

Drinking Water Operator Certification Training



Module 22: Inorganics Removal

Revised January 2006

This course includes content developed by the Pennsylvania Department of Environmental Protection (Pa. DEP) in cooperation with the following contractors, subcontractors, or grantees:

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Penn State Harrisburg Environmental Training Center

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Unit 1 – Overview of Inorganics

Learning Objectives

- Define and identify sources of undesirable inorganic constituents that may be found in drinking water.
- Provide a brief historical perspective on inorganics removal treatment processes.
- Define the following words:
 - Anions.
 - Cations.
 - Catalyst, as it pertains to treatment for soluble manganese.
 - Colloidal, as it pertains to iron and manganese.
 - Insoluble, as it pertains to metals.
 - Kinetics, as it pertains to oxidation.
 - Oxidation, as it pertains to treatment for soluble metals.
 - pH.
 - pE-pH.
 - Soluble, as it pertains to metals.
 - Solute.

Definition of Inorganics



Inorganics are mineral-based compounds such as metals, nitrates, and asbestos that do not contain organic materials.



Sources of Inorganic Constituents

The following five categories represent some sources of inorganics: naturally occurring; municipal and industrial discharges; non-point and run-off; water in contact with pipe materials; and water treatment by-products.

◆ Naturally Occurring

- ⊕ Mineral weathering (dissolution) and leaching (due to ion exchange in soils) are naturally occurring sources of inorganics that find their way into the water supply.
- ⊕ Solubilization as a byproduct of anaerobic microorganisms' metabolic processes is another naturally occurring source of inorganics that are in the water supply.
- ⊕ The following is a list of the predominant inorganic materials found in natural waters.
 - ◆ Calcium
 - ◆ Magnesium
 - ◆ Sodium
 - ◆ Potassium
 - ◆ Bicarbonate/Carbonate
 - ◆ Sulfate
 - ◆ Chloride

- ◆ The concentration of major inorganic mineral ions as a weighted composite of sample analyses from many rivers around the world is presented below.

Parameter	Concentration (mg/L)
Calcium	15
Magnesium	4.1
Sodium	6.3
Potassium	2.3
Iron	0.67
Silica	13.1
Bicarbonate	58.4
Sulfate	11.2
Chloride	7.8
Nitrate	1

- ◆ **Municipal and Industrial Discharges**



What are some examples of municipal and industrial discharges that contribute inorganics to the water supply?

- ◆ **Non-point Water Pollution**

- ◆ Non-point water pollution is contamination that does not come from a specific location. An example of the opposite of non-point, point pollution, is polluted water flowing out of a pipe.
- ◆ Land under cultivation contributes inorganics to the water supply.
- ◆ Paved areas can produce run-off and contribute inorganics to the water supply.



Examples of non-point pollution that contributes inorganics to the water supply are:

- A. Polluted water from a pipe
- B. Polluted water running off of a fertilized farm field
- C. Polluted water running off of a grocery store parking lot

◆ **Water in Contact with Piping**

- ⊕ The water can lead to corrosion or leaching of pipe materials into the water supply.



What are some inorganics that find their way into the water supply when the water comes in contact with piping?

◆ **Water Treatment By-products**

- ⊕ Residuals from chemicals added as part of the treatment process contribute inorganics.
- ⊕ Reaction products between chemicals (such as disinfectants) and naturally occurring inorganic matter contributes inorganics.



By-products, or products that are formed in water because of a chemical reaction include:

- A. Disinfection By-Products
- B. Pipe Scale
- C. Water Treatment Chemicals

The following chart displays examples of common sources of inorganic contaminants (metals) that are of importance to drinking water.

Parameters	Metals				
	Naturally Occurring	Industrial Discharges	Storm Water Run-off	Distribution System Pipe Corrosion	Water Treatment By-product
Antimony		Petroleum refineries; fire retardants; ceramics; electronics; solder			
Barium	Erosion of natural deposits	Drilling wastes; metal refineries; brick and ceramic manufacturers			
Beryllium		Metal refineries; coal burning factories; electrical, aerospace, and defense industries			
Cadmium	Erosion of natural deposits	Metal refineries; waste from electroplating	Runoff from waste; batteries; paint	Galvanized pipe corrosion	
Chromium (total of valence states III and IV)	Erosion of natural deposits	Steel and pulp mills; waste from electroplating; garbage; fossil fuel combustion			
Lead	Erosion of natural deposits			Corrosion of distribution system lead pipe; household plumbing systems	
Copper	Erosion of natural deposits			Corrosion of household plumbing systems	Copper salts used for algae control in reservoirs
Mercury, Total (inorganic)	Erosion of natural deposits	Refineries; factories	Runoff from landfills and croplands		
Nickel	Erosion of natural deposits				

Parameters	Metals				
	Naturally Occurring	Industrial Discharges	Storm Water Run-off	Distribution System Pipe Corrosion	Water Treatment By-product
Thallium		Leaching from one-processing sites; electronics, glass, and drug factories			
Iron	Erosion of natural deposits; bacteria converting solid ferric hydroxide (FeOH) soluble ferrous ion (Fe ⁺)	Acid mine drainage		Corrosion of distribution pipe	Overdose of iron salt coagulant
Manganese	Erosion of natural deposits; in aquatic environment, anaerobic bacteria convert solid manganese dioxide (MnO ₂) to soluble manganous ion (Mn ⁺)	Discarded batteries; steel alloys; agricultural products			
Aluminum	Erosion of natural deposits				Overdose of alum coagulant
Silver					Some domestic treatment systems
Sodium	Erosion of natural deposits	Many industrial wastes			Sodium hypochlorite, caustic soda, soda ash
Zinc	Erosion of natural deposits			Corrosion of galvanized pipe	Some phosphate-based corrosion inhibitors

The following chart displays examples of common sources of inorganic contaminants (anions and miscellaneous inorganics) that are of importance to drinking water.

Parameters	Inorganic Anions & Miscellaneous Inorganics				
	Naturally Occurring	Industrial Discharges	Storm Water Run-off	Distribution System Pipe Corrosion	Water Treatment By-product
Arsenic	Erosion of natural deposits	Glass and electronics production wastes; smelting of nonferrous metal ores (especially copper)			
Asbestos	Erosion of natural deposits	Mining discharge		Asbestos decay; cement pipe	
Chloride	Erosion of natural deposits				
Sulfate	Erosion of natural deposits				
Nitrate (as N)	Erosion of natural deposits		Leeching from septic tanks; farm fertilizers; feed lots; sewage		
Nitrite (as N)			Leeching from septic tanks; sewage		
Nitrate + Nitrite (both as N)	Erosion of natural deposits		Leeching from septic tanks; farm fertilizer; feed lots; sewage		
Fluoride	Erosion of natural deposits		Fertilizer; aluminum factories; leeching from septic tanks; sewage		Water additive to promote strong teeth
Selenium	Erosion of natural deposits	Petroleum refineries; discharge from mines			
TDS (Total Dissolved Solids)	Erosion of natural deposits				

Chemical Perspectives



- ◆ In **1925** the United States Public Health Service (USPHS) established physical and chemical constituent standards for color, chloride, iron, magnesium and sulfate.
 - ◆ In **1942** the USPHS revised the 1925 standards.
 - ⊕ Tolerance limits (now MCLs) were established for arsenic, fluoride, lead and selenium.
 - ⊕ Recommended limits were established for chloride, copper, iron plus manganese, magnesium, sulfate, zinc and total solids.
- ◆ In **1946** the USPHS revised 1942 standards.
 - ⊕ They added a tolerance limit for hexavalent chromium.
- ◆ In **1962** the USPHS recommended the establishment of non-enforceable contaminant limits for health-related chemical impurities, including barium, cadmium, nitrate, and silver.
 - ⊕ These limits served as the basis for the establishment of the inorganic standards component of the interim drinking water standards in USEPA's 1974 Safe Drinking Water Act (SDWA), and were accepted by all 50 states as guidelines or regulations.
- ◆ In **1974** the USEPA Safe Drinking Water Act was established in a three step process.
 - ⊕ In the first step, EPA promulgated interim regulations based on the 1962 Public Health Service standards. These regulations became effective in June 1977 and included MCLs for 10 inorganic chemicals.
 - ⊕ The second step consisted of a two-year study conducted by the National Academy of Sciences (NAS) intended to gather information on all contaminants in drinking water that may have an adverse health impact.
 - ⊕ In the third step, the EPA promulgated more comprehensive drinking water regulations, and revised existing regulations based on the NAS two-year study results and other research.

Physical Perspectives

- ◆ Water clarity was considered important in the 18th century.
 - ⊕ The removal of particles from water by filtration had been established as an effective means of clarifying water.
 - ⊕ The degree of clarity was not measured.

GENERAL INORGANIC CHEMICAL AND TREATMENT TERMINOLOGY



Anion – an elemental atom or compound with a negative charge.



Cation – an elemental atom or compound with a positive charge.



Catalyst – a substance which can “speed up” a chemical reaction without itself being permanently changed.



Colloidal – dispersion of extremely small particles ($< 1.0 \mu\text{m}$ in size) in water, which cannot settle naturally, primarily due to electrostatic repulsive forces of particle surface charges.



Insoluble – a solid element of compound that is incapable of being dissolved.



Kinetics – speed or velocity of chemical reactions, which depend on factors such as temperature, pH, presence of catalysts, etc.



Oxidation – a chemical in combination with oxygen. A wider definition of oxidation: metal or metal-like element loses electrons to a nonmetal, thereby gaining stability as it transforms from a soluble phase to a solid phase.



pH – measurement of hydrogen ion activity, which affects many chemical reactions. The pH of a solution measures the degree of activity or alkalinity relative to the ionization of the water.



pE-pH – oxidation potential; pE level is raised by adding an oxidant (electron acceptor) and pH level is raised by adding an alkali.



Soluble – dissolved phase of a compound or element.



Solute – the dissolved component of a solution.

Key Points



Five most common sources of inorganics in water are:

- Naturally occurring
- Municipal and industrial discharges
- Non-point water pollution
- Water in contact with pipe materials
- Water treatment by-products



An important perspective or regulation for that includes inorganics in water is:

- The 1974 USEPA Safe Drinking Water Act.

Unit 2 –Inorganics Removal Standards

Learning Objectives

- State one reason for regulating some inorganic constituents by primary maximum contaminant level (PMCL) drinking water standards.
- Identify three inorganic constituents and describe their aesthetic effects in drinking water when exceeding secondary maximum contaminant level (SMCL) drinking water standards.

Regulating These Constituents

- ◆ The Primary Maximum Contaminant Level (MCL) represents the highest level of a contaminant that is allowed by the USEPA in drinking water.
- ◆ MCLs are created to protect the public health, as these contaminants do or may cause chronic or acute health problems.
 - ⊕ MCLs are set as close to Maximum Contaminant Level Goals (MCLGs) [see below] as feasible, using the best available treatment technology, and taking cost into consideration.
 - ⊕ MCLs are enforceable standards.
- ◆ MCLG is a regulatory standard that was established as part of the amendment in 1986 that strengthens the SDWA.
 - ⊕ The MCLG is the level of a contaminant known to occur in drinking water, below which there is no known or expected risk to health, based on toxicology reviews.
 - ⊕ MCLGs allow for a margin of safety and are non-enforceable public health goals.
- ◆ Treatment Technique (TT) is a regulatory standard that was established as part of the amendment to the SDWA in 1977.
 - ⊕ The TT is used in place of the MCL standard if it is not economically or technically feasible to determine the level of the contaminant.

Commonly Found Inorganics with MCL

Table 2.1 Primary Maximum Contaminant Levels

Parameter	MCL	Article I. MCLG
Arsenic - mg/L	0.01	0
Lead - mg/L	0.015 -TT AL	0
Copper - mg/L	1.3 - TT AL	1.3
Nitrate (as N) - mg/L	10	10
Fluoride - mg/L	4	4

MCL = Maximum Contaminant Level
MCLG = Maximum Contaminant Level Goal
TT AL = Treatment Technique Action Level

Effects of These Constituents

- ◆ Secondary Maximum Contaminant Levels (SMCL) are non-enforceable guidelines set by the USEPA for contaminants that may adversely affect the aesthetic quality of drinking water.
- ◆ Secondary standards apply to contaminants that do not pose health concerns.
- ◆ States are encouraged to establish regulations based on these standards.

Commonly Found Inorganics with SMCL

Table 2.2 Secondary Maximum Contaminant Levels

Parameter	SMCL
Article II. Metals	
Iron - mg/L	0.3
Manganese - mg/L	0.05
Aluminum - mg/L	0.05 - 0.2
Copper – mg/L	1.0
Zinc – mg/L	5
Silver – mg/L	0.10
Article III. Anions	
Chloride - mg/L	250
Sulfate - mg/L	250
Article IV. Other Inorganics	
TDS - mg/L	500
Corrosivity	Noncorrosive
Fluoride – mg/L	2
Taste and Odor	3 TON*

*TON = Threshold Odor Number

INORGANICS THAT OCCUR IN DRINKING WATER WITH SECONDARY DW STANDARDS

The table below lists some common secondary standards with their effects, inorganic contributors, and indications.

Table 2.3 Examples of Secondary DW Standards

Standards Related to:	Possible Water Quality Contributor(s)	Possible Indication of:
Metallic taste	Copper, iron, manganese, zinc	Lack of, or non-optimized, corrosion control treatment resulting in corrosion of pipe materials
Salty taste	Total dissolved solids (TDS), sulfate, chloride	Man-made contamination; salt water intrusion
Color	Aluminum, copper, iron, manganese, total dissolved solids (TDS)	Improper and/or inadequate source water treatment; corrosion of pipe materials
Cosmetic effects	Silver	Possible evidence of Argyria, a skin discoloration, due to leaching from home water treatment devices that contain silver for disinfection
Tooth discoloration and/or pitting in children	Fluoride	High levels of fluoride in water supply; excessive fluoride feed
Corrosion and staining	Copper, iron, manganese, zinc,	Lack of, or non-optimized, corrosion control treatment, resulting in corrosion of pipe materials leading to staining (blue-green, reddish, brown, black) of plumbing fixtures, laundry, etc.
Scale and sediments	Iron, manganese, sulfur, calcium, magnesium, Total Dissolved Solids (TDS), Aluminum	High levels of naturally occurring hardness; excessive alkali feed; and/or deficient source water treatment that may result in scale formation and sediments, mineral deposits that build up on the inside of water mains, hot water pipes, boilers, and heat exchangers, which restricts or blocks water flow
Odors	Hydrogen Sulfide	Inadequate oxidation

Hardness



- ◆ Excessively hard water produces scale formation inside water conveyance pipes and pumps, resulting in progressively degraded performance.
- ◆ Hot water increases the tendency of water to produce scale, which seriously degrades domestic, commercial, and industrial hot water system performance and lifespan.
- ◆ Excessive hardness reduces the effectiveness of soaps and detergents.



What consequences could scale from hard water produce?

Hydrogen Sulfide



- ◆ Hydrogen sulfide production is generally limited to groundwater supplies (wells).
- ◆ It may result in rotten egg odors, milky-blue colored water, and corrosion of water conveyance pipe.

Key Points



Primary Maximum Contaminant Level (MCL) Inorganic constituents

- Represents the highest level of a contaminant that is allowed by the USEPA in drinking water
- These contaminants do or may cause chronic or acute health problems
- MCLs are enforceable



Secondary Maximum Contaminant Level (SMCL) Inorganic constituents

- Represents the level of a contaminant that may adversely affect the aesthetic quality of drinking water
- Do not pose health concerns
- SMCLs are non-enforceable



Inorganics not presently regulated that may need treatment

- Hardness
- Hydrogen Sulfide

Unit 3 – Treatment Protocols

Learning Objectives

- List three conditions that may contribute to process selection for inorganics removal.
- Identify common treatments for iron and manganese.
- Identify common treatments for aluminum.
- Identify common treatments for hardness.
- Identify common treatments for nitrates.
- List a common treatment choice for three less common inorganics.

Treatment Selection Considerations

Contaminant Removal

- ◆ The primary contaminant(s) of concern will be the basis for determining which treatment technologies are most appropriate for additional consideration.

Source Water Quality and Variability

- ◆ The nature and variability of the water quality profile will be a primary consideration for the selection of a treatment process.

Reliability

- ◆ Due to the requirement stating that treatment operations often must be maintained around the clock, frequently with long periods of unmanned operations, it is essential that a treatment technology have minimal susceptibility to failures and that redundancy is built into critical components.

Existing Conditions

- ◆ Consideration for incorporating existing water facilities is an important factor for selecting a new treatment process.

Flexibility

- ◆ Treatment technologies must be capable of treating typical and worst case source water quality conditions.
- ◆ Water quality standards are becoming more stringent; whenever possible, the capability to treat anticipated future requirements should be considered in treatment selection.

Utility Capabilities

- ◆ The resources, in terms of staff and finances, are essential factors to consider in treatment selection.

Environmental Compatibility

- ◆ Treatment technologies must abide by all environmental laws, considering such issues as the environmental impacts of construction and the handling the treatment process waste residuals.

Treatment Technology Options

The following tables present inorganic contaminants that may potentially be found in drinking water supplies and the feasible treatment options for each contaminant.

Table 3.1 Treatment Technology Options for Metals

Parameter	GAC	Oxidation	Coagulation/ Filtration	Ion Exchange	Membranes	Lime Softening	Activated Alumina	Corrosion Control	Sequestration
Antimony			X		X				
Barium				X (Cation)	X	X			
Beryllium			X	X	X	X			
Cadmium			X	X (Cation)	X	X		X	
Chromium ⁽⁺³⁾			X	X (Cation)	X	X			
Chromium ⁽⁺⁶⁾			x	X (Anion)	X	X			
Copper								X	
Iron		X	X	X (Cation)	X	X		X	X
Lead								X	
Manganese		X	X	X (Cation)	X	X		X	X
Mercury	X		X		X	X			
Molybdenum				X (Anion)	X				
Nickel				X (Cation)	X	X			
Thallium				X (Anion)			X		
Zinc				X (Cation)	X	X		X	

⁽¹⁾ Membranes

NF Nanofiltration (membranes containing slightly larger diameter pores than RO; used primarily for softening hard water and for removing disinfectant by-product precursors, or organics)

RO Reverse osmosis (membranes primarily used for desalination of seawater and for removal of salts from brackish water; also capable of removing synthetic organic chemicals)

ED Electrodialysis/Electrodialysis Reversal (membrane process primarily used to demineralize brackish water and seawater, and to soften hard water; limited to removing ionic contaminants; not effective for removing pathogens and organics)

GAC Granular Activated Carbon

Table 3.2 Treatment Technology Options for Inorganic Anions and Miscellaneous Inorganics

Parameter	GAC	Oxidation	Coagulation/ Filtration	Ion Exchange	Membranes ⁽¹⁾	Lime Softening	Activated Alumina	Corrosion Control	Sequestration
Arsenic (+3)			X (w/preoxidation)	X	X	X (w/preoxidation)	X	X	
Arsenic (+5)			X	Article V.	X	X (w/preoxidation)	X	X	
Boron				X	X	(i) X			
Nitrate				X	X				
Nitrite				X	X				
Nitrate and Nitrite				X	X				
TDS					X				
Chloride					X				
Sulfate				X	X				
Selenium (+4)			X	X (Anion)	X	X	X		
Selenium (+6)				X (Anion)	X	X	X		
Fluoride					X		X		
Calcium & Magnesium Hardness				X (Cation)	X	X			X

⁽¹⁾ Membranes

NF Nanofiltration (membranes containing slightly larger diameter pores than RO; used for softening hard water and for removing disinfectant by-product precursors, or organics)

RO Reverse osmosis (membranes primarily used for desalination of seawater and for removal of salts from brackish water; also capable of removing synthetic organic chemicals)

ED Electrodialysis/Electrodialysis Reversal (membrane process used to demineralize brackish water and seawater, and to soften hard water; limited to removing ionic contaminants; not effective for removing pathogens and organics)

GAC Granular Activated Carbon

Introduction

Common Sources of Iron and Manganese

◆ Rivers

- ⊕ Most iron and manganese is in the particulate form.
- ⊕ Levels can vary widely, primarily depending on turbidity levels.



Yellow springs, near Yellow Springs, Ohio, formed by iron-precipitating microflora (water from limestone)

◆ Reservoirs and Lakes

- ⊕ Lower levels of reservoirs and lakes may become anaerobic (depleted of oxygen due to a lack of mixing with the upper layers above the thermocline), which results in solubilization of some of the constituents of the bottom sediments, including iron and manganese.
- ⊕ Higher levels of iron and manganese may occur during periods of reservoir/lake turnover (inversion), typically due to the upper portion of the lake/reservoir sinking as the temperature becomes colder, which displaces the lower levels and brings more concentrated levels of iron and manganese closer to the surface.
- ⊕ If multiple raw water intake levels are available, it may be valuable to establish a depth water quality sampling program to aid in the decision-making process for what level of withdrawal to use.

◆ Groundwater

- ⊕ Water quality is generally relatively constant in individual wells, but the quality can vary greatly within the same aquifer or well field.
- ⊕ Iron and manganese are typically in the soluble state. Deciding which wells to use may depend not only on the quantity that a well can produce, but also on the levels of iron and/or manganese.

◆ In-plant sources

- ⊕ If settled solids in sedimentation basins are not removed frequently, anaerobic conditions may occur, resulting in the release of soluble iron and manganese that downstream filtration may not be able to remove.
- ⊕ Also, recycle waters from backwash lagoons and residual dewatering systems may contain higher levels of iron and/or manganese than the raw water.

Definitions

Some definitions that will be helpful for this section, and for your use at the treatment facility, are listed below.



Adsorption – the ability of certain materials (the adsorbent) to retain molecules on its surface in a more or less reversible manner in a mass transfer from water to the material being used as an adsorbent. The most common adsorption processes used in water treatment are granular activated carbon (GAC) and powdered activated carbon (PAC).



Amperometric Titration – a method used to measure concentrations of strong oxidizers (most commonly to accurately measure chlorine residual), among other substances, based on the electric current that flows during a chemical reaction.



Colorimetric Measurement – a means of measuring unknown chemical concentrations in water by measuring a sample's color intensity following a reaction with a chemical reagent. The specific color of the sample that develops is compared with color standards of known concentrations of the parameter, and can be measured using various analytical tools, including color comparison tubes, colorimeters, spectrophotometers.



Demand (as it pertains to oxidation) – the sum of all soluble constituents in a water that will “use up” the oxidant feed. The demand defines the total oxidant dose.



Inversion – the process by which a stratified surface water supply becomes intermixed, typically due to cooling of the surface water as seasonal change occurs from summer to autumn, resulting in the sinking of the cooler, denser surface water to the bottom, displacing the lower portion and causing it to rise to the surface. This typically results in increased levels of inorganic contaminants such as iron and manganese rising to the upper portions of the supply.



Organic complex – element or compound associated with dissolved organic carbon (DOC).



Oxidant – generally a chemical (sometimes aeration) added that converts soluble constituents, such as iron and manganese, into their precipitated forms.



Oxidation – A chemical reaction between an oxidant chemical, such as chlorine, and a soluble constituent, such as manganese, that results in the constituent being converted into its solid form.



Oxidation-Reduction Potential (ORP) or Redox – the electrical potential required to transfer electrons from one element or compound (the oxidant, or oxidizer) to another compound or element (the redundant, or reducer); this is used as a qualitative measure of the state of oxidation at a particular location of interest in the water treatment process. The redox potential of a water reflects its electron activity in the same way that pH reflects hydrogen ion activity.



Precipitation – physical and chemical reactions due to supersaturation of specific dissolved chemical ions that result in the conversion of some or all of those ions into solid particles so that supersaturation no longer occurs and equilibrium is resored to a solution. In other words, precipitation is the separation, from a solution, of a substance made insoluble as the result of a chemical reaction.



Stoichiometry – the method by which the quantities of reactants and products in chemical reactions are determined.



Thermocline – the level (“boundary”) in a stratified surface water supply that separates the warmer, primarily aerobic, upper layer of water from the colder, primarily anaerobic, lower layer of water.



White water effluent – filtered water that undesirably leaks into an area of a filter due to a mechanical problem. For example, a faulty air relief valve or a valve that does not completely close allowing filtered water to leak through.

Common Treatments

- ◆ Compared to the removal of other inorganics, such as calcium and magnesium, iron is not easy to remove from source waters.
- ◆ Oxidation and coagulation are effective pretreatment processes for removal of some inorganics prior to filtration.
- ◆ Oxidation involves converting soluble iron (Fe II) and soluble manganese (Mn II) to the precipitated (solid) compounds ferric hydroxide (Fe(OH)₃) and manganese dioxide (MnO₂), respectively. Depending on the source and turbidity level of the raw water, oxidation may be followed by coagulation, flocculation, sedimentation, and filtration.
- ◆ Ion exchange, appropriate for groundwater only, is suitable when iron is less than 10 mg/L, and low production volumes are required.
- ◆ Sequestration, which is not so much a removal process as it is a stabilization of iron and manganese using polyphosphates (sometimes silicates) to prevent precipitation, is limited to iron levels of 1.0 mg/L or less, and manganese levels of 2.0 mg/L or less, or both combined of 2.0 mg/L or less.

Oxidation/Filtration

Oxidation

- ◆ The first step in selecting an appropriate oxidation treatment process is to identify the particular forms of iron and manganese that occur in the source water. Potential forms of iron and manganese are found in the table below.

Table 3.3 Potential Forms of Iron and Manganese

Water Quality Parameter	Article VI. Chemical Forms			
	Particulate	Colloidal	Dissolved	DOC-complexed
Iron	Ferric ion - Fe III Ferric Hydroxide - Fe(OH) ₃	Particulate < 0.2 μm in size	Ferrous ion - Fe II	Both Fe II & Fe III Typically < 0.1 mg Fe per mg DOC
Manganese	Manganese Dioxide - MnO _{2(s)}	Particulate < 0.2 μm in size	Manganous ion (Mn II) – typical species in raw water Permanganate ion - MnO ₄ ⁻ & Mn (IV)	Not complexed with DOC

Monitoring and Sampling Procedures

◆ Monitoring Procedures

- ⊕ Monitor source water for iron and manganese on a routine basis (particularly surface water supplies).
- ⊕ Monitoring depth samples from reservoir supplies that have multi-level raw water intakes may provide the flexibility to access the best quality water, and may also provide advanced warning of reservoir turnover.

◆ Sampling Procedures

Table 3.4 Sampling Procedures

Water Quality Parameter	Particulate	Article VII. Chemical Forms		
		Colloidal	Dissolved	DOC-complexed
Iron	Collect sample w/o any filtration step for total iron analysis; subsequently subtract soluble iron	Collect sample and immediately filter ⁽¹⁾	Collect sample and immediately filter ⁽¹⁾	Both dissolved iron (Fe II) and particulate/colloidal iron (Fe III) can be significantly complexed by DOC
Manganese	Collect sample w/o any filtration step for total manganese analysis; subsequently subtract soluble manganese	Collect sample and immediately filter ⁽²⁾	Collect sample and immediately filter ⁽²⁾	Minimal

(1) Use 0.45 µm porosity filter paper to separate colloidal and soluble iron from particulate iron, collect a portion of this for analysis to determine the colloidal and soluble iron concentration; filter the remaining portion again, this time with a 0.22 µm porosity filter paper and analyze the filtered sample for iron; this will be the soluble iron concentration. The analytical result of the sample filtered by the 0.45 µm filter paper minus the analytical result of sample filtered by 0.22 µm filter paper should provide a good estimate of the quantity of colloidal iron.

(2) Use 0.45 µm porosity filter paper first to separate colloidal and soluble manganese from particulate manganese, collect a portion of this for analysis to determine the colloidal and soluble manganese concentration; filter the remaining portion with 0.22 µm porosity filter paper* and analyze the filtered sample for soluble manganese. Analytical result of sample filtered by 0.45 µm filter paper only minus analytical result of sample filtered by 0.22 µm filter paper should provide a good estimate of the quantity of colloidal manganese.

Caution: Colloidal iron and manganese may tend to be less than 0.2 µm in size, thus the 0.45 µm and 0.22 µm porosity filter papers that have traditionally been used for separating particulate metals from soluble metals in a sample may not be effective for removing the colloidal portion of particulate iron and manganese. If these larger-porosity filter papers are used, an operator may be led to believe that all of the metal concentration in the filtered portion of the sample is in the soluble state, when in fact a significant portion may be colloidal. Subsequently the operator may increase the oxidant dose to oxidize the remaining “soluble” metal. An increased oxidant dose may not improve treatment in this circumstance since any colloidal metal is already oxidized, and may in fact result in an excessive oxidant residual. Filter paper having 0.22 µm porosity is a better choice than 0.45 µm porosity for separating the soluble fraction of the metal from the particulate metal. However, if the operator has access to a bench membrane ultrafilter for metals sampling, it would provide the greatest assurance that all of the colloidal iron and manganese has been removed from a sample prior to analysis, and the filtered portion of the sample contains only dissolved metals.

Criteria for Selecting the Oxidant

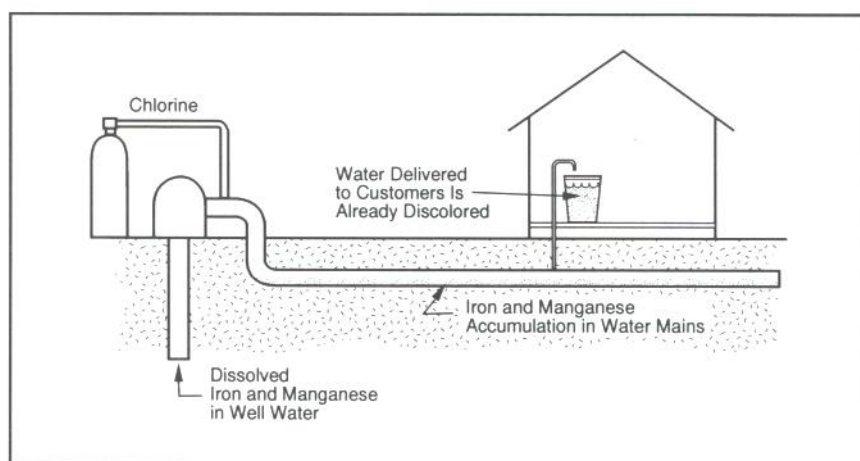
- ◆ There are several types of oxidants from which to choose.

Aeration

- ⊕ Aeration, such as is accomplished with a tray aerator; the process flow is exposed to a very large amount of air. This process is typically used in conjunction with carbon dioxide removal, and is appropriate for groundwater application only. Because oxygen saturated water is corrosive, using aeration in the oxidation process can prove to be a disadvantage.

Chlorine

- ⊕ Chlorine can be in the form of chlorine gas, sodium hypochlorite, and calcium hypochlorite. It is possible that if chlorine is used as the oxidizer before filtration TTHMs can be formed. Another disadvantage to using chlorine as the oxidant is that ferric chloride is formed during the oxidation process. During the greensand filtration process (discussed later in this module) the ferric chloride reacts with the potassium permanganate thus consuming it.



Iron and manganese oxidized by addition of chlorine

Potassium permanganate (*commonly referred to as Greensand*)

- ⊕ Potassium permanganate is a dry granular powder typically put into solution prior to feeding.

Chlorine dioxide

- ⊕ Chlorine dioxide is generated on-site as a product of the reaction between chlorine and sodium chlorite.

Ozone

- ⊕ Ozone is generated on-site as a result of a reaction between an electric arc and oxygen.

- ◆ Oxidant kinetics, or the speed of oxidation, may be a critical factor in determining which oxidant to use.

COMMON TREATMENTS FOR IRON AND MANGANESE

- ⊕ All oxidants react faster with iron than with manganese; this factor may be important when considering the type of oxidants to use and the sequence of addition.
- ⊕ Maximum oxidation reaction rates for iron and manganese are separated by 3 pH units.
 - ◆ Iron oxidation reactions occur fastest at a pH of 6.5 to 7.0.
 - ◆ Manganese oxidation reactions occur fastest at a pH above 10.
- ⊕ Use the criteria in the table below in the context of the specific water supply to be oxidized when performing an evaluation for selecting an appropriate oxidant.

COMMON TREATMENTS FOR IRON AND MANGANESE

Table 3.5 Oxidant Selection Criteria

Oxidant	pH		Temperature		Competitive Demands		Additional Treatment Required ¹	
	Iron	Manganese	Iron	Manganese	Iron	Manganese	Iron	Manganese
Aeration	Strongly influenced by pH: Slow if pH < 6.5; relatively rapid if pH > 7.0. Rate increases 100 fold for every one unit pH increase. Treatment works best a pH range of 8.0 – 9.0.	Too slow if pH ≤ 9.5; fastest at pH = 10	Cold water slows reaction	Cold water slows reaction	If significant DOC, Fe highly resistant to oxidation	Ineffective treatment if significant DOC	Filtration (and coagulation sedimentation if iron ≈> 5.0 mg/L)	Requires the presence of manganese-oxidizing bacteria; Filtration
Chlorine (HOCl)	Fast	pH < 9.5 very slow; for autocatalytic removal on filter media, rapid at pH >7.5	Cold water slows reaction	Cold water slows reaction	DOC creates competitive demand; if Fe is DOC-complexed, highly resistant to oxidation	DOC creates competitive demand; inhibits rate of oxidation	Filtration (and coagulation-sedimentation if iron ≈> 5.0 mg/L)	Filtration; important oxidant for autocatalytic removal of dissolved manganese (Mn II) on oxide-coated media or greensand; minimum Cl ₂ residual = 0.5 mg/L

COMMON TREATMENTS FOR IRON AND MANGANESE

Oxidant	pH		Temperature		Competitive Demands		Additional Treatment Required ¹	
	Iron	Manganese	Iron	Manganese	Iron	Manganese	Iron	Manganese
Potassium Permanganate (KMnO₄)	Instantaneous for pH = 6.0 – 9.0	5.5 – 9.0 reaction very fast; pH <5.5 require reaction time > 2 min.	Minimal effect	Water temp. below 35°F requires reaction time > 2 min.	DOC creates competitive demand; If Fe is DOC – complexed, highly resistant to oxidation	DOC creates competitive demand	Filtration (and coagulation-sedimentation if iron ≈> 5.0 mg/L)	Filtration (and coagulation if colloidal manganese is formed prior to filtration); sedimentation if colloidal manganese ≈ > 2.0 mg/L
Chlorine Dioxide (ClO₂)	Instantaneous	Instantaneous for pH = 6.0 – 9.0	Minimal effect	Minimal effect	DOC creates competitive demand; if Fe is DOC – complexed it is highly resistant to oxidation	DOC creates competitive demand	Filtration (and coagulation-sedimentation if iron ≈> 5.0)	Filtration (and coagulation if colloidal manganese is formed prior to filtration); sedimentation if colloidal manganese ≈ > 2.0 mg/L

COMMON TREATMENTS FOR IRON AND MANGANESE

Oxidant	pH		Temperature		Competitive Demands		Additional Treatment Required ¹	
	Iron	Manganese	Iron	Manganese	Iron	Manganese	Iron	Manganese
Ozone (O₃) (aq)	Instantaneous	Faster at low pH	Minimal effect	Minimal effect	DOC creates competitive demand; if Fe is DOC - complexed highly resistant to oxidation	Ineffective treatment if DOC significant; presence of bicarbonate alkalinity may increase removal under high DOC conditions	Filtration (and coagulation-sedimentation if iron ≈ > 5.0 mg/L)	Filtration (and coagulation if colloidal manganese is formed prior to filtration)); sedimentation if colloidal manganese ≈ > 2.0 mg/L

(1) All surface water supplies require at least filtration, regardless of iron and manganese levels, to assure removal of pathogenic microorganisms.

Initial Dosing

- ◆ Theoretical dose calculations are only a starting point when trying to determine the optimal dose for an oxidant.
- ◆ Typically there are other water quality constituents that also have an oxidant demand; the oxidant dose has to factor in these other demands.
- ◆ After establishing the oxidant to be used and calculating the theoretical oxidant dose based on soluble iron and manganese analyses, conduct bench-scale testing to determine the total oxidant demand.
 - ⊕ Using jar test equipment, test the theoretical oxidant dose, as well as doses greater and less than this dose.
- ◆ The chart below lists the theoretical oxidant doses for soluble iron and manganese.

Table 3.6 Theoretical (Initial) Dosing

Oxidant	Soluble Iron (Fe II)	Soluble Manganese (Mn II)
Aeration - Dissolved Oxygen (O ₂)	0.14 mg O ₂ / mg Fe II	0.29 mg (O ₂)/ mg Mn II
Chlorine (HOCl)	0.64 mg HOCl/ mg Fe II	1.30 mg HOCl/ mg Mn II
Potassium Permanganate (KMnO ₄)	0.94 mg KMnO ₄ / mg Fe II	1.92 mg KMnO ₄ / mg Mn II
Chlorine Dioxide (ClO ₂)	1.20 mg ClO ₂ / mg /Fe II	2.45 mg ClO ₂ / mg /Mn II
Ozone (O ₃) (aq)	0.43 mg O ₃ / mg Fe II	0.88 mg O ₃ / mg Mn II

Filtration

- ◆ Granular media, primarily for filtration of iron and manganese, can be used in either open, gravity flow filters or pressure filters (tanks).
 - ⊕ Open filters are typically used for surface water supplies.
 - ⊕ Pressure filters are typically used for groundwater treatment.
- ◆ Two types of granular media used for iron and manganese removal are presented below: manganese greensand and anthrasand.

Manganese Greensand

- ◆ Manganese greensand is typically used for groundwater sources containing levels of iron and/or manganese that require treatment.
- ◆ Processed from glauconite greensand by saturating the surface with manganous ions, the media utilizes the natural ion exchange properties of greensand.
 - ⊕ Following saturation, the media is soaked in a strong oxidizing solution that converts the manganous ions to a hard black manganese dioxide coating.
 - ⊕ The coating makes up about 4 mg per 1000 mg of greensand.
 - ⊕ It is easy to detect when the media coating is stripped because the underlying greenish color of the glauconite sand will be uncovered.
 - ⊕ Stripping can be avoided by using the continuous regeneration process. After the oxidation process, potassium permanganate (KMnO_4) is added before it enters the greensand bed. The KMnO_4 will oxidize any trace amounts of soluble iron and manganese and should be added so that a slight excess remains. This slight excess is reduced to a manganese oxide by the greensand. These oxides will precipitate on the greensand, maintaining a continuous regeneration. Over dosing of KMnO_4 will produce pink water while under dosing will produce brownish water.
- ◆ Greensand filters typically have an anthracite media cap (12 inch to 24 inch depth) that serves to remove iron, thereby reducing fouling and clogging of the greensand.
 - ⊕ Anthracite has been found to be more effective than sand for iron removal, even when the same size of media is used; anthracite apparently has an adsorption capacity for iron.
 - ⊕ The maximum hydraulic loading rate for anthracite media is up to 4 times greater than for sand, 8 gpm/sq ft versus 2 gpm/ sq ft.
 - ⊕ There is a relationship between the loading rate, area of the filter, and the amount of water to be treated for iron and manganese removal.
- ◆ Greensand depth typically ranges between 16 inches and 24 inches.
- ◆ Manganese greensand capacity is as follows:
 - ⊕ Capacity for manganese: 5,000 mg per ft^3 of greensand.
 - ⊕ Capacity for iron: 10,000 mg per ft^3 of greensand.
- ◆ Soluble manganese removal primarily occurs by autocatalytic adsorption on the manganese dioxide (MnO_2)-coated media, followed by oxidation of the adsorbed soluble manganese on the media; this process of manganese removal is suitable when iron and manganese levels in the source water are less than 1.0 mg/L.
- ◆ Manganese that was previously removed and oxidized on the greensand has an adsorption capacity for soluble manganese, thereby keeping the greensand continuously regenerated

COMMON TREATMENTS FOR IRON AND MANGANESE

- ⊕ Adsorbed soluble manganese is subsequently oxidized by the continuous feeding of an oxidant (preferably chlorine) to form manganese dioxide (MnO_2).
- ⊕ Only chlorine is required for oxidation.
- ◆ Filter backwash is required when headloss reaches a predetermined endpoint, or when iron and/or manganese begin to break through the filter.
 - ⊕ The freeboard, the space above the filter media, allows for the media bed expansion during the backwash process.
 - ⊕ Air wash is important in conjunction with water wash.
 - ⊕ Insufficient backwashing causes the thickness of the filter media to increase. This can cause problems such as: decreased flow through the filter media, failure to remove additional insoluble iron and manganese, and loss of media during the backwash process.
 - ⊕ Excessive backwash flow rate can also cause loss of filter media.
 - ⊕ Backwash waste water can be collected for reuse and the settled precipitates sent to a sanitary sewer or drying bed.



Exercise

Calculate the filtration rate in gpm/ft^2 for a filter with a surface length of 30 feet and a width of 20 feet when the flow through the filter is 5 MGD.

Tip: Be sure to complete any necessary unit conversions.

Step 1: Calculate filter area

$$\text{Filter Bed Area} = (20 \text{ ft.})(30 \text{ ft.}) = 600 \text{ sq. ft.}$$

Step 2: Convert flow rate to GPM

$$\left(\frac{5,000,000 \text{ gal}}{\text{day}}\right)\left(\frac{1 \text{ day}}{24 \text{ hr}}\right)\left(\frac{1 \text{ hr}}{60 \text{ min}}\right) = 3472 \text{ gal/min}$$

Step 3: Calculate filtration rate

$$\text{Filtration Rate} = \left(\frac{3472 \text{ gal}}{\text{min}}\right)\left(\frac{1}{600 \text{ sq. ft.}}\right) = 5.8 \text{ gpm/sq. ft.}$$

Is this an acceptable loading rate for a manganese greensand filter? Tip: Refer to the information about greensand filters on page 3-17.

COMMON TREATMENTS FOR IRON AND MANGANESE

- ◆ Advantages to using manganese greensand are plentiful.
 - ⊕ It has the optimum grain size and shape to retain oxidation and precipitation products of iron and manganese.
 - ⊕ No on-site batch chemical preparation is required to form a manganese dioxide media coating.
 - ⊕ Media reconditioning is generally not required because the coating is firmly attached to the greensand.
 - ⊕ Manganese dioxide coating is not removed during backwash.
 - ⊕ No detention time is required for oxidation prior to filtration.
 - ⊕ Manganese greensand acts as an oxidation-reduction (redox) buffer, adsorbing a slight overdose of potassium permanganate, and continuing (temporarily) to remove iron and manganese if an underdose of oxidant should occur.
 - ⊕ Manganese greensand is not proprietary.

- ◆ Of course, there are some disadvantages to manganese greensand.
 - ⊕ Minimum pH required is 6.2
 - ⊕ If prefilter pH adjustment is required, the pH should not be adjusted above 6.8 to 7.0 to prevent the formation of non-filterable iron colloids.
 - ⊕ The small effective size (ES) of the media grains results in high cleanbed headloss.
 - ⊕ The media has limited oxidative capacity.
 - ⊕ Exhausted media must be regenerated with potassium permanganate.
 - ⊕ High pressure drops, in excess of 8 psi, should be avoided in order to minimize media fracturing.
 - ⊕ Raw water silica levels of 10 mg/L or more require feeding of sodium aluminate to prevent stripping of the greensand coating.

Anthrasand

- ◆ Anthrasand is generated on-site (*in situ*).

- ◆ A base material of anthracite and sand (sized for a conventional filter) is coated with a thin layer of manganese dioxide (MnO_2).
 - ⊕ Media is placed in the filter vessel and soaked for a prescribed period with a manganous salt solution prior to oxidizing the manganous ion to manganese dioxide (MnO_2) using $KMnO_4$.

COMMON TREATMENTS FOR IRON AND MANGANESE

- ◆ Conventional filters will eventually become “anthrasand filters” if the following conditions are met:
 - ⊕ Manganese occurs in the raw water;
 - ⊕ A preoxidant is fed continuously;
 - ⊕ pH is greater than 7.0;
 - ⊕ Most of the manganese remains in the soluble state by the time it contacts the filter media.

- ◆ Iron and manganese removal occurs by autocatalytic reaction with the oxide-coated media.
 - ⊕ The presence of free chlorine in the filter-applied water results in two sequential reactions.
 - ◆ First, soluble manganese (Mn II) is adsorbed to the oxidized surface adsorption sites (manganese dioxide coating) of the media grains.
 - ◆ Then, the oxidized surface of the media grains catalyzes the oxidation of Mn II to manganese dioxide (MnO₂) by free Cl₂; this process regenerates Mn II adsorption sites and also minimizes Mn II desorption.

- ◆ Free chlorine residual and solution pH are key for effective treatment with anthrasand.
 - ⊕ Minimum chlorine residual (0.5 mg/L to 1.0 mg/L) assures that free chlorine regenerates media surface sites.
 - ◆ Without the maintenance of a chlorine residual, the media capacity is defined by the initial number of adsorption sites present.
 - ◆ Without the presence of an oxidant, Mn II is removed onto the media by adsorption only, with a potential for desorption. Mn II is soluble manganese; it only becomes part of the coating when it converts to manganese dioxide, a solid. An oxidant is required for that conversion to occur.
 - ◆ The addition of stronger oxidants than chlorine to filter-applied water results in essentially instantaneous oxidation, producing manganese dioxide colloidal solids; the retention of these colloidal solids may be poor and could potentially result in premature manganese breakthrough and/or increased loss of head.
 - ◆ The capture of KMnO₄-oxidized Mn II colloidal particles may require coagulant feed.
 - ⊕ Solution pH of greater than 7.0 increases the sorption capacity of oxide-coated media.
 - ◆ The rate of Mn II uptake on the surface of manganese dioxide coatings is rapid and apparently is a direct function of the number of available adsorption sites.

- ◆ Anthrasand’s greatest advantage is its inherent resistance to attrition due to the hardness of the base media.

- ◆ A significant disadvantage to anthrasand is the difficulty establishing a manganese dioxide coating.
 - ⊕ Unlike greensand, anthracite and sand do not have natural ion exchange properties or grain surface areas that are increased by many pockets and crevices.

Coagulation/Filtration



Coagulation Tank – City of Roanoke, VA

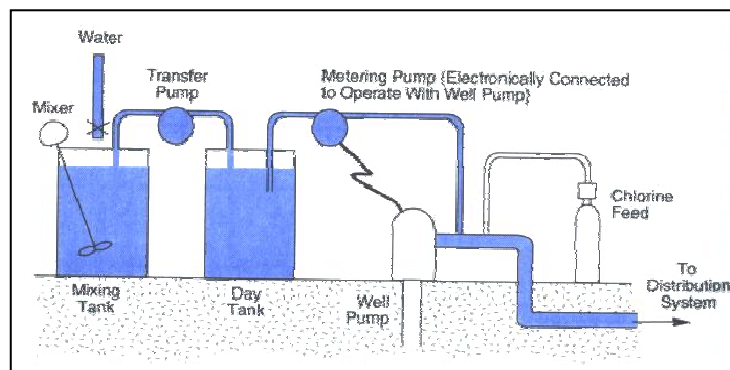
Coagulation

- ◆ Coagulation involves the addition of a chemical compound to destabilize colloidal and suspended particles, which otherwise are kept in suspension by electrostatic forces.
- ◆ Oxidized manganese, in particular, has colloidal properties that require coagulation of the negatively-charge colloids so that downstream solids/liquids separation processes are able to remove these constituents.
- ◆ The addition of calcium ions (such as from feeding lime) reduces the coagulant dose required due to neutralization MnO_2 colloidal surface charges.
 - ◆ A settling or clarification step may be required if iron and manganese are greater than about 5mg/L, in order to minimize solids loading into downstream filters.

Filtration

- ◆ The filtration process can be the same as that described under oxidation. In fact, coagulation often follows oxidation and precedes filtration.

Sequestration



Sequestering chemical feed equipment

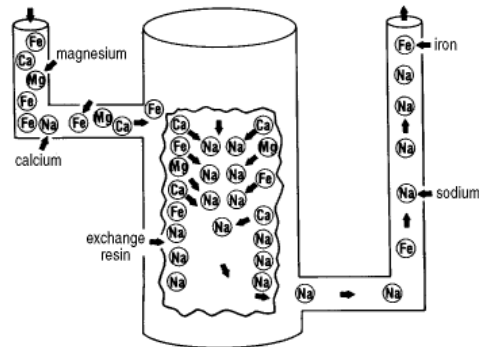
Source: Principles and Practices of Water Supply Operations



Sequestration uses a chemical, generally a polyphosphate compound, to keep metals such as iron and manganese dispersed in distributed water, preventing the tendency of these contaminants to otherwise create aesthetic problems. However, the dispersing properties of sequestration are lost when water is heated; this may result in colored water and staining from the hot water tap.

- ◆ The maximum soluble iron level that can be practically and economically treated is around 1.0 mg/L. The maximum soluble manganese level that can be practically and economically treated is around 2.0 mg/L.
- ◆ The sequestrant is typically a polyphosphate product such as sodium hexametaphosphate or tripolyphosphate.
- ◆ The sequestrant is fed at the ratio of 5:1 phosphate to iron, or 2:1 phosphate to manganese. If both elements are present, the 2:1 ratio is suitable.
- ◆ The sequestrant must be fed prior to the addition of any oxidant.
- ◆ Chlorine residuals must be maintained in the distribution system when feeding one of these products.
- ◆ pH is recommended at 7.0 to 7.5.

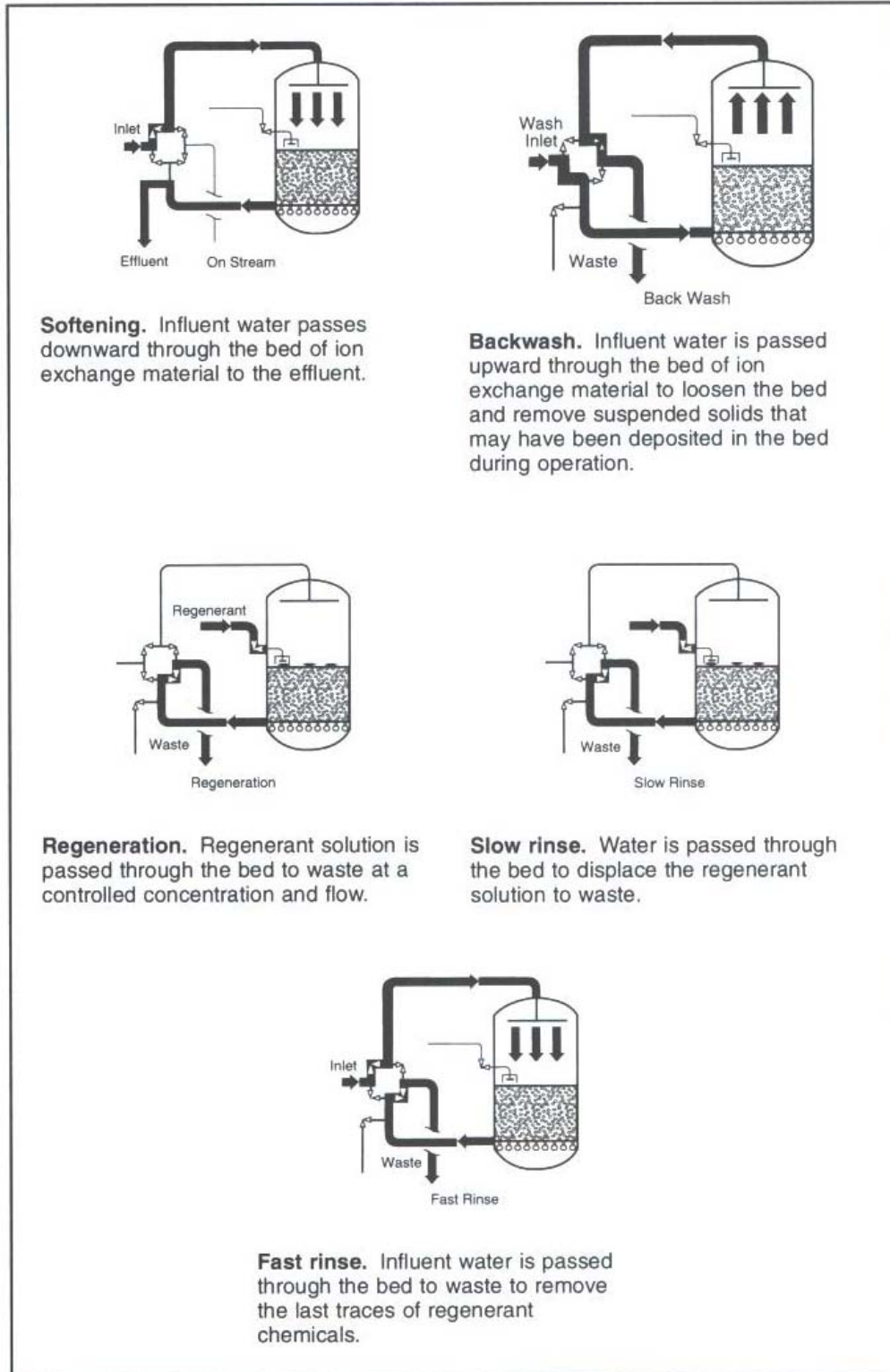
Ion Exchange



Ion exchange is only used for groundwater supplies that are low in particulate matter. Ion exchange consists of a chemical process that reversibly transfers ions between a special type of material and the water solution passing through it.

- ⊕ The special material is usually a synthetic resin.
- ⊕ The specific type of resin used depends of the contaminant ion to be removed; the resin has a selective affinity for the ions of one element over another; ions of the element previously saturated onto the resin are replaced with the target contaminant ions of another element due to preferential selection for this ion by the resin.
- ◆ The primary reason for selecting the ion exchange process is to reduce water hardness; removal of iron and manganese is generally secondary with this process.
- ◆ A rule of thumb for predicting the amount of iron removed with this process is 0.5 mg/L of iron is removed for every 1 mg/L of hardness reduction.
- ◆ Manganese-zeolite softening is the original ion exchange process for softening.
 - ⊕ Zeolite is a naturally occurring mineral that has ion exchange properties, acts as an oxidizing contact media, an adsorber of soluble manganese, and a filter medium.
 - ⊕ The manganese coating added to the zeolite acts as an oxidizing contact media, an adsorber of soluble manganese, and a filter medium similar to greensand and anthrasand.
 - ⊕ This media is used for groundwater treatment only.
 - ⊕ It is not appropriate for source waters containing iron levels that exceed 5.0 mg/L.
 - ⊕ For large municipal suppliers, the maximum source levels of both iron and manganese is 1.0 mg/.
 - ⊕ Iron and manganese must be in the dissolved form to prevent bed fouling.
 - ⊕ pH must be greater than 7.5.

COMMON TREATMENTS FOR IRON AND MANGANESE



Courtesy of Infilco Degremont, Inc., Richmond, Va.

Four cycles in the ion exchange process

Other Treatments

Biological Filtration

- ◆ Bacterial populations growing within the filter bed causes the precipitation of soluble iron and manganese as a byproduct of their metabolic processes, with each metal precipitating under separate conditions.
 - ⊕ Manganese bacteria require a different pH than iron bacteria; therefore, when this process is done intentionally, a pH adjustment likely will precede it.

Membranes

- ◆ Membrane filtration is a process that uses controlled diffusion through pressure-driven thin films of extremely small porosity. Membrane types are generally distinguished by the minimum particle size they can remove or the dissolved material to be removed, and the net driving pressures.
- ◆ Reverse osmosis (RO) and nanofiltration (NF) can be effective for removal of soluble iron and manganese, provided that an acid is fed prior to the membranes to prevent manganese precipitation.
- ◆ Microfiltration (MF) and ultrafiltration (UF) can be effective, provided that preoxidation and/or coagulation steps occur prior to the membranes.

Softening Precipitation

- ◆ As with ion exchange, the primary reason for selecting lime/soda ash precipitation is to reduce water hardness; iron and manganese removal, occurring concurrently, is generally of secondary importance.

Treatment at the Source

- ◆ Surface water can be treated by aeration to maintain dissolved oxygen throughout the water column of the supply, thereby preventing reservoir stratification and consequent conditions that might cause iron and manganese precipitates contained in bottom sediments to become dissolved.
- ◆ Groundwater treatment involves air injection into the well for oxidation of soluble iron and manganese.

Erosion of natural deposits and overdose of alum coagulant from water treatment by-product are the common sources of aluminum. The most common reasons for aluminum residuals are an overdose of aluminum sulfate (alum) from the treatment facility, incorrect pH for alum coagulation, and water temperatures below 4°C.

pH Adjustment

- ◆ The pH and water temperature of the mixed water (after alum has been added) have a significant impact on aluminum residual levels, as indicated by the following aluminum chemistry:
 - ⊕ Minimum aluminum solubility (maximum aluminum hydroxide precipitation) at 25°C occurs at pH 6.3.
 - ⊕ Minimum aluminum solubility (maximum aluminum hydroxide precipitation) at 4°C occurs at pH 6.8.
- ◆ If the pH varies significantly from the level that provides minimum aluminum solubility at the respective water temperature, then significant soluble aluminum could pass through the downstream treatment processes and eventually form aluminum floc and scales in the distribution system.

Coagulation/Filtration



- Coagulation initiates the aggregation of particles into soft, semisolid masses called flocs, which are subsequently removed by clarification and/or filtration processes. Typically a metal salt, such as aluminum sulfate, or other chemical compound is added to the water to neutralize particle negative charges that would otherwise keep the particles in suspension.
- ◆ Some pretreatment factors to be considered for optimum coagulation are listed below.
 - ⊕ Filtered turbidity must be less than or equal to 0.3 ntu in 95% of monthly readings in order to comply with EPA regulations. The typical drinking water industry goal is less than 0.1 ntu.
 - ⊕ The PA DEP has a particle count goal of 25 particle counts per mL; there is no particle count regulation.
 - ⊕ Raw water pH of 6.5 to 7.0.
 - ⊕ Streaming Current Detector (SCD) readings should be maintained at a set point that was previously established based on known optimized coagulation conditions.
 - ⊕ Jar tests with a series of coagulant doses help define the optimal coagulant dose for existing source water and plant conditions.
 - ⊕ TOC (total organic carbon) removal to meet EPA percent removal goals are contained within the TOC treatment technique in the EPA Disinfectant Byproduct Rule.
 - ⊕ Filter run time and loss of head should both be considered; the longer run times and lower rates of headloss are desirable for efficient plant operations. Common drinking water industry goals are maximum headloss goal of 8 feet, and minimum run times of 48 hours.

Definitions



Alkali – certain soluble salts containing cations, such as of sodium, potassium, magnesium and calcium, that have the property of combining with acids to form neutral salts. The most commonly used alkali in water treatment contains either sodium (caustic soda, soda ash) or calcium (lime).



Alkalinity, Total – capacity of water to neutralize acids due to the water's content of carbonate, bicarbonate, hydroxide and possibly minor amounts of other anions; alkalinity concentrations are generally expressed in terms of mg/L of calcium carbonate equivalent.



Alkalinity, Bicarbonate (HCO_3^-) – a form of alkalinity that occurs when pH is less than 8.3, commonly referred to as natural alkalinity.



Alkalinity, Phenolphthalein – that portion of total alkalinity that occurs above a pH of 8.3, which may include bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and hydroxide (OH^-) anions.



Buffer – a water whose chemical makeup neutralizes acids or bases without a significant change in pH.



Buffer Capacity – a measure of the capacity of a water to resist a change in pH.



Calcium Carbonate Equivalent (CaCO_3) – an expression of the concentration of various water quality constituents in terms of their equivalent value to calcium carbonate.



Gram Equivalent Weight – gram molecular weight of a compound (or gram atomic weight, for an element) divided by the valence state of that compound or element.



Hardness, Total – the presence of divalent metallic cations (primarily calcium and magnesium) in water due to the dissolution of minerals in geologic formations by natural waters. Although there is no specific hardness level that defines at what point a water is considered hard, there is a general understanding that a water having a total hardness less than 75 mg/L (as CaCO_3) is considered soft, and above 150 mg/L (as CaCO_3) is considered hard.



Hardness, Calcium – that portion of total hardness due only to calcium.



Hardness, Carbonate – that portion of total hardness which is chemically equivalent to alkalinity; the dissolution by water of calcium and magnesium from minerals containing carbonate and bicarbonate are the predominant source of carbonate hardness.



Hardness, Magnesium – that portion of total hardness due to magnesium ions.



Hardness, Noncarbonate – that portion of total hardness in excess of alkalinity; the dissolution of calcium and magnesium compounds of sulfate and chloride, or silicates in water are the predominant source of noncarbonate hardness. Noncarbonate hardness equals the total hardness minus the carbonate hardness.



Lime, Hydrated – limestone treated under controlled conditions so that the calcium oxide (CaO) portion has been converted to calcium hydroxide (Ca(OH)₂).



Lime, Quick – a material that is mostly calcium oxide (CaO) that is capable of reacting with water to form hydrated lime.



Mole – the molecular weight in grams of a compound or element. Mole is the same as gram molecular weight.



Normality – the number of gram equivalent weights per liter of solution.



Percent Saturation – the amount of a substance that is dissolved in a solution, compared with the amount that could be dissolved in the solution, expressed as a percent.



Recarbonation – process in which carbon dioxide is bubbled through water in order to depress pH; in lime/soda ash softening, the last stage of treatment used to stabilize water by minimizing the formation of any additional precipitates.



Regeneration – chemical process by which a chemically-coated filter media (e.g. ion exchange media) is returned or restored to a productive treatment condition.



Scale – the precipitation of previously dissolved ions onto materials in contact with water; there are four essential types of scales: calcium carbonate (calcite); magnesium hydroxide (brucite); calcium sulfate (gypsum); and silica.



Slake – to mix with water so that hydration occurs, such as slaking of lime.



Supersaturated – unstable condition in water whereby a substance is contained at a concentration greater than the saturation concentration for that substance.



Titration – analytical method whereby a chemical solution of known strength is added drop by drop until a specific end point is reached, identified by a color change, precipitate or pH change. This is the most commonly used method for determining levels of alkalinity and hardness in water treatment plant operator labs.



Total Dissolved Solids (TDS) – surrogate for ionic strength in water, consisting mainly of dissolved inorganic salts. Since dissolved ions serve as a weak conductor of an electric current, there is a relationship between TDS and conductivity. Although this relationship is site specific, typically it is in the range of 55% to 70% of the conductivity reading.

Ion Exchange

- ◆ Remember that in the ion exchange process, a reversible exchange of different ions occurs using a special type of media, synthetic resin.
- ◆ For softening, a cation-based resin is used to exchange sodium ions for calcium ions; following resin exhaustion (saturation with calcium), it is typically regenerated with a strong sodium hydroxide solution.

Lime Softening

Chemical Precipitation

- ◆ Lime softening is a chemical precipitation process.
- ◆ In this process calcium ions, Ca^{+2} , are precipitated as calcium carbonate, and magnesium ions, Mg^{+2} , are precipitated as magnesium hydroxide; both reactions occur by increasing pH with the addition of alkali chemicals, such as lime and/or soda ash.
- ◆ Stoichiometric quantities of lime, $\text{Ca}(\text{OH})_2$, and soda ash, Na_2CO_3 , are added to raise the pH value of the water so that calcium carbonate, CaCO_3 , and magnesium hydroxide, $\text{Mg}(\text{OH})_2$, are at their minimum solubilities, resulting in precipitation of the quantities in excess of the solubility limits for these compounds.
- ◆ There are three types of chemical precipitation used for water softening: lime only; lime/soda ash; and lime/soda ash with recarbonation.
- ◆ The type of chemical precipitation process selected to soften a particular water supply will depend primarily on the goals of treatment since each process will produce a water containing a different level and/or type of hardness, as indicated in the next sections of the workbook.

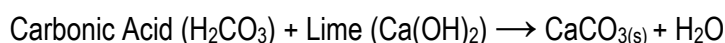
Lime/Soda Ash Softening

- ◆ The advantages to this type of softening are many.
 - ⊕ It removes both carbonate and noncarbonate hardness.
 - ⊕ It removes iron and manganese.
 - ⊕ It disinfects bacteria and viruses due to elevated pH.
 - ⊕ It removes excess fluoride.
 - ⊕ It can control corrosion and scale formation when followed with additional treatment to stabilize the product water.

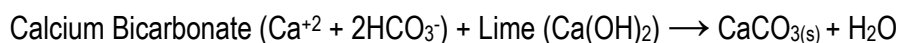
- ◆ There are a few disadvantages.
 - ⊕ It cannot remove all of the hardness.
 - ⊕ The process is operator intensive, requiring close attention to process controls in order to maximize efficiency in hardness removal, water stability, and costs.
 - ⊕ It generates large quantities of residual sludge as a result of the precipitates; the sludge must be handled and then disposed.

Reactions of Lime/Soda Ash Softening

The primary driver of treatment is the addition of an alkali chemical to initiate precipitation of calcium and magnesium ions. However, neutralization of naturally occurring carbon dioxide acidity must occur first before the pH can be increased significantly. This is the first reaction step presented below. The entire softening/precipitation process is represented in five reaction steps below. Note that (s) refers to the fact that a solid is precipitated from these reactions.



The precipitation of calcium carbonate hardness is represented below.



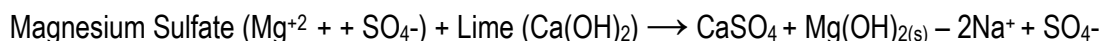
The precipitation of calcium noncarbonate hardness is represented below.



The precipitation of magnesium carbonate hardness is represented below.



The precipitation of magnesium noncarbonated hardness is represented below.



Stability

- ◆ Supersaturation of calcium carbonate and magnesium hydroxide often occurs at the end of lime/soda ash softening as a result of excess lime feed.
 - ⊕ This results in softened water with a pH of 10.9.
 - ⊕ The addition of carbon dioxide to slightly depress the pH will result in more complete precipitation of calcium carbonate and magnesium hydroxide.

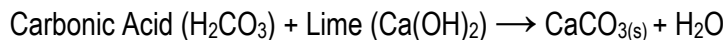
- ◆ Stability reactions occur through a two-stage process.
 - ⊕ Carbon Dioxide is added to lower pH to 10:4.
$$\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_{3(s)} + \text{H}_2\text{O}$$
 - ⊕ Carbon Dioxide is added again to lower pH to 9.8.
$$\text{CaCO}_3 + \text{CO}_2 \rightarrow \text{Ca(HCO}_3)_2$$

Lime Softening

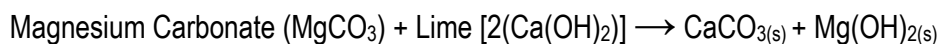
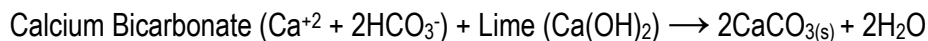
- ◆ Lime softening removes carbonate hardness only.

Reactions of Lime Softening

The neutralization of naturally occurring carbon dioxide acidity (as carbonic acid) is represented below.

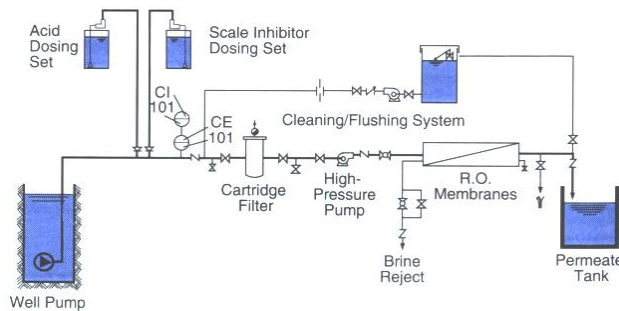


The precipitation of calcium carbonate hardness is represented below.



Softening Membrane Filtration

- ◆ Softening membranes, technically referred to as nanofiltration (NF) use a pressure-driven and diffusion-controlled layer of thin synthetic film that is only permeable to constituents smaller than a particular size, approximately 0.001 μm in size.
- ◆ There is one influent to the membrane module, known as the feed, and two membrane module discharges, known as the permeate (treated water) and the concentrate (reject, or wastewater).



Source: American Engineering Services, Inc., Tampa, Fla.

Pretreatment Requirements

- ◆ Scale inhibitor and/or acid is required to minimize scale formation on the membranes.
- ◆ If turbidity is greater than 0.2 ntu and/or the silt density index (SDI) is greater than 2, prefiltration will be required with microfiltration, ultrafiltration, or conventional filtration.
- ◆ The potential for biofouling (iron bacteria slime) requires the continuous feeding of a disinfectant, such as chloramines.
- ◆ The potential for organic fouling requires enhanced coagulation followed by microfiltration, ultrafiltration, or conventional filtration.

Sequestration

- ◆ Sequestration stabilizes the primary components of hardness to prevent their precipitation. This process is only effective at low levels of hardness and is not really intended to soften water.

Common sources of Nitrate are erosion of natural deposits and leeching septic tanks, farm fertilizers, feed lots and sewage in storm water run-off situation.

Ion Exchange

- ◆ This treatment is limited to groundwater supplies, and was explained in an earlier section.
- ◆ Anion-based resins are used to remove nitrates.
- ◆ If turbidity is greater than 0.2 ntu, prefiltration will be required.
- ◆ In order to prevent resin fouling, do not aerate prior to ion exchange treatment.

Membrane Filtration

- ◆ Membrane filtration for nitrate removal utilizes the concept of membrane filtration presented earlier by using a reverse osmosis (RO) type membrane.
- ◆ RO typically achieves 85% to 95% nitrate removal.
- ◆ Pretreatment includes using a scale inhibitor and/or acid to minimize scale formation on the membranes.
- ◆ If turbidity is greater than 0.2 ntu and/or the silt density index (SDI) is greater than 2, prefiltration will be required to prevent fouling of the membrane.
- ◆ Membrane filtration has a significant advantage of near-total automation.



Photo Courtesy of Hammers International

Membrane Filtration

- ◆ Membrane filtration for total dissolved solids (TDS) uses either the concept presented previously involving a pressure-driven process in which the flow diffuses through thin film, or an electrically driven membrane process called Electrodialysis Reversal (EDR).
 - ◆ The pressure-driven process can be RO or NF.
 - ◆ Pretreatment requirements for RO and NF depend on the source water quality, but typical pretreatment includes the addition of scale inhibitors and acid to prevent calcium carbonate deposition.
 - ◆ Nanofiltration (NF), also known as the softening membrane, is primarily used to soften water, but will also remove other dissolved minerals that contribute to TDS, including sulfates.
 - ⊕ The size of particles removed by NF are in the range of $< 0.001\ \mu\text{m}$ down to $0.0001\ \mu\text{m}$ in size.
 - ⊕ Membrane applied pressures required are in the range of 70 psi to 140 psi.
 - ⊕ There is greater than 97% removal of sulfates.
 - ◆ Reverse Osmosis (RO) is primarily used for removing salts from brackish or seawater, but will remove virtually all dissolved minerals.
 - ⊕ The particle sizes removed by RO are down to $0.0001\ \mu\text{m}$ in size.
 - ⊕ Membrane applied pressures required are in the range of 140 psi to 700 psi.
 - ◆ Electrodialysis/Electrodialysis Reversal (ED/EDR) utilizes electrically-driven membrane processes that are used for demineralization of seawater, saltwater and freshwater.
- ◆ Ion exchange can also be used to remove TDS and sulfates. An anion-based resin is used. The process has been explained in earlier sections of the workbook. Remember that ion exchange is used for groundwater sources only.

COMMON TREATMENTS FOR LESS COMMON INORGANICS

Table 3.7 Potential Treatments for Less Common Inorganics

Parameter	GAC	Oxidation	Coagulation/Filtration		Ion Exchange		Membranes	Lime Softening	Activated Alumina	Sequestration
			Alum	FeCl ₃	Anion	Cation				
Arsenic (III)			w/preoxidation	F	L		(RO, NF, ED) G - F	w/preoxidation	w/preoxidation	
Arsenic (V)			if pH <7.5 E	E	E		(RO, NF, ED) E	if pH 10 to 10.8 G	E	
Boron							(RO, NF)			
Nitrate					E		(RO, ED) G			
Nitrite					x		(RO)			
Nitrate and Nitrite					x		(RO) G			
TDS							(RO, ED)			
Chloride							(RO, ED)			
Sulfate					E		(RO, NF, ED)			
Selenium (IV)				pH <7.5	E		(RO, ED) E	L - P	E - G	
Selenium (VI)					E		(RO, ED) E	L - G	L - G	
Fluoride	E (Bone Char)						(RO, ED) E	G	E	
Calcium & Magnesium Hardness						x	(RO, ED, NF)	x		x

GAC Granular Activated Carbon
 NF Nanofiltration
 RO Reverse Osmosis
 ED Electrodisalysis/Electrodialysis Removal

E = Excellent (90% to 100% removal)
 G = Good (70% to 90% removal)
 F = Fair (40% to 70% removal)
 L = Low (20% to 40% removal)
 P = Poor (0 to 20% removal)
 x = Insufficient Data to Classify

Arsenic

- ◆ Arsenic is among the most widely distributed elements in the earth's crust.
 - ⊕ Approximately 5,000 community water systems out of 70,000 that use groundwater supplies have arsenic levels that exceed 5 µg/L.
 - ⊕ The new MCL for arsenic is 10µg/L.
- ◆ Treatment is dependent on the chemistry of arsenic, which primarily exists in two inorganic states in drinking water supplies.
 - ⊕ Arsenite (As III), also arsenious acid (HAsO_2) is difficult to remove.
 - ⊕ Arsenate (As V), also arsenic acid (H_3AsO_4) is by far the easier form of arsenic to remove.
 - ⊕ Therefore, pretreatment is often included in arsenic treatment processes to oxidize As III to As V.
- ◆ Arsenic generally occurs in the anionic form, pH dependent, since solubilities of oxides are high.

Treatment Processes

Precipitation without Preoxidation

- ◆ Coagulation/filtration can be used to remove arsenate (As V) by co-precipitation with, or is adsorption to, either ferric hydroxide floc (at pH <8.5) or aluminum hydroxide floc (at pH <7).
 - ⊕ The flocs are subsequently removed by sedimentation and/or filtration, resulting in more than 90% removal of arsenic.
- ◆ Arsenic removal by lime softening involves adsorption onto magnesium hydroxide flocs (at pH <10.5).
 - ⊕ The flocs are subsequently removed by sedimentation and/or filtration, resulting in more than 90% removal of arsenic.
- ◆ A preoxidation step, resulting in oxidation of any arsenite (As III) to arsenate (As V) can result in 100% removal of arsenic using the processes listed above.

Adsorption

- ◆ Adsorption is a physio-chemical process where arsenic ions are adsorbed onto a granular media substrate.
 - ⊕ Several types of alumina-based media can be used for effective arsenic removal.
 - ◆ Activated alumina (AA) can be used.
 - ◆ Granular ferric hydroxide (GFH) can also be used.

Ion Exchange

- ◆ Strong base anion exchange resins are a proven treatment technology for arsenic removal.
 - ⊕ These resins can be regenerated with several different salt solutions.
 - ◆ Hydroxide ions are used.
 - ◆ Chloride ions are also used.



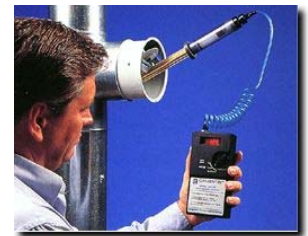
Since these resins have an even stronger affinity for sulfate anions than for arsenic, the concentration of sulfate in the feed water determines the capacity of the resin for arsenic.

Membrane Filtration

- ◆ Through molecular size rejection, nanofiltration and reverse osmosis membrane types can exclude arsenic.
- ◆ Membranes permeable to larger size particles, such as ultrafiltration and microfiltration, also can be effective for arsenic removal if preceded by a coagulation step.

Hydrogen Sulfide

- ◆ Hydrogen sulfide, a compound that produces a “rotten egg” smell, is generally a problem restricted to groundwater supplies since the bacteria that cause the production of hydrogen sulfide (H_2S) do not grow in the presence of oxygen.
- ◆ H_2S is often associated with iron and manganese in groundwater located near swampy areas.
- ◆ The solubility of H_2S in water decreases with increasing temperature.
- ◆ The amount of total sulfide present as H_2S is dependent upon pH.
 - ⊕ At a pH of 8.0, only 10% of total sulfide is H_2S .
 - ⊕ At a pH of 7.0, 50% of total sulfide is H_2S .



H_2S Water Quality Issues

- ◆ H_2S makes water unpalatable due to the smell; the oxidation byproduct of H_2S is also aesthetically displeasing due to the milky blue turbidity that is generated.
- ◆ H_2S consumes greensand capacity, reducing capacity for iron and/or manganese.
- ◆ H_2S is corrosive to copper pipes.

H₂S Treatment Alternatives

- ◆ Use granular activated carbon (GAC); a proprietary type of catalytic carbon, known as Calgon Carbon, is used specifically for H₂S removal.
- ◆ Use an oxidizing filter, such as anthrasand, preceded by chlorine addition pH adjustment.
- ◆ Use manganese greensand, with the capacity for hydrogen sulfide of 2,000 to 3,000 mg of H₂S per ft³ of greensand.
- ◆ Use aeration (pressure type) followed by filtration, as in venturi/air release and retention by turbidity removal filter.
 - ⊕ A Venturi creates a partial vacuum, drawing outside air into the flow stream. The entrained outside air oxidizes the H₂S in the process flow.
- ◆ Use chemical oxidation with chlorine, followed by filtration.
 - ⊕ Theoretically, 8.5 mg/L of Cl₂ is required per 1.0 mg/L of H₂S.
 - ⊕ The most important factor in H₂S removal is contact time.
 - ◆ Given enough time and an oxidizing agent, all dissolved sulfides can be converted to sulfates.
 - ◆ A minimum DT of 20 minutes is required for chlorine oxidation of H₂S. DT is the contact time between the oxidant chemical and the water being treated.
 - ⊕ A pH range of 6.5 to 7.3 is optimal.
 - ⊕ Cl₂ oxidation of H₂S will result in free sulfur, which produces a milky blue turbidity.
 - ◆ Sulfur chlorination is practical only if this turbidity can be removed; do not assume that normal filtration will be effective due to the colloidal nature of turbidity.
 - ⊕ Pilot testing may be desirable.
- ◆ Chemical oxidation with potassium permanganate, followed by filtration, is also effective for H₂S removal.
 - ⊕ The kinetics of reaction are essentially instantaneous.
 - ⊕ A molar ratio of 4:3, KMnO₄ to H₂S, is required to oxidize hydrogen sulfide. In other words, for every 1 mg/L of H₂S to be treated, 1.3 mg/L of KMnO₄ is required.
- ◆ Chemical oxidation with ozone, followed by filtration, can also be effective for H₂S removal.
 - ⊕ The kinetics of reaction are essentially instantaneous.
 - ⊕ A molar ratio of 5:3, O₃ to H₂S, is required to oxidize hydrogen sulfide with ozone.

COMMON TREATMENTS FOR LESS COMMON INORGANICS

Table 3.8 Miscellaneous Trace Metals and Their Potential Treatments

Parameter	GAC	Oxidation	Coagulation/Filtration		Ion Exchange		Membranes	Lime Softening	Activated Alumina	Sequestration
			Alum	FeCl ₃	Anion	Cation				
Antimony										
Barium						E	E	E pH 9.5-10.8		
Beryllium										
Cadmium			E pH 8.5	E pH >8.0		E	E	E		
Chromium (III)			E	E		E	E	E pH >10.5		
Chromium (V)	E (bone char)			P	L		E	E	E	
Copper			X	X		X				
Lead			E	E			E	E		
Mercury	E						G - F			
Molybdenum					X		X			
Nickel						X	X			
Silver			G	G		E	E	G		
Thallium					X					
Zinc						X	X	X		

GAC Granular Activated Carbon
 NF Nanofiltration
 RO Reverse Osmosis
 ED Electrodialysis/Electrodialysis Removal

E = Excellent (90% to 100% removal)
 G = Good (70% to 90% removal)
 F = Fair (40% to 70% removal)
 L = Low (20% to 40% removal)
 P = Poor (0 to 20% removal)
 x = Insufficient Data to Classify

Parameters and Equipment Commonly Used for Monitoring the Effectiveness of Oxidation Processes

Water Quality Analyses

Iron and Manganese

- ◆ Typical sample sources are from raw water and filtered effluent.
 - ⊕ The purpose of sampling raw water is to determine the dose of oxidant(s) required, based on iron and manganese analyses.
 - ⊕ The purpose of sampling filtered water is to determine the effectiveness of the oxidation/filtration process, including oxidant dose and particle capture on the filter media.
- ◆ Soluble (grab) samples require that the sample be filtered immediately upon collection (before any soluble portion of the metal has a chance to oxidize from exposure to air) through an extremely small porosity filter medium, preferably a membrane ultrafilter, to assure that the metals in the filtered portion are truly in the soluble state and not just colloidal.
- ◆ Only the soluble fraction of the total iron and manganese levels creates an oxidant demand.
 - ⊕ Identifying the soluble concentrations of these metals helps to determine the oxidant dose.
- ◆ Both the soluble and total metals samples should be preserved with nitric acid to pH less than 2.

Free Chlorine Residual

- ◆ Typical sample sources are filtered influent (or applied) and filtered water.
- ◆ A chlorine residual of 0.5 mg/L to 1.0 mg/L should be maintained in the filter effluent to assure complete oxidation of soluble iron and manganese.
 - ⊕ DPD or amperometric titration can be used for measuring chlorine residuals.
 - ◆ DPD is a commonly used reagent/method for measuring chlorine residuals in the field and at small facilities.
 - ◆ Amperometric titration is more accurate for measuring chlorine residuals, and is commonly used at larger facilities.
- ◆ The sample must be analyzed immediately, as chlorine can off gas from solution.

Permanganate Residual

- ◆ Typical sample source is from filter applied water.
- ◆ Samples are taken to assure that slight permanganate residual is being applied to the filter to maintain the filter media in the regenerated condition.
 - ⊕ Observation is generally sufficient to detect a permanganate residual; a slight pink color should be noticeable.
- ◆ The sample should be observed immediately.

Analytical Equipment

- ◆ Field test kits that might be used include:
 - ⊕ Color comparator can be used for iron and manganese (not recommended), as well as free chlorine-DPD (adequate for distribution system checks).
 - ⊕ Portable colorimeter is used for iron and manganese, color, and free chlorine-DPD.
 - ⊕ Portable spectrophotometers are used for analyzing iron and manganese, color, free chlorine-DPD, and permanganate residual.



- ◆ Bench analytical equipment includes:
 - ⊕ Colorimeter.
 - ⊕ Spectrophotometer.
 - ⊕ Amperometric titration (oxidant only).
 - ⊕ Oxidation-Reduction Potential (ORP) meter.
- ◆ On-line analytical equipment includes:
 - ⊕ DPD Colorimetric (chlorine only).
 - ⊕ See Method 408.E of *Standard Methods of the Examination of Water and Wastewater*.
 - ⊕ Oxidation-Reduction Potential (ORP) meter.

Parameters and Equipment Commonly Used for Monitoring Coagulation and Flocculation Processes

Water Quality Indicators

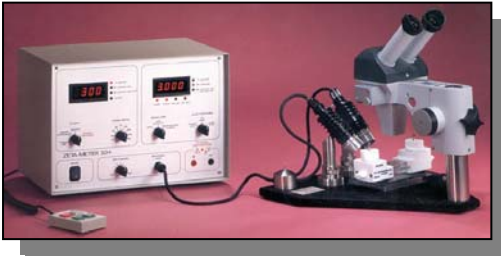
- ◆ Charge density measurement is an indication of relative charge neutralization of particles in water following coagulation and, therefore, can be an indication of the degree of coagulation.
- ◆ pH is measured because coagulation has a specific pH range where it is most effective, depending upon the coagulant used and the goals of treatment.
- ◆ Turbidity measurements are used as one of the primary indicators of treatment plant performance and also helps to predict the coagulant demand.
- ◆ True color is apparent color with turbidity removal; true color helps to predict the coagulant demand.
- ◆ Alkalinity is measured because each coagulant and dose requires that at least a minimum level of alkalinity be available in the source water order for coagulation to be effective.
 - ⊕ Measurement of this parameter aids in determining if additional alkali, such as lime, should be added, and how much is needed.
- ◆ Temperature can have a significant effect on coagulation and oxidation kinetics; cold water significantly slows the speed of floc formation and impacts the optimum pH when using conventional coagulant salts, such as alum and ferric sulfate.
- ◆ Floc characteristics, such a size, density, and water clarity between floc particles, provide a visual evaluation.
 - ⊕ The evaluation is often conducted with a jar test and helps to determine optimum pretreatment conditions.

Analytical Equipment

- ◆ Field test kits include the following:
 - ⊕ A portable pH meter measures pH.
 - ⊕ Titration and colorimeter measure alkalinity.
 - ⊕ A portable turbidimeter measures turbidity.
 - ⊕ A portable spectrophotometer measures true color.



- ◆ Bench analytical equipment includes the following:
 - ⊕ Zeta potential meter measures charge density.
 - ⊕ pH is measured with a bench pH meter.
 - ⊕ Alkalinity is measured with burette titration.
 - ⊕ A bench turbidimeter is used for turbidity measurement.
 - ⊕ Color can be measured with a bench spectrophotometer.
 - ⊕ Jar test apparatus is used to determine coagulant doses and floc characteristics.
 - ⊕



Zeta meter



pH meter

- ◆ On-line analytical equipment includes the following:
 - ⊕ SCD, or Streaming Current Detector, monitors charge density.
 - ⊕ An on-line pH transmitter measures pH.
 - ⊕ On-line turbidimeters monitor turbidity.

Parameters and Equipment Commonly Used for Monitoring Clarification and Conventional or Membrane Filtration

Water Quality Indicators

- ◆ Processed turbidity should be maintained at a constant level, regardless of the raw water turbidity.
 - ⊕ Clarification: Maintain turbidity at less than 2.0 ntu (and preferably less than 1.0 ntu as a goal).
 - ⊕ Filtration: Maintain turbidity at less than 0.10 ntu as a goal.
- ◆ Particle counts should be maintained at a consistent low level, regardless of the raw water particle counts.
 - ⊕ Maintain filtered particle counts at the lowest level possible, using 25 counts/mL or less as a goal.
- ◆ True color should be consistently reduced to a low level, regardless of the raw water true color.
 - ⊕ Maintain at less than 5 color units (c.u.) in the filter effluent (with zero as a goal).
- ◆ Coagulant residual for aluminum assists with optimizing the alum dose.
 - ⊕ An aluminum level that is higher than the raw water level may indicate an overdose of alum or incorrect mixed water pH.
- ◆ Coagulant residual measurement for iron may assist in optimizing ferric chloride or ferric sulfate doses.
 - ⊕ An iron level in the clarified or filtered water that is higher than the raw water iron level may indicate an overdose of ferric chloride or ferric sulfate.

Analytical Equipment

- ◆ Field test kits should include:
 - ⊕ Portable turbidimeter for measuring turbidity.
 - ⊕ Portable color colorimeter or field spectrophotometer for measuring color, aluminum, manganese, and iron.



Turbidimeter

- ◆ Bench analytical equipment should include:
 - ⊕ Bench turbidimeter for measuring turbidity.
 - ⊕ Bench particle counter for measuring particle counts.
 - ⊕ Bench spectrophotometer for monitoring UV254, color, aluminum, manganese, and iron.

- ◆ On-line analytical equipment includes:
 - ⊕ Turbidimeter.
 - ⊕ Particle counter.

Key Points



Treatment selection considerations for inorganic removal include:

- Contaminant to be removed
- Source water quality and variability
- Reliability
- Existing conditions
- Flexibility
- Utility capabilities
- Environmental compatibility



Treatment Technology Options

- Granular Activated Carbon (GAC)
- Oxidation
- Coagulation/Filtration
- Ion Exchange
- Membranes
- Lime Softening
- Activated Alumina
- Corrosion Control
- Sequestration



Treatments for Iron and Manganese

- Common sources: Rivers, reservoirs, lakes, groundwater and in-plant sources
- Oxidation and Coagulation – effective as pretreatment processes
- Oxidation – transforming soluble into solid compounds, followed by coagulation, flocculation, sedimentation and filtration
- Ion exchange – appropriate for groundwater low in particulate matter only
- Sequestration – used to stabilize iron and manganese
- Less common treatments: Biological filtration, membranes, softening precipitation and treatment at the source



Treatments for Aluminum

- Common sources: Erosion of natural deposits and overdose of alum coagulant from water treatment by-product
- pH Adjustment – The pH and water temperature have significant impact on aluminum residual levels
- Coagulation/Filtration – Coagulation initiates the aggregation of particles into flocs, followed by clarification and/or filtration



Treatments for Hardness

- Common sources: Water conveyance pipes and pumps
- Ion exchange – used for softening with a cation-based resin
- Lime softening – the three types of chemical precipitation are: lime only, lime/soda ash and lime/soda ash with recarbonation
- Softening Membrane Filtration – used when constituents are smaller than a particular size
- Sequestration – effective at low levels of hardness



Treatments for Nitrate

- Common sources: Septic tanks, farm fertilizers, feed lots and sewage
- Ion Exchange - appropriate for groundwater only
- Membrane Filtration – Significant advantage of near-total automation



Treatments for total dissolved solids, Sulfates

- Common sources: Erosion of natural deposits
- Membrane Filtration – Pretreatment requirements depends on the source water quality
- Ion Exchange - appropriate for groundwater only



Treatments for Arsenic

- Among the most widely distributed elements in the earth's crust
- Coagulation/Filtration – preoxidation step can result in 100% removal of arsenic
- Lime Softening – preoxidation step can result in 100% removal of arsenic
- Adsorption – used with activated alumina or granular ferric hydroxide as media
- Ion Exchange - appropriate for groundwater only
- Membrane Filtration – effective if preceded by a coagulation step



Treatments for Hydrogen Sulfide

- Generally a problem restricted to groundwater supplies.
- GAC, oxidizing filter, manganese greensand, aeration followed by filtration, chemical oxidation (with chlorine, potassium permanganate or ozone) followed by filtration.



Monitoring effectiveness of Oxidation Processes

- Water Quality Analyses: Iron and Manganese, free Chlorine residual, Permanganate residual
- Analytical Equipment



Monitoring effectiveness of Coagulation and Flocculation Processes

- Water Quality Indicators
- Analytical Equipment



Monitoring effectiveness of Clarification and Conventional or Membrane Filtration

- Water Quality Indicators
- Analytical Equipment

**Exercise**

Match the letter of the definition to the word it describes.

- | | |
|------------------------|--|
| 1. ____ Solute | A. A chemical reaction between an oxidant chemical, such as chlorine, and a soluble constituent, such as manganese, that results in the constituent being converted into its solid form. |
| 2. ____ Supersaturated | |
| 3. ____ Precipitation | B. An elemental atom or compound with a negative charge. |
| 4. ____ Oxidation | C. A water whose chemical makeup neutralizes any acids or bases added, without a significant change in pH. |
| 5. ____ Anion | D. The dissolved component of a solution. |
| 6. ____ Cation | E. Unstable condition in water, whereby a substance is contained at a concentration greater than the saturation concentration for that substance. |
| 7. ____ Buffer | F. An elemental atom or compound with a positive charge. |
| | G. The separation from a solution of a substance made insoluble as the result of a chemical reaction. |

Select or complete the answers for the question. Note that some questions have more than one answer.

8. Sources of inorganic constituents are:
- A. Natural sources
 - B. Non-Point Pollution, such as runoff from a farm field
 - C. An industry that discharges contaminants through a pipe
9. Primary Maximum Contaminant Levels (MCLs) protect acute and chronic health problems.
- A. True
 - B. False
10. Secondary Maximum Contaminant Levels (SMCLs) protect against:
- A. Nuisance and aesthetic problems in treated water.
 - B. Health concerns.
 - C. Radioactive contamination.

13. Common treatments for iron and manganese are oxidation, ion exchange, and:
 - A. Facial
 - B. Sublingual
 - C. Sequestration
 - D. Heat Treatment

14. Identify two common treatments for aluminum.

15. Identify two common treatments for hardness.

16. Identify one common treatment for nitrates.

17. List two less common inorganics and one treatment for each.

18. The ion exchange process is commonly used for the treatment of water from an uncovered surface reservoir.
 - A. True
 - B. False

19. Pretreatment techniques before the filtration process are:
 - A. Oxidation
 - B. Backwashing
 - C. Pre-Soaking
 - D. Coagulation

20. A chemical process that reversibly transfers ions between resin (media) and the water being treated is known as:
 - A. Ion sharing
 - B. Ion resonating
 - C. Ion disinfection
 - D. Ion exchange