



Properties and Use of Two Iron Hydroxide Impregnated Anion Exchange Resins for Arsenic Removal

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Outline

1. Arsenic in drinking water
2. Materials synthesis and characterization
3. Laboratory batch studies
4. Field trials
5. Conclusions



US Drinking Water Regulations

- Maximum Contaminant Level (MCL) for Arsenic in drinking water lowered from 50 $\mu\text{g}/\text{L}$ to 10 $\mu\text{g}/\text{L}$ by the US Environmental Protection Agency (EPA) in January 2006.
- Estimated that 4,000 water providers and several million domestic wells in the US out of compliance.
- New Jersey imposed a more stringent 5 $\mu\text{g}/\text{L}$ MCL.
 - Other states also contemplating lower MCL.
- Water systems above the new MCL must implement an arsenic remediation strategy.
 - Local legislation starting to appear that also affects domestic wells.



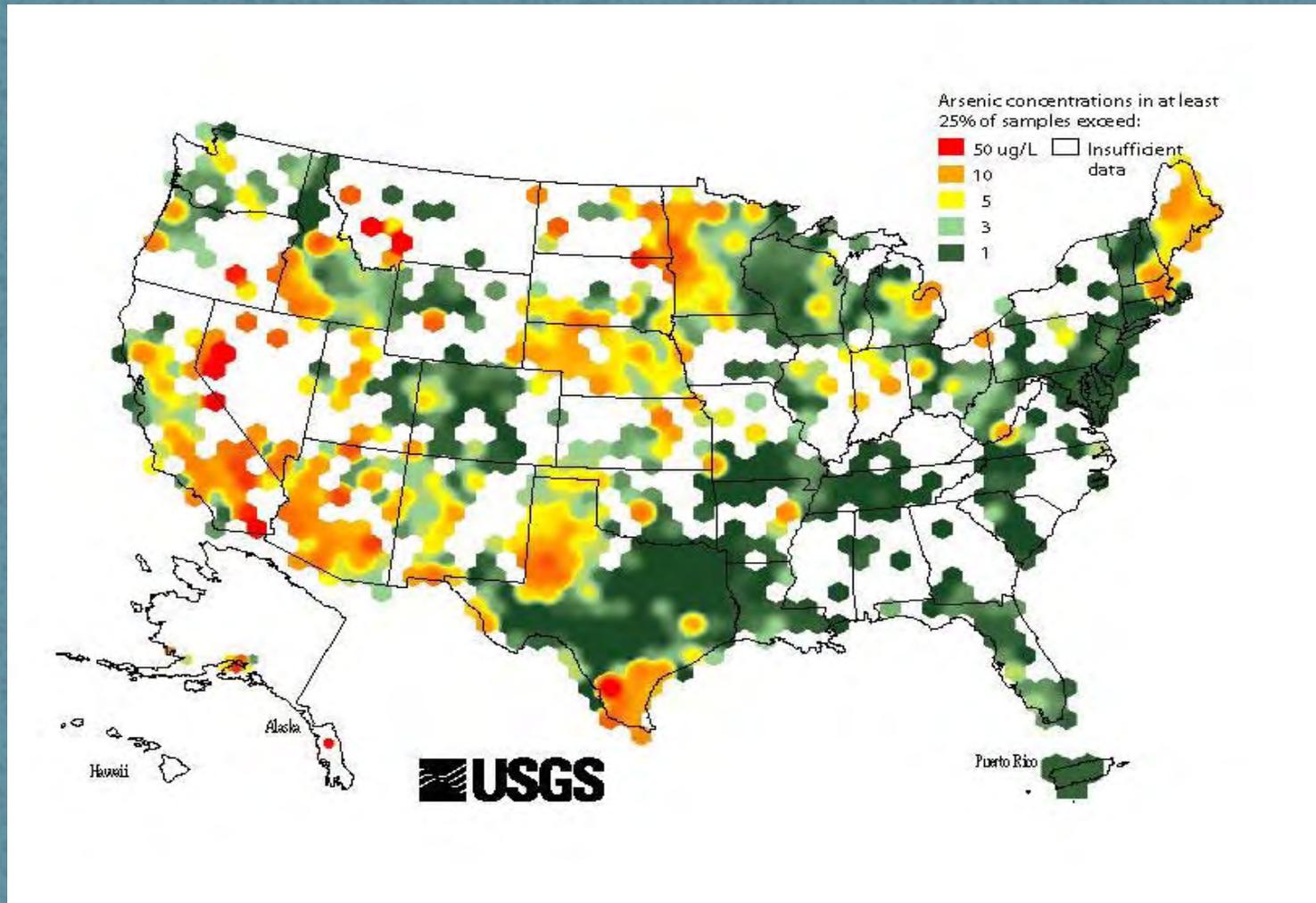
Long Term Exposure to Elevated Arsenic in Drinking Water

- Long term (chronic) exposure to ppb levels of arsenic causes range of ailments.
 - Lung, kidney, liver and bladder cancer association with arsenic in drinking water is well established.
- Higher levels (> 0.1 ppm) can cause skin lesions and discoloration.
 - Estimated in Bangladesh that 35 million people exposed arsenic levels greater than 10 ppb.

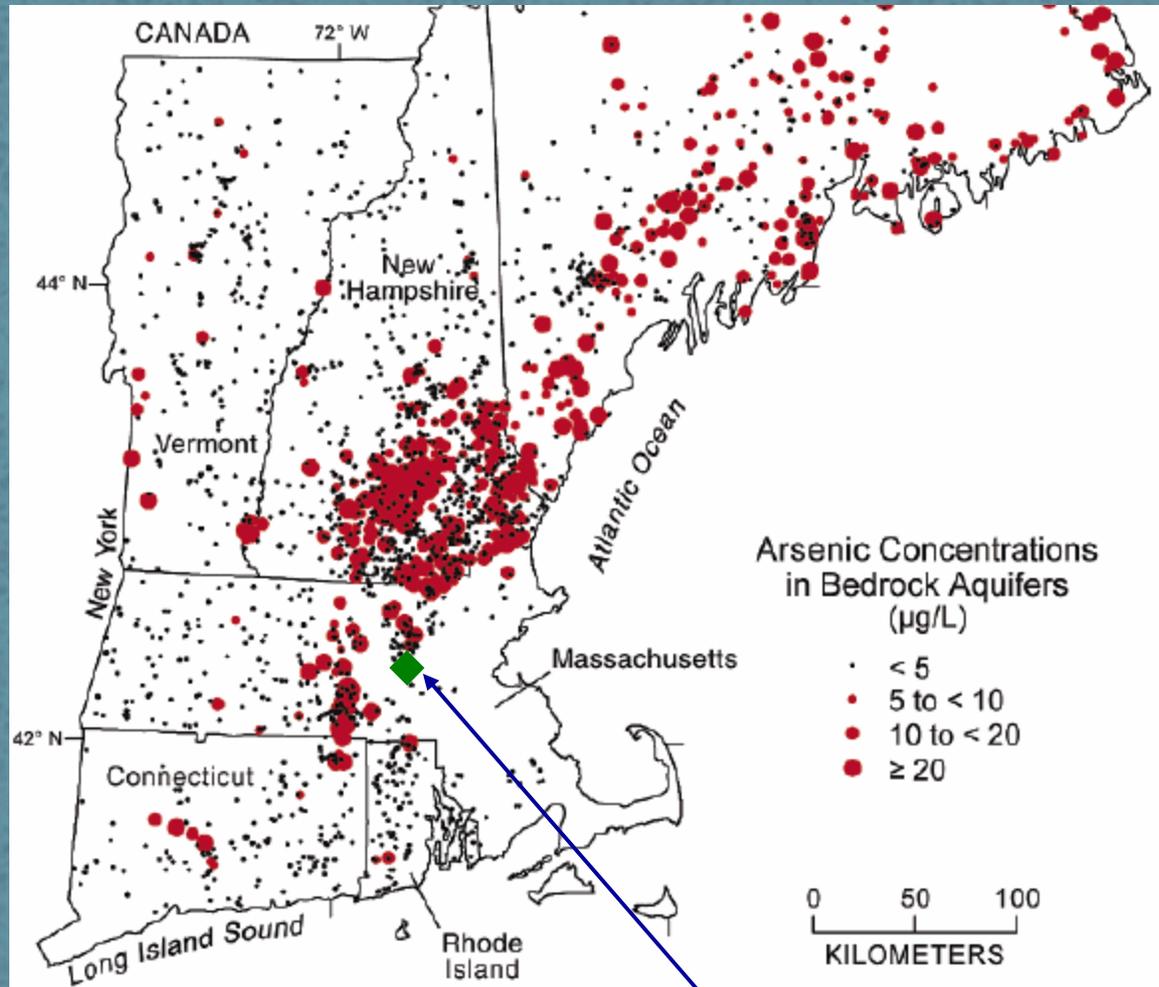
Arsenic - Induced Skin Lesions in Bangladesh



Arsenic in US Groundwater



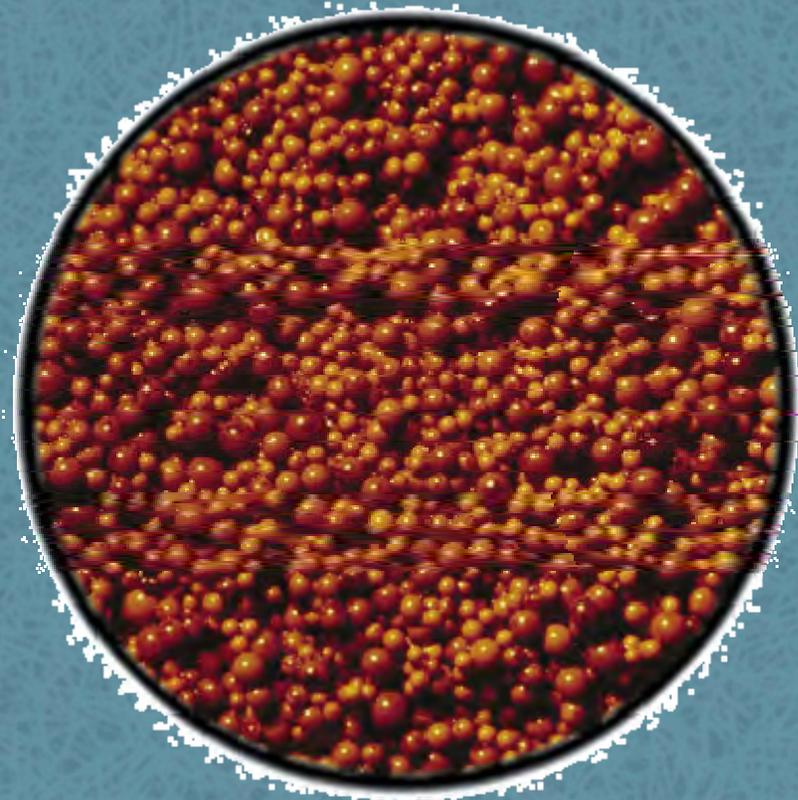
Why Arsenic is of Interest to SolmeteX



SolmeteX

ArsenX^{np} media

- Standard ion exchange resin size distribution (300 – 1200 µm).
- Iron throughout resin bead.
- Opaque mustard/brown colored.
- Support is a macro-porous strong base anion exchange resin.





ArsenX^{np} - Synthesis and Characterization

- Multistep process to disperse iron hydroxide throughout an anion exchange resin bead.
 - Concept developed by Arup SenGupta at Lehigh University.
(A.K. SenGupta & L.H. Cumbal, US Patent No. 7,291,578, November 2007)
- Synthesis optimized and scaled up by SolmeteX.
- Commercial product, ArsenX^{np}, manufactured under license by The Purolite Company in Philadelphia, USA
- NSF-61 certified for drinking water applications.



ArsenX^{np} – Synthesis chemistry

1. Contact anion exchange resin with an anionic oxidant, e.g. hypochlorite, persulfate, permanganate.

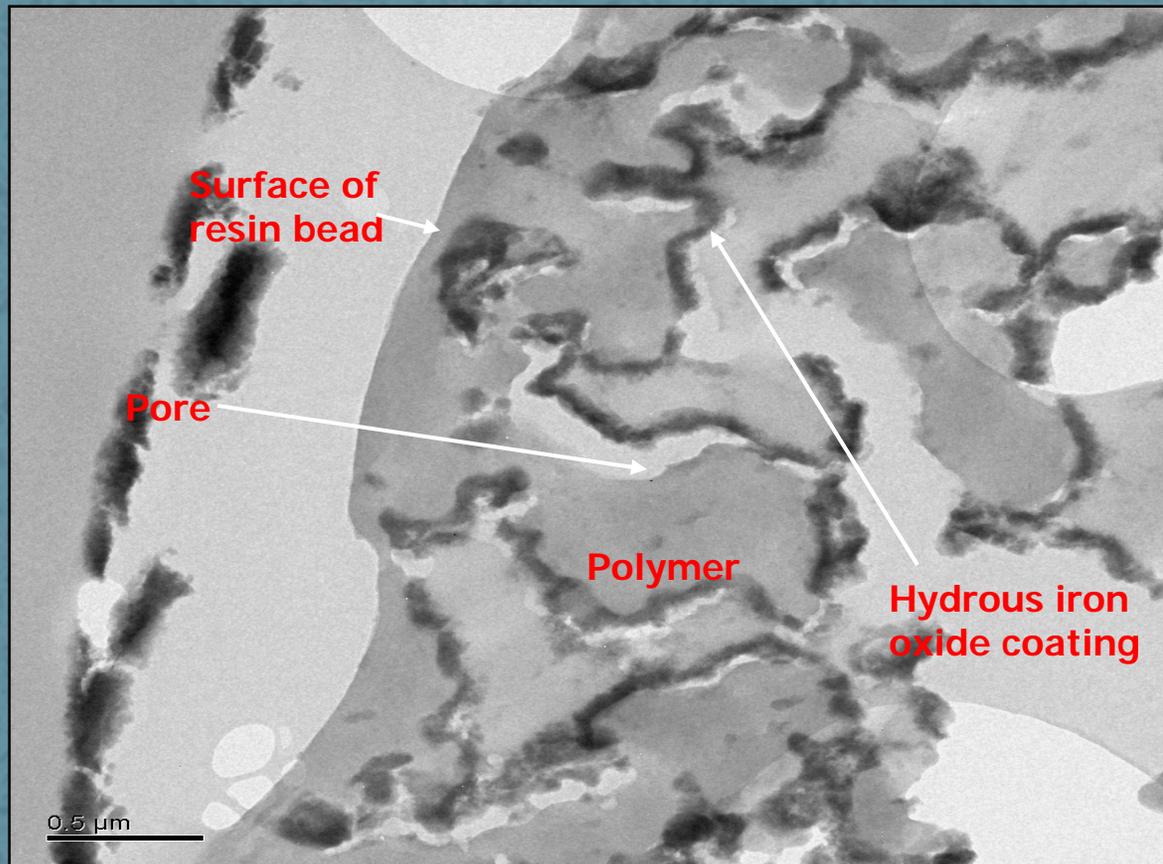


2. Contact oxidant-loaded resin with an Fe(II) solution to precipitate ferric hydroxide.



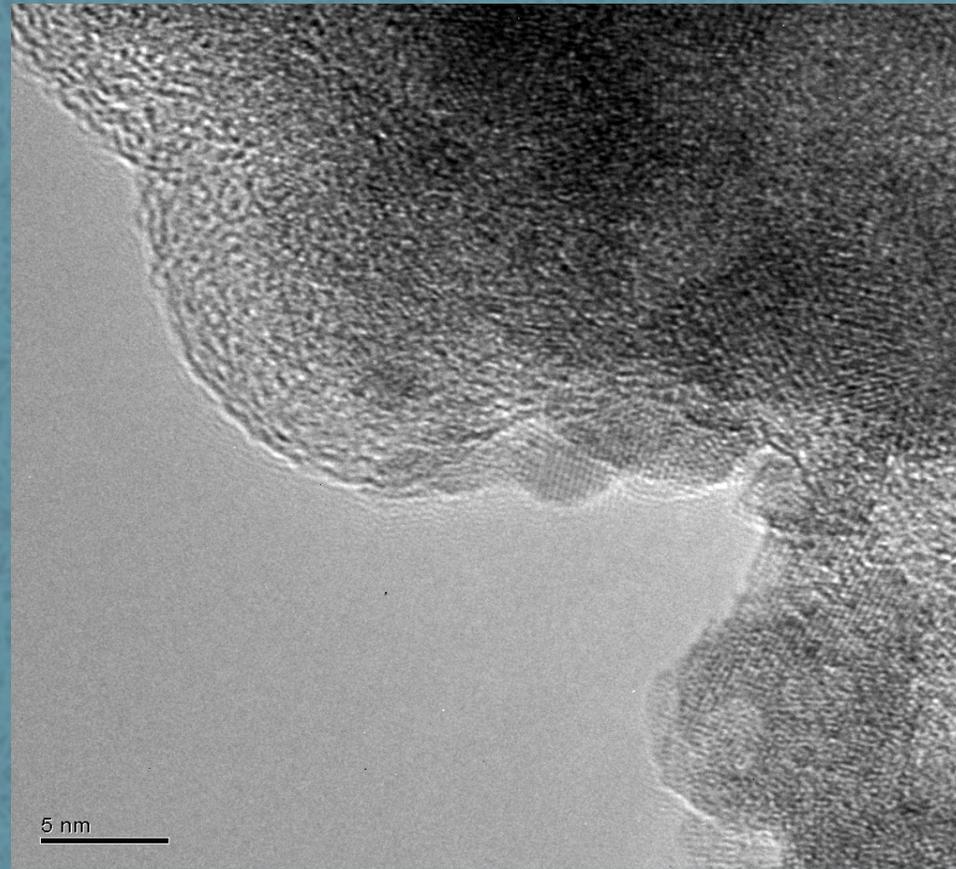
3. Wash final product to remove unbound iron hydroxide and raise pH to ~7.

ArsenX^{np} TEM Micrograph



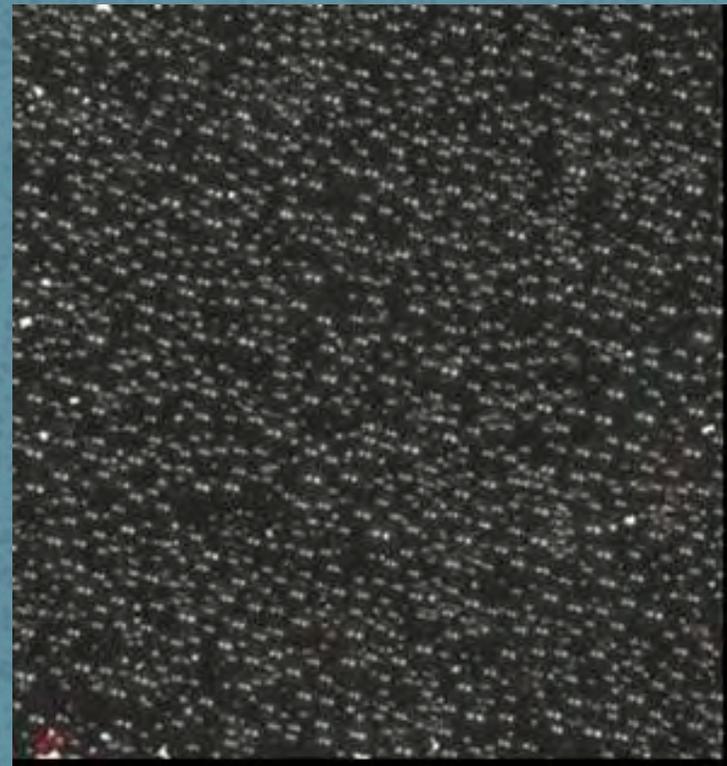


High Magnification ArsenX^{np} TEM Image



npRio media

- Standard ion exchange resin size distribution (300 – 1200 μm).
- Iron throughout resin bead.
- Dark red/black translucent beads.
- Support is a microporous gel-type strong base anion exchange resin.





npRio – Synthesis

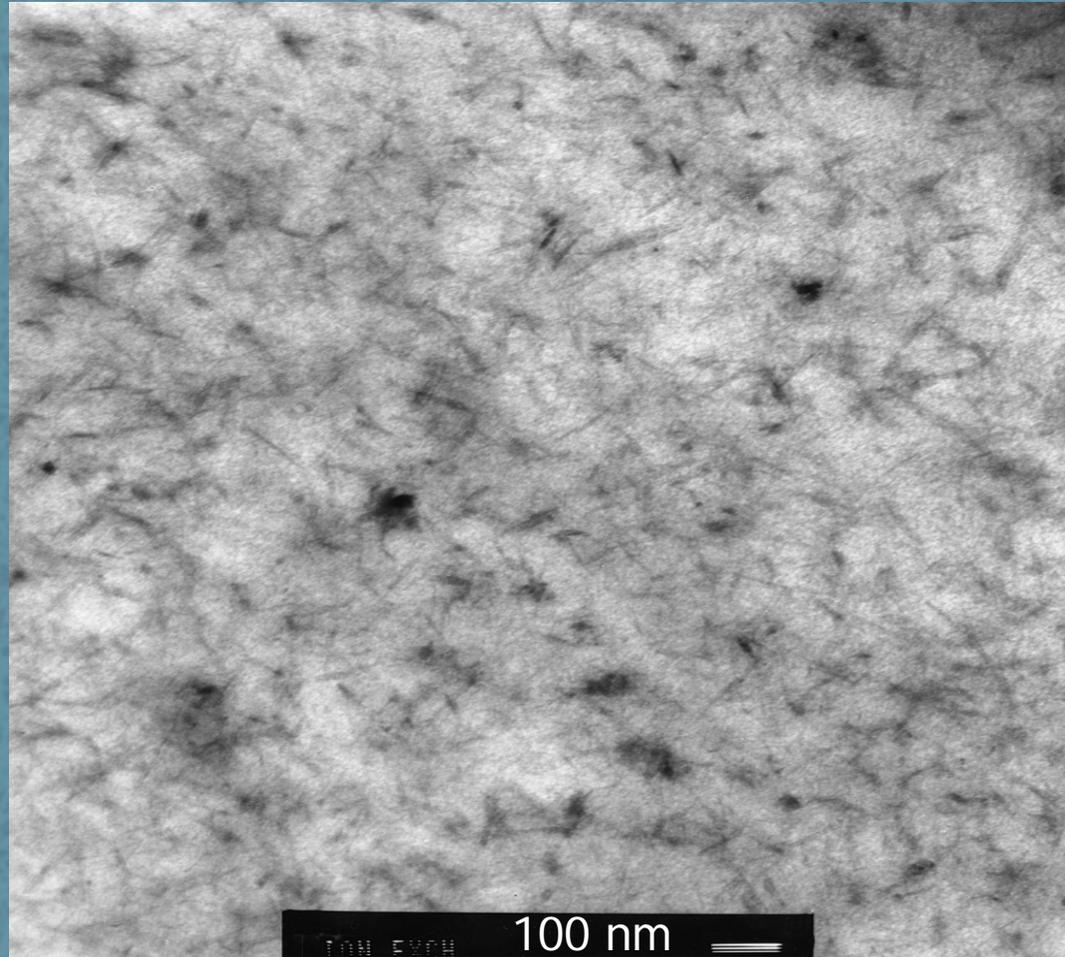
- Ion exchange FeCl_4^- anion onto anion exchange resin.



- Contact loaded resin with an alkaline solution to deposit ferric hydroxide *in situ* within the bead.
- Neutralize resin and wash to remove any unbound ferric hydroxide.
- npRio commercially manufactured under license by Basin Water in Memphis, TN.
- NSF-61 certified for drinking water applications.



npRio TEM micrograph





ArsenX^{np} and npRio Comparison

Property	ArsenX ^{np}	npRio
Iron Content (Dry weight)	~250 mg/g	~300 mg/g
Base Bead	Macroporous AIX	Gel Type AIX
Bead Size	300 – 1200 μm	300 – 1200 μm
Physical appearance of oxide particles	Nanoparticle coating around macropores	Discrete lath-shaped nanoparticles
Form of Hydrous Iron Oxide	Low crystallinity goethite	X-Ray amorphous
Point of Zero Charge (pH_{pzc})	8.8 – 9.0	6.5 – 7.5



As(V) Isotherm Capacity – Experimental Procedure

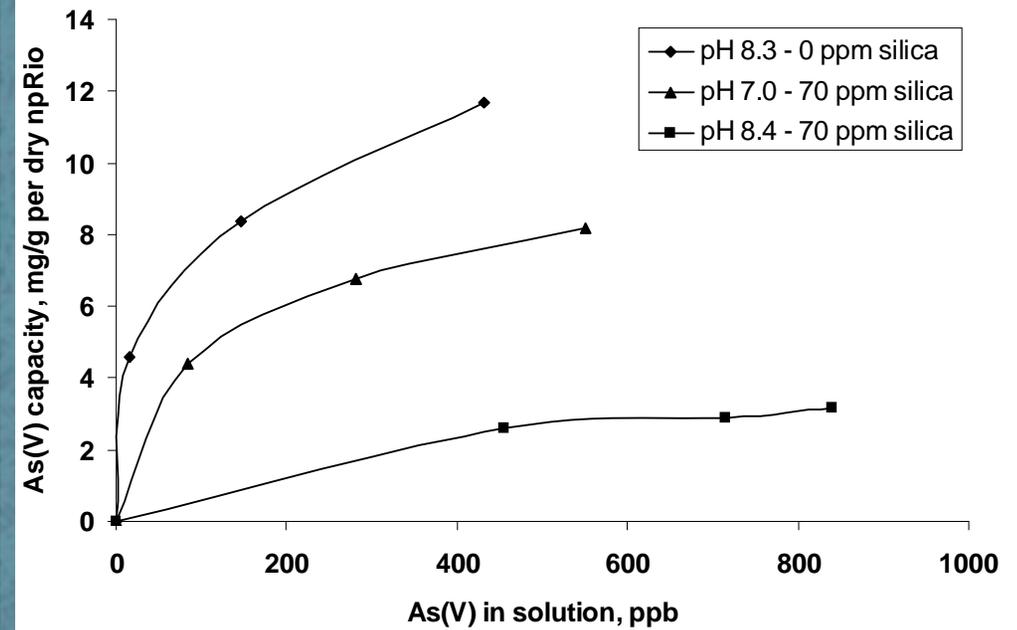
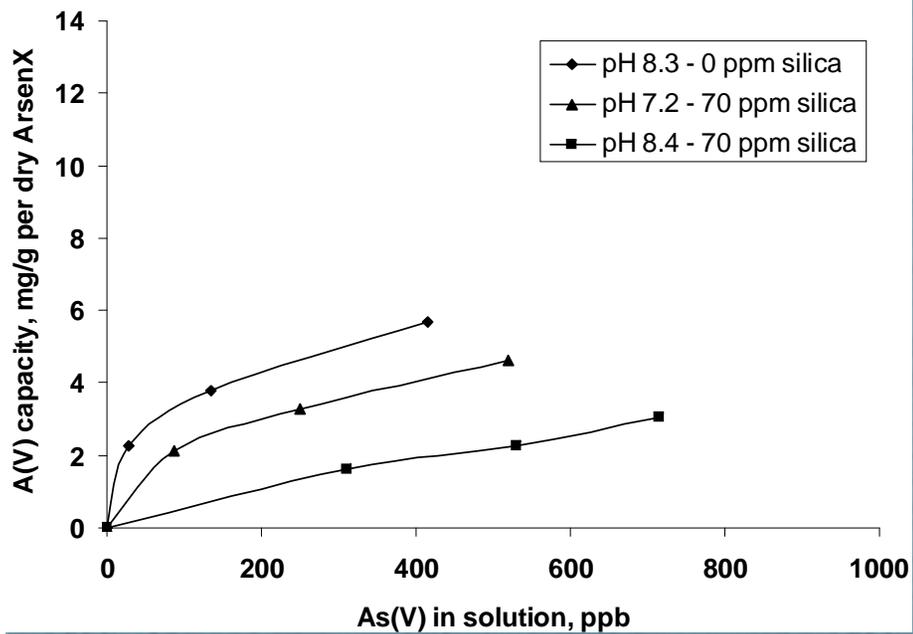
- 0.025, 0.050 and 0.100g of media equilibrated overnight with 200 ml solution containing 1 ppm arsenic(V) in matrix of 120 ppm sulfate, 33 ppm chloride 100 ppm bicarbonate.
- Silica content varied from 0 – 70 ppm SiO₂.
- pH adjusted using HCl or NaOH within range pH 7.0-9.0.
- Residual arsenic content of solution determined and isotherms plotted.



Selected As(V) Isotherm Results

ArsenX^{np}

npRio





As(V) Static Capacity Summary

- As(V) capacity of both media decrease with increasing pH.
- Increased silica decreases arsenic capacity for both media.
- npRio has higher initial arsenic capacity in low pH/low silica solutions but is affected more than ArsenX^{np} by increases in pH and silica.
- At pH 8.4, 70 ppm SiO₂, arsenic capacities of ArsenX^{np} and npRio are similar but very low (~ 3 mg/g).
- Batch data suggested that npRio would have higher arsenic capacity than ArsenX^{np} under majority of conditions.



Field Trials

- Two locations selected for trials: Paxton, MA and Bow, NH.
- ~ 3L of each media run simultaneously with an empty bed contact time of 3 minutes.
- Paxton – 2" ID columns, 57" height.
Bow – 4" ID columns, 16.5" height.
- Run in down-flow configuration. Samples taken at intermediate points in column to obtain information on arsenic adsorption kinetics.
- Arsenic breakthrough curves plotted as a function of processed bed volumes.

Field Test Pilot Systems

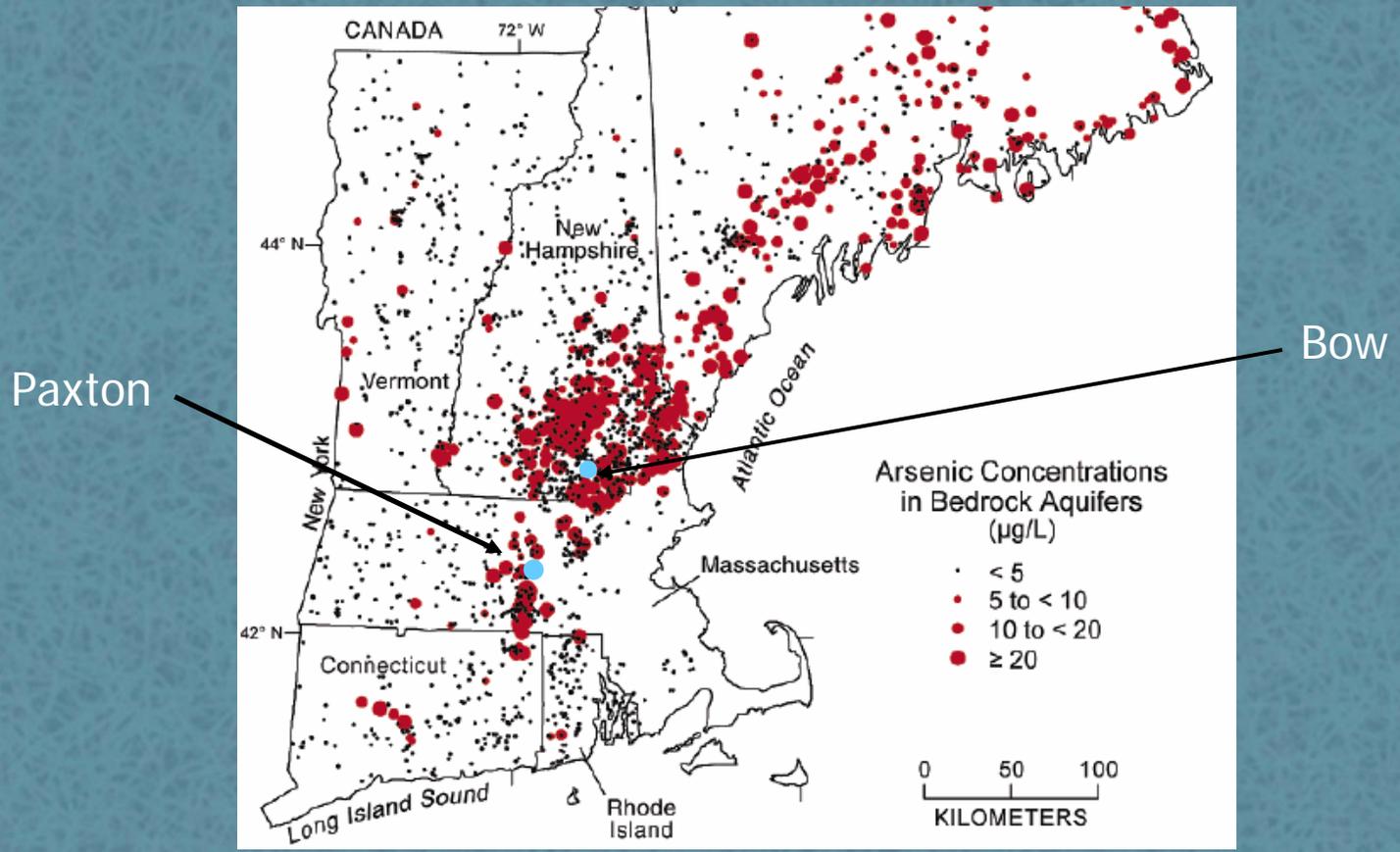
Paxton, MA



Bow, NH



Location of Test Sites





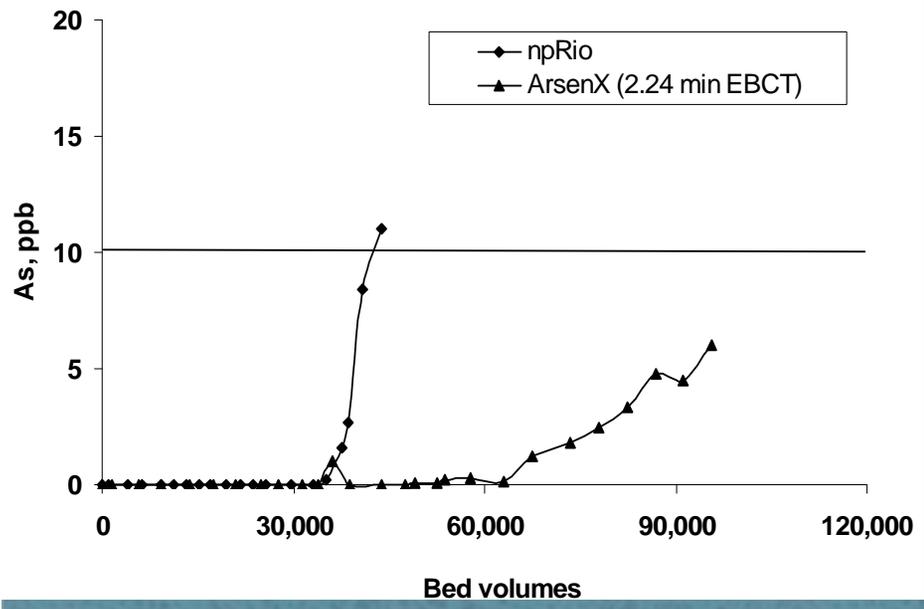
Water Quality at Field Test Sites

Parameter	Paxton, MA	Bow, NH	Units
pH	6.7	7.7	
Arsenic	21	44	ppb
Iron	0.03	0.06	ppm
Hardness	89	83	ppm CaCO ₃
Silica	13	20	ppm
Chloride	55.3	41	ppm
Sulfate	20.7	15.5	ppm
Fluoride	0.2	0.8	ppm
Phosphate	<150	<100	ppb

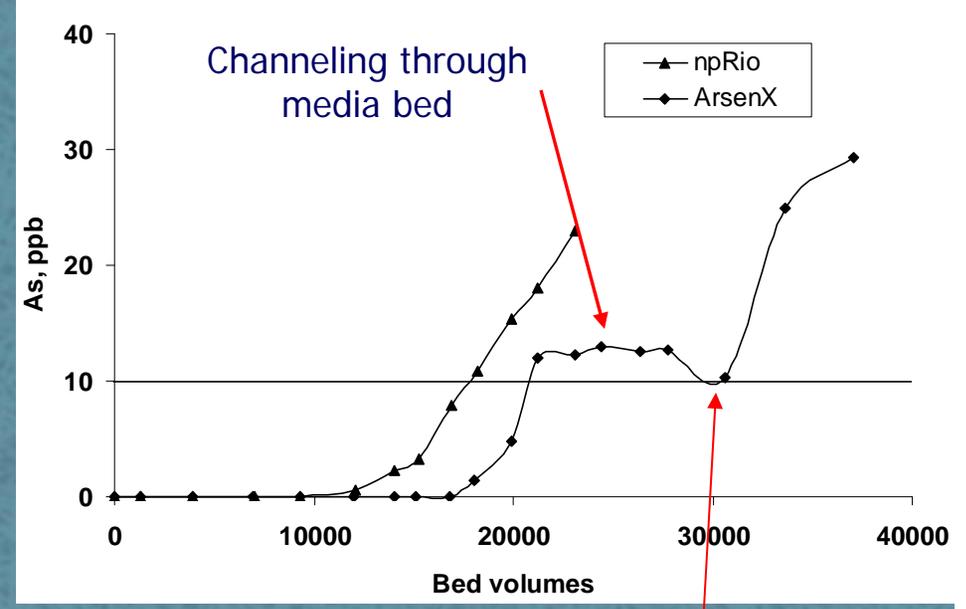


Arsenic Breakthrough Curves

Paxton, MA



Bow, NH



Estimated Breakthrough



Field Trials - Results

- npRio broke through much earlier than ArsenX^{np} at both sites:
 - Paxton: 104,000 BVs (estimated) for ArsenX^{np} vs 43,000 BVs for npRio.
 - Bow: 30,000 BVs for ArsenX^{np} vs 18,000 BVs for npRio.
- Laboratory batch tests under similar pH and silica conditions suggested npRio would outperform ArsenX^{np}.
- Why the difference between lab batch tests and field column trials?



Analysis of Spent Columns

- Twice as much silica on spent npRio at Paxton compared to ArsenX^{np}.
- Suggests higher affinity of npRio for silica, even at low pH
 - Interference with As adsorption.
- Higher NOM levels on ArsenX^{np} than npRio.
 - Expected for a macroporous resin.
- Laboratory tests using humic acid showed little impact on performance of either media.



Conclusions

- Two commercial hybrid iron oxide media evaluated for arsenic removal.
- Form of iron oxide very important for optimum arsenic affinity and tolerance for interfering species, such as silica.
- Static batch tests not always useful for comparing different media.
- Hypothesized that silica adsorption and polymerization on npRio physically blocked access to arsenic adsorption sites as well as directly competed with arsenate anion.
- Microporous gel-type resin more susceptible to blocking of active adsorption sites than a macroporous resin.



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Arsenic

Listener

Questions

Answered!

Arsenic

