Workshop on the Design and Operation of Adsorptive Media Processes for the Removal of Arsenic from Drinking Water

August 10-11, 2004
Westin Cincinnati Hotel
Cincinnati, OH

Sponsored by
Water Supply and Water Resources Division
National Risk Management Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency

TUESDAY, AUGUST 10, 2004

7:30 am	**Registration**
8:30 am	**Welcome and Introduction** Sally Gutierrez and Tom Sorg, USEPA, Office of Research and Development, National Risk Management Research Laboratory, Water Supply and Water Resources Division
Session I	**Adsorption Fundamentals / Bench Scale Testings**
9:00 am	**Fundamentals of Arsenic Adsorption: An Overview** Dr. Dennis Clifford, University of Houston
9:30 am	**Isotherm Testing: Procedures and Application of Results** Dr. Gary Amy, University of Colorado Boulder
10:00 am	**RSSCTs for Arsenic Testing: Procedures and Applications** Dr. Paul Westerhoff, Arizona State University
10:30 am	**Break**
Session II	**Process Design — Media Performance**
11:00 am	**Adsorption Media for Arsenic Removal** Darren Lytle, USEPA
11:30 am	**Arsenic Occurrence and Co-Occurrence, Implications for Adsorptive Media Treatment** Dr. Philip Brandhuber, HRD Inc.
12:00 pm	**Lunch**
1:30 pm	**Media Performance: Laboratory Studies** Dr. Gary Amy, University of Colorado Boulder
2:00 pm	**Media Performance: Laboratory and Pilot Studies** Dr. Xiaoguang Meng, Center for Environmental Systems, Stevens Institute of Technology
2:30 pm	**Media Performance: City of Mesa, AZ Experience** Michelle De Haan, Damon S. Williams Associates (Presented by Dr. Paul Westerhoff, Arizona State University)
3:00 pm	**Break**
3:30 pm	**Pilot-Scale Evaluation of Adsorptive Media for Arsenic Removal** Dr. Abraham Chen, Battelle
4:15 pm	**Open Discussion**
5:00 pm – 6:30 pm	**Hospitality Hour** Sponsored by Water Quality Association

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Session III — **System Design and Operation**

8:00 am — **Critical Design Considerations**
Eric Winchester, ADI International Inc.

8:45 am — **Tank/Bed Configurations: Series, Parallel, Redundancy**

Small System Configuration Options
Bernard Lucey, New Hampshire Department of Environmental Services

Arsenic Treatment Systems: Design and Operation, Michigan's Approach
Patrick Cook, Michigan Department of Environmental Quality

9:30 am — **Break**

10:00 am — **Pre-Treatment Considerations**
Gregory Gilles, AdEdge Technologies, Inc.

10:30 am — **Arsenic Media Handling**
Richard Dennis, Severn Trent Services, Inc.

11:00 am — **Monitoring and Operation of Adsorptive Media Systems for Arsenic Removal**
Glen Latimer, Jr., Kinetico Incorporated

11:30 am — **Lunch**

Session IV — **System Evaluation, Costs and Residuals**

1:00 pm — **Round 1 Arsenic Removal Technology Demonstration: Evaluation Approach**
Chris Coonfare, Battelle

1:30 pm — **Treatment Costs: Capital and Operational**
Lili Wang, Battelle

2:00 pm — **Residuals: Quantities, Characteristics and Disposal Options**
Tom Sorg, USEPA, Office of Research and Development

2:30 pm — **Adjourn**

SPEAKER BIOGRAPHIES

Workshop on the Design and Operation of Adsorptive Media Processes for the Removal of Arsenic from Drinking Water

SPEAKER BIOGRAPHIES

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Dr. Gary Amy
Professor of Environmental Engineering
Department of Civil, Environmental and Architectural Engineering
University of Colorado Boulder
Campus Box 428
Boulder, CO 80309
Phone: 303-492-6274
Email: gamy@spot.colorado.edu

Dr. Gary Amy is a Professor of Environmental Engineering at the University of Colorado at Boulder. He has a Ph.D. in Civil/Environmental Engineering from the University of California at Berkeley.

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Dr. Philip J. Brandhuber
Project Manager
HRD Inc.
303 East 17th Avenue, Suite 700
Denver, CO 80203
Phone: 303-764-1527
Email: philip.brandhuber@hdrinc.com

Dr. Philip Brandhuber is an expert in the removal of inorganic contaminants from drinking water. He has more than 22 years of experience in engineering, including 10 in water quality and drinking water treatment.

His work has focused on the treatment of inorganic contaminants using advanced treatment technologies including membrane filtration, ion exchange and adsorptive treatment. He was the Principal Investigator for the recently completed American Water Works Association Research Foundation's (AwwaRF) *Research Partnership for Hexavalent Chromium Removal* and Co-Principal Investigator for the AwwaRF project *Impacts of Water Quality on the Performance of Adsorptive Arsenic Treatment Media*. He was a member of the EPA panel responsible for selecting arsenic treatments for small systems and advised EPA on the impacts of the recently promulgated Arsenic Rule. He was Lead Engineer for the City of Alamosa's Arsenic Treatment Recommendation Project. Currently he is heading an American Water Works Association (AWWA) sponsored study mapping national perchlorate occurrence. Dr. Brandhuber is a member of the American Society of Civil Engineers (ASCE) and the AWWA, where he serves on the Inorganic Contaminant and Membrane Research Committees.

Dr. Brandhuber has a B.S. in Mechanical Engineering from the University of Dayton, a M.S. in Management from Boston University, and a M.S. and Ph.D. in Civil Engineering from the University of Colorado at Boulder.

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SPEAKER BIOGRAPHIES

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Dr. Abraham Chen
Deputy Department Manager
Battelle
505 King Avenue
Columbus, OH 43201-2693
Phone: 614-424-5641
Email: chena@battelle.org

Dr. Abraham (Abe) Chen is a researcher and the Deputy Department Manger of the Environmental Restoration Department at Battelle in Columbus, Ohio. He has a Ph.D. degree in Environmental Science in Civil Engineering from the University of Illinois at Urban-Champaign. Since 1997, Abe and his staff at Battelle have provided arsenic research support to U.S. EPA, including the Arsenic Removal Technology Demonstration Program under EPA's Arsenic Rule Implementation Research Program. This paper reports the results of several pilot-scale studies, evaluating the performance of several commercially available adsorptive media for arsenic removal.

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Dr. Dennis Clifford
Professor of Environmental Engineering
Cullen College of Eng.
University of Houston
Engineering Bldg. 1, Room N127
Houston, TX 77204-4003
Phone: 713-743-4266
Email: daclifford@uh.edu

Dr. Dennis Clifford is Professor of Environmental Engineering in the Department of Civil and Environmental Engineering at the University of Houston where he conducts research and teaches courses in Water Chemistry and Physical-Chemical Treatment Processes. He is a Professional Engineer with more than thirty years experience in water treatment with special emphasis on the removal of inorganic and radioactive contaminants from drinking water. He has researched the subject of arsenic removal from water for more than 20 years. Professor Clifford's doctoral degree in Environmental Engineering was earned at the University of Michigan on the subject of multicomponent ion exchange for drinking water treatment. His bachelor and master's degrees in Chemical Engineering were earned at Michigan Technological University and the University of Michigan. The title of his presentation today is "Fundamentals of Adsorption for Arsenic Removal from Water."

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SPEAKER BIOGRAPHIES

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Patrick L. Cook
Water Treatment Specialist
Michigan DEQ
P.O. Box 30630
Lansing, MI 48909-8130
Phone: 517-241-1242
Email: cookp@michigan.gov

Pat Cook is the Water Treatment Specialist for the Michigan Department of Environmental Quality, Drinking Water Division. Pat has a Bachelor of Science degree in civil engineering from Michigan State University and is a registered professional engineer in the State of Michigan.

Pat has been employed by the Michigan DEQ for 16 years, the last 2 as a treatment specialist. He has been involved in many projects relating to arsenic removal, including design, treatment selection and operation.

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Chris Coonfare
Principal Research Scientist
Battelle
3990 Old Town Ave., Suite B-104
San Diego, CA 92110
Phone: 619-574-4822
Email: coonfare@battelle.org

Mr. Chris Coonfare is a Principal Research Scientist at Battelle Memorial Institute. With Battelle since 1995, Mr. Coonfare currently serves as the Study Lead for three of the twelve sites under Round 1 of the EPA Arsenic Removal Demonstration Program. His responsibilities as a Study Lead include the oversight and management of site demonstration activities, conducting operator training on data and sample collection, reviewing operational and analytical data, and preparing Study Plans and reports. He has been designated as a Regional Team Leader under the recently awarded second round of the Program, and will be responsible for coordinating the demonstration activities at sites throughout the western United States. Mr. Coonfare holds a B.A. in Geology from Wittenberg University in Springfield, Ohio, and is a Registered Geologist in the State of California.

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SPEAKER BIOGRAPHIES

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Michelle De Haan
Senior Scientist/Associate
Damon S. Williams Associates
2533 E. Camelback Road, Suite 700
Phoenix, AZ 85016
Phone: 602-217-1022
Email: mdehaan@dswa.net

Michelle De Haan is a Senior Scientist and Associate at the Damon S. Williams Associates Phoenix, AZ office where she manages several projects related to drinking water regulatory compliance and gaining compliance with the Arsenic Rule. She has a B.S. in Chemistry from the University of South Carolina and managed the City of Scottsdale drinking water program for 9-years prior to joining DSWA. She has participated in three recent EPA Arsenic Panels, which screened new Arsenic technologies for further research funding and for installation of Arsenic demonstration systems for small water systems. She is the project manager for several Arsenic projects in Arizona including projects for cities of Chandler, Mesa, and Peoria and Deer Valley Unified School District.

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Richard S. Dennis
Separation Products Manager
Severn Trent Services, Inc.
5415 W. Sligh Ave., Suite 102
Tampa, FL 33634
Phone: 813-886-9331
Email: rdennis@severntrentservices.com

Mr. Rich Dennis received his bachelor's degree in Chemical Engineering from Lehigh University in 1973. After starting his career with DuPont, he worked on several chemical separation projects for IMC at their Mulberry, Florida phosphate complex. These included water demineralization, phosphoric acid defluorination and purification, and uranium extraction.

In 1986, AST (now Calgon Carbon) hired him to direct new process development programs employing the ISEP®, a continuous ion exchange contactor. Rich was employed by TETRA Technologies in 1992 to direct their Higgins Loop™ continuous ion exchange system business. Since then, the Higgins Loop™ has been commercialized in a variety of applications ranging from chemicals production to drinking water nitrate removal. It is now being used for the purification of produced waters generated in the coal bed methane industry of Wyoming.

With Severn Trent Services acquisition of TETRA, Rich is now the Product Manager for separation technologies that include the Higgins Loop™ and SORB 33™ arsenic adsorption. Since May 2000 he has directed the domestic STS Arsenic Removal program utilizing technology originally developed by Severn Trent Water in the U.K. He managed the first pilot test at Rio Rancho, NM and has initiated over 20 other arsenic test programs in the U.S. He has been a leader in optimizing the SORB 33™ technology for As Removal and designing economical treatment systems of all sizes.

Rich is a member of the AWWA, AIChE & SME organizations.

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SPEAKER BIOGRAPHIES

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Gregory C. Gilles
Vice President
AdEdge Technologies, Inc.
3560 Financial Center Way, Suite 5
Buford, GA 30519
Phone: 678-835-0052
Email: greg@adedgetechnologies.com

Greg Gilles is currently Vice President and Principal of AdEdge Technologies in Atlanta, Georgia. AdEdge develops, markets, and sells adsorbent-based water treatment systems and products for drinking water, environmental, and commercial / industrial applications. With 20 years of engineering and applied technology expertise, Mr. Gilles leads AdEdge's municipal and commercial water treatment products group providing new business development, designing new technology applications, conducting training, and providing field and startup services in support of its packaged treatment systems.

Mr. Gilles has a MS in Environmental Science and a BA in Biology / Chemistry from Indiana University. He has worked in the field of arsenic and heavy metals treatment technology for over 15 years and has designed and implemented multiple successful systems. He has authored numerous technical publications and articles on the subject and is a frequent conference and seminar speaker around the U.S. His practical experience in arsenic treatment includes the entire range from laboratory and field pilots to full-scale evaluations for a variety of technologies and products. In 2001, Mr. Gilles received one of the prestigious R&D 100 Awards honoring the top 100 inventions of the year for the arsenic treatment unit (ATU) designed for treating potable water in small rural communities in third world countries. Mr. Gilles participated as an *ad hoc* contributor to EPA's National Drinking Water Advisory Council's Cost Work Group on the arsenic rule. He has also served on various committees with NSF International, the Water Quality Association, and American Water Works. He holds one U.S. process technology patent and one pending for the design of an arsenic treatment system for community drinking water used in India and Bangladesh.

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SPEAKER BIOGRAPHIES

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Sally Gutierrez
Director, WSWRD
USEPA/ORD
26 W. Martin Luther King Drive
Cincinnati, OH 45268
Phone: 513-569-7683
Email: gutierrez.sally@epa.gov

Sally Gutierrez was appointed as Director of the Water Supply and Water Resources Division within the National Risk Management Research Laboratory in Cincinnati, Ohio, in February 2000. She is responsible for leading a research program for treatment and control of microbes and chemicals in drinking water to support the promulgation and implementation of drinking water standards. Her staff consists of engineers, chemists, microbiologists and ecologists located in Cincinnati and Edison, New Jersey. She is EPA's lead on the treatability research program for arsenic in drinking water. She is also responsible for implementing a research program to support implementation of measures to control contaminants in impaired water bodies across the nation. Prior to coming to EPA, Sally worked for the State of Texas as the Director of the Water Quality Division of the Texas Natural Resource Conservation Commission. She holds a Master of Science degree from the University of Texas School of Public Health.

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Glen Latimer, Jr.
Manager Municipal Water Systems
Kinetico Incorporated
10845 Kinsman Road, P.O. Box 193
Newbury, OH 44065 USA
Phone: 440-564-5397
Email: glatimer@kinetico.com

Glen Latimer manages the Community Water Systems at Kinetico Incorporated. Glen holds a bachelor's degree in mechanical engineering from Youngstown State Universirty and is a member of both the Water Quality Association and American Water Works Association.

He is directly involved with the development of treatment systems that provide potable water for enitre municipalities and has designed and managed projects in a number of states.

Glen, with his knowledge of various water treatment methods, has contributed to numerous articles that have been published in industry publications such as the AWWA Journal. He currently holds two United States patents to Kinetico Incorporated. He also has another patent pending. Glen has been involved in the water treatment industry with Kinetico for 20 years.

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SPEAKER BIOGRAPHIES

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Bernard Lucey, P.E.
Senior Engineer
New Hampshire Department of Environmental Services
P.O. Box 95, 29 Hazen Drive
Concord, NH 03301
Phone: 603-271-2952
Email: blucey@des.state.nh.us

Mr. Lucey has a B.S. in Civil Engineering and a M.S. in Sanitary Engineering from Northeastern University, Boston. Mr. Lucey is a registered professional engineer in the state of NH and member of the New Hampshire, New England and American Water Works Associations.

Mr. Lucey has worked for Boston areas consultant engineers and, since 1973, for the NH Department of Environmental Services. He has also been a member of the adjunct faculty at the University of Massachusetts at Lowell from 1980-2002 teaching courses related to water distribution and treatment.

Mr. Lucey is the NH lead for arsenic and was a member of the EPA peer review committee for the EPA Design Manuals: Removal of Arsenic from Drinking Water by Adsorptive Media and Ion Exchange.

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Darren Lytle
Environmental Engineer
USEPA
26 W. Martin Luther King Dr.
Cincinnati, OH 45268
Phone: 513-569-7432
Email: lytle.darren@epa.gov

Darren Lytle received his B.S. in Civil Engineering from the University of Akron in 1990. In 1991 he received a M.S. in Environmental Engineering from the University of Cincinnati, and he is in the process of completing a Ph.D. from the University of Illinois in Environmental Engineering.

Darren was hired on by the U.S. Environmental Protection Agency in 1991 as an environmental engineer with the drinking water research group. Over the years he has conducted drinking water research in the areas of lead and copper corrosion control, filtration, iron control and most recently arsenic removal.

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SPEAKER BIOGRAPHIES

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Xiaoguang Meng, Ph.D., PE
Associate Professor
Center for Environmental Systems
Stevens Institute of Technology
Castle Point on Hudson
Hoboken, NJ 07030
Phone: 201-216-8014
Email: xmeng@stevens-tech.edu

Dr. Xiaoguang (spells Shiaoguang) Meng is an associate professor at the Center for Environmental Systems, Stevens Institute of Technology in Hoboken, New Jersey. He has a B.S. degree in Chemistry, a M.S. degree in Marine Chemistry and a Ph.D. in Environmental Engineering. His research is focused on adsorption of arsenic and heavy metals by ides and physicochemical treament of inorganic pollutants in water.

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Tom Sorg
Engineer
USEPA
26 W. Martin Luther King Dr.
Cincinnati, OH 45268
Phone: 513-569-7370
Email: sorg.thomas@epa.gov

Tom Sorg is a Research Engineer for the Water Supply and Water Resources Division, Office of Research and Development, USEPA, Cincinnati, OH. He has a B.S. and M.S. in Civil/ Environmental Engineering from the University of Notre Dame. He is a registered PE in the State of Ohio.

Tom has 40 years of experience with environmental programs of the Federal Government; the last 31 years with the drinking water research and development program of USEPA. For 25 years, Tom has been Chief of the Inorganics and Particular Control Branch of the Drinking Water Research Division. His special emphasis of research work has been on drinking water treatment technology for the removal of inorganic and radionuclide contaminants from water supplies, including the removal of arsenic. During the past 5 years, his research has focused on treatment technology to remove arsenic from drinking water in support of the revised arsenic MCL of 10 ug/L. This effort has included the responsibility of the Arsenic Removal Full Scale Demonstration Program. Tom has authored over 60 publications on drinking water treatment. He is a member of AWWA and AAEE.

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SPEAKER BIOGRAPHIES

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Lili Wang
Principal Research Scientist
Battelle
505 King Ave.
Columbus, OH 43201
Phone: 614-424-7407
Email: wangl@battelle.org

Ms. Lili Wang is a registered professional engineer and a Principal Research Scientist with Battelle. Lili has a B.S. degree in Environmental Engineering from Tsinghua University and an M.S. degree in Environmental Sciences from the Ohio State University. Since 1997, Lili has played a leading role in providing arsenic research support to U.S. EPA. Lili currently serves as the Deputy Program Manger for the Arsenic Removal Technology Demonstration Program. The presentation involves a show-and-tell of a cost-estimating program developed for small adsorptive media and IX systems.

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Dr. Paul Westerhoff
Associate Professor
Department of Civil and Environmental Engineering
Arizona State University
Engineering Center, G-Wing, Room ECG 252
Tempe, AZ 85287-5306
Phone: 480-965-2885
Email: p.westerhoff@asu.edu

Paul Westerhoff has been in Department of Civil and Environmental Engineering at Arizona State University since 1995, and is currently an associate professor. He obtained a Ph.D. from the University of Colorado at Boulder, a MS from University of Massachusetts and BS from Lehigh University. His teaching and research interests are related to water quality, water treatment, and water distribution. He belongs to AWWA, IOA, ACS, ASEEP, and AWPCA. He serves on the water reuse, particulate, taste and odor, and university student affairs AWWA committees. He was awarded the 1999 JAWWA Best Paper Award. His current research includes investigating NOM characteristics, oxo-anion reactions/removal, oxidant reactions, assessing/controlling/treating sources of tastes and odors, and wastewater reuse.

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SPEAKER BIOGRAPHIES

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Eric L. Winchester
Vice President
ADI International Inc.
1133 Regent Street, Suite 300
Fredericton, NB Canada E3B 3Z2
Phone: 506-451-7407
Email: elw@adi.ca

Mr. Eric Winchester is Vice President of ADI International Inc. and heads up the development and marketing of the Company's arsenic removal technology. Mr. Winchester is a registered professional engineer, with a Civil engineering degree from the University of New Brunswick, Canada, and has over 30 years experience in water supply and treatment. He lead the development of MEDIA G2®, a patented and regenerable iron-based adsorption filter media, from its initial research in 1995. Since 1995, Mr. Winchester was involved in obtaining certification of MEDIA G2® under NSF Standard 61, was awarded patents in Canada, United States and other countries, and oversaw the design, supply and installation of over 15 full-scale arsenic removal systems.

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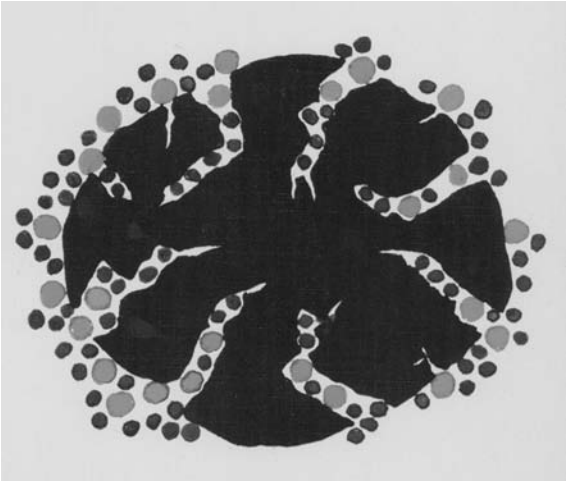
SESSION I

Adsorption Fundamentals / Bench Scale Testings

Fundamentals of Adsorption for Arsenic Removal from Water

Dennis Clifford
University of Houston

Adsorption is taking stuff (arsenic) out of water and putting it onto a solid adsorbent with micro and macro pores.



Application of Adsorption to Wastewater Treatment
W. W. Eckekfelder, Jr., Ed., 1981

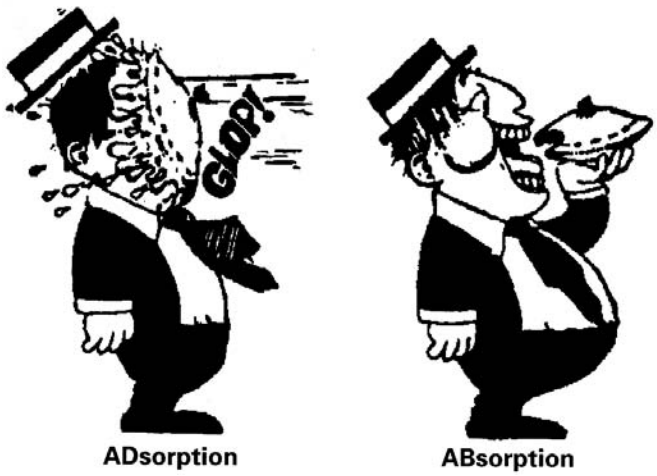
More Specifically

- ***Ad*sorption** is contaminant removal from water by attachment onto the surface of a porous solid adsorbent (GAC, AAl, GFH/GFO).
  - Physical Adsorption, low energy, reversible
  - Chemical Adsorption, high energy, irreversible
- ***Ab*sorption** is contaminant removal by dissolution/reaction in another phase

  Removal of CO_2 by bubbling through NaOH soln.

  CO_2 (g) + NaOH(aq) → $NaHCO_3$(aq)
- ***Sorption*** covers all mechanisms and is the removal of a "sorbate" (contaminant) by a "sorbent" (adsorbent).

Here is the difference between Adsorption and Absorption



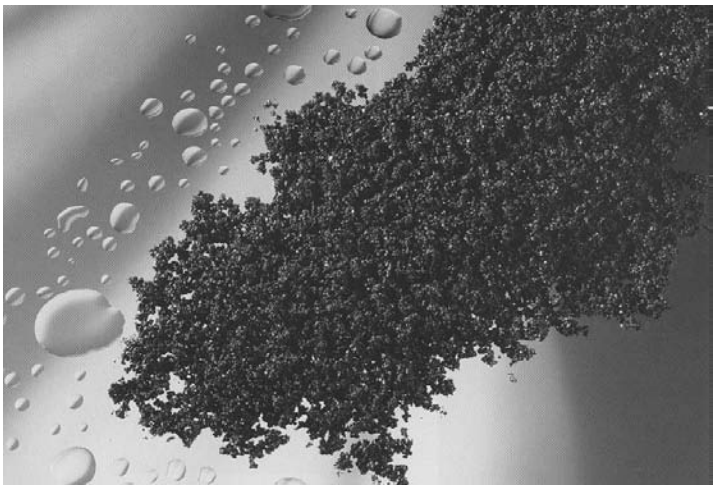
"Sorption": A General Term Covering Many Processes

- Physical Adsorption; <20 kJ/mol
  - GAC + N_2 = GAC •N_2, Reversible
- Chemical Adsorption; up to 800 kJ/mol
  - $\underline{=}C + O_2 \rightarrow \underline{=}CO$; Irreversible
- Surface Complexation (Ligand Exchange)
  - $FeOOH + HAsO_4^- \rightarrow FeO{\bullet}HAsO_4 + OH^-$
- Ion Exchange (Softening with IX Resin)
  - $2RNa + Ca^{2+} = R_2Ca + 2\ Na^+$; < 8kJ/mol
- Surface Precipitation

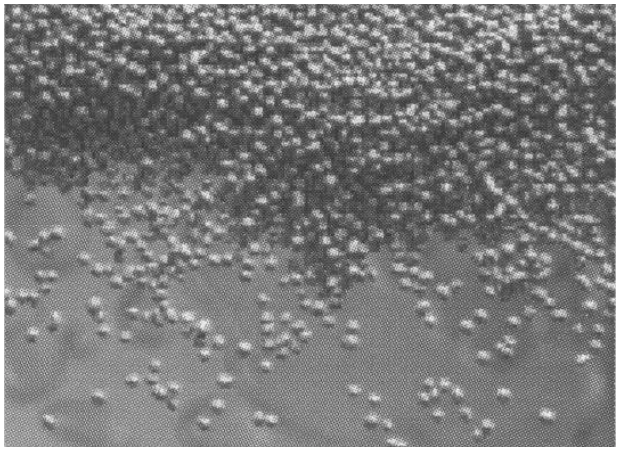
Common ***Sorbents*** (Porous Solids) for Water and Wastewater Treatment

- Activated Carbon (GAC 16x40, PAC <325)
- Polymeric Adsorbents (XAD Resins, 16x50)
- Activated Alumina (AlOOH, 28x48)
- Granular Ferric Hydroxide/Oxide, GFH/O)
- Zeolites (Aluminosilicate ion exchangers)
- Ion Exchange Resins (Cation and Anion, 16x50)

Granular Ferric Hydroxide



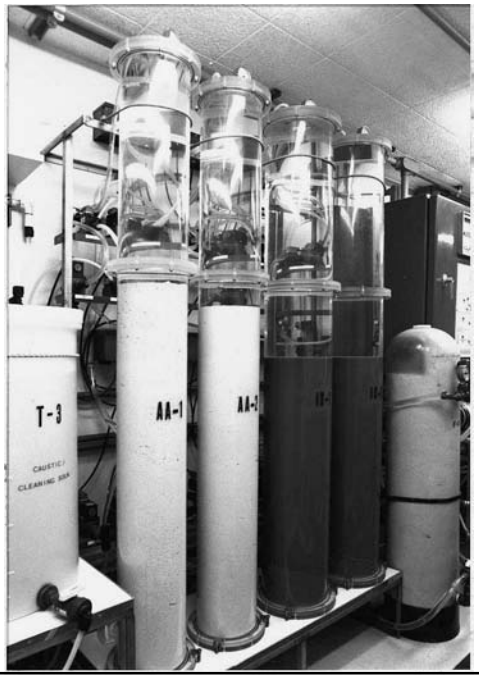
Granular Ferric Oxide, GFO



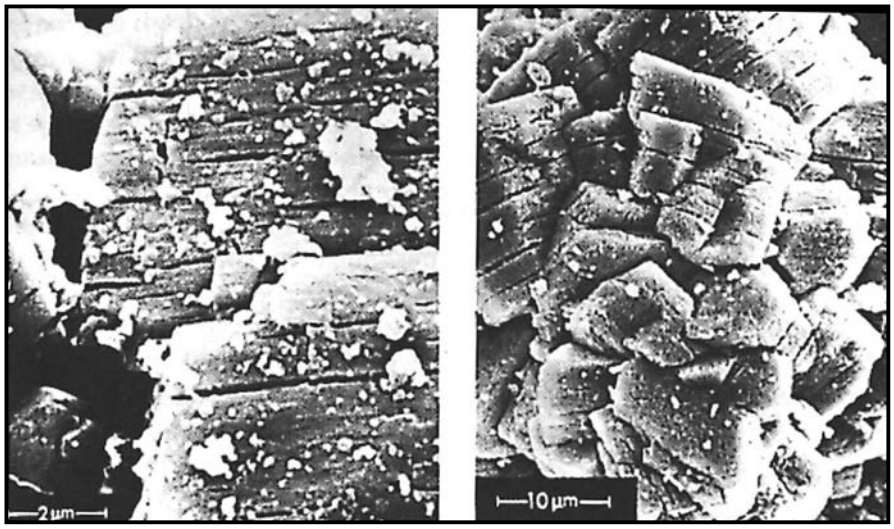
GFH Magnified

GEH® is a pure synthetic ferric hydroxide with approx. 75 % porosity and a specific surface area of 250 300 m²/g.

Activated Alumina in Columns



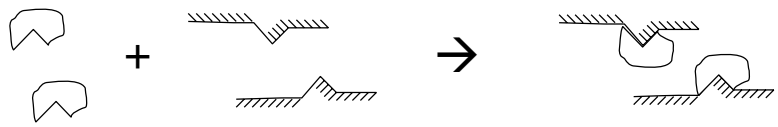
Highly Magnified Activated Alumina



Characterization of Sorbents, AAl

- Surface area: 200-300 m^2/g
- Pore volume, 0.2-0.5 cm^3/g
- Pore size distribution, micro and macro pores.
- Bulk density, 50 lbs/ft^3
- Skeletal density, 3 g/cm^3
- Particle size: 28 x 48 mesh (0.6-0.3 mm)
- pH at Zero Charge Point, pH_{ZPC}

Modeling The Adsorption Process



Contaminant ion or molecule

Porous adsorbent with active sites

Contaminants adsorbed onto internal surface sites

$$A + S \rightarrow A \bullet S$$

The "Adsorption Isotherm" describes the extent of adsorption at equilibrium.

- **Isotherm:** Constant temperature plot of solid-phase concentration (A•S) vs liquid-phase concentration of contaminant (A).
- **Example:** Simple linear isotherm

$$C_{A,Solid} = KC_{A,liquid}$$
$$q_{A,equil.} = KC_{A,equil.}$$
$$q_e = KC_e$$

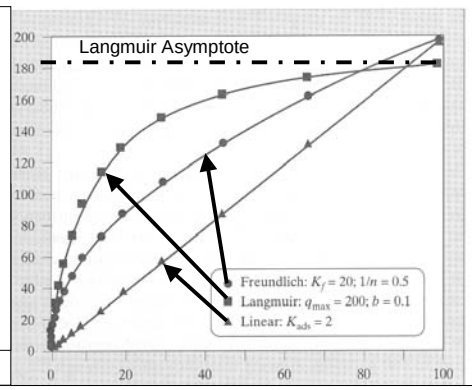
Common Isotherm Equations

Linear: $q_e = K_{ads} C_e$

Langmuir: $q_e = q_{max} \frac{bC_e}{1 + bC_e}$

Freundlich: $q_e = K_f C_e^{1/n}$

q_e, Solid-phase concentration, mg A/g AAl, y-axis

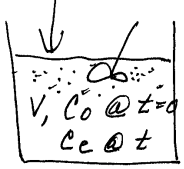


C_e, Aqueous-phase concentration, mg A/L, x-axis

Construction of an Isotherm from Batch Equilibrium Data

Nomenclature

$D = \frac{mg\ PAC}{L}$

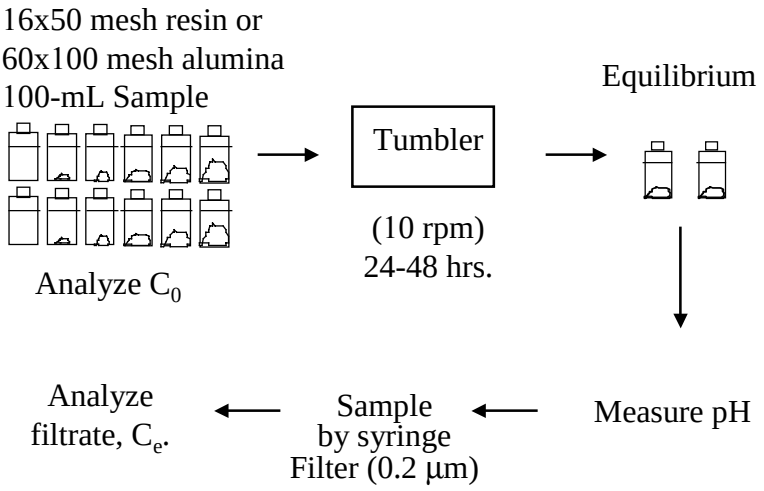


V = volume of liquid, L
C_0 = initial conc. of contaminant, mg A/L
M = mass of adsorbent added to reactor, mg PAC
D = dosage of adsorbent, mg PAC/L
$D = \frac{M}{V}$ = mg PAC/L of water

<u>Test Procedure</u>
(1) Grind adsorbent into powder
(2) Place volume, V, of water into reactor (or bottle).
(3) Add mass (M) to volume (V) of water.
$D = \frac{M}{V}$ = mg PAC/L of water.
(4) Mix, shake, or tumble mixture for 30 min to 7 days.
(5) Settle, centrifuge, or filter out the spent PAC.
(6) Measure C_e, mg A/L, at equilibrium.
(7) Repeat steps 2-6 for other dosages of PAC.
(8) Using data from each batch equilibration, construct an isotherm.

Equilibrium Isotherm Tests:

"Bottle-Point" Method for Resins and Adsorbents



Adsorption of arsenic onto aluminum and iron oxides involves:

- Surface complexation (ligand exchange or inner-sphere complex formation)
- Ion Exchange (weak ionic attraction in the diffuse layer)
- Surface precipitation

Chemistry of the Solid-Water Interface,
Werner Stumm, Wiley-Interscience, 1992

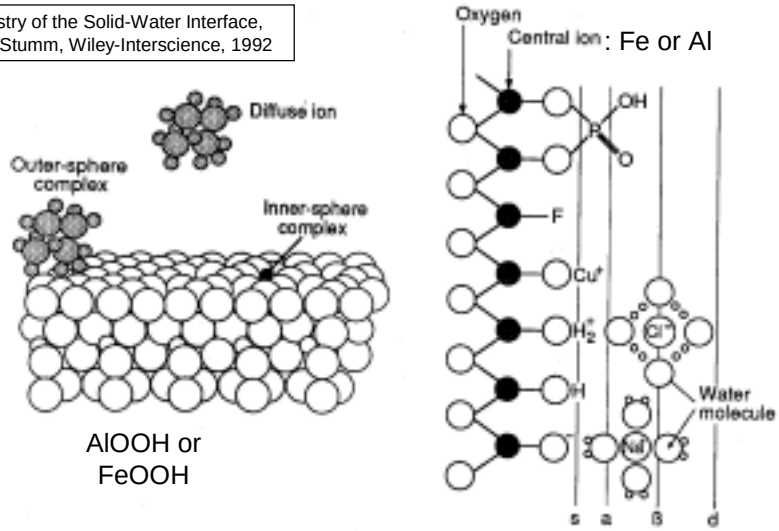
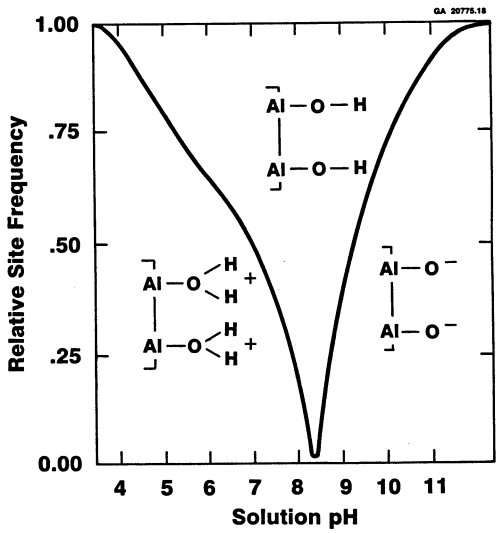


Figure 2.4

Surface complex formation of an ion (e.g., cation) on the hydrous oxide surface. The ion may form an inner-sphere complex ("chemical bond"), an outer-sphere complex (ion pair) or be in the diffuse swarm of the electric double layer. (From Sposito, 1989)

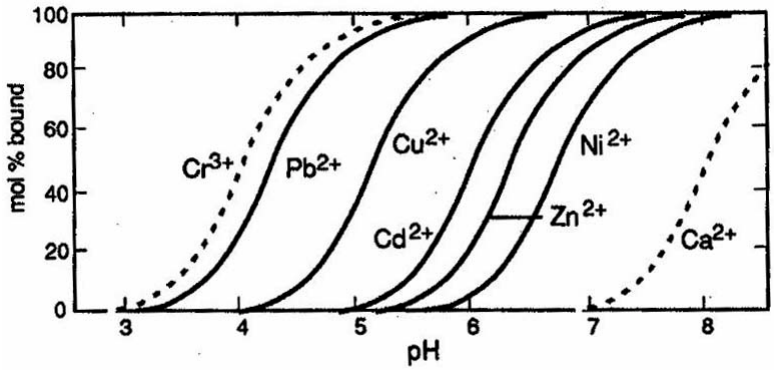
Fig. b shows a schematic portrayal of the hydrous oxide surface, showing planes associated with surface hydroxyl groups ("s"), inner-sphere complexes ("a"), outer-sphere complexes ("β") and the diffuse ion swarm ("d"). (Modified from Sposito, 1984)



Relative Site Distribution of an Alumina Surface

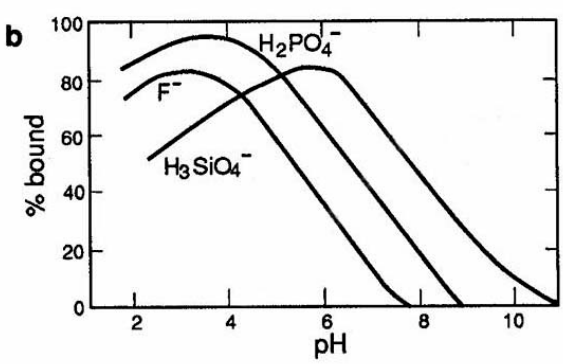
. W. Novak, Jr. and R. R. Burr, "Investigations of ion adsorption interactions using flow calorimetry", Alcoa Report 6-887-31

Cation Sorption onto FeOOH by Outer-Sphere Surface Complex Formation



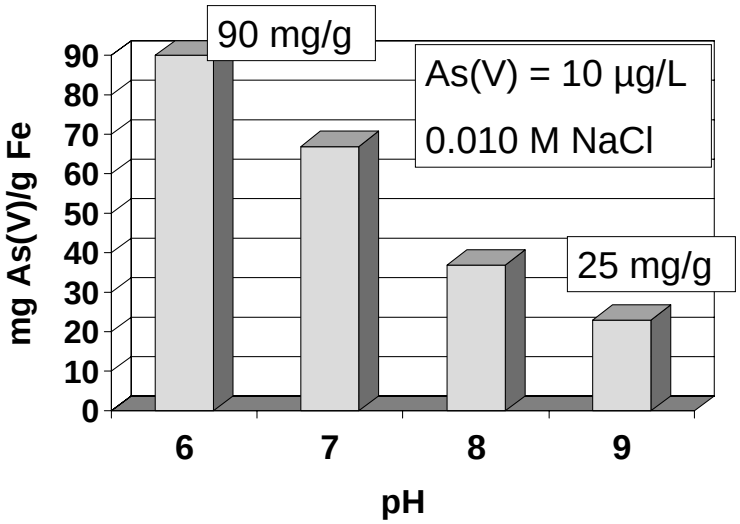
[TOT-Fe] = 10^{-3} M, 2 x 10^{-4} M reactive sites/L, [TOT-Me] = 5 x 10-7 M, I = 0.1 M $NaNO_3$

Anion Adsorption onto FeOOH

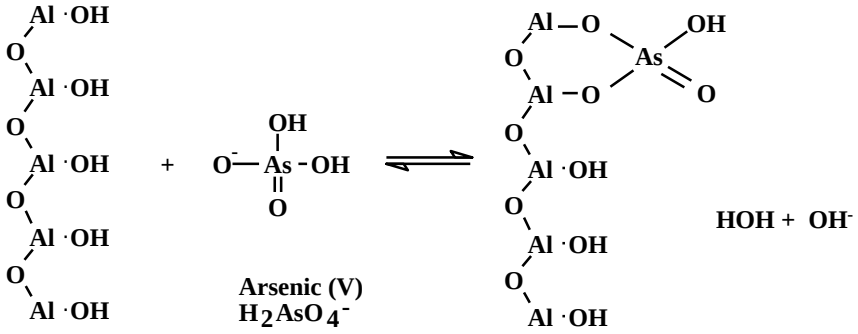


Binding of phosphate, silicate, and fluoride on goethite (α-FeOOH); the species shown are surface species. (6.0 g FeOOH/L, P_T = 10^{-3} M, Si_T = 8 x 10^{-4} M.) Sigg and Stumm, 1981

Effect of pH on GFH Performance



AAl—Arsenic Ligand Exchange



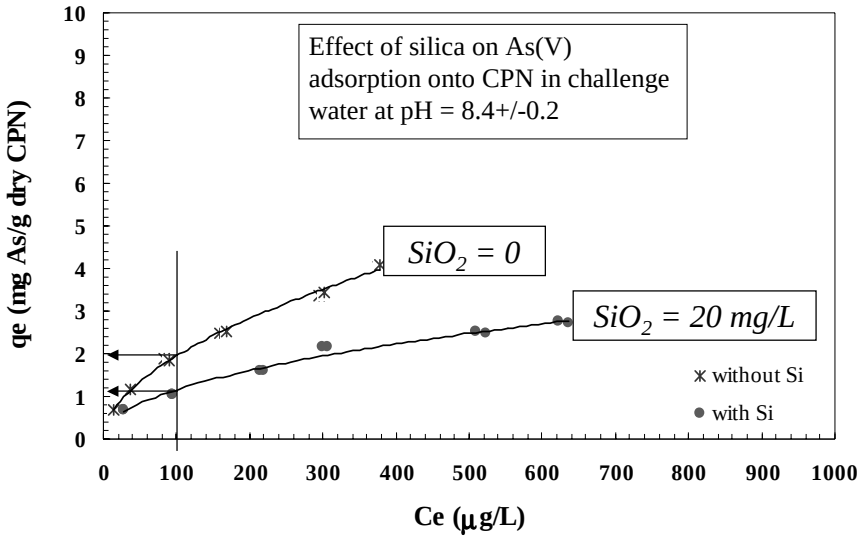
Alumina
AlOOH
FeOOH
Zr, Ti oxides

Competing Ligands:
$H_2PO_4^-$
$Si(OH)_3O^-$

Arsenic on
AlOOH
FeOOH

Hydroxide

Isotherms for adsorption of As(V) onto CPN AAl



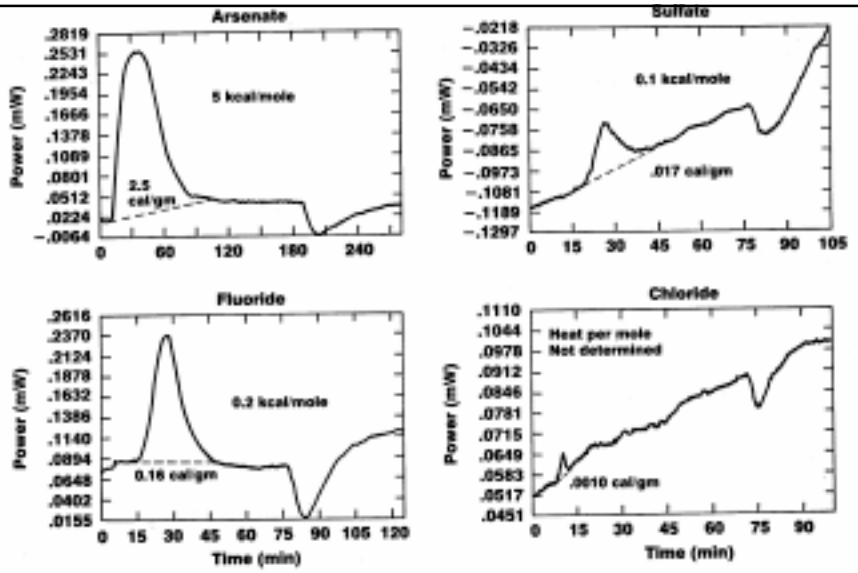
Adsorption Thermodynamics

$$\Delta G_{ads} = \Delta G_{coul} + \Delta G_{chem} + \Delta G_{soln}$$

ΔG_{coul} = Free energy from coulombic interactions

ΔG_{chem} = ΔG from specific chemical reactions, e.g., covalent surface bonds

ΔG_{soln} = ΔG from changes in hydration of the sorbent, sorbate, and any other counter ions.



Heats evolved from adsorption of anions onto CPN Activated Alumina. pH 6.0, C_I = 100 mg/L, T = 25.5°C

J. W. Novak, Jr. and R. R. Burr, "Investigations of ion adsorption interactions using flow calorimetry", Alcoa Report 6-887-31

Competing Ligands Sequence Activated Alumina (and FeOOH)

$\underline{OH^-}$ > $H_2AsO_4^-$ > $H_2PO_4^-$ > $HSeO_3^-$ >

$Si(OH)_3O^-$ > VO_3^-, F^- ≫ TOC^- >

SeO_4^{2-}, SO_4^{2-} >> Cl^-, NO_3^-, HCO_3^- >

H_3AsO_3

Summary

- Adsorption of arsenic is its removal from water by concentration onto a porous adsorbent such as AlOOH or FeOOH.
- Adsorption of arsenic onto AlOOH and FeOOH is usually described using standard isotherms based on simple models, but it’s a very complcated process.
- Surface complexes and ion pairs are formed, pH increase lowers arsenic adsorption. Competing anions such as silicate, phosphate, fluoride, vanadate,and sulfate also reduce arsenic adsorption.

Isotherm Testing: Procedures and Application of Results

Gary Amy
Professor of Environmental Engineering
University of Colorado USA

Terminology

- (ad)sorption ⇨ accumulation @ solid/solvent interface
- (ad)sorbent ⇨ solid phase material
- (ad)sorbate ⇨ target compound(s)
  - arsenate (or arsenite) ✓
  - single vs. multi-sorbate
    - interferants
    - competition
- solvent ⇨ water
- knowledgebase ⇨ activated carbon + organics

Adsorbent Forms and Properties

- Granular vs. Powdered
  - Fixed Bed vs. Slurry Reactor (or Membrane)
- Porous vs. Non-Porous
  - e.g., GFH vs. SMI
  - Kinetics
- (Specific) Surface Area (m^2/g)
- (Surface) Charge (pH_{ZPC})
- Site Density ($\#/nm^2$)
- Mineralogy
  - Crystaline vs. Amorphous
  - Various Iron Oxides, etc. vs. Ion Exchange Resins
  - Strictly Adsorbent vs. Reactive media (e.g., MnO_2)

Influential Factors

- Temperature
  - Exo- versus Endothermic ⇨ *Isotherm*
  - Exo ⇨ adsorption ∝ 1/temperature;
    Endo ⇨ adsorption ∝ temperature
  - Adsorption
    - Generally exothermic
    - But higher diffusion at higher temperature often offsets higher temperature effects
- pH
  - $H_2AsO_4^-$ vs. $HAsO_4^{2-}$
- Interferants
  - e.g., Phosphate

Mechanisms of Arsenic Adsorption

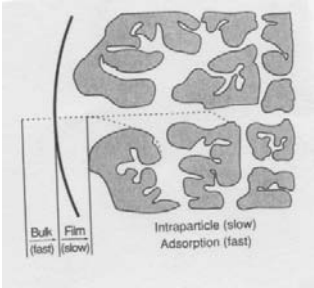
- Physical Adsorption ✖
  - van der Waals Forces
- Chemisorption ✓
  - Surface Complexation
- Exchange Adsorption ✓
  - Ion Exchange

Adsorption Mechanisms

- Chemisorption:
  - Ligand (L) Exchange
    $>X\text{-}OH + L^- \leftrightarrow >X\text{-}L + OH^-$
  - Surface Complexation
    $>X\text{-}OH + HAsO_4^{2-} \leftrightarrow X\text{-}OHAsO_4^{2-} + H^+$
- Exchange Sorption:
  - $>X\text{-}Cl + L^- \leftrightarrow >X\text{-}L + Cl^-$
- Influential Factors
  - pH: $H_2AsO_4^-$, $HAsO_4^{2-}$
  - pH_{ZPC} of Adsorbent; if pH < pH_{ZPC}, "+"
  - Inner (bond) vs. Outer Sphere Complexes (ion pair)

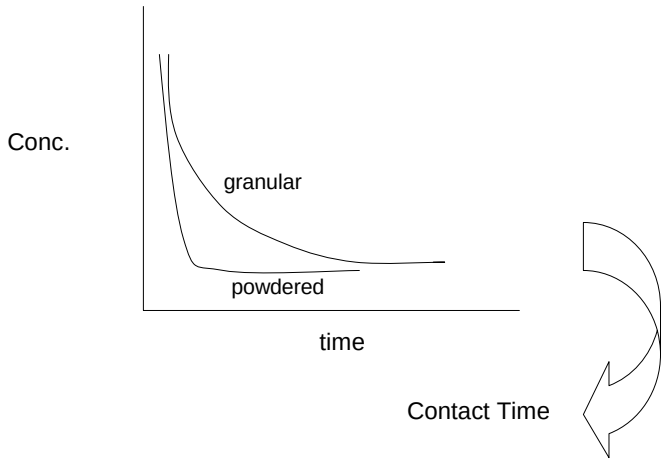
Mass Transfer Steps

- (External) Film Diffusion
- (Internal) Pore and/or Surface Diffusion
  - Generally Rate-Limiting
- Surface Reaction

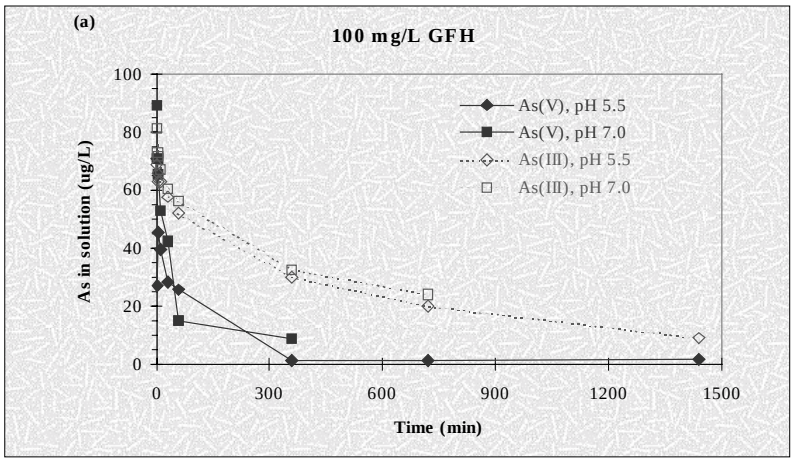


Kinetics

Kinetics

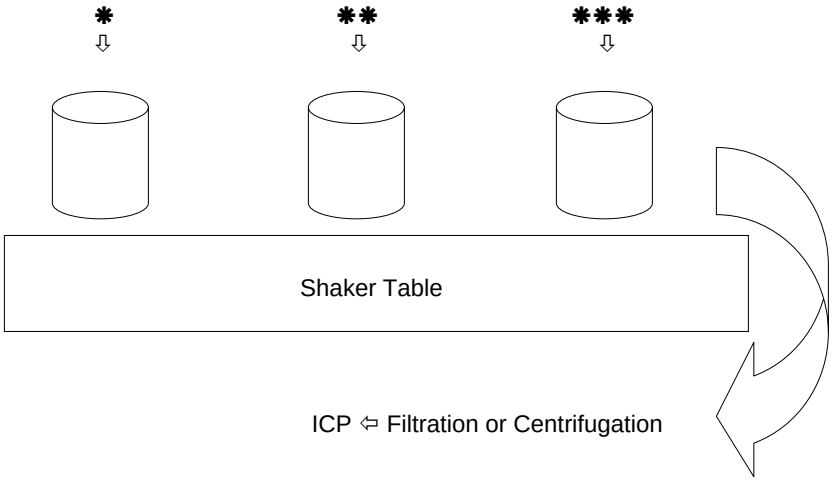


Kinetics



Other Studies: up to 96 hours

Bottle Point Isotherms



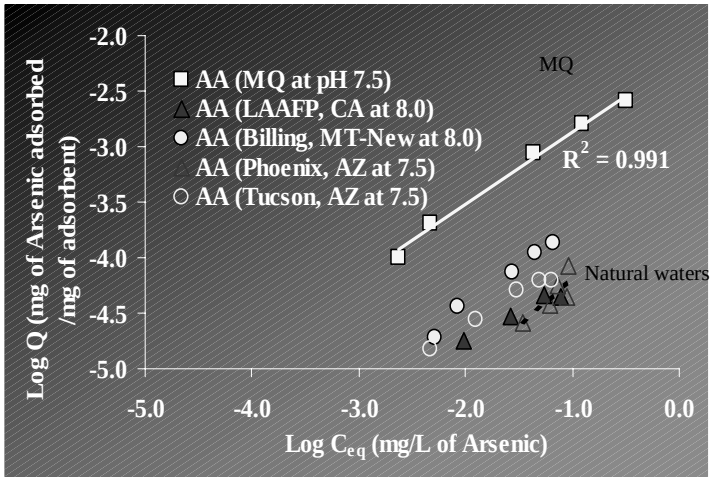
Bottle Point Experiments

- Concentration Constant ⇨ Vary Adsorbent
  - natural water
- Adsorbent Constant ⇨ Vary Concentration
  - e.g., synthetic water
- Multi-Adsorbate
  - C_0 of arsenic and interferant affects isotherm

(Equilibrium) Isotherms

- $q = x/m = (V(C_0 - C))/m$
  - q ⇨ solid phase conc. (e.g., ug/mg)
  - C ⇨ equil. water-phase conc. (e.g., ug/L)
    - Initial (C_0) vs. Equilibrium (C)
  - m ⇨ adsorbent concentration (e.g., mg/L)
  - V ⇨ volume (e.g., L)
  - x ⇨ mass adsorbed (e.g., ug)
- Batch Equilibrium Tests
  - Equilibration Time:
    - Powdered ⇨ minutes to hours
    - Granular ⇨ hours to days
    - Pulverize granular media?

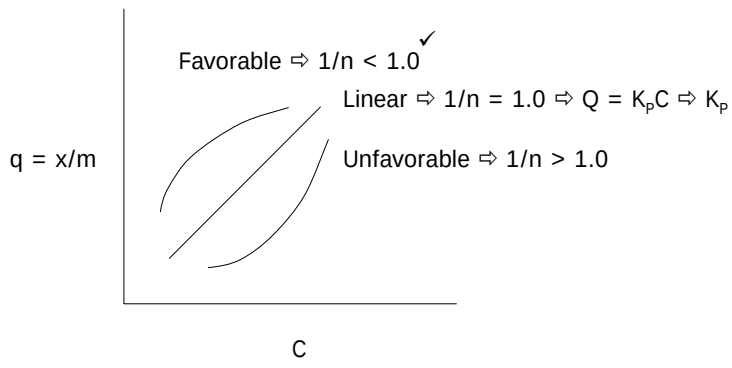
Activated Alumina Isotherms



Isotherm Equations

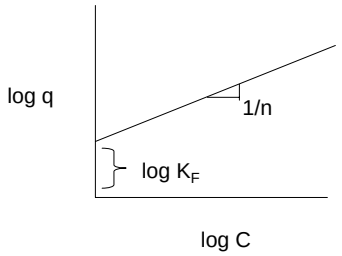
- Freundlich
  - Empirical; good data fit of intermediate range data
  - $q = K_F C^{1/n}$ (or $q = KC^n$ in Europe)
  - q ⇨ solid phase conc. (ug/mg, moles/g, etc.)
  - C ⇨ equil. water-phase conc. (ug/l, moles/L, etc.)
  - K_F & 1/n ⇨ empirical constants
    - K_F ⇨ capacity parameter (units!)
    - 1/n ⇨index of „favorable“ vs. „unfavorable“ adsorption
- Langmuir
  - Theoretical; good fit of higher and lower range data
  - $q = (Q_{max}K_L C)/(1 + K_L C)$
  - Q_{max} ⇨ max. surface conc.
    - indicative of „monolayer“ coverage or site saturation ✓
  - K_L ⇨ constant

Favorable vs. Unfavorable Adsorption



Determination of Isotherm Constants – cont.

- Linearization of Freundlich Equation
  - log q = log K_F + 1/n log C
  - log-log plot
    - Intercept ⇨ K_F
    - Slope ⇨ 1/n



Determination of Isotherm Constants – cont.

- Linearization of Langmuir Equation
  - $1/q = 1/Q_{max} + (1/bQ_{max})(1/C)$
  - Plot of 1/q vs. 1/C
    - Intercept ⇨ $1/Q_{max}$
    - Slope ⇨ $1/K_L Q_{max}$

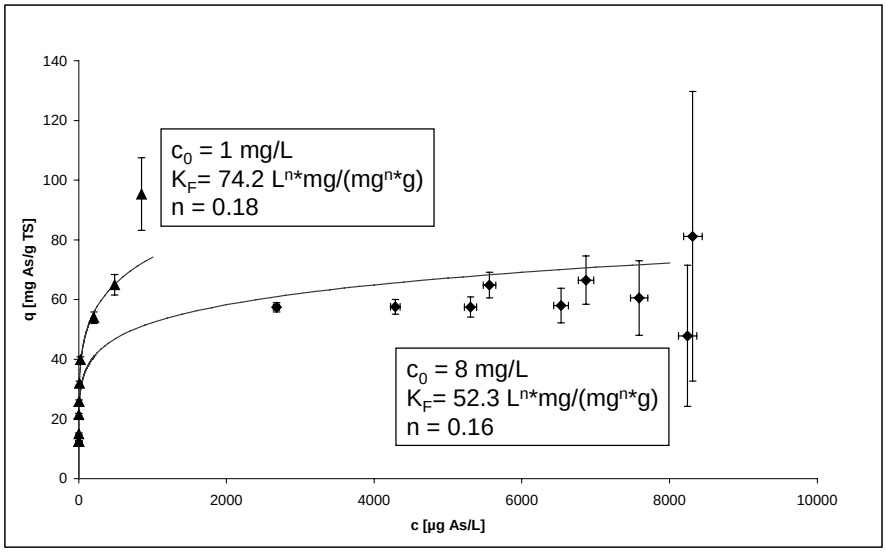
Adsorption Capacity

- q vs. C
  - q_{eq} vs. C_{eq}
  - q_0 vs. C_0
  - q_{10} or q_{50} vs. C = 10 or 50 ug/L
  - mass based q (ug/mg)
    vs. surface area based q (ug/cm^2)

A *Robust* Isotherm

- Lower Level Resolution
  - Adsorbate Limited
- Higher Level Resolution
  - Adsorbent Limited

Isotherm: Higher and Lower Concentration Ranges



Adsorption of Mixtures

- Multiple Adsorbates
- Reduced Single Adsorbate Capacity

Competitive Langmuir Equation

- $q_i = (Q_{max,i}K_{L,i}C_i)/(1 + \sum_{j=1}^{n}(K_{L,j}C_j))$
  - n ⇨ number of (ad)sorbates
  - C_i ⇨ equil. conc. of i sorbate in a j sorbate mixture
  - q_i & $K_{L,i}$ ⇨ single sorbate parameters
- For two (Ad)sorbates:
  - $q_1 = (Q_{max,1}K_{L,1}C_1)/(1 + K_{L,1}C_1 + K_{L,2}C_2)$
  - $q_2 = (Q_{max,2}K_{L,2}C_2)/(1 + K_{L,1}C_1 + K_{L,2}C_2)$
  - $Q_{max,1}$, $Q_{max,2}$, $K_{L,1}$, $K_{L,2}$ ⇨ derived from single sorbate experiments
  - C_1, C_2 ⇨ derived from competitive sorbate experiments
  - q_1, q_2 ⇨ calculated from competitive adsorption

Information Provided by Isotherms

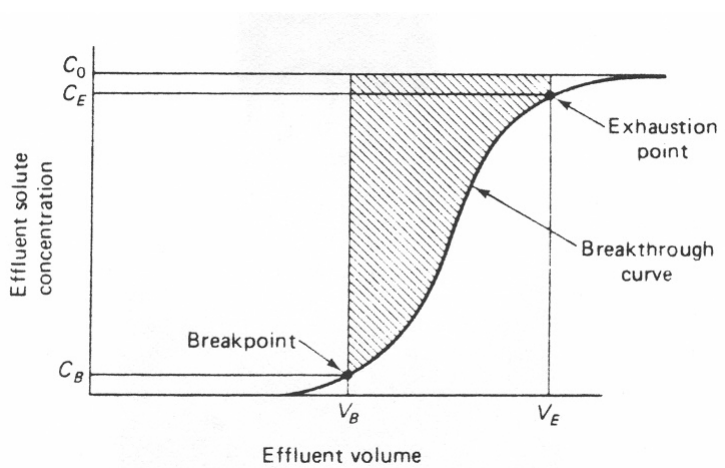
- Powdered Adsorbent Applications
  - If m is specified, C = ?
    - $q = x/m = (V(C_0 - C))/m = = K_F C^{1/n}$
  - If C is specified, m = ?
    - $q = x/m = (V(C_0 - C))/m = = K_F C^{1/n}$
- Granular Adsorbent Applications
  - Column-mode capacity ⇨ q_0 (vs. C_0)

How does isotherm capacity relate to column capacity?

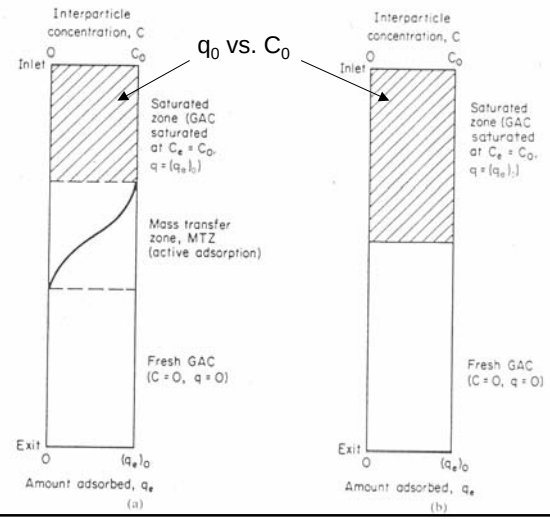
GAC Column Performance

- C(oncentration) to Breakthrough or Exhaustion vs.
  t(ime) or
  V(olume), ΣV, or
  B(ed) V(olumes), BVs =$\Sigma V/V_{empty}$

Fixed Bed Column: Idealized Breakthrough Curve (BTC)



Adsorption Column with (a) and without (b) MTZ



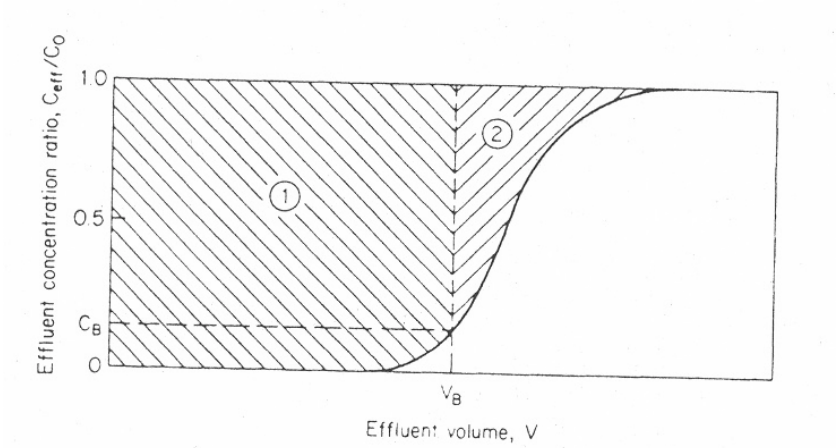
Mass Adsorbed at Breakthrough or Exhaustion

- Integration of BTC: C (mg/L) vs. V (L)

$$\int_{V=0}^{V=V} (C_0 - C)dV \quad \Big\} \quad x \overset{m}{\Rightarrow} x/m \Rightarrow q$$

$V \Rightarrow V_B$ or V_E

Integration of BTC



Breakthrough Capacity ⇨ ① x C_0
Exhaustion Capacity ⇨ ① + ② x C_0
Capacity Utilization (%) @ Breakthrough ⇨ ①/① + ② x 100
Stoichiometric Breakthrough @ C/C_0 = 0.5

Adsorbent Utilization Rate (AUR)

- AUR (mass/volume)

  $$\text{AUR} = \frac{\text{mass of adsorbent in column}}{\text{volume treated to breakthrough, } V_B}$$

- From BTC:

  AUR = $\rho_{adsorbent}$ (g/L)/BVs to breakthough

- From Isotherm:

  AUR (g/L) = $(C_0)/q_0$

  - g/L = mg/L ÷ mg/g

Adsorbent Bedlife (BVs)

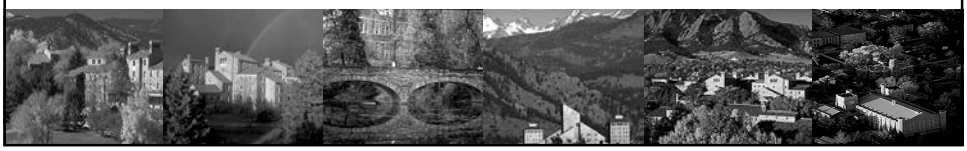
- From BTC:
  - BVs @ breakthrough
- From Isotherm:

  Bed-Life = $q_0/C_0 \times \rho_{adsorbent}$
  - Bed-Life ⇨ BVs
  - q_0 ⇨ mg/g
  - C_0 ⇨ mg/L
  - $\rho_{adsorbent}$ ⇨ apparent density of adsorbent (g/L)
  - dimensionless = mg/g ÷(mg/L) x g/L

Summary

- Isotherms provide an equilibrium estimate of capacity
- Isotherms provide an tool for rapid screening of candidate adsorbents and interferants
- Isotherms provide insight into column capacity

gamy@spot.colorado.edu



Rapid Small Scale Column Test (RSSCT) – Procedures for Arsenic Studies and Application of Results

Paul Westerhoff
Associate Professor

Department of Civil & Environmental Engineering
Arizona State University, Tempe, AZ
August 2004

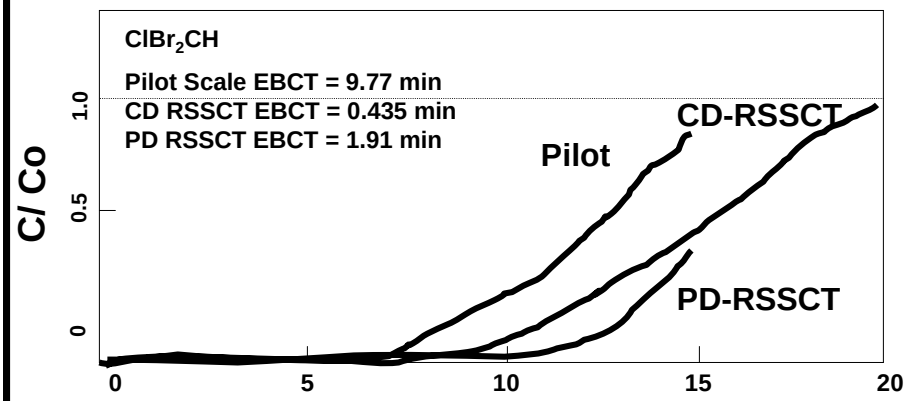
Objectives for Talk

- Describe advantages of RSSCTs for arsenic adsorptive media testing
- Describe basis for applying RSSCTs
- Demonstrate use of RSSCTs

What is an RSSCT?

- Rapid Small Scale Column Tests (RSSCTs) were initially developed by Crittenden and others for evaluating organic compound removal on activated carbon
- Fundamentally, the concept is to scale the hydrodynamics and mass transport from full-sized media in a pilot or full scale reactor *down* to smaller test media in a small-scale bench-top continuous flow test

Rapid Small Scale Column Tests (RSSCTs) For GAC versus Pilot GAC Data



Liters of Water Treated / Gram of GAC

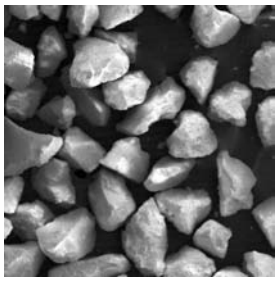
Crittenden et al.

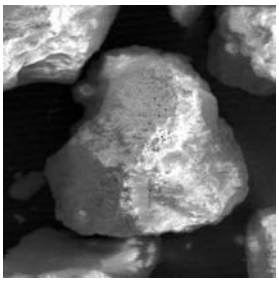
Advantages of RSSCT

- RSSCTs can be conducted in a fraction of the time required of pilot tests (1% to 10% of the time)
- RSSCTs require less water than pilot tests, and can be conducted under controlled laboratory conditions
- RSSCTs are generally cheaper than pilot tests
- RSSCTs are continuous flow tests and allow evaluation of dynamic behavior and competition reactions that are more representative than batch tests
- RSSCTs were used during the USEPA ICR for organic carbon removal
- RSSCTs facilitate comparison of media and water quality effects

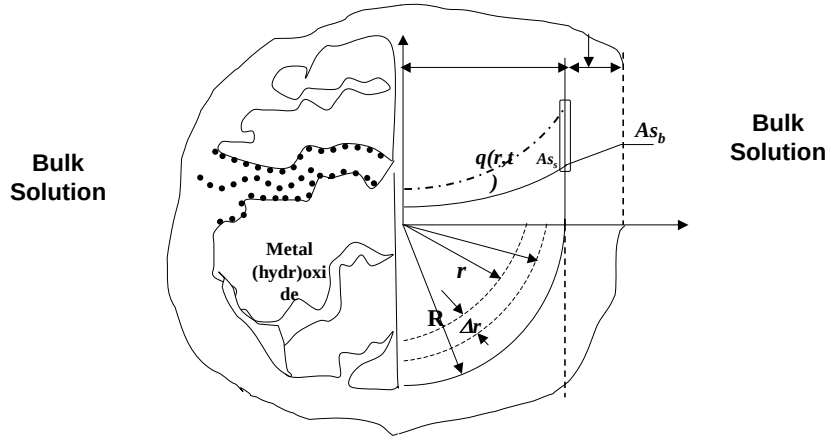
Today's Question

Are RSSCTs suitable for evaluating arsenic removal by porous metal (hydr)oxide medias?





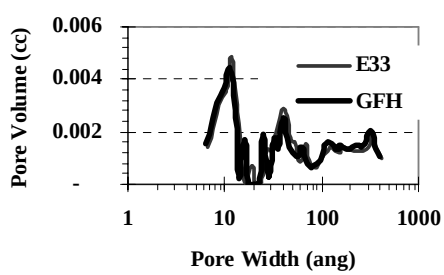
Porous Adsorbents

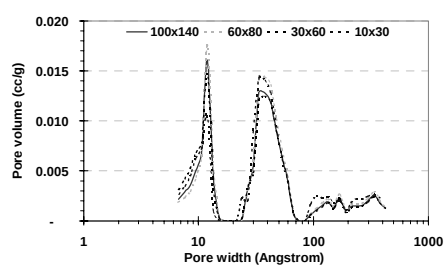


$$\frac{\partial q(r,t)}{\partial t} = D_s\left(\frac{\partial^2 q(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial q(r,t)}{\partial r}\right)$$

Basis for RSSCT

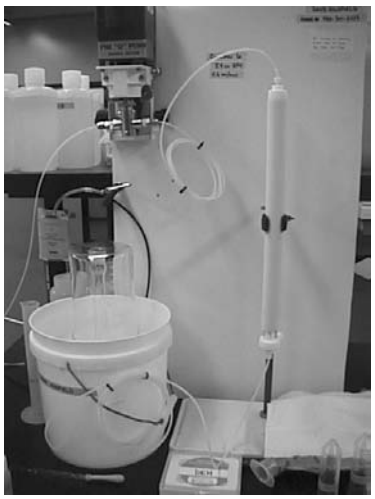
- Key assumption - Internal mass transport is limiting (therefore only applicable to microporous materials)
- GFH surface area is 230 m^2/g and E33 is 130 m^2/g
- GFH and E33 have comparable pore structure
- Pore size distribution is nearly independent of particle radius (r_p) or mesh size
- Conclusion: Internal mass transfer is probably important & RSSCTs could be viable testing technologies





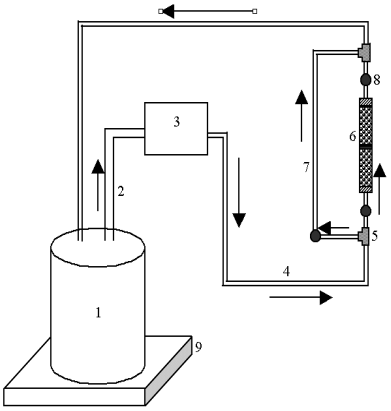
Results

- Differential Column Batch Reactor (DCBR) Study
- RSSCTs with different particle diameters
- RSSCTs versus pilot performance
- Application of RSSCTs for arsenic removal media



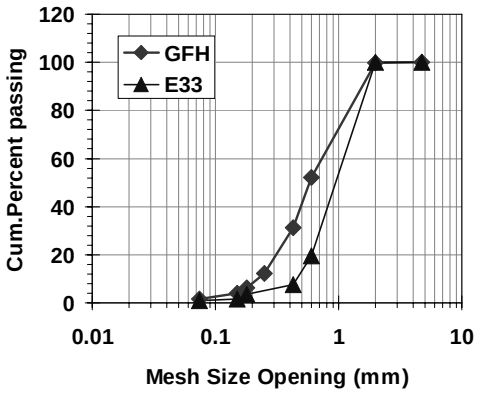
DCBR Apparatus

- DCBR Apparatus is used to determine internal mass transfer coefficients
- Results are used to evaluate applicability of RSSCT scaling theory

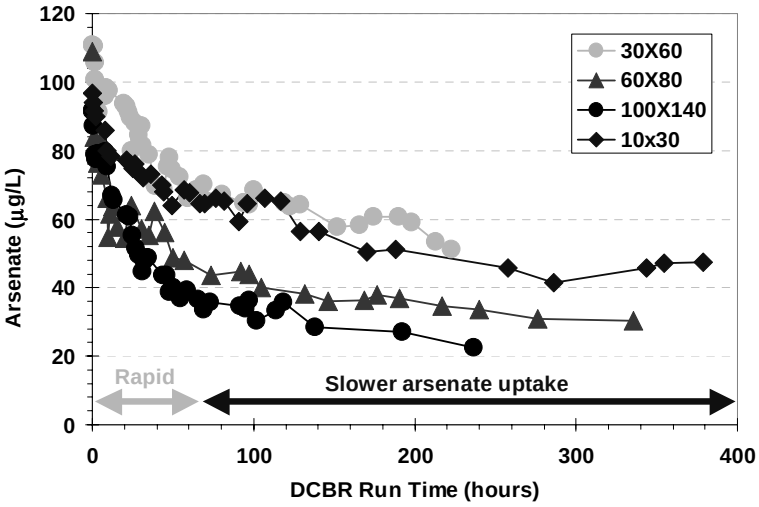


Differential Column Batch Reactor (DCBR)

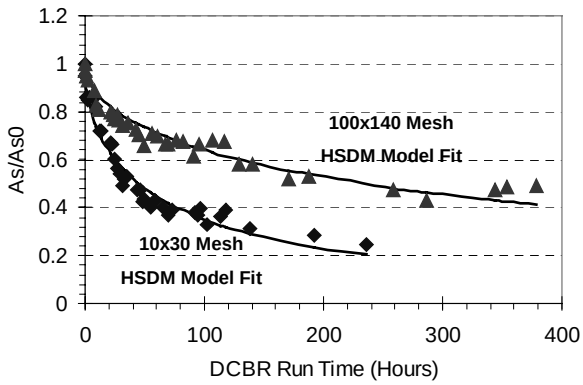
Adsorbent Material Sieved into discrete particle / mesh sizes



DCBR Data for Various Mesh Sizes



DCBR Results & Modeling with GFH



Equilibrium Isotherm

$q = K C^{1/n}$

$K = 4.0$ & $1/n = 0.3$

$$SPDFR = \frac{\rho_p D_s (D_p = 0) q_0}{\varepsilon_p D_L As_0}$$

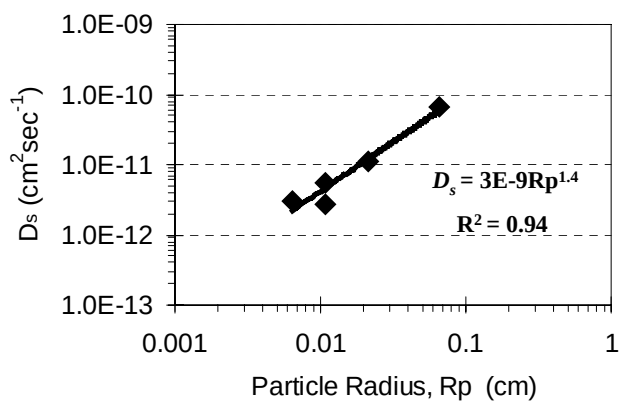
- SPDFR Ranged 6 ~150

$$Bi = \frac{k_f d_p C_0}{2 D_s \rho_p q_0}$$

- Bi ranges 7 ~57

$$\frac{\partial q(r,t)}{\partial t} = D_s \left(\frac{\partial^2 q(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial q(r,t)}{\partial r} \right)$$

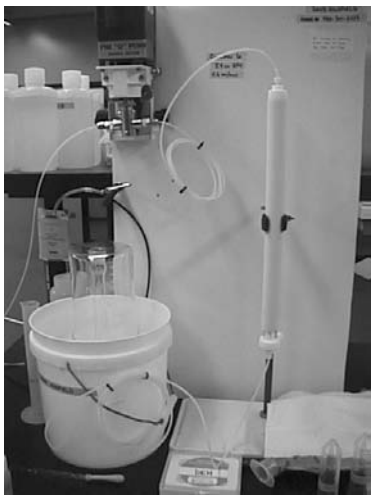
Fitted Surface Diffusivities



Conclusion: Surface diffusivity is *not* constant, but proportionate to GFH particle radius

Results

- Differential Column Batch Reactor (DCBR) Study
- RSSCTs with different particle diameters
- RSSCTs versus pilot performance
- Application of RSSCTs for arsenic removal media



Validating RSSCTs

Approach:
Vary Particle Radius (R_{SC}) used in RSSCT columns

and

scale RSSCTs to a common sized pilot column that uses a larger adsorbent particle radius (R_{LC})

RSSCT Scaling Relationships

- Empty bed contact times (EBCTs) are scaled based upon particle radius (R)
- Constant Diffusivity (CD)
  - $D_{S,small\ column\ media} \approx D_{s,large\ column\ media}$
  - $R_{SC} \neq R_{LC}$
  - X = 0

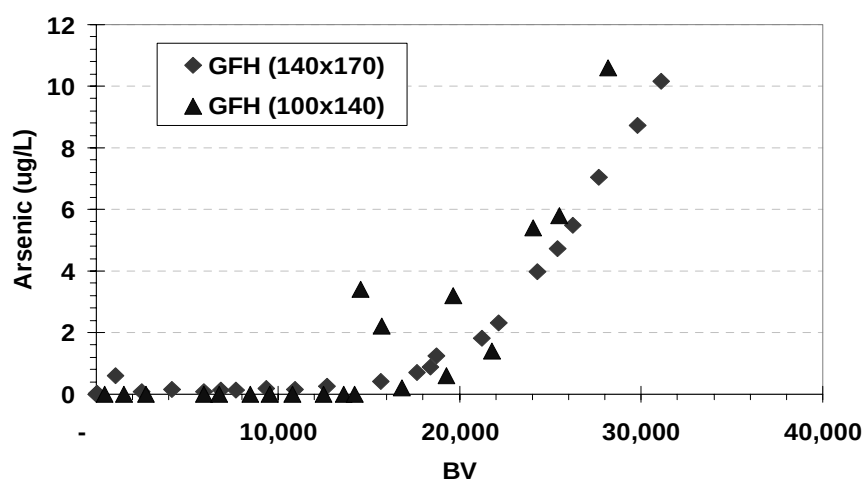
$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left(\frac{R_{SC}}{R_{LC}}\right)^{2-x}$$

- Proportional Diffusivity (PD)
  - Diffusivity is proportional to adsorbent radius
  - From D_s data with DCBR
    X = 0.6 (assume X=1)

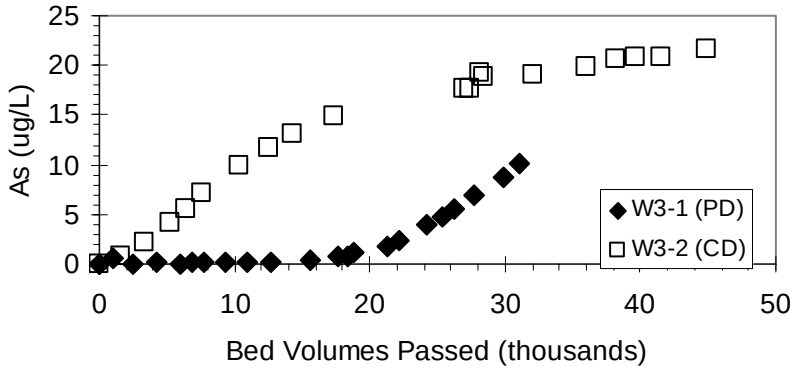
$$x = \frac{Log\left(\frac{R_{SC}}{R_{LC}}\right)}{Log\left(\frac{D_{s,SC}}{D_{s,LC}}\right)}$$

- PD approach should be valid for GFH

PD Scaling "works" with different GFH Mesh Sizes



Comparison of CD versus PD RSSCTs



Results

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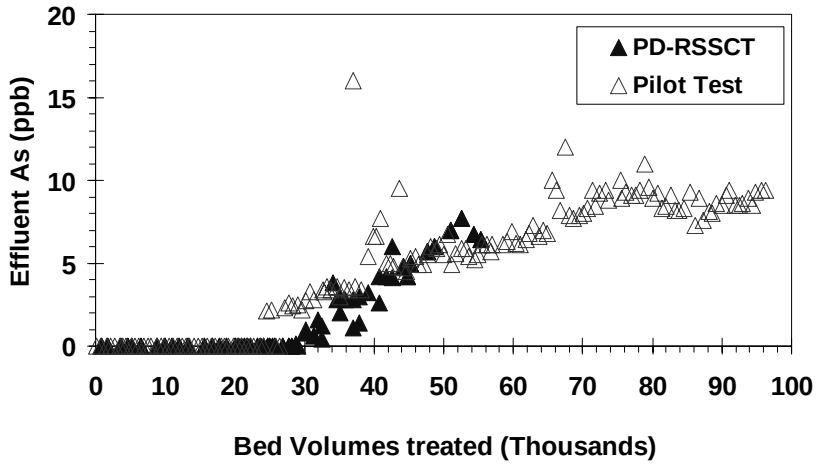
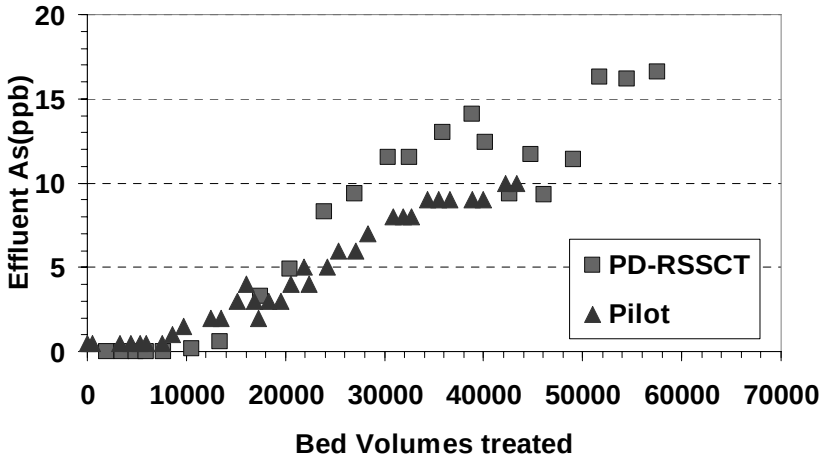
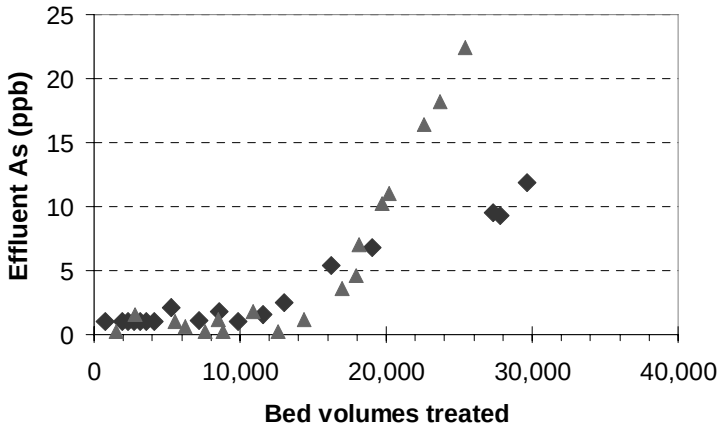
RSSCT-PD vs Pilot (GFH)



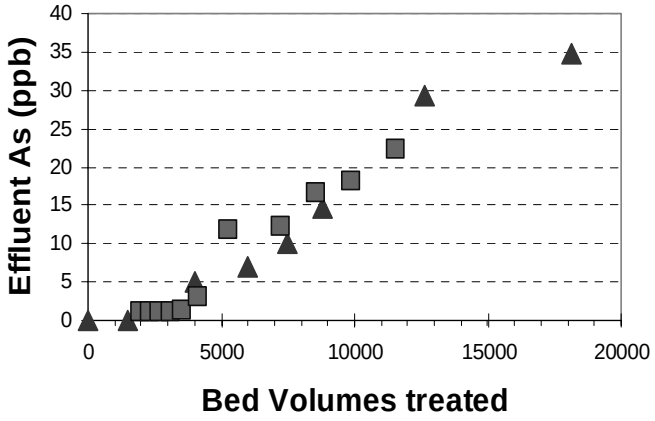
RSSCT-PD vs Pilot (GFH)



RSSCT-PD vs Pilot (E33)



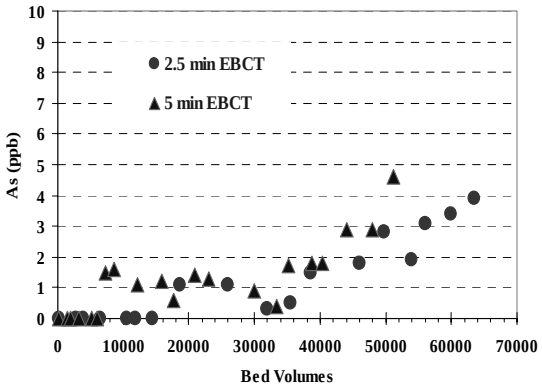
RSSCT-PD vs Pilot (E33)



Results

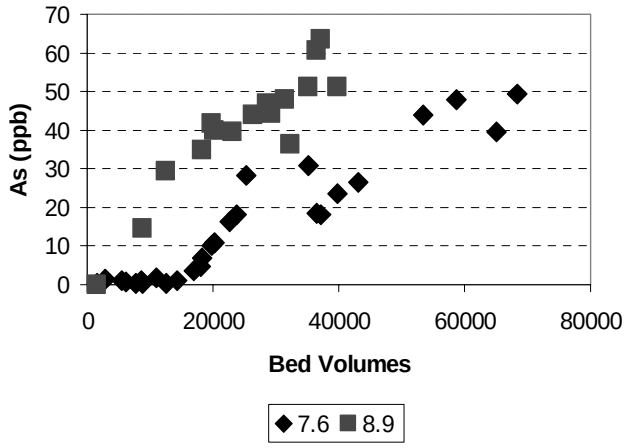
- Differential Column Batch Reactor (DCBR) Study
- RSSCTs with different particle diameters
- RSSCTs versus pilot performance
- Application of RSSCTs for arsenic removal media

Effect of EBCT (E33)

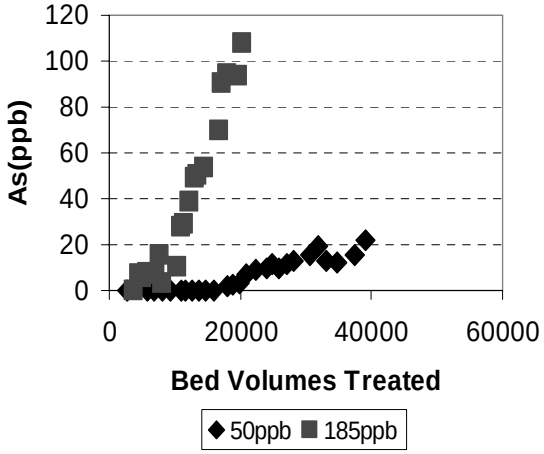


- No Statistical benefits of increasing EBCT 2.5 to 5min

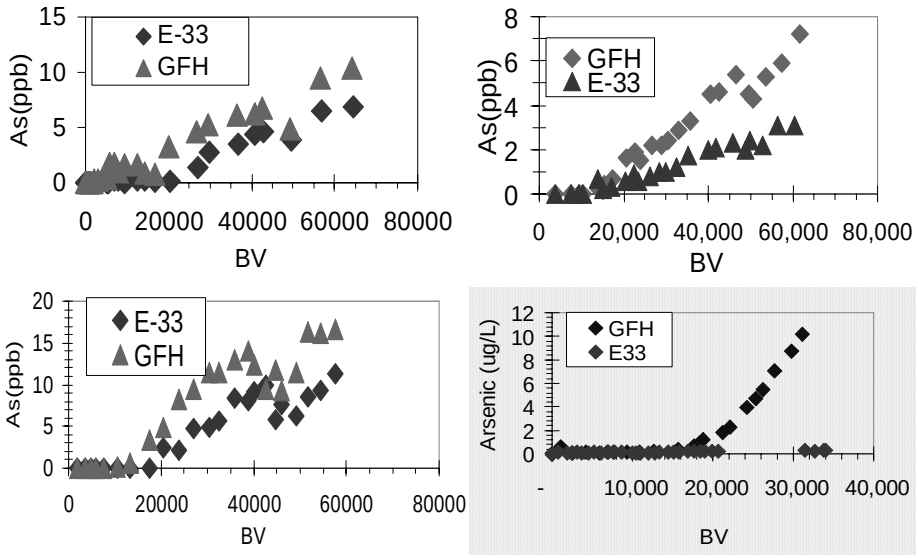
Effect of pH



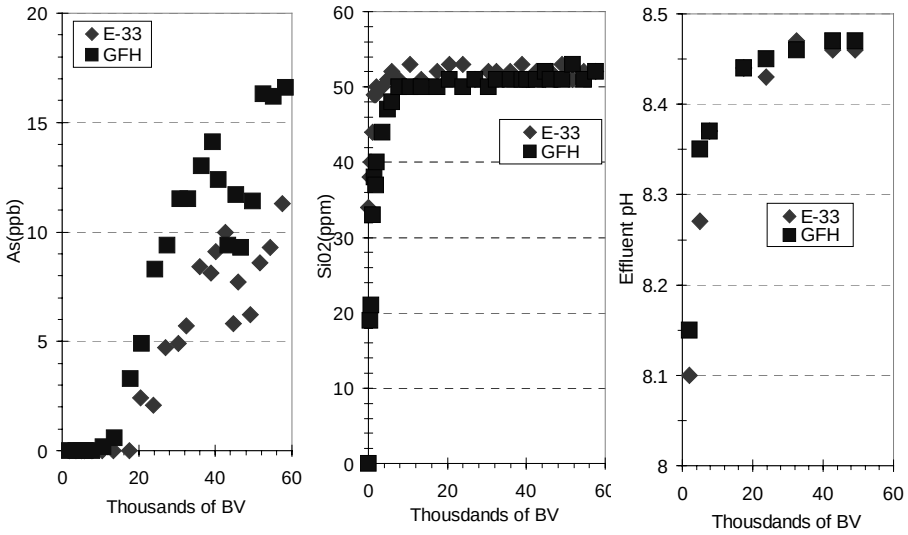
Effect of Initial Arsenate Concentration



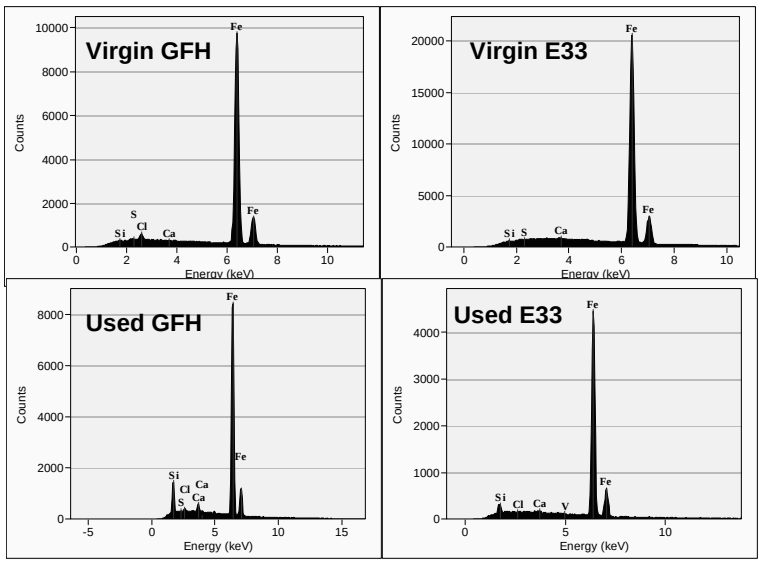
Comparison E33 & GFH



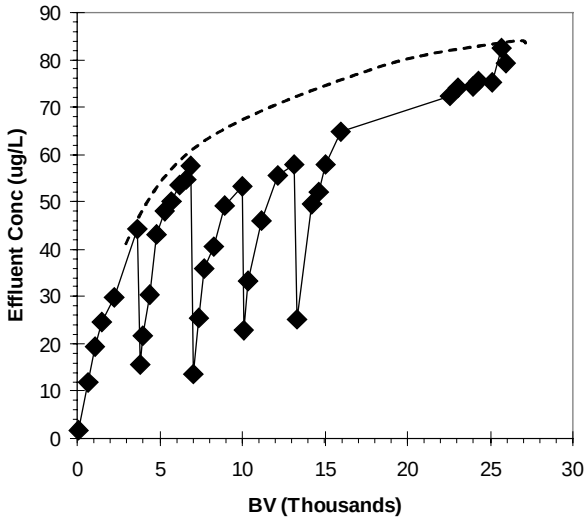
Why difference in Arsenate removal with E33 & GFH



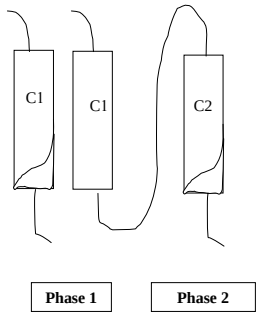
Elemental Surface Composition from SEM with EDX

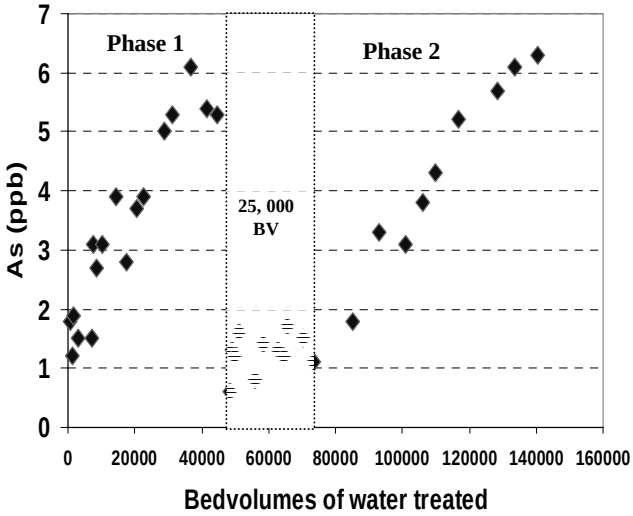


Intermittent Column Operation



Series Column Experiments: E33





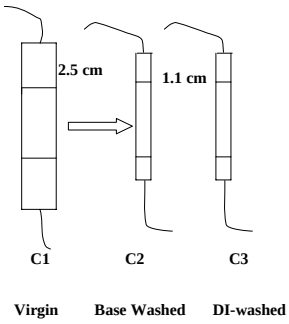
Simulated EBCT:

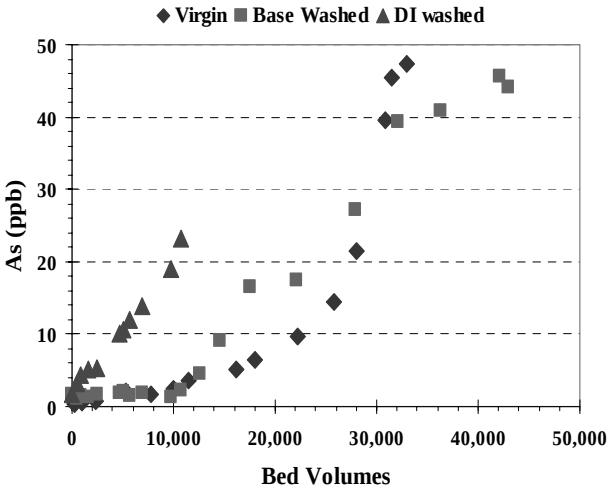
C1 - 2.5 min

C2 - 2.5 min

C2 was connected when effluent conc. was 5ppb, after 7 days ~ 48,000 BVs

Regeneration of Packed Bed E33





Tap Water Spiked with

As: 50 ppb

Silica : 20 ppb

pH : 8.2

EBCT: C1, C2 and C3 ~ 2.5 min

Summary

- We have recently demonstrated that RSSCTs can be used to evaluate porous arsenic adsorption media (GFH, E33, MetSorbG, Fe-AA, AA, FerriSorb)
- ASU is currently comparing FS-AA, GFH, and E33 against USEPA demonstration facilities at 4 sites
- RSSCTs can facilitate media selection and optimization or effect of water quality
- RSSCTs can facilitate evaluation of packed-bed operational modes (parallel vs series)
- We have run RSSCTs continuously, but many full-scale systems operate intermittently or in cyclic patterns; RSSCTs give a "conservative" breakthrough curve and actual performance using non-continuous operation would be greater than predicted by RSSCTs

Paul Westerhoff, Ph.D.

Arizona State University

Associate Professor

Department of Civil & Environmental Engineering

http://ceaspub.eas.asu.edu/pwest/

p.westerhoff@asu.edu

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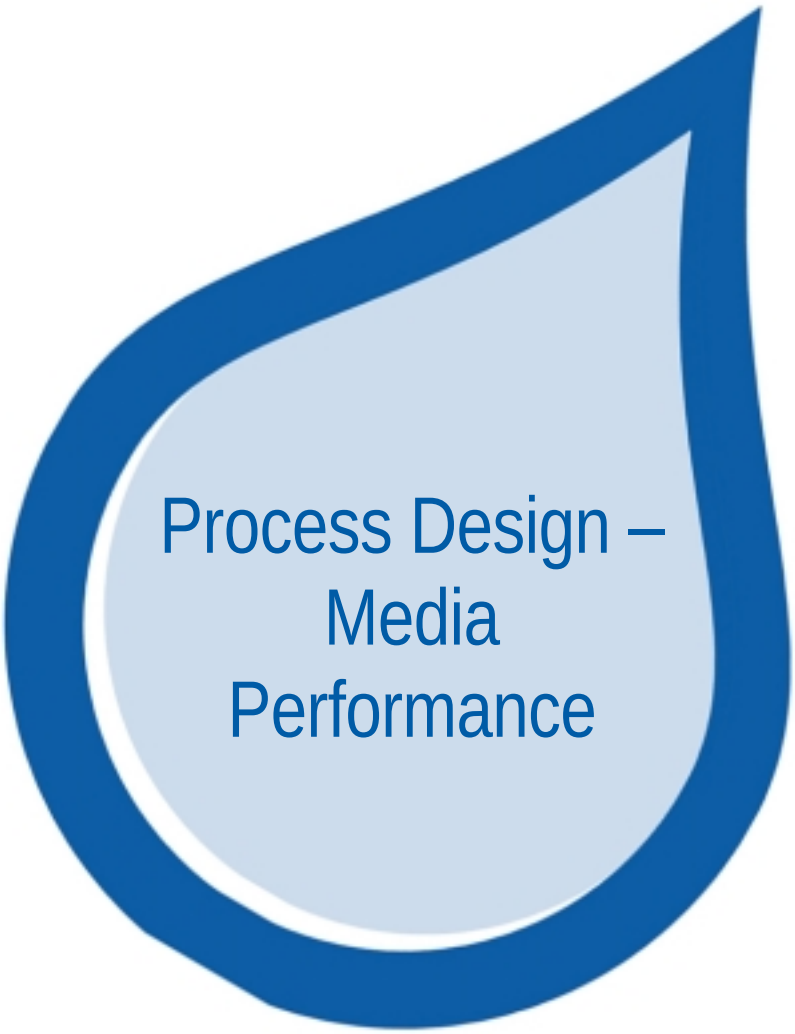
SESSION II



ADSORPTION MEDIA FOR ARSENIC REMOVAL

Darren A. Lytle, Jeremy M. Payne, Thomas J. Sorg
U.S. Environmental Protection Agency
ORD, NRMRL, WSWRD, TTEB,
Cincinnati, Ohio 45268

Lytle.darren@epa.gov

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Objective

- Introduce adsorption media used for arsenic removal
- List properties of arsenic adsorption media

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History

- Aluminum
  - Activated Alumina in use past 20-30 years
- Fe minerals adsorb Arsenic
  - Goethite, Hematite, Zero
- First iron based materials emerged in the 1990's
- Key – Produce a robust yet affordable material

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Properties that Impact Arsenic Removal

- Mineralogy
- Surface Area
- Zeta Potential (Point Zero Charge)
- Crystal Size
- Additives

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Fundamental Materials

- Alumina
  - Activated Alumina
  - Modified Alumina
- Iron
  - Iron Minerals
  - Iron Coated
- TiO_2
- Modified Zeolite
- Zirconium

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Disclaimer

- Mention of company or trade names does not imply U.S.EPA endorsement or the endorsement of the authors.

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Iron Based Media

Product	Manufacturer	Material
GFH	GEH Wasserchemie GmbH and Co. (USFilter)	$Fe(OH)_3$ and FeOOH Akagenéite (ß-FeOOH)
Bayoxide E33	Bayer (Severn Trent, AdEdge)	90% FeOOH (Goethite)
Media G2	ADI	Ferric hydroxide coated diatomite
ARM 200	Engelhard	(Hematite)
SMI-III	SMI	Sulfur modified iron

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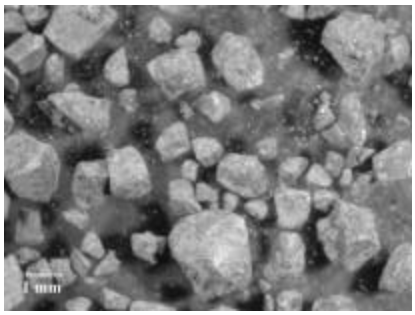
Granular Ferric Hydroxide (GFH)

- GEH Wasserchemie GmbH and Company (U.S. Filter)
- Akagenéite (ß-FeOOH)
- Commercially available
- NSF approved
- Shipped wet



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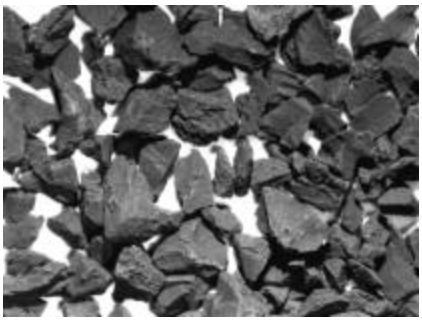
E33 Bayoxide

- Bayer (Severn Trent, AdEdge)
- Goethite (a-FeOOH)
- Commercially available
- NSF approved



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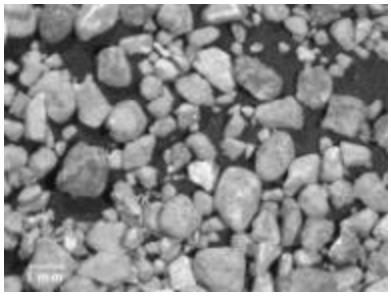
Media G2

- ADI International
- Ferric hydroxide coated calcined diatomite
- Commercially available
- NSF approved



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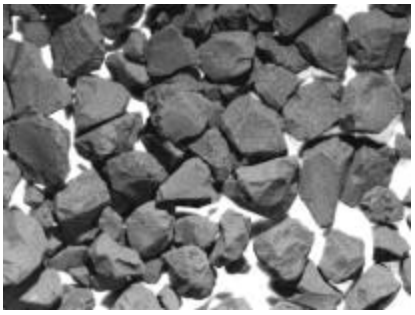
ARM 200

- Engelhard Inc.
- Hematite
- Commercially available
- NSF approved



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Alumina Based Media

Product	Manufacturer	Material
AA-400G	Alcan Chemicals	Activated Alumina
AA-FS50		Activated Alumina with proprietary additives (Boehmite-AlOOH)
ARM-100	Engelhard Inc.	Alumina with proprietary promoters
CPN-AA	Alcoa	Activated Alumina
Aqua-Bind EP	Apyron Technologies	Activated Alumina
Aqua-Bind MP	Apyron Technologies	Metal Oxide composite

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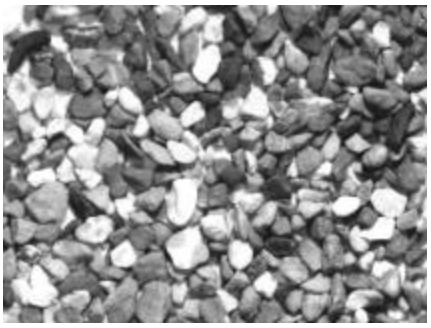
AAFS-50

- Alcan Chemicals
- Activated alumina Bohmite – AlO(OH)
- Commercially available
- NSF approved



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Other Media

Product	Manufacturer	Material
MetSorb	Hydroglobe	anatase (TiO_2)
As:X^{np}	McPhee Environmental	polystyrene
Z-33	Water Remediation Technology	Modified Zeolite
Isolux	Magnesium Elekton	Zirconium Hydroxide

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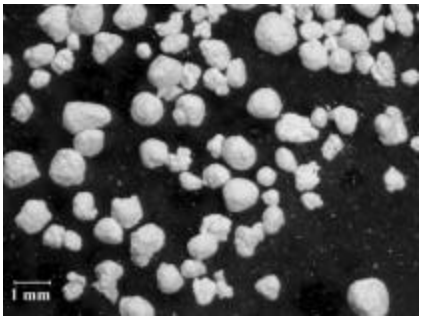
MetSorb

- Hydroglobe Inc.
- Microporus TiO_2 (Rutile)
- Commercially available
- NSF approved



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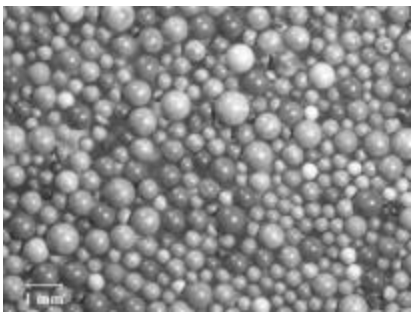
$As:X^{np}$

- Solometex (McPhee Environmental Supply)
- Porous polystyrene beads with iron oxide dopants
- Commercially available
- NSF approved



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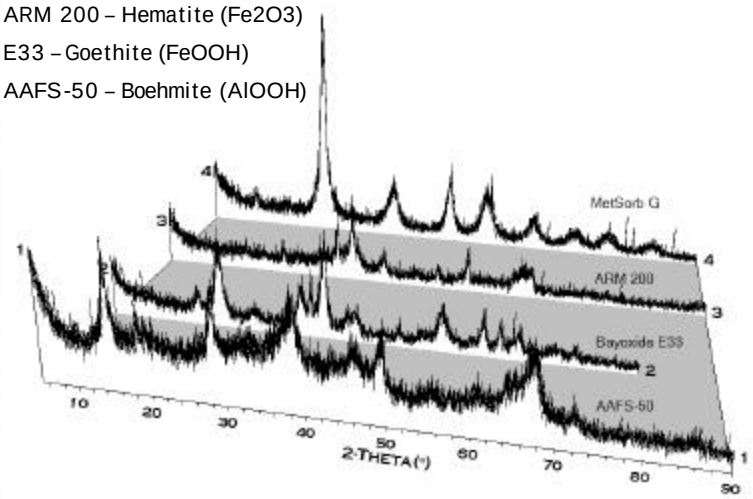
Mineralogy

MetSorb – Anatase (TiO2)

ARM 200 – Hematite (Fe2O3)

E33 – Goethite (FeOOH)

AAFS-50 – Boehmite (AlOOH)



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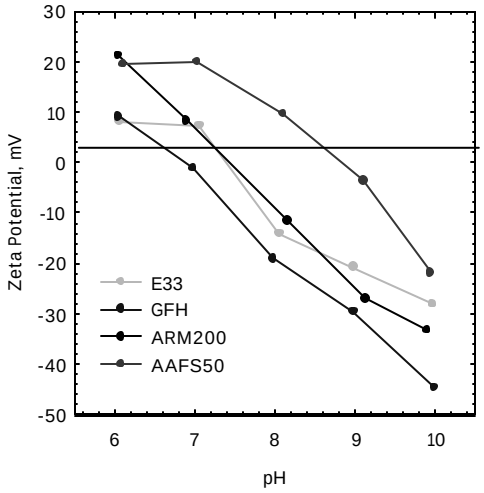
Zeta Potential



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Surface Area

Product	Material	BET surface Area (M^2/g)	Bulk Density (g/cm^3)
GFH	FeOOH (akagenéite)	(290.2)	1.25
AAFS-50	AlOOH (boehmite)	(240.4)	0.91
MetSorb G	TiO_2 (Anatase)	(205.8)	0.75
E33	FeOOH (goethite)	(140.2)	0.45
ARM 200	Fe_2O_3 (Hematite)	(138.0)	0.76
Media G2	FeOOH coated diatomite	(14.2)	0.75

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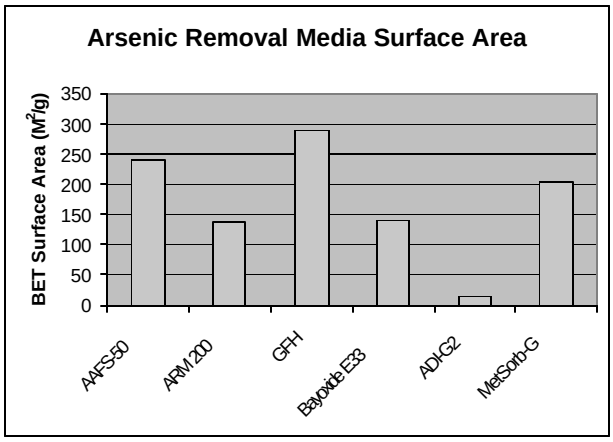
Surface Area



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Evaluation Criteria

- Cost
- Ability to reduce arsenic
- As(III) vs. As(IV)
- Bed Volumes before disposal/regeneration
- Competitive adsorption

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Evaluating Media

- Literature review
- Comparing other sites
- Bench/Pilot tests

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Conclusions

- Wide variety of base materials available
- Mineralogy, surface area, zeta potential differ
- Link between properties and arsenic removal are unclear
- Changing area of development

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Acknowledgments

- Battelle Memorial Institute
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- Christy Frietch
- Tim Hodapp
- Jessica Lewis

Arsenic Occurrence and Co-occurrence, Implications for Adsorptive Media Treatment

Phil Brandhuber[1]
Nicole Graziano[2]

[1]HDR Engineering
[2]McGuire Environmental Consultants

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What is Occurrence and Co-occurrence? Why do we Care?

- Arsenic occurrence
  - How much arsenic is present and where
- Arsenic co-occurrence
  - What other contaminants are present in waters containing arsenic
- Adsorptive media treatment performance sensitive to water quality

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What do we Know About Arsenic Occurrence and Co-occurrence?

- Arsenic occurrence
  - AWWA, National Arsenic Occurrence Survey (Frey et.al)
  - USGS, Arsenic Occurrence Analysis (Welsh et.al)
- Contaminant co-occurrence
  - EPA, Co-occurrence of Drinking Water Contaminants (SAIC)

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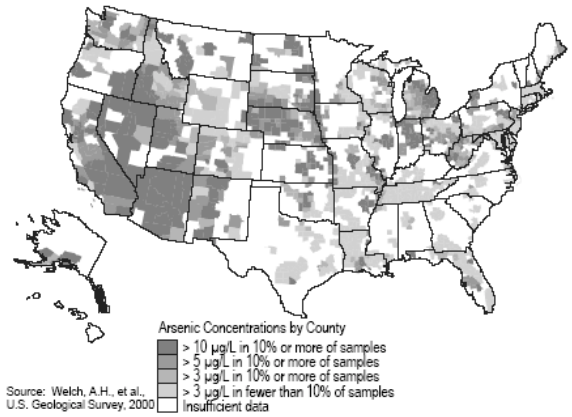
Arsenic Occurrence – USGS Study



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Objectives of AwwaRF Occurrence and Co-occurrence Analysis

- Part of AwwaRF Project 2731
  - Evaluate arsenic occurrence on a geophysical basis
  - Understand range of concentrations of water quality parameters which co-occur with arsenic
  - Provide guidance on conditions to evaluate performance of adsorptive media

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Features of Analysis

- Retrospective
  - use existing USGS NWIS data
- Limited to groundwater
- Geographically dispersed and geologically varied
- Focused on waters suitable for consumption with appropriate treatment
- Contained in a data base

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Data Base Development

Step 1
Extract suitable NWIS groundwater records for arsenic and co-occurring parameters

⇩

Step 2
Eliminate duplicate records and purge stations which are not of drinking water quality

⇩

Step 3
Treat records recorded as non-detect (ND)
- Eliminate ND's whose detection levels (DL) are too high to be meaningful
- Eliminate ND's recorded as 0 or where DL's are unreasonably low
- For use in statistical analysis, estimate values of remaining ND's at 0.5 x DL

⇩

Step 4
Create "Groundwater Arsenic Co-occurrence Database"

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Criteria for Inclusion in Data Base

USGS	AwwaRF
Arsenic analytical method	Reported detection limit
Filtered arsenic	Unfiltered arsenic
Single analysis at site	Mean value at site
• Exclude sites (arsenic) – > 50ºC – TDS > 2000 mg/L	• Exclude sites (arsenic) – Failed arsenic QC – Unacceptable co-occurring contaminant water quality – Geologic event sampling

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Data Acceptance Criteria

Parameter	Unit	Acceptable Data		Acceptable Detection Limit
		Minimum	Maximum	
Alkalinity	mg/L	2	1000	-
Arsenic	ug/L	0.5	150	≤10
Calcium	mg/L	0.5	500	≤1
Chloride	mg/L	0.5	500	≤10
Fluoride	mg/L	0.1	10	≤0.1
Iron (dissolved)	ug/L	5	8000	≤10
Iron (total)	ug/L	5	8000	≤10
Potassium	mg/L	0.5	50	≤1
Magnesium	mg/L	0.1	100	≤0.1
Manganese (dissolved)	ug/L	1	1500	≤10
Manganese (total)	ug/L	2	1500	≤10
Sodium	mg/L	0.3	500	≤10

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Data Acceptance Criteria

Parameter	Unit	Acceptable Data		Acceptable Detection Limit
		Minimum	Maximum	
Nitrate	mg/L	0.1	50	≤1
pH	-	0	14	-
Phosphate (total)	ug/L	0.1	500	≤0.1
Selenium	ug/L	.5	200	≤10
Silica	mg/L	0.1	150	≤0.1
Sulfate	mg/L	2	500	≤10
TDS	mg/L	10	1500	-
Temperature	ºC	0	50	-
Total Hardness	mg/L	10	1000	-
Well Depth	feet	N/A	N/A	-
Chromium (total)	ug/L	1	500	≤10

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AwwaRF Groundwater Arsenic Co-occurrence Database

- Robust database of groundwater arsenic occurrence and co-occurrence
  - 9867 total sites
    - 8414 sites; mean As < 5 ug/L
    - 963 sites; mean 5 ug/L ≤ As < 20 ug/L
    - 490 sites; mean As ≥ 20 ug/L
  - 8546 sites with co-occurrence data
- 44 of 50 states represented in database

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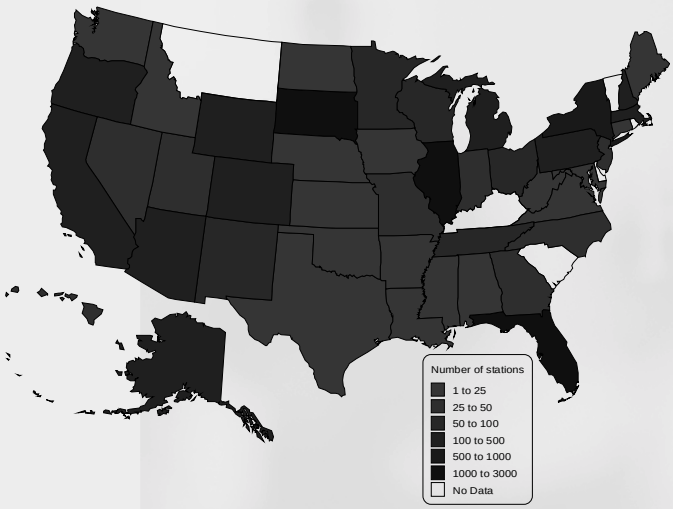
Number of Sites in Database by State



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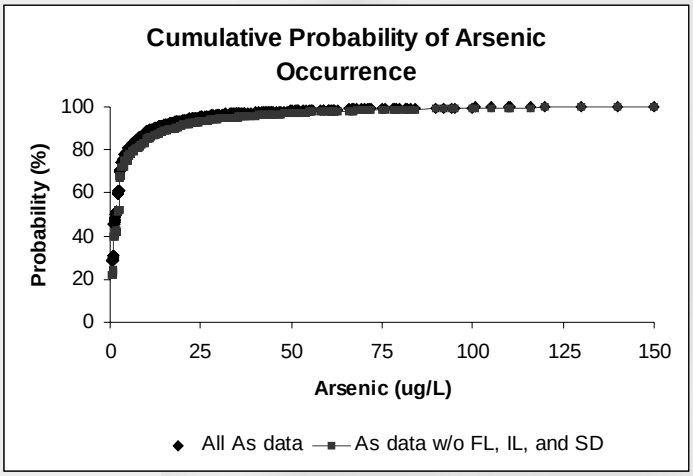
Cumulative Probability Distribution of Arsenic in Groundwater - all Sites



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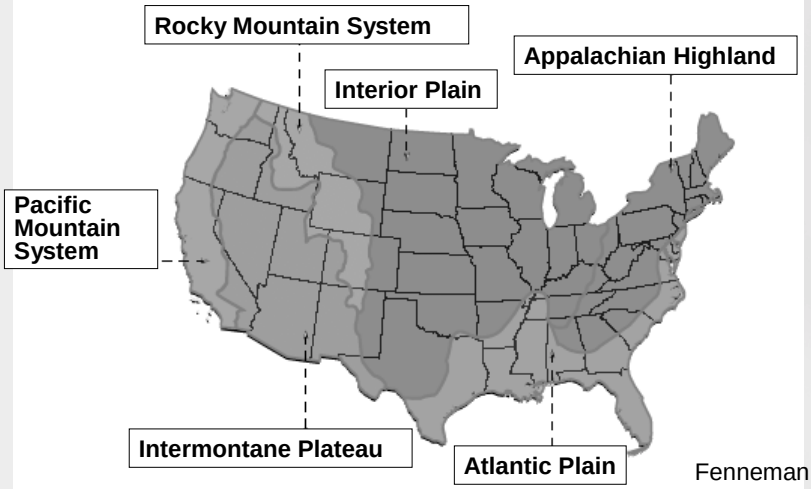
Physiographic Regions of the US



Fenneman 1931

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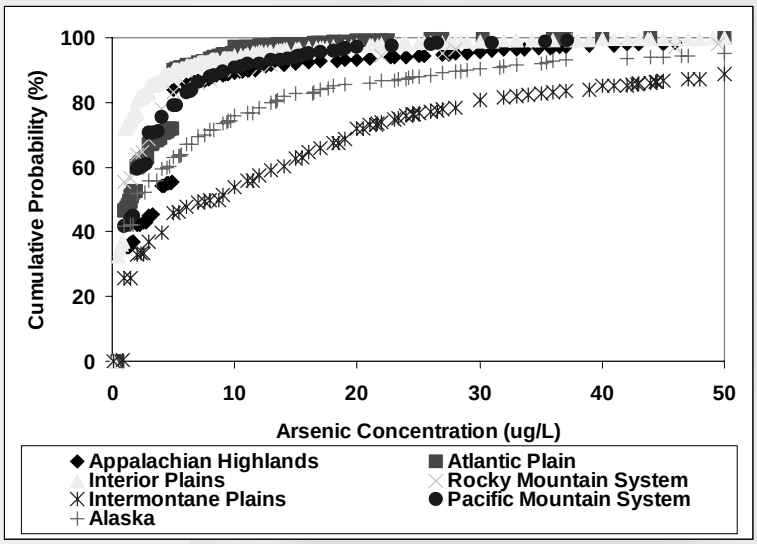
Arsenic Occurrence by Physiographic Region



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Comparison of AwwaRF and USGS Analysis

Arsenic concentration in ug/L

Region	USGS			AwwaRF		
	Sites	Mean	Median	Sites	Mean	Median
Appalachian	2212	3	1	701	6	4
Atlantic	2047	2	1	2155	3	1
Interior	3947	5	1	5505	3	1
Rocky Mt	1028	7	1	108	6	1
Intermontane	4640	15	3	591	18	9
Pacific	2401	9	2	343	5	2
Alaska	-	-	-	418	11	2
Hawaii	-	-	-	46	-	-
Total	16275			9867		

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Binning of Arsenic Occurrence

Bin	Range	Description
1	As < 5 ug/L	Low Arsenic
2	5 ug/L ≤ As < 20 ug/L	Moderate Arsenic
3	As ≥ 20 ug/L	High Arsenic

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50th Percentile Concentration of Co-occurring Parameters

Parameter	Unit	Arsenic Bin			Trend
		Low As	Moderate As	High As	
Alkalinity	mg/L $CaCO_3$	262	246	286	⇨
Calcium	mg/L	53	55	43	◐
Chloride	mg/L	20	31	33	⇨
Fluoride	mg/L	0.2	0.3	0.5	⇨
Hardness	mg/L $CaCO_3$	140	204	197	⇨
Iron (dissolved)	ug/L	80	385	120	⇨
Iron (total)	ug/L	99	1656	2016	⇨
Magnesium	mg/L	13	12	18	⇨
Manganese (dissolved)	ug/L	20	30	30	⇨

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50th Percentile Concentration of Co-occurring Parameters

Parameter	Unit	Arsenic Bin			Trend
		Low As	Moderate As	High As	
Manganese (total)	ug/L	17	44	45	⇨
pH	-	7.3	7.7	7.8	⇨
Phosphate	mg/L P	0.05	0.13	0.34	⇨
Potassium	mg/L	2	2.5	4	⇨
Silica	mg/L SiO_2	10	14	18	⇨
Sodium	mg/L	30	43	87	⇨
Sulfate	mg/L	22	27	31	⇨
TDS	mg/L	374	389	436	⇨
Temperature	° C	13.5	14	14	⇨

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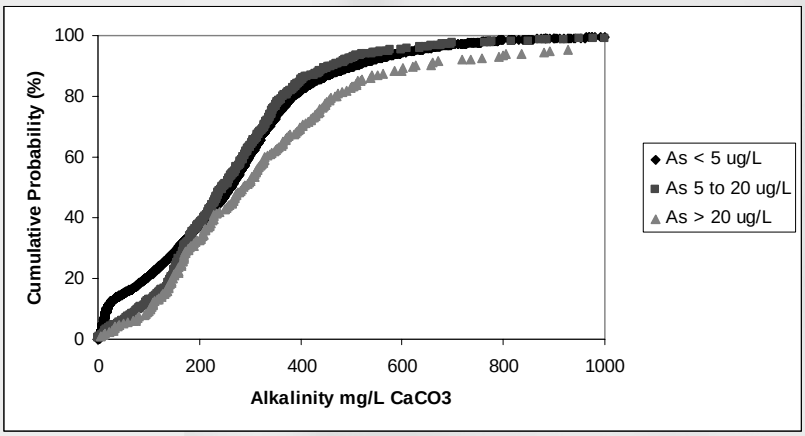
Cumulative Probability Distribution of Alkalinity by Binned Arsenic Concentration



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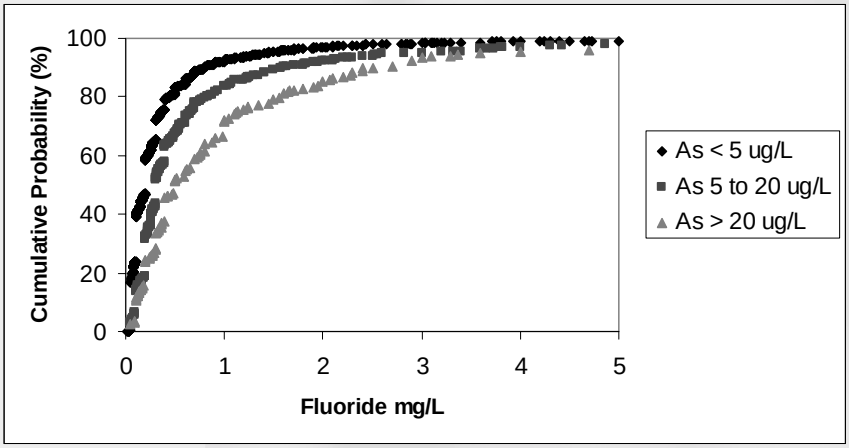
Cumulative Probability Distribution of Fluoride by Binned Arsenic Concentration



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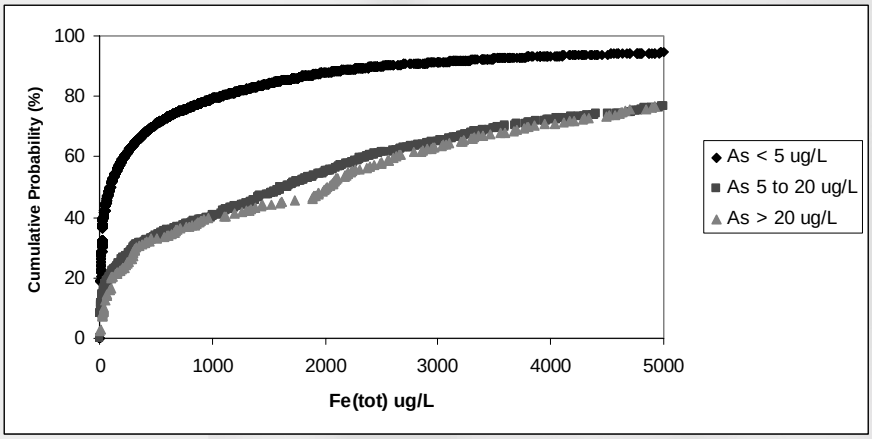
Cumulative Probability Distribution of Iron(total) by Binned Arsenic Concentration



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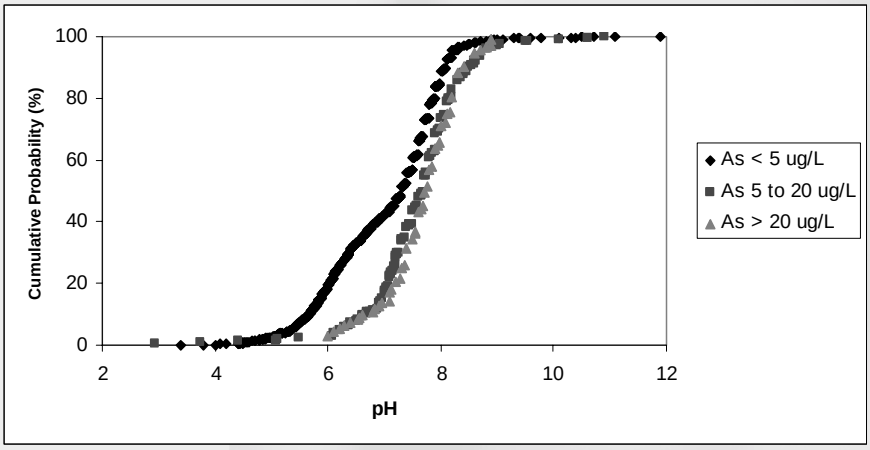
Cumulative Probability Distribution of pH by Binned Arsenic Concentration



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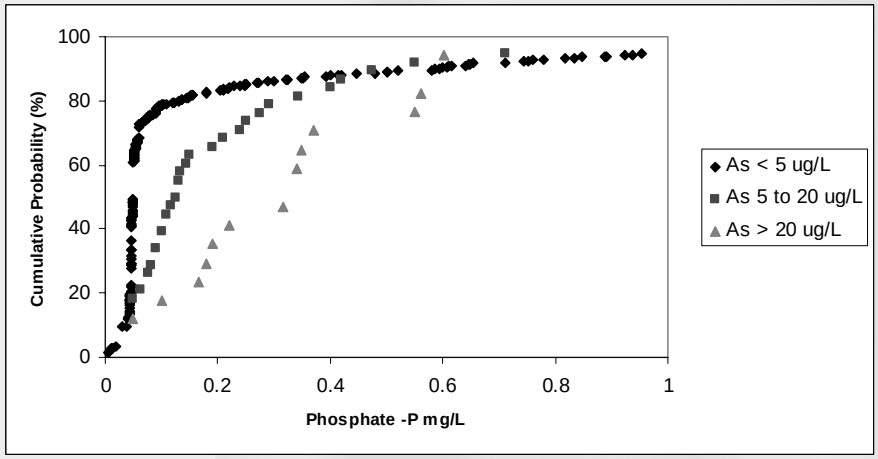
Cumulative Probability Distribution of Phosphate by Binned Arsenic Concentration



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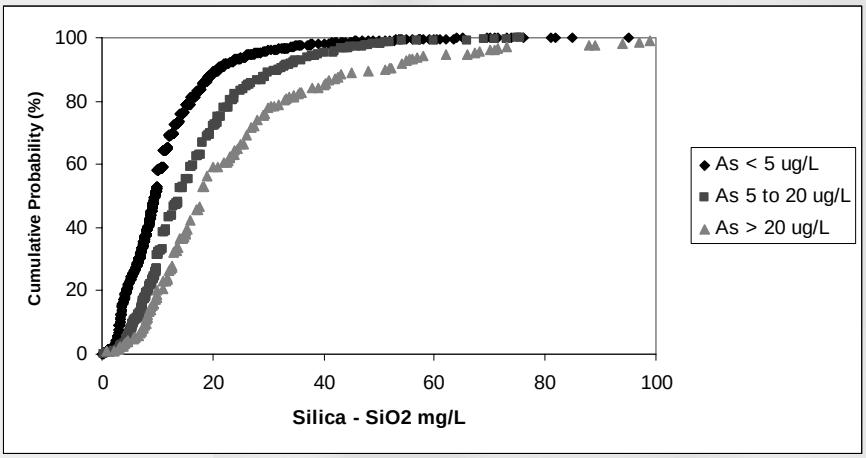
Cumulative Probability Distribution of Silica by Binned Arsenic Concentration



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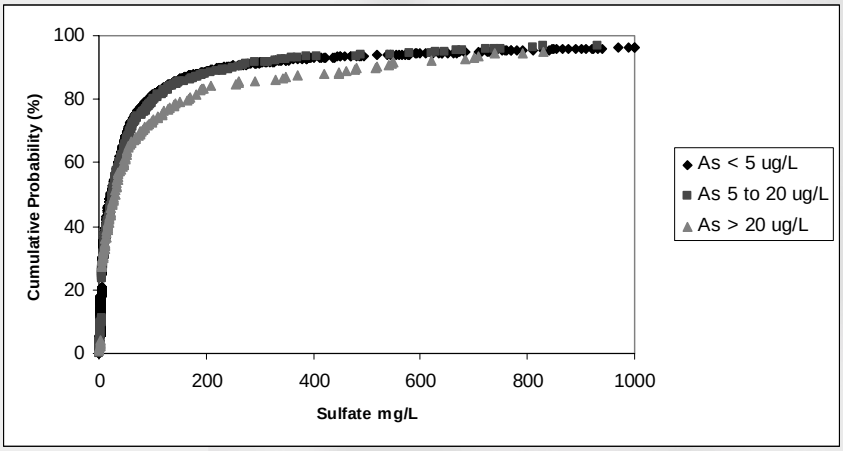
Cumulative Probability Distribution of Sulfate by Binned Arsenic Concentration



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Comparison of NSF Challenge Water to Co-occurrence Data

Parameter	Unit	NSF Water	Moderate As Water		
			50th	75th	90th
Sodium	mg/L	74	43	120	330
Calcium	mg/L	40	55	106	174
Magnesium	mg/L	13	12	26	50
Alkalinity	mg/L –CaCO3	150	246	344	466
Chloride	mg/L	71	31	84	273
Fluoride	mg/L	1	0.3	0.7	1.6
Sulfate	mg/L	50	27	79	260
Nitrate	mg/L -N	2	1	5.3	14.8
Phosphate	mg/L -P	0.12	0.13	0.28	0.55
Silica	mg/L – SiO2	20	14	21	32
TDS	mg/L	307	374	572	1090

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Summary

- Co-occurrence database developed from retrospective analysis of USGS data
- Quality of arsenic bearing water differs from non-arsenic bearing waters
- NSF challenge water is roughly representative of a 50th percentile co-occurring water
  - Media may see more aggressive conditions at many locations

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Acknowledgements

- Project Funding – AwwaRF
  - Traci Case and PAC
- University of Colorado
  - Gary Amy
- MEC
  - Ruth Hund

Most of the project was performed while employed by McGuire Environmental Consultants

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Media Performance: Laboratory Studies (Impact of Water Quality Parameters on Adsorbent Treatment Technologies for Arsenic Removal)

Gary Amy[1], Hsiao-Wen Chen[1],
Urs von Gunten[2], Martin Jekel[3], Kashi Banerjee[4]
[1]University of Colorado USA
[2]EAWAG SWITZERLAND
[3]Technical University – Berlin GERMANY
[4]USFilter USA

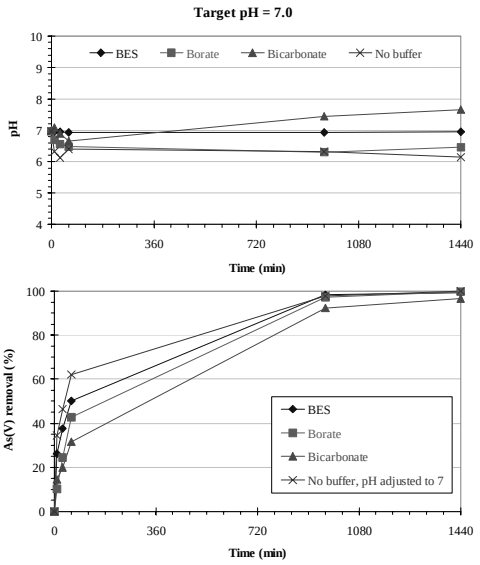
Experimental Approach

- Batch Tests
  - Preliminary Screening of Candidate Adsorbents
    - Selection of Non-Adsorbing Buffer
    - Kinetics (contact time)
    - Isotherms (absence of interferants)
  - Intensive Testing of Selected Adsorbents
    - Physical-Chemical Properties of Adsorbents
    - Isotherms (presence of interferants)
    - NSF Challenge Water and Utility-Supplied Waters
- Column Tests
- TCLP/WET Tests

Preliminary Screening Experiments – Candidate Adsorbents

- AA-400G (activated alumina (AA))
- AA-FS50 (iron impregnated AA)
- MIEX (amagnetized ion exchange resin)
- Bayoxide E33 (granular ferric oxide (GFO))
- Granular Ferric Hydroxide (GFH)
- Metsorb (titanium dioxide)
- Z33-Revision B (iron modified zeolyte)
- ARM 100 (alumina based, with proprietary promoters)
- Sulfur Modified Iron Version III (SMI)
- ViroClear Bauxsol F3 (Bauxite Clay)
- Geothite (α-FeOOH)
- Pyrolusite (β-MnO_2)

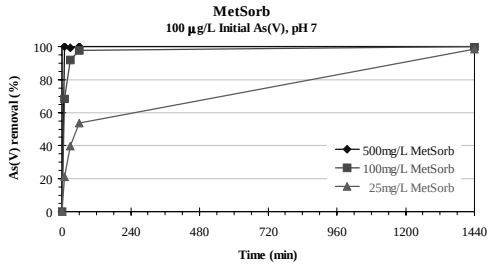
Non-Adsorbing Buffer (w/ GFH)

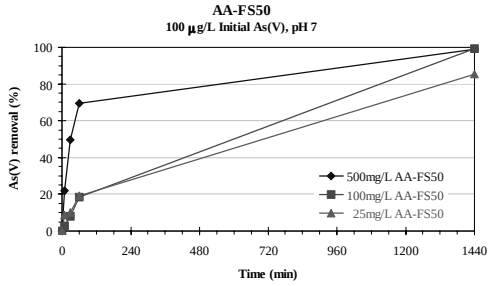


None (Milli-Q)
Bicarbonate
Borate
BES
(N,N-Bis(2-hydroxyethyl)-2-aminoethanesulfonic Acid)

2 mM BES Buffer

Kinetics



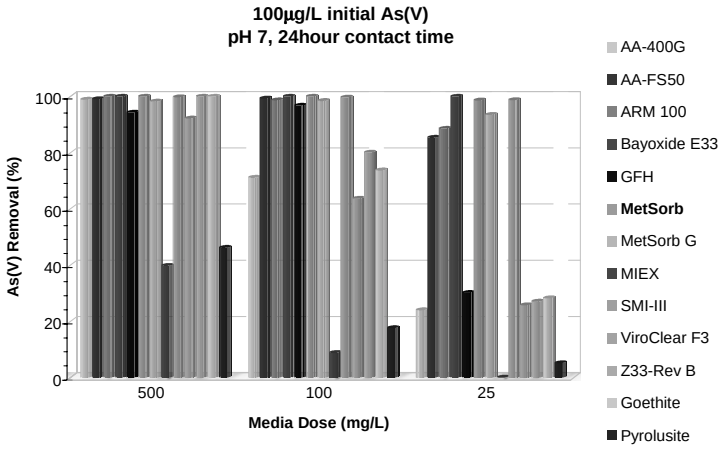


Rapid Kinetics:
Bayoxide E33
ARM 100
Metsorb
MIEX
Pyrulosite

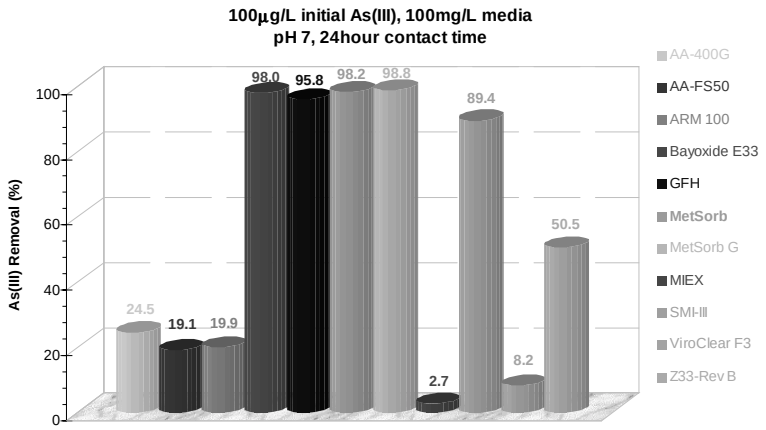
24 hours ⇨ Pseudo-Equilibrium

Slower Kinetics:
AA-400G
AA-FS50
GFH
Z33
Goethite

Preliminary Screening Experiments – % Removal of As(V) by Candidate Adsorbents



Preliminary Screening Experiments – % Removal of As(III) by Candidate Adsorbents



Intensive Testing – Selected Adsorbents

- Bayoxide E-33
- GFH
- MetSorb G
- AA-FS50
- Z33 (Revision b)

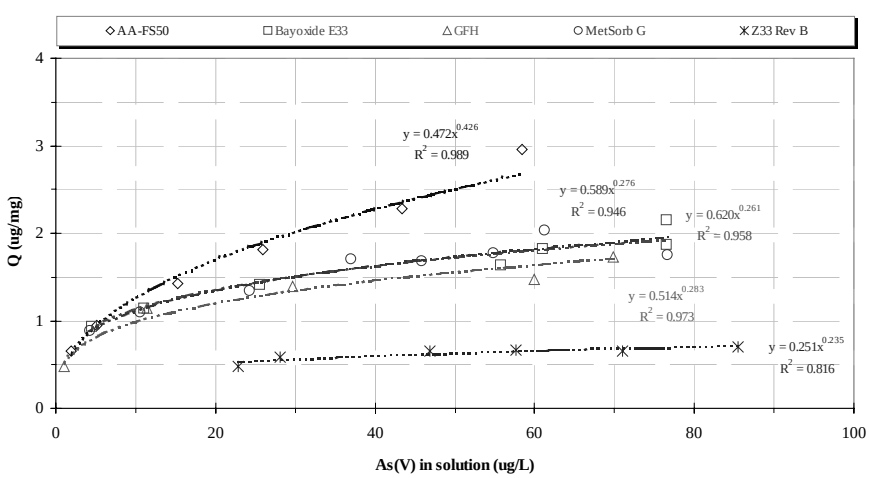
Criteria: As(V) capacity, As(III) capacity, and other factors

Physical/Chemical Properties of Adsorbents

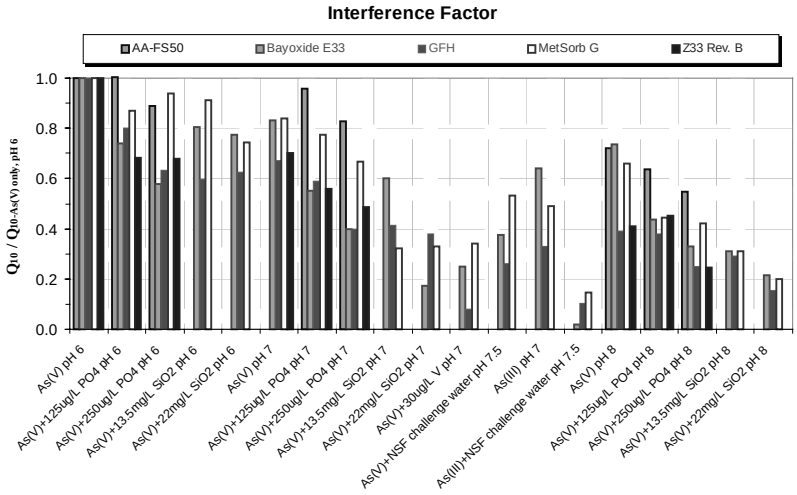
Adsorbent	Property				
	Grain Size (mm or mesh)*	Bulk Density (g/mL)	pH_{ZPC}	Surface Area (m^2/g) (BET)	Mineral Identity (by XRD)
AA-FS50	28-48 mesh	0.75 (dry)	7.28	246	Aluminum oxide Hydrate (Boehmite)
E33	0.5 – 2.0 mm (10-35 mesh)	1.19 (wet)	8.28	119	Iron oxide hydrate (Goethite)
GFH	0.32 - 2.0 mm	1.19 (wet)	7.57	242	Iron oxide (Akaganeite)**
Metsorb G	16 – 50 mesh	0.78 (dry) 0.88 (wet)	4.68	166	Titanium oxide (Anatase)
Z33	100-140 mesh	0.88	4.79	36.9	Calcium aluminum silicate hydrate (Heulandite)
SMI	n/a	2.15	n/a	4.46	n/a

*10 mesh = 0.1 inches = 0.254 cm = 2.54 mm
**Traces of Hematite and Geothite also identified in contrast to previous studies

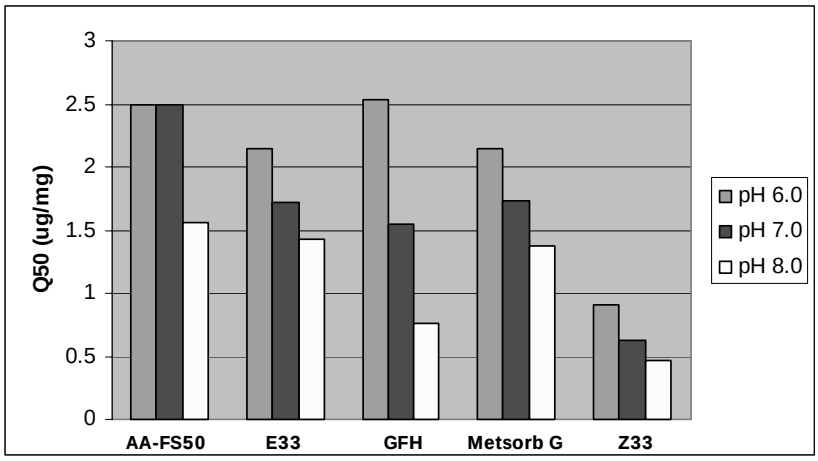
As(V) Adsorption Isotherms @ pH 7.0
(Single Solute)



Summary of Interference Factors (Ratio of As(V) Capacity to that at pH 6.0 in the Absence of Interferents)



As(V) Adsorption: pH Effects on Q_{50} (Q_{50} in equilibrium with C = 50 ug/L)

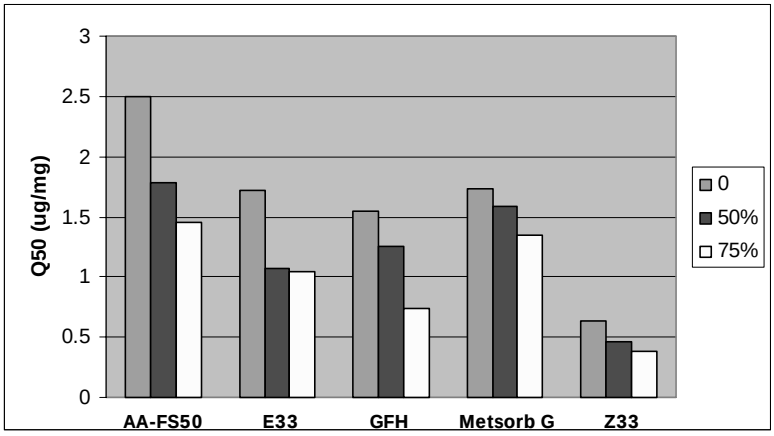


Concentrations of Interferents based on U.S. Co-Occurrence Survey

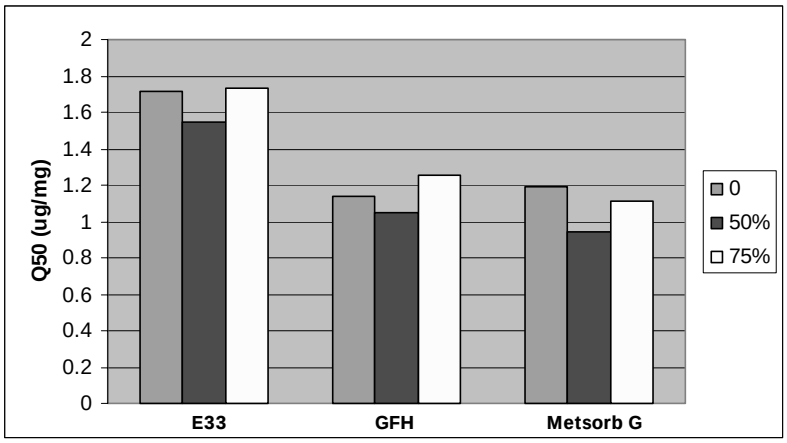
Component*	Units	50 Percentile Concentration	75 Percentile Concentration
Phosphate	ug/L as PO_4^{3-}	125	250
Silicate	mg/L as SiO_2	13.5	22
Vanadate	ug/L as V	18	30

*Others: Fluoride, Sulfate, Carbonate

As(V) Adsorption: PO_4^{3-} Effects @ pH 7.0

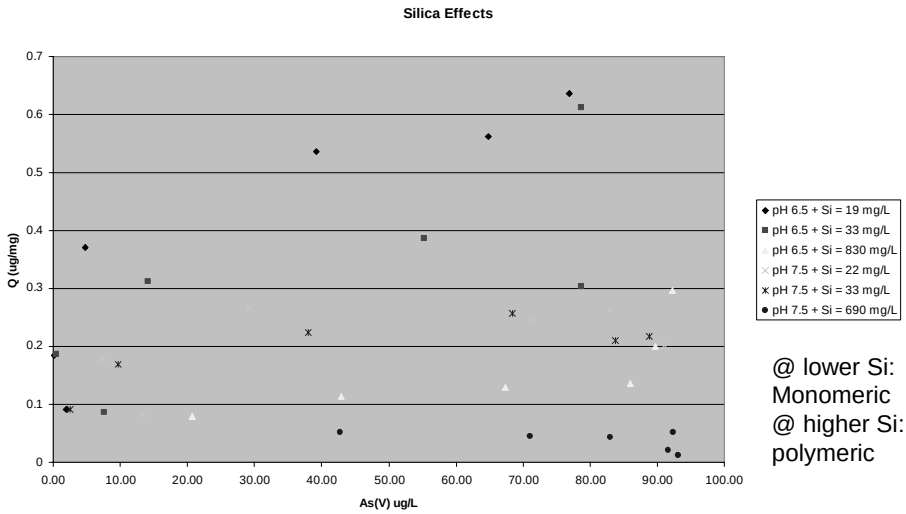


As(V) Adsorption: SiO_2 Effects @ pH 7.0



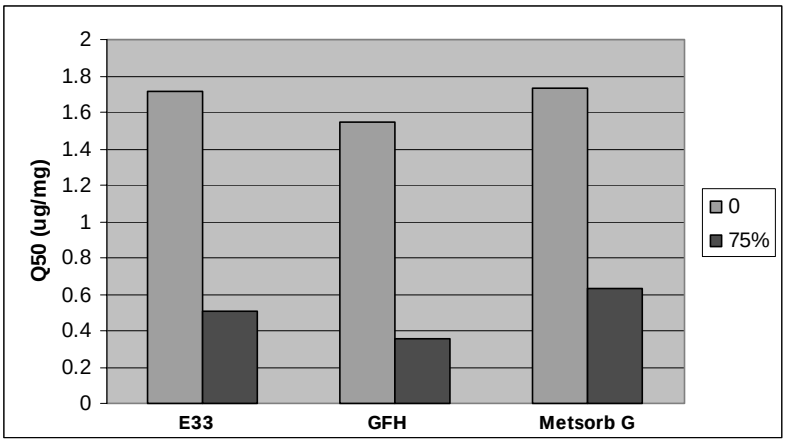
Monomeric vs. Polymeric Silica?

Isotherms for GFH with As(V) at Varying pH Levels and Silica Concentrations

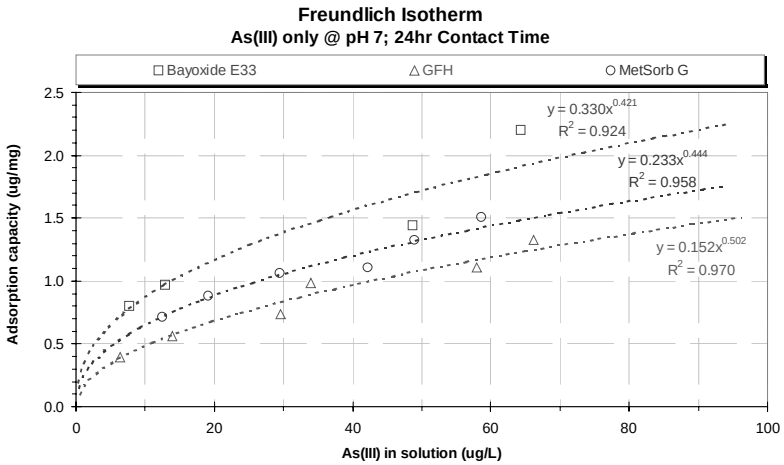


@ lower Si: Monomeric
@ higher Si: polymeric

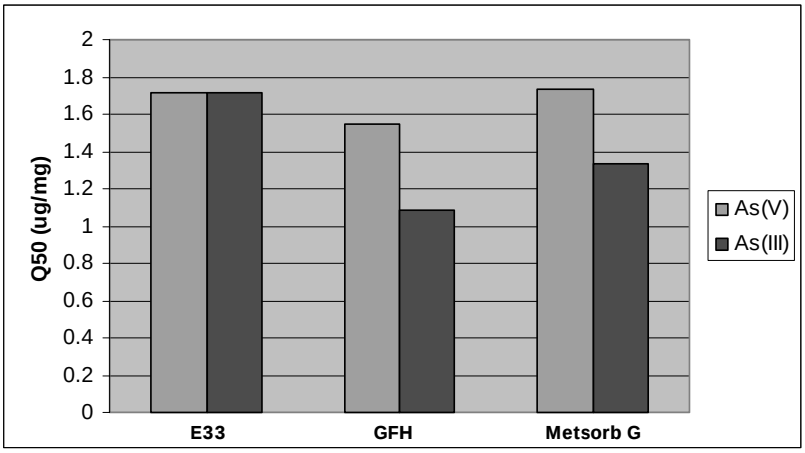
As(V) Adsorption: V Effects @ pH 7.0



Isotherms for As(III) at a pH of 7.0: Absence of Interferants.



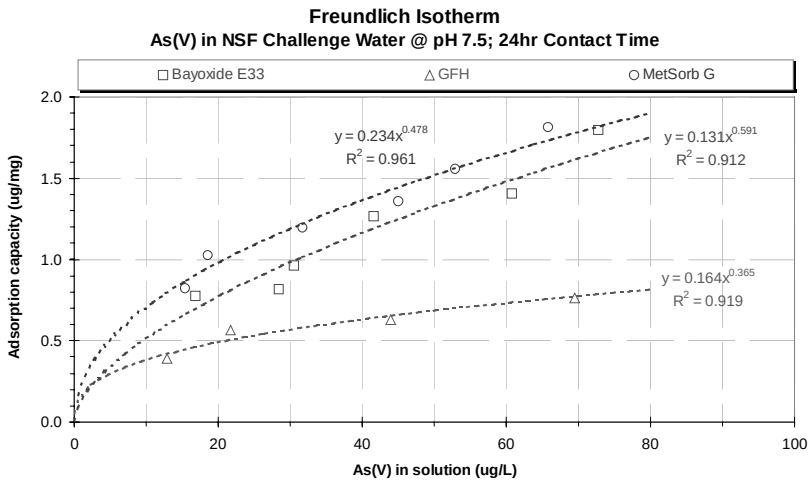
As(V) vs. As(III) Adsorption @ pH 7.0



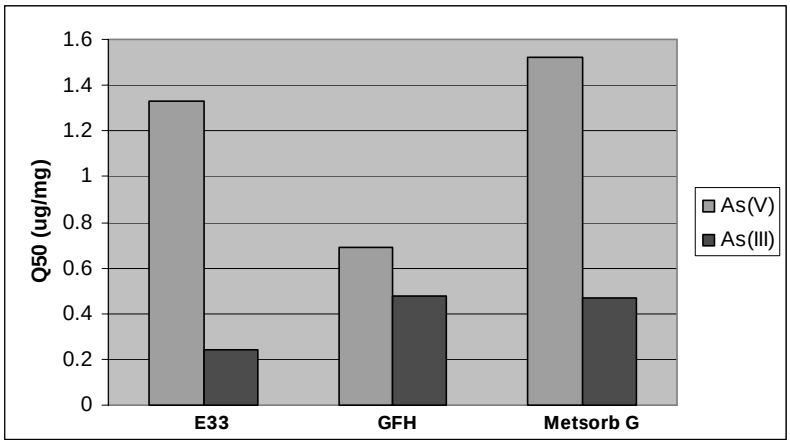
Ionic Composition of Standardized (NSF) Challenge Water (pH = 7.5)

Component	Concentration (mg/L)	Component	Concentration (mg/L)
Na^+	74	SO_4^{2-}	50
Ca^{2+}	40	NO_3^--N	2.0
Mg^{2+}	13	F^-	1.0
HCO_3^-	183	PO_4^{3-}-P	0.04
Cl^-	71	SiO_2	20

Isotherms for As(V) in NSF *Challenge* Water



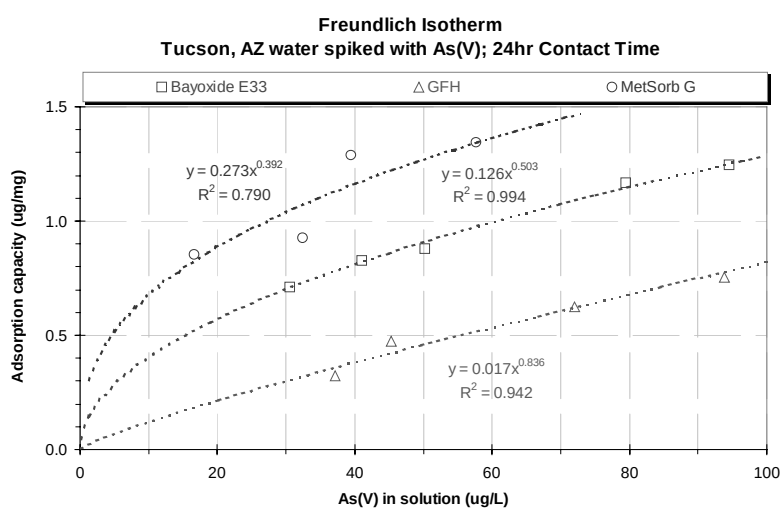
As(V) vs. As(III) Adsorption: NSF Test Water



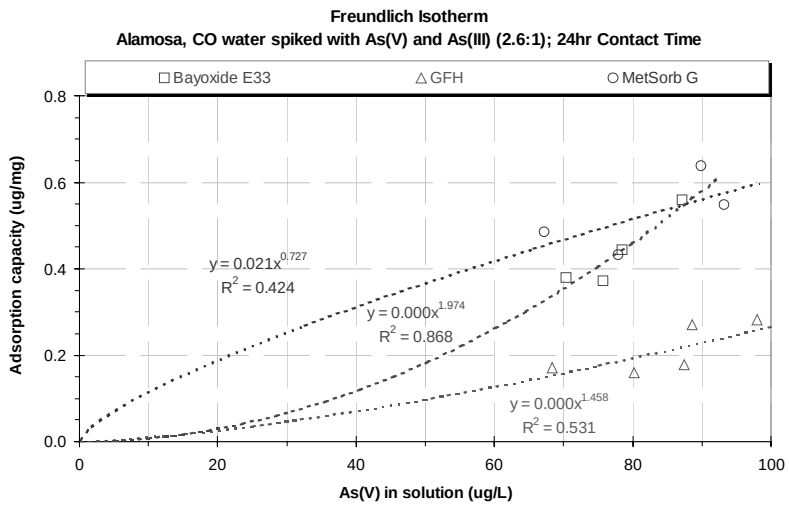
Water Quality Summary of Utility-Supplied Waters

Parameter	Water			
	Tucson AZ	LADWP CA	El Paso TX	Alamosa CO
V (ug/L)	66	5	6	125
SiO_2 (mg/L)	28	28	28	93
PO_4^{3-} (ug/L)	18	78	35	26
pH	7.9	7.7	8.5	8.3
As_{total} (ug/L)	12.6	25.6	22.9	40.9
As(V) (ug/L)	12.6	25.6	12.4	29.6
As(III) (ug/L)	0	0	10.5	11.4

Isotherms for Utility-Supplied Water: Tucson AZ Groundwater



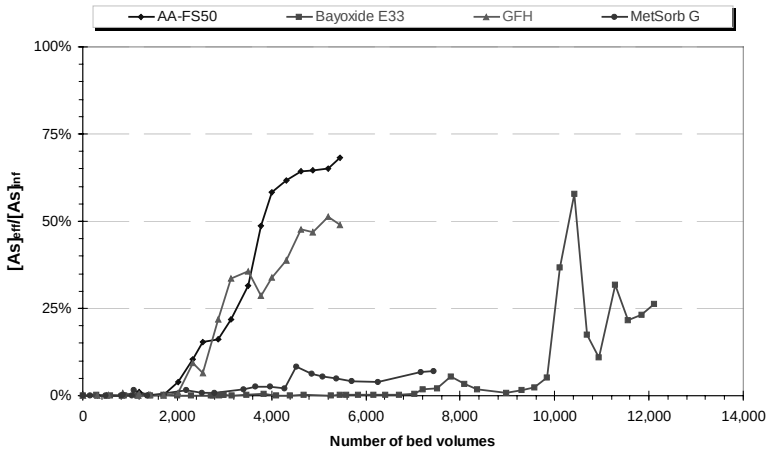
Isotherms for Utility-Supplied Water: Alamosa CO Groundwater



Experimental Conditions Employed in Column Tests

	Adsorbent			
	Bayoxide E33	AA-FS50	GFH	Metsorb G
EBCT (min)	5	5	5	5
HLR (cm/min)	8.2	4.1	2.0	2.0
D (cm)	40	20	10	10
A (cm^2)	1.3	5.1	5.1	1.3
Media mass (g)	20	110	59	9.3
BV/hour	12	12	12	12
$As(V)_0$ (ug/L)	250	1,000	1,000	1,000

Breakthrough Curves (BTCs) for Column Tests with NSF Challenge Water



Column-mode versus Batch-mode Capacities

Adsorbent	Column-Mode (ug/mg) (integration of BTC)	Batch-Mode (ug/mg) (Q_{100} from isotherm)
Bayoxide E33	6.55	1.99
AA-FS50	3.46	n/a
GFH	3.51	0.87
Metsorb G	9.44	2.11

•High initial As concentration in column tests
•24-hour psuedo-equilibrium time in batch tests
(inadequate in establishing true equilibrium for porous adsorbents?)
•another mechanism of As(V) removal other than adsorption (e.g., surface precipitation)

TCLP and WET results for spent media from column tests

	TCLP As (ug/L)		WET As (ug/L)	
	Avg	Std dev	Avg	Std dev
Bayoxide E33	0.3	0.0	88	1.4
GFH	0.1	0.2	1023	32
AA-FS 50	12.8	1.1	1337	37
Metsorb	1.6	0.1	129	13

Summary

- Each Adsorbent Independently
  - AA-FS50 showed moderate decrease in capacity as pH increased, significant decrease in capacity in the presence of fluoride (results not shown), and small impact by phosphate
  - Bayoxide E33 media showed only slight pH effect but exhibited significant impacts by phosphate and vanadium with some silica effects
  - GFH showed a decrease in performance as pH increased, with phosphate, silica, and vanadium exhibiting adverse effects
  - MetSorb G showed a decrease in performance as pH increased, with phosphate, silica, and vanadium exhibiting effects, although the interferent effects were less at lower pH
  - Z33 performance decreased as pH increased and phosphate had a significant effect

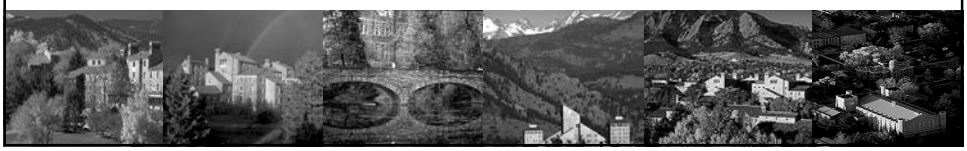
Summary – cont.

- Adsorbent Comparisons
  - The two iron oxide media (Bayoxide E33 and GFH) and Metsorb G generally showed comparable capacities although GFH performance dropped sharply at highest pH; interferant effects were lowest for Metsorb G (pH_{ZPC}: E33 > GFH)
  - The iron-modified activated alumina (AA-FS50) showed higher capacity than the two iron oxide media and Metsorb G at lower pH, but a lower capacity at higher pH, indicating more of a pH dependency
  - The iron-modified zeolite (Z33) generally exhibited the lowest capacity (lowest specific surface area)
  - As(III) capacity:
    - As(V) > As(III)
    - E33 > Metsorb G > GFH

Acknowledgements

- AWWA Research Foundation
- U.S. EPA
- Phil Brandhuber HDR (MEC)

gamy@spot.colorado.edu



MEDIA PERFORMANCE: LABORATORY AND PILOT STUDIES

Xiaoguang Meng, Sunbaek Bang
Maria E. Pena, and Chuanyong Jing, George Korfiatis
Stevens Institute of Technology
Center for Environmental Systems,
Hoboken, NJ 08904, xmeng@steven.edu

Manish Patel
New Jersey Department of Environmental Protection
P.O. Box 409, Trenton, NJ 08625

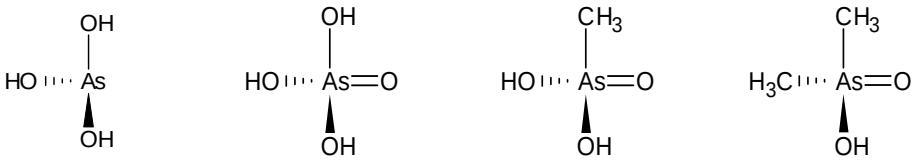
Overview

1. Basics of As adsorption by metal oxides and hydroxides
2. Batch adsorption results
3. Laboratory filtration results for removal of As(V) from the challenge water
4. Field pilot filtration results for removal of As(V) and As(III)
5. Field pilot filtration results for removal of As(III), As(V), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA)

Adsorbents Tested

1. Granular TiO_2
2. Granular ferric oxide (GFO)
3. Granular ferric hydroxide (GFH)
4. Activated alumina (AA)
5. Iron-modified activated alumina

Common Arsenic Species



As(III) As(V) MMA DMA

Parameters affecting As removal

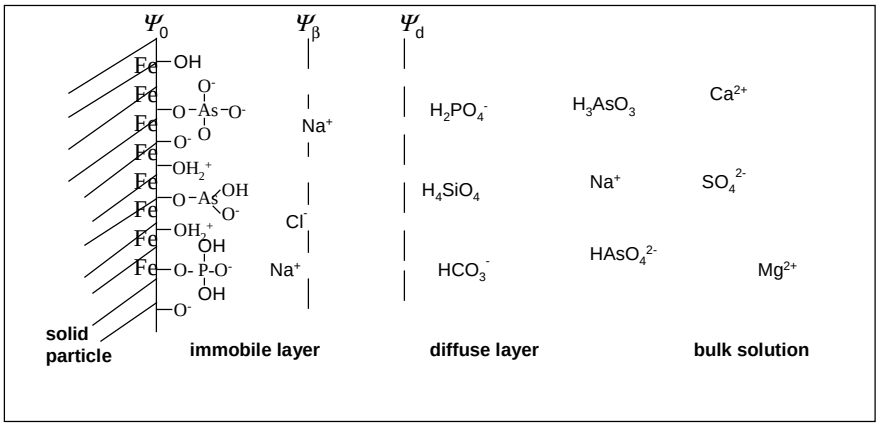
Properties of adsorbents

1. Activity and content of surface sites:
   Ti-OH, Fe-OH, Al-OH
1. Surface potential
   (pH_{ZPC}:TiO_2=5.8, α-FeOOH=7.8, α-Al_2O_3=9.1)
3. Specific surface area
4. Particle sizes
5. Pore size distribution

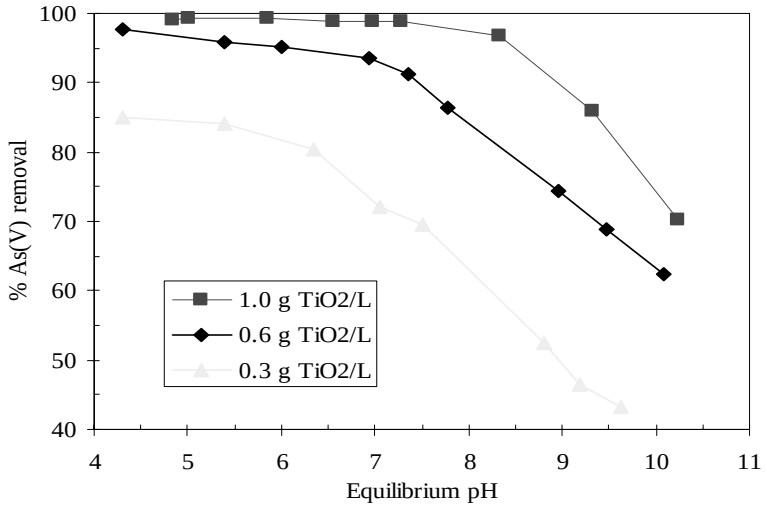
Water chemistry

- ⌘ pH
- ⌘ Phosphate, silicate, bicarbonate

Surface Adsorption Model

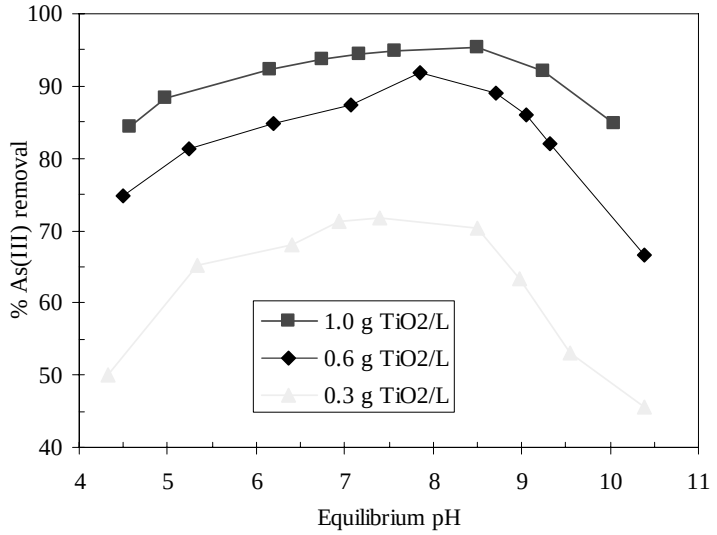


Batch Adsorption of As(V) by TiO_2



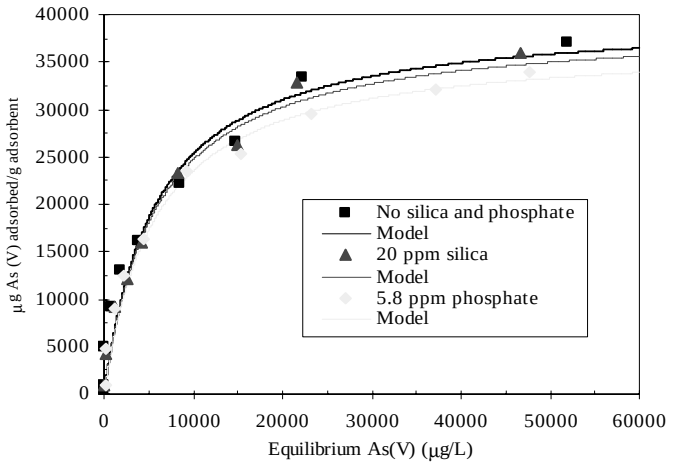
As=300 μg/L in spiked groundwater, mixing time=2 hr

Batch Adsorption of As(III) by TiO_2



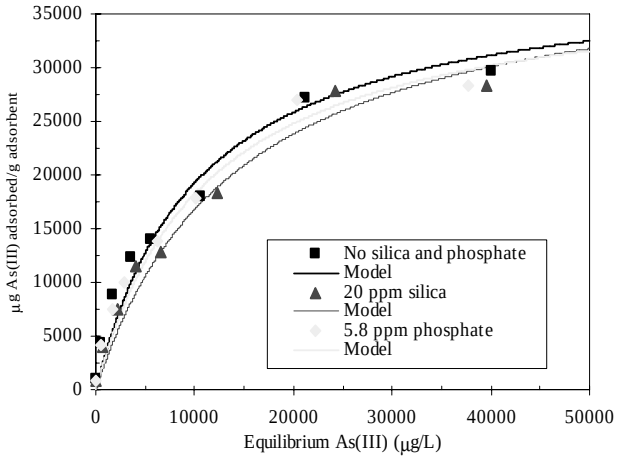
As=300 μg/L in spiked groundwater, mixing time=5 hr.

Effect of Si and P on As(V) adsorption



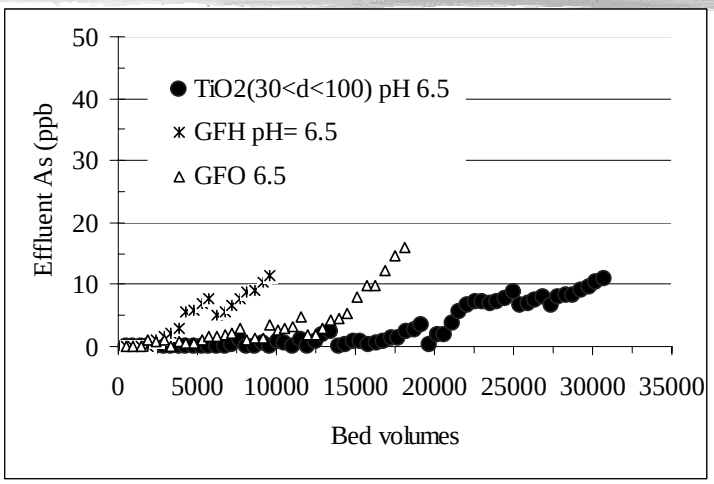
TiO_2=1.0 g/L, 2 hr, pH_{eq} = 7.0±0.1, Simulated groundwater (Ca = 100, Mg =20, Na =50 mg/L)

Effect of Si and P on As(III) adsorption



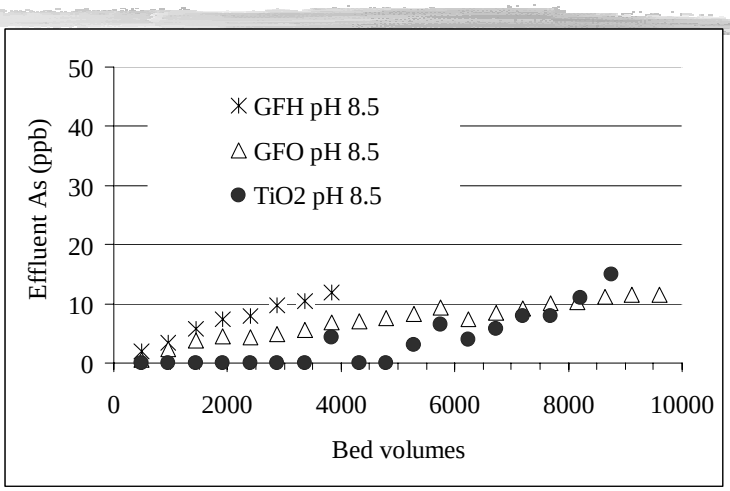
TiO_2=1.0 g/L, 5 hr, pH_{eq} = 7.0±0.1, Simulated groundwater (Ca = 100, Mg =20, Na =50 mg/L)

Laboratory Filtration of As(V) from the Challenge Water



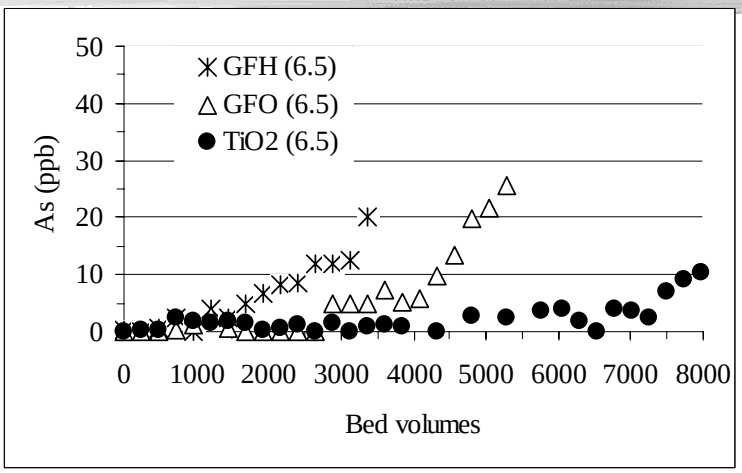
As(V)=50 ppb, pH=6.5, 0.04 mg/L PO4, 20 mg/L SiO2, 250 mg/L NaHCO3, column D=2.54cm, H=7cm, bed volume=35ml, EBCT=15sec, 50/50 cycle, NSF53.

Laboratory Filtration of As(V) from the Challenge Water



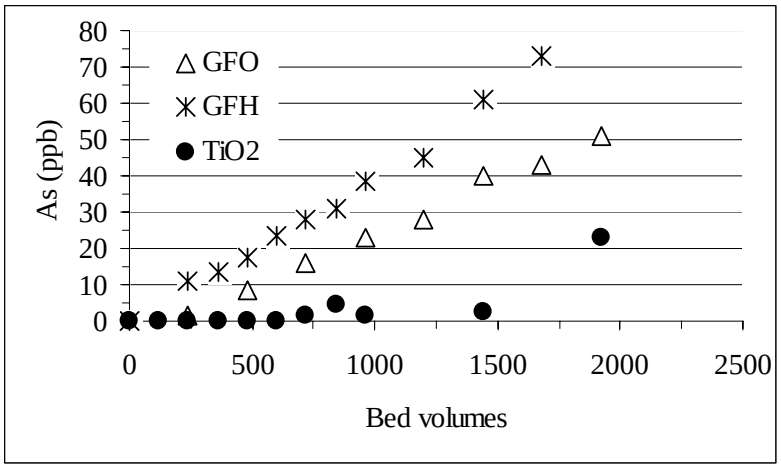
As(V)=50 ppb, pH=8.5, column D=2.54cm, H=7cm, bed volume=35ml, EBCT=15sec, 50/50 cycle

Laboratory Filtration of As(V) from the Challenge Water



As(V)=300 ppb, pH=6.5, column D=2.54cm, H=7cm, bed volume=35ml, EBCT=15sec, 50/50 cycle

Laboratory Filtration of As(V) from the Challenge Water



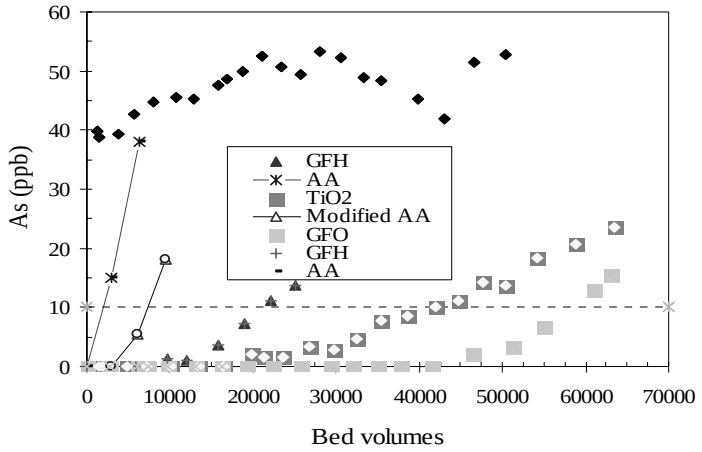
As(V)=300 ppb, pH=8.5, column D=2.54cm, H=7cm, bed volume=35ml, EBCT=15sec, 50/50 cycle

Filters tested in Hopewell, NJ

Chemical Properties of groundwater in Hopewell Borough

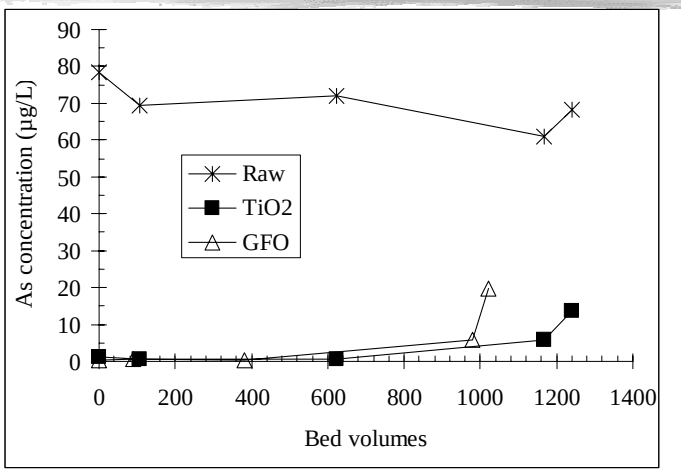
Alkalinity	130 mg $CaCO_3$/L
Calcium	40 mg/L
Magnesium	12 mg/L
Silica	20 mg/L
Iron	<0.02 mg/L
Sulfate	62 mg/L
pH	7.92
ORP	243 mV
As(V)	~45 µg/L

Removal of As from Groundwater in Hopewell, NJ

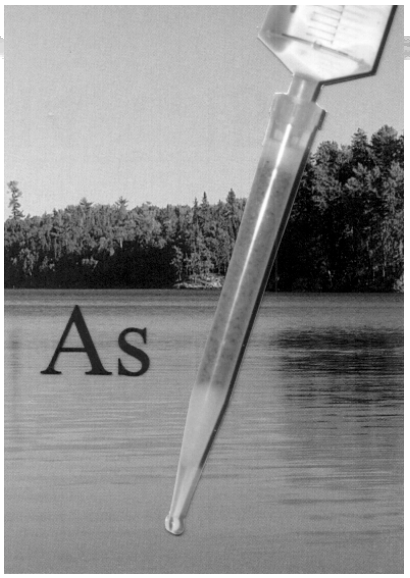


Bed volume=3 L,EBCT = 3 min

Removal of As(III) from Well Water in NJ



Water pH=7.3, ~80% As(III), BV=1.5 L, EBCT = 5 min,

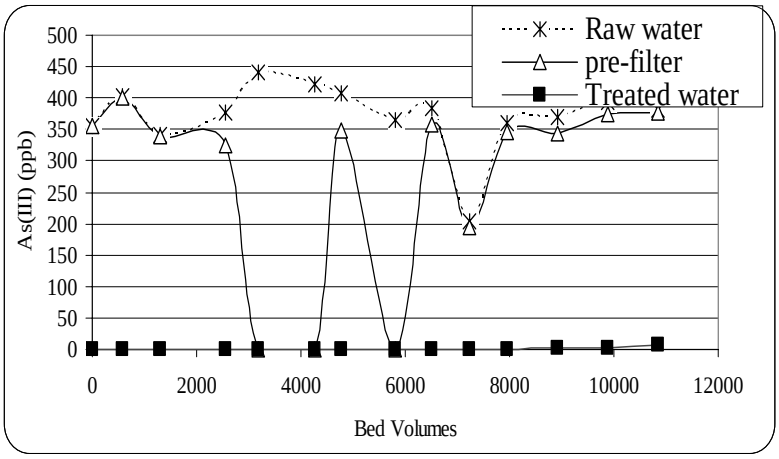


Speciation cartridge used for separation of As(V) and As(III), rapid flow, no pH adjustment

Chemical Properties of Groundwater at a Superfund Site

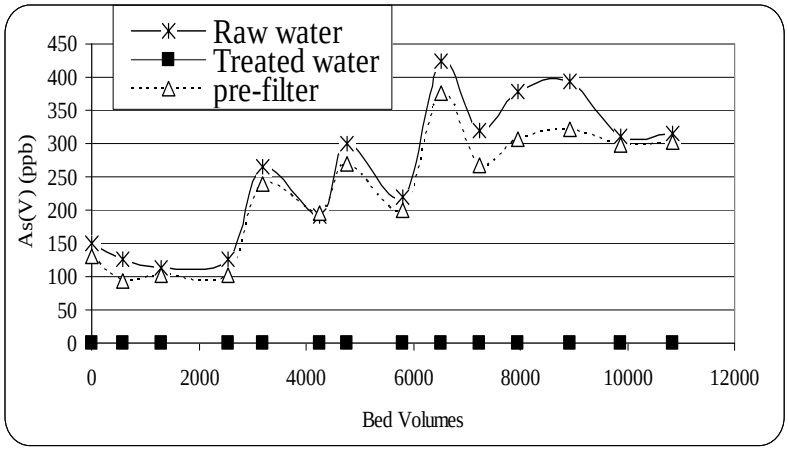
pH	5.5 – 6.2
As(III)	205-440 μg/L
As(V)	112-425 μg/L
MMA	104-301 μg/L
DMA	123-490 μg/L

Removal of As(III) from Groundwater at a Superfund Site



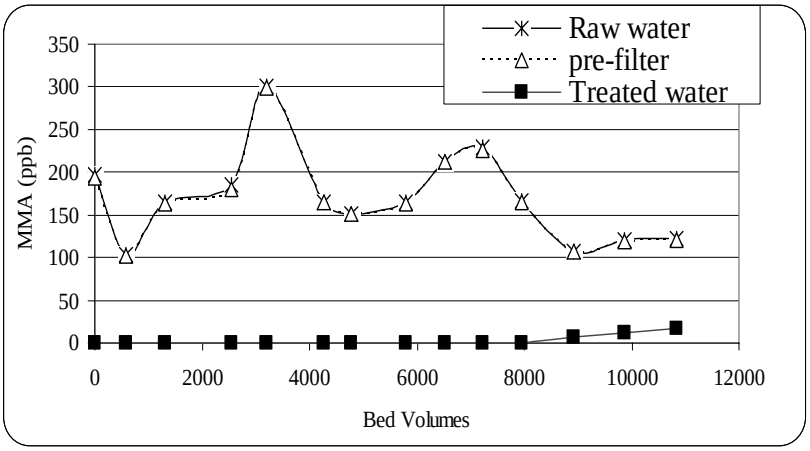
TiO_2 BV=3 L, EBCT = 6 min

Removal of As(V) from Groundwater at a Superfund Site



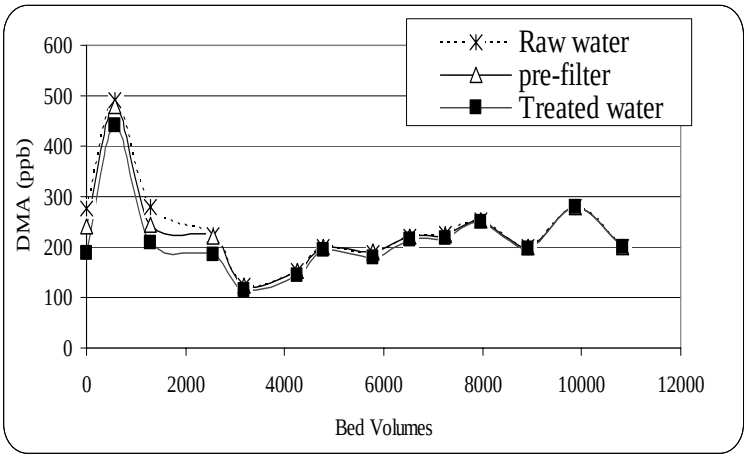
TiO_2 BV=3 L, EBCT = 6 min

Removal of MMA from Groundwater at a Superfund Site



TiO_2 BV=3 L, EBCT = 6 min

Removal of DMA from Groundwater at a Superfund Site



TiO_2 BV=3 L, EBCT = 6 min

Conclusions

- TiO_2 and GFO are more effective for removal of As(V) than other adsorbents tested in the present work.
- Phosphate and silicate do not have significant effect on the removal of arsenic by TiO_2.
- TiO_2 is effective for removal of MMA.
- The adsorbents are not effective for removal of As(III) from an anoxic well water.

Media Performance City of Mesa, AZ Experience

EPA Arsenic Workshop
August 10, 2004

Michelle De Haan, DSWA
Eric Dole, DSWA
Paul Westerhoff, ASU
Alan Martindale, City of Mesa

Today's Presentation

- City of Mesa Arsenic Compliance Situation
- Technologies Being Tested in Mesa
  - Adsorptive Media
  - Ion Exchange
- Results from Bench and Pilot Testing

City of Mesa Arsenic Rule Compliance Situation

- Supplies
  - Surface Water – 136 MGD
  - 38 Wells – 90 MGD
- 22 Wells impacted because of new MCL
  - 14 Wells > 10 ppb
  - 8 Wells within 20% MCL (8 ppb)

Arsenic Removal Technology Testing in Mesa

- Project Goal
  - Determine most appropriate technologies
  - Focus on Falcon Field Well #4 Water
    - 34 ppb Arsenic
    - 7.7 pH
    - 39 ppm Silica (as SiO_2)
    - 15 ppb Vanadium
    - 0.017 ppm Phosphate (as P)
- Adsorptive Media
  - Bench Testing
  - Pilot Testing
- Ion Exchange
  - Pilot Testing

Adsorptive Media Arsenic Treatment

- Advantages
  - Low cost
  - Simple installation
  - Simple operation
  - Not limited to sole source
  - Fully automated turn-key systems available
- Limitations
  - Only removes As(V)
    - Some media
  - Lack of As selectively
  - Interferences
  - Releases
  - pH dependant
  - Waste disposal concerns

Adsorptive Media Bench Testing

- Screen adsorption treatment technologies
  - Two phases of bench testing
    - Batch Testing
    - Rapid Small Scale Column Testing (RSSCT)

ASU Graduate Students Conducting Bench Testing Under Direction of Paul Westerhoff, Ph.D.

Adsorptive Media Bench Testing

- City criteria for media selection for piloting
  - pH adjustment
  - Adsorption capacity
  - Cost & operational considerations
  - NSF approval status

Adsorption Medias in Bench Testing Program

Activated Alumina (baseline)
Iron Modified AA
ZVI w/ Silica (AsRT) developed by the University of Connecticut
Granular Ferric Hydroxide (GFH) supplied by U.S. Filter
Bayoxide E33 supplied by Severn Trent
Sulfur Modified Iron (SMI) III
Z33 supplied by Water Remediation Technology
Metsorb G supplied by HydroGlobe

Adsorptive Media Bench Testing

Phase I – Batch Tests

- Screen several adsorption media for % arsenic removal with Mesa water
- Compare media at 3 pHs to determine if pH adjustment required for pilot testing
  - Ambient (7.7)
  - 7.0
  - 6.5

Phase II – RSSCT Tests

- Conduct continuous flow column experiments with better performing Phase I adsorbents
- Determine predicted media life for each media
  - Expressed in bed volumes

Adsorptive Media Bench Testing

- Batch Test Results
  - Media performance ranked from highest to lowest

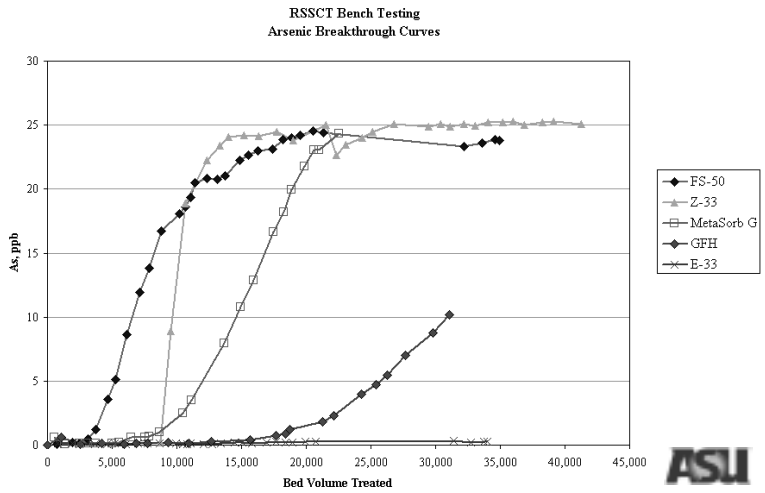
    SMI~ ZVI > Bayoxide E33 > GFH ~ AA ~ FS50 > Z33
  - Iron release problems with ZVI and SMI
    - Decided to discontinue testing of ZVI & AA

Adsorptive Media Bench Testing

- RSSCT Results
  - Media performance ranked from highest to lowest

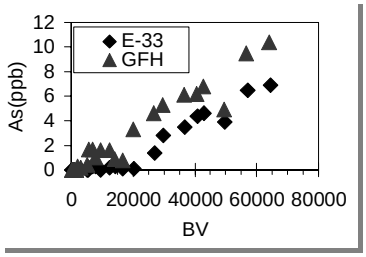
    Bayoxide E33 > GFH >Metsorb G > Z33 > FS50
  - RSSCT bed volumes not calculated for SMI due to upflow design requirements
    - Additional iron release testing conducted

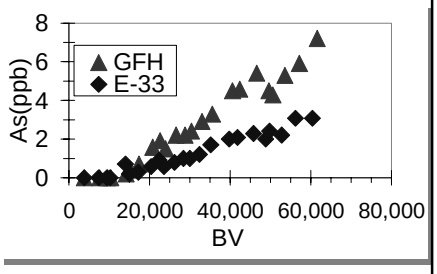
Adsorptive Media Bench Testing

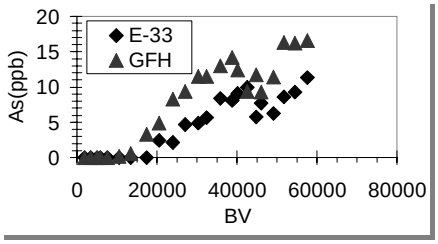


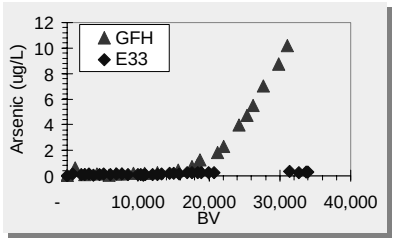
Adsorptive Media Bench Testing

RSSCT Comparison E33 & GFH for 4 GWs in Arizona









Prof. Paul Westerhoff, Civil and Environmental Engineering, ASU (Tempe, AZ)

DSWA Criteria Matrix – Adsorptive Media to be Pilot Tested

- DSWA evaluated ASU bench testing results & other criteria for media selection by descending order of importance
  - NSF approval status
  - Bed volumes/$/lb
  - Bed volumes treated
  - Iron release issues
  - pH adjustment requirement potential
- Z-33 > SMI-III > Bayoxide E33 > GFH ~ FS50

Adsorptive Media Pilot Testing

- Pilot testing completed with Z33, GFH, Bayoxide E33
- Additional pilot testing with As:X^{np} developed by SolmeteX

Loading GFH Media

Adsorptive Media Pilot Testing

- Pilot testing conducted in DSWA pilot system
- Media
  - As:X^{np}
  - Bayoxide E33
  - GFH
  - Z33
- Design Factors
  - Downflow
  - Parallel
  - 8” Columns

Bayoxide E33 & GFH Media

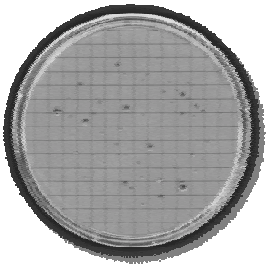
Adsorptive Media Pilot Testing

- Start-up
  - Media handling - safety
  - Conditioning procedures
- Routine Operation
  - 5 minute EBCT
  - 5.7 gpm/ft^2
- Routine Maintenance
  - Backwash driven by Δ P
  - Backwash disposal
  - Media disposal

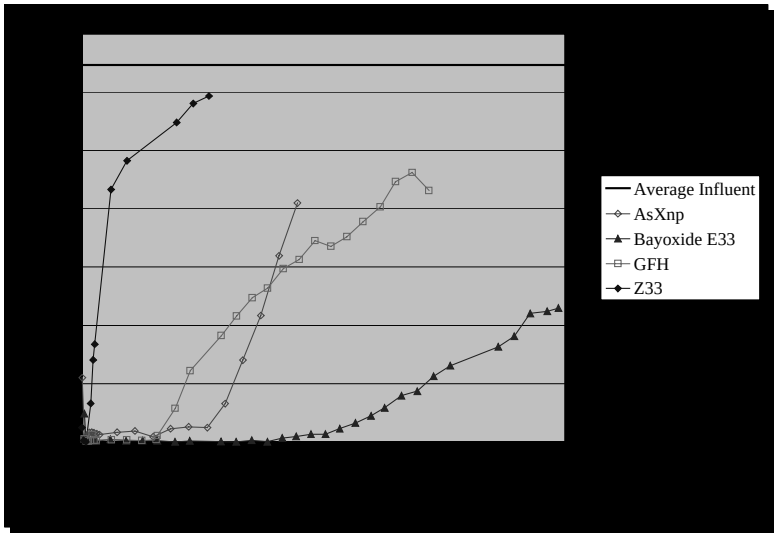
Conditioning GFH & Bayoxide E33

Adsorptive Media Pilot Testing

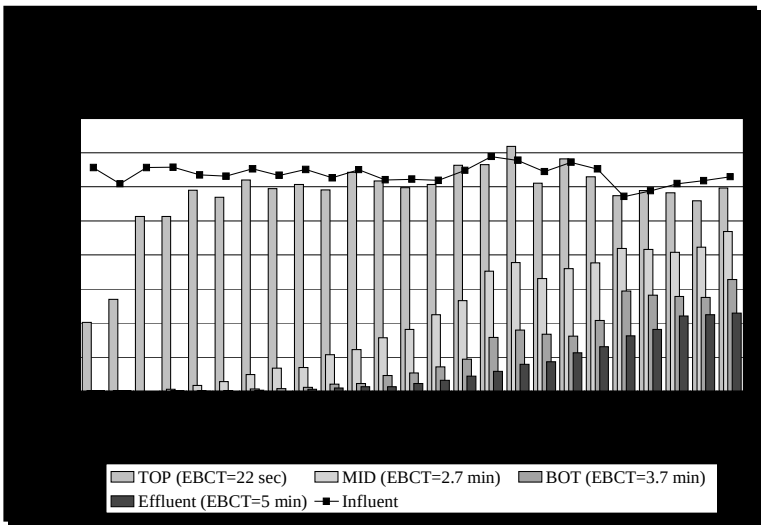
- Constituents of concern for this water
  - Arsenic
  - Silica
  - Vanadium
  - Heterotrophic Plate Count
  - Contaminant releases



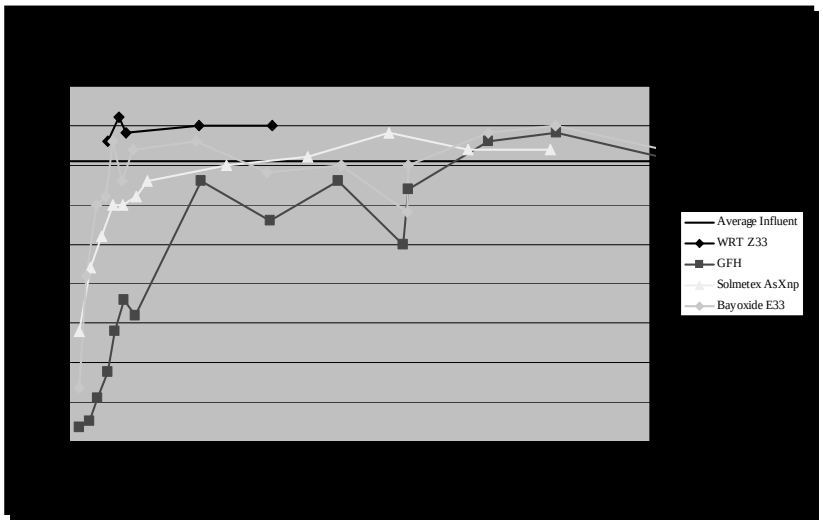
Adsorptive Media Pilot Testing



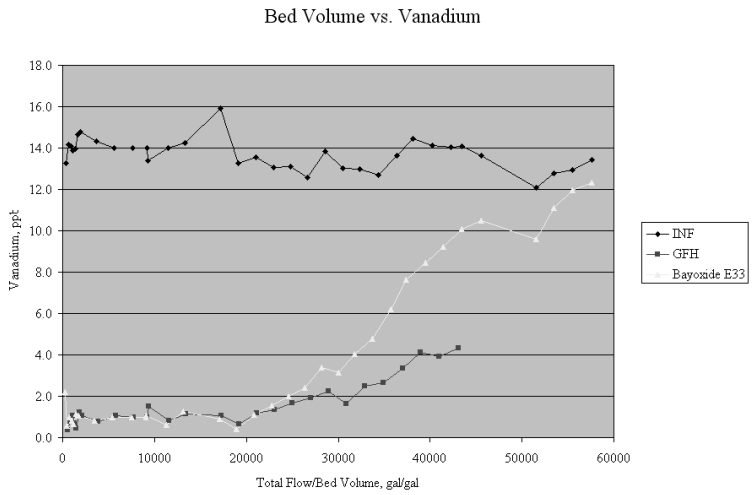
Adsorptive Media Pilot Testing



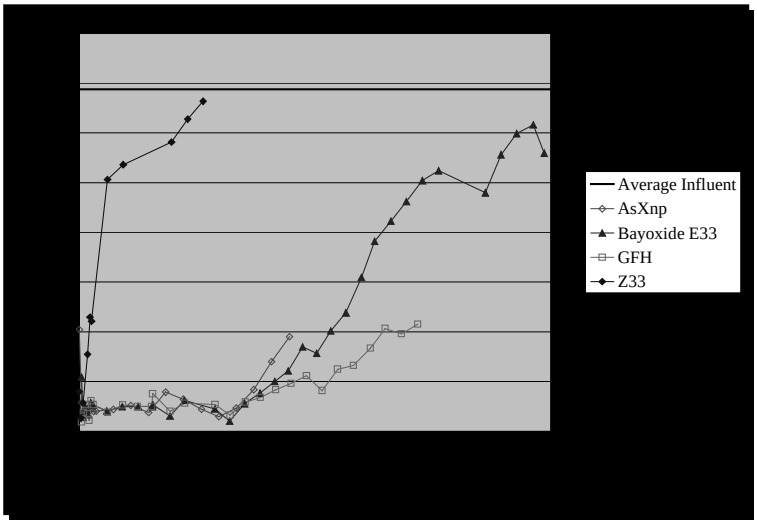
Adsorptive Media Pilot Testing



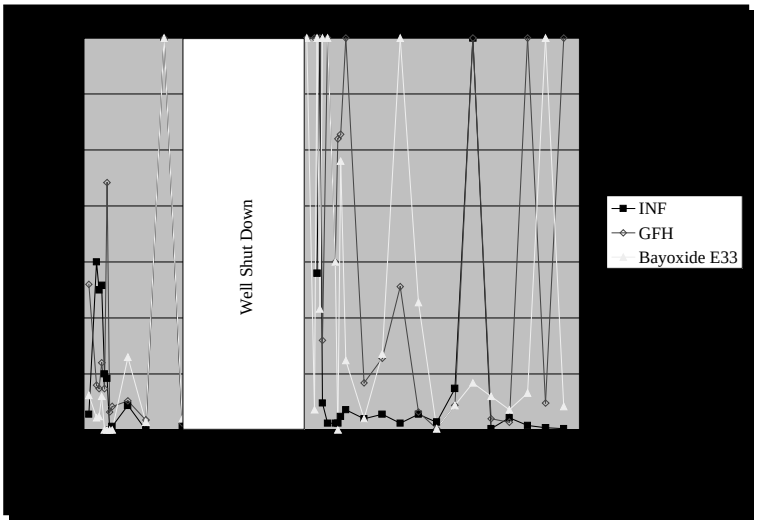
Adsorptive Media Pilot Testing



Adsorptive Media Pilot Testing



Adsorptive Media Pilot Testing

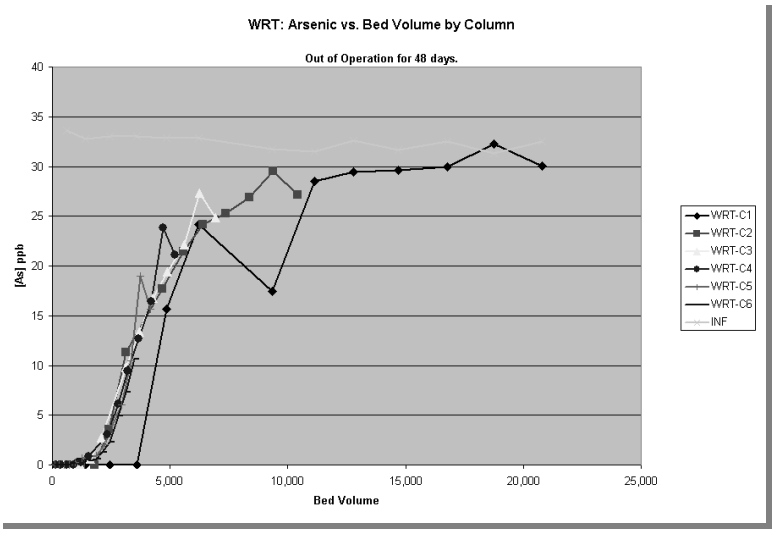


Adsorptive Media Pilot Testing

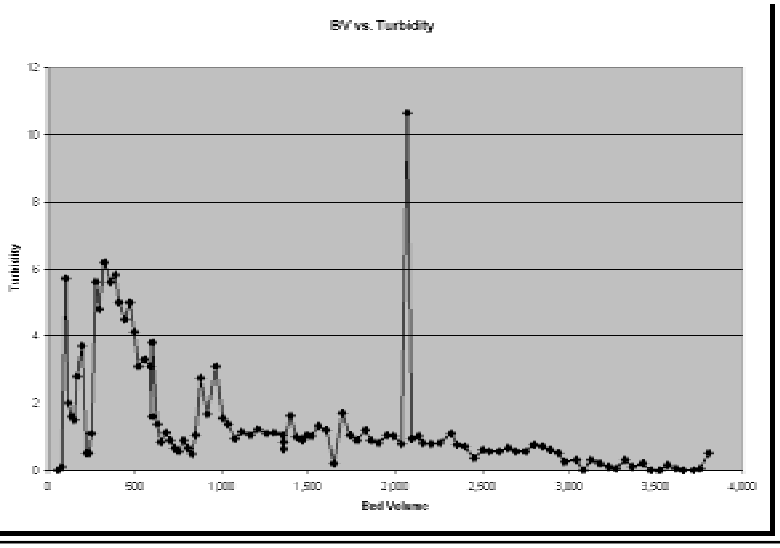
- Pilot testing conducted in Water Remediation Technology (WRT) pilot plant
- Media – Z-33
- Design
  - Upflow
  - Series configuration
    - Six columns

WRT Pilot Columns

Adsorptive Media Pilot Testing



Adsorptive Media Pilot Testing



Lessons Learned

- Bench testing can be used to screen better media with specific waters
  - RSSC Testing may be used as a tool to predict media behavior if there is not time to pilot test
- Media may remove Arsenic differently due to specific water qualities
  - Sometimes they behave similarly, other times not
- Operational constraints must be tested prior to serving water to distribution system
  - Ensure media well preped by manufacturer to avoid iron leaching (Fe/Mn field kits available)
  - Ensure media releases are avoided (measure turbidity)
  - Avoid Iron-bacteria and biofilm growth
- Operational tools can be designed to predict breakthrough

Take Home Message

- Get to know your water!
  - Collect samples for arsenic impacted contaminants at all wells above 10 ppb or within margin of safety (8 ppb)
  - Compare your water quality data to pilot test sites with similar water
  - Determine if pilot testing required for your water
  - Get started if you have not already

Acknowledgements

- Presenter – Paul Westerhoff, Ph.D.
- Co-authors
  - Eric Dole, Paul Westerhoff, Alan Martindale
- City Mesa
  - Alan Martindale, Laura Natalie, Dave Bates, R.E. Eck, Matt Rexing, Gary Smith, Jen Hetherington, Harry Brown, Bill McCarthy, Bill Haney
- ASU
  - Paul Westerhoff, Mohammad Bzaman, Smitha Raghavan
  - ASU NSF Water Quality Center

Questions?

Contact Information

Michelle De Haan
Damon S. Williams Associates
2355 E. Camelback Road
Suite 700
Phoenix, AZ 85016
602-217-1022
mdehaan@dswa.net
www.dswa.net

Battelle

The Business of Innovation

Pilot-Scale Evaluation of Adsorptive Media for Arsenic Removal

Abe Chen, Ph.D.,P.E. and Lili Wang, P.E., Battelle

Tom Sorg, P.E. and Darren Lytle, U.S. EPA

August 10, 2004

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- Licking Valley School District generously allowed the use of its facilities for on-site testing since 2001
- Several adsorptive/oxidizing media manufacturers, distributors, and vendors provided samples
- Many Battelle staff provided field and laboratory support

Outlines

- Experimental design rationale
- Pilot-plant design and test conditions
- Results of As(V) adsorption tests
- Results of As(III) adsorption tests
- Conversion of As(III) to As(V)
- Observations and conclusions

Outlines

- Experimental design rationale
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- Results of As(V) adsorption tests
- Results of As(III) adsorption tests
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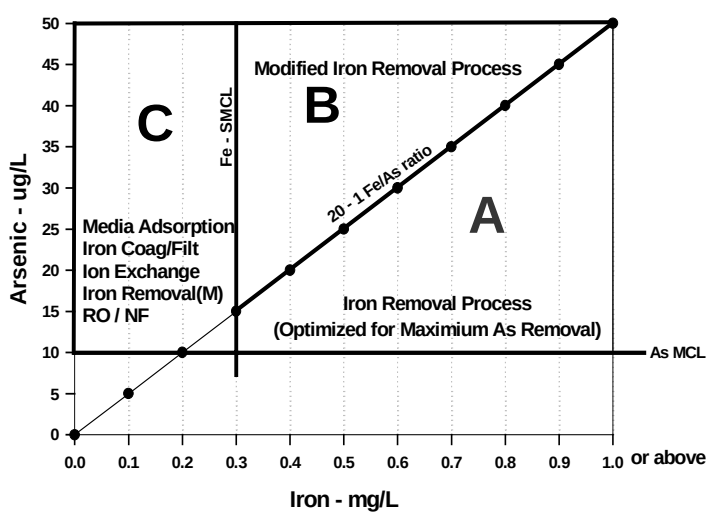
- Observations and conclusions

LVHS Water Quality

Analyte	Concentration Range
pH	7.7–8.0
Temperature (°C)	11.0–22.3
As_{total} (µg/L)	53–79
$As_{soluble}$ (µg/L)	56–73
$As_{particulate}$ (µg/L)	<0.1–16
As(V) (µg/L)	<0.1–13
As(III) (µg/L)	42–68
Fe_{total} (µg/L)	1,077–1,725
$Fe_{soluble}$ (µg/L)	795–1308
Mn_{total} (µg/L)	148–202
$Mn_{soluble}$ (µg/L)	146–185

Analyte	Concentration Range
Alkalinity (mg/L as $CaCO_3$)	200–245
Hardness (mg/L as $CaCO_3$)	165–187
NO_3-NO_2 (mg/L as N)	0.3
Silica (mg/L)	2.2
Sulfate (mg/L)	4.0
Sulfide (mg/L)	<1.0
Phosphate (mg/L)	<0.10–0.11
TOC (mg/L)	1.4
DO (mg/L)	1.0–1.7
ORP (mV)	-30-24

Technology Selection Chart



Experimental Approach

- As(V) adsorption tests
  - Pretreatment using solid oxidizing media to remove iron and Mn and convert As(III) to As(V)
- As(III) adsorption tests
  - No pretreatment
- Solid oxidizing media (SOM) tests

Outlines

- Experimental design rationale
- Pilot-plant design and test conditions
- Results of As(V) adsorption tests
- Results of As(III) adsorption tests
- Conversion of As(III) to As(V)
- Observations and conclusions

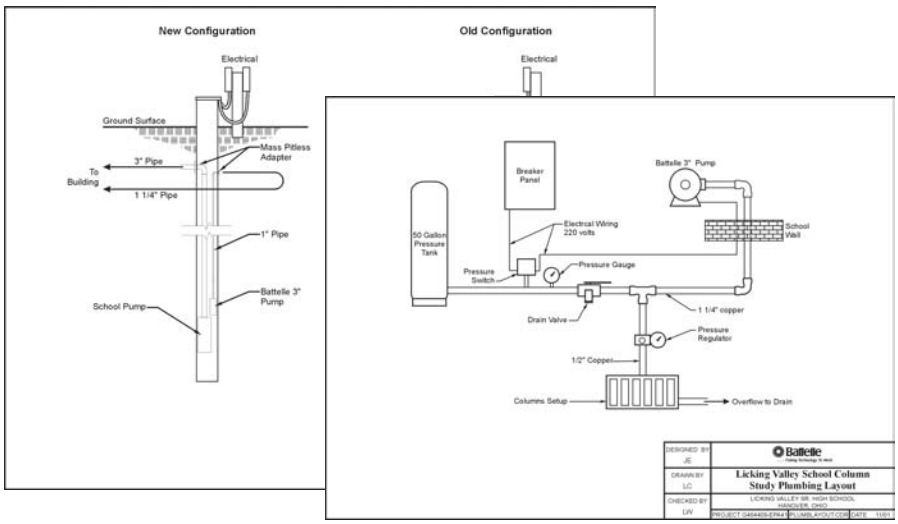
Pilot Study on Adsorptive Media

- Adsorptive media (13)
  - Alumina-based media (5)
    CPN; AAFS50; Aqua-Bind XP, MP; ARM100
  - Iron-based media (4)
    G2; E33; GFH; ARM200
  - Others (4)
    Titanium oxide-based media: MetSorb
    Nanoparticle selective resin: As:X^{np}
    Zeolite-based media: Zeocros B321
    F-400 GAC
- Solid oxidizing media (3)
  - Filox[a,b], Pyrolox[a], Brim

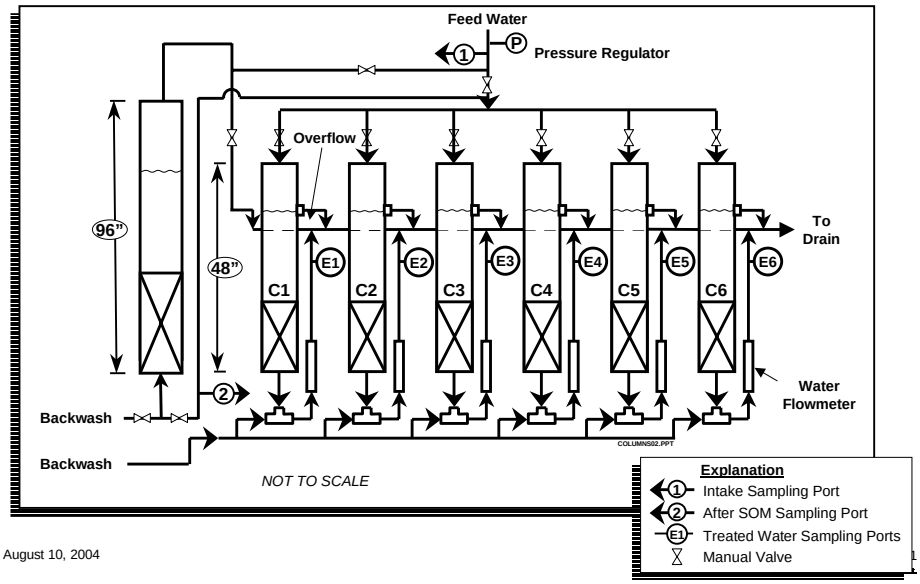
(a) Also known as Pyrolusite

(b) Currently branded as Metlease

Source Water Supply Schematic



Pilot-Plant Schematic



Properties of Alumina-Based Media

Parameter	CPN AA	AAFS50	Aqua Bind XP	Aqua Bind MP	ARM-100
Manufacturer	Alcoa	Alcan	Apyron	Apyron	Engelhard
Mesh size	28 × 48	28 × 48	28 × 48	28 × 48	18 × 50
Bulk Density, g/cm3 (lbs/ft3)	0.75 (47)	0.91 (57)	0.56-0.62 (35-39)	0.61-0.67 (38-42)	0.5 (32)
BET surface area ,m^2/g	300-340	200-250	190-230	190-250	200-260
Active ingredient	94.1% Al_2O_3	80-85% Al_2O_3 + proprietary additive	Alumina metal oxide composite	Alumina metal oxide composite	Alumina-based

Properties of Iron-Based Media

	G2	ARM-200	E33	GFH
Manufacturer	ADI	Engelhard	Bayer	USFilter
Mesh size	0.32 mm (Effective size)	40 × 80 (Mesh size)	10 × 35 (Mesh size)	0.32-2 mm (Effective size)
Bulk Density, g/cm^3 (lbs/ft^3)	0.75 (47)	0.72-0.80 (45-50)	0.45 (28)	1.22-1.29 (76-81)
BET surface area, m^2/g	27	NA	142	127
Active ingredient	Diatomaceous earth (Si-based) impregnated with a coating of ferric hydroxide	Iron-based	Iron oxide composite (90.1% FeOOH)	52-57% $Fe(OH)_3$ and β- FeOOH

Properties of other Adsorptive Media

Parameter	As:X^{np}	Metsorb	Zeocros B321	GAC
Manufacturer	Solmetex	HydroGlobe	Unknown	Calgon
Mesh size	0.3-0.6mm (Effective size)	NA	NA	12 X 40 (Mesh size)
Bulk Density, g/cm^3 (lbs/ft^3)	0.74-0.81 (45-50)	0.8 (50)	NA	0.53 (33)
BET surface area, m^2/g	NA	NA	NA	800
Active ingredient	Nano particle selective resin with iron oxide as a functional group	Titanium oxide	Zeolite based media	Activated carbon

NA = not available

Properties of Solid Oxidizing Media

Parameter	Filox-R ™	Pyrolox	Birm ®
Manufacturer	Matt-Son	American Minerals	Clack Corporation
Mesh size	12 × 40	8 × 20	9 × 35
Bulk Density, g/cm^3 (lbs/ft^3)	1.8 (114)	2.0 (125)	0.7–0.8 (44–50)
BET surface area, m^2/g	NA	NA	NA
Active ingredient	75–85% MnO_2	MnO_2	<0.01% MnO_2

NA = not available

Test Conditions - Adsorption Columns

- Conditions applied to both As(V) and As(III) tests
- Media wet loading to remove fines
- System operated under constant pressure at about 15 psi
- Bed dimension 2” diameter × 12” long
- Bed volume 620 mL
- Flowrate 125−135 mL/min
- EBCT 4.8 ± 0.2 min
- No pH adjustment
- No backwash for adsorptive beds

Test Conditions - Pretreatment column

- Test conditions applied to As(V) tests only
- Dual media Birm and Filox
- Bed dimension 6” diameter × 16” long (8” per SOM)
- Bed volume 3,700 mL × 2
- Flowrate 750−810 mL/min
- EBCT 4.8 ± 0.2 min per SOM
- Backwash twice a week

Sampling and Analysis

- Sampling/speciation weekly at inlet, after pretreatment (for As[V] tests only), and after each adsorption column
- Speciation for total and particulate As, As(V), and As(III); total and soluble Fe, Mn, and Al
- Metals analysis
  - EPA Method 200.8
  - Perkin Elmer Sciex Model 6000 ICP/MS equipped with a crossflow pneumatic nebulizer and an auto-sampler
  - Detection limits of 0.1, 30, 0.5, and 11 µg/L for As, Fe, Mn, and Al, respectively
- On-site analysis
  - pH, DO, ORP, and temperature using a WTW multi-340i meter

Outlines

- Experimental design rationale
- Pilot-plant design and test conditions
- Results of As(V) adsorption tests
- Results of As(III) adsorption tests
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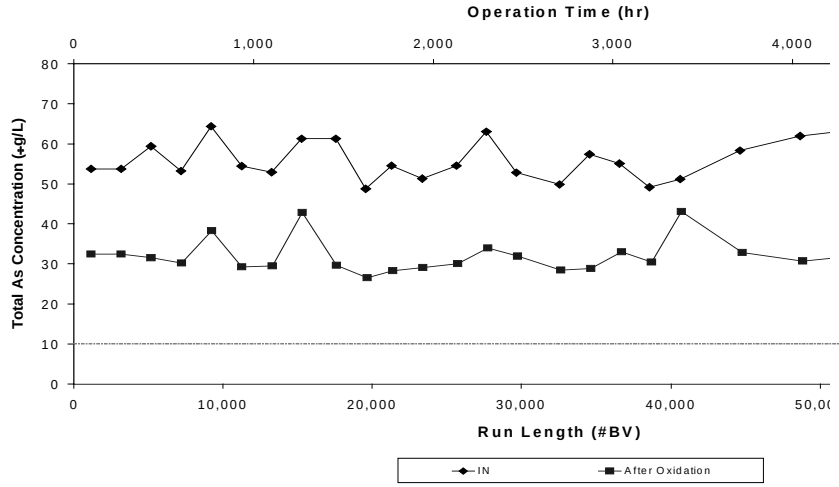
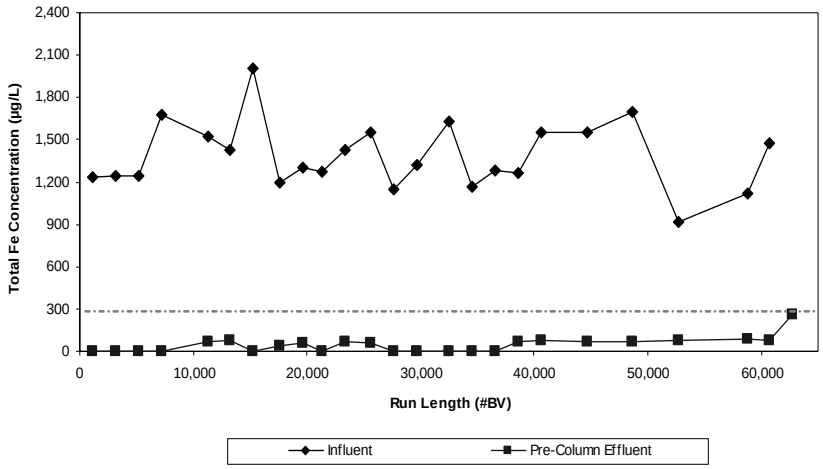
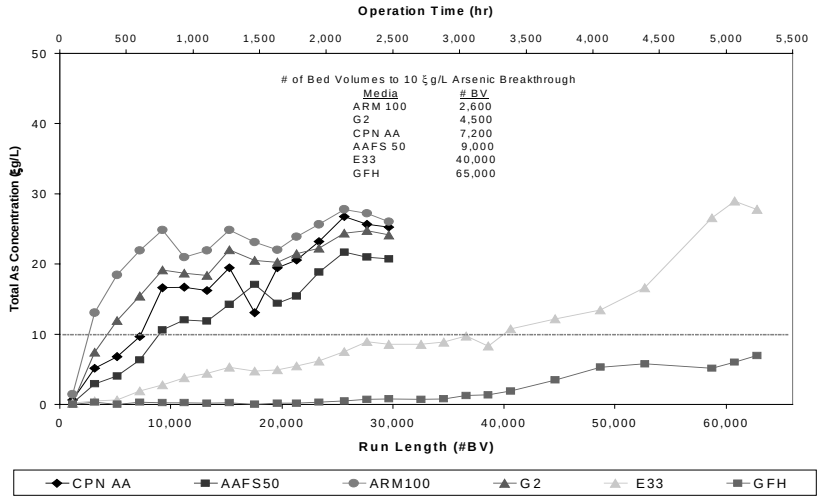
As(V) Test: Pretreatment - Arsenic



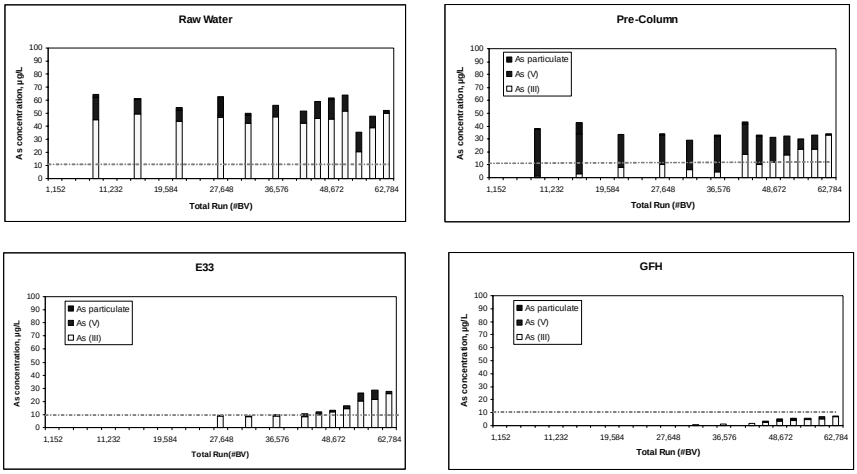
As(V) Tests: Pretreatment - Iron



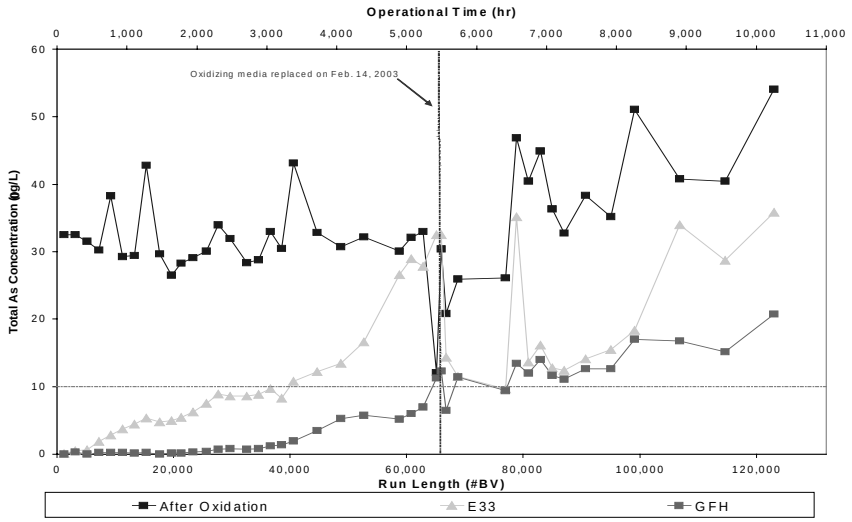
As(V) Tests: Breakthrough Curves



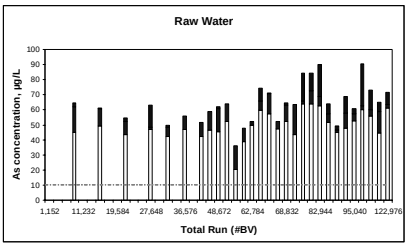
As(V) Tests: Speciation Results

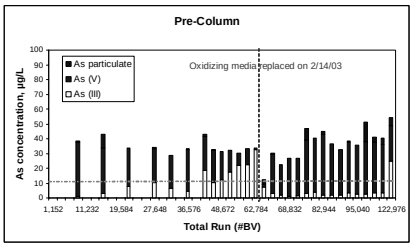


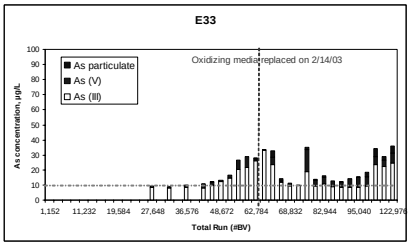
As(V) Tests: Breakthrough after SOM Re-bedding

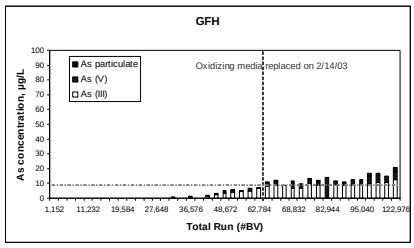


As(V) Tests: Speciation Results after SOM Re-bedding









As(III) Mass Balance

Media	As(III) Entered during Run 1	As(III) Removed during Run 1	As(III) Removal (%)	As(III) in Treated Water during Run 2
E33	323	**54**	17	**155**
GFH	323	**296**	92	**101**

During Run 2:

- As(V) was the predominating species in the influent to both E33 and GFH
- As(III) was the predominating species in the GFH effluent, indicating displacement (???)
- The amount of As(III) in the E33 effluent was more than that removed by E33 during Run 1 – what does it mean?

Outlines

- Experimental design rationale
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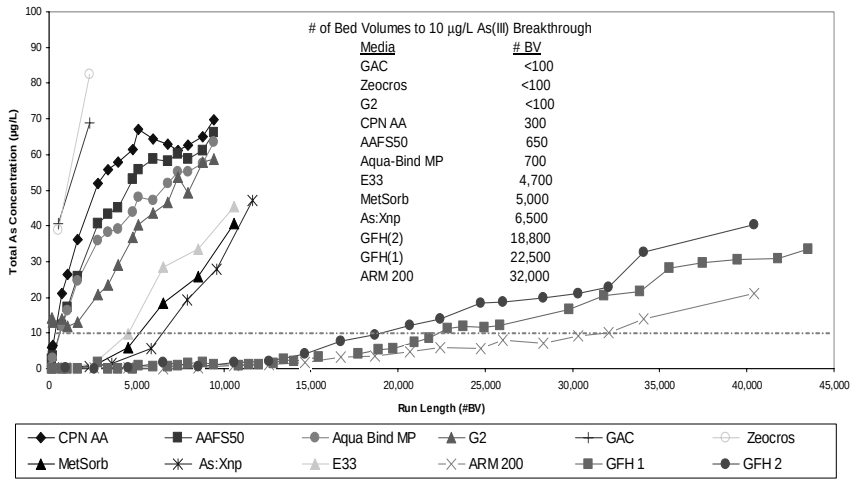
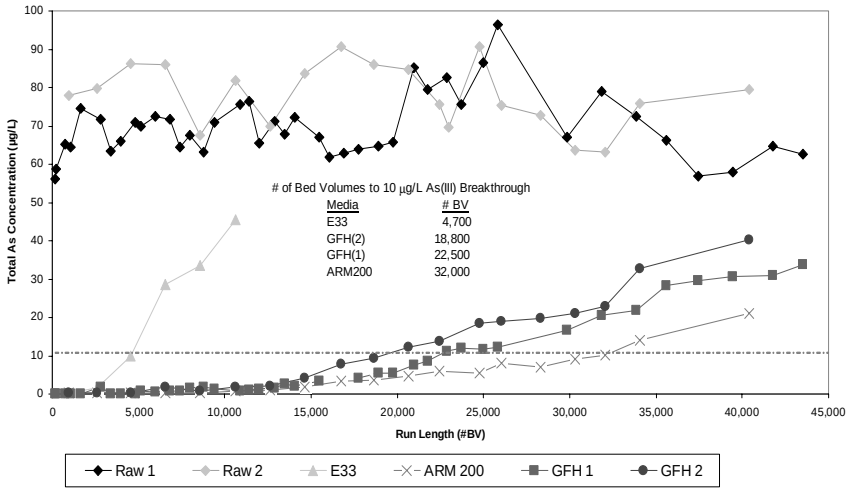
- Results of As(III) adsorption tests
- Conversion of As(III) to As(V)
- Observations and conclusions

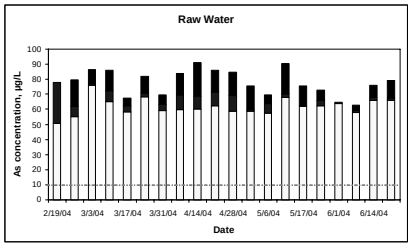
As(III) Tests: Breakthrough Curves

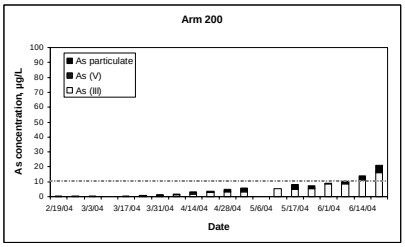


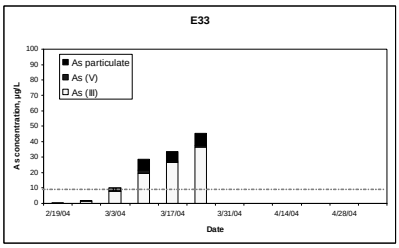
As(III) Tests: Breakthrough from E33, GFH and ARM 200

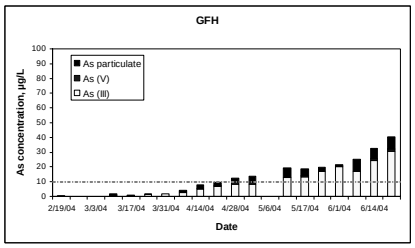


As(III) Tests: Speciation Results

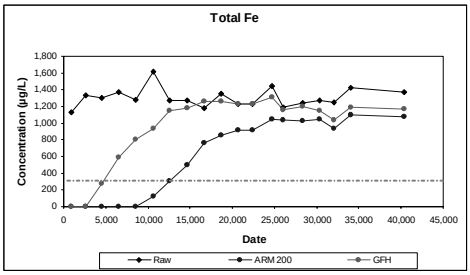


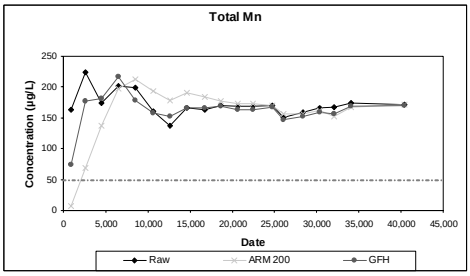






As(III) Tests: Fe and Mn Breakthrough

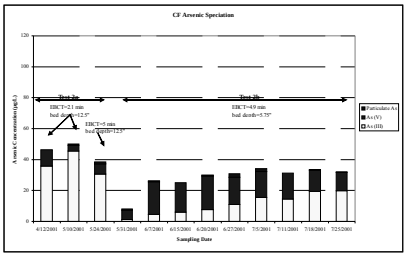


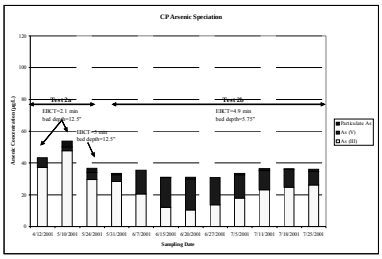


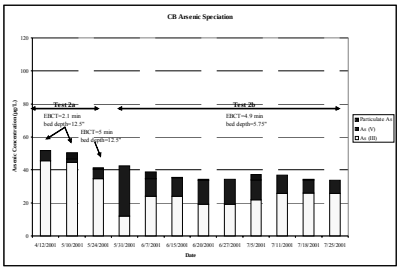
Outlines

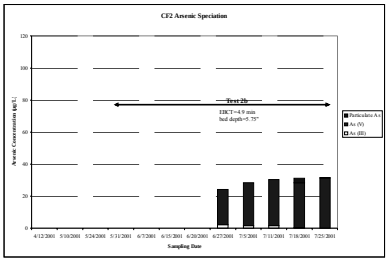
- Experimental design rationale
- Pilot-plant design and test conditions
- Results of As(V) adsorption tests
- Results of As(III) adsorption tests
- Conversion of As(III) to As(V)
- Observations and conclusions

As Conversion with Filox or Birm/Filox

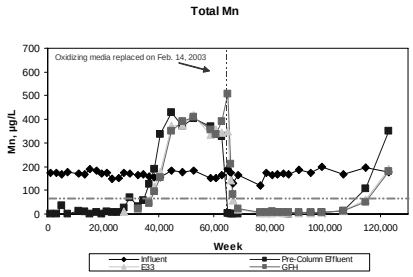


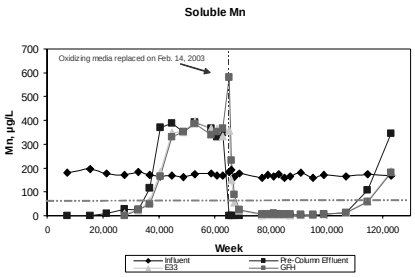






As(V) Tests: Mn Leaching from Oxidizing Media





Outlines

- Experimental design rationale
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- Results of As(V) adsorption tests
- Results of As(III) adsorption tests
- Conversion of As(III) to As(V)
- Observations and conclusions

Observations and Conclusions

- In general, iron-based media outperformed Al-based media for arsenic removal with media life ranging from 2,000 to 9,000 BVs for Al-based media and 40,000 to 65,000 BVs for E33 and GFH.
- Adsorptive media had much higher capacities for As(V) than for As(III). However, ARM 200 and GFH had a long media life of 34,000 and 24,000 BVs for As(III), respectively.
- As(III) can be released from adsorptive media through displacement or surface-mediated conversion (?).
- Solid oxidizing media can be used as a pretreatment step before adsorptive media. Frequent backwash is essential to effectively remove Fe and/or convert As(III) to As(V).

SESSION III

Critical Design Considerations For Adsorptive Media For Arsenic Removal

Eric Winchester, Vice President

ADI International Inc.

Critical Design Considerations

- Process Design
- Sizing of Adsorber Vessels
- Secondary Process Considerations

Design Input Data

- Chemical analysis of the water.
- Treated water compliance standard.
- Regulatory design standards.
- Residuals disposal.
- Design flow rates and consumption.

Design Input Data

Chemical Analysis

- Arsenic and pH: adsorption capacity increases with As conc. And decreases with high pH.
- Certain elements may interfer with adsorption capacity - silica, iron, sulfate, chloride.
- Other metals are adsorbed also.

Design Input Data

Compliance & Design Standards

- EPA MCL - 10 ppb
- Other Agencies: 3 to 10 ppb

- Min/Max operating parameters, e.g., gpm/sf
- NSF Standard 61
- EPA/NSF ETV Program
- Other, e.g., ASME code

Design Input Data

Residuals

- Initial media conditioning - backwash, rinse, disinfection.
- Normal backwash and rinse during use.
- Regeneration chemicals.
- Spent media.

Design Input Data

Flow Rates & Consumption

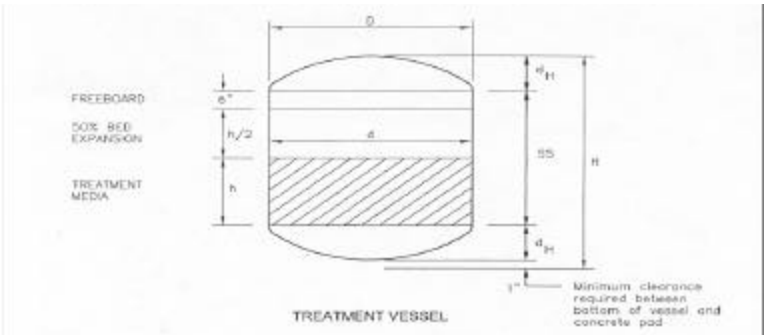
- Well pump capacity used to hydraulically design system - physical size of filters, piping, chemical feed.
- Consumption used to estimate media life and operating cost.

Design Options

- Selection of adsorptive media.
- With or without pH adjustment.
- Spent media regeneration, or one-time use & disposal.
- Series or parallel operation.
- Manual or automatic control.

Design and Cost Considerations

- Empty Bed Contact Time (EBCT).
- Series or parallel operation.
- pH adjustment.
- Regeneration capability.
- Oxidation - As III to As V.



TREATMENT VESSEL

SYMBOLS

q – TREATED WATER FLOW RATE (gpm)
d – TREATMENT BED DIAMETER (ft.), $d = \sqrt{4q/\pi h}$
h – TREATMENT BED DEPTH (ft.)
V – TREATMENT BED VOLUME – $\frac{\pi d^2}{4} h$ (ft.^{3})
M_d – DENSITY OF TREATMENT MEDIA (lb./ft.^{3})
M_w – WEIGHT OF MEDIA (lbs.)
D – OUTSIDE DIAMETER OF TREATMENT VESSEL (ft.)
d_H – DEPTH OF DISHED PRESSURE HEAD (ft.)
H – OVERALL HEIGHT OF SKID MOUNTED TREATMENT VESSEL (ft.)
SS – STRAIGHT SIDE (ft.)

GIVEN

$d > h/2$, $3'-0" < h < 6'-0"$
$H = 2\,d_H + h + h/2 + 8" + 1"$
$D = d + 1"$
$M_d = 45$ lb./ft.^{3} (VARIES WITH MEDIA IN VESSEL)
$M_w = M_d \times V = 48V$ (lb.)

Figure 3-5. Treatment Bed and Vessel Design Calculations

Design & Cost Considerations

EBCT

- Range - 3 to 10 minutes
- Activated alumina - 5 min +
- ADI's MEDIA G2 uses 8 to 10 min, results in a unit flow rate of 2.5 to 3 gpm/sf
- The lower the EBCT, the higher the unit flow rate.

Design & Cost Considerations

EBCT & Bed Volumes

- The lower the EBCT, the smaller the size of vessels.
- Adsorption capacity determines the no. of bed volumes or the quantity of water treated in gallons before arsenic break-through.

Design & Cost Considerations

Bed Volumes

- Why not use a longer EBCT and larger bed volume to increase the total amount of treated water before break-through?
- Initial cost may be a factor.
- Ask whether lower service flow rates (gpm/sf) can be tolerated.
- Ask whether there are any minimum flow limitations under NSF 61 standard, i.e., gpm/cf of media or a max use level.
- There is a diminishing return on increasing EBCT related to performance and adsorption capacity.

Design & Cost Considerations

Series or Parallel

- Advantage of series:
- Redundancy and safety.
- Maximum use of media capacity.
- More flexible for scheduling of media change-outs.

Design & Cost Considerations

Series or Parallel

- Disadvantages of series:
- Increased capital cost due to number and size of filters.
- Larger foot print.
- Higher pressure drop.
- Need for larger backwash rates.

Design & Cost Considerations

pH Adjustment

- Disadvantages:
- Increased complexity of operation.
- Trained operators needed to address handling & safety issues.
- Loss of pH control may cause arsenic desorption of some media (ask the vender for details).

Design & Cost Considerations

pH Adjustment

- Advantages:
- In many cases, results in lower As concentration in treated water.
- Increased adsorption capacity & hence longer media life.
- Same pH chemicals are then available for media regeneration.

Design & Cost Considerations

Regeneration

- Disadvantages:
- Increased complexity.
- Another waste stream for disposal.
- May not be economical for non-pH adjusted water.

Design & Cost Considerations

Regeneration

- Advantages:
- Substantial increase in media life (Not all media can regenerated).
- Less frequent media change-outs.
- Lower operating cost.

Design & Cost Considerations

Oxidation - As III to As V

- Chlorine used for disinfection will oxidize As III to As V for easier removal and longer bed life.
- For some media, exposure to chlorine will degrade performance, e.g., activayed alumina.

Sizing of Adsorber Vessels

- Empty Bed Contact Time (EBCT).
- Media bed depth.
- Bed expansion.
- Unit flow rate.
- Parallel or series operation.

Secondary Process Considerations

- Need for pH feed-back control and alarms when pH corrected.
- Re-adjust pH after treatment ?
- Manual vs automatic control.
- Filter internals – no different than conventional multi-media filters.
- Pre-treatment.

Critical Design Considerations For Adsorptive Media For Arsenic Removal

Eric Winchester, Vice President

ADI International Inc.

www.adi.ca

Arsenic Treatment – Equipment Configuration

Bernie Lucey, P.E.
NH Department Of Environmental Services
PO Box 95 Concord NH 03302-0095

603-271-2952

Contexts of Arsenic In NH

- Very small PWSs 0-100 gpm
- Without full-time operator presence
- Limited operator skill and experience
- Treatment assumption –
  - adsorptive media treatment almost exclusively

- 700 com./110 Arsenic; 450 NTNC/40 Arsenic.
- 20 Existing Arsenic Treatment Systems;
  - 15-Adsorptive Media; 4 POU/POE (RO); 1-RO (full scale)

Treatment Concept I POU/POE

- POU typically at kitchen sink
  - Adv: Utility owned, maintained, and monitored
  - Dis: high level of utility and state oversight
- POE typically at foundation wall
  - Adv: Utility owned, maintained, and monitored
  - Dis: high level of utility and state oversight

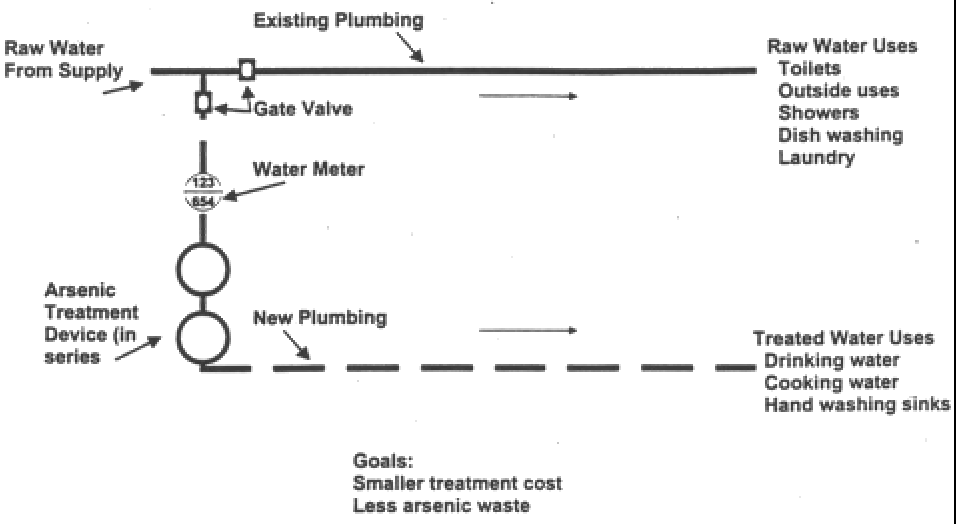
POU Treatment

Treatment Concept IA
Non-Community Non-transient

Modified POU/POE Treatment System.

- **Develop a dual water system within the building - open interior layout:**
  - Existing plumbing remains–untreated water.
  - New plumbing – has treated water.
- **Requirements:**
  - All faucets must be labeled (Drinking vs Not Treat.)
  - All plumbing requires color coding/25'.

Appendix D: POE/POU Concept - Dual Plumbing System



Treatment Concept II
Parallel Configuration

Pat Cook
State of Michigan

Treatment Concept III
Series Configuration

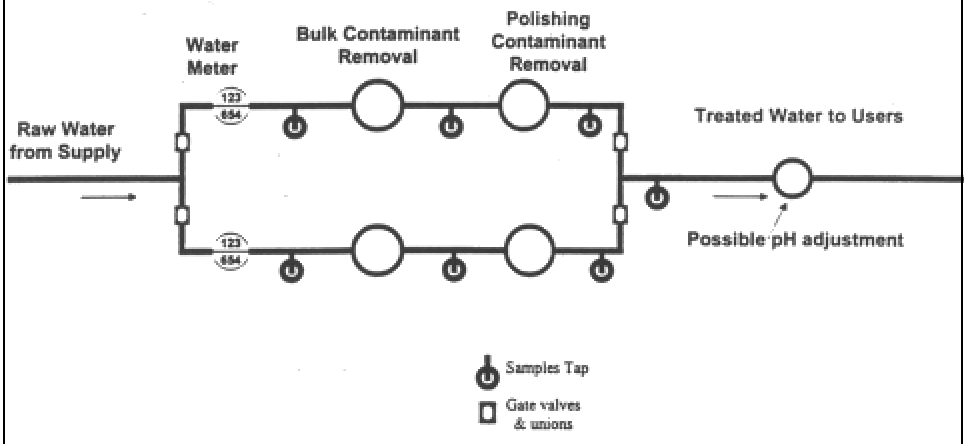
Two tanks per train:

Lead tank does the majority of removal.

Lag tank polishes and addresses breakthrough.

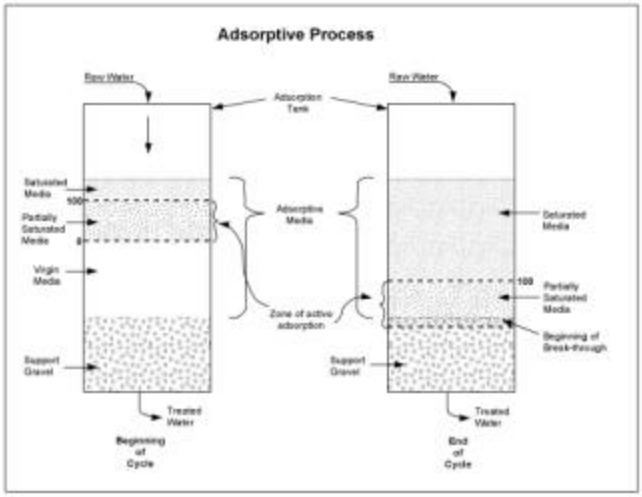
- Allows breakthrough in first tank without the need for immediate operator response.
- Achieves maximum adsorption of arsenic on media.

Appendix E: Adsorption Treatment - Series Configuration



Adsorption Rules

- **The greater the arsenic concentration the greater the amount that can be held by the adsorbent medias.**
- **Where media is effective for Arsenic III;**
  - **Breakthrough will likely be sooner; total holding capacity will be lower.**
- **Bed is physically backwashed every month. Backwash upsets the boundary of the active absorption band.**
-
- **Breakthrough will be faster than predicted in literature references due to monthly backwash upset.**



Series Configuration

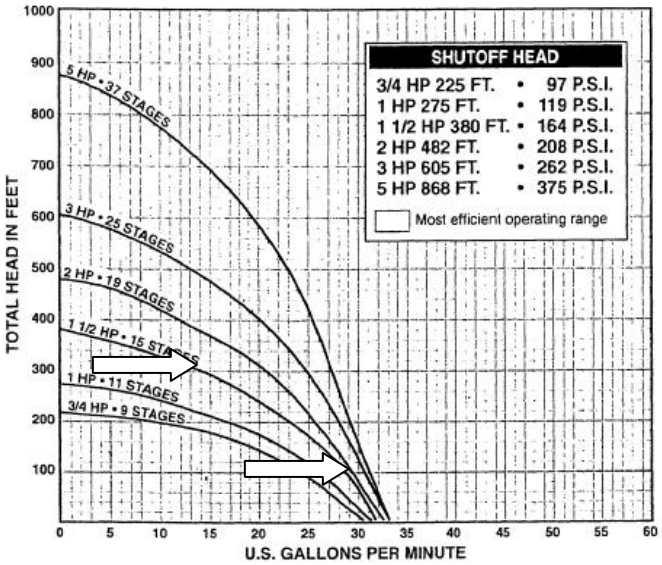
- In NH series is the recommended configuration.
  - **Media: Use once then rebed**
  - **pH: Do not adjust ambient pH.**
- Series is much more operator friendly/tolerant.
- Some savings realized in adsorptive media per changeout.
- Higher first capital cost and initial media cost.

Other Design Considerations

Varying Source Water Pump Flows

- **In NH the typical well with Arsenic is into bedrock 400 ft deep; Typical static is 50-100 feet.**
- **Max. drawdown during pumping is likely to 300 ft.**
- **Change in pumping rate between initial and long term pumping can be 25-200 % lower as drawdown increases.**

Typical Pump Curve



Response to Pumping Variation

- Possible Responses:
  - **Install flow restrictor to limit flow to no greater than that at maximum drawdown.**
  - **Do not install restrictor and size treatment tank for the flow rate associated with minimum drawdown (static water level).** ***Preferred Option***

Other Design Considerations
Is Preoxidation Needed?

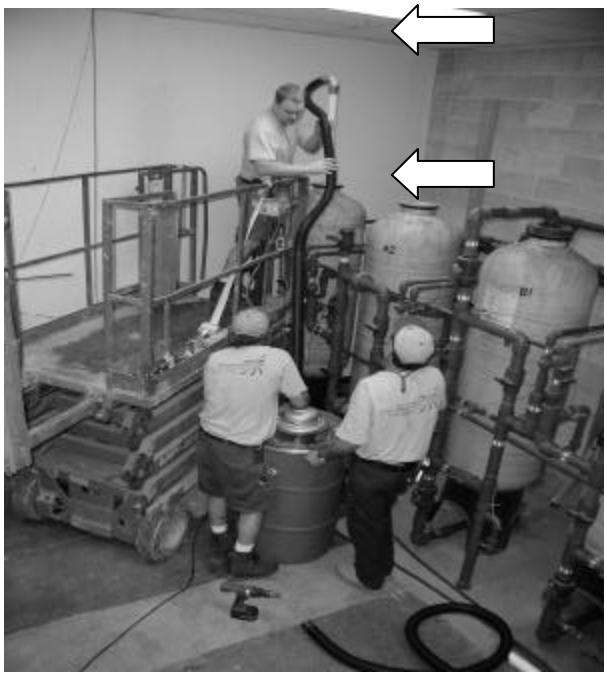
- **Is there Arsenic III ?**
  - **If yes. We recommend oxidation even if the media can remove As III.**
- **Is Arsenic III present seasonally** ?
  - **Oxidation will address the future unknown.**
- NH Policy
- **Pretreatment will not be initially required since many medias will address As III. HOWEVER, Arsenic media holding capacity is typically less with As III.**
- **Initial quarterly monitoring. Then begin accelerated monitoring at 75% of estimated bed capacity.**
- **Leave plumbing fittings for oxidant feed as a retrofit.**

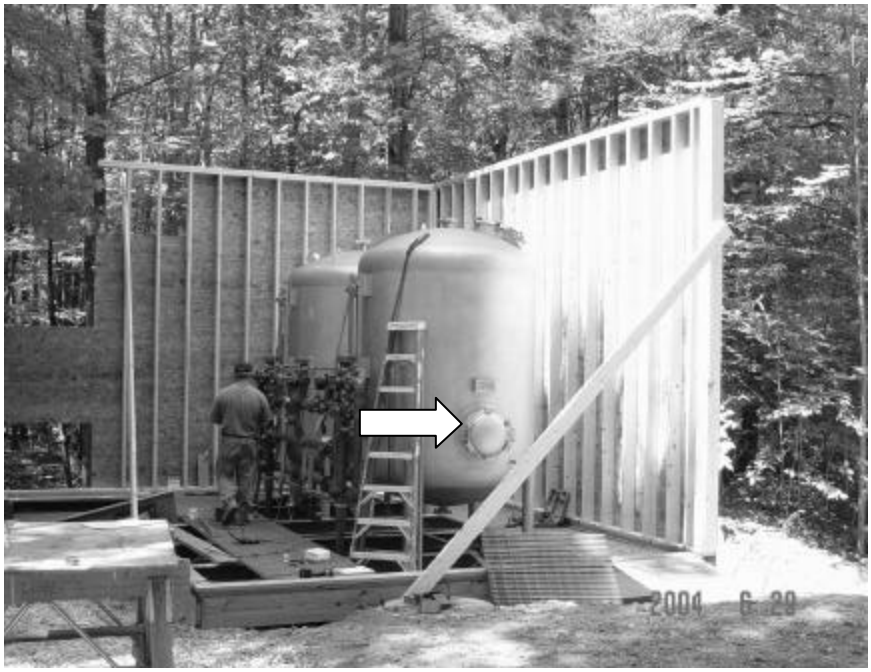
Other Design Considerations
Dust During Media Rebedding

- Funnel to guide media into tank.
- Note garden hose and spray nozzle connected to funnel to reduce dust.
- Vent fan needed.
- Dusk mask for workers.

Other Design Considerations Spent Media Removal

- No side tank removal provisions
  - Provide adequate headroom between top of tank and underside of ceiling.
- Discharge port on side wall of tank
  - Wash out media into low rise decant tub.
- Some medias may adsorb radionuclides
  - Proper equipment location, staff training.
  - Recommend exposure badges.

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Other Design Considerations Duration of Backwashing

- Problem
  - Fines in adsorptive media need to be backwashed and pH level of media may need to be diluted.
- Solution:
  1. Sample faucet
  2. Transparent spool piping
  3. Air gap in piping
- Influent/effluent pressure gauges

Evaluating New Media

- Setup small pilot studies using 3”x10” cartridges running to waste.
  - Have throttling gate valve and water meter.
- Run pilot to initial arsenic breakthrough.
- Evaluate all media types and keep detailed records.
- EPA study and recommendations pending.

Arsenic Treatment Systems - Design and Operation: Michigan's Approach

EPA Arsenic Workshop

Cincinnati, Ohio

Aug 10-11, 2004

State of Michigan

Department of Environmental Quality

Pat Cook, P.E.

Michigan DEQ

Water Division

cookp@michigan.gov

517-241-1242

Michigan Water System Inventory

- 1,457 Community (Type 1) water systems
  - 75 surface water sources
  - 278 customers supplies
  - 1,104 ground water sources
- ~10,600 Non-community (Type 2) water systems
  - ~2,600 Non-transient non-community
  - ~8,000 Transient non-community

Arsenic in Michigan

- ~150 community water supplies will exceed the 10 ppb standard
- ~200 non-community non-transient water supplies will exceed the 10 ppb standard
- No surface water sources are expected to exceed the new MCL of 10 ppb

Arsenic in Michigan

Huron
Sanilac
Tuscola
Genesee
Lapeer
Oakland

MI DEQ – Water Division "Arsenic Policy"

- DEQ – Water Division has created an Arsenic Policy to assist water systems, consulting engineers and manufactures in designing and operating arsenic removal systems.
- Mainly for Type 1 or community water systems

Arsenic Policy

WATER DIVISION
POLICY AND PROCEDURES

NUMBER:	WD-03-020
SUBJECT:	DESIGN AND OPERATIONAL REQUIREMENTS FOR ARSENIC REMOVAL TREATMENT SYSTEMS FOR COMPLIANCE WITH THE ARSENIC MCL
EFFECTIVE DATE:	OCTOBER 20, 2003 PAGE: 1 OF 6

ISSUE:

Effective January 23, 2006, all community water supplies and nontransient noncommunity water supplies must comply with the revised arsenic maximum contaminant level of 0.010 milligrams per liter (mg/l), or 10 parts per billion (ppb). This policy will establish design criteria to be used by water systems when designing, installing, maintaining, and monitoring an effective arsenic removal treatment system.

AUTHORITY:

R 325.10601 (Rule 601) and R 325.10604c (Rule 604c) of the Administrative Rules adopted under the Safe Drinking Water Act, 1976 PA 399, as amended (Act 399), covering drinking water standards for specific contaminants, including inorganics, that shall be met by a supplier of water to assure the protection of the public health. In addition, Section 325.1004 (2) of Act 399 states, "Upon receipt of the plans and specifications for a proposed waterworks system, the department shall evaluate the adequacy of the proposed system to protect the public health by supplying water meeting the state drinking water standards."

What is NOT Allowed:

- Point-of-Use (POU) devices will not be allowed to comply with MCL's for Type 1 systems, but Point-of-Entry (POE) devices will be allowed in certain circumstances.
- Blending of water in the distribution system to reduce levels below 10 ppb
- Exemptions or variances as allowed in the Federal Arsenic Rule

New Systems/Sources

- Any new systems and/or sources that begin operation after January 22, 2004, must meet the 10 ppb standard before going on-line.

Initial Monitoring Requirements

- Groundwater Systems will be asked to collect the first compliance sample during the 1st quarter of 2005 from each entry point to the distribution system (EPTDS)
- Surface water systems must sample annually and complete sampling by December 31, 2006

Initial Monitoring Requirements

- If the first quarter sample in 2005 is less than 10 ppb, and there is no other sample result since 1996 showing As over 10 ppb, system will be in compliance and quarterly sampling may stop with DEQ approval.
- Otherwise, continue to sample quarterly in 2005

Compliance Requirements

-Violation based on 4 quarters of monitoring

- Unless a sample will cause the running annual average to exceed the MCL
- All samples collected during any one quarter will be averaged for compliance determination
- Violation if running annual average exceeds MCL

Standby or Emergency Sources

- Not required to install treatment on a well if it is not needed to meet “firm capacity” requirement
- *Firm capacity = the capacity of each water system component with the largest unit taken out of service.*
- True standby or emergency wells will also not be required to install treatment
- Should notify public if any source is being used if levels exceed the MCL

Design Requirements

- Pilot studies are <u>usually</u> required
- Pilots are not needed if proposed treatment units are being used at other systems with similar raw water quality
- Permits are required for ALL installations (including NTNCWS)

Design Requirements

- Items to take into Consideration
  - # and location of wells
  - Technology to be used/pilot data available?
  - Backwash frequencies and volumes
  - Backwash water disposal options
  - Series or parallel installation
  - Maintenance considerations (out of service)
  - Pre-oxidation
  - Iron, sulfate levels
  - Others

Sizing/# of Treatment Units

- For systems with one Entry Point to the Distribution System (EPTDS)

  -The entire capacity of the treatment system must, as a minimum, equal the firm capacity rating of the water system

  -At least two treatment units

  -Preferred method would be to have firm capacity of the treatment system equal to the firm capacity of the water system

Sizing/# of Treatment Units Example: One EPTDS

- Small water system has two,100 gpm wells in a common well house
- Install in parallel, two (2) 100 gpm treatment units

OR

- Install in parallel, three (3) 50 gpm treatment units

Sizing/# of Treatment Units

- <u>For systems with multiple Entry Points to the Distribution System (EPTDS)</u>

The firm capacity of the treatment system must equal the firm capacity rating of the water system

Firm capacity = the capacity of each water system component with the largest unit taken out of service.

Sizing/# of Treatment Units Example: Multiple EPTDS

- System has fours wells (100, 200, 250 and 300 gpm) all in different well houses. Firm capacity = 550 gpm
- Install treatment units in each well house equal to the well capacity serving that particular well house (i.e. one 100 gpm unit for the 100 gpm well, two 100 gpm units for the 200 gpm well, etc.)
- Treatment capacity in each well house should equal the capacity of the well

Existing Treatment Systems

- Many systems in Michigan were installed to remove iron, but also remove arsenic
- Some have one, large treatment unit to remove both iron and arsenic (aerolators)
- These systems will not be required to build redundant plants until major upgrades/improvements are needed

Point of Entry Requirements

Point of entry devices (on service lines providing treated water for entire building) are allowed under the following conditions:

1. All units must be owned, controlled and maintained by water system owner
2. 100% participation
3. Alarms included
4. ANSI/NSF approved units must be used
5. Operation and Monitoring plans must be approved by state

Operational Requirements

- Operators must have “D” or Limited Treatment licenses
- Collect arsenic samples from the effluent of each treatment unit weekly (via field test kit or certified lab)
- Collect compliance sample quarterly

Types of Treatment

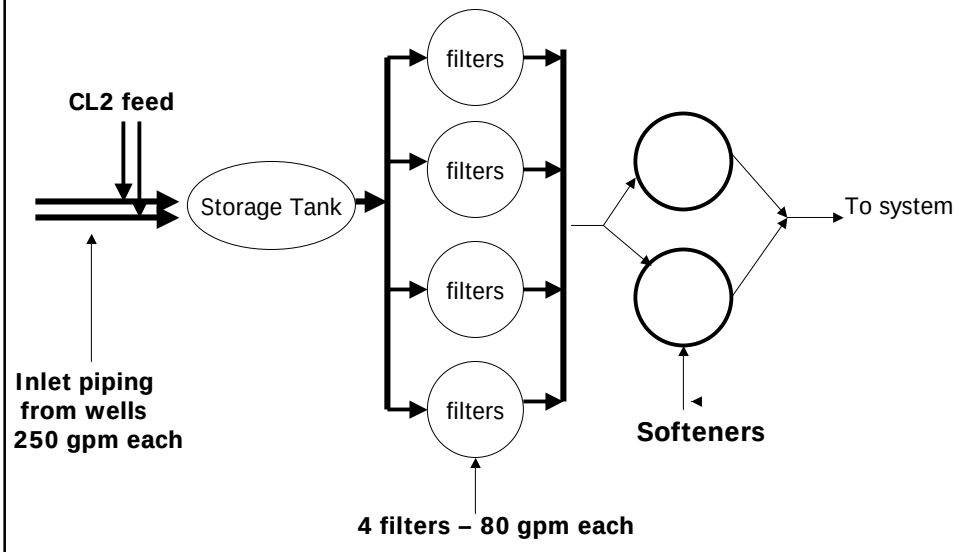
- Severn-Trent SORB 33 media
- ADI- G2 media
- Ad-Edge AD33 media
- Layne – OX media (piloted)
- Ondeo–Ferazur biological process (piloted)
- Conventional oxidation/precip/filtration
- Potassium permanganate/greensand
- Membranes (RO)

Whitmore Lake Apts

Whitmore Lake Apts

1. 125 unit apartment complex
2. Arsenic levels around 20 ppb
3. 2 - 250 gpm wells with hydropnuematic storage
4. 4 - 80 gpm each GFH adsorption media filters
5. Chlorine feed (pre-oxidation)
6. Softening
7. Backwash water to sanitary sewer

Whitmore Lake – Well House



Whitmore Lake Apts

Whitmore Lake Apts

Whitmore Lake Apts

Questions

ISSUE:

Effective January 23, 2006, all community water supplies and nontransient noncommunity water supplies must comply with the revised arsenic maximum contaminant level of 0.010 milligrams per liter (mg/l), or 10 parts per billion (ppb). This policy will establish design criteria to be used by water systems when designing, installing, maintaining, and monitoring an effective arsenic removal treatment system.

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DEFINITIONS:

Community Water Supply (CWS) – A public water supply that provides year-round service to not fewer than 15 living units, or that regularly provides year-round service to not fewer than 25 residents. Examples include municipalities, such as cities, villages, and townships; apartment complexes; manufactured housing communities; condominiums; and nursing homes.

Nontransient Noncommunity Water Supply (NTNCWS) – A noncommunity supply that serves not fewer than 25 of the same individuals on an average daily basis more than six months of the year. Examples include places of employment, schools, and day care centers.

Maximum Contaminant Level (MCL) – The maximum permissible level of a contaminant in water that is delivered to any user of a public water supply.

Operator In Charge (OIC) – A properly certified operator who is designated by the owner of a public water supply as the responsible individual in overall charge of a waterworks system, or portion of a waterworks system, who makes decisions regarding the daily operational activities of the system that will directly impact the quality or quantity of drinking water.

Firm Capacity - As applied to wells, pumping stations, or units of treatment systems, means the production capacity of each respective part of the water system with the largest well, pump, or treatment unit out of service.

Entry Point to the Distribution System (EPTDS) – A point where treated water enters the distribution system, after treatment and before the first customer. In most cases, this is where public water systems have to collect samples to determine compliance with the arsenic standard. For purposes of this policy, the compliance sample location will be called the "plant tap."

Point-of-Entry Treatment Device (POE) – A treatment device applied to the drinking water entering a household or building for the purpose of reducing contaminants in the drinking water throughout the house or building. These treatment devices are usually installed on the service line as it enters a building.

Point-of-Use Treatment Device (POU) – A treatment device applied to a single tap used for the purpose of reducing contaminants in the drinking water at one tap. These treatment devices are usually installed near or at the kitchen tap.

BACKGROUND:

The final arsenic rule was published in the Federal Register (66 FR 6976) on January 22, 2001, with an extended effective date of March 22, 2002. The rule applies to all CWSs and NTNCWSs and establishes a new arsenic MCL of 0.010 mg/l (10 ppb) that becomes enforceable on January 23, 2006, for existing systems. Also, the rule requires all new systems or systems that use a new source of water that begin operation after January 22, 2004, to demonstrate compliance with the MCL within a period of time specified by the state. It is the intent of the Michigan Department of Environmental Quality (MDEQ), Water Division (WD), to require any new systems or systems that use a new source of water that begin operation after January 22, 2004, to demonstrate compliance with the MCL before serving water to the public.

POLICY:

Initial Monitoring Requirements

For sources that exist prior to January 22, 2004 - The arsenic rule requires groundwater systems to sample for arsenic at each sampling point once every three years. The first compliance period starts January 1, 2005, and ends December 31, 2007. The WD is planning to require all groundwater systems to conduct quarterly sampling from each sampling point starting the first quarter of 2005. If the 2005 first quarter results are under 10 ppb **and** there is no other sample result from the same sampling point since January 1, 1996, equal to or over 10 ppb, the system will be determined in compliance and quarterly monitoring may stop if approved by the WD. If the 2005 first quarter results are equal to or over 10 ppb, **or** there are other sample results from the same sampling point since January 1, 1996, equal to or over 10 ppb, quarterly monitoring must continue for the remainder of 2005. If the running annual average (RAA) after four consecutive quarters of sampling exceeds the MCL, the system is in violation of the MCL.

Surface water systems will be required to sample annually from each sampling point and the first sample must be collected by December 31, 2006.

For new sources that come on-line after January 22, 2004 – Each new source must comply with the 10 ppb MCL before the source begins serving water to the public. If arsenic levels in a new source are below 10 ppb, the source is considered in compliance with the arsenic standard. Also, if the new source comes on-line between January 22, 2004, and January 1, 2005, the EPTDS must be sampled the first quarter of 2005 similar to the existing systems listed previously.

If the new source has arsenic levels over 10 ppb, the source may not serve water to the public until a properly designed treatment system, approved by the WD, is permitted and installed. After the new source (including treatment) is on-line, the EPTDS must be sampled at least quarterly. If the RAA after four consecutive quarters of sampling is below the MCL, the system is in compliance.

If a water system plans to use a source of water that has no arsenic treatment system and has knowledge that the source has arsenic levels over 10 ppb (i.e., a standby or emergency well), or plans to bypass or take out of service an arsenic treatment unit that will allow water to go to the distribution system with arsenic levels over 10 ppb, the system must contact the MDEQ immediately and collect arsenic samples weekly from the plant tap or at another frequency specified by the MDEQ. Also, the system should issue a public notice to the affected water customers, preferably at the time the source is placed in service.

Compliance Calculations

For systems monitoring more than once per year, compliance with the MCL is determined by an RAA at each entry point to the distribution system or other sampling point approved by the WD. Systems monitoring annually or less frequently whose result exceeds 10 ppb must revert to quarterly sampling. Systems triggered into increased monitoring will not be considered in violation of the MCL until they have completed one year of quarterly sampling. If any sample result may cause the RAA to exceed the MCL at any sampling point (i.e., the result is greater than four times the MCL) the system is out of compliance with the MCL immediately.

Systems may not monitor more frequently than specified by the WD to determine compliance unless they have applied to and obtained approval from the WD. If a system does not collect all required samples when compliance is based on an RAA of quarterly samples, compliance will be based on the RAA of samples collected. If a sample result is less than the method detection limit, zero will be used to calculate the RAA.

The WD may require confirmation samples for any results. All confirmation samples approved to be collected by the WD within a specific monitoring period will be averaged with the original result to calculate a quarterly average. The quarterly averages will be used to determine the RAA.

If an arsenic MCL violation has occurred, the water system should contact the WD immediately and public notification will be required. A Tier 2 public notice must be issued in accordance with R 325.10403 and R 325.10405 of Act 399 as soon as possible, but no later than 30 days after the violation has occurred.

Design, Operation, and Oversight of Arsenic Removal Treatment Systems

The design of arsenic treatment removal systems must take into consideration many factors to reliably and consistently keep arsenic concentrations below 10 ppb in the water delivered to the public. The type of treatment will depend upon the characteristics of the water to be treated, including, but not limited to, raw water arsenic concentrations, oxidation state of the arsenic in the raw water (arsenic III or V), iron levels, sulfate levels, pH, plus waste streams and backwash disposal options.

Many treatment technologies are available to remove arsenic. Treatment options consist of coagulation/filtration, coagulation assisted microfiltration, lime softening, activated alumina, ion-exchange (anion), oxidation/filtration and adsorptive/absorptive filter medias. Any emerging treatment technologies will also be considered. Water supplies planning to install an arsenic removal system may be required to run pilot studies. If a pilot study is not going to be completed, documentation must be submitted to the WD showing adequate treatment of water at other water systems using the same type of proposed treatment and having similar raw water quality.

The final design of arsenic removal systems will be based on the number and location of wells, disposal options, and the ultimate treatment technology to be used. Treatment systems may be installed in parallel, in series, and as a single pass or multiple pass configuration. The design must take into consideration that treatment systems will have to be taken out of service periodically for routine maintenance and/or repair. Below are some common types of system layouts and items that need to be taken into consideration when designing an arsenic removal system for each scenario.

Systems with several EPTDSs (i.e., two or more wells with each well located in a separate well house) -The firm capacity of the entire arsenic removal system must equal, as a minimum, the firm capacity rating of the water system. Systems are strongly encouraged to install treatment systems at each EPTDS that may exceed the 10 ppb standard. While systems are not required to have redundant treatment units at each EPTDS, the rated capacity of the treatment units at each EPTDS should equal the raw water capacity serving that particular EPTDS.

Systems with one EPTDS (i.e., two or more wells that have a common well house or one treatment plant) – As a minimum, two treatment units must be installed. The capacity of the entire arsenic removal system must equal, as a minimum, the firm capacity rating of the water system. The preferred design is to have the firm capacity of the treatment system equal the firm capacity rating of the water system. This will allow one unit to be taken out of service while the other unit(s) can remain on-line and still meet maximum day demands.

If an existing system has just one large treatment unit, and the unit satisfactorily removes arsenic below 10 ppb, a second treatment unit will not be required until major upgrades or improvements are needed to the treatment system.

Blending Options – This option is available for systems that have some sources of water (wells) above and some below, 10 ppb of arsenic should only be considered in unusual circumstances. This

option will allow water systems to blend the water of two or more wells before entering the distribution system to keep arsenic levels less than 10 ppb. An example is blending of water from one well with arsenic of 2 ppb with water from another well with arsenic of 14 ppb. If the wells have similar pumping capacities, the resulting arsenic concentration will be 8 ppb, which will meet the new standard. The blending of water must take place prior to entering the distribution system and operational guidelines for using this option must be reviewed and approved by the WD before being implemented. Systems should be aware that by using this option, the firm capacity rating of the water systems may be decreased by the WD. Also, the system must have a valid reason for not installing treatment on the well(s) with high arsenic levels.

POUs and POEs – Due to capital and operational costs, this option should only be considered by small systems, typically less than 100 service connections. POUs are usually installed near or at the kitchen sink and POEs are installed on the service line as it enters a building. All of these types of treatment units must be owned, controlled, and maintained by the public water supply and must be equipped with alarms to indicate the unit has failed or is not operating properly. All or 100 percent of customers must participate for a system to be eligible for this option. If the American Standards National Institute/National Sanitation Foundation has issued product standards applicable to a specific type of POU or POE treatment device, units meeting those standards shall be used. Supplies shall obtain WD approval for their POU/POE operational oversight and monitoring plans.

Proper operation and oversight is critical for arsenic removal systems. All systems with arsenic removal treatment units must designate an OIC and backup operator. The OIC must have, as a minimum, a limited treatment or "D" certification and provide regularly scheduled visits to the water supply in accordance with Drinking Water and Radiological Protection - Policy 03-017, Community Water Supply Systems – Required Operations Oversight.

Monitoring of treatment systems will be determined on a case-by-case basis at the discretion of the WD. For operational purposes, individual treatment units (i.e., each filter) should be sampled at least once per week. Samples collected at each treatment unit effluent can be analyzed by either a certified lab or a field test kit acceptable to the WD. Compliance monitoring at each EPTDS for supplies that have arsenic removal systems will be required to sample at least quarterly, and the analyses must be done at a laboratory certified for arsenic analysis. Refer to the example sampling scenarios attached to this policy for additional guidance.

PROCEDURE:

Responsibility	Action
Water Division District Staff	Incorporates this policy and procedure as part of the permit process to construct arsenic treatment systems and uses this policy and procedure to evaluate proposals from consulting engineers, developers, and water systems. Plans, specifications, and/or permit applications for arsenic treatment systems that are inadequate in design or application information will be returned to sender. Review arsenic monitoring results collected by the CWS to determine compliance with the arsenic MCL.
CWS Owner	An Act 399 construction permit shall be obtained from the MDEQ for arsenic treatment systems prior to commencing installation. Conduct arsenic monitoring as required by the department and submit results to the WD.

APPROVED: Richard A. Powers, Chief
Water Division

DATE: October 20, 2003

EXAMPLES – ARSENIC REMOVAL SYSTEM DESIGN, MONITORING AND OPERATIONAL OVERSIGHT

Example No. 1 – A water supply has two wells, each 100 gallons per minute (gpm) and share a common well house (i.e., one EPTDS). Both of the wells have arsenic levels over 10 ppb. The firm capacity rating of 100 gpm is adequate to meet maximum day demands. Following the recommendation of the policy for systems with one EPTDS, the firm capacity rating of the treatment system should equal the firm capacity rating of the water system.

Design - Install three, 50 gpm treatment units (adsorptive/absorptive media, activated alumina, etc.) in parallel within the well house or two (2) 100 gpm treatment units in parallel. In the first scenario, there would be a total treatment capacity of 150 gpm and a firm capacity rating of 100 gpm. In the second scenario, there would be a total treatment capacity of 200 gpm and a firm capacity rating of 100 gpm. Both of these arrangements will allow one treatment unit to be taken out of service while still being able to meet maximum day demands.

Oversight – For D-4 systems, an OIC shall visit the water treatment facilities at least once per week. For D-1, D-2, and D-3 systems, the OIC shall visit the water treatment facilities daily. Effluent from each treatment unit (filter) should be tested weekly for arsenic using a field test kit acceptable to the WD. A quarterly plant tap sample shall be collected and submitted to a state approved lab for compliance purposes. It is recommended that a split sample should be tested with the field test kit at the same time the quarterly plant tap sample is collected for verification analysis.

Testing should increase to once per day frequency on any treatment unit that indicates an effluent concentration of greater than 5 ppb. Increased sampling should continue until at least two subsequent tests indicate the arsenic concentration for each treatment unit is below 5 ppb. Treatment units that continue to exhibit effluent concentrations greater than 5 ppb shall undergo routine maintenance (i.e., backwashing) and retested in accordance with above testing protocol until the arsenic concentration is less than 5 ppb.

In the event that a test indicates an arsenic concentration of greater than 10 ppb, the treatment unit shall be taken out of service immediately and an arsenic sample shall be collected from the plant tap and submitted to a state approved laboratory for arsenic analysis. If backwashing does not return the concentration to less than 5 ppb, a service technician shall be called.

Example No. 2 – A water system has fours wells (100, 200, 250, and 300 gpm) and are located in different locations within separate well houses (i.e., four EPTDS's). All of the wells have arsenic levels over 10 ppb. The firm capacity of the water system (550 gpm) is adequate to meet maximum day demands. Following the recommendation of the policy for systems with several EPTDSs, the firm capacity rating of the treatment system must equal the firm capacity rating of the water system.

Design – Install treatment units in each well house in some combination equal to the well capacity serving that particular well house. As an example, you could install three, 100 gpm treatment units or one 300 gpm unit in the well house where the 300 gpm well is located. This arrangement will allow either the largest capacity well or the largest capacity treatment unit to be taken out of service while still being able to meet maximum day demands.

Oversight – Operational oversight and sampling of each treatment unit should be the same as in Example No. 1.

Example No. 3 - A water system has fours wells (200, 250, 350, and 400 gpm) that pump to a common pipe that leads to an existing iron/arsenic treatment plant, which consists of one 1,200 gpm treatment unit (i.e., one EPTDS). All of the wells have arsenic levels over 10 ppb. The firm capacity of the wells (800 gpm) and the total capacity of the treatment plant are adequate to meet maximum day demands.

Design - Since there is only one treatment unit, the system's firm capacity rating for the treatment system is 0 gpm. This is not the preferred method of design, but will be allowed if the existing treatment system is adequately removing arsenic to below 10 ppb. When major improvements are needed to the treatment system, a minimum of two treatment units equal to the firm capacity of the system will be required.

If this is a system installing treatment for the first time, the design (at a minimum) would have to include at least two treatment units equal to the firm capacity of the well system (i.e., two 400 gpm treatment units). A more flexible design to provide better reliability would be to install four 300 gpm treatment units that would provide a treatment firm capacity of 900 gpm.

Oversight – For D-4 systems, the OIC must visit the plant weekly. For D-1, D-2, and D-3 systems, the OIC must visit the plant daily. The plant tap should be sampled weekly using a field test kit acceptable to the WD. A quarterly plant tap split sample shall be collected. One split should be tested with the field test kit and the other split sample should be submitted and analyzed for arsenic at a state approved laboratory for verification analysis.

Testing should increase to once per day frequency on any plant tap sample that indicates an effluent concentration of greater than 5 ppb. Increased sampling shall continue until at least two subsequent tests indicate the arsenic concentration for each treatment unit is below 5 ppb. Treatment units that continue to exhibit effluent concentrations greater than 5 ppb shall undergo routine maintenance (i.e., backwashing) and retested in accordance with above testing protocol until the arsenic concentration is less than 5 ppb.

Example No. 4 – A water system has two wells, one well with an arsenic concentration of 2 ppb and the other with an arsenic concentration of 14 ppb. The wells have equal pumping capacities and pump to a common pipe before entering the distribution system. Therefore, the resulting arsenic concentration when both wells are operating is 8 ppb.

Design – In this case, treatment will be required to be installed on the source with arsenic levels of 14 ppb, unless waived by the WD. If a waiver is approved by the WD, the telemetry or well system controls must be set up so that both wells operate simultaneously to achieve adequate blending and dilution. Water meters or hour meters shall be installed for each well to make certain that both wells are pumping the same amount of water. Systems must be aware that eventually the well with the lower arsenic levels will be out of service, allowing only the well with an arsenic level over 10 ppb to pump water to the system.

Oversight – For D-4 systems, the OIC must visit the plant weekly. For D-1, D-2, and D-3 systems, the OIC must visit the plant daily. Both wells and the plant tap should be sampled monthly using a field test kit acceptable to the WD. The plant tap must also be sampled quarterly and submitted to a state approved lab for MCL compliance determination.

Example No. 5 – A 30-home subdivision has two wells that both have arsenic levels over 10 ppb. The homeowners have chosen to install POUs in each home to comply with the arsenic MCL. All 30 homeowners have agreed to participate.

Design – The POUs must be installed at or near the kitchen tap and all units must be owned, controlled, and maintained by the owner of the water system (homeowners association, developer, private utility company, etc.). All treatment units must have alarms indicating that the unit is not working properly or has reached its maximum design life.

Oversight – Since this is a D-4 system, the OIC must visit the water system weekly. Approximately 10 percent of the treatment units shall be sampled quarterly and submitted to a state approved lab. The quarterly sampling should be rotated among the homes so that every unit is sampled at least once every three years.

If any sample result exceeds 10 ppb, a confirmation sample must be collected from the same location as soon as possible. If the confirmation sample also exceeds 10 ppb, that particular treatment unit must be replaced or repaired immediately and all other units must be scheduled for repair or replacement as soon as possible.

Adsorption Pre-Treatment Considerations

EPA Workshop on the Design and Operation of Adsorption Media Processes for the Removal of Arsenic from Drinking Water
August 10-11, 2004

Greg Gilles
Vice President
AdEdge Technologies, Inc
Atlanta, Georgia
678-835-0052
greg@adedgetechnologies.com

Topics

- Importance of Pre-Treatment
- Common Interferents for Adsorption
- Pre-Treatment Technologies and Project Examples for:
  - Suspended solids, Sediment
  - Iron, manganese, sulfides
  - High pH
  - Organics, Tannins
  - Bacteria and Biofilms

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Why Pre-Treatment?

- Preserves the media for intended purpose
- Prevents premature exhaustion of media
- Reduces affects of interferents that can blind adsorption sites or foul media
- Prevents blocking of pore based adsorption sites where 90% of adsorption takes place
- Lowers long-term operation and maintenance costs
- Improves aesthetics of water (e.g., Secondary MCL)

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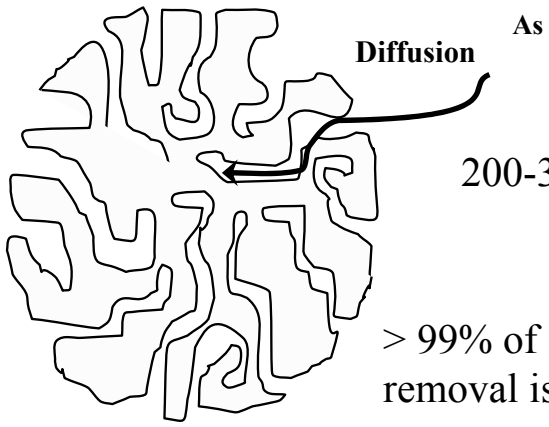
Accessible area of Granular Media



200-300 m^2/g

> 99% of surface for removal is internal

Source: M. Edwards June, 2003

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Common Myths

- I can effectively use my media bed as a filter for other contaminants and backwash when needed
- Specialty adsorption medias can remove multiple contaminants in addition to arsenic with equal effectiveness without negative consequences
- Naturally occurring iron is always beneficial in arsenic adsorption processes since iron has an affinity for arsenic
- All medias are affected similarly by interferants
- pH adjustment for high pH waters will always be the most economical approach

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Pre-Treatment Considerations begin in the design stage with understanding of the site specific water chemistry

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AdEdge Technologies, Inc.
AD33 Adsorption System
System Sizing and Budget Estimate Form

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Arsenic Reduction - Small Water Systems
Application - Site Profile Form

Customer Confidential

Contact Information

Customer / Utility:		**Date (mm/dd/yy) :**	
Site or Well Location:		**Main Contact :**	
Local Engineer / Firm:		**Phone:**	
Operator:		**Fax:**	
		Email:	
Other Pertinent Notes:			

System Parameters / Site Specific Info

System Type / Application:		(municipal / utility, school, recreational, trailer park, subdivision, other)
Population Served:		
Number of Connections:		
Design Flow (GPM):		(Max design flow rate)
Ave Flow (GPM):		(Typical demand)
Gallons per day:		(Ave throughput per day)
Est. Usage (Gals / Year):		(Best estimate)
Existing Pretreatment In Place:	Describe:	
Existing Disinfection:	Yes / No If Yes, Type: Cl_2 gas / HOCl / ClO_2 / Chloramine / Ozone / Other	
Disinfection Injection Point:	Pump Shaft / Storage Tank / Downstream	
Pump Operation:	Constant / Intermittant / Other	
Pump Discharge Pressure (psi):		
Electrical Power Availability:		
Storage Tank Present at the site:	Yes / No If Yes, Size and location:	
Hydropneumatic Tank Present:	Yes / No If Yes, Size and location:	
Building present:	Yes / No If Yes, Available space in existing building:	
Any additives ie, phosphates, fluoride:	Yes / No If Yes, Specify type and injection point:	
Discharge Options:	Sanitary Sewer (POTW) / Drainage Ditch / Evap. Pond / Other	

Water Analysis
(enter all available)
**** denotes priority parameters**

Most Important Water Parameters

pH **			**Antimony**		mg/L Sb
Total As **		mg/L As	**Sulfides****		mg/L
As(III)		mg/L	**Chromium**		mg/L Cr
Alkalinity		mg/L @ CaCO3	**Fluoride**		mg/L F
Hardness **		mg/L @ CaCO3	**Lead**		mg/L Pb
Silica **		mg/L SiO2	**Vanadium ****		mg/L Va
Phosphate **		mg/L P04	**Molybdenum**		mg/L Mo
Sulfate **		mg/L SO4	**Selenium**		mg/L Se
Iron **		mg/L Fe	**Turbidity**		NTU
Manganese **		mg/L Mn	**Suspended Solids**		mg/L

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Parameters for Pre-Treatment

- Suspended solids / sediment
- Iron and/or manganese
- High pH
- Sulfides
- Organics, Tannins
- Bacteria, Biofilms

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Common Pre-treatment Scenarios

Condition	Recommendation
Suspended Solids / Sediment	Pre-filtration: cartridge, bag, or media
High pH > 8.5	Adjust pH to 7.0+/ – with HCL, H_2SO_4 or CO_2 gas
High pH and Silica Where pH > 8.5, SiO2 > 30 mg/l	Adjust pH to 7.0-7.5 to reduce interference
High Iron and / or manganese Fe > 0.3 mg/l, Mn > 0.05 mg/l	Pre-treat for iron: oxidation / filtration or media oxidation / filtration
High arsenic + Predominant As (III) present	Pre-oxidation of As (III) to As (V) for optimal longevity and performance
Sulfides	Pre-treat to oxidize sulfides
Organics / Tannins	Chemical oxidation or IX resin specific for organics
Bacteria / Biofilm	Oxidation / shock treatment

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Project Examples and Field Applications

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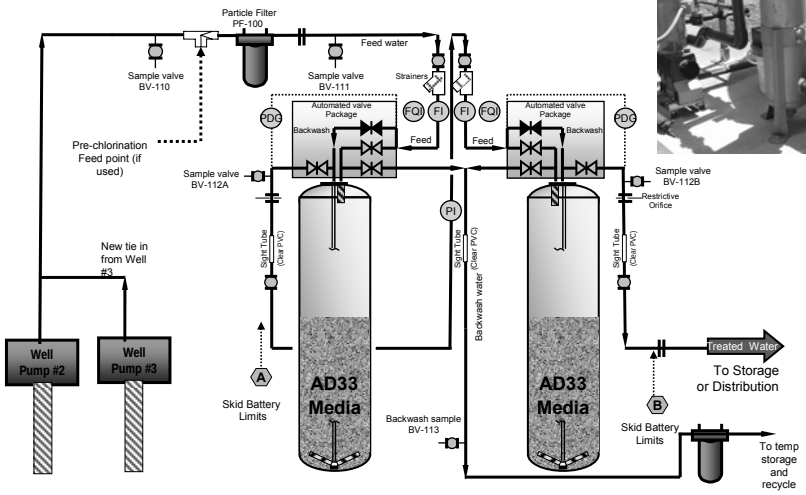
Rimrock - Arizona
Montezuma Haven Wells
Series Operation



Rollinsford, New Hampshire

- EPA Demo Site
- 100 gpm system
- pH 8.4 typical
- pH adjustment with CO_2 gas
- 58,000 gallons/day
- Arsenic influent = 40-50 ppb
- Operational Jan, 2004

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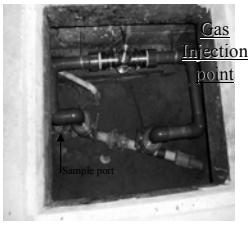
pH Adjustment Using CO_2
(Rollinsford, NH)



- 100 gpm flow rate, 12 hours/day
- (3) 50 lb gas cylinders on-line
- Delivery pressure approx. 100 psi
- 2-4 scfh injection rate through CO_2 membrane
- pH monitoring probe and control panel
- CO_2 cylinder change-out approx every 3 weeks

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Membrane based CO_2 Injection for pH Adjustment

- Has some advantages over acid
  - Health and safety
  - Low operating costs
- Rapid pH adjustment with very short contact time
- Higher initial capital cost
- Requires monitoring system for control and measurement
- Natural de-gassing after treatment raises pH
- Depending on water quality, probes and membrane may require periodic cleanings

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Oxidation of As(III) to As(V)

	Effective		Not Effective
Cl_2	√		
O_3	√		
$KMnO_4$	√		
NH_2Cl		√	
ClO_2		√	
DO			√
UV			√

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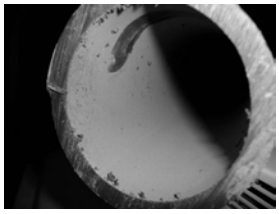
Iron…Friend or Foe?

- Arsenic has a natural affinity for iron
- Naturally occurring iron in water can be maximized in design to help reduce arsenic; efficiencies vary by process and water chemistry
- Iron can foul / plug adsorption and many processes and therefore pretreatment is recommended above certain thresholds
- Combination of iron pretreatment and adsorption polishing is ideal for effectively reducing arsenic to meet MCL



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Iron / Arsenic Removal

One must understand the water chemistry and limitations of the specific media to be able to determine or predict long-term affects on performance

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Factors to Consider

- What are the treatment goals?
- The concentration of iron and manganese
- Oxidation state
- pH, Alkalinity, and Hardness
- Dissolved oxygen for some treatment types
- Presence of iron and manganese bacteria

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Fe/Mn Treatment Methods

- Softening
- Aeration + Filtration
- Oxidation / Filtration Processes
  - AD26 Catalytic Media
  - Mn Greensand with KMnO4 regeneration
  - Pyrolusite
- Sequestering for Low Concentrations

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Iron, Manganese Pre-Treatment

- Softening
  - Only recommended where both iron/manganese and hardness are high
  - Effective for water containing less than 2-4 mg/L of dissolved colorless iron or < 0.5 mg/L manganese
  - Adds sodium to the drinking water and creates brine disposal problems.
- Oxidation / Filtration Removal
  - Media and non-media based options
  - pH value is important
  - Best results with chemical oxidants e.g., Cl_2 or $KMnO_4$
  - Contact time
  - Aeration can be used rather than chemicals
- Greensand with $KMnO_4$
  - pH should preferably be over 7.5
  - Requires either intermittent or continuous regeneration.

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Project Profile: Michigan

- Elementary School
- Location: Oakland County, Michigan
- AdEdge APU-40 Adsorption system w/ GFO media
- Influent Arsenic: 37-50 ppb
- 40 gpm design flow
- Installation May, 2003
- Water Conditioning used for Iron and Hardness Removal (0.8 mg/L Fe)
- Effluent arsenic below detection after treatment

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Project Profile: Kenai, Alaska

- US Fish and Wildlife Service
- Design flow: 50 gpm
- Location: Kenai, Alaska
- Influent Arsenic: 51 ppb
- Installation March 21, 2003
- 26 cubic feet Adsorption Media
- Iron 2.6 mg/L; using softening system
- pH 7.3
- Effluent < 2 ppb As

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Pilot – Nursery Site, Florida

- AdEdge AD33 Pilot
- 2 gpm flow rate
- EBCT of 7.5 min/vessel
- (2) 12-in vessels in series
- Iron 1 – 1.5 mg/L
- pH approx 7.1
- 5-micron prefilter
- Arsenic influent 1.5 – 2.2 mg/L
- Treatment goal 0.250 mg/L
- Continuous operation 24 hr, 7 day/week

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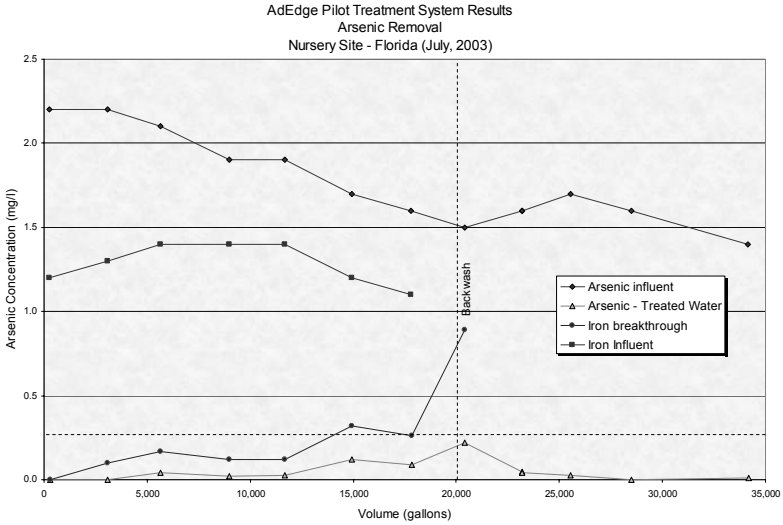
Arsenic / Iron Treatment



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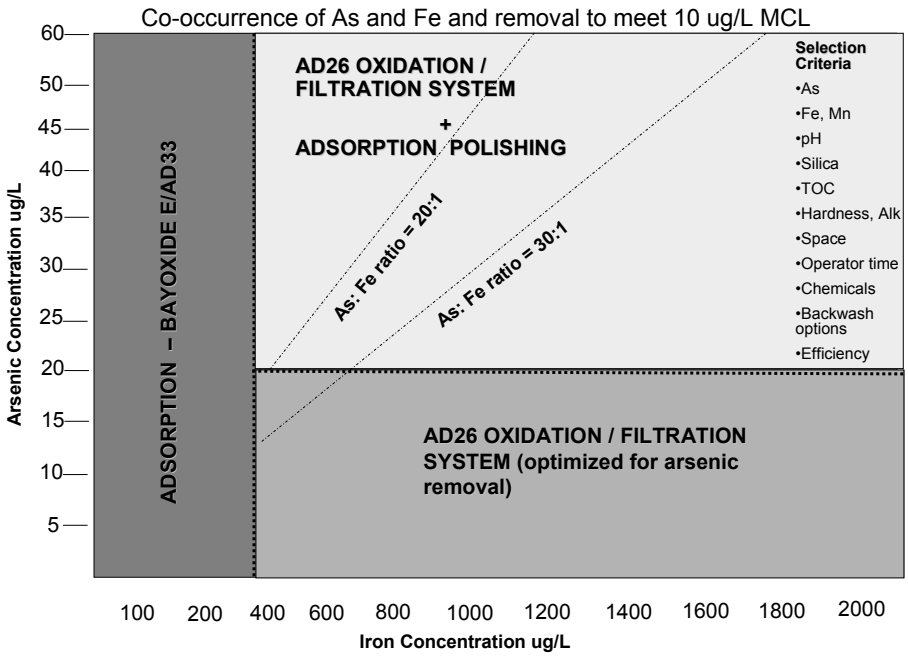
Treatment Selection



AdEdge AD26 Systems

- Oxidation / Filtration Process
- Designed for Iron, Manganese and Sulfide + low level arsenic removal to meet MCLs
- Utilizes catalytic MnO_2 media for efficient removal of Fe, Mn and co-precipitation of As
- Stand alone or used as pre-treatment for Sorb 33 Systems
- Used most efficiently with hypochlorite addition
- Media lasts 5-10 years or more, no regeneration, only backwash

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World War II Memorial Site
Washington, DC

- Groundwater Treatment
- (2) 30 gpm AD26 and (2) Sorb 33 Systems
- Contaminants: Iron, Manganese, and Arsenic
- 20' below grade in vault beneath monument
- Arsenic influent 20-60 ppb
- Iron 0.5 – 10 ppm
- Mn 0.05 – 2 ppm
- 2 ppb treatment limit
- Operational June, 2004
- Operated by National Park Service

National WWII Monument

AD26 Iron pretreatment + APU-40 System
Washington, DC

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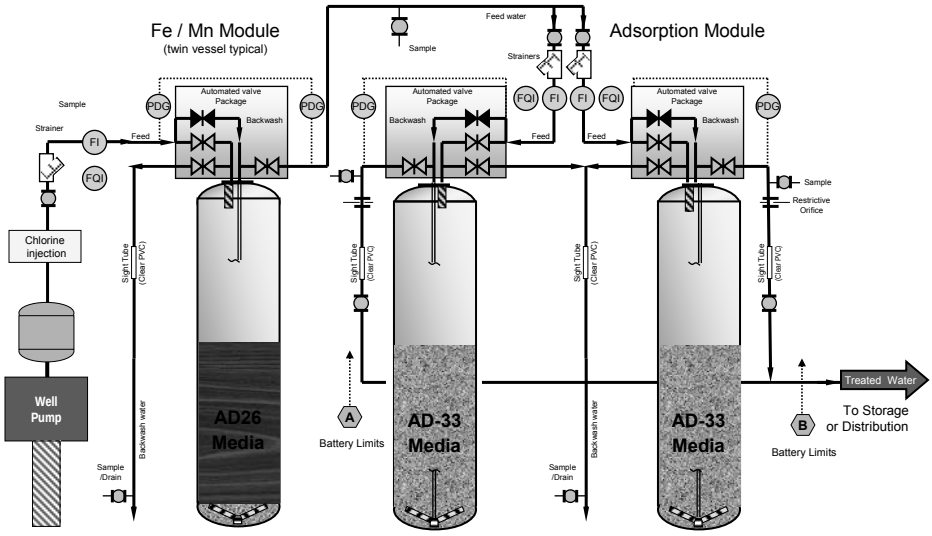
Process Flow Diagram
AdEdge AD33 Arsenic Reduction System
System with Iron / Manganese Pretreatment



Project Profile: Alaska

- Commercial System
- Location: Yakatat, Alaska
- Arsenic: 80-90 ppb
- 25 gpm System serving regional airport
- Installed May, 2002
- 20 cubic feet AD33 Adsorption Media
- Pre-Treatment: Ozone pretreatment for Fe, Mn, and bacteria; GAC, Softening
- Effluent arsenic - Non detect

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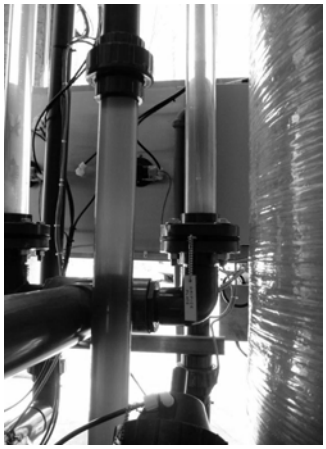
Pre-Treatment Backwashing

- Removes co-precipitated iron, manganese and arsenic particulates that are filtered
- Often performed at differential pressure set points or manually
- Performed typically 1-3x/week depending on water profile
- Rates from 8-25 gpm/sq foot for various products
- Non-hazardous water can be discharged to POTW, septic in most cases



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Sequestering Agents

- Polyphosphate based products or others
- Complexes / chelates iron
- Reduces or interferes with adsorption processes (phosphate interference)
- If used, inject <u>after</u> the treatment system to avoid negative impact to adsorption media

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Sulfides

- Sulfides can bind with media
- Sulfides act as an interferent and/or competitor for adsorption sites on iron-based medias; form low solubility precipitants as well
- H_2S result often of bacterial reduction of SO_4; detected at levels around 0.05 mg/L
- Obvious aesthetic issues
- Co-occurrence with iron, As (III), reducing conditions

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Organics

- Naturally occurring organics from decay of plant material
- Humic and other types of organic acids
- Not much study on the affects to adsorption medias
- More often issue in surface water rather than groundwater
- Oxidation using Chlorine, ClO_2, Ozone are common methods of destruction
- IX resins are available for Tannin removal

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Biofilms and Biofouling

- Heterotrophic plate count bacteria are ubiquitous in water systems
- Mostly non-harmful and non-pathogenic
- Can cause fouling and performance issues for adsorption systems
- Less likely in systems using disinfectants
- System and/or media may require periodic shock treatments if accumulations observe
- Bacteria "carry through" can bring arsenic or other contaminants with it

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Pre-Treatment Monitoring

- Sample contaminant of concern after pretreatment unit to determine effectiveness
- Frequency of sampling should be at least as frequently as arsenic samples are obtained
- Field test kits offer rapid methods
- Be aware of laboratory analyte interferences and detection limits

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Other Pre-Treatment Issues

- Backwashing water quality and quantity
- Discharge Options
  - POTW or Septic
  - Filter and/or coagulate and discharge or recycle
  - Evaporation pond
- Presents some challenges for remote / rural systems with no POTW or Septic options
- Residuals Management (if not direct discharged)
- Pre-treatment capital costs can be 50% or more of adsorption system costs depending on method

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Conclusions

- Do your homework up front on the water chemistry to avoid surprises
- If in doubt about the affects on performance, consider pre-treatment or piloting
- The role and benefits of naturally occurring iron for arsenic removal to meet the MCL must be evaluated on a case-by-case basis and designed carefully
- Pre-treatment cost/benefit ratio must factor in:
  - prolonged life of adsorption media
  - Lower life-cycle costs
  - Improvement to aesthetics
- Consider residuals management for pre-treatment scenarios

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As Removal from Drinking Water
Adsorption Media Handling

EPA Workshop on Adsorptive Media Processes

Richard S. Dennis
Severn Trent Water Purification, Inc.
August 11, 2004

Discussion Topics

- Media Characteristics
- Packaged Media Delivery & Handling
- Adsorber Loading
- Residuals Handling
- Media Conditioning & Backwashing
- Media Regeneration
- Spent Media Removal
- Media Disposal

Adsorptive Media Characteristics

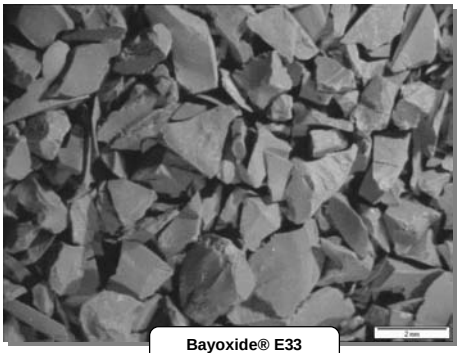
- **Bulk Density & Specific Gravity**
  - Higher Lb/Ft³ = Greater Unit Weight & Higher Fluidization Flows
- **Shape & Size**
  - Granules, Pellets, Spherical Beads, Powder
  - Normal Adsorptive Media Size
    - Low Δ**P** but Lower Unit Capacity
  - Finer Adsorptive Media Size
    - Higher Unit Capacity but High Δ**P**
- **Flowability & Friability**
  - Ease of Loading & Removal
  - Physical Attrition in Handling or Service
- **Miscellaneous**
  - NSF Certification, Consistency, Availability, etc.

Sieve Sizes & Tyler Equivalents

Std Sieve Designation	Sieve Opening mm.	Sieve Opening inches	Wire Dia mm.	Tyler Mesh Size
8.00 mm	8.00	0.312	2.07	2.5
6.73 mm	6.73	0.265	1.87	3
5.66 mm	5.66	0.223	1.68	3.5
4.76 mm	4.76	0.187	1.54	4
4.00 mm	4.00	0.157	1.37	5
3.36 mm	3.36	0.132	1.23	6
2.83 mm	2.83	0.111	1.10	7
2.38 mm	2.38	0.0937	1.00	8
2.00 mm	2.00	0.0787	0.900	9
1.68 mm	1.68	0.0661	0.810	10
1.41 mm	1.41	0.0555	0.725	12
1.19 mm	1.19	0.0469	0.650	14
1.00 mm	1.00	0.0394	0.580	16
841 µm	0.841	0.0331	0.510	20
707 µm	0.707	0.0278	0.450	24
595 µm	0.595	0.0234	0.390	28
500 µm	0.500	0.0197	0.340	32
420 µm	0.420	0.0165	0.290	35
354 µm	0.354	0.0139	0.247	42
297 µm	0.297	0.0117	0.215	48
250 µm	0.250	0.0098	0.180	60
210 µm	0.210	0.0083	0.152	65
177 µm	0.177	0.0070	0.131	80
149 µm	0.149	0.0059	0.110	100
125 µm	0.125	0.0049	0.091	115
105 µm	0.105	0.0041	0.076	150
88 µm	0.088	0.0035	0.064	170
74 µm	0.074	0.0029	0.053	200
63 µm	0.063	0.0025	0.044	250
53 µm	0.053	0.0021	0.037	270
44 µm	0.044	0.0017	0.030	325
37 µm	0.037	0.0015	0.025	400

SORB 33™ - Bayoxide® E33 Media

- **Granular Iron Media – "GIM"**
  - Manufactured for STS by Bayer AG
  - α-Ferric Oxide Hydroxide or α-FeOOH
  - Granular Ferric Oxide (**GFO**) - Crystalline
- **Physical Properties**
  - Appearance – Yellow/Orange
  - Particle Size Distribution – 0.5-2.0 mm
  - Bulk Density – 29 Lb/Ft³
  - Specific Gravity – 3.6 g/cc
  - Flowability – Flows like GAC when flooded
  - Friable Relative to GAC & AA
- **Packaging**
  - 38 Ft³ Supersacks
  - 2 or 4 Ft³ Drums
- **Similar Commercial Product**
  - US Filter's **GFH** – Granular Ferric Hydroxide
  - Manufactured by Wasserchemie - **GEH**



Bayoxide® E33
Granular Ferric Oxide

Media Storage & Delivery

- **Some Medias are Dry; Some are Moist**
- **Media Shelf Life**
  - Life Time from Production (4-30 Months)
  - Storage Requirements – Conditioned or Ambient
  - Product Deterioration – Drying, Surface Loss, etc.
  - Inventory – Responsibility by Supplier or Utility
- **Delivery**
  - Drums, Supersacks or Bulk
  - Larger Unit Volume Minimizes Handling
  - Vessel Accessibility for Media Fills

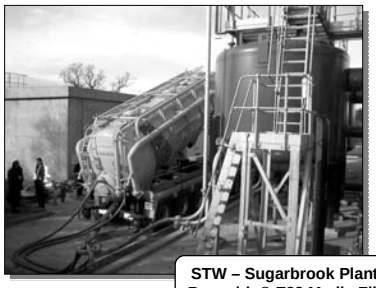
Adsorber Media Loading

- **Solids Handling - Rules of Thumb**
  - Dry Solids Gravity Feed - Simplest
    - Minimal Wastewater & Dust
  - Slurries Hydraulic Feed
    - Next Easiest
    - Wastewater Generation – Reuse Capability
  - Moist Solids from Packaging
    - Labor Intensive with Product Losses
- **Fill Equipment Requirements**
  - Readily Available Equipment
  - Specialized - Availability
- **Regional Media Service**
  - Size, Experience & Specific Know-how

EPA Demo Project
Anthony, NM
SORB 33™ 300 GPM Unit

Adsorber Loading – STW Process

- **Severn Trent Water (STW)**
  - 2nd Largest Utility in the UK
  - 46 MGD of Capacity
  - 60 Vessels @ 16 Sites
- **"Central" Bulk Handling System**
  - Fill Bulk Carbon Tanker from Sacks Off Site
  - Transport Dewatered Media Next Day
  - Pictured Site – Sugarbrook
    - 4 12'-Ø Adsorbers in Parallel
    - 3.6 MGD Total Capacity



STW – Sugarbrook Plant
Bayoxide® E33 Media Fill

Adsorber Loading – STW Process

- **"Central" Bulk Handling System (Cont'd)**
  - Hydraulic Fill of Empty Adsorber from Tanker
  - Partial Media Conditioning during Fill
  - Wastewater Routed to Backwash Water Reclaim
- **Process Assessment**
  - Works Well for STW
  - Labor Intensive & Multiple Media Handling

STW – Sugarbrook Plant
Bayoxide® E33 Media Fill

Adsorber Media Loading

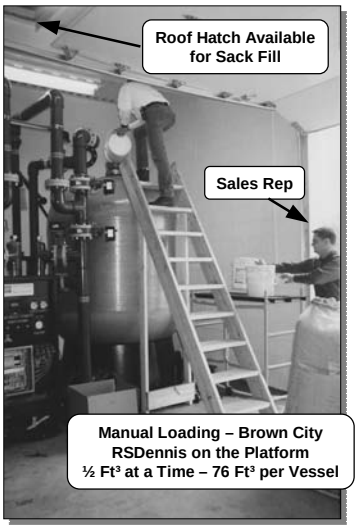
- **Dry Solids Loading**
  - Headroom Access for Sacks or Drums
    - Crane, Boom Truck or Forklift Access
  - Pneumatic Transfer
    - Equipment Intensive – Dust Collection
    - Media Attrition
- **Slurry Loading**
  - Hopper/Eductor Equipment
  - Wastewater Handling
- **Regional Media Service**
  - Size, Experience
  - Specific Know-how

Hopper & Eductor Loading
Nottingham, UK

Media Loading – Dry Gravity Fill

Aqua Pennsylvania Site
Roof Hatch Added for Gravity Fill
30 Minute Fill - 76 Ft³ per Vessel

- Small Systems - <300 Ft³ Inventory
- Roof Hatch Included/Added for Dry Fill
- Boom Truck Access ʷ/4”-Ø Flex Hose
- Both Sites – 300 GPM APU Systems



Manual Loading – Brown City
RSDennis on the Platform
½ Ft³ at a Time – 76 Ft³ per Vessel

Media Conditioning & Backwashing

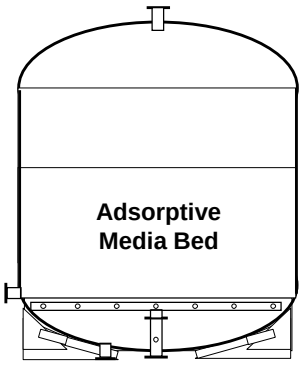
- **Pretreatment Requirements for Service**
  - Media Wetting
  - Conditioning for Fines Removal – Bed Fluidization
  - Regeneration & Rinsing if Media "Conversion" Required
  - Off-line Time Requirements - Backwashing
- **Residuals Handling - Wastewater**
  - Volume Generated & Quality – Toxicity, Solids & Corrosivity
    - Classification & Permits
  - Non-hazardous Liquids – Ditch, Sewer, Evaporation Pond, POTW
  - Solids-bearing Liquids – Decant Tank to Settle & Collect Solids
  - Zero Discharge – Surge Tank to Reclaim Liquid to As System Inlet

Media Regeneration & Spent Waste

- **Need for Media Regeneration**
  - Medias with Low As Capacities - <10,000 Bed Volumes (**BV's**)
  - Co-adsorption of PPM Level Contaminants – Fluoride, etc.

Spent Media Removal

- **Adsorber Vessel Underdrain Type**
  - Header/Lateral or HUB & Spoke
  - Cone Bottom with Screened Nozzles
  - False Bottom with Screened Nozzles or Porous Plate
  - Distribution Gravel Underbedding
- **Media Removal Method**
  - Pressurized Hydraulic Slurry Flow
  - Vacuuming
  - Gravel Underbedding Removal
  - Hydraulic Wastewater Disposal



Header/Lateral w/Underbedding

Spent Media Removal

- **Considerations**
  - Available Off-line Timing for Change-out
  - Vessel Entry Needs – Disinfection, etc.
  - Simple, Complete Removal vs Thorough Process
  - Gravel Underbedding Losses/Replacement
  - Empty Vessel Internals Inspection
- **Severn Trent Water Process**
  - Underdrain: Header/Lateral with Gravel
  - Drain Vessel & Media Bed of Water
  - Vacuum Media from Top Manway to Truck
  - Leave Gravel Underbedding Intact
  - Vessel Entry: Remove Media "Heal" & Inspection
  - Labor Intensive – UK Safety Laws

Spent Media Disposal

- **Spent Media Classification**
  - Hazard Criteria for Leachate: As > 5 mg/L; V > 5 mg/L; Cr > 5 mg/L
  - Non-Hazardous Classification – Passes EPA's TCLP Solids Waste Test
    - TCLP – **T**oxic **C**haracteristic **L**eaching **P**rocedure
  - Hazardous Waste Solids – 3-6 Times More Expensive Disposal
  - Total Mass of As Not Critical to Hazard Classification
- **California Hazard Classification**
  - Soluble Threshold Limit Concentration (STLC) – the "**WET**" Test
    - More rigorous test than TCLP
  - Total Threshold Limit Concentration (TTLC)
    - Total Mass of As in the Solid – Limit is 500 mg/Kg As
    - Some Medias Have As Capacity Greater than this TTLC Limit

Operation And Monitoring Of Adsorptive Arsenic Removal Systems

EPA Arsenic Workshop
Cincinnati, OH
August 2004
Glen Latimer

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Daily Operation Monitoring

- Flow monitoring
- Pressure drop monitoring
- Chemical addition monitoring
- Arsenic performance monitoring

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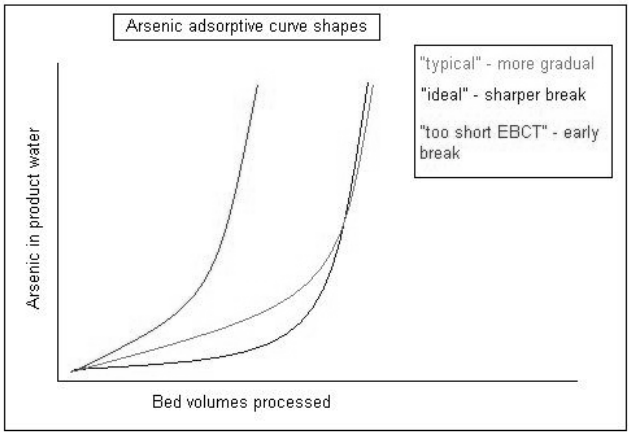
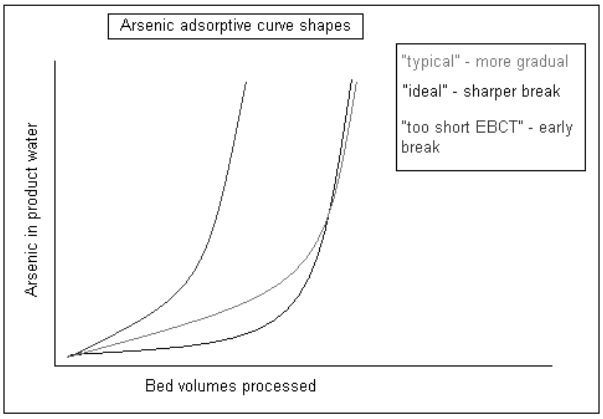
Flow Monitoring - Higher Than Design Flow

- Short EBCT
- Change in breakthrough time
- Change in breakthrough slope



Flow Monitoring - Lower Than Design Flow Effects

- Uneven distribution
- Channeling and wall effects
- Low flow indicating fouling



Pressure Drop Monitoring

- Manual pressure gauges or electronic transmitters can be used
- Suspended solids in feed water (media fouling)
- “Mud ball” forming
- Channeling
- Media fines collecting on lower distributor
- Insufficient flow
- Damage to underdrain
- Media loss

Chemical Monitoring - Chlorine

- Chlorine feed and monitoring
- Chemical storage level
- Residual monitor maintenance
- Loss of oxidation / As^{+3} leakage

Online Chlorine Monitor

Chemical Monitoring - pH Adjust

- **pH Adjustment**
- **Chemical storage level**
- **Probe cleaning and calibration**
- **Loss of pH control / arsenic leakage**

Online pH Monitor

Arsenic Analysis

- **Lab analyses**
  - **Atomic Adsorption (AA)**
  - **Inductively Coupled Plasma Mass Spectrometry (ICP-MS)**
- **Detection limits**
  - **AA: 2.0 ppb**
  - **ICP-MS: <0.50 ppb**
- **Location**
- **Frequency**

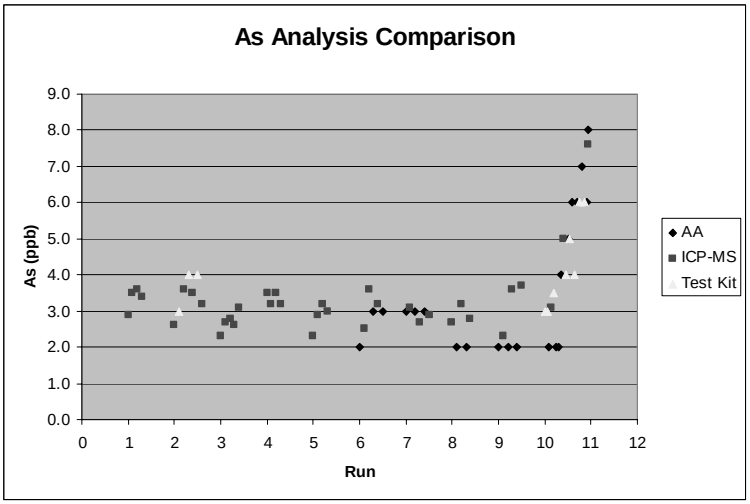
Atomic Absorption (Graphite Furnace)

ICP Mass Spectrophotometer

Arsenic Field Test Kits

- **Valuable for piloting and plant optimization**
- **Limitations**
- **Accuracy**

Arsenic Analytical Comparison



Future On-line Arsenic Analyzers

- Several technologies currently under development
- Extremely valuable in plant optimization as well as monitoring for compliance
- Elimination of 3rd party laboratory testing will result in cost savings for a utility

Arsenic Adsorptive System Control Panel

- PLC based controls
- Minimal automation provides for automatic backwashes
- PID control loop for pH control

Four Column Arsenic Adsorptive Pilot System

- 4 separate column allow for head-to-head testing of different media
- Manual system with instantaneous and totalizing flow meters
- Chemical injection point for oxidant and pH control

Valley Vista Arsenic Adsorption System

- 37 gpm lead/lag design
- PLC controls and actuated valves control basic start/stop and backwash functions
- Backwash waste sent to holding tank and settled water and recycled to raw water feed
- Automated pH control

Valley Vista Arsenic Adsorption System

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SESSION IV

Treatment Costs and Residuals Disposal

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Round 1 Arsenic Removal Technology Demonstration: Evaluation Approach

Chris Coonfare, Wendy Condit, Jeff Oxenham, Lili Wang, and Abe Chen, Battelle, Columbus, Ohio

Tom Sorg and Darren Lytle, U.S.EPA, Cincinnati, Ohio

1

Acknowledgments

- Funding for this effort is provided under Task Order 0019 of the U.S. Environmental Protection Agency Field Evaluation and Technical Support (FEATS) Contract No. 68-C-00-185.

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2

Main Objective

- Conduct full-scale demonstration studies on the removal of arsenic from drinking water supplies at twelve water treatment facilities throughout the United States
- Evaluate the efficiency and effectiveness of the technologies in meeting the new arsenic maximum contaminant level (MCL) of 10 µg/L

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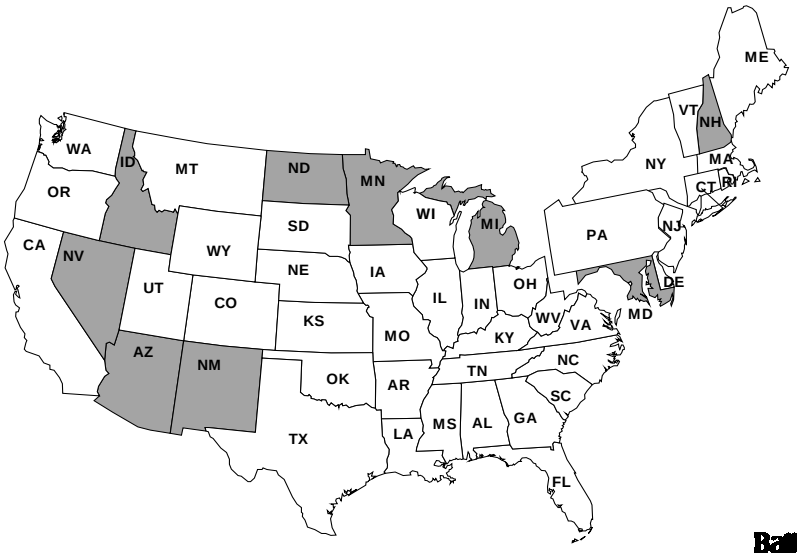
Round 1 – 12 Sites in 9 States



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Sites/Technologies Evaluated

State	Facility	Technology	Vendor	System Flowrate (gpm)	Concentration (µg/L)/ pH Unit		
					As	Fe	pH
NH	Bow	AM (G2)	ADI	70	39	<25	7.7
NH	Rollinsford	AM (E33)	AdEdge	100	36	46	8.4
MD	Stevensville	AM (E33)	Severn Trent	300	19	270	7.3
MI	Brown City	AM (E33)	Severn Trent	640	14	127	7.3
MN	Climax	C/F	Kinetico	140	39	546	7.4
ND	Lidgerwood	SM	Kinetico	250	146	1,325	7.2
NM	Anthony	AM (E33)	Severn Trent	320	23	39	7.7
NM	Nambe Pueblo	AM (E33)	AdEdge	145	33	<25	8.5
AZ	Rimrock	AM (E33)	AdEdge	90	50	170	7.2
AZ	Valley Vista	AM (AAFS)	Kinetico	37	41	<25	8.0
ID	Fruitland	IX	Kinetico	250	44	<25	7.4
NV	Reno	AM (GFH)	USFilter	350	39	<25	7.4

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APU-300 System at Anthony Site

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Demonstration Objectives

- Determine/document construction and operational costs of the new systems or the modifications of existing systems to achieve compliance
- Evaluate performance of the new processes or process modifications of existing treatment for 1 year in achieving compliance
- Determine the operational and maintenance requirements of treatment systems
- Characterize the residuals produced by the processes, quantity, and chemical characteristics
- Evaluate impact of the treatment processes on the distribution systems

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Major Activities

- Conduct introductory meeting with EPA, State drinking water official(s), facility, vendor, and engineering firms
- Issue Letter of Understanding
- Issue performance evaluation study plan
- Establish contract(s) with vendor for equipment/system engineering, site engineering, installation/shakedown, and operator training
- Obtain permit(s)
- Oversee system installation/shakedown
- Provide operator training for sampling and on-site measurements and As speciation
- Track system performance for one year with weekly sampling and monthly As speciation; coordinate O&M and troubleshooting needs
- Prepare progress reports to EPA/prepare reports for Office of Management and Budget
- Prepare final technology evaluation report

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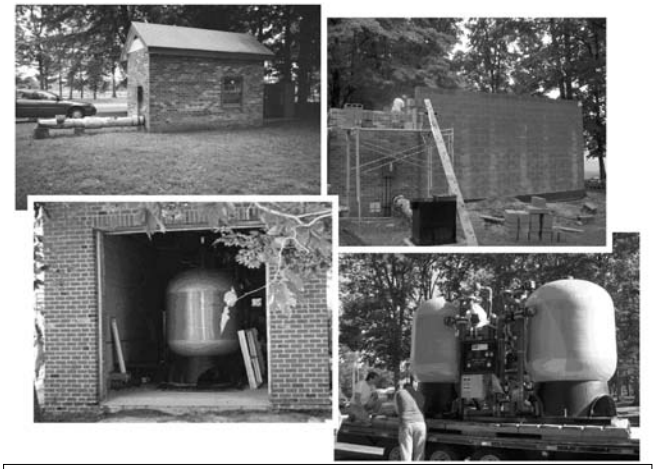
Construction and Installation of the Stevensville, MD System



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Technology Evaluation Approach

- An approach was developed to collect the data required to facilitate the evaluation of the selected arsenic removal technologies. The types of data collected include:
  - System performance and reliability
  - Simplicity of operation and operator skill requirements
  - Cost-effectiveness
  - Residuals
  - Impact on distribution systems

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System Performance: As Removal

- The key evaluation parameter is the ability of the technology to consistently remove arsenic to less than 10 μg/L
- This parameter is tracked through the collection of weekly water samples and monthly arsenic speciation at the treatment plant
- The weekly and monthly samples are analyzed in the laboratories, and results are provided to Battelle's Project Manager and Study Leads for review within two weeks of the collection of the samples

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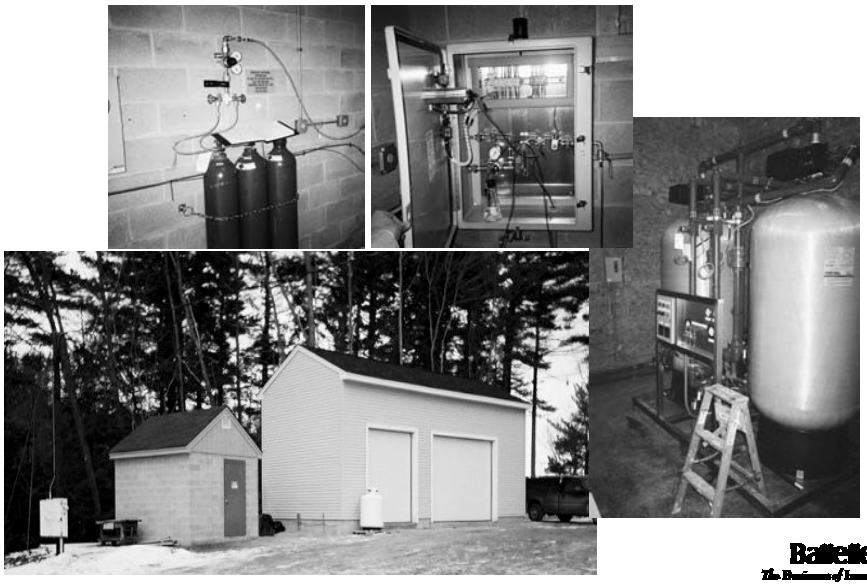
APU-100 System at Rollinsford Site



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System Performance: O&M

- Daily, weekly, and monthly operation and maintenance activities are performed and logged by the plant operator at each site
- The exact types of data vary based on the specific site and system, but general tasks performed daily include leak checks, pressure gauge and flow/hour/watt meter readings, and level checks
- Weekly on-site water quality measurements (including pH, temperature, DO, OPR, chlorine residuals, etc.) are performed using field meters

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System Reliability

- The reliability of the technology is evaluated based upon the unscheduled system downtime and the frequency and extent of any repair/replacement activities
- All unscheduled downtime and repair information is recorded on a Repair and Maintenance Log Sheet provided to the operator by Battelle

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Simplicity of Operation

- The simplicity of system operation and the required level of operator skills is evaluated based on quantitative data and qualitative considerations
  - Time spent operating the system is tracked on a daily Operator's Labor Log Sheet
  - Qualitative considerations include any pre- or post-treatment requirements, the level of system automation, operator skill requirements, an analysis of the preventive maintenance activities, frequency of chemical/media handling, and general operator knowledge required for chemical processes and safety

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System Shakedown at Fruitland, ID

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Cost-Effectiveness

- The cost-effectiveness of a system is evaluated based on capital and operating costs
  - Capital costs include costs for equipment, site engineering, and system installation
  - Operating costs include costs for chemical/media supply, electrical power consumption, and labor hours

Residuals

- Handling of residuals adds cost and complexity to the operation of the arsenic removal systems
- The quantity of aqueous and solid residuals generated at each site is tracked by the plant operator
  - Aqueous residuals include backwash and regeneration waste water
  - Solid residuals include particulates, sediment, or media fragments produced during backwash, as well as spent media or resin

Impact on Distribution System

- Distribution system water samples are collected at three LCR residences and/or non-LCR locations at each site both prior to and during the operation of the arsenic removal system
- Results are used to determine the impact of treatment on the water chemistry in the distribution system and the water quality at consumers' taps

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Key Elements

- Communication
- Operator training
- Sampling logistics
- Data management

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Communication

- Frequent communication allows timely input to the performance evaluation from all parties
- The operator provides O&M data to Battelle daily or weekly
- Battelle shares the analytical data with the utility, keeping them up-to-date on the effectiveness of the technology evaluated
- Battelle reviews the operational and analytical data, sharing ideas with the EPA, the utility, and the vendor, to correct problems rapidly

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Operator Training

- The facility operator receives training from the technology vendor
- Battelle meets with the facility operator at the introductory meeting and during system start-up, providing training on sample collection, arsenic speciation, and field analytical and operational data collection

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Sampling Logistics

- The Battelle Logistics Team coordinates all sampling activities
- Color-coded sample bottles are labeled and packed in coolers along with ice packs, pre-completed air bills, chain-of-custody documents, and sampling instructions, and sent to facility operators
- After coolers are returned to Battelle via overnight courier, the Logistics Team logs in the samples and distributes them to appropriate laboratories

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Data Management

- An organized system is critical to maintaining and evaluating data from a multiple-site demonstration
- System operating parameters are saved and updated weekly in spreadsheet format for easy review
- Analytical results are loaded to an Access database
- All results are reviewed weekly by Battelle's Project Manager and Study Leads before forwarding to EPA and the utilities

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Sampling and Analysis

- Sampling activities include:
  - Source water sampling
  - Treatment plant water sampling
  - Residual sampling
  - Distribution system/fire hydrant sampling
- Analytical activities include:
  - On-site water quality measurements
  - Laboratory analyses for water and solid samples

Arsenic Speciation

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Source Water Sampling

- Source water samples were collected during the initial site visit for detailed water quality characterization
- Source water samples were speciated on-site for particulate and soluble arsenic, As(III), and As(V), as well as other metals (i.e., Fe, Mn, and Al)

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Treatment Plant Water Sample Collection

- Treatment plant water samples are collected weekly throughout the one-year evaluation
  - Samples are collected at sample ports throughout the process stream, including the inlet, after chlorination, after each vessel, and at the combined effluent, as applicable at each site
  - Each sample port is marked with a color-coded label, corresponding to a color-coded set of bottles allocated to samples from that specific tap
  - Speciation samples are collected at a subset of the total ports for each system, and are collected once every four weeks

Backwash Sample Collection

- Backwash/regeneration water is sampled at each site before being discharged to the sewer, settling pond, or other backwash water disposal area. The water samples are typically collected from sample taps installed on the backwash water discharge line
- Samples are analyzed for arsenic and other water quality parameters

On-Site Measurements

- Field measurements of water quality parameters are performed weekly, in concert with the collection of the samples for laboratory analyses.
- Parameters measured on-site include pH, temperature, dissolved oxygen (DO), and oxidation/reduction potential (ORP), chlorine residuals.

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Off-Site Sample Analyses

- Water samples are analyzed by the Battelle ICP-MS Laboratory for arsenic and other metals using EPA Method 200.8
  - Detection limit for As: 0.1 µg/L
- Water quality parameters are analyzed by contract laboratories using standard EPA methods, or equivalent

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System Troubleshooting

- The troubleshooting procedure is defined in the Study Plan prepared for each demonstration
- In the event of an operational problem or repair, the operator is to contact the Battelle Study Lead
- The operator and the Study Lead will work together to correct the problem. If necessary, the Study Lead will consult the vendor for troubleshooting or system repair

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Reporting

- A Performance Evaluation Study Plan was prepared for each system
- A Six-Month and a Final Performance Evaluation Reports are prepared for each system. The reports
  - Summarize the operational and analytical data collected during the evaluation
  - Document the cost, reliability, ease of operation, and other factors necessary to evaluate the technologies, according to the demonstration objectives
- A Final Summary Report is prepared for all 12 systems
- Battelle maintains real-time communications with EPA regarding the status of each demonstration site
- Battelle provides a formal quarterly verbal progress report to EPA for project status and schedule, problems encountered, and corrective actions taken

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Cost Estimating Program for Arsenic Removal by Small Systems

Lili Wang,P.E., and Abraham Chen, Ph.D.,P.E., Battelle
Tom Sorg,P.E., U.S. EPA

August 11, 2004

Acknowledgments

- Funding provided by U.S. EPA under the Physical/Chemical R&D Support Contract (No. 68-C7-0008) and Field Evaluation and Technical Support (FEATS) Contract (No. 68-C-00-185)

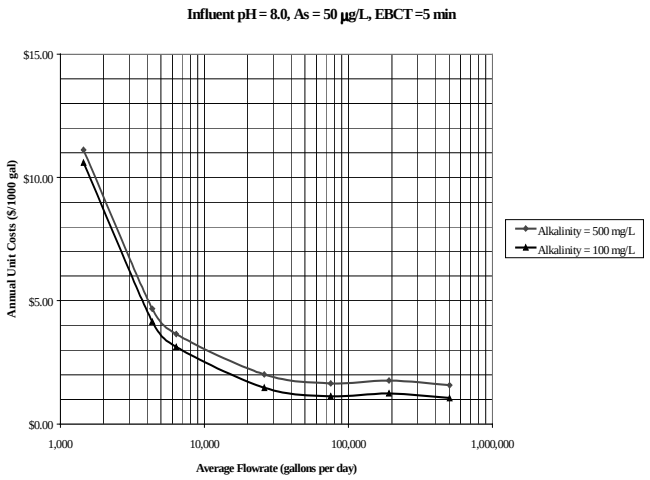
Objectives

- Develop a cost estimator for three arsenic removal processes
  - Adsorptive media throw-away system
  - Adsorptive media with media regeneration
  - Anion exchange
- Provide small systems with a useful tool for selecting a cost-effective treatment technology
- Applicable to systems with capacities ranging from 1,000 to 500,000 gallons per day (gpd)

General Assumptions

- System to be installed as part of an existing facility
- Cost model not including costs associated with:
  - Building
  - Water storage
  - Pre-oxidation to convert As(III) to As(V)
  - Waste disposal (waste production rate is provided)
- Single or multiple trains with two beds in series
- When lead bed detects 50% As breakthrough, it is recharged/ regenerated and returned to service as polishing bed; the lag bed is moved up to lead position

Traditional Cost Curves



Key Features of Cost Estimator

- Graphic user interface (GUI) to allow input of key design and costing parameters
- One-step cost comparison using default parameters
- Step-by-step costing wizards
- Expandable to other arsenic removal media
- Unrestricted access to Microsoft Excel functions, menus, and spreadsheets
- Programming language: Microsoft Visual Basic
- Platform: Microsoft Excel 97 or a higher version for Windows 98, NT, or 2000 platform

System Components

- Adsorptive media throw-away system
  - Adsorptive system*
  - Optional pH adjustment system
- Adsorptive media with media regeneration
  - Adsorptive system*
  - Acid and base feed system
- Anion exchange system
  - IX system*
  - Brine regeneration system

*Including vessels, media/resin, piping, valving, and controls

Key Design Equations

- Design flow

$Q_d = Q/1440 \times 24/TD \times 1.15$

where Q_d = design flow (gal/min)

Q = average daily flow (gal/day)

TD = treatment duration or daily operational hours (hr/day)

- Media bed volume

$V_m = Q_d \times EBCT/7.48$

where V_m = media bed volume (ft^3)

$EBCT$ = empty bed contact time (min) (for single vessel)

Key Design Equations (Cont'd)

- Replacement/regeneration frequency

  $RF = 365/(RL \times (Q_d/Q) \times EBCT)$

  where *RF* = No. of replacement/regeneration per year

  RL = media/resin run length (#BVs)

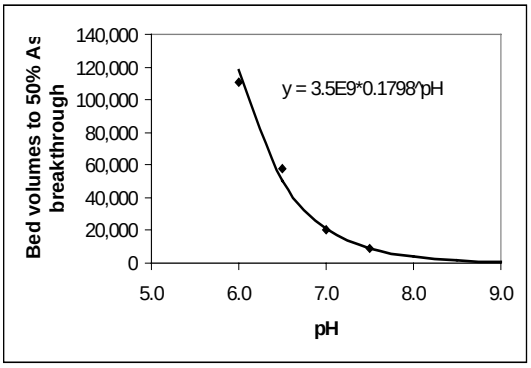
AA Run Length Estimation

$RL = (3.5 \times 10^9 \times 0.1798^{pH}) \times [3.5096 \times C_{As}^{(-0.3755)}]$*

Where *RL* = run length to 50% arsenic breakthrough (#BVs)

pH = raw water pH value

C_{As} = raw water As concentration (µg/L)



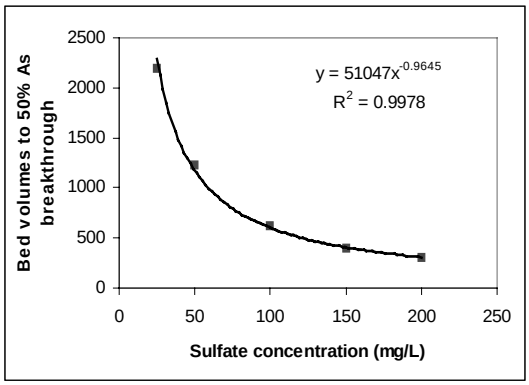
*Based on data from Simms & Azizian (1998)

AIX Resin Run Length Estimation

$RL = 51{,}047x(C_{SO4})^{(-0.9645)*}$

where RL = run length to 50% arsenic breakthrough (#BVs)

C_{SO4} = raw water sulfate concentrations (mg/L)



*Based on Clifford's study (1983)

Cost Breakdown

- Capital cost
  - Direct capital cost
    - Equipment
    - Materials
    - Installation
  - Indirect capital cost
    - Contractor/engineering
    - Permitting
    - Contingency
    - Working capital
    - Startup
- O&M Cost
  - Chemical and material
  - Electrical
  - Labor
- Unit cost ($/1000 gal)
  - Unit capital cost
    - Net interest rate
    - Years of investment
  - Unit O&M cost

Cost Scenario

- General design parameters
  average daily demand = 200,000 gpd
  daily operating time = 12 hr/day
  design flow = 320 gpm
- Raw water quality*
  pH = 7.8
  Alkalinity = 200 mg/L as $CaCO_3$
  As = 40 μg/L
  SO_4 = 4 mg/L
- Media type

Properties	Media 1	Media 2
Media price (per ft^3)	$150	$35
EBCT (min)	5	10
Media run length (#BV)	40,000*	5,000*

* Based on a pilot study at Licking Valley High School, Ohio

Cost Scenario 1

- Input Parameters

	Media 1	Media 2
Media price (per ft^3)	$150	$35
EBCT (min)	5	10
Media run length (#BV)	40,000	5,000

- Model Output

	Media 1	Media 2
Capital Cost	$257,400	$273,200
O&M Cost (per 1000 gal)	$0.63	$1.11
Media life (day)	330	79

Cost Scenario 2

- Input Parameters

	Media 1	Media 2
Media price (per ft^3)	$150	$35
EBCT (min)	5	5
Media run length (#BV)	40,000	5,000

- Model Output

	Media 1	Media 2
Capital cost	$257,400	$149,382
O&M Cost (per 1000 gal)	$0.63	$1.09
Media life (day)	330	40

Cost Comparison: An AIX System

- General design parameters
  - average daily demand = 1,200 gpd
  - daily operating time = 5 hr/day
  - design flow = 5 gpm
  - EBCT = 3.7 min
- Raw water quality
  - pH = 7.5
  - Alkalinity = 85 mg/L as $CaCO_3$
  - As = 50 μg/L
  - SO_4= 24 mg/L
- Comparison

	Model	Actual
Capital cost	$7,835	$11,942
O&M Cost (per 1000 gal)	$10.0	Not available
Media run length (#BV)	2,380	3,000

Residuals Quantities, Characteristics and Disposal Options

Tom Sorg
USEPA
Cincinnati, OH

EPA Workshop on
Adsorptive Media Processes
August 10-11, 2004
Cincinnati, OH

RESEARCH & DEVELOPMENT

Building a scientific foundation for sound environmental decisions

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Residuals

- Backwash Water
- Spent Media

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Backwash Water

- Quantity
- Characteristics
- Disposal Options

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Backwash Water

- Quantity
- Characteristics
- Disposal Options

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Backwash Water

- Quantity (Life of Media)
  - Frequency – dependent on quality of raw water and adsorptive media
    Several days to several months
  - Quantity per backwash
    10 – 15 BV

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Backwash Water

- Quantity (10 /15 BV)

Vessel 63” D x 86” H

80 cu ft media

BWW = 6000 / 9000 gallons

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Backwash Water

- Quantity of BW Water

Stevensville, MD

2 vessels (80 cu ft media/vessel)
7 gpm/ft^2 for 30 minutes
4536 gallons/vessel = 7.5 BV
9072 gallons for system

Frequency – 1/Month

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Backwash Water

- Quantity
- Characteristics
- Disposal Options

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Backwash Water

- Characteristics

Backwash water:

Liquid fraction – dependent on quality of backwash water

Solids fraction – dependent on the solids filtered out of the source water by media

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Backwash Water

- Characteristics – Brown City, MI

Parameter	Units	Raw Water	Backwash Water			
			Unit 1	Unit 2	Unit 3	Unit 4
Turbidity	NTU	_	28	27	38	39
TDS	mg/L	_	648	1010	864	678
Arsenic	**ug/L**	**10-14 (T)**	**5 (S)**	**6 (S)**	**7 (S)**	**7 (S)**
Iron	ug/L	126-260 (T)	<25 (S)	<25 (S)	<25 (S)	<25 (S)
Manganese	ug/L	13-18 (T)	12 (S)	13 (S)	15 (S)	14 (S)

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Backwash Water

- Characteristics – RHC, MI (ADI G2 Media)

Parameter	Units	Raw Water	Backwash Water (filtered sample)
Arsenic	ug/L	35-40	2
Iron	mg/L	**1.2-1.4**	0.003
Manganese	ug/L	23-25	7
Silica	mg/L	20	17

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Backwash Water

- Characteristics – RHC, MI

Parameter	Raw Water mg/L	Solids ug/g	ug element / mg Fe
Arsenic (As)	**0.037 – 0.041**	**3,550** **5,545**	**19.7** **21.1**
Iron (Fe)	**1.2 -1.4**	**201,471** **262,592**	------- -------
Manganese (Mn)	0.02	2,558 3,532	------- -------
Silica (SiO_2)	19 -20	1,971 871	9.8 3.3
Calcium (Ca)	80 - 85	135,697 62,303	------- -------
Magnesium (Mg)	33 - 36	10,285 9,209	------- -------
Phosphorus (P)	<0.065	292 303	1.4 1.2

RESEARCH & DEVELOPMENT

Building a scientific foundation for sound environmental decisions

Backwash Water

- Quantity
- Characteristics
- <u>Disposal Options</u>

RESEARCH & DEVELOPMENT

Building a scientific foundation for sound environmental decisions

Backwash Water

Disposal Options

Dependent on:

1. State regulations

2. Site specific conditions
   - Sewer (POTW)
   - Holding pond
   - Land discharge
   - Stream discharge
   - Recycle of liquid fraction & solids disposal

RESEARCH & DEVELOPMENT

Building a scientific foundation for sound environmental decisions

Backwash Water

Arsenic Demonstration Project, Round 1
Nine Adsorption Technology Projects

Backwash water disposal

- 2 Recycle
- 2 Pond
- 1 Ditch
- 4 POTW

RESEARCH & DEVELOPMENT

Building a scientific foundation for sound environmental decisions

Residuals

- Backwash Water
- Spent Media

RESEARCH & DEVELOPMENT

Building a scientific foundation for sound environmental decisions

Spent Media

- Landfill
  Hazardous/non-hazardous
- Recycle

The End!

Thank You!

Questions!

LIST OF PARTICIPANTS

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LIST OF PARTICIPANTS

Mr. Roderick Abinet
Special Applications Manager
Kemiron Companies, Inc.
3211 Clinton Parkway Ct., Suite 1
Lawrence, KS 66047
Phone: 785-842-7424
E-mail: dplanas@kemiron.com

Mr. Jeffrey Adams
Environmental Engineer
US EPA
26 W Martin Luther King Dr.
Cincinnati, OH 45268
Phone: 513-569-7835
E-mail: adams.jeff@epa.gov

Dr. Gary Amy
Professor
University of Colorado
Civil Engineering
Boulder, CO 80309
Phone: 303-492-7315
E-mail: gamy@spot.colorado.edu

Dr. Alicia Aragon
Post-Doc
Sandia National Laboratories
PO Box 5800
Albuquerque, NM 87185
Phone: 505-844-5426
E-mail: alicia17@unm.edu

Mr. Bruce Bartley
Technical Manager
NSF International
789 Dixboro Rd.
Ann Arbor, MI 48105
Phone: 734-769-8010
E-mail: bartley@nsf.org

Mr. Joseph Bellisomo
Chemist
PACS Inc.
409 Meade Dr.
Coraopolis, PA 15108
Phone: 724-457-6576
E-mail: Barbpacs@aol.com

Ms. Gretchen Berryman
Graduate Student
Western Kentucky University
1 Big Red Way
Bowling Green, KY 42101
Phone: 270-745-8725
E-mail: berryge@wku.edu

Mr. Dennis Bitter
Manager
Severn Trent Services
21520 Yorba Linda Blvd.
Suite G200
Yorba Linda, CA 92887-5531
Phone: 714-692-9384
E-mail: dbitter@severntrentservices.com

Dr. David Bjorkquist
Principal Scientist
Procter & Gamble
8700 Mason Montgomery Rd.
Mason, OH 45040
Phone: 513-622-4302
E-mail: bjorkquist.dw@pg.com

Mr. Francis Boodoo
Technical Sales Manager
Purolite
150 Monument Rd., Suite 202
Bala Cynwyd, PA 19004
Phone: 610-668-9090
E-mail: fboodoo@puroliteusa.com

Mr. Richard Boren
VP Technology
EnviroScrub Technologies
1650 W 82nd St., Suite 650
Bloomington, MN 55431
Phone: 952-884-7337
E-mail: richboren@att.net

Dr. Philip Brandhuber
Project Manager
HDR
303 E 17th Ave., Suite 700
Denver, CO 80203
Phone: 303-764-1527
E-mail: philip.brandhuber@hdrinc.com

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LIST OF PARTICIPANTS

Dr. Adele Buckley
VP Tech & Research
OCETA
63 Polson St.
Toronto, Ontario M5A 1A4 Canada
Phone: 416-778-5281
E-mail: abuckley@oceta.on.ca

Mr. Steve Canter
President
Environmental Engineering Service
1054 Monroe Rd., Suite 302
Lebanon, OH 45036
Phone: 513-934-1512
E-mail: scanter@enveng.com

Mr. Matthew Carr
Business Development Manager
Orica Watercare
33101 E Quincy Ave.
Watkins, CO 80137
Phone: 303-268-5292
E-mail: matt.carr@orica.com

Dr. Abraham Chen
Manager
Battelle
505 King Ave.
Columbus, OH 43201
Phone: 614-424-5641
E-mail: chena@battelle.org

Dr. Amy Chen
Materials Scientist
Inframat Corporation
156-J River Rd.
Willington, CT 06279
Phone: 860-487-3838
E-mail: achen@inframat.com

Dr. Wei-Chih Chen
VP Product Development
Apyron Technologies, Inc.
3342 International Park Dr.
Atlanta, GA 30316
Phone: 678-904-6581
E-mail: wcchen@apyron.com

Dr. Virginia Ciminelli
Professor
Federal University of Minas Gerais - UFMG
R. Espírito Santo 35
Belo Horizonte, Minas Gerais 30160-030 Brazil
Phone: 55-31-3238-1800
E-mail: ciminelli@demet.ufmg.br

Dr. Dennis A. Clifford
Professor
University of Houston
Civil and Environmental Eng. Dept.
Eng. Bldg. 1
Houston, TX 77204-4003
Phone: 713-743-4266
E-mail: daclifford@uh.edu

Mr. Dan Cloyd
Environmental Spec. 3
Ohio EPA
401 E Fifth St.
Dayton, OH 45402-2911
Phone: 937-285-6844
E-mail: dan.cloyd@epa.state.oh.us

Miss Wendy Condit
Research Scientist
Battelle
505 King Ave.
Columbus, OH 43201
Phone: 614-424-3501
E-mail: conditw@battelle.org

Mr. Pat Cook
Treatment Specialist
Michigan DEQ
PO Box 30630
Lansing, MI 48909-8130
Phone: 517-241-1242
E-mail: cookp@michigan.gov

Mr. Chris Coonfare
Principal Research Scientist
Battelle
3990 Old Town Ave., Suite B104
San Diego, CA 92110
Phone: 619-574-4822
E-mail: coonfare@battelle.org

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LIST OF PARTICIPANTS

Ms. Rachel Copeland
Research Assistant
UC/US EPA
26 W. Martin Luther King Dr.
Cincinnati, OH 45220-2242
Phone: 513-569-7210
E-mail: copelar@email.uc.edu

Mr. Thomas Davis
President
Tonka Equipment Company
13305 Watertower Circle
Plymouth, MN 55441
Phone: 763-559-2837
E-mail: tdavis@tonkawater.com

Dr. Sreedevi Dawadi
Post Doctorate Research Associate
Western Kentucky University
1 Big Red Way
Bowling Green, KY 42101
Phone: 270-745-8725
E-mail: sree.dawadi@wku.edu

Mr. Richard S. Dennis
Separation Products Manager
Severn Trent Services, Inc.
5415 W Sligh Ave., Suite 102
Tampa, FL 33634
Phone: 813-886-9331
E-mail: rdennis@severntrentservices.com

Mr. George Dimotsis
Manager, Research & Development
Sybron Chemicals Inc., A Lanxess Company
200 Birmingham Rd.
Birmingham, NJ 08011
Phone: 609-893-1100
E-mail: gdimotsis@sybronchemicals.com

Mr. Daryl Enfield
Environmental Engineer
Iowa Department of Natural Resources
401 SW 7th St., Suite M
Des Moines, IA 50309-4611
Phone: 515-725-0285
E-mail: daryl.enfield@dnr.state.ia.us

Mr. James Farmerie
Product Manager - Clarification
F.B. Leopold Company, Inc.
227 S Division St.
Zelienople, PA 16063
Phone: 724-453-2120
E-mail: jfarmerie@fbleopold.com

Mr. Phil Fatula
Market Segment Manager - Chemical & Environmental
Sybron Chemicals Inc., A Lanxess Company
100 Bayer Rd., Bldg. 14
Pittsburgh, PA 15205
Phone: 412-777-4157
E-mail: phil.fatula@Lanxess.com

Mr. Joe Feldhaus
Grantee
US EPA
26 W Martin Luther King Dr.
Cincinnati, OH 45268
Phone: 513-383-8779
E-mail: feldhaus.joe@epamail.epa.gov

Mr. Lance FitzGerald
Director of Product Development
Culligan International
One Culligan Pky.
Northbrook, IL 60062
Phone: 847-559-7661
E-mail: ltfitzgerald@culligan.com

Ms. Christy Frietch
Engineering Technician
US EPA
26 W Martin Luther King Dr.
Cincinnati, OH 45268
Phone: 513-569-7901
E-mail: frietch.christy@epa.gov

Mr. Brian Fuchs
Municipal Sales
Calgon Carbon
1 Top of the Oaks
Chadds Ford, PA 19317
Phone: 610-358-4733
E-mail: bfuchs@calgoncarbon-us.com

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LIST OF PARTICIPANTS

Mr. Dan Gallagher
Student
US EPA - Cincinnati NRMRL - Arsenic Removal Implementation Team
26 W Martin Luther King Dr.
Cincinnati, OH 45268
Phone: 513-569-7625
E-mail: gallagher.daniel@epa.gov

Mr. John Gandee
Senior Engineer
SI Group
155 Tri County Pky., #250
Cincinnati, OH 45246
Phone: 513-771-3617
E-mail: jgandee@thesigroup.com

Mrs. Angel Gebeau
Drinking Water Engineer
Earth Tech
200 Indiana Ave.
Stevens Point, WI 54481
Phone: 715-342-3023
E-mail: angel.gebeau@earthtech.com

Mr. Shane Gernand
Environmental Chemist
General Electric Global Research
One Research Circle
Bldg. K, Rm. 3B29
Niskayuna, NY 12309
Phone: 518-387-5654
E-mail: gernand@research.ge.com

Mr. Josh Gesick
Research Engineer
ADA Technologies, Inc
8100 Shaffer Pky., Suite 130
Littleton, CO 80127
Phone: 303-874-7370
E-mail: joshg@adatech.com

Mr. Gregory C. Gilles
Vice President
AdEdge Technologies, Inc.
3560 Financial Center Way, Suite 5
Buford, GA 30519
Phone: 678-835-0052
Email: greg@adedgetechnologies.com

Dr. Anirban Gupta
Assistant Professor
Bengal Engineering College
College Rd.
Howrah, West Bengal 711103 India
Phone: 0091-33-26322049
E-mail: guptaanirban@hotmail.com

Ms. Sally Gutierrez
Director, WSWRD
Office of Research and Development, USEPA
26 W Martin Luther King Dr.
Cincinnati, OH 45268
Phone: 513-569-7683
E-mail: gutierrez.sally@epa.gov

Mr. Mariano Haensel
Environmental Specialist
Ohio EPA
401 E Fifth St.
Dayton, OH 45402
Phone: 937-285-6113
E-mail: mariano.haensel@epa.state.oh.us

Ms. Katherine Hais
Conference Coordinator Assistant
SAIC
11251 Roger Bacon Dr.
Reston, VA 20190
Phone: 703-318-4678
E-mail: haisk@saic.com

Mr. Charles Hammel
Vice President & CTO
Enviroscrub Technologies Corp.
1650 W 82nd St., Suite 650
Minneapolis, MN 55431
Phone: 952-884-7337
E-mail: chammel@truevine.net

Mr. Marc Hancock
Compliance Assistance Specialist
Indiana Dept of Environmental Management
2525 N Shadeland, PO Box 6015
Indianapolis, IN 46206-6015
Phone: 317-308-3113
E-mail: mhancock@dem.state.in.us

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LIST OF PARTICIPANTS

Mr. Syed Ahsanul Haque
Hydrologist/Water Resources Engineer
CEGIS (Center for Environmental & Geographic Information Services)
House # 6
Road #23/C
Gulshan-1, Dhaka 1212 Bangladesh
Phone: 8821570-2
E-mail: shaque@cegisbd.com

Ms. Lorelle Harris
Chemical Engineer
Enviroscrub Technologies Corp
1650 W 82nd St., Suite 650
Minneapolis, MN 55431
Phone: 763-232-1458
E-mail: harr0520@umn.edu

Mr. Joseph Harrison
Technical Director
Water Quality Association
4151 Naperville Rd.
Lisle, IL 60532
Phone: 630-505-0160
E-mail: jharrison@mail.wqa.org

Mr. F. Gary Hayne
Civil Engineer
USDA, RD
9173 W Barnes Dr., #A1
Boise, ID 83709-1574
Phone: 208-378-5619
E-mail: gary.hayne@id.usda.gov

Mr. Terry Heller
Technical Sales
Purolite Co.
150 Monument Rd.
Bala Cynwyd, PA 19004
Phone: 800-343-1500
E-mail: tlheller@sbcglobal.net

Mr. Tim Hodapp
Research Assistant
US EPA
26 W Martin Luther King Dr.
Cincinnati, OH 45268
Phone: 513-569-7294
E-mail: hodapp.tim@epa.gov

Mr. Abul Hossain
Managing Director
Hydrotech(BD) Ltd.
29 W Panthapath
Dhaka, Bangladesh 1205 Bangladesh
Phone: 880-2-9131394
E-mail: hydrotechbdltd@yahoo.com

Mr. Md. Anwar Hossain
Assistant Professor
Dept. of Farm Structure, Bangladesh Agricultural University, Mymensingh-2202
Teaching and Research
Mymensingh-2202, Bangladesh
Phone: 88-0172-205902
E-mail: anwar_bau@yahoo.com

Mr. Albert Ilges
Arsenic Program Manager
AWWA Research Foundation
6666 W Quincy Ave.
Denver, CO 80235
Phone: 303-347-6123
E-mail: ailges@awwarf.org

Dr. Christopher Impellitteri
Environmental Engineer
USEPA-ORD-WSWRD
26 W Martin Luther King Dr.
Cincinnati, OH 45268
Phone: 513-487-2872
E-mail: impellitteri.christopher@epa.gov

Mr. Cherno Jallow
Health Journalist
Daily Onserver
St. Matty Junction. Bakau.
New Town
Banjul, p m b 131, The Gambia 220
Phone: 00220 4394578
E-mail: cherno_j@yahoo.com

Mr. Subhash Jha
Program Manager
Nebraska Department of Health & Human Services
Regulation & Licensure
301 Centennial Mall S, PO Box 95007
Lincoln, NE 68509-5007
Phone: 402-471-0524
E-mail: subhash.jha@hhss.state.ne.us

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LIST OF PARTICIPANTS

Mr. Dinkar Joshi
Environmental Journalist
Youth Awareness Environmental Forum (YAEF)
Environmental Library, PO Box 8975
Godawari Area, Bade Gaon, Lalitpur
Kathmandu, EPC-104 Nepal
Phone: +977-1-4487517
E-mail: dinkarjoshi@hotmail.com

Dr. Leonid Kaledin
Research Scientist
Argonide Corporation
291 Power Ct.
Sanford, FL 32771
Phone: 407-322-2500
E-mail: kaledin@argonide.com

Dr. Peter Kwasowski
Technical Director
ClifMar Associates Ltd.
University of Surrey
Guildford, Surrey GU2 7XH United Kingdom
Phone: 44-1483-857469
E-mail: peter@clifmar.com

Mr. Glen Latimer
Manager Municipal Group
Kinetico, Inc.
10845 Kinsman Rd.
Newbury, OH 44255
Phone: 440-564-4282
E-mail: glatimer@kinetico.com

Ms. France Lemieux
Manager, Materials and Treatment Division
Water Quality and Health Bureau, Health Canada
2720 Riverside Dr.
AL: 6604B
Ottawa, Ontario K1A 0K9 Canada
Phone: 613-941-3166
E-mail: France_Lemieux@hc-sc.gc.ca

Mr. Gary Lewis
Research Intern
Battelle
505 King Ave.
Columbus, OH 43201
Phone: 614-424-7206
E-mail: lewisg@battelle.org

Ms. Jessica Lewis
Student Assistant
US EPA
26 W. Martin Luther King Dr.
Cincinnati, OH 45268
Phone: 513-569-7415
E-mail: lewis.jessica@epa.gov

Miss Jody Lipps
Researcher
Battelle
505 King Ave.
Columbus, OH 43201
Phone: 614-424-5842
E-mail: lippsj@battelle.org

Ms. Maria Lucente
Environmental Specialist 2
Ohio EPA
122 S Front St., PO Box 1049
Columbus, OH 43216-1049
Phone: 614-644-2752
E-mail: maria.lucente@epa.state.oh.us

Mr. Bernard Lucey, P.E.
Senior Engineer
New Hampshire Department of Environmental Services
29 Hazen Dr., PO Box 95
Concord, NH 03301
Phone: 603-271-2951
E-mail: blucey@des.state.nh.us

Mr. Darren Lytle
Environmental Engineer
US EPA
26 W Martin Luther King Dr.
Cincinnati, OH 45268
Phone: 513-569-7432
E-mail: lytle.darren@epa.gov

Dr. Hubert MacDonald
Principal Scientist
PACS Inc.
409 Meade Dr.
Coraopolis, PA 15108
Phone: 724-457-6576
E-mail: Barbpacs@aol.com

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LIST OF PARTICIPANTS

Ms. Alina Martin
Environmental Specialist
SAIC
11251 Roger Bacon Dr.
Reston, VA 20190
Phone: 703-318-4678
E-mail: martinali@saic.com

Dr. Heath Mash
Chemist
US EPA
26 W Martin Luther King Dr.
Cincinnati, OH 45268
Phone: 513-569-7713
E-mail: mash.heath@epa.gov

Mr. Dilshad Masih
Student
Tokyo Institute of Technology
4259-G1-16 Nagatsuta, Midori-ku
Yokohama, 226-8502 Japan
Phone: +81-090-6155-9638
E-mail: dilshad@chemenv.titech.ac.jp

Mr. Sam Mason
Research Scientist
Kinetico Incorporated
10845 Kinsman Rd.
Newbury, OH 44065
Phone: 440-564-9111
E-mail: sam.mason@kinetico.com

Ms. Andrea Matzke
Environmental Health Scientist
US EPA
1200 Pennsylvania Ave. NW, MC 4606M
Washington, DC 20460
Phone: 202-564-3842
E-mail: matzke.andrea@epa.gov

Dr. James Maynard
Professor
University of Cincinnati
345 College Ct.
Rm. 500 Geology/Physics
Cincinnati, OH 45221-0013
Phone: 513-556-5034
E-mail: maynarjb@uc.edu

Ms. Sarah McCall
Research Scientist
Battelle Memorial Institute
505 King Ave.
Columbus, OH 43201
Phone: 614-424-4628
E-mail: mccalls@battelle.org

Mr. Andrew McClure
Senior Marketing Manager
Calgon Carbon Corporation
PO Box 717
Pittsburgh, PA 15102
Phone: 412-787-6761
E-mail: amcclure@calgoncarbon-us.com

Mr. John McDaniel
Environmental Specialist 2
Ohio EPA
401 E Fifth St.
Dayton, OH 45402-2911
Phone: 937-285-6117
E-mail: john.mcdaniel@epa.state.oh.us

Dr. Xiaoguang Meng, PE
Associate Professor
Center for Environmental Systems
Stevens Institute of Technology
Castle Point on Hudson
Hoboken, NJ 07030
Phone: 201-216-8014
Email: xmeng@stevens-tech.edu

Mr. Greg Millsap
Business Development Manager
Dow Chemical
2030 Dow Center
Midland, MI 48674
Phone: 989-636-6506
E-mail: gmillsap@dow.com

Mr. Jon Mogan
Technical Manager
Alcan Specialty Aluminas
4000 Development Dr.
Brockville, Ontario K6V 5V5 Canada
Phone: 613-342-7462
E-mail: jon.mogan@alcan.com

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LIST OF PARTICIPANTS

Ms. Olga Morales-Sanchez
RDS - Environmental
Rural Community Assistance Corporation
PO Box 1223
Dona Ana, NM 88032
Phone: 505-382-6992
E-mail: olgams@rcac.org

Mr. Christopher Morss
V.P. Remediation Services
USFilter
6611 San Leandro St.
Oakland, CA 94621
Phone: 925-519-5617
E-mail: morssc@usfilter.com

Ms. Cecilia Naughton
Environmental Specialist
Iowa DNR
401 SW 7th St., Suite M
Des Moines, IA 50309
Phone: 515-725-0289
E-mail: cecilia.naughton@dnr.state.ia.us

Mr. Roy Ney
Senior Engineer
Iowa DNR
401 SW 7th St., Suite M
Des Moines, IA 50309
Phone: 515-725-0360
E-mail: roy.ney@dnr.state.ia.us

Mr. Marty Norton
Engineer
USDA-Rural Development
100 Centennial Mall N, Suite 308
Lincoln, NE 68508
Phone: 402-437-5560
E-mail: marty.norton@ne.usda.gov

Mr. Isaac Osei-Gyan
Student
UNESCO-IHE, Institute for Water Education
PO Box 3012
Locker 62
Delft, 2601 DA Netherlands
Phone: 316-421-89220
E-mail: oseigyan@yahoo.com

Mr. Jeffrey Oxenham
Research Scientist
Battelle
505 King Ave.
Columbus, OH 43201
Phone: 614-424-3657
E-mail: oxenhamj@battelle.org

Mr. Dan Patel
Principal Engineer
Southern Company Services
42 Inverness Center Pky., Bin B426
Birmingham, AL 35242
Phone: 205-992-7697
E-mail: dvpatel@southernco.com

Mr. Jeremy Payne
Research Assistant
US EPA
26 W Martin Luther King Dr.
Cincinnati, OH 45268
Phone: 513-569-7088
E-mail: payne.jeremy@epa.gov

Ms. Kathleen Pinto
Environmental Specialist
Ohio EPA
Lazarus Government Ctr.
PO Box 1049
Columbus, OH 43216-1049
Phone: 614-644-3558
E-mail: kathy.pinto@epa.state.oh.us

Mr. Tom Poeton
Environmental Engineer
US EPA Region 6
1445 Ross Ave.
Suite 1200, 6WQ-SD
Dallas, TX 75202-2733
Phone: 214-665-2757
E-mail: poeton.tom@epa.gov

Dr. Jian Qiu
Staff Scientist
Pall Corporation
25 Harbor Park Dr.
Port Washington, NY 11542
Phone: 516-671-7568
E-mail: jian_qiu@pall.com

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LIST OF PARTICIPANTS

Mr. Shaidur Rahaman
Campaigner
Noble Social Development Program - NSDP
140 S Bishil
Mirpur-1, Dhaka 1216 Bangladesh
Phone: ++88-02-9010084
E-mail: nsdp@dhaka.net

Mr. Patrick Ransom
Environmental Engineer/Economist
SAIC
11251 Roger Bacon Dr.
Reston, VA 20190
Phone: 703-318-4681
E-mail: ransomp@saic.com

Dr. Regu Regunathan
President
ReguNathan & Associates, Inc.
1490 Jasper Dr.
Wheaton, IL 60187
Phone: 630-653-0387
E-mail: Regu5@yahoo.com

Mr. Bill Reid
Senior Sales Representative
Alcan Specialty Aluminas
525 S Washington St., Suite 9
Naperville, IL 60540-6641
Phone: 630-527-1213
E-mail: bill.reid@alcan.com

Mr. Jeffrey Reynhout
Project Manager
Wade Trim
400 Monroe, Suite 310
Detroit, MI 48226
Phone: 313-961-8650
E-mail: jreynhout@wadetrim.com

Mr. Dan Rice
Project Manager
The Dow Chemical Company
1691 N Swede Rd., Larkin Lab
Midland, MI 48674
Phone: 989-636-0570
E-mail: drice@dow.com

Mrs. Gail Risto
Research Scientist
Alcan Specialty Aluminas
4000 Development Dr.
Brockville, Ontario K6V 5V5 Canada
Phone: 613-342-7462
E-mail: gail.risto@alcan.com

Mr. Peter Ritchey
Business Development Manager
Calgon Carbon Corporation
500 Calgon Carbon Dr.
Pittsburgh, PA 15205
Phone: 412-787-6859
E-mail: pritchey@calgoncarbon-us.com

Mr. Mark Rowzee
Education Director
Water Quality Association
4151 Naperville Rd.
Lisle, IL 60532
Phone: 630-505-0160
E-mail: mrowzee@mail.wqa.org

Dr. Robert V. Russo
VP, Business Development
HydroGlobe, Inc.
1200 Florence-Columbus Rd.
Bordentown, NJ 08505
Phone: 609-499-3542
E-mail: rrusso@hydroglobe.com

Mr. Mark Ruutel
R&D Manager
ClifMar Associates Ltd.
SBMS
University of Surrey
Guildford, Surrey GU2 7XH UK
Phone: 44-0-1483-686444
E-mail: mark@clifmar.com

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Cincinnati, OH

LIST OF PARTICIPANTS

Dr. Ali Safarzadeh-Amiri
Senior Technical Director
Ontario Centre for Environmental Technology Advancement (OCETA)
63 Polson St.
Toronto, Ontario M5A 1A4 Canada
Phone: 416-778-5281
E-mail: aamiri@oceta.on.ca

Mr. Anuj K. Saha
Managing Principal
VEETech, P. C.
942 Millbrook Ave., Suite 6
Aiken, SC 29803
Phone: 803-641-0085
E-mail: anujsaha@netzero.com

Mr. Asit Saha
President
Pegasus Technical Services, Inc.
10901 Reed Hartman Hwy., Suite 203
Cincinnati, OH 45242
Phone: 513-793-0094
E-mail: asit@pegasustechserv.com

Mr. Ramana Reddy Sama
Process Engineer
VEETech P.C.
942 Millbrook Ave., Suite 6
Aiken, SC 29803
Phone: 803-641-2299
E-mail: ramanareddy_sv@yahoo.com

Dr. Kirk Scheckel
Soil Scientist
US EPA
5995 Center Hill Ave.
Cincinnati, OH 45224
Phone: 513-487-2865
E-mail: Scheckel.Kirk@epa.gov

Mr. Wayne Schuliger
Director, Engineering
PACS Inc.
409 Meade Dr.
Coraopolis, PA 15108
Phone: 724-457-6576
E-mail: Barbpacs@aol.com

Mr. David Secor
Environmental Specialist
Ohio EPA
401 E Fifth St.
Dayton, OH 45402-2911
Phone: 937-285-6114
E-mail: dave.secor@epa.state.oh.us

Dr. Malcolm Siegel
Principal Member Tech Staff
Sandia National Laboratories
1515 Eubank SE, MS 0750
Albuquerque, NM 87185
Phone: 505-844-5426
E-mail: msiegel@sandia.gov

Dr. Tony Singh
Research Associate
Indian Institute of Technology, Delhi
Chemical Engineering, IIT, Hauz Khas
Delhi, Delhi 110016 India
Phone: 919899569590
E-mail: tony_iitd@yahoo.com

Ms. Jennifer Sjolin
Environmental Engineer
US EPA
1200 Pennsylvania Ave. NW
Washington, DC 20460
Phone: 909-544-3582
E-mail: matzke.andrea@epa.gov

Mr. Tom Sorg
Engineer
US EPA
26 W. Martin Luther King Dr.
Cincinnati, OH 45268
Phone: 513-569-7370
E-mail: sorg.thomas@epa.gov

Mr. John Spotts
Director of Technical Services
Apyron Technologies, Inc.
3342 International Park Dr.
Atlanta, GA 30316
Phone: 678-904-6584
E-mail: jspotts@apyron.com

Workshop on the Design and Operation of Adsorptive Media Processes for the Removal of Arsenic from Drinking Water
August 10-11, 2004
Cincinnati, OH

LIST OF PARTICIPANTS

Mr. Jeffery Stark
Environmental Specialist
Ohio EPA
401 E 5th St.
Dayton, OH 45402-2911
Phone: 937-285-6118
E-mail: jeff.stark@epa.state.oh.us

Mr. Joseph Strouse
Team Leader
Texas Commission on Environmental Quality
PO Box 13087
Austin, TX 78711-3087
Phone: 512-239-6953
E-mail: jstrouse@tceq.state.tx.us

Mr. Charles Thomas
Engineer
NMED/Drinking Water Bureau
4131 Montgomery Blvd. NE
Albuquerque, NM 87114
Phone: 505-841-9476
E-mail: chuck_thomas@nmenv.state.nm.us

Mr. Michael Thompson
E.I. 2
LDHH-Office of Public Health
6867 Bluebonnet Blvd.
Suite 222, Box 3
Baton Rouge, LA 70810
Phone: 225-765-5048
E-mail: mthompson@dhh.la.gov

Dr. Craig Turchi
Sr. Research Engineer
ADA Technologies
8100 Shaffer Pky., #130
Littleton, CO 80127
Phone: 303-792-5615
E-mail: craigt@adatech.com

Miss Julia Valigore
Research Intern
Battelle
505 King Ave.
Columbus, OH 43201
Phone: 614-424-5304
E-mail: valigorej@battelle.org

Mr. John Van Newenhizen
Director of Research
Culligan International
One Culligan Pky.
Northbrook, IL 60062
Phone: 847-205-5734
E-mail: jvannew@culligan.com

Dr. Fredrick Vance
Research Specialist
The Dow Chemical Company
1776 Building
Midland, MI 48623
Phone: 989-636-0390
E-mail: fwvance@dow.com

Mrs. Karen VanderKooi
Scientist
Access Business Group
7575 Fulton E
Ada, MI 49355
Phone: 616-787-0258
E-mail:
karen_vanderkooi@accessbusinessgroup.com

Ms. Kimberly Walsh
Business Development Mgr-Filtration
EaglePicher Filtration & Minerals
9785 Gateway Dr., Suite 1000
Reno, NV 89521
Phone: 775-824-7646
E-mail: kim.walsh@eaglepicher.com

Mrs. Lili Wang
Research Scientist
Battelle
505 King Ave.
Columbus, OH 43201
Phone: 614-424-7407
E-mail: wangl@battelle.org

Dr. Paul Westerhoff
Associate Professor
Arizona State University
Civil and Environmental Engineering, Box 5306
Tempe, AZ 85287-5306
Phone: 480-965-2885
E-mail: p.westerhoff@asu.edu

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LIST OF PARTICIPANTS

Ms. Sherri Westphal
Territory Manager
Tonka Equipment Company
13305 Watertower Circle
Plymouth, MN 55441
Phone: 763-559-2837
E-mail: swestphal@tonkawater.com

Mr. Dan Williams
Engineer Technician
US EPA
26 W. Martin Luther King Dr.
Cincinnati, OH 45268
Phone: 513-569-7237
E-mail: williams.daniel@epa.gov

Mr. Eric Winchester
VP
ADI International, Inc.
1133 Regent St.
Fredericton, NB E3B3Z2 Canada
Phone: 506-451-7407
E-mail: elw@adi.ca

Ms. Amy Wolfe
Intern
Hedin Environmental
195 Castle Shannon Blvd.
Pittsburgh, PA 15228
Phone: 412-600-6015
E-mail: wolfeamy_@hotmail.com

Mr. Wm Young
Master Service Tech
Water Treatment Equipment, Inc.
915 US Route 1
Yarmouth, ME 04096-6931
Phone: 207-846-5061
E-mail: wyoung01@maine.rr.com