

6. Groundwater Treatment

6.1. Introduction

Compared to surface water sources, many groundwater supplies are characterized by reduced seasonal variability and microbial counts, lower turbidity, and lower concentration of synthetic organic substances. Because of this, and its normally high overall quality, groundwater is often preferred to surface water as drinking water source. When it does not contain excessive mineral concentrations or contaminants, groundwater may be suitable for direct pumping to the distribution system and consumption, without prior treatment. However, this depends on specific regulations, typically on a country (federal) level. For example, in the United States, the Ground Water Rule, published in 2006 (US Federal Register, 2006), requires only those groundwater systems that are identified as being at risk of fecal contamination to disinfect water. "At-risk" supplies are identified by using sanitary surveys and periodic monitoring of fecal indicator organisms conducted, on a frequency determined by the size of the system, under the Total Coliform Rule (US Federal Register, 1989). Secondary disinfection (i.e., maintaining chlorine residual through the distribution system) is, instead, mandatory, regardless of the initial quality of raw water. Often the treatment of groundwater is limited to the removal of inorganic contaminants such as iron and manganese and disinfection (see Fig. 6.1 for a typical schematic for this type of system). This, by no means, implies that groundwater cannot be contaminated, as discussed in Chap. 5. When contaminants are found above the concentrations specified by the regulatory agencies or tolerated by the public, treatment of groundwater is required before consumption.

Groundwater treatment processes are designed to remove a variety of natural and anthropogenic contaminants. Efficacy, capital, and operation and maintenance (O&M) costs, and owner's preference determine the selection of a specific treatment technology. Individual process units are arranged in a "treatment train" to achieve the removal of multiple contaminants from the water. At the municipal scale, commonly used processes include some form of oxidation, coagulation/clarification process, filtration, and disinfection (a flow schematic for a typical conventional groundwater treatment process is presented in Fig. 6.2).

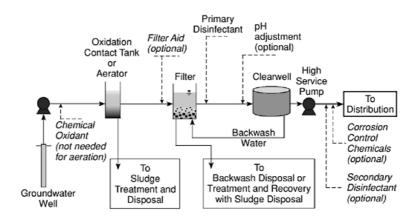


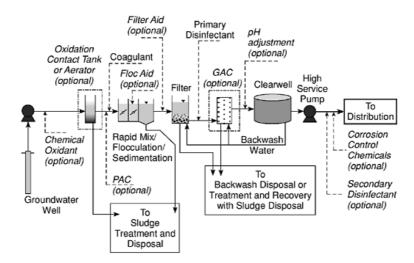
Figure 6.1 Basic groundwater treatment plant with iron and manganese oxidation and removal.

In cases where an individual household or a small number of connections is served by an individual well, it is often more economical to install a treatment system directly at the location where water is consumed. Point of entry (POE) and point of use (POU) devices are designed for this particular use (USEPA, 2006a). POE devices treat all water entering a single home, business, school, or facility, while POU devices treat only the water from a particular faucet. Typically, POE/POU devices rely on the same treatment technologies used by centralized treatment plants. However, it should be noted that POU/POE systems are designed to function at much higher specific flow rate than those for municipal systems. For example, flow rates for ion-exchange resins up to 70 m 3 /m 2 h (approximately 30 gpm/ft 2) are used in POU/POE versus 2.5 to 12 m 3 /m 2 h (approximately 1 to 5 gpm/ft 2) in municipal systems. POU units are typically installed under the kitchen sink, providing



purified water for drinking and cooking, while other water faucets deliver untreated water for washing and cleaning. This configuration provides treatments only where needed thus helping to contain the O&M costs of the treatment. POE units are instead typically installed to treat all the water that is entering a single home, building, or facility.

Figure 6.2 Conventional drinking-water treatment plant. GAC: granular activated carbon.



Municipal systems that supply water to larger communities, small systems treating water only for a few users, and individual well owners use a variety of technologies to remove contaminants from groundwater water. The most commonly used of these technologies are described in the following sections.

6.2. Oxidation

In groundwater treatment, oxidation is typically implemented at the plant headworks. The selection of oxidant type, dose, and reaction time depends on the type of contaminant to be removed and overall raw water quality conditions.

The simplest method of oxidation is aeration and is often used for oxidation of iron, manganese, and arsenic and the removal of hydrogen sulfide and volatile organic compound (VOC). Aeration is a physical process aimed at transferring oxygen from air to water, decreasing carbon dioxide dissolved in water and stripping volatile compounds from water. The efficiency of the exchange process is typically enhanced by providing a large surface area. Aeration systems may be classified into four general categories: waterfall aerators, diffusion or bubble aerators, mechanical aerators, and pressure aerators (AWWA and ASCE, 1998). For oxidation of groundwater, waterfall aerators are often used. The more common types include spray aerators, multiple-tray aerators, cascade aerators, cone aerators, and packed columns. The selection of the specific type of aerator system depends on several factors, such as required transfer efficiency, footprint, and cost.

Chemical oxidants used in groundwater treatment are chlorine, permanganate, chlorine dioxide, and ozone. Table 6.1 presents the standard potentials of common chemical oxidants used in water treatment.

Many of these oxidants are also used as disinfectant and can be added both at the plant headworks to provide oxidation and disinfection or/and downstream in the treatment process for disinfection purposes (further information on disinfection is provided later in this chapter).

Traditionally, chlorine has been the most common oxidant used by small groundwater systems because, in addition to its effectiveness, it requires limited equipment and capital investment both in the gaseous (Fig. 6.3) and in the liquid forms (Fig. 6.4), and relatively low O&M costs. However, stricter standards for and concerns over disinfection by-products (DBPs), which are formed by the reaction of chlorine with natural organic matter (NOM), have caused many plants to discontinue the practice of prechlorination, i.e., the addition of chlorine at the plant headwork (USEPA, 1999a). Many water treatment plants have



switched to alternative oxidants. Permanganate is widely used, especially by systems with high concentrations of manganese, which is more difficult to oxidize than iron. One problem posed by permanganate is that the dosage has to be carefully targeted.

Table 6.1 Oxidation Potential of Common Water Treatment Oxidants

Oxidizing Compound	Standard Half-Cell Potential (V)
Ozone	2.08
Hydrogen peroxide	1.78
Hypochlorite ¹	1.64
Permanganate	1.68
Chlorine dioxide ²	0.95
Hypochlorous acid ¹	1.48
Monochloramine	1.40
Chlorine gas ¹	1.36
Dichloramine	1.34

¹ Chlorine is available as chlorine gas and as dry and aqueous hypochlorite. Chlorine gas hydrolyzes rapidly in water to form hypochlorous acid (HOCI) (White, 1999).

An insufficient dosage will not provide adequate oxidation, while overfeeding can lead to pink water entering the distribution system. Pink water does not pose a health hazard but can cause customer concern and complaints. Furthermore, overfeeding can cause operational problems in conventional filters by contributing to the formation of mudballs (spherical conglomerate of sand and silt, which form in the top layer of granular filters due to inadequate backwashing).

Ozone is the strongest oxidant available in water treatment (see Table 6.1). It is very reactive and must be produced on site. It does not form chlorinated DBPs although, depending on the quality of the source water, may form other DBPs. Because of the relatively high capital and O&M costs, ozonation is more frequently used by larger systems (Singer and Reckhow, 1999; Kawamura, 2000).

² The oxidation potential of chlorine dioxide may be misguiding, as it is a very effective oxidant due to its selective (only reacts with certain compounds) characteristics (White, 1999). Source: Singer and Reckhow, 1999; Stumm and Morgan, 1996.



Figure 6.3 Gaseous chlorine feed system. (From USEPA, 1999a.)

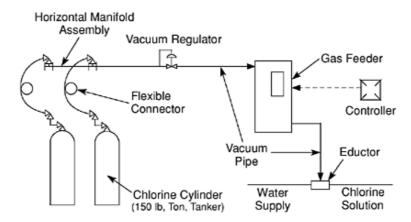
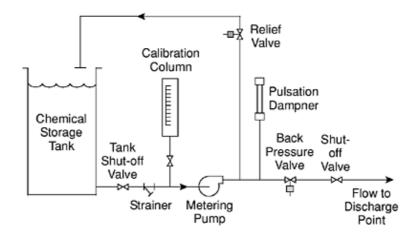


Figure 6.4 Hypochlorite feed system. (From USEPA, 1999a.)



Chlorine dioxide is another very strong oxidant that in recent years has gained more attention because it does not form chlorinated DBPs and capital and operational costs are lower than those for ozone. Like ozone, it is highly reactive and must be produced on site. Dosage of chlorine dioxide must be carefully calibrated because residual concentrations greater than 0.4 mg/L in the water delivered to consumers cause taste and odor problems (USEPA, 1999a; Singer and Reckhow, 1999).

Further details on the oxidation of specific contaminants are given later in this chapter.

6.3. Clarification

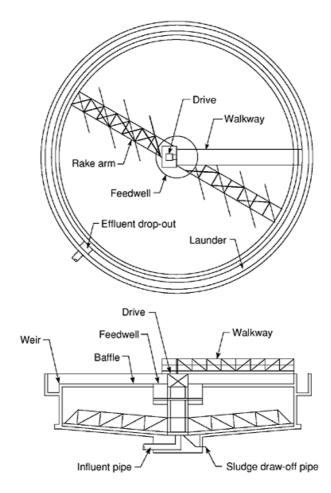
Following oxidation, a clarification step is commonly used to promote the aggregation and settling of suspended and dissolved constituents such as clay, silt, finely divided inorganic and organic matter, soluble organic compounds, algae, and microscopic organisms including microbes. Conventional clarification comprises three steps. First is the addition of coagulant or a pH-adjustment chemical in the flash mixer to destabilize (reduction of the electrostatic repulsion) particles and, therefore, promote their agglomeration. Second is the flocculation step where water is gently mixed to produce larger and heavier "flocs" (agglomerated particles). The third step is settling in which heavier particles and the flocs formed during the previous steps settle by gravity at the bottom of a tank (see Fig. 6.5 for an illustration of a circular radial flow clarifier). Extensive reviews of this process unit are found in Gregory et al. (1999) and Letterman et al. (1999).

Variations on the clarification process include (1) high rate clarification, which involves using smaller basins and higher surface loading rates than conventional clarifiers, and (2) dissolved air flotation, which uses rising air bubbles to float flocs to the surface of a tank where the material is skimmed off (LeChevallier and Au, 2004; Gregory et al., 1999).



The most commonly used coagulants are alum (aluminum hydroxide), iron salts, and polyaluminum chloride (PACI). Coagulant dosages vary, based on several factors including water pH, alkalinity, turbidity, quality of suspended solids (size and negative charge), concentration of TOC (a measure of the concentration of organic substances), and water temperature. Typical dosages for sources with low turbidity (less than 2 NTU), low TOC (less than 2.5 mg/L), low alkalinity (less than 30 mg/L), and average temperature around 15°C range between 5 and 15 mg/L for ferric salts; 10 to 25 mg/L for alum; and 2 to

Figure 6.5 Circular radial flow clarifier. (AWWA and ASCE, 1998; McGraw-Hill, printed with permission.)



8 mg/L for PACI. Significantly larger dosages (>30 mg/L for ferric salts and >50 mg/L for alum) are normally required for groundwaters with higher TOC and lower temperatures. Various types of polymer additives with different molecular weights and charge may also be added to improve particle removal and filterability at the flash mix or flocculation step, or as sole coagulant in place of metallic coagulant. The selection of the appropriate polymer is based on water quality, point of addition, and treatment objectives.

As alternative to coagulation/flocculation, chemical precipitation through softening achieved through the addition of lime or caustic (sodium hydroxide) to increase pH can be used in the clarification step for removing particulate matter if hardness removal is one of the treatment objectives.

The performance of the clarification process is dependent on many factors, including physical design of the facility, concentration and type of particulate to be removed, type and dosage of coagulant, pH, ionic strength, temperature, and concentration of NOM. Turbidity is an expression of the optical property that causes light to be scattered and absorbed by particles and molecules rather than transmitted through water (USEPA, 1999a). Although not a true measurement of particle concentration, turbidity is used to measure the performance of the clarification process. High turbidity is an indication of potential for drinking water contamination with microbial agents because suspended particles can "shelter" microbes from



disinfectants (USEPA, 1999b, 1999c). Typically, a turbidity of less than 2 NTU is often considered a minimal target for the clarification effluent.

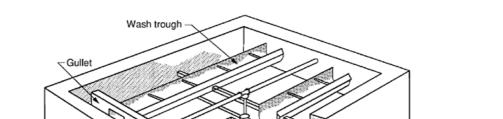
Finally, the treatment of many groundwater supplies may not require the flocculation and sedimentation steps. For high-quality source waters, such as those characterized by low turbidity, in-line coagulation can be implemented by directly adding coagulant to the raw water pipeline before direct filtration. The addition of the coagulant improves the filterability of particles, thus improving filter performance (LeChevallier and Au, 2004).

6.4. Filtration

Following clarification, a filtration step is often used to remove remaining particulates. In most treatment plants, filtration is the final step to accomplish removal of suspended solids. Filtration consists of passing water through a bed of granular filter media such as sand, anthracite, or other filtering material. Most of the suspended matter in the influent water is retained onto the media. Filtered water should be clear with turbidity below 0.2 NTU (Binnie et al., 2002). Media size, filtration rates, effectiveness of the clarification system, and filter-aid polymer addition greatly affect filter performance. In the United States, the USEPA mandates (as of January 1, 2002) that the turbidity of the filter effluent combined for all filters in a drinking water plant may never exceed 1 NTU, and must not exceed 0.3 NTU in 95 percent of daily samples in any month (USEPA, 2006b).

6.4.1. Rapid Sand Filters

Rapid sand filters are the most common type of granular filter used in municipal water treatment. They consist of concrete boxes filled with one or more layers of porous media such as sand and anthracite (see Fig. 6.6). In some cases, a layer of granular activated carbon (GAC) may also be placed in filter to adsorb chemicals and DBP precursors dissolved in water. Typical loading rates for these filters are 5 to 12 m 3 /m 2 h (approximately 2 to 5 gpm/ft 2) of filter bed surface area. Water enters the filter from above the media and flows by gravity downward through the filter media. At the bottom of the filter unit water it is collected in the underdrain system, where it is removed from the filter. The filter is cleaned through the "backwash" process, which consists of reversing the flow of water through the filter, to remove the solids accumulated on the media surface and within the media bed. Air can be added to the backwash water to improve scouring of the solids. At the end of the backwash cycle, backwash water and the solids it contains are removed from the filter with a series of collection troughs. Rapid sand filtration requires advanced operator training and skills, particularly for starting and conducting backwash operations and bringing back filters on line without affecting the quality of finished water. Extensive monitoring is required during operation of media filtration units.



Surface wash unit

─ Filter media ← Gravel Underdrain blocks

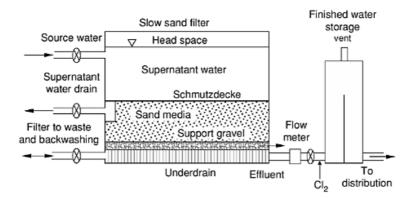




6.4.2. Slow Sand Filters

Slow sand filters are a form of filtration that has been in use for nearly two centuries (USEPA, 1999b). Typically, they are not preceded by coagulation or flocculation processes and can treat water with turbidity up to 50 NTU (Schultz and Okum, 1984). Hydraulic loading rates for this type of filter range from 0.1 to 0.4 m³/m²h, or approximately 0.2 to 1.0 gpm/ft² (Huisman and Wood, 1974; Schultz and Okum, 1984). The filter media is contained in a box and is composed of a bed of relatively uniform in size and fine-grained sand, which is supported by a layer of gravel (see Fig. 6.7). Similarly to rapid sand filters, water flows down the filter media drawn by gravity. Water is treated as a combination of physical straining and biological removal to remove suspended solids, and some microbes. Removal of solids by physical straining occurs within the upper 0.5 to 2 cm of the sand layer. During operation, a layer of dirt and biologically active organisms develops at the surface and within the uppermost part of the sand. This layer is known as the "schmutzdecke" and is essential to the effectiveness of the filter in removing suspended solids and reducing turbidity (Huisman and Wood, 1974; Schultz and Okum, 1984; USEPA, 1999b; Binnie et al., 2002). When the filter becomes clogged by the removed impurities, the top layer of the media is scraped off to start a new filter cycle. The cleaning can be done by unskilled labor (Schultz and Okum, 1984). Depending on water quality, filter runs between cleaning can last up to 2 to 6 months (Kawamura, 2000). Slow sand filters can effectively remove suspended solids; however, they have been found to have limited capability for removing clay particles and color (AWWA and ASCE, 1998). Their simplicity of operation, low cost of installation, simple design, and no power requirements make them a very effective "lowtech" method of treating water, especially for urban and rural communities of low-income areas (WHO, 2007). Prefabricated slow sand filter units are also on the market. These systems are particularly suitable for installation in small communities where construction capabilities are limited and in emergency situations.

Figure 6.7 Typical covered slow sand filter installation. (From AWWA and ASCE, 1998; McGraw-Hill; printed with permission.)

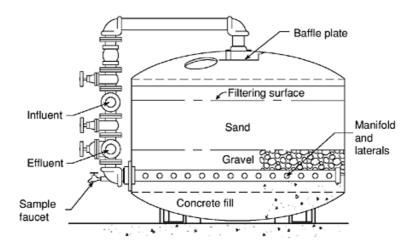


6.4.3. Pressure Filters

Pressure filters and rapid sand filters have many similar characteristics. They use the same types of media, and the removal of suspended solids is accomplished in the same way. Their efficacy to remove suspended solids and reduce turbidity is also similar (USEPA, 1999b). The main difference is that in pressure filters the media is contained within a pressurized vessel, usually made of steel (see Fig. 6.8). Pressure, not gravity, is the driving force to push water through the media. Some of the major advantages of pressure filters are that they have a compact design since they do not require several feet of water above the filter bed to provide a static pressure head and that water leaves the filter under pressure. The latter occurrence eliminates the need for repumping water before delivery to the distribution systems and the potential for air binding, which is sometimes associated with rapid sand filters. The disadvantages of pressurized filters include the absence of visual observation of the filter during operation and the propensity to experience turbidity "breakthrough" because of the high pressure driving the filtration process (USEPA, 1999b).



Figure 6.8 Typical cross section of a pressure filter. (From Cleasby and Logsdon, 1999; copyright McGraw-Hill; printed with permission.)



6.4.4. Precoat Filters

This type of filter uses a thin layer of very fine media such as diatomaceous earth or perlite, which is supported by a permeable rigid structure or fabric element. Water is forced through the media by pressure or vacuum. The media physically strains solids from the water. When the surface cake of strained solids builds up to impart a headloss that does not allow an efficient filtration process, cake and media are washed out from the support and a new layer of media is deposited in a slurry to start a new filtration cycle (USEPA, 1999b; LeChevallier and Au, 2004).

Typically, loading rates are in the range of 1.2 to 5 m³/m²h (approximately 0.5 to 2 gpm/ft²). Advantages of this process include relatively low capital cost and no need for the clarification. Disadvantages include the inability to handle water with high turbidity, the potential for particle breakthrough if the precoat phase is not properly done or cracks develop in the precoat layer during operation, and the poor capability to remove color-and taste- and odor-causing compounds (USEPA, 1999b).

6.4.5. Bag and Cartridge Filters

Bag and cartridge filters are used to remove microbes and turbidity. The filtration process for these units is based on physical screening—particles larger than the filter pore size are removed. The pore size of these filters is typically designed to be small enough to remove protozoa such as *Cryptosporidium* and *Giardia*. However, smaller particles, including viruses and most bacteria, can pass through the filters. Bag and cartridge filters can be used only for water with low-turbidity loadings, because high turbidity can quickly clog them. Upon fouling, bag filters can be backwashed, while cartridge filters must be replaced. A disinfectant is typically added to water before it enters cartridge filters to inhibit bacterial growth in the unit. In larger systems, these filters typically find their application as pretreatment to protect reverse osmosis (RO) membranes or other process units sensitive to suspended solids. They are easy to operate and maintain, which makes them suitable for small systems and for POE/POU applications (LeChevallier and Au, 2004).

6.4.6. Ceramic Filters

Ceramic filters can remove bacteria and parasites by passing water through a porous ceramic cartridge. The volume of water that can be treated with these filters is small, and their application is limited to kitchen sink units that produce drinking and cooking water. These filters are not able to remove all viruses if they are present in the water, and additional disinfection should be provided. Ceramic filters tend to plug up quickly if the water contains significant loads of particulate matter.

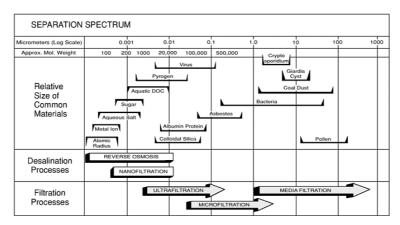


A type of "low-tech" ceramic filtration system (Filtron) developed by Dr. Fernando Mazariegos of the Central American Industrial Research Institute (ICAITI) is used in low-income areas and emergency situations to purify water (Potters for Peace, 2007). This filtration system is composed of a porous clay filter medium, a larger storage recipient canister or a bucket with a lid, and a spigot attached to the bottom. Water is poured in the clay filter at the top and percolates into the storage vessel. Users can draw water from the spigot. The clay filter is manufactured with a simple process that can be easily replicated on a local level, which includes a mix of local terra-cotta clay and a combustible material such as sawdust or rice husks. The three ingredients are mixed together. A hand-operated press and two-piece aluminum mold can be used to form the clay filter. The combustible material burns out in the firing process, leaving a network of fine pores (ranging between 0.6 and 3.0 .µm). After firing, the filter is coated with colloidal silver to inhibit bacterial growth (Potters for Peace, 2007). The Asociación Guatemalteca para la Familia de las Americas (AFA Guatemala), in association with other organizations, conducted a study from 1993 to 2005 on the effectiveness of this filter. The study found that the filters could reduce diarrhea by 50 percent (references in Johnson, 2006). Bench-scale testing has shown that the majority of the bacteria and protozoa are removed mechanically through the filter's fine pores. The colloidal silver inactivates 100 percent of the bacteria (Lantagne, 2001). The effectiveness of the filter in inactivating or removing viruses is unknown.

6.5. Membrane Filtration

Membranes are the new generation of water filters that are slowly replacing conventional filters due to their ease of operation and robust performance. Membrane filtration can also be considered, to a certain extent, as a form of disinfection because it can completely remove those pathogens whose size is larger than the pore size of a specific type of membrane (see Fig. 6.9). Capital and O&M costs, which used to be a deterrent for widespread implementation of membrane filtration, have considerably declined in recent years, making membranes a very attractive treatment alternative. Small membrane units are also used at POE/POU for the purification of groundwater from individual wells.

Figure 6.9 Pressure-driven membrane process classification (Westerhoff and Chowdhury, 1996; copyright McGraw-Hill; printed with permission.)



The membrane filtration process is driven by pressure (or vacuum) to force water to the other side of a semipermeable membrane while retaining impurities and some of the feed water. The most commonly used membranes for drinking water treatment are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Detailed descriptions of the fundamentals, design, and operation of these processes are available in Mallevialle et al. (1996), Taylor and Weisner (1999), and USEPA (2005a).

There are a variety of membranes of different materials and operational configurations (referred as modules) available on the market. Nearly all membranes used in drinking water are made of synthetic polymers. NF and RO are made of semipermeable cellulose acetate (CA) or polyamide materials, while UF and MF are membranes made of CA, polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), polypropylene (PP), polysulfone (PS), polyethersulfone (PES), or other polymers (USEPA, 2005a).



Membranes are characterized by their capability to exclude (or reject) a solute (also referred as pore size) or by molecular weight cutoff (MWCO). The MWCO is expressed in terms of Daltons: a unit of mass designating 1/16 of the lighter and most abundant isotope of oxygen. Typically, manufacturers use the MWCO value—the nominal molecular weight of a known species that is always being rejected at a specific percentage under specific test conditions—to characterize individual types of membranes. However, as MWCO protocols vary among manufacturers, there is a certain level of ambiguity in defining the "true" cutoff of a membrane (Taylor and Weisner, 1999).

UF and MF are membranes made of polymeric porous material designed specifically to remove suspended solids via a sieving mechanism based on the size of the membrane pores. The distribution of pore sizes characteristic of each membrane varies with material type and manufacturing process. UF membranes are characterized by a pore size range of approximately 0.01 to 0.05 μ m (nominally 0.01 μ m) or less (USEPA, 2005a). UF is the primary membrane technology for the removal of viruses that, in general, range in size from about 0.01 to 0.1 μ m. At the lower end of the UF spectrum some larger organic macromolecules, including DBP precursors, can be retained by the membrane. Typical MWCO for UF membranes used in water treatment is approximately 100,000 Da. The range of pore sizes for MF membranes is 0.1 to 0.2 μ m (nominally 0.1 μ m) (USEPA, 2005a). MF is primarily effective for removing turbidity and larger pathogens such as *Giardia* or *Cryptosporidium*, and some species of bacteria that are larger than 0.1 μ m. In general, it is not an effective means for virus treatment, although some virus removal by MF has been reported in the literature. This removal is generally attributed to formation of a cake layer on the surface of the membrane. By the same process, MF can remove coagulated organic matter. In terms of module configuration, typically MF and UF are supplied in hollow-fiber membranes. MF and UF membranes must be regularly backwashed and chemically cleaned on recurrent intervals (USEPA, 2005a). The disposal options for residuals from these operations must be taken into consideration during the planning and design phases.

RO and NF membranes employ the process of RO to remove dissolved contaminants from water. NF and RO are made of semipermeable CA or polyamide materials. The typical range of MWCO is less than 100 Da for RO membranes, and between 200 and 1000 Da for NF membranes (USEPA, 2005a). RO is often used for the desalination of sea and brackish water, but also has high rejection capability for many synthetic organic compounds (SOCs) (Taylor and Weisner, 1999). NF is used, primarily, for softening or the removal of dissolved organic contaminants. NF and RO membranes are specifically designed for the removal of total dissolved solids (TDS) and not particulate matter. They are not intended to be sterilizing filters and some passage of particulate matter due to manufacturing imperfections may occur. Further, because these membranes cannot be backwashed, particulate matter can cause rapid irreversible fouling. Therefore, NF and RO are not typically used to directly treat raw water with significant concentrations of suspended solids. NF and RO use spiral-wound membranes (Fig. 6.10). A typical schematic for these systems is shown in Fig. 6.11. RO and NO filtration produce a continuous stream of concentrated brine, and the membranes must undergo chemical cleaning on a periodic basis. Both residuals must be disposed of. RO and NO do not require backwash (USEPA, 2005a).

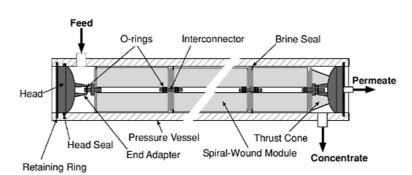
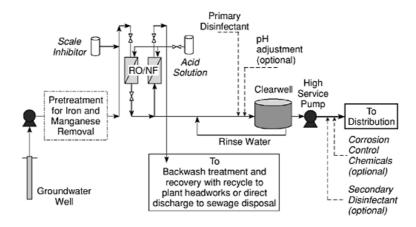


Figure 6.10 Typical spiral-wound (NF/RO) module pressure vessel. (From USEPA, 2005a.)

An additional type of membrane filtration is electrodialysis (ED). In this process water does not pass through the membrane and only contaminant ionic species are transported across selectively permeable membranes driven by an electric potential (USEPA, 2005a).



Figure 6.11 Schematic of a reverse osmosis/nanofiltration treatment system.



A variation of ED is electrodialysis reversal (EDR) in which the polarity of the electrodes is periodically reversed to change the direction of ion movement, in order to reduce scaling. As water is not physically filtered, ED and EDR do not provide a physical barrier to pathogens and suspended solids. The USEPA recognizes their effectiveness for removing dissolved ionic constituents but does not strictly consider them as filters (USEPA, 2005a).

6.6. Carbon Adsorption

The manufacturing of GAC for drinking water treatment involves a process of grinding, roasting, and activation of the source materials—such as bituminous coal, coconut shell, petroleum coke, wood, and peat—with high-temperature steam. The end product is a porous material with very high internal surface area and high adsorptive properties.

GAC filters can be placed after conventional filters as an additional process in conventional treatment (postcontactors) or in place of conventional filter media (Kawamura, 2000), since GAC media is able to remove suspended particles as efficiently as conventional media. But the main reason for using GAC is its capability for removing organic compounds. GAC can effectively remove SOCs such as aromatic solvents (benzene, toluene, and nitrobenzenes), chlorinated aromatics (PCBs, chlorobenzenes, and chloronaphthalene), phenol and chlorophenols, polynuclear aromatics (acenaphthene and benzopyrenes), pesticides and herbicides (DDT, aldrin, chlordane, and heptachlor), chlorinated aliphatics (carbon tetrachloride and chloroalkyl ethers), high-molecular-weight hydrocarbons (dyes, gasoline, and amines) (Tech Brief, 1997; Faust and Aly, 1999; Snoeyink and Summers, 1999), and methyl tertiary butyl ether (MTBE) (Stocking et al., 2000). GAC can be used to remove natural organic compounds such as humics (DBP precursors) and taste- and odor-causing compounds (Snoeyink and Summers, 1999).

During operation, when the adsorption capacity of a GAC filter is eventually exhausted, the media must be replaced and regenerated. Depending on the quality of the water to be treated and filtration rates, the interval between media replacement may be months or years. Pretreatment to reduce organic loading and remove suspended solids that may decrease the adsorptive capacity of GAC or clog the adsorption column is, in some cases, a valuable option. Powdered activated carbon (PAC) is rarely used in groundwater treatment with the exception of hydrogen sulfide removal.

6.7. Ion Exchange and Inorganic Adsorption

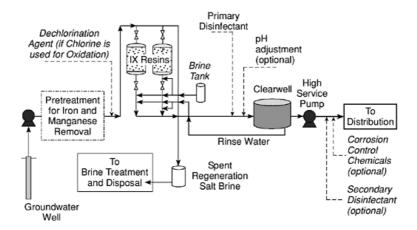
lon exchange is a reversible chemical process wherein a charged molecule is removed from solution by exchange for a similarly charged ion attached to a solid matrix. In water treatment, the solid matrix is provided by resins composed of synthetic or natural high-molecular-weight polymeric or inorganic material. These resins have high porosity and, consequentially, large surface-area-to-weight ratio. This high ratio provides a large number of adsorption sites for the removal



of pollutants. Typically, resins are in the form of small (less than 1 to 2 mm in diameter) beads that are packed in a filter column.

Examples of charged (anionic or cationic) constituents that can be removed through ion exchange include the calcium (hardness) and other metals, nitrates, heavy metals, arsenic, fluoride, and radionuclides. Ion exchange is most effective for water sources that have relatively stable quality (like most groundwater sources) and low loading of suspended solids and organic matter. In some cases, disposal of water used for regenerating ion-exchange resins can be a problem as it contains high salt concentration and can negatively affect the performance of the wastewater plant. Otherwise, ion exchange is a relatively simple inexpensive process that requires low capital costs and labor. Ion-exchange media targeting specific compounds (e.g., nitrate and perchlorate) have been developed, improving the performance of this technology in situations where several ions may be competing for the same adsorption sites (Montgomery, 1985; Clifford, 1999). The schematic of a typical ion-exchange treatment system is shown in Fig. 6.12.

Figure 6.12 Schematic of an ion-exchange treatment system.



Activated alumina is a physical and chemical process for the removal of ions by adsorption. It is used in a similar way to ion-exchange resins. In this process, water flows through the alumina-packed bed typically contained in a fiberglass canister. The contaminant is adsorbed onto the surface of the alumina. Activated alumina is used in the removal of constituents such as arsenic, uranium, beryllium, selenium, silica, fluoride, and humics. Once the adsorptive capacity of activate alumina is exhausted, the media is replaced or regenerated (Montgomery, 1985; Clifford, 1999).

6.8. Biological Treatment

Biological water treatment processes are used in small and large municipal water treatment plants in Europe and are now gaining some consideration in North America. Biological treatment involves optimizing conditions to promote a permanent active biofilm for the biodegradation or conversion of unwanted constituents such as biodegradable organic matter, taste- and odor-causing substances, some SOCs, iron and manganese, and arsenic. Granulated active carbon is an excellent media to support the growth of bacteria (particularly when preceded by ozonation), which can be used to promote the biological removal of certain compounds. However, biological growth must be controlled to avoid operational problems such as sloughing-off of clumps of microbial growth from the filter and transport of microbes to the distribution on activated carbon fine particles that may be present in the plant effluent, which may cause high bacterial counts in the distribution system and taste and odor problems (AWWA and ASCE, 1998; Geldreich and LeChevallier, 1999). Disinfection of the GAC effluent is, therefore, recommended to ensure its acceptable microbiological quality before discharge into receiving surface water bodies.

6.9. Distillation



Distillation uses temperature change to evaporate and condense water. Metals and other mineral contaminants are generally retained in the boiling chamber, and purified water is collected in the condensate chamber. Some organic contaminants are not removed by this process. Because of the high energy cost and reject heat, this system is typically used only by small-scale installations and POE/POU devices for groundwater treatment. However, it is used in many large-scale systems in the Persian Gulf region for the desalination of sea water.

6.10. Disinfection

Typically, some form of disinfection is the last step in the treatment process to ensure that the water is microbiologically safe (free from bacteria, viruses, and protozoan parasites) before the water is consumed. Because water quality deteriorates as soon as it enters the distribution system, many utilities apply a secondary disinfectant to maintain the microbiological quality of water. Water in the distribution system can be contaminated by a variety of pollution sources, such as backflow, pipe leaks and intrusion, and bacterial regrowth in the distribution pipes. In the United States, the USEPA mandates that treated water contains sufficient excess disinfection chemical to maintain a residual in the distribution system and to ensure that no microbial regrowth and recontamination occur in the water as it is being distributed (USEPA, 1999a, 2006b). However, the idea of the need for a residual disinfectant is not universally accepted. For example, some European municipalities do not implement secondary disinfection.

The advantages and disadvantages of various disinfection methods are presented in Table 6.2, and the effectiveness of various disinfection methods for various pathogens are listed in Table 6.3.

6.10.1. Chlorine

Free chlorine can be introduced to water directly as a primary or secondary disinfectant. Chlorine is effective for disinfection of bacteria, viruses, and some protozoa (e.g., *Giardia*). However, the protozoan *Cryptosporidium* has demonstrated resistance to disinfection by chlorination. The major problem with chlorine is that it is known to react with organic substances and form variety of halogenated DBPs, including significant amounts of three halo methanes (THMs) and halo acetic acids (HAAs). In general, more THMs and HAAs are produced during chlorination than with all other disinfection methods. Further, excessive concentrations of chlorine can be harmful to human health. The USEPA has set a maximum residual disinfectant level (MRDL) for chlorine of 4.0 mg/L (USEPA, 1999a, 2006b; Singer and Reckhow, 1999). Besides disinfection, chlorine is used to achieve several other objectives during treatment (for example, oxidation and previously mentioned in this chapter). Table 6.4 summarizes some of the reasons for adding chlorine and other process considerations.



Table 6.2 Summary of Advantages and Disadvantages of Disinfection Techniques

Consideration	Chlorine	Chloramines	Ozone	Chlorine Dioxide	UV
Equipment reliability	Good	Good	Good	Good	Medium
Relative complexity of technology	Less	Less	More	Medium	Medium
Safety concerns	Low to high ¹	Medium	Medium	High	Low
Bactericidal	Good	Good	Good	Good	Good
Virucidal	Good	Medium	Good	Good	Medium
Efficacy against protozoa	Medium	Poor	Good	Medium	Good
By-products of possible health concern	High	Medium	Medium	Medium	None
Persistent residual	High	High	None	Medium	None
pH dependency	High	Medium	Low	Low	None
Process control	Well developed	Well developed	Developing	Developing	Developing
Intensiveness of operations and maintenance	Low	Moderate	High	Moderate	Moderate
¹ Safety concern is high for gaseous chlorine Source: Earth Tech (Canada), 2005.	, but it is low for h	ypochlorites.			

Table 6.3 Effectiveness of Disinfectants on Selected Pathogens

Disinfectant		Microorg	anism Reduction Ability	
	E. Coli	Giardia	Cryptosporidium	Viruses
Chlorine	Very effective	Moderately effective	Not effective	Very effective
Ozone	Very effective	Very effective	Very effective	Very effective
Chloramines	Very effective	Moderately effective	Not effective	Moderately effective
Chlorine dioxide	Very effective	Moderately effective	Moderately effective	Very effective
Ultraviolet radiation	Very effective	Very effective	Very effective	Moderately effective
			conditions and they are only to dose, contact time, and wate	



Table 6.4 Typical Chlorine Applications in Drinking Water Treatment and Doses

Application Typical	Dose	Optimal pH	Reaction Time	Effectiveness	Other Considerations
Disinfection	Min. 2 mg/L ¹ in effluent ²	7-8.5	"CT" requirements	Good for virus and bacteria Fair for protozoa	DBP formation possible Taste and odor problems
Iron oxidation	0.62 mg/mg Fe	7.0	Less than 1 hour	Good	
Manganese oxidation	0.77 mg/mg Mn	7-8 9.5	1-3 hours minutes	Slow kinetics	Reaction time increases at lower pH
Biological growth control	1-2 mg/L	6-8	NA	Good	DBP formation
Taste/odor control	Varies	6-8	Varies	Varies	Dosage and effectiveness depends on compound DBP formation
Color removal	Varies	4.0- 6.8	Seconds to minutes	Good	DBP formation may result in taste and odo problems at high dosages
Zebra mussels	2-5 mg/L 0.2-0.5 mg/L ¹		Shock level Maintenance level	Good	DBP formation
Asiatic clams	0.3-0.5 mg/L ¹		Continuous	Good	DBP formation

¹ Residual, not dose.

Modified from USEPA, 1999a.

The forms of chlorine most commonly used in water disinfection are chlorine gas, liquid sodium hypochlorite, and (especially for smaller installations) calcium hypochlorite. Selection of the most appropriate addition method for a specific application should take into consideration several factors such as safety, cost and operation requirements, stability, availability, odor-control ability, corrosiveness, solubility, and ability to respond instantaneously to initiation and rate changes.

6.10.2. Chloramines

Chloramines are often used as a secondary disinfectant because of their capability to maintain disinfection residual for a long time in the distribution system and because they form less DBP compared to chlorine (USEPA, 1999a; Singer and Reckhow, 1999; Faust and Aly, 1999). However, in recent years, concern over the formation of N-nitrosodimethylamine (NDMA), iodoacetic acid (the most genotoxic DBP to mammalian cells ever identified), and leaching of lead from pipes have raised many doubts over the extensive use of chloramination to replace chlorination (Renner 2004a, 2004b; Edwards and Dudi, 2004). Similarly to chlorine, the USEPA has set an MRDL of 4.0 mg/L (as total chlorine) for chloramines (USEPA, 2006b).

² For systems implementing secondary disinfection.



6.10.3. **Ozone**

Ozone is very effective against a wide range of microorganisms, including bacteria, viruses, and protozoa. However, ozonation can form DBPs such as haloketones, aldehydes, ketoacids, carboxylic acids, and other forms of biodegradable organic matter, which must be adequately controlled, typically by a biologically active granular media filter, to avoid increased biofilm production within the transmission system. Further, in waters with sufficient bromide concentrations, ozonation can result in the formation of bromate and other brominated DBPs. Bromate is a regulated DBP (0.010 mg/L in the USA) and limits the use of ozone for many water supplies (USEPA, 1999a, 2006b; Singer and Reckhow, 1999).

Ozone is not used for secondary disinfection because, due to its highly reactive nature, ozone residual cannot be sustained for an extended duration. Generally, ozone is more costly than other commonly used disinfectants/oxidants. Its use is typically justified when disinfection objectives include inactivation of chlorine-resistant protozoa or where advanced oxidation is required for DBP, taste and odors, and color control.

6.10.4. Chlorine Dioxide

Chlorine dioxide is a powerful oxidant typically used as preoxidant (i.e., added at the plant headworks), because of its capability of enhancing the removal of iron and manganese. However, in recent years it has been increasingly used as a primary disinfectant due to its effectiveness for the inactivation of protozoa and bacteria (USEPA, 1999a).

Chemically, chlorine dioxide (ClO $_2$) is unstable and degrades to form by-products chlorite (ClO $_2$) and chlorate (ClO $_3$). The presence of all three species, chlorine dioxide, chlorite, and chlorate, is a health concern, and taste and odor complaints are also often associated with the use of chlorine dioxide (USEPA, 1999a; White, 1999). In the United States the first two are regulated; the MRDL for chlorine dioxide is 0.8 mg/L and the MCL for chlorite is 1 mg/L (USEPA, 2006b).

6.10.5. Ultraviolet Light Disinfection

When ultraviolet (UV) light is applied to a microorganism, DNA and RNA absorb the light energy and their structure is altered. These alterations inhibit DNA replication and diminish the capability of the microorganism to infect a host. UV light can be effectively used for primary disinfection. Generally, it has been observed that the more complex the microorganism, the more sensitive it is to UV inactivation. This means that UV is most effective for the disinfection of protozoa and least effective for the disinfection of viruses. Particularly, UV is effective for the disinfection of chlorine-resistant protozoa (i.e., *Giardia* and *Cryptosporidium*) (USEPA, 1999a, 2006c).

UV disinfection is a physical process rather than a chemical disinfectant. For this reason, there is no residual disinfectant associated with UV light, and an additional disinfectant (e.g., chloramines or chlorine) must be applied to achieve secondary disinfection. At the dosages appropriate for drinking water application, UV light is not believed to be an effective oxidant. However, when used in combination with another oxidant such as ozone, UV light can enhance the oxidation of contaminants. UV light can promote a free radical reaction pathway that increases the potency of ozone when used as an oxidant (USEPA, 1999a, 2006c).

To date, there is no evidence to suggest that UV irradiation results in the formation of any DBPs; however, little research has been performed in this area. Most of the research regarding application of UV light and DBP formation has focused on the impact on chlorinated DBP formation as a result of UV application prior to the addition of chlorine or chloramines.

One of the main drawbacks with UV is the possibility of microbes passing through at times the lamp is operating off specification. At low UV intensities, some microbes have shown the ability to repair damage done by UV light. Thus, it is important that drops in lamp intensity are minimized (USEPA, 2006c).



6.11. Corrosion Control

Corrosion is of concern for all drinking water suppliers because of its potential impact on aesthetics, economics, and human health. Discoloration and metallic taste caused by corrosion raise customer concern over the quality of drinking water. The reduced life of metallic and asbestos—cement pipe is a major economic loss due to corrosion. Leaching of toxic elements including lead, copper, cadmium, and asbestos into the finished water from the plumbing within a home and or well pump can present a health threat.

The presence of high concentrations of nitrate and sulfate ions may cause low pH in some groundwater. Low pH (typically, less than 7.0) inhibits the formation of a protective calcium carbonate scale on pipe and increases metal solubility. This requires that the pH of water is adjusted before being delivered to the distribution system. In many cases, pH is controlled by adding lime or caustic soda. In addition to raising the pH, lime increases the alkalinity and calcium content of water. Caustic soda converts excess CO 2 (if present) to alkalinity species. Some utilities also use chemical corrosion inhibitors in combination with pH control or alone to limit the effects of corrosion. Phosphate, zinc phosphate, and silicates are widely used corrosion control additives. The effectiveness of these chemicals for a specific system needs to be carefully evaluated and tested before full-scale implementation (DVGW/AWWARF/AWWA, 1996).

6.12. Removal of Specific Constituents from Groundwater

Removing specific contaminants in an affordable and effective manner is a challenge for groundwater providers and well owners. Specific treatment strategies employed to remove some of the most common contaminants found in groundwater are described below.

6.12.1. Iron and Manganese Removal

Until recently, it was thought that neither iron nor manganese causes adverse health effects and that high concentrations of these elements were only responsible for aesthetic effects. However, in recent study, Hafeman et al. (2007) have suggested that exposure to high manganese concentrations in drinking water may contribute to Bangladesh's extremely high infant mortality. In terms of aesthetic effects, water containing high concentrations of iron can discolor water, spot laundry, and stain plumbing fixtures. In addition, the growth of iron-oxidizing bacteria can result in abnormal taste and odor and can contribute to the growth of iron bacteria in distribution systems (Kawamura, 2000). Manganese causes similar reactions problems to form "black water" and can result in brownish-black stains on contact surfaces. Levels of 0.5 mg/L of iron and 0.05 mg/L of manganese are known to cause objectionable taste (Montgomery, 1985; Faust and Aly, 1999).

In general, iron and manganese problems arise in water containing low oxygen levels and high iron and manganese concentrations. The reason is that both iron and manganese are soluble under anoxic conditions, and problems occur when this type of water is pumped to the surface. When chemical equilibrium is changed upon exposure to the atmospheric pressure, the precipitation of iron and manganese will occur in plumbing, on fixtures, and on clothing, dishes, and utensils. These conditions are typical of waters that do not have regular contact with the atmosphere, such as groundwater from confined aquifers and deep wells. However, sometimes oxygen-poor conditions can also occur in relatively shallow wells that have stagnant water. In low-alkalinity groundwaters (less than 50 mg/L), iron concentrations can be up to 10 mg/L (or greater) and manganese concentrations up to 2 mg/L (Kawamura, 2000).

6.12.1.1. **Oxidation**

Iron and manganese removal is one of the most common objectives of groundwater treatment. Many systems remove iron and manganese with a combination of oxidation, coagulation/precipitation, and filtration. Oxidation is normally placed at the



plant headworks to changes the form of iron and manganese from the bivalent form (Fe ² + or Mn ² +), which is soluble to the trivalent form (Fe ³ + or Mn ³ +), which is both insoluble and colored (Mongtomery, 1985). Oxidation methods used in drinking water treatment are aeration, chlorine, permanganate, ozone, and chlorine dioxide (Kawamura, 2000). Oxidant dosages required for the oxidation of iron and manganese are reported in Table 6.5.

Table 6.5 Oxidant Doses Required for Oxidation of Iron and Manganese

Oxidant	Iron (II) (mg/mg Fe)	Manganese (II) (mg/mg Mn)			
Chlorine, Cl ₂	0.62	0.77			
Chlorine dioxide, CIO ₂	1.21	2.45			
Ozone, O ₃	0.43	0.88 1			
Oxygen, O ₂	0.14	0.29			
Potassium permanganate, KMnO ₄	0.94	1.92			
¹ Optimum pH for manganese oxidation using ozone is 8−8.5.					
Source: Reckhow et al., 1991; Williams and Culp, 1986; Langlais et al., 1991.					

Cascading tray aerators are used for iron and manganese oxidation. In waters where iron and manganese form complexes with humic substances or other organic molecules, aeration is not effective because oxygen is a weak oxidant and cannot break the bonds between metal and organics. Further, the oxidation of manganese by oxygen is a slow process (on the order of hours) unless the pH is raised above 9.5 (USEPA, 1999a).

Chlorine, permanganate, ozone, and chlorine dioxide are very effective for converting iron and manganese to insoluble compounds. The presence of high concentrations of NOM can hinder the oxidation of iron and manganese and increase oxidant demand. This situation may pose a problem in terms of overfeeding of oxidant. Elevated concentrations of chlorine can result in high DBP formation. High permanganate concentrations can carry through the plant and result in pink water reaching the distribution system. High ozone dosages can turn the oxidation of manganese to permanganate, which may result in pink color to develop in the water. High chlorine dioxide residuals can cause taste and odor problems.

6.12.1.2. Coagulation/Precipitation

Following the oxidation step, a clarification is commonly used to remove small iron and manganese particulate. Manganese colloids are sometimes difficult to remove because of their small size and high specific surface area if the clarification process is not carefully optimized and may end up being removed by the downstream filters or carried through the plant and end up in the distribution system.

In alternative to coagulation/flocculation, chemical precipitation is through softening, and this process can also remove iron and manganese particles. Softening is, however, too expensive for removing these two metals alone. But when it is used for hardness removal it can also be used for removing iron and manganese. The high pH used during the softening process results in rapid oxidation and precipitation of iron and manganese. Also, the two metals can be removed by incorporation in calcium and magnesium precipitate (Montgomery, 1985; Faust and Aly, 1999).

6.12.1.3. Filtration



Filtration is usually the last step for removing iron and manganese either following sedimentation or, depending on water quality conditions, directly following oxidation. Generally, manganese oxidation determines the hydraulic detention time needed before filtration because it has a slower oxidation reaction rate than iron. Different types of filters are used for the direct removal of iron and manganese (Montgomery, 1985).

The most commonly used type of filter for removing iron and manganese for small-and medium-sized treatment plants is pressure manganese greensand filter. Greensand is manufactured using grains of the zeolite mineral glauconite—a green clay mineral. The glauconite is treated with various chemicals to produce a durable greenish-black coating that has ion-exchanging properties. This coating behaves as a catalyst, facilitating the chemical oxidation necessary for the removal of iron and manganese. As water is passed through the filter, soluble iron and manganese are removed from solution and oxidized to form insoluble iron and manganese. Insoluble iron and manganese will build up in the greensand filter and must be removed by backwashing. The greensand is regenerated by feeding continuously or intermittently a permanganate solution.

Anthracite/sand dual media can also be used for iron and manganese removal. In this case, the oxide coating is obtained after the installation in the filter boxes by feeding permanganate. Also, in this case, the coating acts as a catalyst for the oxidation of iron and manganese. Precoat filtration can also be used in potable water systems for removing low concentrations of iron and manganese precipitants after oxidation.

6.12.1.4. **Ion Exchange**

Ion exchange is usually considered for removing iron and manganese only if water hardness is also a problem. This method is suited to remove only low concentrations (less than 0.5 mg/L combined) of these metals because of the risk of precipitation and rapid clogging of the media. Removal of iron by ion exchange should be run in the absence of oxygen to prevent oxidation and precipitation of iron and manganese oxides. Iron and manganese precipitates can coat and foul the media requiring acid or sodium bisulfate washing to resume operations. Further, ion exchange is not effective if the iron has combined with organic material, or if the growth of iron bacteria, which secrete large amounts of iron oxide, is not adequately controlled (Montgomery, 1985; Faust and Aly, 1999; Kawamura, 2000).

6.12.1.5. Biological Treatment

lon and manganese removal can be achieved by biological filtration. To optimize biological removal, the unit feed water should have low levels of oxygen and should not be chlorinated. After the biological step, aeration and disinfection are usually required to stabilize treated water (for more information of this topic see Sharma et al., 2005).

6.12.1.6. Sequestration

In systems with low concentrations of iron and manganese of, respectively, less than 1.0 and 3.0 mg/L, polyphosphates can be added as a sequestering agent before iron and manganese come in contact with air or an oxidant to prevent precipitation. Normally, a dosage of 2 to 4 ppm of a polyphosphate compound, such as sodium hexametaphosphate (SHMP), sodium tripolyphosphate (STP), or tetrasodium pyrophosphate (TSPP), forms colorless phosphate complexes. This method is effective in mitigating the negative effects of iron and manganese precipitation. However, consumers may still be affected as iron and manganese precipitation still takes place when water is heated—creating deposits in water heaters, boilers, and kitchen pots—and when water age—affecting areas at the margins of the distribution system or served by tanks where water is held for a long time (Kawamura, 2000).

6.12.2. **Hardness**

Excessive water hardness can result in soap deposits, scaly deposits in plumbing, appliances and cookware, and decreased cleaning action of soaps and detergents. It is caused by high concentration of dissolved calcium and magnesium. Other



bivalent ions such as strontium, barium, zinc, and aluminum can also have some minor effects on hardness levels. Table 6.6 presents a classification of different types of water according to their hardness content.

Total hardness is calculated by summing up the concentrations of bivalent metals expressed as mg CaCO₃/L and is differentiated between carbonate and noncarbonated hardness. Carbonate hardness is the portion of hardness where ions are associated with carbonate and bicarbonate compounds. The most common source of this type of hardness is when groundwater flows through aquifers formed of limestone or chalk. Noncarbonate hardness is associated with chloride, sulfate, and other anions, and it is typical of groundwater passing through sedimentary formations containing high concentrations of sulfates.

Table 6.6 General Hardness Scale

Description	Milligrams per Liter as CaCO ₃
Soft	0-60
Moderately hard	61-120
Hard	121-180
Very hard	More than 180
From USGS, 2007.	

Because of the tangible effects of high hardness levels, it is quite common to treat groundwater. However, because of concerns over the association between softened water and heart diseases, some systems prefer not to remove hardness.

For large potable systems, the most common method to soften water is precipitative softening by lime, lime—soda ash, or caustic soda. The selection of one of these processes depends on costs, concentration of TDS, sludge production, prevalent type of hardness, and chemical storage issues. In general, softening with caustic soda is more costly than lime and lime—soda ash. In most cases, lime and lime—soda ash softening lower TDS while caustic soda increases their concentration. More sludge is produced by lime and lime—soda ash than by caustic soda. Water mostly containing carbonate hardness can be softened by lime alone. However, if noncarbonate hardness is significant, lime and lime—soda ash may be used in combination to obtain the desired degree of hardness reduction. Chemical stability during storage and clogging of feeding systems are issues for softening plants. Hydrated lime absorbs water and carbon dioxide forming lumps, and quicklime may slake. Conversely, caustic soda does not deteriorate during storage and does not clog feeding lines. High concentrations of carbon dioxide should be reduced before precipitative softening because its removal through precipitation requires the use of more chemicals and more sludge is produced. An aeration step can be used for this purpose (Montgomery, 1985; AWWA and ASCE, 1998; Kawamura, 2000).

In precipitative softening plants, it is very important to carefully monitor pH. Typically, precipitative softening is conducted by raising the pH of water to approximately 10 for calcium carbonate precipitation. When the removal of magnesium is also required, the pH needs to be increased up to approximately 11. Operating the plant at an improper pH can lead to the precipitation and deposition of lime in the filter bed. This may lead to the "cementification" of media with consequent irreparable damages to the integrity of the media (AWWA and ASCE, 1998; Kawamura, 2000).

Water softened by chemical precipitation is characterized by high potential for carbonate scale formation. Recarbonation through the application of carbon dioxide and pH control is often used post precipitation to lower pH and mitigate scaling downstream of the softening process unit within the plant and in the distribution system. Scale formation can also be



controlled by the application of low levels of polyphosphates (1 to 10 ppm) to inhibit scale formation (AWWA and ASCE, 1998; Kawamura, 2000).

Smaller potable systems are less likely to use precipitative softening because of high capital costs and operational complexity associated with this process. A popular alternative is ion exchange. Water is passed through a column filled with resins beads where bivalent ions are exchanged with sodium ions. For potable uses, only a portion of the total flow needs to undergo this process before being blended with untreated water to lower sodium concentration. Other less commonly methods that are used to lower hardness are EDR and RO/NF.

6.12.3. **Nitrates**

Nitrate contamination is a common problem for many groundwater supplies. In most cases, it is a result of the application of fertilizers containing nitrogen, livestock facilities, or sewage disposal areas. However, in some instances, high nitrate concentrations can originate from natural deposits of nitrates. The main concern with high concentrations of nitrate in drinking water is methemoglobinemia, which causes "blue baby" syndrome, especially in bottle-fed infants younger than 6 months of age, and the potential conversion of nitrate into carcinogenic nitrosamine. The current MCL set by the USEPA (USEPA, 2006b) for nitrate in drinking water is 10 mg/L as nitrate-nitrogen (NO 3-N). The WHO guideline (WHO, 2006) for nitrate is 50 mg/L as nitrate (NO 3); note that 10 mg/L NO 3-N = 44.3 mg/L NO 3.

The most common treatment processes used to reduce nitrates in drinking water are ion exchange and RO. In the ion-exchange process, a portion of the flow is passed through a special resin, which replaces nitrate anions with another ion, usually chloride. Because sulfate is preferentially exchanged over nitrate by chloride anions, special resins that preferentially remove nitrates are normally used. These special resins (IX process) that are used to remove nitrate/nitrite also reduce the possibility of nitrate "dumping" (release of a large amount of nitrates that may occur when the ion-exchange column is saturated).

An example of the application of the ion-exchange process is reported at the Village of White Oak Water System in North Carolina, USA (Mitchell and Campbell, 2003). This system supplies water to 42 homes from a single 95 L/minute (25 gpm) well. High nitrate concentrations above 10 mg/L (nitrogen) were detected in the raw water. After pilot testing, the water provider chose to install ion-exchange units to reduce nitrate levels. The design includes a 50–50 flow split, so that only 50 percent of the flow is treated. This allowed the reduction of costs and volume of reject water. After blending of the treated and untreated water, the residual nitrate levels are on average 3 mg/L (as nitrogen), well below the 10 mg/L MCL. The reject water from backwash of the ion-exchange units is collected in a storage tank and transported to a wastewater treatment plant for treatment.

Although nitrate is not very well rejected by most membrane materials, RO can be used for nitrate removal. Typical rejection rates for nitrate removal are around 90 percent, and they are sufficient to lower nitrate to acceptable concentrations. An example of the application of RO for nitrate removal is the system in the greater Milan area, Italy (Elyanow and Persechino, 2005). GE Italba installed 13 RO membrane plants in nine locations to control high nitrate concentrations from a series of wells providing drinking water. The nitrate concentrations in these wells range between 50 and 60 mg/L (NO 3), and the treatment goal was to lower nitrate levels to less than 40 mg/L (NO 3), while discharging in the sewer a waste stream with a nitrate concentration lower than 132 mg/L. To minimize treatment costs, permeate from the RO plants is blended with untreated raw water at a ratio of approximately 20 percent permeate to 80 percent blend water. The average water recovery for the RO plants averages around 60 percent, but considering blending actual recovery ranges between 77 and 88 percent. The system is run by a central control and data logging room in the GE Milan office.



Table 6.7 Example of General Electric (GE) Electrodialysis Reversal for Nitrate Removal

	Bermuda	Delaware	Italy
Production (m ³ /hour)	94.6	63.1	47.3
Recovery (%)	90	90	90
Desalting stages	3	3	3
Feed nitrate (mg/L NO ₃)	66	61	120
Product nitrate (mg/L NO ₃)	8.8	4.5	37
Feed TDS (mg/L)	278	11	474
NO ₃ removal (%)	86.7	92.6	69.2
TDS removal (%)	81	88	53
From Elyanow and Persechino, 2005.			

ED reversal process is also used for nitrate removal, using the electrostatic properties of nitrate anions, and, especially where high recovery is required, EDR has been implemented as it has demonstrated recoveries greater than 90 percent (Elyanow and Persechino, 2005). This technology has been used by several plants across the world. For example, General Electric reports that plants in Bermuda, Delaware, and Italy have achieved reliable service (nearly 10 years) and nitrate removal rates from 69 to 93 percent. Performance data from these plants are summarized in Table 6.7. Recent upgrades to this technology have improved the performance of EDR systems (Elyanow and Persechino, 2005).

At the POE/POU scale, RO is the most frequently used point-of-use-sized treatment system for nitrate/nitrite removal. It is the most cost-effective method for producing only a few liters of treated water per day. Ion exchangers can also be used. However, because of the risk of "dumping" mentioned earlier in this section, only nitrate-specific resins should be used. Distillation is used at the POE/POU scale, since it is a very energy-intensive technique, not suited for larger-scale installations. It involves boiling and collecting water after condensation. Nearly all nitrates are removed in the process. However, it should be pointed out that just boiling the water does not remove nitrates; on the contrary, it increases their concentration.

6.12.4. Total Dissolved Solids

TDS refer to all dissolved solids that are present in water. Typically, these comprise inorganic salts such as calcium, magnesium, potassium, sodium, bicarbonates, chloride and sulfate, some organic materials, and soluble minerals (e.g., iron and manganese, arsenic, aluminum, copper, and lead). TDS originate from dissolution of minerals in geologic formations, sewage, urban runoff, and industrial wastewater.

In practice, TDS are measured by filtering a sample of water through a very fine filter (usually $0.45\mu m$), which removes the suspended solids, evaporating the filtrate and weighing the residue after evaporation (US Federal Register, 2007). It is important to notice that this type of test provides a qualitative measurement of the overall amount of dissolved solids, but it does not give any information on the specific nature of the solids. Thus, TDS should only be used as a general indicator of water quality.



Table 6.8 Classification of Source Water, According to Quantity of Dissolved Solids

Water Source	Total Dissolved Solids (mg/L)
Potable water	<1000-1200
Mildly brackish water	1000-5000
Moderately brackish water	5000-15,000
Heavily brackish water	15,000-35,000
Average sea water	35,000
Sources: WHO, 2006; NRC, 2004.	

High TDS levels do not per se pose a public health concern; however, they may create aesthetic problems such as limiting the effectiveness of detergents, corroding plumbing fixtures, resulting in scale formation, and causing salty or brackish taste. Driven by these considerations, the USEPA has set a secondary minimum contaminant level of 500 mg/L. The WHO (2006) guidelines for drinking water quality do not suggest a health-based value for TDS. However, it is noted that drinking water with high levels of TDS (greater than 1200 mg/L) may be objectionable to consumers, and extremely low concentrations of TDS may as well be unacceptable because of its flat, insipid taste (WHO, 2006). By comparison, seawater has an average TDS of about 35,000 mg/L. In Table 6.8, a classification of source water according to the concentration of dissolved solids is presented.

The selection of treatment options for elevated TDS depends on the type of dissolved species to be removed. If the high TDS concentration is due to a constituent such as calcium, magnesium, and iron, removal is possible through a softening or ion-exchange process (see hardness removal). If the problem is, instead, associated with an elevated concentration of sodium or potassium salts, removal techniques include RO, ED, or distillation.

In recent years, desalination with RO and ED due to advances in technologies and decreasing capital and operating costs has become an option for the development and management of water resources. This is of great importance in regions where freshwater supplies are limited; especially in arid inland areas where the groundwater is characterized by high TDS and in coastal regions. Desalination of groundwater can be implemented for directly providing potable water to communities in areas where brackish groundwater is found underground or to limit the overexploitation and degradation of groundwater sources.

Numerous RO and ED desalination plants are in operation in the Western Region of the United States, Middle-East, Mediterranean Region, Central Asia, and North Africa for treating brackish groundwater for potable, irrigation, and industrial uses. Large RO desalination plants have been built to supply water for major urban centers (see Table 6.9), but smaller-sized plants have also have been installed to provide water for smaller communities.

For example, as one of several water management initiatives for limiting the overexploitation of the Hueco and Mesilla Bolson aquifers, El Paso Water Utilities, and Ft. Bliss,



Table 6.9 World's Largest Brackish Groundwater Desalination Plants

Location	Capacity (m ³ /d)	Start of Operation				
Malaga, Spain	165,000	2001				
Al Wasia, Saudi Arabia	200,000	2004				
Negev Arava, Israel	152,000	2006				
Zara Maain, Jordan	145,000	2005				
Undisclosed location, Iraq	130,000	2005				
El Paso, USA	104,000	2007				
Gwadar, Pakistan	95,000	2006				
Bandar Imam, Iran	94,000	2002				
Sources: Wagnick/GWI, 2005; El Paso Water Utilitie	Sources: Wagnick/GWI, 2005; El Paso Water Utilities, 2007.					

Texas, have jointly begun to operate a 104,000 m 3/day (27.5 mgd) desalination plant. This facility contributes to the stabilization of the levels of fresh groundwater by intercepting and treating brackish groundwater before it intrudes into historically freshwater areas and limiting the need for pumping of freshwater. For the two cities, brackish water represents an important alternative and plentiful water source in addition to surface water from the Rio Grande. The amount of brackish water in the Hueco and Mesilla Bolson aquifers exceeds the amount of potable water by approximately 600 percent (El Paso Water Utilities, 2007; Hutchison, 2007). In the desalination plant, the brackish water is filtered to reduce suspended solids and then is passed through RO membranes (approximately 83 percent recovery rate). The permeated (desalted) water from the RO process is blended with water from freshwater wells and, after pH adjustment and disinfection, is pumped into the distribution system. The concentrated brine from the desalination process is disposed of through injection into an underground rock formation (El Paso Water Utilities, 2007).

Another example is the Al Wasia Treatment Plant commissioned by the Saudi Arabia Ministry of Agriculture to supply to the city of Riyadh. The plant is expected to start operation in 2007 and treat 200,000 m 3/day (approximately 53 mgd) of brackish groundwater through softening, sand filtration, and RO membranes. The reject flow from the membranes will be finally conveyed to an evaporation pond, where it is further concentrated by solar energy.

Typically, RO treatment decreases the pH of treated water due to the removal of part of the constituents of the dissolved alkalinity. The EDR system does not lower pH as much, and the treated water tends to have a pH closer to that of source. However, both processes decrease TDS to very low concentrations. Pumping water with low pH and TDS in a distribution system can have negative consequences on water quality, especially if the pipes are used to carry water with different chemical characteristics. Suppliers of desalinated water must evaluate the impact of changing water chemistry on corrosion and pipe scale stability and implement adequate preventive measures. These measures can include blending of desalinated water with other water sources before entering the distribution system and adding chemicals such as sodium hydroxide (caustic soda) or lime—to raise the pH to the 7.5 to 8.0 units range—and corrosion inhibitors.

6.12.5. Radionuclides

Radioactive minerals are commonly present in bedrock aquifers. They are soluble in water, and, in some wells, radionuclides



can be found at concentrations that exceed drinking water standards. There are different processes for the removal of different radionuclides. A general problem linked with the removal of these contaminants is that most treatment processes concentrate the radioactivity. Thus, handling and shielding of the treatment devices and waste must then be provided.

The following methods can be used for the removal of radionuclides (Montgomery, 1985; Faust and Aly, 1999):

- Distillation is capable of removing all types of mineral radionuclide types in one treatment process with the exception of radon gas. Because of the high energy costs associated with providing the heat source for distillation, this method is only practical as a POU/POE device.
- RO and EDR remove uranium, radium-226 and radium-228, gross alpha, gross beta, and proton emitters. There is no
 concern about the accumulation of radioactive substances in the membrane, as rejected particles are carried away in the
 waste stream
- Cation exchangers can remove radium-226 and radium-228 and some gross alpha contaminants and that portion of the gross alpha that is positively charged.
- Anion exchange can be used to remove uranium and the negatively charged fraction of gross alpha. Particularly, uranium is removed only above pH 6.0 when it becomes negatively charged (below pH 6.0, uranium may be either an anion or nonionic). Above pH 8.2, uranium may precipitate and, as a solid, is not removed by anion exchange. Thus, ion exchange for uranium has to occur within the pH 6 to 8 window.
- When an oxidation filter such as potassium permanganate greensand is used to treat iron and manganese, removal of radionuclides (in particular radium) can also be expected.
- Some removal of radionuclides (especially uranium, radium-226, and radium-228) may also occur during coagulation/sedimentation and lime softening. To determine if these processes provide sufficient removal, it is necessary to monitor the treated water to determine the effluent concentration of radionuclides.

A special case among groundwater radioactive contaminants is represented by radon. Radon is a radioactive gas produced by the natural radioactive decay of radium and uranium during the weathering of rocks. According to the United States National Research Council (NRC, 1999): "Of all the radioisotopes that contribute to natural background radiation, radon presents the largest risk to human health." Radon is particularly harmful to the lungs through breathing of the gas. Water can transport the gas from the soil into households, and exposure can take place when taking shower, doing laundry, or washing dishes. Radon represents a greater problem for individual well users and small systems than for large systems, because radon decays relatively quickly (3.825-day half-life) and storing water (as done by most large systems) considerably reduces public exposure. In the United States, radon is not yet regulated at the federal level; however, the USEPA has proposed (1999 Federal Register 64 FR 59246) new regulations to reduce the public health risks from radon. Water should be treated where it enters a house or building. POU devices, such as those installed on a tap or under the sink, are not effective and should not be used for radon removal because they treat only a small portion of the water used in a house or building and do not address radon vapors that are released during showers or laundry. Aeration, GAC, and POE GAC are the recommended technologies for radon removal (NRC, 1999; USEPA, 2003). Aeration is the most efficient method. Proper venting of the aeration systems to the atmosphere must be installed to avoid indoor contamination. Removal by activated carbon requires large amounts of carbon media and long contact times. When activated carbon is used, it should be placed in sealed canisters to avoid leaks of accumulated gas. Furthermore, special consideration should be given to the disposal of the spent media or cartridge disposal because of radon accumulation to high concentrations (USEPA, 2003).

6.12.6. Hydrogen Sulfide

Hydrogen sulfide, H₂S, is found in groundwater as a result of the bacterial decomposition of vegetation and other organic matter under anoxic conditions. It can cause taste and odor problem such as rotten-egg odor and metallic taste even at very low concentrations. Furthermore, it reacts with many metals, causing black stains or black deposits of iron sulfite.



Aeration can be used to remove hydrogen sulfite from water, and groundwater supplies are often aerated for this reason. Oxidation is also often used to reduce sulfur species and limit taste and odor problems. Chlorine, ozone, permanganate, and hydrogen peroxide have been successfully used for this purpose. Adsorption through GAC or PAC is capable of adsorbing H $_2$ S. This is a particularly advantageous system to use for H_2 S at the POU/POE (Montgomery, 1985; Faust and Aly, 1999).

6.12.7. Volatile Organic Compounds and Synthetic Organic Compounds

Organic chemicals may be present in groundwater because of contamination from various sources. Many of these compounds represent serious public health threats if consumed in drinking water. In general, the three treatment methods that have been shown to be effective in removing organics from drinking water are aeration, adsorption using activated carbon, and oxidation. Carbon adsorption with GAC is effective for removing both VOCs and SOCs. Treatment with PAC is effective for removing some of the SOCs.

VOC chemicals, including trichloroethane and tetrachloroethane, are easily removed by air stripping. The off-gases from the air-stripping process must be further treated to avoid pollution of the atmosphere. Air stripping can be accomplished through packed tower aeration, incline cascade aeration, or membrane air stripping. In all cases, GAC columns are typically used to remove VOCs from off-gas.

Some organic contaminants will chemically react with oxygen and oxygen-like compounds. After this treatment, the resultant compounds either may be fully neutralized or will have a lower level of hazard. Further treatment may still be necessary.

Oxidizing chemicals could include potassium permanganate, hydrogen peroxide, and hypochlorite. Ozone oxidation is effective for removing certain classes of VOCs and SOCs, and certain RO membranes and UV treatment can also be effective against VOCs and SOCs (Montgomery, 1985; AWWA and ASCE, 1998; Faust and Aly, 1999; Kawamura, 2000).

6.12.8. Total Organic Carbon

Total organic carbon (TOC) is a gross measurement that quantifies the amount of NOM in water. TOC per se is not a harmful chemical, but its combination with disinfectant, and particularly with chlorine, results to the formation of DBPs, which are regulated compounds and pose a risk to public health. Further, natural organic compounds must be removed to improve the aesthetic quality of water (color) and to reduce the growth of biofilms in the distribution system as they constitute a food source for the bacterial population. Effective treatment strategies to remove TOC form water include the following (Singer, 1999; Letterman et al., 1999):

- Enhanced coagulation (low pH)
- Modified lime-softening (pH greater than 10 and addition of small amounts of ferric- or aluminum-based coagulants)
- o GAC columns
- Ozone/biofiltration
- Synthetic iron-based resins
- RO

6.12.9. Arsenic

Arsenic occurs naturally in rock and soil and is released to groundwater due to its solubility. In recent years, arsenic contamination of groundwater has received increasing attention. The WHO guideline and the US and EU standard for arsenic



is 10 parts per billion (ppb). According to an assessment conducted by the National Academy of Sciences (NAS), consumption of water with this concentration of arsenic still poses a significant health hazard (NAS, 2001). An individual drinking 2 L of water per day with 10 ppb of arsenic has a lifetime risk of fatal bladder or lung cancer greater than 1 in 300. This is far greater than the risk that the USEPA has traditionally used for cancer-causing compounds, which is no larger than 1 in 10,000.

As part of the regulatory process for lowering arsenic standards, the USEPA identified seven best available technologies (BATs) at the municipal scale in the Final Arsenic Rule based on removal efficiency, history of full-scale operation, geographic applicability, costs based on large and metropolitan water systems, service life, compatibility with other water treatment processes, and ability to bring all of the water in a system into compliance (US Federal Register, 2001). The performance of most of these treatment technologies is contingent on the state of oxidation of arsenic. Arsenic is removed more efficiently as arsenic V than arsenic III. Arsenic V ions are negatively charged, and they can be removed efficiently by several processes through electrostatic interaction. On the contrary, arsenic III is uncharged and its removal from water is difficult. All the BATs identified by the USEPA are for arsenic V, and preoxidation may be required to convert arsenic III to arsenic V before treatment (USEPA, 2000; US Federal Register, 2001).

6.12.9.1. Ion (Anion) Exchange

lon exchange removes arsenic anions by exchange with chloride or other anions. There are several designs of ion-exchange systems. Some are nonproprietary, while others are proprietary designs by various manufacturers. Ion exchange combined with an oxidation pretreatment step has been shown to reduce total arsenic effluent concentrations as low as 0.003 mg/L (Health Canada, 2006). Laboratory studies using ion-exchange columns treating water with an arsenic concentration of 0.021 mg/L have achieved effluent concentrations as low as 0.002 mg/L (Clifford et al., 1999). A variety of adsorption media have been developed for treating arsenic. Sulfate, TDS, selenium, fluoride, and nitrate compete with arsenic for adsorption sites and can shorten run length. Suspended solids and iron precipitation can clog the adsorption column. Systems containing high concentrations of these constituents may require pretreatment. A typical schematic of an ion-exchange system in presented in Fig. 6.12. The groundwater is first oxidized with chlorine (or an alternative oxidant) and then passed to a filter cartridge to remove silt and salt. If chlorine is used for oxidation, a dechlorination agent should be added before the resin to limit the rapid deterioration of the resin and the potential for NDMA formation in the resin. The dechlorination agent is expected to increase the concentration of TDS in the filtered water. The brine from regeneration usually contains high TDS and arsenic. Often it cannot be discharged or accepted by a wastewater treatment plant. In those cases when the residual cannot be discharged it is treated with iron salts. The resulting sludge containing high levels of arsenic is then disposed of in a landfill while the supernatant is treated in an evaporation pond.

6.12.9.2. Activated Alumina

Activated alumina is a granular media manufactured for the purpose of removing ions from water. It is prepared by dehydration of aluminum hydroxide at high temperature. It has high adsorptive capacity, and it is the most common arsenic removal process for municipal-scale treatment of arsenic. Several studies have reported high arsenic removal efficiencies. A pilot study has reported effluent arsenic levels of <0.01 mg/L (Health Canada, 2006; Simms and Azizian, 1997). Activated alumina preferentially adsorbs arsenate over sulfate and other major ions; therefore, it is able to achieve long run lengths. The performance is sensitive to pH, which must be kept in the 5.5 to 6 range for optimum performance. This means that acid must be added upstream of the activated alumina column. After treatment, the pH must be adjusted before releasing into the water distribution system to avoid corrosion problems. It is possible to regenerate the media, but regeneration is incomplete and requires the addition of a strong base followed by acid neutralization. Replacement with new media and landfilling of the exhausted media is the other alternative. Operationally, the safest configuration is to have two columns operating in a series, with the first column removing the bulk of the arsenic and the second column providing a polishing step. When the medium in the first column is exhausted, it is replaced, and the two columns are switched using the first column for the polishing step. In this way, the column with the fresher media is always the last step, making the event of a breakthrough less likely. The waste produced from activated alumina processes includes the water caustic solution used in the regeneration process and the



arsenic removed from the media. Typically, the combined volume of these waste streams is less than 1 percent of the processed water.

6.12.9.3. RO Membrane Technologies

RO is effective for removing both positive and negative forms of arsenic. However, because RO is nonselective in its rejection of contaminants and fouling, it requires frequent backwashing and water rejection can be high (on the order of 20 to 25 percent). The waste of a large portion of water may be an issue in water-scarce regions, which may prompt the implementation of more efficient, although more costly, recovery processes.

Although RO is included among the BATs for its high removal efficiency, based on costs of treatment and brine disposal, it is unlikely that it would be installed exclusively for arsenic removal.

6.12.9.4. Modified Coagulation/Filtration

Arsenic can be removed by coagulation with both aluminum and ferric hydroxide coagulants. Adsorbed arsenic is removed by precipitation or/and filtration. The optimal pH for adsorption is around 7 for aluminum and up to 8 for ferric hydroxides. Silica is known to compete with arsenic for adsorption onto ferric hydroxides particularly when pH is above 7. High concentrations of TOC may also reduce arsenic removal capabilities. The disadvantage of this treatment process includes the production of large amounts of arsenic-contaminated sludge that, depending on the arsenic concentration, might need to be disposed of in a hazardous waste landfill and large settling tanks. Typically, groundwater systems are not designed for particulate removal and use small clarification facilities. Because of high costs, it is unlikely for this process to be installed solely for the removal of arsenic.

6.12.9.5. Modified Lime Softening

Arsenic is effectively removed by the lime-softening process as long as the pH is high enough to precipitate $Mg(OH)_2$ (normally 10.5 or higher). As per conventional treatments, the production of arsenic-contaminated sludge is a disadvantage and the selection of lime softening solely for arsenic removal is not cost effective.

6.12.9.6. Electrodialysis Reversal

EDR can, in some instances, produce effluent water quality comparable to that of RO. A major advantage of EDR is that the system is fully automated and it requires limited operator attention, and no chemical addition. However, EDR systems are, in general, more expensive than other membrane systems including RO. Furthermore, typical recovery rates are low: in the 70 to 80 percent range. This may be a factor preventing the use of this technology in regions where water is scarce. Other options are more cost effective and have much smaller waste streams.

6.12.9.7. Oxidation/Filtration

This removal process is based on the coprecipitation of arsenic with iron during iron removal. The presence of a sufficiently high concentration of iron is critical to obtain significant removal of arsenic. One study conducted by Subramanian and coworkers (1997) suggested that a 20:1 iron to arsenic ratio result in lower removal rates. For a lower 7:1 iron to arsenic ratio, a 50 percent arsenic removal rate was reported. Competition with other ions is not a major factor limiting the effectiveness of this technology. Although a preoxidation step is not needed, when the arsenic is present as arsenic III, sufficient contact in an aerobic environment needs to be provided for the conversion to arsenic V. This USEPA suggests that this inexpensive technology may be appropriate for systems treating raw water with high iron and low arsenic concentrations. Table 6.10 summarizes the maximum arsenic removal rates as reported by the USEPA in the final version of the Arsenic Rule in 2001 (US Federal Register, 2001).



Additional technologies not listed as BAT by the USEPA but reputed to be effective to some extent for arsenic treatment are described below.

Table 6.10 USEPA Best Available Technologies for Arsenic Removal and Removal Rates for Arsenic V (Preoxidation May Be Required)

Treatment Technology	Maximum Percent Removal
Ion exchange (sulfate ≤50 mg/L)	95
Activate alumina	95
Reverse osmosis	>95
Modified coagulation/filtration	95
Modified lime softening (pH > 10.5)	90
Electrodialysis reversal	85
Oxidation/filtration (20:1 iron:arsenic)	80
Source: US Federal Register, 2001.	

6.12.9.8. Coagulation/Membrane Filtration

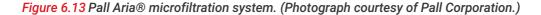
The use of small doses (less than 10 mg/L) of ferric coagulant (added inline) in combination with MF or UF membranes removes arsenic. Arsenic adsorbs to the small floc formed by the ferric coagulant and then is filtered with the membrane. Typically, ferric dosages range between 5 and 20 mg/L, depending on the quality of raw water. This method reduces the amount of sludge produced, as there is no need for a large settleable floc to be formed. Other advantages of this technology include low chemical dosages and a smaller footprint compared to conventional treatment. Similar to conventional treatment, a pH above 8 or the presence of high levels of silica or TOC can reduce the arsenic removal performance of this technology. Membranes require occasional cleaning with caustic soda and citric acid to remove dissolved organic matter that may clog pores and reduce the efficiency of filtration. The frequency of the cleaning depends on the quality of the water to be treated. Typically, membranes must be backwashed to remove the ferric—arsenic precipitate that collects on the surface on the membrane. Backwash is, typically, started every 30 to 60 minutes, depending on the type of membrane and ferric dose. This process has two waste streams: the spent chemical-cleaning solution, which does not contain significant levels of arsenic but high concentrations of sodium and organic carbon, and the spent backwash water, which contains high concentrations of arsenic. The first stream is commonly discharged directly to the sanitary sewer. The second can be discharged to the sewer (if TDS concentrations are low) or decanted and returned to the head of the plant. The concentrated solids from the decanted can be normally discharged in the sanitary sewer.

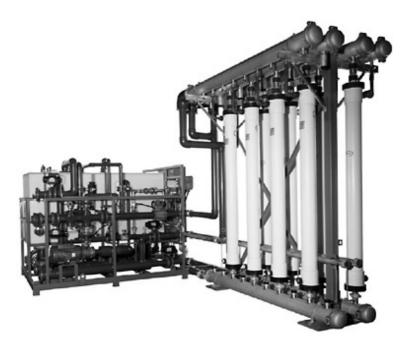
Pilot tests conducted at Albuquerque, New Mexico, on iron coagulation followed by a direct MF showed that this process can effectively remove arsenic V and yield arsenic concentrations consistently below 2 mg/L (Clifford et al., 1997). Although there is extensive full-scale experience of coagulation and MF as separate processes, there are no full-scale applications of the combined coagulation/MF process (USEPA, 2000).

A full-scale application of this technology is provided by the Pall Aria [®] MF systemr (Fig. 6.13). To optimize arsenic removal, ferric chloride is added to the water before filtration. Arsenic anions are adsorbed onto positively charged ferric hydroxide



particles, which are then removed by MF. Backwash is used to remove the ferric hydroxide-arsenic cake from the membrane surface. One of such systems has been installed for the Fallon





Paiute-Shoshone Tribe in Fallon, Nevada, to comply with the USEPA arsenic MCL. It is reported that at this location the Pall Aria $^{(0)}$ system is able to reduce arsenic from concentrations as high as $160\mu g/L$ to undetectable levels, less than 2 ppb (Wachinski et al., 2006).

6.12.9.9. Granular Ferric Hydroxide

Granular ferric hydroxide (GFH) is a very promising technology based on arsenic adsorption onto iron-based granular media. It can effectively remove arsenic up to pH 8. Preoxidation is not required. High levels of silica and phosphate reduce arsenic removal through this process. The medium is contained in a filter vessel. Similarly to the operation of a conventional filter, water enters the filter from the top and is filtered through the media bed. As water is being filtered, the amount of arsenic being adsorbed onto the media increases. When the adsorptive capacity of the media is used up, the arsenic concentration in the treated water increases to a breakthrough value. At or before breakthrough, the operator must switch the operation to another filter with fresh media. It is possible to regenerate GFH with caustic; however, because of potential headloss issues, it may be more suitable for one-time use (US Federal Register, 2001). The simplicity of this process makes it very attractive for small installations and single-well applications.

6.12.9.10. Nanofiltration

NF membranes primarily reject arsenate by electrostatic repulsion. They do not foul as easily and can be operated at higher recovery than RO. Sato et al. (2002) compared the performance of rapid sand filters and NF for arsenic removal. When arsenic concentration in the raw water exceeded 50 μ g/L, NF achieved 95 percent arsenic V removal and 75 percent arsenic III removal without chemical addition. Rapid sand filtration was ineffective for the removal of soluble arsenic III. Sato et al. (2002) suggested that NF membrane can be used with any type of water for arsenic removal.

6.12.9.11. Greensand Filtration



In manganese greensand filtration, the arsenic contained in the raw water is oxidized as it passes through the filter and is deposited onto the filter media. Similarly to oxidation/ filtration, removal is dependent on water quality and particularly on the iron-to-arsenic ratio (Subramanian et al., 1997). In laboratory studies conducted by Subramanian et al. (1997) using tap water spiked with high concentrations (200 mg/L) of arsenic III, removal increased from 41 percent to more than 80 percent as the Fe/As ratio increased from 0 to 20. Sulfate and TDS did not seem to strongly affect arsenic removal. A full-scale study showed arsenic removal rates ranging between 90 and 98 percent (an average effluent arsenic concentration of $2.2 \mu g/L$), with an influent arsenic concentration of $54 \mu g/L$ for the greensand system in Village Kelliher, Saskatchewan, Canada (Magyar, 1992). This water was characterized by a total iron concentration of 1.79 mg/L (a 33 Fe/As ratio) and an average pH between 7.2 and 7.3. Potassium permanganate was added before the filters at a feed rate of about 2.3 mg/L. The filters were operated at a continuous pressure between 4.0 and 5.5 psig and a flow rate of 76 gpm (4.8 L/s). The Guideline Technical Document on Arsenic prepared by Health Canada (2006) suggests that this technology is appropriate for systems that do not require high arsenic removal, because of the high iron to arsenic ratio that is required to obtain high arsenic removal rates. Furthermore, because of its simplicity of operation and relatively low cost, it may be attractive for installations in remote areas and developing countries.

6.12.9.12. Additional Technologies

Additional technologies that have received some attention for their arsenic removal capabilities include the following:

- Slow sand filters: removal without preoxidation of up to 96 percent from groundwater containing 14.5 to $27.2\mu g/L$ arsenic (Pokhrel et al., 2005).
- Biological activated carbon filter: removal of up to 97 percent of arsenic without preoxidation and 99 percent after ozone addition (Pokhrel et al., 2005).
- Nano-sized polymer beads: 100 percent removal from Idaho groundwater at pH greater than 7 and in the presence of significant concentrations of silica in experiments conducted by the Idaho National Laboratory (Patel-Predd, 2006).
- Titanium-based media: the Dow Chemical Company manufactures the ADSORBSIA™ GTO™, a granular titanium oxide media designed with strong affinity for arsenic, lead, and other heavy metals.
- Synthetic ceramic materials: Kinetico Inc. of Newbury, Ohio, has patented the Macrolite[®] pressure filtration process based on a ceramic media designed tor remove arsenic.

6.12.9.13. POU and POE Treatment Devices for Arsenic Removal

A variety of technologies can be adapted to POE/POU devices to remove arsenic on the residential and commercial scale. These types of devices are affordable and can remove arsenic from drinking water to concentrations below 0.010 mg/L. Before selecting a POE/POU device, the groundwater should be tested to determine the concentrations of arsenic, and substances such as competing ions (e.g., fluoride, iron, sulfate, and silica) and organic matter, which could hinder arsenic removal. Furthermore, because most technology cannot effectively remove arsenic III, an oxidation step should be implemented to convert arsenic III to arsenic V (US Federal Register, 2001).

The most common POE/POU devices available on the market for arsenic removal are RO and steam distillation (Health Canada, 2006), but other their types of systems based on alternative technologies such as adsorption are also becoming more common. RO is easy to service and is affordable. The main disadvantage is the significant volume of reject water that is produced during treatment. Distillation can remove virtually all arsenic in drinking water. It is more complex than RO to operate and service. It is normally used in commercial-scale applications. It should be noted that both RO and distillation remove all minerals including those that are beneficial such as calcium and magnesium. Adsorption/filtration using media such as ferric hydroxide, aluminum, and titanium oxide is becoming increasingly popular for arsenic removal in small water treatment systems because of its relatively simple O&M.



6.12.9.14. Developing Countries' Systems and Applications

High arsenic levels in the alluvial aquifer underlying Bangladesh and India have been recognized as a major environmental and public health problem. Al-Muyeed and Afrin (2006) report that, in most of Bangladesh, arsenic in groundwater has been found to be higher than 0.05 mg/L. In many instances, high iron and arsenic levels have been found to coexist (Al-Muyeed and Afrin, 2006), and groundwater in approximately 65 percent of Bangladesh is characterized by high iron content above 2 mg/L. Al-Muyeed and Afrin (2006) also noted that, with the exception of a few cities and towns, centralized water treatment systems are rare, and a large part of the population is served by individual or community tube-wells. Therefore, the short-term solution of this environmental problem depends on the development of low-cost technologies that can be implemented at the community or household level.

Al-Muyeed and Afrin (2006) conducted an investigation on the efficiency of conventional iron removal plants for arsenic removal operating in small communities in Bangladesh. These systems are typically constructed, including aeration, sedimentation, and filtration steps in small units. The field survey of 60 community plants showed removal rates between 60 and 80 percent for 60 percent of the installations and less than 60 percent for 40 percent of the installations. The pH of water strongly affected arsenic removal, with increasing rates corresponding to increasing pH. For pHs above 7.0, arsenic removal was, in most cases, in excess of 70 percent. As previously mentioned, the removal of arsenic is strongly correlated with the removal or iron (Subramanian et al., 1997), and relatively high arsenic removal rates in excess of 70 percent were observed when Fe concentrations were in the 6 to 8 mg/L range.

A variety of simple POU technologies have been suggested and used for the treatment of contaminated water in rural communities in Bangladesh. Despite their limitations from a technological perspective, they are extremely valuable tools for protecting public health in less affluent communities. Among the most popular and effective technologies are the 3-Kolshi filter and the SONO [®] filter.

6.12.10. Trace Metals and Inorganic Compounds

A variety of trace metals and inorganic compounds can be found in groundwater. The most common treatment removal options for several of these contaminants are summarized in Table 6.11.



Table 6.11 Common Treatment Removal Technologies for Trace Metals and Inorganic Compounds

Compound	Treatment Technology
Antimony	RO
Asbestos	Chemical coagulation/filtration
Barium	Softening and ion exchange
Beryllium	Coagulation/filtration, lime softening, activated alumina, RO, and ion exchange
Cadmium	Chemical coagulation, lime softening, and RO
Chromium	GAC, PAC, coagulation at lower pH, oxidation, and lime softening
Copper	Coagulation at lower pH
Cyanide	Chemical and biological degradation
Lead	RO, distillation, customized GAC, chemical precipitation, and lime softening
Mercury	Coagulation at lower pH and coagulation/filtration
Nickel	Lime softening and RO
Selenium	Coagulation/filtration, lime softening, activated alumina, ion exchange, and RO
Silver	Coagulation/filtration and lime softening
Thallium	Ion exchange and activated alumina
Zinc	Conventional treatment
Fluoride	Activated alumina, coagulation, and lime softening

6.13. Drinking Water Treatment Costs

The cost of water treatment projects is highly variable and difficult to predict because the final cost of facilities depends on site-specific factors such as plant capacity, design criteria and selection of treatment processes, raw water quality, site characteristics, climate, land costs, regulation and permit requirements, status of national and local economic conditions, and cost of contractors.

In the United States, the cost of construction for a basic groundwater treatment plant (including well construction, chemical addition and filtration for iron and manganese removal, pumping, storage, and disinfection facility) and disinfection is in the US \$250 to 500/m ³ (\$1.00 to 2.00/gal) range, depending on plant size and local conditions. As discussed in previous sections, additional process units may be required to achieve other treatment objectives.

In terms of individual treatment technologies, costs for conventional clarification, lime softening, and conventional media filtration are, to a large extent, due to construction and land requirements; therefore, they vary from one location to another. Costs for other process units are more dependent on equipment cost. Indicative average capital costs for various technologies used in groundwater treatment and O&M for some of the individual process units that are often used in



groundwater treatment are presented in Table 6.12. Costs are calculated for installation in the United States, and they include site work, electrical work and instrumentation, contractor overhead, and profit. They do not include land requirements, pretreatment, and sludge disposal options, as these factors are site specific and should be determined for each location.

Table 6.12 Average Costs for Process Units Typically Used in Ground water Treatment (Continued)

	Capital C		t (Including Construction Costs) (\$/m³) (\$/1000 gal)		O&M (\$/m³) (\$/1000 gal)		
Process Unit	Small Plant <4000 m ³ /d (<1 mgd)	Medium Plant 4000–40,000 m ³ /d (1–10 mgd)	Large Plant >40,000 m ³ /d (>10 mgd)	Small Plant <4000 m³/d (<1 mgd)	Medium Plant 4000–40,000 m³/d (1–10 mgd)	Large Plant >40,000 m ³ /d (>10 mgd)	
Oxidation							
Chlorine	14 (53)	5 (19)	1.3 (4.9)	0.021 (0.080)	0.006 (0.021)	0.001 (0.004)	
Permanganate	15 (55)	4.3 (16.4)	1.3 (4.9)	0.024 (0.090)	0.013 (0.050)	0.001 (0.004)	
Chlorine dioxide	95 (360)	15 (56)	6.3 (24)	0.021 (0.080)	0.005 (0.020)	0.003 (0.010)	
Ozone (5 mg/L dose)	33 (125)	21 (78)	10 (36)	0.026 (0.100)	0.007 (0.026)	0.002 (0.007)	
Aeration (packed tower)	84 (318)	40 (150)	12 (45)	0.011 (0.040)	0.005 (0.020)	0.004 (0.015)	
Clarification							
Conventional	284 (1075)	73 (275)	30 (114)	0.001 (0.004)	0.013 (0.050)	0.003 (0.010)	
Upflow	140 (528)	63 (237)	27 (101)	0.023 (0.090)	0.008 (0.030)	0.003 (0.010)	
Media filtration							
Rapid sand	268 (1014)	146 (551)	50 (190)	0.050 (0.190)	0.018 (0.070)	0.018 (0.070)	
Greensand	269 (1018)	147 (556)	52 (198)	0.050 (0.190)	0.018 (0.070)	0.018 (0.070)	
Pressure	455 (1725)	89 (340)	83 (314)	0.016 (0.060)	0.034 (0.013)	0.018 (0.070)	
Softening							
Lime softening	205 (777)	64 (241)	41 (155)	0.026 (0.100)	0.011 (0.040)	0.001 (0.005)	
lon exchanger softener	201 (761)	90 (339)	55 (208)	0.021 (0.080)	0.006 (0.022)	0.004 (0.015)	

Table 6.12 Average Costs for Process Units Typically Used in Ground water Treatment (Continued)

	Capital Cost (Including Construction Costs) (\$/m³) (\$/1000 gal)			0&M (\$/m³) (\$/1000 gal)		
Process Unit	Small Plant <4000 m ³ /d (<1 mgd)	Medium Plant 4000–40,000 m ³ /d (1–10 mgd)	Large Plant >40,000 m ³ /d (>10 mgd)	Small Plant <4000 m ³ /d (<1 mgd)	Medium Plant 4000–40,000 m³/d (1–10 mgd)	Large Plant >40,000 m ³ /d (>10 mgd)
Membrane filtration						
MF/UF	302 (1145)	183 (691)	167 (633)	0.40 (1.5)	0.066 (0.250)	0.028 (0.110)
RO/NF	957 (2623)	507 (1920)	320 (1210)	4 (15)	1.3 (4.8)	0.276 (0.015)
Electrodialysis reversal	172 (650)	121 (456)	102 (385)	0.150 (0.580)	0.120 (0.470)	0.250 (0.940)
GAC	819 (3101)	599 (2266)	553 (2093)	0.558 (2.113)	0.390 (1.490)	0.231 (0.873)
lon exchange	14 (54)	9.8 (37)	6.7 (25)	0.05 (0.19)	0.036 (0.14)	0.025 (0.009)
Disinfection						
Chlorine	19 (71)	6.7 (25)	2.6 (9.9)	0.025 (0.090)	0.007 (0.026)	0.001 (0.004)
Ozone (5 mg/L)	44 (166)	27 (103)	17 (64)	0.026 (0.100)	0.009 (0.034)	0.002 (0.008)
Chloramines	26 (98)	9.2 (35)	3.2 (12)	0.0004 (0.0016)	0.0004 (0.0016)	0.0004 (0.0016)
Ultraviolet radiation	44 (165)	29 (111)	23 (87)	0.090 (0.034)	0.03 (0.007)	0.003 (0.012)
Corrosion control	30 (113)	6.1 (23.2)	2.8 (11)	0.004 (0.015)	0.0024 (0.009)	0.001 (0.004)
(lime or soda ash)						

Sources: USEPA, 2005b; Culp/Wesner/Culp, 2000; Cotton et al., 2001.

Table 6.13 Indicative Prices of Common Water Treatment Chemicals in the United States



Chemical	Use	Cost in \$/kg (\$/lb)
Chlorine gas	Disinfection/oxidation	0.23 (0.5)
Sodium hypochlorite 12.5%	Disinfection/oxidation	0.36 (0.8) as free Cl ₂
Ammonia, anhydrous	Chloramines formation	0.18 (0.4)
Ammonia, aqueous	Chloramines formation	0.23 (0.5)
Liquid oxygen (LOX)	Ozone production	0.06 (0.13)
Sodium chlorite (NaClO ₂) 80%	Chlorine dioxide production	1.14 (2.5)
Potassium permanganate 80%	Oxidation	1.14 (2.5)
Aluminum sulfate (alum), dry	Coagulation	0.05-0.1 (0.1-0.2)
Ferric sulfate, dry	Coagulation	0.07-0.08 (0.15-0.18)
Ferric chloride, dry	Coagulation	0.07-0.08 (0.15-0.18)
Ferrous sulfate, dry	Coagulation	0.07-0.08 (0.15-0.18)
PACI, liquid	Coagulation	0.05 (0.11)
Anthracite coal	Filter media	0.07 (0.15)
Cationic polymer	Coagulation aid	0.3 (0.7)
Anionic polymer	Flocculation, filter aid	1.14 (2.5)
Sulfuric acid	pH control	0.03 (0.06)
Sodium chloride, salt	Hypochlorite production and ionic exchange regeneration	0.01 (0.03)
Lime, quick	Softening, lime precipitation, and pH control	0.02 (0.05)
Lime, hydrated	Softening, lime precipitation, and pH control	0.02 (0.06)
Caustic soda, dry	pH control	0.07-0.08 (0.15-0.18)
Soda ash, dry	pH control	0.07 (0.15)
Activated carbon, granular	Removal of dissolved contaminants, T&O compounds	0.45 (1.0)
Powdered activated carbon	Removal of dissolved contaminants, T&O compounds	0.3 (0.7)
Carbon dioxide, liquid	Recarbonation	0.08 (0.17)
Citric acid	Membrane cleaning	0.36 (0.8)
Hydrofluosilicic acid	Fluoridation	0.1 (0.2)
Phosphoric acid	Corrosion control	0.2 (0.45)



Chemical	Use	Cost in \$/kg (\$/lb)
Zinc orthophosphate, liquid	Corrosion control	0.45 (1.0)

Water treatment chemicals represent a major component of the cost of treatment. Chemicals used in drinking water should be high-grade food additive class or approved by the local regulatory agencies (Kawamura, 2000). Table 6.13 provides indicative prices (for the US market) of most chemicals commonly used in water treatment and their uses. In addition to price, other factors that should be considered in the selection of a specific chemical include appropriateness, supply reliability, sludge formational and disposal costs, possible effects on other process units, environmental impact, dosing and maintenance issues, and safety.

Finally, a variety of coagulant aids derived from natural products are available for the treatment of drinking water. They include adsorptive clays (e.g., bentonite and fuller's earth) and limestone to improve the coagulation of high-color or low-turbidity sources, and a variety of natural polyelectrolyte coagulant aids. The price of these chemicals tends to be low, although dosage requirements tend to be high. Because of their low cost and local availability, they have been mainly used in developing countries.

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