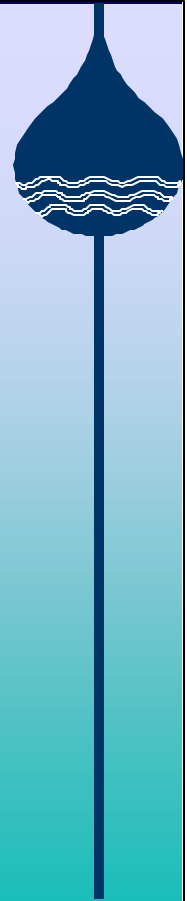


# Arsenic

## Mitigation Strategies

- The purpose of this training session is acquaint Primacy Agency decision makers, technical assistance providers, and other public health officials with the requirements of the final Arsenic Rule.
- This presentation covers strategies systems can use to lower the amount of arsenic in finished water. It is one part of an overall training session on the Arsenic Rule conducted by EPA during 2002. Other presentations cover the disposal of residuals generated by arsenic treatment, monitoring and reporting and other Arsenic Rule topics.
- This presentation is based on EPA's draft document *Arsenic Treatment Technology Design Manual for Small Systems*. The document summarizes available data and presents it in an easy-to-use format. The manual and the decision trees were designed to help a system operator, assistance provider, or regulator determine whether a system has an arsenic problem and the best methods for mitigating. The *Design Manual* also includes detailed cost and labor estimates.
- Other useful resources on arsenic treatment are available through the EPA Office of Ground Water and Drinking Water's Arsenic web page at <http://www.epa.gov/safewater/arsenic.html>. Also see the EPA Office of Research and Development's web page at [www.epa.gov/ORD/NRMRL/arsenic/](http://www.epa.gov/ORD/NRMRL/arsenic/).
- In addition, the American Water Works Association (AWWA) is developing a book that examines arsenic treatment technologies, however, it is not focused as much on small systems and is more technical in nature.

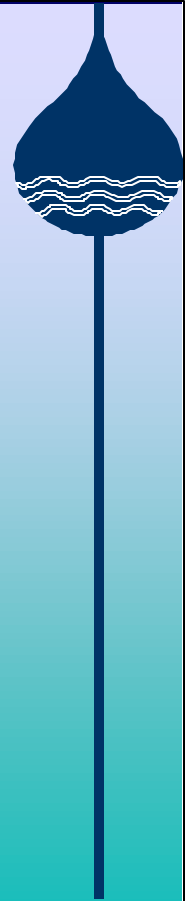
# Presentation Summary



- **BAT**
- **Arsenic**
  - **Arsenite vs. Arsenate**
  - **Speciation**
  - **Oxidation**
- **Monitoring and planning**
- **Zero treatment options**
- **Treatment options**
  - **Existing technologies**
  - **New technologies**
    - **Most likely new technologies**
- **Piloting**
- **Regulatory considerations**
- **POE/POU**
- **Workshop**

- This presentation is structured as follows:
  1. Brief discussion of best available technologies (BAT). This segment is brief because most small systems impacted by the Arsenic Rule will probably not use a BAT.
  2. Discussion of arsenic chemistry. The difference between arsenite [arsenic (III)] and arsenate [arsenic (V)] will impact removal.
  3. Brief discussion of monitoring and planning. Most systems, especially early on, need to think about monitoring as part of their planning options.
  4. Explanation of zero treatment options, which are preferable where they are possible.
  5. Step-by-step discussion of treatment options, including a discussion of technologies that are the most promising for small systems.
  6. Overview of pilot testing.
  7. Regulatory issues will be considered throughout the presentation.
  8. Finally, an introduction to point-of-use (POU) treatment units.
  9. This presentation is meant to be accompanied by a treatment technology workshop, in which training participants use the decision trees from this presentation to make suggestions about appropriate technologies for a series of example systems.

# Best Available Technologies (BAT)



- **High removal efficiency**
- **History of full-scale operation**
- **General geographic applicability**
- **Reasonable cost based on large systems**
- **Reasonable service life**
- **Compatibility with other treatment processes**
- **Able to bring all of a system's water into compliance**

- Section 1412(b)(4)(E) of the Safe Drinking Water Act (SDWA) states that each National Primary Drinking Water Regulation (NPDWR) which establishes an Maximum Contaminant Level shall list the technology, treatment techniques, and other means that the Administrator finds to be feasible for purposes of meeting the MCL. Technologies are judged to be a BAT when the following criteria are satisfactorily met:
  - (1) The capability of a high removal efficiency;
  - (2) A history of full-scale operation;
  - (3) General geographic applicability;
  - (4) Reasonable cost based on large and metropolitan water systems;
  - (5) Reasonable service life;
  - (6) Compatibility with other water treatment processes; and,
  - (7) The ability to bring all of the water in a system into compliance.
- Systems are not required to use BATs to achieve compliance with an MCL. Any technology that is accepted by the State primacy agency and achieves compliance with the MCL is allowed. However, if a system is unable to meet the MCL with its chosen technology, the system is not eligible for a variance unless it has installed a BAT and still cannot achieve compliance. For more information on variances and exemptions see the Arsenic State Implementation Guidance (EPA 816-K-02-018) at [http://www.epa.gov/ogwdw/ars/pdfs/regguide/ars\\_final\\_!mainguide\\_9-13.pdf](http://www.epa.gov/ogwdw/ars/pdfs/regguide/ars_final_!mainguide_9-13.pdf).

Technology	Maximum % Removal
Activated Alumina	95
Coagulation/Filtration	95
Ion Exchange	95
Lime Softening	90
Reverse Osmosis	>95
Electrodialysis	85
Oxidation/Filtration	80

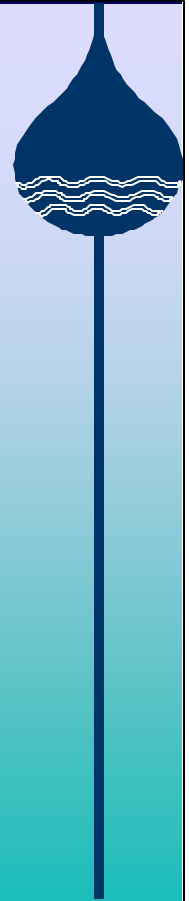
- EPA identified 7 BATs in the Final Arsenic Rule using its listed criteria (66 FR 6976 at 6981). EPA determined these technologies to be the BATs for the removal of arsenic in drinking water based on a demonstration of efficacy under field conditions taking cost into consideration (40 CFR 141.62(c) and SDWA 1412(b)(4)(D)). All of these BATs are for arsenic V. Pre-oxidation may be required to convert arsenic III to arsenic V (40 CFR 141.62(c)).
- This table shows the seven BATs identified by EPA in the Final Arsenic Rule and also the maximum percent of arsenic removal that can be reasonably obtained from these technologies. These technologies include:
  - Activated Alumina, with a maximum removal of 95%;
  - Coagulation/Filtration (not BAT for systems with fewer than 500 service connections), with a maximum removal of 95%;
  - Ion Exchange, with a maximum removal of 95%;
  - Lime Softening (not BAT for systems with fewer than 500 service connections), with a maximum removal of 90%;
  - RO, with a maximum removal of over 95%;
  - Electrodialysis, with a maximum removal of 85%; and,
  - Oxidation/filtration, with a maximum removal of 80%. To obtain high removal rates with oxidation/filtration, the iron to arsenic ratio must be at least 20:1 (40 CFR 141.62(c)).
- A brief discussion of the major issues surrounding the usage of each technology is given in the preamble to the Final Arsenic Rule. More details about the treatment technologies and costs can be found in EPA's *Technologies and Costs for the Removal of Arsenic From Drinking Water*, December 2000.

## Small System Compliance Technologies in 40 CFR 141.62 (d)

Treatment Technology	Affordable for listed category
Activated Alumina (central, POU, POE)	All size categories
Ion exchange	All size categories
Oxidation/Filtration	All size categories
Coag Assisted Micro	501-3,300 and 3,301-10,000
Reverse Osmosis (central)	501-3,300 and 3,301-10,000
Reverse Osmosis (POU)	All size categories
Coagulation/Filtration	501-3,300 and 3,301-10,000
Lime Softening	501-3,300 and 3,301-10,000

- The technologies examined for BAT determinations were also evaluated as small system compliance technologies (SSCTs). EPA must list SSCTs for three sizes of small systems: systems serving between 25 and 500 people, systems serving between 501 and 3,300 people, and systems serving between 3,301 and 10,000 people (SDWA 1412(b)(4)(E)(ii)). EPA has listed SSCTs that may achieve compliance with the arsenic MCL and that are affordable and applicable to small drinking water systems.
- This table identifies the SSCTS and the system size categories for which they are SSCTS.
- Because EPA has listed SSCTs, small systems:
  - Will have the latitude to choose the type of treatment technology that is most cost effective and appropriate (from an operation and maintenance standpoint).
  - Are not eligible for a *small system variance* since EPA has determined that SSCTs exist for all three system size categories.
  - May be eligible for a *general variance* under SDWA 1415(a) if they have installed or agreed to install the BAT but, due to source water quality, will not be in compliance with the MCL.
- For more information on variances, exemptions, and small system compliance technologies, see the Arsenic State Implementation Guidance (EPA 816-K-02-018). Also see (EPA 816-R-02-008A), *Complying With the New Drinking Water Standard for Arsenic: Small Entity Compliance Guide*, which is a guide designed to help small systems comply with the Rule.

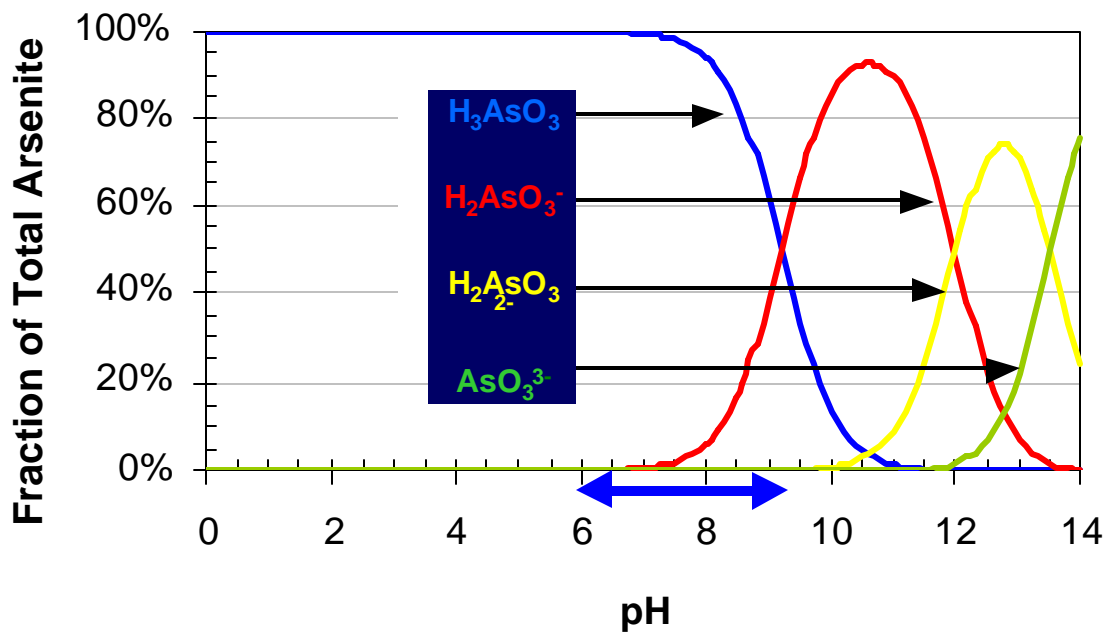
# Arsenic Chemistry



- **Found in water in two oxidation states**
  - **Arsenite (trivalent As III)**
  - **Arsenate (pentavalent As V)**

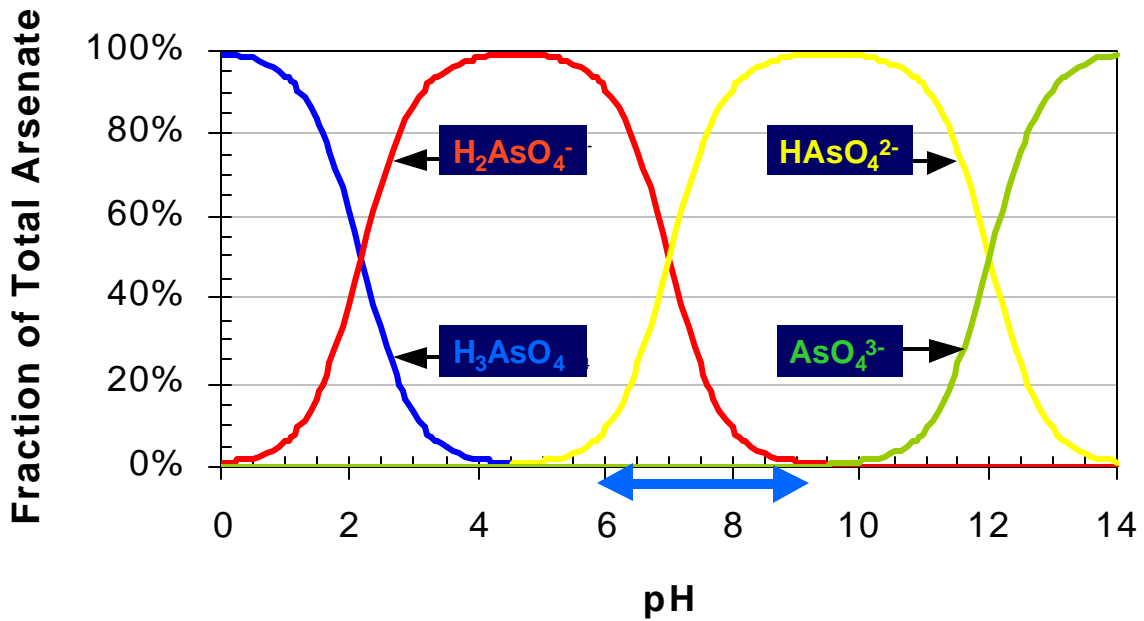
- Soluble arsenic generally exists in either the +3 (tri-) or +5 (penta-) valence state, depending on local oxidation-reduction conditions. Arsenic (III) is also known as arsenite; arsenic (V) is also known as arsenate.
- Under anaerobic conditions, arsenic exists primarily as arsenic (III) (arsenite). Under aerobic conditions, arsenic exists primarily as arsenate (pentavalent).
- Anaerobic conditions are common in deep groundwater sources. Conversely, surface waters generally contain much higher levels of dissolved oxygen, which support an aerobic environment.
- Arsenic is introduced into the aquatic environment from both natural and manmade sources. Typically, however, arsenic occurrence in water is caused by the weathering and dissolution of arsenic-bearing rocks, minerals, and ores. Although arsenic exists in both organic and inorganic forms, the inorganic forms are more prevalent in water and are considered more toxic. Therefore, the focus of this presentation is on inorganic arsenic.

## Disassociation of Arsenite



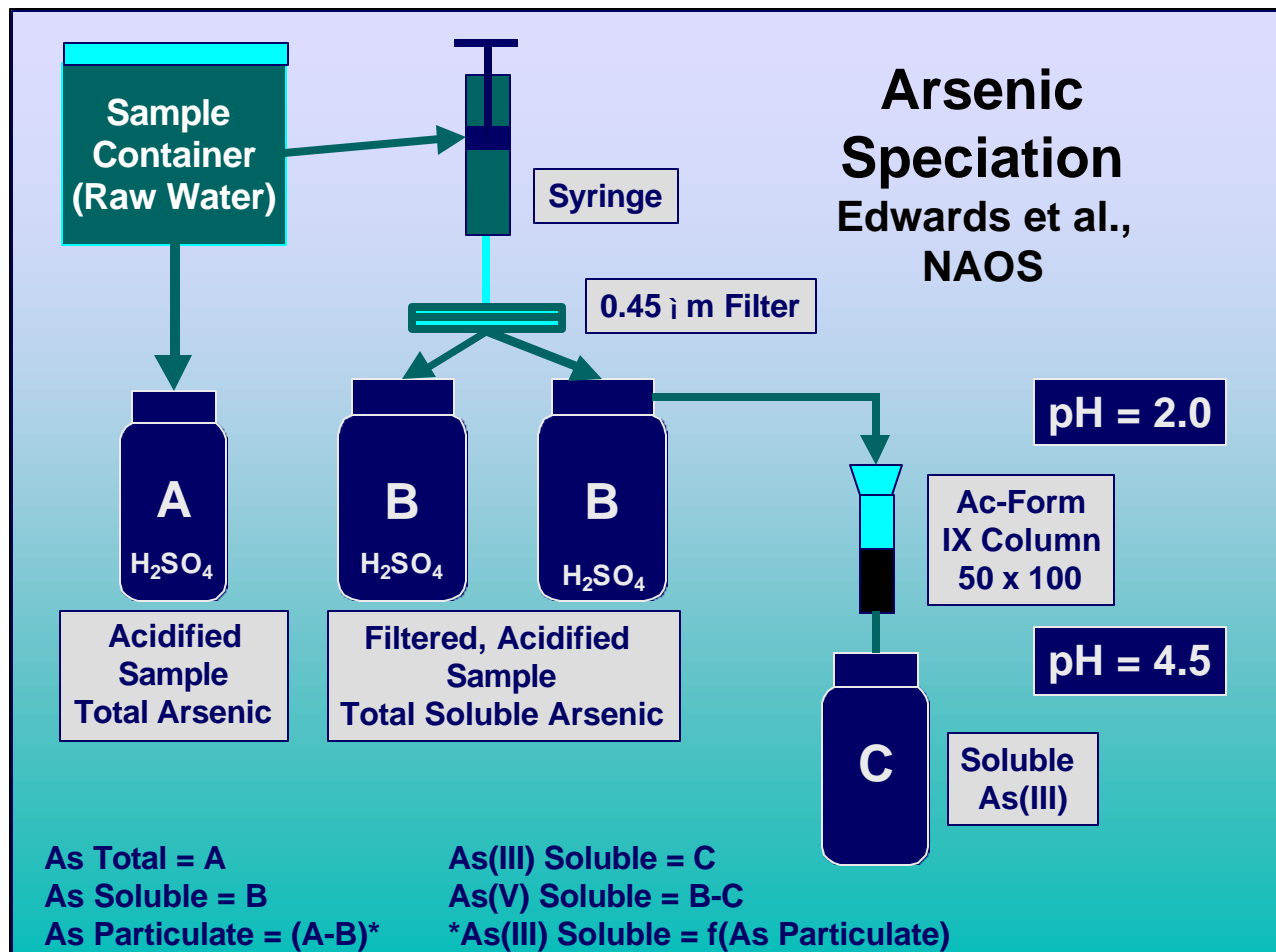
- The dissociation of both arsenite and arsenate is pH-dependent. The kinetics of dissociation are nearly instantaneous.
- This figure shows that, in the pH range of natural water, which typically is between 6 and 9, arsenite occurs as an uncharged particle,  $H_3AsO_3$ .

## Disassociation of Arsenate



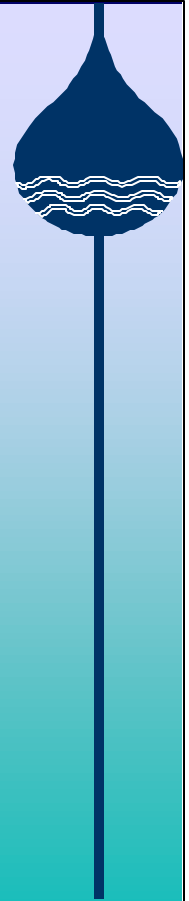
- This figure shows that, in the pH range of natural water, which typically is between 6 and 9, arsenate occurs as a charged particle,  $H_2AsO_4^-$  or  $HAsO_4^{2-}$ .
- Chemical speciation is a critical element of arsenic treatability. Negative surface charges facilitate removal by adsorption, anion exchange, and co-precipitative processes.
- Since the net charge of arsenite is neutral at natural pH levels, this form is not easily removed. However, the net molecular charge of arsenate is negative (-1 or -2) at natural pH levels, enabling it to be removed with greater efficiency.
- Conversion to arsenate is a critical element of any arsenic treatment process. This conversion can be accomplished by adding an oxidizing agent such as chlorine or permanganate. Selection of the most appropriate oxidation technology is discussed later in this presentation.





- Arsenic speciation is the determination of the relative concentrations of arsenite and arsenate. If arsenic speciation indicates that high levels of arsenite are present in source water, the water system may need to install pre-oxidation equipment to convert arsenite to arsenate prior to treatment.
- Following Edwards et al., arsenic can be speciated as follows:
  1. Collect a water sample. If acidified and analyzed directly, this sample would yield total arsenic, including both particulate and soluble arsenic.
  2. Pump the sample through a 0.45 micron filter to remove particulate As.
  3. Add sulfuric acid to adjust the pH to 3.
  4. Split the sample and conduct total soluble arsenic analysis on one half. The result is the concentration of arsenate and arsenite combined.
  5. Filter the second half through Dowes anion exchange resin.
  6. Conduct total soluble arsenic analysis on the second, anion-exchange-treated half. The result is the concentration of arsenate.
  7. The concentration of arsenite can be calculated by subtracting the concentration of arsenate from the concentration of total soluble arsenic.

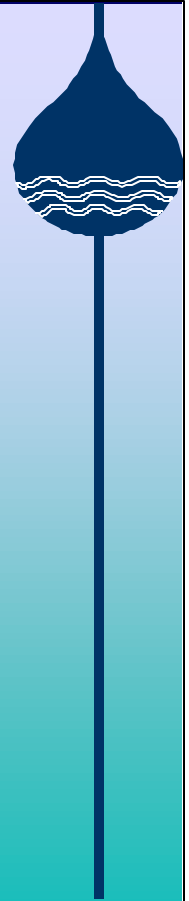
## But, For Practical Purposes....



- **Plan on oxidation by chlorination**
  - **Virtually all technologies remove arsenic V better than arsenic III**
  - **Many (most?) States will require disinfection**

- From the perspective of protecting public health, pre-oxidation using chlorination will probably be necessary, and systems may not need to perform speciation.
  - Most small systems are ground water systems, and ground water supplies typically contain high levels of arsenite. Because all technologies detailed here remove arsenate better than arsenite, pre-oxidation will probably be necessary.
  - Many States will require disinfection when treatment is installed.
  - Conversion to arsenate can be accomplished by providing an oxidizing agent at the head of any proposed arsenic removal process. However, chlorination is the only process capable of both oxidizing arsenite to arsenate and introducing a residual into the distribution system.

# Mitigation Techniques



- **Alternative source**
- **Blending**
- **Centralized treatment**
  - **Techniques**
    - **Side-stream treatment**
    - **Full treatment**
  - **Existing technologies**
  - **New technologies**
- **Point-of-use (POU)**

- Problematic arsenic levels in drinking water can be mitigated in several different ways.
- The selection of the most appropriate method for a particular water system should be based on feasibility issues, system constraints, and costs. This presentation will address the following mitigation approaches:
  - **Alternative source** - abandonment of the problematic source(s) and switching to other source(s) within the system or purchasing from a neighboring system. Systems with multiple sources that do not all have arsenic problems should first analyze whether they can meet the standard without installing treatment; systems located near other systems may wish to investigate purchasing finished water.
  - **Blending** - The combination of multiple water sources to produce a stream with an arsenic concentration below the MCL. Blending should be a second choice for systems.
  - **Centralized treatment** - The processing of a high arsenic water stream to reduce the arsenic concentration to below the MCL. Centralized treatment can be used to treat the full stream of influent water, or it can be used for side-stream treatment, which is the centralized treatment of a portion of the high arsenic water stream and subsequent blending of this stream back with the untreated portion to produce a water that meets the MCL.
    - Centralized arsenic treatment can be produced either by modifying an existing treatment technology or by installing new treatment equipment.
  - **POU** - Only the water to be used for human consumption is treated at the utility at a point after the water exists the distribution system (e.g., at a household faucet).

# Pre-Oxidation Processes (Chlorine & Permanganate)



- **Chlorine**

- **Pros**

- **Low cost**
    - **Primary and secondary disinfectant**
    - **MnO<sub>x</sub> media regenerant**

- **Cons**

- **Disinfection byproducts**
    - **Membrane fouling**
    - **Handling and storage requirements**



- Reduced inorganic arsenic (arsenite) should be converted to arsenate to facilitate removal. This step is critical for achieving optimal performance for all processes described in this presentation. We will assume that oxidation is necessary and that it will be put in place with all treatment options.
- Chlorine and permanganate both oxidize arsenite to arsenate within one minute in the pH range of 6.3 to 8.3.
- Chlorine can be added either as a gas or as liquid hypochlorite. For new chlorine feed installations, these alternatives should be evaluated carefully. Gas chlorine will lower the pH. This may be useful to improve treatment but may contribute to Lead and Copper Rule problems and will probably not be used by small systems. Sodium hypochlorite will raise the pH. The stoichiometric oxidant demand is 0.95  $\mu\text{g/L}$  of chlorine (as  $\text{Cl}_2$ ) per  $\mu\text{g/L}$  of arsenite (as As).
- Benefits of chlorine:
  - Low relative cost (\$0.20/lb);
  - Primary disinfection capability;
  - Secondary disinfectant residual; and,
  - MnO<sub>x</sub> media regenerant.
  - Lack of interference from dissolved iron, manganese, sulfide, and total organic carbon (TOC).
- Drawbacks of chlorine:
  - Formation of disinfection by-products (DBP) when organic matter is present;
  - Membrane fouling. A GAC filter is often placed ahead of the membrane to remove chlorine, but GAC filters can introduce biological growth into the system and that growth may also be indicative of anaerobic conditions, which might convert arsenate back to arsenite; and,
  - Special handling and storage requirements.

# Pre-Oxidation Processes (Chlorine & Permanganate)

- **Permanganate**

- **Pros**

- **Doesn't react with membranes**
    - **No regulated disinfection byproducts**
    - **Ease of handling and storage**
    - **MnOx media regenerant**

- **Cons**

- **Relatively costly**
    - **Not a primary or secondary disinfectant**

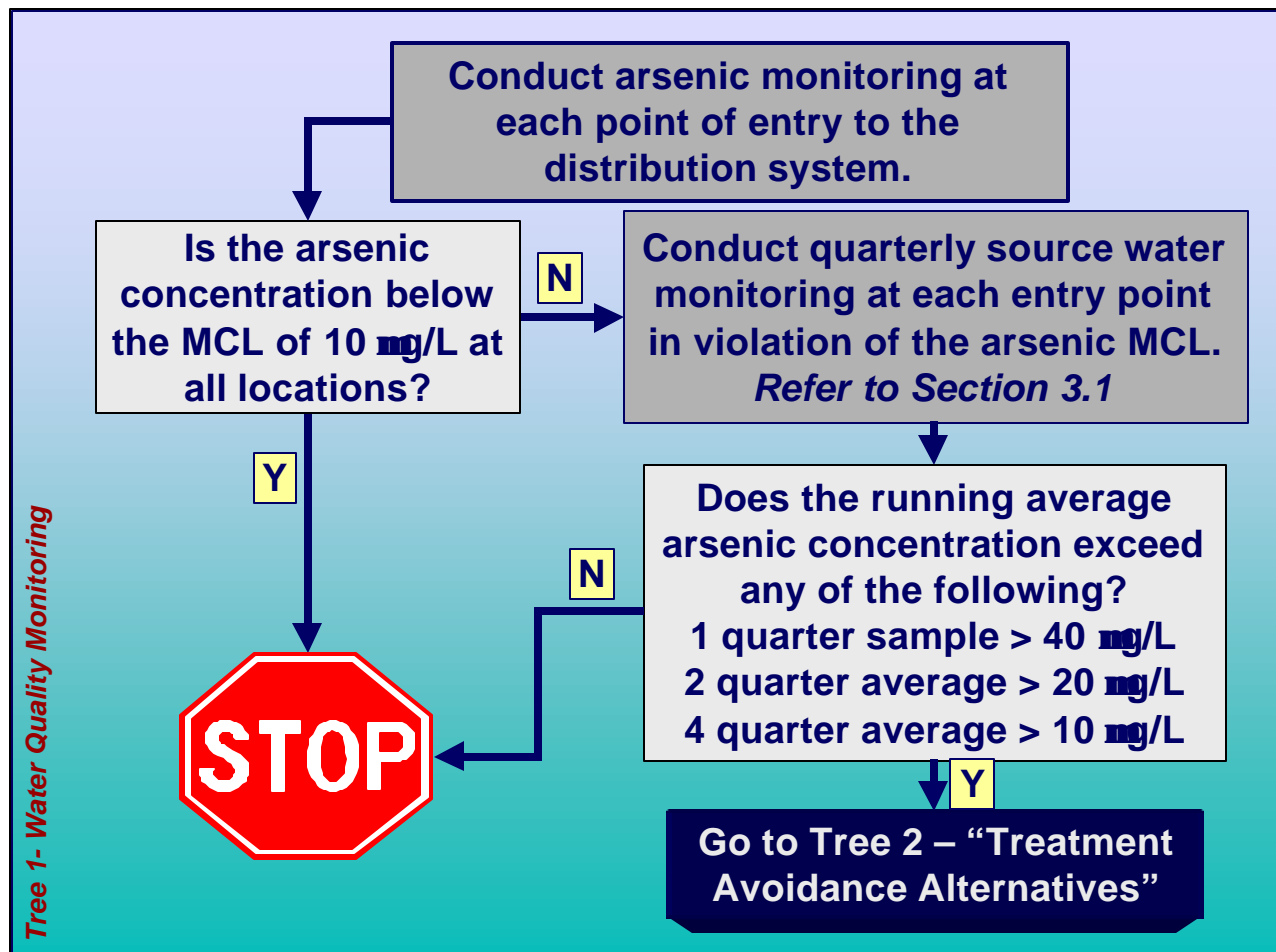


- Permanganate is a powerful oxidizing agent that is commonly used in iron and manganese removal processes. Potassium permanganate exists in solid, granular form and is readily soluble in water (6.4 g/L at room temperature). The stoichiometric demand is 0.49  $\mu\text{g/L}$  of permanganate (as Mn) per  $\mu\text{g/L}$  of arsenite (as As).
- Benefits of permanganate:
  - Unreactive with membranes;
  - No formation of disinfection by-products;
  - Ease of handling and storage;
  - MnOx media regenerant; and,
  - Lack of interference from dissolved iron, manganese, sulfide, and TOC.
- Drawbacks of permanganate:
  - High relative cost (\$1.35/lb);
  - No primary disinfection capability;
  - Does not provide a secondary disinfectant residual; and,
  - Formation of manganese particulates ( $\text{MnO}_2$ ). To prevent the accumulation of these deposits in the distribution system, they must be removed via filtration.
- The choice of chemical oxidant should be based primarily on the arsenic treatment technology to be employed and secondarily on other factors, such as cost and ease of use. Water systems that already employ chlorine or permanganate addition will usually be able to optimize their processes to provide concurrent arsenite oxidation.
- There are other oxidizing agents, although none is as effective as chlorine or permanganate for the oxidation of arsenite:
  - Ozone rapidly oxidizes arsenite but its effectiveness is significantly diminished by the presence of sulfides or organic carbon;
  - Chlorine dioxide and monochloramine are ineffective in oxidizing arsenite; and,
  - Ultraviolet (UV) light, by itself, is also ineffective. However, if the water is spiked with sulfite, UV photo-oxidation may be possible.

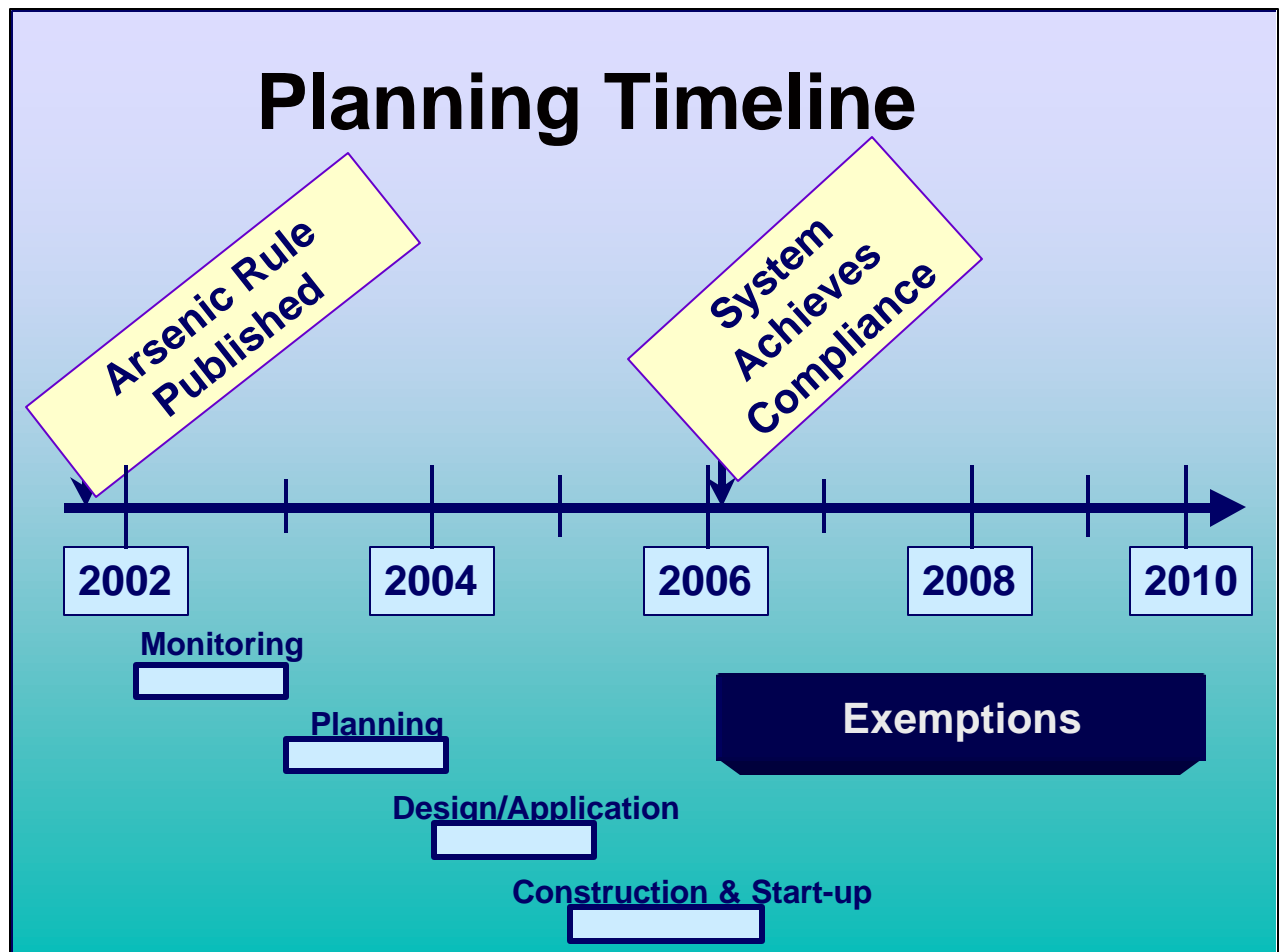
# Decision Tree Overview

- **Step 1: Water Quality Monitoring**
    - Tree 1: Water Quality Monitoring
  - **Step 2: Treatment Avoidance Alternatives**
    - Tree 2: Treatment Avoidance Alternatives
  - **Step 3: Optimizing Existing Treatment**
    - Tree 3: Optimizing Existing Treatment
    - Tree 3a: Enhanced Coagulation/Filtration
    - Tree 3b: Enhanced Lime Softening
    - Tree 3c: Iron & Manganese Filtration
  - **Step 4: Selecting New Treatment**
    - Tree 4: Selecting New Treatment
    - Tree 4a: Ion Exchange Processes
    - Tree 4b: Adsorption Processes
    - Tree 4c: Membrane Processes
- 

- The *Arsenic Treatment Technology Design Manual for Small Systems* provides decision trees to guide systems, regulators, assistance providers, and others through the process of determining appropriate treatment technologies for a given system.
  1. The first step in the process is to monitor source water to determine if the system has an arsenic problem at any of its entry points.
    - If there is a problem, then systems should first consider an alternate source or blending.
    - If an alternate source or blending is not feasible, then the system should consider optimizing its existing treatment.
  4. Finally, if no alternatives exist, the water system will need to install new treatment.
- The decision trees provided in this presentation are correlated with the *Design Manual*. When a decision tree refers to a section (for example, Section 3.1), that section of the *Design Manual* will provide more information on this topic.
- A draft of the *Design Manual* is posted on EPA's website at <http://www.epa.gov/safewater/smallsys/arsenicdesignmanualpeerreviewdraft.pdf>. The final document will also be posted here.



- The first determination that must be made is whether the water system will have difficulty complying with the revised arsenic MCL of 10 µg/L.
- The system should monitor for arsenic at each entry point to the distribution system. Because there may be temporal or seasonal variation in arsenic levels, this monitoring should ideally occur over an extended period of time.
- If arsenic is below 10µg/L at all entry points to the distribution system, then the system will be in compliance with the revised MCL and does not need to consider arsenic mitigation.
- If arsenic is above 10 µg/L at even one entry point to the distribution system, then the system will need to develop mitigation strategies.



- Systems need to start planning for compliance with the Arsenic Rule now. There are many steps that need to occur before the system will achieve compliance.
  1. Systems should monitor for arsenic to assess whether they have a problem.
  2. If necessary, systems need to consider their mitigation options and plan which ones are likely to be feasible. Systems may also need to apply for funding.
  3. Engineers will need to design or optimize treatment technologies. Systems should make sure to pilot new technology prior to full-scale installation.
  4. Construction and start-up will also take time.
- States may choose to issue exemptions to systems to provide them with more time to come into compliance with the Rule while protecting public health. For more information on exemptions see Appendix D of the Arsenic Implementation Guidance.



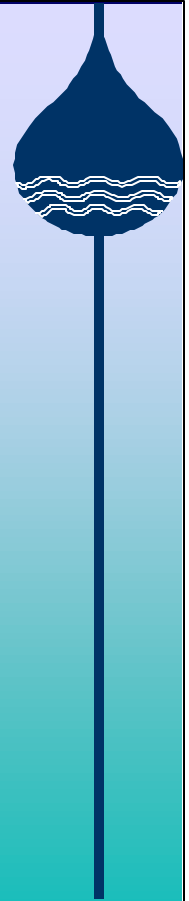


# Zero Treatment Options

## Alternative Source Blending

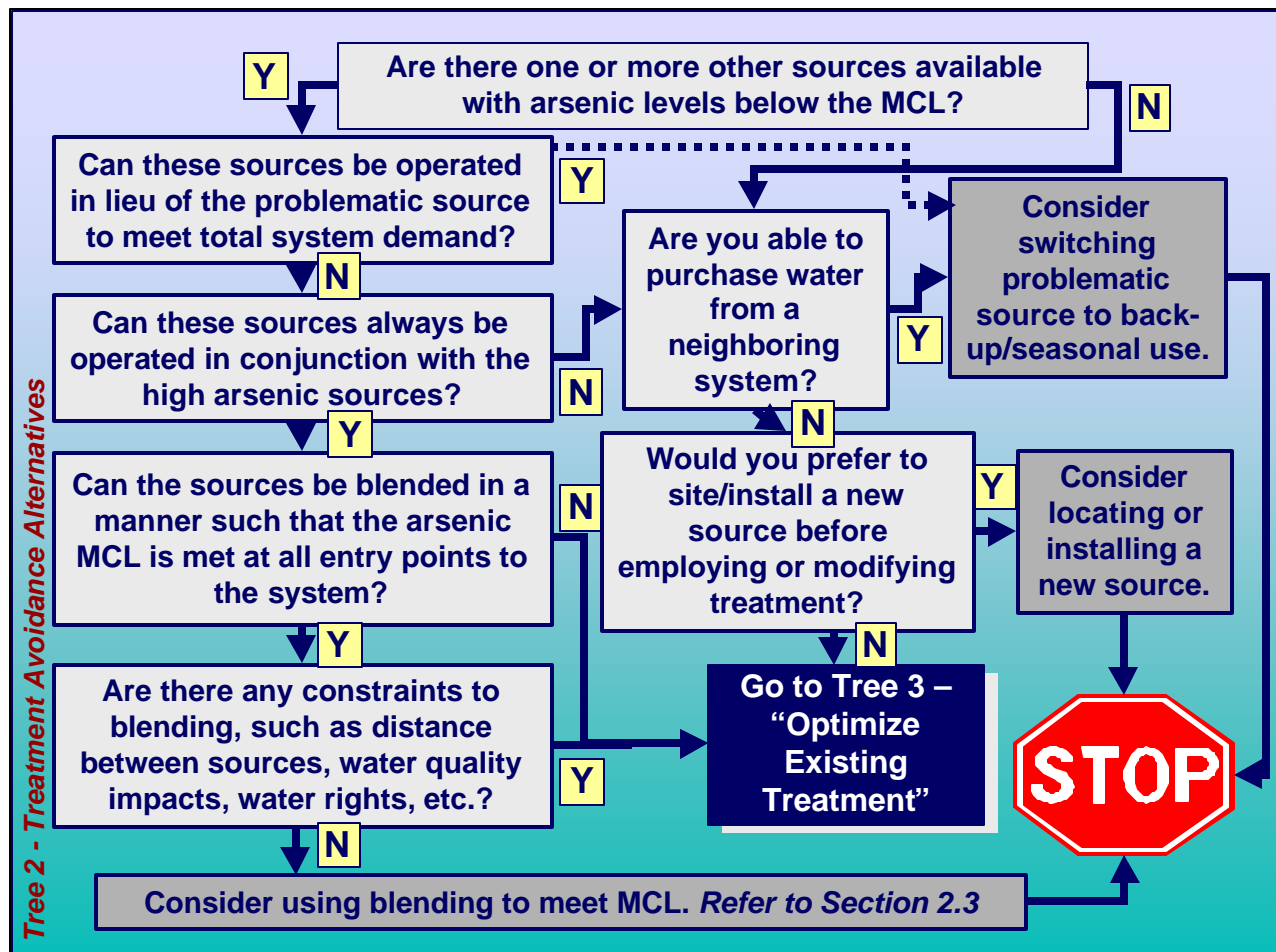
- The revised arsenic MCL must be met at all entry points to the distribution system. Therefore, community water systems (CWSs) and non-transient non-community water systems (NTNCWSs) that utilize multiple sources will need to consider a mitigation strategy for each source that exceeds the revised MCL.
- Where possible, systems should consider zero treatment options. Not only are these options often less costly, but they also avoid the creation of residuals.
- Zero treatment options include using alternative sources and blending.

# Alternative Source(s)



- **Abandon high arsenic source(s)**
- **Use sources that meet standards**

- Perhaps the simplest approach is abandonment of the high arsenic water source and procurement of a new source that meets the arsenic MCL.
- This option is most realistic for utilities with multiple water sources where at least one source can be relied upon to produce water with arsenic below the MCL. There may, however, be other constraints to switching primary sources, such as inadequate treatment capacity or water rights.
- Many small utilities only maintain a single water source and do not have the flexibility of simply switch production to another location. The utility then has two options:
  - (1) Locate or install a new source; or,
    - Purchase water from a nearby system.
- New source installations may or may not be more costly than treatment.
- Another option is to switch a high arsenic water source from full-time production to seasonal or peaking use only. When used, it would be blended with low arsenic water sources before entry to the distribution system. This is allowed under federal regulations, as long as the running annual average at the entry point to the distribution system does not exceed the MCL. Individual State requirements may differ.

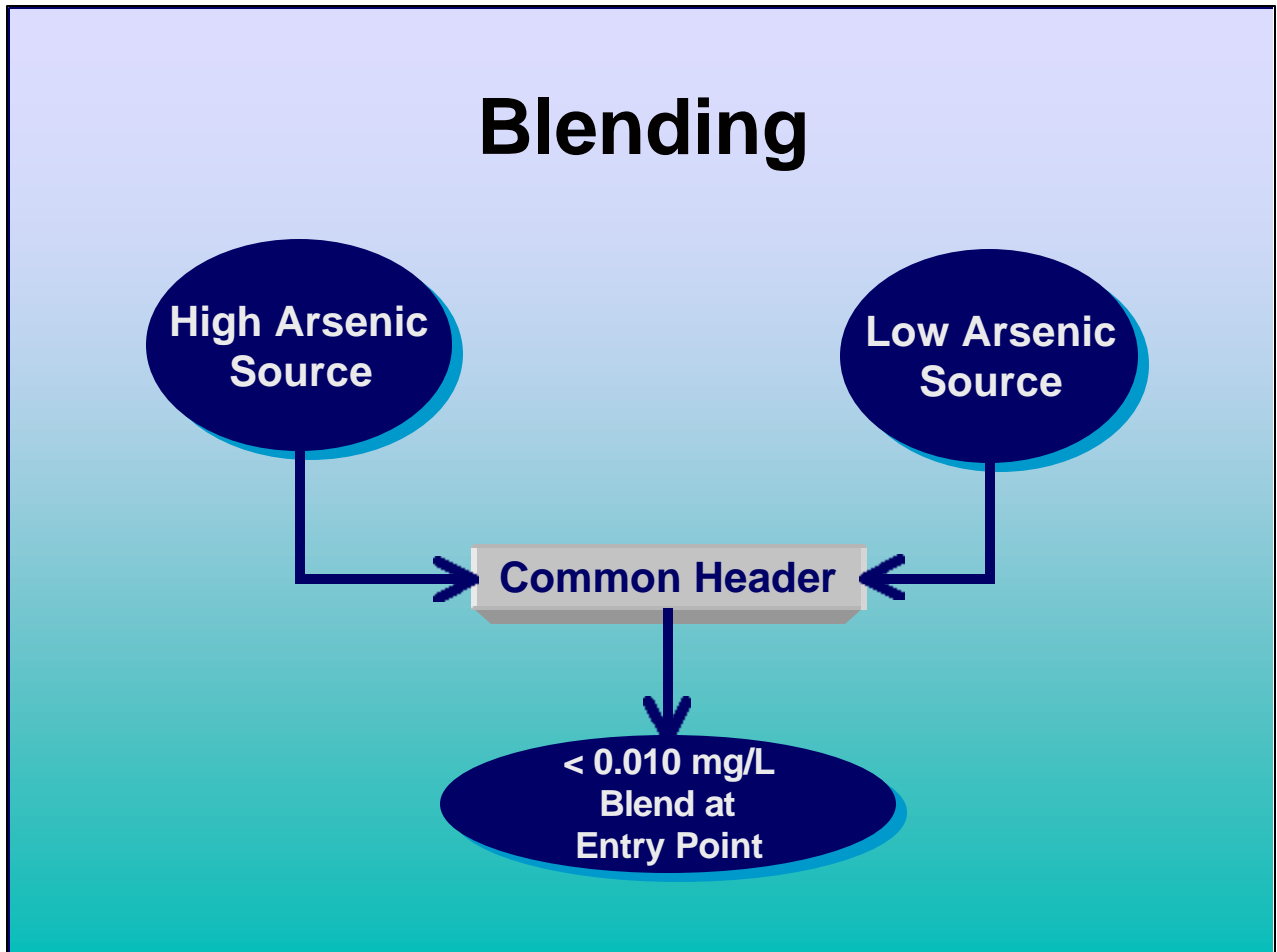


- This decision tree shows that, if a system has one or more sources available with arsenic levels below the MCL, and these sources can be operated in lieu of the problematic source(s) to meet the total system demand, then one option available is to switch the problematic sources to back-up or seasonal use.
- If the system has low arsenic sources available, and these sources can always be operated in conjunction with the high arsenic sources, then the water system may be able to produce finished water below the MCL by blending these sources. In order for blending applications to be appropriate, the wells with low arsenic levels must be reliable on a continuous basis.
  - To determine whether blending is possible, the system should solve the following mass balance inequality:

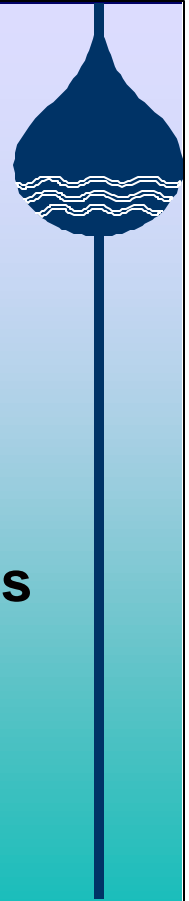
Where  $Q_i$  = Minimum reliable flow rate at source  $i$

$C_i$  = Maximum arsenic concentration at source  $i$  (in  $\mu\text{g/L}$ )

- Generally, the total arsenic concentration in the blended stream is set below the MCL by a safe margin ( $\frac{\sum Q_i \cdot C_i}{\sum Q_i} < \text{MCL}$ )
- If there are no constraints on blending, and blending is allowed by the State, then the system may be able to use blending to produce finished water below the MCL.
- If neither abandoning a source of supply or blending is an option, then a system will probably need to modify or install treatment.



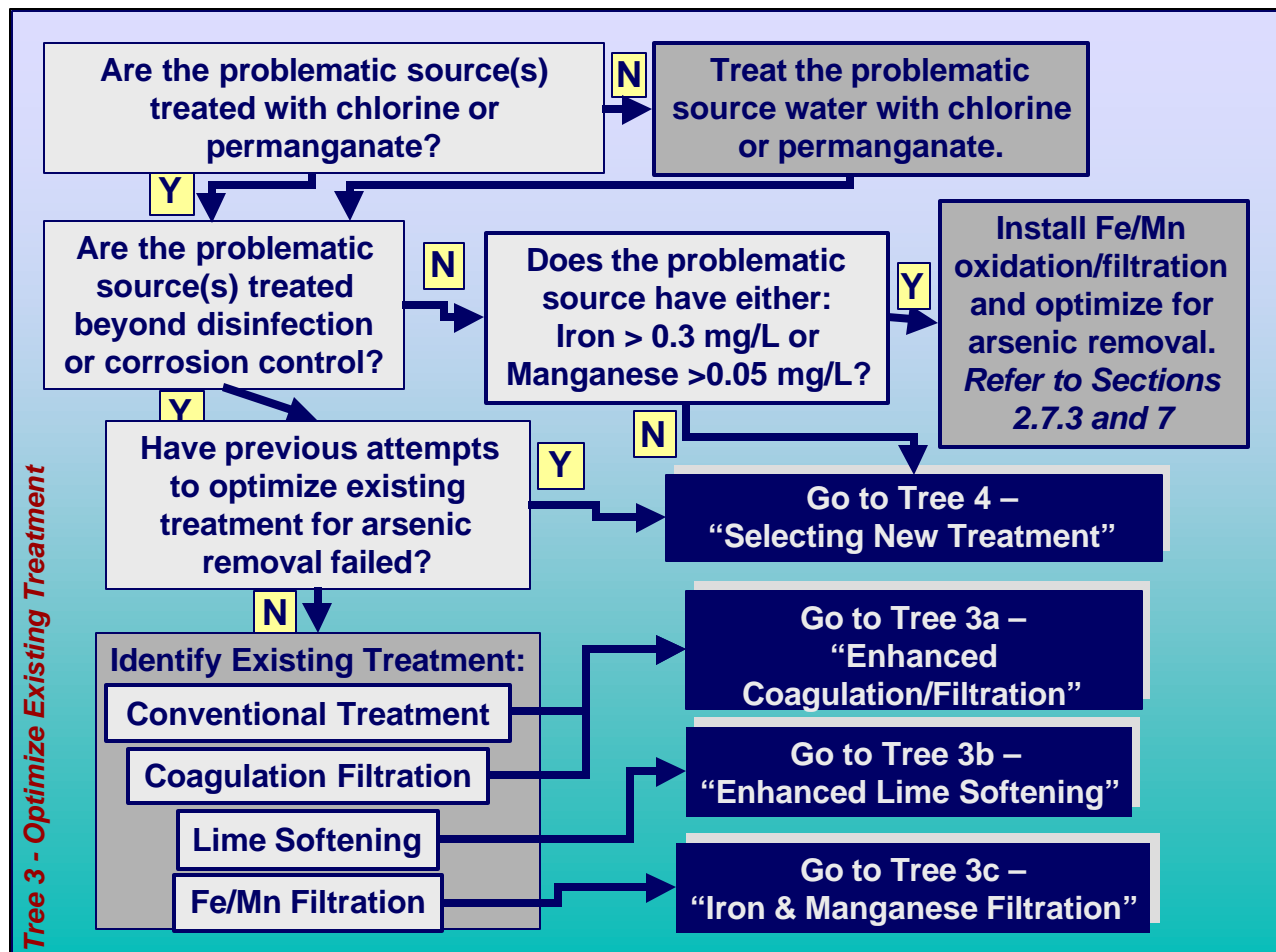
- Blending is a viable mitigation strategy for conservative inorganic substances, such as arsenic. Blending involves mixing waters from two or more different sources *prior* to distribution. At its simplest, a high arsenic source (with arsenic levels above the revised MCL) and a low arsenic source (with arsenic levels below the revised MCL) are fed into a combined header.
- Water systems and State regulators need to consider the relative flow rates and the consistency of operation of the two sources to ensure that finished water is consistently below the revised arsenic MCL. In most cases, even if a system can achieve compliance through blending, it will need to replace its pumps or otherwise ensure that it will achieve compliance with the blend.
- Sidestream treatment involves splitting flow, treating one stream, and blending it with the untreated stream prior to distribution. Blending and sidestream treatment can be used independently or in a variety of combinations.
- Sidestream treatment is feasible when a water source exceeds the revised MCL by a relatively small margin. This approach is viable because most arsenic treatment processes (operated under optimal conditions) can achieve at least 80% arsenic removal and, in many cases, this high level of performance is not needed to meet the MCL.
- Some treatment processes (e.g., RO) may have significant water losses associated with them. Water loss is incoming water that does not exit the system as treated water. Water losses frequently occur as a stream used to dispose of waste. Typical treatment efficiencies and water losses for processes operated under normal conditions should be taken into account when considering sidestream treatment.



# Treatment Options

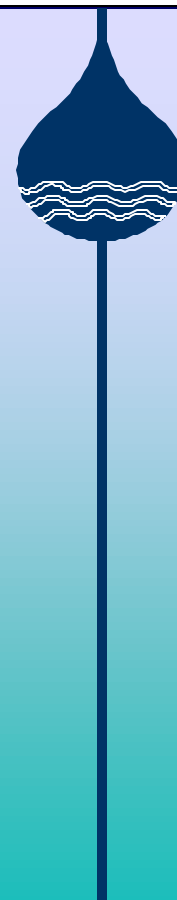
**Optimization of Existing Technologies**  
**Addition of New Technologies**

- A system will need to optimize existing treatment or install new treatment if it has high arsenic sources but cannot achieve compliance through either an alternate source or blending.
- The system should first determine whether any of its existing treatment is capable of removing arsenic even though it may not be doing so currently. The system should first attempt to optimize its existing technology before adding additional treatment.



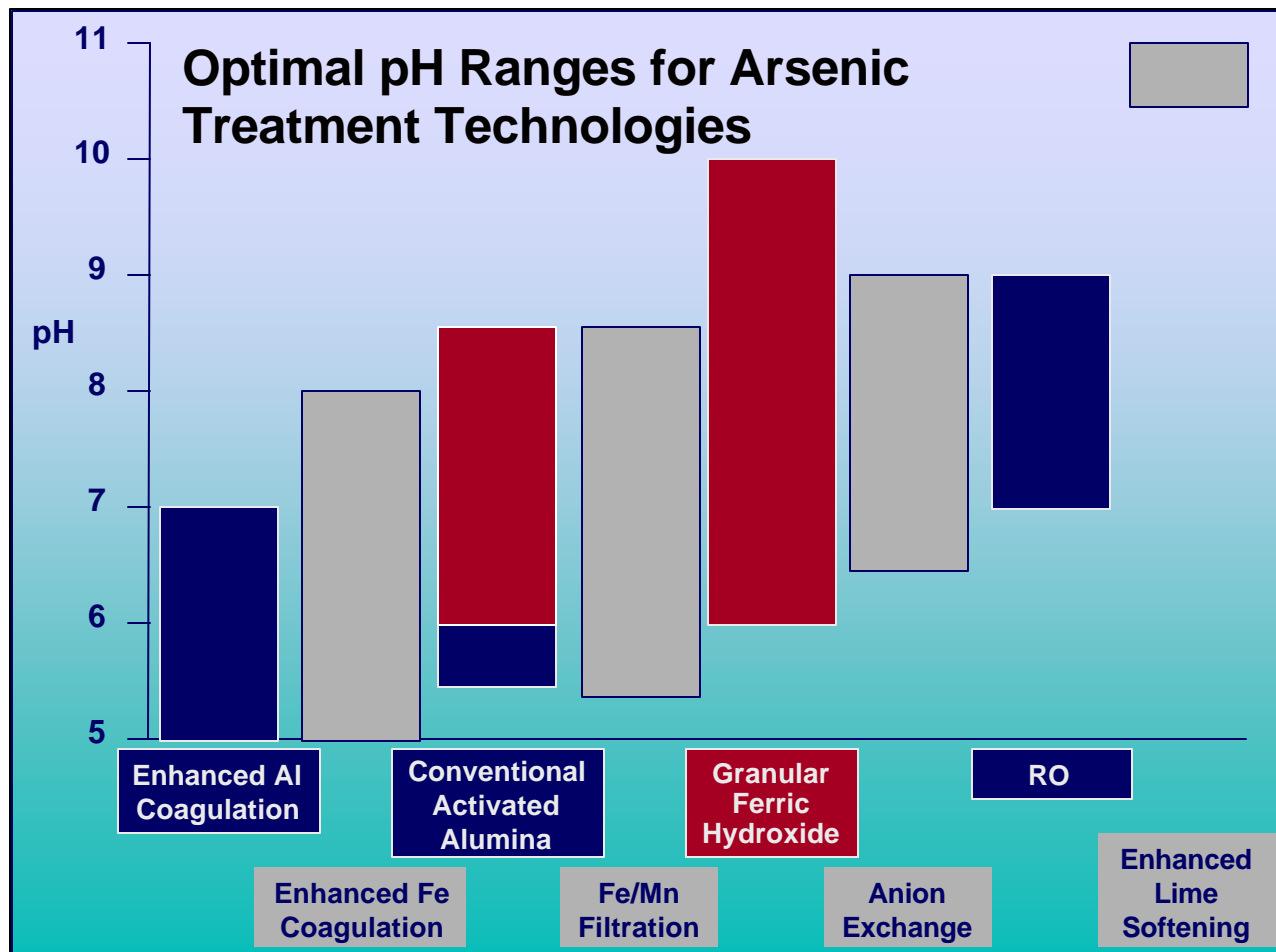
- The system should next determine whether it has existing treatment that could be modified for arsenic treatment. If it has any of these technologies in place, it should investigate in more detail whether optimization for arsenic is feasible.
- If the system does not have any of these technologies in place but has sources that have high levels of iron or manganese, it may be cost-effective and desirable for the system to take care of these secondary contaminants and arsenic at the same time by installing an oxidation/filtration or greensand plant.

# 4 Categories of Technologies



- **Sorption Processes**
  - Ion Exchange (IX)\*
  - Activated Alumina (AA)\*
  - Granular Ferric Hydroxide (GFH)
- **Iron & Manganese Removal**
  - Oxidation & Filtration\*
- **Membrane Processes**
  - RO\*
  - Nanofiltration
- **Chemical Precipitation Processes**
  - Coagulation Assisted Microfiltration
  - Enhanced Coagulation / Filtration\*
  - Enhanced Lime Softening\*

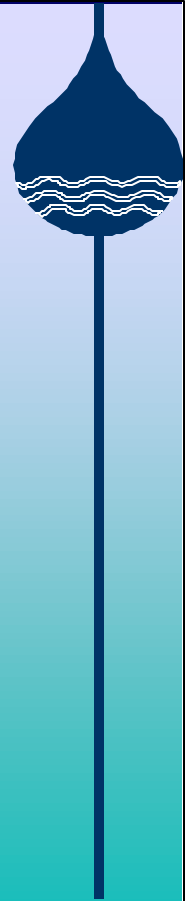
- There are four categories of technologies that have proven successful for arsenic removal: Sorption Processes, Iron and Manganese Removal, Membrane Processes, and Chemical Prescription Processes.
- Coagulation-assisted microfiltration could also be considered a membrane process; it consists of using a coagulant to adsorb arsenate and then removing the coagulant through a membrane.
- The technologies shown in red are likely to be cost-effective only if they are currently in place for other treatment purposes. Iron and manganese oxidation/filtration may be an exception if iron and/or manganese levels are currently problematic. Lime softening may also be an exception if water hardness is currently problematic.
- The technologies designated with an asterisk have been designated as BAT for the Arsenic Rule.
- Small systems without existing treatment are most likely to use sorption processes. Iron & manganese removal, coagulation/filtration, and lime softening are only likely to be used by systems that have existing treatment or at least problems in these areas. The membrane processes are also unlikely to be used. RO (RO) is quite expensive and can waste large amounts of water, so it is only likely to be installed if there are other contaminants that need to be removed [sulfate, total dissolved solids (TDS), etc.] or if it is used in a POU compliance strategy.
- One technology not shown is direct filtration with ferric chloride addition, which has shown promise as an emerging technology.



- This slide provides a summary of the optimal pH ranges for common treatment technologies. Although the technologies may remove arsenic at pHs outside of their optimal ranges, their removal efficiencies are much lower. Many of the arsenic treatment technologies require pH adjustment for optimization of performance. Sorption and coagulation processes are particularly sensitive to pH and function most effectively at the lower end of the natural pH range.
- In addition to affecting arsenic treatability, pH also can have a significant effect on disinfection, coagulation, and chemical solubilization/precipitation within the distribution system.
- Enhanced coagulation is defined as “the addition of sufficient coagulant for improved removal of disinfection byproduct precursors by conventional filtration treatment” (40 CFR 141.2). Enhanced alum coagulation is the operation of a conventional filtration plant in a mode that removes TOC, which is used as surrogate for disinfection byproduct precursors. Coincidentally, optimizing for TOC removal also achieves high arsenic removal. Alum coagulation operates best at a pH of 5 to 7. Systems that use alum for coagulation but still have arsenic in their treated water should consider adding more alum to decrease the pH or switching to iron as a coagulant.
- Enhanced iron coagulation can operate at a higher pH than alum coagulation, frequently up to pH 8. Either ferric chloride or ferric sulfate is used as a coagulant.
- Conventional activated alumina (AA) operates best between a pH of 5.5 and 6. Systems using AA frequently need to adjust the pH twice: once to lower it for treatment and once to raise it after treatment to avoid corrosion of the distribution system. Conventional AA is therefore not practical for the smallest systems.
- Iron/manganese removal operates over a wide pH range, between 5.5 and 8.5
- The removal efficiency of granular ferric hydroxide (GFH) increases as the pH decreases down to approximately 6, but GFH will also can achieve arsenic removal at up to pH 10.
- Anion exchange (AX) is able to remove arsenic between pH 6.5 and pH 9.
- Enhanced lime softening is defined as “the improved removal of disinfection byproduct precursors by precipitative softening” (40 CFR 141.2). Adding lime to increase the pH up to 10.5 or 11 causes the precipitation of magnesium hydroxide, which adsorbs both TOC and arsenic.
- Based on the natural pH of water, which is usually between pH 6 and 9, GFH is likely to be the treatment of choice for small systems without existing technologies. Although AX is also effective over this pH range, disposal issues may preclude many small systems from considering it. Conventional AA has too limited a pH range to be widely used, but new modified media, which can be operated over a broader pH range and are more selective for arsenic, may show promise.



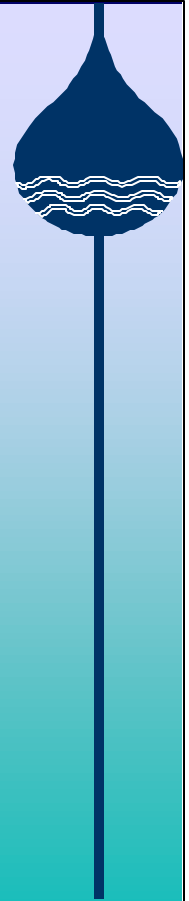
# Innovative Technologies



- **Adsorbents**
  - **MIEX** (magnetic ion-exchange)
  - **HIOPs** (hydrous iron oxide particles)
  - **SMI** (sulfur modified iron)
  - **IOC-M** (iron oxide coated microsands)
  - **GFH** (granular ferric hydroxide)
- **Coagulation**
  - **Coagulation assisted membrane filtration**

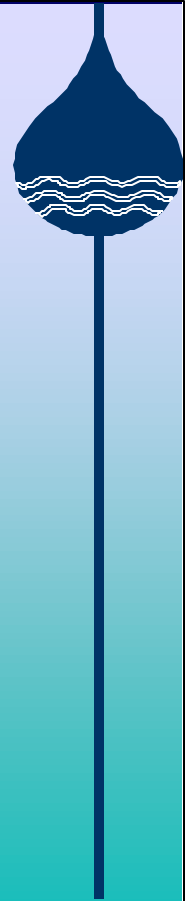
- There are several innovative technologies that show promise for arsenic treatment. None of these are designated BAT or SSCT because they do not have a proven history of full-scale operation and/or success over a range of water qualities. However, they may prove effective; systems should complete piloting prior to use.
- Most of the adsorbents have some type of iron coating, and coagulation-assisted membrane filtration uses iron coagulation followed by microfiltration.
- The two technologies in red are discussed later in this presentation.

# BULLETIN!



- **Adsorptive technologies**
  - **Likely to be the treatment of choice for many small systems**

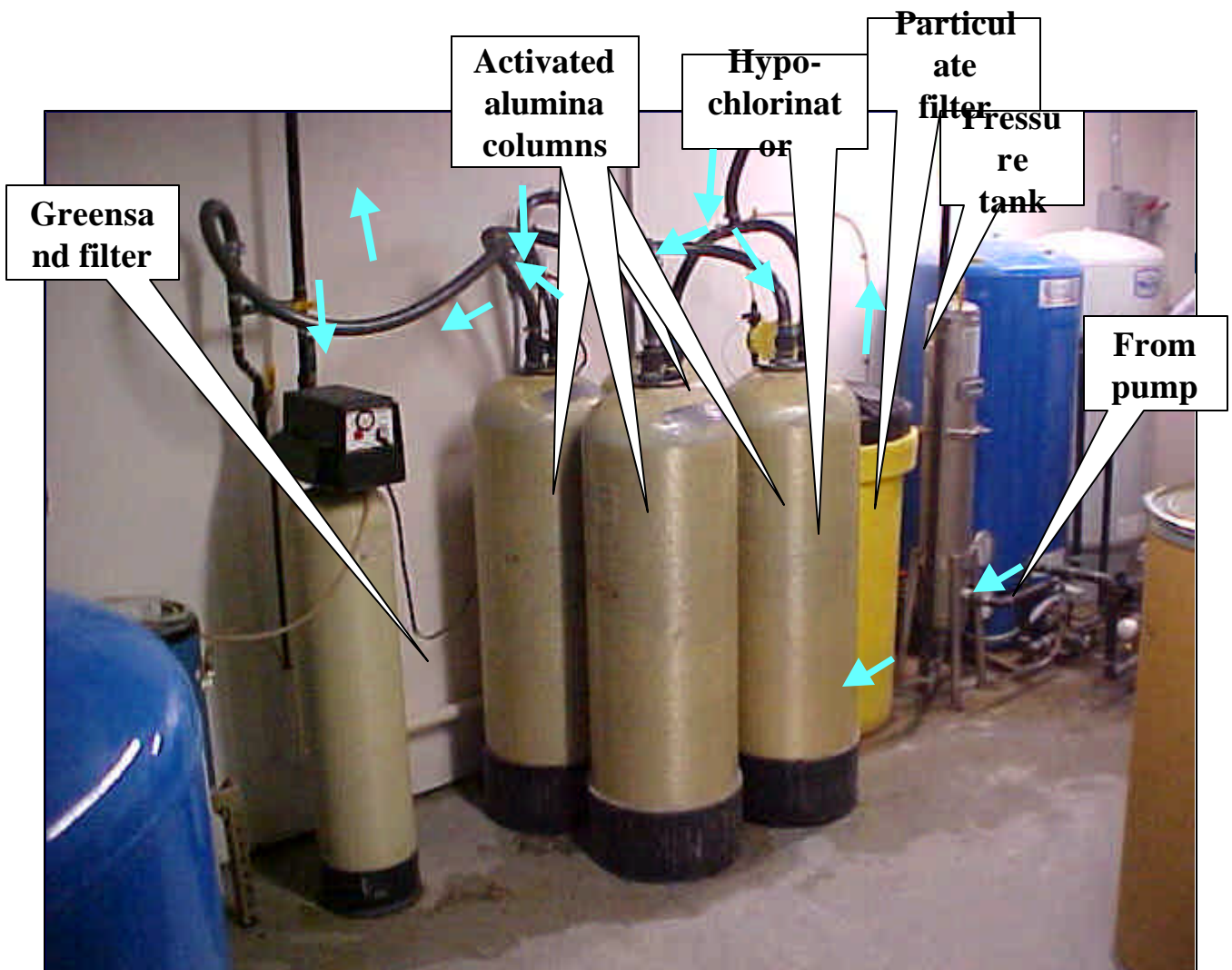
- Adsorptive technologies are likely to be the treatment of choice for many small systems.
- Adsorptive technologies are likely to:
  - Achieve high arsenic removal over a wide pH range;
  - Avoid competition from commonly occurring co-contaminants (sulfate, nitrate, etc);
  - Be used in relatively simple treatment trains; and,
  - Not be hazardous waste when used on a throw-away basis.
- However, there may be exceptions. One small system (Three Forks, Montana) has piloted adsorptive technologies and found them ineffective for their source water; the system will next pilot coagulation. This example illustrates that many questions still remain with arsenic treatment and that more research needs to be done. It also points to the necessity for pilot testing prior to full-scale installation.



# Activated Alumina

## Full Scale Operation at a Small Community PWS

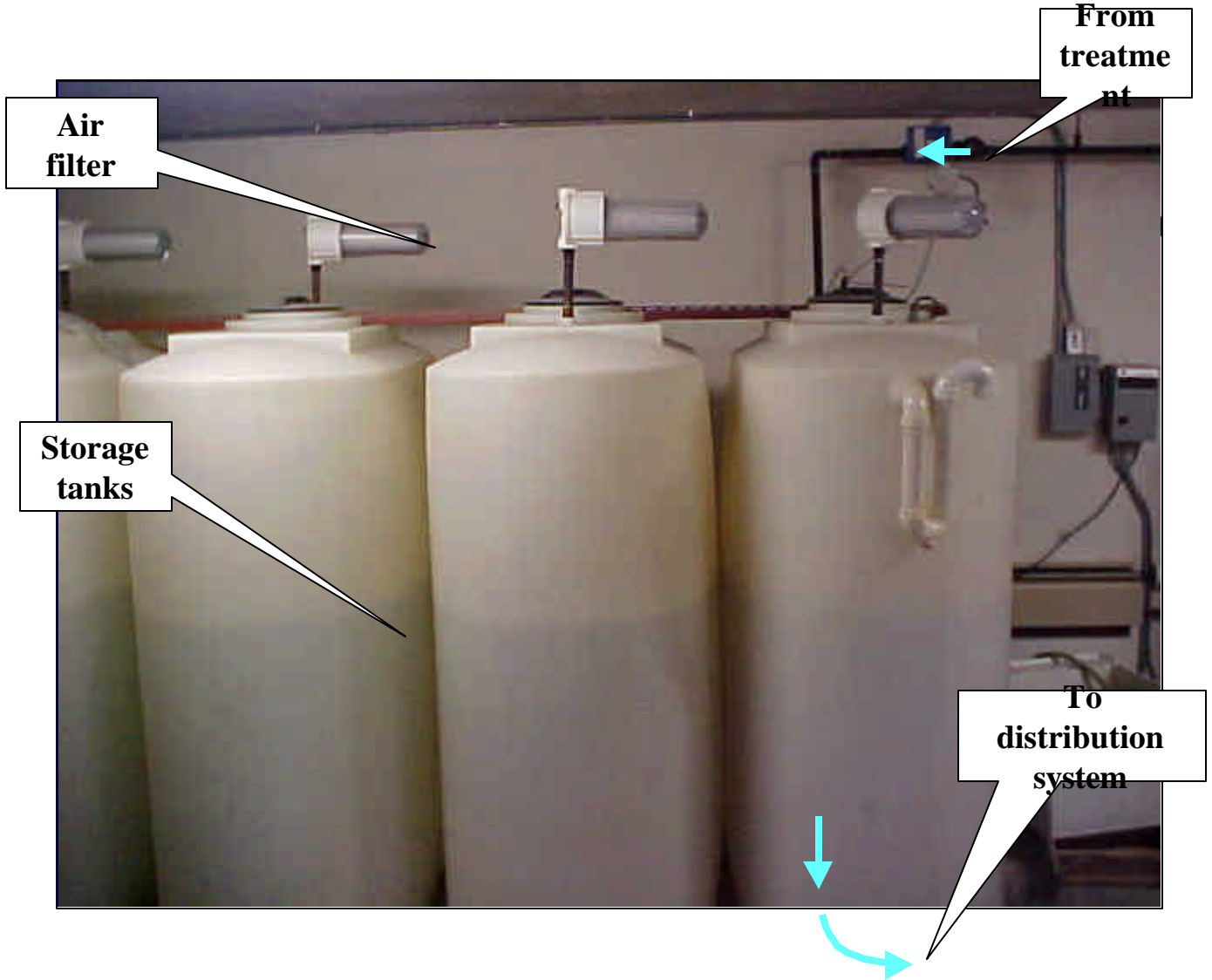
- This is an example of a full-scale activated alumina installation at a small community water system.
- This system is located near of Boston, Massachusetts. The small CWS serves a 40-unit apartment building (approximately 60 residents).
- The level of arsenic in its influent well water usually varies between 150 and 450  $\mu\text{g/L}$ , though it is quite variable and has reached 1100  $\mu\text{g/L}$ .
- The system has not speciated the arsenic in its influent water.
- The system has a back-up well located a few yards away and drilled into the same aquifer.
- The arsenic appears to be primarily naturally occurring; there is a band of high-arsenic containing rocks that runs through that part of Massachusetts. However, the area also used to have a lot of orchards that probably used arsenic compounds for pest control, and some arsenic could be reaching the well from surface recharge.
- The activated alumina treatment units used by the system were installed in 1993 and remove arsenic consistently to 5  $\mu\text{g/L}$ .



- From the outdoor well, the water is brought into a basement room and into a captive air pressure tank to reduce water hammer. The water then passes through a hypochlorinator with a pump that injects chlorine for oxidation and disinfection. The water passes through the 3-micron particulate filter, which removes sand and other particles that would foul the treatment technology.
- The water is then split. Each half of the stream passes through two activated alumina tanks in series. These tanks are made of fiberglass and are 14" in diameter and 48" high, containing 2 cubic feet of media. The peak design flow is 9 gallons per minute (gpm). In each tank, the water is dispersed at the top of the chamber, filters down through the media, is collected at the bottom, and passes back up through a pipe running up the middle.
- The water is then run through a greensand filter to remove manganese, which is also high in the source water (90-100  $\mu\text{g/L}$ ).
  - Greensand filters are also effective at removing arsenic, but arsenic levels in the water passing through the filter are already quite low so this filter probably does not remove much arsenic.
- The activated alumina tanks are filled half-full with media. This should only be necessary for tanks that are backwashed; during backwashing, the media expands. These tanks are not backwashed and could be filled to within 6" to 8" of the top; only enough head space to ensure adequate dispersal of water over the top of the media is necessary.

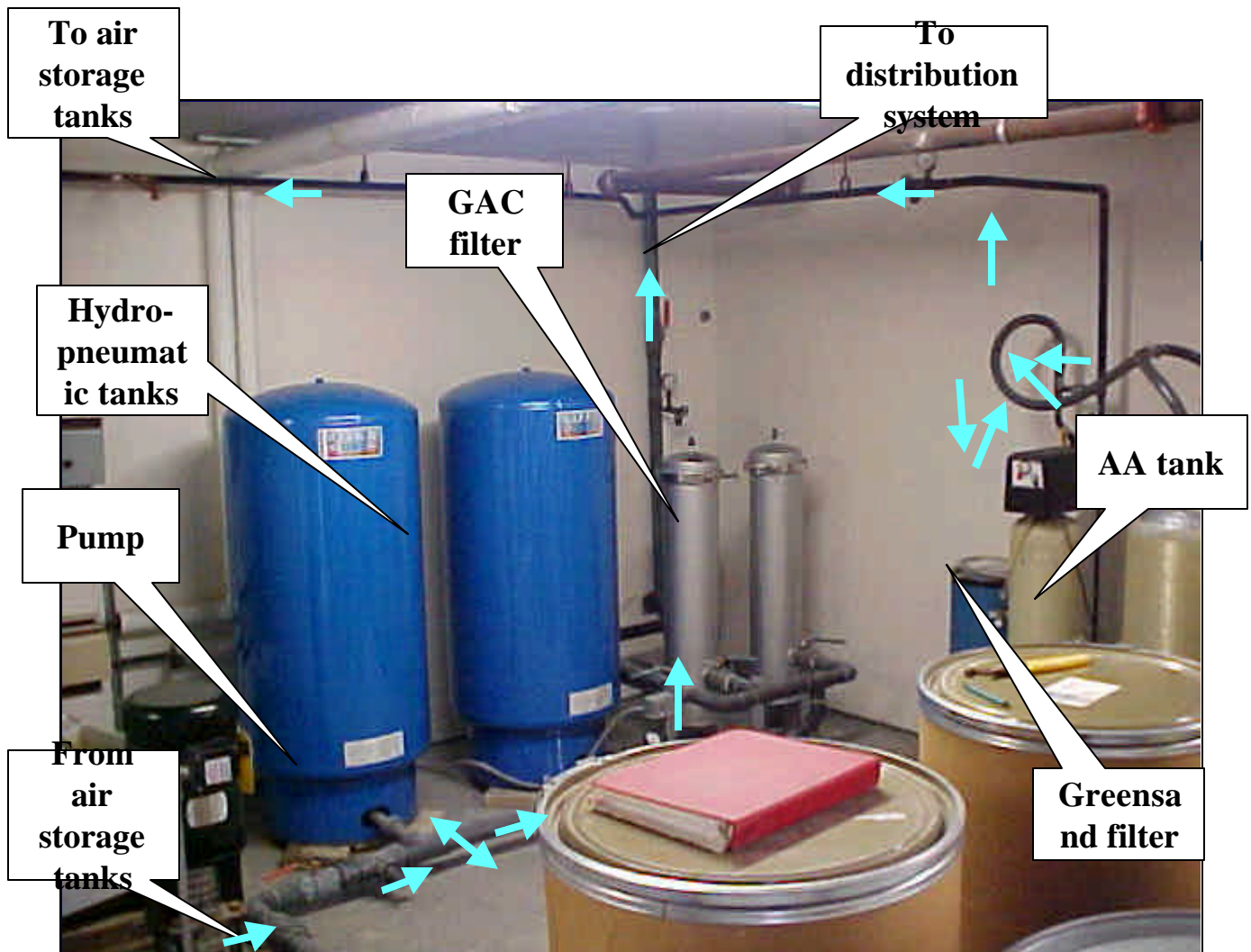


- The State requires the system operator, a licensed operator who is responsible for managing several small systems and a local municipality, to collect and analyze monthly samples of the raw water, weekly samples after the first two tanks (and before the second two tanks), and weekly samples of the finished water (after all four tanks).
- From years of sampling, the operator knows that he needs to replace the media every six weeks to avoid breakthrough in the finished water. Every six weeks, he physically removes the first two tanks, moves the next two into their place, and then adds two more tanks filled with fresh media that were waiting off to the side. During the next six weeks, the media in the removed tanks is taken out and replaced with fresh media. A hazardous waste disposal company is used to remove the spent media, although it has never been tested to determine whether it is hazardous. The fresh media is bought in bulk approximately once a year.
- Replacing the media every six weeks ensures that, very soon after arsenic is detected after the first two tanks, the media is replaced.
  - In the past, when the operator has delayed replacing the media at that point, high levels of arsenic have occurred in the finished water. Therefore, the second tank is loaded to exhaustion almost as soon as breakthrough occurs after the first.
    - This probably happens because the chlorine does not have enough contact time to fully oxidize the arsenic before it is passed through the first two tanks.
  - Systems should ensure that they provide adequate mixing time for oxidation of arsenite to arsenate; a couple of minutes and some mixing should be adequate. If this contact time is provided, then a system should be able to wait to change out the media in the first two tanks, letting them run to near exhaustion while using the second two tanks as guard columns to ensure low levels of arsenic in the finished water.



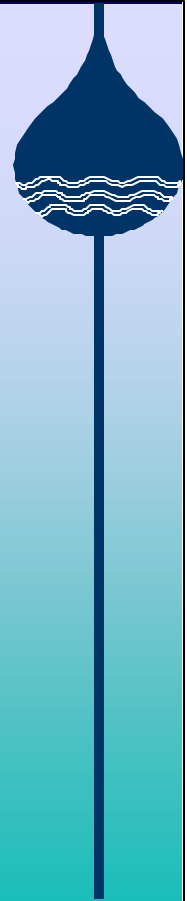
- The water is stored in four large tanks in the same room used for treatment. The room is fairly large-sized (16' by 20'), which allows for adequate room for treatment and storage. The tanks are at room pressure and are fitted with air filters to ensure air is filtered before it comes into contact with the treated water.
- The well pump (and therefore the activated alumina unit) does not operate continuously. The storage tanks are fitted with a sensor so that, when the water level drops below a specified point, the well pump turns on. When they are full, it shuts off.





- A 7.5 horsepower pump takes suction out of the storage tanks and pumps the treated water into hydropneumatic storage tanks, which provide short-term demand by the distribution system. After leaving these hydropneumatic storage tanks, the water passes through GAC filters, which improve aesthetic properties, and goes into the distribution system, which is the interior piping of the apartment complex.
- Most small systems will probably look similar to this system prior to installation of treatment: a wellhead and a couple of pressure tanks. This system was able to add and maintain treatment relatively easily. Having sufficient room to install treatment was beneficial.
- Pilot testing will help systems determine sampling frequencies and change-out schedules, which will vary for each system based on water quality, size of treatment units, and other system-specific factors.

## Vessel Costs

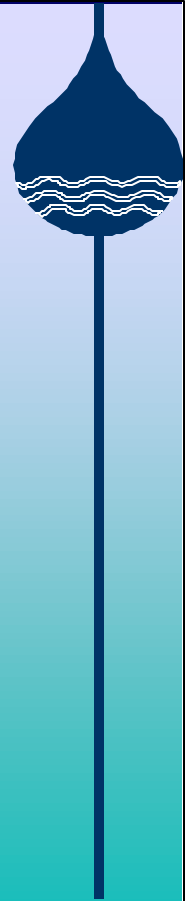


- **12" X 52" = \$192**
  - **4.7 gpm @ 5 minute EBCT; Surface Loading Rate of 6 gpm/ft<sup>2</sup>**
- **24" X 60" = \$1,147**
  - **19 gpm @ 5 minute EBCT; Surface Loading Rate of 6.0 gpm/ft<sup>2</sup>**
- **36" X 72" = \$2,174**
  - **53 gpm @ 5 minute EBCT: Surface Loading Rate of 7.5 gpm/ft<sup>2</sup>**

- A complete small treatment or piloting system, including two empty 10" x 52" vessels, a pre-filter to take out sediments, meters on each vessel, piping, valves, sample ports etc., costs \$994.
- If the size is increased to 12" x 52", the cost for each empty fiberglass vessel would be \$192. The interior volume of the vessel would be 3.4 cubic feet. If the vessel is operated on a throw-away basis, not much head space is necessary; assume that the vessel can hold 3.14 cubic feet of media with a media depth of 48". A 2 to 10 minute empty bed contact time (EBCT) is recommended for activated alumina or granular ferric hydroxide; longer EBCTs usually result in better removal. For granular ferric hydroxide, loading rates of up to 10 gallons per minute per square foot are allowable. With a 5 minute EBCT ( $3.14 \text{ cf} \times 7.48 \text{ gal/cf} = 23.5 \text{ gallons} / 5 \text{ min.} = 4.7 \text{ gpm}$ ) and a loading rate of 6 gallons per minute per square foot, the system could produce 4.7 gallons per minute ( $5 \text{ gpm} / \text{surface area of media} = 5 \text{ gpm} / 0.785 \text{ sf} = 6.4 \text{ gpm/sf}$ ).
- If 24" x 60" units are used, the price jumps to \$1,147 per vessel. Assuming one foot of head space (4' of media), a 5 minute EBCT, and a loading rate of 6 gallons per minute per square foot, 19 gallons per minute can be achieved.
- If 36" x 72" vessels are used, the price is \$2,174 per vessel. Assuming one foot of head space, a 5 minute EBCT, and a loading rates of 7.5 gallons per minute per square foot, up to 53 gallons per minute of treated water can be produced.
- If the maximum momentary demand is 106 gallons per minute, six vessels that are each 36" x 72" would be necessary (three trains with one in standby). A system should take its expected maximum day and maximum momentary demand into account when sizing a plant

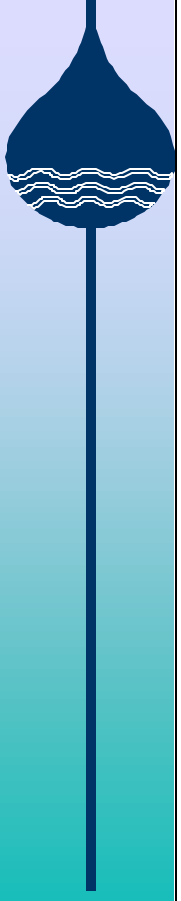


# Optimization of Existing Technologies



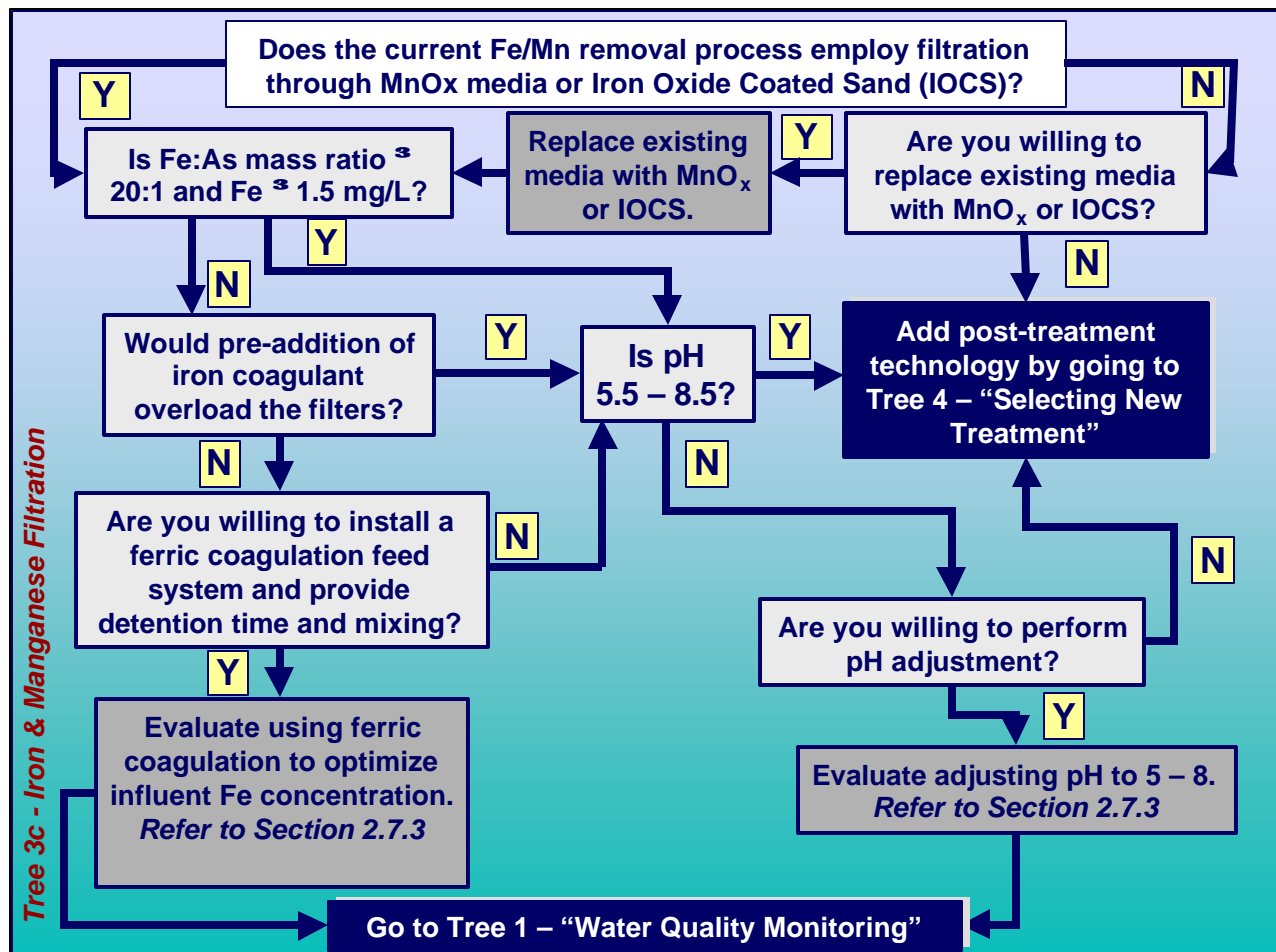
- **Iron and Manganese Removal**
  - Oxidation/Filtration
- **Enhanced Coagulation/Filtration**
- **Enhanced Lime Softening**

- Systems that cannot achieve low enough levels of arsenic through zero treatment options should first explore whether they can optimize existing technologies.
- All three of these technologies have been designated BAT for arsenic removal.

A decorative graphic on the right side of the slide, consisting of a dark blue teardrop shape at the top, containing three white wavy lines representing water. A thin dark blue vertical line extends downwards from the bottom of the teardrop, ending near the bottom of the slide's background.

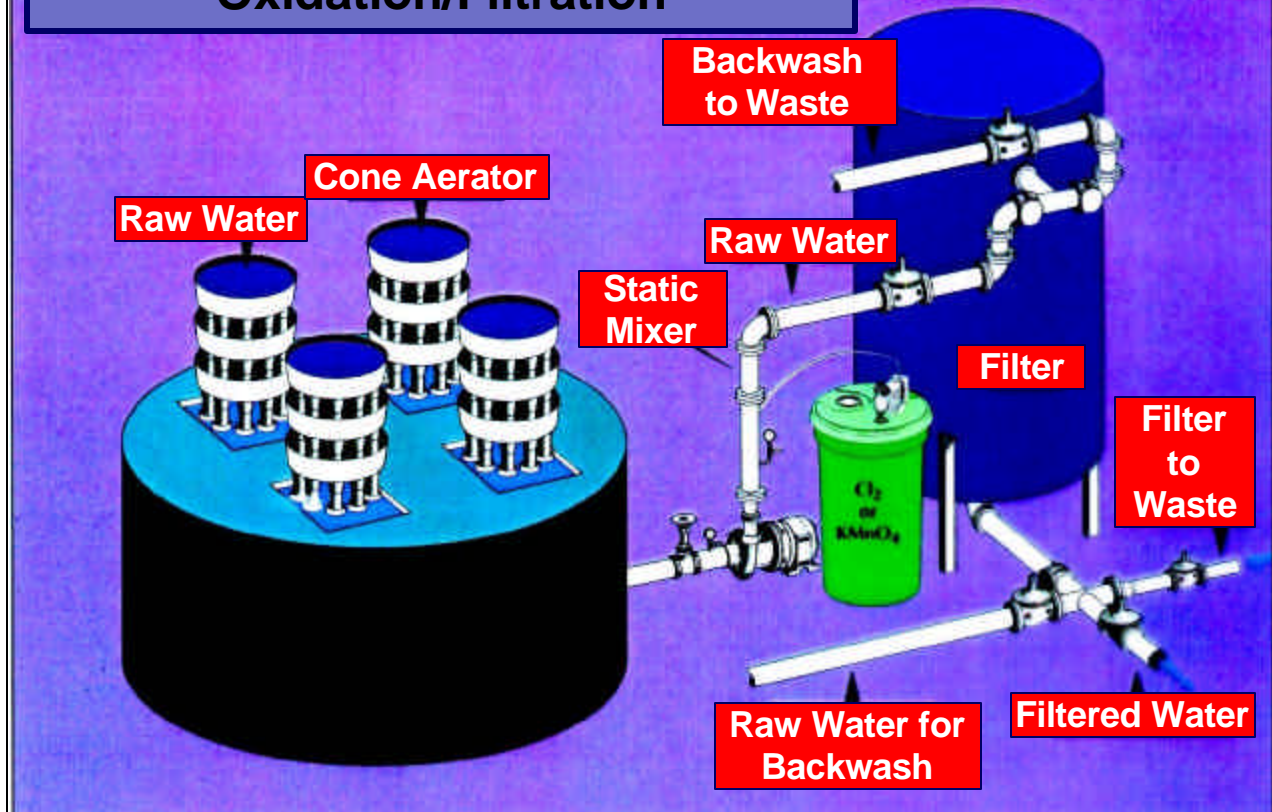
# Iron and Manganese Removal Oxidation/Filtration

- Iron and manganese removal plants have been determined to be effective at removing arsenic. Arsenic removal can occur in a traditional treatment plant with mixing and settling basins or can be through granular media.

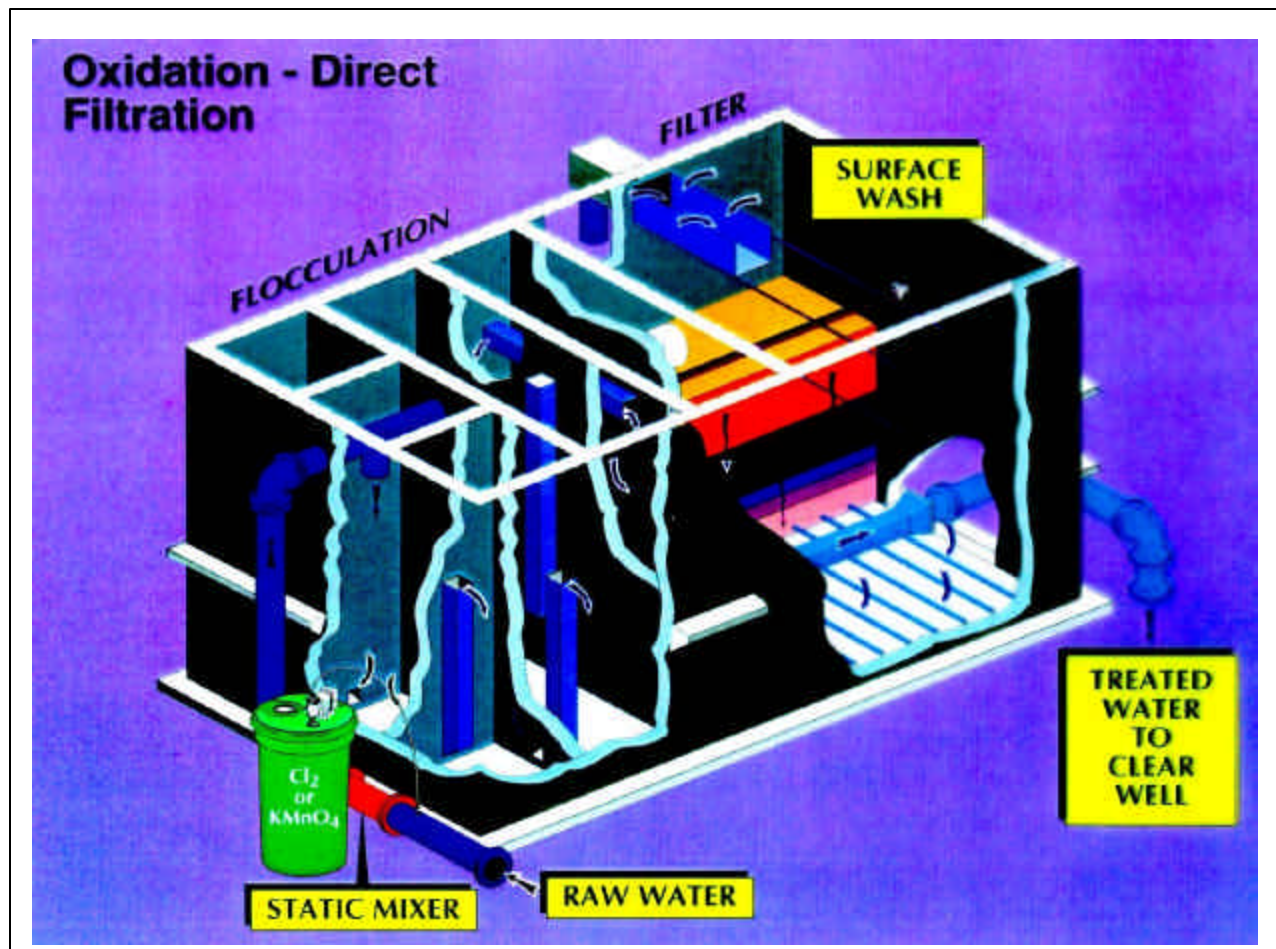


- Systems that have an iron and manganese removal system in place but have arsenic levels greater than the revised MCL in their treated water should use this decision tree.
- Although arsenic may be removed by adsorption/co-precipitation with manganese, iron is much more efficient for arsenic removal. The arsenic removal efficiency is strongly dependent on the initial iron concentration and the ratio of iron to arsenic. In general, iron should be present at 1.5 mg/L or greater, and the iron:arsenic mass ratio should be at least 20:1. These conditions customarily result in an arsenic removal efficiency of 80 - 95%. In some cases, it may be appropriate to add ferric coagulant to the beginning of the iron removal process to optimize arsenic removal.
- The effectiveness of arsenic co-precipitation with iron is relatively independent of source water pH in the range 5.5 to 8.5 but decreases outside of this range. Therefore, water systems with high influent levels of arsenic but a pH value outside of this range may be able to increase arsenic removal through pH adjustment.
- If the water system is unwilling or unable to make any of these adjustments, or if piloting indicates that they will not be successful, then the system will need to install additional treatment for arsenic removal.

## Iron and Manganese Removal Oxidation/Filtration

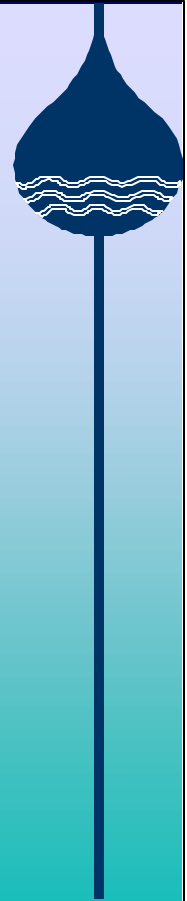


- Oxidation/filtration can be used as a special case of pressurized granular-media filtration where the granular media catalyzes the oxidation and precipitation of iron and manganese.
- Manganese-oxide ( $\text{MnO}_x$ ) media, which include manganese greensand and pyrolucite, are commonly used in oxidation/filtration processes because of their unique adsorptive and catalytic capabilities. Greensand is manufactured by coating glauconite with manganese dioxide, while pyrolucite is a naturally mined ore composed of solid manganese dioxide. Greensand media has been shown to be capable of removing up to 80% of arsenic by oxidation/adsorption.
- In oxidation/filtration processes, water is passed through a column of  $\text{MnO}_x$  media which adsorbs and catalyzes the oxidation of the iron and manganese. The filtering capacity of the granular  $\text{MnO}_x$  media then retains the precipitated iron, manganese, and arsenic until it is backwashed out of the column. Backwashing creates waste water and sludge, which the water system must properly dispose.
- Arsenic appears to be removed primarily by the iron precipitates as opposed to those of manganese. Water systems with low levels of influent iron (less than 1.5 mg/L or less than 20:1 ratio with arsenic) may want to consider adding ferric chloride prior to oxidation.
- It is generally recommended that green sand be preceded by a 12 inch anthracite cap to filter any iron particulates formed by oxidation from the air.
- In order for greensand to retain its adsorption and catalytic oxidation capabilities, the media must be regenerated with permanganate or chlorine.
  - *Continuous regeneration:* Typically these oxidants are added ahead of the filter where they provided continuous oxidation of the contaminants as well as regeneration of the  $\text{MnO}_x$  media. Arsenic that is not oxidized is adsorbed onto the  $\text{MnO}_2$  surface on the greensand particles.
  - *Intermittent regeneration:* In some circumstances, aeration can achieve near complete oxidation, in which case the arsenic-containing iron particulates are removed by the anthracite layer on top the  $\text{MnO}_x$  media. Any remaining arsenic is then oxidized and adsorbed onto the  $\text{MnO}_x$  media. Periodically the greensand must be regenerated with chlorine or permanganate. This method is preferred where raw water quality interferes with oxidation.



- In a traditional iron and manganese removal plant optimized to remove arsenic, the raw water is first oxidized by chlorine or permanganate. The arsenate then adsorbs onto the iron hydroxide. Then, as the iron hydroxide precipitates, arsenic is trapped and ultimately filtered out of solution.
- Arsenic appears to be removed primarily by the iron precipitates as opposed to those of manganese. Water systems with low levels of influent iron (less than 1.5 mg/L or less than 20:1 ratio with arsenic) may want to consider adding ferric chloride prior to oxidation.
- High levels of natural organic matter (NOM), orthophosphates, and silicates weaken arsenic removal efficiency by competing for sorption sites on iron hydroxide precipitates.
- The filter media must be periodically backwashed to dislodge solids and restore hydraulic capacity. Backwash water is typically a high-volume, low solids (less than 0.1%) waste stream. The specific amount of solids will depend on several factors, including raw water iron levels, coagulant addition (if any), filter run length, and background solids concentration.

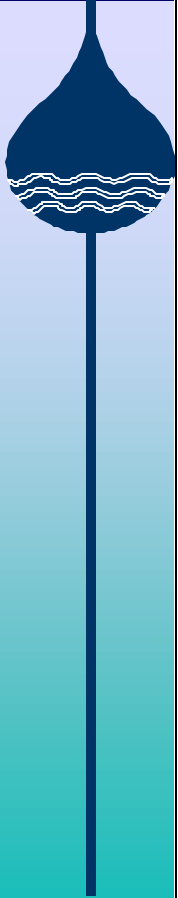
# Residuals Produced



- **Liquids**
  - Backwash water
  - Supernatant
- **Solids**
  - Sludge
  - Media

- Package plants for iron removal exist that might make the technology attractive for some situations, particularly when the ground water has high iron and/or manganese. Pressure filters are common for this type of situation.
- This picture is of an interestingly shaped package iron removal plant in the southeast part of Indiana. The water is oxidized with aeration toward the top of the cylinder. Chlorine is then added and mixing time is provided. The water then passes through a greensand filter before reaching a clear well at the base. A nearby building has pumps that suction out and pump to the distribution system.
- Iron and manganese filtration creates both liquid and solid residuals.
  - Liquid wastes include backwash water and supernatant from the settling of backwash water.
    - Two treatment options are available for liquid residuals: (1) indirect discharge and (2) dewatering and sludge disposal. Water intended for indirect discharge will be subject to technically based local limits (TBLLs) placed by the publicly owned treatment works (POTW) on total dissolved solids (TDS) and arsenic. Dewatering can be accomplished by gravity thickening, followed by other mechanical or non-mechanical techniques. Settling basins can be used to provide gravity clarification, while the supernatant can be decanted and recycled to the process head.
    - Liquid residuals may also be recycled as backwash or by recycling to the facility headworks.
  - Solid wastes include spent media and sludges.
    - MnOx media can be regenerated repeatedly, but it will need to be replaced periodically. Spent media will probably need to be placed in a landfill.
    - Sludges will be produced from filtration or from settling of the backwash. Sludges can be passed through a small filter press for dewatering. The resultant sludge can be disposed of in a conventional landfill if it passes the paint filter liquid test (PFLT, showing it has no free liquid) and the toxicity characteristic leaching procedure (TCLP, showing it is not hazardous). Previous studies have indicated that typical ferric coagulation-filtration sludge will pass the TCLP test by a substantial margin (Fields, 2000b).
- Additional information on residuals is provided in the Residuals presentation.

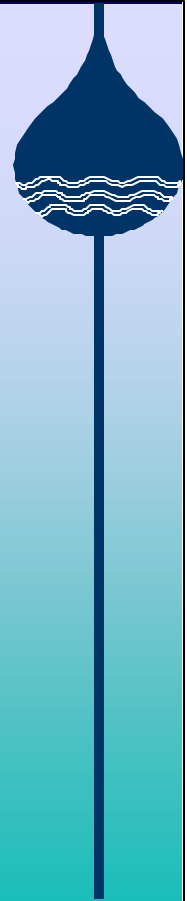




# Enhanced Coagulation/Filtration

- Enhanced Coagulation/Filtration drives pH down so can adsorb arsenic onto metal hydroxides.
- Coagulation is the process of destabilizing the surface charges of colloidal and suspended matter to allow for the agglomeration of particles. This process results in the formation of large, dense floc, which is amenable to removal by clarification or filtration.
- Coagulation/filtration processes, both conventional and pressurized, can be optimized to remove dissolved inorganic arsenic from water. The removal process is thought to occur by a combination of:
  1. Adsorption - Arsenic is adsorbed onto the metal hydroxide precipitates; and,
  2. Inclusion - The arsenic becomes entrapped as the particle continues to agglomerate.
- The efficiency and economics of the system are contingent upon several factors, including the type and dosage of coagulant, mixing intensity, and pH. In general, however, optimized coagulation-filtration systems are capable of achieving over 90% removal of arsenic and producing water with less than 5  $\mu\text{g/L}$  of arsenic. Influent arsenic levels do not appear to impact the effectiveness of this treatment process.
- Coagulation/filtration was listed as a SSCT in the Arsenic Rule.

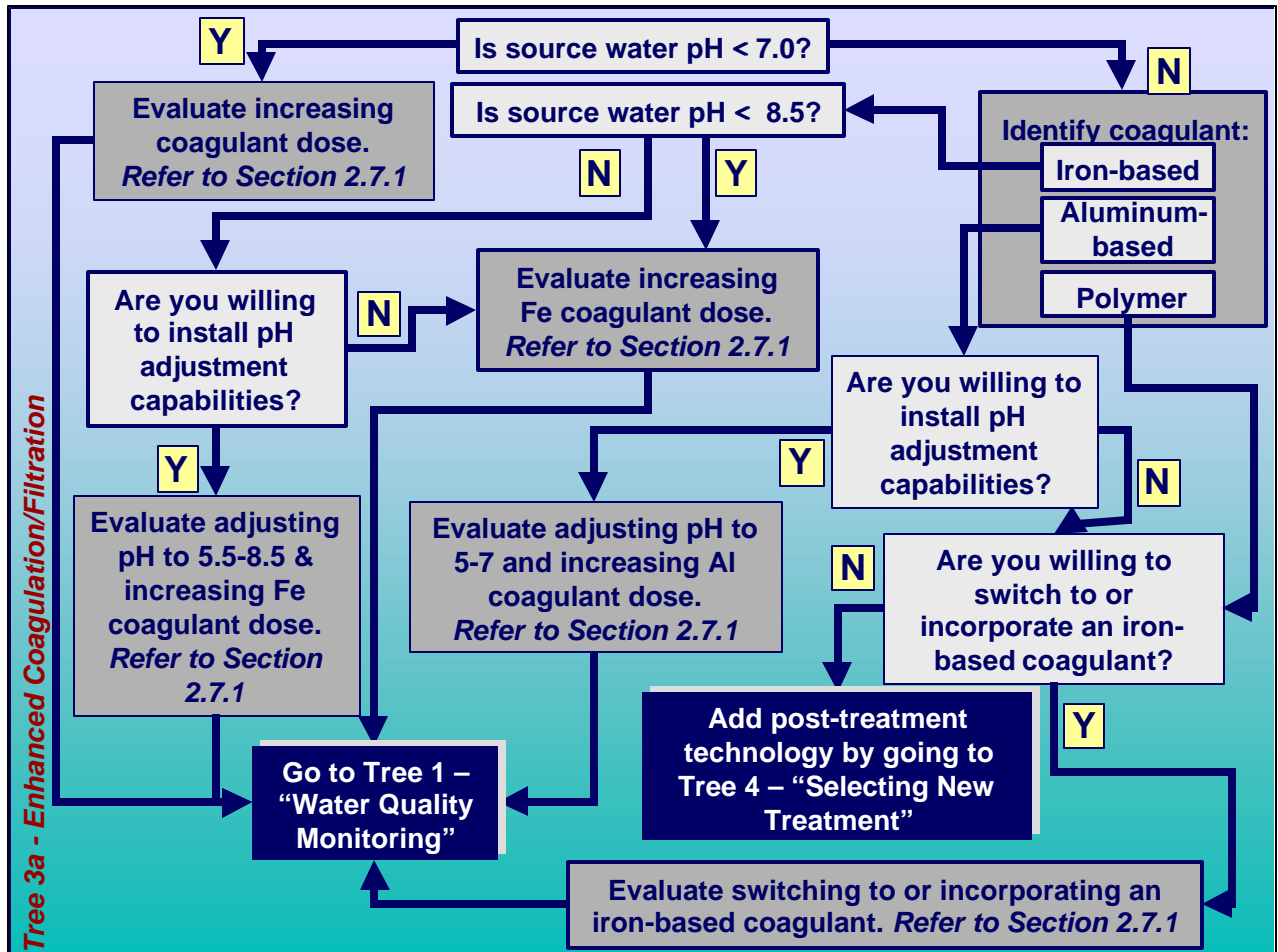
# Enhanced Coagulation/Filtration



- **Defined in Stage 1 D/DBP Rule**
  - Operating for removal of disinfection byproduct precursors
- **Alum & Ferric Chloride (most common)**
  - Metal hydroxide species formed
  - pH range
    - 6 – 7 for Alum
    - 6 – 8 for Ferric Chloride

- Enhanced coagulation was defined by the Stage 1 Disinfectants and Disinfection Byproducts Rule (Dec 16, 1998; 63 FR 69390) as “the addition of sufficient coagulant for improved removal of disinfection byproduct precursors by conventional filtration treatment” (40 CFR 141.2).
- The most widely used coagulants for water treatment are aluminum and ferric salts, which hydrolyze to form aluminum and iron hydroxide particulates, respectively.
- Metal hydroxide solubility is a function of pH so arsenic removal is pH dependent.
  - Alum removes arsenic in a range of pH 5 to 8, with an optimum range of pH 6 to 7.
  - Ferric chloride removes arsenic in a range of pH 4 to 9, with an optimum range of pH 6 to 8.
- Iron-based coagulants, including ferric sulfate and ferric chloride, are more effective at removing arsenic than their aluminum-based counterparts. This is because iron hydroxides are more stable than aluminum hydroxides in the pH range 5.5 to 8.5. A fraction of the aluminum remains as a soluble complex, which is incapable of adsorbing arsenic and can pass through the filtration stage. At pH values above 7, the removal performance of aluminum-based coagulants drops markedly. Feed water pH should be adjusted to the appropriate range prior to coagulant addition. Post-filtration pH adjustment may be necessary to optimize corrosion control and comply with other regulatory requirements.
- Several batch studies have demonstrated that arsenic removal is positively related to coagulant dosage. However, specific dose requirements needed to meet arsenic removal objectives were contingent upon the source water quality and pH. Effective coagulant dosage ranges were 5 – 25 mg/L of ferric chloride and as much as 40 mg/L of alum.
- Arsenite is not effectively removed because of its overall neutral charge under natural pH conditions. Therefore, pre-oxidation is recommended.





- If a water system has a coagulation/filtration plant and still has an arsenic problem, then it should evaluate optimizing that plant for arsenic removal.
- Changes that the plant might take to increase arsenic removal include:
  - Adjusting the pH;
  - Increasing coagulant dose; and,
  - Changing coagulant.
- If the water system is unable to make any of these adjustments, or if piloting indicates that they will not be successful then the system will need to install additional treatment for arsenic removal.



- Conventional coagulation/filtration processes like slow-sand filtration use gravity to push water through a vertical bed of granular media that retains the floc and are typically used within surface water treatment plants. They are less commonly used for treatment of groundwater supplies since these sources usually contain much lower concentrations of suspended solids, organic carbon, and pathogenic microorganisms. Installation and operation of a conventional coagulation/filtration process solely for arsenic removal is uneconomical.
- This is a photograph of a coagulation/filtration plant near San Francisco, California with flocculators and sedimentation basins.



- This photograph shows the floc, which contains arsenic, precipitating in the clarifier. The filters also remove a small amount of arsenic.
- Coagulation/filtration can also be performed in pressurized granular-media filtration columns. Here, a pressure differential forces the water down through a bed of granular media. Although this method is less common than conventional gravity filtration, prepackaged granular-media filtration systems are available and can be economical as new installations for small utilities wishing to treat water for arsenic.

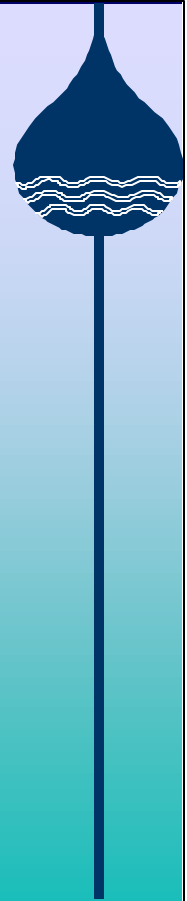
# Residuals Produced

- **Liquids**
  - Backwash water
  - Supernatant
- **Solids**
  - Sludge



- Coagulation/filtration produces both liquid and solid residuals.
  - Liquid wastes include backwash water and supernatant from the settling of backwash water.
    - Two treatment options are available for liquid residuals: (1) indirect discharge and (2) dewatering and sludge disposal. Water intended for indirect discharge will be subject to TBLLs placed by the POTW on TDS and arsenic. Dewatering can be accomplished by gravity thickening, followed by other mechanical or non-mechanical techniques. Settling basins can be used to provide gravity clarification, while the supernatant can be decanted and recycled to the process head.
    - Liquid residuals may also be recycled as backwash or by recycling to the facility headworks.
  - Solid wastes primarily consist of sludges.
    - Sludges will be produced from filtration or from settling of the backwash. Sludges can be passed through a small filter press for dewatering. The resultant sludge can be disposed of in a conventional landfill if it passes the PFLT, showing it has no free liquid, and the TCLP, showing it is not hazardous. Previous studies have indicated that typical ferric coagulation-filtration sludge will pass the TCLP test by a substantial margin (Fields, 2000b).

# Enhanced Coagulation/Filtration

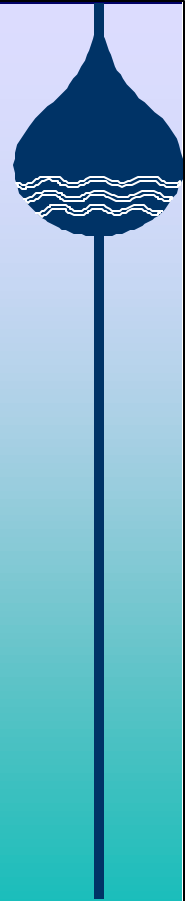


- **Pros**
  - **Uses existing technology**
  - **Can be optimized for arsenic removal**
  - **Disinfection Byproduct Precursor (DBPP) removal**
- **Cons**
  - **Generally only cost effective for existing technology**
  - **Increased chemical use**
  - **More sludge**
  - **Lead/Copper; in-plant corrosion**

- Benefits of enhanced coagulation/filtration:
  - It uses existing technology. A water system will probably find it more cost-effective to optimize this treatment than to install new treatment. In addition, the operator will already be familiar with the system.
  - It can be optimized for arsenic removal. Systems may be able to make relatively minor changes in operating procedures and achieve over 90% removal of arsenic.
  - Modifying coagulation/filtration systems for arsenic removal by lowering the pH or increasing coagulant dosage can also remove disinfection byproduct precursors, which are also regulated by EPA.
- Drawbacks of enhanced coagulation/filtration:
  - It is generally only cost effective if it is an existing technology. Due to the large capital investment necessary to install a coagulation/filtration plant, systems are unlikely to install one solely to comply with the Arsenic Rule.
  - Optimizing a coagulation/filtration plant for arsenic removal may necessitate increasing the coagulant dosage. This increases the amount of chemicals used by the water system, which may both increase costs and increase the risk to operator safety.
  - Increasing the coagulant dosage will also increase the amount of sludge produced, because more floc will be produced. The system will then have to dispose of more sludge.
  - Optimizing a coagulation/filtration plant for arsenic removal may necessitate lowering the pH during treatment. The lowered pH may create in-plant corrosion and, if not adjusted prior to release into the distribution system, may lead to problems with Lead and Copper Rule compliance.

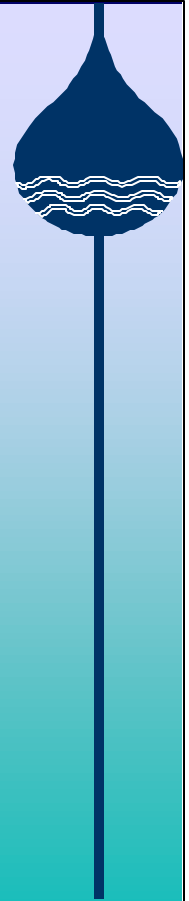


# Case Study: Billings, MT



- Billings, Montana draws water from the Yellowstone River, which carries arsenic leached from rocks in Yellowstone National Park, which is located just upstream. Arsenic levels can reach 20 to 30  $\mu\text{g/L}$  in the raw water. Billings recognized the public health hazards associated with arsenic and has been removing it for over 20 years.

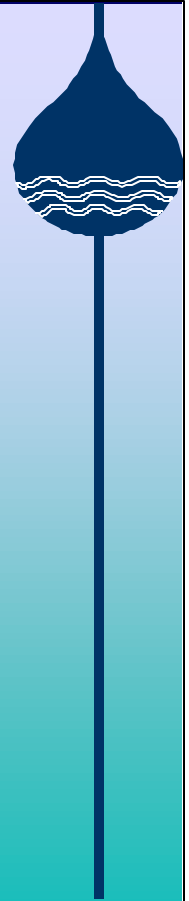
# Yellowstone River Water Quality



- **Flow:** - 1100 – 20,000cfs
- **pH:** - 7.8 – 8.9 s.u.
- **Turbidity:** - 1.5 – 2000 NTU
- **Arsenic:** - 5 – 17 ppb
- **Alkalinity:** - 41 – 166 ppm
- **Iron:** - <50 – 8200 ppb
- **Temperature:** - 0 - 23°C

- The influent water used by Billings has the following characteristics:
  - Flow: 1100 – 20,000cfs
  - pH: 7.8 – 8.9
  - Turbidity: 1.5 – 2000 NTU; can flash to 4000 NTU
  - Arsenic: 5 – 17 µg/L
  - Alkalinity: 41 – 166 mg/L
  - Iron: <50 – 8200 µg/L
  - Temperature: 0 - 23°C
- The influent water quality is extremely variable. It varies both seasonally and with storms located upriver on its tributaries.

# Billings WTP

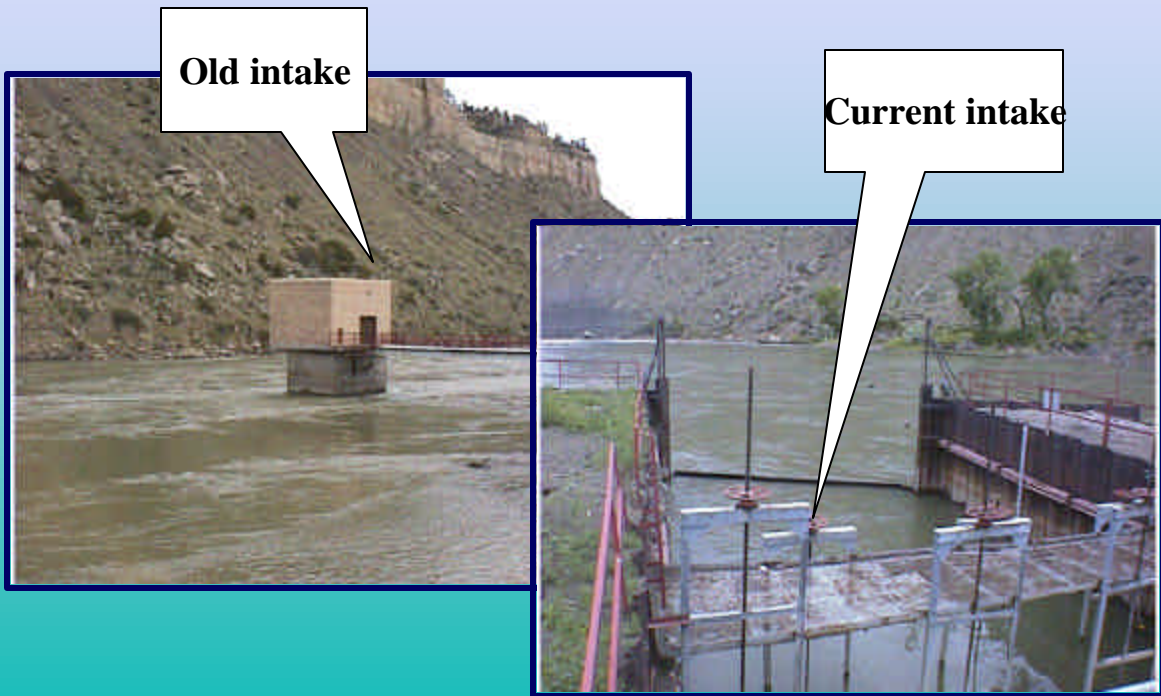


- **Plant: Conventional / In-line filtration**
- **Population served: 91,000**
- **Capacity: 100 MGD / 50 MGD**
- **Built: 1915 – present**

- The Billings Water Treatment Plant is a conventional plant using in-line filtration.
- It serves a population of 91,000.
- The plant has a design capacity of 100 million gallons per day (MGD), but, because the operators insist on extremely low finished turbidity, they can only achieve 50 MGD.
- The original treatment plant was adapted from an existing dam in 1915. The treatment plant has been continuously modified since that time.



# Yellowstone River Intake

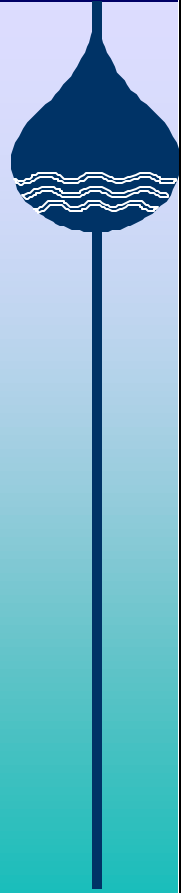


- These are the intakes used by Billings.
  - The picture on the left is of the old intake, which was damaged by floating debris several years ago.
  - Currently, the system uses the tail race for an old dam located at the site.
- Note how turbid the water is.



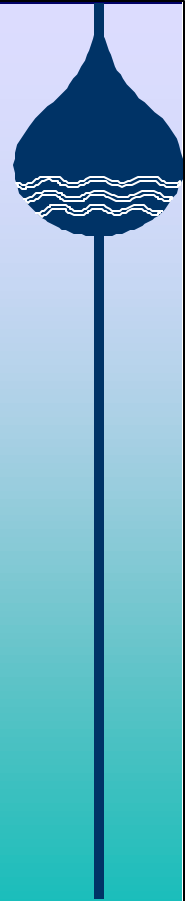
- This photograph shows the water in the winter when it is extremely clear. At these times, the water is also extremely cold and very difficult to treat.

# Sedimentation/ Flocculation



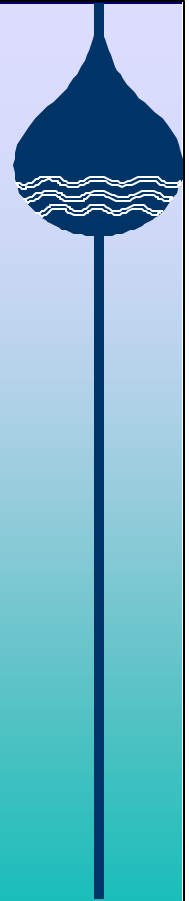
- This sedimentation/flocculation basin at the Billings system illustrates the treatment plant. Because water enters the basin through the tail race, the level of water in the basin depends on the stage of the river. Therefore, detention time in the basin varies significantly. Floating mixers are used in the basin.

# Billings Filter Basin



- Billings uses outdoor filter basins.

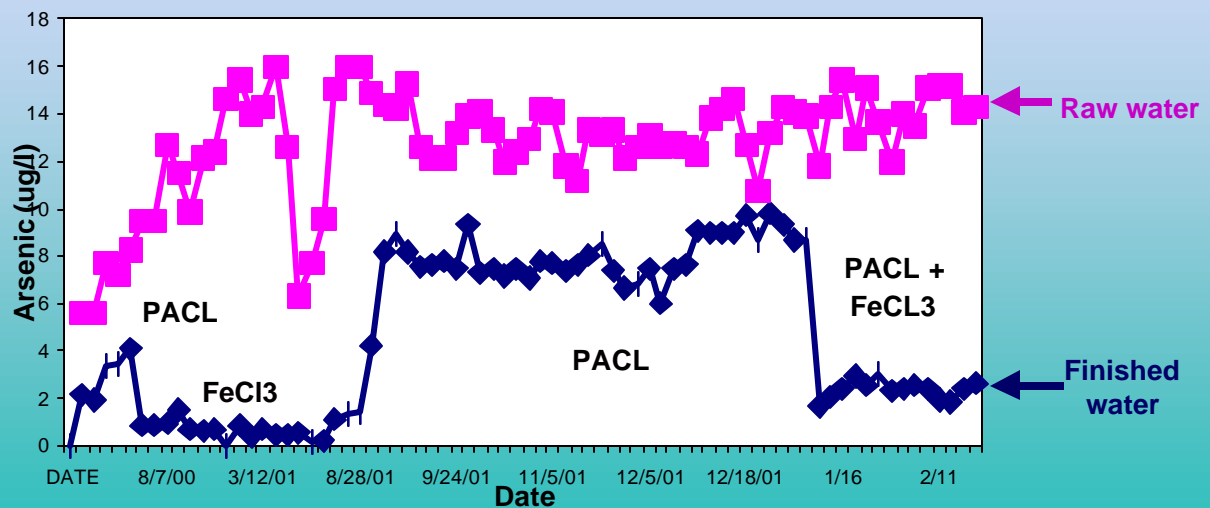
# Water Quality Problems



- **Cold water coagulation**
- **Corrosion problems - Pb/Cu**
- **Arsenic**

- Billings faces several water quality problems:
  - The very cold water temperature in the winter (approximately 0° C) makes coagulation difficult;
  - pH adjustment to decrease the pH creates corrosion problems, which are regulated by the Lead and Copper Rule, in the distribution system; and,
  - High levels of arsenic in the influent water challenge the treatment plant.

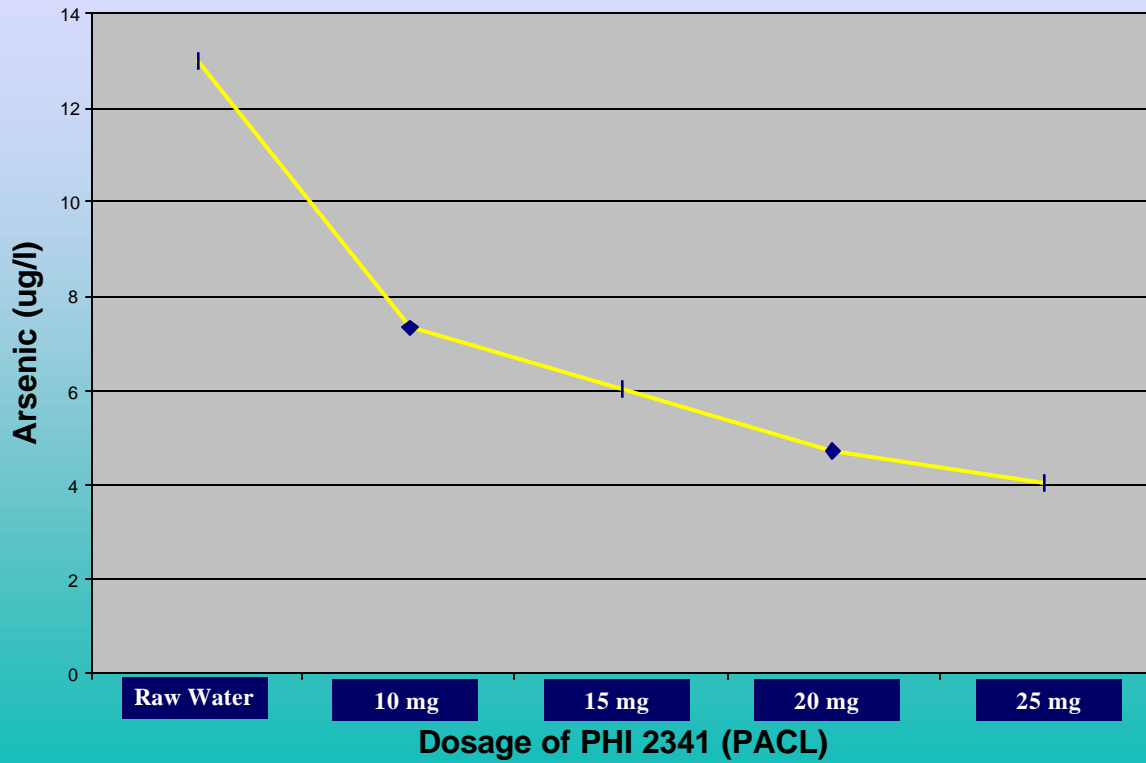
# Yellowstone Raw Water vs. Finished Water



PACL = Poly-Aluminum Chloride  
FeCL3 = Ferric Chloride

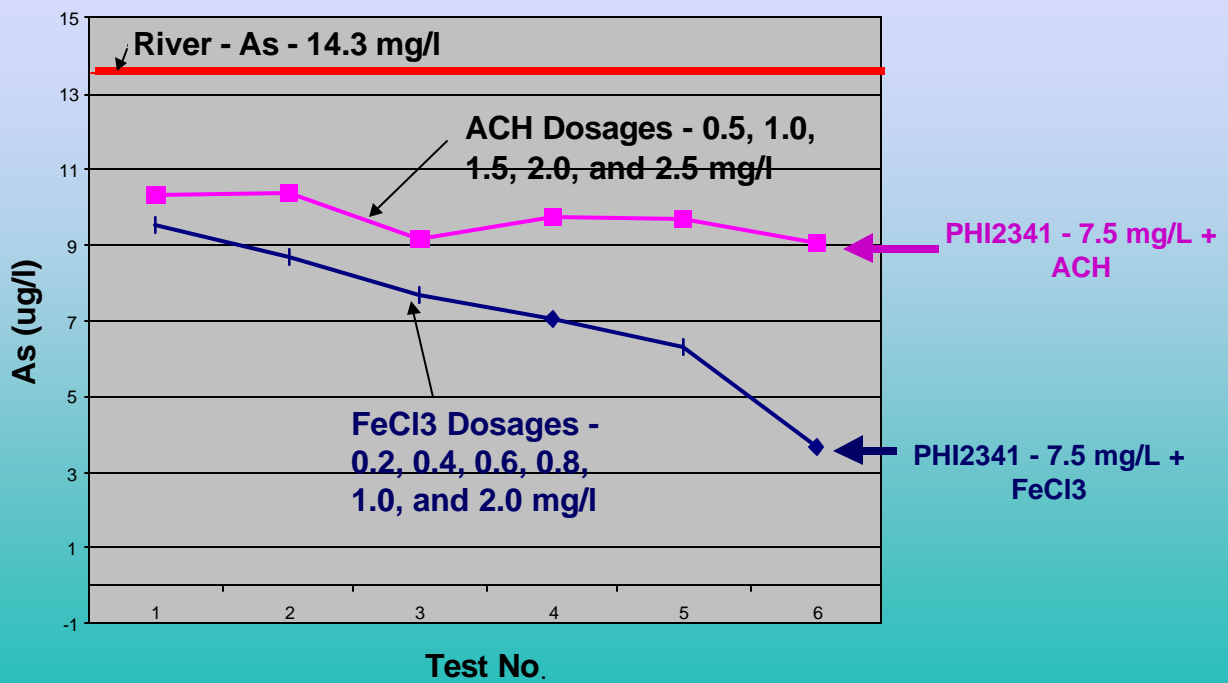
- In the 1980s, Billings switched coagulants to ferric chloride, which they discovered could remove both turbidity and arsenic. However, ferric chloride is difficult and potentially dangerous to handle, and they tried switching to poly-aluminum chloride (PACL). Because levels of arsenic in their influent level were below the arsenic MCL of 50  $\mu\text{g/L}$ , they used the whole plant to pilot the new coagulant.
- Initially, PACL removed nearly all of the arsenic, but levels began rising again. Billings then switched back to ferric chloride and achieved extremely high removal again. They tried PACL one more time for an extended period and found that it could remove arsenic consistently to 8 to 10  $\mu\text{g/L}$  but could not decrease it any lower. Finally, they decided to use a blend of PACL and ferric chloride. Currently, they continue to add PACL and 2 mg/L of ferric chloride and achieve arsenic levels in the finished water of 2 to 3 mg/L. Billings believes that it could add 1 mg/L of ferric chloride and achieve the same arsenic removal, but its feed pumps are too large and cannot feed less than 2 mg/L.
- The Billings plant was able to optimize its treatment trains for multiple purposes. They are able to produce finished water with low levels of arsenic and are able to significantly decrease their use of ferric chloride, resulting in increased operator safety.

## Billings Jar Test 1/25/2002



- This jar test shows how increasing the PACL dosage improves the removal of arsenic. The raw water level of 13  $\mu\text{g/L}$  is reduced to 6  $\mu\text{g/L}$  by 15 mg/L of PACL and to 4  $\mu\text{g/L}$  by 25 mg/L of PACL.

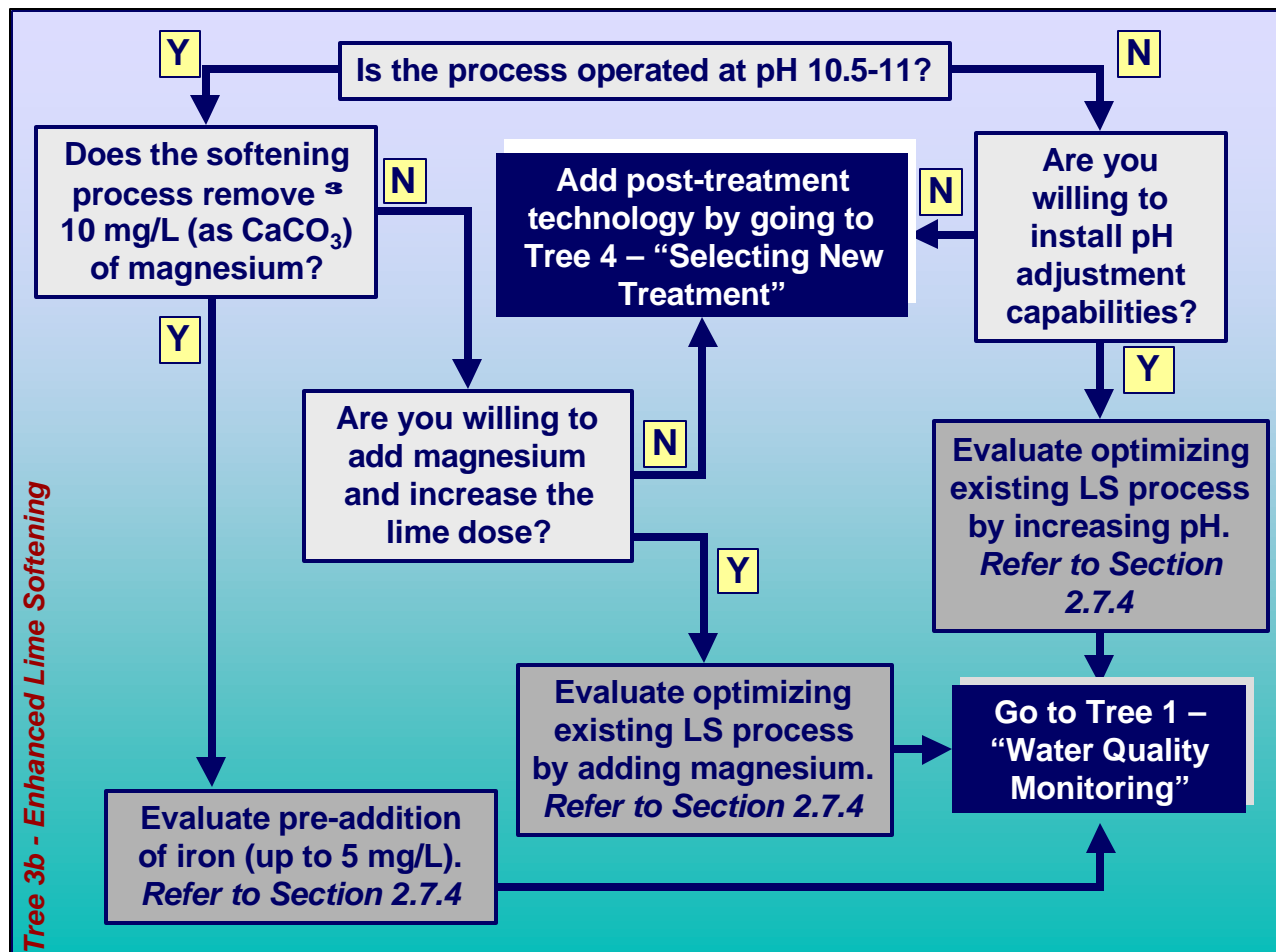
## Billings Jar Test of ACH (PACL) vs. FeCl



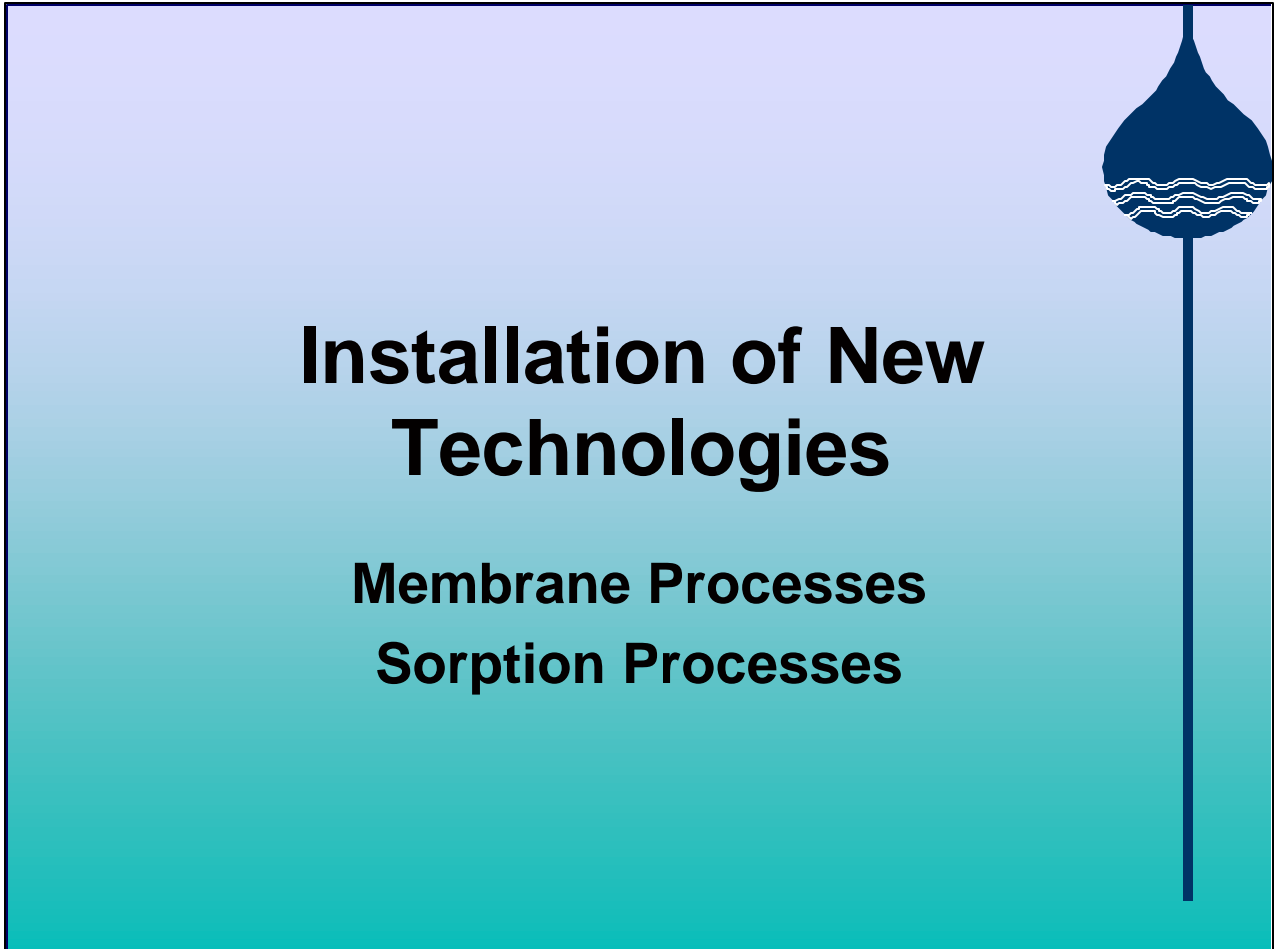
- This jar test shows how low levels of ferric chloride are much more effective than low levels than PACL at arsenic removal. The raw water level of 14.3  $\mu\text{g/L}$  is reduced to approximately 6  $\mu\text{g/L}$  by 1 mg/L of ferric chloride (compare to 15 mg/L of PACL from the other jar test) and to less than 4  $\mu\text{g/L}$  by 2 mg/L of ferric chloride (compare to 25 mg/L of PACL). On the other hand, increasing the PACL dosage from 0.5 to 2.5 mg/L decreases the level of arsenic slightly, from 10  $\mu\text{g/L}$  to 9  $\mu\text{g/L}$ .







- This decision tree helps water systems with existing lime softening plants that will still have a problem meeting the revised arsenic MCL to determine whether changing their operating procedures can sufficiently increase their arsenic removal. Options available to these systems include:
  - Raising their pH to 10.5 or above. Magnesium hydroxide, which adsorbs arsenic, is only precipitated above pH 10.5.
  - Adding magnesium and increasing the lime dosage. Arsenic removal by calcium carbonate is poor, so systems for which most hardness is calcium may be able to increase arsenic removal by adding magnesium and then precipitating it with increased amounts of lime.
  - Adding up to 5 mg/L of iron prior to softening. The addition of iron before softening can increase arsenic removal; however, competition between arsenic and carbonate for sorption sites on the iron hydroxide reduce the removal efficiency to levels below those of a normal coagulation/filtration process.
- While the total volume of waste produced from lime softening is typically higher than that produced by coagulation/filtration and co-precipitative processes, the arsenic concentration in the sludge is generally lower because more solids are produced. Typical solids concentrations are 1 to 4%. Prior to disposal, this waste residual will require thickening and dewatering, most likely via mechanical devices. The resultant sludge is anticipated to pass the TCLP test (Fields, 2000a).

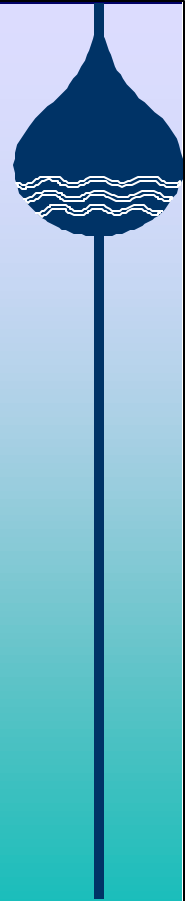


# Installation of New Technologies

## Membrane Processes Sorption Processes

- Water systems that are not able to reduce arsenic levels to below the revised MCL through alternative methods will need to install new technologies.
- Most new technologies will use membrane processes and sorption processes.
- The most practical ways for such systems to achieve compliance are likely to be with sorption processes:
  - Ion exchange;
  - Activated alumina (conventional or modified);
  - Granular ferric hydroxide or proprietary sorption processes; and,
  - Coagulation assisted membrane filtration.
- Membrane processes, especially nanofiltration or RO, may also be chosen when high levels of TDS or other contaminants must be removed.

# Raw Water Testing



- **Primary parameters**

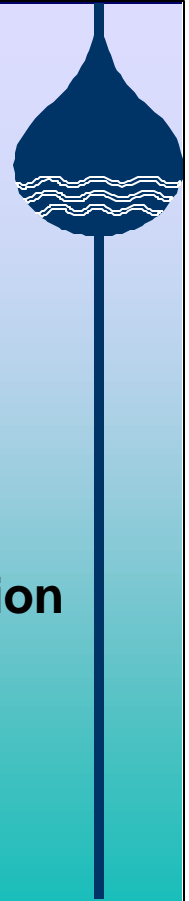
- Total arsenic
  - Arsenite
  - Arsenate
- Chloride
- Fluoride
- Iron
- Magnesium
- Manganese
- Nitrate/Nitrite
- Orthophosphate
- pH
- Silica
- Sulfate
- Total Dissolved Solids (TDS)

- **Secondary parameters**

- Alkalinity
- Aluminum
- Calcium
- Turbidity
- Hardness

- Prior to installing new treatment for arsenic, a system should test for all of these primary and secondary parameters.

# Design Information



- **Capacity of source(s)**
- **Location of source(s)**
- **Maximum day water use**
  - Gravity storage
- **Peak instantaneous demand**
  - Hydropneumatic systems
- **Target finished water arsenic concentration**
- **Other**
  - Publicly Owned Treatment Works (POTW)
  - Land
  - Labor
  - Acceptable water loss

- Certain system information is necessary when designing new treatment including:
  - Number of source(s) and their respective arsenic levels
  - Capacity of source(s)
  - Location of source(s)
  - Maximum day water use if gravity storage will be used. When using gravity storage, a water system must be able to produce in 24 hours enough water for a maximum day. The system can rely on gravity storage during that day but it cannot rely on the storage for more than 24 hours, because 30 maximum days may occur consecutively.
  - Peak instantaneous demand if hydropneumatic storage will be used. Hydropneumatic systems have no long-term storage and therefore must be able to treat the water at the maximum rate at which it is used.
  - The target finished water arsenic concentration, which is likely to be 10 to 20% below the revised arsenic MCL. Comparing the target finished concentration with the raw water concentration will determine what the removal efficiency is necessary.
  - Other information:
    - Whether a POTW is available and the TBLLs it sets on the waste streams it accepts.
    - How much land is available for construction and waste disposal.
    - How many operators the system has or is able to acquire, and their level of certification.
    - An acceptable rate of water loss.
    - What the Primacy Agency is going to require in terms of redundancy, polishing unit requirements, process control, etc. Also, whether it will allow split treatment and, if so, how it will be monitored.

## 2 Systems With 100 Service Connections

- **System 1:**
  - Gravity Storage = Max. Day
  - 2 wells with single entry point

**62,500 gpd = 65 gal/min  
960 min/day**

- **Assume:**
  - 125 gpcpd avg.
  - 2 people/connection
  - Max = 2.5 x avg.
  - 16 hour/day pumping
  - 62,500 gpd = max day

**Figure two trains @  
35 gal/min each**

**Provides Max Day &  
Average Day with  
Largest Treatment Unit  
Out of Service**

- To compare gravity storage and hydropneumatic storage, consider two systems with 100 service connections. Each system has two wells with a single entry point.
- The first system has gravity storage.
- The following conservative assumptions will be made:
  - Each person consumes 125 gallons per day.
  - There are 2 people per service connection.
  - A maximum day is twice an average day.
  - The pumps only operate 16 hours per day.
  - The system needs to supply 62,500 gallons (100 connections \* 2 people per connection \* 125 gallons per person on an average day \* 2.5 for a maximum day) on a maximum day.
- Because the system has gravity storage, it needs to produce 62,500 gallons over the course of the whole day. There are 960 minutes in 16 hours, so it needs to produce 65 gallons per minute.
- The system could install two treatment trains each capable of treating 35 gallons per minute. This will provide for the maximum day (with a little bit of redundancy) and provide for an average day with the largest treatment train out of service, as is required by most Primacy Agencies.

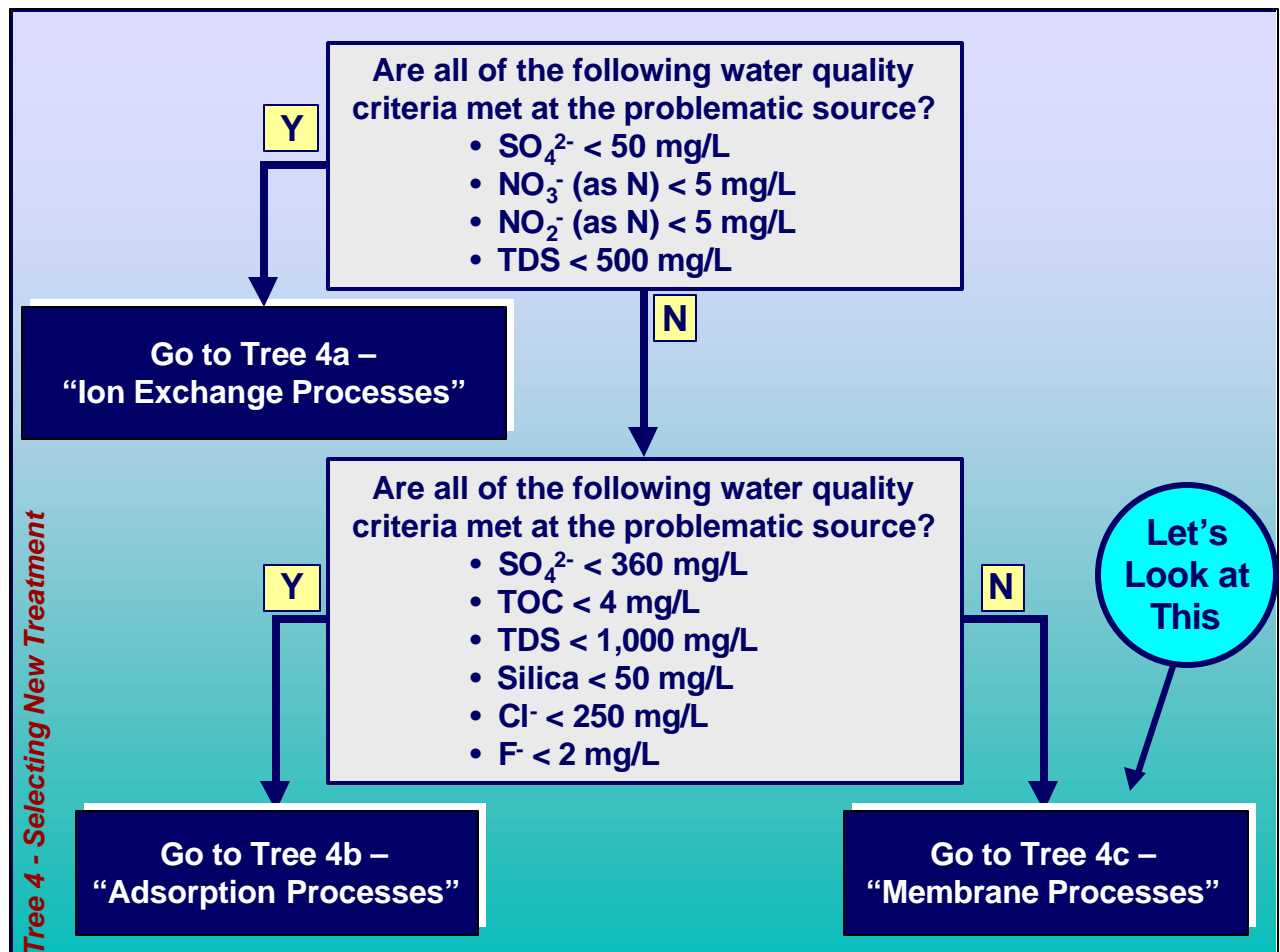
## 2 Systems With 100 Service Connections

- **System 2:**
  - Hydropneumatic tanks
  - 2 wells with single entry point
- **Assume:**
  - 125 gpcpd avg.
  - 2 people/connection
  - Max = 2 x avg.
  - 16 hour/day pumping
  - 62,500 gpd = max day

**Salvato: Probable  
Max. Momentary Demand =  
140 gpm**

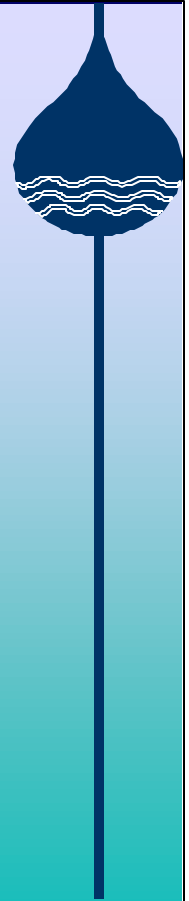
**Figure 4 trains @  
50 gal/min each  
Provides Max Momentary  
Demand  
with  
Largest Treatment Unit  
Out of Service**

- The second system has hydropneumatic storage.
- The same conservative assumptions will be made:
  - Each person consumes 125 gallons per day.
  - There are 2 people per service connection.
  - A maximum day is twice an average day.
  - The pumps only operate 16 hours per day.
  - The system needs to supply 62,500 gallons (100 connections \* 2 people per connection \* 125 gallons per person on an average day \* 2.5 for a maximum day) on a maximum day.
- Because the system has pneumatic storage, it has no long-term storage capabilities. Therefore, its production is driven not by the maximum day demand but by the maximum momentary demand. Salvato's charts can be used to determine the maximum momentary demand, which is approximately 140 gallons per minute for this system.
- The system could install four treatment trains each capable of treating 50 gallons per minute. This will provide for the probably maximum momentary demand (with a little bit of redundancy) with the largest treatment train out of service, as is required by most Primacy Agencies.
- Treatment costs, both installation and operations, will be much higher for this system, so hydropneumatic systems should evaluate the cost effectiveness of storage when putting in treatment.



- Water systems that cannot use zero treatment options and that cannot successfully optimize their current treatment will need to install new treatment.
- This part of the presentation will examine the three types of treatment processes that small systems are likely to install:
  - Membrane Processes;
  - Chemical Precipitation Processes; and,
  - Sorption Treatment Processes.
- First, a look at membrane processes, which are an unlikely option for arsenic removal.





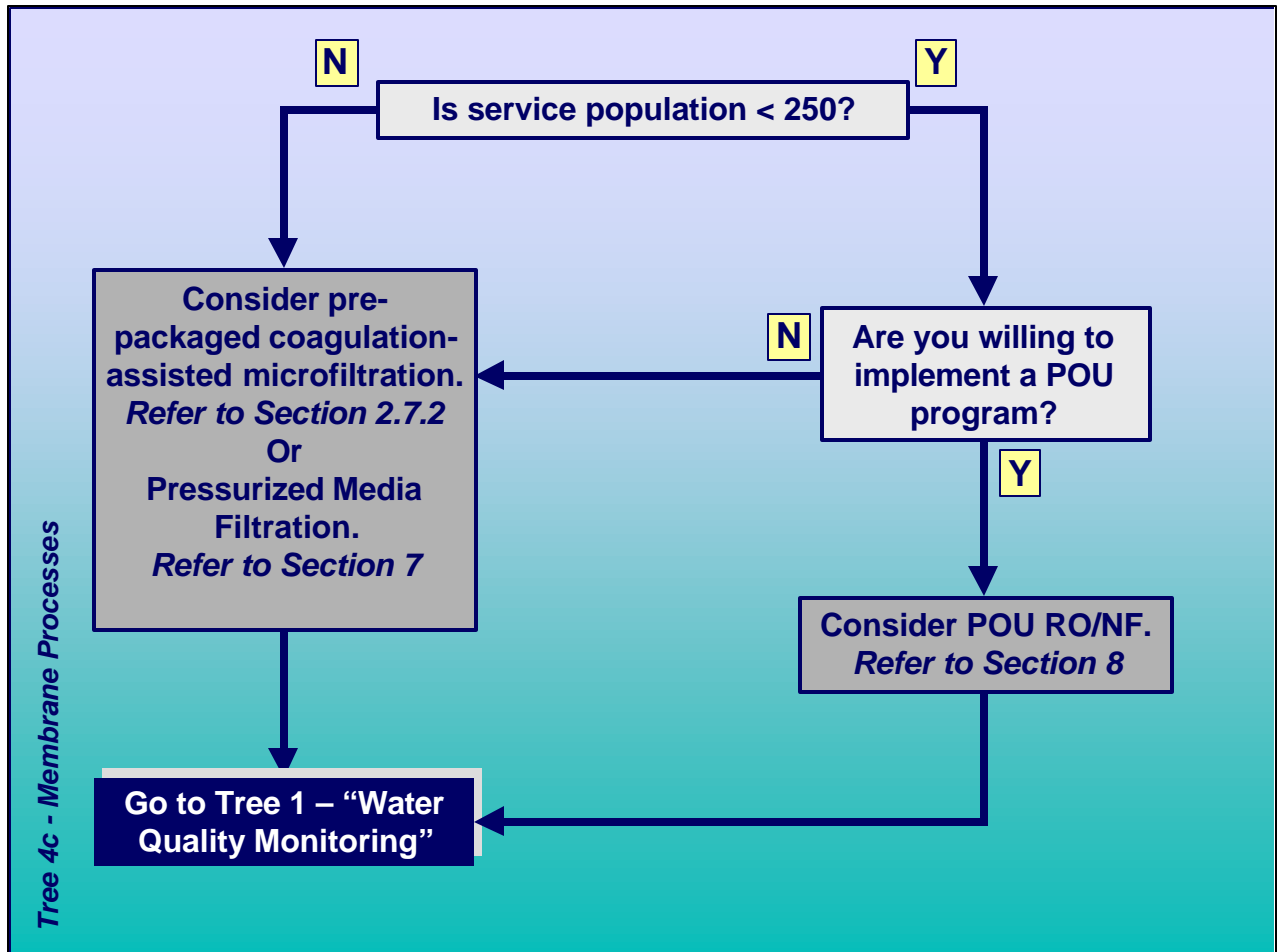
# Membrane Processes

**RO**

**Nanofiltration**

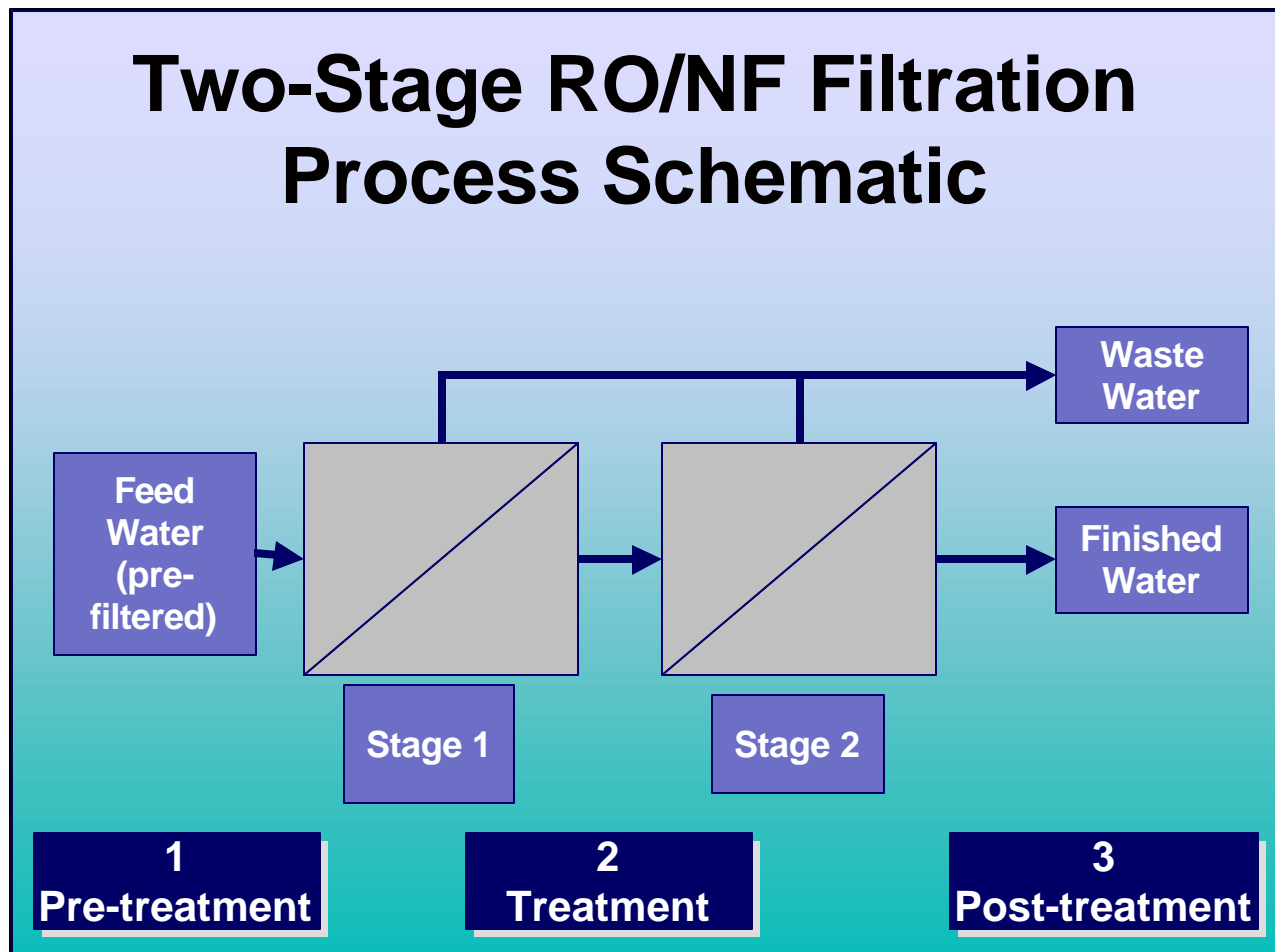
**Coagulation Assisted  
Microfiltration**

- Systems currently without treatment must install new treatment processes.
- Generally these systems will have low turbidity water and are unlikely to opt for processes involving membranes. Nanofiltration and RO (the latter is a BAT), which are quite expensive, are most commonly used for treatment of highly brackish water. However, they may be more practical and cost-effective for systems that have multiple contaminants. For example, a system with high arsenic and high levels of TDS may choose to install a RO system to remove both contaminants.
- Systems are more likely to use coagulation assisted filtration processes.
- Coagulation assisted microfiltration is shown in blue since it was listed as a SSCT in the Arsenic Rule.
- RO is shown in red since it was listed as a SSCT in the Arsenic Rule.

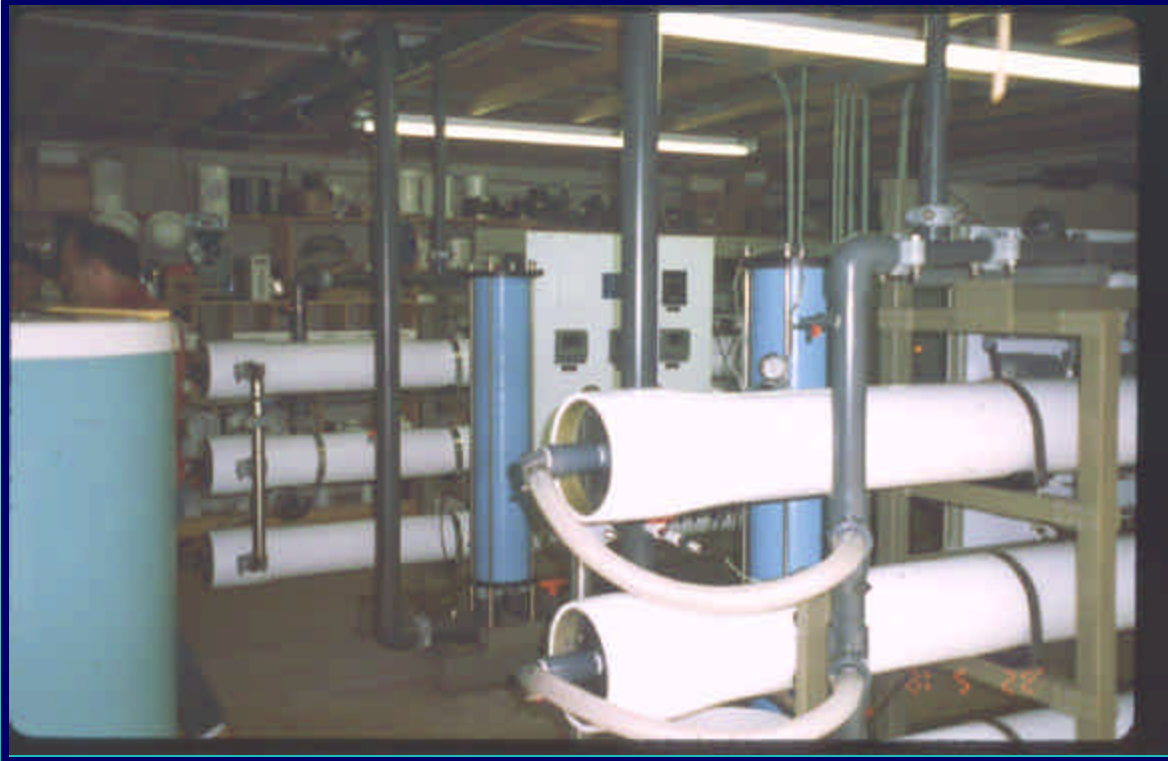


- Small systems are most likely to consider RO POU devices (if they serve fewer than 300 people) and pre-packaged coagulation-assisted microfiltration.

# Two-Stage RO/NF Filtration Process Schematic

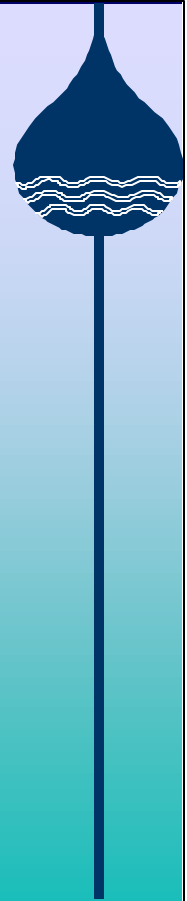


- Membranes are a selective barrier, allowing some constituents to pass while blocking the passage of others. The movement of constituents across a membrane requires a driving force (i.e., a potential difference between the two sides of the membrane). RO and nanofiltration both use pressure as a driving force; microfiltration may use a vacuum.
- RO and nanofiltration employ a similar technique to remove contaminants from water. In both technologies, a high-pressure force (100-150 psi for RO, 50-150 psi for nanofiltration) is used to force water through a membrane. Treated water is collected on the other side; contaminants and rejected water (up to 70% of influent water) are unable to pass through. Nanofiltration is typically capable of removing compounds with molecular weights over 400 g/mol; RO membranes, which have even smaller pores than nanofiltration membranes, can remove low molecular weight organic molecules and salts.
- This simplified schematic shows a two-stage RO or nanofiltration treatment unit. Water is first pre-treated, with at least filtration to remove particles that could damage the membrane. The water then passes through the first membrane. The reject stream from the first membrane is passed through the second membrane. The water that passes through either membrane is post-treated and distributed.
- Chemical feed points, backwashing and chemical cleaning systems are not shown in the schematic.
- Source water parameters of concern for RO and nanofiltration include:
  - Arsenic, which determines the required removal efficiency;
  - Sodium, chloride, and sulfate;
  - Calcium and magnesium, which can cause membrane scaling; and,
  - Silica, metal hydroxides, colloid, and bacteria, which can cause membrane fouling.
- Studies indicate nanofiltration and RO can treat water to below the revised arsenic MCL provided the arsenic exists as (or is converted to) arsenate. Increasing the pH increases arsenite removal but also, above pH 7, may increase scaling.



- The nanofiltration plant is located on the east coast of Florida south of Jacksonville. Its source water contains high levels of TDS, sulfate, and hydrogen sulfide gas. The plant splits its influent stream into several treatment trains. Within each treatment train, there are three membranes. The reject water from the first membrane is passed through a second membrane, and the reject water from that membrane is passed through a third. This process minimizes water loss.
- In general, most water systems using nanofiltration or RO have high TDS source water, either from sea water or some other cause.

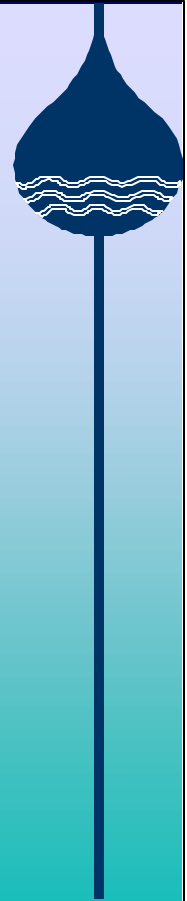
# Residuals



- **Liquids**
  - High total dissolved solids (TDS) in waste water
- **Solids**
  - Membranes

- RO is possible for very small CWSs and NTNCWSs. For example, this picture shows a RO unit inside a Native American school that faces high TDS in its source water. The school uses the high- TDS water to flush toilets and water grass. A portion of the water is treated by a RO unit and stored. Pumps then take suction out to drinking fountains and the cafeteria.
- Membrane processes will create the following residuals:
  - A liquid waste stream, which will contain high TDS; and,
  - Spent membranes.

# RO/Nanofiltration



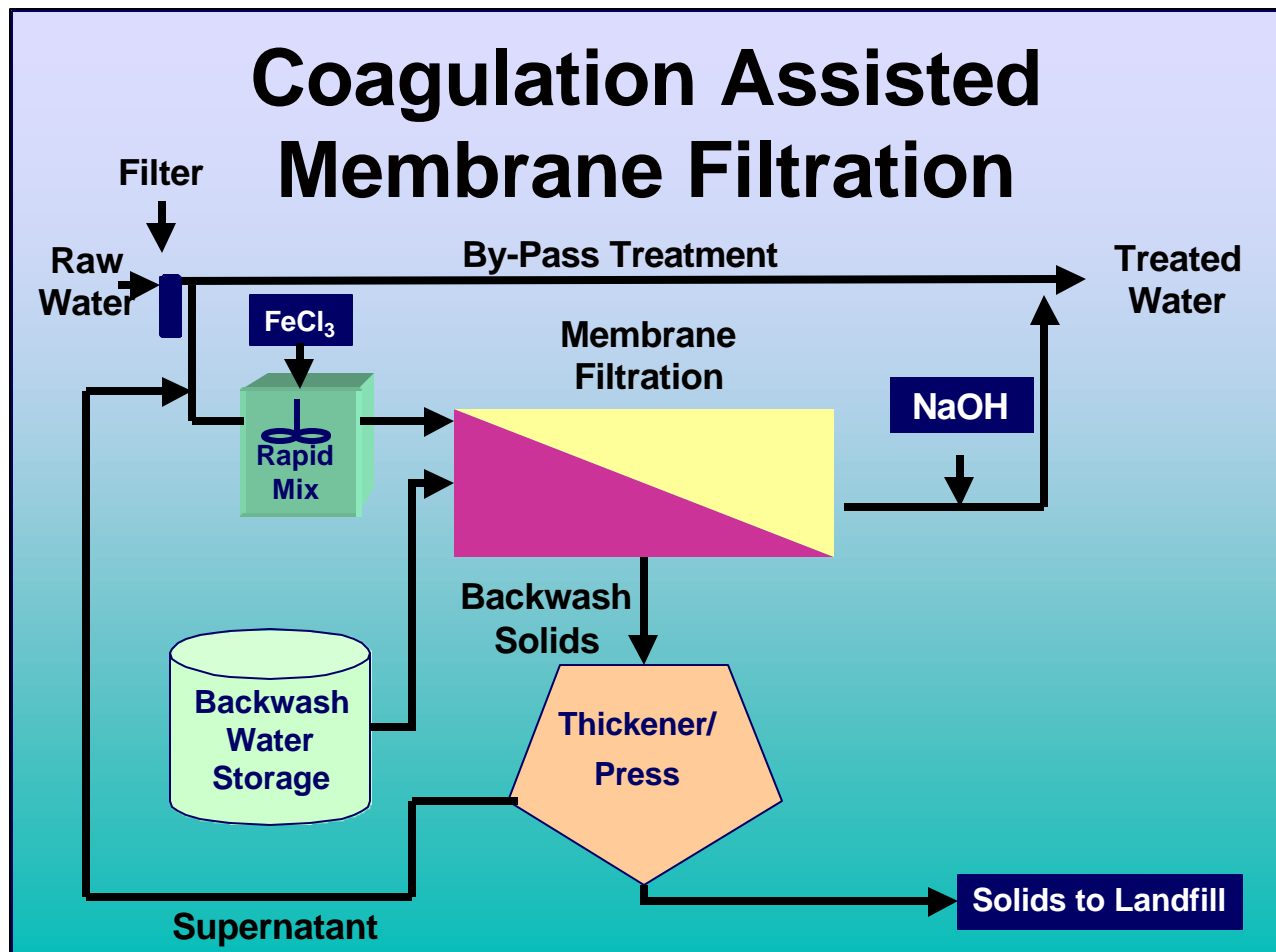
- **Pros**

- Effective for arsenic removal
- RO may not require oxidation process
- Effective for removal of other contaminants
- Applicable for POU or POE

- **Cons**

- Pretreatment often required
- May require
  - Oxidant
  - pH adjustment
- Energy requirements
- Residuals
- Post treatment
- Water loss

- Benefits of RO and nanofiltration:
  - They are effective for arsenic removal. RO, which has been designated BAT for arsenic, can remove over 95% of the arsenic in influent water in a full-scale installation. Nanofiltration can remove up to 90% of arsenic.
  - RO may not require pre-oxidation, especially at high pH (above 7).
  - Both RO and nanofiltration can remove many other contaminants.
  - RO can be used at the point of use or point of entry. It has been designated a SSCT for POU use. RO is probably too expensive for most small systems unless it is used in POU applications.
- Drawbacks of RO and nanofiltration:
  - Pretreatment is often required to reduce membrane fouling and scaling. If chlorination is used for oxidation or disinfection, it should be removed before the membrane to prevent membrane damage.
  - Treatment of arsenite will usually require either oxidation or pH adjustment, especially for nanofiltration.
  - Both processes have high energy requirements to maintain the pressure gradient across the membrane.
  - Residuals production can be significant, especially with RO. A large stream of high-TDS water is created.
  - Post treatment may be necessary.
  - Water loss can be significant, up to 70% of influent for RO (although typically 10 to 20% for both processes). Water loss can be minimized by using a two-step or three-step process in which water rejected by one membrane is run through others.

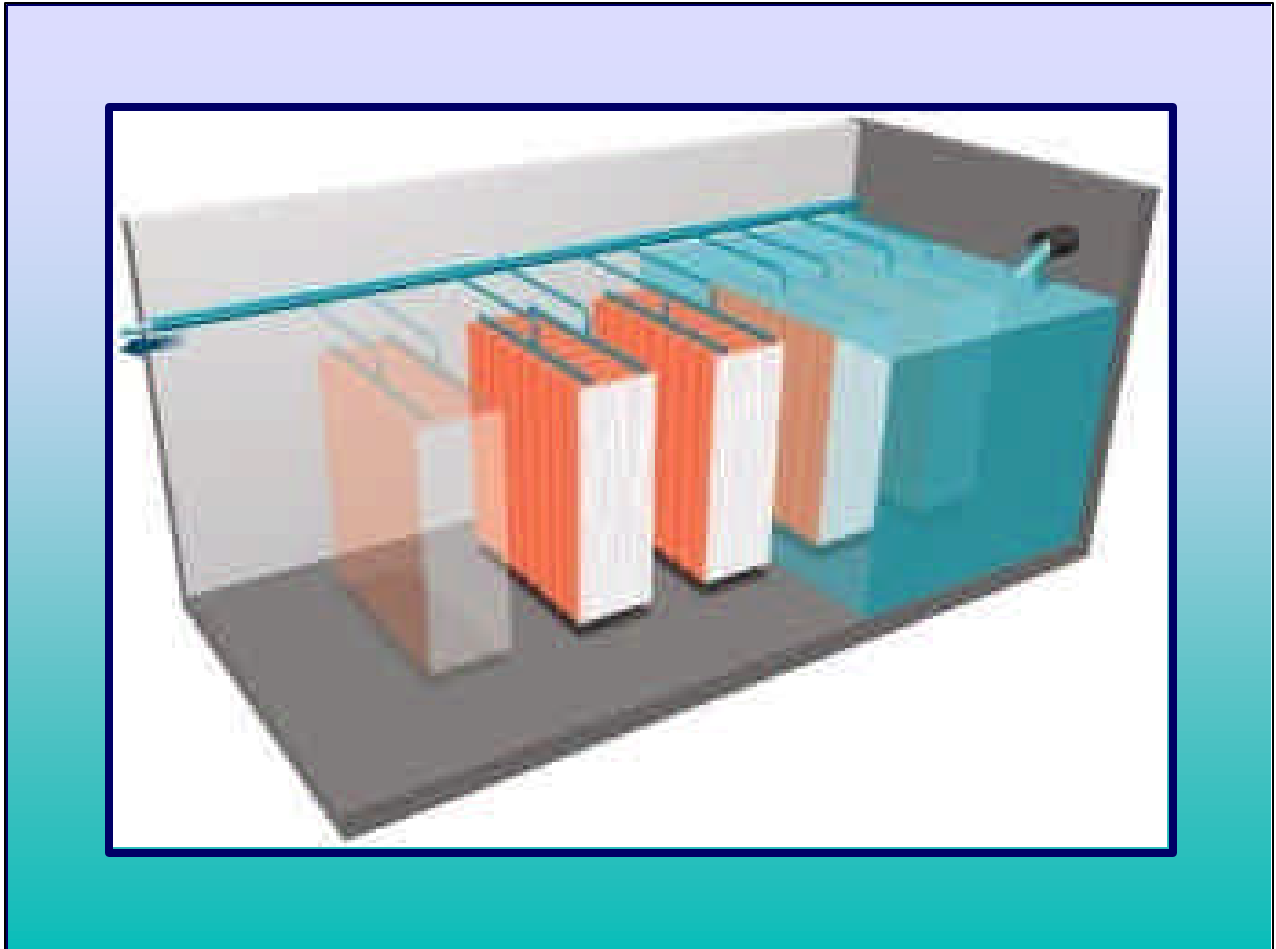


- In coagulation assisted membrane filtration, a coagulant (usually ferric chloride) is used to form floc containing arsenic, and a membrane is then used to remove the floc. Coagulation assisted membrane filtration may be able to remove smaller floc sizes than a conventional gravity filter, so smaller amounts of coagulant may be required.
- As this schematic shows, the raw water is first filtered first to remove debris that could damage or clog the membranes. If necessary, arsenite would be oxidized to arsenate, which is more easily removed by the process. pH and/or alkalinity adjustment might be necessary for optimizing coagulation.
- Ferric chloride is then added during rapid mix to form floc. The arsenic adsorbs to the precipitated floc and may co-precipitate with the coagulant. To be effective for arsenic removal, the floc needs time, at least 5 minutes, to form large enough particles for filtration. The coagulated water passes through the membrane and the water and arsenic/floc are separated. pH adjustment might be necessary after treatment.
- Silicate can interfere as it can complex with the ferric hydroxide precipitate. Silicate interference is usually only a problem with conditions involving high pH, high silicate, and high arsenite.
- Package coagulation-assisted membrane filtration plants are available on the market and may be an option for small systems.



- This coagulation-assisted membrane filtration plant in Erie, Colorado, is used for the removal of bacteria in surface water. A similar set-up could be used for arsenic removal.
- The vertical white tubes are the membrane filtration units that remove arsenic-containing floc.





- The filters used in coagulation-assisted membrane filtration are meant to be put in existing filter basins. Suction is then used to take water through them. In the set up used in Erie, Colorado, air bubbling devices are used underneath to reduce head loss across membranes.

# Coagulation Assisted Membrane Filtration

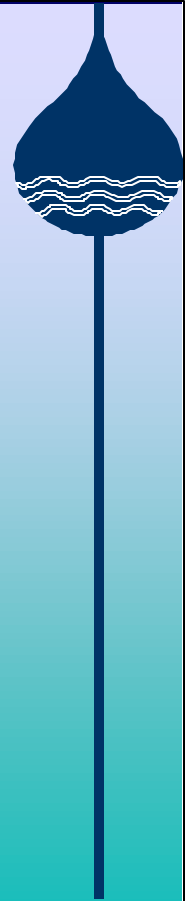
- Coagulant required



**Membrane Filtration**

- Both ferric chloride and alum can be used in coagulation assisted membrane filtration. Ferric chloride can achieve higher removal rates, especially at a higher pH and with arsenite, but may be more difficult to handle.

# Coagulation Assisted Membrane Filtration



- **Pros**
  - Minimal residuals
  - Very little water loss (< 0.1 %)
  - Relatively easy process control
  - Low chemical requirements
- **Cons**
  - High equipment costs
  - Finished water adjustment may be necessary
    - pH
    - Fluoride

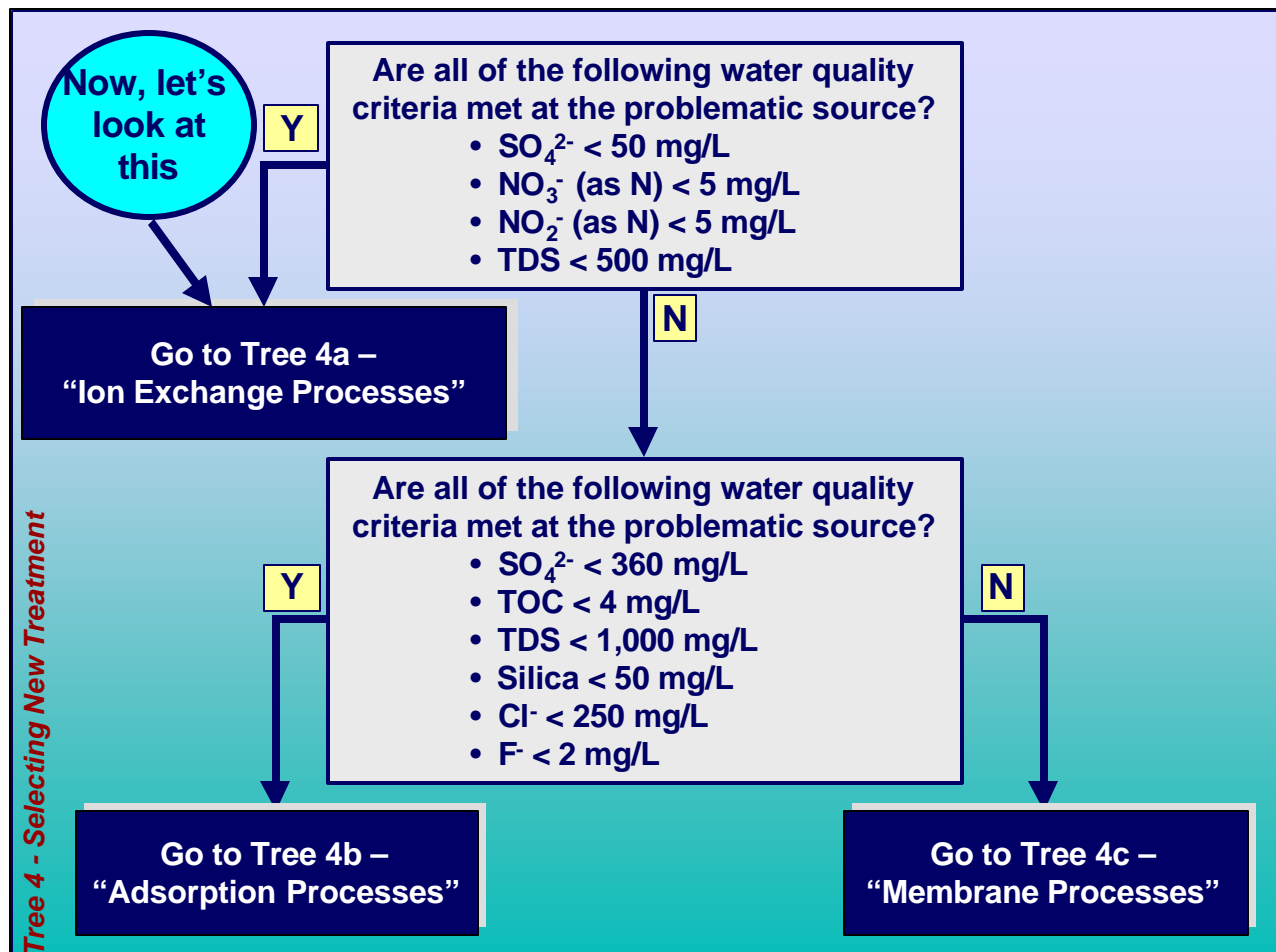
- Benefits of coagulation assisted membrane filtration include:
  - Relatively low residuals production. The sludge that is produced is typically thickened and the water recycled.
  - Very little water loss.
  - Relatively easy process control. The process tends to be relatively predictable, lending itself to package plant production.
  - Low chemical requirements, minimizing operation and maintenance costs and sludge production.
- Drawbacks to coagulation assisted membrane filtration include:
  - High capital equipment costs; and,
  - Finished water adjustment may be necessary for pH and fluoride.

# **Chemical Precipitation Processes**

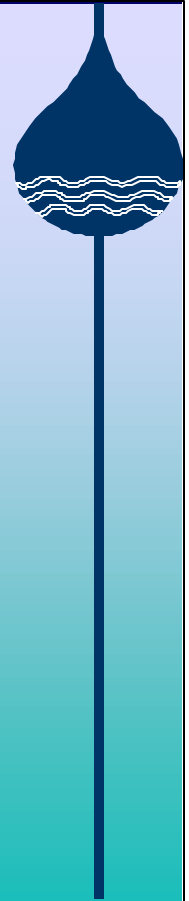
**Enhanced  
Coagulation/Filtration  
Enhanced Softening**

**Generally not as cost effective as new technologies.  
Therefore, more of an “optimization” of existing  
technologies issue**

- Because of their high capital costs, chemical precipitation technologies are an unlikely option for Arsenic removal. Water systems with existing coagulation/filtration or softening plants should consider optimizing them for arsenic removal.



- Water systems that need to install new treatment and have source water that meet all of the following water quality criteria may wish to consider utilizing an ion exchange processes:
  - Less than 50 mg/L sulfate;
  - Less than 5 mg/L nitrate;
  - Less than 5 mg/L nitrite; and,
  - Less than 500 mg/L TDS.
- High levels of sulfate can compete with arsenic for removal by ion exchange resins.
- Arsenic is adsorbed preferentially to nitrate and nitrite. However, high nitrate and nitrite levels can be problematic because of a phenomenon known as chromatographic peaking: arsenic, nitrate, and nitrite are all adsorbed onto fresh media. As the free adsorption sites become limited, arsenic replaces some nitrate and nitrite on their adsorption sites. The concentration of nitrate and nitrite in the effluent can increase above levels in the influent, which may be dangerous for consumers.
- High TDS levels can adversely affect performance.



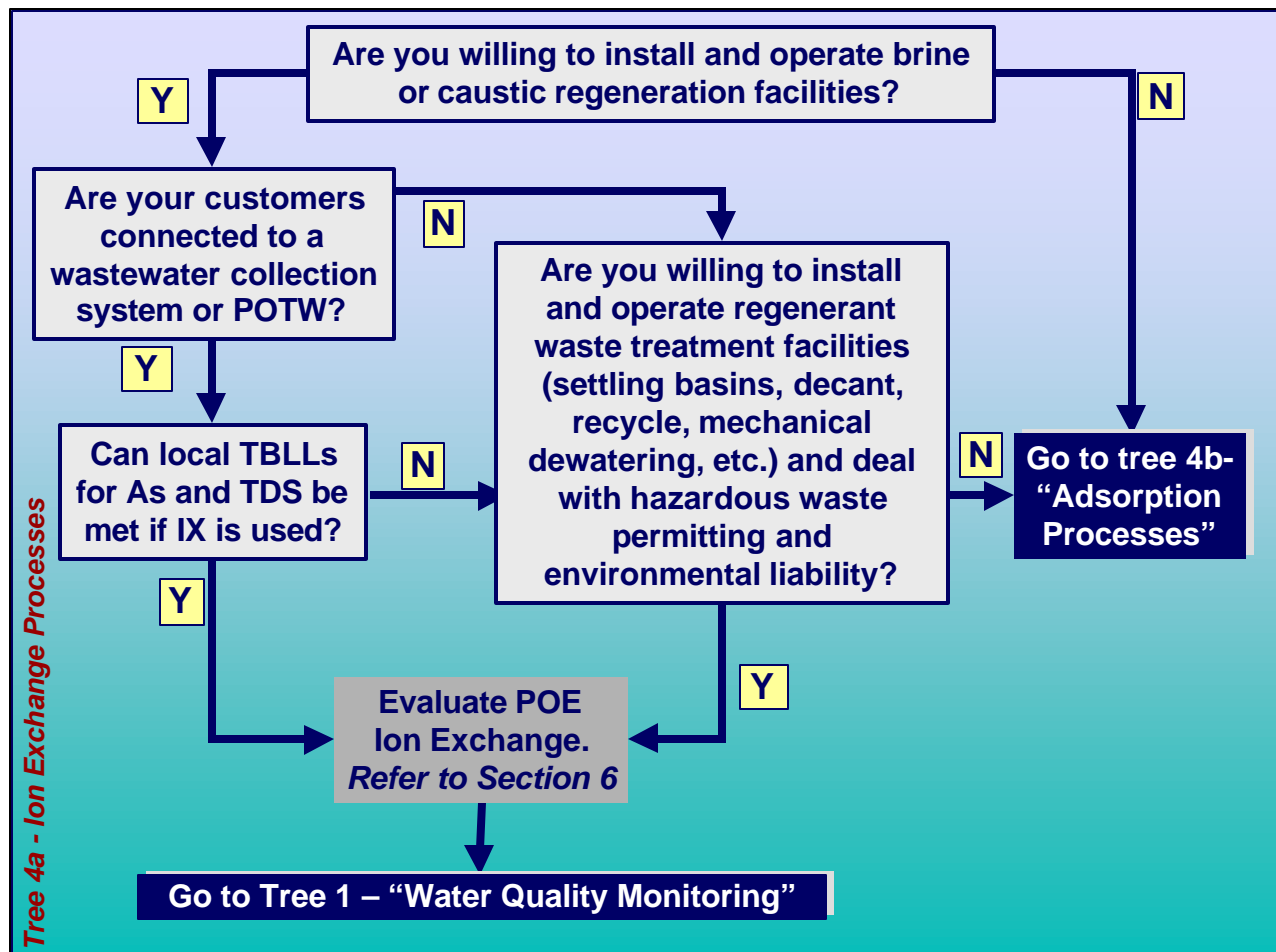
# Sorption Treatment Processes

**Ion Exchange**

**Activated Alumina**

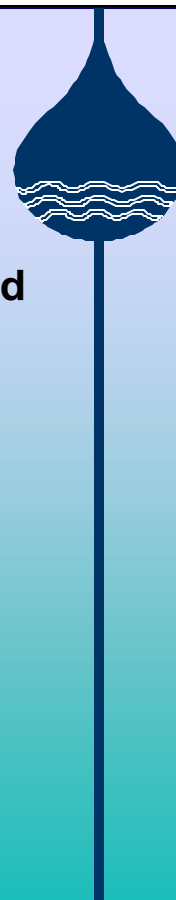
**Granular Ferric Hydroxide**

- Sorption treatment processes include ion exchange, activated alumina, and granular ferric hydroxide. This presentation will first consider ion exchange.
- Ion Exchange and Activated Alumina are shown in red since they were listed as a BATs in the Arsenic Rule. They were also listed as SSCTs for all sizes of small system categories.



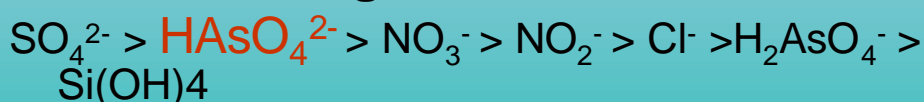
- Water systems that are not willing to install brine or caustic regeneration facilities are unlikely to find ion exchange cost effective. Resins become exhausted relatively quickly but can be repeatedly regenerated.
- Because ion exchange generates a high-TDS liquid waste stream with high arsenic levels, systems without access to a POTW or other waste disposal facility will be unlikely to be able to afford ion exchange. POTWs establish TBLLs, which set limits on the concentrations of contaminants in the waste streams they accept. For more information on disposal to a POTW see the Residuals presentation.

# Ion Exchange



- **Physical-chemical process**
  - Ions exchanged between a solution phase and solid resin phase
  - Strong-base anion exchange resin
  - Insensitive to pH in range of natural waters

- **Exchange affinity is a function of net surface charge**

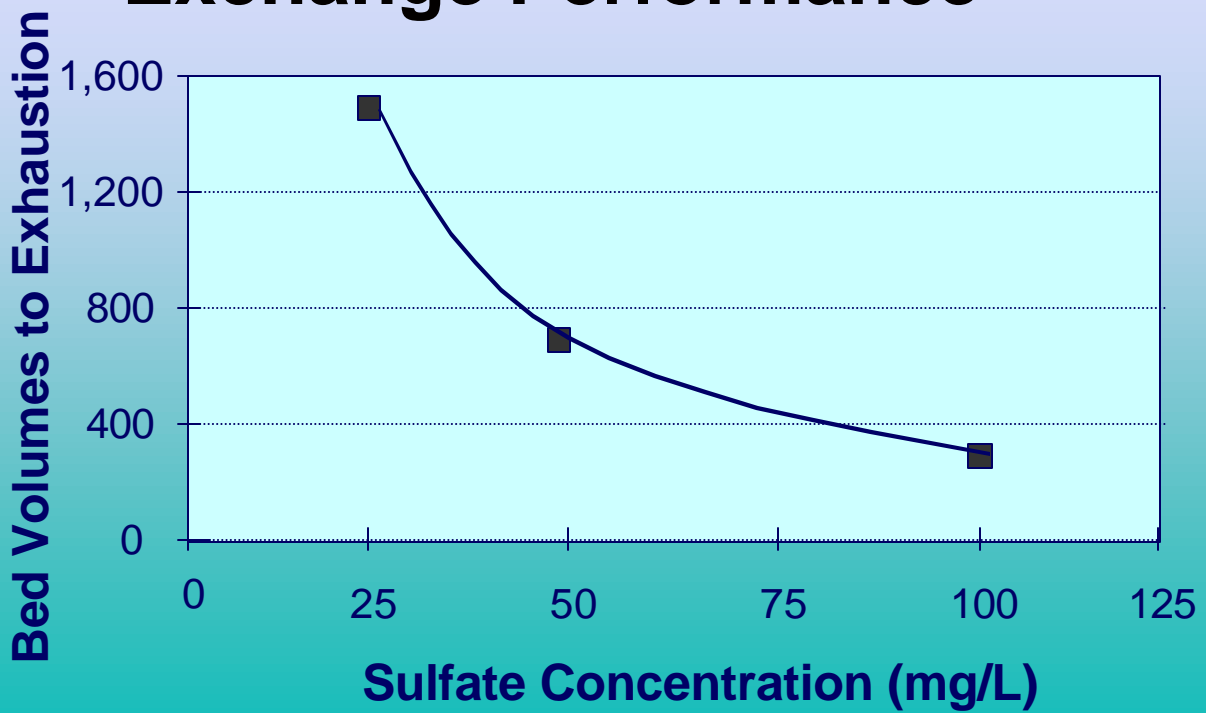


- **High TDS can adversely affect the performance**

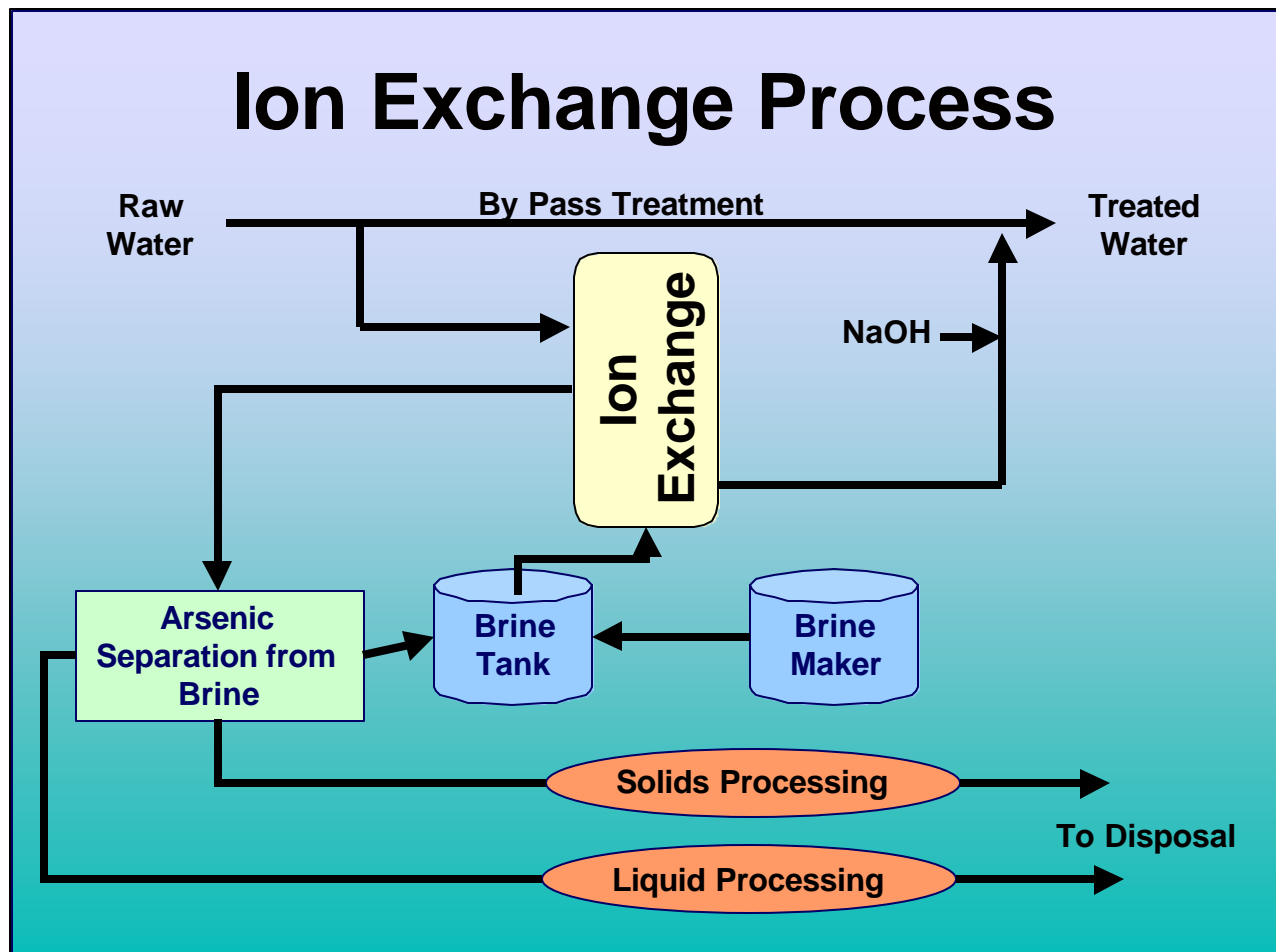
- Ion exchange is a physical/chemical process by which an ion in the solid form is exchanged for an ion in the feed water. This solid phase is typically a synthetic resin which has been chosen to preferentially adsorb the particular contaminant of concern. To accomplish this exchange of ions, feed water is continuously passed through a bed of ion exchange resin beads until the resin is exhausted. Exhaustion occurs when all sites on the resin beads have been filled by contaminant ions. At this point, the bed is regenerated by rinsing the ion exchange column with a regenerant, which is a concentrated solution of ions initially exchanged from the resin.
- There are several different types of ion exchange resins. A strong-base anion exchange resin is best for removing arsenic. Ion exchange removals with strong-base resins is typically not sensitive to pH in the range of pH 6.5 to 9.0, so it is generally not necessary to adjust pH prior to using ion exchange for arsenic removal.
- The exchange affinity varies among anions in naturally occurring water. Therefore, the efficiency of the IX process for arsenic removal will vary depending upon the concentration of other anions, particularly sulfate, which is removed preferentially to arsenic.
- One of the primary concerns with using IX for arsenic removal, particularly with small systems, is the phenomenon known as chromatographic peaking. This can actually cause the arsenic concentration in the treated water to exceed that of the raw water.
- Influent water with high levels of sulfate is particularly prone to chromatographic peaking.



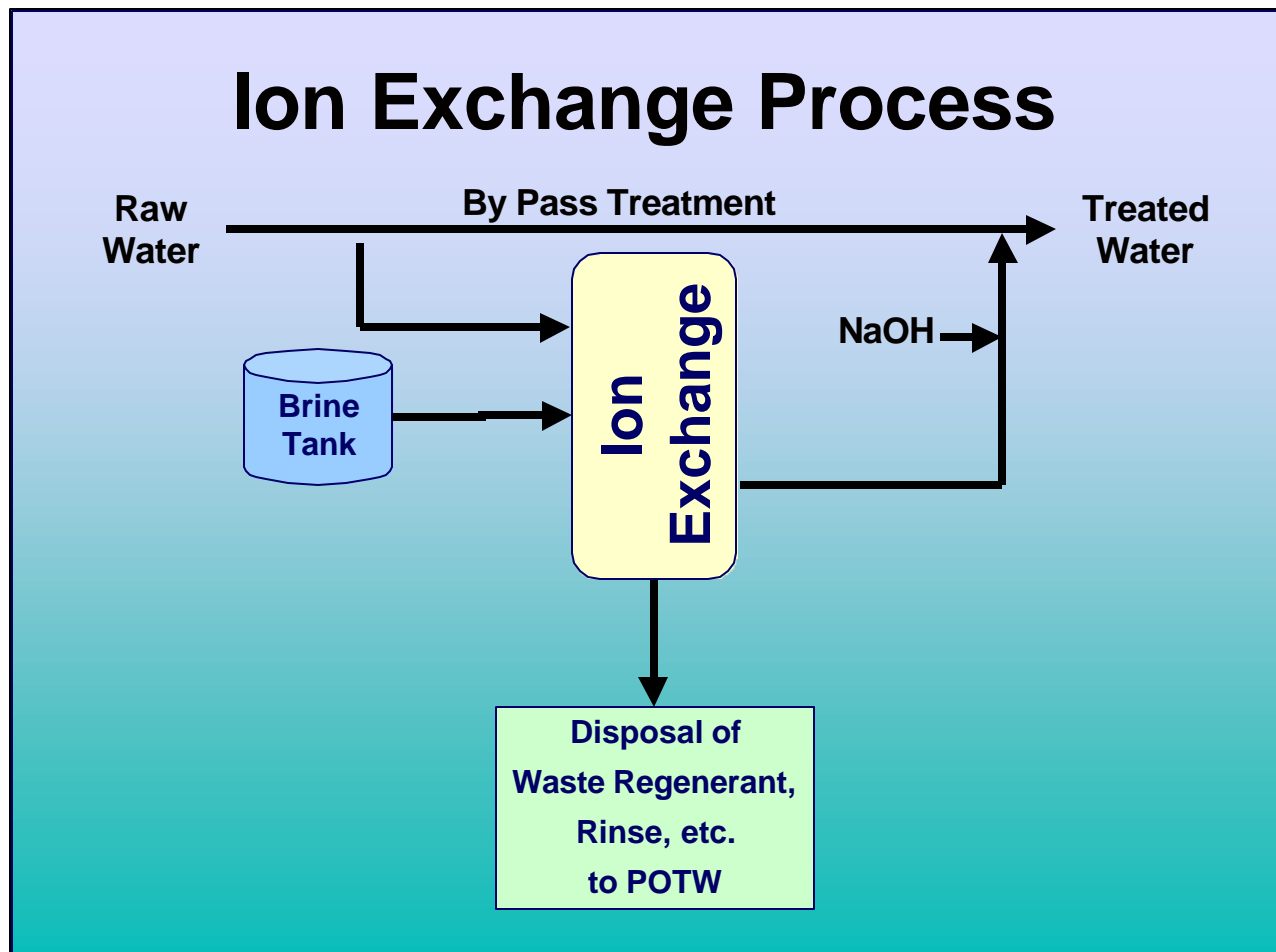
## Effect of Sulfate on Ion Exchange Performance



- This chart, which is from Clifford's work, shows how high levels of sulfate can dramatically decrease the capacity of ion exchange resins for arsenic, resulting in a shortened period of time before exhaustion.
- Ion exchange is recommended for water systems with sulfate concentrations in the influent water less than 50 mg/L.



- The ion exchange process involves passing water through a bed containing ion exchange resin. After the process pH adjustment may be necessary.
- Exhausted resins can be regenerated using a three step process:
  1. Backwashing for removal of particulates (may not be necessary if pre-filtration is in place);
  2. Passing a brine rinse through the resin; and,
  3. Performing a final rinse.
- Typically 3 to 5 bed volumes of brine waste are produced per regeneration. The brine stream may be recycled for further use, as in this diagram, but this will further concentrate arsenic in the stream and make disposal difficult unless arsenic is first removed from the brine.
- Only large water systems are likely to reuse brine.



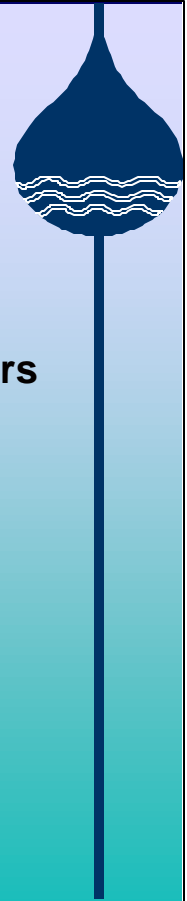
- Small systems are much more likely to dispose brine directly to a POTW instead of recycling it.
- The ion exchange process can be modified in two ways:
  - Advanced IX Operations: Two ion exchange columns are used in series. Arsenic is eluted from the upstream column and passed through the second column in a rotating process. The goal is to keep minimal amounts of arsenic from entering the finished water or the brine. Because arsenic levels in influent water are very low (parts per billion), this process can be repeated for many cycles.
  - Indefinite Brine Recycling: Barium chloride is added to the brine at a 1:1 molar ratio to precipitate barite ( $\text{BaSO}_4$ ). This increases the chloride concentration of the brine stream and may allow the brine to be used indefinitely.

# Anion Exchange



- This photograph is of the anion treatment unit installed by a small community with nitrate problems. In the late 1980s, when the community installed a cation exchange treatment system for its nitrate problems, it also installed an anion exchange system. The system is still using the original resins.

# Ion Exchange



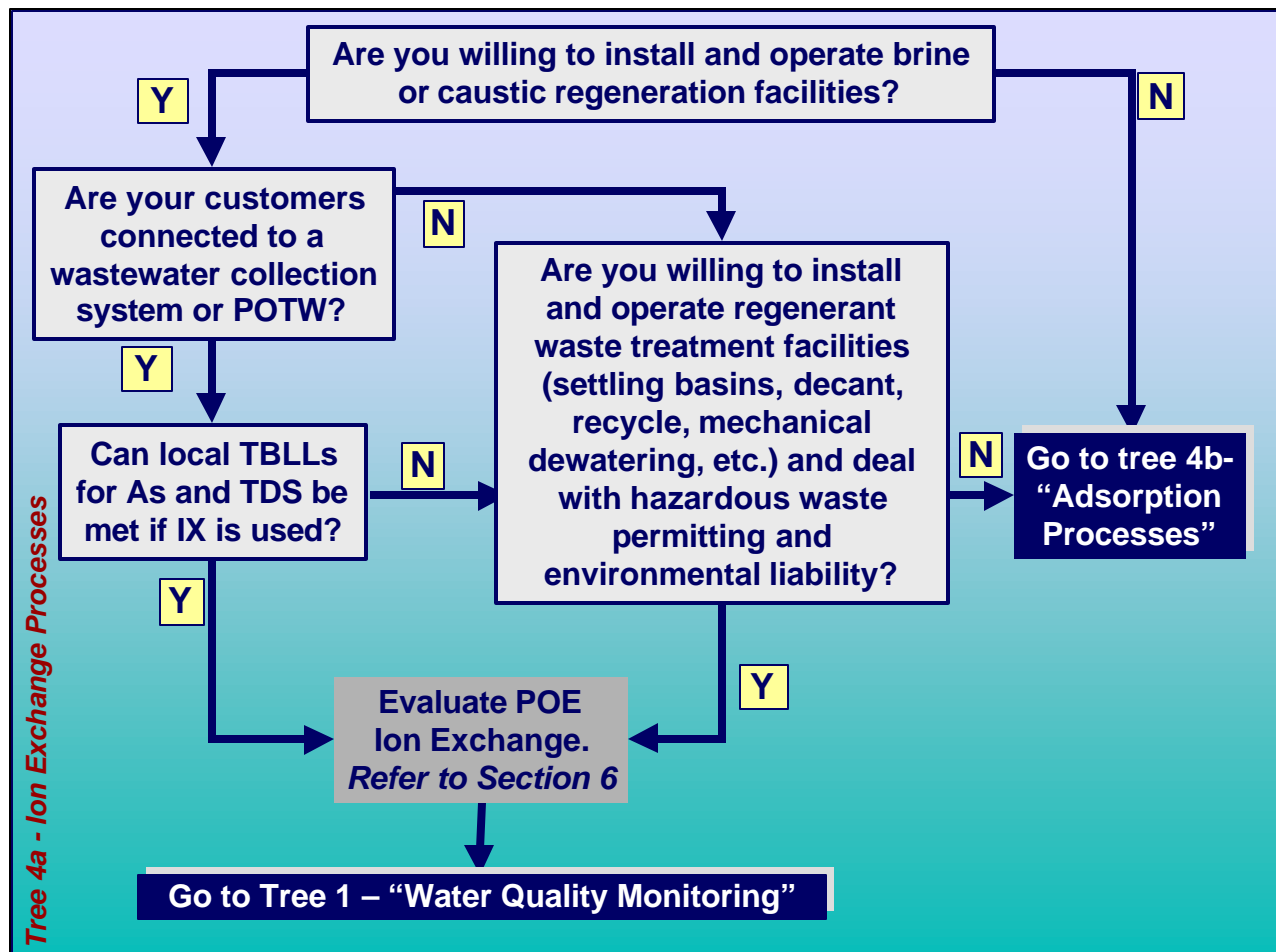
- **Pros**

- Operates on demand
- Short contact time (flow insensitive)
- Insensitive to pH over the range of natural waters
- Lower chemical requirement (except for NaCl) than for activated alumina (AA) or coagulation microfiltration
- Appropriate for small systems

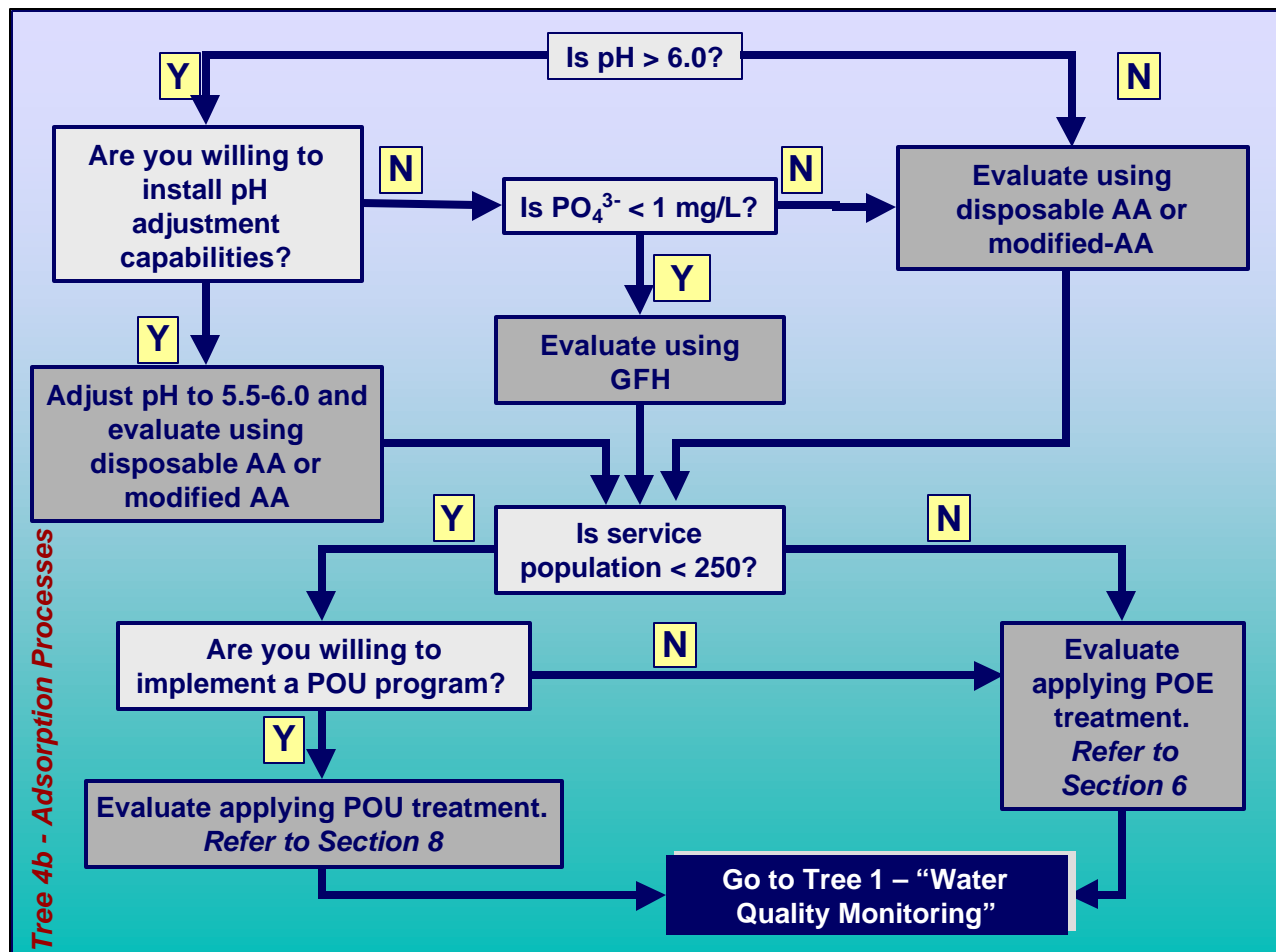
- **Cons**

- Large volumes of salt
- Sulfate can be a problem
- Finished water pH adjustment may be required
- Chromatographic peaking
- Large volumes of brine for disposal

- Benefits of ion exchange for arsenic removal include:
  - Ion exchange can operate on demand, instead of in continuous operation, so it can be used by hydropneumatic systems;
  - It requires a relatively short EBCT;
  - It performs optimally between pH 6.5 and 9, which is the range of natural water;
  - It has a lower chemical requirement (except for sodium chloride) than activated alumina or coagulation assisted membrane filtration; and,
  - It may be appropriate for small systems with access to a POTW.
- Drawbacks of ion exchange for arsenic removal include:
  - It requires large volumes of salt;
  - Sulfate competes with arsenic for adsorption sites, which may both limit run lengths and lead to chromatographic peaking;
  - Finished water pH adjustment may be required;
  - Chromatographic peaking of arsenic (caused by competition with sulfate) or nitrate and nitrite (caused by competition with both sulfate and arsenic) is possible; and,
  - Large volumes of brine, which may be hazardous, require disposal.



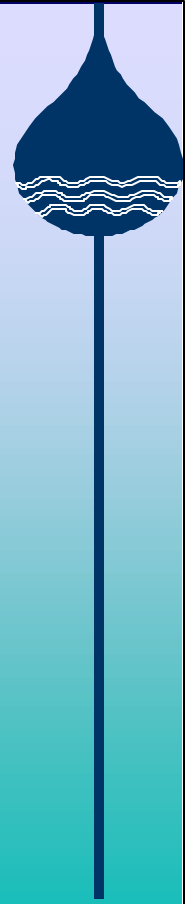
- Systems for which ion exchange is not feasible should investigate sorption processes. Sorption processes are likely to be the treatment of choice for many small systems.



- Activated alumina is most effective at low pH (below 6) and low phosphate concentrations (tentative cut-off established at 1 mg/L). There is a 30% reduction in adsorptive capacity for every 0.2 mg/L of phosphate above 0.4 mg/L, so 1 mg/L of phosphate represents an approximate 65% reduction at 1mg/L. If the source water has a pH above 6, the system is unwilling to install pH adjustment, and the concentration of phosphate is greater than 1 mg/L, the system should pilot granular ferric hydroxide (GFH).
- POU and POE treatments are options for small systems.

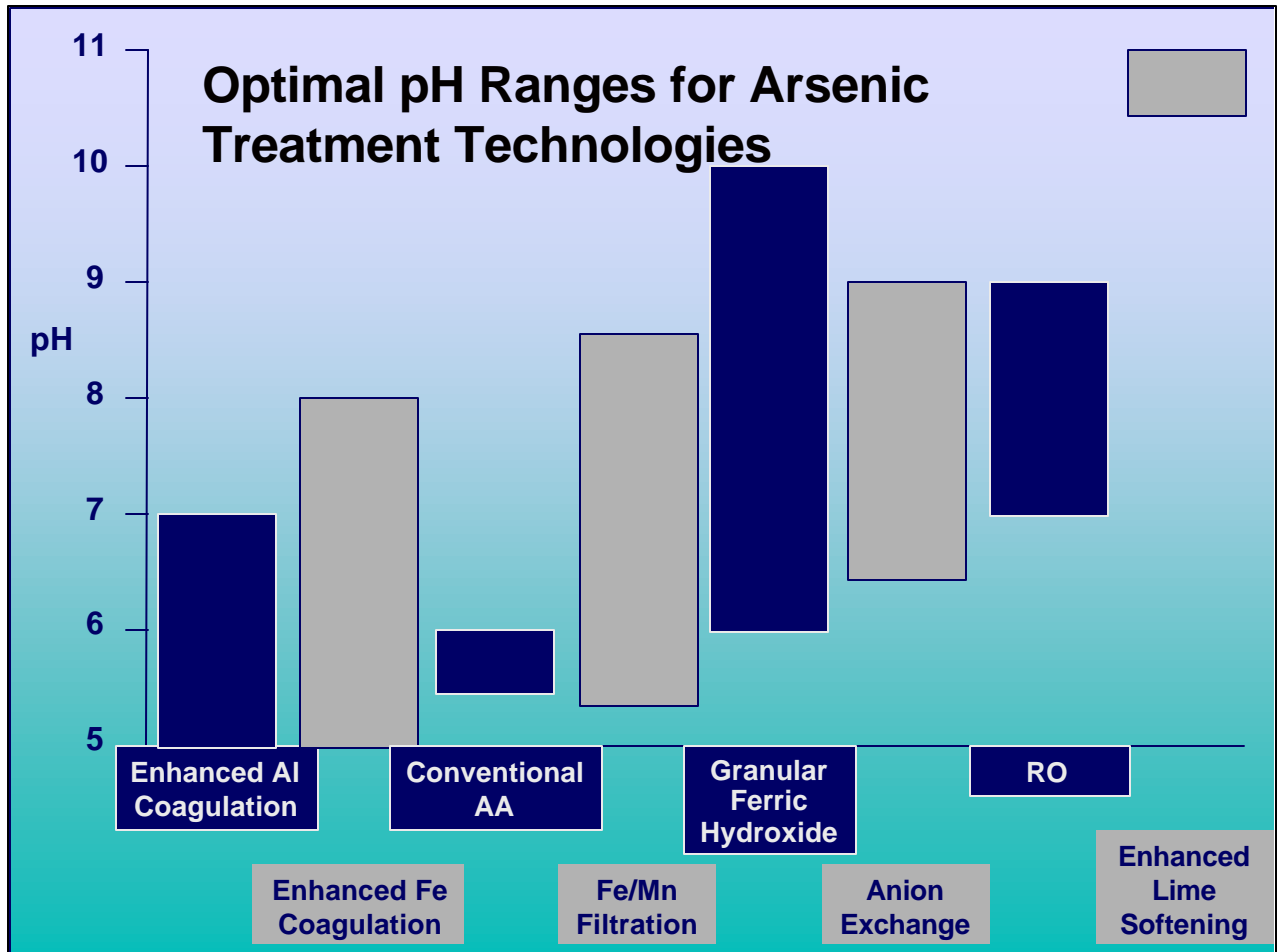
# Sorption Processes (Continued)

## Activated Alumina



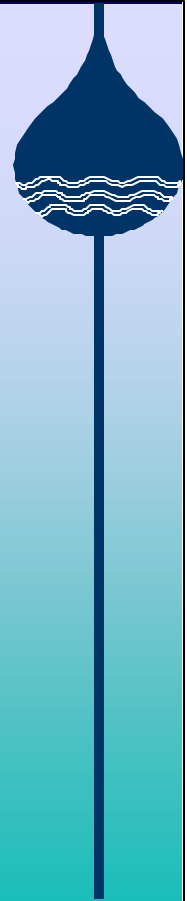
- Activated alumina, like ion exchange, is a sorption process. Ions in the feed water are adsorbed to the oxidized activated alumina surface.
- There are fewer competing ions for activated alumina, and chromatographic peaking does not occur, but arsenic still faces some competing ions with activated alumina.
- Small systems will probably use activated alumina on a throw-away basis (i.e., with no regeneration). Large systems may be more willing to handle the concentrated acids and waste products that regeneration entails.



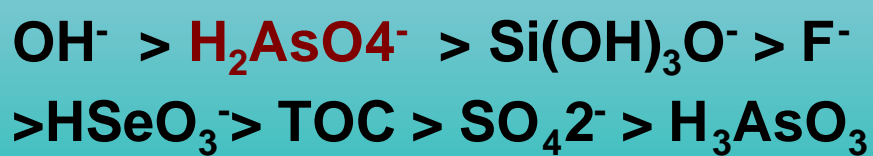


- Activated alumina works best between pH 5.5 and 6, but it can be modified to work at a higher pH and still be cost-effective.

# Activated Alumina

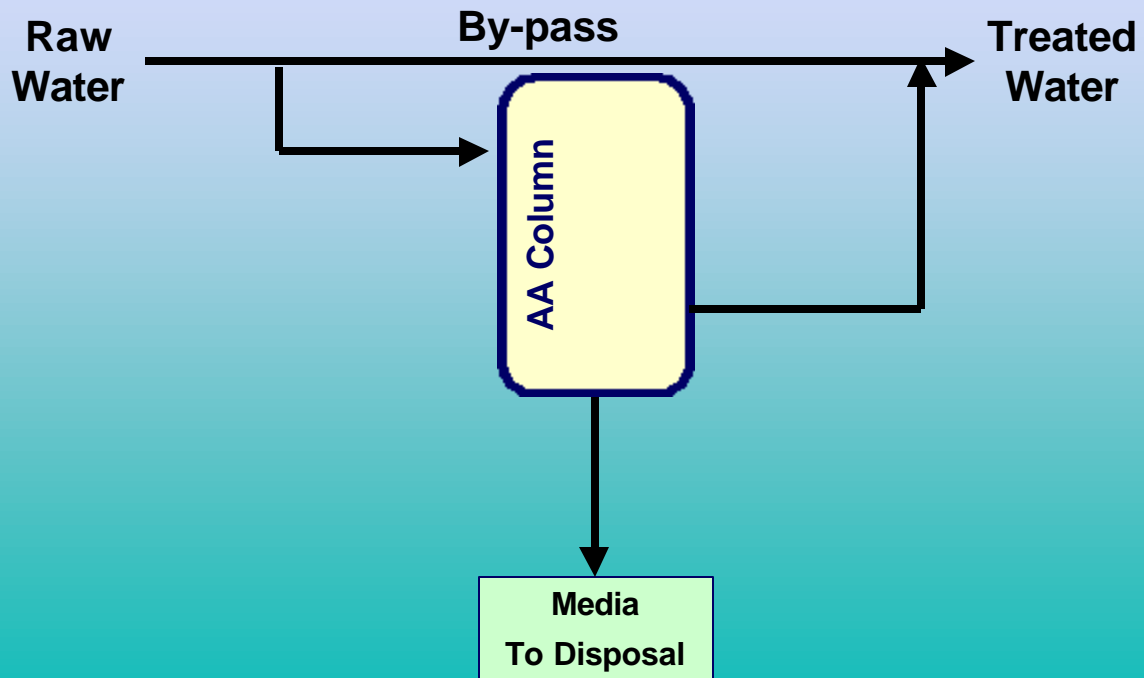


- Porous granular media (aluminum trioxide) with ion exchange properties
- Competing ions

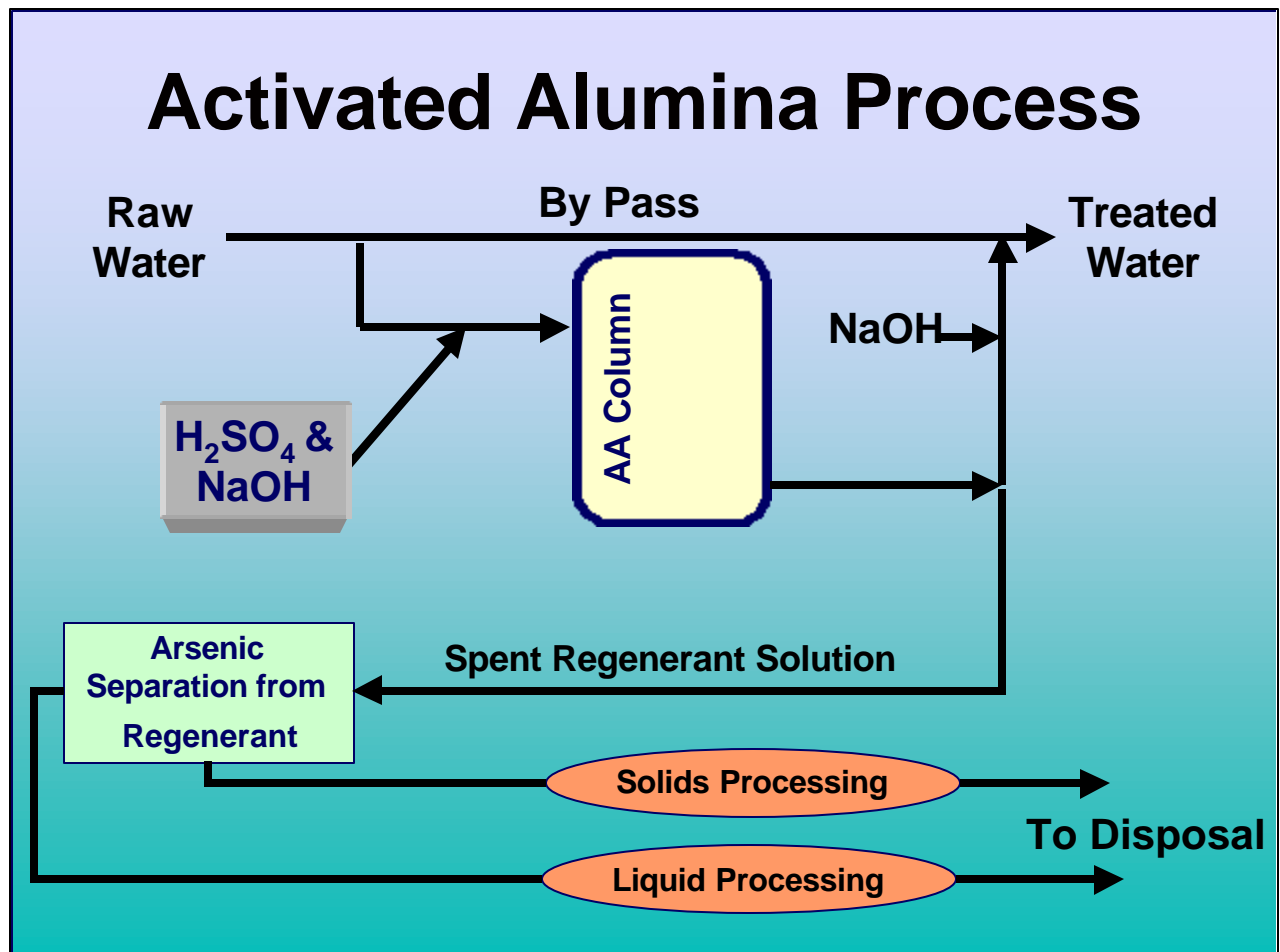


- Activated alumina has typically been used as a technology for fluoride removal. It is used in packed beds. Feed water is continuously passed through the bed to remove contaminants, including arsenic, which are exchanged with surface hydroxides on the alumina.
- When the media is exhausted, it may be regenerated through a sequence of rinsing with regenerant (typically a concentrated solution of sodium hydroxide), flushing with water, and neutralizing with a strong acid (typically sulfuric acid). However, many small systems may find disposable activated alumina a cost-effective option.
- The selectivity sequence for activated alumina is shown. Levels of competing ions impact the performance of activated alumina but not in the same manner or to the same extent as ion exchange. Note that the hydroxide ion is the only molecule preferentially adsorbed to arsenate.
- Activated alumina can operate on demand, which makes it an option for hydropneumatic systems.

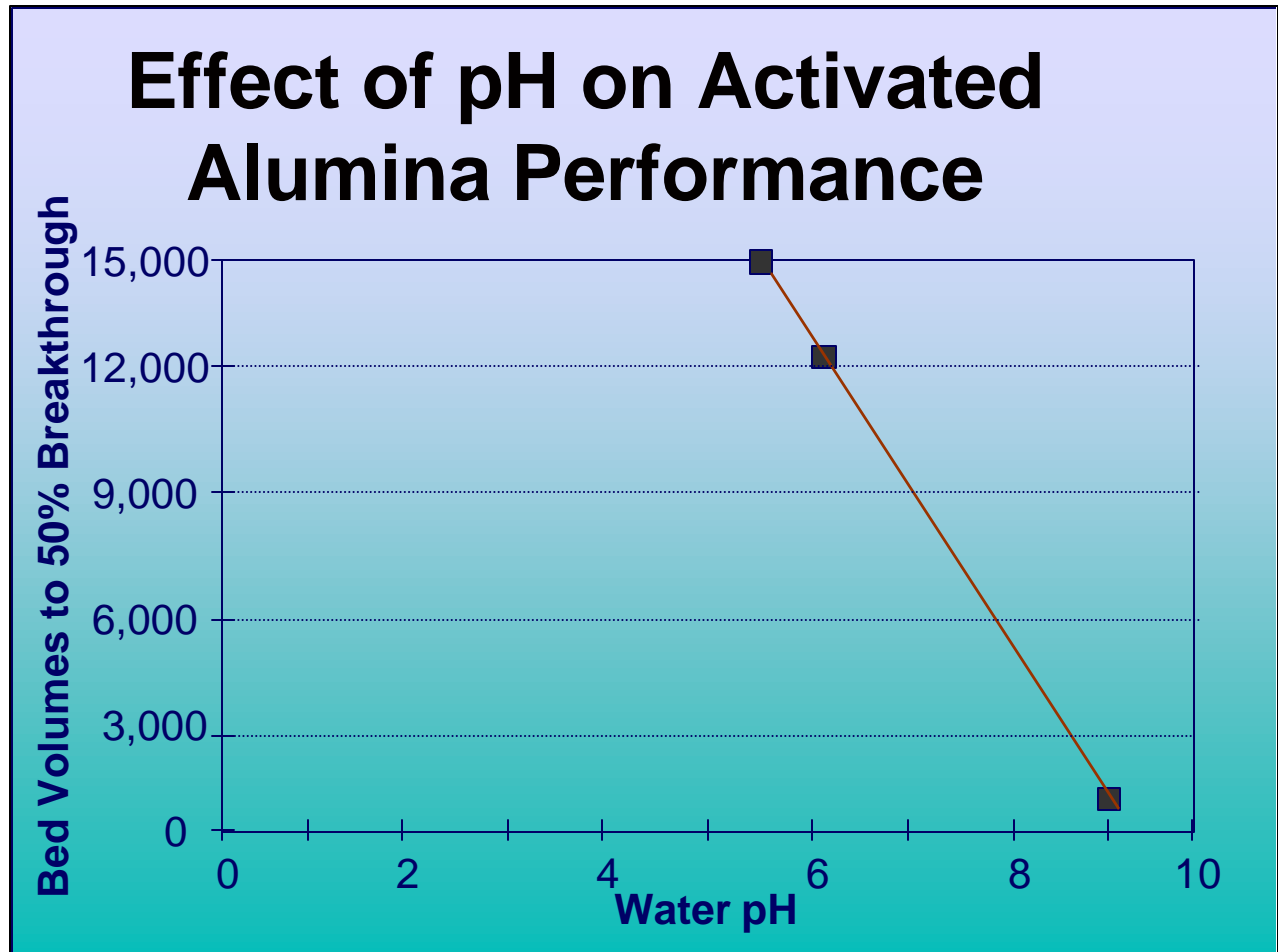
# Activated Alumina Process (Throw-Away)



- Activated alumina can be regenerated. Many small systems, however, will probably operate it on a throw-away basis.
- When operated as a throw-away process, the activated alumina bed is used to exhaustion, the media is disposed, and fresh media is installed. This method does not require strong acids or bases to be handled or stored.



- Alternatively, activated alumina can be regenerated.
- In this mode of operation, the activated alumina bed is used to exhaustion. Prior to regeneration the exhausted column must be backwashed to remove entrained particles, break up clumps of alumina, and reclassify the media to eliminate channeling and packing.
- Following the 5 - 10 minute backwash, a two-step regeneration is practiced:
  1. NaOH is added to replace the arsenic ions with hydroxide ions ( $\text{OH}^-$ ); and,
  2. Sulfuric acid is added to neutralize the media.
- A slow rinse follows to displace the regenerant and conserve chemicals.
- Total waste water is about 4% of the blended product water.
- Spent regenerant may be discharged to a POTW if it meets the TBLLs. If arsenic levels in the regenerant are too high for disposal, water systems may be able to use intermediate processing to remove arsenic from the regenerant prior to disposal. The concentrated arsenic may then be disposed of separately as solid waste.
- Regeneration is probably not appropriate for small systems. In addition to handling strong acids and bases, the system will need to manage waste disposal issues.
- Finally, a percentage of the activated alumina media dissolves during each regeneration cycle and must be replaced.



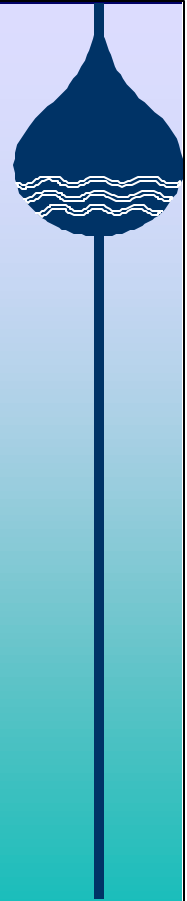
- pH has a strong influence on activated alumina performance.
- A pH of 8.2 is significant because it is the “zero point charge” for activated alumina.
- Below this pH, activated alumina has a net positive charge resulting in a preference for adsorption of anions, including arsenic.
- Acidic pH levels are generally considered optimum for arsenic removal with activated alumina.
- This chart shows that the capacity of activated alumina (as measured by the number of bed volumes before arsenic removal decreases below 50%) decreases linearly and sharply from a pH of 5.5-6 to a pH of 9 (S.W. Hathaway and F. Rubel, Jr., 1987, Removing Arsenic from Drinking Water, *J. AWWA* 79(8):61-65).

## Water Quality Interferences with Activated Alumina Adsorption

Parameter	Problem Level
<b>Chloride</b>	<b>250 mg/L</b>
<b>Fluoride</b>	<b>2 mg/L</b>
<b>Silica</b>	<b>50 mg/L</b>
<b>Iron</b>	<b>0.5 mg/L</b>
<b>Manganese</b>	<b>0.05 mg/L</b>
<b>Sulfate</b>	<b>720 mg/L</b>
<b>Dissolved Organic Carbon</b>	<b>4 mg/L</b>
<b>Total Dissolved Solids</b>	<b>1,000 mg/L</b>

- Several constituents of water can interfere with the arsenic removal process by competing for adsorption sites or clogging the media with particulates. This chart shows some of the most widely recognized water quality parameters that interfere with arsenic removal and the level above which they are often problematic.
- There are several emerging varieties of proprietary activated alumina media, which are commonly referred to as “modified AA.” They typically have been modified with iron or in other ways improve the adsorptive capacities and/or strengthen the affinity for arsenic. Many of these media can achieve high arsenic removal in the presence of interfering substances and in high pH conditions.

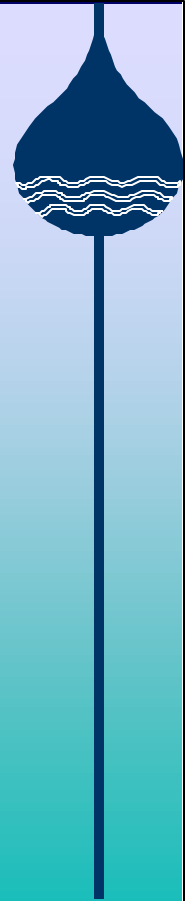
# Activated Alumina



- **Pros**
  - Operates on demand
  - Relatively insensitive to TDS and sulfate
  - High quality finished water possible
  - Highly selective for arsenic and fluoride
  - Disposable media option
  - Affordable

- Benefits of activated alumina for arsenic removal include:
  - Activated alumina can be operated on demand and therefore used by hydropneumatic systems;
  - Activated alumina is relatively insensitive to TDS and sulfate, which can be problematic for anion exchange;
  - Activated alumina is capable of achieving high arsenic removal percentages;
  - Activated alumina is highly selective for arsenic and fluoride and does not exhibit chromatographic peaking;
  - Systems may use activated alumina on a disposable basis, avoiding caustic management and waste disposal issues; and,
  - Activated alumina may be affordable for small and large systems.
- When using activated alumina on a throw-away basis, small systems are likely to operate two or more beds in series to allow the complete exhaustion of the first bed, maximizing the investment in that media, while limiting the amount of arsenic in the finished water with the second column, which is commonly known as a guard column.

# Activated Alumina



- **Cons**
  - **Regeneration**
    - **Both acid and base required**
    - **Causes loss of removal efficiency**
    - **Produces significant volume of spent regenerant**
  - **Pre- and post-pH adjustment**
  - **Media tend to dissolve**
  - **Slow adsorption kinetics**
  - **Removes fluoride**
  - **Waste disposal**

- Drawbacks of activated alumina for arsenic removal include:
  - Regeneration is probably not suitable for small systems, making it likely to be used by small systems as a throw-away option. Regeneration is difficult because:
    - Regeneration requires both a strong acid and a strong base, which are difficult and potentially dangerous to manage and use;
    - Regeneration decreases removal efficiency and results in the loss of media;
    - The regeneration process results in a significant volume of spent regenerant, which may be difficult to dispose without intermediate processing.
  - Activated alumina is most effective at low pH, so pH adjustment before and after the treatment process may be necessary;
  - Media dissolves over time and is therefore not available for arsenic removal. Media dissolution is increased by regeneration.
  - The slow adsorption kinetics of arsenic to activated alumina necessitate a relatively long EBCT, which increases the amount of media necessary to treat a given flow of water.
  - Activated alumina removes fluoride, which at low levels may reduce cavity formation.
  - The generation of arsenic-containing residuals that must be disposed.



# Emerging Disposable Media

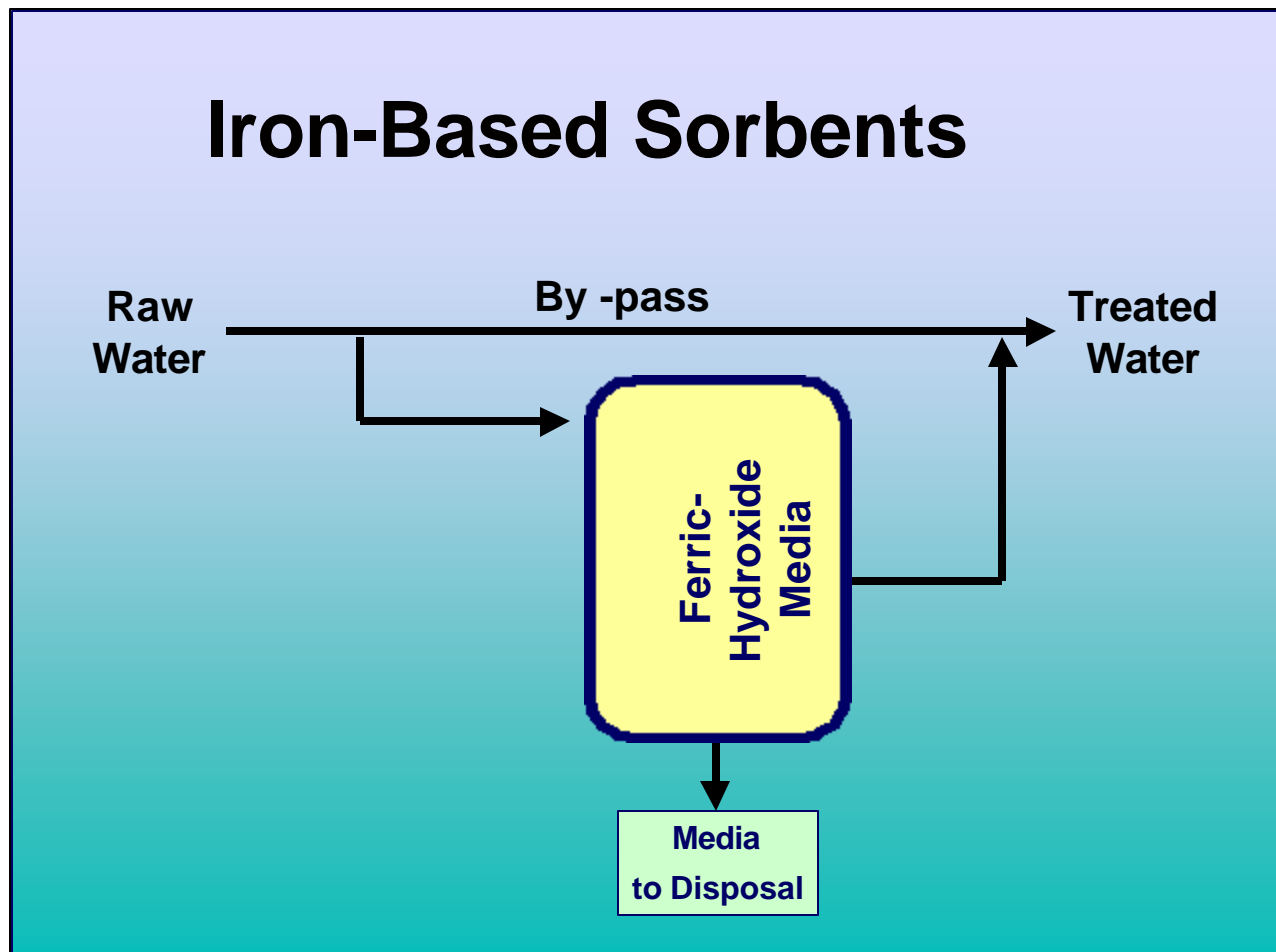


- **Conventional AA**
- **Iron-Modified AA**
- **High Porosity AA**
- **Proprietary AA**
- **Granular Ferric Hydroxide**

- **High As removal at natural pH**
- **Disposable; no regeneration required**
- **No hazardous wastes produced**
- **NSF 61 certified**

- There are several emerging adsorptive media that are currently being tested. In addition to conventional activated alumina, these media include:
  - Iron-modified activated alumina;
  - High porosity activated alumina;
  - Proprietary activated alumina; and,
  - Granular ferric hydroxide.
- To be successful, the media should meet the following criteria:
  - The media has a high capacity to adsorb arsenic at a neutral pH, so upstream pH adjustment is not required;
  - The media is disposable with no on-site regeneration required;
  - The spent media is non-hazardous; and,
  - The media has been certified to NSF standard 61, “Drinking Water System Components - Health Effects.”
- The photograph shows an outdoor pilot testing system used in Scottsdale, Arizona. Four media were pilot tested simultaneously: ion exchange, iron-modified activated alumina, high porosity activated alumina, and granular ferric hydroxide.

# Iron-Based Sorbents



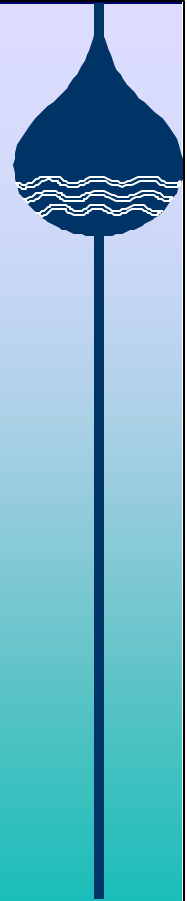
- Most small systems are likely to use iron-based sorbents in this configuration
- The affinity of iron-based sorbents is strong for arsenic under pH conditions of natural waters. Therefore, it may be possible for the media to treat much more water (i.e., a much greater number of bed volumes) before exhaustion without pH adjustment.
- Similarly to activated alumina, an EBCT of 5 minutes and a loading rate of 5 GPM per square foot are recommended.
- Phosphate may compete aggressively with arsenate for adsorption sites.
- Exhausted media has passed the TCLP test, so non-hazardous disposal may be possible (although systems must make sure to appropriately test their own wastes).

# Pilot Testing



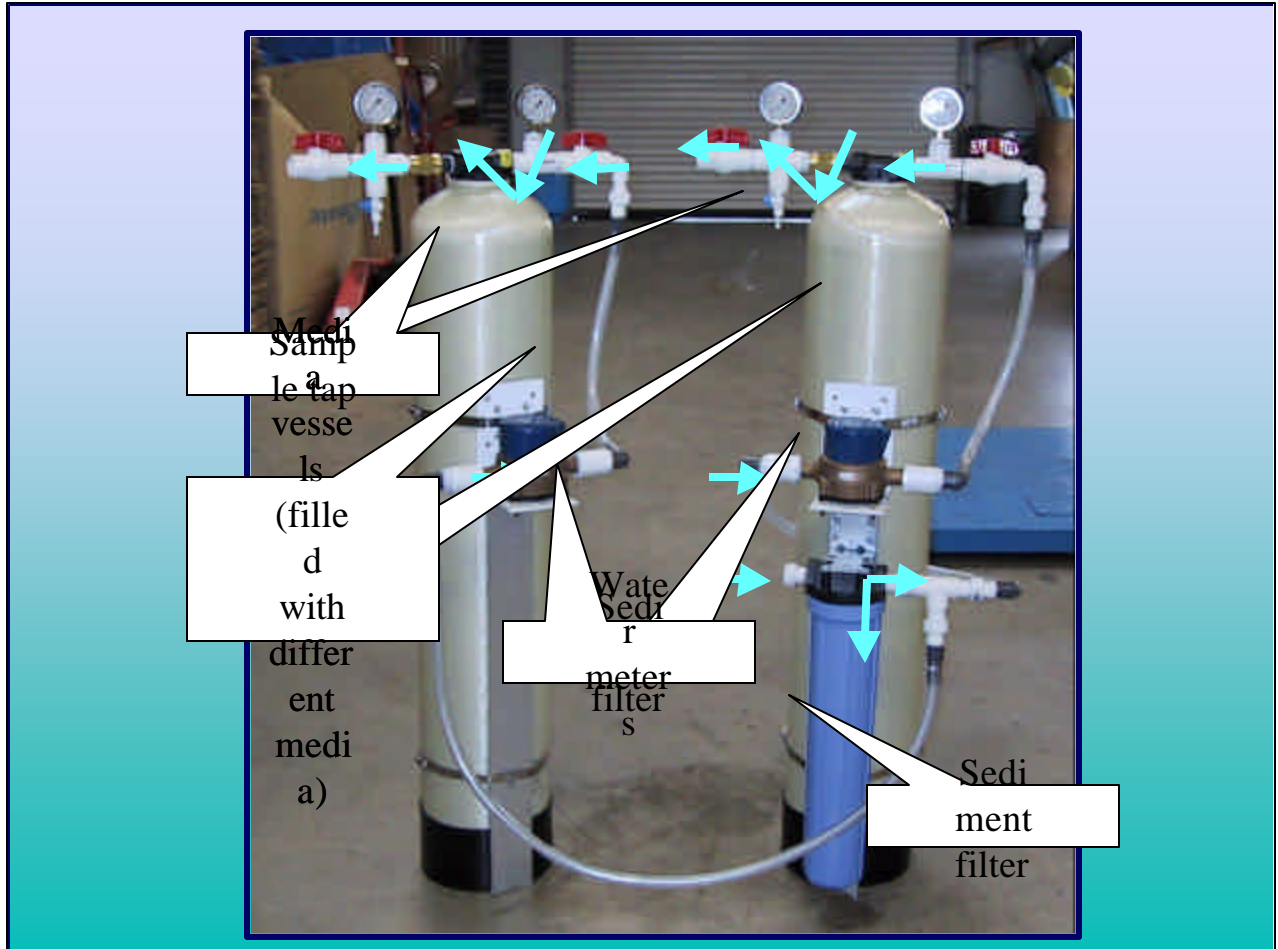
- Pilot testing is highly recommended prior to the final selection and installation of arsenic treatment. System-specific water quality and challenges can impact the suitability of treatment technologies.
- This is a pilot testing unit installed in Scottsdale, Arizona. Four media were pilot tested simultaneously: ion exchange, iron-modified activated alumina, high porosity activated alumina, and granular ferric hydroxide. The vessels were supplied by Severn Trent.

# Pilot Testing – Scottsdale

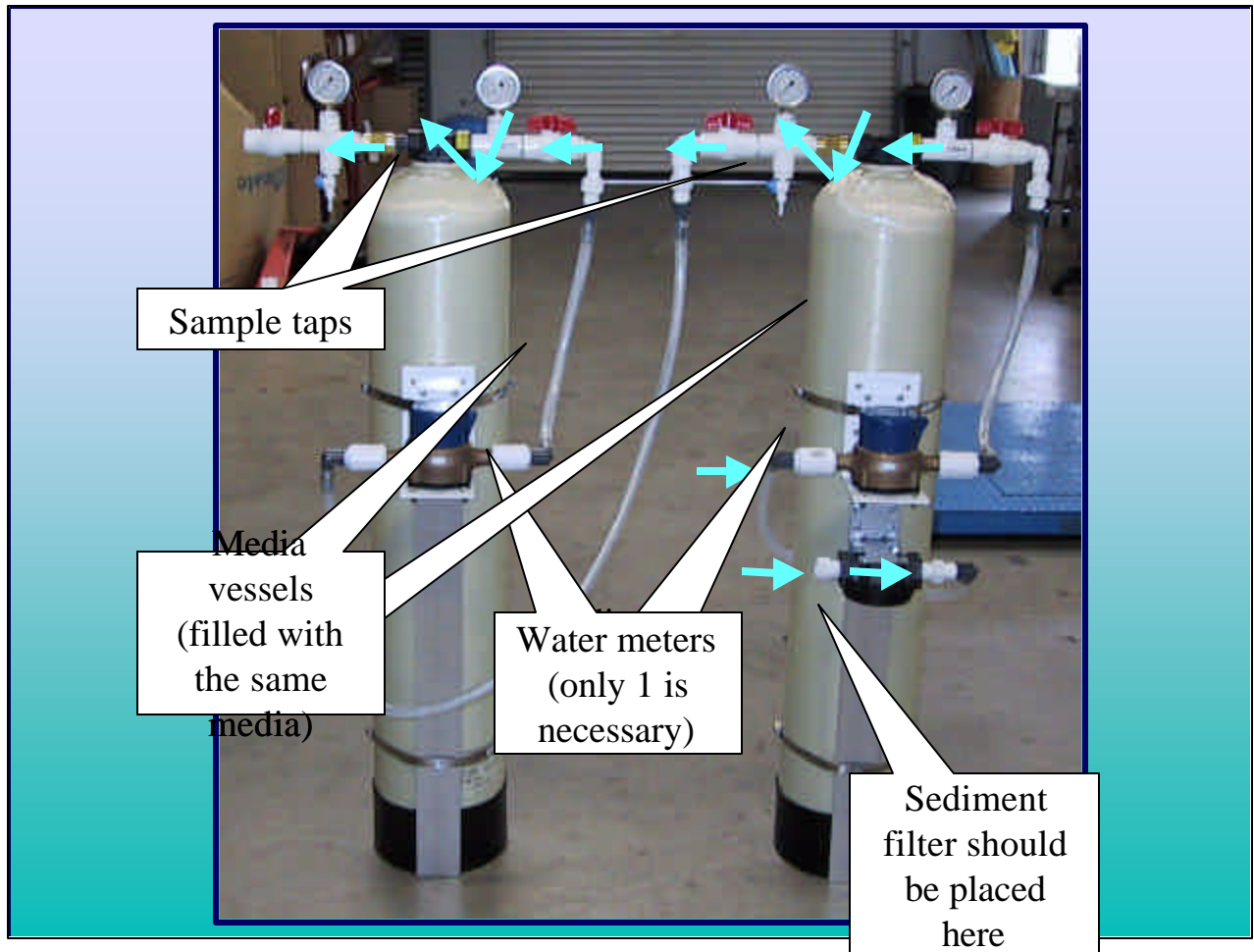


- **High water temperature caused problems with ion exchange (IX) testing**
  - Scaling of control system
- **All media become more effective as pH approaches 6.0**
- **Guard columns needed**
  - Unpredictable peaks with pH excursions
- **AA > MCL**
  - 72,000 bed volumes
- **GFH near non-detection**
  - > 62,000 bed volumes

- Pilot testing of the four media in Scottsdale led to several interesting observations that will be used in the selection of full-scale treatment:
  - The ion exchange unit was recalled to HDR's lab in December 2001. The Scottsdale water temperature was higher than that of the water used for bench scale testing. The higher temperature caused unexpected barium sulfate scaling of the control mechanism and resulted in insufficient control of the pilot testing process.
  - Generally, all the adsorptive media seem to be more effective as they move toward raw water pH of 6.0. This means, for best removal, pH would normally have to be adjusted at the front and back ends of treatment. The experimenters at Scottsdale plan to test at pH 7.0 (some natural waters are at this pH) and pH 6.0, which would require pH adjustment.
  - Guard columns are likely to be needed. For example, an excursion in pH to 8.0 caused raw water spikes of up to 0.083 mg/L even from the granular ferric hydroxide, which is three or four times raw water concentrations. Clearly, flow pacing of pH control needs to be in place.
  - The water treated with activated alumina exceeded the MCL by 72,000 bed volumes.
  - Granular ferric hydroxide is produced in Germany and shipped to North America wet. The granular ferric hydroxide unit has treated more than 62,000 bed volumes and is still near no detect.

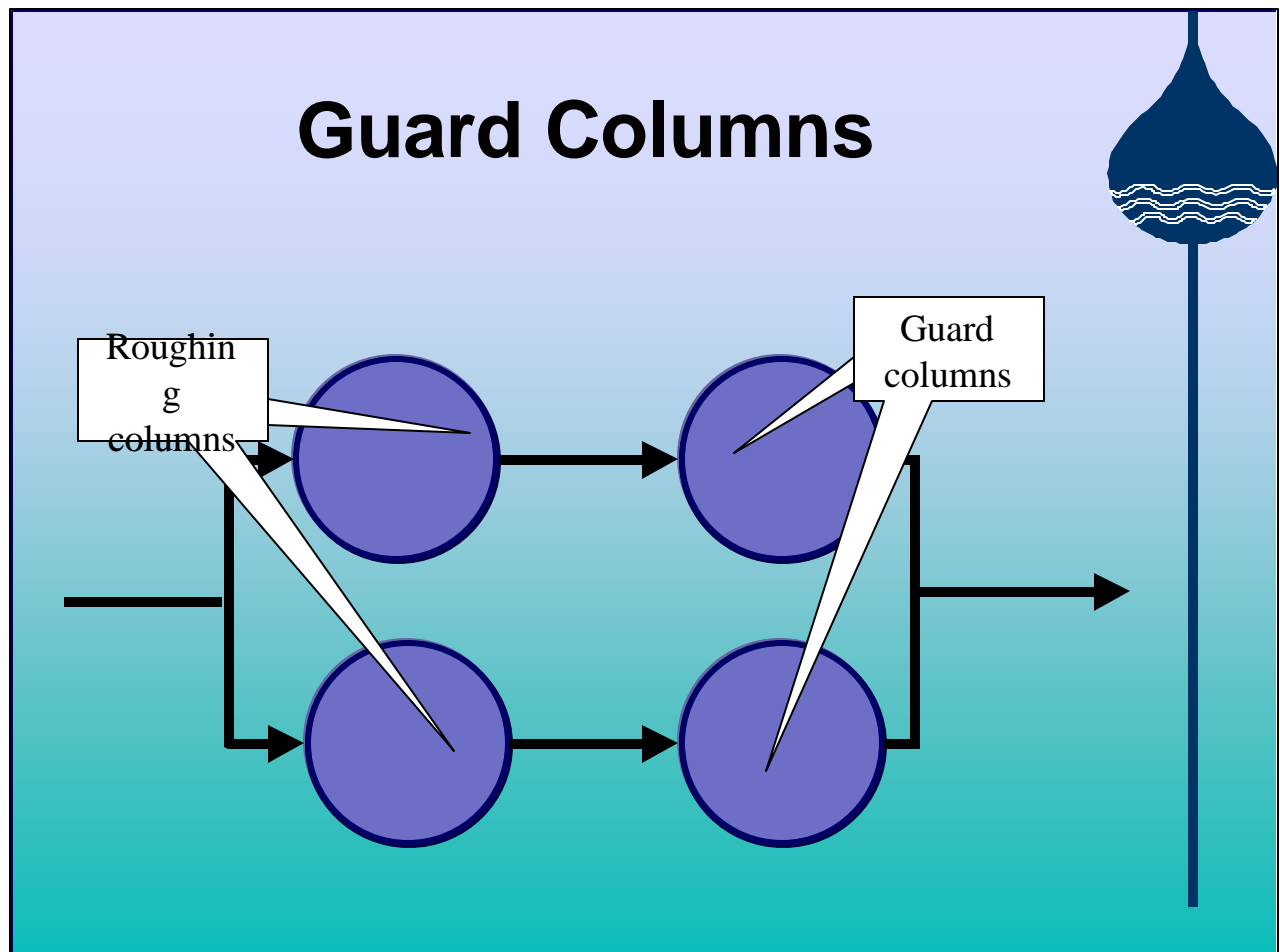


- This photograph shows a small treatment plant that can be used for pilot testing or for treatment in a small water system.
- This photograph shows the vessels aligned for parallel treatment, which would be used for pilot testing. Water enters through the sediment filter (in the blue canister) and is split into two streams. Each stream passes through a flow meter, through media, and by a sample tap. This treated water can then be distributed or run to waste. This set-up allows two different media to be tested: the effluent from each can be analyzed separately and compared.



- This photograph shows the vessels aligned for treatment in series, which would be used for actual treatment. Water passes through the sediment filter, through a flow meter, through media, by a sample tap, through more media of the same type, and by another sample tap. This treated water can then be distributed. The second flow meter in the set-up above is unnecessary. This set-up provides a roughing and guard column to ensure the effective utilization of the media while providing safe drinking water to consumers.





- It is recommended that systems using adsorptive media operate at least two tanks in series. If there are multiple treatment trains (for example, there are two in the illustration shown), then there should be at least two tanks in series in each train. The first tank is called the roughing column. The second is called the guard or polishing column.
- These columns are operated in rotation with a third column. When the roughing column is exhausted, it is removed from the sequence, the guard column becomes the roughing column, and a different vessel with new media becomes the guard column. The media in the exhausted roughing column is then replaced with fresh media and will become the guard column in the next cycle. The units will usually be designed with a series of valves so that the tanks do not have to be physically switched, although cross-connection issues should be taken into account.
- Samples are taken from both between the two vessels and from after the second vessel. The level of arsenic samples between the two vessels indicates when the first column is becoming exhausted and should be changed out. Pilot testing should be used to gauge the typical length of time necessary for exhaustion to occur.
- The guard column ensures that, even if the concentration of arsenic in the water after the first column exceeds the MCL, the treated water after the guard column is below the MCL. There are two reasons why this is useful:
  - There is a danger of chromatographic peaking (i.e., the production of water with a contaminant concentration that exceeds the influent concentration) with any type of adsorptive media. Activated alumina and granular ferric hydroxide are less prone to chromatographic peaking than ion exchange, but there is still a danger.
  - Having the second column in place allows the use of the media in each column to be maximized. By running the first column to near complete exhaustion (i.e., to producing water near the influent concentration), the water system can ensure that all of its capacity is used prior to disposal. The guard column is then in place to ensure that enough arsenic is removed before the water enters the distribution system.

## Scottsdale Well

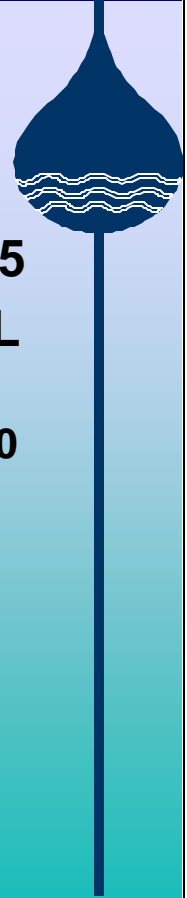
- High pH and silica caused poor performance
- Slight pH reduction improved GFH more than AA
- With pH of 6.5m, GFH > 60,000 bed volumes

Parameter	(mg/L)
Arsenic	0.031 to 0.041
Fluoride	1.3
Hardness	31
Iron	0.5
Manganese	<0.010
Nitrate	2
Orthophosphate	
pH	8.7 to 9.2
Silica (as SiO <sub>2</sub> )	25.3
Sulfate	23
Alkalinity	120
TDS	370

- pH control proved to be critical to the water quality parameters faced by the Scottsdale system. Here the raw water pH, after chlorination, ranged from 8.7 to 9.2. Silica was between 24.4 and 27.6 mg/L. A ten micron cartridge filter provided pre-treatment to keep sand out of the media.
- The granular ferric hydroxide and both activated alumina media performed worse than expected due to high pH and silica. The granular ferric hydroxide only treated approximately 3,500 bed volumes at the natural pH before exhaustion. These media are therefore not feasible at Scottsdale without pH adjustment.
- After pH adjustment, the activated alumina and high-porosity activated alumina media had similar capacities. Iron-modified activated alumina performed better, and granular ferric hydroxide performed the best. The granular ferric hydroxide costs three times as much, delivered, as the iron-modified activated alumina. Therefore, even though it may not perform as well, iron-based activated alumina may be more cost-effective at some locations. A cost analysis would have to be done at each site.
- The Scottsdale system had problems with the pH feed and ensuring a stable pH.
- A slight pH adjustment had a greater beneficial effect on the performance of granular ferric hydroxide than on activated alumina. After adjusting the pH to about 6.5, the granular ferric hydroxide was able to treat more than 60,000 bed volumes.
  - The columns used in the Scottsdale pilot test were set up in the following arrangement:



# Tucson



- **pH**      **7.2 – 7.5**
- **Silica**    **34 mg/L**
  - **GFH still under MCL after 70,000 bed volumes**

- System operators in Tucson, Arizona, have also pilot tested adsorptive media for arsenic removal.
- The granular ferric hydroxide media cost about three times as much, delivered, as the activated alumina.
- The pH varied between 7.2 and 7.5 and the concentration of silica in the raw water was about 34 mg/L.
- The granular ferric hydroxide was still producing effluent water with arsenic concentrations below the MCL after 70,000 bed volumes.

# Century Well – Full Scale

- **Head Space?**
  - Capital cost reduction
- **4' Diameter X 5' High**
  - 50 gpm currently with 5 minutes EBCT
    - (32" of media)
  - Up to 90 gpm
- **\$0.5 Million**
  - (Mn removal, office, storage, etc.)
- **\$10 – 20,000 for a single vessel**



- The Century full-scale pilot test in Paramount, California is being used to evaluate the performance of four media: three activated aluminas and granular ferric hydroxide.
- Traditional wisdom suggests that headspace is needed for media expansion during backwash, and accordingly the vessels were only filled two-thirds with media. Backwashing does not, however, appear to be necessary or desirable with the media used here when used on a throw-away basis. Therefore, it seems reasonable that more media can be loaded into the vessels. This should reduce capital costs per unit volume produced.
- The columns are 4 feet in diameter and 5 feet high, hold about 450 gallons of media, and provide an EBCT of 5 minutes at up to 90 gallons per minute. Currently, only 32 inches of media is used, which provides 50 gallons per minute.
- Granular ferric hydroxide has performed the best at this site. The raw water pH is 7.8 to 7.9, and granular ferric hydroxide appears to be better at higher pH than the activated aluminas. The next phase of the pilot test will occur after granular ferric hydroxide exhaustion, when the pH will be adjusted to 7.0. It is anticipated that the use of one 55 gallon barrel of sulfuric acid every two days will be required for pH adjustment.
- The existing piloting system cost about \$500,000, including manganese removal treatment, an office, a storage building, etc. Each vessel costs between \$10,000 and \$20,000.

## Century Well

Arsenic still below MCL after >30,000 bed volumes

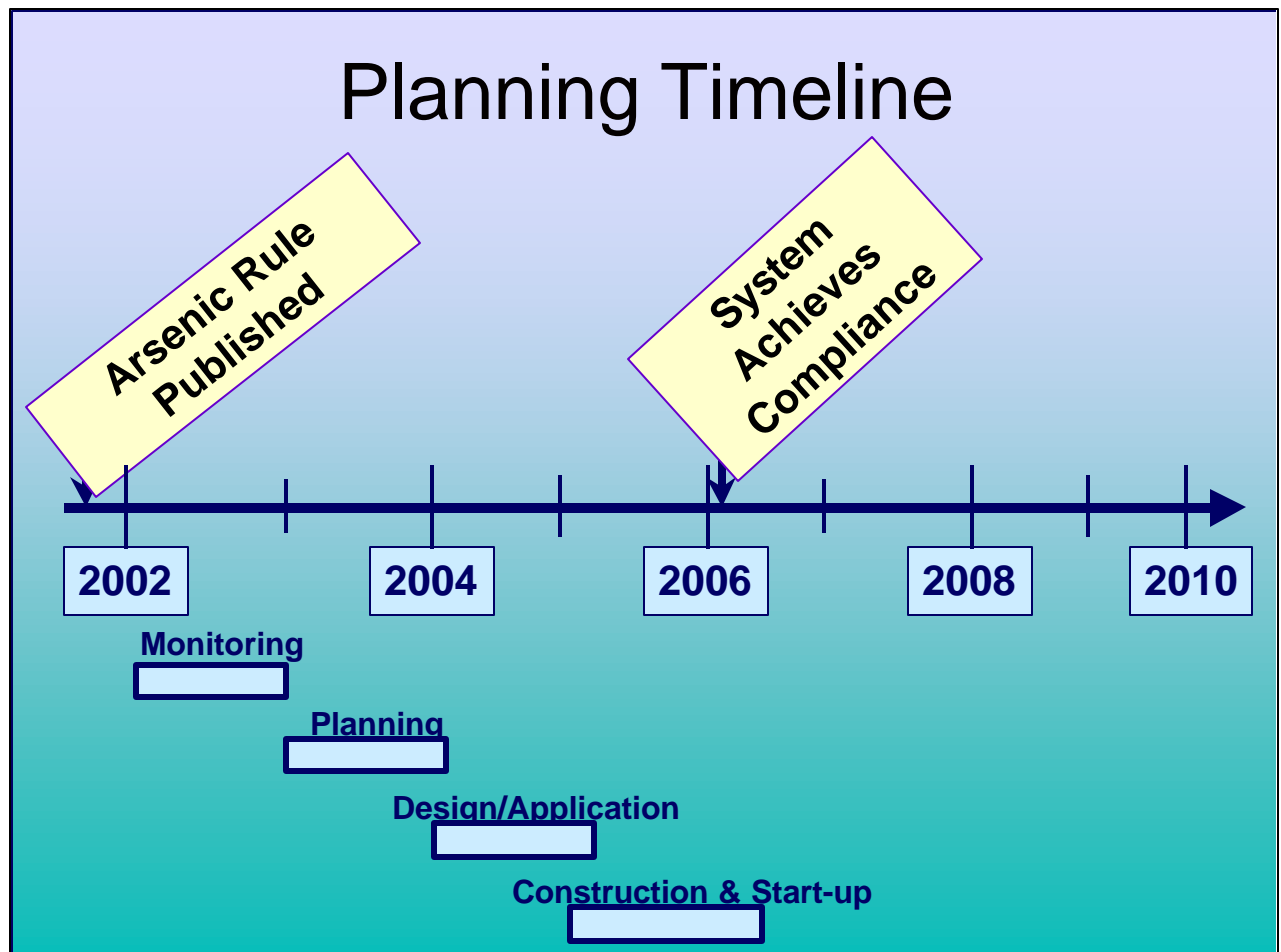
GFH seems to be more attractive with high pH & silica

*But*

GFH 3 times the cost delivered

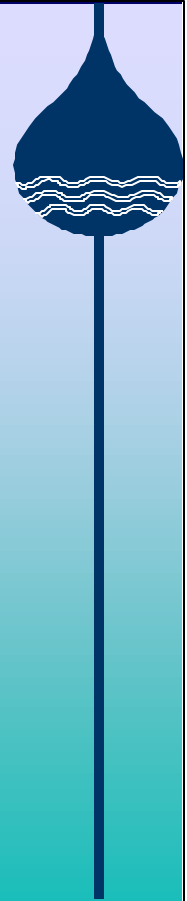
Parameter	(mg/L)
Arsenic	0.015 to 0.020
Fluoride	0.27
Hardness	210
Iron	0.011
Manganese	0.144
Nitrate	
Orthophosphate	
pH	7.6 to 8.0
Silica (as SiO <sub>2</sub> )	20.5
Sulfate	60
Alkalinity (CaCO <sub>3</sub> )	195
TDS	368

- The manganese concentration in the source water is quite high at the Century well in California (0.144 mg/L) and is being removed prior to arsenic removal by four Pyrolusite pressure vessels in parallel.
- The arsenic concentration from the granular ferric hydroxide is still well below 0.010 mg/L after more than 60,000 bed volumes. Again, the high pH and silica seem to make the granular ferric hydroxide more attractive than the activated alumina. After the granular ferric hydroxide vessel starts producing finished water above the MCL, a reduction in pH is planned for the duration of the study.



- Systems need to leave time for pilot testing when planning how to meet the revised arsenic MCL by January 23, 2006.
- Pilot testing is critical to revealing how different media will perform under various operating conditions for system-specific parameters.

# Piloting Potential Technologies



- **Arsenic removal**
  - **Compliance**
  - **Cost**
- **Waste production and disposal**
  - **Compliance**
  - **Cost**

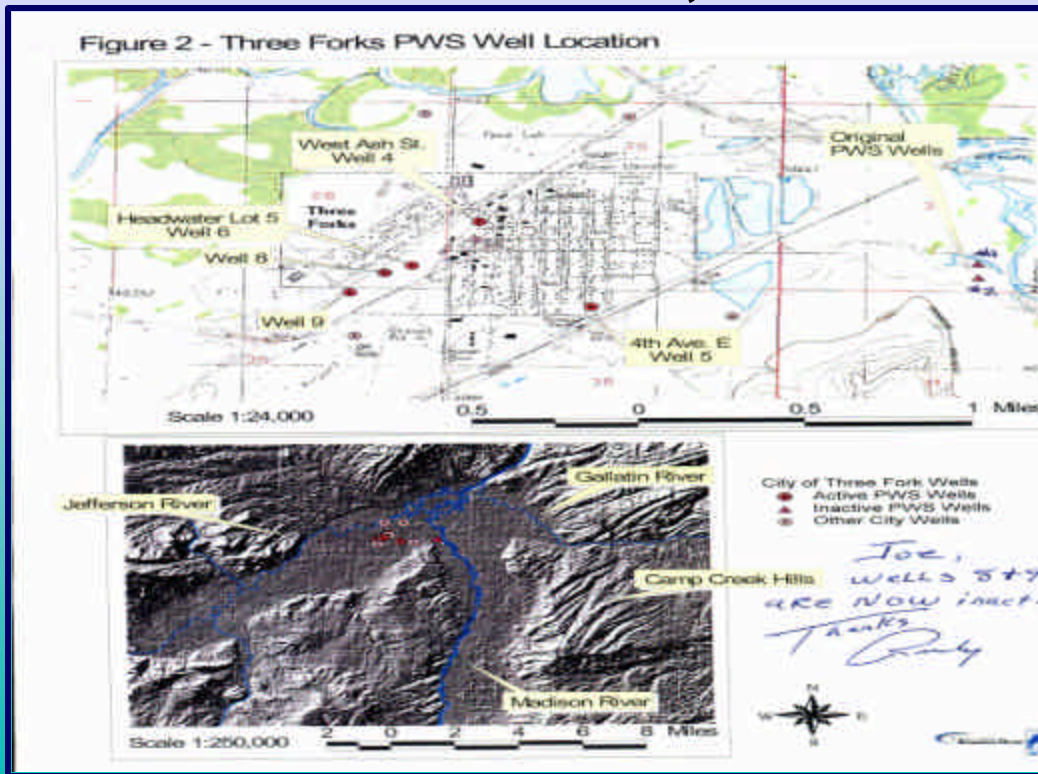
- When piloting potential technologies, water systems need to consider both arsenic removal and waste disposal.
- Systems must be in compliance with all applicable regulations for both arsenic removal and waste disposal, and pilot testing offers an opportunity to ensure that all requirements will be met.
- In addition, systems can use pilot testing to find lower-cost solutions.

# Three Forks, MT



- Three Forks, Montana, is a small water system that is out of compliance with the current arsenic MCL. The system is in the process of pilot testing various technologies and has not yet been successful.

# Three Forks, Mt



- This map shows the location of the wells used by the Three Forks system.

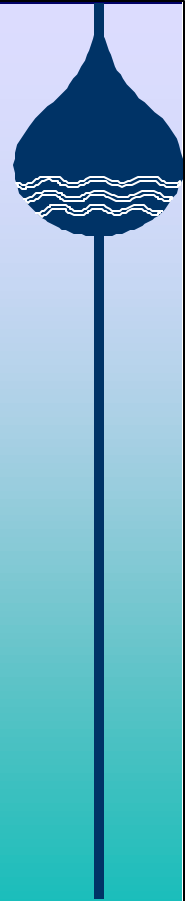




- This photograph shows the existing Three Forks water treatment building. Because the system is in a cold climate, all of its pilot testing and treatment equipment must be indoors, which increases costs.



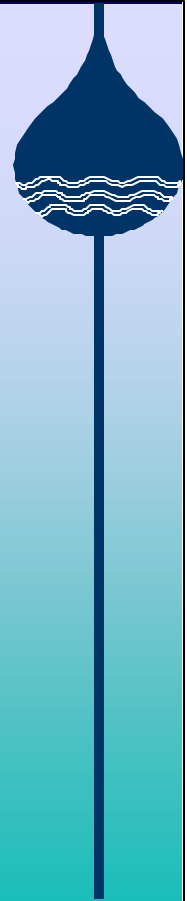
# Water Quality



- **pH:** - 7.4 su
- **Arsenic:** - 0.072 mg/L
- **Silica:** - 48.6 mg/L
- **Iron:** - <0.03 mg/L
- **TDS:** - 321 mg/L
- **Alkalinity:** - 246 as CaCO<sub>3</sub>
- **Fluoride:** - 2.5 mg/L

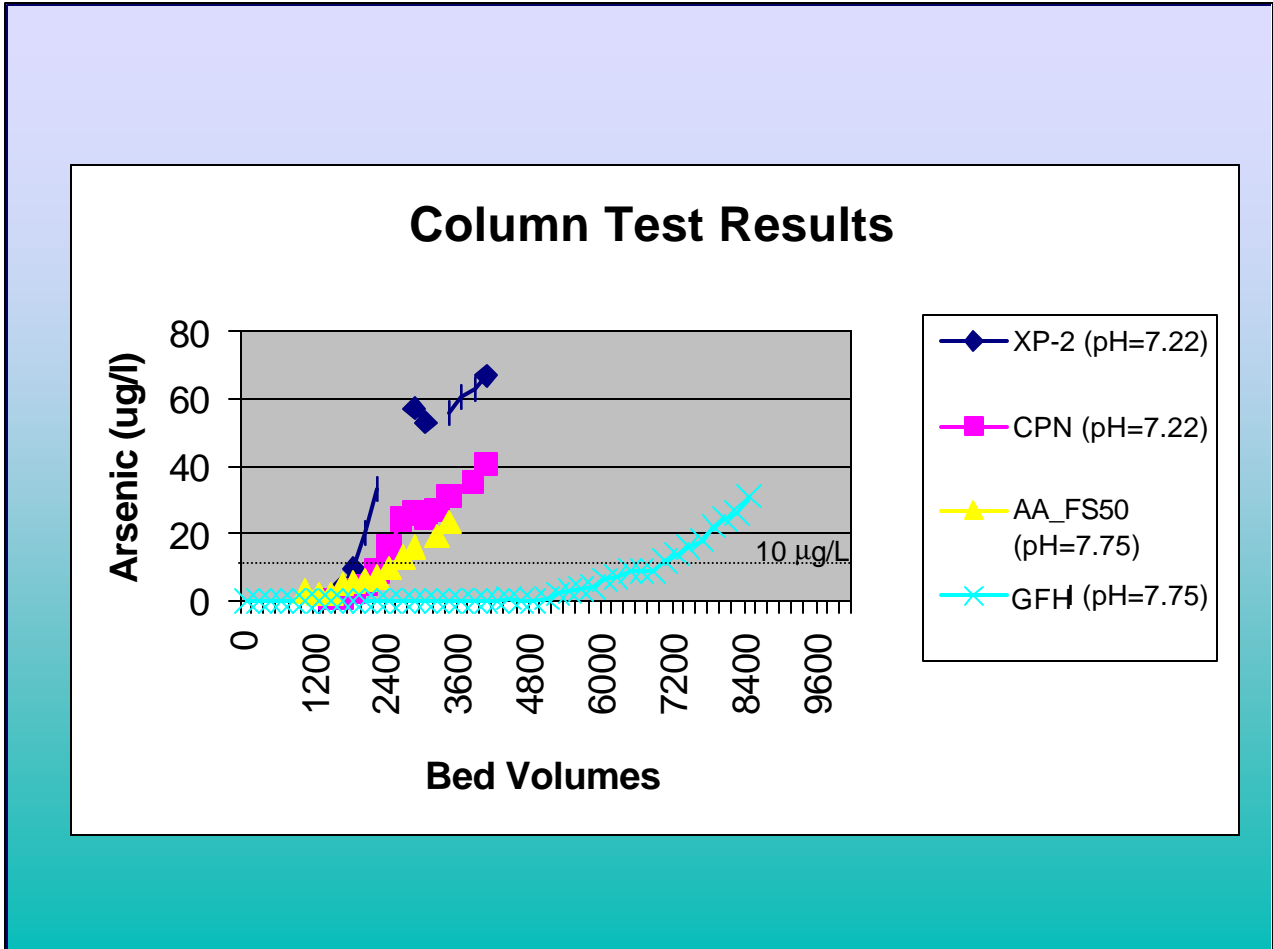
- The water quality parameters faced by the Three Forks system, include:
  - pH: 7.4 su
  - Arsenic: 0.072 mg/L
  - Silica: 48.6 mg/L
  - Iron: <0.03 mg/L
  - TDS: 321 mg/L
  - Alkalinity: 246 as CaCO<sub>3</sub>
  - Fluoride: 2.5 mg/L

# Media Types for Column Tests



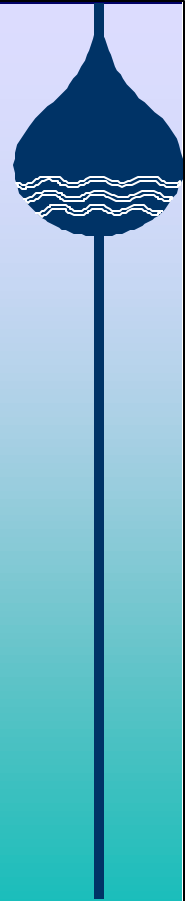
- **Aqua-Bind XP-2**                      **1760 bed volumes**
- **Alcoa CPN**                              **2230 bed volumes**
- **Alcan AA-FS50**                      **2480 bed volumes**
- **GFH**                                      **6370 bed volumes**

- The four media used at Three Forks for column tests were:
  - Aqua-Bind XP-2, a metal oxide composite manufactured by Apyron Technologies, which treated 1760 bed volumes before arsenic breakthrough;
  - CPN, a granular activated alumina manufactured by Alcoa, which treated 2,230 bed volumes before arsenic breakthrough;
  - AA-FS50, a surface-modified (iron-coated) activated alumina manufactured by Alcan Chemicals, which treated 2,480 bed volumes before arsenic breakthrough; and,
  - Granular ferric hydroxide, manufactured in Germany and distributed in the United States by US Filter, which treated 6,370 bed volumes before arsenic breakthrough.



- This plot shows the breakthrough curves for each media.
- The XP-2 media (the metal oxide composite) was able to maintain low levels of arsenic for the shortest period of time.
- The two activated alumina media showed breakthrough shortly afterward.
- The granular ferric hydroxide, however, was able to maintain levels of arsenic below the MCL for nearly three times as long.

# Protocol

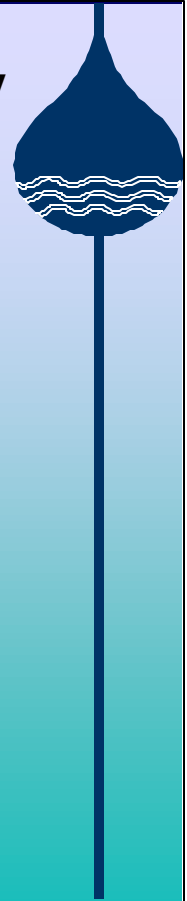


- **Objectives**
- **Media Description**
- **Process Description**
- **Project Schedule**
- **Project Documentation**
- **WQ Data Collection and Analysis**
- **QA/QC**
- **Residual Management and Disposal**

- The Three Forks pilot test was designed considering the following factors:
  - Objectives;
  - Media description;
  - Process description;
  - Project schedule;
  - Project documentation;
  - Water quality data collection and analysis;
  - Quality assurance/quality check (QA/QC); and,
  - Residual management and disposal.

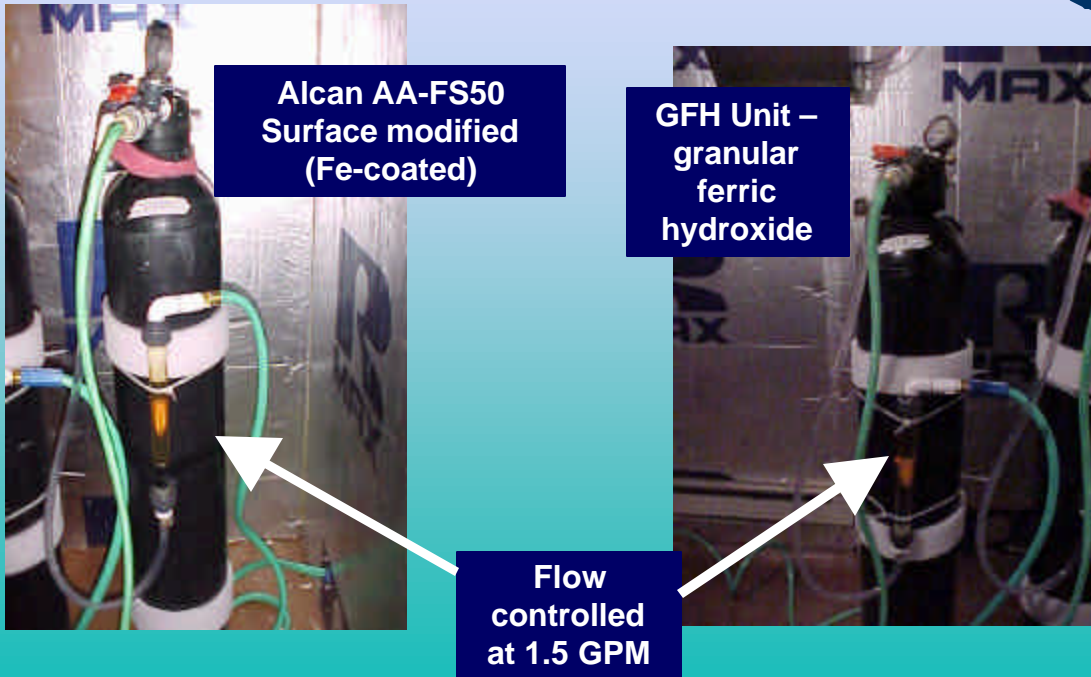
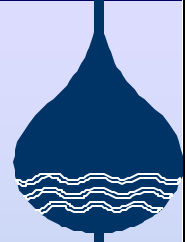
## Table - 1 Sampling and Analysis Frequency

Parameter	Raw Water	GFH	Surface modified AA
Arsenic	Daily for first week 2x/week thereafter	Daily for first week 2x/week thereafter	Daily for first week 2x/week thereafter
Total Coliform	1x/week	1x/week	1x/week
pH	Monthly	Monthly	Monthly
Alkalinity	Monthly	Monthly	Monthly
Aluminum	Monthly	Monthly	Monthly
Calcium	Monthly	Monthly	Monthly
Hardness	Monthly	Monthly	Monthly
Iron	Monthly	Monthly	Monthly
Magnesium	Monthly	Monthly	Monthly
Manganese	Monthly	Monthly	Monthly
Silica	Monthly	Monthly	Monthly
Temperature	Monthly	Monthly	Monthly
TOC	Monthly	Monthly	Monthly



- This table shows the sampling and analysis frequency for various parameters in the raw water, water treated by granular ferric hydroxide, and water treated by iron-coated activated alumina.

# On-Site Pilot



- These pictures show the two tanks used for the surface-modified activated alumina and granular ferric hydroxide at the on-site pilot at Three Forks.

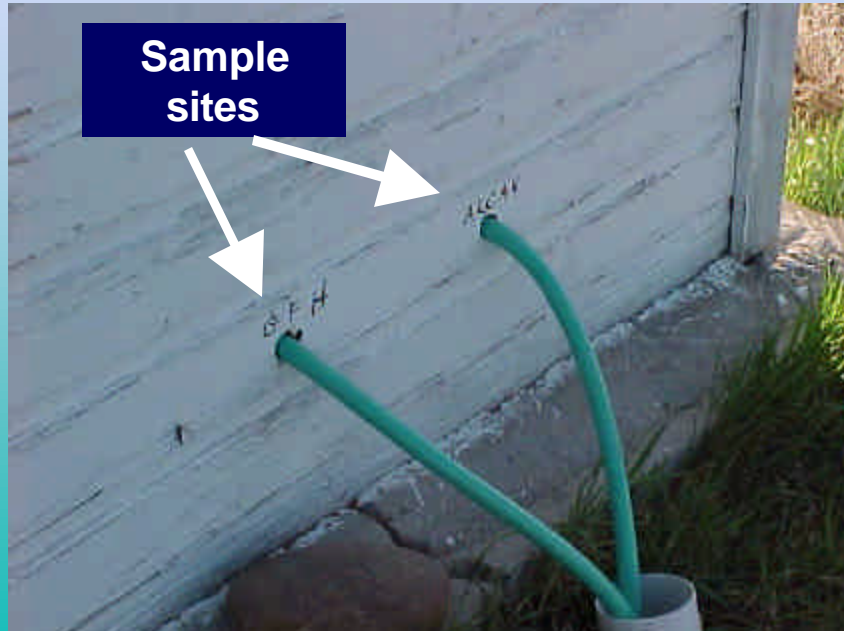
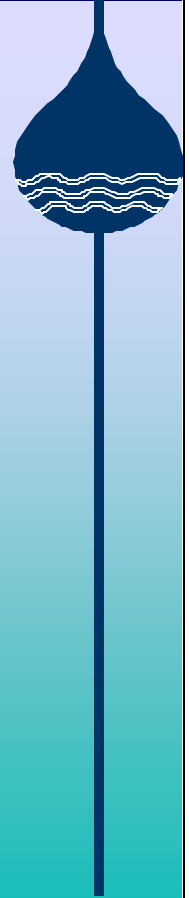
# On-Site Pilot



**Feed and  
backwash  
line**

- This photograph shows the feed and backwash lines at Three Forks.

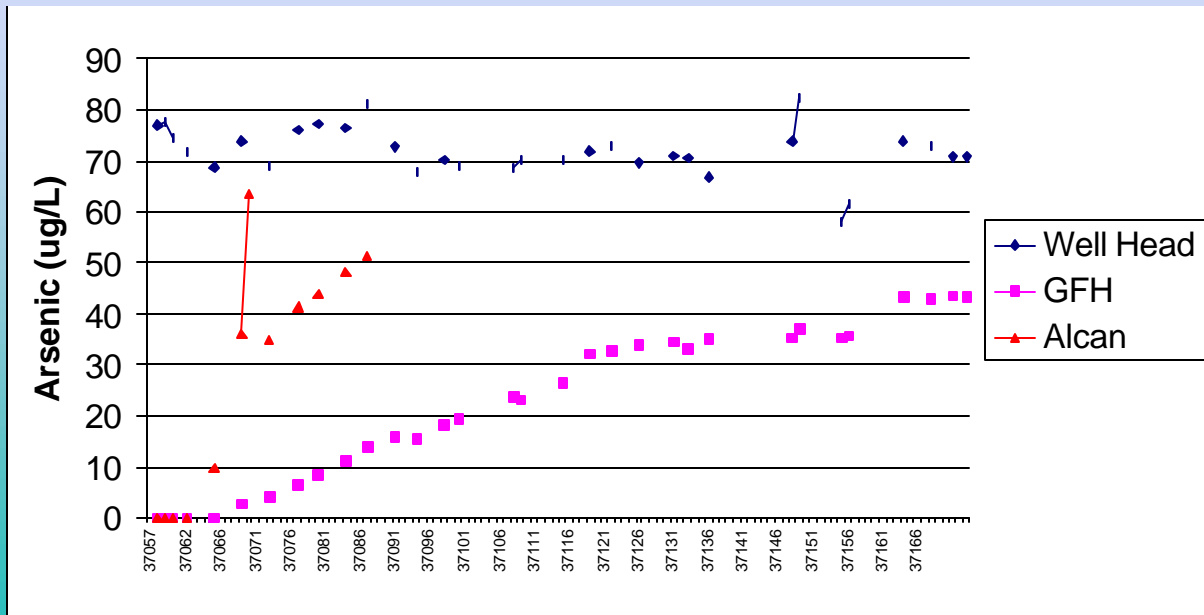
# On- Site Pilot



- Sample taps were plumbed into the Three Forks pilot system to allow for easy and frequent sampling.

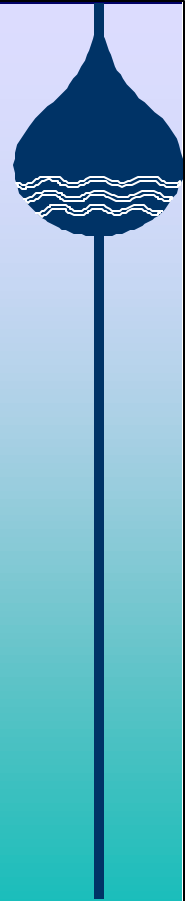


## Well Head and Effluent Arsenic Concentrations at Three Forks



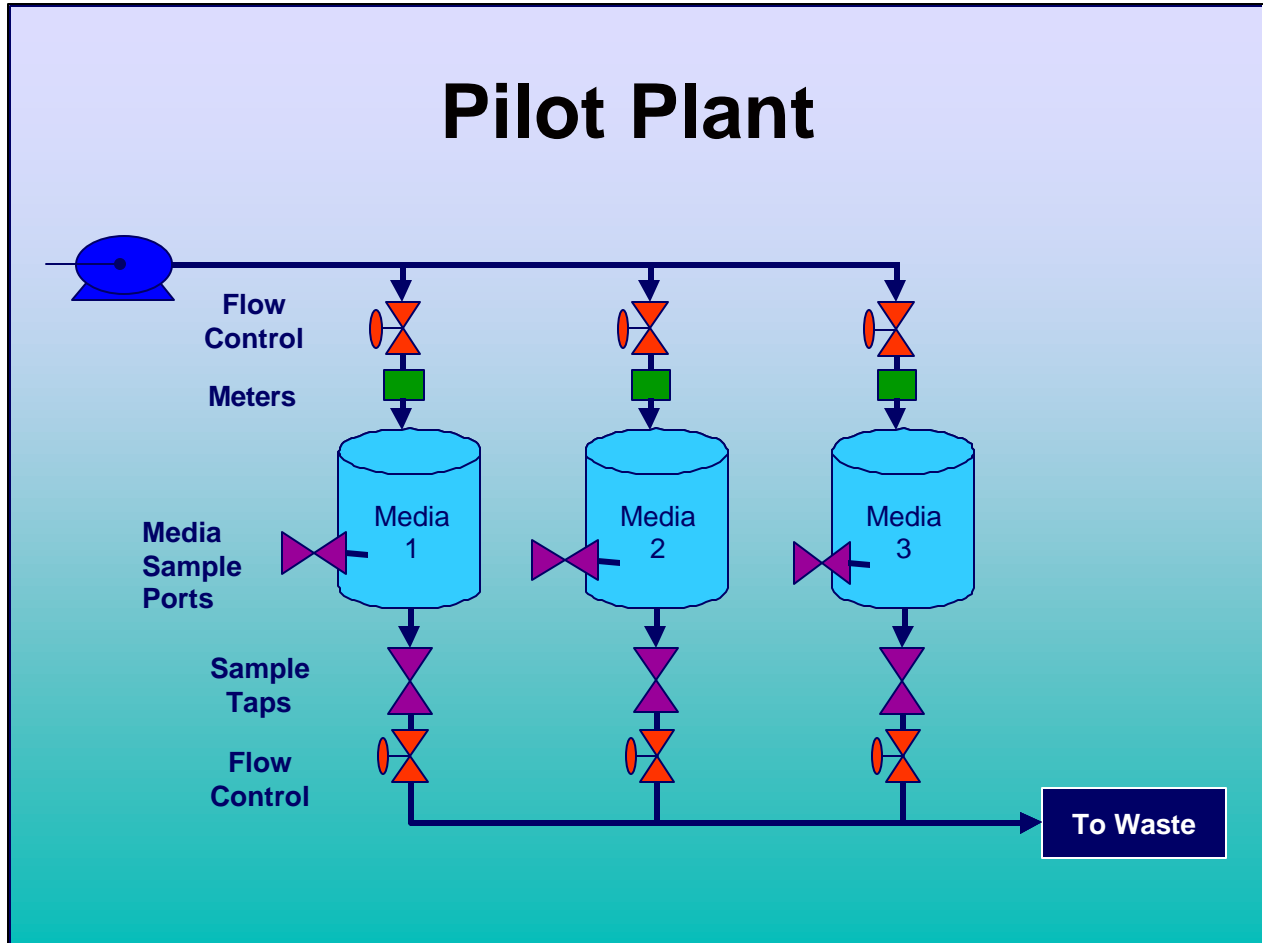
- This plot shows that arsenic concentration over time in the raw water, after the granular ferric hydroxide, and after the surface-modified Alcan activated alumina.
- Breakthrough of 10 µg/L occurred much later in the granular ferric hydroxide than in the modified activated alumina.
- Even after breakthrough, the granular ferric hydroxide continued to remove arsenic from the raw water (i.e., the concentration of arsenic in the water treated by the granular ferric hydroxide was below the concentration of arsenic in the raw water). This result suggests that granular ferric hydroxide would be effect in series, because the media still has a lot of capacity left even when the water it produces exceeds the MCL. If operated in series, the first roughing column could continue to be used to exhaustion even after its effluent water exceeds the MCL while the second guard column removes the remaining arsenic from the water.

# Three Forks



- Three Forks is not satisfied with the four media it has tested so far and is continuing to look for an effective treatment technology. It is planning to try a coagulation-assisted membrane filtration plant next.
- Systems similar to Three Forks with challenging water quality characteristics would be solid candidate's for the EPA Office of Research and Development's Treatment Technology Research Demonstration program.

# Pilot Plant

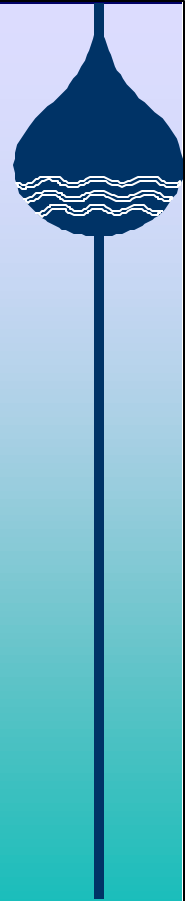


- This schematic shows an example of how a pilot plant may be configured. The water from the well head is split into several streams that run through different media in parallel. Each train is fitted with flow control, a flow meter, and a sample tap. The streams are then combined prior to distribution or disposal.

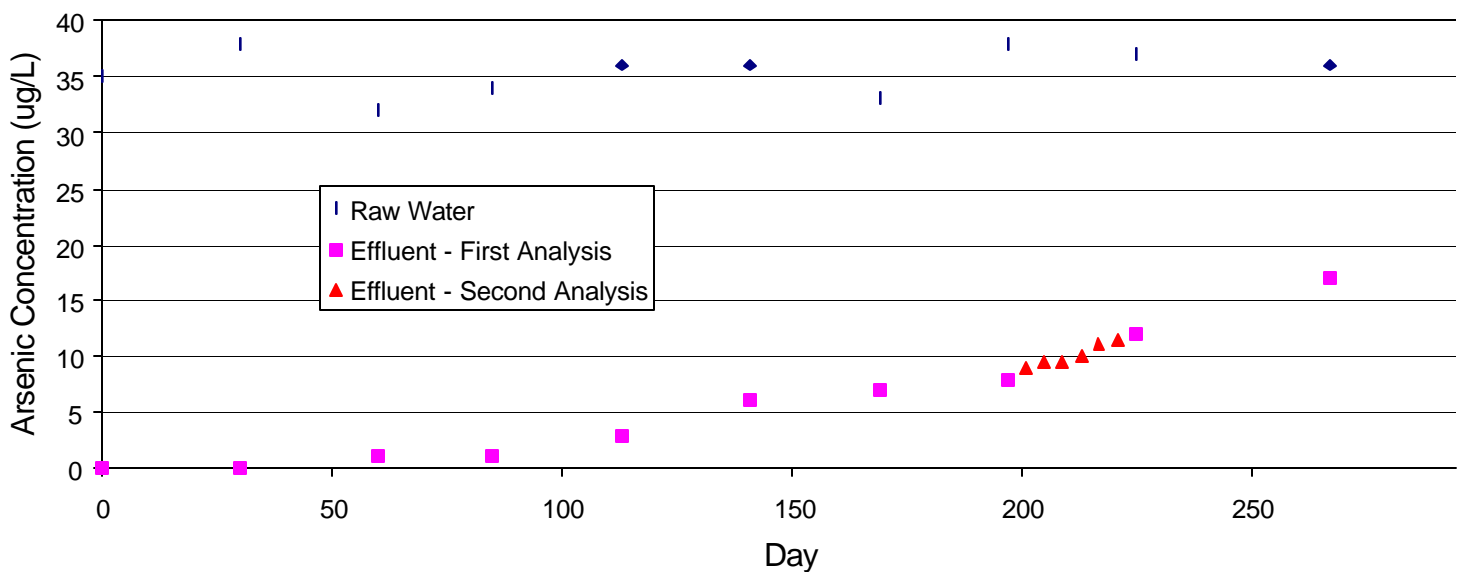
# Pilot Test Monitoring

- Raw Water

- Finished Water

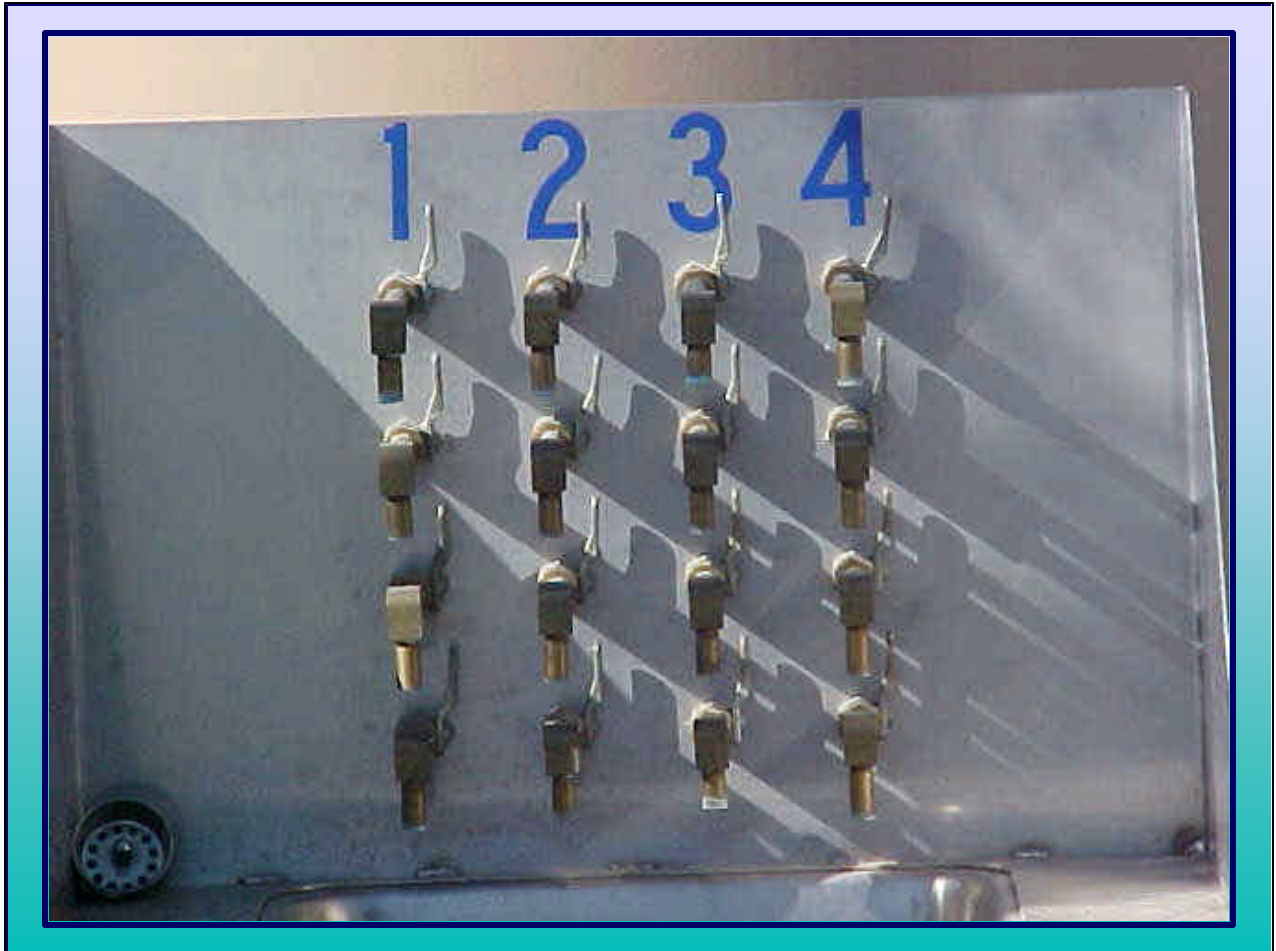


- Pilot test monitoring should include both the raw and the finished water. If multiple tanks in series are used, samples should also be taken between the tanks.
- More water samples should be taken than are initially analyzed. After treatment is installed, the concentration of arsenic in the treated water tends to be relatively constant for a period of time before it rises to breakthrough. Analyzing frequent samples can be expensive and is unnecessary except during the crucial period of breakthrough. Because arsenic samples can be stored for up to 6 months, frequent samples can be taken but only some samples (e.g., every tenth sample) sent for analysis. After the results are received back from the laboratory, the system can then decide if there are any periods that it would like to examine in depth and send those samples for analysis. For example:



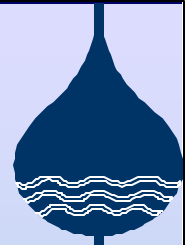


- The pilot plant in Paramount, California, was designed with pilot testing in mind. Each media vessel has three internal and one finished water sampling taps. These taps are connected to a sampling sink, making sample collection as easy as possible for operators.



- This photograph shows a close-up of the well organized and labeled sample sink at Paramount.

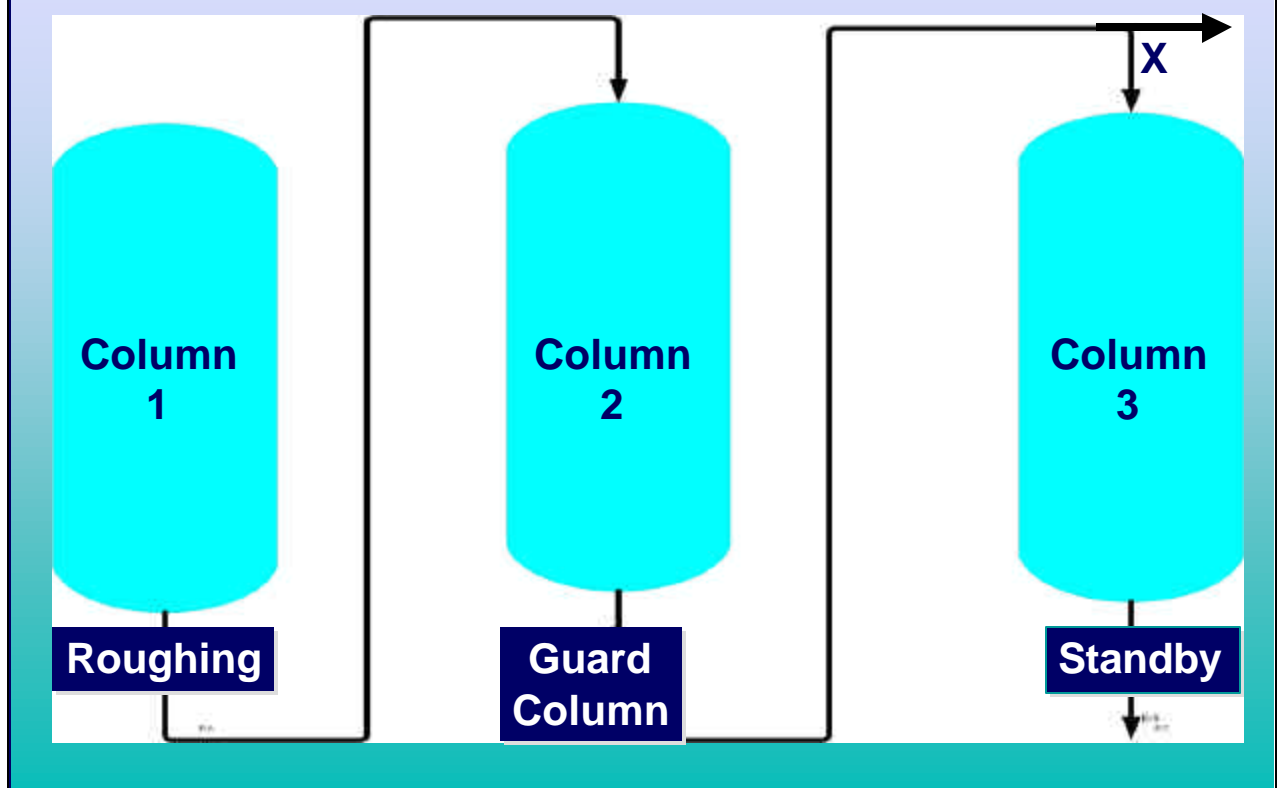
# Regulatory Design Considerations



- **Configuration**
  - Parallel
  - Series
  - By-pass
  - Pre-treatment
  - Post-treatment
- **Redundancy**
- **Loading rates**
- **Process control monitoring**

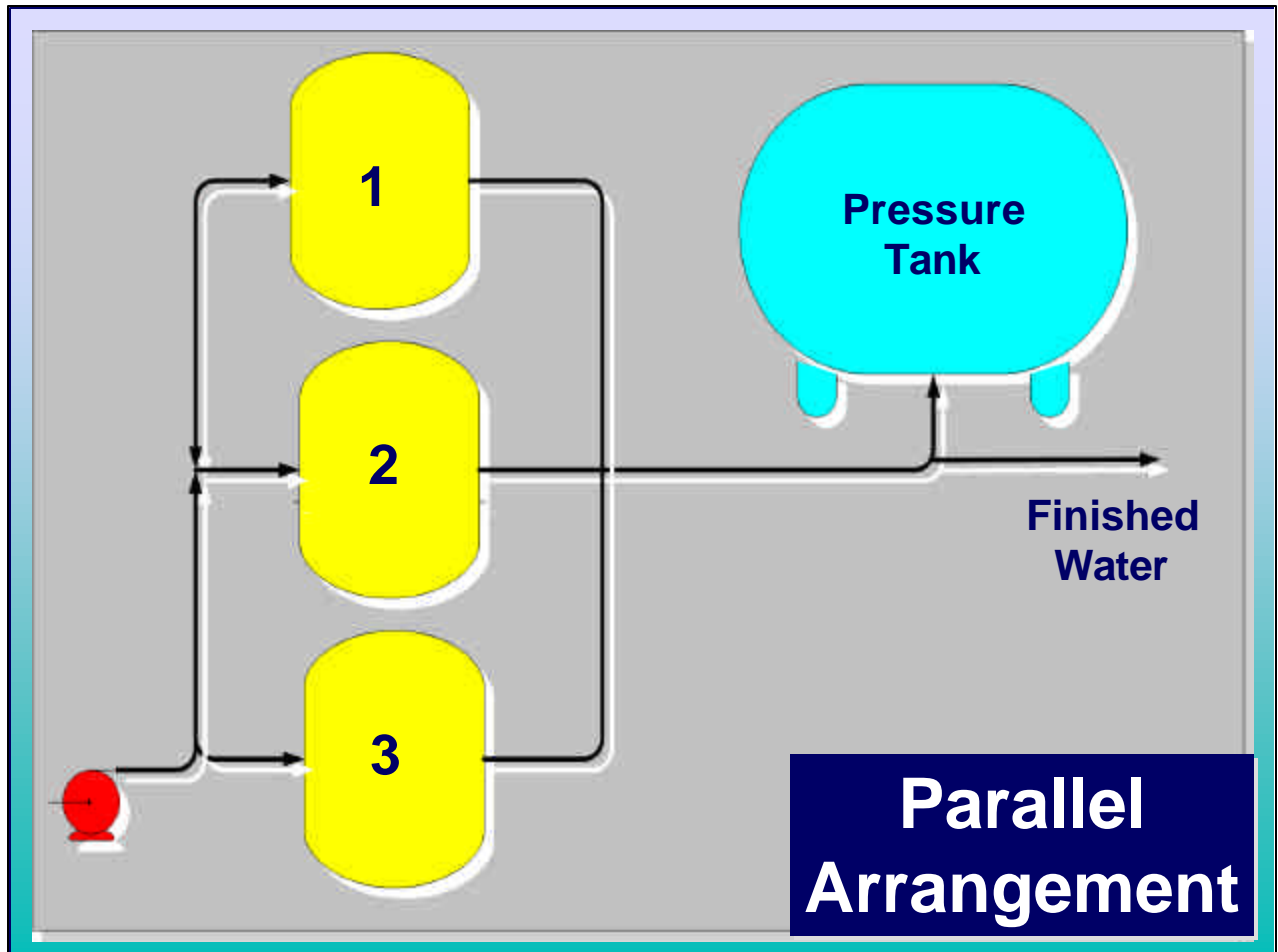
- The federal regulations give States the flexibility to determine how they will ensure that systems will comply with the revised arsenic MCL. The federal regulations do not include requirements on the following points, though it is recommended that States consider the following factors when drafting their regulations and guidance documents:
  - Acceptable plant configuration.
    - Parallel operation may not be enough to ensure that treated water consistently meets the MCL, especially if an adsorptive media is used. It is recommended that States require systems to install a guard column in each treatment train using adsorptive media.
    - States may also wish to consider how to regulate systems using treatment by-pass to treat a portion of the stream and blend it with raw water to ensure that the finished water is always below the MCL.
    - States may also wish to require certain pre-treatment (such as chlorination for oxidation) and post-treatment (such as pH adjustment).
  - Redundancy. Realizing that mechanical failure and maintenance occur, most States will require that a system design some redundancy into its system, such as being able to treat an average day flow while its largest unit is off-line.
  - Loading rates. The loading rate is the flow rate that a given quantity of media can treat. The loading rate is necessary in the calculation of the EBCT. Assuming too high a loading rate can underestimate the amount of media necessary to remove arsenic reliably. Typical loading rates for adsorptive media range up to 7.5 gallons per minute per square foot.
  - Process control monitoring involves collecting frequently from a variety of locations within the plant (not just from the finished water) to ensure that the plant is operating properly on a day-to-day basis. The State may wish to require the system to maintain records of frequent process control monitoring.

## Columns in Series



- Because of the risks associated with chromatographic peaking, regulators might expect small systems to use something similar to the above schematic. The first adsorptive media column in the series (the roughing column) is designed to take out the majority of the arsenic. The treated water is then passed through the second column (the guard column) and, should column 1 be operated past the point of exhaustion to maximize the use of the media, column 2 will remove arsenic to below the MCL.
- When column 1 requires regeneration, valves are used to switch column 2 to the first in the series with column 3 becoming the guard column. The media in column 1 is then regenerated or disposed and replaced. The column is then put in standby mode.
- Sampling for arsenic or sulfate should be done upstream of the effluent (i.e., between the two columns) to ensure that chromatographic peaking does not occur.





- Small systems often use pressure (hydropneumatic) tanks. Pressure tanks have limited storage capabilities, so the system must be able to treat the instantaneous maximum demand, which can be quite high even for a small system. To provide a sufficient EBCT of, say, 5 minutes at the instantaneous maximum demand, the system will need to provide several media tanks in parallel. Having several tanks can be quite expensive. An analysis should be performed to see if re-pumping from storage, combined with source water treatment at lower flows, would be more cost effective.

# Field Tests



- Field testing is an alluring alternative to laboratory analytical analysis. If field tests were accurate, sensitive, and safe, they would be useful because:
  - Field tests are less expensive than laboratory analysis. The cheapest field test kits cost less than a dollar per sample, whereas laboratory analysis can cost \$15-25 per sample. More accurate field testing protocols may necessitate the purchase of portable laboratory equipment (for example, a colorimeter for \$500 or more), which could conceivably be shared by several small systems.
  - Field tests would provide more immediate results than laboratory analysis. Instead of waiting for two or more weeks to receive results, systems could know the arsenic level within minutes.
  - As a result of these two factors, field tests would be useful for frequent process control, to check on the system more frequently than required by the Primacy Agency to ensure the proper removal of arsenic.
- There are several kinds of field testing systems available.
  - Portable labs, are large and expensive, but also deliver low detection limits and large detection ranges, produce quantitative results, and are quite durable.
  - Test kits or test strips, are smaller, quicker, cheaper, and easier but do not offer the accuracy of portable labs. Companies advertise them for education or for the indication of possible problems but make no claims about their precision. In *Field Sampling and Analysis Technologies Matrix and Reference Guide*, 1998, EPA stated that these chemical colorimetric kits “should only be used as an indication or screening device” and could only detect compounds at levels down to 0.5 mg/L in water.
- This photograph illustrates a Hach test kit that uses zinc for arsenic detection.



- In the Hach test, a measured amount of water is placed in a covered vial. An additive is used to reduce all the arsenic to arsenic (III). The water is acidified with hydrochloric acid and a zinc solution is added. When zinc is added to water containing hydrochloric acid, the zinc corrodes to form  $Zn^{+2}$ , accompanied by the vigorous release of  $H_2$  gas and concurrent reduction of arsenic (III) to arsine ( $AsH_3$ ) gas. Finally, the amount of arsine gas produced is measured by a test strip inserted into the head space at the top of the vial. There are two forms of the Hach test. The more expensive version compensates for the presence of hydrogen sulfide in the test water. The less expensive version does not compensate for hydrogen sulfide; if water containing hydrogen sulfide needs to be sampled, a piece of gauze must be inserted into the cap to absorb the hydrogen sulfide gas before it contacts the test strip.

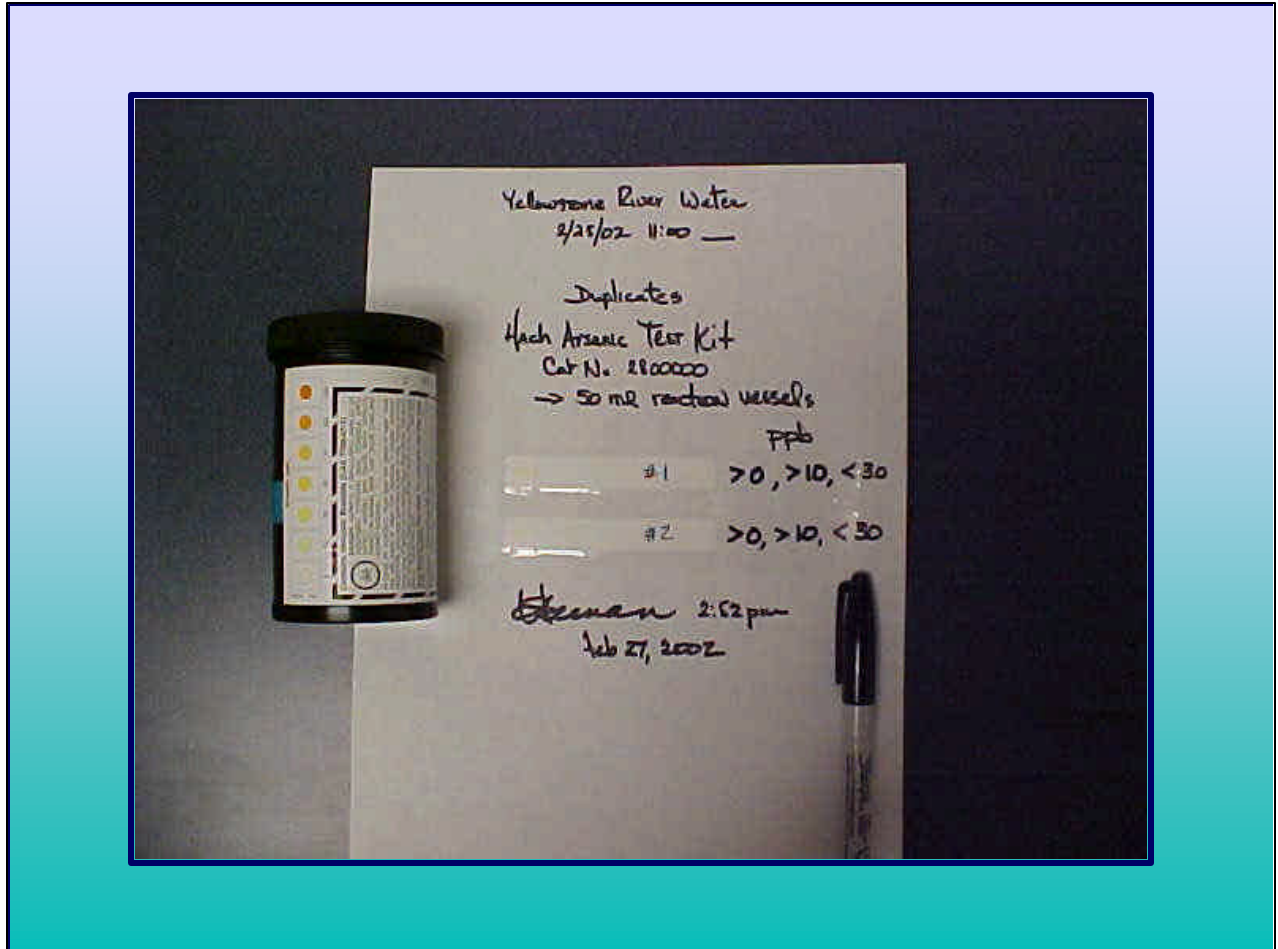


- The sample size is measured with a line on the side of the test container. Filling the container exactly to the line can be difficult in small systems where the sample tap is difficult to access.



- A spot on the test strip at the top of the container turns color in response to the concentration of arsine gas produced. The tester then compares this color with sample color swatches on the test strip bottle label, which are labeled with the appropriate concentration of arsenic in the water sample.

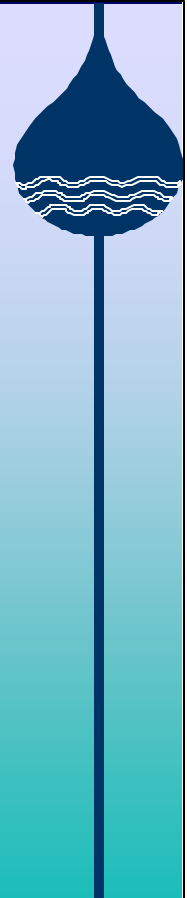




- Neither version of the Hach test appears to be able to measure arsenic reliably below 20 to 30  $\mu\text{g/L}$ ; at these concentrations, the color produced is too faint to be distinguished by eye.
- Therefore, although this test kit could be used for rough process control, it will not be of much use to water systems trying to detect arsenic levels at or below the revised MCL.
- A similar process that uses  $\text{BaBH}_4$  (sodium borohydride), which seems to be better suited for the generation of arsine gas at levels below 5  $\mu\text{g/L}$ , is currently being developed.



# Point of Use Technologies

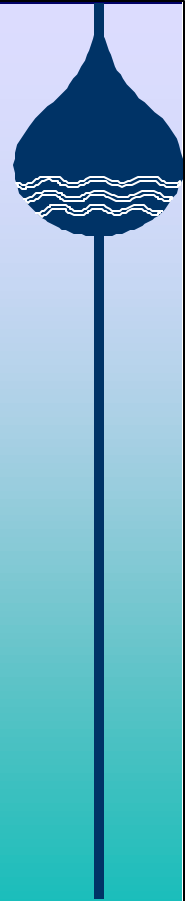


- **Ion exchange**
  - Chromatographic peaking
- **Activated alumina**
- **Granular ferric hydroxide**
- **RO**

- Technologies currently available at the POU include ion exchange, activated alumina, granular ferric hydroxide, and RO.
  - Activated alumina and RO POU were designated as small system compliance technologies (SSCTs) for the Arsenic Rule.
  - Ion exchange POU was not designated as a SSCT because of the potential for chromatographic peaking and run lengths that would typically be less than six months.
  - Granular ferric hydroxide was not designated as a BAT or SSCT because of the lack of published data showing performance for a range of water qualities and the lack of published information on the cost of the media.



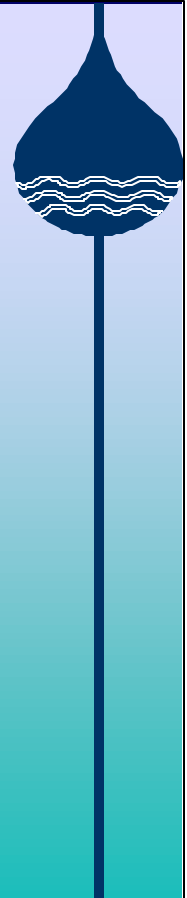
# Point of Use



- **Regulatory considerations**
  - **Technology**
  - **Configuration**
    - **Add-on technologies**
  - **Maintenance**
    - **Monitoring**
    - **Replacement**
  - **Chlorine residual**
  - **Compliance**

- Regulatory considerations influencing POU devices include:
  - Deciding which technologies are appropriate for the source water;
  - Determining appropriate configurations for arsenic treatment, especially when consumers may already have POU devices in their homes or wish to install other add-on technologies;
  - Having the system or its contractor enter the consumers' homes for monitoring and filter replacement;
  - Maintaining of a chlorine residual in the distribution system; and,
  - Calculating compliance.

# Point of Use



- Water systems serving fewer than 250 consumers may wish to consider point-of-use treatment devices (POU). Whole-house, or point-of-entry (POE) treatment, is necessary when exposure to the contaminant by modes other than consumption is a concern; this is not the case with arsenic. Single faucet, or POU, treatment is preferred when treated water is needed only for drinking and cooking. POU devices may be especially suitable for systems that have a large flow, of which only a minor part is directed for potable use.



# **Point-of-Use for Arsenic Control**

**Gretchen Rupp  
Montana Water Center  
April 11, 2002**

- This portion of the presentation is adapted from a presentation given by Gretchen Rupp of the Montana Water Center on April 11, 2002.
- The most protective compliance option is centralized treatment. For very small systems which have no other alternative, Point of Use devices can be an effective compliance tool.

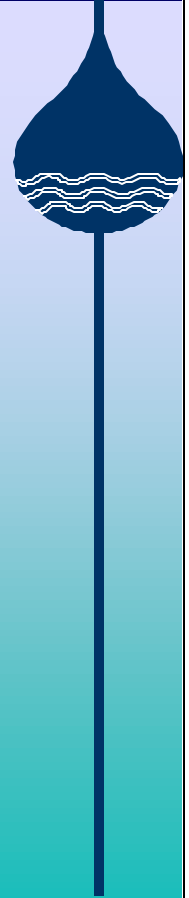
# The Demonstration Project

- **Conducted by Dr. Chuck Moretti, University of North Dakota**
- **Water Center sponsorship**
- **October 2000 - February 2002**
- **21 residences in Oakes, ND.**



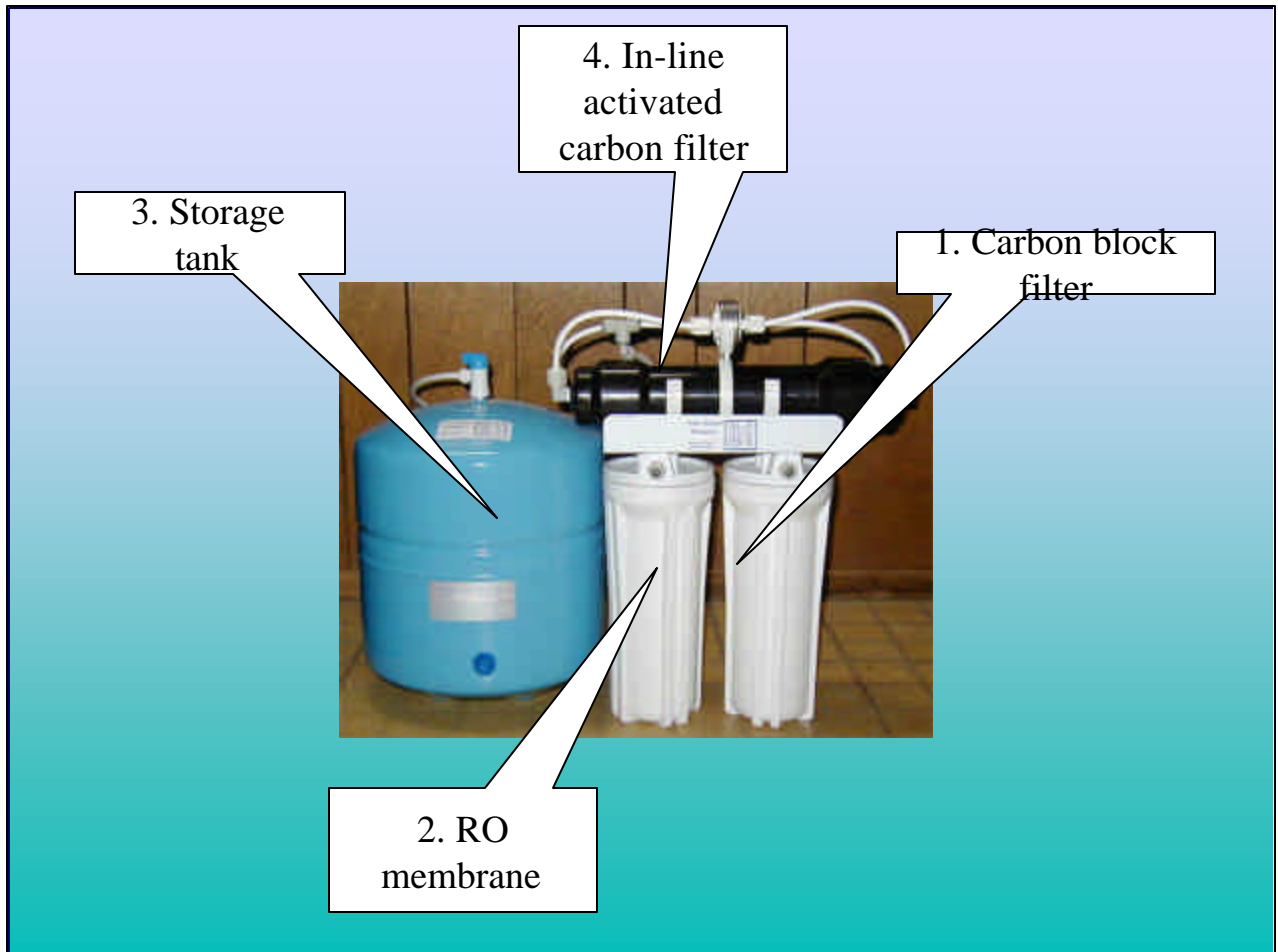
- The Montana Water Center sponsored a demonstration project at 21 residences in Oakes, North Dakota. The project was conducted by Dr. Chuck Moretti of the University of North Dakota and occurred from October 2000 through February 2002.

## Configuration of the POU-RO

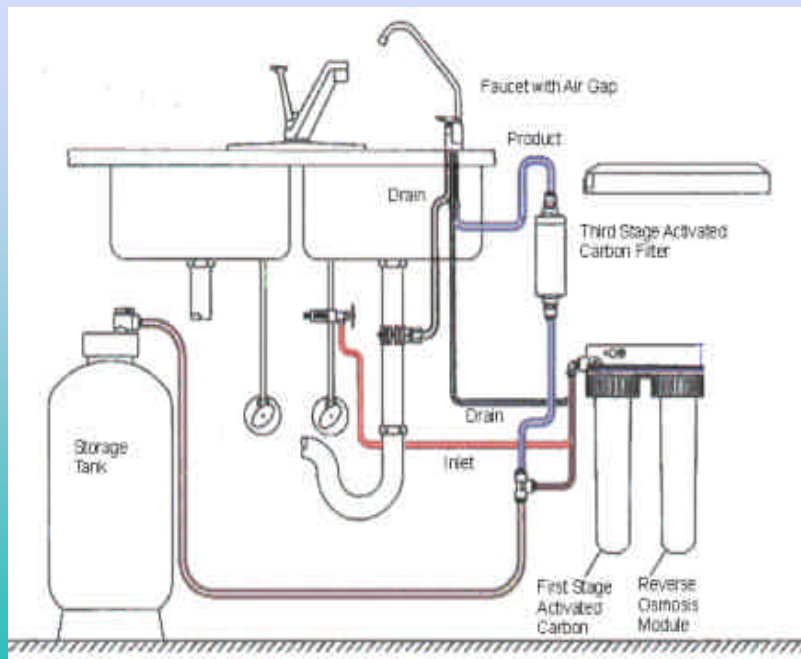


- **Stage One – 5-micron carbon block filter to remove chlorine, sediment, taste & odor**
- **Stage Two – RO membrane module producing 15-30 gpm @ 40-80 psi**
- **Stage Three – Storage tank**
- **Stage Four – Activated carbon filter**

- The demonstration project used four-stage POU RO devices.
  1. A 5 micron carbon block filter, which removed chlorine, sediment, taste, and odor;
  2. An RO membrane module producing 15 to 30 gallons per minute at 40 to 80 psi;
  3. A storage tank, which allows water to be stored instead of relying on the relatively slow RO process; and,
  4. An activated carbon filter to polish the water and improve its aesthetic qualities. The filter is located after the storage tank to minimize the risk of bacterial colonization of the treated water.



- This photograph shows the RO POU treatment unit used in Oakes, North Dakota.



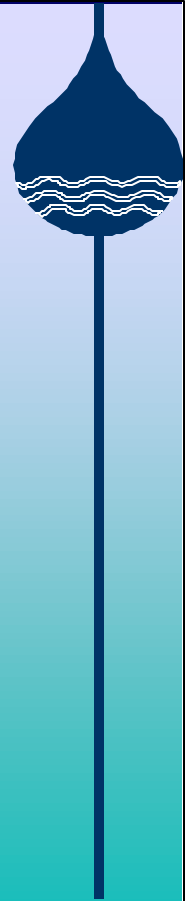
- This is the schematic showing the installation of a POU RO unit under a sink in Oakes, North Dakota. The blue indicates treated water feeding into a dedicated tap at the sink; the red indicates reject water disposed to waste.



- This photograph shows a RO POU unit installed under a sink. Note the dedicated faucet on top of the sink.

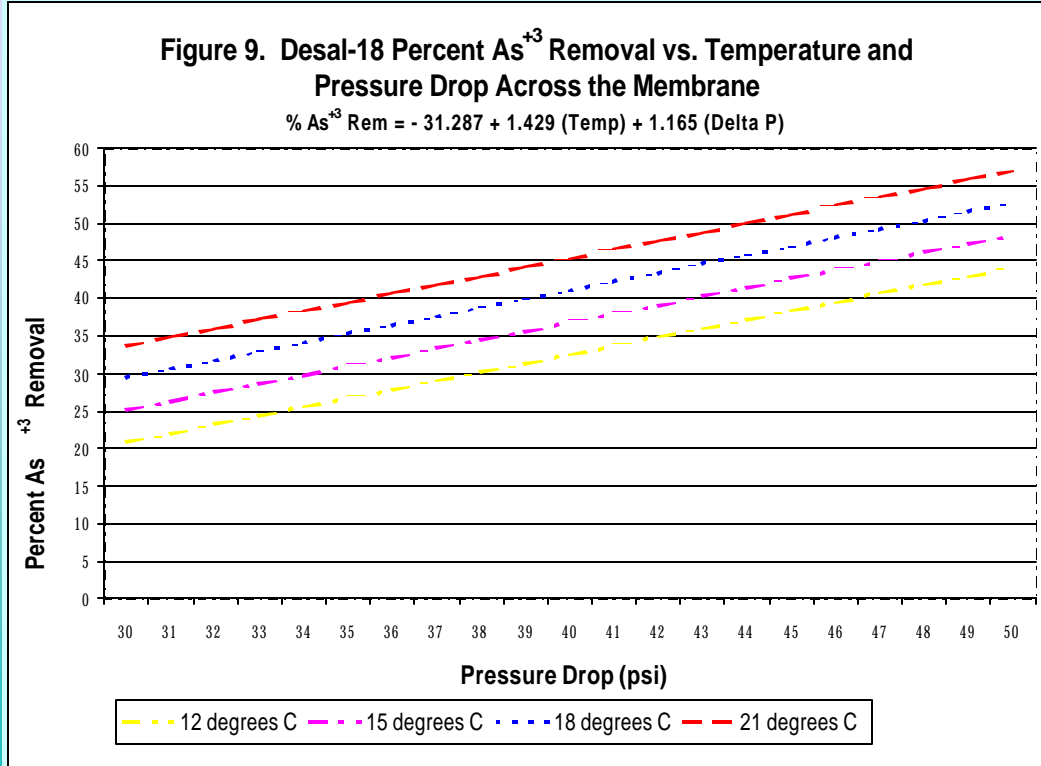


## First - Laboratory Evaluation of Two Units



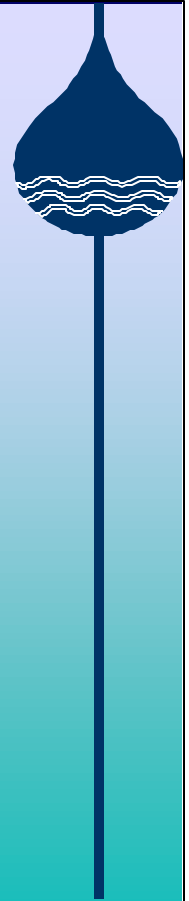
- **Dechlorinated Grand Forks water spiked with As(III) to 20 mg/L**
- **Tested Desal and Filmtec thin-film composite POU-RO units**
- **Examined As(III) removal, water production, water recovery**

- The first step in the POU evaluation was a laboratory test of two units.
  - The raw water used was dechlorinated water from Grand Forks, North Dakota, spiked with arsenite to a concentration of 20 µg/L.
  - The two membranes tested were Desal and Filmtec thin-film composite (TFC) membranes. Several types of RO membranes are used in POU and POE treatment. The most common are cellulose acetate (CA) and TFC membranes. While CA membranes are more resistant to deterioration from chlorine than TFC membranes, they are not as widely used today because TFC membranes exhibit superior contaminant removal rates, even in conditions of low pressure, in a wide range of pH.
  - The test evaluated arsenite removal, water production, and water recovery (i.e., the percentage of the raw water that was treated and not rejected).



- This chart shows the arsenite removal achieved by the Desal membrane with different pressure losses and at different temperatures. Note that, in general, arsenite removal is improved by higher temperatures.

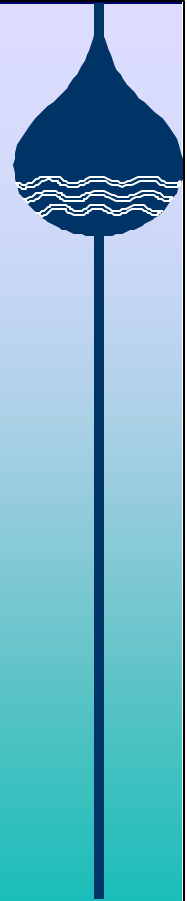
## Field Pilot Test



- **Filmtec or Desal units installed in 21 homes in Oakes, ND**
- **Source water: Untreated groundwater with 10-20  $\text{mg/L}$  of total arsenic.**
- **Membrane integrity monitored for six months, as permeate electrical conductivity.**

- The next stage of the comparison was a field pilot test at 21 homes.
- The source water used was untreated ground water. The level of arsenic in the ground water ranged from 10 to 20  $\mu\text{g/L}$ .
- The membrane integrity was monitored for six months by measuring the electrical conductivity of the permeate (the treated water). An electrical conductivity meter measures total dissolved solids; if the solids level rises, then the membrane may be damaged.

# Conclusions of the Field Pilot Tests

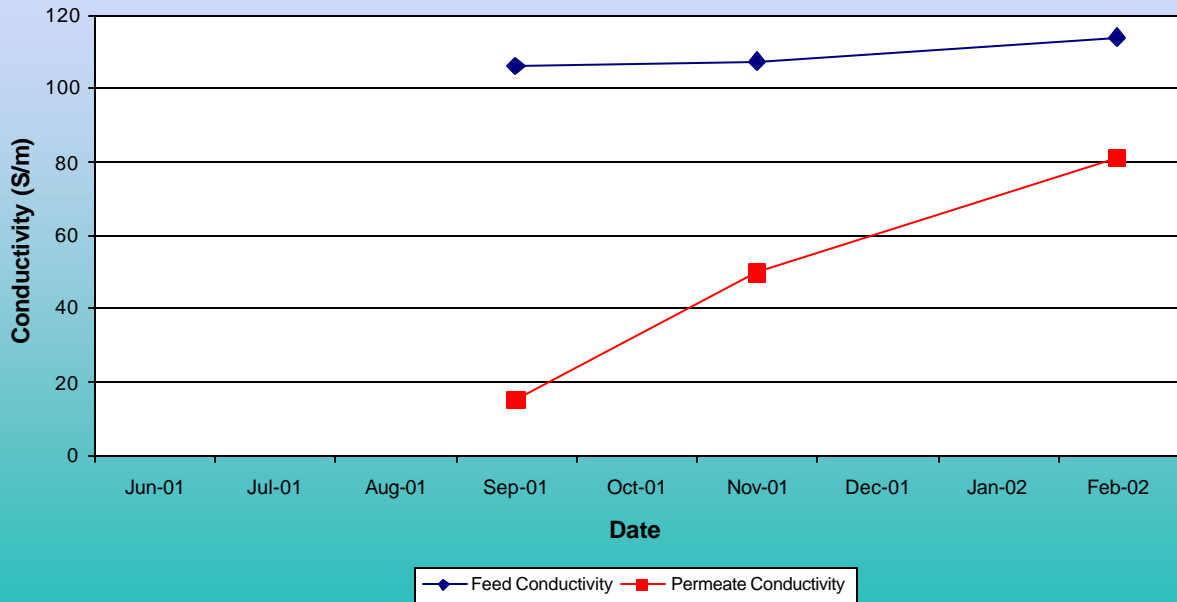


- **The concentration of total arsenic in the permeate  $\leq 1$  ppb**
- **Membrane failure a very gradual process**
- **Arsenic does not begin to pass a failing membrane until permeate EC reaches 50% of feed water EC**

- The field pilot tests in Oakes showed that:
  - For the six month test period, the concentration of total arsenic in the permeate was maintained at  $1 \mu\text{g/L}$  (one tenth of the MCL) or below;
  - Membrane failure is a very gradual process; and,
  - Arsenic does not begin to pass a failing membrane until the permeate electrical conductivity reaches 50% of the feed water electrical conductivity.
- Electrical conductivity measurements are relatively quick and inexpensive. Having maintenance personnel test electrical conductivity on their routine household visits may provide timely enough information to prevent arsenic from passing a failing membrane.

# POU RO Conductivity Data

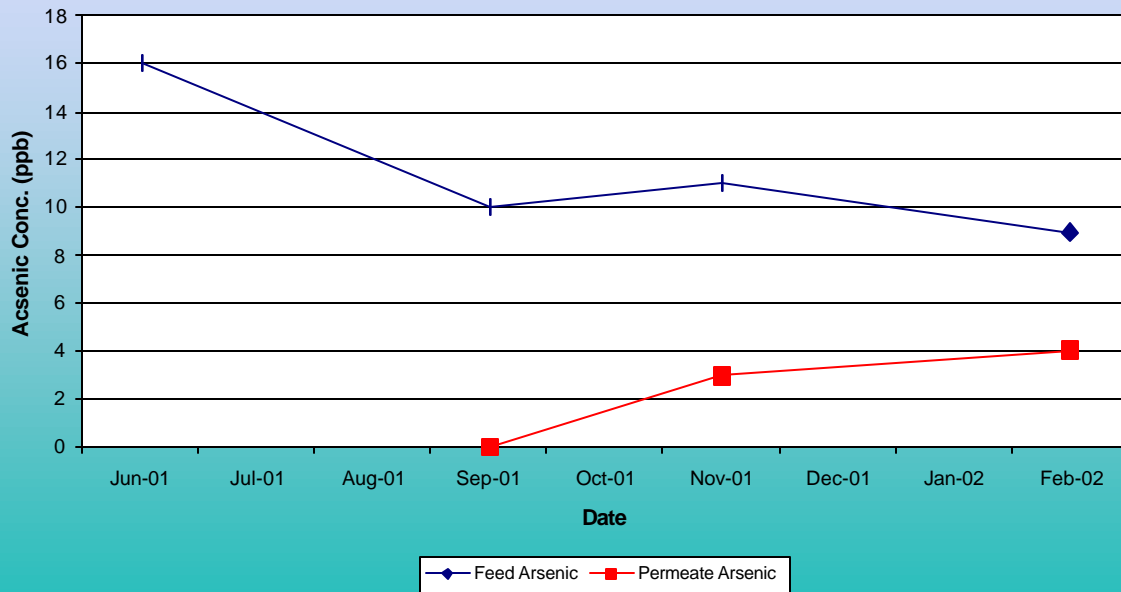
(Membrane Degradation Indicated)



- This plot shows how the permeate conductivity rises toward the feed water conductivity over time as the membrane slowly fails.

# POU RO Arsenic Data

(Membrane Degradation Indicated)



- This plot shows how the concentration of arsenic in the treated water rises toward the concentration of arsenic in the field water as the membrane degrades.



# Selecting Strategies

## Decision Trees

- The decision trees included in the presentation are adapted from the *Arsenic Treatment Technology Design Manual for Small Systems* and are meant to help systems and regulators decide between the many arsenic treatment options available. The decision trees offer guidance only; all treatment technologies should be pilot tested prior to installation.

# Decision Tree Overview

- **Step 1: Water Quality Monitoring**
  - Tree 1: Water Quality Monitoring
- **Step 2: Blending**
  - Tree 2: Blending
- **Step 3: Optimizing Existing Treatment**
  - Tree 3: Optimizing Existing Treatment
  - Tree 3a: Enhanced Coagulation/Filtration
  - Tree 3b: Enhanced Lime Softening
  - Tree 3c: Iron & Manganese Filtration
- **Step 4: Selecting New Treatment**
  - Tree 4: Selecting New Treatment
  - Tree 4a: Ion Exchange Processes
  - Tree 4b: Sorption Processes
  - Tree 4c: Membrane Processes

- The *Arsenic Treatment Technology Design Manual for Small Systems* provides decision trees to guide systems, regulators, assistance providers, and others through the process of determining appropriate treatment technologies for a given system.
  1. The first step in the process is to monitor source water to determine if the system has an MCL problem at any of its entry points.
  2. If there is a problem, then systems should first consider blending or purchasing.
  3. If blending or purchasing is not feasible, then the system should consider optimizing its existing treatment.
  4. Finally, if no alternatives exist, the water system will need to install new treatment.
- The decision trees provided in this presentation are correlated with the *Design Manual*. When a decision tree refers to a section (for example, Section 3.1), that section of the *Design Manual* will provide more information on this topic.
- For copies of the *Design Manual* including the decision trees see EPA's website <http://www.epa.gov/safewater/ars/implement.html>.