Arsenic Treatment Technology Design Manual for Small Systems

Arsenic Treatment Technology Design Manual for Small Systems

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Executive Summary

In January 2002, the U.S. Environmental Protection Agency (USEPA) published a final Arsenic Rule in the Federal Register. This rule established a revised maximum contaminant level (MCL) for arsenic at 10 μ g/L. All community and non-transient, non-community (NTNC) water systems, regardless of size, will be required to achieve compliance with this rule by February 2006.

This Manual is intended to serve as a resource for small municipal drinking water systems that may be affected by provisions of the Arsenic Rule. For the purpose of this Manual, small is defined as 10,000 or fewer connections. Average water demand for these size systems is normally less than 5 million gallons per day (MGD).

Provided below is a checklist of activities that will normally take place in order to comply with the new arsenic rule. Many of the items on this checklist reference a section in this Manual that may help in completing the activities.

Arsenic Mitigation Checklist

- 1. Monitor arsenic concentration at each entry point to the distribution system. (Section 1.3.1)
- 2. Determine compliance status. This may require quarterly monitoring. See Section 1.3.2 for details on Arsenic Rule compliance. Decision Tree 1, *Water Quality Monitoring* may also assist.
- 3. Determine if a non-treatment mitigation strategy such as a source change or blending can be implemented. See Sections 2.2 and 2.3 for more detail and Decision Tree 2, *Treatment Avoidance Alternatives*.
- 4. Measure water quality parameters. See Section 3.1.1 for more detail on water quality parameters that are used in selecting a treatment method.
 - Arsenic, Total Nitrite
 - Arsenate
 - Arsenite
 - Chloride
 - Fluoride
 - Iron
 - Manganese

• pH

Orthophosphate

- Silica
- Sulfate
- Total Dissolved Solids (TDS)
- Total Organic Carbon

- Nitrate
- 5. Determine the design criteria. See Section 3.1.2 for more detail on design parameters that are used in selecting a treatment method.
 - Existing Treatment Processes
 - Target Finished Water Arsenic Concentration

- Technically Based Local Limits (TBLLs) for Arsenic and Total Dissolved Solids (TDS)
- Domestic Waste Discharge Method
- Land Availability
- Labor Commitment
- Acceptable Percent Water Loss
- Maximum Source Flowrate
- Average Source Flowrate
- State or primacy agency requirements that are more stringent than those of the USEPA.
- 6. Select a mitigation strategy using the decision trees provided in Section 3.2. These trees lead to the following mitigation strategies.
 - Treatment Avoidance & Treatment Minimization Strategies
 - Source Change
 - Blending Before Entry to Distribution System
 - Sidestream Treatment
 - Enhance Existing Treatment Processes
 - \circ Enhanced Coagulation/Filtration
 - Enhanced Lime Softening
 - Iron/Manganese Filtration
 - Treatment (Full Stream or Sidestream and Blending)
 - Ion Exchange
 - Activated Alumina Adsorption
 - Granular Ferric Hydroxide
 - Point-of-Use Treatment Program
 - Activated Alumina Adsorption
 - Granular Ferric Hydroxide
 - $\circ \ \ \, {\rm Reverse \ Osmosis}$
- 7. Calculate planning-level capital and O&M costs for the mitigation strategy using the costs curves provided in Section 4. Include costs for arsenic removal and waste handling. If a side-stream treatment method is being used (treating a portion of the stream and blending it back in with the remaining untreated water), costs should be based only on the flowrate of the water being treated. If this planning level cost is not within a range that is financially possible, consider using different preferences in the decision trees.
- 8. Evaluate design considerations for the mitigation strategy. See Section 2.7 for enhancing existing treatment processes and Sections 6 through 8 for the design of new treatment processes.
- 9. Pilot the mitigation strategy. Although not explicitly discussed in this Manual, piloting the mitigation strategy is a normal procedure to optimize treatment variables and avoid implementing a strategy that will not work for unforeseen reasons.
- 10. Develop a construction-level cost estimate and plan.

- 11. Implement the mitigation strategy.
- 12. Monitor arsenic concentration at each entry point to the distribution system to ensure that the arsenic levels are now in compliance with the Arsenic Rule.

Table ES-1 provides a summary of information about the different alternatives for arsenic mitigation found in this manual.

Factors	Sorption Processes			Membrane Processes
	Ion Exchange	Activated Alumina ²	Granular Ferric Hydroxide	Reverse Osmosis
	IX	AA	GFH	RO
USEPA BAT	Yes	Yes	No ³	Yes
Can treat arsenic levels up to: ¹	160 •g/L	160 •g/L	16 - 400 •g/L	160 •g/L
Other Contaminants Treated	SO_{4} -2	F-	PO_{4} -3	TDS
Pre-Oxidation Required	Yes	Yes	Yes	$Possible^4$
Operator Skill Required	High	Low	Low	Medium
Recommended Water Quality	pH 6.5 - 9 < 5 mg/L NO ₂ . < 5 mg/L NO ₃ . < 50 mg/L SO ₄ . ² <500 mg/L TDS	$\begin{array}{c} {\rm pH}\ 5.5 - 6\\ < 250\ {\rm mg/L}\ {\rm Cl}^{\circ}\\ < 2\ {\rm mg/L}\ {\rm F}^{\circ}\\ < 360\ {\rm mg/L}\ {\rm S0}_{4}^{\circ 2}\\ < 50\ {\rm mg/L}\ {\rm Silica}\\ < 0.5\ {\rm mg/L}\ {\rm Fe}^{+3}\\ < 0.05\ {\rm mg/L}\ {\rm Mn}^{+2}\\ < 1,000\ {\rm mg/L}\ {\rm TDS}\\ < 4\ {\rm mg/L}\ {\rm TOC}\\ \end{array}$	pH 6 - 10 < 1 mg/L PO4 ^{.3}	No Particulates
Waste Generated	Spent Resin, Spent Brine, Backwash Water	Spent Media, Backwash Water	Spent Media, Backwash Water	Reject Water
Other Considerations	Large volume of potentially hazardous brine waste, Nitrate Peaking, Carbonate Peaking affects pH	Feed and product pHs require adjustment, Modified AA Available	GFH is very expensive ⁵	High Water Loss (15-75% of feed water)
Appropriate as a New Treatment for Small Systems	Possible	Yes	Yes	POU Only
Applicable for POU	Possible	Yes	Yes	Yes
POU Cost	Not Applicable	Medium	Medium	Medium
POE Cost	High	Medium	Medium	High

Table ES-1. Arsenic Treatme	nt Technologies Summa	ry Comparison	(1 of 2).
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¹ The maximum recommended arsenic levels are calculated from removal rates that are typical for large systems and assume a safety factor of 20%. Small systems, which have additional constraints, may not be able to remove as high of concentrations of arsenic from water.

² Activated alumina is assumed to operate in a non-regenerated mode.

³ GFH's track record in the US is not established enough to be considered as a BAT.

⁴ Pre-oxidation for RO in not always required but will always increase the removal efficiency.

⁵ GFH is currently only manufactured in Europe. With increased domestic use, manufacturing of GFH or another iron based sorbent will occur and significantly decrease the cost.

Factors	Precipitative Processes			
	Coagulation Assisted Micro- Filtration	Oxidation Filtration	Enhanced Coagulation Filtration	Enhanced Lime Softening
	CMF	OxFilt	CF	LS
USEPA BAT	No	Yes	Yes	Yes
Can treat arsenic levels up to: ¹	40 •g/L	40 •g/L	160 •g/L	80 •g/L
Other Contaminants Treated	Fe ⁺³ , DBP Precursors, Particulates, Pathogens	Fe ⁺³ , Mn ⁺² , Particulates	Fe ⁺³ , Mn ⁺² , DBP Precursors, Particulates, Pathogens	Ca ⁺² , Mg ⁺² , Particulates
Chlorination Required	Yes	Yes	Yes	Yes
Operator Skill Required	High	Medium	High	High
Recommended Water Quality	pH 5.5 - 8.5	pH 5 - 8, >1.5 mg/L Fe ⁺³ , >0.05 mg/L Mn ⁺² , Fe:As 20:1 (by mass)	pH 5.5 - 8.5	pH 10.5 - 11 up to 5 mg/L Fe ⁺³
Waste Generated	Backwash Water, Sludge	Backwash Water, Sludge	Backwash Water, Sludge	Backwash Water, Sludge (high volume)
Other Considerations	None	None	None	Treated water requires pH adjustment
Appropriate as a New Treatment for Small Systems	Yes	Yes	No	No
Applicable for POU	No	No	No	No
POU Cost	N/A	N/A	N/A	N/A
POE Cost	Medium	High	High	High

Table ES-1. Arsenic Treatment Technologies Summary Comparison (2 of 2).

¹ The maximum recommended arsenic levels are calculated from removal rates that are typical for large systems and assume a safety factor of 20%. Small systems, which have additional constraints, may not be able to remove as high of concentrations of arsenic from water.

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List of Acronyms and Abbreviations

AA	Activated Alumina
As	Arsenic
As(III)	Arsenite
As(V)	Arsenate
ASTM	American Society for Testing and Materials
AWWA	American Water Works Association
AwwaRF	American Water Works Association Research Foundation
BAT	Best Available Technology
BV	Bed Volume
cft	Cubic feet
Cl-	Chloride
Cl_2	Chlorine
\mathbf{CMF}	Coagulation-Assisted Microfiltration
\mathbf{CT}	Disinfectant Concentration Times Contact Time
CWA	Clean Water Act of 1987
DBP	Disinfection By-Product
D/DBPR	Disinfectant/Disinfectant By-Product Rule
EBCT	Empty Bed Contact Time
F-	Fluoride
Fe	Iron
FeCl_3	Ferric Chloride
\mathbf{ft}	Feet
FTW	Filter-To-Waste
g	Gram
gal	Gallon
GFH	Granular Ferric Hydroxide
gpd	Gallons per Day
gph	Gallons per Hour
gpm	Gallons per Minute
h	Hour
H_2O	Water
${ m H}_2{ m SO}_4$	Sulfuric Acid
HAA	Haloacetic Acid
HCl	Hydrochloric Acid
HOCl	Hypochlorous Acid
IX	Ion Exchange
kg	kilogram
kWh	Kilowatt Hour
L	Liter
LACSL	Land Application Clean Sludge Limit
lb(s)	Pound(s)

LS	Lime Softening
m	Meter
MCL	Maximum Contaminant Level
mg	Milligram
μg	Microgram
MGD	Million Gallons per Day
mL	Milliliter
mm	Millimeter
Mn	Manganese
MnO_2	Manganese Dioxide
MnO _x	Manganese Oxide
MnO ₄ -	Permanganate
MSHA	Mine Safety and Health Administration
MTZ	Mass Transfer Zone
Ν	Nitrogen
NaOCl	Sodium Hypochlorite
NaOH	Sodium Hydroxide
NF	Nanofiltration
NIOSH	National Institute for Occupational Safety and Health
NO_2^-	Nitrite
NO ₃ -	Nitrate
NOM	Natural Organic Matter
NPDES	National Pollutant Discharge Elimination System
NTU	Nepthelometric Turbidity Units
O&M	Operations and Maintenance
OCl-	Hypochlorite
OH·	Hydroxide
Р	Phosphorus
PFLT	Paint Filter Liquids Test
Hq	Negative Log of Hydrogen Ion Concentration
POE	Point-of-Entry
POTW	Publicly Owned Treatment Works
POU	Point-of-Use
psi	Pounds per Square Inch
RCRA	Resource Conservation and Recovery Act
RO	Reverse Osmosis
S	Sulfur
SBR	Strong Base Resin
\mathbf{scf}	Standard Cubic Feet
scfm	Standard Cubic Feet per Minute
sft	Square feet
$\mathrm{SO}_4{}^{2\text{-}}$	Sulfate
TBLL	Technically Based Local Limit
TC	Toxicity Characteristic

TCLP	Toxicity Characteristic Leaching Procedure
TDS	Total Dissolved Solids
THM	Trihalomethane
TOC	Total Organic Carbon
UFC	Uniform Fire Code
USEPA	United States Environmental Protection Agency
UV	Ultra-Violet
wt%	Weight Percent
WWTP	Wastewater Treatment Plant
У	Year

Equation Nomenclature

Symbol	Definition	Units
β	Individual Stage Water Recovery Rate	%
BV _e	Bed Volumes to Exhaustion	-
C _{As,1}	Arsenic Concentration of Source 1	μg/L
C _{As,2}	Arsenic Concentration of Source 2	μg/L
C _{o,i}	Initial Concentration of Species i	mg/L
C _{f,i}	Final Concentration of Species <i>i</i>	mg/L
C _{FeCl3}	Ferric Chloride Stock Solution Concentration	wt%
C _i	Concentration of Species <i>i</i> in the Feed Stream	mg/L
C _{MCL}	Arsenic MCL	μg/L
C_{MnO_4}	Permanganate Stock Solution Concentration	mg/L
C _{R,i}	Concentration of Species i in the Retentate	mg/L
C _{Source}	Concentration of Arsenic at the Source	μg/L
C _{TDS}	Concentration of Total Dissolved Solids	g/L
δ_{Cl_2}	Chlorine Dose	mg/L as Cl ₂
δ_{FeCl_3}	Ferric Chloride Dose	mg/L
δ_{MnO_4}	Permanganate Dose	mg/L as Mn
D	Column Diameter	Ft
D_{Cl_2}	Ultimate Chlorine Demand	mg/L as Cl ₂
$\mathrm{D}_{\mathrm{MnO}_4}$	Ultimate Permanganate Demand	mg/L as Mn
3	Arsenic Rejection Rate	%
Е	Overall Rejection Rate	%
Es	Individual Stage Contaminant Rejection Rate	%
EBCT	Empty Bed Contact Time	minutes
F	Freeboard Allowance	%
γ_i	Normality of Species <i>i</i>	eq/mole
G_{BW}	Backwash Flux	gpm/sft
G _R	Regeneration Flux	gpm/sft
Gs	Service Rate	gpm/sft
H	Column Height	ft
h _j	Height of Media Layer j	${ m ft}$
i	Annual Inflation Rate	%
m	Mass of Media Added	g
М	Chlorine Mass Flow	lb/day of Cl ₂
\overline{M}_{Brine}	Brine Molarity	mole/L
MWi	Molecular Weight of Species <i>i</i>	mg/mole
n	Number of Stages	

Symbol	Definition	Units
N	Normality of Media	eq/L of resin
\overline{N}	Normality of Feed Stream	eq/L
n _i	Normality of Species <i>i</i> in Feed Stream	eq/L
n _P	Number of Parallel Treatment Trains	-
P ₁₉₉₈	Year 1998 Cost	\$
P _{Current}	Current Cost	\$
Q	Design Flow Rate	gpm
\mathbf{Q}_1	Flowrate of Source 1	gpm
Q ₂	Flowrate of Source 2	gpm
Q_{BW}	Backwash Flowrate	gpm
Q_{Cl_2}	Hypochlorite Metering Pump Rate	gph
Q_{FeCl_3}	Ferric Chloride Metering Pump Rate	mL/min
Q_{MnO_4}	Permanganate Metering Pump Rate	gph
Q _{Source}	Total Source Flowrate	gpm
Q _{Split}	Flowrate to be Split off and Treated	gpm
Q _{Total}	Flowrate of the Final Blended Stream	gpm
$ ho_{ m B}$	Bulk Density of Media	g/L
ρ_{FeCl_3}	Density of Ferric Chloride	kg/L
$ ho_j$	Bulk Density of Media <i>j</i>	lbs/cft
R_{Cl_2}	Desired Chlorine Residual	mg/L as Cl ₂
S	Sorption Capacity of Media	eq/g of resin
s _i	Sorption Capacity of Media for Species <i>i</i>	eq/g of resin
t	Storage Time	days
τ	Optimal Filter Run Time	h
t_{BW}	Backwash Duration	minutes
t _{FTW}	Filter-To-Waste Duration	minutes
t _R	Regeneration Duration	minutes
<u>V</u>	Storage Capacity	gal
V	Volume of Solution Added	L
V _{WW}	Volume of Wastewater	gal
\mathbf{W}_{j}	Weight of Media j	lbs
Y _{Current}	Current Year	-
σ	Safety Margin	%
ω	Treatment Water Loss	%
Ζ	Depth of Sorptive Media	ft

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Section 1 Background

1.1 Purpose of this Manual

This Manual is intended to serve as a resource for small municipal drinking water systems that may be affected by provisions of the Arsenic Rule. For the purpose of this Manual, small is defined as 10,000 or fewer connections. Average water demand for these size systems is normally less than 5 million gallons per day (MGD).

1.2 How to Use this Manual

This Manual includes general arsenic treatment information, cost evaluation tools, and detailed design considerations for specific treatment technologies. The Manual is organized to enable the user to make educated decisions about the most appropriate treatment approach(es) to address arsenic concerns prior to getting involved in detailed design considerations. The user should read Sections 1 through 3 in sequence, then use the treatment selection guidance provided in Section 3 to move to the most appropriate cost and design considerations sections (Sections 4 through 8).

Section 1 provides background information on the arsenic rule, waste disposal regulation, and arsenic chemistry which is useful in understanding the remainder of the Manual.

Section 2 provides descriptions and background information for established arsenic mitigation strategies, with emphasis on those that are both most technically and financially suitable for small systems. The reader should use this section to gather background information on the various arsenic mitigation strategies and determine the volume flowrate to be treated if treatment is selected as the mitigation strategy.

Section 3 describes the considerations required to make an informed treatment method selection. Decision trees are provided to guide the user to the most applicable mitigation or treatment strategy. The selected process is the one that has the highest chance of achieving the most cost effective solution for the particular water source, given the parameters used in the decision making process.

Section 4 enables the reader to quickly estimate the planning-level costs for the selected treatment process. This section is intended for those systems that have identified the need to install new arsenic treatment. Based on the cost estimate,

the utility can then decide if the selected treatment process is economically feasible. If it is not, the user can repeat the decision trees and apply different parameters. It is important that the cost curves provided are for planning-level considerations only and are not used as the primary decision-making tools.

Section 5 presents pre-oxidation alternatives and design calculations. This section is relevant to those water systems which have selected a treatment alternative and do not currently employ oxidation at the source(s) with arsenic concerns.

Sections 6-8 are intended for those systems that have identified the need to install new arsenic treatment technologies. These sections provide detailed design information on each of the primary arsenic treatment technologies.

After the mitigation strategy has been reviewed, the reader should evaluate the cost and constraints of the mitigation strategy. For strategies that involve modification of an existing process, a test should be run. For strategies that involve a new process, a pilot plant test should be run. After the tests have been performed and the results analyzed, the reader should re-evaluate whether the strategy will reduce the arsenic concentration below the Maximum Contaminant Level (MCL).

1.3 Regulatory Direction

1.3.1 The Arsenic Rule

The former arsenic MCL was 50 μ g/L, as established under the 1975 National Primary Drinking Water Regulations. As part of the 1996 Safe Drinking Water Act (SDWA) Amendments, the Environmental Protection Agency (USEPA) was directed to conduct health effects and cost/benefit research for proposal of a new Arsenic Rule in 2000. The USEPA sought to establish a revised MCL that maximized health risk reduction while balancing costs and benefits.

In June 2000, the USEPA proposed a revised arsenic MCL of 5 μ g/L, and requested public comment on alternative MCLs of 3, 10, and 20 μ g/L. The USEPA published a final rule in the Federal Register in January 2001. This rule established a revised arsenic MCL of 10 μ g/L, and identified the following as Best Available Technologies (BATs) for achieving compliance with this regulatory level:

- Ion Exchange (IX)
- Activated Alumina (AA)
- Oxidation/Filtration
- Reverse Osmosis (RO)

- Electrodialysis Reversal
- Enhanced Coagulation/Filtration
- Enhanced Lime Softening

This regulation would apply to all community water systems and non-transient, non-community (NTNC) water systems, regardless of size.

Compliance with the Arsenic Rule will be required by February 2006. The running annual average arsenic level must be at or below the 10 μ g/L at each entry point to the distribution system. However, for smaller systems, point-of-use (POU) treatment can be instituted instead of centralized or point-of-entry (POE) treatment.

1.3.2 Arsenic Rule Compliance

In order to determine compliance, all affected water systems must begin monitoring arsenic at each entry point to the system by January 23, 2006. Analytical results for arsenic are rounded to the nearest 1 μ g/L for reporting and compliance determination. If any sample is above the 10 μ g/L MCL, quarterly monitoring must be performed. The water system is deemed out of compliance if any of the following are true:

- Any Single Result > $40 \mu g/L$
- Average of First Two Quarters > 20 µg/L
- Running Annual Average > 10 µg/L

1.3.3 Other Drinking Water Regulations

In an attempt to comply with one drinking water regulation, it is possible to compromise treatment performance or compliance with other drinking water regulations. Therefore, in an effort to conform with the Arsenic Rule, community water systems should be cognizant of potential system-wide, regulatory and operational impacts. In particular, compliance with the following regulations should be considered.

- Lead and Copper Rule (LCR)
- Enhanced Surface Water Treatment Rule (ESWTR)
- Disinfectant/Disinfectant By-Products Rule (D/DBPR)

Many of the arsenic treatment technologies require pH adjustment for optimization of performance. Figure 1-1 provides a summary of the optimal pH ranges for several arsenic treatment technologies. Sorption and coagulation processes are particularly sensitive to pH, and function most effectively at the lower end of the natural pH range.



Figure 1-1. Optimal pH Ranges for Arsenic Treatment Technologies.

In addition to affecting arsenic treatability, pH also can have a significant effect on disinfection, coagulation, and chemical solubilization/precipitation within the distribution system.

Lead and Copper Rule

Lead and copper in tap water is primarily due to corrosion of plumbing system components within buildings, including copper pipes, lead-based solder used to join segments of copper pipe, and faucets made from brass. Alkalinity and pH play a critical role in providing passive protection from corrosion. In general, the optimum pH range for minimizing corrosion of lead and copper is 7.5-9.0. Therefore, post-treatment pH adjustment is recommended for many of the treatment techniques provided in Figure 1-1.

Enhanced Surface Water Treatment Rule (ESWTR)

Disinfection efficacy is also related to pH if chlorine is used. The biocidal potential of chlorine is enhanced as the pH is reduced. Therefore, utilities that are currently required to meet a CT (disinfectant concentration times contact time) standard should receive disinfection benefit from pH reduction at the head of the treatment process. Post-treatment pH adjustment for corrosion control should be conducted after CT requirements are met.

Coagulation and flocculation processes are also related to pH. The formation of floc is improved as the pH is reduced, within the range 5-8. However, iron and aluminum-based coagulants also consume alkalinity, thereby decreasing the buffering capacity of the water.

Disinfectant/Disinfectant By-Products Rule (D/DBPR)

Chlorine reacts with natural organic matter (NOM) to form halogenated disinfection byproducts, particularly trihalomethanes (THMs) and haloacetic acids (HAAs). Therefore, incorporating pre-chlorination to convert arsenite to arsenate could increase the occurrence of these regulated chemicals. The Stage 1 D/DBPR, which became effective in January 2002, establishes running annual average MCLs of 80 μ g/L and 60 μ g/L for THMs and HAAs, respectively. The Stage 2 D/DBPR, scheduled for promulgation in 2002, will further tighten these standards.

1.3.4 Waste Disposal Regulations

Waste disposal is an important consideration in the treatment selection process. Arsenic removal technologies produce several different types of waste, including sludges, brine streams, backwash slurries, and spent media. These wastes have the potential for being classified as hazardous and can pose disposal problems. Table 1-1 provides a summary of the available waste disposal options and associated criteria. These are further discussed in the following paragraphs.

Table 1-1. Waste Disposal Options.				
Waste Type	Disposal Method (Criteria)			
	• Direct Discharge (CWA, NPDES)			
Liquid	• Indirect Discharge (TBLLs)			
	• On-Site Sewerage (POU systems)			
	Land Application (LACSL)			
Solid (sludge, media)	Conventional Landfill (PFLT, TCLP)			
	Hazardous Landfill (PFLT)			

Liquid waste streams must meet the Toxicity Characteristic (TC) in order for the waste to be classified as non-hazardous. The current arsenic TC is 5.0 mg/L. Those liquid waste streams that contain more than 5.0 mg/L of arsenic would be in violation of the Toxicity Characteristic and therefore classified as a hazardous waste. Many of the arsenic removal technologies also remove other constituents. The waste stream must be analyzed for these other substances that may be in concentrations above their respective TCs. Because of RCRA (Resource Conservation and Recovery Act) requirements and cost restrictions, on-site treatment or off-site disposal of hazardous waste is considered infeasible for small water systems. Indirect discharge may be an option since wastes that pass through a sewer system to a Publicly Owned Treatment Works (POTW) are exempt from RCRA regulation. Solids waste streams are subject to the Toxicity Characteristic Leaching Procedure (TCLP). These solids waste streams should be dewatered via mechanical or non-mechanical means to generate sludge for use in the TCLP. This test is used to simulate the potential for leaching in a landfill setting. The TCLP leachate must meet the TC in order for the waste to be classified as non-hazardous.

There are five realistic methods for the disposal of arsenic waste streams.

Landfill Disposal

Historically, conventional landfills have been commonly used for the disposal of non-hazardous solid wastes emanating from treatment processes. However, the hazard potential of arsenic may limit the feasibility of this alternative.

Dewatered sludge and spent media can be disposed in a conventional (nonhazardous) landfill if the waste passes both the Paint Filter Liquids Test (PFLT) and the TCLP. The PFLT is used to verify that there is no free liquid residual associated with the waste. However, if the TCLP extract contains arsenic above the TC, the waste residuals must be disposed in a designated and licensed hazardous waste landfill. These landfills are strictly regulated under RCRA and have extensive monitoring and operational guidelines. As such, the costs of disposal are relatively high. As with conventional landfill disposal, waste sludges must not contain free liquid residuals.

A critical element of hazardous waste disposal is the cradle-to-grave concept. The party responsible for generating the hazardous waste forever retains liability and responsibility for the fate and transport of the waste.

Direct Discharge to Surface Waters

Direct discharge refers to the disposal of liquid waste streams to nearby surface waters, which act to dilute and disperse the waste by-products. The primary advantage of direct discharge is reduced capital and O&M costs due to the elimination of residuals treatment. The feasibility of this disposal method is subject to provisions of the National Pollution Discharge Elimination System (NPDES). The allowable discharge is a function of the ability of the receiving water to assimilate the arsenic without exceeding water quality criteria established under the Clean Water Act. Different water quality criteria exist depending on the classification of the receiving water. The ambient arsenic criteria for waters used for fish consumption and drinking water consumption are 0.14μ g/L and 0.0175μ g/L, respectively. The NPDES criteria used to calculate allowable discharge limits include ambient contaminant levels, low flow conditions of the receiving water, and design flow of the proposed discharge.

Indirect Discharge

The discharge of liquid waste streams to a municipal wastewater treatment plant (WWTP) is a potential disposal alternative. In this case, the waste stream will be subject to Technically Based Local Limits (TBLLs) established as part of the WWTP's Industrial Pretreatment Program. TBLLs are established in order to protect WWTP operation, assure compliance with NPDES permits, and prevent an unacceptable level of accumulation of contaminants in the process sludge and biosolids. The TBLLs are computed for each WWTP to take into account the background levels of contaminants in the municipal wastewater. In addition, the estimated flow contributed by the water treatment plant, as compared to the background municipal flow, is used to calculate the allowable contaminant loading to the WWTP.

Land Application

Dedicated land application of concentrated sludge is allowed under certain conditions. The Land Application Clean Sludge Limit (LACSL) specifies that the arsenic concentration must not exceed 41 mg/kg. If this threshold is exceeded, then land application is limited to 41 kg per hectare. Application is dependent upon several variables, including soil and sludge chemistry, land use designations, and the type of vegetation in the application area.

On-Site Sewerage

Liquid waste streams from reverse osmosis POU devices should be suitable for disposal in an on-site sewerage or septic system. Figure 1-2 illustrates a typical flow diagram for RO POU water treatment and on-site waste disposal.



Arsenic is concentrated in the RO retentate during normal process operation. However, eventually this retentate is combined with other domestic wastewater in the septic tank. Because the amount of water consumed is small relative to the total flow entering the dwelling, the concentration of arsenic in the *blended* wastewater is nearly identical to that in the influent stream.

1.4 Health Effects

Motivation to reduce the arsenic MCL is driven by the findings of health effects research. Over the past several years, numerous toxicological and epidemiological studies have been conducted to ascertain health risks associated with low-level exposure to arsenic via ingestion.

Ingestion of inorganic arsenic can result in both cancer and non-cancer health effects (NRC, 1999). Arsenic interferes with a number of essential physiological activities, including the actions of enzymes, essential cations, and transcriptional events in cells (NRC, 1999). The USEPA has classified arsenic as a Class A human carcinogen. Chronic exposure to low arsenic levels (less than 50 μ g/L) has been linked to health complications, including cancer of the skin, kidney, lung, and bladder, as well as other diseases of the skin, neurological, and cardiovascular system (USEPA, 2000).

The primary mode of exposure is ingestion of water containing arsenic. Dermal absorption of arsenic is minimal; therefore, hand washing and bathing do not pose a known risk to human health. For this reason, point-of-use devices were approved as small system compliance technologies.

1.5 Arsenic Chemistry

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 Manual is on inorganic arsenic.

Total arsenic is the sum of both particulate arsenic, which can be removed by a 0.45-micron filter, and soluble arsenic. Soluble arsenic generally exists in either the +3 (tri-) or +5 (penta-) valence state, depending on local oxidation-reduction conditions. Under anaerobic conditions, arsenic exists primarily as arsenite (trivalent). 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.

The dissociation of both arsenite and arsenate is pH-dependent, as depicted in Figure 1-3 and Figure 1-4, respectively. The kinetics of dissociation are nearly instantaneous.



Figure 1-3. Dissociation of Arsenite {As(III)}.



Figure 1-4. Dissociation of Arsenate {As(V)}.

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 (6-9), 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 should be based on several considerations, including cost, integration with existing treatment, disinfection requirements, and secondary effects. This is discussed further in Section 2.4. This page intentionally left blank.

Section 2 Arsenic Mitigation Strategies

2.1 Description of Arsenic Mitigation Strategies

Problematic arsenic levels in drinking water can be mitigated in several different ways. This Manual will address the following mitigation strategies:

- Source Change The abandonment of the problematic sources(s) and subsequent switch to other source(s) within the system or purchase from a neighboring system.
- Blending The combination of multiple water sources to produce a stream with an arsenic concentration below the MCL.
- Centralized or Point-of-Entry (POE) Treatment The processing of the high arsenic water stream to reduce the arsenic concentration to below the MCL.
- Sidestream Treatment The centralized treatment of a portion of the high arsenic water stream and subsequent blending back with the untreated portion of the stream to produce a water that meets the MCL.
- Point-of-Use Treatment (POU) Only the water to be used for human consumption is treated by the utility at a point after the water exits the distribution system (e.g., at a household faucet).

There are three primary categories of available treatment processes. Technologies that have been designated as BATs are noted with an asterisk.

- Sorption Treatment Processes
 - Ion Exchange*
 - Activated Alumina*
 - Granular Ferric Hydroxide
- Membrane Treatment Processes
 - Reverse Osmosis*
- Precipitation/Filtration Processes
 - Enhanced Coagulation/Filtration *
 - Coagulation-Assisted Microfiltration
 - Oxidation/Filtration*
 - Enhanced Lime Softening*

The selection of the most appropriate method should be based on feasibility issues, system constraints, and costs.

2.2 Source Change

Perhaps the simplest approach for remedying a high arsenic source 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 for producing 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 switching production to another location. In this particular case, the utility has two options: (1) locate or install a new source, or (2) purchase water from a nearby system if an intertie exists. 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 at the federal level, as long as the running annual average at the entry point to the distribution system does not exceed the MCL. Individual state requirements may preclude this option.

2.3 Blending and Side-Stream Treatment Prior to Distribution

The revised arsenic MCL must be met at all entry points to the distribution system. Therefore, community water systems that utilize multiple sources will need to consider a mitigation strategy for each source that exceeds the revised MCL.

Blending and sidestream treatment are viable mitigation strategies for conservative inorganic substances, such as arsenic. Blending involves mixing waters from two or more different sources *prior* to distribution. Sidestream treatment involves splitting flow, treating one stream, and blending it with the untreated stream prior to distribution. These strategies can be used independently or in a variety of combinations, as illustrated in Figure 2-1 through Figure 2-4. The purpose of blending and sidestream treatment is to reduce the overall level of treatment required, or eliminate the need for treatment altogether.


Figure 2-1. Blending.







Figure 2-2. Treatment and Blending.





2.3.1 Blending

Stand-alone blending (Figure 2-1) is only a consideration when a water system has multiple sources, one (or more) with arsenic levels above the MCL and one (or more) with arsenic levels below the MCL. The flow required from each source can be determined by performing a conservative mass balance. In order for blending applications to be appropriate, the wells with low arsenic levels must be reliable on a continuous basis.

Generally, the target arsenic concentration of the final blended stream is set below the MCL by a safe margin (e.g., 10-20% below the MCL). The following equation can be used to determine the required flowrate from the low arsenic source (Q_2) which, when blended with flow from the high arsenic source (Q_1), will produce water with an arsenic concentration a safe margin below the MCL.

$$Q_2 = Q_1 \cdot \left(\frac{[1 - \sigma] \cdot C_{MCL} - C_{As,1}}{C_{As,2} - [1 - \sigma] \cdot C_{MCL}} \right)$$
Eqn. 2-1

Where:

 $\begin{array}{ll} Q_1 &= Flowrate \ of \ Source \ 1 \ (gpm) \\ Q_2 &= Flowrate \ of \ Source \ 2 \ (gpm) \\ C_{As,1} &= Arsenic \ Concentration \ of \ Source \ 1 \ (\mu g/L) \\ C_{As,2} &= Arsenic \ Concentration \ of \ Source \ 2 \ (\mu g/L) \\ C_{MCL} &= Arsenic \ MCL \ (\mu g/L) \\ \sigma &= Safety \ Margin \ (\%) \end{array}$

For example, suppose that water from Sources 1 and 2 in Figure 2-1 contain arsenic concentrations of 15 μ g/L and 6 μ g/L, respectively. The final arsenic MCL is set at 10 μ g/L, and assume that the water system wants to provide a 20% safety margin (i.e., produce water with 8 μ g/L of arsenic). Assuming the maximum flowrate from Source 1 is 700 gpm, the minimum required flowrate from Source 2 is 2,450 gpm and is calculated as follows:

$$Q_{2} = 700 \text{ gpm} \cdot \left(\frac{\left[1 - 0.2\right] \cdot 10 \ \mu\text{g/L} - 15 \ \mu\text{g/L}}{6 \ \mu\text{g/L} - \left[1 - 0.2\right] \cdot 10 \ \mu\text{g/L}}\right) = 2,450 \text{ gpm}$$

2.3.2 Sidestream Treatment

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., reverse osmosis) 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 are provided in Table 2-1. In the simple case of sidestream treatment from a single source (Figure 2-5), the flowrate of the split stream requiring treatment can be calculated using Equation 2-2. The resulting total treated flowrate can be calculated using Equation 2-3.

$$Q_{\text{Split}} = Q_{\text{Source}} \left(\frac{C_{\text{Source}} - [1 - \sigma] \cdot C_{\text{MCL}}}{C_{\text{Source}} [1 - (1 - \omega)(1 - \varepsilon)] - \omega \cdot [1 - \sigma] \cdot C_{\text{MCL}}} \right)$$
Eqn. 2-2

$$Q_{\text{Total}} = Q_{\text{Source}} - \omega Q_{\text{Split}}$$
 Eqn. 2-3

Where:

Q _{Source}	= Total Source Flowrate (gpm)
Q_{Split}	= Flowrate to Split Off for Treatment (gpm)
Q _{Total}	= Flowrate of the Final Blended Stream (gpm)
C _{Source}	= Arsenic Concentration of the Source (μ g/L)
C _{MCL}	= Arsenic MCL (µg/L)
σ	= Safety Margin (%)
ω	= Treatment Water Loss (%)
3	= Arsenic Rejection Rate (%)



Figure 2-5. Sidestream Treatment.

For example, suppose a water system operates a single well at a maximum flowrate of 500 gpm. The well contains 12 μ g/L of arsenic. Further, assume that the final arsenic MCL is set at 10 μ g/L, and that the water system wants to provide a 20% safety margin (i.e., produce water with 8 μ g/L of arsenic). The utility has selected a reverse osmosis process which has demonstrated an arsenic removal efficiency of 95% at a water loss of 40%. Using Equation 2-2, approximately 47% of the total source flowrate (or 237 gpm) should be split and sent to the RO treatment unit. The final (blended) flowrate is 405 gpm.

$$Q_{\text{Split}} = 500 \text{ gpm} \cdot \left(\frac{12 \,\mu\text{g}/\text{L} - [1 - 0.2] \cdot 10 \,\mu\text{g}/\text{L}}{12 \,\mu\text{g}/\text{I}[1 - (1 - 0.4)(1 - 0.95)] - 0.4 \cdot [1 - 0.2] \cdot 10 \,\mu\text{g}/\text{L}}\right) = 237 \text{ gpm}$$
$$Q_{\text{Total}} = 500 \text{ gpm} - 0.4 \cdot 237 \text{ gpm} = 405 \text{ gpm}$$

Treatment	Arsenic Removal Efficiency	Water Loss
Sorption Processes		
Ion Exchange	$95\%^{1}$	0%
Activated Alumina (Throw-Away Media)	$95\%^1$	0%
Granular Ferric Hydroxide	$50-98\%^{2}$	0%
Iron and Manganese Removal Processes		
Oxidation/Filtration (Greensand)		
With Ferric Chloride Addition	$80\%^1$	$\leq 2\%$
Without Ferric Chloride Addition	50%	$\leq 2\%$
Membrane Processes		
Reverse Osmosis	$>95\%^{1}$	$15-75\%^{2}$
Nanofiltration	$30-95\%^2$	$15\%^2$
Precipitative Processes		
Coagulation Assisted Microfiltration	$90\%^{1}$	0%
Enhanced Coagulation/Filtration		
With Alum	$< 90\%^2$	0%
With Ferric Chloride	$95\%^1$	
Enhanced Lime Softening	$90\%^{1}$	0%
Point-Of-Use Treatment Processes		
POU Reverse Osmosis	$>95\%^{1}$	$10-80\%^{2,3}$
POU Activated Alumina	$90\%^{1}$	0%
POU Granular Ferric Hydroxide	$50-98\%^2$	0%
1 USEPA 2000 Table 3-12		

Table 2-1. Typical Treatment Efficiencies and Water Losses.

JSEPA 2000, Table 3-12.

² USEPA 2000.

³ NSF Intl., 2001.

2.4 **Pre-Oxidation Processes**

Reduced inorganic arsenic (arsenite) should be converted to arsenate to facilitate This step is critical for achieving optimal performance of all unit removal. processes described in this Manual. Conversion to arsenate can be accomplished by providing an oxidizing agent at the head of any proposed arsenic removal process. Chlorine and permanganate are highly effective for this purpose. They oxidize arsenite to arsenate within one minute in the pH range of 6.3 to 8.3. 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. Ultraviolet (UV) light, by itself, is also ineffective. However, if the water is spiked with sulfite, UV photo-oxidation shows promise for arsenite conversion (Ghurye and Clifford, 2001). Based on these considerations, only chlorine and permanganate are discussed in this Manual.

Table 2-2 provides a summary of the benefits and drawbacks associated with the use of chlorine and permanganate oxidation technologies. The choice of chemical oxidant should be based primarily on the arsenic treatment technology to be employed (as described in Section 3), and secondarily on factors provided in Table 2-2. Many small water systems employ chlorine disinfection, either alone or as part of a larger treatment process. In most of these instances, the existing chlorination process can be optimized to provide concurrent arsenite oxidation. The same is true for those systems employing permanganate addition.

Table 2-2. Comparison of Oxidizing Agents.			
Oxidant	Benefits	Drawbacks	
Chlorine	 Low relative cost (\$0.2/lb.) Primary disinfection capability Secondary disinfectant residual MnO_x media regenerant 	 Formation of disinfection by-products Membrane fouling Special handling and storage requirements 	
Permanganate	 Unreactive with membranes No formation of disinfection by- products Ease of handling and storage MnO_x media regenerant 	 High relative cost (\$1.35/lb.) No primary disinfection capability Does not provide secondary disinfectant residual Formation of Mn particulates 	

2.4.1 Chlorine

Issues associated with pre-chlorination are: (1) sensitivity of the treatment process to chlorine; (2) disinfection by-product (DBP) formation potential; and (3) code requirements associated with chemical storage and handling. Chlorine can be added either as a gas or as liquid hypochlorite. For new chlorine feed installations, these alternatives should be evaluated with respect to capital and operating costs, O&M requirements, code restrictions, containment requirements, footprint, and safety concerns, among other issues. Gas feed is typically conducted with either 150-pound cylinders or 2,000-pound (1-ton) containers, depending on the rate of chlorine consumption. Small systems normally use the 150-pound cylinders. Liquid hypochlorite can either be generated on-site (0.8% strength), or purchased as commercial strength (12.5%) liquid hypochlorite.

The oxidation-reduction reaction for chlorine (as hypochlorite) is provided in Equation 2-4. The stoichiometric oxidant demand is $0.95 \ \mu g/L$ of chlorine (as Cl_2) per $\mu g/L$ of arsenite (as As).

$$OCl + H_3AsO_3 \rightarrow Cl + H_3AsO_4$$
 Eqn. 2-4

The ability of chlorine to convert arsenite to arsenate was found to be relatively independent of pH in the range 6.3 - 8.3. Based on laboratory oxidation studies (Ghurye, 2001), chlorine applied in a stoichiometric excess

of 3 times was capable of converting over 95% of arsenite within 40 seconds. Similar conversion efficiencies were obtained in the presence of dissolved iron, manganese, sulfide, and total organic carbon (TOC).

2.4.2 Permanganate

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 (60 g/L at room temperature). Most applications involve metering of a permanganate solution.

The oxidation-reduction reaction for permanganate is provided in Equation 2-5. The stoichiometric oxidant demand is $0.49 \,\mu$ g/L of permanganate (as Mn) per μ g/L of arsenite (as As).

$$MnO_{4} + 1.5 H_3AsO_3 + H^+ \rightarrow MnO_2 + 1.5 H_3AsO_4 + 0.5 H_2O$$
 Eqn. 2-5

The ability of permanganate to convert arsenite to arsenate was found to be relatively independent of pH in the range 6.3 - 8.3. Based on laboratory oxidation studies (Ghurye, 2001), permanganate applied in a stoichiometric excess of 3 times was capable of converting over 95% of arsenite within 40 seconds. Similar conversion efficiencies were obtained in the presence of dissolved iron, manganese, sulfide, and TOC.

The primary drawback to the use of permanganate is the formation of manganese particulates (MnO_2). To prevent the accumulation of these deposits in the distribution system, they must be removed via filtration.

2.5 Sorption Treatment Processes

The following three forms of sorption treatment are addressed: (1) ion exchange, (2) adsorption to activated alumina media, and (3) adsorption on granular ferric hydroxide media.

2.5.1 Ion Exchange

Ion exchange (IX) is a physical-chemical process in which ions are swapped between a solution phase and solid resin phase. The solid resin is typically an elastic three-dimensional hydrocarbon network containing a large number of ionizable groups electrostatically bound to the resin. These groups are exchanged for ions of similar charge in solution that have a stronger exchange affinity (i.e., selectivity) for the resin. In drinking water treatment, this technology is commonly used for softening. Arsenic removal is accomplished by continuously passing water under pressure through one or more columns packed with exchange resin, as illustrated in Figure 2-6. Arsenate can be removed through the use of strongbase anion exchange resin (SBR) in either chloride or hydroxide form. These resins are insensitive to pH in the range 6.5 to 9.0 (USEPA, 2000; reference to Clifford et al., 1998). The following paragraphs discuss factors that affect IX system efficiency and economics.



Figure 2-6. Ion Exchange Process Flow Diagram.

The exchange affinity of various ions is a function of the net surface charge. Therefore, the efficiency of the IX process for arsenate removal depends strongly on the solution pH and the concentration of other anions, most notably sulfates and nitrates. These and other anions compete for sites on the exchange resin according to the following selectivity sequence (Clifford, 1999).

$$SO_{4^{2}} > HAsO_{4^{2}} > NO_{3^{\circ}}, CO_{3^{2^{\circ}}} > NO_{2^{\circ}} > Cl^{\circ}$$

High levels of total dissolved solids (TDS) can adversely affect the performance of an IX system. In general, the IX process is not an economically viable treatment technology if source water contains over 500 mg/L of TDS and/or over 50 mg/L of sulfate (SO₄²⁻). Figure 2-7 illustrates the effect of sulfate ions on the performance of IX media. Although this relationship will not be exactly the same for all waters, it does provide a general indication of the impact of sulfates on IX treatment.



Figure 2-7. Effect of Sulfate on Ion Exchange Performance (Clifford, 1999).

One of the primary concerns related to IX treatment is the phenomenon known as chromatographic peaking, which can cause arsenic and nitrate levels in the treatment effluent to exceed those in the influent stream. This can occur if sulfates are present in the raw water and the bed is operated past exhaustion. Because sulfate is preferentially exchanged, incoming sulfate anions may displace previously sorbed arsenic and nitrate. In most groundwaters, sulfates are present in concentrations that are orders of magnitude greater than arsenic. Therefore, the level of sulfates is one of the most critical factors to consider for determining the number of bed volumes that can be treated. Careful monitoring of the effluent stream, operation of the bed to a known volume setpoint (followed by regeneration), and parallel column operation are useful techniques for avoiding chromatographic peaking. Frequently, the bed volume setpoint is based on the breakthrough of sulfate. The kinetics of breakthrough are rapid; therefore a margin of safety should be provided.

Hydraulic considerations associated with IX include empty bed contact time (EBCT); resin fouling; and headloss. The recommended EBCT range is 1-5 minutes. The presence of suspended solids in the feed water could gradually plug the media, thereby increasing headloss and necessitating more frequent backwashing. Therefore, pre-filtration is recommended if the source water turbidity exceeds 0.3 NTU. Mineral scaling and mica can also foul exchange resin.

Resin which has been used to exhaustion can be regenerated on-site using a two-step process: (1) contacting with brine (for chloride-form SBR) or caustic soda (for hydroxide-form SBR) and (2) clean water rinse.

Single-pass regeneration of anion exchange media typically produces 4-5 bed volumes of brine waste (USEPA, 2000; reference to AwwaRF, 1998). In a study conducted by the USEPA (October 2000), dissolved arsenic concentrations in spent brine ranged from 1.83 mg/L to 38.5 mg/L, with an average value of 16.5 mg/L. It is anticipated that for most sources with arsenic levels above 10 μ g/L and sulfate levels below 50 mg/L, the spent regenerant will contain at least 5.0 mg/L of dissolved arsenic. This brine stream can be mixed with backwash and rinse water in an equalization basin to reduce the overall dissolved arsenic concentration prior to disposal.

Liquid waste streams (less than 0.5% solids) are evaluated directly against the TC to characterize hazard potential. Those liquid waste streams that contain more than 5.0 mg/L of arsenic would be in violation of the Toxicity Characteristic and therefore classified as a hazardous waste. Because of RCRA requirements and cost restrictions, on-site treatment or off-site disposal of hazardous waste is considered infeasible for small water systems. Indirect discharge may be an option since wastes that pass through a sewer system to a POTW are exempt from RCRA regulation. The critical factor dictating the feasibility of this option will be TBLLs for arsenic and TDS. Water systems that elect to use brine recycle will further concentrate the dissolved arsenic and solids, making it more unlikely that the stream will meet local TBLLs.

Replacement of ion exchange media may be required over time. Based on previous studies, spent IX resin should pass the TCLP, enabling it to be disposed of in a conventional landfill. This is true regardless of whether or not the media has been regenerated prior to conducting the TCLP.

2.5.2 Activated Alumina

Activated alumina (AA) is a porous, granular material with ion exchange properties. The media, aluminum trioxide, is prepared through the dehydration of aluminum hydroxide at high temperatures. AA grains have a typical diameter of 0.3 to 0.6 mm and a high surface area for sorption.

In drinking water treatment, packed-bed AA adsorption is commonly used for removal of silica, natural organic matter, and fluoride. The removal of arsenic by AA adsorption can be accomplished by continuously passing water under pressure through one or more beds packed with AA media, as illustrated in Figure 2-8. The efficiency and economics of the system are contingent upon several factors, as discussed in the following paragraphs.



Figure 2-8. Activated Alumina Process Flow Diagram.

The level of competing ions affects the performance of AA for arsenic removal, although not in the same manner nor to the same extent as IX. The following selectivity sequence has been established for AA adsorption:

$$OH^{\cdot} > H_2AsO_4^{\cdot} > Si(OH)_3O^{\cdot} > F^{\cdot} > HSeO_3^{\cdot} > TOC > SO_4^{2\cdot} > H_3AsO_3^{\cdot}$$

The selectivity of AA towards arsenite is poor, owing to the overall neutral molecular charge at pH levels below 9.2. Therefore, pre-oxidation of arsenite to arsenate is critical. Several different studies have established the optimum pH range as 5.5-6.0, and demonstrated greater than 98% arsenic removal under these conditions. Activated alumina column runs operated under acidic pH conditions are 5 to 20 times longer than under natural pH conditions (6.0-9.0), as depicted in Figure 2-9. However, many small utilities elect to conduct AA treatment under natural pH conditions. In these cases, the savings in capital and chemical costs required for pH adjustment and media regeneration offset the costs associated with decreased run length.



Figure 2-9. Effect of pH on Activated Alumina Performance (USEPA, 2000; original data from Hathaway and Rubel, 1987).

Several constituents can interfere with the adsorption process, either by competing for adsorption sites or clogging the media with particulate matter.

Table 2-3. Water Quality Interferences with AA Adsorption.			
Parameter	Problem Level		
Chloride	250 mg/L		
Fluoride	2 mg/L		
Silica	50 mg/L		
Iron	0.5 mg/L		
Manganese	0.05 mg/L		
Sulfate	720 mg/L		
Dissolved Organic Carbon	4 mg/L		
Total Dissolved Solids	1,000 mg/L		

These constituents, and their corresponding problematic levels, are summarized in Table 2-3.

Hydraulic considerations associated with AA adsorption include empty bed contact time and headloss. For most types of AA media, the recommended EBCT range is 3-10 minutes. The presence of suspended solids in the feed water could gradually clog the media, thereby increasing headloss. Pre-filtration is recommended for sources where the turbidity exceeds 0.3 NTU.

The technologies and market for alumina-based adsorptive media continue to expand. There are several emerging proprietary media, commonly referred to as modified AA, which contain alumina in a mixture with other substances such as iron and sulfur. In some instances, these media have greater overall adsorptive capacities, enhanced selectivity towards arsenic, and/or greater overall operational flexibility than conventional AA, thus making them more cost-effective. To account for this industry growth, the decision trees in Section 3 include a treatment alternative known as modified-AA. If this endpoint is reached, the water system should strongly consider more detailed investigation into current, innovative media. The relevance of these types of media to a particular application can be determined through a capacity study, as discussed in Section 6. It is recommended that all media used in water treatment be approved under NSF Standard 61.

AA media can either be regenerated on-site or disposed of and replaced with fresh media. On-site regeneration of AA media typically produces 15-25 bed volumes of caustic soda waste. Because of the high pH of the regeneration process, roughly 2% of the AA media dissolves during each regeneration sequence. Therefore, the waste solution typically contains high levels of TDS, aluminum, and soluble arsenic. In most cases, this arsenic level will exceed the 5.0 mg/L TC, and the waste stream will be classified as a hazardous liquid. Further, it is unlikely that indirect discharge will be a viable option as arsenic levels are expected to exceed most TBLLs. Backwashing may also be necessary to prevent cementation of the media, which can occur as a result

of dissolution caused by chemical addition during regeneration. For these reasons, regeneration of AA is considered an infeasible option for most small water systems.

The alternative for systems considering AA adsorption is the use of throwaway media, operated with or without pH adjustment. The savings in O&M requirements and residuals disposal may offset the cost of periodically replacing the media. For this option, systems must provide an equalization basin for backwash water (if applicable) and a staging area to store spent media prior to disposal. Throwaway AA media is expected to pass the TCLP test, enabling it to be disposed of in a conventional landfill (Wang, 2000).

2.5.3 Granular Ferric Hydroxide

Adsorption on granular ferric hydroxide (GFH) media is an emerging treatment technique for arsenic. The sorption process has been described as chemisorption (Selvin, 2000), which is typically considered to be irreversible. It can be applied in fixed bed pressure columns, similar to those for AA. Due to limited performance research, it has not yet been designated as a BAT by the USEPA.

The few studies conducted with GFH media have revealed that the affinity of this media for arsenic is strong under natural pH conditions, relative to AA. This feature allows GFH to treat much higher bed volumes without the need for pH adjustment. However, similar to AA, optimal GFH performance is obtained at lower pH values. The recommended operating conditions include an EBCT of 5 minutes and a loading rate of 5 gpm/sft.

Phosphate has been shown to compete aggressively with arsenate for adsorption sites. Each 0.5 mg/L increase in phosphate above 0.2 mg/L will reduce adsorption capacity by roughly 30% (Tumalo, 2002).

Exhausted GFH media has successfully passed the TCLP test. (MacPhee, 2001).

2.6 Membrane Treatment Processes

Membrane separation technologies are attractive arsenic treatment processes for small water systems. They can address a numerous of water quality problems while maintaining simplicity and ease of operation. The molecular weight cut-off of microfiltration (MF) and ultrafiltration (UF) processes necessitates the use of a coagulation stage to generate arsenic-laden floc. However, nanofiltration (NF) and reverse osmosis (RO) units have a much larger retention spectrum, and can be used as stand-alone arsenic treatment under most water quality conditions. Figure 2-10 provides a block flow diagram for a RO/NF membrane process.



Figure 2-10. Membrane Process Flow Diagram.

Nanofiltration is a pressure-driven membrane separation process, which acts to remove NOM, large molecules, and ions by both physical (size exclusion) and electrostatic mechanisms. The membrane surface is composed of either cellulose acetate or polyamide and contains pores less than 0.01 micron in size. The arsenic removal efficiency of NF processes is dependant on the feed water characteristics. Since particles with higher charges are more likely to be electro-statically repulsed, NF is much more effective at removing arsenate than arsenite. Therefore, preoxidation is recommended. Further, divalent arsenate is more likely to be retained than monovalent arsenate. Therefore, the optimum pH range is above 7.0. The driving force for separation is the pressure gradient maintained across each membrane. Typical NF operating pressures are between 50 and 150 psi. Under natural pH conditions, arsenate rejection rates (i.e., treatment efficiency) are usually 60 - 70% per stage (at a water recovery of 80 - 90%).

Reverse osmosis is a pressure-driven membrane separation process capable of removing dissolved solutes from water by means of particle size, dielectric characteristics, and hydrophilicity/hydrophobicity. Most RO membranes are made of cellulose acetate or polyamide composites cast into a thin film. The semipermeable (non-porous) membrane is then constructed into a cartridge called an RO module, typically either hollow-fiber or spiral-wound. Reverse osmosis is capable of achieving over 95% removal of arsenic in a single pass. As an added benefit, RO also effectively removes several other constituents from water, including organic carbon, salts, dissolved minerals, and color. The treatment process is relatively insensitive to pH. In order to drive water across the membrane surface against natural osmotic pressure, feed water must be sufficiently pressurized with a booster For drinking water treatment, typical operating pressures are between pump. 100 and 350 psi. Water recovery is typically 60 - 80%, depending on the desired purity of the treated water. In some cases, particularly POU applications, RO units are operated at tap water pressures. This results in a significantly lower water recovery.

Multiple RO/NF units can be applied in series to improve the overall arsenic removal efficiency. Figure 2-11 illustrates a 2-stage RO/NF treatment process. The overall rejection rate for a multi-staged RO/NF treatment process can be calculated as:

$$E = 1 - (1 - E_s)^n$$
 Eqn. 2-6

Where:

E = Overall Rejection Rate (Treatment Efficiency)

 E_{S} = Individual Stage Contaminant Rejection Rate

n = Number of Stages



Figure 2-11. Two-Stage RO/NF Treatment Process Schematic.

Indirect discharge to a POTW or direct discharge to an on-site sewerage system are considered the most viable residuals disposal option. For those systems considering indirect discharge, the retentate must meet local TBLLs for arsenic. The arsenic concentration in the retentate can be calculated using equation 2-7.

$$C_{R,i} = \frac{C_i \cdot E_s}{1 - \beta}$$
 Eqn. 2-7

Where:

 $C_{R,i}$ = Concentration of Species *i* in the Retentate (mg/L)

 C_i = Concentration of Species *i* in the Feed Stream (mg/L)

 E_s = Individual Stage Contaminant Rejection Rate (%)

 β = Individual Stage Water Recovery Rate (%)

Membrane fouling can occur in the presence of NOM and various inorganic ions, most notably calcium, magnesium, silica, sulfate, chloride, and carbonate. These ions can be concentrated (in the retentate) to concentrations an order of magnitude higher than in raw water. This can lead to the formation of scale on the membrane surface, which in turn can cause a decline in arsenic rejection and water recovery. Further, the membrane surface can act as a substrate for biological growth. Membrane cleaning can restore treatment performance; however, the cleaning process is difficult and costly. The rate of membrane fouling depends on the configuration of the module and feed water quality. Most RO modules are designed for cross-flow filtration, which allows water to permeate the membrane while the retentate flow sweeps rejected salts away from the membrane surface. In many cases, pre-filtration (commonly through sediment or granular activated carbon) is worthwhile. This minimizes the loading of salt precipitates and suspended solids on the membrane surface, thereby extending run length, improving system hydraulics, and reducing O&M requirements.

Some membranes, particularly those composed of polyamides, are sensitive to chlorine. Feed water should be dechlorinated (if applicable) in these instances. Another potential concern associated with RO treatment is the removal of alkalinity from water, which in turn could affect corrosion control within the distribution system. If feasible, this problem can usually be avoided by conducting sidestream treatment for arsenic removal.

2.7 Precipitation/Filtration Treatment Processes

The following three chemical precipitation processes are addressed: (1) enhanced coagulation-filtration, (2) coagulation-assisted microfiltration, and (3) enhanced lime softening. Figure 2-12 provides a block flow diagram for the precipitation/filtration processes.



Figure 2-12. Oxidation/Filtration Process Flow Diagram.

2.7.1 Enhanced Coagulation/Filtration

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. The most widely used coagulants for water treatment are aluminum and ferric salts, which hydrolyze to form aluminum and iron hydroxide particulates, respectively.

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.

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.

Coagulation/filtration processes, both conventional and pressurized, can be optimized to remove dissolved inorganic arsenic from water. The mechanism involves the adsorption of arsenic to an aluminum or ferric hydroxide precipitate. The arsenic becomes entrapped as the particle continues to agglomerate. Arsenite is not effectively removed because of its overall neutral charge under natural pH conditions. Therefore, pre-oxidation is recommended. 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 μ g/L of arsenic. Influent arsenic levels do not appear to impact the effectiveness of this treatment process.

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. The optimal pH ranges for coagulation with aluminum and ferric salts are 5 to 7 and 5 to 8, respectively. 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.

2.7.2 Coagulation-Assisted Microfiltration

Coagulation-Assisted Microfiltration (CMF) uses the same coagulation process described above. However, instead of the granular media filtration

step, the water is forced through a semi-permeable membrane by a pressure differential. The membrane retains the floc formed in the coagulation step.

The use of pre-packaged coagulation-assisted microfiltration systems is a realistic possibility for new installations where water quality precludes the use of sorption treatment. Due to limited performance research, it has not yet been designated as a BAT by the USEPA. This section is devoted to CMF.

The primary water quality concern associated with removal of arsenate by CMF processes is the presence of silica. Within the pH range 7 to 9, silica particles aggressively compete with arsenic for sorption sites on the precipitates. Also, silica can promote fouling of membrane filters.

The membrane must be periodically backwashed to dislodge solids and restore hydraulic capacity. Backwash water is typically a high-volume, low solids (less than 1.0%) waste stream. The specific amount of solids will depend on several factors, including coagulant type, dosage, filter run length, and ambient solids concentration. Two treatment options are available for this waste stream: (1) indirect discharge (for systems treating less than 10 MGD), and (2) dewatering and sludge disposal.

Water intended for indirect discharge will be subject to TBLLs for TDS and arsenic. Dewatering can be accomplished by gravity thickening, followed by other mechanical or non-mechanical techniques. Settling basins can be used to allow settleable solids to drop out of solution via gravity, while the supernatant can be decanted and recycled to the process head. The solids can be slurried out periodically and 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 Liquids Test (no free liquid) and the TCLP. Previous studies have indicated that typical CMF sludge will pass the TCLP test by a substantial margin (Fields, 2000a).

2.7.3 Oxidation/Filtration

Oxidation/filtration is a special case of pressurized granular-media filtration where the granular media catalyzes the oxidation and precipitation of iron and manganese.

Manganese-oxide (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.

In oxidation/filtration processes, water is passed through a column of MnO_x media which adsorbs and catalyzes the oxidation of the iron and manganese. The filtering capacity of the granular MnO_x media then retains the precipitated iron and manganese until it is backwashed out of the column.

In order for greensand to retain its adsorption and catalytic oxidation capabilities, the media must be regenerated with permanganate or chlorine. Typically, these oxidants are added to the water stream ahead of filtration, where they provide continuous oxidation of iron, manganese, and arsenite, as well as regeneration of MnO_x media.

If arsenic is present in the water, it can also be removed via two primary mechanisms: adsorption and co-precipitation. First, soluble iron and arsenite are oxidized. The arsenate then adsorbs onto the iron hydroxide. Then, as the iron hydroxide precipitates, arsenic is trapped and ultimately filtered out of solution.

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 Fe:As 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. However, 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. Two treatment options are available for this waste stream: (1) indirect discharge and (2) dewatering and sludge disposal.

Water intended for indirect discharge will be subject to TBLLs for 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. The solids can be slurried out periodically and passed through a small filter press for dewatering. The resultant sludge can be disposed of in a conventional landfill if it passes the PFLT (no free liquid) and the TCLP. Previous studies have indicated that typical ferric coagulation-filtration sludge will pass the TCLP test by a substantial margin (Fields, 2000b).

2.7.4 Enhanced Lime Softening

Lime softening (LS) is a chemical-physical treatment process used to remove calcium and magnesium cations from solution. The addition of lime increases the pH of solution, thereby causing a shift in the carbonate equilibrium and the formation of calcium carbonate and magnesium hydroxide precipitates. These precipitates are amenable to removal by clarification and filtration.

Lime softening is generally considered cost-prohibitive as a primary arsenic treatment technology. However, for water systems that use lime softening to reduce hardness, the process can be enhanced for arsenic removal. The removal mechanism involves adsorption of arsenate to magnesium hydroxide particulates. These particulates are generated in the presence of excess lime within the pH range 10.5 - 11. Arsenic removal by co-precipitation with calcium carbonate is poor (less than 10%).

The amount of waste residual produced by lime softening is dependent on the hardness removed. While the total volume of waste produced from LS is typically higher than that produced by coagulation – filtration and coprecipitative processes, the arsenic concentration in the sludge is generally lower because more solids are produced. Typical solids concentrations are 1 - 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).

2.8 Point-of-Use Treatment

Under the final Arsenic Rule, point-of-use (POU) devices are approved as small system compliance technologies. However, the rule required that the devices be owned, controlled and maintained by the public water system or by an agency under contract with the water system. Therefore, the responsibility of operating and maintaining the devices cannot be passed to the customer.

POU devices are particularly attractive for removing contaminants that pose (solely) an ingestion risk, as is the case with arsenic. This is because a very small fraction of the total water supplied to a given household is ultimately consumed. In most cases, the POU unit is plumbed into the kitchen faucet.

The primary advantage of employing POU treatment in a small system is reduced capital and treatment costs, relative to centralized treatment. On the downside, however, these programs generally incur higher administrative and monitoring costs to make sure that all units are functioning properly. Previous studies have suggested that POU programs are an economically viable alternative to centralized treatment for systems serving roughly 50 - 250 people.

Most POU devices do not address the issue of pre-oxidation. Water systems may need to conduct centralized chlorine treatment to convert reduced arsenic to arsenate. The technologies that are most amenable to POU treatment include column adsorption with AA or GFH and RO. The primary criteria for selecting an appropriate POU treatment device are arsenic removal performance and cost.

Section 3 Arsenic Treatment Selection

3.1 Selection Criteria

The task of navigating through the alternative arsenic treatment technologies involves several technical considerations. Although nearly all of the unit processes previously presented could be used for arsenic reduction at an arbitrary site, some are more economically viable under specific circumstances. The first and most important consideration is the type of treatment currently employed. Although most water systems today have been designed without the need for arsenic removal, many current practices may accomplish incidental removal. Optimization of these processes is a realistic option.

3.1.1 Source Water Quality

Source water quality dictates the performance of the removal processes identified in Section 2. In turn, process performance, associated O&M requirements, and residuals disposal dictate the economics of a particular treatment approach. Therefore, it is important that utilities conduct thorough up-front monitoring of water quality at all active sources to make the most informed treatment selection decision.

Tables 3-1 and 3-2 provide a summary of recommended monitoring parameters and associated analytical methods. The parameters are divided into two categories: (1) Key and (2) Other. Key parameters are those most critical to evaluating the treatment performance potential of various arsenic removal processes. These parameters should be monitored multiple times over the course of several weeks or months to capture variability in concentrations. Other parameters should be monitored at least once in order to optimize the selected arsenic treatment method.

Parameter	USEPA Method	Standard Method ³	\mathbf{ASTM}^4
Arsenic, Total ¹	200.7, 200.9	3113B, 3114B	D2972-93B, D2972-93C
Arsenite		3500-As B	
Arsenate		3500-As B	
Chloride ²	300.0	4110B, 4500-Cl-D, 4500-Cl-B	D4327-91, D512-89B
Fluoride ^{1,2}	300.0	4110 B, 4500-F B, 4500-F C, 4500-F D, 4500-F E	D4327-91, D1179-93B
Iron ²	200.7, 200.9	3120 B, 3111 B, 3113 B	
Manganese ²	200.7, 200.8, 200.9	3120B, 3111B, 3113B	
Nitrate ¹	300.0, 353.2	4110 B, 4500-NO ₃ -F, 4500-NO ₃ -D, 4500-NO ₃ -E	D4327-91, D3867-90A, D3867-90B
Nitrite ¹	300.0, 353.2	4110 B, 4500-NO ₃ -F, 4500-NO ₃ -E, 4500-NO ₂ -B	D4327-91, D3867-90A, D3867-90B
$Orthophosphate^1$	365.1, 300.0	4500-P F, 4500-P E, 4110 B	D515-88A, D4327-91
pH ^{1, 2}	150.1, 150.2	4500-H+ B	D1293-95
Silica ¹	200.7	4500-Si D, 4500-Si E, 4500-Si F	D859-95
Sulfate ²	300.0, 375.2	$\begin{array}{c} 4110 \text{ B,} \\ 4500\text{-}\mathrm{SO}_4 \text{ F,} \\ 4500\text{-}\mathrm{SO}_4 \text{ C, D,} \\ 4500\text{-}\mathrm{SO}_4 \text{ E} \end{array}$	D4327-91, D516-90
Total Dissolved Solids ²		2540 C	
Total Organic Carbon	415.1		

Table 3-1. Key Water Quality Parameters to be Monitored.

References:

¹USEPA Approved Methods for Drinking Water Analysis of Inorganic Chemicals and other parameters.

²USEPA Recommended Methods for Secondary Drinking Water Contaminants.

³18th and 19th editions of Standard Methods for the Examination of Water and Wastewater, 1992 and 1995, American Water Works Association (AWWA).

⁴Annual Book of ASTM Standards, 1994 and 1996, Vols. 11.01 and 11.02, American Society for Testing and Materials (ASTM).

Parameter	USEPA Method	${\bf Standard} \\ {\bf Method}^{3}$	\mathbf{ASTM}^4
Alkalinity ¹		2320B	D1067-92B
Aluminum ²	200.7, 200.8, 200.9	3120 B, 3113 B, 3111 D	
Calcium ¹	200.7	3500-Ca D, 3111 B, 3120 B	D511-93A, D511-93B
Magnesium ¹	200.7	3113 B, 3120 B, 31500-Mg E	D511-53B, D511-93B
Turbidity	180.1		
Water Hardness	215.1, 242.1		

Table 3-2.	Other Water	Quality	Parameters to	o be Monitored.
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References:

¹USEPA Approved Methods for Drinking Water Analysis of Inorganic Chemicals and other parameters.

²USEPA Recommended Methods for Secondary Drinking Water Contaminants.

³18th and 19th editions of Standard Methods for the Examination of Water and Wastewater, 1992 and 1995, American Water Works Association (AWWA).

⁴Annual Book of ASTM Standards, 1994 and 1996, Vols. 11.01 and 11.02, American Society for Testing and Materials (ASTM).

3.1.2 Process Design Basis

There are several design criteria and assumptions that should be established prior to navigating the decision trees and cost tables. These include the following:

- Maximum flowrate per source
- Average flowrate per source
- Target finished water arsenic concentration
- Method of domestic waste discharge
- TBLLs for arsenic and TDS
- Land availability
- Labor commitment
- Acceptable percent water loss

3.2 Process Selection Decision Trees

Decision trees are useful tools for narrowing the field of available treatment technologies to those which are most economically viable for a particular system. This is accomplished through a series of input-output blocks, which direct the user along the path towards the best technologies. While they do not always point to a single solution, they allow the user to rapidly eliminate some technologies which are cost-prohibitive for a specific application.

It is critical that the reader employ these decision trees, rather than cost correlation curves, as the primary tool for selecting an arsenic mitigation strategy. These trees take into account system-specific conditions and user preferences.

Frequently, decision trees are used to guide the user to the ultimate question: "Does this treatment method meet the MCL?" In most cases, this requires pilot-testing to answer. This approach was not applied in this Manual. Rather, the decision trees guide the user to the technologies that are expected to work best for their particular situation. In some cases, the pathway is contingent upon a water system's willingness to impose a particular change in their operating scheme. These decision-making scenarios were presented only for cases where it may be economically advantageous to make such a change. However, there may be other restrictions (i.e., operating labor, space) to making the operational changes in question. In other cases, there may be more than one equally viable technology. At that point, the water system should further evaluate its preferences with respect to costs and labor commitments, and capabilities with respect to residuals disposal and facility expansion.

The decision trees employ the following labeling scheme:



The question/decision block requests information or user preference in the form of a yes/no or multiple-choice question. With the exception of Tree 1 – Water Quality Monitoring, the action box is used as the stopping point for a particular branch of the decision tree. This box provides the recommended follow-up action given system-specific constraints and preferences. The reference box simply directs the user to another portion of the decision tree.

If a user reaches an action box pertaining to switching sources, blending, or existing treatment optimization, they should refer to Section 2 for more specific information. If a user reaches an action box pertaining to new treatment installation, they should refer to Section 4 for cost information and Sections 6-8 for specific design detail. For the latter case, pilot-testing is also recommended.

The decision trees are intended for use as an iterative tool. If a utility proceeds to a specific action box, conducts follow-up cost estimation, process optimization, and/or pilot-testing, and the results indicate that the selected strategy may be ineffective or infeasible for arsenic removal, the user can restart the tree and modify preferences.

The following assumptions were made in the development of the decision trees:

- Pre-oxidation will be conducted at a centralized location or at each POE.
- Optimization of existing treatment process is economically preferable over new installations.
- Construction of new settling or media filtration technologies is not appropriate for the sole purpose of arsenic removal.
- Small water systems would opt for disposable adsorptive media rather than conduct on-site regeneration.
- Small systems would not generate hazardous waste for either on-site treatment or off-site disposal.

Decision Tree Overview

Step 1) Water Quality Monitoring

D Tree 1 – Water Quality Monitoring

Step 2) Treatment Avoidance Alternatives

D Tree 2 – Treatment Avoidance Alternatives

Step 3) Optimizing Existing Treatment

- I Tree 3 Optimizing Existing Treatment
 - Tree 3a Enhanced Coagulation/Filtration
 - Tree 3b Enhanced Lime Softening
 - $\cdot~$ Tree 3c Iron & Manganese Filtration

Step 4) Selecting New Treatment

u Tree 4 – Selecting New Treatment

- Tree 4a Ion Exchange Processes
- Tree 4b Sorption Processes
- Tree 4c Membrane Processes

Figure 3-1. Decision Tree Overview.





Figure 3-2. Decision Tree 1 - Water Quality Monitoring.



Figure 3-3. Decision Tree 2 – Treatment Avoidance Alternatives.





Figure 3-4. Decision Tree 3 - Existing Treatment Optimization.



Figure 3-5. Decision Tree 3a - Enhanced Coagulation/Filtration.





Figure 3-6. Decision Tree 3b - Enhanced Lime Softening.





Figure 3-7. Decision Tree 3c - Iron/Manganese Filtration.





Figure 3-8. Decision Tree 4 - Selecting New Treatment.



Tree 4a

Figure 3-9. Decision Tree 4a - Ion Exchange Processes.





Figure 3-10. Decision Tree 4b - Adsorption Processes.



Figure 3-11. Decision Tree 4c - Membrane Processes.

Table 3-3 provides a summary of information about the different alternatives for arsenic mitigation found in this manual.
Factors	S	Membrane Processes		
	Ion Exchange	Activated Alumina ²	Granular Ferric Hydroxide	Reverse Osmosis
	IX	AA	GFH	RO
USEPA BAT	Yes	Yes	No ³	Yes
Can treat arsenic levels up to: ¹	160 •g/L	160 •g/L	16 - 400 •g/L	160 •g/L
Other Contaminants Treated	${ m SO}_4$ -2	\mathbf{F}^{\cdot}	PO_{4} -3	TDS
Pre-Oxidation Required	Yes	Yes	Yes	$Possible^4$
Operator Skill Required	High	Low	Low	Medium
Recommended Water Quality	pH 6.5 - 9 < 5 mg/L NO ₂ . < 5 mg/L NO ₃ . < 50 mg/L SO ₄ . ² <500 mg/L TDS	$\begin{array}{c} \rm pH~5.5\cdot6 \\ < 250~mg/L~Cl^{\circ} \\ < 2~mg/L~F^{\circ} \\ < 360~mg/L~SO_{4}^{-2} \\ < 50~mg/L~Silica \\ < 0.5~mg/L~Silica \\ < 0.05~mg/L~He^{+3} \\ < 0.05~mg/L~Mn^{+2} \\ < 1,000~mg/L~TDS \\ < 4~mg/L~TOC \end{array}$	pH 6 - 10 < 1 mg/L PO4 ^{.3}	No Particulates
Waste Generated	Spent Resin, Spent Brine, Backwash Water	Spent Media, Backwash Water	Spent Media, Backwash Water	Reject Water
Other Considerations	Large volume of potentially hazardous brine waste, Nitrate Peaking, Carbonate Peaking affects pH	Feed and product pHs require adjustment, Modified AA Available	GFH is very expensive ⁵	High Water Loss (15-75% of feed water)
Appropriate as a New Treatment for Small Systems	Possible	Yes	Yes	POU Only
Applicable for POU	Possible	Yes	Yes	Yes
POU Cost	Not Applicable	Medium	Medium	Medium
POE Cost	High	Medium	Medium	High

Table 3-3. Arsenic Treatment Technologies Summary Comparison.(1 of 2)

¹ The maximum recommended arsenic levels are calculated from removal rates that are typical for large systems and assume a safety factor of 20%. Small systems, which have additional constraints, may not be able to remove as high of concentrations of arsenic from water.

² Activated alumina is assumed to operate in a non-regenerated mode.

³ GFH's track record in the US is not established enough to be considered as a BAT.

⁴ Pre-oxidation for RO in not always required but will always increase the removal efficiency.

⁵ GFH is currently only manufactured in Europe. With increased domestic use, manufacturing of GFH or another iron based sorbent will occur and significantly decrease the cost.

(/						
Factors	Precipitative Processes					
	Coagulation Assisted Micro- Filtration	Oxidation Filtration	Enhanced Coagulation Filtration	Enhanced Lime Softening		
	CMF	OxFilt	CF	LS		
USEPA BAT	No	Yes	Yes	Yes		
Can treat arsenic levels up to: ¹	40 •g/L	40 •g/L	160 •g/L	80 •g/L		
Other Contaminants Treated	Fe ⁺³ , DBP Precursors, Particulates, Pathogens	Fe ⁺³ , Mn ⁺² , Particulates	Fe ⁺³ , Mn ⁺² , DBP Precursors, Particulates, Pathogens	Ca ⁺² , Mg ⁺² , Particulates		
Chlorination Required	Yes	Yes	Yes	Yes		
Operator Skill Required	High	Medium	High	High		
Recommended Water Quality	pH 5.5 - 8.5	pH 5 - 8, >1.5 mg/L Fe ⁺³ , >0.05 mg/L Mn ⁺² , Fe:As 20:1 (by mass)	pH 5.5 - 8.5	pH 10.5 - 11 up to 5 mg/L Fe ⁺³		
Waste Generated	Backwash Water, Sludge	Backwash Water, Sludge	Backwash Water, Sludge	Backwash Water, Sludge (high volume)		
Other Considerations	None	None	None	Treated water requires pH adjustment		
Appropriate as a New Treatment for Small Systems	Yes	Yes	No	No		
Applicable for POU	No	No	No	No		
POU Cost	N/A	N/A	N/A	N/A		
POE Cost	Medium	High	High	High		

Table 3-3. Arsenic Treatment Technologies Summary Comparison.(2 of 2)

¹ The maximum recommended arsenic levels are calculated from removal rates that are typical for large systems and assume a safety factor of 20%. Small systems, which have additional constraints, may not be able to remove as high of concentrations of arsenic from water.

Section 4 Planning-Level Treatment Costs

This section presents information the reader can use to calculate planning-level capital and operation and maintenance (O&M) costs for the treatment method selected in Section 3. All the charts are from *Technologies and Costs for Removal of Arsenic from Drinking Water* (USEPA, 2000). This information will give the reader only a rough estimate of the selected treatment process costs so that relative costs can be evaluated. If the costs are too high, the reader is encouraged to re-evaluate the criteria used in the treatment selection process in Section 3.

It is critical that the reader employ the decision trees in Section 3, rather than the cost correlation curves provided in this section, as the primary tool for selecting an arsenic mitigation strategy. The trees take into account system-specific conditions and user preferences. Comparing planning-level costs without consideration of the technical issues incorporated in the decision trees may lead the utility to an inappropriate technology.

The cost curves incorporate different mathematical models for different sized systems. Because of this, there are step changes between the model outputs in some of the charts. If the system being sized falls at a flowrate that lays on one of these step changes, the reader is encouraged to use an average cost number and then perform a more site specific cost evaluation.

Capital cost charts are based on the maximum flowrate for which the facility was designed (i.e., design flowrate). The design flowrate should be slightly higher than the treated flowrate determined in Section 3. The capital costs include: process costs (including manufactured equipment, concrete, steel, electrical and instrumentation, and pipe and valves), construction costs (including site-work and excavation, subsurface considerations, standby power, contingencies, and interest during construction), engineering costs (including general contractor overhead and profit, engineering fees, and legal, fiscal, and administrative fees) and the costs associated with retrofitting, permitting, piloting testing, housing, and system redundancy (where prudent). The capital costs do not include costs associated with additional contaminants or land.

The O&M costs are based on the average flowrate that the facility is expected to treat. The O&M costs are based on the following assumptions:

- Electricity costs of \$0.08/kWh,
- Diesel fuel costs of \$1.25/gallon,
- Natural gas costs of \$0.006/scf,
- Large systems labor costs of \$40/h (or loaded labor costs of \$52/h),

- Labor costs for small systems of \$28/h,
- Building energy use of 102.6 kWh/sft/y.

All of the costs presented in the charts are given in year 1998 dollars. To convert to the current year costs, use the formula:

$$P_{\text{Current}} = P_{1998} (1+i)^{(Y_{\text{current}}-1998)}$$
 Eqn. 4-1

Where:

 $\begin{array}{ll} P_{Current} &= Current\ Cost \\ P_{1998} &= Year\ 1998\ Cost\ (from\ the\ charts) \\ i &= Annual\ rate\ of\ inflation\ (\sim 2.5\% - 3\%) \\ Y_{Current} &= Current\ Year \end{array}$

4.1 Pre-Oxidation System Costs Using Chlorine

- A new chlorination system is installed.
- A dose of 1.5 mg/L of free chlorine is added to the treated flow.
- Very small systems (i.e., less than 0.1 MGD) use 15% sodium hypochlorite feed stock and are designed to handle dosages as high as 10 mg/L.
- Larger systems use gas chlorination.



Figure 4-1. Chlorination Capital Costs.



Figure 4-2. Chlorination O&M Costs.

4.2 Ion Exchange System Costs

- A new IX system is installed.
- Capital Cost Design Assumptions:
 - $\circ~$ Pre-oxidation is required but not included in these costs.
 - $\circ~$ Cost includes a redundant column to allow the system to operate during regeneration.
- O&M Cost Design Assumptions:
 - Run length when sulfate is at or below 20 mg/L is 1500 bed volumes (BV). Run length when the sulfate is between 20 and 50 mg/L is 700 BV.
 - $\circ~$ Labor rate for small systems is \$28/hour. The loaded labor rate for large systems is \$52/hour.
- Waste is discharged to a POTW (i.e., indirect discharge).



Figure 4-3. Ion Exchange (<20 mg/L SO₄²) Capital Costs.



Figure 4-4. Ion Exchange (<20 mg/L SO₄²) O&M Costs.



Figure 4-5. Ion Exchange (<20 mg/L SO₄²⁻) Waste Disposal Capital Costs.



Figure 4-6. Ion Exchange (<20 mg/L SO₄²⁻) Waste Disposal O&M Costs.



Figure 4-7. Ion Exchange (20-50 mg/L $SO_{4^{2}}$) Capital Costs.



Figure 4-8. Ion Exchange (20-50 mg/L SO_4^{2}) O&M Costs.



Figure 4-9. Ion Exchange (20-50 mg/L SO₄²⁻) Waste Disposal Capital Costs.



Figure 4-10. Ion Exchange (20-50 mg/L SO_4^{2-}) Waste Disposal O&M Costs.

4.3 Activated Alumina System Costs

- A new activated alumina system is installed.
- Activated alumina media is disposed of in a non-hazardous landfill rather than regenerated.
- Capital Cost Design Assumptions:
 - $\circ~$ Natural pH is between 7.0 and 8.3 and is not adjusted.
 - Redundant column included for operation during media replacement.
 - Costs for constructing housing for the equipment are included.
 - $\circ~$ Capital costs include both pre- and post-treatment pH adjustment if pH adjustment is used.
- O&M Cost Design Assumptions:
 - $\circ~$ Power costs are \$0.08/kwh.
 - Run length for natural pH range of 7.0-8.0 is 10,000 bed volumes (BV). Run Length for natural pH range of 8.0-8.3 is 5,200 BV.
 - pH adjustment costs are included.
 - $\circ~$ Labor rate for small systems is \$28/hour. The loaded labor rate for large systems is \$52/hour.



Figure 4-11. Activated Alumina (Natural pH) Capital Costs.



Figure 4-12. Activated Alumina (pH 7-8) O&M Costs.



Figure 4-13. Activated Alumina (pH 8-8.3) O&M Costs.



Figure 4-14. Activated Alumina (pH 7-8) Waste Disposal O&M Costs.



Figure 4-15. Activated Alumina (pH 8.0-8.3) Waste Disposal O&M Costs.



Figure 4-16. Activated Alumina (pH Adjusted to 6.0) Capital Costs.



Figure 4-17. Activated Alumina (pH adjusted to 6.0 - 23,100 BV) O&M Costs.



Figure 4-18. Activated Alumina (pH adjusted to 6.0 - 15,400 BV) O&M Costs.



Figure 4-19. Activated Alumina (pH adjusted to 6.0 - 23,100 BV) Waste Disposal O&M Costs.



Figure 4-20. Activated Alumina (pH adjusted to 6.0 - 15,400 BV) Waste Disposal O&M Costs.

4.4 Granular Ferric Hydroxide System Costs

Granular ferric hydroxide is a relatively new technology and, as such, costs for GFH treatment systems have not yet been determined.

4.5 Greensand System Costs

- A new greensand filtration system is installed.
- Potassium permanganate feed rate of 10 mg/L (however, chlorination will work also.)
- Filter service rate of 4 gpm/sft.
- Backwash flowrate of 10-12 gpm/sft.
- Backwash waste is discharged to a POTW (i.e., indirect discharge).



Figure 4-21. Greensand Capital Costs.



Figure 4-22. Greensand O&M Costs.



Figure 4-23. Greensand Waste Disposal Capital Costs.



Figure 4-24. Greensand Waste Disposal O&M Costs.

4.6 Coagulation Assisted Microfiltration System Costs

- Ferric chloride dose of 25 mg/L.
- For Systems Less Than 1 MGD:
 - Package plants with a service rate of 5 gpm/sft.
 - Sodium hydroxide dose of 20 mg/L for pH control.
 - Standard microfiltration.
- For Systems Larger Than 1 MGD:
 - Rapid mix for 1 minute.
 - \circ Flocculation for 20 minutes.
 - Sedimentation at 1000 gpd/sft using rectangular tanks.
 - Dual media gravity filters running at a service rate of 5 gpm/sft.
- Waste is dewatered before being disposed of in a non-hazardous landfill. Costs are given for dewatering performed by either mechanically or non-mechanically. Land costs are not included in the waste disposal costs



Figure 4-25. Coagulation Assisted Microfiltration Capital Costs.



Figure 4-26. Coagulation Assisted Microfiltration O&M Costs.



Figure 4-27. Coagulation Assisted Microfiltration (w/ Mechanical Dewatering) Waste Disposal Capital Costs.



Figure 4-28. Coagulation Assisted Microfiltration (w/ Mechanical Dewatering) Waste Disposal O&M Costs.



Figure 4-29. Coagulation Assisted Microfiltration (w/ Non-Mechanical Dewatering) Waste Disposal Capital Costs.



Figure 4-30. Coagulation Assisted Microfiltration (w/ Non-Mechanical Dewatering) Waste Disposal O&M Costs.

4.7 Coagulation/Filtration System Enhancement Costs

- A coagulation/filtration system is already installed. Costs are only for system enhancement for arsenic removal.
- Assumptions About The Existing Coagulation/Filtration System:
 - $\circ~$ Existing coagulation/filtration system removes 50% of the arsenic without enhancement.
 - $\circ~$ Ferric chloride dose of 25 mg/L.
 - Polymer dose of 2 mg/L.
 - Lime dose of 25 mg/L for pH control.
 - $\circ~$ Systems less than 1 MGD are package plants with a service rate of 5 gpm/sft.
 - Systems Larger Than 1 MGD:
 - Rapid mix for 1 minute.
 - Flocculation for 20 minutes.
 - Sedimentation at 1000 gpd/sft using rectangular tanks.
 - Dual media gravity filters running at a service rate of 5 gpm/sft.
- Assumptions for the Enhancement of the Coagulation/Filtration System:
 - Additional ferric chloride dose of 10 mg/L.
 - Additional feed system for increased ferric chloride dose.

 $\circ~$ Additional lime dose of 10 mg/L for pH adjustment.



• Additional feed system for increased lime dose.

Figure 4-31. Coagulation/Filtration System Enhancement Capital Costs.



Figure 4-32. Coagulation/Filtration System Enhancement O&M Costs.

4.8 Lime Softening System Enhancement Costs

- A lime softening system is already installed. Costs are only for system enhancement for arsenic removal.
- Lime dosage of 250 mg/L.
- Carbon dioxide dosage of 35 mg/L for recarbonation.
- Assumptions About the Existing Lime Softening System:
 - Systems less than 1 MGD are package.
 - Systems Larger Than 1 MGD:
 - Rapid mix for 1 minute.
 - Flocculation for 20 minutes.
 - Sedimentation at 1500 gpd/sft using circular tanks.
 - Dual media gravity filters running at a service rate of 5 gpm/sft.
- Assumptions for the Enhancement of Existing Lime Softening System:
 - Additional lime dose of 50 mg/L.
 - Additional feed system for increased lime softening dose.
 - $\circ~$ Additional carbon dioxide dose of 35 mg/L for recarbonation.
 - Additional feed system for increased carbon dioxide dose.



Figure 4-33. Lime Softening Enhancement Capital Costs.



Figure 4-34. Lime Softening Enhancement O&M Costs.

4.9 Point-of-Use Reverse Osmosis System Costs

- In an average household, there are 3 individuals using 1 gallon each per day for a total of 1,095 gallons per year.
- Life of POU unit is 5 years.
- Duration of cost study is 10 years.
- Cost of water meter and automatic shut-off valve included.
- No shipping and handling included.
- If the water is chlorinated, dechlorination may be required. Costs for dechlorination are not included.
- Volume discount schedule retail for a single unit, 10 percent discount for 10 or more units, 15 percent discount on more than 100 units.
- Installation time 1 hour unskilled labor (POU)
- Minimally skilled labor \$14.50 per hour (population less than 3,300 individuals).
- Skilled labor \$28 per hour (population greater than 3,300 individuals).
- O&M costs include maintenance, replacement of pre-filters and membrane cartridges, laboratory sampling and analysis, and administrative costs.



Figure 4-35. POU Reverse Osmosis Capital Costs.



Figure 4-36. POU Reverse Osmosis O&M Costs.

4.10 Point-of-Use Activated Alumina System Costs

Costs presented in the following charts make the following assumptions:

• In an average household, there are 3 individuals using 1 gallon each per day for a total of 1,095 gallons per year.

- Life of POU unit is 5 years.
- Duration of cost study is 10 years.
- Cost of water meter and automatic shut-off valve included.
- No shipping and handling included.
- Volume discount schedule retail for a single unit, 10 percent discount for 10 or more units, 15 percent discount on more than 100 units.
- Installation time 1 hour unskilled labor (POU)
- Minimally skilled labor \$14.50 per hour (population less than 3,300 individuals).
- Skilled labor \$28 per hour (population greater than 3,300 individuals).
- O&M costs include maintenance, replacement of pre-filters and membrane cartridges, laboratory sampling and analysis, and administrative costs.



Figure 4-37. POU Activated Alumina Capital Costs.



Figure 4-38. POU Activated Alumina O&M Costs.

4.11 Point-of-Use Granular Ferric Hydroxide System Costs

GFH is a relatively new technology and, as such, the costs for using small GFH units in a POU scheme have not been well defined. Costs for a GFH POU system are anticipated to be similar to those of an activated alumina POU system.

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Section 5 Pre-Oxidation Design Considerations

The conversion of reduced inorganic arsenic to arsenate is critical for achieving optimal performance of *all* unit processes described in this Manual. Conversion to arsenate can be accomplished by providing an oxidizing agent at the head of any proposed arsenic removal process. Chlorine and permanganate are highly effective for this purpose. They oxidize arsenite to arsenate within one minute in the pH range of 6.3 to 8.3. Ozone rapidly oxidizes arsenite but its effectiveness is significantly diminished by the presence of sulfides or TOC. Chlorine dioxide and monochloramine are ineffective in oxidizing arsenite. UV light, by itself is also ineffective. However, if the water is spiked with sulfite, UV photo-oxidation shows promise. Because of these considerations, only chlorine and permanganate are discussed in this section.

5.1 Chlorine

The primary applications of chlorine in water treatment include pre-oxidation, primary disinfection, and secondary disinfection. Several arsenic removal processes, particularly membranes, are chlorine sensitive and/or intolerant. In these instances, the utility should consider an alternate oxidation technology. If this is the case, but the utility already has chlorination capabilities in place, the process of modifying the existing system to achieve arsenite oxidation is complicated. One alternative is the application of a pre-chlorination dechlorination—arsenic removal—re-chlorination treatment setup. However, this alternative may be more costly than integrating a permanganate pre-oxidation system.

Chlorine can be added either as liquid sodium hypochlorite (Equation 5-1) or dissolved gas (Equation 5-2). In either case, biocidal hypochlorous acid is generated.

$$NaOCl + H_2O \rightarrow HOCl + NaOH$$
 Eqn. 5-1

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$
 Eqn. 5-2

The first step in selecting the most appropriate method of chlorination is to determine the chlorine flow requirements for the particular application. Chlorine demand can be calculated with equation 5-3.

$$M = \frac{Q \cdot \delta_{Cl_2}}{83.2}$$
 Eqn. 5-3

where:

M = Chlorine Mass Flow (lb/day of Cl₂)

- Q = Design Flow Rate (gpm)
- δ_{Cl_2} = Chlorine Dose (mg/L as Cl₂)

Careful consideration should be given to the chlorine dose estimate. Most waters contain substances (other than arsenite) that exert chlorine demand. In many cases, these substances compete for chlorine more aggressively than arsenite. Simple chlorine demand bench testing can be used to ascertain the instantaneous and ultimate chlorine demand of particular water. The applied chlorine dose should account for these factors, as well as the desired disinfectant residual concentration.

$$\delta_{\text{Cl}_2} = D_{\text{Cl}_2} + R_{\text{Cl}_2}$$
 Eqn. 5-4

Where:

 δ_{Cl_2} = Chlorine Dose (mg/L as Cl₂)

 D_{Cl_2} = Ultimate Chlorine Demand (mg/L as Cl₂)

 R_{Cl_2} = Desired Chlorine Residual (mg/L as Cl_2)

The chlorine demand for stoichiometric conversion of arsenite to arsenate is $0.95 \ \mu g/L$ of chlorine (as Cl₂) per $\mu g/L$ of arsenite (as As). This demand is three orders-of-magnitude smaller than typical chlorine dose rates.

Selection of the type of chlorination system should include consideration of capital and operating costs, O&M requirements, code restrictions, containment requirements, footprint, and safety concerns. This Manual will address the following options, which are considered most viable for small water systems:

- 150-lb gas feed system
- Commercial liquid hypochlorite feed system
- On-site hypochlorite generation system

The application of ton cylinders is not practical for small water systems, and is not discussed here.

5.1.1 Chlorine Gas

Chlorine cylinders (150-lb) contain pressurized chlorine liquid, with a small amount of vapor headspace. Feed systems are typically designed for gas phase withdrawal, either positive pressure or vacuum differential type. The latter is recommended for systems that have daily chlorine requirements below 500 lbs.

An example flow diagram of a vacuum differential feed system is shown in Figure 5-1. Figure 5-2 shows a typical schematic of a gas chlorination system. Chlorine gas is dissolved in carrier water, which is subsequently flow-paced into the system flow. Key appurtenances associated with this setup include the vacuum regulator valve, automatic switchover valve, and gas feeder (injector). The cylinders are typically mounted on electronic scales to allow for estimation of the remaining useful life.



Figure 5-1. Typical Gas Chlorination Process Flow Diagram.

Although chlorine gas feed systems are simple and non-intensive, there are some important operating conditions to note. The cylinders should be kept out of direct sunlight and maintained between 50 and 80°F. One spare cylinder should be provided for each cylinder that is in service. Finally, withdrawal should be limited to 40 lbs of chlorine per day per cylinder.



Figure 5-2. Gas Chlorination System Schematic (U.S. Filter Wallace & Tiernan).

The 1997 Uniform Fire Code (UFC) mandates the installation of equipment for mitigating an accidental chlorine leak. Total containment vessels have been designed for this purpose. Figure 5-3 depicts a total containment vessel and loader in the loading position. Figure 5-4 shows a total containment vessel in the operating position.



Figure 5-3. Total Containment Vessel Schematics for 150-lb Cylinders (TGO Technologies).



Figure 5-4. Total Containment Vessel for 150-lb Cylinders (TGO Technologies).

5.1.2 Commercial Liquid Hypochlorite

Liquid sodium hypochlorite can be purchased as a 12-15% strength solution. The solution must be delivered to the facility by tanker trucks or in drums on a regular basis. The solution is stored on-site in a tank and metered into the system by a small pump. Figure 5-5 shows a flow diagram for a typical liquid hypochlorite process. Figure 5-6 is a typical flow schematic for a flooded suction hypochlorite metering system.



Figure 5-5. Typical Liquid Hypochlorite Process Flow Diagram.



Figure 5-6. Liquid Hypochlorite System Schematic (U.S. Filter Wallace & Tiernan).

The flow rate of 12.5% strength liquid hypochlorite required to meet chlorine mass flow requirements can be approximated by Equation 5-5. This flow rate should be used to size the metering pump, as well as provide an estimate of chemical operating costs.

$$Q_{Cl_2} = \frac{M}{30.2}$$
 Eqn. 5-5

Where:

Q_{Cl₂} = Hypochlorite Metering Pump Rate (gph) M = Chlorine Mass Flow (lb/day of Cl₂)

The required capacity of the storage tank is contingent upon the desired frequency of tanker truck deliveries. Tanks are commonly sized to provide 7-21 days of storage. Because commercial strength liquid hypochlorite is a Class 1 Liquid Oxidizer, storage of more than 4,000 pounds represents a non-exempt quantity and requires special precautions. The volume required may be calculated as follows.

$$V = 24 \cdot (Q_{Cl_2} \cdot t)$$
 Eqn. 5-6

Where:

V = Storage Volume (gal)

 Q_{Cl_2} = Hypochlorite Metering Pump Rate (gph)

t = Storage Time (days)

5.1.3 On-Site Hypochlorite Generation

On-site generation of sodium hypochlorite is accomplished by adding electricity to saturated (32%) brine. The strength of hypochlorite produced is 0.8%, below the hazardous material threshold of 1%. These systems can be constructed piecewise or purchased as pre-packaged units.

Figure 5-7 shows a typical flow diagram for an on-site hypochlorite generation system. The equipment requirements of an on-site generation system, which can be seen in Figure 5-8, include a salt saturator, hypochlorite storage tanks, electrolyzers, rectifiers, controls, and hypochlorite metering pumps. The following material inputs are required per pound of chlorine generated: 3.5 lb NaCl salt, 15 gallons of water, and 2.5 kWh of electrical energy.

Figure 5-9 shows an on-site hypochlorite generator that will produce up to 36 pounds of chlorine per day.



Figure 5-7. Typical On-Site Hypochlorite Generation Process Flow Diagram.


Figure 5-8. On-Site Hypochlorite Generation System Schematic (U.S. Filter Wallace & Tiernan).



Figure 5-9. On-Site Hypochlorite Generation System (Severn Trent Services).

5.2 Permanganate

The primary applications of permanganate (MnO_4) in water treatment include pre-oxidation (particularly for iron and manganese) and taste and odor control. Potassium permanganate exists in solid, granular form, but is typically applied as a saturated liquid (60 g/L at room temperature).

Permanganate is not biocidal against drinking water pathogens, so there should be negligible residual leaving the treatment works. Manganese particulates (MnO_2) are produced as a result of permanganate oxidation reactions. To prevent the accumulation of these deposits in the distribution system, post-filtration treatment must be applied.

Potassium permanganate is a Class 2 Solid Oxidizer. The storage of more than 250 lbs necessitates special hazardous waste precautions. Potassium permanganate can be purchased in a variety of quantities, including 55-lb (25-kg) pails, 110-lb (50-kg) kegs, and 330-lb (150-kg) drums. The solids can be stored indefinitely if kept in a covered container and maintained in a cool, dry environment. Special handling and safety requirements should be employed when working with solid potassium permanganate, including the use of goggles, rubber gloves, and an approved NIOSH-MSHA dust and mist respirator.

Careful consideration should be given to the permanganate dose estimate. Most waters contain substances (other than arsenite) that exert oxidant demand. In particular, permanganate reacts aggressively with organic materials. Permanganate may also be consumed during the regeneration of MnO_x media. The applied dose should account for all of these factors.

$$\delta_{MnO_4} = D_{MnO_4}$$
 Eqn. 5-7

Where:

 δ_{MnO_4} = Permanganate Dose (mg/L as Mn)

 $D_{MnO_{4}}$ = Ultimate Permanganate Demand (mg/L as Mn)

The application of potassium permanganate is straightforward. Permanganate solution is prepared by loading solid potassium permanganate into a storage silo. A feeder meters the permanganate into a dry hopper which allows the solids to be pulled into a water stream where it dissolves. The permanganate solution is then stored in a solution tank until it is metered into the water to be treated. This process is shown in the flow diagram in Figure 5-10. For small systems looking to maintain simplicity, manually loading solids into a solution tank filled with water to create batch quantities of permanganate solution is recommended.

Pre-packaged drum inverters (Figure 5-11) and dry feeders (Figure 5-12) are available in several different styles, including gravimetric weigh-belt and volumetric (hopper) type.



Figure 5-10. Typical Permanganate Process Flow Diagram.



Figure 5-11. Permanganate Dry Feed System (Merrick Industries, Inc.).



Figure 5-12. Permanganate Dry Feed System (MetCon Engineering).

The stock solution is then metered into the water system with the use of a small pump. The flow rate of solution required to meet the dose requirements are contingent upon the strength of the stock solution, according to equation 5-8.

$$Q_{MnO_4} = \frac{60 \cdot (Q \cdot \delta_{MnO_4})}{C_{MnO_4} - \delta_{MnO_4}}$$
Eqn. 5-8

Where:

 Q_{MnO_4} = Permanganate Metering Pump Rate (gph)

Q = Design Flowrate (gpm)

 δ_{MnO_4} = Permanganate Dose (mg/L)

 C_{MnO_4} = Permanganate Stock Solution Concentration (mg/L)

5.3 Comparison of Pre-Oxidation Alternatives

Table 5-1 provides a review of issues pertinent to the four pre-oxidation methods previously discussed.

Criteria	150-lb Chlorine Gas Feed System	Liquid Sodium Hypochlorite System	On-Site Hypochlorite Generation System	Permanganate Solution Feed System
Safety and Regulatory Issues	 Sites storing over 2,500 lbs require an EPA Risk Management Plan. OSHA PSM regulations applicable for sites storing over 1,500 lbs. Secondary containment vessels or chemical scrubbers are required to meet fire code. 	 HazMat regulations for safety and handling apply. Potential for corrosive vapors in the presence of moisture. Emergency response plan required with local fire department. Secondary containment required. 	 Below 1% threshold for hazardous classification. Exempt from HazMat regulations. No secondary containment requirements. 	• Solid permanganate poses dust and inhalation hazard.
Space Requirements	• Space requirements are moderate. Total containment vessels generally require a smaller footprint than chemical scrubber facilities.	• Space requirements are small, assuming the UFC exempt criteria are met.	• Space requirements are large. There must be room for salt storage, brine tanks, hypochlorite holding tanks, electrolytic equipment, as well as instrumentation & control and power.	• Space requirements are small. Additional space may be required for storage of solid permanganate.
Chemical Characteristics	 Pressurized chlorine gas in liquid form. Depresses pH of water slightly. Scrubber requires storage of caustic soda. 	 12-15% (delivered) sodium hypochlorite solution. Degrades over time. Decay of solution creates chlorate byproduct. Increases pH of water slightly. 	 Stable sodium hypochlorite solution (0.8%). Constant application concentration. Chlorate formation low to none. Increases pH of water slightly. 	 Stable permanganate solution, generally 3-4%. Reacts rapidly with dissolved organics.
Chemical Delivery	Chlorine gas cylinders delivered.	• Liquid hypochlorite delivered by tanker truck.	• Salt delivered in 50-lb bags or 2000-lb totes.	 Solid permanganate available in 25-kg pails, 50-kg kegs, and 150-kg drums.
Labor	• Change cylinders periodically.	Periodic tanker truck delivery.Dilution procedures.	Salt delivery.Weekly loading of salt into brine tank.	 Load dry feeder. Dilution procedures.
Operation and Maintenance	 Low level of O&M for total containment. Moderate level of O&M to maintain scrubber system. 	• Low day-to-day O&M. Long-term material maintenance could be a problem because of corrosive effects of liquid hypochlorite.	• Moderate O&M, mainly associated with salt handling. Change electrode cells every five years.	• Low day-to-day O&M for automated systems.
Off-Normal Operation	-	• A temporary bleach solution can be mixed in the storage tank.	• A temporary bleach solution can be mixed in the day tank.	-
Community Relations	• Chlorine is a toxic gas.	HazMat signage required.	• No HazMat regulations. Hydrogen byproduct vented to atmosphere.	-

Table 5-1. Comparison of Pre-Oxidation Alternatives.

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Section 6 Sorption Process Design Considerations

This section describes the design of sorptive processes, including activated alumina, modified activated alumina, granular ferric hydroxide, and ion exchange. For reasons previously cited, the discussion about AA, modified-AA, and GFH are restricted to non-regenerable applications. Conversely, ion exchange is most economically feasible when used in a regenerable process.

6.1 Process Flow

Despite the availability of several different types of sorptive treatment processes, the overall treatment approach for each is similar. Pre-treatment consists of necessary oxidation to convert arsenic to its pentavalent form, as well as optional pH adjustment and pre-filtration stages. Next, the water is fed through a column packed with sorptive media. Post-treatment consists of an optional pH adjustment stage. Typically, the entire process is carried out under pressure.



Figure 6-1. Typical Sorption Treatment Process Flow Diagram

Pre-filtration is strongly recommended when the source water turbidity is above 0.3 NTU. Suspended solids in the feed water can clog sorption sites and impair process hydraulics. Common pre-filtration media include sand, anthracite, and granular activated carbon (GAC). For smaller systems, backwashable cartridge filters may also be appropriate.

The performance of AA treatment is highly pH-sensitive. Treatment conducted under acidic conditions (pH 5.5-6.0) can be expected to produce run lengths 5 to 20 times longer than treatment conducted under natural pH conditions. As a result, in the decisions trees in Section 3, conventional AA is only recommended over GFH when the pH is naturally low or the system is willing to adjust the pH below 6.0. In most cases, pH adjustment will require chemical addition of a strong acid, such as sulfuric (H₂SO₄) or hydrochloric (HCl) acid. Dose requirements depend on the background pH and buffering capacity of the water.

6.2 Column Rotation

Sorption processes are conducted using two or more columns in series, with at least one column on standby. This setup is utilized to prevent arsenic leakage into the finished water. The number of columns to be placed in series depends on the estimated lifetime of each column and the desired monitoring and media change-out or regeneration frequency.

Figure 6-2 illustrates the different flow modes (for Column 1) used in sorption treatment processes. The first sorption column in the treatment process is referred to as the lead column, and the remaining sorption columns are referred to as lag columns. The last on-line column is sometimes referred to as a polishing column.



Normal Operation Mode

Figure 6-2. Sorption Treatment Process Flow Modes.

The lead column serves as the primary arsenic removal location. The lag column provides a polishing step and is intended to capture arsenic breakthrough as soon as it occurs from the lead column. The columns are operated in this manner until arsenic breakthrough of the lead column occurs, which is detected by periodic, manual monitoring. Breakthrough is initially defined as the time when the effluent arsenic concentration is equal to 50% of the feed water arsenic level. This number can be adjusted after piloting or operation to optimize the economics of the process. At this point, adsorptive sites on the lead column have become saturated and the column should be taken off-line for media replacement or regeneration.

The lag column is then promoted to the lead column position. The standby column becomes the last column in the series. After the column being regenerated is ready for use, it is set in standby mode to wait for the next column rotation.

6.3 Sorption Theory

To understand operation of sorption processes, it is important to understand fundamental ion exchange theory. An important consideration in sorption processes is the mass transfer zone (MTZ), which can be viewed as a wave or a zone of activity (i.e., non-equilibrium between liquid and media phases) for a particular contaminant. As depicted in Figure 6-3, the MTZ also represents the front of the exhaustion zone for a particular contaminant. Exhaustion zones and MTZ waves are typically considered for the target contaminant (i.e., arsenic) and any species that have a higher exchange affinity for the media. Arsenic must compete with other anions for exchange sites according to the selectivity sequence for the particular media (see Section 2). Previously sorbed arsenic can be displaced by anions of higher selectivity. Exhaustion and mass transfer zones order themselves according to the selectivity sequence, as illustrated in Figure 6-3. Other sorbed contaminants, such as carbonate (CO_3^{2-}) and nitrate (NO_3^{-}), would be present further down from the arsenate MTZ.



Figure 6-3. Multi-Component Ion Exchange.

6.3.1 Non-Regenerated Sorption Processes

For the purpose of this Manual, processes utilizing activated alumina, modified-AA, or GFH media are referred to as non-regenerated sorption treatment. These technologies are most applicable to small utilities when used as a one-time application with subsequent media disposal and replacement.

Processes utilizing conventional AA are only recommended when the solution pH is less than 6.0. At this pH, the hydroxide (OH⁻) concentration is less than 0.2 μ g/L. Since this is at least an order-of-magnitude less than the arsenic concentration, hydroxide provides little competition against arsenic for exchange sites. There are several types of modified-AA which have demonstrated enhanced arsenic removal performance under natural pH conditions (6.0-9.0) but these have not been designated as BATs by the USEPA.

GFH treatment has been described as chemisorption (Selvin, 2000), which is typically considered to be irreversible. Therefore, although phosphate and arsenic compete for sorption sites, neither has the ability to displace the other. In this instance, there is a single exhaustion zone and MTZ comprised of both arsenate and phosphate contaminants.

6.3.2 Ion Exchange Processes

Arsenate can be removed through the use of strong-base anion exchange resin (SBR) in either chloride or hydroxide form, although the former is more commonly used for drinking water applications. The expense and low capacity of ion exchange resin generally renders it uneconomical for one-time application and disposal. Instead, periodic regeneration should be applied to restore the exchange capacity of the resin.

Figure 6-3 illustrates a resin-phase loading profile down an IX column for treatment of hypothetical natural water containing arsenic and sulfate. As arsenic is exchanged with anions on the SBR, the arsenic band develops and its MTZ moves downward. The same phenomenon is true for sulfate ions. However, because of its higher exchange affinity, sulfate anions displace the arsenic, thereby forcing the arsenic-exhausted region and the arsenic MTZ downward further.

An important consideration in the application of IX treatment is the potential for chromatographic peaking of nitrate (NO_{3}) and nitrite (NO_{2}). These contaminants pose an acute health risk, and as such are regulated under the Safe Drinking Water Act (SDWA) with primary MCLs of 10 mg/L (as N) and

1 mg/L (as N), respectively. According to the selectivity sequence provided in Section 2.5.1, nitrate and nitrite will also replace chloride on exchange sites, although with less preference than arsenate or sulfate. As a result, the region of nitrate and nitrite activity will reside further down the column (relative to the activity of sulfate and arsenate), as illustrated in Figure 6-4. These species will chromatographically peak before arsenate, and this peaking could produce water that does not meet the aforementioned MCLs. Utilities that purvey water with measurable quantities of nitrite or nitrate should be aware of this phenomenon and plan column operation to avoid this occurrence.



Figure 6-4. Activity of Nitrate and Nitrite During Ion Exchange.

The removal of carbonate (CO_{3^2}) by IX resin can also lead to a pH drop of 0.5 to 1.0 units, particularly at the beginning of a run. This impact can be minimized by post-treatment addition of soda ash or caustic soda. Pilot testing is recommended to evaluate the impact on pH for the specific water in question.

6.4 Media Capacity Evaluation

Finding a good adsorbent for arsenic in drinking water applications has relatively little to do with the interaction of the adsorbent with arsenic *per se*; rather, the real challenge is to find an adsorbent whose interactions with other constituents of the solution do not interfere too severely with the arsenic-adsorbent interaction. The decision trees were constructed with this focus in mind.

Once a particular sorption technology has been chosen with the aid of the decision trees, there are a wide variety of media alternatives. Depending on site-specific

water quality, some types of media may be more effective than others. A useful and simple method for evaluating different media types is to perform a batch capacity study. A capacity study allows the user to determine the amount of arsenic (and other ions) that can be adsorbed per unit mass of media under varying conditions.

The test involves preparing a mixture of the arsenic-containing solution and the test media. The solution should be the actual source water and not synthesized water, as the presence of other ions may impact the sorption process. Pre-oxidation and pH adjustment (if applicable) should be conducted to produce the oxidant residual and solution pH to be used in the final design. Following these steps, but prior to media addition, the following water quality analyses should be performed:

- For AA and modified-AA media: solution pH, total arsenic
- For GFH media: solution pH, total arsenic, total phosphate
- For IX resin: solution pH, total arsenic, total sulfate

These are referred to as critical parameters for a particular media. Assuming there is a measurable oxidant residual, it is reasonable to approximate the arsenate concentration as the measured arsenic concentration.

The next step involves addition of the test media. The media and solution should be allowed to remain in contact for the proposed empty bed contact time (EBCT) of the particular media. Some form of continuous gentle agitation should be provided. To ascertain the optimal sorption capacity, the goal is to add enough media to produce a distinct, measurable change in the concentration of the critical parameter(s), but not so much media that the solution concentration is changed drastically. A concentration change of 10-30% is a reasonable target. This is a trial-and-error approach and may require several iterations. At the end of the contacting period, the solution should be filtered from the media and analyzed for the critical water quality parameters.

The sorption capacity of the media can be calculated as:

$$S = \sum_{i} s_{i}$$
 Eqn. 6-1

$$s_{i} = \frac{\overline{V} \cdot \gamma_{i} \cdot (C_{o,i} - C_{f,i})}{MW_{i} \cdot m}$$
 Eqn. 6-2

Where:

S = Sorption Capacity of Media (eq/g resin)

- s_i = Sorption Capacity of Media for Species *i* (eq/g resin)
- \overline{V} = Volume of Solution Added (L)
- γ_i = Normality of Species *i* (eq/mole)
- m = Mass of Media Added (g)

 MW_i = Molecular Weight of Species *i* (mg/mole)

 $C_{o,i}$ = Initial Concentration of Species *i* (mg/L)

 $C_{f,i}$ = Final Concentration of Species *i* (mg/L)

For AA and modified-AA processes, the following species should be considered: hydroxide and arsenate. For GFH processes, the following species should be considered: phosphate and arsenate. For IX processes, the following species should be considered: sulfate and arsenate. Table 6-1 and Figure 6-5 provide values for use in equation 6-2.

Table 6-1. Constants for Exchange Capacity Calculations.				
Species	Molecular Weight (mg/mole)	Normality (eq/mole)		
Hydroxide	17,000	1		
Sulfate	32,060 as S	21		
Arsenate	74,922 as As	Use Figure 6-5		
Phosphate	30,974 as P	Use Figure 6-5		

¹ For pH > 2



Figure 6-5. Normality of Arsenate and Phosphate Versus pH.

The following example is intended to provide guidance on the use of Equations 6-1 and 6-2. Consider a hypothetical capacity study designed to evaluate the sorption capability of a particular SBR. Suppose the following data were obtained from a beaker to which 100 mL (0.1 L) of the (pre-oxidized) water had been mixed with 10.0 mg (0.01 g) of the exchange resin.

Table 0-2. Data for Meura Capacity Example 1 robiem.				
Parameter	Experimental Results			
i ur unicotor	Start	End		
Solution pH	6.9	6.7		
Arsenic	0.030 mg/L as As	0.029 mg/L as As		
Sulfate	15.0 mg/L as S	11.9 mg/L as S		

Table 6-2.	Data for	Media	Capacity	Example	Problem.
	Data IOI	mound	Cupacity	L'Admpie	I I ODICIII.

The pH data should be used in conjunction Figure 6-5 to determine the normality of arsenate (γ). As shown in the following figure, the normality of arsenate is roughly 1.4 equivalents per mole at the average solution pH of 6.8. From Table 6-1, the normality of sulfate is 2.



Figure 6-6. Normality of Arsenate Versus pH for Example Problem.

The sorption capacity can be calculated for each species as follows:

 $s_{\text{Arsenate}} = \frac{(0.1 \text{ L}) \cdot (0.03 - 0.029 \text{ mg/L}) \cdot (1.4 \text{ equiv/mole})}{(74,922 \text{ mg/mole}) \cdot (0.01 \text{ g})} = 1.87 \times 10^{-7} \text{ eq/g resin}$ $s_{\text{Sulfate}} = \frac{(0.1 \text{ L}) \cdot (15.0 - 11.9 \text{ mg/L}) \cdot (2.0 \text{ equiv/mole})}{(32,060 \text{ mg/mole}) \cdot (0.01 \text{ g})} = 1.93 \times 10^{-3} \text{ eq/g resin}$

The total sorption capacity (S) is equal to the sum of the individual sorption capacities for sulfate and arsenate.

$$S = 1.93 \times 10^{-3} \text{ eq/g} + 1.87 \times 10^{-7} \text{ eq/g} = 1.93 \times 10^{-3} \text{ eq/g resin}$$

Eqn. 6-3

The capacity of the media is typically reported as normality, which has units of equivalents per liter of resin. Normality is related to the sorption capacity through equation 6-3. In many instances, the manufacturer can provide the estimated normality of the specific resin, which can then be compared to the results of the capacity study. Chloride-form strong base anion exchange resins have typical normalities of 1.0 to 1.4 eq/L.

 $N = S \cdot \rho_B$

Where:

N = Normality of Media (eq/L resin)

S = Sorption Capacity of Media (eq/g resin)

 $\rho_{\rm B}$ = Bulk Density of Media (g/L)

The estimated useful media life (measured as bed volumes of water treated) can be calculated based on knowledge of the media normality and feed water quality. Equations 6-4 through 6-6 are provided for this purpose.

$$BV_e = \frac{N}{\overline{N}}$$
 Eqn. 6-4

$$\overline{N} = \sum_{i} n_{i}$$
 Eqn. 6-5

$$n_{i} = \frac{C_{i} \cdot \gamma_{i}}{MW_{i}}$$
 Eqn. 6-6

Where:

 BV_e = Number of Bed Volumes to Exhaustion

N = Normality of the Media (eq/L resin)

 \overline{N} = Normality of the Feed Stream (eq/L)

 n_i = Normality of Species *i* in Feed Stream (eq/L)

 C_i = Concentration of Species *i* in Feed Stream (mg/L)

 MW_i = Molecular Weight of Species *i* (mg/mole)

 γ_i = Normality of Species *i* (eq/mole)

The following calculations reference the previous example problem. The optimal sorption capacity of the SBR was calculated as 1.93×10^{-3} eq/g resin. Assuming the bulk density of the media is 41 lbs/cft (657 g/L), the normality of the media is 1.27 eq/L.

$$N = (1.93 \times 10^{-3} \text{ eq/g}) \cdot (657 \text{ g/L}) = 1.27 \text{ eq/L}$$

In order to calculate the useful bed lifetime, the normality of the feed stream must be determined.

$$n_{\text{Arsenate}} = \left(\frac{0.03 \text{ mg/L}}{74,922 \text{ mg/mole}}\right) \cdot (1.4 \text{ eq/mole}) = 5.61 \times 10^{-7} \text{ eq/L}$$
$$n_{\text{Sulfate}} = \left(\frac{15 \text{ mg/L}}{32,060 \text{ mg/mole}}\right) \cdot (2.0 \text{ eq/mole}) = 9.36 \times 10^{-4} \text{ eq/L}$$

The normality of the feed stream (\overline{N}) is equal to the sum of the individual normalities for arsenate and sulfate.

$$\overline{N} = 5.61 \times 10^{-7} \text{ eq/L} + 9.36 \times 10^{-4} \text{ eq/L} = 9.36 \times 10^{-4} \text{ eq/L}$$

Finally, the treatment capacity of the media (prior to regeneration or replacement) can be calculated from the normalities of the media and the feed stream.

$$BV_{e} = \left(\frac{1.27 \text{ eq/L}}{9.36 \times 10^{-4} \text{ eq/L}}\right) = 1,357 \text{ Bed Volumes}$$

6.5 **Process Design & Operational Parameters**

Design and operational parameters for sorption treatment processes vary significantly depending on the specific technology chosen, and to a lesser degree on the media type. The most appropriate way to identify the optimal engineering parameters for a particular treatment application is to conduct on-site pilot column studies with the media of interest.

Regenerable IX processes involve three operating modes: (1) Loading; (2) Regeneration; and (3) Rinsing. Loading can be conducted with flow in either the downward or upward direction, although the former is more common in water treatment applications. Once the column is fully loaded it should be taken off-line. The next step is regeneration with concentrated brine (for chloride-based SBR) or caustic soda (for hydroxide-based SBR), which can be conducted in either the downward or upward direction. The latter case is generally more effective, although care must be taken to prevent fluidization of the media. Prior to returning the column to service, water rinsing should be conducted to displace regenerant solution from the column. Slow rate and fast rate rinsing should be conducted in sequence, with each displacing about 2-3 bed volumes of solution per column.

Table 6-3 details key design and operational parameters for AA, GFH, and IX processes. As described in Section 2, non-regenerable AA and GFH process are

recommended for small utilities. Therefore, rinsing and regeneration data is only provided for ion exchange processes.

Table 6-3. Typical Sorption Treatment Design and Operating Parameters.					
Parameter	IX	AA	GFH	Units	
Media Bulk Density	41-44	35-42	72	lbs/cft	
Minimum Column Layers					
Freeboard	50%	50%	50%		
Ion Exchange Resin	24-40			in.	
Activated Alumina		24		in.	
Granular Ferric Hydroxide			32-40	in.	
Operating Conditions					
Maximum Service Rate	2-24	2-10	5-8	gpm/sft	
Minimum Empty Bed Contact Time	1-10	0.5-5	5	min.	
Maximum Pressure Differential	14	5	3.5	\mathbf{psi}	
Regeneration Conditions					
Brine Strength	1-5			mole/L	
Downflow Rate	2-6	_	_	gpm/sft	
Upflow Rate	0.4-4			gpm/sft	
Rinsing Conditions					
Slow Rinse Rate	0.4-4			gpm/sft	
Fast Rinse Rate	2-20			gpm/sft	
Displacement Requirements	4-6			bed volumes	

Table 6.2 Trusical Soundian Tractment Design and Operating Dependence

6.6 Column Design

Dedicated filter vessels should be used for pre-filtration and sorption treatment. This separation is advised because the density of typical filter media, such as sand and anthracite, exceeds that of most types of sorptive media. Therefore, if the media were placed in a single column (with the filter media initially on top), stratification would occur over time and during backwashing. Gradually, the filter media would work its way down the column where it would no longer be capable of pre-filtering solids.

The vessels should be made from typical, well-known materials of construction such as carbon steel or fiberglass. The vessels should have distribution and collector systems that provide a uniform distribution of fluids during all phases of the operation. More detail on these accessories is provided in Section 7. Also, it is advisable to install sight-glasses in order to check resin levels.

Columns placed in series are referred to as a treatment train. The utility should evaluate the number of parallel treatment trains based on the desired redundancy.

Figure 6-7 shows a commercially available multiple-column ion exchange treatment train.



Figure 6-7. Ion Exchange System (U.S. Filter).

6.6.1 Column Diameter

Once the number of parallel treatment trains has been established, column diameter can be calculated based on the recommended service rate of the particular media and the design flowrate. Service rate is the flowrate per unit of cross-sectional area and is proportional to the linear velocity of the fluid through the bed. Recommended maximum service rates are provided in Table 6-3. Column diameter (D) can be calculated using the equation:

$$D = \left(\frac{4Q}{\pi n_{\rm P}G_{\rm S}}\right)^{0.5}$$
 Eqn. 6-7

Where:

D = Column Diameter (ft)

Q = Design Flowrate (gpm)

 n_{P} = Number of Parallel Treatment Trains

 $G_s =$ Service Rate (gpm/sft)

The benefits of lower service rates include a sharper MTZ and potentially better media utilization. However, a lower service rate also translates into a larger column footprint. Consider an example where IX will be used to treat a design flowrate of 65 gpm. The utility has decided to provide 2 active parallel treatment trains. Based on a recommended maximum service rate of 10 gpm/sft, the column diameter should be 2 feet.

$$D = \left(\frac{4 \cdot 65 \text{ gpm}}{\pi \cdot 2 \cdot 10 \text{ gpm/sft}}\right)^{0.5} = 2 \text{ ft}$$

6.6.2 Column Height

The depth of sorptive media required can be calculated based on the selected service rate and consideration of the minimum empty bed contact time. Values of EBCT are provided in Table 6-3.

$$Z \ge \frac{G_{s} \cdot EBCT}{7.48}$$
 Eqn. 6-8

Where:

Z= Depth of Sorptive Media (ft)G_s= Service Rate (gpm/sft)EBCT= (Minimum) Empty Bed Contact Time (min)

Returning to the previous example, suppose the specific resin selected had a minimum EBCT of 3 minutes. The total depth of sorptive media required for the primary treatment columns would be 4 feet.

$$Z = \left(\frac{10 \text{ gpm/sft} \cdot 3 \text{ min}}{7.48}\right) = 4 \text{ ft}$$

The depth of sorptive media (Z) should then be used in conjunction with the column freeboard to determine column height. For ease of change-out, all columns should be sized similarly.

$$H = Z \cdot (1 + F)$$
 Eqn. 6-9

Where:

H = Column Height (ft)

Z = Depth of Sorptive Media (ft)

F = Freeboard Allowance (%)

For the previous example, if the freeboard requirement was 50% of media depth, the column height should be 6 feet.

$$H = (4 ft) \cdot (1 + 0.5) = 6 ft$$

Therefore, for this particular example, the design should include two parallel treatment trains each consisting of three columns (i.e., lead, polishing, and backup). All columns should be 2 feet in diameter by 6 feet tall and contain 4 feet of media. The process flow diagram for this example is provided as Figure 6-8.



Figure 6-8. Process Flow Diagram for Example Problem.

The following constraints should also be considered:

- Small column aspect ratios (i.e., H:D <1) can lead to flow maldistribution.
- Large column heights can lead to excessive pressure drop.
- The available building footprint.
- The available building height.

6.7 Media Regeneration/Replacement Frequency

It is advantageous for a utility to obtain a rough estimate of the optimal operating time until media exhaustion occurs. This is important for establishing an appropriate O&M and monitoring schedule.

The optimal filter run time until media exhaustion can be calculated as:

$$\tau = \frac{BV_e \cdot EBCT}{60}$$
 Eqn. 6-10

Where:

τ = Optimal Filter Run Time (hr)
 BV_e = Number of Bed Volumes to Exhaustion
 EBCT = Empty Bed Contact Time (min)

Columns should be operated until 50% arsenic breakthrough occurs. Therefore, the actual filter run time will be less than the calculated optimal filter run time (τ) .

The deviation will depend on the efficiency of the sorption/exchange process and the width of the MTZ.

Consider an example where the estimated lifetime of a particular combination of media and raw water was 1,357 bed volumes (continuing from example in Section 6.4). If the columns are sized to provide an EBCT of 3 minutes, the optimal run time until media exhaustion is 68 hours.

$$\tau = \frac{(1,357 \text{ Bed Volume}) \cdot (3 \text{ min})}{60 \text{ min/hr}} = 68 \text{ hr}$$

6.8 Regeneration of Ion Exchange Resin

Ion exchange resins are essentially unusable for arsenic removal unless they can be efficiently regenerated. Because of the high selectivity of SBR for sulfate (SO₄²⁻), the exchange capacity would be exhausted within a few days for many natural waters. The cost of the virgin resin is far too great to dispose of it at that time.

Chloride-based SBR can be regenerated with concentrated brine (1-5 mole/L) in either the upflow or downflow mode. The more concentrated the regenerant solution, the greater the fraction of the bed that is regenerated. It should be noted, however, that regeneration efficiencies are generally less than 100%. Therefore, successive runs can be expected to be shorter in duration.

For a conventional IX process, spent regenerant will contain arsenic and sulfate in a ratio approximately corresponding to their concentration in the raw water. If the water contains a moderate amount of competing ions, it is possible that the brine waste will contain less than 5.0 mg/L of arsenic, and thus will meet the TC. However, in most instances, the liquid waste stream will contain more than 5.0 mg/L of arsenic. This will force utilities to consider disposal and waste treatment options.

Based on previous studies (AwwaRF, 2000), roughly 4 bed volumes of spent brine are produced per regeneration. The regeneration duration can be calculated as:

$$t_{R} = \frac{29.9 \cdot Z}{G_{R}}$$
 Eqn. 6-11

Where:

 t_R = Regeneration Duration (min) Z = Depth of Sorptive Media (ft) G_R = Regeneration Flux (gpm/ft²) Following regeneration, this brine can either be disposed of via indirect discharge (assuming local TBLLs are met) or stored for recycle. In the case of recycle, it may be necessary to add salt to bring the strength of the brine back to the range 1-5 mole/L.

Rinsing with water is typically conducted afterwards to flush out residual brine and prepare the column for normal operation. Generally 4 to 6 bed volumes of rinse water are generated per step.

Ion exchange resin typically lasts 4-8 years before chemical and mechanical degradation necessitates media replacement.

6.9 Waste Handling Systems

This section addresses three types of waste: backwash water from pre-filters, spent regenerant, and spent media.

The two most probable methods for disposal of backwash water from pre-filters are indirect disposal through a municipal POTW or by settling the solids, recycling supernatant, and sending the solid sludge to a landfill.

Regarding brine used in IX regeneration, there are two waste disposal options. Spent brine that contains less than 5.0 mg/L of arsenic can either be disposed of via indirect discharge or treated on-site. The feasibility of indirect discharge of regenerant waste will be dictated by local TBLLs for TDS. The concentration of total dissolved solids in the spent regenerant can be approximated as:

$$C_{\text{TDS}} = 58.4 \cdot \overline{M}_{\text{Brine}}$$
 Eqn. 6-12

Where:

 C_{TDS} = Concentration of Total Dissolved Solids (g/L) \overline{M}_{Brine} = Brine Molarity (mole/L)

When indirect discharge is not an option, the utility must deal with the waste onsite. The most common approach for treating brine waste (containing less than 5.0 mg/L of arsenic) is chemical precipitation with iron-based salts and subsequent solids thickening. Thickening can be conducted using a settling basin, or for more rapid results, mechanical dewatering equipment. The brine decant can then be sent to an evaporation pond.

Spent brine used in the regeneration of arsenic-laden resin will most likely be classified as hazardous. Therefore, manipulating the chemical form of the waste onsite constitutes treatment of a hazardous waste, which has extensive permit, as well as cost implications. As a result, when the brine waste stream contains over 5.0 mg/L of arsenic, indirect discharge to a conventional sewer system is considered the only viable option for small utilities. When this option is unavailable, on-site regeneration of arsenic-laden resin should not be performed. Rather, the resin should be disposed of at a conventional landfill and replaced with fresh resin.

The appropriate disposal method for spent resin is dependent on the results of the TCLP, as described in Section 1.

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Section 7 Pressurized Media Filtration Process Design Considerations

This section describes the design of a typical pressurized granular-media filtration system including sand filtration, GAC filtration, and iron and manganese oxidation/filtration systems. Iron and manganese oxidation/filtration systems can utilize several different types of media such as greensand, pyrolucite, MTM, Anthrasand, BIRM, and iron oxide coated sand (IOCS). The most common of these is greensand. Although the following information describes a pressurized greensand filter, it can be applied to any pressurized granular media filtration system.

7.1 Process Flow

In a typical media filtration process, seen in Figure 7-1, the raw water is first put through a pre-oxidation step. This converts the arsenic to the oxidized arsenate form and provides the oxidant for any iron and manganese oxidation that may occur. If a MnO_x is being used as the filter media, this oxidation step also provides the oxidant for the continuous regeneration of the MnO_x media.

After pre-oxidation, a coagulant addition step may be performed if the iron concentration or the Fe:As ratio is low. Next, the water is passed through filters containing granular media before being sent to the distribution system. Typically, three or more filters are provided in parallel.



Figure 7-1. Typical Media Filtration Process Flow Diagram.

Media filters are operated in three different modes: (1) Filtration; (2) Backwash; and (3) Filter-To-Waste (FTW). In the operating mode, all filters are fed in parallel with flow in the downward direction. The effluent is sent to the distribution system as shown in Figure 7-2.

After some time of operation, solids captured by the filtration media will impede the flow and increase the differential pressure across the filter. To restore hydraulic capacity, the filter will have to be backwashed. To do this, effluent from one or more filters is diverted to the third filter. The backwash flow is in the upward direction, which fluidizes the granular media and washes the accumulated solids out of the filter. In some instances, air scouring is conducted prior to fluid backwashing. Air scouring bubbles large volumes of air upward through the filter. This assists in breaking apart conglomerates of filtered material, allowing the subsequent fluid backwash to more easily remove the captured solids. An air scour also reduces the volume of backwash waste that is generated.



Figure 7-2. Media Filtration Process Flow Modes.

After backwashing, the media is allowed to settle and downward flow is reinstated with the filter effluent going to waste. This repacks the column, setting it up for operation. It also reduces amount of particulate matter that gets into the distribution system. After the FTW mode, the filter is returned to standard operation.

7.2 Process Design & Operational Parameters

Table 7-1 lists design and operational parameters typical of media filtration systems.

Parameter	Value	Units			
Media Bulk Density					
Anthracite Media ¹	50	lbs/cft			
Greensand Media ²	85	lbs/cft			
Garnet Media ³	140	lbs/cft			
Support Gravel ⁴	100	lbs/cft			
Column Layers					
Freeboard ^{1,2}	50%	of Anthracite and Greensand			
Anthracite Media ¹	10-18	in.			
Greensand Media ^{2,5}	20	in.			
Garnet Media ³	4	in.			
Support Gravel ⁴	18-30	in.			
Operational Parameters					
Service Rate ⁶	3-12	gpm/sft			
Max Pressure Differential	8	psi			
Backwash Parameters					
Backwash Service Rate ²	10-12	gpm/sft			
Backwash Duration	15	min			
Backwash Frequency	1-7	days			
Bed Expansion ²	40%	minimum			
Air Scouring Rate	0.8 - 2.0	scfm/sft			
Filter-to-Waste Parameters					
FTW Service Rate ²	3-5	gpm/sft			
FTW Duration	5	min			

Table 7-1	Typical	Groonsand	Column	Design and	Onersting	Parameters
Table 7-1.	Typical	Greensand	Column	Design and	Operating	rarameters.

¹Recommendation by Clack Corporation, Anthracite, Form No. 2354.

² Recommendation by Clack Corporation, Manganese Greensand, Form No. 2349.

³ Recommendation by Clack Corporation, Garnet, Form No. 2355.

⁴ Recommendation by Clack Corporation, *Filter Sand and Gravel*, Form No. 2352.

⁵ Clack Corporation, *Manganese Greensand*, Form No. 2349 recommends 30" but can be significantly lower if used with continuous regeneration.

⁶ Recommendation by Clack Corporation, *Manganese Greensand*, Form No. 2349 for manganese removal.

7.3 Filter Design

Typically, granular-media pressure filters have multiple layers of media selected to maintain a coarse-to-fine grading from the top to bottom of the filter. The coarse, upper layer provides rough filtration and the bulk of the particulate retention while the fine, lower layer provides superior filtration. This scheme allows for longer runs times while maintaining filtration quality. A typical oxidation/filtration filter is shown in cross-section in Figure 7-3.



Figure 7-3. Schematic of a Vertical Greensand Pressure Filter.

In oxidation/filtration, the primary layer in the filter is made of a media that catalyzes iron and manganese oxidation, promotes its precipitation, and filters out the precipitate. Arsenic is removed by the co-precipitation with the iron and, to a lesser degree, the manganese. Greensand is the most common of these types of material. Greensand is glauconite sand coated with a thin layer of MnO_2 . Other materials that function similarly are pyrolucite (solid MnO_2 media), BIRM (aluminum silicate sand impregnated with MnO_2), and Anthrasand (anthracite coated with MnO_2).

Because the greensand is very fine, 16-60 mesh, it is susceptible to being overloaded with solids. To reduce the solids loading on the greensand a layer of filter coal such as anthracite is put on top. This layer also provides an area for the iron floc to coagulate. Because of anthracite's low density, the filter coal will naturally stratify as the top layer after backwash.

In order to keep the greensand from being slurried out the under-drain, a layer of filter garnet is placed below it. This filter garnet has a particle size of 8-12 mesh and a density almost 50% greater than the greensand. This puts the filter garnet below the greensand after stratification.

The bottom layer is support granite, which allows the water to flow easily into the lower distribution system and exit the filter. Because of its larger size, the support granite is not fluidized during backwash. Instead, it assists in distributing the backwash flow evenly throughout the filter.

When the media is backwashed, it will expand by up to 50%. To accommodate this, the filter is designed with freeboard. Freeboard is the amount of empty space in the filter between the upper layer of media and the upper distribution manifold. The height of this freeboard is dependent on the media but is generally 40-50% of the fluidized media.

Every filter will have an upper and lower distribution manifold. The upper manifold distributes the influent and collects the backwash water. The lower manifold collects filtered water and distributes backwash water. There are numerous designs for these distribution manifolds. Smaller diameter filters may have a hub-lateral design shown in Figure 7-4. Larger diameter columns may have a header-lateral design, shown in Figure 7-5. The header-lateral design gives a more even distribution of the flow, which is much more important for the lower manifold, as flow distribution directly affects the effectiveness of the backwash.



Figure 7-4. Hub-Lateral Distribution System (Johnson Screens).



Figure 7-5. Header-Lateral Distribution System (Johnson Screens).

Typical media filtration installations include several filters in parallel. This allows one to be taken offline while the others continue to work. It also allows the other filters to provide the backwash water necessary to backwash a single filter. Figure 7-6 shows one potential valving arrangement that allows the use of multiple filters. Figures 7-7 and 7-8 show pictures of commercially available pressurized media filters.



Figure 7-6. Multiple Media Filter Setup.



Figure 7-7. Pressurized Media Filter (U.S. Filter).



Figure 7-8. Packaged Arsenic Filtration System (Kinetico).

7.3.1 Filter Diameter

The primary design variable for the granular media filters is the service rate. This is the flowrate the filters handle per horizontal cross-sectional area of media. Typical service rates for greensand filters range between 4 and 10 gpm/sft. Using this information, the number of filters, and the maximum flowrate for which the filters are designed (i.e., design flowrate), the filter diameter can be calculated using equation 7-1.

$$D = \left(\frac{4Q}{\pi n_{\rm P}G_{\rm S}}\right)^{0.5}$$
 Eqn. 7-1

Where:

D = Column Diameter (ft)

Q = Design Flowrate (gpm)

 n_{P} = Number of Parallel Treatment Trains

 $G_s =$ Service Rate (gpm/sft)

For the example of 3 parallel filters designed to treat a maximum of 300 gpm of water at a filter service rate of 5 gpm/sft, the filter diameter should be 5 feet.

$$D = \left(\frac{4 \cdot 300 \text{ gpm}}{\pi \cdot 3 \cdot 5 \text{ gpm/sft}}\right)^{0.5} = 5\text{ft}$$

7.3.2 Media Weight

The weight of each media layer can be calculated using the following equation:

$$W_{j} = \frac{\pi D^{2} h_{j} \rho_{j}}{4} \qquad \text{Eqn. 7-2}$$

Where:

 W_i = Weight of Media Layer *j* (lbs)

D = Column Diameter (ft)

 h_i = Height of Media Layer j (ft)

 ρ_i = Bulk Density of Media *j* (lbs/cft)

For the previously calculated 5-ft filters, using 1 ft of anthracite, 2.5 ft of greensand, 0.25 ft of filter garnet, and 2 ft of support granite, the media weights per filter are 982 lbs of anthracite, 4,172 lbs of greensand, 916 lbs of filter garnet, and 3,927 lbs of support granite, respectively. Typical densities for each of the media can be found in Table 7-1.

$$W_{\text{Greensand}} = \frac{\pi (5 \text{ ft})^2 (2.5 \text{ ft})(85 \text{ lbs/cft})}{4} = 4,172 \text{ lbs of greensand (per filter)}$$

7.4 Waste Handling System Design

Both the backwash water and the FTW water from granular media filtration processes pose disposal issues. The backwash flowrate can be calculated using the equation:

$$Q_{BW} = \frac{\pi}{4} D^2 G_{BW}$$
 Eqn. 7-3

Where:

 Q_{BW} = Backwash flowrate (gpm) G_{BW} = Backwash flux (gpm/sft) D = Column Diameter (ft)

The FTW flowrate is typically the same as the flowrate used in the filtration mode. Therefore, the volume of wastewater produced by the backwash and FTW modes can be calculated using the equation:

$$V_{WW} = Q_{BW} \cdot t_{BW} + \frac{Q}{n_{P}} t_{FTW}$$
 Eqn. 7-4

Where:

V_{WW} = Volume of Wastewater (gal)

 Q_{BW} = Backwash Flowrate (gpm) t_{BW} = Backwash Duration (min) Q = Design flowrate (gpm) n_{P} = Number of Parallel Treatment Trains

 t_{FTW} = Filter-To-Waste Duration (min)

For example, assume the same 3-filter system as before (5-foot diameter, 300gpm design flowrate, and 5 gpm/sft service rate) has a backwash rate of 12 gpm/sft, a backwash time of 15 minutes and a filter-to-waste time of 5 minutes. The required backwash flowrate is then 236 gpm/filter and the wastewater volume created is 4,040 gallons per backwash per filter.

$$Q_{BW} = \left(12 \ \frac{gpm}{sft}\right) \frac{\pi (5 \ ft)^2}{4} = 236 \ gpm (per \ filter)$$

$$V_{WW} = \left(236 \frac{\text{gpm}}{\text{Filter}}\right) \left(15 \frac{\text{min}}{\text{Backwash}}\right) + \left(\frac{300 \text{ gpm}}{3 \text{ Filters}}\right) \left(5 \frac{\text{min}}{\text{Backwash}}\right) = 4,040 \frac{\text{gallons}}{\text{Filter} \cdot \text{Backwash}}$$

The wastewater can be disposed of in several different ways. The two most probable methods are indirect disposal through a municipal POTW or by settling the solids and recycling the supernatant and sending the solids to a landfill.

In the indirect discharge through a municipal POTW, a holding tank may be desired to eliminate the surging to the municipal POTW system. In the liquid recycle/solids disposal method, a settling tank or basin is required. The holding basin or tank should be sized to hold at least two backwash/FTW cycles. In the above example, this leads to an 8,100-gallon tank.

7.5 Coagulant Addition System Design

The efficiency of arsenic co-precipitation to iron floc may vary depending on the concentration of iron and the iron:arsenic ratio. Optimal performance is obtained with an iron concentration of 1.5 mg/L or greater and an iron:arsenic mass ratio of at least 20:1. If the raw water does not meet these two parameters, iron addition may be required to provide enhanced coagulation. Ferric chloride (FeCl₃) is commonly available for use in potable water systems and can be obtained as a 38-wt% liquid. The volumetric flowrate ferric chloride solution required to meet a predetermined dose rate can be calculated with equation 7-5.

$$Q_{\text{FeCl}_3} = \frac{Q \cdot \delta_{\text{FeCl}_3}}{90.96 \cdot C_{\text{FeCl}_3} \cdot \rho_{\text{FeCl}_3}}$$
Eqn. 7-5

Where:

Q_{FeCl} = Ferric Chloride Metering Pump Rate (mL/min)

Q = Design flowrate (gpm)

 δ_{FeCl} = Ferric Chloride Dose (mg/L)

 C_{FeCL_2} = Ferric Chloride Stock Solution Concentration (wt%)

 ρ_{FeCl_3} = Density of Ferric Chloride (kg/L)

For example, if the design rate was 300 gpm of water to be treated and the water needed an additional 1.0 mg/L of iron, a 38-wt% solution of ferric chloride with a density of 1.42 kg/L could be added to the water at a rate of 6.1 mL/min to provide the required iron.

$$Q_{\text{FeCl}_3} = \frac{(300 \text{ gpm})(1 \text{ mg/I})}{90.96 (0.38)(1.42 \text{ kg/I})} = 6.1 \text{ mL/min}$$

The required storage capacity for the ferric chloride solution can be calculated using equation 7-6.

$$V = \frac{Qt \,\delta_{FeCl_3}}{239 \cdot C_{FeCl_3} \cdot \rho_{FeCl_3}}$$
 Eqn. 7-6

Where:

V = Storage Volume (gal)

Q = Design flowrate (gpm)

 δ_{FeCl_3} = Dose Rate of Ferric Chloride mg/L)

t = Storage Time (days)

 $C_{FeCl_{2}}$ = Ferric Chloride Stock Solution Concentration (wt%)

 ρ_{FeCl_3} = Density of Ferric Chloride (kg/L)

Using the same example and specifying 14 days of ferric chloride storage, the required storage volume would be 32.6 gallons.

$$V = \frac{(300 \text{ gpm})(14 \text{ days})(1 \text{ mg/I})}{239 (0.38)(1.42 \text{ kg/I})} = 32.6 \text{ gal}$$

A generalized flow diagram for a ferric chloride chemical addition system is shown in Figure 7-9. The ferric chloride should be stored in a tank made of either fiberglass-reinforced polyester or rubber-lined steel tanks. A flow meter installed along the main water line is used to pace the addition of ferric chloride to the water flowrate. An isolation valve and check valve are used in the connection to the water line. After the ferric chloride addition, the water is mixed with an inline mixer and the dosed water is sent to the filters.



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Section 8 Point-Of-Use Treatment

Point-of-use (POU) devices were approved as small system compliance technologies for meeting the revised arsenic MCL. POU devices are attractive for removing contaminants that pose (solely) an ingestion risk, as is the case with arsenic. This is because a very small fraction of the total water supplied to a given household is ultimately consumed. In most cases, the POU unit is plumbed into the kitchen faucet. As such, the kitchen tap would be the only source from which water should be collected for consumption.

The primary advantage of employing POU treatment in a small system is reduced capital and treatment costs, relative to centralized treatment. On the downside, however, it is the utility's responsibility for maintenance of the equipment. Therefore, these programs generally incur higher administrative and monitoring costs to make sure that all units are functioning properly. POU programs are an economically viable alternative to centralized treatment for systems serving up to 80-90 connections (USEPA, 2001).

The primary criteria for selecting an appropriate POU treatment device are arsenic removal performance and cost. Additional considerations include the following:

- Minimal attention required
- Simplicity
- Can be used in on-demand mode
- Small footprint

- Does not produce hazardous waste
- Damage-proof
- Error-proof
- Under-the-counter application

8.1 Treatment Alternatives

The technologies that are most amenable to POU treatment include column adsorption with AA, GFH, or RO with pre-filtration. The decision trees in Section 3 lead to the most appropriate POU technology among these choices.

8.1.1 Column Adsorption

The use of disposable activated alumina in a POU device is recommended only in instances where the pH of water in the distribution system is near or below 6.0. Because of concerns with lead and copper corrosion, pH values in this range are not common. Modified activated alumina and GFH provide improved treatment capacity across a broader pH range, and are thus recommended for higher pH values. In either case, these technologies are used in column or cartridge operation. Column operation has the advantages of simple operation, low maintenance, low relative cost, small under-thecounter footprint, and high treatment capacity. Additionally, the breakthrough kinetics of sorption technologies are slow and more readily detected by routine monitoring.

Figure 8-1 shows how POU adsorption equipment is typically connected to kitchen plumbing.



Figure 8-1. Point-Of-Use Adsorption Setup (Kinetico).

Adsorption columns are typically operated to a set volume to prevent arsenic leakage. This is accomplished through the use of a metered cartridge which provides flow totalization and will automatically shut-off water flow once the unit reaches the prescribed volume limit. Figure 8-2 shows a cross-section of one manufacturer's adsorption cartridge.



Figure 8-2. Metered Automatic Cartridge (Kinetico).

8.1.2 Reverse Osmosis

Point-of-use RO devices are recommended for treating arsenic-rich water containing high levels of sulfates or phosphates. When operating at typical tap pressures, RO devices commonly achieve greater than 95% arsenate rejection at a water recovery of 10-25%. Most units are designed with preand post-filters. Pre-filtration through granular media is applied to reduce solids loading and extend membrane life. For chlorine-sensitive membranes, pre-filtration typically utilizes a dechlorinating media such as GAC. Post-filtration utilizes carbon or arsenic adsorbent media and serves as a final polishing step.

Although the cost of RO POU devices is relatively high compared to other possible options, the immediate improvement of the overall water quality could make it very attractive to customers. The potential disadvantages associated with RO systems include poor water recovery, disposal of the reject stream, and high capital cost.

The most common types of membranes used for RO applications are cellulose acetate, thin-film polyamide composites, and sulfonated polysulfone. The membranes are manufactured in various forms, including tubes, sheets, and hollow fibers. The membrane is then constructed into a cartridge called an RO module, either spiral wound or hollow fiber. Most RO POU devices operate at tap water pressure, and therefore have relatively poor water recoveries. Permeate is sent to a bladder tank large enough to meet on-demand requirements. Typical production rates range from 5-15 gpd.

Over time, the membrane surface will require cleaning in order to maintain performance. This capability is built in to most RO devices. Depending on the specific design, the water source for washing the membrane surface may either be feed water or permeate.

Figure 8-3 shows how POU RO equipment is typically connected to kitchen plumbing.



Figure 8-3. Point-Of-Use Reverse Osmosis Setup (Kinetico).

8.2 Implementation Considerations

The new rule requires that POU devices be owned, controlled and maintained by the public water system or by an agency under contract with the water system. Therefore, the responsibility of operating and maintaining the devices cannot be passed to the customer. The implications of this requirement to the utility are significant.

The implementation of a centrally managed POU program is very different from application of centralized treatment. In many cases, the customer's acceptance of the treatment unit is affected by familiarity with the technology, the need for treatment, the appearance of the unit, and other subjective factors.

Many homeowners currently employ some form of POU treatment such as carbon filtration or water softening. These products are generally used to enhance aesthetic properties of water, and are therefore used voluntarily. Under a centrally managed POU treatment program, all customers would be required to employ treatment devices in their home. As such, utility staff or contractors would need access inside individual homes to install treatment devices, make plumbing modifications, and make periodic O&M checks. The extent of customer acceptance and potential for resistance associated with this utility-customer interface are not well known.

8.2.1 Program Oversight

The utility must decide whether it wants to implement the POU program inhouse or contract out the necessary services. In one case, the utility would be the main contact with the customer, and utility staff would be responsible for installation, monitoring, record-keeping, and O&M activities. This raises several important issues. First, many small utilities often have difficulty finding the time and budget to hire, train, and retain operators. Second, utilities that elect to keep the work in-house must provide staff training on installation and O&M procedures. Third, the utility should consider the liability implications of entering individuals' homes to conduct work. If the utility decides to contract out the services, the vendor would be the main contact with the customer and the utility would need to monitor the contractor.

8.2.2 Cost

There are a number of cost elements involved in conducting a POU program. These include:

• Capital cost of POU devices. The typical cost ranges of RO devices and adsorption cartridges are \$300-\$1,000 and \$100-\$300 each, respectively.

- Installation labor. Installation of each device is anticipated to take 30 to 60 minutes assuming no significant plumbing modifications are necessary.
- Installation parts
- Replacement parts. Carbon-based pre-filters typically cost between \$15-50. New membranes typically cost about \$150.
- Water quality analyses. Arsenic can be measured by a commercial laboratory for approximately \$10-\$20 per sample.
- O&M labor.

8.2.3 Monitoring

Monitoring will need to be conducted for each and every installed POU device, though only one-third within the same year. This can be conducted by the utility, the contractor, or by the customer. In the latter case, the utility would still be responsible for providing and collecting sample containers, as well as specific instructions that can be used by the customer to conduct the sampling.

The monitoring requirement will cover such items as water quality (arsenic levels), pressure drop, and cumulative volume treated. It would be ideal to have a set of criteria addressing both quantitative and qualitative issues that would be monitored or assessed periodically.

A monitoring schedule should be established based on considerations of water quality and the treatment technique employed. Given raw water quality, most vendors can provide an estimated lifetime of the specific treatment before breakthrough occurs. Section 6 also includes discussion of methods that can be used to estimate useful sorbent life. Any monitoring plan should include a significant safety margin to prevent exposure to arsenic-rich water. The monitoring schedule can always be revised based on the actual performance of the POU devices or pilot studies.

8.2.4 Operations and Maintenance

Periodic O&M is necessary to ensure that the devices are functioning properly and producing tap water in compliance with the arsenic MCL. Operations and maintenance activities consist of both regular scheduled tasks as well as emergency troubleshooting responses.

The sorbent media or RO membrane must be replaced periodically, based on the results of monitoring. The arsenic rule also stipulates that the POU device be equipped with mechanical warnings to ensure that customers are automatically notified of operational problems. Many devices include a programmable indicator which tracks cumulative water use, and serves as a convenient visual guide for the remaining life of the POU device. However, it is not recommended that the utility depend solely on the customer for POU servicing. Rather, there should be an established schedule that is made public to the community and adhered to.

8.2.5 Customer Involvement

Customer education and 100% community participation are necessary elements of a POU program. To facilitate this, customers should be provided advanced written notice of the monitoring and O&M schedule.

8.2.6 Waste Handling

The type of waste produced from a POU device will depend on the treatment employed. Reverse osmosis treatment will produce a continuous liquid waste stream (i.e., retentate) that should be suitable for disposal in an on-site or community sewerage system (see Section 2). Conversely, with column adsorption treatment, the only waste is exhausted media, which is produced on a periodic basis.

8.3 Device Certification

POU devices should be certified according to the following ANSI/NSF standards.

- ANSI/NSF 53 (1998): Drinking Water Treatment Units Health Effects
- ANSI/NSF 58 (1997): Reverse Osmosis Drinking Water Treatment Systems
- ANSI/NSF 61 (1999): Drinking Water System Components Health Effects

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