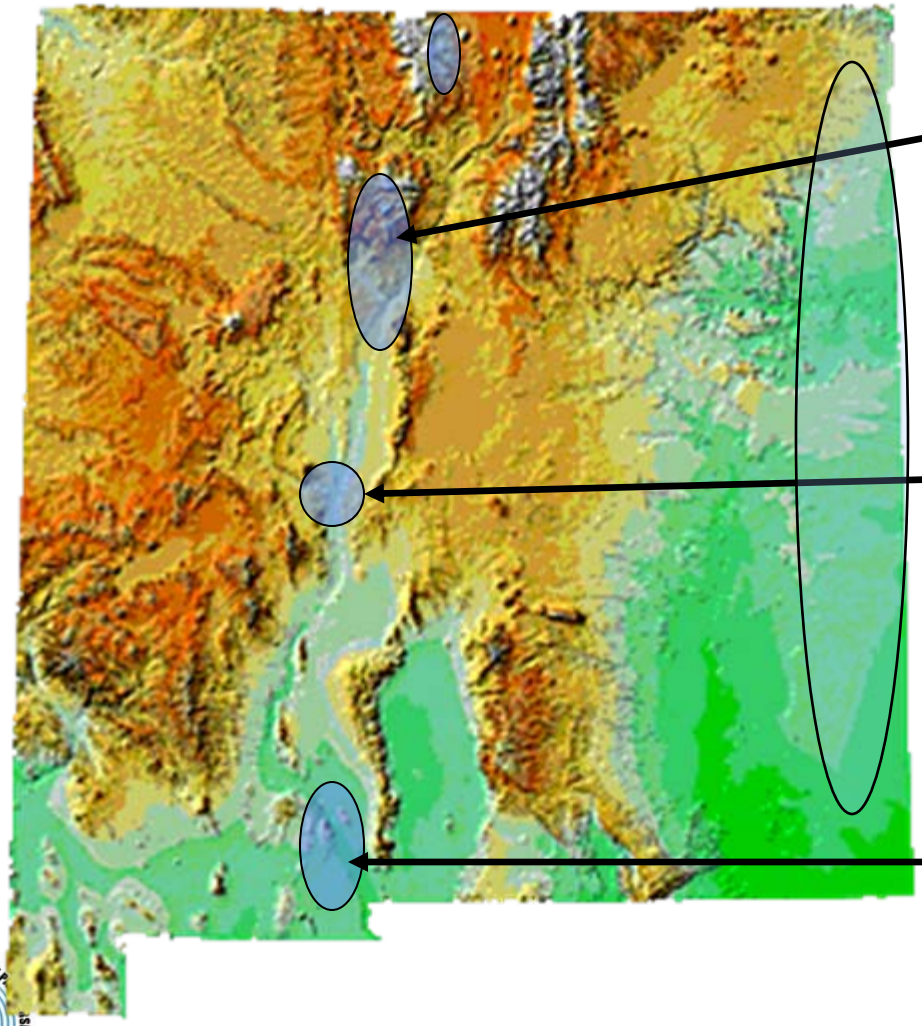
High Arsenic in New Mexico's Waters



- **Abundant in silicic volcanics**
  - **derived volcaniclastic sediments and associated hydrothermal systems**
- **Arsenic enrichment by Potassium Metasomatism**
  - **low temperature alteration common in closed hydrographic basins in arid climates**
- **Mixing of deep geothermal waters and shallower surface influenced waters**

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Pilot Tests in New Mexico

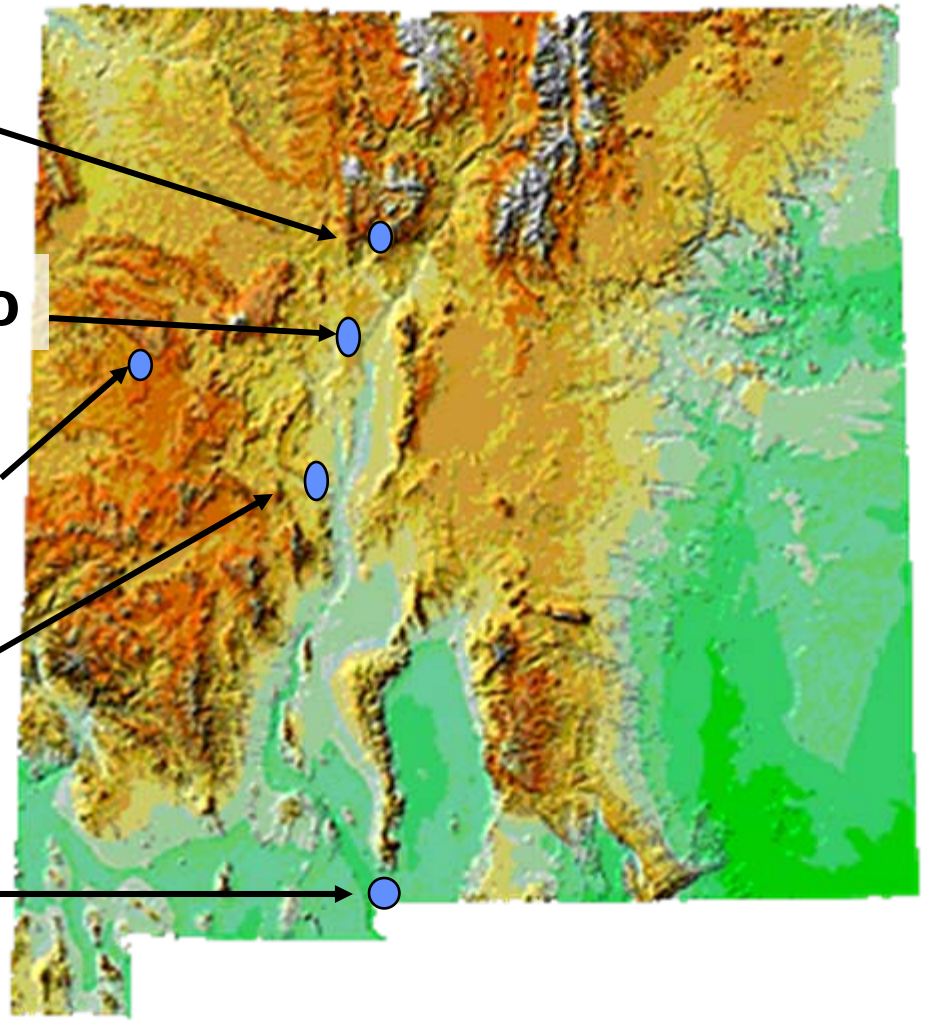
Jemez Pueblo

Rio Rancho

Ramah NR

Socorro

Anthony



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Socorro Springs, Socorro, NM

- 100% groundwater source for drinking water
- 2 warm springs (90^{o}F) provide 500 gpm, 35 – 55 ppb As(V) by gravity flow.
- Formerly site of tap for bottled water company;
- Optimal F for oral health
- Phase 1: Feb-Oct 2005
  - Tested
    - Fe oxides: E33, ARM200
    - Resin - AsX^{np}
    - Ti-oxide - Metsorb
    - Zr-oxide - Isolux
  - EBCT study of E33
    - 2,4,5 min

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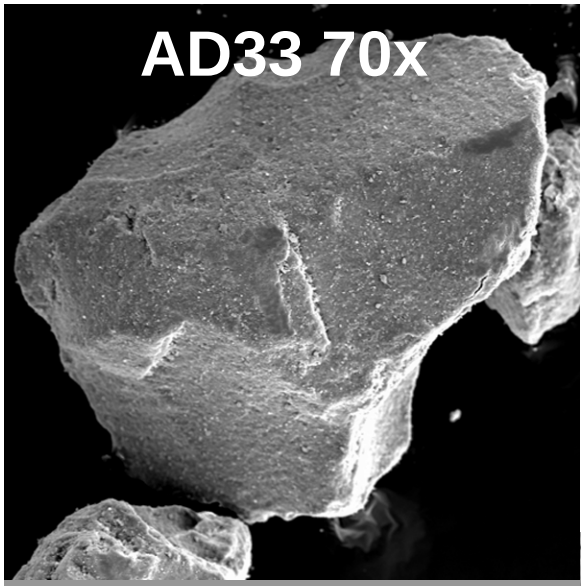
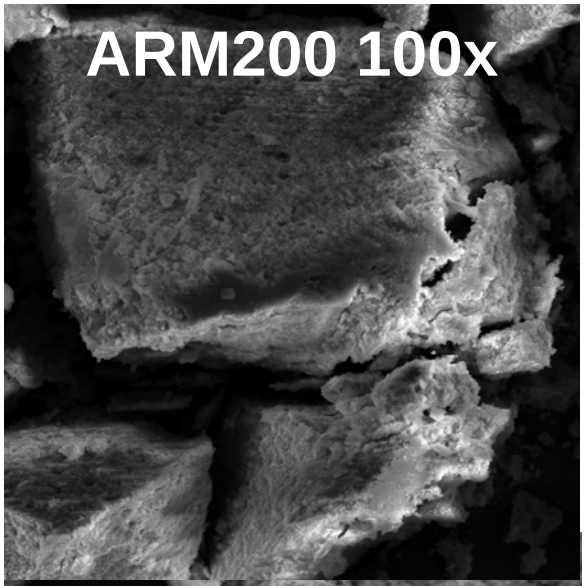
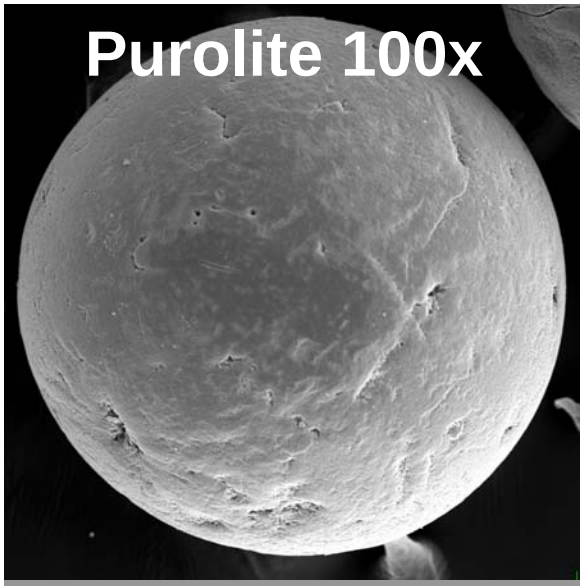
Chemical Compositions of Media

Media	Constituents (XRD)	Dominant Elements (EDS)
Isolux 302M	Amorphous zirconium oxide/hydroxide	Zr, O
Metsorb	Crystalline TiO_2 (*Anatase*)	Ti, O
ARM200	Amorphous Iron oxide/hydroxide (or very poorly crystalline *Hematite*)	Fe, O
ArsenX^{np}	Amorphous iron oxide/hydroxide Resin impregnatation	Fe, O, C
E33 (AD33)	Iron oxide/hydroxide (*Goethite*)	Fe, O

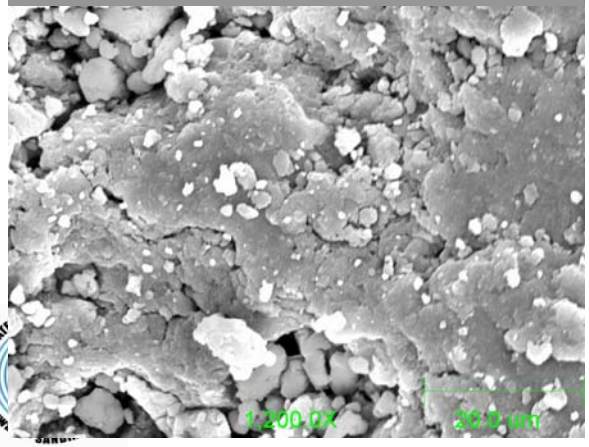
SEM Photos of Adsorptive Media



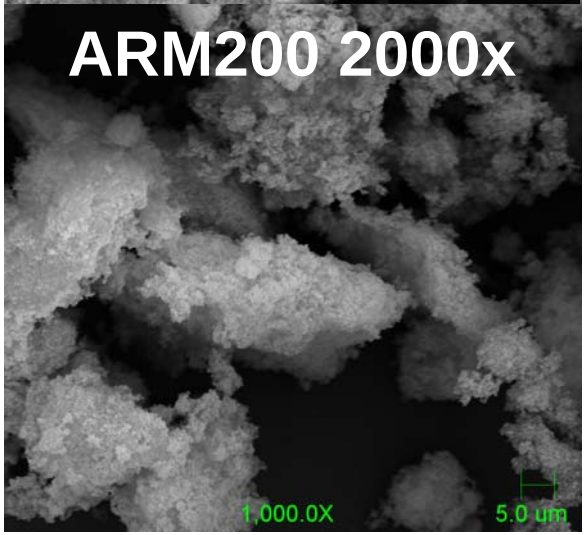




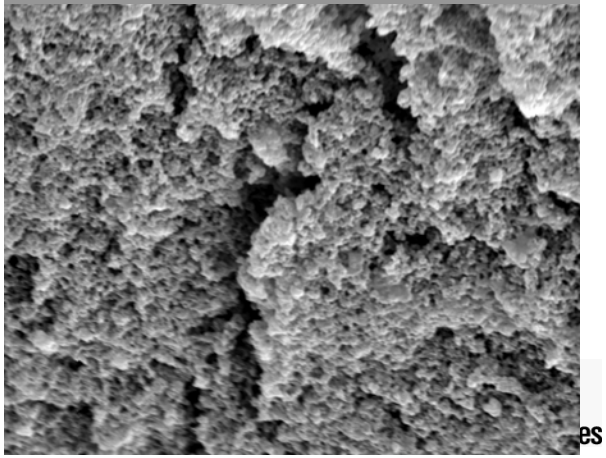
AD33 1200x



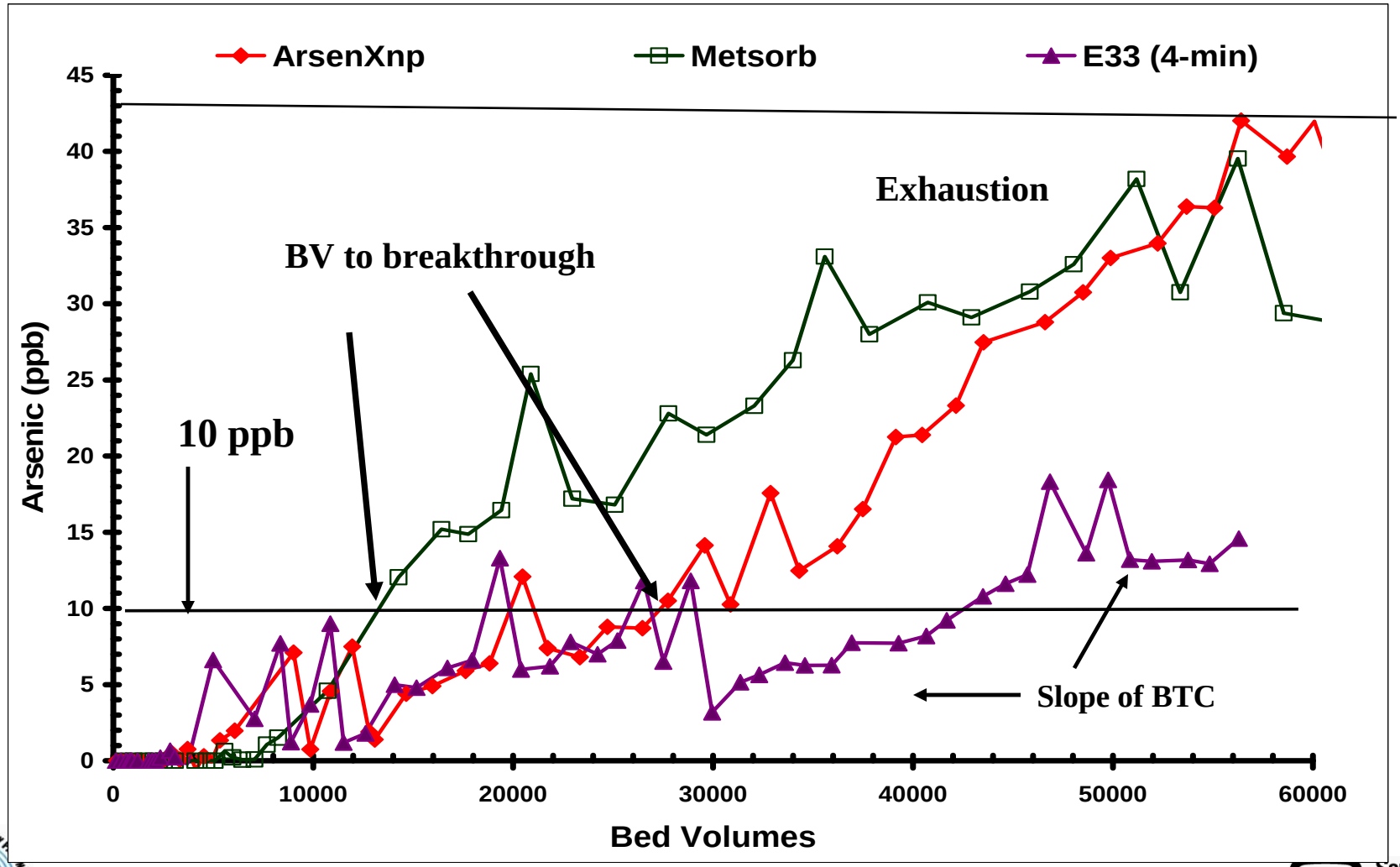
ARM200 2000x



Purolite 1200x



Comparison of Media Performance



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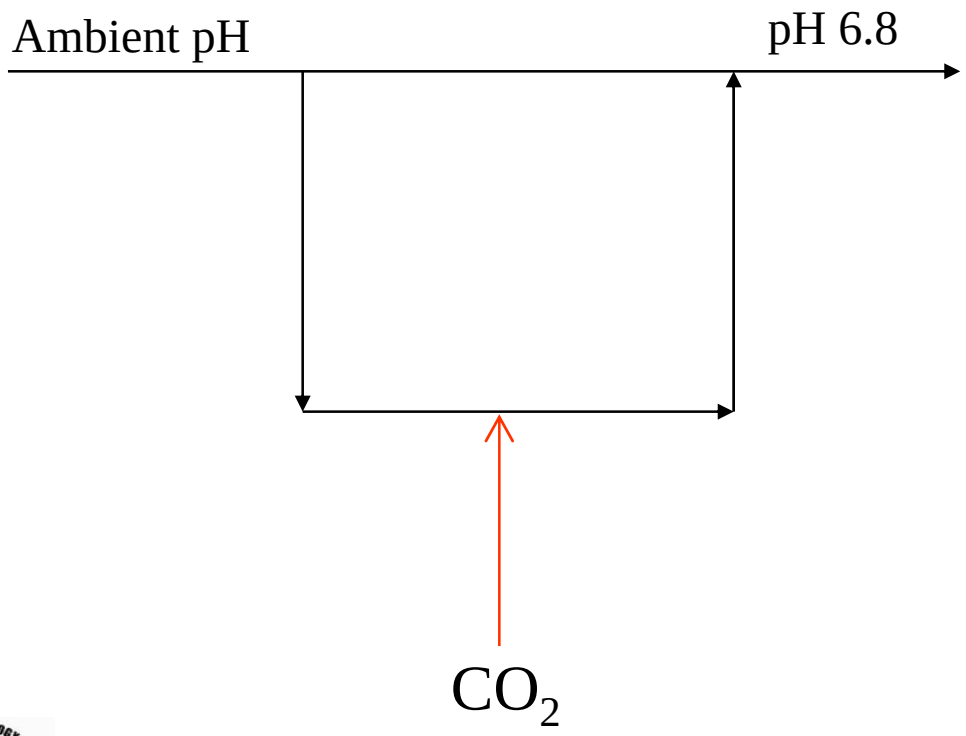
Media Performance in Socorro, NM

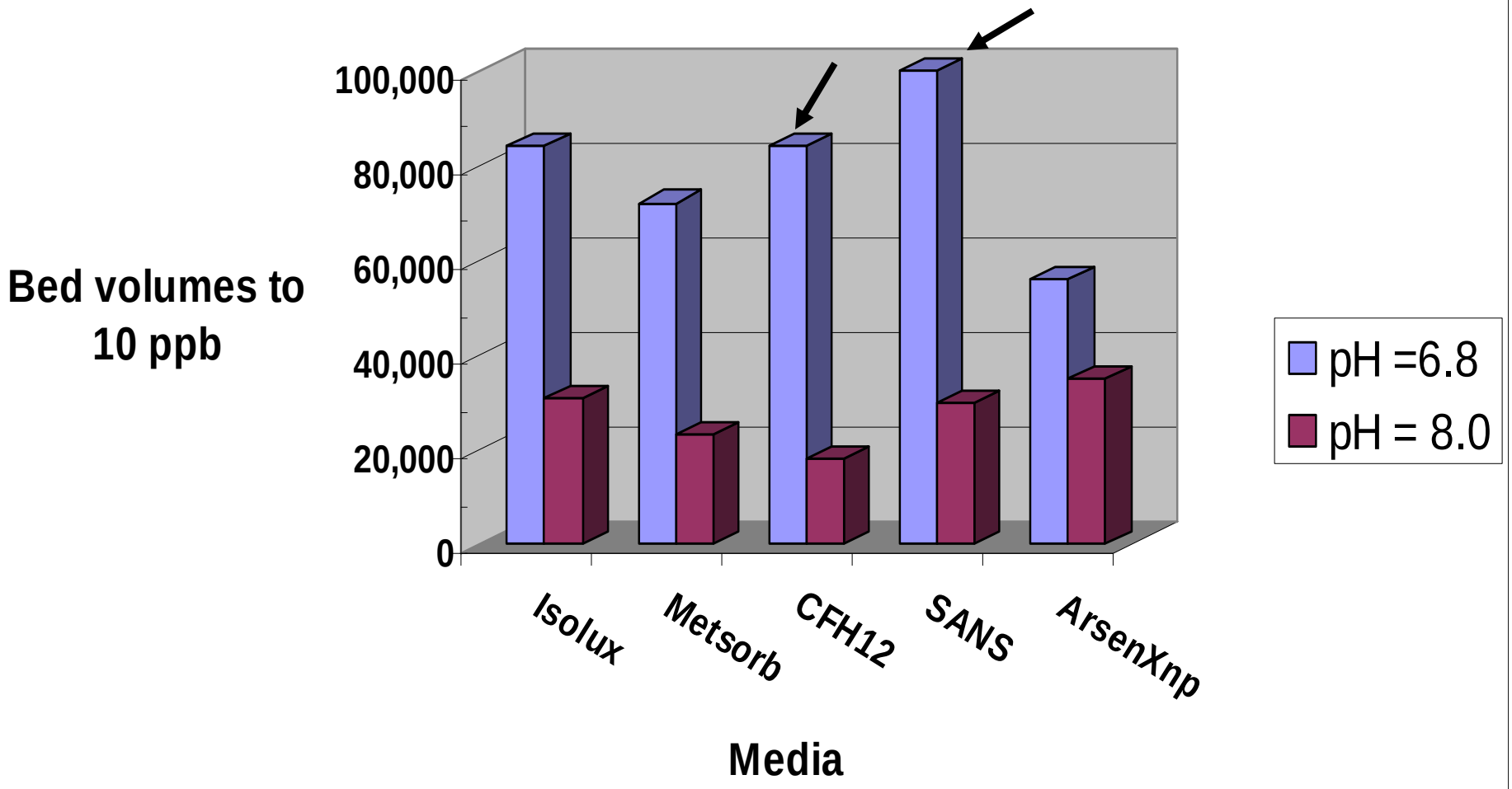
Ambient pH vs. pH 6.8

Phase 2b:

- **pH Adjustment using CO_2 gas**



Media Performance in Socorro, NM
Phase 2 (pH = 6.8 vs. 8)



Rapid Testing Methods

Full scale treatment

12-24 months

Reduce time and costs required to determine the most effective adsorptive treatment technology for small rural systems.

Pilot scale

6-12 months

RSSCT & isotherm

Days-weeks

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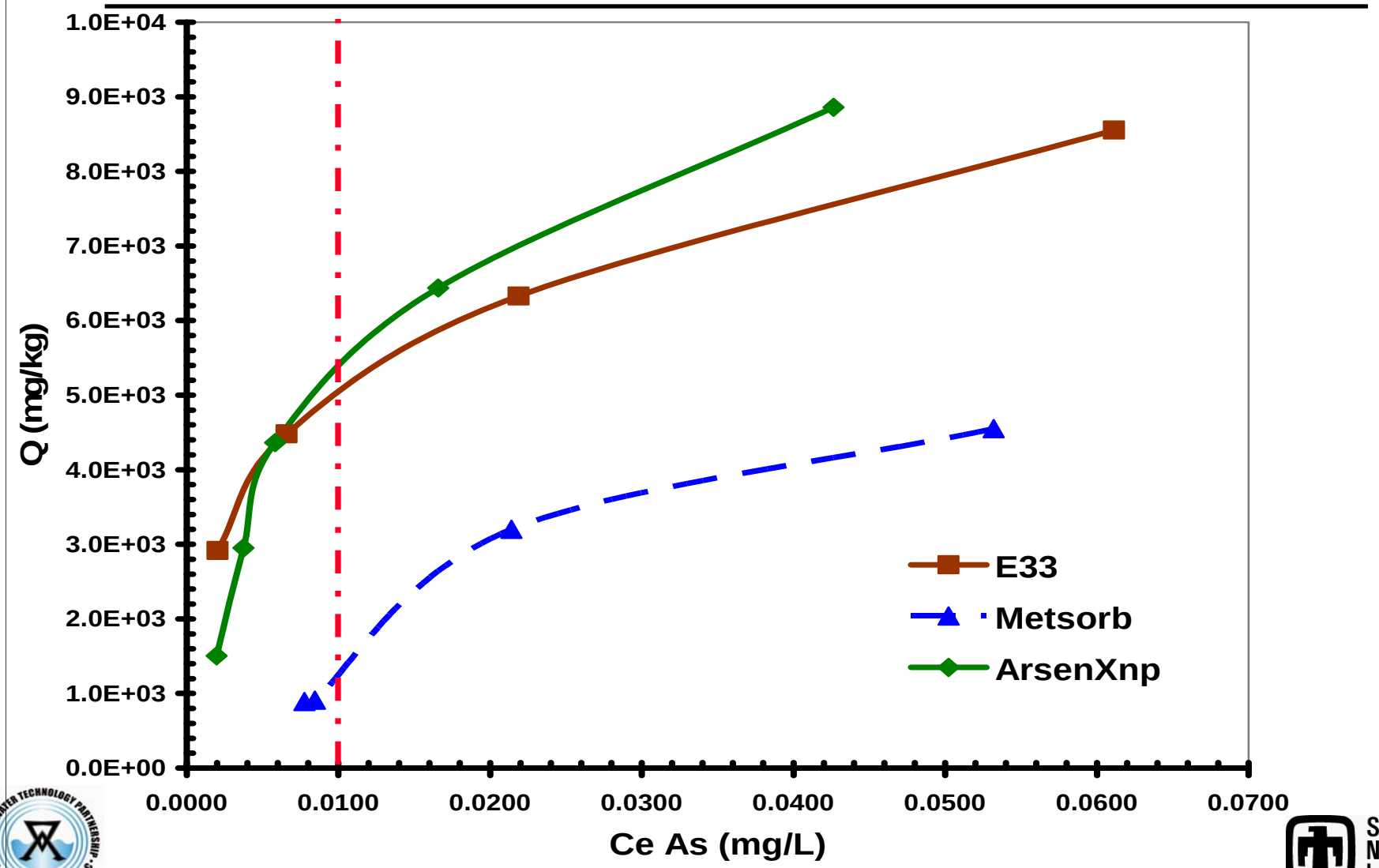
Predicting Media Performance

- **Materials characterization**
  - **Pre-test and post studies, temperature-ageing studies**
  - **XRD, Surface area (BET), pore size distribution**
  - **Particle morphology and surface chemistry**
  - **Attrition loss**
  - **Post-mortem pore fluids and solids**
- **Batch sorption studies**
  - **Kinetic (15^{o}C and 40^{o}C)**
  - **Isotherms (linear, Freundlich, Langmuir)**
- **Rapid small scale column tests (RSSCTS)**
- **Develop simple model that could predict media performance from Lab tests**

Batch Isotherm Results (Socorro, NM)



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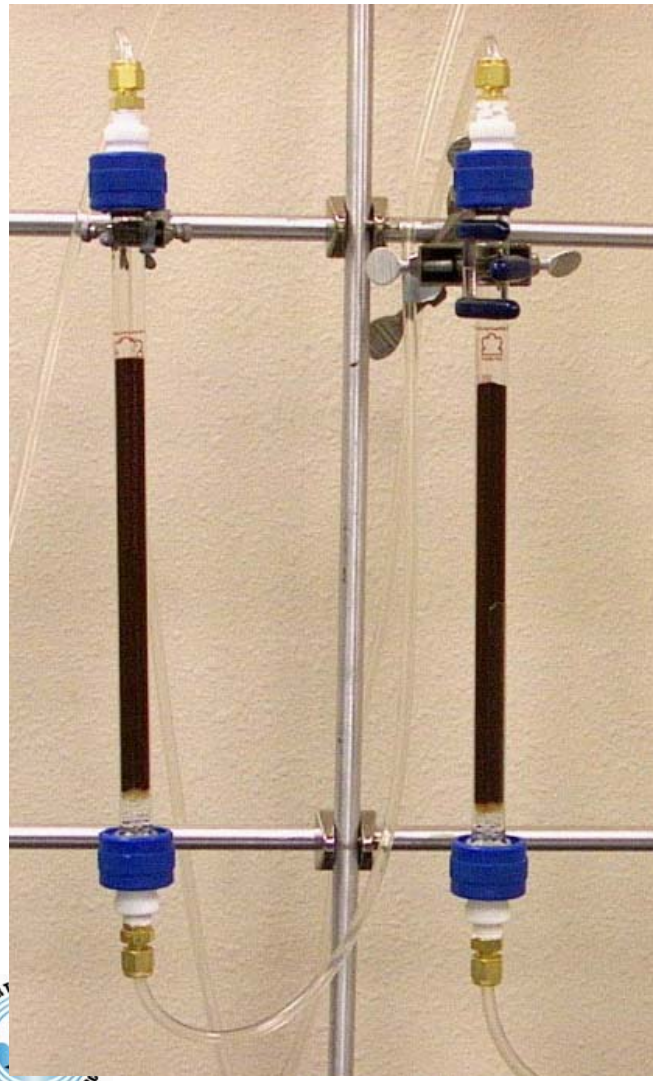
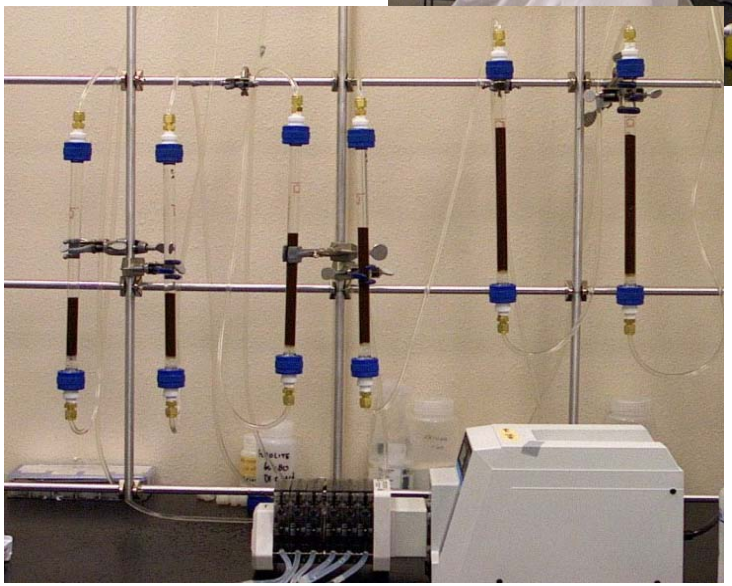
RSSCT Design and Practice

- Crush media to much smaller sizes; Reduce column diameter
    - Smaller media, faster kinetics
- Apply a higher hydraulic loading rate
    - Smaller boundary layer, faster kinetics
    - Reduces external mass transfer resistance
- Shorter EBCT (Empty Bed Contact Time)
- Dimensional analysis and similitude
    - Attention to dimensionless parameters
- Two RSSCT designs:
    - Proportional Diffusivity: duration 2-5 weeks
    - Constant Diffusivity: duration 2-10 days

Socorro PD RSSCTs





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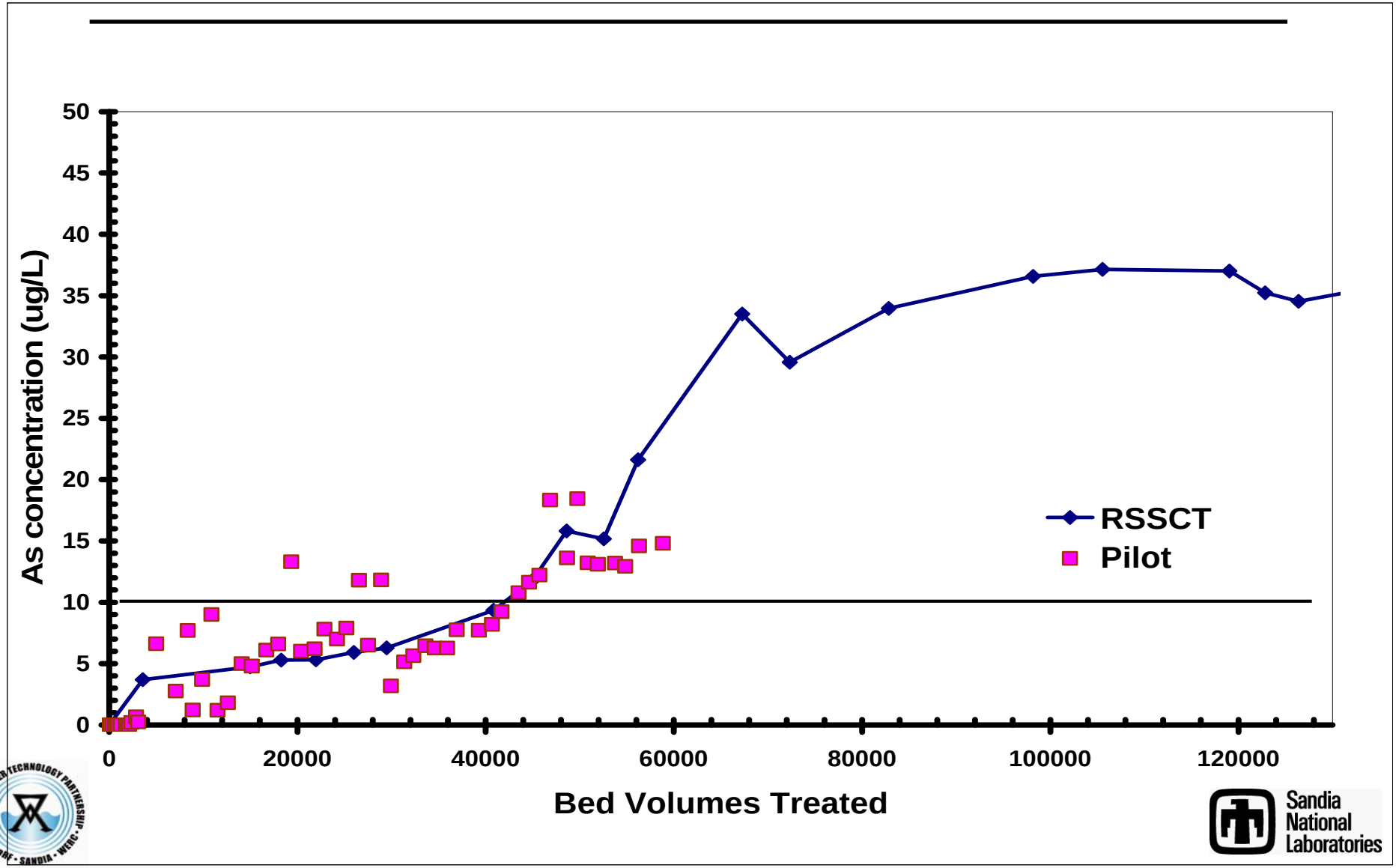
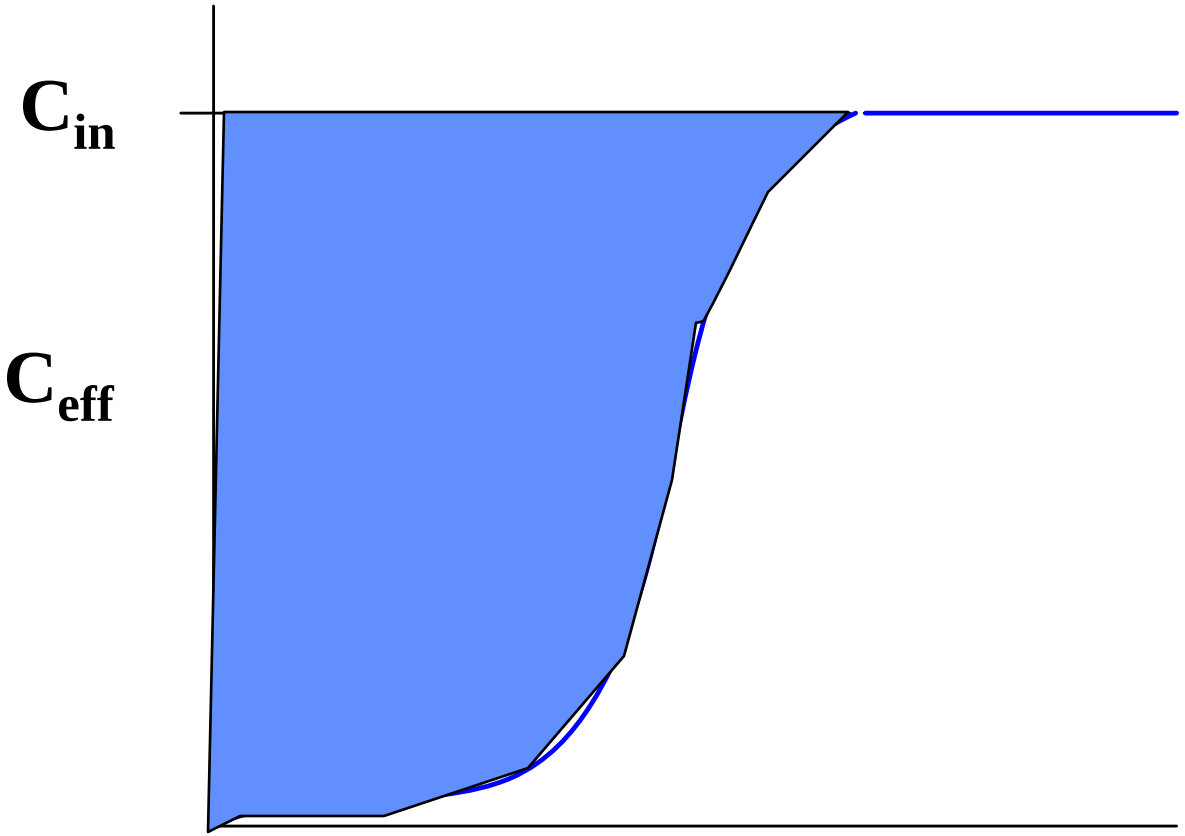
Socorro I Pilot and RSSCT Breakthrough Curves for E33 (4 min. EBCT)



Calculation of Column Arsenic Loading Capacity



Agreement Among Estimates of Arsenic Sorption Capacity from Different Tests

	E33	ARM200	Metsorb
BV to 10ppb (pilot)	43,000	8,600	13,000
As at 10ppb (pilot)	3.56 mg/g	0.6 mg/g	0.7 mg/g
BV to 10ppb (RSSCT)	43,000 (PD)	6000 (CD)	12,800 (PD)
As at 10 ppb (RSSCT)	3.39 mg/g (PD)	0.42 mg/g (CD)	0.69 mg/g (PD)
As at 10 ppb (Freundlich)	5.0 mg/g	3.6 mg/g	1.2 mg/g

BV = bed volumes, PD = proportional diffusivity, CD = constant diffusivity

As = capacity calculated from loading or batch test

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Ongoing Research

- Can a comprehensive lab-based study of media properties replace the need to carry out site-specific field tests for predictions of media performance?
  - Relate pore structure to performance?
  - Effect of major ions on performance?
  - Effect of hydraulic properties on performance?
    - Backwashing may create fines and decrease BVs
- Comparison to full-scale treatment plant results?

Helping Communities

- **Information gathered at Vendors Forum and Pilots available on Sandia Pilot project website:**
  - **http://www.sandia.gov/water/arsenic.htm**
- **WERC developed Comprehensive Arsenic Tool (CoAsT)**
  - **available at: http://www.arsenicpartners.org**
    - **Summaries of BATs**
    - **Several cost models**
    - **Decision tree**
- **Sandia Rural Outreach Program and New Mexico Small Business Assistance Program**
  - **Outreach to individual communities in New Mexico**

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Summary: Managing the public health threat of arsenic

- Strong evidence exists that exposure to high levels (> 100 ppb) is associated with significant health effects but association at lower levels (10-50 ppb) is less clear.
- The new MCL for arsenic in US stretches limits of state-of the art in different aspects of water quality policy.
  - Occurrence, toxicity, cost
  - Unintended consequences of new MCL
- Work at Sandia National Laboratories aims to reduce cost.
  - Objective pilot tests of new adsorptive media
  - Development of rapid testing techniques
  - Understand basic principles of treatment processes
- Important work remains in helping communities deal with the new Arsenic Standard.
  - Optimum solution may not be obtainable due to regulatory and scientific constraints.

AWTP Team Members

Sandia National Laboratories:

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Thank you for your attention

Questions?

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For More Information:

Arsenic Partnership Website

http://www.arsenicpartners.org/

Sandia Website

http://www.sandia.gov/water/arsenic

→ **Papers, Presentations, Vendor Information, Pilot Results**

WERC CoAsT Website

http://www.werc.net

→ **Click on Outreach tab, then CoAsT**

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