CHAPTER 4

WATER TREATMENT AND PURIFICATION

This chapter describes water treatment methods used to partially remove and replace various impurities from a feedwater stream, water-conditioning additives used to neutralize impurities and inhibit corrosion, and pure water systems used to remove all impurities from the feedwater to a level at or below limits desired by the end user.

Information is presented on basic water chemistry, impurities found in water, water analysis, and impurity measurement. Also discussed are general selection criteria for the removal or reduction of specific impurities from water. Separate sections cover water-conditioning systems for boiler feedwater, water-conditioning systems for cooling water, and the generation of purified water.

For purposes of discussion only, the term *water treatment* is intended to mean only the removal and/or replacement of undesired impurities in feedwater with more desirable impurities. The resultant water is not pure. *Water conditioning* is intended to mean the addition of chemicals to water for the purposes of inhibiting corrosion and neutralizing undesirable impurities. *Pure water systems* is intended to mean the production of water pure enough for pharmaceutical and laboratory applications. The explanations and definitions given are simplified ones.

CODES AND STANDARDS

There are many codes and standards that apply to various systems. Among them are:

1. Potable water treatment shall comply with the 1986 Safe Drinking Water Act and Amendments.
2. Potable water treatment shall comply with EPA technologies describing contaminant removal.
3. Pure water treatment shall comply with the following, depending on the purity of the water desired:

a. CAP and ASTM reagent-grade water
b. USP standards for water purity
c. AAMI standards
d. NCCLS standards
e. SEMI and ASTM electronics-grade water standards (outside the scope of this handbook)

BASIC WATER CHEMISTRY

Water to be treated is known variously as raw water, feedwater, or source water. Water that has been treated is known as treated water, product water, or solute. Impurities that dissolve in water are called electrolytes. The dissolved impurities dissociate (separate) to form negatively and positively charged atoms called ions. The positively charged atoms are called cations because they migrate to the cathode electrode; the negatively charged atoms are called anions because they migrate to the anode electrode. The ions in solution act almost independently. For example, magnesium sulfate dissociates to form positive magnesium ions and negative sulfate ions. Ions are often referred to as salts in reverse osmosis water production.

When a compound dissolves in water, the molecules of the compound separate, disperse among the molecules of water, and then are held in suspension. When the solubility limit is reached, those same compounds become suspended solids because there is no chemical reaction. Dissolved materials cannot be removed by filtration.

Some types of liquids cannot be dissolved. They break down into extremely small particles and then disperse into water, but do not dissolve. These liquids are called immiscible liquids, and the resulting small particles are known as colloids. Colloidal material is composed of suspended particles at the upper end of the size range for ions and molecules, from 0.001 to 1.0 μm. Other liquids, such as oil and grease, cannot separate into smaller particles and become dispersed, but simply remain in suspension. If they are lighter than water, they float on top. If heavier, they sink below the surface.

All acid compounds in water chemistry consist of hydrogen combined with an acid radical. Since the acid radical moves around as a unit, it is convenient to view an acid radical as an integral anion unit. When a metal radical and an acid radical combine, they form a class of chemicals called salts. When a metal cation and a hydroxide anion combine, a base results.

The valence of any element is the measure of its chemical combining power compared to that of a hydrogen atom, which has the assigned value of 1. An element with a valence of $+2$ can replace two hydrogen atoms in a compound; with a valence of -2, it can react with two hydrogen atoms. When atoms combine to form compounds, a cation atom must combine with an anion atom and, in addition, the valences of the two basic elements must be equal in order to form the compound.

Most of the basic chemical reactions in water treatment consist of rearranging cation and anion atoms using their valences. As can be seen in Table 4.1, hydrogen has a valence of one and sulfate has a valence of two. When combined to form sulfuric acid, two hydrogen atoms are required to form the combination, resulting in the formula H_2SO_4. The chief exception is the case where carbonates and bicarbonates are destroyed by heating or aeration, giving off carbon dioxide.

The term *equivalent weight* is the weight in pounds of any element that could combine with 1 pound of hydrogen. Since the valence of an element is proportional to its combining power, the equivalent weight is based on its valence. This is illustrated in Table 4.1.

TABLE 4.1 Important Elements, Acid Radicals, and Acids in Water Chemistry

Element	Symbol	Atomic weight	Valence	Equivalent weight
Aluminum	Al	27.0	3	9.0
Barium	Ba	137.4	2	68.70
Calcium	Ca	40.1	2	20.05
Carbon	C	12.0	Variable	—
Chlorine	Cl	35.46	Variable	35.46
Fluorine	F	19.0	1	19.0
Iron (ferrous)	Fe''	55.8	2	27.9
Iron (ferric)	Fe'''	55.8	3	18.6
Hydrogen	H	1.0	1	1.0
Magnesium	Mg	24.3	2	12.15
Nitrogen	N	14.0	Variable	—
Potassium	K	39.1	1	39.1
Oxygen	O	16.0	2	8.00
Phosphorus	P	31.02	Variable	—
Sodium	Na	23.0	1	23.0
Sulfur	S	32.0	Variable	—
Silicon	Si	28.06	4	7.01

Acid radicals	Formula	Molecular weight	Valence	Equivalent weight
Bicarbonate	HCO_3	61.0	1	61.0
Carbonate	CO_3	60.0	2	30.0
Chloride	Cl	35.46	1	35.46
Nitrate	NO_3	62.0	1	62.0
Hydroxide	OH	17.0	1	17.0
Phosphate	PO_4	95.0	3	31.66
Sulfite	SO_3	80.0	2	40.0
Sulfate	SO_4	96.06	2	48.03

Acid	Formula	Molecular weight	Equivalent weight
Carbonic acid	H_2CO_3	62.0	31.0
Hydrochloric acid	HCl	36.46	36.46
Phosphoric acid	H_3PO_4	98.0	32.67
Sulfuric acid	H_2SO_4	98.1	49.05
Sulfurous acid	H_2SO_3	82.1	41.05

Miscellaneous compounds	Formula	Molecular weight	Equivalent weight
Aluminum hydroxide	$Al(OH)_3$	78.0	26.0
Calcium bicarbonate	$Ca(HCO_3)_2$	162	81.0
Calcium carbonate	$CaCO_3$	100	50.0
Calcium sulfate	$CaSO_4$	136	68.0
Carbon dioxide	CO_2	44.0	22.0
Ferric hydroxide	$Fe(OH)_3$	107	35.6
Magnesium carbonate	$MgCO_3$	84.3	42.1
Magnesium hydroxide	$Mg(OH)_2$	58.3	29.1
Magnesium sulfate	$MgSO_4$	120	60.1
Sodium sulfate	Na_2SO_4	142	71.0

WATER IMPURITIES

Natural or source water is never pure. Water picks up impurities as it comes into contact with the ground or, when percolated through the earth, mineral formations. It also contains dissolved gases and dust picked up by rain, snow, and hail or by surface water in contact with the air above the water level. Water is classified as surface water when it comes from sources such as lakes and rivers and as ground water when it comes from streams, wells, or other aquifers originating underground.

SUSPENDED MATTER (PARTICULATES)

Turbidity

Turbidity is a general term used to describe any form of insoluble matter, or suspended solids, suspended in water. Color is often used to describe turbidity and may be used when referring to water containing decaying vegetation. However, turbidity is used most often when referring to mineral particulates, such as silt, that are usually the most plentiful substances in the water. Other commonly occurring impurities are liquids, such as oil, and the residue caused by decaying vegetation. Coarse particles that settle rapidly when water is standing are referred to as sediment; fine particles that remain in suspension are called silt.

Microorganisms

Microorganisms are bacteria and viruses. They are living forms of particulate matter. Their unusual physiology allows them to grow and multiply in water containing only trace levels of nutrients. The presence of these nutrients in untreated water is an indicator of the presence of microorganisms (if the temperature is favorable for their growth). Although microorganisms are suspended solids, the treatment required for their removal or neutralization puts them in a separate category.

Pyrogens cause fever, and pathogenic organisms (such as leageonella) cause diseases of any kind. Endotoxins, which are fragments derived from the cell walls of gram-negative bacteria, are considered the most important and widely occurring group of pyrogens. Other organic growths include algae (a primitive form of plant life), fungi (plants that lack the chlorophyll required for photosynthesis), and bacteria that exhibit both plant and animal characteristics. Bacteria are further subdivided into slime bacteria, which secrete slime; iron bacteria, which thrive on iron; sulfate-reducing bacteria, which live by consuming sulfate and converting it to hydrogen sulfide gas; and nitrifying bacteria, which use ammonia and whose byproduct results in the formation of nitric acid.

Several methods of measurement are used, including viable count assays, direct count epifluorescent microscopy, scanning electron microscopy, and biochemical techniques. The most common means of measuring bacterial contamination is the viable count method, in which the water being measured is passed through a sterile nutrient medium, and the number of colonies appearing on the medium is counted after a period of time is allowed for growth. These are called colony forming units or CFUs. Endotoxins are measured in endotoxin units per milliliter (EU/mL). A popular form of measurement for endotoxins is the limulus amoebocyte lysate

(LAL) test, in which a blood extract of the horseshoe crab becomes turbid in the presence of bacterial endotoxins. This detection technique uses optical density (turbidity level) measured over a period of time.

Other Organisms

This form of impurity is also applied to larger living things such as clams, mussels, and their larvae. They tend to clog water inlets of salt- and fresh-water and may also find their way into the piping system of a facility. See the section on nonpotable water systems for further discussion.

DISSOLVED MINERALS AND ORGANIC SUBSTANCES

Organic Substances

Dissolved organic substances typically found in water include both manmade and natural substances. Manmade impurities include herbicides, pesticides, trihalomethanes, surfactants, and detergents. Naturally occurring impurities include lignins, tannins, humic and fulvic acid, and other biodecomposition products.

Alkalinity

All natural water contains some alkalinity. Alkalinity is a measure of the quantity of dissolved earth minerals in water, and reflects the water's ability to neutralize acids. It is mainly the sum of the carbonate, bicarbonate, and hydroxide ions in water, with borate, phosphate, and silicate ions partially contributing to the total. It is reported as the ppm equivalent of calcium carbonate. Alkalinity is regarded as the most important characteristic in determining the scale-forming tendency of water.

Alkalinity is measured using two end-point indicators. The phenolphthalein alkalinity, or P alkalinity, measures the strong alkali in the solution. The methyl orange alkalinity, or M alkalinity, measures all of the alkalinity present in the solution. M alkalinity is often called total alkalinity because it also includes P alkalinity. Alkalinity is not a measure of pH.

Iron

The most common form of iron is ferrous bicarbonate. It is also considered a form of hardness of water. Iron causes problems with many ion exchange resins.

Magnesium

The most common forms are magnesium carbonate, magnesium bicarbonate, and magnesium chloride. These impurities tend to deposit scale on surfaces they come in contact with.

Silica

The three most common kinds of silica are soluble, colloidal, and particulate. Soluble silica is often referred to as reactive silica, and colloidal silica is sometimes called nonreactive or polymeric. The most common form in solution is silicon oxide; in suspension it is found as a fine colloid. These impurities tend to deposit a scale on surfaces they come in contact with and form a gelatinous mass on RO membranes.

Sodium and Potassium

Both elements form similar salts, with the three most common being sodium or potassium chloride, sodium or potassium carbonate, and sodium or potassium bicarbonate.

Chlorides and Sulfates

The most common forms are dissolved salts of sodium, potassium, calcium, and magnesium. These impurities tend to deposit a scale on surfaces they come in contact with.

Hardness

Hardness is the total amount of calcium, magnesium, iron, and other metallic elements that contribute to the ‘‘hard’’ feel of water. Carbonate, sulfate, and chloride salts of these elements are responsible for most of the scaling deposited on pipe walls and boilers. Generally accepted practice limits the term *hardness* to include only calcium and magnesium. Often, water is characterized in general terms by the amount of hardness, expressed in mg/L as $CaCO_3$, as follows:

Soft	0 to 75 mg/L as $CaCO_3$
Moderate	76 to 150 mg/L as $CaCO_3$
Hard	151 to 300 mg/L as $CaCO_3$
Very hard	Over 300 mg/L as $CaCO_3$

Trace Elements

Trace elements are present in very small quantities and are only considered problems if the amount is above an accepted level for the purpose for which the water is to be used. Examples are lead, cadmium, copper, barium, silver, lithium, zinc, chromium, mercury, arsenic, and selenium.

DISSOLVED GASES

The most common dissolved gases in natural raw water are oxygen, carbon dioxide, nitrogen, and hydrogen sulfide. In addition, water obtained from a potable water supply usually has chlorine and fluorides present, added for public health. Of increasing concern is the presence of radon gas in many water supplies obtained from wells.

Oxygen is the basic factor in the corrosion process and must be present for the corrosion of metals. Removal or reduction reduces the corrosiveness of the water.

For chlorine, no pretreatment is usually necessary for feedwater containing less than 1 ppm. When more than 1 ppm of chlorine is present, an activated carbon filter is recommended.

WATER ANALYSIS AND IMPURITY MEASUREMENT

GENERAL

Analyzing a water sample is the process of finding the quantity of various impurities present. In order to accomplish this, the quantities must be presented in a logical and understandable manner to allow for easy and practical interpretation. It is of utmost importance that the initial analysis of incoming water be accurate and contain a worst-case scenario and that the desired output quality be established prior to the selection of any treatment system.

The most accurate analysis of a water sample is done by laboratories specializing in this type of work. Sterile containers must be used and several samples must be taken over a period of time to ensure that peak readings and average values will be obtained. There are also many field tests that are not as accurate as laboratory tests but give an accuracy acceptable to the user.

The results of the analysis can be expressed in many ways. A common method is to report the concentration of ions in solution by the weight of an element or compound per liter of water, expressed as milligrams per liter of water (mg/L). Another method is expressed in parts per million (ppm), which can be expressed either by the weight of an impurity compared to the weight of water, abbreviated w/w (weight to weight), or by the volume of the impurity compared to the volume of water, abbreviated v/v. Other units are also used, such as grains per gallon (gpg) and equivalents per million (epm). mg/L differs from ppm in expressing a proportion in weight per volume. This finds specific use in analysis of saline waters. Where the specific gravity of a liquid is around 1, mg/L and ppm are equal. Grams per gallon (gpg) is a term used in the discussion of ion-exchange equipment capabilities, where 1 gpg = 17.1 ppm.

As previously explained, compounds break down into ions when dissolved. Although chemists can measure the amounts of each ion present in a sample, it is not practical to find the total amount of each compound that actually went into solution. In practice, the actual method of analysis measures ions only. Using the ionic form in measurement when reporting impurities makes it easier to interpret the results.

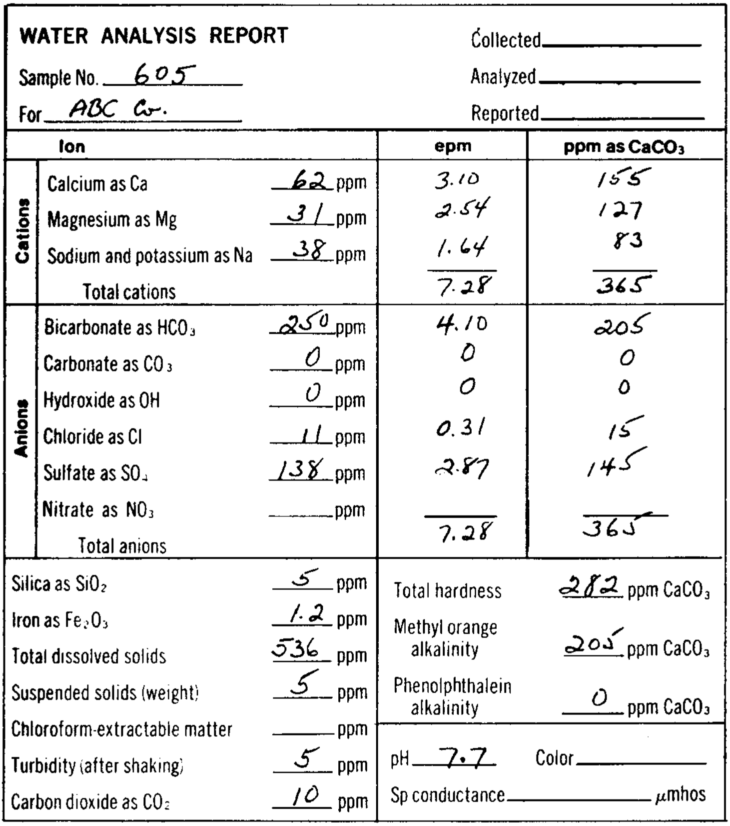
To further simplify reporting, it is desirable to reduce all ions present in solution to a common denominator. The common denominator is calcium carbonate. This is accomplished by comparing the equivalent weight of all ions present and expressing them as the ppm anion and cation equivalent of calcium carbonate. The main reason for this is that the molecular weight of calcium carbonate is 100 and its equivalent weight is 40. This method of expression is a widely accepted, but not universal, standard for reporting water analysis. Table 4.2 presents the conversion factors used for major impurities. Figure 4.1 illustrates a typical water analysis report indicating impurities in ppm, equivalents useful in calculating reacting chemicals, and a comparison of positive and negative ions.

pH

When alkalines (bases) are mixed in water, hydroxyl ions result. In a mixture of acid and water, hydrogen ions result. pH is a measurement of the hydrogen-ion

TABLE 4.2 Converting ppm of Impurities to ppm of Calcium Carbonate

Cations	Ionic ppm multiplier	Anions	Ionic ppm multiplier
Hydrogen	50.00	Hydroxide	2.94
Ammonium	2.78	Chloride	1.41
Sodium	2.18	Bicarbonate	0.82
Potassium	1.28	Nitrate	0.81
Magnesium	4.10	Bisulfate	0.52
Calcium	2.50	Carbonate	1.67
Ferrous	1.79	Sulfate	1.04
Ferric	2.69		
Cupric	1.57	Other	
Zinc	1.53		
Aluminum	5.55	Carbon dioxide	2.27
Chromic	2.89	Silica	1.67



WATER ANALYSIS REPORT

Sample No. 605
For ABC Co.

Collected
Analyzed
Reported

	Ion		epm	ppm as CaCO₃
Cations	Calcium as Ca	62 ppm	3.10	155
	Magnesium as Mg	31 ppm	2.54	127
	Sodium and potassium as Na	38 ppm	1.64	83
	Total cations		7.28	365
Anions	Bicarbonate as HCO_3	250 ppm	4.10	205
	Carbonate as CO_3	0 ppm	0	0
	Hydroxide as OH	0 ppm	0	0
	Chloride as Cl	11 ppm	0.31	15
	Sulfate as SO_4	138 ppm	2.87	145
	Nitrate as NO_3	ppm		
	Total anions		7.28	365

Silica as SiO_2	5 ppm	Total hardness	282 ppm $CaCO_3$
Iron as Fe_2O_3	1.2 ppm	Methyl orange alkalinity	205 ppm $CaCO_3$
Total dissolved solids	536 ppm	Phenolphthalein alkalinity	0 ppm $CaCO_3$
Suspended solids (weight)	5 ppm		
Chloroform-extractable matter	ppm		
Turbidity (after shaking)	5 ppm	pH 7.7	Color
Carbon dioxide as CO_2	10 ppm	Sp conductance	μmhos

FIGURE 4.1 Typical water analysis report.

concentration of a solution. Since the balance of hydroxyl (cation) and hydrogen ions (anion) must be constant, changes in one ion concentration produces a corresponding change in the other. The pH value is calculated from the logarithmic reciprocal of the hydrogen-ion concentration in water. The pH scale ranges from 0 to 14, with 0 being acid and 14 being alkaline. 7.0 is neutral. A change of one unit represents a tenfold increase (or decrease) in strength. pH is not a measure of alkalinity.

Specific Resistance

Specific resistance is a measure of the amount of electrolytes in water. It measures the ability of 1 cm^3 of a sample solution at a given temperature to resist the flow of an electrical current. It is based on the activity of the compounds, i.e., ionized salts, dissolved in water and varies with the temperature of the water. It is the most practical method of measuring impurities from a given sample. Resistance is given in ohms; pure water has a resistance of 18.3 megaohms (MΩ). Resistivity conversions are given in Table 4.3.

TABLE 4.3 Resistivity and Conductivity Conversion

Grains/gal* as $CaCO_3$	ppm as $CaCO_3$	ppm NaCl	Conductivity, μmho/cm	Resistivity, MΩ/cm
99.3	1700	2000	3860	0.00026
74.5	1275	1500	2930	0.00034
49.6	850	1000	1990	0.00050
24.8	425	500	1020	0.00099
9.93	170	200	415	0.0024
7.45	127.5	150	315	0.0032
4.96	85.0	100	210	0.0048
2.48	42.5	50	105	0.0095
0.992	17.0	20	42.7	0.023
0.742	12.7	15	32.1	0.031
0.496	8.5	10	21.4	0.047
0.248	4.25	5.0	10.8	0.093
0.099	1.70	2.0	4.35	0.23
0.074	1.27	1.5	3.28	0.30
0.048	0.85	1.00	2.21	0.45
0.025	0.42	0.50	1.13	0.88
0.0099	0.17	0.20	0.49	2.05
0.0076	0.13	0.15	0.38	2.65
0.0050	0.085	0.10	0.27	3.70
0.0025	0.042	0.05	0.16	6.15
0.00099	0.017	0.02	0.098	10.2
0.00070	0.012	0.015	0.087	11.5
0.00047	0.008	0.010	0.076	13.1
0.00023	0.004	0.005	0.066	15.2
0.00012	0.002	0.002	0.059	16.9
0.00006	0.001	0.001	0.057	17.6
none	none	none	0.055	18.3†

*Grains per gal = 17.1 ppm ($CaCO_3$).

†Theoretical maximum.

Specific Conductance

Specific conductance measures the ability of 1 cm^3 of a sample solution at a given temperature to conduct an electrical current. It is the reciprocal of the resistance, in ohms. Since it is the opposite of resistance, it is given the name mho, which is ohm spelled backwards. The actual conductance is so small it is measured in micromhos (μmho, one millionth of a mho). For example, at 70°F (19°C) demineralized water with ½ ppm dissolved salt has a conductance of 1 μmho. Pure water has a conductance of 0.036 μmho. Conductivity conversions are given in Table 4.3. Specific conductance in actual practice is normally measured by probes suspended in the stream of water.

Total Suspended Solids

This figure is the sum of all of the suspended material found in a water sample and is commonly measured in either parts per million (ppm, w/w), or milligrams per liter (mg/L). For all practical purposes, these two forms of measurement are equal to each other (1 ppm 1 mg/L).

Turbidity in water is classified by the size of the particulates in micrometers (1/1000 of an inch) and tested by a light interference method, known as nephelometric. This test compares the color of the water sample to a standard color scale, which indicates the total suspended solids based on this comparison. The most common reporting method is the nephelometric turbidity unit (NTU). The higher the number, the more turbid the water.

The NTU measures the color of a beam of light passed through a water sample. A common standard for potable water is the Standard Method for the Examination of Water and Wastewater by the American Public Health Service, which uses formazin as the standard for producing a known volume of turbidity. The standard color scale to which it is compared is derived from the platinum cobalt unit (PCU). Other methods used less frequently are the comparator tube determination using formazin, called the formazin turbidity unit (FTU), and the original test, the Jackson turbidity unit (JTU), named for the man who developed the standard candle used to compare the color of the candlelight through the sample to a color standard. The most accurate method of measuring solids is the gravimetric method, in which a known quantity of water is evaporated and the resulting solids weighed.

The most effective devices for removing turbidity are filters and strainers. The equipment chosen to accomplish this task depends for the most part on the size and type of solids to be retained. Other factors include materials composing the device, the nature of the raw water, flow rate requirements, particle removal target, initial and operating costs, and maintenance requirements. Filters and strainers are discussed in Chap. 3.

Total Dissolved Solids (TDS)

Often referred to as dissolved inorganics and mineral salts, TDS is the sum of all the dissolved minerals including chlorides, sulfates, and carbonates. Dissolved solids contribute to scale deposit and corrosion of piping and equipment. When dissolved in water, mineral salts form positively charged ions, mostly sodium and calcium, and negatively charged ions, mostly chlorides and sulfates.

Total Organic Carbon (TOC)

TOC is a measurement of the carbon level in water and is widely used to determine the level of contamination of water by organic compounds. These compounds contribute to corrosion, cause problems in manufacturing, and usually indicate the presence of endotoxins in water for pharmaceutical use.

The measurement is generally complicated and dependent on the expected level. For high levels, the organic compound is first converted to carbon dioxide which is then measured by infrared absorption. Gas stripping is required to remove other forms of carbon ions from dissolved mineral compounds. For PPB levels, photolytic oxidation is used and the resultant carbon dioxide measured.

Silt Density Index (SDI)

The SDI is a measure of the fouling potential of a feedwater source. Since colloids and other solids can be any size in the submicrometer range, there is no direct method to measure their concentration in feedwater. The SDI is found by passing the feedwater through a 0.45-μm rated Millipore filter at 30 psi (207 kPa), and then applying the following formula:

$$\text{SDI} = \frac{1 - \dfrac{t_1}{t_2} \times 100}{T} \tag{4.1}$$

where t_1 = initial time, in seconds, needed to collect 500-mL sample of water through fresh 0.45-μm filter, 47 mm in diameter
t_2 = time in seconds to filter and collect second 500-mL sample after exposing same filter as above for 15 min to flow of feedwater
T = total test time, in minutes, typically 15 min; for high SDI, T may be less

To obtain an accurate test, the filter should not have become more than approximately 74 percent plugged by the end of the elapsed time. If this figure is exceeded, the test should be repeated using a shorter overall elapsed time. A Millipore filter is the only membrane currently approved by the ASTM for determining the SDI. The higher the SDI, the greater potential for fouling.

Many manufacturers of RO cartridges recommend allowable SDI figures for feedwater. For hollow-fiber modules the maximum SDI is 3, and for spiral-wound modules the maximum SDI is 4. For continuous deionization, an SDI of 4 or less is recommended. In practice, when water has an SDI greater than 4, a 4-μm depth prefilter is recommended. In addition to the 4-μm filter, an additional 1-μm filter is recommended downstream. The use of a 4-μm filter in the feedwater stream is always recommended as a precaution against fouling regardless of the potential SDI.

DEPOSITS AND CORROSION

The contaminants previously discussed will cause piping system fouling by depositing materials on the walls of the pipe, thereby reducing the efficiency of the system and reducing the thickness of the pipe wall by corrosion, which will eventually cause failure of the piping system. Following is a brief discussion of these categories and treatment methods as they apply to most systems.

DEPOSITS

Scale and Sludge

Scale is a solid deposit on the walls of a pipe resulting from precipitation of dissolved solids in the fluid stream. Scale reduces heat transfer and interferes with the flow of water by increasing the friction of the fluid against the walls of the pipe. Boiler scale consists of calcium, magnesium, iron, and silica minerals. It is prevented by pretreating water before it enters the boiler to remove much of the scale-forming ingredients or by adding effective chemicals to feedwater to adjust pH, prevent corrosion, and prevent deposits from occurring.

Sludge is a sticky and adherent deposit in the feedwater, which results from the settling out of suspended matter from several sources. One source is an excess of iron, generally iron oxide (rust) and iron carbonate (a corrosion product). Other sources are mud, dirt, and clay that tend to collect and adhere in areas of low circulation. Sludge is prevented by filtering the incoming feedwater and adding chemical dispersants to keep the solids in suspension. They are removed by blowdown. Mud, dirt, and clay are rarely encountered except where the feedwater comes from surface sources.

Condenser scale deposits consist of calcium carbonate, calcium sulfate, or silica minerals when their concentrations exceed their solubility or their pH exceeds saturation, causing these minerals to come out of solution. This is prevented by controlling the pH, diluting the circulating water to prevent concentration, and adding chemicals to inhibit and prevent scale formation.

Biological Fouling

Microbiological fouling is caused by the growth of bacteria, algae, fungi, and other organisms. Their growth is helped by a favorable water temperature, favorable pH, and the presence of oxygen and food. Slime is the buildup of microbes and their waste products and also dust and other suspended matter.

Microbial control consists of sterilization, disinfection, and sanitation. Sterilization is defined as the lethal disruption of all bacteria, molds, and yeasts and the elimination of biofilm and spores. Numerically, it is a 12 log reduction in bacteria. Disinfection is a 6 log reduction of microbials. Sanitation is generally considered to be the killing of the vegetative organisms and it minimizes the presence of bacteria and endotoxins. Numerically, it is a 3 log reduction in bacteria.

There are different methods of controlling biofouling. The method selected depends on the intended use of the treated water and the proposed materials of the system components. Chemicals, ultraviolet radiation, heat, filtering, and ozone are the most commonly used.

CORROSION

Corrosion is the loss and eventual failure of metals and alloys from the electrochemical reaction between water and the pipe material. It is separated into two basic types: general and localized. General corrosion describes the potential dissolution of pipe over its entire exposed surface. Localized corrosion affects only a small area of the pipe surface.

General Corrosion

This is a breakdown of the pipe material at a uniform rate over its entire surface by direct chemical attack. It is caused by the loss of the protective passive film that forms on the surface of the pipe coupled with a chemical reaction occurring between the pipe material and the chemical in the fluid.

Galvanic Corrosion. This type of corrosion occurs in a liquid medium (called an electrolyte) when a more active metal (anode) and a less active metal (cathode) come in contact with one another and form an electrode potential. When this occurs, the more active (noble) metal will tend to dissolve in the electrolyte and go into solution.

Intergranular Corrosion. This occurs in the pipe wall when material in the grain boundary of some alloys is less resistant to the corroding agent than the grains themselves, and the bonds between the grains are destroyed.

Erosion Corrosion. This is caused by a wearing away of the pipe wall, usually as a result of excessive fluid velocity or constant wearing away by solids in the water striking the walls of the pipe.

Localized Corrosion

This takes place on small areas of the surface, usually at high rates, and takes various forms:

1. Stress-corrosion cracking is the physical deterioration and cracking of the pipe wall caused by a combination of high operating temperature, tensile stress on the pipe and chemicals in the fluid stream.
2. Pitting is characterized by deep penetration of the metal at small areas of the surface, concentrating in small cells, without affecting the entire surface.
3. Crevice-attack corrosion occurs at junctions between surfaces (often called crud traps) where a crack exists that allows an accumulation of a corroding agent.

Conventional corrosion treatment of feedwater for boilers and cooling water systems consists of pH control and chemical corrosion inhibitors. Dissolved gases are removed by deaeration.

PREDICTING SCALE FORMATION AND CORROSION TENDENCIES

GENERAL

A common and costly water-caused problem is the formation and deposit of mineral scale. Although scale deposits may contain a complex mixture of mineral salts, the primary constituent is calcium carbonate.

Most salts are more soluble in hot water than cold water. Calcium and magnesium salts, on the other hand, dissolve more readily in cold water than hot. As a result, they tend to deposit on surfaces when there is a rise in temperature. The following are the primary factors which affect this tendency:

1. Alkalinity
2. Hardness (calcium)
3. pH
4. Total amount of dissolved solids
5. Temperature

pH

The pH value reflects the ratio of bicarbonate to carbonate alkalinity. A higher pH value indicates a greater carbonate content of the water, and the increased tendency of calcium and magnesium carbonates to precipitate out of solution. Also, the higher the temperature, the greater the tendency of dissolved solids to precipitate out of solution because of their property of inverse solubility.

LANGELIER SATURATION INDEX (LSI)

In the 1930s, W. F. Langelier studied the primary factors that effected the tendency of water to form deposits of mineral scale on heat transfer equipment. As a result of this work, the Langelier index was created. The index is based on numerical values given to the factors that affect deposits. This index is best known as the Langelier saturation index (LSI).

The LSI is actually a calcium carbonate saturation index. It is based on the assumption that water with a scaling tendency will tend to deposit a corrosion-inhibiting film of calcium carbonate and thus be less corrosive. A water with non-scaling tendency will tend to dissolve protective films and thus be more corrosive. The interpretation of the LSI is based on numerical values given in Table 4.4. The LSI is calculated as follows:

$$\mathrm{LSI} = \mathrm{pH} - \mathrm{pHs} \tag{4.2}$$

TABLE 4.4 Prediction of Water Tendencies by the Langelier Index

Langelier saturation index	Tendency of water
2.0	Scale-forming and for practical purposes noncorrosive
0.5	Slightly corrosive and scale-forming
0.0	Balanced, but pitting corrosion possible
−0.5	Slightly corrosive and nonscale-forming
−2.0	Serious corrosion

where LSI = Langelier saturation index
pH = value obtained from testing the water in question
pHs = value calculated for the pH of saturation for the calcium carbonate present in the water in question

The most accurate method for calculating pHs is to use the following formula:

$$\text{pHs} = (9.3 + A + B) - (C + D) \tag{4.3}$$

The numerical values of *A, B, C,* and *D* for substitution into Eq. (4.3) are found in Table 4.5. A more empirical method to find pHs is to use the chart in Fig. 4.2.

TABLE 4.5 Numerical Values for Substitution in Eq. (4.3) to Find the pHs of Saturation for Water

Total Solids	A	Ca as $CaCO_3$	C	M. Alkalinity	D
50–330	0.1	10–11	0.6	10–11	1.0
400–1000	0.2	12–13	0.7	12–13	1.1
Temp, °F	B	14–17	0.8	14–17	1.2
		18–22	0.9	18–22	1.3
32–34	2.6	23–27	1.0	23–27	1.4
36–42	2.5	28–34	1.1	28–35	1.5
44–48	2.4	35–43	1.2	36–44	1.6
50–56	2.3	44–55	1.3	45–55	1.7
58–62	2.2	56–69	1.4	56–69	1.8
64–70	2.1	70–87	1.5	70–88	1.9
72–80	2.0	88–110	1.6	89–110	2.0
82–88	1.9	111–138	1.7	111–139	2.1
90–98	1.8	139–174	1.8	140–176	2.2
100–110	1.7	175–220	1.9	177–220	2.3
112–122	1.6	230–270	2.0	230–270	2.4
124–132	1.5	280–340	2.1	280–340	2.5
134–146	1.4	350–430	2.2	350–440	2.6
148–160	1.3	440–550	2.3	450–550	2.7
162–178	1.2	560–690	2.4	560–690	2.8
178–194	1.1	700–870	2.5	700–880	2.9
194–210	1.0	880–1000	2.6	890–1000	3.0

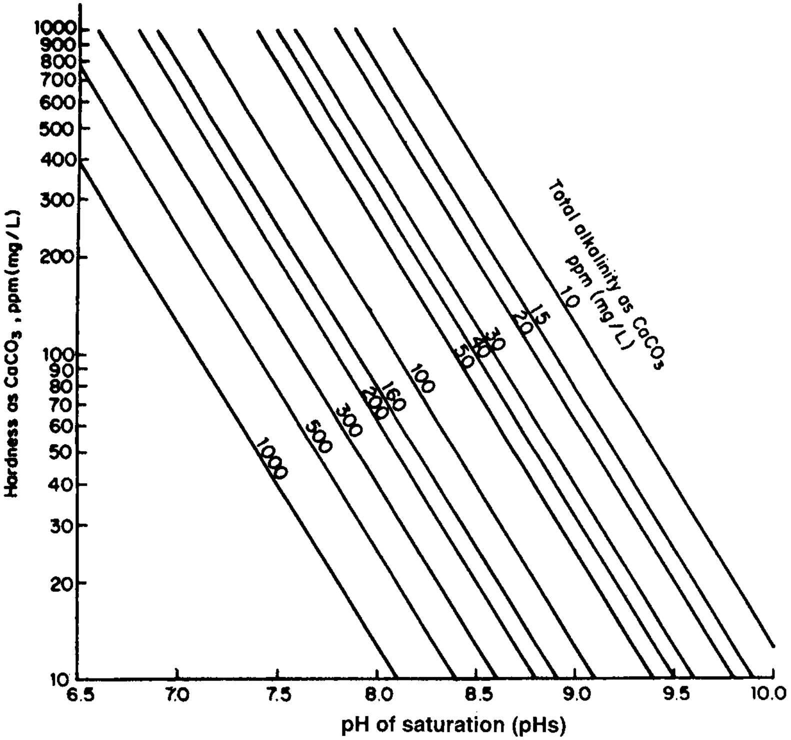


FIGURE 4.2 pH of saturation for water.

RYZNAR STABILITY INDEX (RI)

Also referred to as simply the stability index (SI), the RI is an empirical method used to predict scale-forming tendencies of water. The RI is calculated from the following formula using the same definitions used for the LSI:

$$RI = 2\ pHs - pH \qquad (4.4)$$

The RI is always positive. When it falls below 6.0, scale formation is possible and becomes more probable with decreasing RI. For an interpretation of the RI, refer to Table 4.6.

AGGRESSIVENESS INDEX (AI)

Developed by the EPA, the aggressiveness index is used rarely as a guideline to find the corrosive tendency of potable water. AI is calculated as follows:

TABLE 4.6 Prediction of Water Tendencies by the Ryznar Index

Ryznar index	Tendency of water
4.0–5.0	Heavy scale
5.0–6.0	Light scale
6.0–7.0	Little scale or corrosion
7.0–7.5	Significant corrosion
7.5–9.0	Heavy corrosion
9.0 and higher	Intolerable corrosion

$$\mathrm{AI} = \mathrm{pH} + \log_{10}(\text{alkalinity} \times \text{hardness}) \tag{4.5}$$

Values less than 10 indicate aggressive water, values between 10 and 12 indicate moderately aggressive water, and values more than 12 indicate nonaggressive water.

TECHNOLOGY AND COMPONENT DESCRIPTION

AERATION

Aeration is a gas transfer process in which water is brought into contact with air for the purpose of transferring volatile substances to or from the raw water. It is used most often to remove undesirable gases such as carbon dioxide, hydrogen sulfide, and methane. Aeration, by introducing oxygen, is also used to remove iron and manganese and to lower the amount of volatile organic compounds (VOCs) from ground water. The following are criteria for its use:

1. Reduction of carbon dioxide by 90 percent is obtained by near saturation with oxygen. Carbon dioxide dissolved in ground water will consume lime in the lime-soda softening process without any accompanying softening. Generally accepted practice indicates that aeration is not economical for carbon dioxide concentrations in water of less than 10 mg/L. The cost of the lime saved should be compared to the cost of purchasing and operating the proposed aerator.

2. Aeration will partially remove VOCs from raw water by oxidation, making them insoluble. They would then be coagulated and removed from the water.

3. Aeration alone could be used for the removal of hydrogen sulfide in concentrations of 2 mg/L or less. Above this level, it could be used in conjunction with chlorination, which oxidizes hydrogen sulfide.

4. Iron and manganese can be removed by aeration if this cannot be done by other methods. These metals are oxidized to form insoluble hydroxides which precipitate out at proper pH levels. They can then be removed by settlement or filtered out of the water stream. Each ppm of dissolved oxygen will oxidize about 7 ppm of iron or manganese.

Several types of aerators are commonly used: waterfall, diffusion (or bubble), and mechanical. The most commonly used system in utility water treatment is the waterfall.

Waterfall aerators are made in several types: cascade, spray nozzle, and multiple tray. They operate by having the raw water enter the unit from the top and fall by gravity to the bottom, using various methods to evenly distribute and disperse the water throughout the unit. The most common waterfall aerator is the naturally ventilated, multiple tray type. This unit consists of a series of trays, one above the other, with perforated, slot, or mesh bottoms. The trays are filled with 2 to 6 in (40 to 140 mm) of a medium such as coke, stone, or ceramic balls to improve water distribution and gas transfer as well as providing catalytic oxidation in the medium. The vertical openings between trays range from 12 to 30 in, depending on the number of trays required. Water loading on the trays is usually in the range of 10 to 20 gpm/ft^2. Efficiency can be improved by the use of enclosures and forced air blowers to provide counterflow ventilation.

The simplest type of aerator is the diffusion type which bubbles compressed air up through the water tank. The large volume of air required limits the diffusion aerator to smaller flows of water. Air requirements vary from 0.1 to 0.2 SCFM per gallon of water aerated. A detention time is necessary, ranging from 10 to 30 mm. Advantages of this type of aerator are the freedom from cold weather operating problems, very low head loss, and the possibility of using this process for chemical mixing.

The mechanical aerator consists of an open impeller operating on the water surface of a tank. It is not as efficient as either of the two systems previously described, and so, longer retention times are necessary. This unit is also free from cold weather problems and can be used for chemical mixing.

CLARIFICATION

Clarification is a process to reduce or remove turbidity, silt, and sediment present in the raw water supply. The water can be treated with chemicals or filtered, depending on the amount of impurities present and the volume of water to be treated. If treated with chemicals, time is required for the solids to settle out of suspension. The chemical treatment process is usually reserved for large volumes of water.

Suspended and colloidal particles will normally be in the range of 0.1 to 10 μm in size. They stay apart because negatively charged ionized matter is absorbed on their surfaces and thus they repel each other. A measure of the charge that surrounds the colloid is known as the "zeta potential." These negative charges are reduced by the use of positively charged chemicals called coagulants. Coagulants, through a chemical reaction, reduce the zeta potential and allow the colloids to cluster to form a larger, jellylike mass called floc. In a process called flocculation, colloidal particles, bacteria, and organic matter are mechanically brought together into larger and heavier particles. These particles are now too heavy to remain suspended, and so, they settle out of the water to the bottom. This process is called sedimentation.

Clarification of large volumes of water is done in a basin. First, the coagulant(s) must be introduced with a strong action in order to completely disperse and mix the chemicals with the incoming water. Often, some of the sludge produced by flocculation is mixed with the coagulant. After coagulation is accomplished, the mixture is then gently mixed in order to allow the now larger particles to settle rapidly to the bottom of the tank. This settling process is called sedimentation. The particles and chemicals that settle out are called sludge, which must be removed from the tank and disposed of. Most clarifier designs do both processes in the same operating unit.

The chemical coagulant used most frequently is aluminum sulfate, called alum or filter alum. Other coagulants used often are sodium aluminate and potash alum. Iron coagulants include ferric sulfate, ferris sulfate, and ferric chloride. Organic polyelectrolytes, which are high molecular weight polymers, are also employed in low dosages to increase the effectiveness of treatment.

It is usually a matter of trial and error to find the correct amount of alum. This is because the amount depends on the size and quantity of suspended solids of the raw water, retention time prior to flocculation, water temperature, and the amount of mixing. All of these conditions change from day to day.

As with almost every process, there is more than one method appropriate to achieve a desired goal when the demand for water is not very large. One alternative flocculation method is to produce a finer floc which can be removed by an appropriate filter system. By eliminating a large settling basin, a high quality water can be produced more quickly with smaller equipment.

DEAERATION

Dissolved gases in the water supply can produce corrosion and pitting. They must be removed prior to using the water for most purposes. These gases are oxygen, carbon dioxide, hydrogen sulfide, and ammonia.

Although carbon dioxide and hydrogen sulfide can be removed by aeration, in many cases it is easier and less expensive to remove them by deaeration. This process operates on the principle of raising the water temperature to the saturation point for the existing pressure. There are two types of deaerators, steam and vacuum. When heated water is needed, for example, for boilers, the steam type is preferred. When cold water is required, the vacuum type is used.

Steam deaerators break up water into a spray or thin film, then sweep the steam across and through it to force out the dissolved gases. Using this method, oxygen can be reduced to near the limit of detectability. Designs fall broadly into spray, tray, and combination units. Typical deaerators have a heating and deaeration section and a storage section for hot, deaerated water. Often, a separate tank is provided to hold an additional 10-mm supply of deaerated water. The direction of steam may be crossflow, downflow, or countercurrent. The majority of the steam condenses in the first section of the unit. The remaining mixture of noncondensable gases is discharged to the atmosphere through a vent condenser.

Vacuum deaerators use a steam jet or mechanical vacuum pumps to develop the required vacuum used to draw off the unwanted gases. The vessel has a packing material inside, and the inlet water is introduced to the top of the unit and passed down through this packing. Deaerated water is stored at the bottom of this vessel. The steam or vapor vacuum located at the top of the unit discharges the unwanted gases. The vacuum unit is far less efficient than the steam one, and is most often used in demineralizer systems to reduce the chemical operating cost and the demineralizer size, and to protect anion exchange resins from possible oxidation damage.

DECARBONATION

Decarbonation is rarely used but should be considered if the bicarbonate level in the feedwater is in the range of 14 to 20 mg/L or higher. Decarbonation is usually accomplished by the use of filtered air counterflowing through the water stream and stripping out the carbon dioxide.

DEALKALIZING

Dealkalizing is a process that reduces the alkalinity of feedwater. This can be done either with or without the use of acid regenerent. Without the acid, the regenerent used is salt, and the process is often called salt splitting. The salt-splitting process exchanges all bicarbonate, sulfate, and nitrate anions for chloride anions. For best results, it is recommended that deionized water be used as feedwater. Where hard, alkaline, low sodium water is available, the use of a weak acid resin should be considered.

The entire regeneration cycle is similar to that previously described for a water softener. It is not uncommon to use the same salt and regenerent piping to accommodate both the softener and dealkalizer. Some caustic soda may be added (1 part caustic soda to 9 parts salt) to reduce leakage of alkalinity and carbon dioxide. Since this can cause hardness leakage from the dealkalizer, a filter downstream of the processed water is necessary.

A weak acid resin can also be used. The process transfers the alkaline salts of calcium and magnesium to the weak acid resin. This process should include degasification if required by the product water. The weak acid process operates at a very high utilization factor, near the theoretically required amount. Hydrochloric acid is preferred for regeneration rather than sulfuric acid. This process is very sensitive to the flow rate, temperature, and contaminant level of the feedwater. These changing conditions must be considered by the manufacturer in the design of the process. The entire regeneration cycle is similar to that of cation ion exchange column.

DISTILLATION

In its basic form, distillation is the boiling of feedwater, condensing the steam produced from the feedwater, and collecting the condensate which yields a water product that is theoretically free of nonvolatile impurities. There are three methods currently used to produce distilled water: single-stage, vapor compression, and multieffect distillation.

Single-Stage Distillation

This is the most simple still. Feedwater enters the still, then is evaporated and condensed in a single stage. Cooling water is required to condense the steam produced. This type of still will produce water of approximately 1 MΩ/cm, with higher purity possible with optional equipment that removes dissolved gaseous impurities. This still has a small footprint, is not labor intensive, and will tolerate feedwater with a high level of impurities.

Vapor Compression Distillation

Vapor compression, sometimes called thermocompression distillation, is a method of evaporation in which a liquid is boiled inside a bank of tubes. The vapor generated then passes through a mist eliminator that removes any water droplets. The pure vapor is withdrawn by a compressor in which the energy imparted results in a compressed steam with increased pressure and temperature. The high-energy-compressed steam is discharged into an evaporator. At this point, the steam gives up most of its energy (latent heat) to the water inside the tubes. More vapor is generated and the process is repeated. The condensate (distilled water) is withdrawn by the distillate pump and is discharged through a two-stream heat exchanger.

The excess feedwater that did not evaporate is also pumped through an exchanger. Both the distillate and the blowdown are cooled, and the feedwater is preheated prior to entering the evaporator. These exchangers minimize the energy consumption of the system and eliminate the need for additional cooling water. The system operates continuously once it is started. Additional makeup heat, usually supplied by steam, is required for continuous operation. Vapor compression is generally considered more economical for large quantities of water and does not require a high quality feedwater for proper operation. The vapor compression still is moderate both in initial and operating costs.

Refer to Fig. 4.3 for a schematic diagram of a vapor compression distillation unit.

Multieffect Distillation

Multieffect distillation units use the principle of staged evaporation and condensation to generate distilled water. Each stage is called an effect. Distilled water is produced in each effect by condensing the steam generated by the evaporation of high purity feedwater in the previous stage. The initial driving force for the evaporation is power steam applied to the shell side of the first effect vessel. The multieffect still has the highest initial cost and lowest operating cost, and it requires the highest quality feed-water of all the stills.

The feedwater enters the vessel and its pressure is boosted by the feed pump. The feedwater flows through a coil in the condenser, which allows it to pick up heat from the condensing steam. This preheated feedwater flows through the feed control valve and into the tube side of the first effect. The first effect level controller senses the feedwater level and signals the feed control valve to maintain the desired level. Power steam is introduced into the unit and flows through the steam control valve and into the shell side of the first effect.

Temperature sensors sense the temperature on the tube side of the first effect and signal the steam control valve to maintain the required temperature. This steam condenses on the outside of the tubes of the first effect, giving up its latent heat of vaporization to the feedwater inside of the tubes, causing the water to boil and generate vapor.

The pure steam generated in the first effect is introduced into the shell side of the second effect. The pure steam condenses, producing distilled water, while giving up its latent heat to the high purity feedwater inside the second effect tubes, which in turn causes the feedwater to boil and generate vapor. Each effect operates at a lower pressure than the previous effect in order to provide the temperature difference that allows the transfer of heat. The pure steam generated in the tube side of the first effect by the condensing power steam passes through the mist eliminator to remove any entrained water droplets. Feedwater from the first effect passes through an orifice and into the tube side of the second effect. The first effect pure steam enters the shell side of the second effect and is condensed on the outside of the tubes.

The condensate (distilled water) passes through an orifice and enters the shell side of the third effect. Feedwater in the second effect passes through an orifice and into the tube side of the third effect.

After passing through the mist eliminator, the last effect pure steam enters the condenser and condenses on the outside of the condenser coils. This distilled water from the last effect and the distilled water from the previous effects is cooled by the cooling water of the condenser. The distilled water exits the condenser and enters the distillate pump, where it is pumped through the distillate control valve and through the storage-dump valve. The condenser level controller senses the distillate level and signals the control valve to maintain the desired level.

Noncondensable gases in the condenser are vented to the atmosphere. The condenser temperature is maintained at a predetermined level by the cooling water flow. The unit is protected by pressure relief valves along with high and low level alarms.

Refer to Fig. 4.4 for a schematic diagram of a multieffect distillation unit.

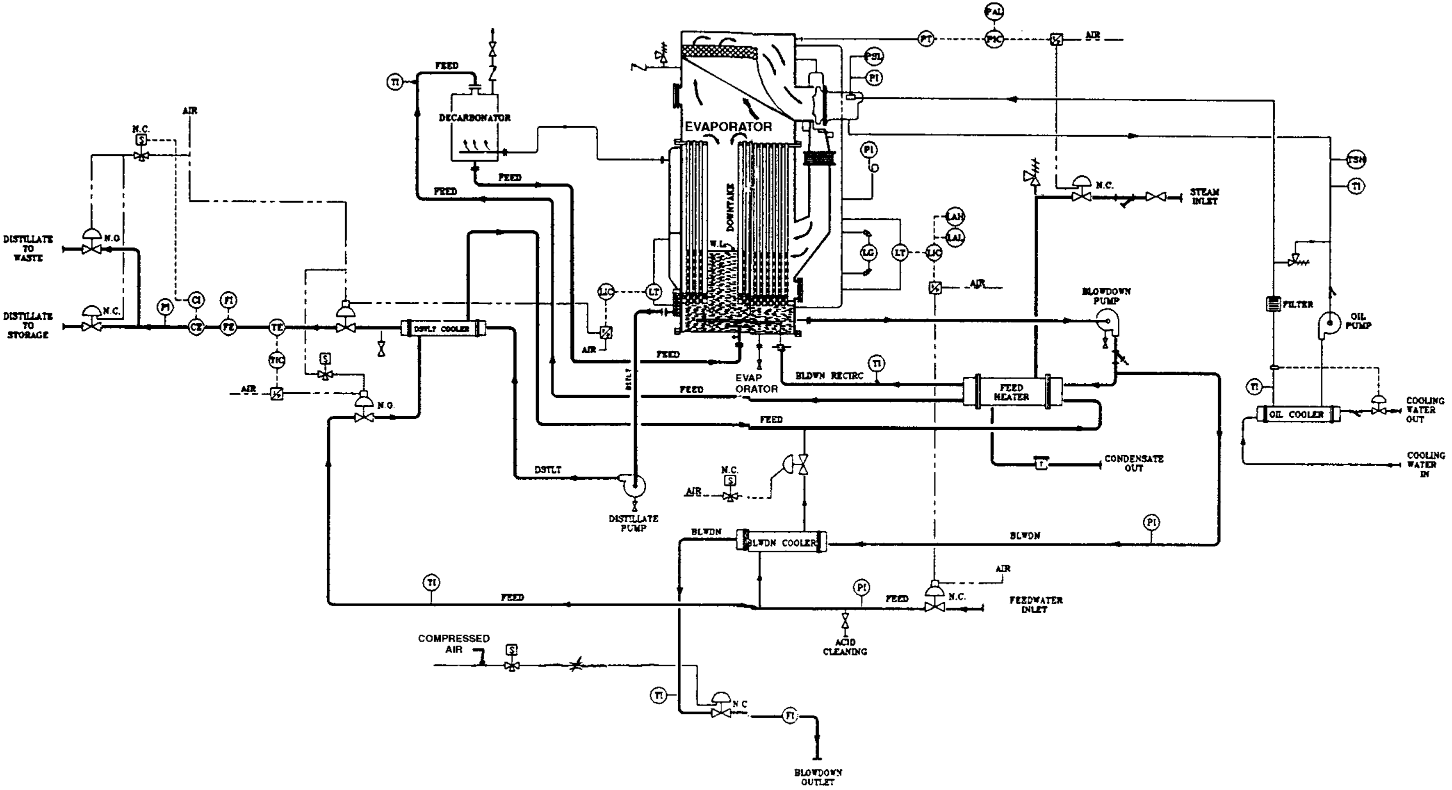


FIGURE 4.3 Detail of vapor compression still.

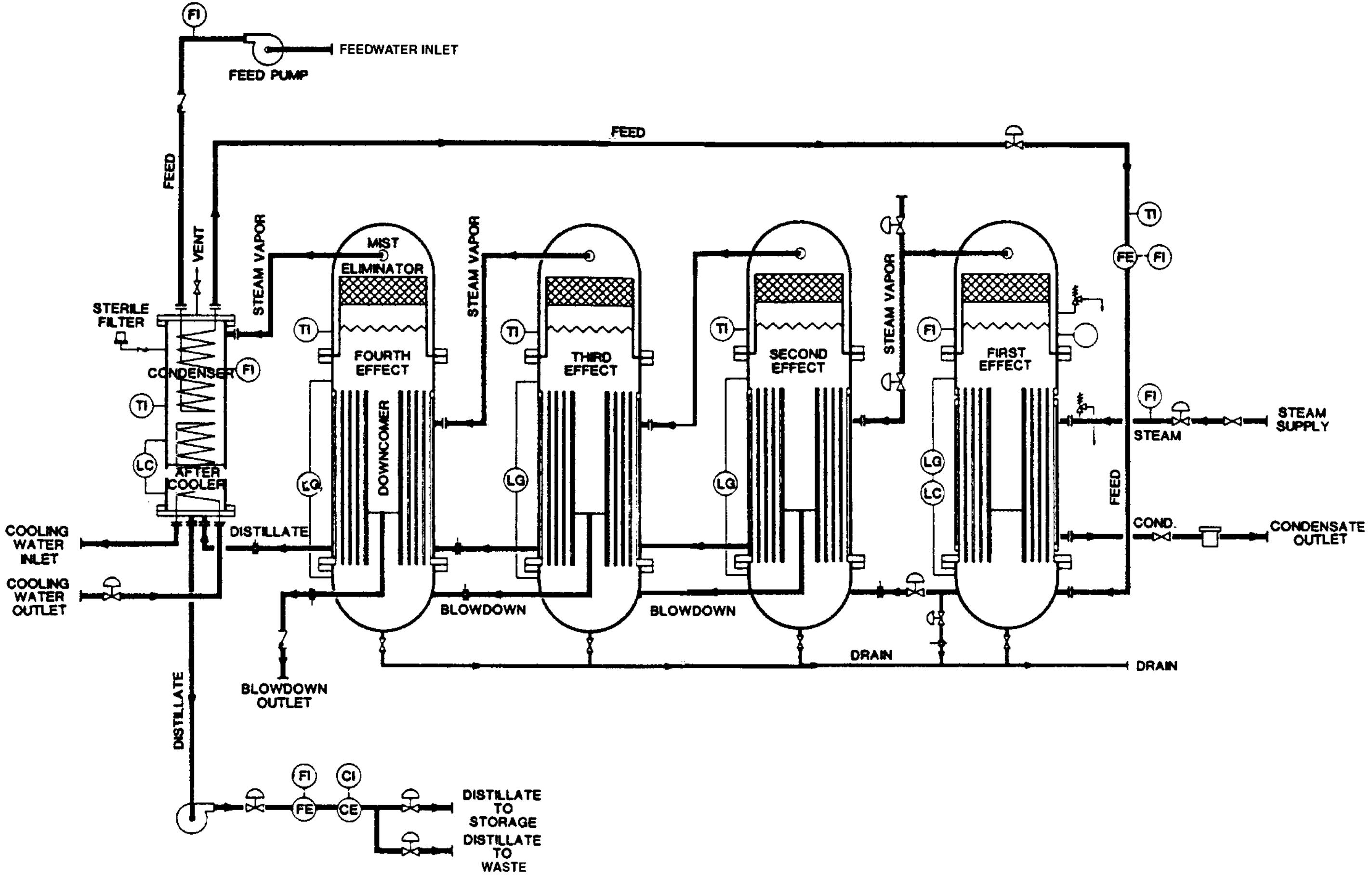


FIGURE 4.4 Detail of miltieffect still.

FILTRATION

Deep Bed Sand Filtration

Deep bed filters are designed to remove coarse suspended particulates larger than 10 μm in size. They are pressure-type filters that use either multigraded sand or multimedia in the filter. Particulate removal on the order of 98 percent should be expected. For additional discussion, refer to Sand Filters in Chap. 3.

Sand-only filters for laboratory water systems should generally operate at a face velocity of about 4 gpm/ft^2 of cross-sectional bed area. Multimedia filters operate at about 6 gpm/ft^2 of cross-sectional bed area. Since these values are general in nature, it is important to operate these units at the velocities recommended by the individual manufacturers.

The multimedia filter achieves a more uniform distribution of filter media throughout the bed and is considered a more effective type of filter. A typical multimedia filter for laboratory use consists of a top layer of anthracite having a 1.1-mm grain size and 1.5 specific gravity, a middle layer of sand having a 0.5-mm diameter grain size and a specific gravity of 26, and a bottom layer of garnet having a 0.2-mm grain size and 4.2 specific gravity. Normal operational flow rate is from 6 to 15 gpm/ft^2 of bed area.

Backwashing is required to clean the filter, with the effluent discharged to the sanitary drainage system. A backwash flow rate of 10 to 15 gpm/ft^2 is generally required for effective cleaning.

Activated Carbon Filtration

Activated carbon is used to remove dissolved, nonionic organics such as residual chlorine disinfectants, trihalomethanes, and chlorimines, as well as a major portion of naturally occurring dissolved organic material, from municipal water supplies. The non-ionic organics tend to coat ion-exchange resins and all types of membranes. For additional discussion, refer to Activated Carbon Filters in Chap. 3.

System designers are reluctant to use the activated carbon filter in the generation of PW because of the development of significant levels of bacteria in the unit itself. This can be controlled by periodically sanitizing with pure steam or hot water with a temperature greater than 80°C. The need for sanitizing can be determined only by testing the water. Because of this sanitizing, the interior of the filter housing should be lined or coated. When using potable water as feedwater, stainless steel housings should be avoided because of the possible chloride stress corrosion and chloride pitting resulting from the chlorine in the feedwater. A typical detail of a packed bed activated carbon unit is illustrated in Fig. 4.5.

ION EXCHANGE AND REMOVAL

Ion exchange is the basic process where specific ions in a feedwater stream are transferred onto an exchange medium called resin, and exchanged for different ions of equal charge. When the ion exchange process is used to treat water only for removal of hardness, it is generally known as water softening. When the ion exchange process is used to treat water for the removal of ions to produce pure water, it is often referred to as deionization or demineralization.

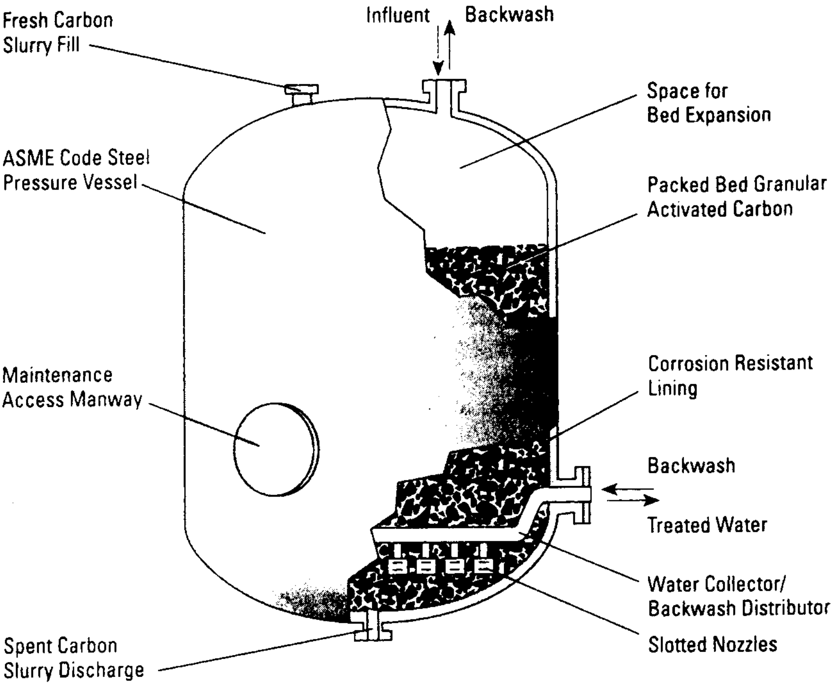


FIGURE 4.5 Schematic detail of large-scale granular activated carbon filter.

The deionization/demineralization process uses different types of resin to exchange first anions and then cations, which will result in the removal of all ions from feedwater when carried to completion. When all of the ionic components devolved in water are removed by ion exchange, the water is said to be deionized or demineralized. The ion exchange process is also used to remove dissolved inorganics. Water softening only exchanges some types of ions for others less detrimental for the intended end use of the water. Table 4.7 lists the common anions and cations typically found in water. Ion exchange will not remove significant amounts of organics, bacteria, pyrogens, or turbidity.

TABLE 4.7 Typical Cations and Anions Found in Water

Cations	Anions
Calcium	Carbonates
Magnesium	Bicarbonates
Sodium	Sulfates
Potassium	Chlorides
Iron	Nitrates
Manganese	Silica

Regenerable Ion Exchange

Regenerable ion exchange is a batch process where ions in raw water are transferred onto a resin medium in exchange for other ions bonded to that medium as the raw water percolates through them. This is accomplished by having the ions in the raw water adsorbed onto a bed of exchange resins and replaced with an equivalent amount of another ion of the same charge. This action continues until the medium has reached its exchange capacity, where it is no longer capable of exchanging ions. Water softening and deionization are the two most common ion exchange processes.

There are two general types of deionizers, working and polishing. The working type is used for the initial removal of the bulk of ions from feedwater or as an ion exchange process alone (such as hardness removal) if the purification is a single process. A polishing type is used to purify feedwater after an initial run through a working ion exchange system.

Resins

Resin exchange media include natural inorganic aluminum silicates (sometimes called zeolites or greensands), bentonite clay, synthetic gelatinous resins, and synthetic organic resins. Most processes use the synthetic resins. Resins are graded by purity and consistency of bead size.

Resin is manufactured in the form of a large number of spherical beads, typically about 0.4-mm diameter. These beads have weakly bonded ions present on their surface that are used for the exchange process. Because the process must exchange ions of the same charge, ion exchange resins are composed of either anion or cation exchange resins. Manufacturers are constantly making new resins for different ion removal purposes.

Traditional deionization exchanges cations with H^+ ions (acids) and anions with OH^- ions (bases). Although not 100 percent effective, the end result of these two exchange processes combines the ions remaining in the feedwater to create deionized or demineralized water as the end product.

There are a large number of ion exchange resins available. Each of them has been formulated to obtain optimum performance for different impurities. The affinity for specific ions in solution is termed the *selectivity coefficient.* The number of charges (valence) available on a particular ionic medium is a major factor in the selection of specific resins to remove the desired impurities, and is based on an analysis of raw water. These resins are contained in a vessel often referred to as a column. The actual resin bed could be supported by a mat of graded gravel, screen-wrapped pipe, or perforated plates, which also act to evenly distribute feedwater over the entire resin bed. The size of the resin beads in the vessel also creates an effective depth filter. This filtering action leads to fouling and unpredictable operating runs because of an accumulation of particulates.

Anion resins could be either strong or weak bases. A common anion resin is divinyl benzene, a gelatinous bead. Anion resin type 1 premium has a very close tolerance of bead size. Anion resin type 1 regular is generally used for maximum silica reduction. Resin type 2 is used most often unless type 1 is specifically requested. There is a difference in cost and capacity between the two resins. In general the higher cost of the type 1 resin is considered acceptable in order to obtain a more efficient and longer-lasting resin. Weak base exchangers are not effective in the removal of carbon dioxide or silica. They remove strong acids more by adsorption than by ion exchange. The end result is the same, and the efficiency of weak base regeneration for acid salt removal is far superior to that of the strong base material doing the same job. Thus weak base units are superior when the feedwater is high in sulfates and chlorides.

The two cation exchange resins used most often are strong or weak acids. Strong cation resins remove all cations regardless of the anion with which they are associated. These resins have a moderate exchange capacity and require a strong acid regenerant such as hydrochloric or sulfuric acid.

The deionization process can be arranged as either a two step (dual bed) or single step (mixed bed) process. In the dual bed process, one vessel contains the anion exchange resins and the second vessel, the cation exchange resin. In the mixed bed unit, a single vessel contains a mixture of both resins. The dual bed arrangement produces water that is less pure than that produced by a mixed bed, but the dual bed has a greater removal capacity. A typical mixed bed contains 40 percent cation resins and 60 percent anion resins. Dual beds are easier to regenerate. It is not uncommon to have a dual bed exchanger, often referred to as a working exchanger, installed in front of a mixed bed to remove the bulk of the impurities, and then have the mixed bed, often called a polishing exchanger, further purify the water to the desired high level. A typical single-bed ion exchange unit is illustrated in Fig. 4.6. A typical dual-bed ion exchange unit is illustrated in Fig. 4.7. A typical mixed-bed ion exchange unit is illustrated in Fig. 4.8. The piping and valve arrangement for different manufacturers may be different.

Regeneration Cycle

The ion exchange process is reversible. As the water continues to pass through the ion exchange resin beds, the number of ions on the resin beads available for

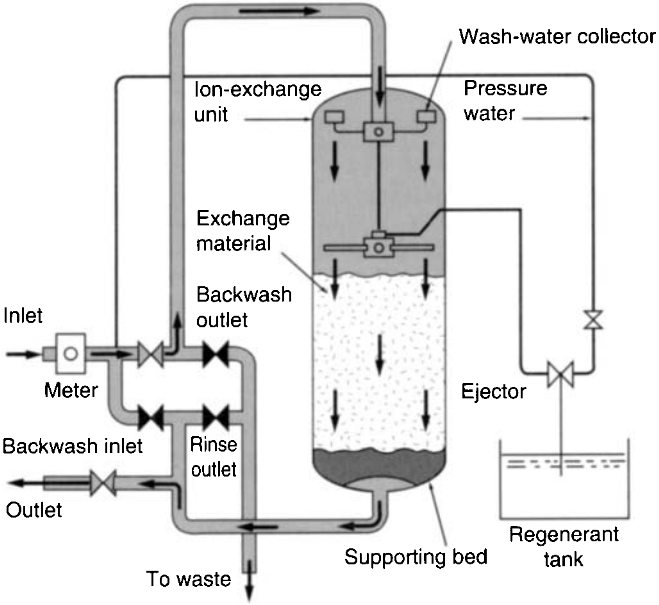


FIGURE 4.6 Typical single bed ion exchanger.

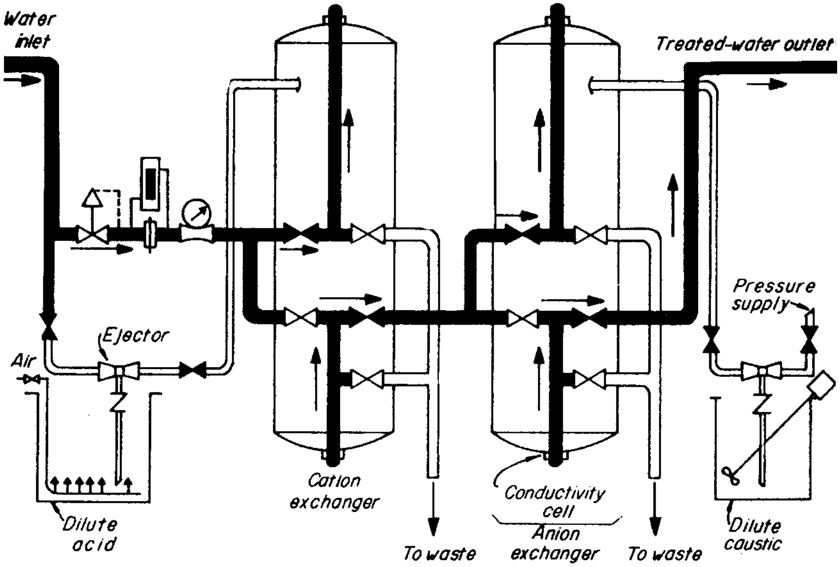
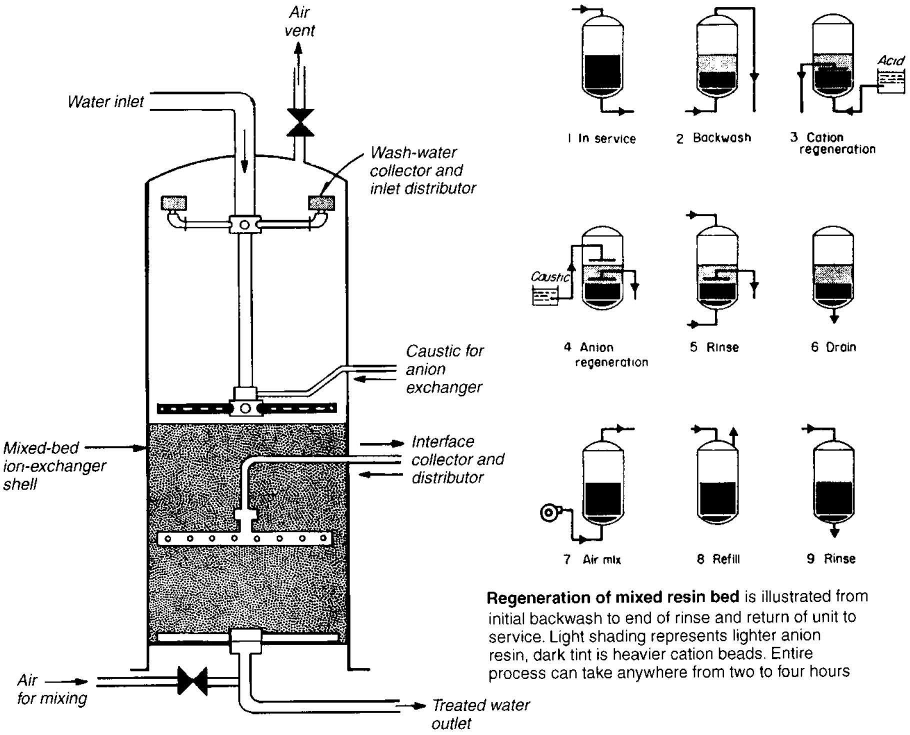


FIGURE 4.7 Typical dual bed ion exchanger.



Regeneration of mixed resin bed is illustrated from initial backwash to end of rinse and return of unit to service. Light shading represents lighter anion resin, dark tint is heavier cation beads. Entire process can take anywhere from two to four hours

FIGURE 4.8 Typical mixed bed ion exchanger.

exchange declines with time and gradually becomes exhausted. This starts first at the water entry to the vessel and progresses down the bed. When the resin has reached the limit of exchange, the bed is said to have reached its exchange capacity. It is then necessary to take the column out of service to be regenerated.

Regeneration, which is the reverse of deionization, is the term used for the replacement of the ions removed by the feedwater. Regeneration generally consists of three steps: (1) backwashing, (2) application of regenerating solution, and (3) rinsing. Regeneration can be performed either cocurrently (in the same direction as the flow of feedwater) or countercurrently (in the opposite direction of the flow of feedwater). All of the water used for regeneration must be routed to a drain of adequate size. In addition, the acid and caustic must be neutralized prior to discharge into a public sewer system. It is common practice to combine the acid and caustic waste streams to neutralize the effluent to the greatest extent possible. Additional acid or caustic may have to be added to the final effluent to produce a pH acceptable to the local authorities.

Backwashing is a countercurrent operation that accomplishes two purposes. The first is to remove any particulates that have accumulated in the resin bed and on the beads. The second is to regrade the resin beads so that new beads are on the top of the bed, which is where the heaviest duty from the beads is required. This is done by having the resin bed expanded by the reverse flow of water from its normal packed condition during use. Individual manufacturers have established the required flow rate of backwash that should be maintained. Too high a flow rate will blow resin out of the tank and into the drain. The flow rate of water should be high enough to scrub the beads together to increase the cleaning action. Higher than recommended flow rates will only waste water and provide no additional benefits.

The two chemicals used to regenerate cation resin beds are either a 93 percent solution of sulfuric acid or a 30 to 32 percent solution of hydrochloric acid, also called mureatic acid. As they flow through the columns, they replace the retained cations with hydrogen ions from the acid. Hydrochloric acid is used most often because it has the greatest efficiency; the amount of hydrochloric acid used is one-fourth the amount of sulfuric acid. Sulfuric acid is much lower in cost and is used when there is a large quantity of resin to be regenerated, making its use practical. The chemical used most often for regenerating anion resins is a 40 percent mixture of sodium hydroxide, which replaces the retained anion ions with hydroxyl ions. For mixed bed units, the resins must be separated prior to regeneration.

The quality of the chemicals used for regeneration has an important effect on the maintenance of exchange capacity. Although chemically pure ingredients are not required, some contaminants found in these chemicals collect on the resins and eventually will cause difficulty in operation.

Technical grade acids, free of oils and other organic materials, are acceptable for regeneration of cation resins. They should be 66 degrees Baumé (°Bé), free of suspended matter and light in color. They should mix freely with water and not form any precipitate. Acid-containing inhibitors should not be used. Sulfuric acid is usually the most economical for large-scale use. Hydrochloric acid should be technical grade, a minimum of 30 percent HCl by weight (18°Bé) and shall not contain excessive amounts of iron and organic materials. HCl obtained by the salt-aid or the hydrogen-chlorine process has been found satisfactory. HCl obtained by the hydrolysis of chlorinated organic chemicals should be avoided, particularly if used to treat potable water.

Anion exchange resins are regenerated with 76 percent sodium hydroxide, which must be low in iron, chlorides, and silica to avoid fouling the strong base anion exchangers. Weak base anion exchangers are most economically regenerated with technical grade flake sodium hydroxide. Strong base exchangers are best regenerated using nylon or rayon grade sodium hydroxide, also 76 percent. If purchased in a 40 percent solution, use the grade previously indicated. All caustics must have a maximum of 2 ppm chlorates.

The flush cycle is the shortest. It is a cocurrent process whose purpose is to flush away any remaining residue of the regeneration liquids and to repack the bed in preparation for the new run.

The entire regeneration cycle typically takes about 1 h. If the process requires continuous operation, a duplicate set of equipment is installed so that one is in use while the other is being regenerated.

To estimate the frequency of regeneration, first, find from the manufacturer the exchange capacity in grains of the selected resin bed. Next, from the analysis of the raw water find the average TDS level and convert this figure into grains per gallon. Dividing the flow rate in gallons into the grain capacity of the resin bed will give the time it takes to saturate the resin bed before regeneration is required.

Service Deionization

Service deionization is not another form of deionization but rather, a different type of equipment arrangement. In the regenerable type, the DI equipment is permanent and the regeneration is done on site by operations or maintenance personnel, who must handle and store the chemicals used for regeneration.

The service DI system uses individual cartridges or tanks for the anion, cation, and mixed beds. When the individual cartridges are exhausted, the supplier replaces them with recharged units on site and the exhausted cartridges are removed to be regenerated at the supplier's premises. This arrangement considerably reduces the initial cost of the equipment, eliminates the need to store chemicals, and frees the operations or maintenance personnel from the job of regenerating the units. In addition, it saves water that does not have to be used for backwash. However, the operating costs are higher than for the permanent bed type.

Continuous Deionization

Continuous deionization (CDI), also known as electrodeionization (EDI), is a continuous water purification process that uses direct current, an alternating arrangement of cation- and anion-permeable ion exchange membranes that form parallel flow compartments (concentrating compartments) on either side of an additional flow compartment containing a thin layer of mixed bed ion exchange resin (diluting compartment). The components, called a cell pair, are installed in a plate and frame device where the flow compartments form various flow paths for the product and wastewater. This arrangement is illustrated schematically in Fig. 4.9.

The feedwater flows through the diluting compartment. When a DC field is applied across the pair of membranes, ions move from the diluting stream, through the ion beads and the membrane into the concentrate stream, thereby producing separation. With an alternating arrangement of cell pairs, the cations and anions are trapped in the concentrate stream where they are routed to drain. The resin bed serves as a highly conductive medium through which the ions flow. The various flow streams are hydraulically independent allowing a high volume of high purity water (product) and a low volume of concentrate (waste).

The resin-filled diluting compartment (cell) creates a low level resistance path for ions. At the outlet of the diluting cell, under the proper combination of flow, temperature, water conductivity, and voltage, the ion exchange resins will regenerate

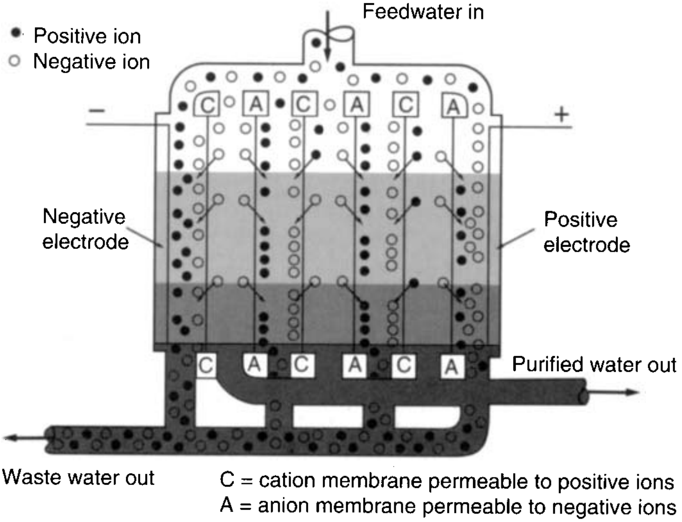


FIGURE 4.9 Schematic operation of a continuous deionization unit. In a continuous deionization cell, electric field pulls positive ions in feedwater through cation-permeable membranes (C), negative ions through anion-permeable membranes (A). Blockage by next membrane confines all ions to one set of channels, purified water to other set. Result: one purified stream, one waste stream.

automatically without the use of added chemicals. This process is continuous, and results in a steady supply of high purity water from the diluting compartment.

CDI is very sensitive to feedwater impurities. Experience has shown that very few natural or potable feedwater supplies can meet the required feedwater specifications without softening. Typical feedwater system requirements are the same as those for potable water. Individual manufacturers may have other specific requirements. Because of these requirements, most processes that purify water for pharmaceutical applications use CDI for polishing purposes after RO. Another disadvantage of this process is that the membrane used is incompatible with standard chemical sanitizing agents and sensitive to the frequency of sanitizing.

Water Softening

Water softening is a process that reduces or removes the dissolved impurities that cause hardness in water. This is commonly done by either of two methods: adding lime-soda ash to the raw water (for very large volumes) or passing the raw water through an ion exchange process.

Lime-Soda Addition. The lime-soda ash method uses either hydrated lime or quicklime along with soda ash. When added to water, these chemicals react with the dissolved calcium and magnesium carbonate to form insoluble compounds. These compounds precipitate out of solution and are passed through a filter to remove them. They are then discharged to drain. This process is usually carried out during the clarification process rather than as a separate process and is reserved for large volumes of water.

Ion Exchange. The ion exchange process is a cation exchange used to remove insoluble and scale-forming iron, calcium, magnesium carbonate, and other multivalent cations, which are the primary causes of hardness, and replace them with sodium ions, which do not contribute to hardness. The removal of these impurities prevents the buildup of insoluble scale precipates on the piping and reverse osmosis membrane. Ion exchange is accomplished by passing the water through a bed of granular sodium cation exchange resin. This process is commonly called sodium cycle ion exchange.

The resin bed typically occupies about two-thirds of the tank. The other one-third is needed for expansion of the resin bed during backwash. A generally accepted range of 0.4 to 3 gpm/ft^3 of resin is used to determine the volume of resin and cycle time of the unit.

Microbial growth inside the unit is a concern in softening systems used for pharmaceutical and some laboratory purposes. The water softener is regenerated with a brine solution that does not destroy bacteria. The liquid brine solution storage and regeneration equipment also allow microbial growth in storage tanks that are exposed to the atmosphere. An alternative is to use a dry storage system, which generates a salt solution from water mixed with salt pellets only when necessary for regeneration. The dry storage system controls microbial growth better than wet systems, but constant maintenance is required to monitor the brine tank. The quality of the salt in all systems should be checked periodically to ensure that there are no added substances present.

The regeneration cycle is similar to that previously discussed. The difference is that salt is used to regenerate the resin bed. Industrial water softeners use rock salt for economy. Rock salt, because of its high mineral content, requires a special tank called a dissolver to dissolve the rock salt in water prior to use. The water softener is similar to the schematic single bed ion exchanger illustrated in Fig. 4.6.

Ion Exchange System Design Considerations

One of the major decisions that must be made when selecting an ion exchange system is how much leakage to allow. Leakage is the presence of unwanted ions in the final treated water. The amount of leakage is a function of the completeness of the resin regeneration. For water softening, generally accepted leakage amounts range from 0.1 to 1 ppm. Since total regeneration of the resin bed is impractical, most water softeners operate at one-half to two-thirds of their ultimate capacity. There is sodium leakage from cation exchangers and silica leakage from anion exchangers. Normally, mixed bed units have negligible leakage.

In general, adequate purification of the water stream for high purity applications is not possible in one pass through the system, so a polisher is necessary. A mixed-bed ion exchange system has an initial cost about 74 percent less than a dual bed system when used as a polisher. A single pass RO system is about equal to a dual-bed ion exchange system.

Usually, if the water demand for a facility is less than about 40 gpm, the greatest benefit will be derived from simpler and less costly equipment at the expense of higher operating costs. For this water demand, it is usual to have a mixed bed unit without a degasifier, which is not required. For systems with a requirement of 200 gpm or more, most of the systems installed have multiple bed units and a degasifier.

Manufacturers must be consulted for the specific system, resin selection, and the required equipment.

Where applicable, the use of weakly acidic and weakly basic resins minimizes chemical costs and reduces losses to waste because of high regenerative capacity.

There are some problems, such as microbial growth, associated with water softeners. Sanitization is usually accomplished during regeneration. Iron buildup in the unit could pass through to downstream purification equipment unless operating personnel constantly monitor the water quality.

MEMBRANE FILTRATION AND SEPARATION

Membrane filtration and separation is a general term for a water purification process that removes contaminants from feedwater by means of a thin, porous barrier called a membrane. When used as a filter, a membrane is capable of removing impurities of a much smaller size than other types of filters. Filters of this nature are often called ultrafilters and nanofilters.

A semipermeable membrane limits the passage of selected atoms and/or molecules in a specific manner. Membrane filtration and separation, when used to produce pure water, is characterized by having the feedwater flow parallel to the membrane (often called tangential flow). Not all of the feedwater is recovered. Many of the membranes used are also available as both depth filters and, in single thickness, disk filters. There are two general categories of membrane filtration: reverse osmosis using a semipermeable membrane and filtration using ultrafiltration and nanofiltration membranes.

Reverse Osmosis

Reverse osmosis (RO) is a broad-based water purifying process involving osmosis and ionic repulsion. Osmosis is the spontaneous passage of nonvolatile solute molecules (impurities such as sodium chloride) in a solvent (such as water) through a semipermeable membrane. This membrane is called semipermeable because it allows the solvent to diffuse, or pass through, but is impervious to the solute.

In the natural osmosis process, when two solutions of different concentrations are separated by a semipermeable membrane, water molecules from the less concentrated solution will spontaneously pass through the membrane to dilute the more concentrated solution. This continues until a rough equilibrium is achieved. The driving force is a difference of pressure, called the osmotic pressure or concentration gradient, that exists across the membrane and is based on the degree of concentration of contaminants. The pressure in the stronger solution is lower than that in the weaker solution. This pressure is what drives the flow of solvent. The flow or flux will continue until the osmotic pressure is equalized, which then results in a higher pressure on the concentrated solution side that is equal to the osmotic pressure.

Reverse osmosis is the flow of solvent in the direction opposite to that of natural osmosis. If enough pressure is applied to the more concentrated solution, which in these discussions is water, pure water is diffused through the membrane leaving behind the bulk of the contaminants. These contaminants are continuously flushed to drain, thereby removing them from the system. The purified water is called permeate and the contaminant-containing water is called reject or the reject stream. In some cases, the reject stream is referred to as salt. The performance characteristics of the selected membrane determine how large a system is required. The flow rate is measured in membrane flux, which is a measurement of the flow rate of permeate that will pass through a given area of the membrane at a specific temperature and pressure. The ratio of purified water flow to the feedwater flow is called recovery. Most applications require a minimum 40 percent recovery rate to be considered practical. Rejection characteristics are expressed as a percent of the specific impurities retained and depend on ionic charge and size.

Membrane Module Configurations. There are four types of membrane module configurations used for RO applications: hollow fiber, spiral wound (SWRO), tubular (TRO), and plate and frame. Hollow fiber and spiral wound are the most common configurations. In each design, maximum turbulence is necessary to avoid concentration polarization.

Hollow-Fiber Reverse Osmosis. The hollow-fiber configuration, illustrated in Fig. 4.10, consists of a perforated tube manufactured from ceramic, carbon, or porous plastic with inside diameters ranging from ⅛ to 1 in (8 to 25 mm). They require rigid support when mounted inside the pressure vessel. Feedwater can be introduced either into the center or outside depending on the manufacturer of the RO module. Fouling resistance is low.

Spiral Wound Reverse Osmosis (SWRO). This configuration, illustrated in Fig. 4.11, typically achieves a large surface area per unit volume. In this design, a flat membrane is formed around a fabric spacer closed on three sides with the open side terminating in a perforated produce water tube. The unit is then placed in a pressure vessel. Feedwater permeates through the membrane and flows radially inside the enclosure toward the product tube.

Tubular Reverse Osmosis (TRO). This configuration, illustrated in Fig. 4.12, consists of a perforated tube manufactured from ceramic, carbon, or porous plastic with larger inside diameters than the hollow fiber configuration. The membrane is installed on the inside of the tube. A number of tubes are installed inside a pressure vessel. Feedwater enters the tube and permeates through the membrane to be collected on the outside. The feedwater channels are much more open than the SWRO and less subject to fouling.

Plate and Frame. This configuration, illustrated in Fig. 4.13, consists of a membrane that is fixed to a grooved plastic or metal plate with several plates stacked together in a frame that includes feedwater and drain ports. As the feedwater flows across the membrane surfaces, the purified water penetrates the membrane and flows along the frame for collection. The retentate continues to flow and could be recirculated or directed to drain.

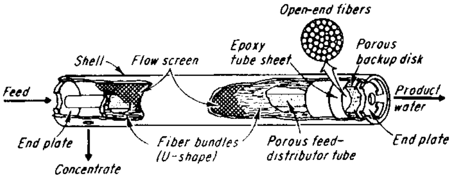


FIGURE 4.10 Hollow fiber reverse osmosis configuration.

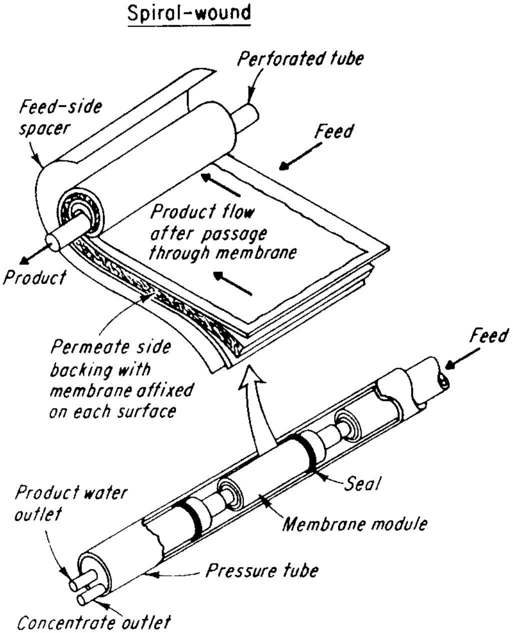


FIGURE 4.11 Spiral wound reverse osmosis configuration.

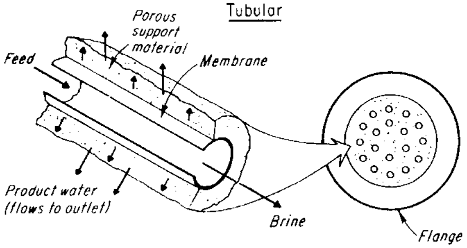


FIGURE 4.12 Tubular reverse osmosis configuration.

This configuration is used mostly for filtration and rarely for RO systems. Packing density is low and resistance to fouling is very high. It is used for small to medium volumes, generally less than 20 gpm.

Membrane Selection

System performance is determined by considering the following factors that influence the capacity of the individual membranes selected:

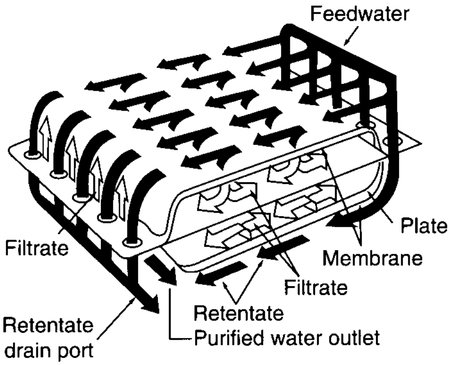


FIGURE 4.13 Plate and frame reverse osmosis configuration.

1. Operating pH
2. Chlorine tolerance
3. Temperature of the feedwater
4. Feedwater quality, usually measured as SDI
5. Types of impurities and previous feedwater treatment
6. Membrane flux
7. Number of operating hours
8. Resistance to biodegradation and ability to be sanitized
9. Rejection characteristics. Typical RO systems remove the following contaminants to the following levels:

Inorganic ions	93–99%
Dissolved organics (>300 MW)	>99%
Particulates	>99%
Microorganisms	>99%

The selection of a system configuration must consider the following:

1. Maximum recovery
2. Fouling properties and resistance
3. Production rate per unit volume

There are only a small number of polymers that have the necessary characteristics to function as semipermeable membranes:

1. Thin film composite of various polymer materials
2. Polyamide
3. Cellulose acetate
4. Cellulose triacetate
5. Polysulfone

TABLE 4.8 Comparison of Reverse Osmosis Polymers

	Thin film composite	Polyamide	Cellulose acetate	Cellulose triacetate	Polysulfone
pH Stability	2–12	4–11	2–8	4–7.5	3–11
Chlorine tolerance	Fair-poor	Poor	Good	Fair-good	Good
Biological resistance	Good	Good	Poor	Fair-good	Good
Temperature limit for stability, °F (°C)	122 (45)	95 (35)	95 (35)	86 (30)	95 (35)
Typical rejection ionic species, %	>90	>90	90	90	90
Flux	High	Low	Low-medium	Low-medium	High

Typical characteristics and a comparison of these membranes are given in Table 4.8.

Filtration

Ultrafiltration and nanofiltration describe membranes that are categorized by their pore size. Ultrafiltration membrane pore sizes range from 0.001 to 0.02 μm. Nanofiltration membranes have pore sizes that will allow the passage of solids to 10,000 daltons. The 10,000-dalton cutoff is recommended for the complete removal of pyrogens. Typical recovery rates for ultrafilters range between 95 and 98 percent, with the remainder flushed to drain.

A membrane is manufactured by bonding the membrane onto a porous, supporting substrate and then configuring it into elements. These filters are generally used for pretreatment in the removal of colloids, bacteria, pyrogens, particulates, and high molecular weight organics. Spiral wound and hollow fiber are the two configurations used most often.

MICROBIAL CONTROL

Chemicals

The most common disinfection method is the addition of oxidizing or nonoxidizing chemicals. Chemicals could be either biocides, which are substances that kill microbes, or biostats, which prevent the further growth of microbes. Commonly used chemicals are chlorine, chlorine compounds, hydrogen peroxide, and acid compounds.

In order to be effective, the chemical must have a minimum contact time in the water. In addition, a residual amount of the chemical must be present to maintain disinfection.

Chemicals add impurities to the water and are not generally suitable for a pure water environment. They disinfect potable and process water and equipment by injection directly into the fluid stream by means of a metering pump. They must be removed from feedwater used for purification. Chlorine may produce trihalomethanes.

Ultraviolet Radiation

Ultraviolet (UV) radiation is an in-line process. UV light is generated using mercury vapor lamps. The UV spectrum is divided into three wavelengths: UVA (315–400 nm), UVB (280–315 nm), and UVC (less than 280 nm). Only UVB and UVC wavelengths can economically produce the intensity and energy output necessary for the intended germicidal treatment. Federal standard 209E and aseptic guidelines issued by the FDA provide some guidance for the use and application of UV irradiation.

The 254-nm wavelength operates in the germicidal region, sterilizing by destroying bacteria, mold, viruses, and other microorganisms. This wavelength is preferred for pure water systems and will significantly reduce the multiplication of organisms.

The 185-nm wavelength operates in the ozone-forming region, where it has the ability to break down organic molecules to carbon dioxide by the photooxidation process. It slowly breaks the bonds in organic molecules by direct radiation, and also oxidizes organisms by the formation of hydroxyl radicals. The UV spectrum is illustrated in Fig. 4.14.

A flow rate of approximately 2 ft/s is an industry standard for effective sanitization of purified water. Flow rate through the UV device should be reduced compared to that of the circulation loop to extend the necessary contact time. The recommended location is ahead of deionization equipment.

Problems include generation of ions that lower the resistivity of water and the possible leaching of silica from the quartz sleeve of the UV device. Glass, plastic, rubber, and similar materials exposed to UV radiation will eventually crack, etch, discolor, and flake. Tests have shown that only half the energy used by a new bulb

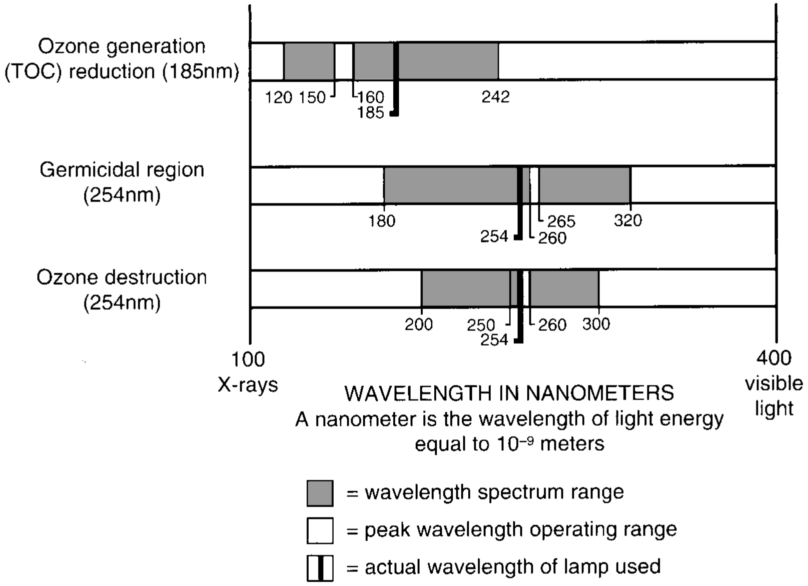


FIGURE 4.14 UV wavelength spectrum.

is actually transmitted to the water and that in time an additional 25 percent of the output will be lost compared to a new bulb.

Filtering

A filter will remove organisms from the fluid stream. Generally accepted practice is to use a 0.2-μm absolute filter for the removal of bacteria. However, some authorities question the effectiveness of this practice. Recommended current practice is to use a membrane filter with an absolute rating (cutoff) of 10,000 daltons. Cartridge filtration is the most common method.

Heat

Heating to 80°C (175°F) will effectively sanitize water under pressure. The heating can be accomplished by using steam, electricity, or other heat exchangers. It is common practice to circulate purified water at this temperature, and use heat exchangers to lower the water temperature at each point of use if necessary.

Ozone

Ozone (O_3) is an oxidizing gas generated from gaseous oxygen or catalytically from water. The most popular method to produce ozone is by a corona-discharge generator converting the oxygen in air to ozone. The air is passed between two electrodes where an electrostatic discharge across the gap converts oxygen to ozone. A schematic drawing of a corona-discharge generator is illustrated in Fig. 4.15.

The ozone system consists of a feed gas treatment unit, an ozone generator, a water-ozone contact mechanism, and a destruction unit to eliminate any residual ozone.

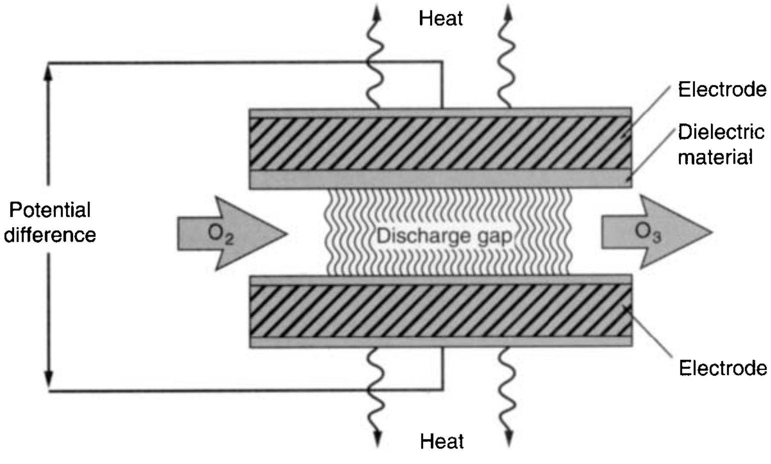


FIGURE 4.15 Principle of corona-discharge ozone generator.

1. *Feed gas treatment.* The gas reaching the generator must have all particles larger than 0.3 μm and 95 percent of particles larger than 0.1 μm removed. In addition, aerosols, moisture, and hydrocarbons must be removed, as required by the manufacturer. This purification is usually supplied as part of a package.

2. *Ozone generator.* The three basic types of generators are the Lowther plate unit, Otto plate unit, and tube units. They differ only in the manner they are cooled. Ozone generators use large amounts of electrical power, generally between 15 and 26 kWh per kilogram of O_3.

3. *Water-ozone contact mechanism.* Ozone and water at a pH of 7.5 or less are mixed in direct contact with one another by the use of static or mechanical mixers, injectors, or columns that optimize the dissolution of the gas.

4. *Destruction unit.* Depending on the generator, ozone concentrations can vary from 100 to 3000 ppm. Because high concentrations are harmful to humans and metals, the ozone should not be allowed to escape to the atmosphere without being treated to a level below 0.1 ppm. Destruction can be accomplished by catalytic, thermal, or activated carbon. Thermal units operate at a temperature of 300°C and generally require a 3 to 5 min contact time to be effective.

The mechanism for ozone oxidation is through the generation of hydroxyl radicals. The gas is directly injected into the water stream. Problems with this method include incomplete oxidation of organic compounds and slow operation. Action is enhanced with the application of UV radiation at 185 nm.

WATER TREATMENT

This section will describe the various methods and equipment used to treat water for various purposes.

UTILITY WATER TREATMENT

Water from wells, rivers, lakes, and streams is commonly used for cooling and washing. Clarifying and treating this water in order to meet the purity requirements of the proposed end use requires good monitoring and quick reactions to raw and treated water fluctuations. If the water is to be recirculated, the treatment methods are more stringent. If the water is to be discharged into the environment, local codes must be followed regarding allowable chemical amounts present in the wastewater in order to avoid the need for waste treatment.

Initial Filtering

If the supply is from surface water, a coarse or fine screen is usually placed at the intake to keep out fish and other large debris. Coarse screens are usually ½-in diameter bars with a clear opening of 1 to 3 in. Fine screens could have openings of approximately ⅜-in square, with the water velocity through the screen limited to about 2 ft/s. If the quantity of water is small enough, basket strainers can be used. In climates where freezing may occur, the inlet should be placed far enough below the low water level to prevent freezing.

Clarification

After initial filtering, clarification is required to obtain water that meets the standards for proposed use. The selection of the clarifier is based on the volume of water to be treated and the final quality desired. If the volume of water is small and the raw water is not very turbid, filters may be used.

Biological Control

In order to control microorganism fouling of the system, they must be destroyed, if possible, or at least inactivated (to keep them from reproducing) and then removed from the water stream. This is usually accomplished by chlorination, filtration, UV radiation, ozone generation, and special adsorbents.

Chlorination is the least costly and most common method. The action of chlorine requires a contact time and the establishment of a residual chlorine amount. A range of 0.5 to 1.0 ppm is generally acceptable for typical water.

Water Softening

Water softening should be considered to reduce the hardness in the utility water system when used for recirculated cooling purposes.

BOILER FEEDWATER CONDITIONING

In a boiler, energy in the form of heat is transferred from a fuel source to water to create steam. When subject to elevated temperature and pressure, the composition of the raw boiler water supply undergoes radical changes.

The effects of dissolved gases are magnified. The dissolved minerals may deposit a scale on the transfer surface, which will effect the heat transfer process. The result will be a reduction in the heat transfer rate, reduction in the flow rate, and increased damage from corrosion. A wide range of treatment methods is available depending primarily on the impurities found in raw water, operating pressure of the boiler, and makeup rate of water. These methods include mechanical treatment; addition of chemicals to prevent deposits, inhibit corrosion, or neutralize impurities detrimental to the proposed end use of the water; and the use of dispersants to keep particulates in suspension.

The treatment starts with an accurate feedwater analysis. This is compared to final treatment objectives established by the user and the boiler manufacturer. The degree of removal is determined by the difference in the two analyses. Recommended standards for boiler feedwater and steam quality are given in Table 4.9.

A boiler water treatment program must do the following:

1. Reduce or remove hardness to control scale by either mechanical (external) or chemical (internal) treatment
2. Maintain proper levels of alkalinity to assure that proper chemical reactions can occur
3. Control dissolved oxygen and carbon dioxide through deaerating and adding an oxygen scavenger
4. Maintain proper levels of conditioners so that the suspended solids remain in suspension and can be easily eliminated through blowdown
5. Optimize boiler blowdown

Mechanical removal of hardness is accomplished most often by water softening using an ion exchange process, where the insoluble calcium and magnesium ions are replaced with highly soluble sodium ions. A strong acid resin in sodium form, often referred to as zeolite, is commonly used. Real zeolite is in reality a naturally occurring mineral that is no longer widely used because of its high cost. Artificial resins are more efficient and cost effective for most uses.

The adjustment of pH is accomplished by the injection of dilute sulfuric or hydrochloric acid, sodium hydroxide, or sodium carbonate. This requires close monitoring.

Feedwater oxygen and carbon dioxide are normally removed with deaerators before the feedwater enters the boiler. In addition to mechanical deaeration, it is recommended that a chemical oxygen scavenger be added to the water to quickly eliminate any remaining traces of oxygen. Many scavengers are in use but the most

TABLE 4.9 Recommended Boiler Feedwater Limits and Steam Purity

Drum pressure, psig	Range TDS* boiler water, ppm max.	Range total alkalinity† boiler water	Suspended solids boiler water, ppm max.	Range TDS‡ steam, ppm (max. expected value)
		Drum-type boilers*		
0–300	700–3500	140–700	15	0.2–1.0
301–450	600–3000	120–600	10	0.2–1.0
451–600	500–2500	100–500	8	0.2–1.0
601–750	200–1000	40–200	3	0.1–0.5
751–900	150–700	30–150	2	0.1–0.5
901–1000	125–625	25–125	1	0.1–0.5
1001–1800	100		1	0.1
1801–2350	50		n/a	0.1
2351–2600	25		n/a	0.05
2601–2900	15		n/a	0.05
		Once-through boilers		
1400 and above	0.05	n/a	n/a	0.05

*Actual values within the range reflect the total dissolved solids (TDS) in the feedwater. Higher values are for high solids, lower values are for low solids in the feedwater.

†Actual values within the range are directly proportional to the actual value of TDS of boiler water. Higher values are for the high solids, lower values are for low solids in the boiler water.

‡These values are exclusive of silica.

n/a = not available.

Source: American Boiler Manufacturers Association.

popular scavengers are sulfites (up to 1000 psig) and compounds of hydrazine. Hydrazine is being replaced by diethylhydroxylamine (DEHA), carbohydrazide, hydroquinone, and isoascorbic acid.

Chemicals can be added to the boiler feedwater for two purposes. One is to keep the hardness salts in solution so they will not cause scaling. The second is to precipitate them out of solution to allow the particulates to be disposed of during blowdown. There are many effective materials, generally blends of component chemicals used to accomplish this. The most common are polymers, phosphates, and carbonates that are designed to optimize the precipitation of calcium, magnesium, and iron. Modern treatment has made hardness deposits much less common, but iron deposits more common because of the return of condensate to the boiler.

Boiler blowdown is the bleeding off of some water from the boiler. When steam is generated from feedwater, impurities are left behind and will accumulate in time. When the level of impurities becomes too high, a portion of the water is discharged to drain. This is called blowdown. Blowdown could be intermittent or continuous.

COOLING WATER CONDITIONING

This section will discuss the basic principles used for controlling scale, corrosion, and biological fouling of water used in evaporative cooling towers and condensation systems.

The basic reason for treatment of cooling water is to keep any dissolved solids from depositing onto any piping or equipment. This is accomplished by not allowing the dissolved solids to reach the saturation point. This is usually expressed as the cycle of concentration, which compares the amount of dissolved solids in the feedwater with the amount of dissolved solids of the circulating water. As an example, if the feedwater has a TDS of 100 ppm and the circulating water has a TDS of 300 ppm, a cycle of concentration of 3 has been reached. The cycle of concentration is reduced by bleed-off (blowdown) from the system.

Scale

The basic treatment for scale in cooling water systems is to add inhibitors to keep the scale from depositing itself on the walls of the pipe. The inhibitors are similar to those used for boiler water treatment, with the addition of surfactants that change the surface characteristics of the pipe to prevent deposition and aid in removal if deposits occur.

Corrosion

The corrosion potential of the water is indicated by the Langelier or Ryznar indexes. Corrosion treatments consist of pH control and chemical inhibitors. These are recommended by the manufacturers of the chemicals and the equipment to ensure compatibility. The pH of the circulating water is usually controlled to a point near 7.5 to decrease the scale-forming tendency. The addition of a dilute acid is used most often. A corrosion inhibitor often adds compounds that increase the tendency of scale to occur; therefore, a balance must be reached.

Biological Fouling

Microbial control is achieved with the addition of biocides, either oxidizing or nonoxidizing depending on their chemistry and killing action. Ozone is also commonly used.

Biocide treatment is intended to shock microbes initially with a heavy dose and then allow the concentration of the compounds to fall to a level of 25 percent of the initial dose. This is a generally accepted lower limit below which the biocide is not considered effective. Often, because of several different strains of microbes present, more than one biocide may be required. A contact time is required that must be approved by the chemical manufacturer.

These chemicals are added by means of a chemical feed pump discharging directly into the piping system. The levels must be closely monitored with alarms established by performance indicators based on operating experience.

POTABLE WATER TREATMENT

Water used for human consumption or intended to be part of food products must be treated to comply with the Safe Drinking Water Act (SDWA), local regulations, and also the Surface Water Treatment Rule, which is a part of the SDWA. In addition, compliance with regulation 10CFR141 is required. Substances that affect the quality of potable water are classified in four major categories:

1. *Physical.* Physical characteristics related to the appearance of the water include color, turbidity, taste, and odor. Physical quality is corrected mostly through the use of various types of filters.
2. *Chemical.* The chemical characteristics of water are related to dissolved minerals (mostly hardness), gases, and organics. The chemical quality of water is adjusted by the use of water softeners, ion exchange, RO units, and activated charcoal units to remove organic impurities.
3. *Biological.* This characteristic is concerned with microorganisms that will affect the health of the consumer. Biological treatment requires the use of biocides

TABLE 4.10 Water Treatment Technology for Small Potable Water Systems

Technology	Advantages	Disadvantages
	Filtration	
Slow sand	Operational simplicity and reliability, low cost, ability to achieve greater than 99.9 percent *Giardia* cyst removal	Not suitable for water with high turbidity, requires large land areas
Diatomaceous earth (septum filter)	Compact size, simplicity of operation, excellent cyst and turbidity removal	Most suitable for raw water with low bacterial counts and low turbidity (<10 ntu), requires coagulant and filter aids for effective virus removal, potential difficulty in maintaining complete and uniform thickness of diatomaceous earth on filter septum
Reverse osmosis membranes	Extremely compact, automated	Little information available to establish design criteria or operating parameters, most suitable for raw water with turbidity <1 ntu, usually must be preceded by high levels of pretreatment, easily clogged with colloids and algae, short filter runs, concerns about membrane failure, complex repairs of automated controls, high percent of water lost in backflushing
Rapid sand/ direct filtration package plants	Compact, treats a wide range of water quality parameters and variable levels	Chemical pretreatment complex, time-consuming; cost

(*Continued*)

TABLE 4.10 Water Treatment Technology for Small Potable Water Systems (*Continued*)

Technology	Advantages	Disadvantages
	Disinfection	
Chlorine	Very effective, has a proven history of protection against waterborne disease, widely used, variety of possible application points, inexpensive, appropriate as both primary and secondary disinfectant	Potential for harmful halogenated by-products under certain conditions
Ozone	Very effective, no THMs formed	Relatively high cost, more complex operation because it must be generated on-site, requires a secondary disinfectant, other by-products
Ultraviolet radiation	Very effective for viruses and bacteria, readily available, no known harmful residuals, simple operation and maintenance for high-quality waters	Inappropriate for surface water, requires a secondary disinfectant
	Organic contaminant removal	
Granular activated carbon	Effective for a broad spectrum of organics	Spent carbon disposal
Packed-tower aeration	Effective for volatile compounds	Potential for air emissions issues
Diffused aeration	Effective for volatile compounds and radionuclides	Clogging, air emissions, variable removal efficiencies
Advanced oxidation	Very effective	By-products
Reverse osmosis	Broad spectrum removal	Variable removal efficiencies, wastewater disposal
	Inorganic contaminant removal	
Reverse osmosis	Highly effective	Expensive waste removal
Ion exchange	Highly effective	Expensive waste removal
Activated alumina	Highly effective	Expensive waste removal
GAC	Highly effective	Expensive waste removal

and biostats to eliminate and reduce the number of microbes present in the water and to create a residual amount of the chemical to maintain the required level of action required by code.

4. *Radiological.* This is concerned primarily with radon in areas where the water may have come in contact with radioactive substances. Retention and aeration will lower the radon count to acceptable limits in approximately 8 h.

A synopsis of general treatment methods for small potable water systems that shows general advantages and disadvantages is given in Table 4.10.

WATER PURIFICATION

This section will discuss pure water used for laboratory and pharmaceutical purposes. The various systems will be broadly defined and general guidelines for their production, storage, and distribution will be provided.

Ultrapure water used in production of food products and electronics industries is outside the scope of this handbook. For information on guidelines for water purity in the electronics industry, refer to the Semiconductor Equipment Manufacturers Institute, Mountain View, California.

The total water treatment system consists of three interrelated phases: pretreatment, purification, and distribution (including posttreatment). Purification methods include distillation, ionization, membrane filtration, and other approved processes. WFI water can only be produced by distillation or membrane filtration. Processes needing ultrapure water used for specific applications often use pure water as feedwater and they further purify it to meet those specific requirements at the point of use.

CODES AND STANDARDS

The required quality of purified water depends on the application. Various codes have specifically defined water quality for use in various industries. Among them are:

1. 21 CFR 210 or cGMP for drugs
2. 21 CFR 211 or cGMP for finished pharmaceuticals
3. USP/NF official water nomographs
4. Federal Food, Drug, and Cosmetic Act

LABORATORY SYSTEMS

For laboratory work, all applications do not require the same quality of water. The American Society for Testing and Materials (ASTM), the College of American Pathologists (CAP), the National Committee for Clinical Laboratory Standards (NCCLS), and the Association for the Advancement of Medical Instrumentation (AAMI) have all developed standards for water used in laboratories depending on their intended use. These standards are summarized in Tables 4.11 (ASTM, CAP), 4.12 (NCCLS), and 4.13 (AAMI). ASTM electronics grade water standard is given in Table 4.14 for reference only. There are two types of pure water categories in the NCCLS specifications:

> Type I, called reagent grade water, is used for analysis of trace matter and other critical applications.
>
> Type II, called analytical grade water, is suitable for all but the most critical procedures.

TABLE 4.11 ASTM Reagent-Grade Water Specifications

	Type I	Type II
Resistivity (Megohm-cm compensated to 25°C)	18.0	1.0
TOC (ppb)	100	50
Sodium (ppb)	1	5
Chlorides (ppb)	1	5
Silica (ppb)	3	3

TABLE 4.12 NCCLS/CAP Reagent Water Specifications

	Type I	Type II
Resistivity (Megohm-cm @ 25°C)	10	1.0
Silicate (mg/L SiO_2)	0.05	0.1
TOC (ppb)	Activated carbon (not required by CAP) or distillation or RO	Not specified
Particulates	0.22 micron filter	Not specified
Bacteria (cfu/mL)	10	1000

Additional purification may be required for selected clinical laboratory procedures such as:

1. Preparation of water with minimal pyrogen levels for cell culture
2. Preparation of bacteria-free water for direct fluorescent detection of bacteria as in Legionella direct fluorescent antibody testing or direct fluorescent stains of mycobacteria
3. Preparation of water with minimal organic content for HPLC.

TABLE 4.13 AAMI/ANSI Water Quality Standards

Contaminant	Suggested maximum level, mg/L
Calcium	2 (0.1 meq/L)
Magnesium	4 (0.3 meq/L)
Sodium	70 (3 meq/L)
Potassium	8 (0.2 meq/L)
Fluoride	0.2
Chlorine	0.5
Chloramines	0.1
Nitrate (N)	2
Sulfate	100
Copper, barium, zinc	0.1 each
Arsenic, lead, silver	0.005 each
Chromium	0.014
Cadmium	0.001
Selenium	0.09
Aluminum	0.01
Mercury	0.0002
Bacteria	200 (cfu/mL)

Source: Association for the Advancement of Medical Instrumentation (AAMI) "Hemodialysis Systems Standard," March 1990. Adopted by American National Standards Institute (ANSI), 1992.

TABLE 4.14 ASTM Electronics-Grade Water Standard*

	Grade			
Assay	E-I	E-II	E-III	E-IV
Resistivity, minimum, MΩ·cm at 25°C	>18.0* >17.0*	17.5† >16.0†	12	0.5
SiO_2 (total), max, μg/L	5	10	50	1000
Particle count per milliliter	1	3	10	100
Particle size limit, μm	0.10	0.5	1.0	10
Viable bacteria, max	1/1000 mL	10/1000 mL	10/1 mL	100/1 mL
Copper, max, μg/L	1	1	2	500
Zinc, max, μg/L	0.5	1	5	500
Nickel, max, μg/L	0.1	1	2	500
Sodium, max, μg/L	0.5	1	5	1000
Potassium, max, μg/L	2	2	5	500
Chloride, max, μg/L	1	1	10	1000
Nitrate, max, μg/L	1	1	5	500
Phosphate, max, μg/L	1	1	5	500
Sulfate, max, μg/L	1	1	5	500
Total organic carbon, max, μg/L	25	50	300	1000
Endotoxins	0.03EU‡	0.25EU‡	N/A§	N/A§

*Above 18 MΩ·cm 95% of the time, not less than 17.

†17.5 or greater 90% of the time, not less than 16.

‡EU = Endotoxin unit.

§N/A = not applicable.

Source: ASTM Standard D5127-90.

PHARMACEUTICAL WATER

The pharmaceutical industry in most countries is regulated. In the United Sates, the industry is regulated by the Food and Drug administration (FDA), which takes guidance from several sources, including the Pharmaceutical Research and Pharmaceutical Manufacturers of America (PhRMA), the United States Pharmacopoeia (USP) and updates from the Pharmacopoeia Forum (PF), published by the U.S. Pharmacopeial Convention. Each country has its own governing and guiding agencies.

Information in this handbook refers to standards of the United States. The standards include USP 24/NF 19, January 1, 2000, as given in Tables 4.15 and 4.16.

PURIFIED WATER TYPES

1. *Compendial water.* This is a general term that includes all types of purified water and water for injection intended to be used in any final pharmaceutical drug dosage form.
2. *Purified water* (PW). The quality of the feedwater shall meet drinking water standards. The final product shall contain no added substances. The USP re-

TABLE 4.15 Standards for Purified Water and Water for Injection

Parameter	Standard
TOC	550 ppb Carbon
Conductivity	1.3 μS/cm @ 25°C 0.1 μS/cm @ 20°C
Bacteria (guidelines <1231>)	PW: 100 cfu/mL WFI: 10 cfu/100 mL
Bacterial endotoxins	WFI: 0.25 USP EU/mL

Notes: μS/cm = microSiemens per centimeter
cfu/mL = colony forming units per milliliter
EU/mL = endotoxin units per milliliter

TABLE 4.16 Standards for Packaged PW, WFI, and Sterile PW

Parameter	Standard
pH	5.0 to 7.0
Chloride (mg/L)	0.5
Sulfate (mg/L)	1.0
Ammonia (mg/L)	0.03
Calcium (mg/L)	1.0
Carbon dioxide (mg/L)	5.0
Oxidizable substances	pass USP Permanganate test
Bacteria	
*Purified Water (cfu/mL)	100
*WFI (cfu/100 mL)	10
Sterial PW	pass the USP Sterility test <71>
Endotoxin WFI (EU/mL)	0.25

Note: *Limits are guidelines in General Chapter <1231>
Source: U.S. Pharmacopeial Convention Inc., Reference 8.

quirement with added substances has always been concerned with additions to the final product and not to the feedwater. It is commonly interpreted by USP that substances may be added to the feedwater provided that they are removed to an acceptable level during the final treatment process. PW is used as the feedwater for preparation of compendial water.

3. *Sterile purified water.* This type, including some Sterile Water for Inhalation, is made using purified water as a raw water source, sterilized and suitably packaged. It contains no antimicrobial agent.
4. *Bacteriostatic purified water.* PW sterilized and suitably packaged. It contains no antimicrobial agent.
5. *Water for injection* (WFI). This type is made using PW as a raw water source that must be further purified by distillation or RO. Bacteria and endotoxins must be reduced to the required level.
6. *Sterile bacteriostatic water for injection.* WFI sterilized and suitably packaged. It contains no antimicrobial agent.

7. *Sterile water for inhalation.* WFI sterilized and suitably packaged. It contains no antimicrobial agent except when used in humidifiers or similar devices subject to contamination, or other added substances.
8. *Sterile water for irrigation.* WFI sterilized and suitably packaged. It contains no antimicrobial agent.

PHARMACEUTICAL WATER TREATMENT PROCESS

Pharmaceutical water treatment takes raw water that meets drinking (potable) water standards and removes sufficient contaminants from that water in a treatment plant to meet the standards for the various types of compendial waters. It takes a number of treatment steps in order to process raw water into PW and other subsequent pure water types.

Each individual treatment plant will have a different configuration. A typical configuration is illustrated in Fig. 4.16. The intent of Fig. 4.16 is to show a process flow and include most of the equipment and general arrangement found in a typical plant. It is not intended to indicate that this is the best or only manner to arrange the process.

All pharmaceutical water shall start with potable water as a raw water source. Potable water usually contains a residual of some oxidizing biocidal agent to control disease causing microorganisms. Typically either chlorine or chlorimine is the oxidizing agent, and it is used in sufficient quantities to achieve a free chlorine residual necessary to achieve it purpose. There are no requirements regarding the amount

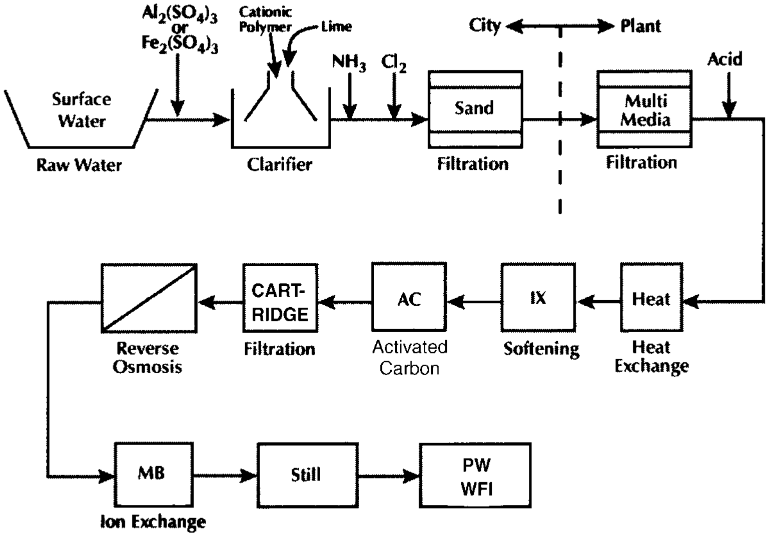


FIGURE 4.16 Pharmaceutical water treatment plant configuration.

of TOC or endotoxins present. The TOC is subject to seasonal variances, with the lowest level usually occurring in the wintertime.

Multimedia filtration. One of the first steps commonly found in the treatment process is multimedia filtration. Its purpose is to remove the bulk of suspended contaminants larger than 30 microns.

Acid injection. Some treatment plants must add acid injection somewhere in the system. The purpose of the acid is primary for scale control It is shown in Fig. 4.16 before the heat exchanger because calcium carbonate is more likely to scale out when water is hot. If there is little hardness (calcium, and magnesium ions) or alkalinity (hydroxide, bicarbonate and carbonate ions) in the feedwater, acid may be eliminated. Another common reason to use acid is to minimize damage to cellulose acetate membranes if it is a downstream RO process component. These membranes are easily damaged at any pH level, but at a pH level of 5.5 to 6, the damage is minimized.

Heat exchange. Feedwater is heated to lower the pumping costs for an RO unit because the warmer the water, the less pressure is required to pump water through an RO membrane. Another reason is that warmer water accelerates the rate of diffusion and chemical reactions. Generally speaking, for every 18°F (10°C) rise in temperature, the speed of chemical reactions doubles.

Softening. A water softener controls scale by removing the hard, scale forming cations like calcium and magnesium, and exchanging (replacing) them with non-scale forming sodium ions.

Activated carbon units. Often called activated carbon beds or activated carbon filters, these filters remove chlorine or chlorimine compounds from the feedwater to protect both RO membranes and DI resins from the oxidizing action of the chlorine and chlorimine compounds. A second, less common reason is to remove certain organic compounds. Organic compounds are molecules that always contain carbon, usually contain hydrogen and frequently contain other atoms. They are called organic because prior to human intervention all organic compounds came from living organisms.

Cartridge filtration. This filter is installed upstream of the RO units as an additional protection against suspended solids. RO membranes will foul if sufficient suspended solids are not removed by the multi-media filter.

Reverse osmosis. RO is a membrane that removes a bulk of the suspended solids and contaminants, which is, typically, 98 to 99+ percent of ionic contaminants and 95 to 99+ percent of dissolved TOC. A single pass through the RO will typically not meet PW or WFI standards. A double pass system, where the processed water from one RO unit is processed again through another unit, may be allowable. Distillation units are more commonly used to provide PW and WFI quality water.

Ion exchange. Following an RO unit, it is generally required to further reduce the contaminant level. This is done typically using a mixed bed deionization unit. This cold be combined with electrodeionization (EDI), also known as continuous deionization (CDI) to further polish RO water. The resultant water is not pyrogen free.

Distillation. In order to achieve PW and WFI quality, most treatment plants use distillation (stills) as a final step. A still heats the feedwater to the boiling point, and the resulting steam condensate typically meets required standards. There are various types of stills that require different feedwater quality; therefore, alternative upstream requirements other than that shown in Fig. 4.16 may be necessary. Distillation produces water that is pyrogen free.

FEEDWATER

Feedwater quality, which is source dependent, is the first parameter to be identified in the design of a pure water system. The source strongly influences the pretreatment options and may dictate the purification methods. There is a wide difference in types and concentrations of various impurities possible, depending on whether the feedwater is obtained from a public utility or privately, such as from a well or other surface or groundwater source. Surface waters are usually high in particulates, colloids, and organics. Underground waters tend to have low levels of particulates, colloids, and organics, and relatively high levels of calcium and magnesium hardness and alkalinity (bicarbonates). Source water from agricultural areas often has high levels of nitrates, phosphates, and organic pesticides. Water from public utilities has residual chlorine, fluorides, and chlorimines as well as iron oxides and other pipe-related impurities. It is important to establish or obtain historical water analysis data from different times and seasons of the year in order to properly design a system with enough flexibility to obtain the required purity under worst case conditions.

It is an FDA requirement that the feedwater for USP Purified Water and WFI systems meet the EPA guidelines for potable water. Of particular concern is the microbial level. The water should be virtually free of coliform, which is a pathogenic marker organism. The feedwater must also meet the 400 cfu/ml, the maximum value specified in USP XXII. Another requirement is that it shall contain no added substances. This is an issue that appears to be interpreted differently by individuals and organizations involved in the design of PW systems. There are systems presently in use that appear from an overall perspective to violate this position. Items such as the chlorination of raw water supplies, acid addition to adjust pH, and the use of ozone to control microbial growth are subject to interpretation. All of the concerns should be resolved during the application phase for FDA approval and validation of the system.

PURIFICATION SYSTEM DESIGN

General

Specific methods of purification are capable of removing various types of impurities better than others. None can be depended on to remove all the impurities necessary to achieve the purity level required for USP purified water. It is accepted practice to use a combination of technologies, each of which is designed to remove a specific type of impurity.

The methods used to produce this water are dependent on the feedwater supplying the facility. In most instances, that feedwater has a high level of some classes of contaminants. It is much more economical to pretreat that water to remove the bulk of large quantities and/or the more concentrated of those impurities, and then use the purification equipment to ‘‘polish’’ the water to the desired purity level. In some cases, the removal of individual impurities is necessary to allow the use of specific types of purification equipment.

Pretreatment

General. Pretreatment is considered for two reasons: to prevent potential damage to the membrane selected and to increase membrane filtration quality. The need for pretreatment is determined by an analysis of the raw water supply. The decision is generally governed by the cost efficiency of the pretreatment method, specifically whether the cost of purchasing and installing the pretreatment equipment will reduce the initial cost of the main treatment equipment and lower the operating cost of the system as a whole enough to justify its installation.

Water Temperature. Membrane productivity (flux) is usually rated with feedwater at 77°F, and is inversely proportional to the feedwater viscosity. When the water temperature is lower, additional membrane area is required. The flux increases with increased feedwater temperature. Heating the feedwater lowers the viscosity. The water can be heated with a separate water heater or with a blending valve using domestic hot water mixed with feedwater to provide the necessary temperature.

pH Adjustment. The selected membrane will have an optimum pH operating range. When using drinking water standards, this problem is rarely encountered. In order to achieve it, a dilute acid is injected into the feedwater if necessary.

Filtration. Filters are used to remove suspended solids originating from any source. If continuous production is required, a duplex arrangement should be installed so that the filters can be backwashed or replaced with no interruption in service.

Sand and Multimedia Filters. A common initial method for gross particulate removal from source water is a pressure multimedia sand filter if suspended solids are greater than 0.2 ppm. If lower, a 5- to 10-μm cartridge filter is often used. Experience has found that cartridge replacement is not economical as compared to the cost of backwashing.

Cartridge Filters. Used to remove lesser amounts of particulates prior to the central purification equipment, an in-line 5-μm cartridge depth filter should be installed to eliminate any particulates that would clog or interfere with operation of the central purification equipment. This filter is recommended if the SDI is less than 4, and is generally required if the level is more than 4. If the level is more than 4, an additional 1-μm cartridge filter is recommended downstream of the main filter.

Carbon Filtration. Following the removal of gross particulates, a granulated carbon filter is provided to remove residual disinfectants (chlorine, chlorimine, etc.), dissolved organics (oils, pesticides, surfactants, etc.), and suspended organics (humic and fulvic acids, etc.).

Flow rates through this filter are usually in the range of 1.0 to 4.0 gpm/ft^2 of filter area depending on the quantity of organics and chlorimines of the entering water. The higher the quality, the higher the flow rate. Also the higher the quality of water, the slower the flow rate.

The problem with carbon filtration is its tendency to harbor microbial growth due to the removal of chlorine. Frequent sanitizing is necessary, usually with potassium permanganate, sodium hydroxide, or steam. If steam is selected, the tank should be constructed of type 316L stainless steel.

Water Softening. If the hardness is high, it is necessary to provide a water softener to reduce the calcium and magnesium present to the level required by the membrane selected. Water softening is recommended if the iron content exceeds 0.4 ppm.

The softener is another device that harbors microbial growth. Sanitizing with potassium permanganate is generally used.

Biological and TOC Reduction. UV units and ozone generators are generally used to remove microorganisms and to remove TOC prior to the feedwater reaching the RO units. Materials used in the system must be compatible with them. There is a reluctance to use any chemical to remove microorganisms due to FDA restrictions against adding chemicals to the feedwater. However, the addition of chlorine to disinfect the feedwater is commonly used because it is cost effective and can be easily removed by GAC filters.

Biocide Removal. A far greater source of feedwater for most facilities is potable water. The water contains a residual amount of chlorine necessary to comply with code for drinking water quality. To remove this residual chlorine, a granulated activated charcoal filter is provided. An organic trap may also be required if organics are very high.

CENTRAL PURIFICATION EQUIPMENT

The basic methods used to produce high purity water are distillation, ion exchange, and reverse osmosis. The method used will depend on the purity desired and limitations on initial or operating cost.

Storage

Storage of water will reduce the size of the purification equipment. Storage tanks are constructed from FRP, PP, and SS. The bottom of the tank is dished or conical to aid in complete drainage. It is an established fact that high purity water degrades in storage. The four major sources of this degradation are:

1. Water will extract contamination from any container.
2. Bacteria will grow and secrete waste products.
3. Organics from solvents and shedding of clothing can diffuse through the air and dissolve in the water.
4. Laboratory personnel secrete urea in perspiration and respiration that can cause the formation of ammonia in stored laboratory water.

The tank for USP water should be airtight and equipped with a nonshedding, 0.2-μm hydrophobic filter for venting. For WFI systems, the tank should be type 304L or 316L stainless steel, pressure rated to a minimum of 35 psig pressure, 30 in Hg vacuum, 180 grit, and electropolished. It is common practice to have a nitrogen gas blanket in the vapor space above the water in the storage tank to reduce the possibility of airborne contamination. The tank should have a jacket to maintain a temperature of 80°C and be insulated and provided with a rupture disk.

The discharge from the tank should be from the center bottom of the tank to allow complete circulation of the stored water. The water return should be at the top of the tank and be equipped with a spray ball or spray ring. This minimizes microbial growth by continuously washing the upper areas of the tank.

Sterilization. It is common practice to provide an in-line UV sterilization device to reduce microorganisms that may be present in the water. Another common method is to heat purified water to a temperature of 80°C (177°F) to prevent microorganism growth, and circulate it to maintain the sterile condition. Another possibility is installation of a filter that will remove any organic particulates.

Piping Distribution Network

The piping material for USP water should be fabricated from virgin PP, PVDF, or SS. Plastic pipe should be butt-joint heat-fused and SS pipe should be orbital welded. Piping material for WFI water should be SS, 180 grit and electropolished. Fittings must have extended ends for orbital welding. All couplings must be sanitary triclamp. Insulation must be nonchloride bearing and designed for a temperature of 80°C. Velocity in the system should be approximately 6 to 9 ft/s for supply from the storage tank to the system and 3 to 6 ft/s in the return leg. Th4s is accomplished by the installation of a back-pressure regulator. These velocities are recommended to scour the pipe interior and prevent the formation of biofilm.

The pipe should be sloped at a ⅛-in pitch to allow complete drainage of the network. Dead legs of more than 6 pipe diameters are not permitted by cGMP requirements. To prevent future plastic pipe sagging from interfering with drainage, continuous support is recommended. Using PP as a baseline, PVDF is twice the cost and SS four times the cost installed.

Valves must be consistent with the piping materials. Prior to the RO or DI units, full bore ball valves are recommended. In the purified loop, SS diaphragm valves with an EPDM or Teflon diaphragm and a backing ring should be used. Sample valves (usually needle type) should be provided in areas of the system to allow samples to be taken at strategic points.

Pumps for purified water should be of sanitary design using a double mechanical seal with product water as the lubricant for the seals. WFI pumps should be type 316L SS, 180 grit and electropolished. A casing drain should be provided.

System Design Considerations

USP/WFI water is used in the pharmaceutical manufacturing process and often becomes part of the product. Because of this, all aspects of the purification system and distribution network are subject to inspection and validation by the FDA, which has the responsibility to determine if the quality of water used is adequate.

The FDA has specific guidelines for selection of stills and RO equipment used for production of WFI. In contrast, PW systems can utilize different types of purification equipment, since the microbial and chemical quality can vary depending on the proposed use of the water.

The purpose of any guidelines or standards is to verify that all pertinent purity requirements of the equipment and distribution system conform to current good manufacturing practice (cGMP), are capable of consistently producing water of the required quality, and are capable of delivering water that meets the acceptance criteria for water that comes in contact with product. This investigation also includes verification that the purification equipment selected be capable of producing water of the required purity, that the quality of installation for the distribution network produces a piping network capable of delivering water of the required quality to all outlets, and that the continuing quality of system operation, maintenance, and ongoing testing will consistently provide water of the desired purity.

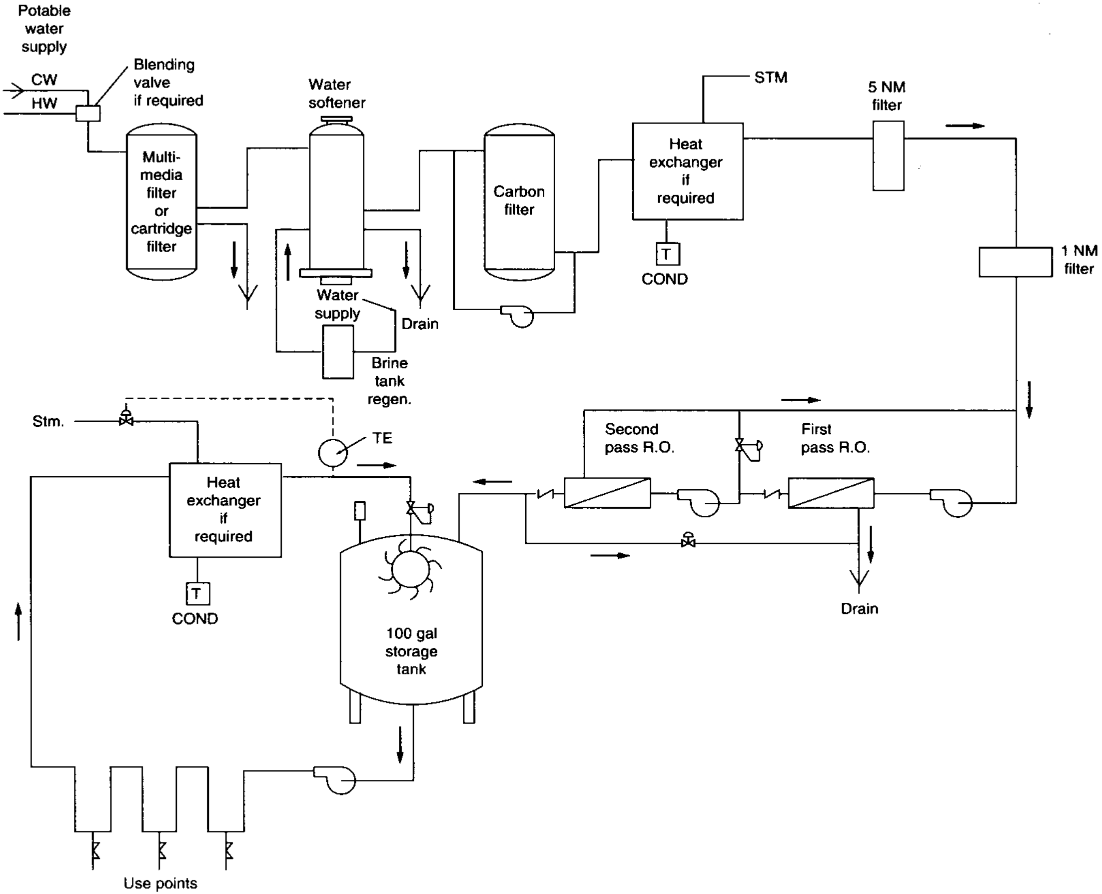


FIGURE 4.17 Typical pharmaceutical water flow diagram.

One typical pharmaceutical water purification flow diagram is shown in Fig. 4.17.

REFERENCES

Blake, R. T., *Water Treatment for HVAC and Potable Water Systems,* McGraw-Hill, New York.

Brown, J., N. Jayawardena, and Y. Zelmanovich, ''Water Systems for Pharmaceutical Facilities,'' *Pharmaceutical Engineering Magazine,* pp. 14–23, July/August 1991.

Cartwright, Peter S., ''Reverse Osmosis and Nanofiltration System Design,'' *Plumbing Engineer Magazine,* pp. 45–49, March 1994.

Collentro, W. V., ''Pharmaceutical Water,'' Parts 1 and 2, *Ultrapure Water Magazine,* November/December 1992.

Dow Chemical Corporation, ''Water Conditioner Manual,'' 1988.

Gorry, M., P. Amin, and D. W. Richardson, Sr.,''Take the Guesswork out of Demineralizer Design,'' *Chemical Engineering Magazine,* pp. 112–116, March 1994.

Janoschek, R., and G. C. du Moulin, ''Ultraviolet Disinfection in Biotechnology: Myth vs Practice,'' *BioPharm Magazine,* pp. 24–27, January/February 1994.

Meyrick, C. E., ''Practical Design of a High Purity Water System,'' *Pharmaceutical Engineering Magazine,* pp. 20–27, September/October 1989.

Nalco Chemical Company, *The Nalco Water Handbook,* 2nd ed., McGraw Hill, New York, 1988. Nussbaum, O. J., ''Treating Cooling Water,'' *Heating/Piping/Air Conditioning Magazine,* pp. 63–67, February 1992.

Parekh, B. S., ''Get Your Process Water to Come Clean,'' *Chemical Engineering Magazine,* pp. 71–85, January 1991.

Sendelbach, M. G., ''Boiler Water Treatment,'' *Chemical Engineering Magazine,* pp. 127–132, August 1988.

Stenzel, M. H., ''Remove Organics by Activated Carbon Adsorption,'' *Chemical Engineering Progress Magazine,* pp. 36–43, April 1993.

Yeh, K. L. and S. H. Lin, ''Looking to Treat Wastewater-Try Ozone,'' *Chemical Engineering Magazine,* pp. 113–116, May 1993.