

HANDBOOK *of*
WATER *and*
WASTEWATER
TRREATMENT
TECHNOLOGY

PAUL N. CHEREMISINOFF

Handbook of Water and Wastewater Treatment Technology

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Preface

This handbook is a collection of exact and useful information relating to the treatment of water and wastewater for municipal, sanitary, and industrial uses. The operations and processes implemented by users of water are numerous and an attempt has been made to reduce those described to the practical limits of a single volume. Preference has been given to those unit operations and processes which have the most general application and serve a broad range of users.

Treatment of material is primarily descriptive, although the text is liberally supplemented with diagrams and drawings. Wherever possible, the theory governing the processes and equipment described is briefly given to clarify the discussion. The intention was to give sufficient information to provide the thoughtful reader with a satisfactory understanding of the subject. This book should be useful to civil, environmental, manufacturing, petrochemical, and chemical engineers, as well as plant operators and technicians.

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1

Water Characteristics

Both individuals and industry produce liquid and solid wastes. The liquid portion, wastewater, is essentially water supply after it has been fouled by use. From the standpoint of sources of generation, wastewater may be defined as a combination of the liquid of water-carried wastes removed from residences, institutions, and commercial and industrial establishments together with such groundwater, surface water, and storm water as may be present. The ultimate goal in wastewater management is the protection of the environment commensurate with economic, social, political, and health concerns.

With increasing density of population and industrial expansion, the need for treatment and disposal of waste has grown. The specific reasons for sewage and waste treatment are as follows.

HEALTH CONCERNS

Disease-producing organisms, especially those causing diarrhea, may be present in sewage. Little is known about the presence of toxic substances produced by bacterial decomposition of certain organic substances, although a variety of degradation products are formed. From a health standpoint, the greatest problem of pollution is its effect on public water supplies by overloading the treatment devices so that they pass intestinal organisms, and by producing intestinal irritants

in water which are not removed by filtration. Sewage pollution of bathing waters and shellfish areas may result in epidemics such as typhoid or other intestinal diseases as well as contamination of the food chain. Sewage treatment which reduces the pollution and kills intestinal organisms assists in the production of a safe drinking water at a lower cost, prevents contamination of shellfish, and permits bathing, water sports, and recreation.

ESTHETIC CONCERNS

The discharge of sewage into streams and water courses produces odors and discoloration, results in nuisances from sludge, and interferes with bathing facilities and recreation.

PROPERTY DAMAGE

The discharge of sewage affects industrial water supplies by changing the character of the water. Odors and gases in sewage affect real estate by causing paints to discolor as well as damage to boats. Some treatment of wastewaters is usually necessary before disposal. The methods of treatment adopted must be sufficient to ensure the necessary degree of purification required to suit the means of disposal.

Most unit operations and processes used for wastewater treatment are constantly undergoing continual and intensive investigation from the standpoint of implementation and application. As a result, many modifications and new operations and processes have been developed and implemented; more need to be made to meet increasingly stringent requirements for environmental enhancement of water. In addition to the developments taking place with conventional treatment methods, alternative treatment systems and technologies are also being developed and introduced.

AVAILABLE TREATMENT SYSTEMS

The treatment process chosen is a function of several factors:

- Flow rate
- Waste strength and toxicity
- Availability of land
- Esthetics
- Discharge standards
- Climatic conditions
- Degree of permanence desired
- Costs

For example, in remote areas where land is inexpensive and climate is favorable, a percolation/evaporation pond may provide simple zero discharge solution, whereas in a suburban community in which the ultimate discharge enters surface waters, an esthetic and high-performance plant which may include some type of tertiary facility would be more appropriate. Table 1 shows the various wastewater treatment options in use. Materials removed during water/wastewater treatment is called sludge, and Table 2 lists the options for its management.

CHARACTERISTICS OF WASTEWATER

An understanding of the nature of wastewater is essential in the design and operation of collection, treatment, and disposal facilities and in the engineering management for environmental quality.

The physical properties and the chemical and biological constituents of wastewater and their sources are listed in Table 3. The important contaminants of interest in wastewater treatment are listed in Table 4. Wastewater characterization studies are conducted to determine the physical, biological, and chemical characteristics and the concentrations of constituents in the wastewater as the best means of reducing the pollutant concentrations.

EFFECTS OF POLLUTION

Effects of pollution can be manifested by many characteristics and variations in degree when pollution enters the aquatic environment. Specific environmental and ecological responses to a pollutant will depend largely on the volume and strength of the waste and the volume of water receiving it. Within each response there can be many changes in magnitude and degree. A classic response that has often been described is the effects of organic wastes that may be discharged from sewage-treatment plants and certain industries. As these wastes enter the receiving water, they create turbidity, decrease light penetration, and may settle to the bottom in substantial quantity to form sludge beds. Wastes are attacked by bacteria and this process of decomposition consumes oxygen from the water and liberates essential nutrients that in turn stimulate the production of some forms of aquatic life.

Upstream from the introduction of organic wastes is a clean water zone or one that is not affected by pollutants. At the point of waste discharge and for a short distance downstream there is formed a zone of degradation where wastes become mixed with the receiving waters and where the initial attack is made on the waste by bacteria and other organisms in the process of decomposition.

Following the zone of degradation there is a zone of active decomposition that may extend for miles or days of stream flow, which depends in large measure on the volume of the waste by the stream and the temperature of the water.

Table 1 Wastewater Treatment Options

	Primary treatment		Secondary treatment	
	Pretreatment	Chemical	Physical	Dissolved organics and colloidal material is removed
Wastewater	Screening and Grit Removal	Neutralization	Flotation	Activated Sludge
	Equalization and Storage	Coagulation	Sedimentation	Contact Stabilization
	Oil Separation	Hydrolysis		Trickling Filter Aerated Lagoon Ozonation
				Sedimentation
				Coagulation Sedimentation Filtration
				Carbon Adsorption Ion Exchange Distillation Reverse Osmosis Electrodialysis

Table 2 Options for Sludge Management

Disposal	Sludge treatment	Sludge disposal
	Aerobic Digestion	
Chlorination Ozonation	Anaerobic Digestion	Incineration
Receiving Waters or Reuse	Wet Combustion	Land Fill
Controlled or Transported	Centrifugation	Soil Conditioning
Discharge		
Ocean Disposal	Thickening	Ocean Disposal
Surface Application or	Vacuum Filtration	
Ground Water Seepage	Lagooning, or	
	Drying Beds	
Evaporation + Incineration		

Biological processes that occur within this zone are similar in many respects to those that occur in a typical sewage treatment plant. Within this zone, waste products are decomposed and those products that are not settled as sludge are assimilated by organisms in life processes.

A recovery zone follows the zone of active decomposition. The recovery zone is essentially a stream reached in which water quality is gradually returned to that which existed prior to the entrance of pollutants. Water quality recovery is accomplished through physical, chemical, and biological interactions within the aquatic environment. The zone of recovery may also extend for many miles, and its extent will depend principally on morphometric features of the waterways. The zone of recovery will terminate in another zone of clean water or area unaffected by pollution that is similar in physical, chemical, and biological features to that which existed upstream from the pollution source.

Organic Wastes

The effects of organic wastes on the receiving stream often become confused with a specific stream because additional sources of pollution may enter the environment before the receiving water has been able to assimilate the entire effects of an initial source. When this occurs, the effects of subsequent introductions become superimposed on the initial source and the total effect may confine large reaches of stream to a particular zonal classification.

Effects of organic wastes in the static water environment, as opposed to the flowing water environment, are modified by the features of the receiving water. Zonal changes for flowing water do exist but may be compressed in great measure either laterally or vertically when the discharge is to a lake or estuary. Such compression may tend to decrease the severity of pollution that is often observed in the flowing water environment and, on the other hand, may increase

Table 3 Physical, Chemical, and Biological Characteristics of Wastewater and Their Sources

Characteristic	Sources
Physical Properties	
Color	Domestic and industrial wastes, natural decay of organic materials
Odor	Decomposing wastewater, industrial wastes
Solids	Domestic water supply, domestic and industrial wastes, soil erosion, inflow-infiltration
Temperature	Domestic and industrial wastes
Chemical Constituents	
Organics	
Carbohydrates	Domestic, commercial, industrial wastes
Fats, oils and grease	Domestic, commercial, industrial wastes
Pesticides	Agricultural wastes
Phenols	Industrial wastes
Proteins	Domestic and commercial wastes
Surfactants	Domestic and industrial wastes
Others	Natural decay of organic materials
Inorganics	
Alkalinity	Domestic wastes, domestic water supply, ground water infiltration
Chlorides	Domestic water supply, domestic wastes, ground water infiltration, water softeners
Heavy metals	Industrial wastes
Nitrogen	Domestic and agricultural wastes
pH	Industrial wastes
Phosphorus	Domestic and industrial wastes, natural runoff
Sulfur	Domestic water supply, domestic and industrial wastes
Toxic compounds	Industrial wastes
Gases	
Hydrogen sulfide	Decomposition of domestic wastes
Methane	Decomposition of domestic wastes
Oxygen	Domestic water supply, surface water infiltration
Biological Constituents	
Animals	Open watercourses and treatment plants
Plants	Open watercourses and treatment plants
Protista	Domestic wastes, treatment plants
Viruses	Domestic wastes

Table 4 Important Contaminants of Concern in Wastewater Treatment

Contaminants	Reason for importance
Suspended solids	Suspended solids can lead to the development of sludge deposits and anaerobic conditions when untreated wastewater is discharged in the aquatic environment.
Biodegradable organics	Composed principally of proteins, carbohydrates, and fats, biodegradable organics are measured most commonly in terms of BOD and COD. If discharged untreated to the environment, their biological stabilization can lead to the depletion of natural oxygen resources and to the development of septic conditions.
Pathogens	Communicable diseases can be transmitted by the pathogenic organisms in wastewater.
Nutrients	Both nitrogen and phosphorus, along with carbon, are essential nutrients for growth. When discharged to the aquatic environment, these nutrients can lead to the growth of undesirable aquatic life. When discharged in excessive amounts on land, they can also lead to the pollution of ground water.
Refractory organics	These organics tend to resist conventional methods of wastewater treatment. Typical examples include surfactants, phenols, and agricultural pesticides.
Heavy metals	Heavy metals are usually added to wastewater from commercial and industrial activities and may have to be removed if the wastewater is to be reused.
Dissolved inorganic solids	Inorganic constituents such as calcium, sodium, and sulfate are added to the original domestic water supply as a result of water use and may have to be removed if the wastewater is to be reused.

substantially the development of biotic nuisances such as algae or rooted aquatic plants that may develop from the nutrients released with and decomposed from the introduced organic materials.

Organism communities that may be related to pollution principally are those that are usually associated with the bed or bottom of the waterway; those that attach themselves to objects such as rocks, aquatic plants, brush, or debris submerged in the water; those that are essentially free floating and are transported by currents and wind, such as plankton and other microscopic forms; and those motile free-swimming organisms such as fish. Considering each of these common organism groups, a number of observations can be made on their reaction to the introduction of organic wastes to a flowing stream.

Upstream from waste sources such limiting factors as food and intense

competition among organisms and among organism groups, predation, and available habitat for a particular species will limit organism populations to those that can be sustained by the particular environment. Most often the limiting factor will be available food. Within this population, however, there will exist a great number of organism species. Thus, the old biological axiom for an environment unaffected by pollution is one that supports a great number of species with the total population delimited largely by food supply.

Introduction of organic wastes causes conditions of existence for many organisms that become substantially degraded. Increased turbidity in the water reduces light penetration, which in turn will reduce the volume of water capable of supporting photosynthesizing plants. Particulate matter in settling will flocculate small floating animals and plants from the water. As the material settles, sludge beds are formed on the stream bed and many of the areas that formerly could have been inhabited by bottom-associated organisms become covered and uninhabitable.

The zone of degradation is the transition area between the clean water unaffected reach and a zone of decomposition of organic wastes. The dissolved oxygen may be diminished but not completely removed. Sludge deposits may be initiated but are not formed in maximum magnitude or extent. Conditions of existence become impaired, and typically there is a reduction in both the organism population and the number of species that can tolerate this environment.

Within the zone of active decomposition conditions of existence for aquatic life are at their worst. Breakdown of organic products by bacteria may have consumed available dissolved oxygen. Sludge deposits may have covered the stream bed and thus eliminate dwelling areas for the majority of bottom-associated organisms that could be found in an unaffected area. Fish spawning areas have been eliminated, but perhaps fish are no longer present because of diminished dissolved oxygen and substantially reduced available food. Here aquatic plants will not be found in large numbers, because they cannot survive on the soft shifting blanket of sludge. Turbidity may be high and floating plants and animals destroyed. Water color may be substantially affected. When organic materials are decomposed as the food supply is liberated for those particular organisms that are adapted to use this food source. Bacterial and certain protozoan populations may increase to extremely high levels. Bottom-associated organisms such as sludgeworms, bloodworms, and other wormlike animals may also increase to tremendous numbers, because they are adapted to burrowing within the sludge, deriving their food therefrom, and existing on sources and amounts of oxygen that may be essentially nondetectable by conventional field investigative methods. Within the zone of active decomposition, the organism species that can tolerate the environment are reduced to extremely low levels. Under some conditions, those bottom-associated animals that are visible to the unaided eye may be completely eliminated. Because of the tremendous quantity of food

that is available to those organisms that are adapted to use it, the numbers of individuals of the surviving species may become great.

The zone of recovery is essentially the downstream transition zone between the zone of active decomposition and an environment that is unaffected by pollution. This zone features a gradual cleaning up of the environment, a reduction in those features that form adverse conditions for aquatic life, an increase in organism species, and a gradual decrease in organism population because of decreased food supply and the presence of some of the predators that are less sensitive individually to pollutional affects.

Because of variation in response among species to conditions of existence within the environment, and because of inherent difficulties in aquatic invertebrate taxonomy, the ecological evaluation of the total organism community is the acceptable approach in water pollution control studies. Investigators tend to place organisms in broad groups according to the general group response to pollutants in the environment. For example, the general group known as "sludgeworms" is found in both the unpolluted as well as the organically polluted environment. Value as a group lies in the fact that the numbers of individuals within the group are exceedingly low in unpolluted water, whereas in the organically polluted environment, its numbers may be very high. Examples of organisms that may inhabit both the unpolluted and polluted environments are listed in Table 5.

The converse of the effects of pollution on organisms is the effects of organisms on pollutants. Organic wastes, especially, the supply food which in turn produces an abundance of a few types of organisms produced in an unpolluted environment. When consuming organic wastes, the organisms stabilize the waste in a given number of feet or miles of horizontal stream in a manner similar to that in a vertical trickling filter that is designed especially for maximum stabilizing efficiency by the organisms.

As organic wastes become stabilized, other organism types predominate within the aquatic animal community. Midge larvae have been found to taint stream beds a brilliant red with their undulating bodies. Caddisfly larval populations greater than 1000 per square foot of stream bed or mayfly nymphs numbering more than 300 per square foot have been found. Figures 1–3 show representative stream bed-associated animals.

Inorganic Silts

Inorganic silts in the environment reduce severely both the types of organisms present and their populations. Particulate matter settling to the bottom can blanket the substrate and form undesirable physical environments for organisms that would normally occupy a habitat. Erosion silts change environments chiefly by screening out light, by changing heat radiation, by blanketing the stream bottom and destroying living spaces, and by retaining organic materials and other substances that can create unfavorable conditions. Developing eggs of fish and

Table 5 Examples of Organisms Sensitive and Tolerant to Polluted Water, Respectively

Clean water organisms		Clean or polluted water organisms	
Algae	<i>Cladophora</i> (green)	Iron Bacteria	<i>Sphaerotilus</i>
	<i>Ulothrix</i> (green)	Fungi	<i>Leptomitus</i>
	<i>Navicula</i> (diatom)	Algae	<i>Chlorella</i> (green)
Protozoa	<i>Trachelomonas</i>		<i>Chlamydomonas</i> (green)
Insects	<i>Plecoptera</i> (stoneflies)		Oscillatoria (blue-green)
	<i>Negaloptera</i> (hellgrammites, alderflies, and fishflies)		Phormidium (blue-green)
		Protozoa	<i>Carchesium</i> (stalked colonial ciliate)
	<i>Trichopetera</i> (caddisflies)		<i>Colpidium</i> (noncolonial ciliate)
	<i>Ephemeroptera</i> (mayflies)	Segmented Worms	<i>Tubifex</i> (slugeworms)
Clams	<i>Unionidae</i> (pearl button)	Leeches	<i>Limnodrilus</i> (slugeworms)
Fish	<i>Etheostoma</i> (darter)	Insects	<i>Helobdeall stagnalis</i>
	<i>Notropis</i> (shiner)		<i>Culex pipiens</i> (mosquito)
			<i>Chironomus (Tendpipes)</i> <i>plumosus</i> (bloodworms)
	Chrosomus (dace)		<i>Tubifera (Eristalis tenax)</i> (rat-tailed maggot)
		Snail	<i>Physa integra</i>
		Clam	<i>Sphaerium</i> (fingernail clam)
		Fish	<i>Cyprinus carpio</i> (carp)

other organisms may be smothered by deposits of silt. Fish feeding may be hampered by silt deposits. Direct injury to fully developed fish, however, by nontoxic suspended matter occurs only when concentrations are higher than those commonly found in natural water or associated with pollution.

Toxic Metals

Wastes containing heavy metals, either individually or in combination, may be destructive to aquatic organisms and have a severe impact on the aquatic community. A severely toxic substance will eliminate aquatic biota until dilution, dissipation, or volatilization reduces the concentration below the toxic threshold. Generally toxic materials will reduce the aquatic biota except those species that are able to tolerate the observed concentration of the toxicant. Because toxic materials do not offer an increased food supply, such as organic wastes, there is no sharp increase in the population of those organisms that may tolerate a

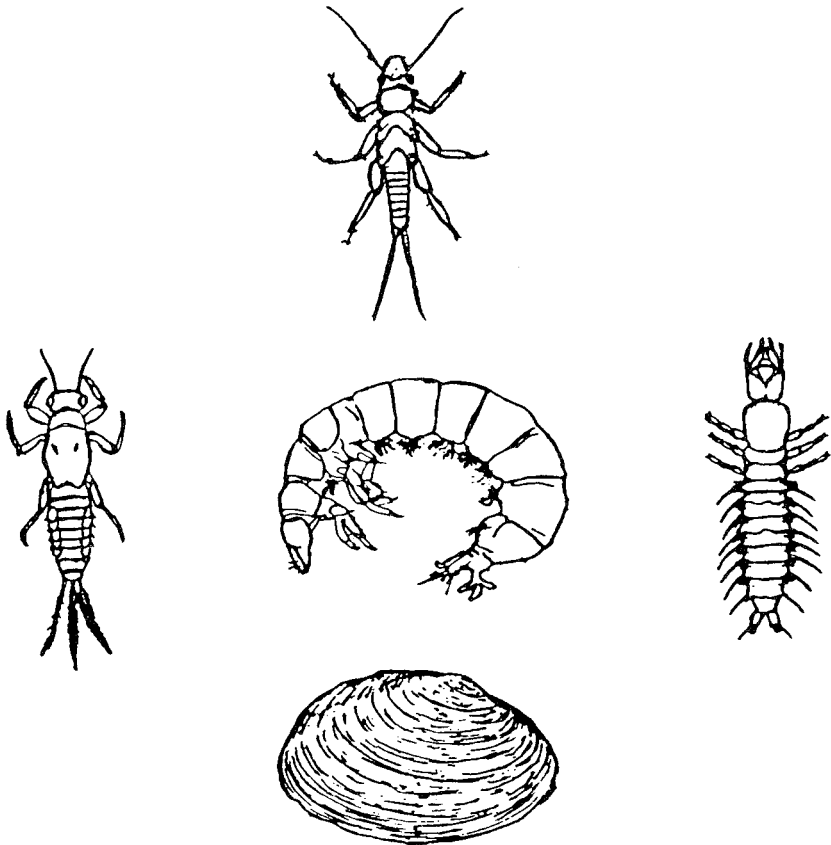


Figure 1 Clean water [sensitive] animals associated with stream beds include the stonefly nymph, mayfly naiad, caddisfly larva, and hellgrammite unionid clam.

specific concentration. The bioassay is an important tool in the investigation of these wastes, because the results from such a study indicate the degree of hazard to aquatic life of particular discharges; interpretations and recommendations can be made from these studies concerning the level of discharge that can be tolerated by the receiving aquatic community.

Temperature

Temperature is a regulator of natural processes within the water environment. It governs physiological functions in organisms, and acting directly or indirectly

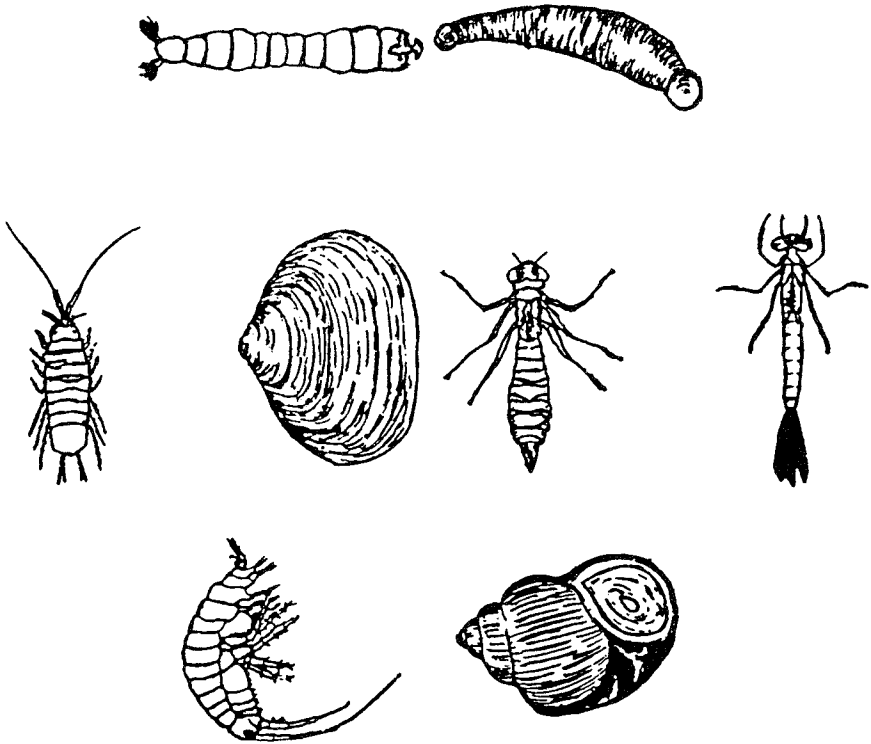


Figure 2 Intermediately tolerant animals associated with stream beds include the scud, sowbug, blackfly larvae, fingernail clam, damselfly nymph, dragonfly nymph, leech, and snail.

in combination with other water quality constituents, temperature affects aquatic life with each change. The effects of temperature changes include, for example, chemical reaction rates, enzymatic functions, molecular movements, and molecular exchanges between membranes within and between the physiological systems and organs of an animal. Because of the complex interactions involved, and often because of the lack of specific knowledge or facts, temperature effects as they pertain to an animal or plant are most efficiently assessed on the basis of net influence on the organism. Depending on the extent of environmental temperature change, organisms can be activated, depressed, restricted, or killed.

Temperature determines those aquatic species that may be present. It controls spawning and the hatching of young, regulates their activity, and stimulates or suppresses their growth and development. Temperature can attract and kill when the water becomes heated or chilled too suddenly. Colder water

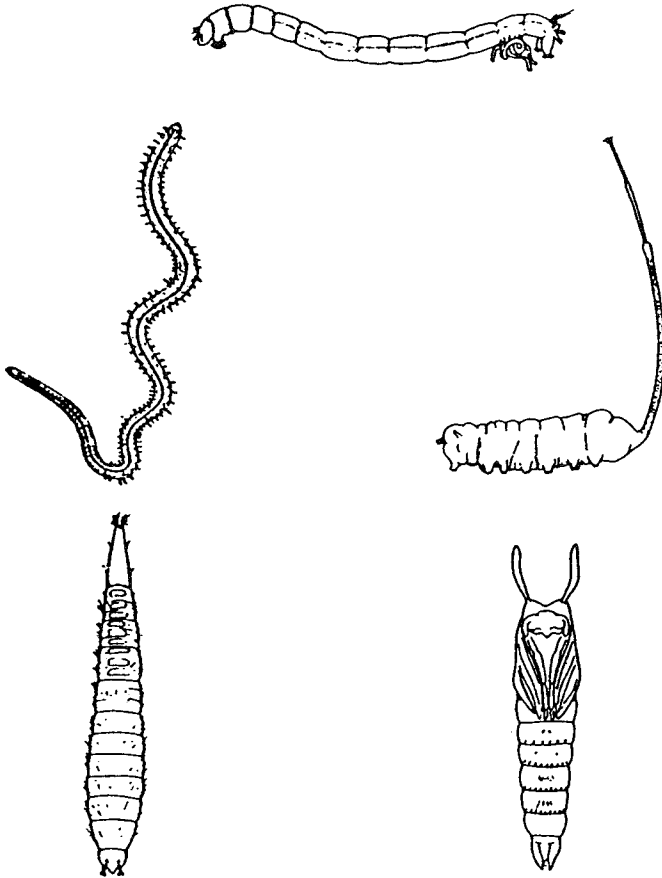


Figure 3 Very tolerant animals associated with stream beds include the bloodworm, midge larvae sludgeworm, rat-tailed maggot, sewage fly larva, and sewage fly pupa.

generally suppresses development and warmer water generally accelerates activity.

Temperature regulates molecular movement and thus determines the rate of metabolism and activity of all organisms, both those with a relatively constant body temperature and those whose body temperature is identical to, or follows closely, the environmental temperature. Because of its capacity to determine metabolic rate, temperature may be the most important single environmental entity to life and life processes.

Variations in temperature of streams, lakes, estuaries, and oceans are

normal results of climatic and geological phenomena. Waters that support some form of aquatic life other than bacteria or viruses range in temperature from 26.6°F in polar sea waters to 185°F in thermal springs. Most aquatic organisms tolerate only those temperature changes that occur within a narrow range to which they are adapted whether it be high, intermediate, or low on this temperature scale.

Within the same species, the effects of a given temperature may differ in separate populations, in various life cycle stages, or between the sexes, and such effects may depend on the temperature history of the individual tested as well as on present or past effects of other environmental factors. Fresh water has the greatest density at 38°F; higher and lower temperatures result in waters with lower density. Seasonally induced temperature changes are greatest in the midlatitudes.

In lakes, insolation warms the surface waters in spring reducing densities compared with the deeper waters until eventually the density differences are sufficient to prevent the wind from mixing the body of water; thermal stratification then occurs. The warm upper layer is well mixed to a depth determined by waves and other wind-induced currents. The cool bottom waters (hypolimnion) become stagnant except for minor currents confined to this stratum. A stratum of sudden temperature changes (thermocline) separates these regions. In autumn, the lake radiates heat, surface temperatures decrease, surface water density increases, and water viscosity increases. Wind aided by reduced density differences between water layers mixes the surface with the bottom waters resulting in a homogeneous water mass. Depending on altitude and local climatic conditions, the lake continues to mix until the following spring in latitudes of less than about 40°F. In latitudes north of about 40°F, winter surface water temperatures are less than 38°F and these are superimposed over the water mass until they are cooled to freezing. An ice cover eliminates wind-induced mixing and stagnation occurs.

Thermal stratification may assume various patterns depending on geographical location, climatological conditions, depth, surface area, type of dam structure, penstock locations, and hydropower use. In general, large, deep impoundments will cool downstream waters in the summer and warm them in winter when withdrawal ports are deep; shallow, unstratified impoundments with large surface areas will warm downstream waters in the summer; water drawn from the surface of a reservoir will warm downstream waters; a reduction in normal flow downstream from an impoundment will cause marked warming in summer; and “runoff-river” impoundments, where the surface area has not been increased markedly over the normal river area, will produce only small changes in downstream water temperatures.

In the deep, stagnant, summer bottom waters as well as in ice-covered waters atmospheric reaeration is absent and oxygen from photosynthesis by plants

is limited. Decomposing organisms (especially those settling to the bottom waters in summer) remove oxygen from the water and the gaseous by-products of decomposition are trapped. Undesirable soluble phosphorus, carbon dioxide, iron, and manganese concentrations increase in these stagnant waters. Designed thermal discharges can reduce some of these problems. Ice cover can be limited and thus allow wind and thermally induced currents to reduce winter stagnation. A deep-water summer discharge could warm hypolimnetic waters to decrease density and permit total water mass mixing where a cold water fishery would not be damaged by such action.

Stratification may occur in streams receiving heated effluents. There are three recognized forms of stream stratification: overflow, interflow, and underflow; the forms are determined by the relationship between the density of the influent and the density of the stream water.

Surface fresh waters in the United States vary from 32 to over 100°F according to the latitude, altitude, season, time of day, duration of flow, depth, and many other variables. Agents affecting natural water temperature are so numerous that no two water bodies, even in the same latitude, are likely to have the same thermal characteristics. Fish and other aquatic life occurring naturally in each body of water are those that have become adapted to the temperature conditions existing there. The interrelationships of species, length of daylight, and water temperature are so intimate that even a small change in temperature may have far-reaching effects. Inhabitants of a water body that seldom becomes warmer than 70°F are placed under stress, if not killed outright, by 90°F water. Even at 75–80°F, they may be unable to compete successfully with organisms for which 75–80°F is favorable. Similarly, the inhabitants of warmer waters are at a competitive disadvantage in cool water.

An animal's occurrence in a given habitat does not mean that it can tolerate the seasonal temperature extremes of that habitat at one time. The habitat must be cooled gradually in the fall if the animal is to become acclimatized to the cold water of winter and warmed gradually in the spring if it is to withstand summer heat. Some organisms might endure a temperature of 92–95°F for a few hours but not for days. Gradual change of water temperature with the season is important for other reasons. An increasing or decreasing temperature often triggers spawning, metamorphosis, and migration. The eggs of some freshwater organisms must be chilled before they will hatch properly.

The temperature range tolerated by many species is narrow during very early development; it increases somewhat during maturity and decreases again in old adults. Similarly, the tolerable temperature range is often more restrictive during the reproductive period than at other times during maturity. Upper lethal temperatures may be lower for animals from cold water than for closely related species from warm water. Many motile organisms such as fish, some zooplankton, certain algae, and some associated animals can avoid critical temperatures

by vertical and horizontal migration into more suitable areas. However, some organisms may be attracted to areas with critical temperatures and succumb on arrival in these areas.

Changes in fish populations can result from many types of artificial cooling and heating of natural waters. These changes result from the discharge of condenser cooling water from thermal electric-generating plants, industrial waste-cooling waters, and other heated effluents and irrigation waters. Streams also are warmed by the sun when the shade from stream bank trees and other vegetation is eliminated. The discharge of cold water from stratified impoundments may provide an ideal habitat for trout and other cold-water fish when sufficient dissolved oxygen is present but not for the warm-water fish that inhabited the stream before impoundment.

For every 18°F increase in temperature, the chemical reaction rate is approximately doubled in an organism or in an environment. Life processes in the water are accelerated with temperature increases and slowed as the water cools. Solubility of gases, including oxygen, in water varies inversely with temperature. In fresh water, the solubility of atmospheric oxygen is decreased by about 55% as the temperature rises from 32 to 104°F under 1 atmosphere of pressure (760 mm Hg). Because all desirable living things are dependent on oxygen in one form or another to maintain the life processes that produce energy for growth and reproduction, dissolved oxygen is of imposing significance in the aquatic environment.

When organism metabolism increases because of higher temperatures, organism development is speeded and more dissolved oxygen is required to maintain existence. But bacterial action in the natural purification process to break down organic materials is also accelerated with increased temperatures, thus reducing the oxygen that could be available in the warmer water. When organisms use larger amounts of oxygen, and when oxygen has been reduced by temperature action and interaction, organisms may perish. Life stages that are especially vulnerable are the eggs and larvae. At higher temperatures, phytoplankton have been found to need greater amounts of certain growth factors such as vitamin B₁₂. For example, at between 96.8 and 98.2°F the vitamin requirement has been found to increase over 300 times for some species.

Fish and other mobile organisms seek a preferred temperature at which they can best survive, which is several degrees below a temperature that is lethal. Larger individuals tend to move out of areas that are too hot, but larvae and juveniles cannot often move fast enough to avoid a sudden temperature increase. Large fish and fish in schools avoid heated areas in summer but may be attracted to such areas in winter. This phenomenon may result in good fishing during the cooler months but an absence of this sport at other times.

Reproduction cycles may be changed significantly by increased temperature, because this function takes place under restricted temperature ranges.

Spawning may not occur at all if temperatures are too high. Thus, a fish population may exist in a heated area only by continued immigration. Disregarding the decreased reproductive potential, water temperatures need not reach lethal levels to wipe out a species. Temperatures that favor competitors, predators, parasites, and disease can destroy a species at levels far below those that are lethal.

Fish food organisms are altered severely when temperatures approach or exceed 90°F. Predominant algal species change, primary production is decreased, and bottom-associated organisms may be depleted or altered drastically in numbers and distribution. Increased water temperatures may cause aquatic plant nuisances when other environmental factors are favorable.

Synergistic actions of pollutants are more severe at higher water temperatures. Domestic sewage, refinery wastes, oils, tars, insecticides, detergents, and fertilizers more rapidly deplete oxygen in water at higher temperatures, and the respective toxicities are likewise increased.

Marine water temperatures do not change as rapidly or range as widely as those of fresh waters. Marine and estuarine fish, therefore, are less tolerant of temperature variation. Although this limited tolerance is greater in the estuarine than in the open water marine species, temperature changes are more important to those fish in estuaries and bays than to those in open marine areas. Marine surf-zone discharge from large-scale coastal power plants may be expected significantly to alter the shore environment for species of invertebrates and fish that are commonly found there.

DISSOLVED OXYGEN

Dissolved oxygen (DO) is a measure of water quality that in the right concentrations is essential not only to keep organisms living but also to sustain species reproduction, vigor, and the development of populations. Organisms undergo stress at reduced DO concentrations that makes them less competitive to sustain their species within the aquatic environment.

Oxygen enters the water by absorption directly from the atmosphere or by plant photosynthesis and is removed by respiration of organisms and by decomposition. Oxygen from the atmosphere may be by direct diffusion or by surface water agitation by wind and waves, which may also release dissolved oxygen under conditions of supersaturation.

In photosynthesis, aquatic plants utilize carbon dioxide and liberate dissolved and free gaseous oxygen at times of supersaturation. Since energy is required in the form of light, photosynthesis is limited to the photic zone where light is sufficient to facilitate this process.

During respiration and decomposition, animals and plants consume dissolved oxygen and liberate carbon dioxide at all depths where they occur. Because

excreted and secreted products and dead animals and plants sink, most of the decomposition takes place in the hypolimnion; thus during lake stratification there is a gradual decrease of dissolved oxygen in this zone. After the dissolved oxygen is depleted, anaerobic decomposition continues with evolution of methane and hydrogen sulfide.

During thermal stratification, dissolved oxygen is usually abundant and is supplied by atmospheric aeration and photosynthesis. Phytoplankton are plentiful in fertile lakes and are responsible for most of the photosynthetic oxygen. The thermocline is a transition zone from the standpoint of dissolved oxygen as well as temperature. The water rapidly cools in this region, incident light is much reduced, and photosynthesis is usually decreased; if sufficient dissolved oxygen is present, some cold-water fish abound. As dead organisms that sink into the hypolimnion decompose, oxygen is utilized; consequently, the hypolimnion in fertile lakes may become devoid of dissolved oxygen following a spring overturn, and this zone may be unavailable to fish and most benthic invertebrates at this time. During the two brief periods in spring and fall when lake water circulates, temperature and dissolved oxygen are the same from top to bottom and fish use the entire water depth.

OTHER IMPURITIES IN WATER

In addition to dissolved mineral matter and dissolved gases, water may contain other impurities such as turbidity and sediment, color and organic matter, tastes and odors, and microorganisms.

Turbidity and Sediment

Finely divided, insoluble impurities that may be suspended in and compromise the clarity of a water are known as turbidity. Suspended impurities may be inorganic in nature, such as clay, rock flour, silt, calcium carbonate, silica, ferric hydroxide, and sulfur, or they may be organic in nature, such as finely divided vegetable, animal matter, oils, fats, greases, and microorganisms. Turbidity may be due to a single substance or more usually to a mixture of substances.

Suspended impurities may range in size from colloidal particles to coarse, sandy materials that can be kept in suspension only by mixing and turbulent flows. Material that is so coarse that it rapidly drops out of suspension is classified sediment. The dividing line between turbidity and sediment is not sharp, and there may be different ideas as to what constitutes turbidity or sediment. Additionally, agglomeration of smaller particles into larger ones is also possible. If the sediment content is sufficiently high, it may warrant preliminary sedimentation before coagulation.

Turbidity is a measure of the opacity of the water as compared with certain arbitrary standards and differs with varying materials and degrees of fineness.

Where the suspended matter is always of the same nature, it is possible to measure the divergence between the observed turbidity and the actual weight of the suspended matter and apply a correction factor to subsequent readings.

The standard method for the determination of turbidity is the Jackson candle method, or suspensions standardized by this method may be used, with or without dilution in other instruments. In the standard Jackson candle turbidimeter, the turbidities are determined from the depths of water through which a light disappears when viewed lengthwise through a tube. In practice, it is customary to use standard suspensions (which have been standardized and diluted by the addition of the calculated amounts of distilled water) for all measurements except extremely low ones.

The term *quiescent* as applied to the waters of lakes, ponds, and reservoirs is a relative one. That is, such bodies of water are relatively quiescent when compared with flowing streams, but wind and wave actions and temperature changes do effect movements in the water even if the inflow and outflow are small in comparison with the size of the body of water so that the effects may be practically negligible. Wind usually tends to push the upper layers of water in the direction to which it is blowing. The movement is greatest at the surface and diminishes downwardly until a plane is reached at which it is practically zero. Below this, the water may return in layers flowing in the opposite direction, slowly under this layer of nearly zero velocity, then increasing in speed in succeeding lower layers until a maximum is reached, after which it tapers off until it again reaches a layer of practically zero movement. Factors such as the shape of the shore line and the sheltering effect of islands may obviously create currents, so that much of the returning water is diverted to another course. Wind also creates waves which have a churning effect and tend to roll waters badly, especially where relatively shallow bodies of water are concerned. It is therefore common experience that many lake, pond, and reservoir waters which are usually clear may become very turbid during and for a period following high winds or storms.

Heavy rainfalls may also increase the turbidity of lakes, ponds, and reservoirs, especially that of the smaller ones. This may be due to dirt or clay being washed in from the banks or from tributaries swollen by heavy rains and carrying unduly heavy loads of turbidity. Obviously, the location of intakes in the proximity of such tributaries may greatly increase the turbidity load in the plant influent. Also, frequently plant intakes are located too close to sewer outlets, so that contamination from this source may occur under certain conditions of wind and currents. Temperature changes may also affect the turbidity of the water, with the greatest effect being noticed when the water is at uniform density, as this permits vertical circulation. Under such conditions, wind and wave action may greatly aggravate the pickup of turbidity from bottom sediments.

In bodies of water that are less than 25 feet in depth, vertical circulation

is possible at all seasons except when the surface is frozen. In deeper bodies, vertical circulation usually occurs when the water is at or near its greatest density, which is at 39.2°F, and the effect on turbidity in certain lakes, ponds, and reservoirs is especially troublesome during the periods of spring and fall turnovers (or overturnings). In areas where freezing temperatures are encountered in the winter, the water on the bottom is stagnant at about the temperature of greatest density. Then in the spring, after the ice has melted, the surface layers increase in density on being warmed, and consequently sink until, when the temperature is about 39.2°F, all of the water is of uniform density and vertical circulation occurs. Then as the upper layers are warmed beyond this point, they become lighter; the body of water tends to stratify and the bottom and lower layers stagnate at about the point of maximum density. In the fall, the upper layers become heavier as they are chilled, until all of the water has reached about 39.27°F, when vertical circulation again is possible. On further cooling, the upper layers become lighter and the period of winter stagnation begins. With many bodies of water, the increase in turbidity at these periods is startling and may persist for several weeks, especially during the fall turnover.

Temperature has an effect on the growth of microorganisms and aquatic plants which, together with their decomposition products, may impart not only turbidity but also color, tastes, and odors to the water supply. Growth of some of these forms takes place in winter and even under the ice, although at greatly reduced rates compared with growth at summer temperatures. The worst contamination with living matter is experienced in small, shallow bodies of water with muddy bottoms.

It is therefore evident that lakes, ponds, and reservoirs, like rivers, must be individually studied as to their possible variations in turbidity and that it is not safe to assume that simply because a few random tests show a negligible turbidity that this will never be exceeded. Likewise, as has been pointed out, the location of the inlet in respect to its depth, distance from the shore, condition of the bottom, proximity to tributaries, and sewers, for example, must also be taken into account.

Turbidity in Ground Waters

Owing to the filtering action of the strata through which ground waters pass, most well and spring waters are free from turbidity. There are exceptions though. Some spring waters, for instance, may be clear the greater part of the time but may show appreciable turbidities after periods of heavy rains. This is especially the case in limestone country where there may be fairly large fissures and crevices through which water containing suspended material may travel. Obviously, any wells tapping such aquifers will show occasional turbidities. Shallow wells also may show turbidities at times; deep wells, with but few exceptions, yield very clear waters. In sandy strata, however, well waters may

contain fine sand which must be removed by sand traps or other settling equipment.

Well waters may also be clear when drawn may develop turbidity on standing in contact with air. Iron-containing waters, for instance, may be sparklingly clear at first but may cloud on exposure to the air and finally deposit yellowish to reddish brown ferric hydroxide. Manganese-bearing waters may also, but usually not so readily, become turbid in contact with the air. Sulfur waters may deposit sulfur in contact with the atmosphere, but in many cases the sulfur is colloidal and is not always apparent in broad daylight. In a darkened room it will, however, show the Tyndall effect when struck by a small beam of light. Sulfur waters may also develop growths of sulfur bacteria, and iron- or manganese-bearing waters may develop growths of iron or manganese bacteria.

High turbidity in a water supply is undesirable for practically all uses except perhaps for certain types of surface condensers. The amount of turbidity which makes a water definitely objectionable varies with the nature of the turbidity and the purpose for which the water is intended. Therefore, tolerances for turbidity may vary.

Removal of turbidity and sediment is if a water supply has a high content of easily settled sediment, it may be advisable to remove a great portion of this by sedimentation tanks, basins, or reservoirs. On the other hand, if the content of heavy, easily settled sediment is small, the sediment and turbidity are usually taken out at the same time by:

- Coagulation and filtration
- Coagulation and settling
- Coagulation, settling, and filtration

Color and Organic Matter

Color is found mostly in surface waters, although some shallow well waters, a few springs, and an occasional deep well water may contain noticeable amounts of color. In general, though, deep well waters are practically colorless. The colors noted in water usually range from a very light straw color, through a yellowish brown, and up to a dark brown. In determining the color of a water, it is the true color that is of interest and not the apparent color. This is expressed as the color standard unit.

The true color of water is that only due to substances in solution; that is, it is the color of the water after the suspended matter has been removed. The accurate determination of color in water containing matter in suspension is impossible. The removal of suspended matter by centrifuging before the color observation is made gives the best results. No filter should be used, since filters may exert marked decolorizing action. The platinum-cobalt method of measuring

color shall be considered as the standard, and the unit of color shall be that produced by 1 mg of platinum per liter.

The color of natural water supplies is usually organic in nature, and augmented in many cases by organic or colloidal iron or manganese. Arbitrary inorganic color standards measure only the relative depth of color of the water and not the mass of the actual coloring agent present. Color in water in large part exists in the form of colloidal suspensions of ultramicroscopic particles. Some of the color may be due to colloidal emulsions. A small part of the color is probably due to noncolloidal material, organic acids, and neutral salts in true solution. The colloidal coloring matter, whether suspensoids or emulsoids, carries an electrostatic charge. This charge may be positive or negative depending on the character and source of the water and varying in different waters. Since these particles carry an electrical charge and are in colloidal suspension, they obey the laws of cataphoresis when an electric current is sent through a colored water. The particles are attracted to the electrode of opposite sign from the charge which they carry. They are discharged, flocculate, and precipitate, with consequent reduction in the color of the water.

Removal of Color and Organic Matter

The soluble organic matter in water is a complex mixture of substances, some of which presumably have a high color and others of which have either a low color or are practically colorless. The intensity of color may be determined against an arbitrary scale, but this does not show the quantity of organic matter producing such a color. Oxygen consumption tests are of value in indicating whether or not excessive amounts of organic matter are present, but they are not translatable into definite amounts of organic matter. Such tests are merely a measure of the quantity of potassium permanganate, which is usually expressed as its available oxygen equivalent that is used up by a given volume of water under certain fixed conditions of time and temperature.

In general, removal or reduction of color and organic matter can be accomplished by coagulation, settling, and filtration. The most widely used coagulant is aluminum sulfate. Iron coagulants, ferric sulfate, and chlorinated coppers are also used. The coagulation is best carried out at the most favorable pH value, which should be determined by experiment: With aluminum sulfate, the optimum point varies over a range from about 5.5 to 6.8 for most waters, but this coagulant has been used at a pH below 5.0 in a few cases, and with waters having rather high mineral contents at a pH as high as 7.5. With ferric coagulants, the range from 3.5 to about 5.5 has been effective for highly colored waters. Ferric coagulants also precipitate well at pH values above 9.0, but a high pH usually tends to keep the color in solution. Addition of clay is valuable in coagulating colored waters which are low in turbidity, and this broadens the pH range at which good coagulation takes place. Activated silica is frequently useful

as a coagulation aid in treating colored waters. Controlled agitation is of importance in securing good floc formation. Settling is of advantage and obviously lessens the load on filters, but settling of the coagulated water when not followed by filtration is often insufficient for good color removal.

Superchlorination is of value in removing color in some waters but has little effect (often below 20%) on the colors of other waters. The value of this method can only be made by experiment, and if it does not have the required effect when dosed to the breakpoint, there is no advantage to be gained by increasing the dosage beyond this. Activated carbon adsorbs some colors, but its adsorptive capacity for others is so uncertain that carbon use is confined almost entirely to taste and odor removal.

Odors are graded according to their nature and intensity. The terms used in the classification are descriptive. The intensity is often described as very faint, faint, distinct, decided, very strong, or by numbers, 0, 1, 2, 3, 4, 5, and so forth, referring to the number of successive dilutions perceptible, which is known as the odor threshold. To the trained observer, such odor determinations are of value in tracing the contamination, but noses are not equally sensitive, so that different observers may variously interpret the same odor. Therefore, both the classification and the intensity of the odor of a given sample of water may be different in the reports of various observers. This does not, by any means, imply that odor tests are worthless, for they are really very valuable, but it does mean that a certain amount of latitude has to be allowed in interpreting the reports of different observers.

Practically all of the odors in natural waters, with the exception of hydrogen sulfide, are organic in nature. Even the odors and tastes noticeable in many chlorinated waters are seldom due to the chlorine but rather to compounds formed by the action of the chlorine on organic matter present in the water. Some of these are so intense that as little as one part per billion is noticeable. These organic tastes and odors are usually confined to surface waters and are either absent or very low in amount in deep well waters.

Disagreeable odors and tastes render waters objectionable for many uses and industrial processes. They are intolerable in water used for beverages or food products, but it is not in these industries alone that odors are objectionable, for many wet-processed materials such as pulp, paper, and textile materials absorb odors.

The removal of inorganic tastes or odors due to hydrogen sulfide or iron has been discussed. Organic tastes and odors may be removed by means of activated carbon, aeration, or aeration followed by activated carbon. Activated carbon may be employed in powdered form in coagulation or settling basins or in granular form in filters. Partial chlorination may intensify certain odors, whereas breakpoint chlorination may destroy them. With surface waters requiring chlorination or superchlorination, it is often advisable to chlorinate first followed

by activated carbon. In some instances, postchlorination in very small doses is then required.

Microorganisms

Microorganisms are common to surface waters but are usually either absent or present in small amounts in deep well waters. Contamination of deep well waters can occur by surface waters seeping down around the casing and, in limestone areas especially, crevices may furnish unobstructed passages for contamination. Shallow wells, some springs, and water from infiltration may also contain appreciable amounts of microorganisms and with iron- or manganese-bearing water iron or manganese bacteria. Deep well waters also may have microorganisms develop in them after they are drawn. Thus, deep well water which has been pumped into an open basin, tank, or reservoir often develops luxuriant growths of algae; or a deep well sulfur water may have clogging growths of sulfur bacteria develop on the trays of an aerator; or bacteria, which reduce sulfates to sulfides, may develop in water mains. In many instances, the point of entry of these organisms is not immediately obvious.

It is in surface waters that organic growths are found in the greater variety and profusion. There are literally many thousands of varieties. Some are visible to the naked eye, others become so at a fairly low magnification, and still others require the highest powers of the microscope. Some are plants and others are animals; in some cases, the exact status is yet unknown. Many of these plants look like animals; on the other hand, many of the animals look like plants.

Microorganisms differ greatly in form, color, and habits as well as in size. The variety of forms, shapes, and patterns is enormous. In one classification alone, the *Diatomacea*, it is estimated that there are over 10,000 species, each of which has its own distinctive shape, pattern, or design of silica shells. The colors of microorganisms also vary; for example, they may be green, yellow, red, pink, brown, blue-green, and in all shades, and some forms are quite transparent and colorless. Some microorganisms live only in sunlight, whereas others thrive in the dark. Some (aerobic) require dissolved air for their existence, whereas others (anaerobic) grow in its absence. They may be nonmotile or motile with various types of appendages that produce numerous methods of locomotion such as rolling, creeping, leaping and rowing, paddling, or swimming. Many of these microorganisms grow, although at reduced rates, in cold water and even under the ice. It is interesting to note that at the other extreme there are some blue-green algae which can live in hot water.

Discoloration and staining of wet-processed materials are frequently caused by microorganisms. Disagreeable tastes and odors, either from the living

microorganisms or their decomposition products, may at times become troublesome. Decomposition of cellulose or other organic substances may be caused by microorganisms that are popularly lumped together as molds and slimes.

In many cooling waters, organic growths are a problem and treatment is necessary. Some of these organic growths are matted and fibrous in appearance, but others are so dense that at times they resemble an inorganic scale. Surface waters usually give the most trouble, especially during the warm summer months, but well waters which contain iron or manganese, usually from shallow wells or from infiltration galleries, frequently cause extremely troublesome and clogging growths of iron or manganese bacteria (*crenothrix* is the term commonly used collectively for these) in piping.

Sulfur waters frequently have threadlike growths that appear on aerator trays and in clear wells. Such waters contain elemental sulfur often in a finely divided, colloidal form. This sulfur may be due to the oxidation of the hydrogen sulfide to water and sulfur by dissolved oxygen, but since this reaction is rather slow, it is believed that the bacteria speed up the process. The sulfate-reducing bacteria, which reduce sulfates to sulfides, are often responsible for the production of shots of black water. These are obtained most frequently from dead ends in mains, and the black color is due to ferrous sulfide.

Tolerances for microorganism will differ according to the types and numbers present and the end use for the water in the various industries. Water that is to be used for drinking purposes should, of course, conform to the public health standards on drinking waters. Where other supplies are used in plants, cross-connections must be avoided and all dangers of back siphonage must be eliminated. Obviously, water that is to be used in the manufacture of beverages or food products must conform to strict standards. Even where products are sterilized in sealed containers, it is shortsighted to allow any water which is not above suspicion to come in contact with them.

The removal, destruction, or prevention of growths of microorganisms may be accomplished by various means. Algae and other chlorophyll-containing plants need sunlight in order to grow. Therefore, if the water can be stored in covered reservoirs, the growth of these organisms can be prevented. Floating rafts have sometimes been employed, but they are not recommended as they usually are not very satisfactory. In open settling basins, activated carbon has sometimes been employed for its light-screening action, but obviously this is somewhat limited in its applications. In large open reservoirs, treatments with measured dosages of copper sulfate are frequently employed. The dosages have to be carefully regulated in order to avoid killing fish.

In most industrial plants, killing and removal of organic growths is best accomplished in the settling basin in the water-treatment plant. This is done with chlorine and coagulation, settling, and filtration to remove the remains. Where chlorine is so used, the process is known as prechlorination, and it is frequently

of value in reducing the dosages of coagulant required. In many cases, however, the bulk of the organic matter is removed by coagulation, settling, and filtration followed by postchlorination. In other cases, both prechlorination and postchlorination may be practiced.

Iron and manganese crenothrix growths are best prevented by removal of these metals followed by chlorination. In the case of sulfur waters, reduction of the hydrogen sulfide should first be carried out after which the water is chlorinated to remove the last traces of hydrogen sulfide and to kill any sulfate-reducing bacteria that may be present. Slimes and molds in such industries as pulp and paper mills are controlled by chlorination or by various other germicides. Where the amounts of water to be handled are relatively small and the content of microorganisms and turbidity is small, settling basins are frequently dispensed with and chlorine or a hypochlorite and a coagulant are added in the line leading to the filters. In these cases, especially if the water demand is not very large, a pressure reaction tank, usually known as a pressure settling tank, is of advantage before the filters. In plants where the cold lime or lime soda process of water softening is employed, the coagulation and settling may be effected in the equipment and used. If the treatment is carried to the caustic stage, a considerable reduction in the bacterial content may be effected, but postchlorination also is usually advisable.

WATER SUPPLIES

Water is used in such vast quantities that in sheer quantity and bulk it far overshadows all other materials. It requires over 250 tons of water to make one ton of steel, over 700 tons to make 1 ton of paper, over 100 tons to make 1 ton of aluminum, and the list could go on and on, for in practically every industry the greatest amount of any material used is water.

Sources may be a surface supply—river, creek, canal, pond, lake, or reservoir—or it may be a ground water supply—deep well, shallow well, spring, mine, or infiltration gallery. Whatever the source, the water will contain impurities, for no natural water supply consists of chemically pure water.

In different water supplies impurities will be varied both in character and amounts present. In fact, in many water supplies, they may at different periods vary over a rather wide range in the same supply. This is especially the case with flowing streams, which may show not only seasonal changes in composition but daily or hourly variations because of rainfalls. On the other hand, water from a large lake or a deep well may be remarkably constant in composition even over a period of many years.

Impurities that may be present in water supplies may be grouped generally as follows:

- Dissolved mineral matter
- Dissolved gases
- Turbidity and sediment
- Color and organic matter
- Tastes and odors
- Microorganisms

Whether or not these impurities are harmful depends on

- The nature and amounts of the impurities present
- The uses to which the water is intended
- The tolerances for various impurities for each use

Treated Water Supplies

The municipal water supply may be chlorinated, aerated, filtered, or softened. Most municipal water supplies, especially of surface origin, are chlorinated whether or not they receive any other treatment. In general, the dosages of chlorine used are very small, so that although the water is rendered safe for drinking purposes, there is little impact on the mineral matter in the water.

With some water supplies, usually surface supplies, chlorination results in objectionable tastes and odors. These chlorine tastes are due to the action of chlorine on certain organic impurities in the water, thereby forming compounds of such marked taste and odor that as little as 1 part in a billion parts of water may be noticeable.

Most filtered municipal water supplies are clear and low in color. If also treated so as to render the filter effluent comparatively nonaggressive, the suspended matter may be so slight as to be of little or no consequence for many industrial uses. In addition, a number of municipal water-treatment plants employ activated carbon for taste and odor removal, but for industrial uses where taste and odor control is important, it is advisable to install dedicated taste and odor removal equipment as an additional safeguard.

Aeration is practiced in many municipal water-treatment plants. The purpose is to reduce hydrogen sulfide content, to reduce tastes and odors, or, in combination with filtration, to remove iron or manganese. In such cases, lime may also be added, especially for manganese removal, to build up the pH value, and such additions may increase the hardness of the water unless partial softening is practiced.

Softened Municipal Water Supplies

Municipal water softening may best be considered separately from other forms of municipal water treatments, because it has so much greater an effect on the dissolved mineral content of the water. Over 1,000 municipalities in this country now partially soften their water supplies.

In general, municipalities do not attempt to soften the water completely but instead merely reduce the hardness to about 85 ppm. Some do not reduce it this far but instead reduce it to only 135 ppm or some intermediate point. Relatively few municipalities reduce it below 85 ppm, and there are even less that soften the water completely. Such partially softened water may be quite suitable for most household uses, but for most industrial uses further softening or treatment is typically required.

Fluoridated Municipal Water Supplies

A large number of municipalities fluoridate their water supplies as a dental health measure. The amount of fluoride added is very small, as the final concentration in the treated water is only 0.7–1.1 ppm, expressed as F (fluorine).

Where a municipal water supply is used in an industry, samples for analysis may be drawn from any convenient tap, and it is simply necessary to allow the water to run for several minutes before sampling and to observe the usual sampling precautions. In such cases, too, records are usually available that will show what variations in composition may be expected. All these records should be carefully studied, for the analysis of a single sample does not necessarily mean that it is representative of the quality of water that may be supplied at all times. Even if the records do not contain complete mineral analyses, they usually will give sufficient information to supplement the knowledge gained from the complete mineral analyses. In the case of most city waters, the manufacturer of water-treating equipment will usually have in its files a number of complete mineral analyses made at different periods.

If the municipality draws its water supply from a large lake or from deep wells tapping the same aquifer, the composition of the water may be remarkably constant. If the water instead is drawn from different well fields, from several sources, from various reservoirs, or from a river or stream variations in composition may be expected and the range of these variations should be known. If records of such variations are not available, a series of periodic analyses should be made or, if time does not permit such a course, allowances should be made for whatever variations in composition may reasonably be expected following a survey of the source or sources of supply.

Units Used in Water Analysis

There are many methods of expressing water analyses. Expressions can be quite complicated. In Table 6, the same quantity of calcium is shown in 28 different forms. It might also be expressed as equivalents per million (epm) or milliequivalents per liter (mEq/L), which are different ways of expressing the same numerical quantity, in this case 2 epm (or 2 mEq/L).

Table 6 The Same Amount of Calcium Expressed in Different Ways

Name	Formula	Parts per million	Parts per 100,000	Grains per US gallon	Grains per imperial gallon
Calcium	Ca	40	4	2.3	2.8
Calcium oxide	CaO	56	5.6	3.3	3.9
Calcium carbonate	CaCO ₃	100	10	5.8	7.0
Calcium bicarbonate	Ca(HCO ₃) ₂	162	16.2	9.4	11.3
Calcium chloride	CaCl ₂	111	11.1	6.5	7.8
Calcium sulfate	CaSO ₄	136	13.6	8.0	9.5
Calcium nitrate	Ca(NO ₃) ₂	164	16.4	9.5	11.5

Water Analysis Units

Numerically there are only four basic units for water analyses, although there are six names for them. These are

- Parts per million (ppm): the number of parts of substance per million parts of water. This same unit is also known by two other names—milligrams per liter (mg/L) or grams per cubic meter (g/m³). All three are numerically equal.
- Grains per US gallon (gpg): the number of grains of substance per 1 US gallon of water (1 grain = 1/7000 pound and 1 US gallon of water weighs 8.33 pounds)
- Parts per hundred thousand (pts/100,000): the number of parts of substance per 100,000 parts of water
- Grains per imperial gallon (gpg imp): the number of grains of substance per 1 British imperial gallon of water (1 grain = 1/7000 pound and 1 imperial gallon of water weighs 10 pounds)

Table 7 gives the interrelations between these basic units and other equivalents such as pounds per thousand gallons and per million gallons both for the US and imperial gallon. The most widely used basic unit is parts per million. Another unit that is commonly used in this country, especially in expressing hardness, is grains per US gallon, and one widely used for the same purpose in other English-speaking countries is grains per imperial gallon. The parts per hundred thousand unit is now much less widely used than formerly, having been largely displaced by parts per million or its equivalents.

In making analyses of fresh waters, the samples are measured by volume at the prevailing temperature and not by weight. Corrections for temperature or specific gravity are practically never made (e.g., boiler salines and brines are

Table 7 Water Analysis Units: Interrelations and Equivalents

1 Part per million (ppm)	
= 1.0	milligrams per liter
= 1.0	grams per cubic meter
= 0.1	parts per 100,000
= 0.0583	grains per US gallon
= 0.00833	pounds per 1,000 US gallons
= 8.33	pounds per 1,000,000 US gallons
= 0.07	grains per imperial gallon
= 0.01	pounds per 1,000 imperial gallons
= 10.0	pounds per 1,000,000 imperial gallons
1 Grain per US gallon (gpg)	
= 17.1	parts per million
= 17.1	milligrams per liter
= 17.1	grams per cubic meter
= 1.71	parts per 100,000
= 0.143	pounds per 1,000 US gallons
= 143.0	pounds per 1,000,000 US gallons
= 1.2	grains per imperial gallon
= 0.171	pounds per 1,000 imperial gallons
= 171.0	pounds per 1,000,000 imperial gallons
1 Part per hundred thousand (pts/100,000)	
= 10.0	parts per million
= 10.0	milligrams per liter
= 10.0	grams per cubic meter
= 0.583	grains per US gallon
= 0.0833	pounds per 1,000 US gallons
= 83.3	pounds per 1,000,000 US gallons
= 0.7	grains per imperial gallon
= 0.1	pounds per 1,000 imperial gallons
= 100.0	pounds per 1,000,000 imperial gallons
1 Grain per British imperial gallon	
= 14.3	parts per million
= 14.3	milligrams per liter
= 14.3	grams per cubic meter
= 1.43	parts per 100,000
= 0.833	grains per US gallon
= 0.119	pounds per 1,000 US gallons
= 119.0	pounds per 1,000,000 US gallons
= 0.143	pounds per 1,000 imperial gallons
= 143.0	pouonds per 1,000,000 imperial gallons

exceptions), and it is assumed that 1 liter weighs one kilogram; that 1 US gallon weighs 8.33 pounds; and that 1 British imperial gallon weighs 10 pounds.

Water Analyses Expressed as Calcium Carbonate (CaCO₃) Equivalents

As noted in Table 6, even when one basic unit such as parts per million is used, it is possible to express part or all of the calcium in seven different ways, each one of which uses a different numerical figure to express the equivalent amount of calcium. This, of course, is an extreme example; for instance, one could hardly imagine anyone using all these values to show parts or all of the calcium present in the same water. However, in a series of analyses made by different analysts, it would be possible to find all forms, although each analysis might use only one, two, or possibly three of them.

If we listed the magnesium equivalents, there would be 7 of them, making a total of 14 different methods of expression for the two constituents that together account for the hardness of water. Since calculations for water treatment were so complicated, it was decided to express the total hardness as the calcium carbonate (CaCO₃) equivalent of all of the hardness constituents. This makes a convenient yardstick; moreover, calcium carbonate has the figure of 100 as its molecular weight, which is a convenient, round, easy number to remember and which is large enough so that practically all of the results appear as whole numbers. Thus, it is customary to express total hardness, calcium hardness, and magnesium hardness as their CaCO₃ equivalents. This equivalent extends to the three forms of alkalinity—bicarbonate, carbonate, and caustic (or hydroxide)—and is convenient to extend this to mineral acidity, which might also be shown as “negative alkalinity.” It is common practice to express the cations of calcium, magnesium, and sodium; the total hardness; the bicarbonate, carbonate, and hydroxide alkalinity; the anions of sulfate, chloride, and nitrate; and mineral acidity in terms of their calcium carbonate (CaCO₃) equivalents in order to simplify the calculations used in water treatment. On the other hand, free carbon dioxide is usually expressed as CO₂ and iron, manganese, silica, and fluoride as Fe, Mn, SiO₂, and F, respectively.

Water Analyses Expressed as Equivalents per Million or Milliequivalents per Liter

The two units, equivalents per million (epm) and milliequivalents per liter (mEq/L), are numerically equal. To express the amount of a substance present in terms of either one, divide the number of parts per million of the substance present by its equivalent weight. The equivalent weights of the common cations and anions in water are Ca 20, Mg 12.2, Na 23, HCO₃ 61, CO₃ 30, OH 17, SO₄ 48, Cl 35.5, and NO₃ 62.

Although equivalents per million epm and milliequivalents per liter are

used, they are not as widely used as the calcium carbonate equivalents. The objection is inconvenience: with these equivalents, many of the figures appear on the right hand of the decimal point, whereas with the calcium carbonate equivalents, especially when expressed in parts per million, most of the figures appear as whole numbers. The equivalents of most of the substances found in water work will be found in the Appendix.

Water Hardness: Methods of Expression

The method of expressing the hardness of a water is as its CaCO_3 equivalent, in parts per million, grains per US gallon, parts per hundred thousand, or grains per imperial gallon. Hardness is also expressed as CaCO_3 equivalents, in parts per million, grains per US gallon or to a limited extent in parts per hundred thousand.

In expressing results of a water analysis, no more than three significant figures should ever be given, for the methods employed do not warrant the use of a greater number. If the application of a factor results in such a figure as 214.64 ppm, it should be rounded off to an even 215 ppm. Even then, it should be understood that the accuracy of the determinations does not extend to +1 in the third significant figure. For certain determinations, two significant figures may be all that are warranted. The chemical factors and equivalents used in water-treatment calculations also need not consist of more than three significant figures. Thus the molecular weight of calcium chlorinate may be taken as 100 instead of 100.09, and the factor for converting Ca to CaCO_3 may be rounded off to 2.50 instead of the more exact 2.497.

WASTES AND WASTE EFFLUENT CHARACTERISTICS

Knowledge of the composition of sewage and industrial wastewaters allows a better assessment of methods of treatment that should be applied before discharge to a receiving body of water. Such knowledge helps to determine whether or not an industrial waste will attack the sewer, whether it should be treated alone or in admixture with sewage—and in what proportions, and whether a single-stage or multistage process should be used. A thorough study of the processes from which various components of an industrial waste arise, together with their composition, may lead to recovery of materials and water saving. Analysis of treated wastewaters is necessary to assess potential toxicity and disease hazards to humans and toxicity to fish and other biota. This is desirable, especially in light of the growing need for reuse and conservation of water, to help decide how to treat the effluents further for use as low-grade water for industrial purposes, and as potable water as well as to meet regulatory requirements of discharge.

The principal source of pollution in sewage is human excreta, with smaller contributions from food, washing, laundry, surface drainage, and so forth.

Industrial wastes, in general, consist of one or more strong spent liquors from specific processes together with comparatively weak waters from rinsing, washing, condensing, floor washing, and so forth. Typically analyses of the sewage itself have to be made for specific substances for particular purposes, such as indole for odor, detergents for foaming, or pesticides for health hazards.

Sampling

The value of analytical work can be reduced if the sampling techniques and programs adopted do not adequately take account of the nature of the wastewater and the wide, often rapid, fluctuations in flow, strength, and composition which occur in wastewaters and effluents. In purely domestic systems, the variations follow a fairly regular pattern, but where industrial wastes are discharged to the sewers other fluctuations will be observed. Continuous industrial processes often give rise to less variation in the wastewater produced than occurs in municipal sewage. Factories operating batch processes, or in which much washing water is used, often give rise to fluctuations in volume and composition of waste. Treatment of wastes by the biological processes reduces the fluctuations, and there is usually little systematic variation in the composition of the effluent.

Equipment used for sampling range from vessels hand operated such as beakers and buckets to sophisticated automatic devices which take constant volume samples at prescribed time intervals or which take volumes proportional to the flow of wastewater. The type of sampler must be suitable for the waste being sampled; for example, any tubes through which the liquid has to pass should be wide enough to prevent clogging by suspended solids. Sometimes it is necessary to analyze the subsamples; in other cases, it is important to know the total pollution load on a treatment plant or to be discharged. For this purpose a composite sample is made by mixing the subsamples in amounts proportional to the flow of liquid at the time of sampling. The time interval between subsamples is commonly 1 hr for sewage, but for industrial wastes more frequent samples may be required. To help decide the frequency of sampling, a knowledge of the manufacturing processes involved is invaluable. In view of postsampling changes, it may be necessary to make provision for preservation of subsamples by refrigeration or addition of a bacterial inhibitors.

The collection of samples for bacterial examination requires sterile conditions, especially where biological effluents are involved. The qualitative estimation of viruses is usually made by using the Moore "swab" technique, in which pads of sterile cotton gauze are immersed in the flowing liquid for a number of hours before being withdrawn for examination.

Sample Preservation

Because of changes which take place on standing, it is desirable that analyses be made immediately after collection. This may not be possible, but it is essential

that for such determinations as dissolved gases, volatile substances, and bacterial numbers the analyses be made within a short time of collection. Of the changes which can occur when bacteria are present, the more important are the absorption of dissolved oxygen, growth and death of bacteria, hydrolysis of urea to ammonia, oxidation of ammonia to nitrite and nitrate, reduction of nitrite to gaseous nitrogen, disappearance of sugars, and formation of volatile fatty acids. Changes in the bacterial count on storage vary widely from sample to sample, probably due to unknown factors. The effect of storage on the 5-day biochemical oxygen demand (BOD) is consistently to lower the value obtained, but there is a wide scatter in the proportional reduction.

Other methods used to preserve samples do not allow the BOD or bacterial count to be estimated but are useful for determination of chemical and physical parameters. The addition of sulfuric acid keeps the suspended solids (SS) constant for 8 days and the chemical oxygen demand (COD) constant for at least 17 days, whereas the addition of the antibiotic polymyxin B, after heating the sample to 80°C for 1 hr, gave constant COD values for at least 6 months on storage at 22–27°C. Mercuric chloride, added at 3–50 mg/L, depending on the concentration of organic matter in the sample, preserved samples for at least 2 weeks for the determination of pH value, COD, total solids, volatile solids (VS), ammonia, nitrite, nitrate, and organic nitrogen but interfere in the determination of phosphate and phenol. It is undesirable to use mercuric chloride in gas-liquid chromatography methods and in the methods for organic carbon involving catalytic gaseous oxidation. Agents such as chloroform, formalin, thymol, and potassium cyanide are ineffective. The method chosen will depend on the situation, and two or more methods of preservation may have to be used for a single series of samples. Whatever method is chosen, the samples should be stored in the dark in full bottles.

Separation and Concentration

Some determinations can be carried out directly on the untreated sample, but because of the very low concentration of many constituents, and also sometimes for convenience, many samples are processed to separate or concentrate the constituent or to remove interfering compounds before analyses are made.

The constituents in suspended solids are best estimated on the dried solids, which are conveniently prepared by lyophilization (freeze drying) of the various solids fractions obtained by successive settlement, differential centrifugation, and ultrafiltration by membrane or Pasteur candle. For most constituents in solution, lyophilization is, again, a useful general concentrating process which prevents loss of heat-labile substances. The method has been used successfully with domestic sewage to yield fine, buff- or tan-colored powders and is especially useful when collecting composite samples over a long period. Recovery by this method of the total solids in solution is high, with the highest proportional loss

being of volatile acids and ammonia; the recovery of the total solids in raw sewage losses are considered to be largely manipulative and nonselective. Sewage and biological effluents have also been concentrated at about 54°C under reduced pressure in rotary and cyclone evaporators designed to minimize loss of heat-labile substances.

Since volatile compounds are preferentially lost by the evaporative methods, special means must be used to determine such compounds in the original sample. Volatile acids and bases have been separated by appropriate steam distillation, whereas some of the neutral volatile compounds have been extracted by solvents. Solvent extraction is also extensively used to separate fats, greases, and detergents from solids using petroleum ether, chloroform, or alkaline methanol; to separate nonvolatile acids and pesticides from solution; and to separate carbohydrates of differing degrees of complexity by successive extraction with aqueous ethanol, perchloric acid, 0.25N HCl, and 72% H₂SO₄. Examples of methods for removing interfering substances prior to analysis are the use of ion exchange resins to remove salts and amino acids before separating individual sugars by paper chromatography and the use of electro dialysis to eliminate nitrite and nitrate from concentrated effluents prior to the determination of sugars by the anthrone method.

Analytical Procedures

Methods are used to determine such parameters as, for example, BOD, COD, and SS. Hitherto most analyses for organic constituents have been made by conventional titrimetric and calorimetric procedures and, after suitable concentration and separation, by long-established chromatographic methods. Examples are amino acids by reaction with higher fatty acids by reversed phase column chromatography. More use is being made of gas-liquid chromatography of aqueous solutions for volatile fatty acids and also of infrared spectroscopy for degradation products of alkylbenzene sulfonates (ABS) and for poly- β -hydroxybutyric acid in sewage microorganisms. The *wet* combustion method for organic carbon has been replaced by high-temperature catalytic oxidation and determination of the carbon dioxide formed by a nondispersive infrared method. Bacterial numbers have been determined by most probable numbers (MPN) or plate counts, and protozoa have been counted by direct microscopic observation.

Sewage Characteristics

Fresh sewage is normally turbid and appears gray to yellow-brown depending on the time of day collected. If industrial wastes are discharged into the sewer, the sewage sometimes takes on the color of the waste. When viewed in ultraviolet light, a colored fluorescence is often seen which is probably due to minor constituents of packaged detergents. Sewage when fresh has a musty, but not offensive, odor; on standing, however, putrefaction sets in and objectionable

odors are produced. Occasionally the odor of an industrial waste is evident or identifiable.

The temperature of sewage is normally a degree or two above that of the water supply; in winter in moderate climates, the temperature range is 8–12°C and in summer 17–20°C. When hot discharges are made to the sewer, higher temperatures are observed, and similarly, infiltration of storm or surface waters can be expected to cause decreases in temperature. Solids suspended in sewage range from colloids up to recognizable matter.

Changes occur in the flow, strength, and composition of sewage hourly, daily, and seasonally; of these, hourly changes are usually greatest. Variations in flow are normally larger, the smaller the community served; the hourly variation is usually 50–200% of the average and can be as wide as 20–300%. The strength and composition also vary considerably during a day, and a fairly regular pattern is followed.

The polluting strength of sewage is assessed by such parameters as 5-day BOD, COD, SS, and ammonia content. The strength varies widely and depends on such factors as the quantity of water used per head of population, the amount of groundwater and surface water entering the sewer, and local habits.

Constituents

Inorganic content of sewage depends on the nature of the water supply from which it is derived as well as on the nature of the polluting material. The major groups present in solution in sewage are sugars, free and bound amino acids, volatile and nonvolatile acids, anionic detergents, and unspecified, ether-soluble neutral compounds, whereas minor groups included bases, amphoterics, phenols, sterols, and various nitrogen-containing substances.

In all fractions of suspended solids, fats, carbohydrates, and proteins are the main identified constituents and together account for 60–80% of the organic matter present.

There are wide variations of fats and greases. For example, total fat and grease is usually 40–100 mg/L, but values as low as 16 mg/L and as high as 1480 mg/L have been reported for sewage containing industrial wastes. Free fatty acids reported include all the saturated ones from C₈ (caprylic) to C₁₄ (myristic), including those whose odd numbers of carbon atoms, the saturated acids C₁₆, C₁₈, and C₂₀, and the unsaturated acids C₁₆-2H, C₁₈-2H, and C₁₈-4H. A number of these acids are bound as esters; free acids as a proportion of total free plus ester acid varies. The major acids are palmitic, stearic, and oleic, which together form the majority—over two-thirds or even as much as 90%; myristic, lauric, and linoleic acids are present in relatively low proportions.

Proteins and amino acids comprise the largest single nitrogen-containing

group in sewage, with the proportion of total organic nitrogen present in this form varying.

A number of N-containing compounds other than amino acids have been found in sewage. Of those derived from urine, urea is the most abundant in fresh material; concentrations as high as 55 mg N/L, but more usual values were in the range 2–16 mg N/L. Changes in urea content are fairly rapid, aerobically and anaerobically, leading to higher ammonia content and lower organic carbon content. Uric acid is present at a fairly constant level of 0.2–1.0 mg/L; hippuric acid has also been detected.

Miscellaneous Constituents

Sterols as a group were thought to be normally present in sewage at 0.1–0.2 mg/L and seldom in excess of 1–2 mg/L. Cholesterol has been reported at 0.04–0.26 and 0.03–0.05 mg/L, whereas the concentration of coprostanol ranges from 0.096 to 0.75 mg/L.

Various pigments derived from plants, e.g., chlorophyll and lycopene, from urine, e.g., urochrome, and from feces, e.g., stercobilin, have been detected in very low concentrations in sewage.

The increasing use of synthetic detergents is reflected in their increasing concentration in sewage.

Organisms present in sewage originate from feces, soil, and water and range from viruses through bacteria and fungi to protozoa and worms. The identity and concentration of such organisms is imprecisely known and effort has been concentrated on organisms pathogenic to humans and the degree to which they are removed by treatment. Many species of the various types of organisms have been described, and in some cases the numbers of individuals of the species have been reported, but nothing like a comprehensive analysis of the total number of organisms present, even of bacteria, is available.

INDUSTRIAL WASTEWATERS

The total polluting load of industrial wastewaters has been estimated to be at least as great as that of domestic sewage. The volume and strength of industrial wastes vary considerably from industry to industry and even within each industry there are wide variations. General properties of wastes from a given industry are usually similar. For many installations there are diurnal variations associated with batch production, a weekly pattern with decreased flow at weekends, or seasonal variations associated with availability of raw materials. Many industrial wastes, especially from the food industry, are similar to domestic sewage and can be purified alone or in admixture with sewage by the usually biological processes. Other wastes are characteristically different. Others cannot be purified

by the usual methods either alone or in admixture with sewage. Some wastes are therefore discharged, with or without treatment, to sewers and others are discharged to rivers or the sea, again with or without prior treatment.

Any given industrial discharge must be examined in detail, not only by analysis of suitable samples but also by examining in detail the processes that produce each of the waste waters that together form the discharge. Table 8 summarizes common impurities found in water, their chemical formula, difficulties caused, and means of treatment.

GROUND WATER CHARACTERISTICS

Ground water technology involves the art and science of investigating, developing, and managing ground water. The technology involves specialized fields of soil science, hydraulics, hydrology, drainage, geophysics, geology, mathematics, agronomy, metallurgy, bacteriology, and electrical, mechanical, and chemical engineering. Ground water engineering is an important source of water. Ground water recovery for water supply—ground water engineering—is important in problems concerning seepage from surface reservoirs and canals, the effects of bank storage, stability of slopes, recharging of ground water reservoirs, controlling of saltwater intrusion, dewatering of excavations, subsurface drainage, and construction, land subsidence, waste disposal, and contamination control.

Ground waters involve the determination of aquifer properties and characteristics and the application of hydraulic principles to ground water behavior for the solution of engineering problems. Determination of aquifer characteristics and the application of data by appropriate methods are essential to the solution of complex problems in which ground water is a factor. The extent to which the determination of aquifer properties and characteristics must be made depends on the complexity of the problem involved. A required investigation may range from cursory to detailed and may entail study or consideration of all or only one or two aquifer properties and hydraulic principles. Conditions often may be so complex as to preclude the determination of finite values and the application of available theory to the solution of some problems. In such cases, solutions may be largely subjective and their reliability dependent on the experience and judgment of the ground water specialist.

Shallow, hand-dug wells and crude water-lifting devices marked the early exploitation of ground water. The introduction of well-drilling machinery and motor-driven pumps made possible the recovery of ground water in large amounts and at increased depths. The benefits of ground water development have become increasingly important. The use of water for domestic purposes usually has the highest priority, followed by industrial requirements, and then agricultural usage (irrigation). Development of the ground water resources has been increasing in

Table 8 Common Impurities Found in Water

Constituent	Chemical formula	Difficulties caused	Means of treatment	Minimum effluent—guarantee
Turbidity	None—expressed in analysis as units	Imparts unsightly appearance to water. Deposits in water lines, process equipment, boilers, etc. Interferes with most process uses.	Coagulation, settling, and filtration	Coagulation—average 5 ppm; filtration—2 ppm
Color	None—expressed in analysis as “units” of color on arbitrary scale	May cause foaming in boilers. Hinders precipitation methods such as iron removal, hot phosphate softening. Can stain product in process use.	Coagulation and filtration, chlorination, adsorption by activated carbon	Coagulation filtration—5 on cobalt scale
Hardness	Calcium and magnesium salts expressed as CaCO ₂	Chief source of scale in heat exchange equipment, boilers, pipe lines, etc. Forms curds with soap, interferes with dyeing, etc.	Softening, distillation, internal boiler water treatment, surface-active agents	Cold lime soda—16 ppm (railway process); hot lime soda—10 ppm; ion exchange—zero
Alkalinity	Bicarbonate (HCO ₃), carbonate (CO ₃), and hydrate (OH), expressed as CaCO ₃	Foaming and carryover of solids with steam. Embrittlement of boiler steel. Bicarbonate and carbonate produce CO ₂ in steam, a source of corrosion.	Lime and lime soda softening, acid treatment, hydrogen zeolite softening, demineralization, dealkalization by anion exchange, distillation, split-stream ion exchange	Cold lime soda—35 ppm; hot lime soda—17 ppm; H ₂ Z ion exchange—zero; anion exchange—10 ppm; split-stream ion exchange—zero
Free mineral acid	H ₂ SO ₄ , HCl, etc., expressed as CaCO ₃	Corrosion	Neutralization with alkalis, anion exchange	Anion exchange—zero

Table 8 (Continued)

Constituent	Chemical formula	Difficulties caused	Means of treatment	Minimum effluent—guarantee
Carbon dioxide	CO ₂	Corrosion in water lines and particularly steam and condensate lines.	Aeration, deaeration, neutralization with alkalis, filming and neutralizing amines	Decarbonator—15 ppm; degasifier—5 ppm; vacuum deaerator—2 ppm; deaerator—zero
pH	Hydrogen ion concentration defined as: $\text{pH} = \log \cdot \frac{1}{(\text{H}^+)}$	pH varies according to acidic or alkaline solids in water. Most natural waters have a pH of 6–8	pH can be increased by alkalis and decreased by acids	
Sulfate	(SO ₄) ²⁺	Adds to solids content of water, but in itself is not usually significant. Combines with calcium to form calcium sulfate scale.	Demineralization, distillation	Demineralization—zero
Chloride	Cl ⁻	Adds to solids content and increases corrosive character of water.	Demineralization. Distillation.	Demineralization—zero
Nitrate	(NO ₃) ⁻	Adds to solids content, but is not usually significant industrially. High concentrations cause methemoglobinemia in infants. Useful for control of boiler metal embrittlement.	Demineralization. Distillation.	Demineralization—zero

Fluoride	F ⁻	Cause of mottled enamel in teeth. Also used for control of dental decay. Not usually significant industrially.	Adsorption with magnesium hydroxide, calcium phosphate, or bone black. Alum coagulation. Anion exchange.
Silica	SiO ₂	Scale in boilers and cooling water systems. Insoluble turbine blade deposits due to silica vaporization.	Cold Lime Soda—15 ppm Hot Lime Soda—1 ppm Na ₂ Z + anion exchange—0.5 ppm Deminerlization—0.01 ppm
Iron	Fe ²⁺ (ferrous) Fe ³⁺ (ferric)	Discolors water on precipitation. Source of deposits in water lines, boilers, etc. Interferes with dyeing, tanning, paper mfr., etc.	Aeration-Filtration—0.3 ppm Manganese Zeolite—0.1 ppm Cation Exchange—zero
Manganese Oil	Mn ²⁺ Expressed as oil or chloroform extractible matter.	Same as iron. Scale, sludge and foaming in boilers. Impedes heat exchange. Undesirable in most processes.	Same as iron. Coagulation Filtration—Clear bright and free from opalescent turbidity as visible to the naked eye in a clean quart glass bottle. Filtration with preformed flocc-Diatomaceous earth.
Oxygen	O ₂	Corrosion of water lines, heat exchange equipment, boilers, return lines, etc.	Vacuum Deaeration—0.1 ppm Open Heater—0.3 ml/L Deaerator—0.005 ml/L

Table 8 (Continued)

Constituent	Chemical formula	Difficulties caused	Means of treatment	Minimum effluent—guarantee
Hydrogen sulfide	H ₂ S	Cause of "rotten egg" odor. Corrosion.	Aeration. Chlorination. Highly basic anion exchange.	Aeration
Ammonia	NH ₃	Corrosion of copper and zinc alloys by formation of complex soluble ion.	Cation exchange with hydrogen zeolite. Chlorination. Deaeration.	Anion Exchange—zero Cation Exchange—zero Aeration
Conductivity	Expressed as micromhos $\mu\Omega$ specific conductance	Conductivity is the result of ionizable solids in solution. High conductivity can increase the corrosive characteristics of a water.	Any process which decreases dissolved solids content will decrease conductivity. Examples are demineralization, lime softening.	Multibed Demineralization—1 mW Mixed Bed Demineralization—0.1 microhm
Dissolved solids	None	"Dissolved solids" is a measure of total amount of dissolved matter, determined by evaporation. High concentrations of dissolved solids are objectionable because of process interference and as a cause of foaming in boilers.	Various softening processes, such as lime softening and cation exchange by hydrogen zeolite, will reduce dissolved solids. Demineralization. Distillation.	

Suspended solids	None	<p>“Suspended Solids” is the measure of undissolved matter, determined gravimetrically</p> <p>Suspended solids plug lines, cause deposits in heat exchange equipment, boilers, etc.</p>	<p>Subsidence. Filtration, usually preceded by coagulation and settling.</p>
Total solids	None	<p>“Total Solids” is the sum of dissolved and suspended solids, determined gravimetrically.</p>	<p>See “Dissolved Solids” and “Suspended Solids” above.</p>

Note: The above minimum effluent guarantees are not applicable to all plants. The effluent water depends on its final end use and the economics of treatment.

recent years as development of surface water sources approaches the point of full potential use.

Precipitation, storage, runoff, and evaporation of the earth's water follow an unending sequence known as the hydrological cycle and are the source of groundwater. During this cycle, the total amount of water in the atmosphere and in or on the earth remains constant even though its form may change. Although minor quantities of magmatic water or water from other deep-seated sources may find its way to the surface, all water is part of the hydrological cycle.

The movement of water within the hydrological cycle consists of water vapor in the atmosphere condensed into ice crystals or water droplets that fall to the earth as rain or snow. A portion evaporates and returns to the atmosphere. Another portion flows across the ground surface until it reaches a stream and flows to the ocean. The remaining portion infiltrates directly into the ground and seeps downward. Some of this portion may be transpired by the roots of plants or moved back to the ground surface by capillarity and evaporated. The remainder seeps downward to join the ground water body.

Ground water returns to the ground surface through springs and seepage to streams where it is subject to evaporation or is directly evaporated from the ground surface or transpired by vegetation. Thus, the hydrological cycle is completed. When sufficient water vapor again gathers in the atmosphere, the cycle repeats. The elements of the hydrological cycle for any area can be quantified.

A basic ground water equation which permits an approach to a quantitative estimate of ground water availability can be established for an area to account for those factors of the hydrological cycle which have a direct effect on flow and storage of ground water. The equation is

$$\Delta S_{gw} = \text{recharge} - \text{discharge}$$

where ΔS_{gw} is the change in ground water storage during the period of study. Theoretically, under natural conditions and over a long period of time, which include both wet and dry cycles, ΔS_{gw} , will be zero and inflow (recharge) will equal outflow (discharge).

The natural recharge to the ground water body includes deep percolation from precipitation, seepage from streams and lakes, and subsurface underflow. Artificial recharge includes deep percolation from irrigation and water spreading, seepage from canals and reservoirs, and recharge from recharge wells. The natural discharge or outflow from the ground water body consists of seepage to streams, flow from springs, subsurface underflow, transpiration, and evaporation. Artificial discharge occurs by wells or drains. If ground water storage in an area is less at the end of the selected period of time than at the beginning, discharge is indicated as having exceeded recharge. Conversely, recharge may exceed discharge.

Recharge from natural sources include the following:

- Deep percolation from precipitation: Deep percolation of precipitation is one of the most important sources of ground water recharge. The amount of recharge in a particular area is influenced by vegetative cover, topography, and nature of soils as well as the type, intensity, and frequency of precipitation.
- Seepage from streams and lakes: Seepage from streams, lakes, and other water bodies is another important source of recharge. In humid and subhumid areas where ground water levels may be high, the influence of seepage may be limited in extent and may be seasonal. However, in arid regions where the entire flow of streams may be lost to an aquifer, seepage may be of major significance.
- Underflow from another aquifer: An aquifer may be recharged by underflow from a nearby, hydraulically connected aquifer.

The amount of this recharge depends on the head differential, the nature of the connection, and the hydraulic properties of the aquifers.

- Artificial recharge: Artificial recharge to the ground water may be achieved through planned systems or may be unforeseen or unintentional. Planned major contributions to the groundwater reservoir may be through spreading grounds, infiltration ponds, and recharge wells. Irrigation applications, sewage effluent spreading grounds, septic tank seepage fields, and other activities have a similar but usually unintentional effect. Seepage from reservoirs, canals, drainage ditches, ponds, and similar water impounding and conveyance structures may be local sources of major ground water recharge. Recharge from such sources can completely change the ground water regimen over a considerable area.

Ground water discharges—losses from the ground water reservoir—occur in the following ways:

- Seepage to streams: In certain reaches of streams and in certain seasons of the year, ground water may discharge into streams and maintain their base flows. This condition is more prevalent in humid areas than in arid or semiarid areas.
- Flow from springs and seeps: Springs and seeps exist where the water table intersects the land surface or a confined aquifer outlets to the surface.
- Evaporation and transpiration: Ground water may be lost by evaporation if the water table is near enough to the land surface to maintain flow by capillary rise. Also, plants may transpire ground water from the capillary fringe or the saturated zone.
- Artificial discharge: Wells and drains are imposed artificial withdrawals on

ground water storage and in some areas are responsible for the major depletion. Ground water moves in response to a hydraulic gradient in the same manner as water flowing in an open channel or pipe. However, the flow of ground water is appreciably restricted by friction with the porous medium through which it flows. This results in low velocities and high head losses as compared with open channel or pipe flow.

An aquifer is a water-bearing bed or stratum of earth, gravel, or porous stone. Some strata are good aquifers, others are poor. The most important requirement is that the stratum must have interconnected openings or pores through which water can move. The nature of each aquifer depends on the material of which it is composed, its origin, the relationship of the constituent grains or particles and associated pores, its relative position in the Earth's surface, its exposure to a recharge source, and other factors.

Rocks—used here to denote all material of the earth, whether consolidated and firm or unconsolidated and loose or soft—are generally classified as sedimentary, igneous, and metamorphic. The geological structure, lithology, and stratigraphy of rocks in an area provide general knowledge of their potentials as aquifers.

In general, the best aquifers are the coarse-grained, saturated portions of the unconsolidated, granular sedimentary mantle which cover the consolidated rocks over much of the surface of the Earth. The widespread presence of unconsolidated sediments is more common at lower elevations in proximity to streams. These sediments consist of stream alluvium, glacial outwash, wind-deposited sand, alluvial fans, and similar water- or wind-deposited coarse-grained, granular materials. In addition, some residual materials resulting from the weathering in place of consolidated rock are good aquifers.

The coarser grained consolidated rocks such as conglomerates and sandstones are also often good aquifers but are usually found below the unconsolidated granular sedimentary mantle. Their value as aquifers depends to a large extent on the degree of cementation and fracturing to which they have been subjected. In addition, some massive sedimentary rocks such as limestone, dolomite, and gypsum may also be good aquifers. These rocks are relatively soluble and over the years solution along fractures or partings may form voids which range in size from a fraction of an inch to several hundred feet. Some of the best-known and most productive aquifers are cavernous limestones.

The value of igneous and metamorphic rocks as aquifers depends greatly on the amount of stress and weathering to which they have been subjected after their initial formation. In general, the crystalline igneous rocks are very poor aquifers if they remain undisturbed. However, mechanical and other stresses cause fractures and faults in these rocks in which ground water may occur. Such openings may range from hairline cracks to voids several inches wide. In general,

these openings disappear with depth and do not yield significant quantities of water below depths of several hundred to a thousand feet.

In coarse-grained crystalline igneous rocks, where in-place weathering has occurred, a thin permeable zone may be found in the transition zone between the sound rock and the thoroughly weathered, usually relatively impermeable, overlying residual material. Some lavas, especially those of viscous basaltic composition, may contain good to excellent aquifers in the zones between successive flows. The scoriaceous upper and lower surfaces of flows are usually porous and permeable, and cooling fractures may be present in a zone extending into the flow from the upper and lower surfaces. Furthermore, coarse-grained sedimentary material may also be present between flows.

An unconfined aquifer is one that does not have a confining layer overlying it. It is often referred to as a free or "water-table" aquifer or as being under "water-table conditions." Water infiltrating into the ground surface percolates downward through air-filled interstices of the material above the saturated zone and joins the ground water body. The water table, or upper surface of the saturated ground water body, is in direct contact with the atmosphere through the open pores of the material above and is everywhere in balance with atmospheric pressure. Movement of the ground water is in direct response to gravity.

A confined or artesian aquifer, as shown in Figure 4, has an overlying, confining layer of lower permeability than the aquifer and has only an indirect or distant connection with the atmosphere. Water in an artesian aquifer is under pressure and when the aquifer is penetrated by a tightly cased well or piezometer,

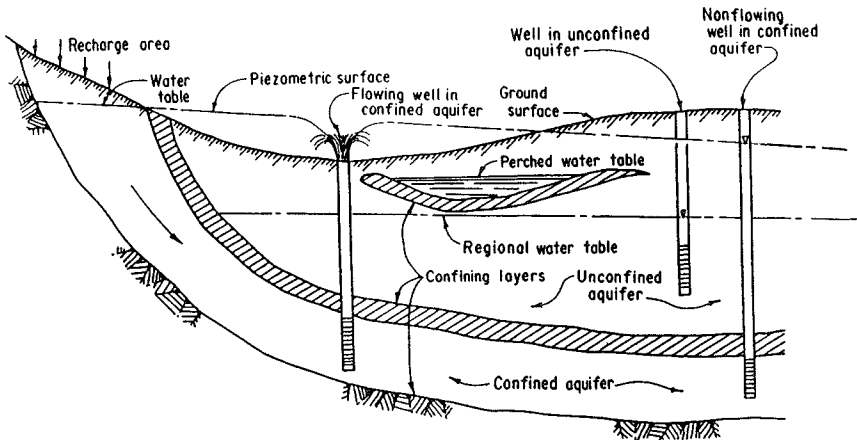


Figure 4 Types of aquifers.

the water will rise above the bottom of the confining bed to an elevation at which it is in balance with the atmospheric pressure and which reflects the pressure in the aquifer at the point of penetration. If this elevation is greater than that of the land surface at the well, water will flow from the well. The imaginary surface, conforming to the elevations to which water will rise in wells penetrating an artesian aquifer, is known as the potentiometric, or piezometric, surface.

Beds of clay or silt, unfractured consolidated rock, or other material with relatively lower permeability than the surrounding materials may be present in some areas above the regional water table. Downward percolating water may be intercepted and a saturated zone of limited areal extent formed. The result is a perched aquifer with a perched water table. An unsaturated zone is present between the bottom of the perching bed and the regional water table. A perched aquifer is a special case of an unconfined aquifer. Depending on climatic conditions or overlying land use, a perched water table may be a permanent phenomenon or one which varies seasonally.

Water may occur in several recognizable subsurface zones under different conditions, as shown in Table 9. The thickness of each zone above the zone of rock flowage varies according to the area and with time. During a period of recharge, the zone of saturation thickens at the expense of the zone of aeration. When discharge exceeds recharge, the zone of saturation thins and the zone of aeration thickens. During periods of recharge, a temporary downward migrating saturated lense may move through the zone of aeration.

Table 9 Status of Water in Various Soil Zones

Zone	Horizon	Condition of water	Condition of soil
Aeration (above water table)	Soil water	Under tension	Unsaturated
	Intermediate	Under tension	Unsaturated
	Capillary fringe	Under tension	Saturated and unsaturated
Saturation (below water table)	Unconfined groundwater	Under pressure but upper surface at atmospheric pressure	Saturated
	Confined or artesian ground water	Under pressure but upper surface above atmospheric pressure	Saturated
Rock flowage		Combined—no free water	Dry

Precipitation typically contains minute amounts of silica and other minerals and dissolved gases such as carbon dioxide, sulfur dioxide, nitrogen, and oxygen which are present in the air and are entrapped as precipitation occurs. As a result, the pH value of most precipitation is below 7 (acidic) and the water is corrosive. On reaching the surface, the water may pick up organic acids from humus and similar materials which increase its corrosive characteristics. While the water is percolating through rock, minerals are attacked by the acid waters and dissolved forming salts which are taken into solution. The amount and character of the salts depend on the chemical composition of the water, the mineralogical and physical structure of the rocks encountered, and the temperature, pressure, and duration of contact.

Nearly all elements may be present in groundwater, and its mineral content varies from aquifer to aquifer and from place to place within an aquifer. Commonly encountered elements and compounds are listed in Table 10.

Less common constituents which are also important because of their effects in use of water are boron (B), manganese (Mn), lead (Pb), arsenic (As), selenium (Se), barium (Ba), copper (Cu), zinc (Zn), hydrogen sulfide (H₂S), methane (CH₄), oxygen (O₂), carbon dioxide (CO₂), and nitrite (NO₂). The mineral content of water is so variable and the acceptable quality for various uses has such a large range that it is not practical to discuss them other than generalities.

Water quality is also important because of its influence on the efficiency and life of equipment. Acidic water with a pH value of less than 7 is usually corrosive; whereas alkaline water (pH > 7) is usually less corrosive. However, alkaline water is likely to form deposits on well screens and on pipes. Hard water with a pH value over 7 may be corrosive and may form deposits if it contains relatively large amounts of sulfate, bicarbonate, and chloride radicals. Gases such as hydrogen sulfide, carbon dioxide, methane, and oxygen may be damaging by both corrosion and cavitation.

Contaminated or polluted water contains organisms and substances that make it unsuitable or unfit for use. Ground water may become contaminated as

Table 10 Chemical Constituents
Commonly Found in Groundwater

Cations	Anions
Calcium, Ca	Bicarbonate, HCO ₃
Magnesium, Mg	Sulfate, SO ₄
Sodium, Na	Chloride, Cl
Potassium, K	Nitrate, NO ₃
Iron, Fe	Fluoride, F
	Silica, SiO ₂

a result of leakage from septic tanks, sewage effluent spreading grounds, garbage dumps, or similar features for the disposal of vegetable and animal waste. Other sources of contamination which are concern are improperly sealed wells, other subsurface structures and excavations, and those areas created by the disposal of oil field brines and industrial wastes through evaporation ponds, spreading fields, and disposal wells.

The distance that organisms may migrate in ground water varies. In general, it should be assumed that in crevassed, fissured, and cavernous rock and in coarse, clean gravels, organically contaminated water may travel as far as several miles. In finer-grained materials, natural filtering action and adsorption may remove such organisms in less than a 100-foot distance. Chemical contaminants may persist indefinitely in ground water. Accordingly, no water should be considered suitable until both chemical and bacterial analyses have shown it to be so.

Differences and changes in the chemical content of water may be useful in determining the source or sources of recharge, direction of flow, and presence of boundaries. The age of water determined by tritium content, carbon 14 dating, and similar analysis may be useful in estimating the age, recharge conditions, or potential direction of flow of ground water or other aspects of ground water hydrology. Also, quality data may be essential in determining the compatibility of water intended for artificial recharge.

Ground water in humid areas maintains the base flow of streams by seepage into stream channels. However, the headwater reaches of some streams may be above the water table and therefore are dry during seasons of low precipitation. In such reaches, seepage from the streambed may charge an underlying aquifer. Some reaches of a stream may be replenished by ground water, whereas others lose water to the ground water reservoir.

In many arid drainage basins, the perennial master streams receive seepage from the ground water reservoir, whereas other streams may be above the water table and streamflow occurs only during periods of high surface runoff. Where the water table is below the streambed, practically all the streamflow may be lost by seepage to the ground water reservoir. Beneath many such streambeds, considerable underflow may be present in the channel fill, although the channel is dry.

It is in the semiarid to arid areas, where irrigation is usually practiced, that water losses from canals and deep percolation from irrigation applications frequently alter natural ground water conditions. Such alterations include water table rise and waterlogging and salination of soils. Artificial drainage by open or buried pipe drains, wells, or other means is often required to lower the water table, maintain a salt balance, and permit the continued production of crops.

Interest has developed in recharging ground water reservoirs with excess surface water. Such recharge is intended to maintain ground water levels, store

water for use during droughts, control salt water intrusion, dispose of treated sewage effluent, or for other purposes. In addition, pollutants such as oil field brines and toxic and radioactive industrial wastes are often disposed of by storing them in deep isolated aquifers.

Because suitable surface water reservoir sites are becoming scarce, interest has increased in the underground storage of water. Although underground reservoirs are not as obvious or as readily recognized as surface reservoirs, they offer a possible alternative in many areas where conventional storage would be costly or otherwise undesirable. As is true of all alternative solutions, each type of reservoir offers advantages and disadvantages.

The major application of ground water has been and probably always will be the provision of a water supply by means of wells and infiltration galleries. Facilities range from isolated individual small wells yielding less than a gallon a minute for domestic and stock purposes to well fields consisting of a number of irrigation, municipal, or industrial water supply wells with individual discharges of more than 5,000 gallons per minute. The small individual well seldom presents a problem if it is designed according to proper engineering practice. Larger installations, particularly those with numerous wells, require evaluation of the aquifer characteristics, estimates of well spacing, drawdowns, quality water, and possibly recharge-discharge relationships. Wells should be designed and pumps selected for economical, long, and trouble-free operation within the capabilities of the aquifer, with the consideration of any possible corrosion and encrustation problems which may be present.

Some aquifers have little measurable recharge or discharge but contain large quantities of water in storage which have accumulated over long periods. Estimates can be made of the desirability of mining the water and the probable economic life of such aquifers under various degrees of development.



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2

Dissolved Matter

INORGANIC MATTER

Natural water supplies, either in their raw state or after treatment, contain dissolved mineral matter. Mineral constituents vary greatly in amounts and relative proportions present in various water supplies. The most abundant are the bicarbonates, sulfates, and chlorides of calcium, magnesium, and sodium that are present as mixtures of their respective anions and cations. Solubilities are given in terms of CaCO_3 (calcium carbonate) equivalents.

Calcium Bicarbonate. Calcium bicarbonate, $\text{Ca}(\text{HCO}_3)_2$, exists only in solution and is formed by the action of water containing carbon dioxide on limestone, marble, chalk, calcite, dolomite, and other minerals containing calcium carbonate according to the following reaction:



Water at 32°F, saturated with carbon dioxide at atmospheric pressure, the solubility of calcium bicarbonate is 1620 ppm. This is the maximum solubility and most natural water supplies do not have calcium bicarbonate contents which even approach this figure. When the temperature is raised, the solubility decreases because of increasing reversal of the

above reaction. In a steam boiler, for example, the reversal is complete and the entire content of calcium bicarbonate breaks down into carbon dioxide, water, and calcium carbonate, which has very low solubility (15 ppm at 3°F and 13 ppm at 212°F).

Magnesium Bicarbonate. Magnesium bicarbonate, $\text{Mg}(\text{HCO}_3)_2$, exists only in solution and is formed by the action of water containing free carbon dioxide on magnesite, dolomite, dolomitic limestone, and other minerals containing magnesium carbonate according to



Water at 3°F, saturated with carbon dioxide at atmospheric pressure, the solubility of magnesium bicarbonate is 37,100 ppm. Although the maximum solubility of magnesium bicarbonate is high, the amounts found in natural water supplies are usually under 75 ppm and seldom reach twice this figure. As the temperature rises, solubility decreases because of an increasing reversal of the above reaction forming first carbon dioxide, water, and magnesium carbonate, which in pure water has a solubility of 101 ppm at 32°F and 75 ppm at 212°F. At higher temperatures, as in a steam boiler, a further change takes place as the magnesium carbonate reacts with water to liberate carbon dioxide and form magnesium hydroxide, which has a very low solubility (17 ppm at 32°F and 8 ppm at 212°F).

Sodium Bicarbonate. Sodium bicarbonate, NaHCO_3 , is commonly known as bicarbonate of soda and baking soda. Solubility in water at 32°F is 38,700 ppm and increases as the temperature rises, but above 100°F it begins to lose carbon dioxide and it completely breaks down into carbon dioxide, water, and highly soluble sodium carbonate at 212°F. In a steam boiler, it reacts with water, so that most of it is converted into carbon dioxide and sodium hydroxide (caustic soda).

Calcium Sulfate. Calcium sulfate, CaSO_4 , occurs as the dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in such minerals as gypsum, alabaster, and selenite; as the anhydrous form (CaSO_4) in the mineral anhydrite; and as the hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) in the material known as plaster of Paris, which is made by the partial dehydration of gypsum.

Magnesium Sulfate. Magnesium sulfate, MgSO_4 , occurs as the heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) that is commonly known as Epsom salt or epsomite when found, e.g., in salt beds, mines, and caverns. Another mineral form is kierserite, which is a monohydrate ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$). It also occurs in other minerals, such as kainite, picromerite, and loweite, as double salts with potassium chloride, potassium sulfate, sodium

sulfate, etc. Unlike calcium sulfate, magnesium sulfate is a very soluble salt, having a solubility of 170,000 ppm at 32°F and 356,000 ppm at 212°F. In steam boilers it is corrosive.

Sodium Sulfate. Sodium sulfate, Na_2SO_4 , occurs as the decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) which is an efflorescent salt that is commonly known as Glauber's salt. It is also known as the mineral mirabilite when found deposited, e.g., in salt lakes, salt beds, and caverns. The anhydrous sodium sulfate of commerce, a by-product of the manufacture of hydrochloric acid from common salt and sulfuric acid, is commonly known as salt cake. Like the other sodium salts found in natural and treated waters, sodium sulfate is very soluble and is not a scale former.

Calcium Chloride. Calcium chloride, CaCl_2 , occurs in natural brines, salt beds, and elsewhere and is obtained as a by-product in the chemical industry. Two mineral forms are tachhydrite, a hydrated double salt with magnesium chloride ($\text{CaCl}_2 \cdot 2\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$) and hydrophilite, an anhydrous form (CaCl_2). It forms several hydrates such as monohydrate ($\text{CaCl}_2 \cdot \text{H}_2\text{O}$), the dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), and the hexahydrate ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$). All at 32°F and 554,000 ppm at 212°F. In steam boilers, it is corrosive.

Magnesium Chloride. Magnesium chloride, MgCl_2 , occurs in sea water, natural brines, salt beds, and elsewhere. Four mineral forms are the anhydrous chloromagnesite (MgCl_2), the hexahydrate bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), the double salt with potassium chloride carnallite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$), and tachhydrite (see above paragraph). Magnesium chloride is deliquescent and highly soluble—362,000 ppm at 32°F and 443,000 ppm at 212°C. It is very corrosive in steam boilers, as it reacts with water at such temperatures to form hydrochloric acid and magnesium hydroxide.

Sodium Chloride. Sodium chloride, NaCl , is most widely known as salt without any qualifying adjective. It is also known as common salt, and the mineralogical name for sodium chloride is halite. It is the chief mineral constituent of sea water (2.7% NaCl) and occurs in salt beds, salt lakes, connate waters, other natural brines, and elsewhere. It is anhydrous in composition, but the crystals often enclose some water so that it often decrepitates on heating. Like the other sodium salts found in natural and treated waters, it has a high solubility and is not a scale former.

Other mineral matter which may be found in natural water supplies may include silica, iron, manganese, nitrates, nitrites, potassium, and mineral acidity. Silica, SiO_2 , occurs in nearly pure form in quartz and many sands. It is also a major constituent of granite, feldspar, clay, and a host of other minerals. It is

found in practically all natural waters and may be present in amounts ranging from as little as 1 ppm or less to over 100 ppm.

Iron is present in most water supplies in small amounts, and if it is present to the extent of 0.1 ppm or less, it may be considered as negligible for most industrial uses. If iron is present in greater amounts than 0.2 or 0.3 ppm, it is usually very objectionable. Manganese is a rarer constituent but is even more objectionable, and tolerances for special uses may be even lower than the tolerances for iron.

Nitrates are usually absent or present only as traces, but there are exceptions, and if appreciable amounts are present, nitrates are determined. Nitrites are either absent or present in such minute amounts that they are rarely determined in industrial water analyses. Ammonia, which possibly might more appropriately be considered under gases, is also usually such a minor constituent that it is seldom determined in industrial water analyses. There are exceptional cases, however, where heavily contaminated waters have given off enough ammonia in the boilers to have an effect on brass valves and fittings.

Potassium, because it is usually present in such small amounts and is so much like sodium in most of its properties, is usually grouped with the sodiums. Fluorides, which may occur in the waters in certain localities in amounts of less than 1 to over 8 ppm, are of importance from a health aspect but are probably of little significance for most industrial uses. A few of the waters in certain western areas contain borates in sufficient amounts to be of importance when used for irrigation. Small amounts of alumina are also commonly found in water supplies, but usually they are of little significance.

Small quantities of carbonate alkalinity may be found, at times, in both natural surface waters and well waters, and objectionable amounts may be present in the so-called alkali waters. Caustic alkalinity is practically never found except in treated waters.

Mineral acidity is found in many waters and some surface waters which have been contaminated by industrial wastes or seepage from mines.

For industrial uses and the usual run of natural and treated water supplies, the mineral constituents shown in Table 1 are the only ones usually considered. As to the amounts of mineral matter dissolved and carried away in solution by natural water supplies. Industrial contamination and contamination from man-made sources require a detailed and full analysis beyond this list.

Alkalinity

Alkalinity can be determined by titration with a standard acid solution, using phenolphthalein and methyl orange as indicators. Results of titration with the methyl orange indicator are expressed as methyl orange alkalinity or total alkalinity. Results of titration with phenolphthalein indicator are expressed as phenolphthalein alkalinity; most natural water supplies contain some free carbon

Table 1 Mineral Constituents Typically Determined in Water Analyses

Name	Formula	Expressed as	Commonly known as
Calcium	Ca	CaCO ₃	Calcium hardness
Magnesium	Mg	CaCO ₃	Magnesium hardness (Total hardness = Calcium hardness + Magnesium hardness)
Sodium	Na	CaCO ₃	—
Bicarbonate	HCO ₃	CaCO ₃	Bicarbonate alkalinity
Carbonate	CO ₃	CaCO ₃	Carbonate alkalinity
Hydroxide	OH	CaCO ₃	Caustic alkalinity
Chloride	Cl	CaCO ₃	—
Sulfate	SO ₄	CaCO ₃	—
Nitrate	NO ₃	CaCO ₃	Mineral acidity
Mineral acid	—	F	—
Fluoride	F	F	—
Silica	SiO ₂	SiSO ₂	—
Iron	Fe	Fe	—
Manganese	Mn	Mn	—

dioxide and show no phenolphthalein alkalinity. If no phenolphthalein alkalinity is present, all of the alkalinity is assumed to be bicarbonate alkalinity. If phenolphthalein alkalinity is present, twice the phenolphthalein alkalinity, if less than or equal to the methyl orange alkalinity, is assumed to be carbonate alkalinity. If twice the phenolphthalein figure exceeds the methyl orange alkalinity, the excess is presumed to be caustic or hydroxide alkalinity.

In solutions as dilute as freshwater supplies are, the salts are not present as such but instead are practically dissociated into the corresponding anions and cations. However, it is often convenient and simpler to visualize some of the salts as if they were undissociated, so it is common practice to refer to the calcium bicarbonate or calcium sulfate content of a water as if these substances were present as undissociated salts instead of as ions. In other cases, it may be simpler to consider the ions that are present.

Hardness

The hardness of a water is due to its calcium and magnesium content. Hardness is expressed in terms of calcium carbonate. Calcium hardness is that hardness due to soluble calcium salts; magnesium hardness is that due to soluble magnesium salts. Total hardness is the sum of the calcium hardness plus the magnesium hardness.

Carbonate hardness (the preferred term), *bicarbonate hardness*, and

temporary hardness are terms for that hardness attributed to the bicarbonates of calcium and/or magnesium. *Noncarbonate hardness* (the preferred term), *sulfate hardness*, and *permanent hardness* are terms for that hardness due to the sulfates chlorides and/or nitrates of calcium and/or magnesium.

The amounts of carbonate and noncarbonate hardness present are determined as follows:

- If the methyl orange alkalinity of the water equals or exceeds the total hardness, all of the hardness is present as carbonate hardness.
- If the methyl orange alkalinity of the water is less than the total hardness, the carbonate hardness equals the alkalinity.
- The noncarbonate hardness, under the conditions above, is equal to the total hardness minus the methyl orange alkalinity.

Calcium Carbonate Scale

Calcium carbonate is much less soluble than magnesium carbonate and both of these are much less soluble than sodium carbonate. It is convenient to visualize the alkalinity as bound first to the calcium, second to the magnesium, and third to the sodium. When a water containing the bicarbonates of calcium, magnesium, and sodium is heated, the calcium carbonate deposits first magnesium carbonate, next, while sodium carbonate is so extremely soluble that no separation in the solid form would occur until the solution was greatly concentrated by evaporation and crystallization takes place. The solubilities of these three carbonates at 212°F are shown in Table 2.

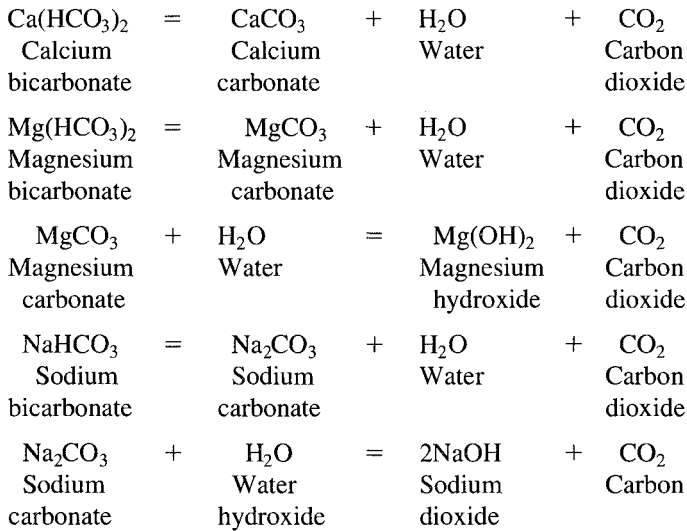
Calcium Carbonate and Magnesium Hydroxide Scale

At the temperatures prevailing in steam boilers, both calcium bicarbonate and magnesium bicarbonate break down to form scale, whereas the calcium scale consists of calcium carbonate, the magnesium deposits as magnesium hydroxide. This is due to the magnesium bicarbonate decomposing first to magnesium carbonate and reacting with the water to form magnesium hydroxide and free carbon dioxide. Sodium bicarbonate undergoes a similar decomposition in a

Table 2 Carbonates: Solubilities of the Carbonates of Calcium, Magnesium, and Sodium at 212°F

Name	Formula	Solubility as CaCO ₃ ppm
Calcium carbonate	CaCO ₃	13
Magnesium carbonate	MgCO ₃	75
Sodium carbonate	Na ₂ CO ₃	289,000

boiler, but since caustic soda is extremely soluble, it remains in solution. These reactions are shown as follows:



Carbon dioxide formed leaves the boiler with the steam. In the case of the sodium carbonate, the conversion to sodium hydroxide often exceeds 80%. The magnesium hydroxide in the scale may lose part of its water content by baking on the tubes and appear partly as magnesium oxide. The solubilities of the hydroxides of calcium, magnesium, and sodium, expressed as parts per million of CaCO_3 , at 212°F are shown in Table 3.

Under higher temperatures and pressures, the solubilities of both calcium carbonate and magnesium hydroxide decrease. At about 210 psi (392°F), the solubility of calcium carbonate is a little less than 5 ppm and that of magnesium hydroxide is only slightly over 1 ppm, expressed as CaCO_3 . Calcium hydroxide also has a solubility that decreases with rise in temperature. At 32°F, its solubility is 2390 ppm, at 212°, 888 ppm, and at 210 psi (392°F), 134 ppm, expressed as

Table 3 Hydroxides: Solubilities of the Hydroxides of Calcium, Magnesium, and Sodium at 212°F

Name	Formula	Solubility as CaCO_3 (ppm)
Calcium carbonate	Ca(OH)_2	888
Magnesium carbonate	Mg(OH)_2	8
Sodium carbonate	NaOH	975000

CaCO_3 . It is not found in a boiler scale unless boiler feed water was grossly overtreated with lime.

Calcium Sulfate Scale

Calcium sulfate is the only scale-forming salt in the noncarbonate hardness for magnesium sulfate, and the chlorides and nitrates of both calcium and magnesium have solubilities exceeding 150,000 ppm by weight expressed as CaCO_3 , even at 32°F and over 356,000 ppm at 12°F. Calcium sulfate, in the form of gypsum, has a solubility curve which, on elevations of temperature, shows a rise up to about 104°F after which it falls until, at 212°F, it is slightly below the solubility at 32°F. At boiler temperatures the curve falls rapidly, until at 322 psi it is only some 40 ppm, expressed as calcium carbonate. Table 4 shows calcium sulfate solubilities.

Tolerance for calcium sulfate in a cooling water should be large—over 1200 ppm expressed as CaCO_3 . This is taken into account in the acid treatment of cooling waters. The blowdown on a cooling pond is regulated so as to maintain the calcium sulfate content below some 100 ppm, expressed as CaCO_3 . Owing to low solubility at the temperatures prevailing in steam boilers and because it forms a very hard and adherent scale, no amount of calcium sulfate can be tolerated in steam boilers.

Thermal Conductivities of Scales

The thermal conductivities (K) of adherent boiler scales, expressed in $\text{Btu/ft}^2/\text{ft/hr}/^\circ\text{F}$ (British thermal units per square foot of area per foot of thickness per hour per 1°F temperature difference) have been found to lie between 0.66 and 2.06 with a mean value of approximately 1.5. The degree of porosity of the scale affects the thermal conductivity, since these pores may be filled with steam instead of water under boiler operating conditions, thus reducing the thermal conductivity in much the same manner as the air cells in the commonly used

Table 4 Calcium Sulfate: Solubilities at 32–428°F

Temperature (°F)	Solubility as CaCO_2	
	(ppm)	(gpg)
32	1293	75.5
104	1551	90.5
212	1246	72.7
338 (100 psi)	103	6.0
392 (210 psi)	56	3.3
428 (322 psi)	40	2.3

heat-insulating materials. There is some evidence that porous scales may have thermal conductivities of only 0.2 Btu/ft²/ft/hr/°F.

Thermal conductivity of firebrick is about 0.75 and steel about 26. Hard-water scales therefore have thermal conductivities of only some 3–8% (average about 5%) of that of steel or about the same as that of firebrick. Hardwater scales are practically as good heat-insulating materials as firebrick. Unfortunately, scale forms in the wrong places, which accounts for its being called misplaced insulation.

Heat-insulating properties of hard-water scales are objectionable not only in steam boilers and water heaters and water-cooled equipment such as condensers, internal combustion engines, and other water-jacketed equipment. Furthermore, these scale deposits do not form a layer which is of even thickness and uniformly distributed over the entire heat transfer area. Instead scale forms most rapidly and consequently is thickest at points where the rate of heat transfer is greatest.

Sodium Salts

Sodium salts that may occur in various natural water supplies are sulfate, chloride, nitrate, bicarbonate, and rarely carbonate. Quantities present in different fresh-water supplies vary over a wide range. For instance in the analyses of the various river lake, spring, and well waters, sodium salts may range from as little as 2% to as much as 98% of the total salts present.

Sodium salts are extremely soluble in either cold or hot water, as is shown in Table 5. Because of these high solubilities, the sodium salts do not form scales, either on heating or in evaporating in the steam boiler, unless the evaporation is carried out to extreme lengths. Also, they do not waste soaps, since soaps that are most widely used are sodium salts of certain of the higher fatty acids. There is no reaction between the sodium salts in water and soap. Strong solutions of sodium salts will throw soap out of solution; an effect is known as salting out. The composition of the soap is unaltered by salting out

Table 5 Sodium Salts and Their Solubilities

Name	Formula	Solubility as ppm of CaCO ₃	
		(at 32° F)	(at 212°F)
Sodium bicarbonate	NaHCO ₃	38400	Decomposes
Sodium carbonate	Na ₂ CO ₃	62600	289000
Sodium chloride	NaCl	225000	241000
Sodium hydroxide	NaOH	370000	965000
Sodium nitrate	NaNO ₃	248000	378000
Sodium sulfate	Na ₂ SO ₄	33200	398000

and it can be redissolved either in fresh water or by diluting the saline solution.

Therefore, for many industrial uses moderate amounts of sodium salts in the water supply are not significant. They do increase the amount of blowdown on the steam boiler, and if much sodium bicarbonate is present, it may be advisable to remove it or to neutralize most of it with sulfuric acid and then to aerate or degasify the acid-treated water before feeding it to the boiler in order to reduce the free carbon dioxide content of the steam.

Sodium salts are objectionable in the processing of manufacture of certain cellulose products, dielectrics, fine drugs and chemicals, synthetic rubber, plastics, photographic materials, silver-plated ware, and other materials. High sodium alkalinity waters are objectionable in high-pressure steam boilers, laundries, and textile plants. Sodium bicarbonate may be removed by a hydrogen cation exchanger and the sulfate, chloride, or nitrate by this treatment followed by treatment with an anion exchanger.

Silica

Silica, in amounts ranging from less than 1 to over 100 ppm, is found in all natural water supplies. In rain, hail, and snow, silica contents range from 0.1 to 2.8 ppm. In the analyses of various surface and ground waters, silica contents range from 1 to 107 ppm. This refers to soluble silica content and not to the silica which may be present in the suspended matter. Suspended matter may be removed from a water supply by coagulation and filtration; such processes have little effect in reducing the soluble silica content.

Silica is particularly objectionable where it may have pronounced scale-forming tendencies. If calcium hardness is present in salines, the scale formed may be a calcium silicate; if soluble alumina is present, an aluminosilicate scale, such as analcite, may be formed; and under other conditions, the scale may consist almost entirely of silica. Silica scales are typically very hard, glassy, adherent, and difficult to remove. Thermal conductivities are usually very low and tube failures can occur with even very thin silica scales. Silica is frequently carried over with steam, forming scale in superheater tubes and on turbine blades. Although this action is usually ascribed to mechanical carryover, silica is soluble to a certain extent in high-pressure steam.

In low- and moderate-pressure steam boilers, silica scale can usually be avoided by maintaining a small excess of phosphate and a ratio of alkalinity to silica of at least 1:1 in the boiler salines. In boilers operated at over 600 psi, treatment of the make-up water to reduce its silica content is frequently necessary. This not only prevents scale in the boilers but also prevents silica deposits on the turbine blades, which may occur even when no serious silica deposits are formed in boilers.

With proper treatment, the silica content of water may be reduced to

unobjectionable amounts. If the water to be treated is a surface water which requires coagulation, the use of ferric sulfate as a coagulant will assist in reducing the silica content. Dolomitic lime or activated magnesia, especially in the hot lime soda process, is effective in treatment. The same materials are also used in the cold lime soda process. In ion-exchange demineralizing processes, silica may be removed by direct anion exchange in a strongly basic anion exchanger which has been regenerated by caustic soda (NaOH).

Iron

Iron is present in practically all water supplies but if amounts present are 0.1 ppm or less, they may be considered as negligible for most industrial uses. The iron in various water supplies may be present in several forms.

In deep well waters, iron, if present in amounts of over 0.1 ppm, is almost always present as the soluble, colorless ferrous bicarbonate. Such waters are usually clear and colorless when first drawn, but on standing in contact with the atmosphere, they may slowly cloud and finally deposit a yellowish to reddish brown precipitate of ferric hydroxide. The amounts of iron present in the great majority of such waters will be found in the range below 5 ppm, with a few in the range of 5–15 ppm, and very few above the latter figure. Iron in the form of ferrous bicarbonate may also be found in carbon dioxide-containing, but oxygen-free, corrosive waters which effect iron pickup from the water mains.

So-called red waters, which are caused either by the action of corrosive waters containing dissolved oxygen on iron piping or by the aeration of a water containing ferrous bicarbonate, have suspended iron in the form of a more or less hydrated ferric oxide.

In some surface waters, iron in amounts of over 0.1 ppm may be present in an organic (chelated) form. Usually such waters will show appreciable color. In acid mine waters or in acid surface waters contaminated with acid mine waters or acid industrial wastes, part or even all of the iron may be present as ferrous sulfate. Such waters may also contain manganese sulfate, aluminum sulfate, free sulfuric acid, and suspended ferric hydroxide. Water supplies containing over 0.2 ppm of iron can be objectionable for industrial uses, and for many uses the tolerance should not exceed 0.1 ppm.

Iron-bearing waters also favor the growth of iron bacteria, called iron crenothrix. Such growths form abundantly in water mains, recirculating systems, and other places and can exert a clogging action and cut down the flow rates. Also, these growths can break loose in large, clogging masses.

Iron present as ferrous bicarbonate may be removed by

- Aeration and filtration
- Cation exchange
- Filtration through manganese zeolite

Iron present as suspended ferric hydroxide may be removed by filtration, which may be preceded by settling. Iron present in organic or colloidal form may be removed by coagulation and filtration. Iron present as ferrous sulfate may be removed by neutralization, aeration, and filtration, which may be preceded by settling.

Manganese

Manganese, rarer in occurrence than iron, can be even more troublesome. In clear, deep well waters, it usually occurs as manganous bicarbonate. Such waters may contain appreciable amounts of ferrous bicarbonate as well as manganous bicarbonate. When first drawn, such waters are clear and colorless, but on standing in contact with air, cloud and then usually deposit the yellowish or reddish brown ferric hydroxide first. This is because the iron oxidizes more readily and at lower pH values than manganese. For air to oxidize manganous bicarbonate rapidly, it is usually necessary to have a pH value of above 9.0. The oxidation is catalyzed if previously formed higher oxides of manganese are present as a contact medium.

When not masked by the color of admixed ferric hydroxide, the oxidized manganese forms gray to black deposits and stains. The color of the manganese crenothrix (manganese bacteria) is also black, and these, like iron bacteria, form clogging growths in pipe lines and recirculating systems, which may break loose in the form of large masses. Very small amounts of manganese—0.2–0.3 ppm—may form heavy incrustations in piping, whereas even smaller amounts may form noticeable black deposits.

In acid mine waters, manganous sulfate is frequently found with the ferrous sulfate. In colored surface waters, manganese, like iron, may be present in an organic or colloidal form. Manganese may also be found as manganous bicarbonate in surface waters, especially in rather quiescent waters such as lakes, ponds, or reservoirs. In such cases, the processes of decay may, especially at the bottom, use up the dissolved oxygen, generate free carbon dioxide, reduce manganese to the manganous, state and dissolve it as manganous bicarbonate.

Manganese present as manganous bicarbonate may be removed by

- Aeration and filtration
- Cation exchange
- Filtration through manganese zeolite

Manganese present as manganous sulfate in acid waters may be removed by neutralization, aeration, and filtration. Manganese present in surface waters in colloidal form may be removed by coagulation, settling, and filtration, but such waters may also contain manganous manganese, which requires oxidation.

Aluminum

Small amounts of aluminum are present in most natural water supplies. Since these are usually of little or no importance for most industrial uses, aluminum is determined separately only in exceptional cases.

Aluminum content of a water may be reduced for special uses by

- Coagulation at a favorable pH value, settling, and filtration
- Passing through a hydrogen cation exchanger
- By the ion-exchanger demineralizing process
- By distillation

The addition of an alum coagulant, adjustment of pH values to a favorable point, settling, and filtration will usually reduce the total alumina content of the water to 0.6–1.5 ppm as Al_2O_3 .

Fluoride

In certain areas, the water supplies and especially, but not exclusively, the ground water supplies show presence of natural fluoride. Communities are now fluoridating their water supplies as a dental health measure. Supplies which are being fluoridated, the amounts added are small ranging from 0.7 to 1.1 ppm, expressed as F (fluorine). Waters which contain a natural fluoride content, in general, most of these fluoride waters will contain from a fraction of a ppm of fluoride, expressed as fluorine, up to about 3 ppm; a few will range from this to 8 ppm; and only in exceptional cases will the content be above this. The solubility of fluorite—calcium fluoride, CaF_2 —is some 16–17 ppm at temperatures of about 65–80°F. This corresponds to about 8 ppm of fluorine. The magnesium salt is over four times as soluble, with a solubility, expressed as MgF_2 , of about 76 ppm at 65°F and the sodium salt is quite soluble—about 4% at 60°F.

Owing to the low solubility of calcium fluoride, it can form scale, but this rarely occurs. For most industrial uses, it is of little or no consequence if the water has a small content of fluoride. Some exceptions include where the material is evaporated with a water containing only 1 ppm of fluoride; this would result in a higher concentration in the finished product.

Mineral Acidity

Water supplies that contain mineral acidity are relatively small in number and are usually confined to

- Mine waters
- Ground waters in the vicinity of mines or contaminated by acid trade wastes
- Surface waters contaminated by mine waters or acid trade wastes

The acid present is almost invariably sulfuric acid. The water may contain sulfates of iron, aluminum, manganese, calcium, magnesium, and sodium. Also, the free carbon dioxide content is usually high and, in the case of acid ground

waters, ferrous bicarbonate is frequently present. In testing such waters, the mineral acidity is determined by titration with a standard solution of sodium hydroxide and using methyl orange as the indicator. The result includes free acid plus any of the acidic substances mentioned above, is noted as free mineral acidity, and is expressed as the calcium carbonate equivalent.

In mines, the free sulfuric acid and metallic sulfates have formed by the oxidation of sulfur-containing materials, notably pyrites. The most common of these is marcasite, or brassy iron pyrites, which yields sulfuric acid and ferrous sulfate on oxidation in the presence of moisture. Pumps, drains, and piping used in removing such acid waters from mines must be made of special, acid-resistant materials or their useful life will be very short. Not all mine waters are acid; many are alkaline with calcium and magnesium bicarbonates. Even in the same mine, waters from some of the levels may be alkaline and from others acid. Some of these acid mine waters seep through strata to emerge later as springs or to be tapped by wells. In passing through carbonate-containing strata, as the acid or iron sulfate is neutralized to a varying extent by the carbonates, corresponding amounts of carbon dioxide are liberated. If the extent of this neutralization is sufficient to neutralize the free sulfuric acid and part of the ferrous sulfate, the resultant water will contain a large part of its iron in the form of ferrous bicarbonate. In certain cases, this neutralization may proceed so far that the originally acid water becomes alkaline.

DISSOLVED GASES

Dissolved gases that may occur in various water supplies are carbon dioxide (CO_2), oxygen (O_2), nitrogen (N_2), hydrogen sulfide, and methane (CH_4).

Carbon Dioxide

Free carbon dioxide is found in varying amounts, in most natural water supplies, and that picked up by rain water from the atmosphere is very small, usually ranges from about 0.5 to 2.0 ppm on freely analyzed samples. Most surface waters also have low contents of free carbon dioxide; ranging from zero to about 5 ppm. In the case of lakes, surface samples will usually range from zero to about 2 ppm, whereas depth samples may show much higher contents.

In most rivers, small amounts of carbon dioxide, ranging from slightly above zero to about 5 ppm, are usually present most of the time. However, since the oxidation of organic matter furnishes carbon dioxide, rivers containing considerable organic matter may at times show much higher quantities of carbon dioxide and contents of 50 ppm or over are occasionally found. Rivers receiving acid mine waters or acid wastes may also show high contents of carbon dioxide. Table 6 shows carbon dioxide solubilities in water at various temperatures.

In addition to the carbon dioxide formed by the decaying organic matter,

Table 6 Carbon Dioxide: Solubilities in Water at Various Temperatures

Temperature		Milliliters per liter (ml/L)	Parts per million (ppm)
(°C)	(°F)		
0	32	1690	3350
5	41	1400	2770
10	50	1170	2310
15	59	996	1970
20	68	855	1690
25	77	733	1450
30	86	637	1260
40	104	491	970
50	122	384	760
60	140	293	580

carbon dioxide may also be picked up from strata or fissures in the Earth's crust. The amount of carbon dioxide contributed to natural surface and ground waters from the atmosphere is practically negligible compared with that contributed by decaying organic matter.

Although most natural waters, freshly sampled, usually have some content of free carbon dioxide, some will show, at times, an appreciable phenolphthalein alkalinity. This is due to photosynthesis; that is, plants, whether large or microscopic, under the influence of sunlight breathe in carbon dioxide and breathe out oxygen. This action does not necessarily stop with the exhaustion of the free carbon dioxide supply but may continue on part of the half-bound carbon dioxide content of the bicarbonates, thus forming the normal carbonate and imparting a phenolphthalein alkalinity to the water.

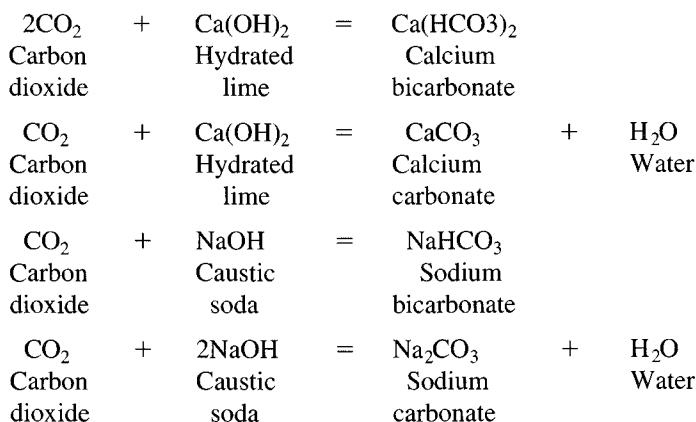
When carbon dioxide dissolves in water, it forms, to a certain extent, a weakly dissociated acid—carbonic acid. (Ionization constant for the first hydrogen, at 18°C, is 3×10^{-7} ; and for the second hydrogen, at 25°C, is 6×10^{-11} .) If the water is free from all traces of alkali, and is saturated with carbon dioxide—about 1450 ppm at 77°F—the pH value is approximately 3.8. This low pH would not be found in natural waters; except for waters containing free mineral acidity or exactly neutral waters, there is some bicarbonate alkalinity always present. Pure distilled water in equilibrium with the carbon dioxide content of the atmosphere will have a pH of about 5.7. Trace of alkalinity will raise this figure, so that most distilled waters in glass vessels will have pH values of around 6.4.

If bicarbonate alkalinity is also present, then the pH value is not dependent on free carbon dioxide alone but instead on the ratio of free carbon dioxide to the methyl orange alkalinity of the water.

Carbon dioxide is corrosive; an example is the attack of oxygen-free condensate on return piping in a boiler system. This attack may be severe owing to the low pH value of condensate which contains carbon dioxide. Natural water supplies, which contain free carbon dioxide but not dissolved oxygen, when passed through pipe, dissolve iron as ferrous bicarbonate. The ferric or ferroso-ferric hydrated oxides react with the iron of the pipe, being first reduced to the ferrous state and then uniting with the free carbon dioxide to form ferrous bicarbonate. This is known as iron pickup and may be stopped by aeration or partial aeration of the water.

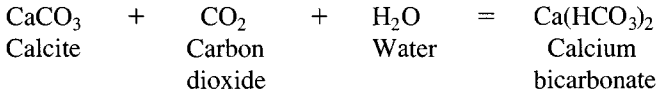
Carbon dioxide is an accelerating factor in dissolved-oxygen corrosion. Water which contains in addition to dissolved oxygen a high content of carbon dioxide in relation to its alkalinity will be much more corrosive than a water which contains a low content of carbon dioxide in relation to its alkalinity. Water having a dissolved oxygen content is much more corrosive if it has a low pH than if it has a high pH. If the calcium alkalinity of the water and its pH value also are such that it is saturated with a calcium carbonate, the corrosion will be greatly reduced, for a very thin film of CaCO_3 will protect the metal. Sodium silicate and caustic soda treatment of water to prevent corrosion are more fully discussed later.

Carbon dioxide may be reduced to certain limits or removed in cold temperatures by means of an aerator, a degasifier, or vacuum deaerator or in hot temperatures by means of a deaerator. Carbon dioxide may also be neutralized by the addition of lime or an alkali such as caustic soda, but these procedures are usually employed only for raw or treated waters which contain relatively small amounts of carbon dioxide. The reactions for forming either the carbonates or bicarbonates are



Carbon dioxide may also be partially removed from water by filtration through a neutralizing filter which employs a bed of calcite granules. Some of

the calcite dissolves in the water forming calcium bicarbonate. In practice it will be found that this automatically brings the pH up to 7.3. or 7.3. Such filters are widely used in the household field of water treatment, in the filtration of coagulated swimming pool waters, and to a certain extent in industry. The reaction is



Solubilities of carbon dioxide from the atmosphere in pure water, at temperatures ranging from 32 to 104°F, are shown in Table 7. In equilibrium with the carbon dioxide content of the atmosphere, pure water can contain only very small amounts of carbon dioxide—from approximately 0.3 to 1.0 ppm. If instead of pure water, water containing amounts of bicarbonate alkalinity is aerated until equilibrium is obtained, it will be found that some of the half-bound carbon dioxide will be given up to the atmosphere, thus converting some of the bicarbonates to carbonates. Removal of free carbon dioxide by aeration is usually not complete enough to establish equilibria. Free carbon dioxide residuals, varying from 3 to over 15 ppm, are usually obtained. Free carbon dioxide removal together with dissolved air may be accomplished by boiling the water and venting off the noncondensable gases. In the usual form of deaerator used for deaerating boiler feed waters, the boiling takes place at or slightly above atmospheric

Table 7 Solubilities of Air, Oxygen, and Nitrogen in Dissolved Air at Atmospheric Pressure and at 0–100°C

Temperature		Milliliters per liter (ml/L)		
°C	°F	air	=	oxygen + nitrogen
0	32	28.64	=	10.19 + 18.45
5	41	25.21	=	8.91 + 16.30
10	50	22.37	=	7.87 + 14.50
15	59	20.11	=	7.04 + 13.07
20	68	18.26	=	6.35 + 11.91
25	77	16.71	=	5.75 + 10.96
30	86	15.39	=	5.24 + 10.15
40	104	13.15	=	4.48 + 8.67
50	122	11.40	=	3.85 + 7.55
60	140	9.78	=	3.28 + 6.50
80	176	6.00	=	1.97 + 4.03
100	212	0.00	=	0.00 + 0.00

pressure. Under vacuum, deaeration is effected by boiling cold water under reduced pressures.

In the vacuum type of deaerator, the degree of deaeration required is usually less than in other deaerators, and since these operate at lower temperatures, decomposition of the bicarbonates is less. Depending on the operating conditions and the content of bicarbonate alkalinity, carbonate alkalinity may or may not develop.

Oxygen and Nitrogen

The solubilities of pure oxygen and pure nitrogen in water, at 32°F and atmospheric pressure, are 48.89 ml/L for oxygen and 23.54 ml/L for nitrogen; the oxygen therefore being a little more than twice as soluble as nitrogen. When air is dissolved in water, the two main components exist in different proportions in solution than they do in the atmosphere. Oxygen constitutes 21% by volume of the atmosphere, on a moisture-free basis, whereas as shown in Table 7, the percentage of oxygen in dissolved air ranges from about 33 to 35%.

The total volume of dissolved air diminishes rapidly with rising temperatures. The solubility of air at 140°F is only about one-third of its solubility at 32°F and at 176°F only about one-fifth, whereas at 211°F its solubility is zero. A method of deaerating water is to boil it and vent off the dissolved gases. According to Henry's law, the solubility of a gas is proportional to the absolute pressure. Therefore, if the pressure is increased, the amount of air that can be held in solution at a given temperature is proportionately increased. The water from a pneumatic tank or pressure aerator may contain much more dissolved air than water saturated with air at atmospheric pressure.

Nitrogen gas is practically never determined in analyzing water, since it is inert and relatively unimportant as far as water treatment is concerned. Certain bacteria, such as found on the roots of clover, peas, and beans, have the ability to take nitrogen out of the air and build compounds. Also, electric discharges through the atmosphere cause some of the nitrogen to combine with oxygen, so that rain water may contain nitrates, which are of value as a plant food. Nitrogen is a rather inert material which has no corrosive effects on metals and, except for air binding, it is of small interest whether or not it is present in a water supply. It is present in surface waters and aerated waters. Also, nitrogen has been found in spring waters and well waters.

Oxygen, however, is an active element which readily combines with many materials. A solution of oxygen in water is very corrosive to those metals—iron, steel, galvanized iron, and brass—which are widely used for containing and transporting water. Low pH values accelerate the rate of dissolved oxygen corrosion and high pH values tend to retard it. With waters containing sufficient calcium, building up the pH value to the calcium carbonate saturation point is usually effective in reducing the rate of corrosion.

Temperature elevations greatly accelerate the rate of corrosion. If all of the dissolved oxygen stayed in solution, if protective films did not form, and if we assumed the reaction followed the general rule of roughly doubling in speed for each 18°F rise in temperature, corrosion would be some 500 times as fast at 194°F than at 39°F. The factor which works in the opposite direction is the diminishing solubility of oxygen with rising temperatures. The greatest rate of corrosion in water heaters takes place at 160–180°F. For corrosion to take place, it is necessary to have liquid water present. Dry steam which contains oxygen is not corrosive, but the condensate formed from such steam is. In condensate return lines, it also can be found that the greatest attack is where liquid water is pocketed, so that proper pitching of the lines so they drain rapidly greatly checks the rates of corrosion.

Dissolved oxygen corrosion can be severe because of air leaking into a system at periods when the steam is off. The pH value of the condensate may also be low owing to the absence or extremely low content of alkalinity in it; even rather small amounts of carbon dioxide will greatly depress the pH value. At low pH values, the carbon dioxide of itself will attack the metal and will greatly accelerate the rate of the dissolved oxygen corrosion when oxygen is present; it is important to keep the carbon dioxide content of the steam low.

As the solubility of air increases directly with the absolute pressure, the content of dissolved oxygen in the water in pneumatic tanks may be much higher than in water saturated with air at atmospheric pressure. The rates of dissolved oxygen corrosion in vessels in contact with such waters may be very rapid.

Dissolved oxygen attacks iron and steel piping with formation of tubercles under each of which is a pit. If a tubercle is rapidly scraped off from a freshly removed piece of pipe, a flash of the green ferrous hydroxide can be seen. The main body of the tubercle consists of a black material, which represents either a hydrated ferrous-ferric oxide or an intimate mixture of ferrous and ferric hydroxides. The outside of the tubercle shows the typical yellowish or reddish brown color of the hydrated ferric oxide.

If tuberculated pipe which has been carrying a water containing dissolved oxygen is later used to carry an oxygen-free water which contains free carbon dioxide, an “iron pickup” frequently occurs and soluble ferrous bicarbonate is found in the water. This is because of reduction by the iron pipe of the ferric and intermediate compounds to the ferrous state and solution by the free carbon dioxide content of the water. Such iron pickups are frequently encountered when a deep well supply is substituted for a surface supply. It can be stopped by aerating the new water supply.

Galvanized iron and brass pipe are attacked by dissolved oxygen just about as rapidly as black iron. In the atmosphere, galvanized iron resists weathering well because of the formation of an adherent basic zinc carbonate. When water containing dissolved oxygen is passed through an internally galvanized pipe, the

adherent basic zinc carbonate does not form. Instead the zinc rapidly oxidizes and washes away. Yellow brass pipe also corrodes rapidly owing to the attack of dissolved oxygen on the zinc of the brass. The result is that the zinc is eaten away leaving a spongy and structurally weak skeleton of copper. As the action is usually localized, perforations and leaks occur long before the main body of the brass has been dezincified. Red brass is less subject to this attack than yellow brass, but it and even copper may be attacked by aggressive waters.

Although this decay of organic matter is using up dissolved oxygen, the plant life of the water (e.g., algae, water plants, certain diatoms) by photosynthesis takes in carbon dioxide and gives out oxygen.

Inhibition of reduction of dissolved oxygen corrosion methods of reducing or inhibiting dissolved oxygen corrosion have been mentioned. The cathodic system of corrosion prevention is used both for tanks and pipe lines. It depends for its action on a film of hydrogen on the surface of the cathode (in these cases, the pipe or tank) protecting the metal against the attack of dissolved oxygen. The current is feeble and power consumption is low, but care in installation, placing of anodes, and painting such as in tanks or of dry surfaces above the water line must be taken.

Hydrogen Sulfide

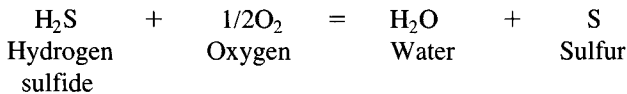
Waters which contain sulfides are commonly known as "sulfur waters." The prominent properties characteristic of hydrogen sulfide gas are an offensive, rotten-egg odor and corrosiveness. The odor is noticeable even in the cold when hydrogen sulfide is present in a water to the extent of 0.5 ppm, and when it is present to the extent of 10 ppm or more, the odor is very offensive. If the water has a high pH value, the odor may be slight; in which a case much of the sulfur may be present as an alkaline sulfide instead of as hydrogen sulfide.

Much of the corrosion deposits from sulfur waters is ferrous sulfide. Corrosion deposits may also consist of FeS_2 instead of FeS . Aeration is widely used for the reduction of the sulfide content of sulfur waters, but the reduction especially in waters of rather high alkalinity is usually only partial. Both hydrogen sulfide and carbon dioxide when dissolved in water are very weakly ionized, and it is possible to displace either one of these substances from its alkaline or alkaline earth salt by blowing a stream of the other gas through the solution. In treating sulfur waters, the carbon dioxide comes out much more easily than the more soluble hydrogen sulfide. Also, as it comes out, the pH value rises, and this upsets the equilibrium between alkaline sulfides and hydrogen sulfide so that the reaction proceeds in the wrong direction for the removal as hydrogen sulfide. Solubilities of hydrogen sulfide are shown in Table 8.

Oxidation of sulfides by dissolved oxygen is apparently a slow process. The oxidation of the hydrogen of the hydrogen sulfide follows:

Table 8 Hydrogen Sulfide: Solubilities at 760 mm and at 0–100° C

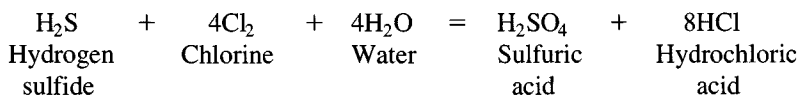
Temperature		Milliliters per liter (ml/L)	Parts per million (ppm)
°C	°F		
0	32	4590	7070
5	41	3900	6000
10	50	3320	5110
15	59	2870	4410
20	68	2500	3850
25	77	2190	3380
30	81	1940	2980
40	104	1530	2360
50	122	1220	1880
60	140	962	1480
80	176	497	765
100	212	0	0



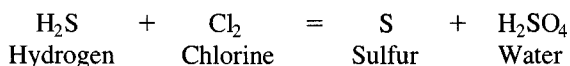
Presumably, then, some of this finely divided sulfur oxidizes further with a sulfate as the final endproduct.

Chlorine may be used to oxidize sulfides, but this process is rather expensive on raw sulfur waters; depending on the pH of the water and the amount of sulfide present, it may take up to eight atoms of chlorine to oxidize one molecule of hydrogen sulfide instead of the two atoms theoretically required to oxidize the hydrogen of the hydrogen sulfide to water and liberate the sulfur. This is because the sulfides are oxidized to sulfates and this oxidation takes place to a great extent even when a deficiency of chlorine is added.

The amount of chlorine required to oxidize 1 ppm of H₂S to the sulfate is 8.32 ppm and the reaction is



The amount of chlorine required to oxidize 1 ppm of H₂S to water and sulfur is 2.08 ppm and the reaction is



Chlorination of waters containing high contents of sulfides would be expensive. Chlorination is of value in eliminating the small residuals from the effluents of other sulfide removal processes.

Methane is commonly given off in stagnant, marshy waters where putrefactive processes are taking place—hence its common name, marsh gas. However, well waters can contain methane. The amounts of methane in these waters ranges from 0.1 to 10 cubic feet per 1000 gallons. This is equivalent roughly to 0.8–87 ml of methane per liter of water. As the solubility of methane at 60°F at atmospheric pressure is only a little over 36 ml/L, a water containing 87 ml/L would effervesce at ordinary temperatures when pressure is released.

DRINKING WATER AND WATER SUPPLY

The municipal water supply should be safe to drink. Many natural water supplies, especially most deep ground water supplies, are perfectly safe as drawn and need nothing more than to be guarded against subsequent contamination. Most surface supplies though, especially in highly populated and industrial areas, and also some ground water supplies are not safe and consequently need treatment to render them safe before they are fed into the distribution systems. There are also some waters which have become so polluted that they are beyond redemption.

Municipal water supplies are generally safe to drink owing to the quality standards and to the strict supervision exercised by the regulatory authorities. This is a most important, since it eliminates municipal water supplies as potential carriers of such waterborne diseases such as cholera and typhoid fever.

In addition to being safe, a drinking water should also be attractive in appearance and palatable, since people do not like to drink a water which has a marked turbidity or a high color, nor do they relish a water which smells like rotten eggs.

Turbidity and Color Removal

Water supply can come from ground water supply, surface water supply, or part of it from a ground water supply and the rest from a surface water supply. Uncontaminated ground water supplies from deep ground are usually clear and practically colorless, but some contain iron and/or manganese and some hydrogen sulfide. Although some surface waters are clear and practically colorless, most of them contain appreciable amounts of turbidity and/or color.

Turbidity in slow sand filtration practice may often be removed without coagulation but has little or no effect in reducing color. In rapid sand filter practice, both turbidity and color are removed by coagulation, settling, and filtration. If the raw water contains large amounts of coarse sediment, then sedimentation may precede these steps.

Sedimentation is effected without the aid of a coagulant, whereas *settling*

refers to the settling of a coagulated water. If raw water contains large amounts of suspended solids, an appreciable percentage of which is coarse enough to be easily removed by sedimentation, then sedimentation preceding coagulation, settling, and filtration may be worthwhile. Impounding of surface water supplies is quite common, and the reservoir formed usually accomplishes a satisfactory degree of sedimentation. Sedimentation basins, with detention periods measured in hours instead of in weeks, months, or even years, may be used if the raw water has a high content of relatively coarse sediment.

Coagulation and Settling

The most widely used coagulant in municipal filtration plants is aluminum sulfate, which is also commonly known as filter alum. The formula is generally given as $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, but the commercial product usually has a lower water content—about 13 or 14 moles instead of 18 moles. It is also available in solution and is shipped in tank cars or tank trucks. Other coagulants used in municipal filtration plants are ferric sulfate, chlorinated copperas (ferrous sulfate), and sodium aluminate.

In raw waters which are high in color and low in turbidity and dissolved mineral matter, a coagulant aid, such as clay, activated silica, or one of the polyelectrolyte coagulant aids may be required. When clay is used, it should be from a tested source, because different clays vary widely in their properties as a coagulant aid. Activated silica is made from sodium silicate by several different processes.

Coagulation and settling may be carried out in various designs of settling basins, tanks and floc-formers, but the suspended solids contact or sludge blanket units have been widely used. In these, coagulation and the development of the floc are carried out while the water is flowing downwardly through an inner section. It then rises and filters upwardly through a suspended blanket of previously formed precipitates in an outer section. Emerging from the upper surface of the blanket, it flows upwardly to the drawoffs from which it passes to the rapid sand filters, which may be divided into two main types: gravity-type and pressure-type filters. Gravity-type rapid sand filters are used in filtering municipal water supplies. The filtration rate is usually 2 gpm/ft² of 2.5–3.0 gpm, but higher rates have been employed. In industrial practice, the standard rate of 3.0 gpm/ft² is used. For the removal of iron and/or manganese from ground waters, pressure-type rapid sand filters can be employed.

The shells of the gravity type rapid sand filters may be made of either concrete or steel. Concrete shells are usually rectangular in shape; the smaller sizes of units are square and the larger ones are oblong. When steel shells are employed, they are cylindrical in shape. Filter medium may be sand or may be crushed and graded anthracite. If the filter medium is sand, the supporting layers under the fine filter sand are coarse sand and several layers of graded gravel. If

the filter medium is anthracite, then the supporting layers may be either graded anthracite or coarse anthracite and graded gravel.

During filtration, the accumulations of strained out material gradually clog the filter bed and build up an increasing resistance to the flow of water through it. When this reaches a pressure drop ranging from about 8–12 feet loss of head in different gravity type filters, the automatic valveless gravity-type rapid sand filters use a 4–5 feet loss of head, the filter unit is taken out of service, cleaned by backwashing, filtered to waste for a few minutes, and then returned to service. Backwash rates for gravity-type sand filters are usually 20 gpm/ft² if not equipped with surface washers and 15 gpm/ft² if equipped with surface washers. Backwash rates for gravity type anthracite filters are usually 15 gpm/ft² if not equipped with surface washers and 12 gpm/ft² if equipped with surface washers. Gravity filters are usually installed in batteries of two or more units.

A separate rate of flow controller is usually employed with each filter unit so as to maintain a uniform rate of flow in spite of the variations in back pressure which occur during the filtration run. For backwashing, usually only one wash rate of flow controller, installed in a common backwash leader, is required, since only one filter unit is backwashed at a time.

Pressure-type rapid sand filters are vertical and horizontal. Vertical pressure filters range in size from 30 to 120 inches in diameter with flow rates of 10–250 gpm per unit at 3 gpm/ft². Horizontal filters are typically 8 feet in diameter and from 10 feet 6 inches to 25 feet in length with capacities ranging from 200 to 510 gpm at 3 gpm/ft². Backwash rates are usually 10 gpm/ft².

In municipal practice, pressure-type filters are used mostly in connection with the treatment of ground waters such as in the removal of iron or manganese from aerated and settled iron-bearing and/or manganese-bearing waters. In industrial applications, pressure-type filters are also employed. In operation, the filter run is continued until the pressure loss rises to some 5–8 psi, when the filter is cut out of service, backwashed, filtered to waste for a few minutes, and then returned to service.

Other filter media employed for special uses include neutralizing filters that have crushed and graded calcite as the filter media for industrial uses to neutralize an aggressive water and automatically raise the pH value to 7.2–7.3 or to stabilize a treated water. Activated carbon filters using granular activated carbon as the filter medium are used for taste and odor removal, chiefly for industrial uses but also to a limited extent for removing tastes and odors from relatively small municipal water supplies. Manganese zeolite filters use granular manganese zeolite as the filter medium and are used both in industrial and municipal practice for removing small amounts (1 ppm or less) of iron and/or manganese from waters containing them as the soluble, divalent bicarbonates.

Disinfection

Disinfection may be accomplished by the use of

- Chlorine
- Chlorine dioxide
- Chloramides
- Hypochlorites
- Ozone

Chlorine, the most widely used disinfectant, is a very strong oxidizing agent. It is available as the liquefied gas in pressure cylinders holding 100, 150, or 2000 lb. It may be applied before other forms of treatment (prechlorination) and/or after other forms of treatment (postchlorination). It may be applied at one or more points in the distribution system (rechlorination).

Chlorine dioxide is a very strong oxidizing agent which, in municipal practice, is made in solution by reacting chlorine with sodium chlorite. It is used for oxidizing disagreeable taste- and odor-producing organic matter as well as for its disinfectant action.

Chloramines are made by the reaction of chlorine with ammonia. The chloramines are not as strong or as rapid oxidizing agents as chlorine or the hypochlorites but are of value in maintaining chlorine residuals.

Hypochlorites are often used in place of liquefied chlorine in treating small water supplies. They are available as "bleaching powder," which is equivalent in oxidizing power to 35% of chlorine or as high-test hypochlorites equivalent to 70% of chlorine.

Ozone is an unstable allotropic form of oxygen made by passing a high-voltage silent electric discharge through a stream of air. It is of value in oxidizing taste- and odor-producing organic matter and has a high bactericidal action but decomposes so rapidly that no residual oxidizing action can be maintained.

Taste and Odor Removal

Objectionable tastes and odors in water are usually due to various organic compounds, except the rotten egg odor of sulfur waters which is due to hydrogen sulfide). As these compounds vary greatly in composition and character in different waters and also from time to time in the same water, it is advisable to make preliminary tests to find the best method of removal.

Many of these compounds have a certain degree of volatility, so that aeration is often of value as a preliminary step. Chlorination may remove some of the odors but with others may intensify them, whereas heavier dosages or the use of chlorine dioxide or ozone may completely remove them. Activated carbon is an excellent taste and odor removal agent. Pulverized activated carbon has been with longer and more intimate contact.