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ABOUT WATER TREATMENT

About water treatment

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Content

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Foreword

Humans have always relied on water. Nowadays, more and more often, it is water that relies on humans. Over the past century, our experts have worked together with partners to address major water treatment challenges and found sustainable solutions to major industrial and societal problems.

Safe, sustainable chemistries are a part of good life – they play a key role in our everyday: ensuring hygiene, safe water, medical supplies, food safety and more. They enable us to utilize scarce resources more efficiently. Chemistry is the high-tech of resource efficiency. Without chemicals, the current level of safe water supply and sustainable wastewater treatment in urban areas cannot be maintained.

The world's future challenges are huge, but we know, from experience, that they can be overcome with science, ingenuity and collaboration.

This Water Handbook describes the methods and processes of water treatment that allow water to be returned to its natural ecological cycle and permit a sustainable society. Happy reading!

Why do we need clean water?

Access to clean, safe water is essential for all life on Earth. The human body contains around 55–60% water, and water is part of every aspect of our lives. We need water to stay alive and hydrated, but we are also dependent on it to grow crops and for the production of goods, to name but a few uses. The availability of clean and safe water has played and will continue to play a major role in the development of healthy, thriving societies.

Water covers 71% of the Earth's surface, and the total volume of water on our planet is estimated at 1,386 million km^3. This might make you think that water is plentiful on our so-called blue planet, but in reality we only have access to a small fraction of this colossal volume. This is because just 2.5% of it is fresh water of which 1.7% is locked up in glaciers and ice caps; the remaining 97.5% is made up of salt water. Of the 0.8% that is available in rivers, lakes, and aquifers, we must share this with the rest of our biosphere. We use water in many different ways: only 7% of available freshwater (or 0.06% of the total water volume on Earth) is used for domestic purposes, whereas 70% is used by agriculture, and 23% by industry. The availability of water is unevenly distributed across the continents, and to make the problem worse, a growing population and increasing income levels create additional water stress, especially in densely populated areas such as cities.

The water on our planet is purified and recirculated in a gigantic solar-powered water cycle. Evaporation transfers water to the atmosphere and it is returned to the soil as condensation and precipitation. This distillation process regulates the temperature on Earth, cooling the soil and the seas and warming the atmosphere. Population growth, urbanization, and the increase in water consumption mean that the natural water cycle can no longer manage water pollution by itself. A network of water-treatment facilities should be incorporated in the human water cycle (Fig. 1:1). According to some studies, the volume of wastewater produced annually from human activity is 380 billion m^3, and this figure is expected to increase by about 25% by 2030 and 50% by 2050. More than 80% of the wastewater produced globally is discharged back into rivers and seas without any treatment, causing a vast environmental problem. In addition, problems such as extensive pesticide and fertilizer use, unauthorized landfilling and illegal dumping, air pollution, and spills from industrial activities lead to further contamination of water bodies. This presents a serious threat to biodiversity and the survival of many aquatic and terrestrial species, and perhaps even the irreparable destruction of whole ecosystems. For us humans, water is becoming increasingly challenging to treat for drinking, recreational, agricultural, and industrial use.

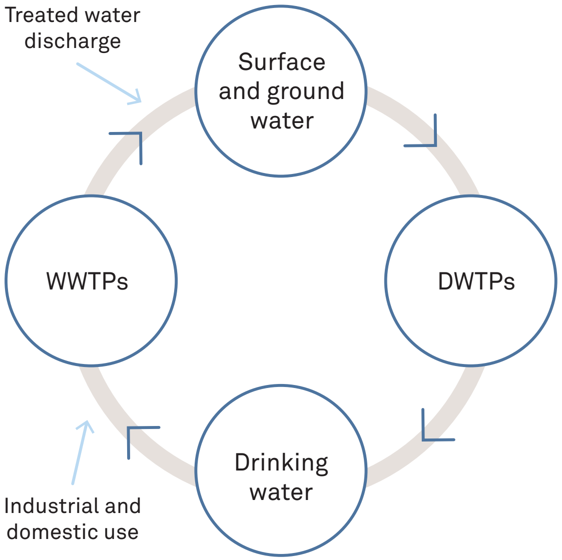


Figure 1.1
The human water cycle (DWTPs – drinking water treatment plants, WWTPs – wastewater treatment plants).

The World Health Organization (WHO) estimates that 80% of all diseases are waterborne. Over one billion people lack access to safe drinking water and four billion people encounter water scarcity throughout the year; along with poor hygiene and sanitation this causes 1.8 million deaths every year. The devastating man-made and natural disasters we have experienced during recent decades, increasing scarcity of natural resources, and other challenges have raised global environmental and social awareness. In 2016, the world's governments came together under the banner of the United Nations (UN) to agree on the kind of world that we must work together to create. This vision of sustainable societies living and prospering in balance with the natural environment was codified in the **UN Sustainable Development Goals (SDGs)**. These 17 goals for 2030 (Fig. 1.2) are shared by all countries, civic groups, and businesses, helping to ensure that individual efforts are complementary.

Two out of the 17 goals are directly related to water quality and life. The first of these is SDG 6, "Clean water and sanitation", which aims to provide safe access to drinking water and equitable sanitation for everyone by 2030, as well as to increase water-use efficacy in all sectors and restore water-related ecosystems. The goal also aims to decrease or eliminate the discharge of pollutants into water bodies and increase water recycling and reuse globally. The second goal related to water is SDG 14, "Life below water", which among other things is targeted at the reduction of marine pollution and the sustainable use of coastal and marine ecosystems. Although only two of the 17 SDGs include quality of water as their main target, there is a broad understanding that all the goals are interlinked. For example, improving the quality of education (SDG 4) can change our view of the relative importance of addressing environmental problems. This in turn results in better decision making in everyday life, starting from the rational use of water by individuals and resulting in investments in wastewater treatment by industry and the adoption of environmental legislation by governments. Similarly, improving the energy efficiency of existing processes and shifting to renewable energy (SDG 7) helps to reduce CO_2 emissions, mitigate climate change, and decrease the acidification of our oceans.

Companies that provide water-treatment solutions play a critical role in rebalancing the water cycle. Working across academia, industry, municipalities, and drinking and wastewater treatment plants, we can reduce the strain on life below water, life on land, and societies. Choosing the right solutions can also have related benefits such as reductions in energy consumption, greenhouse gas emissions, and the extraction of virgin raw materials. In other words, there is a tremendous opportunity to address many of the SDGs through the responsible use, management, and treatment of water.

Clean water and personal hygiene are essential for maintaining good health. In order to ensure a hygienically acceptable supply of water to consumers, water should be treated at drinking water treatment plants (DWTPs); seawater can also be used as drinking water after desalination. More information on sources of fresh water and drinking water treatment techniques can be found in chapter 2 of this handbook. More and more DWTPs and other water-reliant industries have started to integrate the UN SDGs into their strategies

Figure 1.2
The 2030 Agenda for Sustainable Development. UN Sustainable Development Goals.

and operations. Figure 1.3 shows the main SDGs that the water sector works with. The core SDGs for water industries are 6, 7, 11, 13, and 17. At the same time, DWTPs have an important contribution to make to SDG 2, 3, 14, 15, and 16.

The production of **drinking water** is a technical process governed by strict standards. Drinking water is consumed by households but also required for the production of food and beverages, pharmaceuticals, pulp and paper, and other essential products. Moreover, many applications other than domestic use often require a higher degree of water purity and additional treatment stages compared to drinking water production. For example, water for electricity and steam production must be deionized to avoid the precipitation of minerals in boilers and other related equipment. Clean water quality is controlled both locally and globally, with countries either adopting their own water-quality standards or borrowing standards from other countries. For example, the WHO provides guidelines for drinking-water quality, in Europe drinking water quality is regulated inter alia by the European Drinking Water Directive, and the USA has e.g. the Safe Drinking Water Act as a quality standard. The International Organization for Standardization (ISO) provides standards and guidelines for water used in different industries.

The amount of drinking water produced by drinking water treatment plants varies between countries. For example, the USA produces an average of 200 m^3 of water per person per year, whereas in Europe the figure is approximately 90 m^3. The water produced must also meet requirements that ensures its suitability as drinking water even though only a small percentage is used for food and drink.

Domestic and industrial waters become contaminated with a wide variety of pollutants when they are used. More detailed information on the type of pollutants in fresh water sources and **wastewater** from various industries are discussed in this handbook, as well as wastewater treatment technologies. Municipal

Figure 1.3
The core UN SDGs for the water sector

wastewaters are collected by the sewer network and transported to **wastewater treatment plants (WWTPs)** where they undergo treatment to achieve regulatory discharge limits before being released back to water bodies. Wastewater is a mixture of household and industrial effluent, rainwater, and meltwater from snow and ice. High volumes of industrial wastewater are usually treated at the source of production before being discharged into water bodies or the municipal sewer network. Increased water stress caused by pollution, drought, floods, and other factors make it harder and more costly to produce raw water that is of sufficiently high quality for industries. More and more companies are beginning to incorporate circular economy principles into their operations, increasing the importance of recycled raw materials, water recycling and reuse. They are also increasingly implementing zero-liquid discharge (ZLD) technologies in production cycles to allow complete water recovery and separation of contaminants from water into solid forms. Depending on the production process, ZLD technologies may include membrane water treatment methods, crystallization, evaporation, advanced oxidation processes (AOPs), and adsorption.

In general, **water treatment methods** can be separated into physical, biological, chemical, and physico-chemical methods. Physical methods are separation of solid impurities and coarse and fine particles from water using techniques such as screening, filtration, centrifugation, flotation, and membrane technologies. Biological methods are based on microorganisms that consume the pollutants in the water in order to maintain their vital activity. Chemical treatment implies conducting chemical reactions with pollutants – for example oxidation, reduction, or precipitation – to achieve the desired effect. Physico-chemical water treatment combines both chemical and physical treatment, for example chemical coagulation and flocculation followed by a separation step.

Coagulation is the process of destabilizing colloidal particles and then agglomerating them via charge neutralization. In turn, flocculation is the process of agglomerating destabilized particles into bigger flocs. The fastest way to coagulate and flocculate colloidal contaminants in water is to add coagulants and flocculants. The most commonly used coagulants are aluminum and iron salts, while flocculants are usually organic water-soluble polymers. Even though chemical treatment may sound like an unsavoury term, it is a well-established, safe, and non-selective process suitable for removing a wide variety of contaminants. Moreover, chemical and biological treatment are cost-efficient compared to other methods. Chapter 5 of this handbook describes in detail the phenomena that characterize the coagulation and flocculation process.

During chemical and biological treatment, contaminants are transferred from a dissolved and suspended state into aggregated solid particles which are then removed from the water by sedimentation, thus generating **sludge**, a mixture of water and solids. For years municipal sludge was mainly disposed of in landfill, but today it is considered a valuable asset. After several treatment steps (see chapter 4), sludge can become a fertilizer, a source of energy in the form of biogas, or a source of nutrients such as phosphorus (see chapter 6).

Water and sludge treatment are complex processes that benefit from optimization. For example, the environmental impact of these processes can be optimized with the help of **life cycle assessment (LCA)**. LCA helps to identify how, for example, energy and raw material consumption can be reduced or where recycled material could be used in place of virgin raw materials. Efficient use of water treatment chemicals is another essential part of process optimization. Smart process management (see chapter 7) using real-time data to continuously adjust chemical dosing supports improved process efficiency and compliance with regulations; it also enables major cost savings. Modern digital technologies can also be used to avoid overdosing of chemicals, thereby contributing to more responsible consumption and production.

Taking care of the water cycle is crucial for the well-being of society and the sustainable development of our planet.

CHAPTER 2

DRINKING WATER TREATMENT

Drinking water treatment

Most people living in the EU enjoy very good access to high-quality drinking water thanks to a long tradition of drinking water management in many member states. The main sources of fresh water used for drinking water production are surface water and groundwater, but seawater can also be used as a source of raw water if it is desalinated. The share of surface water and ground water used for drinking water production varies widely from country to country. According to the Food and Agriculture Organization of the United Nations (FASO), groundwater is a source of drinking water for about 50% of the global population. In most cases fresh water sources are contaminated with various pollutants, and therefore the raw water requires treatment before it is made available to end users. A variety of treatment methods must be applied depending on the levels of undesirable substances in the raw water and the limits set for water purity.

The priority for the water supplier is to distribute water that meets the requirements set by the authorities, which are based on health considerations. Drinking water must be free of harmful bacteria and viruses, toxic inorganic metals, and organic compounds such as pesticides. The aesthetic characteristics of the water must also be considered, and it must therefore meet certain requirements regarding color, turbidity, odor, taste, and so on.

Extensive knowledge gained in the field of water treatment technologies over the past decades, modern equipment, and various chemical products available on the market today provide excellent opportunities to produce drinking water that satisfies both stringent regulatory requirements and the demands of consumers, even with poor-quality raw water.

Groundwater as a source of raw water

Groundwater forms as a result of water infiltrating the ground and is often the best source of raw water since it is naturally filtered. It collects in aquifers, which are water-bearing permeable rocks like sand, pebbles, and silt, that lie on an impermeable bed consisting of clay, granite, or other rock. Groundwater can be naturally or artificially recharged; for example, in Finland (2018) the water source share was 30% surface water, 43% natural ground water, and 19% artificially recharged groundwater. In densely populated and arid areas groundwater sources are depleted due to the extensive pumping of water. In such areas, either surface water must be used as a supplementary source of raw water, or artificially recharging the groundwater should be considered. There are several ways to artificially recharge aquifers:

- by redirecting surface water, partially treated wastewater, stormwater runoff, or irrigation return flow into the soil through canals across the land surface, infiltration basins, or ponds
- adding irrigation systems, or
- injecting water directly into the aquifer.

As the water passes through high and low permeability rocks it is filtered and purified, reducing its turbidity, odor, and color, as well as levels of humic substances and other contaminants. The concentrations of bacteria, viruses, and single-cell organisms (protozoa) also decrease.

Water dissolves minerals that contain metals such as magnesium, calcium, sodium, iron, and manganese. Concentrations of sulfates, chlorides, and carbonates also contribute to the characteristic composition of groundwater.

Groundwater can in some cases meet acceptable quality standards without any special treatment. In order to protect distribution piping it may be necessary to make the water alkaline and limit the bacteria content by disinfecting it. Alkalization and disinfection are therefore the final stages in most waterworks.

For cases where groundwater requires more extensive treatment, table 3.1 shows the most common undesirable substances, their negative effects, and how they are neutralized or removed.

Life on Earth began in the water around 3000 million years ago. Today, everything living on the planet needs water to survive.

“When you drink water, think of its source.”
Chinese proverb

Table 3.1
Undesirable substances in groundwater and possible treatment methods.

Undesirable substance	Treatment method
Carbon dioxide (CO_2) (dissolved) • causes corrosion in piping	• Add chemicals to increase alkalinity • Filter through alkaline material to increase alkalinity • Aeration
Iron (Fe^{2+}) and manganese (Mn^{2+}) • causes turbidity, odor, and bad taste • leaves deposits/sludge in piping	• Oxidation by aeration; addition of chlorine, potassium permanganate, or ozone followed by filtration • Ion exchange
High hardness (Ca^{2+}, Mg^{2+}) • causes deposits	• Precipitation with lime or other alkali • Membrane technologies • Ion exchange using cationic exchange unit
Nitrate (NO_3^-) and nitrite (NO_2^-) • impairs blood's oxygen uptake	• Ion exchange using anionic exchange unit • Biological treatment • Membrane technologies
Fluoride (F^-) • discolors teeth	• Adsorption • Precipitation coagulation with aluminum sulfate or lime • Ion exchange using anionic exchange unit • Membrane technologies
Pesticides or micropollutants	• Adsorption by activated carbon • Oxidation by UV, ozone, hydrogen peroxide, and others • Membrane technologies • Coagulation/sedimentation • Sand filtration

Surface water as a source of raw water

Surface water is divided into flowing water sources such as rivers and artificial canals, and standing or slow-moving bodies of water, including lakes, reservoirs, and ponds. Lakes are important because of their ability to store water. Water makes a good solvent, which also means it is easily contaminated and consequently rarely clean enough to use without prior treatment. In the European Union the chemical status of surface-water bodies is carefully monitored, with more detailed water quality and water assessment data available from the European Environmental Agency web pages (EEA 2018 water assessment).

Contamination is caused partly by nature and partly by anthropogenic activity, and contaminants can be either soluble or suspended solids. Suspended solids are often defined as the weight of material retained on a filter with a pore size of 1-3 µm when filtering 1 liter of water.

The most common contaminants in surface waters are detailed below.

Mineral particles are natural contaminants such as sand and clay and they make up a large proportion of suspended solids. Mineral particles make the water turbid. Turbidity can be expressed in Formazin Turbidity Units (FTU) or Nephelometric Turbidity Units (NTU); these units are directly comparable, i.e. 1 FTU = 1 NTU. The charge of many inorganic particles in natural waters is controlled by an adsorbed layer of natural organic matter (NOM) and by the salinity and concentration of divalent cations in the water. Suspended solid particles have a substantial organic and biological content of typically 1–20% and therefore have a negative surface charge – this is despite the fact that they could have had a net positive charge before being coated in organic material. During water treatment this organic coating can have a strong impact on the amount of coagulant needed and the rate of coagulation.

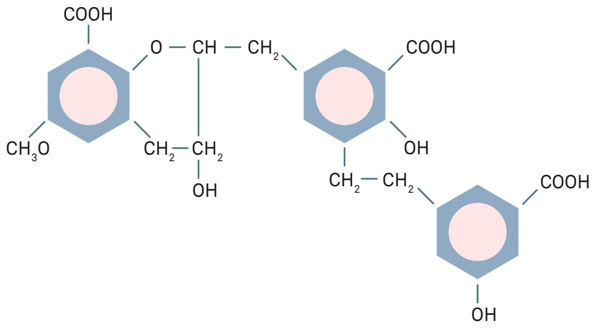
Organic contaminants may be natural in origin or may be waste products from society. Humic acids give water a yellow to golden-brown color and can give water an undesirable odor and taste; they are also precursors for disinfection by-products. These acids are formed when trees, bushes, and leaves decompose. They have aromatic character and contain carboxylic, phenolic, ketone, and methoxy groups; they absorb UV light.

Humic acids precipitate at pH levels below 2 and have a higher molecular weight (1000–10000 g/mol) than fulvic acids (500–2000 g/mol), which are soluble at all pH levels.

Fulvic acids are more prevalent in waters than humic acids: river waters often contain more than eight times more fulvic acids than humic acids. While both types of acid can be precipitated and removed using metal salts, humic acids require less salt to precipitate than fulvic acids, which have a higher negative charge.

Figure 3.2

Possible structure of a fulvic acid.



Of the total amount of organic carbon in surface waters:

- 5–10% derives from proteinaceous compounds
- 10–20% is present as polysaccharides, and
- the remainder is present as humic or fulvic acids

The concentration of organic contaminants is analyzed by measuring the Chemical Oxygen Demand (COD_{Mn}) which is expressed in mg O_2/l. In older standards the concentration of organic contaminants is expressed as a “permanganate value” or in mg $KMnO_4$/l, where 1 mg COD_{Mn}/l is equivalent to about 4 mg $KMnO_4$/l.

Another method is to determine the concentration of Total Organic Carbon (TOC), which is known as a TOC analysis. TOC is usually calculated as the difference between the total amount of carbon (TC) and inorganic carbon (IC). Organic carbon is present in the form of particles and dissolved substances. When water is filtered its dissolved organic carbon (DOC) can be measured; filters with a pore size of around 0.45 µm are typically used for measuring DOC. The absolute major part of the TOC in natural waters is present as DOC.

Chromatographic methods like LC-OCD depict not only the concentration of organic carbon (TOC or DOC) but also the molecular weight distribution (e.g. biopolymers – humic/fulvic substances – neutrals) and share of these species.

Specific UV absorbance (SUVA) is a way to identify the nature of organics in water. Both fulvic and humic acids have a negative charge at typically occurring pHs and contain aromatic groups that absorb UV light with a wavelength of 254 nm. By taking the ratio of UV absorbance at 254 nm expressed as per meter of absorbance divided by the DOC concentration in mg/l, you get the SUVA of the water.

SUVA = (UV_{254}-absorbance/meter)/(mg DOC/l). Humic acids have SUVA values of 5 to 7.5 and fulvic acids of about 4 to 5. Higher SUVA value water contains more humic acids and more of its DOC content can be precipitated.

Table 3.3
Nature of NOM and expected DOC removal for waters with different SUVA values

SUVA	Composition	Usual DOC removal
<2	Mostly non-humic and non-fulvic substances	<25% with aluminum sulfate
2–4	Mixture of aquatic humic and fulvic substances, and other NOM; mixture of molecular weights	25–50% with aluminum sulfate
>4	Mostly aquatic high-molecular-weight humic substances	>50% with aluminum sulfate; 70% removal is possible

Table 3.3 illustrates the nature of NOM and DOC removals expected by alum when treating waters with different SUVA values.

As a result of more advanced analytical methods in recent years, we have become aware of a growing number of organic environmental toxins that biodegrade very slowly, such as polychlorinated biphenyls (PCBs), pesticides, and phenolic compounds, as well as halogenated organic compounds that can be formed during disinfection.

Microorganisms such as bacteria, viruses, parasites, and amoebae are measured in number/ml. They are so small that they are only visible under a microscope, since the smallest particle size visible with the naked eye is about 40 µm (=0.04 mm).

Bacteria are single-celled organisms between 0.2 and 35 µm in size; the most common size range is 0.5 to 5 µm. Bacteria are commonly occurring in wastewater. Normally water is analyzed for the presence of coliform bacteria since these indicate whether there is a risk of pathogenic (disease-causing) bacteria and viruses.

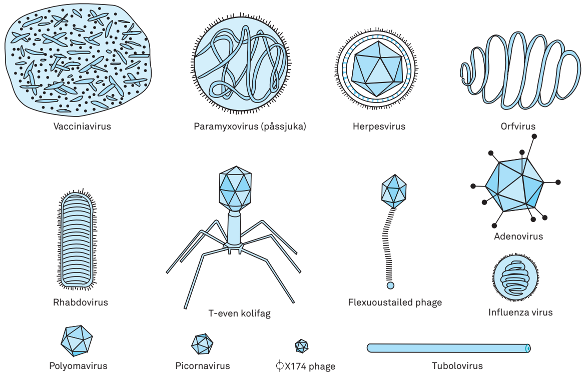
Viruses are considerably smaller than bacteria, with a size of 0.02 to 0.4 µm (20–400 nm). They need living organisms to replicate in.

Protozoa are parasitic single-celled organisms that can cause disease in humans and animals. Some parasite oocysts, e.g. Cryptosporidium, have a spherical shape and a diameter of about 3–7 µm, while Giardia has an oval to spherical shape and measures 5–15 x 8–18 µm.

Lakes are the Earth's water store. Lake water is soft and has a low salt content. Because it often contains algae, humus, and other organic substances that can give it color, odor, and taste, it must be treated prior to distribution.

Figure 3.4

Different types of virus.



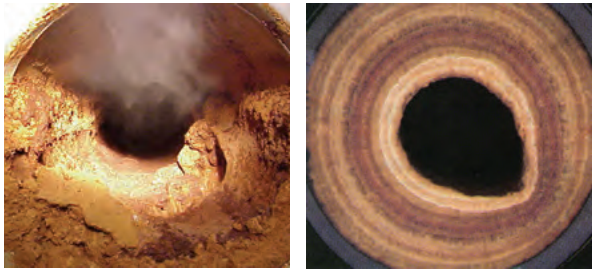
Cryptosporidium and Giardia have been shown to cause serious outbreaks of gastrointestinal infections around the globe and are a major concern in terms of water safety. These parasites are resistant to disinfection with chlorine, and it is important to remove them before water is distributed in order to eliminate the risk of an epidemic.

Chemical precipitation is the treatment method used for the removal of the undesirable substances listed above.

Corrosion is a problem that must be considered during water treatment. Water can behave in a corrosive manner that leads to a reduction in its quality. Depending on the composition of the distribution piping, a variety of substances including copper and iron can be dissolved in and contaminate the water. For example, the presence of DOC can interfere with the oxidation of dissolved iron and manganese and can lead to the corrosion of copper pipes.

During water treatment it is important to produce water of a quality that minimizes corrosion problems. There are several factors that affect corrosion: pH, alkalinity, calcium concentration, presence of disinfectants, and concentrations of inorganic salts and organic compounds. There are three main parameters that influence corrosion and which must be controlled: pH, alkalinity, and calcium concentration. Plastic piping is not affected by pH and alkalinity, but bacterial growth can occur in plastic distribution pipes due to biological film growth inside the pipes.

Different countries have drawn up different recommendations in order to produce potable water with the minimum acceptable corrosion risk (see table 3.5). There are large variations between these recommendations, and it is probable that the prevailing water chemistry in each country has influenced the values.



Depending on the composition of the distribution piping, a variety of substances including copper and iron can be dissolved in and contaminate the water.

Table 3.5

Acceptable water values from a corrosion viewpoint – recommendations from different countries.

Ref. 1: VA-Forsk Rapport 2000-12 "Dricksvatten och korrosion – en handbok för vattenverken" (Drinking water and corrosion – a handbook for waterworks)

	pH	**Alkalinity, mg HCO_3^-/l**	**Calcium, mg/l**	**Chloride, mg/l**	**Sulfate, mg/l**	**COD_{Mn}, mg O_2/l**
Sweden	7.5–9	≥60	20–60	≤100	≤100	≤2
Norway	7.5–8.5	36–60	15–25	≤25	≤25	≤2
Denmark	7–8	≥100	20–200	≤50	≤50	≤1.5
Finland	7.5–8.8	≥36	≤100	≤25	≤50	≤2
Holland	7.8–8.3	≥120	≤150	≤150	≤100	
Germany	6.5–9.5		≤400	≤250	≤250	≤5
England	5.5–9.5	≥30	≥60	≤400	≤250	
USA	6.5–8.5			≤250	≤250	
EU	6.5–9.5					<5

Chemical treatment of surface water

The chemical treatment of surface water may follow the path outlined in figure 3.6. Several process stages may be added or removed, depending on the quality of the raw water.

- **Mechanical separation**, designed to remove larger contaminants.

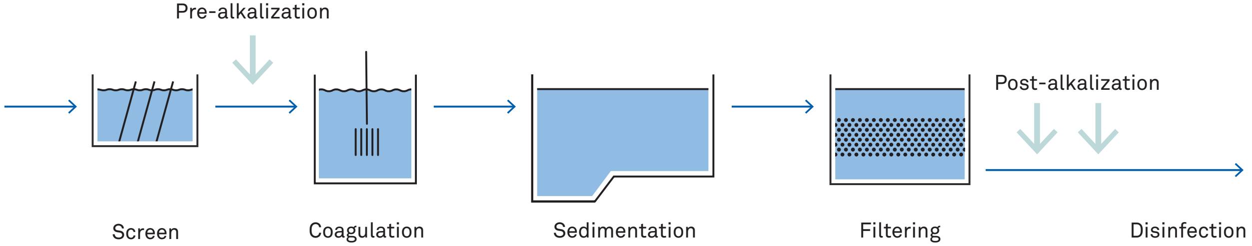
- **Pre-alkalization**, designed to establish the optimum pH for the precipitation process. This stage is omitted in some waterworks, potentially making optimum conditions more difficult to achieve in the chemical flocking stage. However, this can be compensated for to some extent through the choice of coagulant.

- During coagulation in the **chemical coagulation stage**, aluminum salts and polyaluminum salts or iron (III) salts are used as coagulants.

Drinking water treatment plants (DWTPs) sometimes enhance coagulation with, for example, activated silicic acid (water glass) and polyelectrolytes.

- During the **separation stage** the flocs are separated from the treated water by sedimentation or flotation. Most of the precipitated contaminants are removed at this stage.

Figure 3.6
Chemical treatment of surface water.



During sedimentation the flocs are separated by allowing them to settle to the bottom of a sedimentation basin. This happens because the flocs have a higher density than water and therefore tend to sink. The normal surface load in a sedimentation basin is around 0.5 m/h.

Surface load (m/h) = flow (m^3/h)/surface area (m^2)

During flotation, air bubbles become attached to the floc, which then floats up and creates a sludge layer on the surface. Air is dissolved in water at high pressure to create what is known as dispersion water. When the pressure is reduced to atmospheric pressure, microscopic air bubbles are formed that stick to the flocs. This gives them a buoyancy that exceeds the sedimentation forces, so they rise to the surface. A flotation plant can be made more compact since the surface load in a flotation basin can be around 5–10 m/h. The sludge from a flotation plant often has a higher dry solids content than that from a sedimentation plant.

In a **direct filtration process** a coagulant is added just before the raw water reaches the filter. Floc formation takes place in the filter bed, where the flocs are also separated. The coagulation time is considerably shorter (a few minutes) than with conventional coagulation (20–60 minutes). It is preferable to use a coagulant that forms flocs quickly, such as polyaluminum chloride.

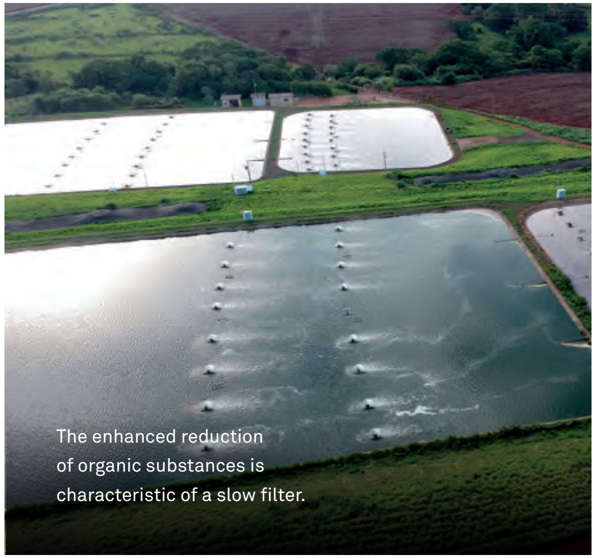

Flocs in a flocculation chamber

- The **rapid sand filter** separates the remaining flocs, i.e. those flocs that were not trapped during the separation stage. A rapid filter has a filtration rate of 5–20 m/h.
- Post-alkalization and **disinfection** are designed to protect the distribution piping from corrosion and prevent bacterial growth respectively.

The process can also be effectively supplemented with slow **filtration**, **infiltration**,or **activated carbon**.

Slow filtration depends on the formation of a biologically active layer that breaks down the remaining organic substances. This reduces the color of the water and the chemical oxygen demand, while also reducing its taste and odor. A slow filter has a filtration rate of <0.4 m/h.

Infiltration involves passing the surface water very slowly (over a period of days or months) through layers of sand and soil. This leads to the separation of suspended solids and the breakdown of organic substances. The water is then pumped back up through the bed. The water quality



The enhanced reduction of organic substances is characteristic of a slow filter.

is similar to that of groundwater, i.e. it has a low uniform temperature and reduced odor and taste, as well as a low concentration of organic substances. The water should be treated prior to infiltration in order to reduce the concentration of suspended and organic matter. In some cases, chemical precipitation is carried out as a preliminary stage before the water goes to the infiltration stage. This is done to prevent this area from being clogged by particulate contaminants and to ensure there is sufficient oxygen to break down organic matter in the filter bed.

If there is a shortage of oxygen in the filter bed, there is a risk of hydrogen sulfide formation and elevated levels of iron and manganese. A reduction in COD_{Mn} of around 80% is achieved after the infiltration treatment stage.

The advantages of infiltration are that the technique is relatively inexpensive and requires only small amounts of chemicals. The filtration rate of an infiltration bed is around 0.1–0.2 m/h.

Water can also be treated with activated carbon if odor and taste are serious problems; this treatment can also remove toxins from the water. The carbon can be added in powder form (PAC, Powdered Activated Carbon) at the time of precipitation, or alternatively the water can be passed through a rapid filter containing Granulated Activated Carbon (GAC). In order to remain effective the carbon in the filter must be replaced or reactivated at regular intervals, usually after one to three years. The lower the contaminant load on the filter, the less often it requires reactivation.

Chemical precipitation of surface water

The purpose of chemical precipitation is to encourage humus and particles to coagulate and form flocs that can then be separated. The choice of coagulant is important to achieve the optimum coagulation and sedimentation characteristics. There is a comprehensive selection of coagulants available on the market today with various special characteristics to optimize the precipitation process.

The two main mechanisms involved in chemical precipitation are described below.

- **Charge neutralization**. The net charge on the surface of the particles is negative. When positive aluminum or iron ions are added they neutralize the charge on the particles; this happens very quickly, in just 0.01–1 seconds. For aluminum sulfate the pH of the water should be between 4.2 and 5.2 to provide optimum conditions; for iron-based products the range is somewhat narrower.

- **Sweep coagulation**. In this phase of floc formation, the particles are bound to the resulting metal hydroxide (aluminum or iron hydroxide) and adsorption takes place. This reaction is a little slower than charge neutralization, occurring within 1–7 seconds. The pH should be between 5.5 and 6.5 for aluminum sulfate; for iron-based products the range is somewhat wider at around 5.5 to 8.

More information on coagulation is provided in the following chapters.

The reaction that takes place in the coagulation process is mainly sweep coagulation, partly because it is often difficult to achieve the rapid and thorough mixing that is required for charge neutralization, and partly because the pH during the precipitation stage is usually in the range of 5.5 to 7.5.

Optimal pH is individual for different coagulants and is best to be determined experimentally. Often, if the target is to maximize the removal of humic substances with iron (III) coagulants, then the optimal pH is 4.5–5.5. If aluminum is used in surface water treatment, the optimal pH is clearly higher at around 6.5–7.5. If the pH is too low, there may be too much residual water-soluble aluminum in the water after treatment.

Disinfection

An essential part of drinking-water quality is to ensure safe and secure water that is free from harmful microorganisms. This has been traditionally guaranteed by monitoring the number of indicator bacteria when the drinking water enters distribution. Current risk-management plans offer improved protection and an emphasis on prevention through good management practice, including a systematic approach to managing the quality of drinking water at all stages from source to tap. This provides the transparency needed to increase trust and confidence in water supplies. General reading and more detailed information is available, for example in The Environmental Protection Agency (EPA) publication, Water Treatment Manual: Disinfection (2011).

The EPA manual highlights that microbial threats to drinking water supplies arise from possible contamination by harmful microorganisms in human and animal excrement. Typically, these microorganisms are classified as bacteria, viruses, protozoa, and helminths (i.e. parasitic worms). Primary disinfection and maintaining a disinfectant residual (secondary disinfection) in distribution systems can be categorized as follows:

Chemical disinfection technologies

- Chlorine or hypochlorous acid – widely used both for primary disinfection and to maintain a residual in distribution systems. Limitations related to chlorination are by-products and taste or odor issues.
- Chlorine dioxide – a more powerful oxidant than chlorine; in its pure form chlorine dioxide does not form trihalomethanes (THMs) but may have dose-related limitations due to inorganic by-products (chlorate and chlorite).
- Monochloramine – prepared in situ by reacting ammonia and chlorine, a process known as chloramination. This substance does not form THMs but it is not practical as a primary disinfectant.
- Ozone – a powerful oxidant and disinfectant when compared with chlorine or chlorine dioxide, but regarded as more expensive (higher capital and operating costs). Ozone offers the additional benefit of destroying organic micropollutants since oxidants are seldom selective, but is limited by its low residual insufficiency for long-term distribution.
- Hydrogen peroxide and peroxone (hydrogen peroxide and ozone) – while hydrogen peroxide is a strong oxidizing agent it has a relatively poor disinfectant capability, though performance can be improved by combining with ozone.

Non-chemical disinfection technologies

- Ultraviolet radiation (UV) – in general UV is a highly effective primary disinfection method for removing protozoa, bacteria, and most viruses but less effective than chlorine against viruses. A secondary disinfectant (e.g. chloramination) may be needed for long-term distribution.

Synergistic benefits can be achieved by combining different chemical disinfection methods or combining a chemical disinfection system with UV disinfection. These methods can be used separately, e.g. applying ozonation before UV to degrade natural organic matter which absorbs UV, or activating hydrogen peroxide with UV to enhance disinfection performance.

A modern potable water plant that uses surface water as a source will typically have several disinfection steps, also known as disinfection barriers. It is normal to have, for example, ozonation, UV, and monochloramine disinfection steps in one plant.

What happens when coagulants are added?

When an acidic substance such as an acid is added to water it raises the concentration of hydrogen ions (H^+), which causes the pH to drop. If the water contains ions that can neutralize the added hydrogen ions then the pH will not drop as much; ions of this type are common in water and are said to have buffering ability. They include hydrogen carbonates, carbonates, and hydroxides.

One measure of this buffering ability is known as the alkalinity of water, usually expressed as mg HCO_3^-/l or milli-equivalents of acid/l. The ions that make the greatest contribution to the alkalinity of water are hydrogen carbonates and carbonates.

The following reaction takes place during chemical precipitation with aluminum sulfate:

$$Al_2(SO_4)_3 + 6(HCO_3)^- \rightarrow 2Al(OH)_3 + 3SO_4^{2-} + 6CO_2$$

The aluminum sulfate reacts with hydrogen carbonate etc. to form aluminum hydroxide. The equation describes that alkalinity (the hydrogen carbonate concentration) decreases and carbon dioxide increases. Both these changes lead to a reduction in pH. At the same time the water receives an excess of sulfate ions. Special measures must be taken to restore the alkalinity and raise the pH, such as adding lime in the form of limestone or slaked lime.

The highly charged Al in the products is optimized for best performance for the different basicities of polyaluminum chloride (see chapter 5 for an explanation of basicity). Low-to-medium basicity products are excellent at reducing particles while maintaining good phosphorus removal properties. These products have a basicity in the range of 25 to 45% (OH/Al ratio of 0.75 to 1.35) and are effective coagulants for treating both drinking water and wastewater. Kemira's high-basicity polyaluminum chlorides (up to 70%, or an OH/Al ratio of 2.1) have been further optimized for particle removal by controlling the formation of Al species in the products. Additional benefits are reduced sludge production, minimized pH adjustment, improved filter operation, and excellent performance in cold-water applications.

In PAX products the aluminum ions are polymerized and have a higher charge than the individual aluminum ions (Al_3^+) in aluminum sulfate, for example, so the charge on the particles is neutralized more effectively. The equivalent reaction for PAX with an OH/Al ratio of 1.5 (i.e. 1.5 moles of OH^- for each mole of Al^{3+}, or 50% basicity) is as follows:

$$2Al(OH)_{1.5}Cl_{1.5} + 3(HCO_3)^- \rightarrow 2Al(OH)_3 + 3CO_2 + 3Cl^-$$

The reduction in alkalinity is lower and less carbon dioxide is produced when PAX coagulants are used. Table 3.7 shows a comparison of two reactions with PAX and aluminum sulfate coagulants and their contribution to carbon dioxide and counter-ion raise when producing 1 mole of $Al(OH)_3$.

The difference is even greater if we choose a PAX product with a higher basicity, such as a PAX-XL.

The higher the charge a product has, the smaller the reduction in alkalinity compared with a standard product. This reduces or even eliminates the need to add alkali in the form of lime or lye.

Table 3.7
Comparison between the number of moles of aluminum sulfate and PAX needed to produce 1 mole of Al(OH)$_3$..

	Aluminum sulfate	PAX
HCO_3^- required	3	1.5
CO_2 produced	3	1.5
Increase in SO_4^{2-}	1.5	0
Increase in Cl^-	0	1.5

Water hardness

The hardness of water and its interaction with carbon dioxide play a central role in the chemistry of water. Hardness depends primarily on the presence of calcium (Ca) and magnesium (Mg). Theoretically, strontium (Sr) and barium (Ba) also contribute to the hardness of water, but these two elements generally occur in such low concentrations that they can be ignored for practical purposes. Hardness is usually expressed on the German hardness scale as °dH and is defined as follows:

$$1\ °dH = 10\ mg\ CaO/l$$

where the total calcium and magnesium content is calculated as calcium oxide (CaO). Some countries use other definitions.

When coagulants such as salts of aluminum or iron are added to surface water they bind themselves to contaminants such as bacteria, coloring agents, and other substances that cause turbidity, producing potable water that is clean and clear.

Calcium hydroxide – carbon dioxide equilibrium

In its natural state, water contains various amounts of dissolved substances. Lime softening is based on hydrated lime, i.e. the use of calcium hydroxide in water treatment. Softening is used to reduce raw water hardness, alkalinity, silica, and other constituents. The one that has the most important effect on the properties of water is calcium hydrogen carbonate.

Calcium hydrogen carbonate does not exist in solid form, but is found in aqueous solutions in an unstable state, which is governed by the equilibrium reaction:

$$\underset{\substack{\text{calcium}\\ \text{ion}}}{Ca^{2+}} + \underset{\substack{\text{hydrogen}\\ \text{carbonate}\\ \text{ion}}}{2HCO_3^-} \longleftrightarrow \underset{\substack{\text{calcium}\\ \text{carbonate}\\ \text{solid}}}{CaCO_3} + H_2O + \underset{\substack{\text{carbon}\\ \text{dixide}\\ \text{(to air)}}}{CO_2}$$

Calcium carbonate, sometimes known as boiler scale, can be deposited in cooking pots and hot water heaters if calcium carbonate and CO_2 are not in equilibrium.

The favored direction of this equilibrium reaction determines the properties of water in terms of aggressivity (corrosiveness) and lime precipitation. Temperature is also critical to this equilibrium reaction. Water that is in equilibrium at room temperature may precipitate lime when it is heated.

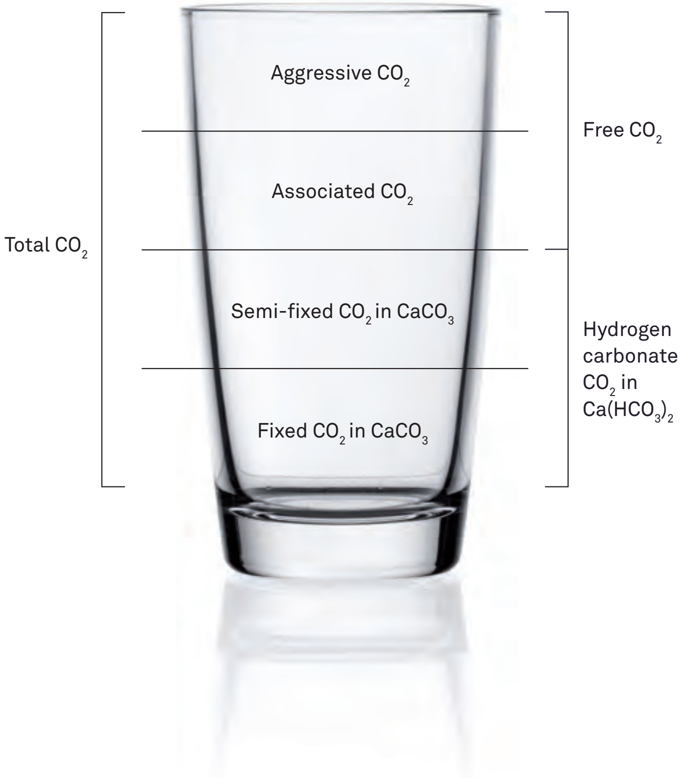
To prevent the precipitation of $CaCO_3$ the water must have a certain concentration of free CO_2, usually referred to as associated CO_2. If the water contains a higher concentration of free CO_2 than is required to keep calcium and hydrogen carbonate in solution then the excess concentration is referred to as aggressive CO_2, which makes the water corrosive. If the water contains a lower concentration of free CO_2 than associated CO_2 then $CaCO_3$ will precipitate, which can cause blockages in distribution piping and deposits on heated surfaces (boiler scale).

The total concentration of carbon dioxide in water can be divided into two main components: free carbon dioxide as described above and hydrogen carbonate carbon dioxide (bicarbonate carbon dioxide).

In the past, the hydrogen carbonate carbon dioxide was further divided to distinguish between the CO_2 that is dissolved in water in the form of hydrogen carbonate (semi-fixed CO_2) and the carbon dioxide that originally came from the calcium carbonate that dissolved to form hydrogen carbonate (fixed CO_2).

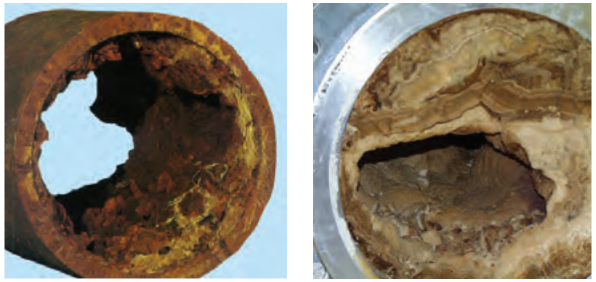
The various states of CO_2 in water are shown in figure 3.8.

Figure 3.8
The various states of carbon dioxide in water.



Calculating the precise theoretical equilibrium state is difficult since the required equilibrium constants, dissociation constants, and solubility products all depend on the temperature and total concentrations of other ions in the water. This means, for example, that water that is in equilibrium at the DWTPs could later precipitate calcium carbonate on a warm surface such as a heat exchanger.

Various attempts have been made to simplify these calculations graphically. Of the many diagrams that can be found in the literature it is worth mentioning Tillman's curve, Langelier's diagram, and Hoover's nomogram, which are among the most commonly used (Figure 3.9 – 3.11). Nowadays there are also simple computer programs for carrying out these calculations.



The corrosion and scaling of water pipes can be a costly side effect of treated drinking water with non-optimal composition.

Figure 3.9

Tillman's curve.

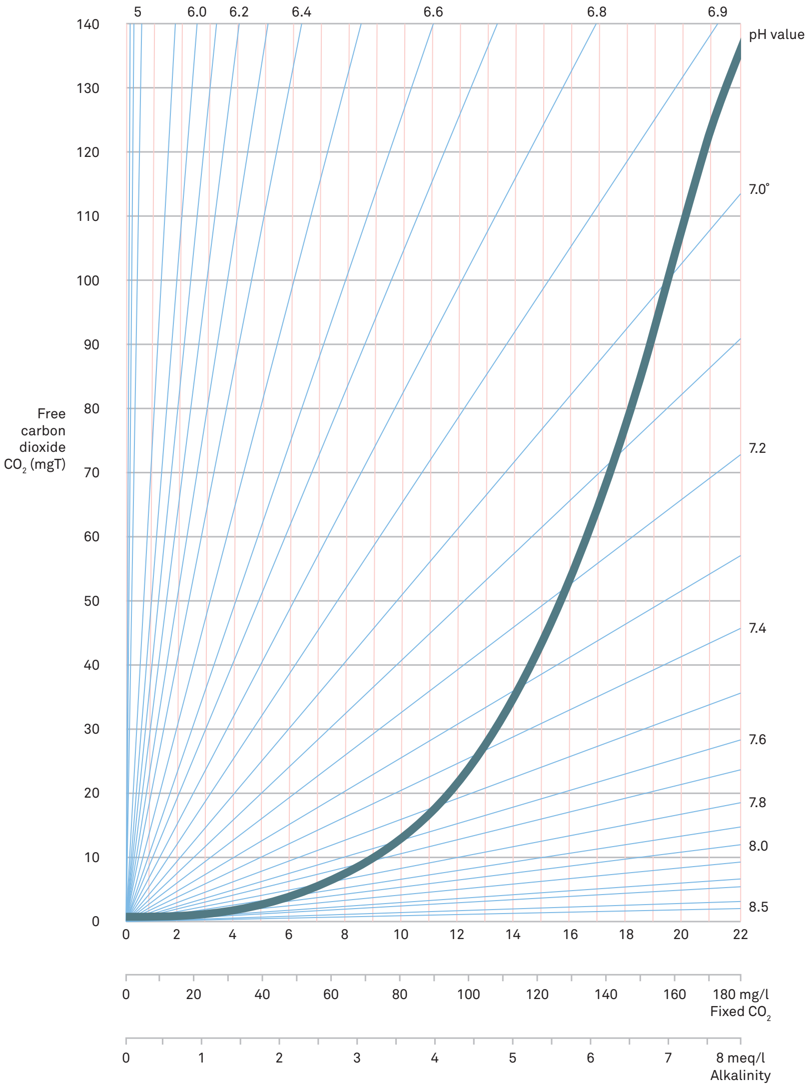
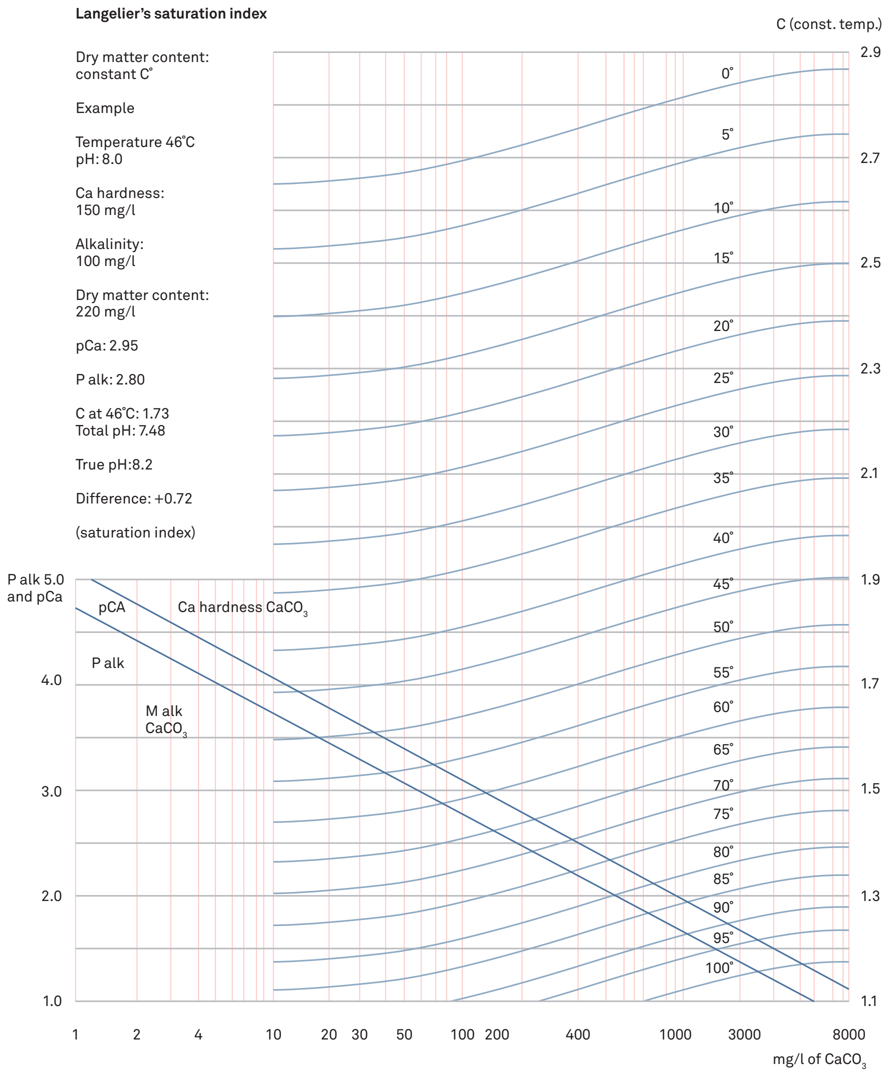


Figure 3.10

Langelier's curve


Langelier's saturation index

Dry matter content:
constant C°

Example

Temperature 46°C
pH: 8.0

Ca hardness:
150 mg/l

Alkalinity:
100 mg/l

Dry matter content:
220 mg/l

pCa: 2.95

P alk: 2.80

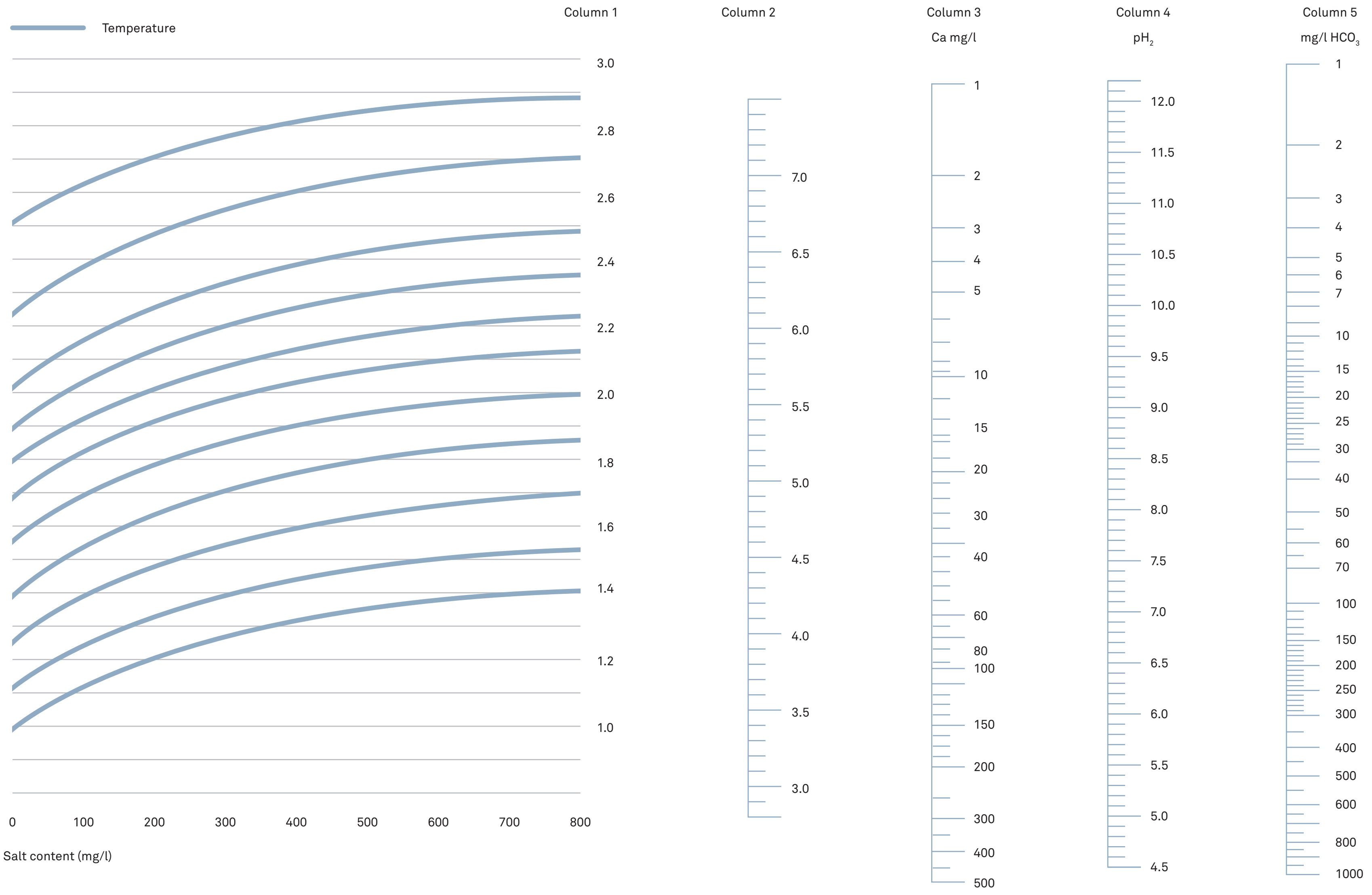
C at 46°C: 1.73
Total pH: 7.48

True pH:8.2

Difference: +0.72

(saturation index)

Figure 3.11
Hoover's nomogram.



Safety issues related to drinking water

Cryptosporidium and Giardia

In recent years greater attention has been given to the causes of outbreaks of illness that have occurred as a result of distributing contaminated water to consumers. One example is the Milwaukee outbreak in 1993, when more than 400,000 people suffered from diarrhea after drinking municipal water. Public health officials in the US voluntarily reported 444 cryptosporidiosis outbreaks to the Center for Disease Control and Prevention (CDC), resulting in 7,465 cases during the period 2009–2017. The cause of these outbreaks was a parasitic protozoan (single-celled organism) called Cryptosporidium. In the dormant state these protozoa are surrounded by protective shells known as oocysts (Cryptosporidium) and cysts (Giardia) that effectively shield them from chlorine disinfection.

The symptoms are stomach cramps, diarrhea, and fever, and the infection is spread by contact between people and between animals and people, as well as indirectly through contaminated water. The infectious dose is low, requiring just 10–100 Cryptosporidium oocysts to cause illness in one person. In the case of Giardia it only takes between 25 and 100 cysts, which means that anything other than very low concentrations is not acceptable in drinking water.

Several species of Cryptosporidium and Giardia are known, but only Cryptosporidium parvum and Giardia intestinalis are known to cause such progressions of illness in people. These organisms are found in surface water such as lakes and rivers.

Oocysts are extremely small, measuring 3 to 5 µm, while cysts are somewhat larger, at 11 to 14 µm. They can be removed using effective chemical precipitation and filtration, or with microfiltration (a form of membrane filtration). Because protozoa behave like particles, a coagulant that is particularly effective at particle reduction should be chosen. The removal efficiency of coagulation and flocculation is about 90% for Cryptosporidium oocyst and Giardia cysts; oocyst absorption was maximal at pH 5.0 and when coagulants were used at higher doses than those used to remove turbidity in water.

The Swedish National Food Administration, SLV, and the Swedish Institute for Infectious Disease Control, SMI, jointly investigated the occurrence of these two protozoa in Swedish surface water sources. The investigation was carried out in autumn 1996 and spring 1997 at 26 surface DWTPs in 21 municipalities, focusing particularly on water sources that were affected by agriculture or sewage. The results showed that 38% of the raw water samples examined contained Cryptosporidium and/or Giardia. The investigation also showed the presence of Cryptosporidium in a potable water sample.

Infections caused by Cryptosporidium and Giardia are spread by contact between people and between animals and people, as well as indirectly through contaminated water.

Persistent organic pollutants (POPs)

Contamination of freshwater systems with industrial, agricultural, and natural chemical compounds is a significant environmental problem. Although most of these organic chemical substances are present at low concentrations, some biodegrade very slowly or can accumulate in the food chain, resulting in undesirable effects on human health and the environment. The Stockholm Convention on Persistent Organic Pollutants is a global treaty (2001, revised in 2017) that aims to prohibit and/or eliminate the production and use of POPs.

Pesticides is the collective name for growth-modifying organic substances that are used to prevent undesirable organisms (such as plants, insects, algae, and fungi) from damaging crops. The following techniques can be used to remove pesticides or POPs from water:

- Separation by adsorption on activated carbon
- Breakdown by oxidation (using ozone, hydrogen peroxide, chlorine, and other substances)
- Biological decomposition on the surface of activated carbon

Who is responsible for water quality?

Water is our most vital commodity, and a whole range of global regulations and national authorities exist to safeguard its quality. Below is a non-exhaustive list of the authorities and directives that govern potable water issues in the European Union.

- **Directive 2000/60/EC** of the European Parliament and of the Council of 23 October 2000 establishing a framework for community action in the field of water policy. Citizens, environmental organizations, nature, and water-using sectors in the economy all need cleaner rivers, lakes, groundwater, and bathing waters.

- **The Environmental Quality Standards Directive (EQSD**), Directive 2008/105/EC, also known as the Priority Substances Directive, which set environmental quality standards (EQS) for the substances in surface waters (river, lake, transitional, and coastal) and confirmed their designation as priority or priority hazardous substances, the latter being a subset of particular concern.

- **The Groundwater Directive (GWD)**, Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration.

- **The Floods Directive (FD)**, Directive 2007/60/EC, which applies to all kinds of floods (river, lakes, flash floods, urban floods, and coastal floods including storm surges and tsunamis), across all EU territory.

- **The Drinking Water Directive, 98/83/EC**, is designed to safeguard the quality of water that is intended for human consumption. The consolidated text of the Directive with its latest amendments including Commission Directive (EU) 2015/1787 can be downloaded from the European Commission website. On February 1 2018 the European Commission adopted a proposal for a revised drinking water directive to improve the quality of drinking water and provide greater access and information.

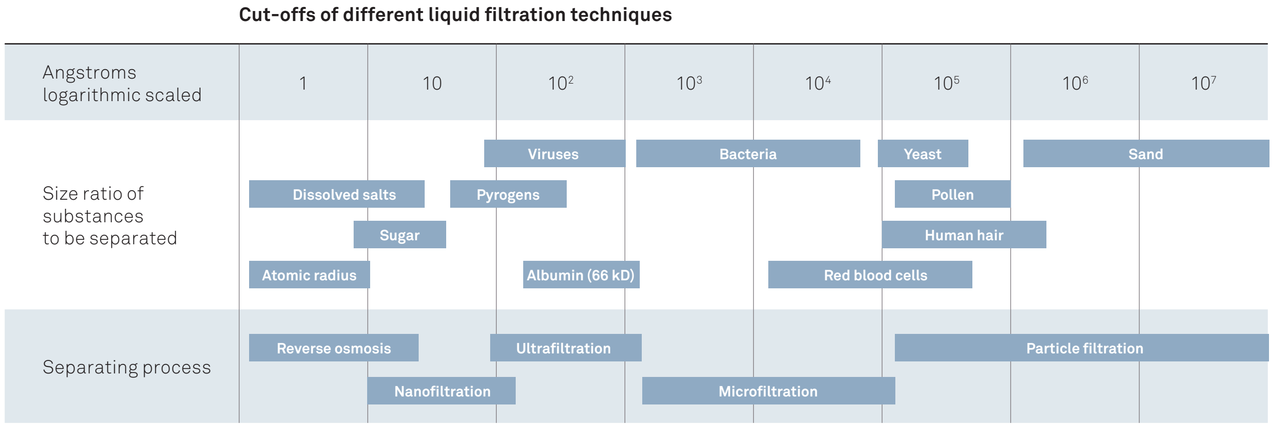
Membrane technologies

Membranes are defined as a selective barrier where the selectivity depends on several parameters such as the size, charge, and the hydrophilicity/hydrophobicity of the membrane and the separated components. The main membrane types used in water treatment processes are ultrafiltration, microfiltration, nanofiltration, and reverse osmosis. These membranes have different pore sizes and thus pressure ranges. Figure 3.12 shows the pore size range for these membranes.

In surface water treatment, when the target is to remove particles, colloidal or dissolved (natural) organic matters, membranes with a larger pore size are used, e.g. microfiltration (MF), ultrafiltration (UF), and/or nanofiltration (NF).

A reverse osmosis (RO) membrane has the smallest pore size and is used to remove dissolved salts from water. The main application of RO is desalination (salt removal) of seawater or brackish water.

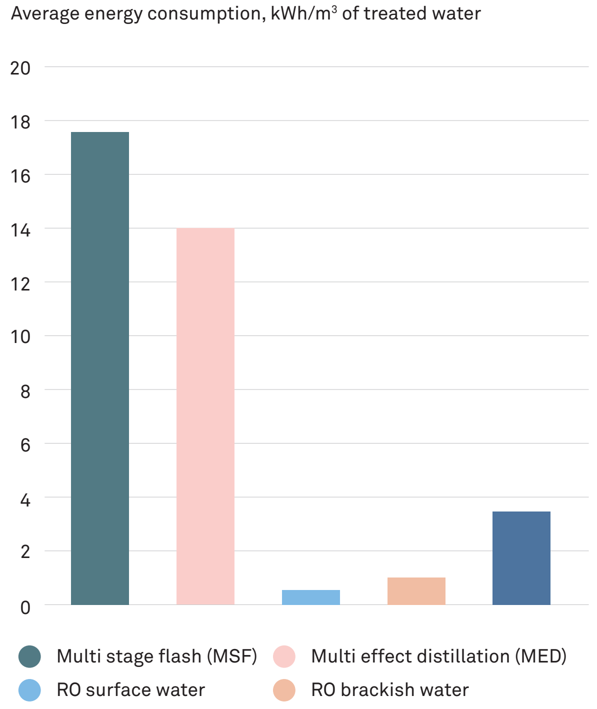
Figure 3.12
Pore size range for different water treatment membranes



Desalination

There are two major types of desalination technologies, thermal and membrane, both of which are used to convert unconventional water sources like seawater and brackish water into drinking or industrial water. Thermal technology was developed prior to membrane technology, and the first commercial thermal plant was constructed in 1951 in Kuwait. Thermal desalination is based on the conversion of water to vapor and then condensation. Due to phase conversion, the energy requirement for this technology is higher than for membrane technology, therefore it is used mostly in countries where the energy price is lower (e.g. Gulf states in the Middle East) or in combination with a power plant where an excess of energy or steam is available. Figure 3.13 shows a comparison of the energy requirements of the different technologies. According to the DA Water Security Handbook produced by the International Desalination Association (IDA) and Global Water Intelligence (January 2019), 45% of the world's desalinated water is generated using thermal desalination. Multi-stage flash (MSF) and multi-effect distillation (MED) are the main technologies used in thermal desalination.

Figure 3.13
Average energy consumption of different desalination technologies.



Desalination with membrane technologies

Reverse osmosis (RO) is the main type of membrane used for desalination. Water from a salty solution is separated through a selective barrier (membrane) with external pressure. Figure 3.14 illustrates the concept of RO. The pressure required to transport water from one side of the membrane to the other depends on the ion concentration or the total dissolved solids (TDS) content of the water. Water with higher TDS requires higher pressure. For example, desalinating seawater with a TDS of between 35 and 40 g/l requires a pressure of about 40–50 bar. Due to the applied pressure the membrane should have a high pressure tolerance. For this reason, RO membranes comprise several layers: a top layer, a support layer, and a base layer. The top (selective) layer has a thickness of 0.2 micrometers and plays a major role in the separation of ions. The porous support and non-woven layers provide mechanical strength. Figure 3.15 shows a cross-section of a membrane taken with scanning electron microscopy.

Figure 3.14
Osmosis and reverse osmosis

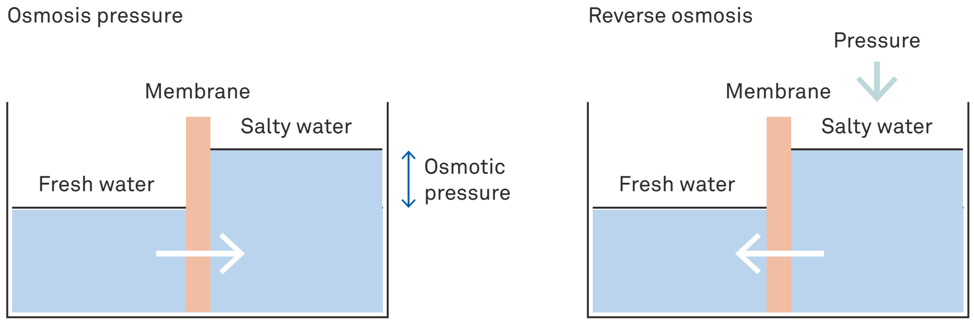
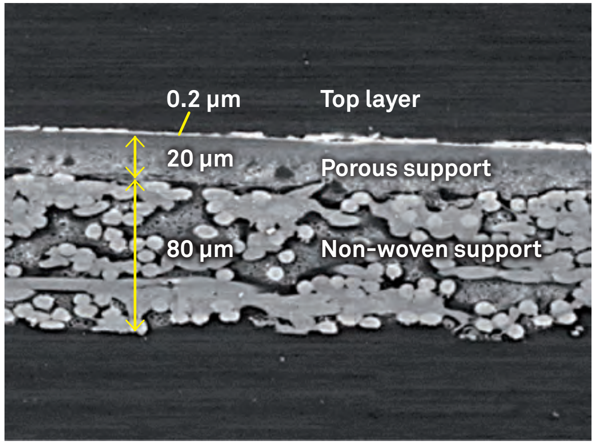


Figure 3.15
Cross-section of RO membrane

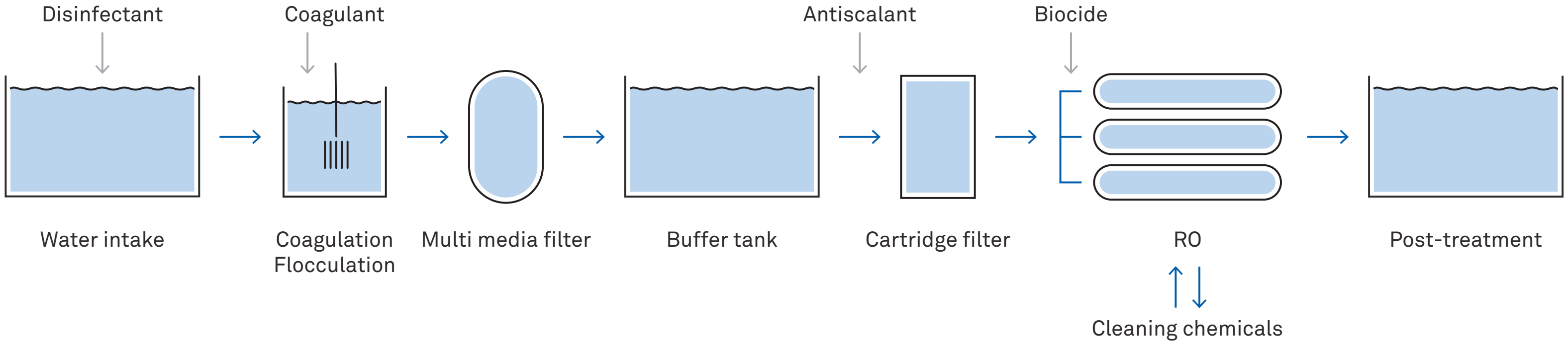


Desalination process

A desalination process consists of several stages including pre-treatment, a membrane process, and post-treatment. Figure 3.16 shows a schematic of a desalination process. The role of pre-treatment is to remove big particles, organics from the water pumped to the RO process. The quality of the treated water before RO is indicated by the silt density index (SDI), which is a standard method used to measure the performance of pre-treatment before the RO membrane. Most membrane manufacturers recommend an SDI value of less than 3.

In the RO process the feed water is separated into two streams. The stream that passes through the membrane has a lower TDS (1–2% of feed) and is called permeate, while the other stream – which contains salts and other components that are retained by the membrane – is known as retentate or reject. The ratio of permeate to feed flow is called recovery. The recovery value depends on the TDS of the feed water and the type of membrane. As rule of thumb, for low-TDS water (brackish water) the value varies between 70 and 90%, while for seawater the value is dramatically lower (30–45%) because of its higher TDS.

Figure 3.16
Schematic of a desalination process



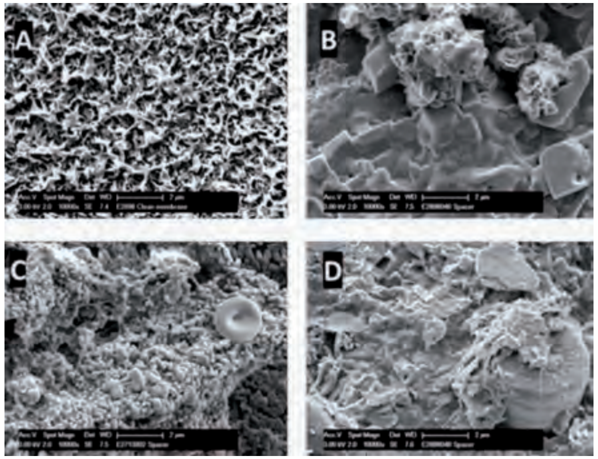
Water reuse

Water scarcity has increased efforts to reuse water from municipal or industrial sources, with membranes like UF, MF, and RO playing a major role. There are several plants around the world that are built to reuse water from treated municipal wastewater, e.g. Orange County (US), Kranji Newater Factory (Singapore), and Sulaibiya (Kuwait). The treated water has the same or better quality as fresh water, however it is currently mainly used for recharging aquifers, preventing saline water intrusion, and for industrial and irrigation uses. There have been some cases where reused water was blended with fresh water for human consumption.

Main challenges

While membrane technologies are the dominant technologies for producing desalinated water and in water reuse applications, there are still challenges preventing their wider adoption, the main one being fouling, which reduces process performance and increases costs. Fouling is classified as colloidal, inorganic, organic, or biofouling. Figure 3.17 illustrates a clean membrane together with different types of fouling. Fouling is unavoidable, but the impact can be reduced through process optimization enabled by chemical management. Several types of chemicals are used in the membrane desalination process to control fouling or increase runnability.

Figure 3.17.
A clean membrane and different fouling types.
A: Surface of clean membrane, B: Inorganic (scale) fouling, C: Biofouling, D: Mixed fouling.



Coagulants

Coagulants are used to remove dissolved organics and suspended/colloidal solids from water. The feed water for RO needs to be very clean and therefore pre-treatment plays a very important role. Iron salts like ferric sulfate and ferric chloride are the main inorganic coagulants used for pre-treatment.

Flocculants

Flocculants play a similar role as in other water treatment applications. Low molecular weight (organic coagulants) and high molecular weight (MW) flocculants are not commonly used in the pre-treatment of water before the RO process because the residuals of flocculants tend to stick to the membrane, causing blockages. When required, a very low dose (<0.5 ppm) for anionic is recommended; for cationic flocculants the dose is even lower (<0.2 ppm).

Biocide

Biocides are used to control microbiological activities and biofouling in membrane processes. Oxidizing biocides such as Na-hypochlorite, chlorine, and chloramine are used in pre-treatment. Residuals need to be minimized before the membrane process due to their adverse effect on the membrane structure. The oxidizing chemicals are added either continuously or in shock dosing. Non-oxidizing biocides are used to control biofouling on the membrane and are also added in shock dosing or continuously. For plants that produce drinking water, continuous dosing of non-oxidizing chemicals is not permitted. Recently, other biocides based on organic acids such as peracetic acids (PAA) and performic acids (PFA) have been introduced for direct use on membranes. Continuous or intermittent dosing (5-10 ppm) of organic acids keeps the surface of the membrane free of biofouling and other types of fouling.

Antiscalants

Antiscalants (scale inhibitors) are used to control scale formation in membrane processes. The scale forms when the ion concentration increases above salt saturation. There are different types of antiscalants commercially available; the main category is polymeric and phosphonate.

pH and alkalinity adjustment

Water desalinated using RO requires post-treatment to increase its pH and alkalinity before it is fit for human consumption. This is usually done by adding lime (sometime in combination with carbon dioxide) or calcium carbonate.

The cost of producing of drinking water

Drinking water is one of the most important resources in everyday life. Consumers expect that their drinking water has a high purity and consistent quality. Authorities and water suppliers put a great deal of effort into ensuring consistently high quality and monitoring the chemical and biological composition of water. As a result, drinking water is one of the most highly controlled resources available.

Before the water ends up in our taps it is subject to a variety of different treatment steps, starting from naturally occurring raw water. Good quality raw water naturally requires less treatment than water of poorer quality.

The cost of coagulants for a chemical precipitation process represents a relatively small proportion of the overall water and sewage cost.

The example in table 3.18 illustrates the approximate percentages of total cost in the production of drinking water using aluminum sulfate at a drinking water plant in a large Swedish municipality. The production process itself accounts for a small share of this total, at approximately 10%.

Chemical consumption accounts for almost 2% of the total cost of producing and distributing drinking water.

Table 3.19 summarizes the typical chemical products produced by Kemira for use in drinking water treatment.

Table 3.18
Exemplary production costs for drinking water in a large municipality in Scandinavia.

	% of total cost
Production (excl. chemicals)	9.7
Distribution	88.5
ALG, aluminum sulfate	1.3
Other chemicals	0.5

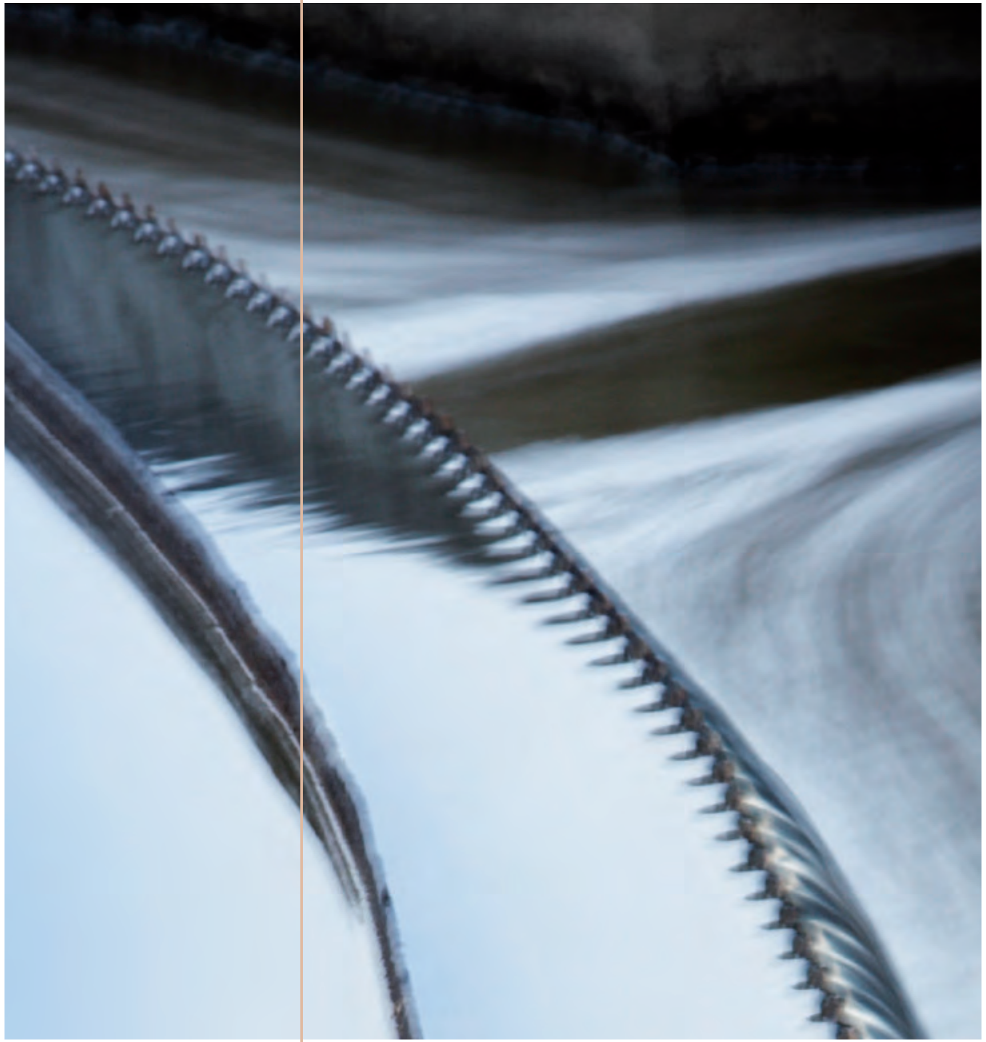
Table 3.19
summarizes the typical chemical products produced by Kemira for use in drinking water treatment.

Brand name	**Active ingredient**	**Main use and characteristics**
Kemira ACL PAX	Polyaluminum chloride	Raw, process, and wastewater treatment
Kemira PAS, PASS	Polyaluminum sulfate	Medium basicity Effective for color, suspended solids, and phosphorous removal.
Kemira ALS	Aluminum sulfate	“Iron-free” products for drinking water applications
Kemira FERIX, e.g., ferric sulfate Kemira PIX, e.g.,ferric chloride	Iron (III) salt	Excellent for drinking water production, wastewater treatment, phosphorous removal, struvite control, and sludge conditioning
KemGuard	Polymeric and phosphonate antiscalant	Scale inhabitation and dispersants


kemira

CHAPTER 3

WASTEWATER TREATMENT



Wastewater is not a new phenomenon; every city throughout history has produced contaminated water. In older civilizations it was simply emptied onto the street, or at best into a ditch. As a result, diseases such as cholera spread easily through cities, and the stench must have been indescribable.

The problem of contaminated water was understood as far back as Roman times. In around 400 BC the Romans laid the first sewer in Rome, known as the Cloaca Maxima. By taking away wastewater in a closed system they succeeded in improving the city environment. There are letters from that time that describe Rome as smelling as sweet as the mountains.

The treatment of wastewater is a more recent invention. The first places to introduce wastewater treatment were industries, which could inflict severe local pollution on the recipient water. This began at the end of the nineteenth century, but it was not until around the 1930s that municipal wastewater treatment became more widespread. Initially the water was simply treated mechanically, but as the years passed and urbanization increased, the treatment methods became more sophisticated. In the early 20th century biological treatment was introduced, first as bio-beds, and in 1914 the activated sludge process was patented – a process solution that, more than 100 years later, is still the dominant technology for wastewater treatment. Chemical phosphorus removal was introduced in the 1960s and has since grown rapidly, followed by nitrogen removal. Today we can purify wastewater to any degree required; it is simply a matter of how much we are willing to pay and what requirements must be met.

Even though the basic principles of mechanical, biological, and chemical treatment have been known for a very long time, development hasn't stopped. We are still learning more and more about the mechanisms behind these treatment methods and how they can be combined and optimized. In the beginning development was more on a macro level, while today it is on the micro or molecular level. With today's knowledge of different water treatment processes, including the availability of many new digital solutions, we can treat wastewater highly efficiently by combining different techniques to great effect.

The nature and composition of wastewater

Contaminants

Wastewater contains a variety of substances. Basically, the content is a picture of what is used upstream. Industrial wastewater might only contain a handful of different impurities, whereas municipal wastewater contains every substance that is used in our daily lives just in different concentrations. The classical way to define wastewater content is to divide the impurities into:

- suspended matter
- oxygen-consuming substances
- nutrient salts
- bacteria
- viruses
- parasite spores and eggs
- toxic metals, also known as heavy metals
- environmentally harmful substances

These contaminants can be classified as dissolved or particulate, and the particulate can be divided into different particle sizes of colloidal, suspended, and sedimentary contaminants (see table 3.1). In order to choose the most suitable treatment process it is important to understand both the composition of wastewater and the particle-size distribution.

80–90% of the nitrogen in wastewater comes from urine.

Another way of classifying contaminants is to divide them into organic and inorganic matter. The organic contaminants are generally composed of around one third each of dissolved, colloidal, and suspended solids. The inorganic material mainly comprises dissolved substances.

Figure 3.1
Definition of particle sizes.

	Dissolved	Colloidal	Suspended	Sedimentary suspended
Particle size, µm	0.1	0.1–1.0	1–100	> 100

Organic contaminants

The term organic substances covers many kinds of substances with different (removal) properties. Table 3.2 shows how the composition of organic substances can vary.

The concentration of organic substances is usually measured as:

- Biochemical oxygen demand (BOD)
- Chemical oxygen demand (COD)
- Total organic carbon (TOC)
- Loss on ignition (LOI)

BOD measures the concentration of biodegradable substances in wastewater. These substances are degraded by bacteria, which consume oxygen. The amount of oxygen the microorganisms used is measured over a period of five days (BOD_5) or seven days (BOD_7) to break down the organic contaminants in water at a temperature of 20°C. BOD is measured in mg oxygen/l.

Figure 3.2
Organic substances in municipal wastewater.

Substance	% organic carbon in wastewater
Carbohydrates	11–18%
Proteins	8–10%
Free amino acids	0.5–1.5%
Higher fatty acids	23–25%
Soluble organic acids	7–11%
Esterified fatty acids (fat)	9–12%
Surfactants	4–6%
Others	25–28%

The following relationship applies to municipal wastewater:

$$\mathbf{BOD_7 = 1.15 \times BOD_5}$$

Ammonium is an oxygen-demanding substance, since oxygen is used to oxidize the nitrogen in the ammonium ion to nitrate. This process uses 4.5 grams of oxygen for every gram of nitrogen. The oxygen consumed by ammonium oxidation is not included in the BOD analysis.

COD is a measure of the concentration of contaminants in the water that can be oxidized by a chemical oxidizing agent. The reaction time is considerably shorter than the analysis of BOD, a maximum of two hours instead of up to a week. Complete oxidation is usually achieved by using potassium dichromate or potassium permanganate at a high temperature in strongly acidic solutions. The amount of oxidizing agent required is a measure of the organic content and is converted into the equivalent oxygen concentration, so values are given in mg oxygen/l or g oxygen/m^3.

The relationship between BOD and COD may appear as in figure 3.3. The ratio of COD to BOD indicates the degree of biodegradability of the wastewater. Low values, i.e. COD/BOD <2, indicates rapidly biodegradable substances, while a high ratio indicates that the material is slowly or non-biodegradable. This relationship cannot be applied generally, but must be determined for each source of wastewater, since there can be major variations depending on its composition. In the case of untreated municipal wastewater, the COD/BOD ratio is usually around 2–3, while the ratio for treated wastewater may be higher than four.

Figure 3.3

Example of the relationship between BOD$_7$ and COD.

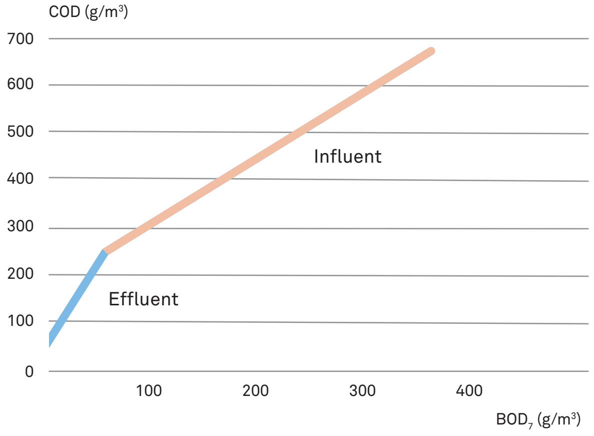
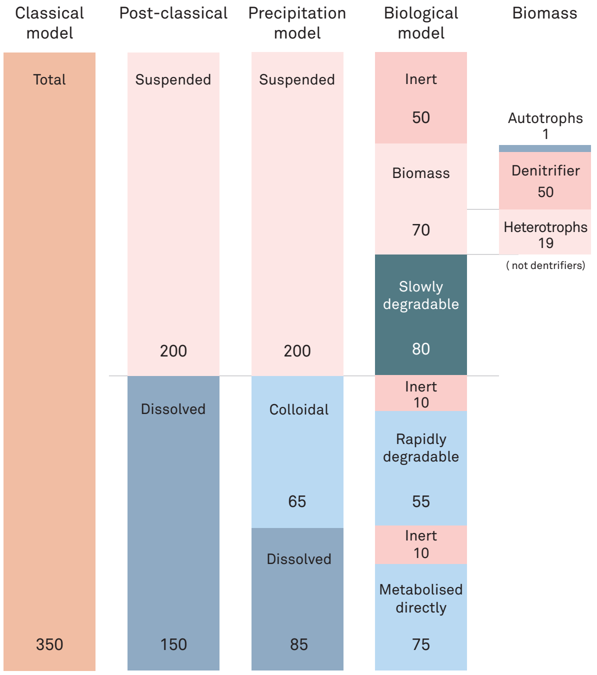


Figure 3.4

COD distribution in wastewater (g COD/m^3). More advanced methods than the classical and post classical models are needed in order to choose an adequate sewage treatment process.

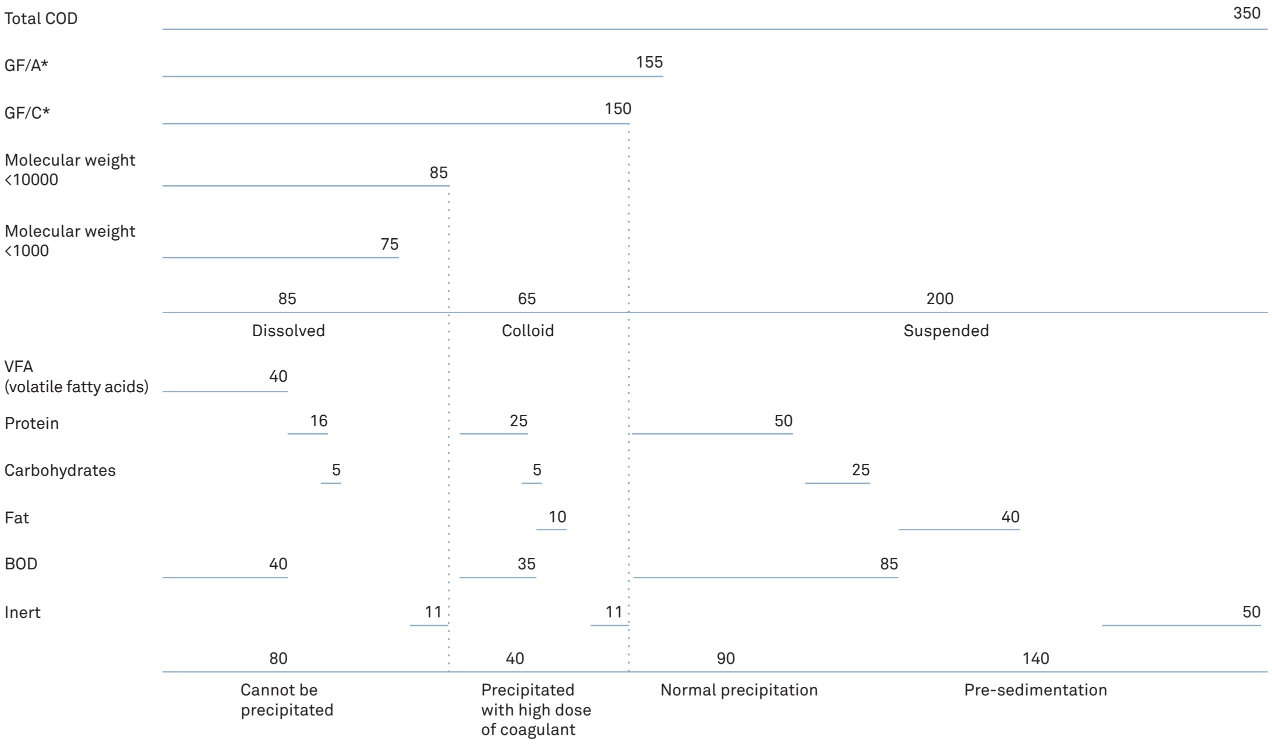


It is also possible to divide COD into substances that are biodegradable and how quickly they are broken down. The composition of wastewater can also be classified according to particle size, volatile fatty acids (VFA), proteins, etc., as shown in figure 3.5.

The HYPRO method

In order to choose the most appropriate treatment process, the wastewater should first be classified in more detail than simply total COD and/or BOD. These analytical methods work well for recipient control but not for operation or selection of a treatment process. Especially in biological processes, the oxygen and nitrate respiration rates are highly dependent on what kind of COD/BOD is available. With the HYPRO method the COD/BOD is defined in more detail in order to better understand what is rapidly available, what can be removed using chemical-physical methods, and what is non-degradable.

Figure 3.5
COD distribution of different organic fractions in wastewater, according to the HYPRO method (g COD/m^3).



** Filtered through a Whatman GF/A resp. GF/C glass fibre filter*

Other organic parameters

LOI is defined as the percentage weight change in a dry substance when a sample is ignited, i.e. heated to 550°C. The assumption is that the losses relate to organic content, i.e. a high LOI corresponds to a high organic content.

TOC is a measure of the content of organic matter, which is determined by measuring the amount of carbon dioxide generated by burning a sample. It is measured in mg C/l.

Advanced analytical methods are constantly being improved, and today it is possible to analyze a huge range of substances to ppb level. Examples of analytical methods used to identify and quantify different substances are mass spectrometer (MS), gas chromatography (GC), liquid chromatography (LC), and IR. To identify specific substances with very low concentrations a combination of several analytical methods is needed. For instance, LC-MS/MS is commonly used to analyze pharmaceuticals in wastewater. With more accurate analysis it is possible to trace potential toxic elements (PTE) or environmentally harmful substances more accurately and at lower concentrations so that environmental risks can be addressed before they cause a problem in the recipient water.

Even at low concentrations some substances can affect the fauna in the recipient water; however, most harmful substances in wastewater are so diluted that they have no environmental impact in the recipient water. On the other hand, in the treatment process toxic substances can become more concentrated in the sludge. Examples of organic substances that can increase in concentration in sludge, and hence need to be carefully monitored, are polychlorinated biphenyls (PCBs), toluene, nonyl phenol, and polycyclic aromatic hydrocarbons (PAHs); inorganic toxic substances like cadmium and mercury can also become concentrated in sludge and therefore must also be carefully monitored.

Microbiological analysis

Microbiological analyses determine the concentrations of bacteria, viruses, and parasite spores. These analyses can be carried out on both influent (untreated) and effluent (treated) wastewater and are normally expressed as number (of bacteria, viruses etc.) per 100 ml of water. Traditionally, bacterial cultures are grown on a growth media specific for the organism in question and then counted. Microscope analysis is another very important traditional method. Genetic/DNA analysis is constantly developing and gives increasingly accurate results that normally tell much more about the sample than traditional analysis methods.

Inorganic substances

The inorganic components in wastewater are mainly dissolved salts in the form of anionic and cationic ions, the majority of which do not need to be removed; however, there are some exceptions. In municipal (and partly in industrial) wastewater, phosphorus and nitrogen-based ions as well as toxic metals should be removed. In industrial applications, the salt content is sometimes so high that it has to be reduced before it is released. For instance, the sulfate or chloride content can be very high and affect the recipient water locally.

Toxic metals are mainly separated with sludge. In general the concentrations are very low in the treated water and have no impact on the environment; however, the removal efficiency is dependent on each specific substance. The table below shows the removal rate of some toxic metals at six municipal wastewater treatment plants (WWTPs) in Sweden.

Figure 3.6
Removal rate of some toxic metals for six municipal wastewater treatment plants with chemical and biological treatment.

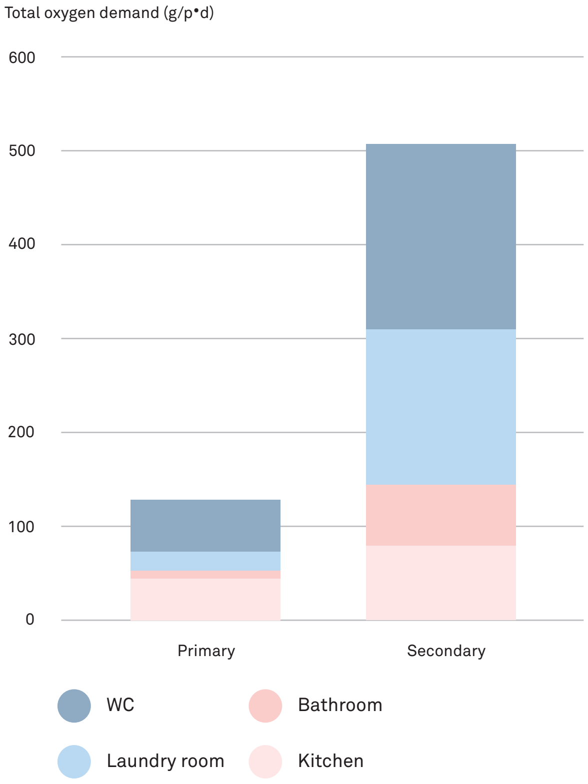
Metal	WWTP A	WWTP B	WWTP C	WWTP D	WWTP E	WWTP F
Ag	100%	97%	97%	97%	97%	97%
Cd	67%	63%	92%	69%	52%	64%
Cr	80%	58%	78%	49%	69%	51%
Cu	74%	81%	90%	91%	81%	77%
Hg	78%	68%	92%	69%	53%	54%
Ni	30%	46%	19%	35%	40%	27%
Pb	90%	76%	95%	78%	74%	70%
Zn	83%	77%	86%	84%	88%	68%

Nutrients

Nitrogen and phosphorus salts are essential for all living organisms but can also be a problem since they are very efficient nutrients. If the concentration is too high in water the growth of algae and other organisms living in the water spirals out of control, i.e. the water is eutrophicated. Eutrophication must be avoided since the biomass that is produced will consume oxygen when it is degraded. This is called secondary oxygen demand in the recipient water. Primary oxygen demand comes from the organic matter (BOD) that is released from the WWTP. The more biomass that is produced in the recipient water, the more secondary oxygen demand is produced. It can easily be that the nutrients in wastewater can cause more oxygen demand than the released BOD, as figure 3.7 shows.

One gram of nitrogen can give rise to around 14 grams of secondary oxygen-demanding organic matter.

Figure 3.7
Primary and secondary oxygen demand.



One gram of phosphorus can give rise to around 100 grams of secondary oxygen-demanding organic matter.

In fresh and brackish waters, phosphates play a more important role in algae production. In salty waters both nitrogen and phosphorus salts cause eutrophication. As well as oxygen-consuming biomass, eutrophication can also produce toxic algae that presents a health risk to both humans and animals; this type of algae can ruin drinking water sources and cause the closure of beaches.

Phosphorus

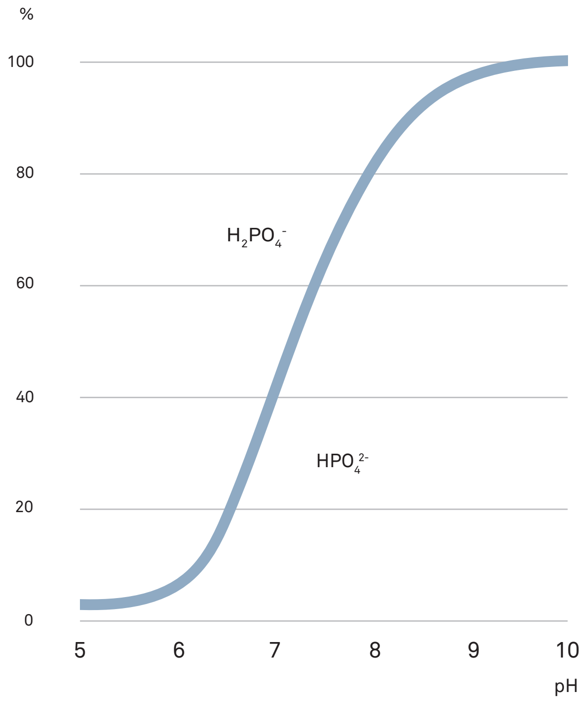
Phosphorus in wastewater is in three main fractions: orthophosphates, polyphosphates, and organically bonded phosphorus, and the total phosphorus value includes all three. Each person contributes approximately 1.5–3.0 g of phosphorus to wastewater each day. On average the human body needs 1.5 g P/day. Most of the phosphorus in wastewater comes from feces and urine.

Organic phosphorus is mainly bonded to solid particles. All bacteria contain nucleic acids, which are rich in phosphorus. Bacteria also have a layer of phospholipids in their cell membranes. Viruses, which are also particles, contain a lot of phosphorus. They have a core of nucleic acids surrounded by a protein layer.

A rule of thumb is that roughly 50% of phosphorus is organic and 50% is phosphate; however, this ratio varies greatly depending on local conditions.

Figure 3.8

The influence of pH on the relative distribution of dissolved orthophosphate with one and two minus charges respectively.



Phosphates mainly originate from urine and historically also from phosphate-based detergents. Since biomass always contains phosphorus, some phosphate is released when biomass is degraded. When biomass is built up in biological treatment some phosphate is taken up. Depending on the pH of the water, the phosphate ion is in different forms. The higher the pH the more will be in the form of orthophosphate ions, the form that is most available for living organisms.

H_3PO_4 ↔ $H_2PO_4^-$ ↔ HPO_4^{2-} ↔ PO_4^{3-}
phosphoric acid **orthophosphate ion**
Low pH **High pH**

The phosphorus concentration is given either as mg/l of total phosphorus (P_{tot}) or mg/l of phosphorus as phosphate (PO_4^{3-}-P).

Instead of using P, the concentration of phosphorus is sometimes given as PO_4^{3-} or P_2O_5. Conversion factors are given in table 3.9.

Table 3.9

Conversion factors for total phosphorus.

P	PO_4^{3-}	P_2O_5
1	3.06	2.29
0.33	1	0.75
0.44	1.34	1

The phosphorus in wastewater can be reduced mechanically, chemically, or biologically. Mechanical treatment separates at the most some tens of percent of the incoming phosphorus; only particle-bound phosphorus can be separated. The biological treatment stage requires phosphorus to support the growth of microorganisms. The biomass in the biological sludge contains around two percent phosphorus. Roughly one gram of phosphorus is required to break down 100 grams of BOD. A conventional biological treatment plant can remove 20–30% of the phosphorus from wastewater, whereas chemical treatment can remove more than 95%.

Nitrogen

The nitrogen load on natural waters mainly comes from atmospheric deposition and agriculture. Table 3.10 shows the different forms of nitrogen in nature. Ammonium salts and nitrates are both easily accessible sources of nitrogen for the production of plant cell matter by nitrogen assimilation.

Atmospheric nitrogen can be fixed by microorganisms. This is the origin of a large proportion of all bound nitrogen.

Table 3.10

Nitrogen in various forms.

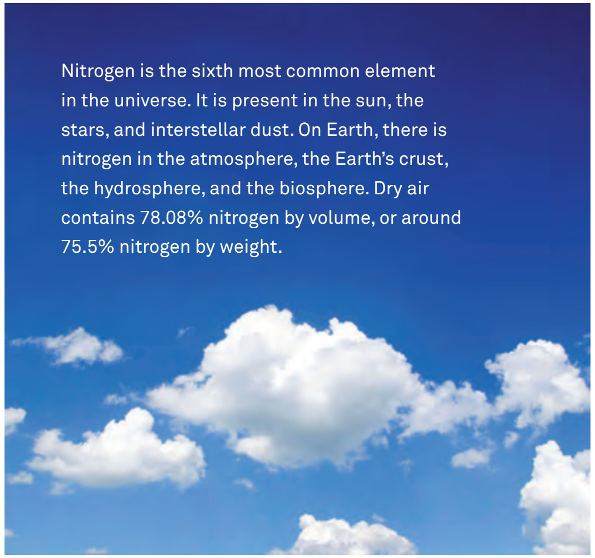
Nitrogen gas (N_2)	Pure nitrogen. Makes up 78% of the Earth's atmosphere.
Ammonium (NH_4^+)	Decomposition product of organically bonded nitrogen. Provides an easily accessible nutrient source for both land-based and aquatic plants. May form ammonia.
Ammonia (NH_3)	Poisonous gas, soluble in water. Formed from ammonium ions in water with high pH.
Nitrate (NO_3^-)	Oxidation product. Forms salts in combination with various metals. Easily accessible nutrient source for plants.
Nitrite (NO_2^-)	Intermediate stage in the oxidation of ammonium to form nitrate.
Proteins	Large molecules that form the building blocks of all living tissue in plants, animals, and people. Nitrogen is an essential component of all proteins, together with carbon, hydrogen, and oxygen.

Ammonium, nitrite, and nitrate are soluble forms of nitrogen that would accumulate in lakes and seas if nitrogen were not continuously removed. This happens naturally on a large scale due to the oxidation of ammonium to produce nitrite or nitrate in a process known as nitrification. The nitrite and nitrate are then reduced to nitrogen gas, which returns to the atmosphere in a process known as denitrification.

High concentrations of nitrate in drinking water are a health hazard and can be very dangerous for infants, since the nitrate can convert into more toxic nitrite.

Nitrogen can be removed from wastewater using biological and chemical-physical methods. Chemical methods are often more costly than biological methods and are used where biological methods are ineffective, for example on difficult industrial wastewater.

About 20% of the nitrogen in wastewater is organically bound; the rest is inorganic nitrogen in the form of ammonium, nitrite, and nitrate. In municipal wastewater more than 95% of the inorganic nitrogen is in the form of ammonium. Nitrate and nitrite are found in the biological treatment process.


Nitrogen is the sixth most common element in the universe. It is present in the sun, the stars, and interstellar dust. On Earth, there is nitrogen in the atmosphere, the Earth's crust, the hydrosphere, and the biosphere. Dry air contains 78.08% nitrogen by volume, or around 75.5% nitrogen by weight.

The concentration of nitrogen is given as total nitrogen in mg/l (N_{tot}). This is the sum of organic nitrogen and nitrogen in the form of ammonium, nitrite, and nitrate. The concentration of nitrogen can also be expressed as Kjeldahl nitrogen, which is the sum of organic nitrogen and nitrogen from ammonium.

Other contamination parameters

Total solids (TS) is another measure of the total concentration of impurities in wastewater. It is the sum of solid and dissolved substances and is expressed in mg/l.

Suspended solids is a measure of the concentration of solid particles in wastewater and is also expressed in mg/l.

Table 3.11 shows approximate typical contaminant concentrations in municipal wastewater, expressed in grams per person equivalent per day (g/person/day).

Table 3.11
Typical contaminant concentrations in municipal wastewater.

Contaminants	g/p·d
Chemical oxygen demand (COD)	120–180
Biochemical oxygen demand (BOD_7)	60–90
Phosphorus (P)	1.0–3.0
Nitrogen (N)	10–14
Suspended solids	70–90
Total solids (TS)	150–250

Table 3.12
Average contaminant concentrations for wastewater of 400 l/(PE·d). Values vary greatly over a 24-hour period.

Contaminant concentration	mg/l
Suspended solids	200
Biochemical oxygen demand (BOD_7)	200
Phosphorus (P)	5
Nitrogen (N)	30

The quantities in the table above are often expressed as person equivalents (PE). Contaminants from industry are often also expressed in person equivalents.

The water consumption of an average household in industrialized countries is normally around 120–200 l per person per day (but values up to 450 l/(PE·d) exist). The amount of wastewater that reaches a treatment plant can be as much as twice this figure due to storm water and groundwater leaking into the system.

Municipal wastewater treatment

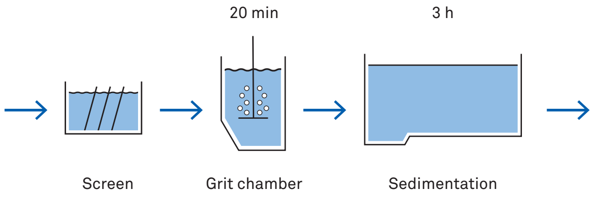
Mechanical treatment

The simplest form of wastewater treatment is to remove the contaminants mechanically. Mechanical treatment is usually carried out in two stages. First, the coarse contaminants are removed by means of screens and sand traps. This step is also called preliminary treatment and exists in all municipal wastewater treatment plants. The remaining suspended solids are allowed to settle in a sedimentation tank. Around 30–70% of suspended solids and around 30% of BOD can be removed from wastewater with mechanical treatment.

The coarser contaminants – such as rags, twigs, scraps of food, etc. – are separated mechanically by passing the water through coarse treatment screens with gaps ranging between 3 and 20 mm wide, which means that relatively large particles pass to the next treatment stage, which is the sand trap.

The sand trap is normally an aerated tank designed specifically to separate heavier particles like sand, gravel, and coffee grounds. The aeration ensures that only the heaviest particles are separated but also supports fat and grease removal. A sand trap normally has a retention time of around 20 minutes.

Figure 3.13
Mechanical treatment stages.




Effluent from mechanical treatment.

After the sand trap, the suspended solids can settle in a sedimentation tank. Depending on the treatment process, this tank is designed to accept 1–3 m^3 of water per m^2 of tank area per hour, i.e. the settling tank has a surface load of 1–3 m/h.

surface load (m/h) = flow (m^3/h)/surface area (m^2)

The normal retention time for water in the settling tank is 2–3 hours, during which 30-70% of the SS are removed from the water but only 30–40% of the BOD.

Since mechanical treatment is poor at removing BOD and removes an even lower percentage of nitrogen and phosphorus, this treatment method is generally inadequate by itself and should therefore only be regarded as a first treatment step.

Mechanical treatment has historically been the dominant process around the world. It is simple, requires only a small investment and is easy to operate. Despite its lack of efficiency, the process does clean water to some extent and is therefore better than no treatment at all. Since mechanical treatment is normally the first treatment stage of a more sophisticated wastewater treatment plant it is also known as primary treatment.

Mechanical treatment produces sludge quantities (primary sludge) of around 50–60 g SS/p·d, which is thickened to a total solids (TS) content of 4–6%, which is equivalent to 0.8–1.5 l/p·d.

Biological treatment

Biological treatment is normally the second treatment stage in a wastewater treatment plant and is therefore also known as secondary treatment. Usually, the water is first treated mechanically and then undergoes a biological treatment stage that is designed to degrade and separate organic contaminants (BOD) by biological means with the support of microorganisms. The contaminants are normally converted into a biological sludge (cell/biomass) and carbon dioxide.

The aeration process in biological treatment can account for more than 50% of a wastewater treatment plant's energy demand.

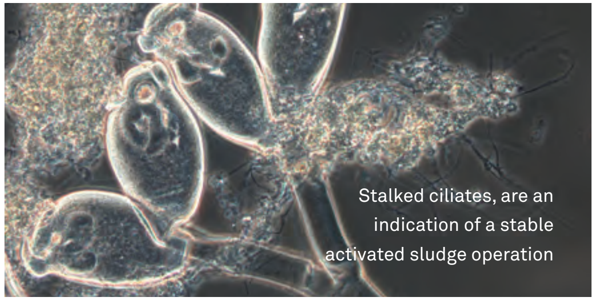
The degradation of organic substances is a complex process that depends on a long series of subsidiary biological reactions. The degradation rate depends on many factors like oxygen content, pH, type of microorganisms available, temperature, contaminant type, presence of toxic substances, and treatment method. The particle size of the contaminants to be removed is also very important. Dissolved organic substances are much easier to degrade than larger particles.

The contaminants in wastewater are primarily degraded by bacteria, which usually specialize in degrading a specific substance or group of substances. As mentioned previously, wastewater contains a variety of different contaminants, which means that several types of bacteria are used in biological treatment. The above-mentioned factors heavily influence the bio-fauna composition.

The bacteria that are used in biological treatment are not the same sort of bacteria we usually think of. They are not disease-causing (pathogenic) bacteria, but naturally occurring bacteria that are found in soil and water. In a biological treatment process high concentrations of these bacteria are used to degrade the impurities in a limited space.

As previously mentioned, secondary treatment is normally designed to degrade and separate organic substances. Nutrient salts, such as nitrogen and phosphorus, are reduced to some extent in a normally loaded, conventional biological treatment system. Only the proportion of nitrogen and phosphorus that is assimilated (taken up) by the cell mass is removed. Usually we would expect this to be equivalent to a BOD/N/P ratio of 100/5/1 based on the influent values. This means that the more biomass produced, the more nutrients are assimilated and hence removed from the water. The biosludge produced, the excess sludge, would contain around 7–10% N and 1–3% P in dry sludge (100% TS).

A biological treatment process also contains other microorganisms than bacteria. A variety of different higher-level species (protozoa and metazoa) are always present in the treatment process. Just as the various species of bacteria have different purposes in the treatment process, these species carry out various tasks in the treatment process. Some live by eating particles and free-swimming bacteria (see activated sludge process); others live on dead or living bacteria and organisms. There are worm-like organisms (oligochaetes) that drill through the biomass and improve water penetration and hence also treatment efficiency.



Stalked ciliates, are an indication of a stable activated sludge operation

There is one thing these organisms all have in common: they support the water treatment process and reduce sludge production. A well-cultivated fauna of protozoa and metazoa is a sign of an effective biological treatment process.

Three types of biological processes are used in wastewater treatment: anaerobic, aerobic, and anoxic degradation.

Anaerobic degradation

An anaerobic process occurs when no oxygen or nitrate is present. The contaminants are degraded anaerobically. Organic substances are converted to methane, carbon dioxide, and water; a small fraction of the organic matter is also converted into new biomass.

Anaerobic degradation is normally only used for the treatment of heavily contaminated industrial wastewater and as a general process for producing biogas and stabilizing sludge, normally called (anaerobic) digestion.

Anaerobic degradation is considerably slower than aerobic processes. Due to the lack of oxygen, the bacteria cannot use the available "food" – the substrate – as effectively, and therefore grow more slowly. A large proportion of the food is used to produce energy and only a small fraction to build up biomass. One (1) kg of COD yields around 0.1 kg of biomass. The rest is used to generate energy for the organism; biogas, a mixture of methane (60-70%) and carbon dioxide (30-40%) with a high energy content, is produced as a by-product.

To increase the degradation rate in an anaerobic process the temperature of the sludge or water is usually increased. The temperature in a digester is normally around 35°C. Municipal wastewater in the Nordic countries usually comes in at a temperature of between 5 and 20°C, which is too low a temperature for an anaerobic process to be considered suitable. Even in warmer parts of the world, where the average temperature is up to 25°C, anaerobic degradation is rarely used in municipal wastewater treatment plants.

In the case of industrial wastewater, especially from the food industry, anaerobic processes can be very attractive as this water sometimes has a high temperature, is highly concentrated, and has low flow rates. More about anaerobic treatment in chapter 6.

Aerobic degradation

This process, which takes place in the presence of oxygen, means that the microorganisms use oxygen in the water to oxidize organic matter into carbon dioxide, water, and biomass.

As mentioned above, due to the presence of oxygen the aerobic treatment process is considerably faster than the anaerobic process. This means that the bacteria can make better use of the substrate and create more biomass. One (1) kg of COD yields around 0.5 kg of biomass, while the rest is used to generate energy.

The aerobic process is also affected by temperature. Too low a temperature reduces the biological activity, but this can be compensated by increasing the concentration of microorganisms. The aerobic treatment process can work well at temperatures down to 5°C and is considerably less temperature-sensitive than the anaerobic process.

When municipal wastewater is treated in an aerobic process the microorganisms may be made to grow on a solid carrier material in what are known as biofilm processes (immobilized cultures, fixed film), or they may be freely suspended in the aqueous phase in the form of biological flocs (suspended cultures, activated sludge).

Anoxic degradation

The anoxic process is similar to the aerobic one, but in this case the bacteria "breathe" by using the oxygen in dissolved nitrate. Anoxic degradation is almost as fast as the aerobic process and considerably faster than the anaerobic process. The degradation process produces biomass, carbon dioxide, water, and nitrogen gas. This process is therefore used for nitrogen removal (see the section on denitrification later in this chapter) since nitrogen is released from the water as nitrogen gas.

Anoxic degradation only works if organic substances (BOD/COD) are present. Bacteria that need organic substances to build biomass are called heterotrophic bacteria. Bacteria that can use carbon dioxide to build biomass are called autotrophic bacteria. One (1) kg of COD yields 0.5 kg of biomass, i.e. the same quantity as aerobic processes. This process must be carried out in the absence of free oxygen, otherwise the denitrifying bacteria are outcompeted by the aerobic bacteria.

Both bio-film bacteria and suspended bacterial cultures can be used for anoxic treatment.

Heterotrophic bacteria need biomass to grow (in the same way as animals)

Autotrophic bacteria can use carbon dioxide to grow biomass (in the same way as plants)

During anaerobic decomposition	1 kg of COD yields 0.1 kg of biomass
During aerobic decomposition	1 kg of COD yields 0.5 kg of biomass
During anoxic decomposition	1 kg of COD yields 0.5 kg of biomass

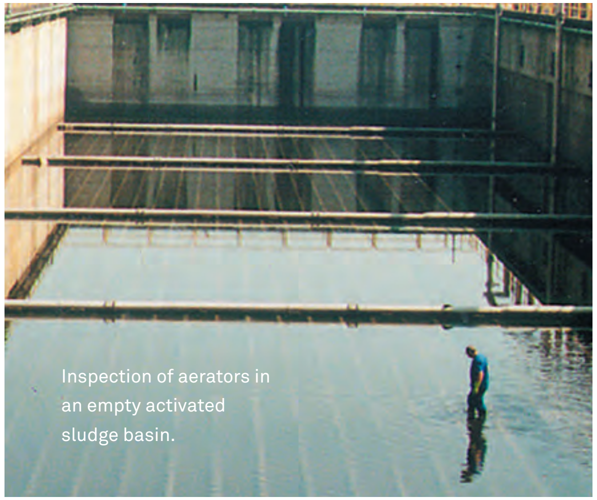
Activated sludge process

In the activated sludge process the biologically active microorganisms are suspended in the water as sludge flocs. A sludge floc, or biofloc, mainly consists of floc-forming bacteria, but other microorganisms are also present.

To create a highly efficient process the microorganisms are concentrated in the activated sludge tank. This is achieved by recycling most of the sludge that is removed from the subsequent sedimentation stage. Since biological treatment is the second stage of the process it is often called secondary treatment and the sedimentation tank for the biosludge is called secondary sedimentation. Some of the sedimented sludge is removed from the process in order to compensate for the continuous growth in biomass (figure 3.14). This sludge is called excess or surplus sludge.

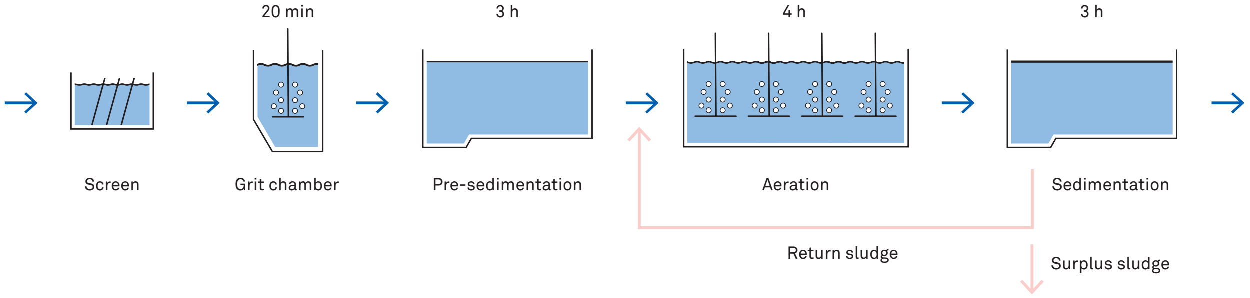
The microorganisms in the activated sludge can take up and degrade dissolved organic contaminants in the water and adsorb suspended colloidal particles. This process results in the formation of carbon dioxide, water, and biomass when water is treated under aerobic conditions.

An activated sludge process can be operated under aerobic, anoxic, or anaerobic conditions. To ensure contact between the bioflocs and the water the activated sludge tank must be mixed, otherwise the bioflocs will settle. Since most activated sludge processes are aerobic (at least partly) the most common way of mixing the sludge is to aerate the water from the bottom of the activated sludge basin. Aeration is also needed to ensure that enough oxygen is present for degradation. In general, more air is needed for this purpose than for keeping the biofloc in suspension. Aeration can also be performed using surface aerators, which spray the water into the air above the surface, forming small droplets of activated sludge that take up oxygen from the air. When the activated sludge process is operating under anoxic or anaerobic conditions, no



Inspection of aerators in an empty activated sludge basin.

Figure 3.14
Activated sludge process.



air can be added. In these cases the activated sludge is kept in suspension with the help of submerged mixers. The organic substances in the water, expressed as BOD, are distributed as follows:

30-50%	are converted to carbon dioxide and water by oxidation
40–45%	are removed from the process as excess sludge
< 10%	are released with the effluent water

The bacteria in an activated sludge process can be divided into three groups: free-swimming, floc-forming, and filamentous.

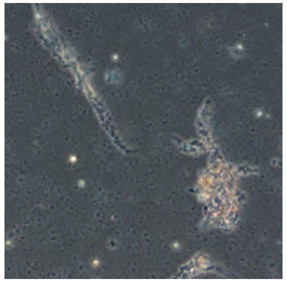
Free-swimming bacteria are single or pair-forming bacteria that are suspended freely in the water and can be likened to very small particles. These bacteria multiply fastest in an activated sludge process. Due to their small size they do not settle in the secondary sedimentation and are lost from the treatment plant. A high concentration of free-swimming bacteria makes it more difficult to meet effluent limits and hence they should be avoided.

There are always free-swimming bacteria in an activated sludge tank as many micro-animals feed on them. If most of them remain uneaten, the treated water will be opaque (cloudy). Low sludge age (see page 65) favors free-swimming bacteria.

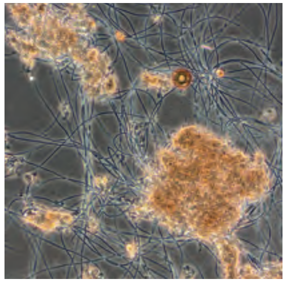
Floc-forming bacteria normally account for the majority of biomass in an activated sludge process and are able to grow in agglomerates because they produce a sticky polysaccharide on the surface that makes them bind together. As a result, they form larger particles (bioflocs) that are large enough to settle in the subsequent sedimentation stage.

Floc-forming bacteria grow slower than the free-swimming bacteria and require a longer retention time (sludge age) to prevent them from being flushed out; the minimum sludge age is one to two days. Free-swimming bacteria are flushed out while the floc-forming bacteria settle in the secondary sedimentation and are recycled to the activated sludge tank. This recycling process means that these slow-growing bacteria can be retained in a process where the retention time of the treated water is much shorter than the bacteria's growth.

The growth and efficiency of the bacteria is also temperature dependent, which means that a low water temperature requires a longer sludge retention time. The retention time is therefore higher during winter than summer.



Free swimming bacteria



Biofloc surrounded by filamentous bacteria

Filamentous bacteria are bacteria that grow “in-line” and form long, hair-like filaments in the biosludge. These bacteria are normally the slowest growing and favor a high sludge age, low temperature, or unusual conditions (like lack of nutrients or oxygen) in the activated sludge process.

A high concentration of filamentous bacteria can cause severe operating problems in an activated sludge plant. Filaments make the sludge voluminous and bulky, meaning that it does not settle easily. The secondary sedimentation tank can become filled with biosludge, which is then discharged with the water from the treatment plant, causing elevated emission levels. Filamentous bacteria also make it difficult to recycle the sludge to the activated sludge tank. Many filamentous bacteria are hydrophobic so they float up to the surface of the activated sludge and sedimentation tanks. This can not only make it challenging to maintain the required effluent limits but also causes many other practical problems such as more difficult sludge handling and disturbances to the biogas process. Finally, the sludge can be more than one meter thick and spread over the whole plant area, leading to a poor-quality working environment.

A healthy biofloc should nevertheless contain a small number of filaments as they give stability to the floc in the same way that the human skeleton supports the body.

Sequence batch reactor

Another way of operating the activated sludge process is to perform both the degradation and sedimentation of flocs in the same reactor. Because this is done in sequences the technology is known as a sequence batch reactor (SBR).

The simplest SBR process would be as follows:

1. The bioreactor containing activated sludge is filled up with wastewater.
2. Aeration starts and BOD is degraded.
3. When BOD is degraded, aeration is closed and the biosludge is allowed to settle.
4. The clear water is decanted from the bioreactor; the better the sludge is able to settle, the more clean water can be separated.
5. A small amount of the biosludge is removed as excess sludge.
6. The process begins again.

SBR technology is discontinuous and needs to be operated accordingly. In municipal WWTPs this is normally done by having more than one bioreactor working in parallel. This means that when a reactor is in settling and decantation mode the other is fed with water and vice-versa. It is also possible to have a buffer tank for the wastewater before the SBR reactor to handle the continuous wastewater flow.

SBR reactors are normally found in smaller treatment plants and in industrial applications. However, the technology is continuously improving and there are plants with capacities of over 100,000 PE that operate with SBR technology. SBR technologies can work under aerobic, anoxic, and anaerobic conditions.

Operating parameters

The most important parameters are set to process organic load, bioreactor and settling tank status, and biomass recycling and removal.

F/M ratio

The sludge load is the ratio between the amount of substrate supplied (= amount of organic matter) and the amount of microorganisms in the activated sludge process. It is calculated as the ratio of the amount of organics entering each day and the existing amount of organic sludge (suspended solids) in the bioreactor.

$$^{F}/_{M} = \frac{\text{Organic load}}{\text{Bioreactor organic solids}}$$

Treatment processes in activated sludge plants can be classified into three main groups depending on the sludge load (F/M): high, normal, or low. The following guide values apply to each group when BOD$_7$ is used to estimate the amount of organics:

Sludge load (F/M)	BOD$_7$ kg/kg VSS per day
High	0.8–1.5
Normal	0.3–0.7
Low	0.05–0.2

Hydraulic retention time (HRT)

HRT is the amount of time it takes the wastewater to pass through a bioreactor.

The average retention time in an activated sludge basin depends on the load on the activated sludge process. A plant with a low load has a large volume and hence a relatively long retention time, while one with a high load is more compact and has a much shorter retention time. If the treatment plant has an effective primary treatment stage (e.g. pre-precipitation) then the volumes can be reduced since most organic substances are removed before the activated sludge process.

$$\text{HRT} = \frac{\text{Bioreactor volume}}{\text{Flow rate}}$$

Table 3.15
Retention times for activated sludge process in municipal wastewater treatment.

Description	Retention time h
Short	0.6–2.0
Normal	2.5–6.0
Long	8–24
Extended	> 24

Sludge age (SRT)

Sludge age (SRT), or mean cell residence time (MCRT), is the average time that sludge solids are maintained in the activated sludge process. It is estimated as the ratio between the existing amount of sludge in the biological treatment stage and the amount of sludge removed each day.

$$\text{SRT} = \frac{\text{Suspended solids in process}}{\text{Suspended solids leaving the process per day}}$$

Table 3.16
SRT for activated sludge process.

Process load	SRT d
High	1.5–3
Normal	3–8
Low	10–30

Mixed liquor suspended solids (MLSS)

MLSS is the concentration of suspended solids in the activated sludge bioreactor; it is normally kept constant in the activated sludge tank but can vary due to flow changes and seasonal differences. Treatment plants with a high sludge age and nitrogen treatment normally have a higher MLSS concentration. The values are in the range 1.5–8 g/l.

The MLSS content is an indication of how active an activated sludge plant is – the higher the concentration, the more bacteria present and hence the higher the activity level. However, MLSS measures all suspended solids in the basin, both organic and inorganic SS, so it does not correlate directly with the bacteria content.

Many treatment plants also analyze mixed liquor volatile suspended solids (MLVSS), which is a measure of the organic content of the activated sludge. It is more directly related to the bacteria content than MLSS. An example that clarifies the difference between MLSS and MLVSS is a case where a municipal WWTP switched from simultaneous precipitation. The VSS content increased from 67% to 78% since the precipitation chemical contributed to sludge production during simultaneous precipitation. With the same MLSS, the biomass concentration was increased by 16% and the capacity could be increased.

Dissolved oxygen (DO)

Oxygen is the electron acceptor in the aerobic respiration process of microbes. The oxygen concentration (DO) in the aerobic process should normally be kept at 1–2 g O_2/m^3. Higher concentrations are normally not needed, while lower concentrations can slow down the treatment process.

The oxygen uptake rate (OUR) of biomass depends on the actual sludge load and the amount of BOD that needs to be removed. With a lower sludge load more oxygen is needed to reduce a given BOD concentration. The reason for this is that oxygen is used for both degrading BOD and to keep the bacteria alive. This is called endogenous respiration. In a low-loaded activated sludge process the activated sludge tanks are larger and retain more biomass, meaning that more endogenous respiration occurs. A low sludge load also leads to nitrification, which increases oxygen consumption considerably. More about nitrification and nitrogen removal can be found on page 92.

Sludge index

The settling characteristics of biosludge are normally measured using the sludge volume index (SVI). It is calculated by dividing the sludge volume, SV_{30}, by the suspended solids content of the sample. Sludge volume is the volume of sludge after 30 minutes of settling in a 1-liter beaker and is expressed in ml/l. The lower the sludge index, the better the sedimentation performance. Normally the sludge volume index is 60–150 ml/g. For sludge volumes lower than 300 ml/l the sludge index is calculated using the formula:

$$SVI = \frac{SV_{30}}{SS}$$

For sludge volumes greater than 300 ml/l the sample should be diluted and resettled. For sludge volumes in the range 300–800 ml/l the following formula can be used to estimate SVI:

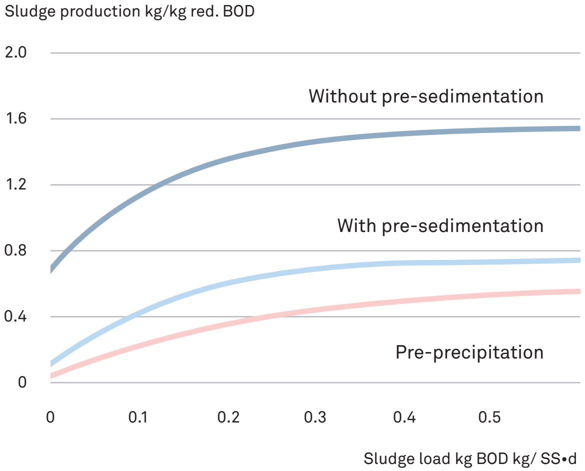
$$SVI = \frac{200 + SV_{30}/3}{SS}$$

A high sludge index indicates that sludge bulking has occurred, probably as a result of a too-high concentration of filamentous bacteria, which make water treatment more difficult because a sludge blanket fills the settling tank.

Sludge production

The amount of excess sludge produced in the activated sludge process depends on the sludge load on the treatment stage but also on what kind of substrate is being degraded. A normally loaded plant with a pre-sedimentation step produces roughly 0.7–0.8 kg of excess sludge per kg of reduced BOD_7, while a low-loaded activated sludge plant produces less sludge. This is illustrated in figure 3.17.

Figure 3.17
The effect of pre-treatment on sludge production as a function of sludge load in municipal wastewater treatment.



Energy consumption

An activated sludge process requires energy. The energy is consumed by the blowing machines that deliver air to the biological treatment step. Removing one kilogram of BOD requires between 0.9 and 1.3 kWh of energy. The energy is not just used for pumping air into the aeration tanks – even if the oxygen concentration is satisfactory, the correct amount of air must be injected to keep the sludge in suspension. If the oxygen requirement is low, then the activated sludge basin can instead be equipped with mixers, which also consume energy but not to the same extent as the aerators.

The energy efficiency of the activated sludge process can be improved by using more efficient blowing machines and air diffusors with an improved design. Reducing the BOD load on an activated sludge naturally also decreases the energy consumption due to the reduced oxygen consumption and sludge volumes.

The BOD load on the biological treatment step can be reduced by pre-precipitation

Treatment efficiency

The degradation rate of BOD depends on the way the activated sludge process is operated. The more time the bacteria are given to degrade the contaminants, the more effective the treatment.

Table 3.18
Degradation rate of BOD in an activated sludge process.

Plant with high load	60–90%
Normal load	85–95%
Low load	90–99%

The degradation rate also depends on the composition of the impurities in the water. If the influent water contains a high proportion of compounds that are difficult to degrade, a longer retention time is required. One example is wastewater treatment in some pulp and paper industries, where the retention time can be several days.

Membrane bioreactor

Membrane technology in biological treatment is in the form of membrane bioreactors (MBR). These use membranes instead of sedimentation to separate the bioflocs in an activated sludge process. The membranes have pores that allow dissolved substances to pass through and filter out particles. When secondary sedimentation is no longer a limiting factor, the bioreactor suspended solids concentration can be increased; the increase is then limited by oxygen transfer to the bioreactor.

The selection of MBR technology instead of a conventional activated sludge process is limited by the higher operating cost due to energy consumption, membrane lifetime, and cleaning requirements, which are a combination of weekly/monthly maintenance and intensive annual procedures. Typical flux through a membrane during its lifetime is in the range 500–3000 m^3/m^2; Fe/Al coagulants and polymers can double the flux. In weekly/monthly maintenance cleaning, moderate chemical concentrations are used and cleaning is done in place (CIP), while in the annual intensive cleaning high chemical concentrations are used and cleaning is done out of place (COP). The cleaning chemicals used are bases, acids, and oxidants.

Anaerobic membrane bioreactor technology (aMBR or AnMBR), which is in early market adoption, uses anaerobic bacteria to treat wastewater in a bioreactor combined with a membrane for solids separation. This technology is mostly used in industrial wastewater treatment.

Biofilm processes

Another way to treat water using microorganisms in a bioreactor is to let them grow on a surface. This is called a biofilm process. Bacteria grow on surfaces everywhere, for instance on the inside of pipes in a sewer system. The challenge is to collect enough bacteria in a limited volume so that the capacity of the bioreactor becomes high enough, which is done by increasing the surface area in the bioreactor. The most common methods used to achieve this are detailed below.

Biological beds/trickling filter

The treatment of wastewater in biological beds is based on a containment (normally circular) filled with carrier material, which should have a large surface where the bacteria can grow. Historically, trickling filters were filled with crushed stone or pumice with a particle size of 70–90 mm and a specific area of 40–60 m^2/m^3. Today, plastic carrier materials with a specific area of 100–250 m^2/m^3 are dominant since they have larger cavities, which reduces the risk of blockages.

A trickling filter is not filled with water. Instead, water is evenly spread over the surface of the filter bed using a sprinkler system with rotating arms where water is released on one side as shown in shown below. The water then trickles down over the carrier materials where a culture of microorganisms degrades the impurities before being collected below the filter for further treatment. It is common that part of the water flow is recirculated to the trickling filter to improve the treatment results.

The water is aerated when it is spread by the sprinkler system. Since the trickling filter isn't filled with water there is a large contact area between water and air in the filter that improves the oxygen transfer further. Assuming that the oxygen transfer is unlimited, the efficiency of the process depends only on the contact area between wastewater and biofilm (carrier materials). It is therefore very beneficial to have a carrier material with a high surface area per volume unit.

Sludge separation

When the growth of microorganisms on the carrier material reaches a certain thickness some of the biofilm is released from the carrier material as suspended solids. This biofilm is normally separated in a sedimentation tank placed downstream of the filter. It should be noted that biological beds release a fraction of finely suspended material that may be difficult to remove. It is therefore recommended that the sedimentation unit is supported by chemical treatment with coagulants. Normally polyaluminum chlorides or polymer blends of polyaluminum chlorides are the most efficient coagulants for removing biofilm residuals. Trickling filters can also be combined with an activated sludge process. If the trickling filter is placed before the activated sludge tank, no separation of excess biofilm is needed after the trickling filter.

Energy consumption

Biobeds were originally an energy-efficient alternative to activated sludge treatment, but the development of new aerators for activated sludge in recent years means that the energy efficiency benefit is now relatively small. In general, the energy consumption is around 0.9 kWh per kg of reduced BOD_7.

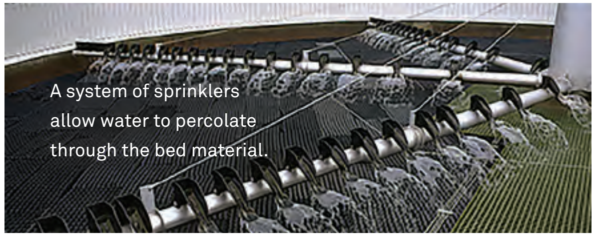
Load

The efficiency of a trickling filter filled with plastic carrier materials is between 2–5 kg BOD_7/m^3 of filter volume per day. In comparison, a stone-filled biobed can treat 0.8–1.2 kg BOD_7/m^3 of bed volume per day.

Biobeds with plastic filler can be useful for treatment prior to an activated sludge process since they are more efficient per volume unit than an activated sludge process.

Treatment efficiency

Biobeds are normally designed for a maximum BOD reduction of 80–85% and are known as heavily loaded biobeds. Further improvements in treatment efficiency require extensive recirculation of wastewater. For economic reasons it is often cheaper to use the activated sludge process instead; it is however possible to use biobeds for nitrification.


A system of sprinklers allow water to percolate through the bed material.

Bio-rotor

The bio-rotor is based on the same principle as the biobed, i.e. the wastewater passes through a carrier material, which in this case is attached to a rotating drum or disc on which the microorganisms grow.

Wastewater passes through a trough in which the bio-rotor is partly submerged. Aeration is achieved by rotating the drum or disc.

The sludge production and treatment efficiency are comparable with those of the biobed.

Energy consumption

This process is normally used in small municipal plants and to treat heavily contaminated industrial wastewater. The load on a bio-rotor can be up to 15–30 g BOD_7 per m^2 of rotor area per day. The energy consumption of a bio-rotor is usually around 1.1 kWh/kg of reduced BOD_7.

Suspended biofilm (MBBR process)

One technology that is more and more commonly used is biofilm processes that use a suspended carrier. This is normally called a moving bed bioreactor (MBBR) process. The biofilm grows on small plastic carrier material that is submerged in the bioreactor tank and kept in suspension by aeration or mixers. The carrier material normally has a density just above that of water, which avoids flotation and minimizes the energy needed to keep the material suspended. A sieve in the outflow of the bioreactor prevents the pieces of plastic from escaping with the water. The biofilm that grows on the carrier material is eventually released and has to be separated after the reactor in the same way as the sludge from a trickling filter or bio-rotor.

The principle of an MBBR unit is similar to an activated sludge process but the biomass is kept in the bioreactor with the carrier materials, where it grows. It is therefore quite easy to convert an activated sludge reactor to an MBBR reactor.

The original process uses a polythene carrier material with a density of 0.95 g/cm^3, formed from small pieces of tube that are 10 mm in diameter and 7 mm long. The pieces have a cross on the inside and fins on the outside to maximize their specific area. The effective specific area when the tank is two-thirds full of carrier material (the typical filling density) is 325 m^2/m^3. There are several different types of carrier material, with the design depending on what kind of wastewater is being treated, the available volume in the bioreactor, and manufacturer-specific differences.

Their high specific area means that MBBR units are compact. The retention time in a plant designed solely for BOD reduction could be as low as 30–60 minutes. A reactor designed for nitrogen reduction has a retention time of three to four hours, compared with 12–18 hours for an activated sludge plant that delivers the same efficiency.

Using suspended carrier material is particularly beneficial when the time comes to upgrade an activated sludge plant that is already operating at its capacity limit. It is then a matter of using as much carrier material as required to achieve the desired treatment efficiency.

This process is also especially suitable for use in combination with chemical post-precipitation in heavily loaded plants since it allows for a highly compact plant design. Due to the short residence time in the bioreactor only dissolved matter is removed. Particulate matter that is more slowly degradable passes the bioreactor and is removed in a chemical coagulation process afterwards.

As with trickling filters, polyaluminum chlorides or polymer blends of polyaluminum chlorides are the most efficient coagulants for removing biofilm residuals.

MBBR technologies can also be combined with an activated sludge process. Doing so makes it possible to keep different microorganisms that need different sludge ages in the same bioreactor. Normally, the slow-growing microorganisms are allowed to grow on the biofilm whereas the faster-growing ones live in the bioflocs in the activated sludge process. An example of this is a process where the bacteria that degrade BOD grow in the bioflocs while the nitrifiers grow on the carrier materials. This kind of reactor is sometimes called a hybrid reactor.

Biological filters

Biological filters are designed in a similar way to traditional sand filters – in other words the water passes upwards or downwards through a bed of a coarse filter material that is usually similar to lightweight expanded clay aggregate (LECA). In this type of process the biofilm grows on the surface of the particles.

The filter needs to be back-washed periodically because it gets gradually blocked by incoming sludge and sludge produced by the treatment process itself. The bioreactor therefore operates on a discontinuous basis, just like a conventional sand filter. Biological filters are very effective and are primarily used on pre-treated water.

Fluidized bed

Another way of building compact biological treatment plants is to use fluidized bed technology. Sand grains of a specific size are used as the carrier material for the microorganisms. Wastewater is pumped up through the bottom of a tank at a constant flow rate, which keeps the grains suspended in the aqueous phase. This ensures extremely good contact between the microorganisms and the water, which means that the retention time can be kept short.

The disadvantage of this process is that it is difficult to operate under aerobic conditions due to limited oxygen transport. It is nevertheless ideal for anoxic operation and can be used for denitrification. If the respiration process is based on nitrate, then a very high bioactivity can be achieved per unit volume. Oxygen cannot dissolve fast enough in the water.

Granulated bioflocs

Granulated biofloc processes are a mix between activated sludge processes and biofilm processes. Instead of letting the biofilm form on a seed of, for instance, sand, biofloc granules can be formed, which are much more compact than bioflocs in an activated sludge process. The principle is otherwise similar to the fluidized bed but the bioflocs form compact granulated flocs without an external seed that behave like the seeded flocs in a fluidized bed.

It is also possible to include settling in the process. The granules settle very rapidly so this can easily be done in the existing bioreactor, like in an SBR process. This technology is commonly used in both aerobic and anaerobic processes.

Another interesting feature of a granulated floc is the possibility to have different functions on different levels of the granule. For instance, in an aerated bioreactor it is possible to have aerobic bacteria on the surface and anoxic or anaerobic bacteria in the middle of the granule. This means that several bioreactions can occur at the same time in a bioreactor without needing to constantly adjust the conditions (by turning the air on and off for instance).

Chemical treatment

The purpose of the chemical treatment of wastewater varies and it can be carried out using several different treatment systems. Generally, the chemical treatment process has a mixing stage in which the coagulant is mixed with the water followed by a coagulation stage where flocs form. These can then be separated in the separation stage by sedimentation, flotation, or filtration.

Direct precipitation

In direct precipitation the precipitation stage is the only treatment stage used after the preliminary treatment. Coagulant is added in the sand trap or after the preliminary treatment. Flocs are formed that can be separated in the following sedimentation tank.

Reduction during direct precipitation

SS	>	90%
BOD	≈	75%
Ptot	>	90%
Ntot	≈	25%

The total hydraulic retention time, i.e. the time the water spends in the treatment process, is three to four hours, although with some separation technologies it can be less than an hour.

The coagulants used are aluminum salts like aluminum sulfate and polyaluminum chlorides, or trivalent iron salts such as ferric chloride or sulfate. Lime can also be used, but due to the high dose rate needed, sludge production is high as well as the pH in treated water.

Bivalent iron salts cannot be used since they cannot form flocs.

Direct precipitation is used in several WWTPs in the Nordic countries and has also gained acceptance as the most cost-effective method in a number of large cities around the world. The process gives a phosphorus reduction of over 90% and a reduction in organic content of around 75%. Table 3.20 shows the results from several Norwegian WWTPs.

Figure 3.19
Direct precipitation. In many cases separate mixing and coagulation chambers are not used.

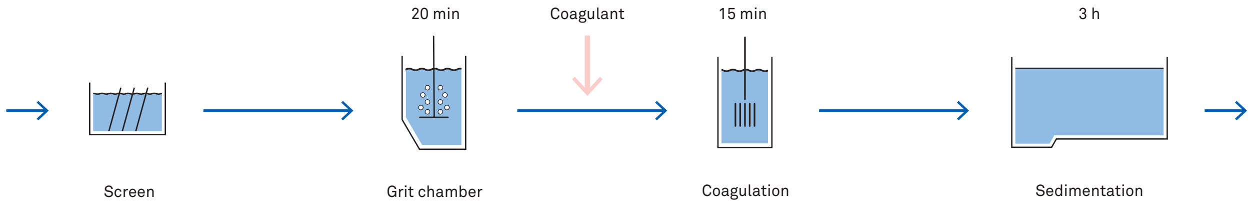


Table 3.20

Direct precipitation. In many cases separate mixing and coagulation chambers are not used.

Parameter	Number of plants	Inlet mg/l	Outlet mg/l	Removal efficiency %
BOD_7	23	167 ± 95	27.2 ± 12.7	80.9 ± 9.6
COD	87	463 ± 251	104 ± 38	74.9 ± 7.9
Ptot	87	5.24 ± 2.53	0.26 ± 0.16	94.0 ± 5.5
SS	78	233 ± 186	16.6 ± 9.6	90.6 ± 7.9

Ref. 1: Ødegaard H. and Karlsson I., Chemical Wastewater Treatment – Value for Money, I: Chemical Water and Wastewater Treatment IV, H.H. Hahn et al (Eds), Springer Berlin Heidelberg New York, pages 191–209, 1994.

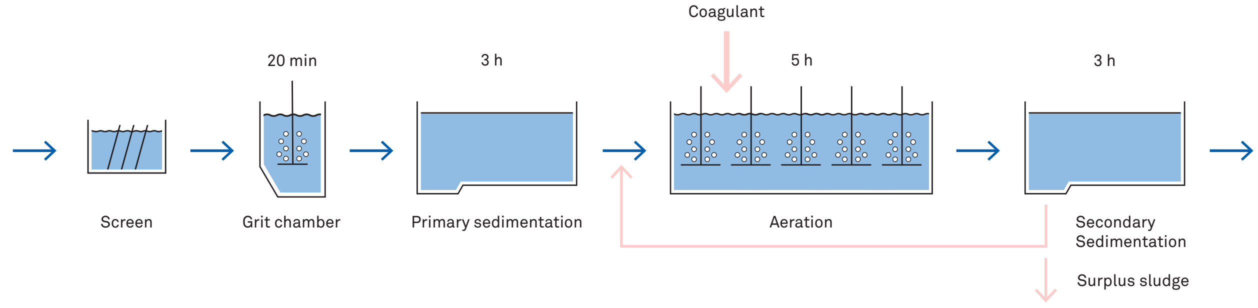
With direct precipitation it is possible to reach phosphorus concentrations as low as 0.3 mg P/l in the treated water. However, reaching this level requires a fairly high chemical dosage and also efficient separation of the chemical flocs. Existing mechanical treatment plants can be converted to effective direct precipitation plants for a very modest investment.

Simultaneous precipitation

Simultaneous precipitation is the name given to a phosphorus reduction process in which chemical phosphorus precipitation takes place at the same time as biological treatment in an activated sludge process. The process is also known as co-precipitation. The biological stage serves as both a coagulation and an activated sludge process. The mixture of biological and chemical sludge is removed in the subsequent sedimentation tank.

The total hydraulic retention time for a WWTP with simultaneous precipitation in our example is around 11.5 hours including pre-sedimentation.

Figure 3.21
Simultaneous precipitation.



Reduction during simultaneous precipitation

SS	>	90%
BOD	≈	90%
Ptot	>	90%
Ntot	≈	25%

This process normally gives a phosphorus content of <0.5–1 mg/l in the treated water.

The coagulant is normally added in the activated sludge tank or at its intake or discharge point. Because phosphorus precipitation takes place at the same time as the biological stage, sludge production is increased, which considerably reduces sludge age (see the section on MLSS/VSS). This reduces the opportunities for nitrification.

The coagulants that are normally used for simultaneous precipitation are aluminum salts or iron salts (bivalent and trivalent), but not lime. Polyaluminum salts can also be used for another purpose than phosphorus removal since they also improve the biosludge properties (see the section on bulking sludge control).


Some wastewater treatment plants in the Nordic countries are built inside mountains

Post-precipitation

Post-precipitation is a suitable method when highly effective phosphorus reduction is needed. Phosphorus is removed chemically from the biologically treated water in a separate treatment stage after secondary treatment. This third treatment step is normally a sedimentation tank but could also be a flotation unit or a filter. Since post-precipitation is the third treatment step after the mechanical and biological steps it is also known as tertiary treatment. The meaning of tertiary treatment has evolved over time, and today it also means any nutrient removal process where phosphorus and nitrogen are removed.

Reduction during post-precipitation

SS	>	90%
BOD	≈	90%
Ptot	>	95%
Ntot	≈	25%

Post-precipitation gives a phosphorus content of less than 0.5 mg/l in the treated water.

The total hydraulic retention time in our example is around 12 hours, including pre-sedimentation.

Post-precipitation is often combined with the recycling of chemical sludge to the pre-sedimentation stage. This results in minor improvements in phosphorus and organic separation in the primary treatment and improved sludge qualities with higher DS content in the sludge. Another benefit is that only two sludge streams have to be processed instead of three.

In addition to the excellent treatment results, a post-precipitation process also provides valuable additional security for the WWTP when the hydraulic loading is high. Sludge loss from the biological treatment can be reduced, meaning that the biological stage can be made more compact while maintaining or even improving BOD reduction.

The coagulants used are aluminum salts (PAX and AVR), iron salts (PIX), or lime; bivalent iron salts cannot be used.

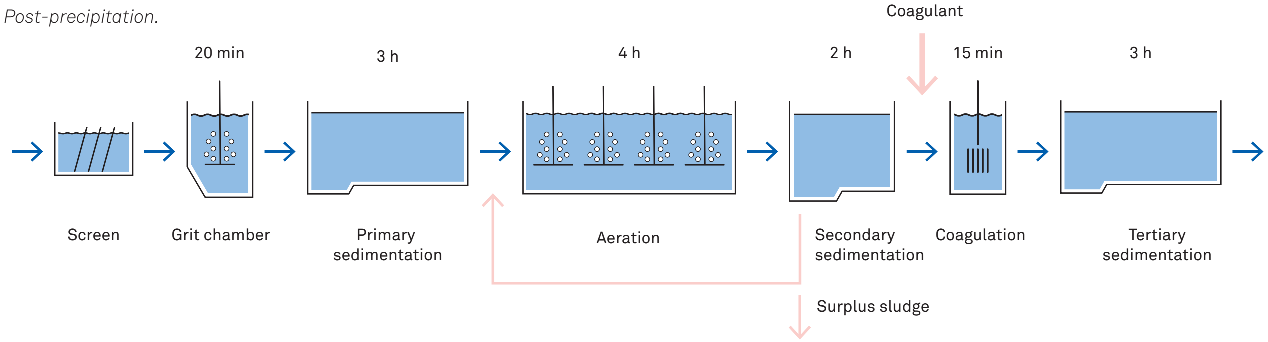


Figure 3.22
Post-precipitation.

Pre-precipitation

Pre-precipitation, also known as chemically enhanced primary treatment (CEPT), is a direct precipitation process where water is chemically treated before the biological treatment step.

Reduction during pre-precipitation

SS	>	90%
BOD	≈	90%
Ptot	>	90%
Ntot	≈	25%

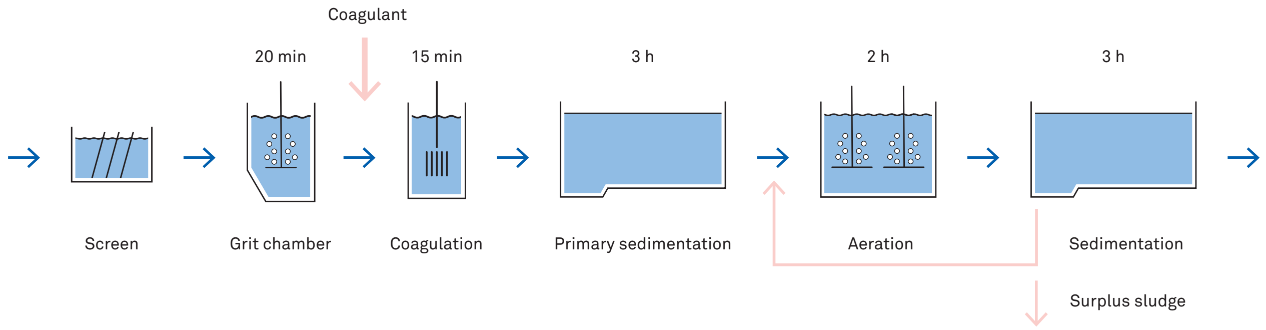
The total hydraulic retention time is around nine hours.

The main purpose with pre-precipitation is to reduce the load on the biological treatment step. Every plant that has primary treatment can be converted to this technology; the only change is that a coagulant is added at a point with turbulent conditions before pre-sedimentation to ensure effective mixing.

Pre-precipitation significantly improves the reduction of organic matter in primary treatment. Phosphorus removal is also improved, and reduction levels can be controlled with the correct choice of coagulant and dosage. The lower load on the biological treatment step results in lower energy consumption and less biosludge production. With pre-precipitation the hydraulic retention time can be reduced or the capacity of the WWTP increased.

The benefit of pre-precipitation is more easily explained with an example. A conventional biological treatment plant must remove 90% of influent organic matter; around 30% of this is removed in a conventional primary

Figure 3.23
Pre-precipitation.
In most cases there is no need for flocculation tanks.

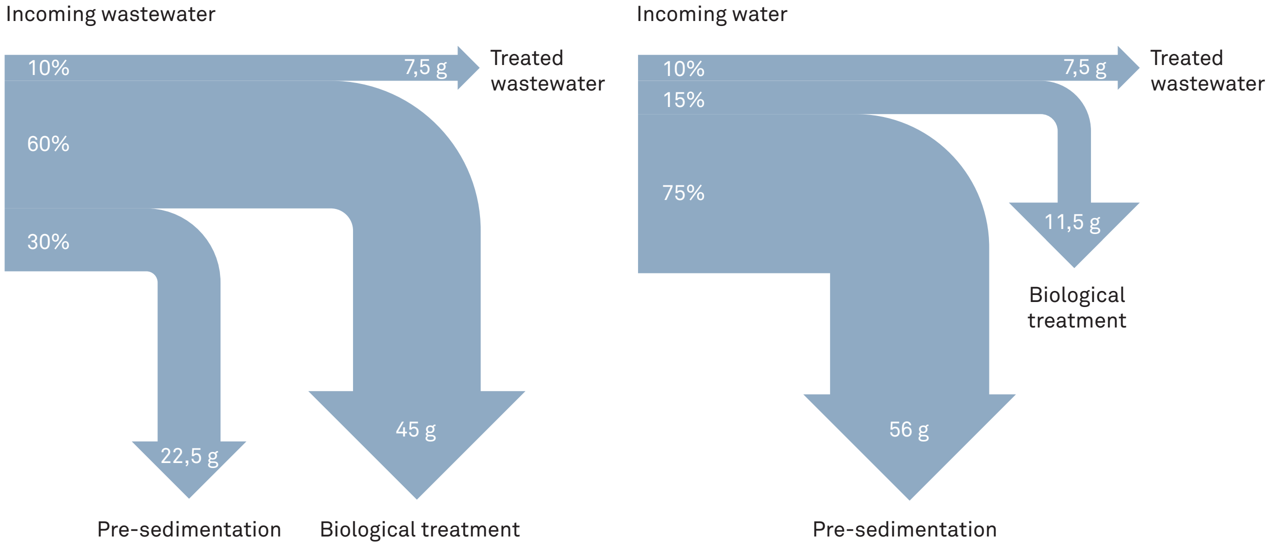


clarifier and the remaining 60% has to be removed in the biological treatment step. Approximately 1.3 kWh of electricity is needed to degrade 1 kg of BOD, resulting in an energy consumption of 20 kWh per person per year to degrade the BOD.

With pre-precipitation the distribution of organic matter changes. The treatment efficiency of BOD in pre-precipitation is up to 75%, leaving just 15% of the BOD to be removed in the biological treatment step. The activated sludge tank needs a much smaller volume and therefore the footprint can be reduced significantly. The energy consumption per person can also be reduced to about 5 kWh per year, which represents a saving of around 75% in the biological treatment step.

Pre-precipitation also increases the amount of biogas produced during the anaerobic digestion of sludge. During conventional biological treatment a large

Figure 3.24
Distribution of removed BOD in a WWTP with and without pre-precipitation.



proportion of the particulate organic material is converted to carbon dioxide. But during pre-precipitation the particulate organic material remains intact in the sludge, which means that it can be converted to methane gas in an anaerobic digester. This means that considerably more methane gas is generated when pre-precipitated sludge is digested than is the case with biological sludge. Biogas generation is of course highly beneficial since it can replace fossil fuels and reduce a plant's carbon footprint.

The sludge production at the WWTP changes with pre-precipitation. More primary sludge is produced with pre-precipitation and less biosludge (excess sludge). If the plant has anerobic digestion, the sludge production after digestion will be on similar levels to a WWTP with simultaneous or post-precipitation. Since biosludge is normally more difficult to dewater, especially if it is an anaerobically digested biosludge, the DS content in sludge might increase by a few percent with pre-precipitation. In case there is no anaerobic digestion of the sludge, a pre-precipitation process normally generates 10–15% more dry sludge.

Another advantage with pre-precipitation is that it acts as a barrier before the biological treatment step. If the load is too high or there are some other disturbances in the biological process, the pre-treatment reduces the severity of these disturbances. The load to a WWTP varies through the day, with the load lowest during the night before a peak in the morning, high load during the day, and then a second peak in the evening. The peak is not only in flow but also in concentration. This means that the load can change multiple times in a fairly short period.

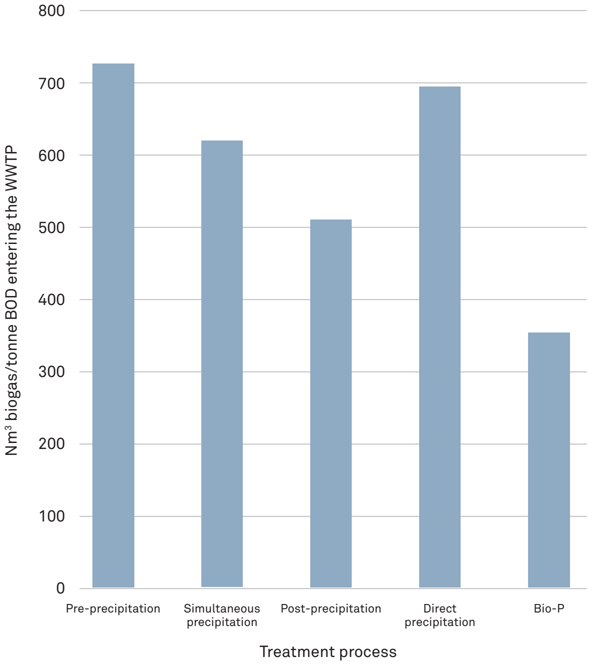
Since biological treatment works best when the load is as constant as possible, pre-precipitation can remove the worst peaks and smooth out the load. With the support of on-line control of the influent flow and water quality it is possible to do this in a highly controlled way. For more information see chapter 7 of this handbook.

As mentioned above, with a pre-precipitation process the energy needed to remove organic matter can be dramatically reduced and biogas production increased. It is therefore possible to improve the energy balance of a WWTP; in some cases the WWTP can be converted to an energy-production plant. With pre-precipitation the influent BOD is an energy source instead of an energy consumer.

In a comparison of 27 environmental reports from Nordic WWTPs, biogas production was compared with influent BOD. Since the BOD can either be converted to biomass and CO_2 or to biogas in anaerobic digestion, this study compared how different water treatment process setups affected biogas production. The biogas potential is calculated as Nm^3 of biogas/tonne BOD$_7$ entering the WWTP. The results are shown in figure 3.25.

Figure 3.25

Biogas production per tonne of BOD$_7$ in influent water for different wastewater treatment process setups.



It is clear that a pre-precipitation plant has a higher biogas potential than the other processes. Even though direct precipitation is a very simple process and doesn’t remove BOD to the same extent as the other processes, it has a high biogas potential due to its high production of primary sludge. The reason why bio-P has a lower potential is unclear, although one reason could be the lack of iron in the sludge. Iron binds sulfides in the anaerobic digester that otherwise would partly poison the biogas process. Another explanation is that the bio-P process needs more organic matter and hence less is available for biogas production.

Ferric, aluminum, and polyaluminum coagulants are all suitable for pre-precipitation and organic (polymer) coagulants can also be used alone or blended with

Table 3.26

Comparison of the different methods of chemical wastewater treatment. The retention time is based on a plant with BOD and P removal only; with nitrogen removal the biological process will need a longer retention time (see also table 3.24).

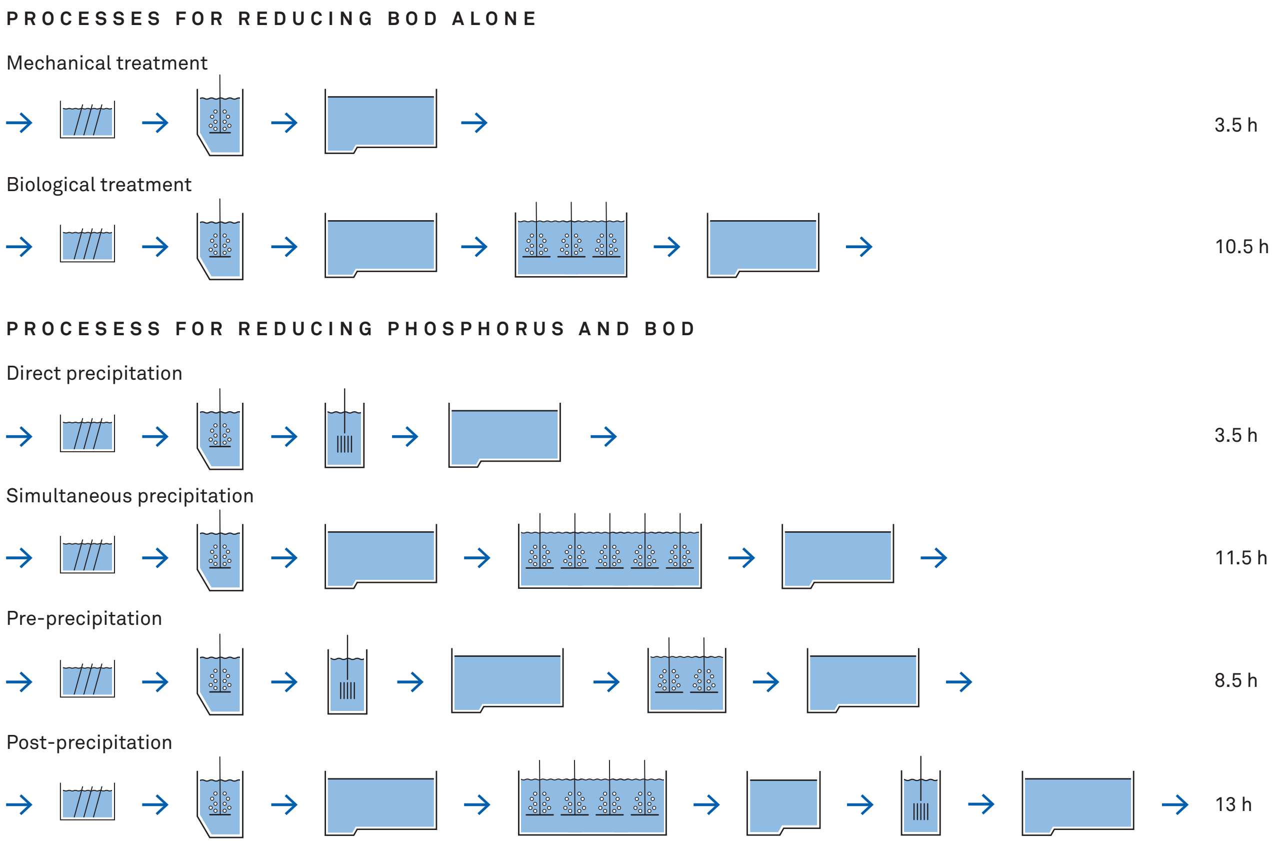
	Treatment efficiency, %				Total treatment time, h
Method	**BOD**	**P**	**Suitable products**		
Direct precipitation	70–80	>90	Aluminum Polyaluminum Ferric	PAX Lime	≈ 3.5
Pre-precipitation	>90	>90	Aluminum Ferric	Polyaluminum	≈ 8.5
Simultaneous precipitation	>90	75–90	Ferrous (Iron(II)) Ferric	Polyaluminum	≈11.5
Post-precipitation	>90	>90	Aluminum Ferric	Polyaluminum Lime	≈12

regular coagulants. The product selection depends on the nature of the water and what is supposed to be removed from it. If only SS need be removed a medium basic polyaluminum chloride or a polymer blend will probably be used, while if phosphate removal is important a ferric salt might be a better option. Alkalinity is a key parameter for the nitrification process in biological treatment, so if the alkalinity of the water is low a polyaluminum coagulant with a higher basicity is a good option since it consumes less alkalinity; lime and ferrous coagulants cannot be used.

A summary of chemical treatment methods

Table 3.25 shows the various processes, treatment results, and suitable precipitation chemicals. Detailed descriptions of these processes can be found in the section on chemical treatment processes.

Figure 3.27
Required retention time for various treatment methods.



Nutrient removal

Chemical phosphorus removal

Chemical phosphorus removal is based on two different mechanisms. Dissolved phosphorus (mainly phosphates) are precipitated as phosphate salts of iron or aluminum (and in a few cases with calcium). The particulate phosphorus is separated by agglomerating the particles into large, easily separated particles using coagulants. Depending on the chemical treatment method, one of the two mechanisms might be more dominant. For instance, in simultaneous precipitation with ferrous sulfate, the precipitation of phosphate is basically the only mechanism.

Products used for chemical phosphorus removal

The chemicals that give a high treatment efficiency for a relatively low cost are:

- Coagulants based on aluminum salts
- Coagulants based on iron salts
- Lime

When the chemicals are added they react with the dissolved inorganic phosphates and precipitate as insoluble salts. Therefore, the coagulants are sometimes referred to as precipitation chemicals. When inorganic coagulants are used, the metal salts also react with water and form metal hydroxides. Since the concentration of phosphate is low in the wastewater, efficient mixing is very important to prevent too much of the coagulant reacting with the water and forming hydroxide flocs.

Hydroxide also has some benefits since the flocs encapsulate precipitated metal phosphates and other suspended solids in the water (sweep coagulation), making the impurities easier to separate. This is typically what happens in a post-precipitation plant. In a direct and pre-precipitation process the initial particle concentration is much higher and particles are mainly separated by the coagulation mechanism as particle charge neutralization.

The chemical reactions are pH dependent, as illustrated in figure 3.27. The solubility of aluminum, iron, and calcium salts is highly dependent on pH. With inorganic coagulants the best results are achieved at slightly acid to neutral conditions. With lime (calcium) the pH needs to be high (9–10) before phosphate salts are precipitated.

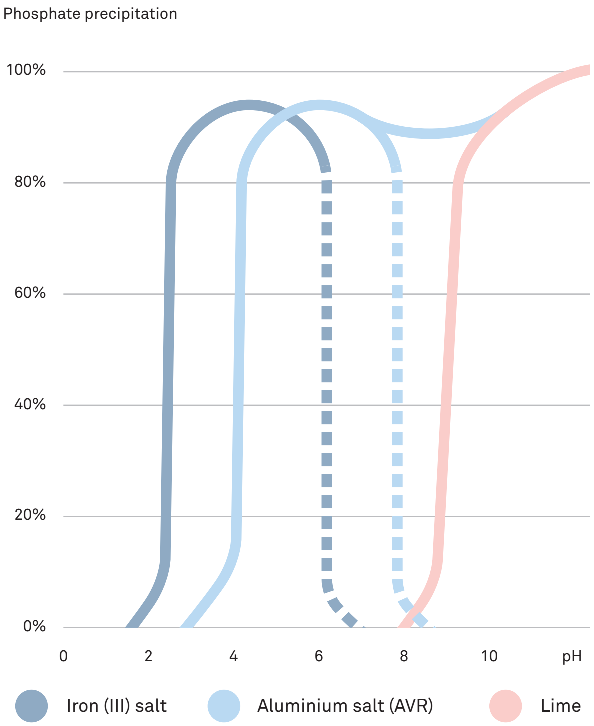
The particles in the water also coagulate to a greater or lesser extent depending on the type of coagulant used (see chapter 5). Generally speaking, highly charged products such as polyaluminum chloride result in more effective coagulation but are less efficient in terms of phosphate precipitation.

Phosphorus removal with aluminum coagulants

The aluminum ion (Al^{3+}) is the most effective ion for precipitating phosphates out of wastewater. Three valent aluminum is found in aluminum sulfate and chloride. Aluminum coagulants can also consist of polymerized aluminum, i.e. polyaluminum coagulants. The products can be polymerized to different degrees. The greater the degree of polymerization, the poorer the ability of the product to precipitate phosphates, since the aluminum ion has already partially reacted with water and has a lower charge per aluminum atom.

Figure 3.28

Orthophosphate precipitation with various coagulants as a function of pH. The dotted lines indicate coagulation in deionized water.



$$3Al^{3+} + 2PO_4^{3-} + 3H_2O \rightarrow (AlOH)_3\,(PO_4)_2 + 3H^+$$

$$Al^{3+} + PO_4^{3-} \rightarrow AlPO_4$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$$

In order to achieve effective precipitation of dissolved phosphorus with aluminum-based products the pH should be kept between 5 and 8.5. Depending on the coagulant type, it can be difficult to form flocs at the upper and lower ends of this pH range. Without flocs it is not possible to settle/separate the precipitated phosphorus, so the pH should preferably be kept between six and eight to ensure effective floc formation. The optimum pH varies from product to product and with water quality.

Theoretically it requires one mole (27 g) of aluminum to precipitate one mole (31 g) of phosphate, i.e. one gram of dissolved phosphorus requires 0.87 g of aluminum. The aluminum does not, however, react solely with the phosphorus in the water, but also with other compounds, including the water itself, which means that in reality it requires 1–1.5 moles of Al per mole of P. The molar ratio between the amount of metal needed and the amount of phosphorus removed is called the beta (ß) factor. A ß-factor of 1–1.5 is equivalent to 0.87–1.3 Al/g of P. If the phosphorus treatment process needs to reach low levels of ortho-phosphate (<0.2-0.3 mg PO_4-P/l), the ß-factor is higher.

Polyaluminum coagulants sometimes requires an even higher ß-factor. A highly charged polyaluminum product may require more than twice the dosage of aluminum to achieve the same reduction rate of dissolved phosphorus as an aluminum sulfate. However, polyaluminum coagulants are considerably more effective at removing suspended solids, i.e. including particle-bound phosphorus. Polyaluminum products are normally active over a wide pH range and have less influence on the alkalinity of the water. The better coagulation characteristics can result in a lower dosage requirement and hence lower sludge production than with aluminum sulfate.

Aluminum-based coagulants can vary to a much greater extent than iron-based coagulants in terms of product properties. It is therefore possible to find a suitable aluminum coagulant for basically any purpose. Another advantage with aluminum coagulants is that the precipitated phosphate remains stable even when the oxygen concentration is low. This reduces the risk of phosphate leakage during anaerobic conditions.


Aluminum is the most common metal in the Earth's crust. It is used as a raw material in the production of coagulants

Phosphorus removal with ferric coagulants

Trivalent iron coagulants (ferric) are either sulfate or chloride based, or a mixture of the two. Ferric nitrate can also be used, but the product is difficult to source and better suited to other water treatment applications.

As with aluminum coagulants, ferric-based coagulants produce phosphorus and hydroxide salts:

$$3Fe^{3+} + 2PO_4^{3-} + 3H_2O \rightarrow (FeOH)_3\,(PO_4)_2 + 3H^+$$

$$Fe^{3+} + PO_4^{3-} \rightarrow FePO_4$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

Iron(III) salts are effective at precipitating phosphates in the pH range 4–8. As with precipitation using aluminum salts, if the calcium ion concentration is high in the water the ferric product gives a relatively good precipitation of orthophosphates in the pH range 6–9. Iron and calcium ions do not produce any precipitation in this range individually. The best results and coagulation performance are obtained in the pH range 5–6, where hydroxide precipitation is most effective. Normally there is no problem with precipitation at considerably higher pH values, as shown in figure 3.15.

The precipitation of orthophosphate requires 1–1.5 moles of Fe^{3+} per mole of P. Even if the ß-factor is the same as for aluminum, more iron is needed on a weight basis due to the higher molecular weight of iron. To remove 1 g of P, 1.8–2.7 g Fe is needed.

Phosphorus removal with ferrous coagulants

Ferrous (iron(II)) coagulants are based on sulfates and chlorides and are normally by-products from different industrial processes. Since ferrous iron doesn't coagulate particles but only precipitates phosphate, it is debatable whether these products should be called coagulants or precipitation chemicals.

$$3Fe^{2+} + 2PO_4^{3-} \rightarrow Fe_3(PO_4)_2$$

The actual dosage of bivalent iron that is required is usually higher than the theoretical dosage (1.5 mol Fe/mol P). A reasonable dosage of iron to precipitate one gram of phosphorus from phosphate is 3.5 grams.

Because of the inability of ferrous coagulants to form flocs they are only useful for simultaneous precipitation, where the iron is oxidized due to the aeration and the resulting flocs are incorporated with the biological sludge. A long aeration period is required to produce acceptable treatment results.

$$4Fe^{2+} + O_2 + 2H_2O \rightarrow 4Fe^{3+} + 4OH^-$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

Each gram of Fe^{2+} that is oxidized requires 0.14 grams of O_2. The oxidation rate of the iron ions is heavily pH dependent. The oxidation rate increases with a higher pH.

One advantage when using iron-based coagulants is their ability to precipitate hydrogen sulfide in water and in anaerobic digestors.

Precipitation with lime

Calcium ions are effective at precipitating orthophosphate as hydroxyapatite when the pH exceeds 10.5. Lime provides the necessary pH increase for precipitation, and polyphosphates are also precipitated.

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$$

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \rightarrow Ca_{10}(PO_4)_6(OH)_2$$

The dosage of lime required is not based on the phosphate content, but primarily on the carbonate content and alkalinity of the water. Carbonate is precipitated as calcium carbonate when the pH is raised above nine. Lime precipitation produces a lot of sludge, although this is easily dewatered. When precipitating with lime the pH of the water must normally exceed 11 to produce a precipitate that can be separated readily. At this pH the original alkalinity of the water is also restored. The alkalinity would normally be reduced through precipitation of the carbonates in the water.

Nitrate-based coagulants

The cations in iron and aluminum-based products are normally sulfate or chloride ions. It is possible to partially or totally replace these with other anions, of which nitrate is the most common. A coagulant that contains nitrates can be used in more ways than a chloride or sulfate-based product.

After pure oxygen, nitrate provides the best source of oxygen for bacteria. The nitrate is broken down into nitrogen gas and water, while organic material is broken down simultaneously to form biomass and carbon dioxide (see also the section on denitrification). Most of the organic matter that is broken down is the more readily degradable type that is dissolved in the water. Dissolved organic material is difficult to precipitate, and then a nitrate salt can be useful.

The main purpose of using nitrate-based coagulants is not normally the removal of organic matter. Since nitrate will be removed in a denitrification process, the counter ion to aluminum or iron disappears. This can be an advantage where a high salt content is a concern, for instance in closed-loop systems.

Nitrate-based products can also be used for odor (hydrogen sulfide) control, as described on page 102.

Dissolved organic matter is difficult to precipitate out but can be degraded by using aluminum nitrate or iron nitrate.

Comparison of coagulants

The various coagulants available have different physical and chemical properties. They are supplied either in a solid form or as a solution. A comparison of these chemicals is shown in table 3.29.

Table 3.29
Physical and chemical properties of a selection of coagulants.

Coagulant	Composition	Supply form	Density t/m³	Metal content %	Metal content Mol per kg
AVR	Al and Fe(III) sulfate	Granules	1	Al 8.2 Fe 0.8	3.1
PIX	$FeClSO_4$ $FeCl_3$ $Fe_2(SO_4)_3$	Liquid	1.4–1.5	Fe 11.5–14	2.0–2.5
PAX	Polymerized Al salts	Liquid Powder	1.2–1.4 0.9	Al 5–10 Al 16	1.9–3.7 5.6
Iron(II) sulfate	$FeSO_4 \cdot 7H_2O$	Crystals	1.2	Fe 18	3.2
Lime	$Ca(OH)_2$	Fine granule Powder	0.6		

Biological phosphorus removal

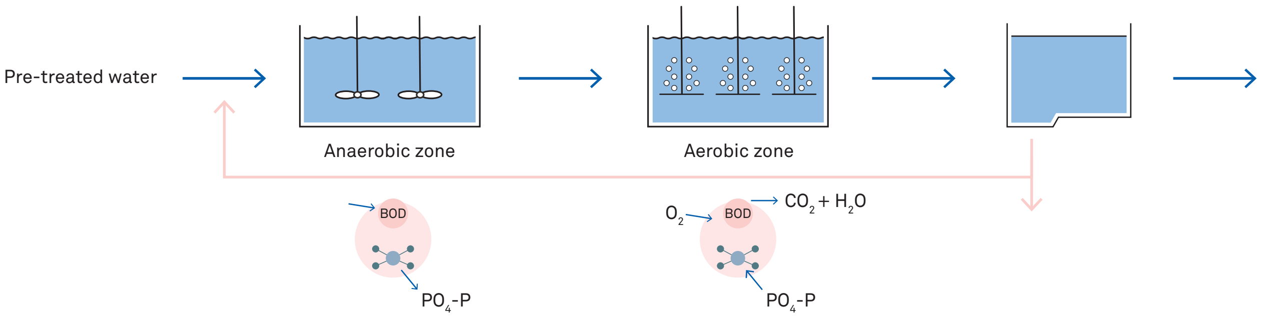
An alternative to chemical phosphorus removal is the biological method known as bio-P or enhanced biological phosphorus removal (EBPR). This method uses the ability of certain bacteria to take up unusually large amounts of phosphate from the water. This enhanced phosphorus uptake is achieved by “stressing” the microorganisms by exposing them alternately to anaerobic and aerobic conditions.

Bio-P bacteria have a greater ability to store energy (phosphate) than other bacteria in a treatment plant. The bacteria can then use this energy under poorer conditions, such as anaerobic conditions. This is exactly what happens in the bio-P process. During the first stage, which is anaerobic – i.e. free from oxygen and nitrate – recycled sludge is mixed with the wastewater. The wastewater contains a lot of “food” (organic matter) but no oxygen (to generate energy). The bacteria want to make use of this food and store it. In order to do this they need energy, and this is where the bio-P bacteria have an advantage over other bacteria due to their ability to store more energy in the form of phosphates. Once this energy has been used, the bacteria release the phosphates. During the anaerobic stage, the concentration of phosphates in the water rises above that of the influent water, while the BOD/COD content falls.

The second, aerobic stage of the bio-P process is the opposite of the anaerobic stage. In this case there is oxygen for energy production but a lack of food (due to competition between organisms). The bio-P bacteria therefore use their stored food to build biomass while also taking the opportunity to store polyphosphates for times when they are in short supply.

During the aerobic stage the phosphorus content of the wastewater is reduced to a level lower than that of the influent water. The bacteria then are recycled by pumping the activated sludge to the anaerobic zone. Some are removed as excess sludge.

Figure 3.30
Biological phosphorus removal.



Under stable operating conditions the above processes give Ptot values of between 0.5 and 2 mg P/l in the treated water. The relatively high value is partly explained by the fact that the suspended material in the treated water has a high phosphorus content. Treated wastewater with a SS content of 20 mg/l can give a phosphorus contribution of 1.2 mg P/l in addition to the contribution to the dissolved phosphorus which is seldom less than 0.3 mg/l.

It is difficult to maintain a stable process because phosphorus immediately goes into solution if the sludge is exposed to anaerobic conditions in the sedimentation basin or during sludge treatment, such as sludge digestion. Although it is possible to achieve effective phosphorus reduction using the bio-P process, it is usually supplemented by chemical precipitation to ensure a stable and high reduction efficiency. It is important for the bio-P process that the sewage contains volatile fatty acids (VFA); since the VFA content in influent water in most wastewaters is limited, this limits the installations of efficient bio-P plants that don't need to be supported with chemical treatment. An alternative is that sludge is hydrolyzed to produce VFA that can be used in the process. For instance, it might be possible to use the primary sludge as a source of VFA.

Most bio-P processes are combined with biological nitrogen reduction.

One challenge with the bio-P process is that the bacteria release phosphate during anaerobic conditions if the biosludge is stored for a long time or anaerobically digested. This phosphate will eventually be recirculated with reject water in the WWTP, increasing the internal load of phosphate in the treatment process. The internal load can be several 10s percent of the total phosphorus load. The high concentration of phosphate can also cause scaling on equipment and in pipes. Most importantly, sludge with a high phosphate content is more difficult to dewater and needs substantially more dewatering polymer.

Nitrogen removal

In municipal wastewater treatment plants that operate nitrogen reduction this is almost exclusively done using biological methods. The following is a description of how the various nitrogen treatment processes work and how they can be made more efficient with the aid of chemical precipitation. Alternative methods of nitrogen reduction are also described.

Biological nitrogen removal

All wastewater treatment plants remove some nitrogen. A small proportion of the total nitrogen content is bound to particles and separated during the primary treatment. If the treatment plant also uses biological treatment, some of the nitrogen will be taken up by the biological sludge since nitrogen is a nutrient and an important building block for all life. This form of nitrogen reduction is called assimilative nitrogen reduction. If these two nitrogen reduction processes are still not sufficient and higher nitrogen reduction is required, a more sophisticated nitrogen treatment process must be introduced.

If most of the nitrogen in wastewater is in the form of ammonium (NH_4^+), biological methods are generally used to remove the nitrogen in a two-stage process – nitrification followed by denitrification. This type of nitrogen treatment process, in which nitrogen is removed from the water as nitrogen gas, is called dissimilative nitrogen reduction. Ammonium is the cation form from ammonia, and as an ion it is difficult to precipitate (see the section on magnesium ammonium phosphate precipitation). Conventional chemical treatment with iron or aluminum salts cannot separate ammonium.

Nitrification

Nitrogen in the form of ammonium must first be converted to nitrate (NO_3^-). This is done using a biological process known as a nitrification. Autotrophic bacteria use oxygen in the air to oxidize ammonium to nitrate in two stages.

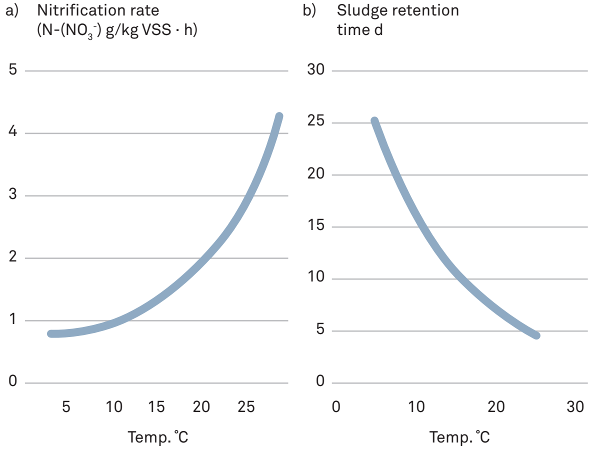
Stage 1	$NH_4^+ + 1.5O_2$	→	$NO_2^- + 2H^+ + H_2O$
Stage 2	$NO_2^- + 0.5O_2$	→	NO_3^-
Stage 1+2	$NH_4^+ + 2O_2$	→	$NO_3^- + 2H^+ + H_2O$

As can be seen from these formulae, the nitrification process produces acid. This reacts with the carbonate in the water, and if the alkalinity of the water is low (low carbonate content) then the pH may drop sharply during nitrification. This inhibits the nitrifying bacteria, since they work best at a pH between eight and nine. The nitrite-oxidizing bacteria do not take up ammonium, but ammonia, which is in equilibrium with the ammonium in the water. At a higher pH a larger proportion of the nitrogen occurs as ammonia and is more readily taken up by the bacteria. If the pH drops below 5.5 the nitrification process will stop completely. The oxidation of nitrite is however favored by a lower pH, so the pH must not be too high in the nitrification process.

Temperature also has a major effect on the rate of nitrification (figure 3.31). It is possible to carry out nitrification at temperatures down to 4°C, but the bacteria work slowly at this temperature. This means that the amount of organic sludge and the reactor retention time should be kept high, which requires large basin capacities and a high sludge age for biological treatment. Because the BOD-reducing bacteria are more effective than the nitrifying bacteria, fast and effective nitrification is achieved when the BOD content is low. Nitrification can take place on a fixed carrier material or in suspended cultures. The former process has shown greater tolerance to variations in pH.

Figure 3.31

a) Nitrification rate at different temperatures. b) Estimate of minimum sludge retention time needed for nitrification at different temperatures.



Denitrification

Denitrification means that microorganisms reduce nitrate to nitrogen gas while oxidizing organic matter in the absence of oxygen (see the equation below). The resulting nitrogen gas is released into the atmosphere.

$$NO_3^- + \text{organic matter} \rightarrow \tfrac{1}{2}N_2 + a{\cdot}CO_2 + b{\cdot}H_2O + OH^-$$

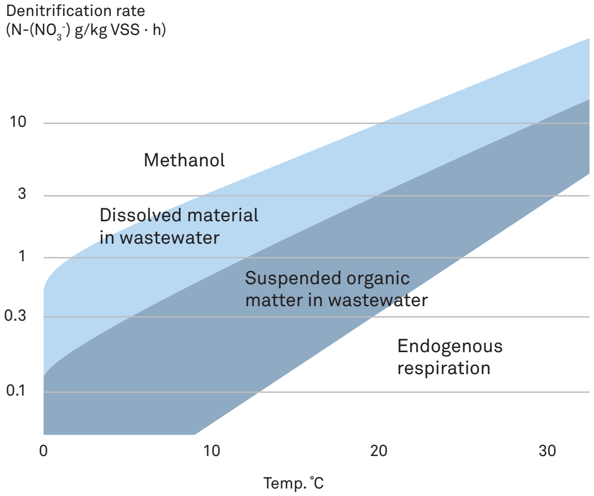
The organisms that can use both oxygen and nitrate for this oxidation process are known as facultative anaerobes. They prefer oxygen, as this gives a slightly higher energy yield. Because of this, oxygen must be excluded from the denitrification process. Anoxic conditions must apply, i.e. the water must be free from dissolved oxygen, but it must contain oxygen bound up as nitrate. These organisms are heterotrophic and need organic carbon as a substrate. The optimum pH for the denitrification process is between seven and nine.

As indicated by the formula, the process leads to an increase in alkalinity. Half of the alkalinity that is lost during the nitrification process is recovered.

The sources of organic matter for denitrification can be divided into two groups, internal and external. When referring to internal carbon sources it means that the organic content of the wastewater itself is used for denitrification. The dissolved fraction of internal organics gives the highest denitrification rate (see figure 3.32). Internal carbon sources also include the degradation of biological sludge during a process known as endogenous respiration. Soluble organics of primary sludge hydrolysis can be used as a readily available source of carbon. The less-accessible precipitated organic matter can be hydrolyzed in concentrated form, as primary sludge, and returned for denitrification in a more accessible form. This allows the treatment plant to be self-sufficient in carbon.

Figure 3.32

Denitrification rate for various organic matter sources.



External carbon sources are easily biodegradable surplus materials – such as methanol, ethanol, acetic acid, and starch – which are added to the process. External carbon sources are expensive, so they should only be used to supplement internal sources.

Table 3.33
Characteristics of some sources of organic matter.

Product	Denitrification rate N-(NO_3^-) g/kg VSS · h	COD content mg O_2/l
Glycol	7–10	1290
Acetic acid	12–16	1070
Propylene glycol	16–17	1680
Methanol	10–15	1500
Ethanol		1600

The denitrification rate is temperature dependent, but not to the same degree as the nitrification rate. The rate of denitrification and the space required depend largely on the composition of the carbon source.

Denitrification processes

There are several ways to set denitrification in relation to the nitrification of the biological treatment process: pre-denitrification, post-denitrification, simultaneous denitrification, or a combination of these. Pre-denitrification and post-denitrification can be usefully combined to obtain optimum benefit from the organic content of the water.

The pre-denitrification process utilizes the degradable organic matter in the influent wastewater as a carbon source. The nitrate that is produced in the subsequent aerobic zone is recirculated. The degree of nitrogen reduction depends on the degree of recirculation. The advantage of this method is that it uses readily available organics in the wastewater. Chemical pre-treatment is not a drawback since the readily available dissolved organic matter is still available after precipitation.

In the post-denitrification process wastewater goes first through an aerobic zone, where organic material is utilized and nitrogen is oxidized. Nitrate reduction can now proceed if degradable organic material is added. The advantage of post-denitrification is that a high proportion of nitrogen can be removed without the need for recirculation.

In a simultaneous denitrification process aerobic and anoxic conditions are combined and repeated in the same treatment basin. This process is typically used in oxidation ditch systems with long retention times.

Reject water from digested sludge dewatering can be treated in a separate biological reactor that operates in a sequence – filling, nitrogen removal (nitrification and denitrification or anammox), sedimentation, and emptying – which then repeats.

Pre-precipitation with nitrogen reduction

In a nitrogen removal process a carbon source is required for denitrification and is easily available in the form of organic material such as dissolved BOD. If the denitrification process uses the BOD in the wastewater as a carbon source it is said that an internal carbon source is used.

WWTPs that use internal carbon sources must use a pre-denitrification process. This process is more energy intensive than a post-denitrification process but can in many cases operate solely with an internal carbon source. Since pre-precipitation removes BOD there is a concern that too much BOD is removed and not enough is available for denitrification. The pre-precipitation mainly removes particulate BOD that is slowly degradable and hence not suitable as a carbon source. A mild to medium pre-precipitation therefore has little to no impact on the denitrification process; it might even be positive since only easily biodegradable substrate is left for the denitrifies. The denitrification zone can then be smaller.

Pre-precipitation can also support the nitrification process. With a high COD/N ratio, the nitrification is slow, therefore a pre-precipitation step that removes some of the COD improves nitrification.

A combined pre-precipitation and post-denitrification process gives the most compact design for a full nutrient removal plant. It is also easier to control since each process step is more well defined and less recirculation is needed.

It is also possible to use the sludge as an indirect carbon source. In the HYPRO process this is done by having a combined pre-precipitation and post-denitrification process. The difference between this and a conventional process is that in the HYPRO process the separated sludge is hydrolyzed. When sludge is hydrolyzed some low-molecule organic substances are released that can be used as a carbon source.

Sludge can be hydrolyzed by biological, enzymatic, chemical, or thermal means. It is preferable from an energy-consumption perspective if the digested sludge is hydrolyzed. If biological hydrolysis is used, primary sludge should be hydrolyzed.

Reduction during the HYPRO process

SS	>	90%
BOD	≈	90%
Ptot	>	95%
Ntot	≈	75%

The total hydraulic retention time is around 12 hours including pre-sedimentation.

See also the section on nutrient-salt reduction.

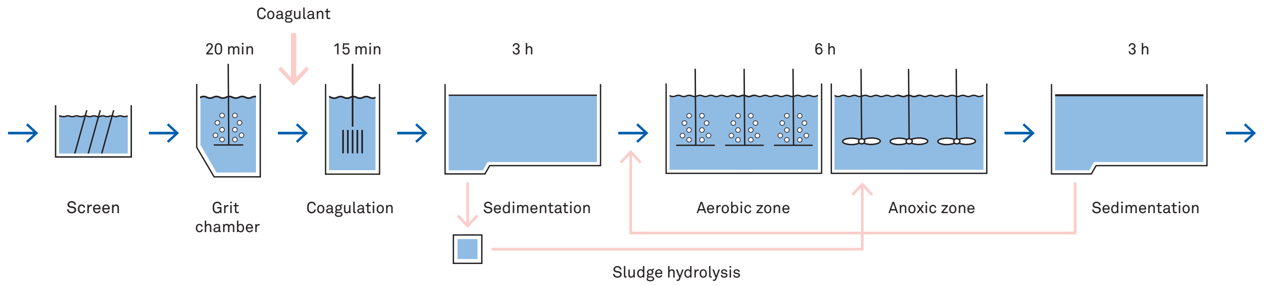


Figure 3.34
The HYPRO process.

Chemical-physical nitrogen treatment methods

Some chemical-physical methods for removing nitrogen are described below. These methods are normally applied to highly contaminated wastewater with high nitrogen concentration. They are therefore used mainly to treat reject waters or industrial wastewaters. The most common methods are stripping and magnesium ammonium phosphate precipitation.

Ion exchange or adsorption

Wastewater is made to pass through an ion exchange filter in which ammonium ions become attracted to the surface of the ion exchange resin. The larger the filters used, the lower the ammonium concentration in the treated water. The ion exchange medium is normally in the form of organic beads with a molecule with high affinity to the specific ion or group of ions incorporated. Natural minerals, such as zeolites, can also be used for ammonium adsorption.

Filters that adsorb ammonium can be regenerated using salts or acids. The wash water, the eluate, can both be considered as a waste and a resource. If the ammonium concentration is high enough the ammonium can be recycled or reused. Zeolite media can also be regenerated but in some cases it is just mixed with the sludge and disposed of.

This method is sensitive to suspended matter in the water and is also relatively costly when large flow rates needs to be treated.

Ammonia stripping

When the pH of wastewater is raised above 11 a large proportion of its ammonium is converted to dissolved ammonia gas. This ammonia can be driven off or stripped by injecting air or passing the wastewater through a column. The ammonia is then recovered in an acidic absorption column. Although this method requires large air-flow rates to treat wastewater it can still be an energy-efficient alternative to biological nitrogen removal as long as the original ammonium concentration is high (approximately 1,000 mg NH_4-N/l or higher). This process is suitable for treating highly contaminated water such as reject water.

The final product is normally highly concentrated ammonium sulfate or nitrate solutions and can be reused as a fertilizer directly on farmland or indirectly via a fertilizer production facility.

Ammonia can also be driven off at high temperature by steam stripping.

Membrane technology

Dissolved nitrogen compounds can also be separated from water in membrane filters, but an ammonium molecule is about the same size as a water molecule, which makes this very challenging. It is somewhat easier to separate nitrate. Because the membranes are highly sensitive to particles and some other impurities an extensive pre-treatment step before the membranes is needed. The membranes have a high pressure demand that makes them highly energy demanding. Because of this, membrane filtration for nitrogen removal becomes very costly and is therefore rarely used.

Struvite precipitation

Magnesium ammonium phosphate (MAP) is a double salt that is also known as struvite. If the water has high concentrations of phosphorus and ammonium and the pH is kept above 7.5–8, precipitation can be achieved by adding magnesium. Struvite precipitation is a well-known reaction in many wastewater treatment plants, particularly those that use the bio-P process. In the pipes after digestion the ammonium and phosphate contents can be high enough to promote MAP precipitation. This undesirable precipitation causes blockages in pipes from scaling. It can be prevented by ensuring that an adequate concentration of coagulant is present in the sludge to bind the phosphates, by using an antiscalant, or by installing a separate struvite precipitation reactor for phosphorus recovery.

The nitrogen content of wastewater is usually considerably higher than the phosphate content. This means that phosphates must be added to achieve effective nitrogen reduction. Adding phosphate is costly and may seem illogical, since one of the requirements the treatment plant must meet is the reduction of phosphorus. Therefore struvite precipitation isn't considered an ammonium removal process but rather a phosphorous recycling technology with the benefit of removing some ammonium as well.

Other chemical methods in wastewater treatment

Bulking sludge control

A bulking sludge problem is when activated sludge becomes voluminous and difficult to settle. SVI is high, normally >150 ml/g. In general, other issues also occur when facing challenges with bulking sludge. Maintaining the effluent standard is the most serious one; heavy foaming is another and can cause fatal problems in anaerobic digesters and also create a poor working environment.

Bulking sludge is a clear indication of an imbalanced biological treatment step and is normally caused by excessive growth of filamentous bacteria, which produce voluminous flocs. It can also be caused by excessive production of exocellular polymers in the bioflocs.

It is important to first identify what is causing the problem since bulking sludge can be caused by many different reasons. A microscope analysis of the sludge and the foam is essential. This will tell if the problem is being caused by exocellular polymers or by filamentous bacteria. Identification of the filamentous bacteria is also important since it shows why the problem has occurred. It is also important to understand the MLSS, content, sludge age, oxygen concentration, etc., in the activated sludge process as well as the chemical composition of the treated water.

With this information it is normally possible to adjust the process. In some cases this is as easy as changing the sludge age or oxygen concentrations, while in other cases more advanced methods incorporating chemical treatment are needed. It is important to use the right chemical product for the right purpose. For instance, extensive production of exocellular polymer can be an indication of phosphorus deficiency, in which case the coagulant dosage should be reduced or the product changed. If no coagulant is used, nutrients (phosphorus) must be added.

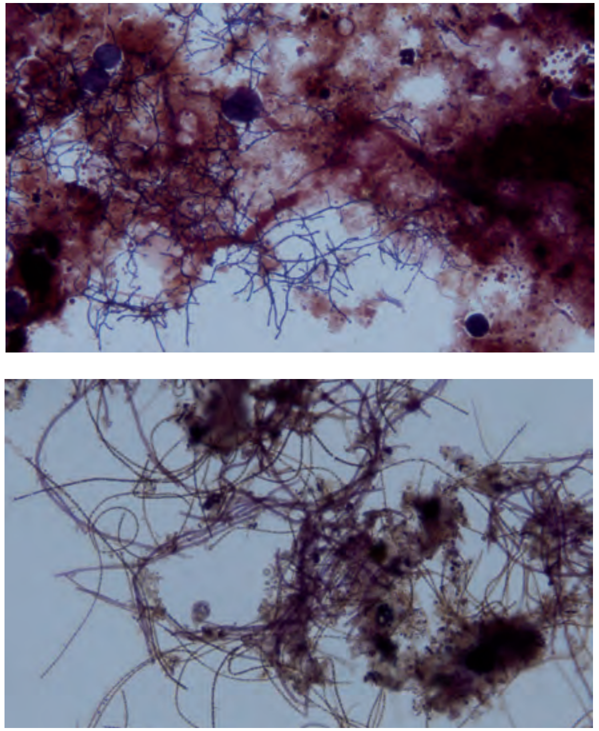
Another method is to add defoamer to the process to reduce foaming problems; however, if it isn't used correctly it can also cause problems with aeration. Polymers, iron, and polyaluminum coagulants are also commonly used to improve conditions at WWTPs.

Since sludge age can be high (sometimes >20 days) and the chemicals aren't killing the bacteria it can take several weeks for sludge ages to reach normal conditions. Normally, positive results are seen long before the full effect is reached. For instance, if a polymer is dosed to the activated sludge it can become more compact and settle more easily but it could still take several weeks before the activated sludge process achieves a healthy state.

There are also some more drastic methods where the purpose is to kill the bacteria that is causing the problem. Normally this is done by adding a strong oxidant that reacts with the bacteria directly. Since the filaments protrude out of the flocs they are more vulnerable than the floc-forming bacteria, which protect each other by growing in groups. However, the activated sludge system is a "living organism" that is sensitive to disturbances, and since it is difficult to find the right dosage of an oxidation chemical the risk of overdosing is high. There are many examples where the entire activated sludge process has been destroyed as a result of overdosing, therefore this drastic treatment method should only be applied in emergency situations when no other method has worked.

Oxidants used are chlorine, hypochlorite, ozone, hydrogen peroxide, and performic acid. Since chlorine-based oxidants form chlorinated organic substances they should be avoided.

Figure 3.35
Two of the most common foam forming filaments seen in microscope after colouring. Above Mycolate (commonly known as Nocardia). Below Microthrix parvicella.



Stormwater treatment

Stormwater conditions occur when the WWTP or sewage network cannot handle the influx of wastewater. This typically happens during heavy rainstorms or when snow melts. Another term for stormwater events is combined sewer overflow (CSO). This term is typically used when the sewage system can't handle all the water in the pipes and needs to release some wastewater, for instance at a pumping station, since the pump doesn't have enough capacity to forward all the water.

A stormwater event means that some of the water is released without sufficient treatment or even with no treatment at all. This can have a harmful impact on the recipient water but also on the WWTP itself since effluent demands are not met. Since WWTPs normally remove >90–95% of the impurities in the water a minor release of untreated wastewater can have a significant impact on the fulfilment of requirements. Phosphorus and bacteria count are normally the most challenging. Chapter 7 describes how to handle bacteria during stormwater events.

Stormwater conditions also affect WWTPs even though they are normally capable of handling at least double the hydraulic flow they are designed for. Normally the biological treatment step is the most sensitive unit during high flows. The secondary sedimentation capacity isn't sufficient and more SS is released, causing values to be too high in treated water. One way to solve this problem is to dose a small amount of polymer in the influent to the secondary settling tanks. Both anionic and cationic polyacrylamides are used for this purpose. The charge of the polymer depends on the sludge characteristics. With the addition of a polymer the surface load on the secondary sedimentation can be increased.

If the flow is too high, part of the wastewater needs to bypass the biological treatment step otherwise there is a risk that a lot of the activated sludge will be flushed away, resulting in consequences for the WWTP that take a long time to recover from. If the water bypasses biological treatment it is normally subject to primary treatment, but in extreme cases even the primary treatment also has to be bypassed.

Chemical treatment can help during stormwater conditions. For example, using a polymer to improve the settling rate in secondary treatment has already been mentioned, and this can also be applied in a primary settling tank. Chemical treatment with coagulants, with or without polymers, can minimize the impact of a stormwater event. This can be done in a conventional primary settling tank, i.e. pre-precipitation, or in units only designed to start up during high flows. Examples of equipment are disc and drum filters with a cut-off between 5 and 50 µm and ballasted sedimentation tanks.

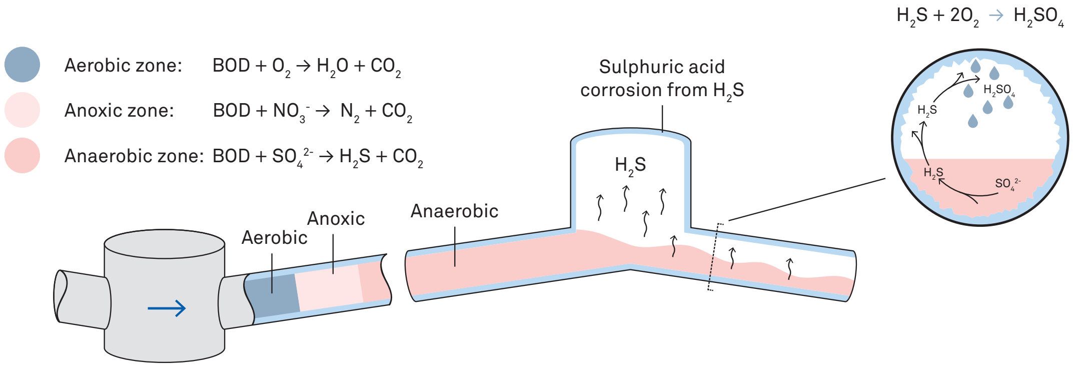
The purpose of stormwater treatment is to rapidly remove as many impurities as possible. This means much harsher physical conditions than normal, and chemical treatment is key to achieving efficient stormwater treatment. Normally coagulants and flocculants are combined: the coagulants are used to agglomerate the small particles while the flocculants build strong flocs that can handle the tough physical conditions.

With efficient stormwater treatment it is possible to reach similar levels as with a well-working direct precipitation plant. BOD can be removed to around 75%, SS and phosphorus to above 90%, and bacteria are also removed to a great extent. There are direct precipitation plants that remove 99% of the inlet bacteria.

Odor control

Odor is something that is frequently associated with wastewater treatment plants and sewers and is often caused by hydrogen sulfide, which is formed by bacteria when water is septic. The bacteria in the water that can break down organic material prefer to use oxygen as an electron acceptor. If oxygen is not present then the next in line is the nitrate ion, followed by the ferric ion (Fe_3^+), and then the sulfate ion. The reactions when using oxygen, nitrate, and sulfate as an electron acceptor are shown in figure 3.36. Because nitrate and ferric ions are rarely present in wastewater it is the sulfate ion that is used as an electron acceptor once the oxygen has been used up. The sulfate ion is then converted to hydrogen sulfide (H_2S). This happens mainly in pressurized sewers.

Figure 3.36
Formation of hydrogen sulfide and sulfuric acid in a sewer pipe.



Hydrogen sulfide is a colorless gas with a distinctive smell of rotten eggs. It is highly toxic and has a very strong smell even at low concentrations. Because hydrogen sulfide is heavier than air there is a risk that the concentration in sewers will reach dangerous levels. There have been several cases of workers being killed by hydrogen sulfide gas while working in sewers.

Hydrogen sulfide is not only smelly and highly toxic, but it can also be converted to sulfuric acid by certain types of bacteria. This takes place in unfilled spaces in sewers. The bacteria live on the inside surface of the pipes and are extremely resistant to acid environments – they can withstand a pH of less than 1. At such low pHs the sewer pipes corrode rapidly, and sooner or later the sewer will collapse. This phenomenon is well known and can be extremely costly. To prevent corrosion and minimize health risks hydrogen sulfide formation must be avoided. The sulfide can also react directly with the concrete and cause corrosion.

Odor control methods

One effective method of odor control is to ensure that the water is always well oxygenated, but this is not possible in pressurized sewer pipes with a long retention time. The state-of-the-art method to address this problem is to add nitrates or iron in combination or separately with the help of smart dosage-control algorithms.

Nitrate salts

Nitrate is a good acceptor of electrons when oxygen is not available. If nitrate is present in the sewer wastewater it drastically reduces the risk of hydrogen sulfide formation.

Nitrate salts have a preventive effect and partially reduce the organic load on the downstream treatment plant. However, it is important not to overdose for two reasons:

1. Excess nitrate releases nitrogen gas which can disrupt the functionality of a pressurized sewer.
2. Excess nitrate increases the N-load to the downstream WWTP.

$$5H_2S + 8NO_3^- \rightarrow 5SO_4^{2-} + 4N_2 + 4H_2O + 2H^+$$

Nitrate-based products that are used to combat hydrogen sulfide formation include calcium, sodium, magnesium, aluminum, and iron nitrates.

Iron salts

Iron ions combine with sulfide ions to form salts with very low solubility. This means that if a bivalent or trivalent iron salt is added to wastewater, it will react with the hydrogen sulfide in the water and prevent it from entering the gas phase. The precipitated salt is always a ferrous iron but a ferric salt can be used for odor control; the reaction is slightly different and elementary sulfur is also produced as shown in the reactions below.

$$Fe^{2+} + S^{2-} \rightarrow FeS$$
$$2Fe^{3+} + 3S^{2-} \rightarrow 2FeS + S_0$$

If trivalent iron is added to the water before hydrogen sulfide has formed it will have a preventive effect as well since the bacteria prefer trivalent iron to sulfate as an electron acceptor.

Prevention through the addition of trivalent iron:

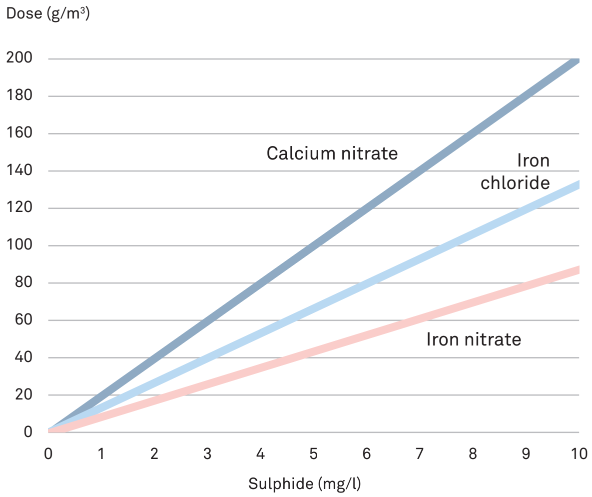
$$Fe^{3+} + BOD \rightarrow Fe^{2+} + CO_2$$

Using iron is a more economical method than using nitrates. It is also less important to control the dosage since excess iron will be used for phosphorus reduction in the WWTP. The disadvantage of iron-based products is that they lead to a small increase in sludge production at the plant.

Ferric nitrate salts

Ferric nitrate is a combination of the two products mentioned above. Because of this, ferric nitrate has a powerful inhibiting effect on hydrogen sulfide formation as well as a good reduction efficiency even if sulfides do form in the sewers. In this respect ferric nitrate is unique in that it can be regarded as a separate product whose characteristics make it far superior to the other two groups of products.

Figure 3.37
Comparison of three different products for sulfide removal.
Iron nitrate is in the form of ferric nitrate.



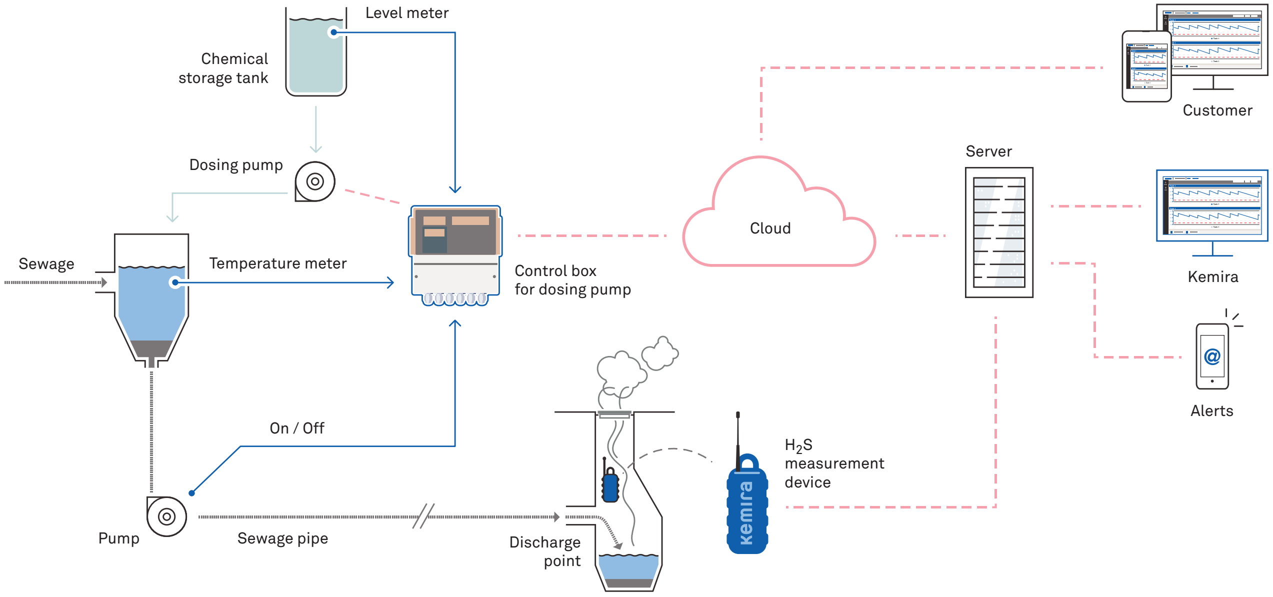
Dosage control

The formation of sulfides in sewer systems depends on a number of parameters, some of the important ones being temperature, redox potential, and retention time in the sewer. Since these parameters vary, a dosage-control algorithm that adjusts the chemical dosage based on real-time data is helpful. There are algorithms that control the dose based on the results (sulfide levels downstream) and algorithms that predict sulfide formation and then dose according to that data. A combination of these two dosing strategies is preferable.

Table 3.38
Typical chemical products for odor control .

Brand name	Active ingredient
Kemira OCC	Ca-nitrate and iron salts
FIN-12	Fe-nitrate
KemConnect OCC	Smart dosing system

Figure 3.39
Example of sulfide dosage control where two algorithms are combined. The data is automatically uploaded to a dashboard for value quantification.



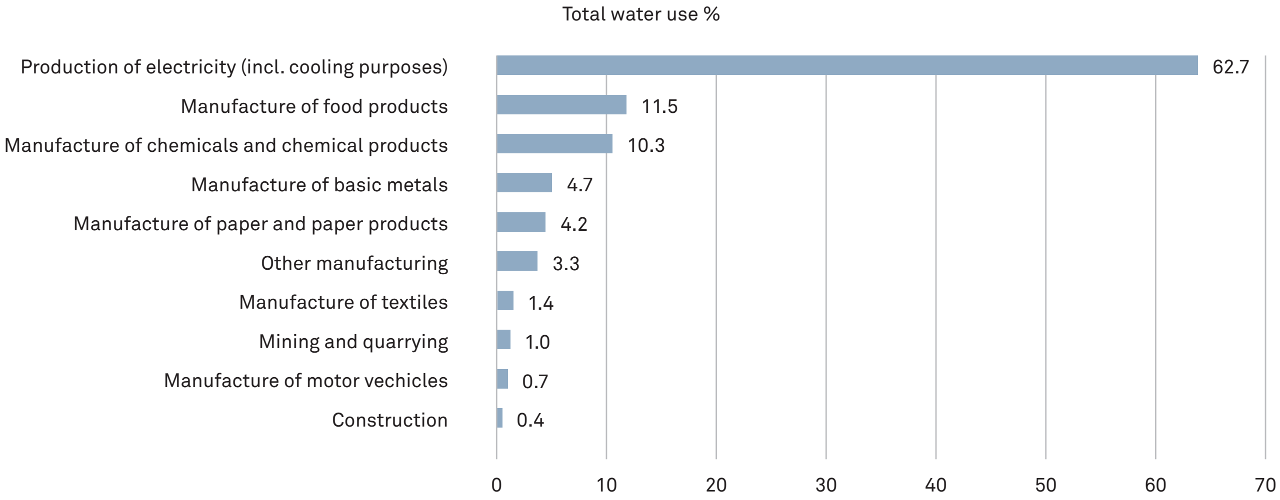
Industrial water

Water types

Untreated water, raw water, can be used for farming, construction, or cleaning purposes. Farmers use it to irrigate crops or give it to livestock to drink, storing it in man-made lakes or reservoirs for long periods of time. Construction industries can use raw water for making cement or for damping down unsealed roads to prevent dust from rising. Raw water from the sea is used only in coastal power plants for cooling purposes.

For industrial processes like inland power generation, the manufacture of food, or paper products, raw water must be treated before being used. The first steps are typically mechanical cleaning, coagulation, flocculation, and sedimentation. Additional treatment steps with membranes or disinfection may also be used.

Figure 3.40
EU average of total water use for industrial categories
(average of 17 EU member states, data from 2009–2011)
Ref.2: Eurostat (online data code: env_wat_cat; env_wat_ind)



During summer the demand for raw water rises dramatically, e.g. for cooling purposes. The hot summer in 2019 resulted in river water shortages in some European countries and a subsequent reduction in raw water supply. This led to power plants having to reduce or even stop power production because of a lack of cooling capacity.

Globally, about 70% of freshwater is used for agricultural purposes. Many countries face serious problems meeting the increasing demand for water from agricultural and other industrial processes. Water reuse can play an important role in supplementing raw water sources.

Industrial wastewater treatment

Process water is usually so contaminated that it cannot be discharged directly into a river or sent to a municipal treatment plant without pre-treatment. In contrast to municipal wastewater, the contaminants that must be removed vary widely, depending on the type of industry.

Industrial wastewater treatment methods

There are many different ways to treat industrial wastewater and the chosen method will mainly depend on what needs to be removed in order to meet the relevant threshold limits.

Table 3.41
Likely contaminants in various industries.

Likely contaminants in industrial wastewater	
Suspended solids	Sand, soil, hydroxides, fibers
Undissolved oxygen-demanding substances	Grease, oil
Dissolved oxygen-demanding substances	Organic material (phenol, sugars, proteins)
Other dissolved substances	Cations, anions, hardness
Colorants	Pigments, dyes, humics
Toxic metals	Cd, Cr, Cu, Zn, Ni, Pb
Nutrient salts	Phosphates, nitrogen compounds

Industry	**Contaminants**
Electricity production (cooling towers)	SS, organic material, hardness, salts
Dairy/meat processing	Grease, oxygen-demanding substances, odor, nutrient salts
Chemical production	Oxygen-demanding substances, toxins, odor, phenols, nutrient salts
Pulp and paper production	SS, organic material, hardness, salts
Mining	SS, toxic metals, nutrient salts
Textile production, dyeing	Paint, oxygen-demanding substances, odor, SS, toxic metals

The following methods are commonly used:

- Mechanical treatment
- Chemical precipitation
- Biological treatment
- Adsorption using activated carbon

- Flotation
- Belt filtration
- Membrane filtration
- Electrodialysis
- Ion exchange

Depending on the required treatment results, various treatment methods may be combined or used independently to achieve the best results. The wastewater flow in industries can be continuous or discontinuous. This means that in some cases treatment is intermittent or wastewater is collected in an equalization tank to even outer flow.

Preliminary treatment

Preliminary treatment describes the very first treatment step, e.g. for river water (surface water). The purpose is to remove tree branches, leaves, and any other material with a coarse screen.

Chemical precipitation

Chemical precipitation is used to reduce the majority of contaminants that occur in raw water and industrial wastewater. The basic steps are coagulation and flocculation followed by sedimentation, filtration, or flotation processes.

Inorganic and organic coagulants are used for precipitation in combination with an anionic organic flocculant to strengthen the flocs. The detailed process steps are different in various industrial applications. Power plants typically use an inorganic coagulant for raw water treatment followed by a sedimentation tank to reduce SS and COD. Further treatment steps include reverse osmosis (RO) before the water is used as feed water for cooling towers.

Wastewater from certain industries, such as dairy and meat processing, may require combinations of inorganic and organic coagulants followed by a flotation unit to remove fat and COD. This pre-treated wastewater is further processed in biological treatment steps before being discharged to a river or a municipal wastewater treatment plant.

Biological treatment

Most biological treatment methods that are used in municipal wastewater treatment are also used in industry. The factor that distinguishes industrial from municipal wastewater is the lack of nutrients in the influent. Phosphorus (phosphoric acid) and nitrogen (urea) must therefore be added separately in order to keep the BOD:N:P ratio at 100:10:1 for effective results.

Anaerobic pre-treatment is applied in many industrial wastewater plants to reduce high loads of easily degradable substances prior to chemical precipitation.

For smaller wastewater flows a sequencing batch reactor (SBR) is often used. This type of treatment combines all biological steps (aerobic aeration, anaerobic mixing, and sedimentation) in a single tank.

Adsorption using activated carbon

Activated carbon has a very large surface area and pores of varying sizes, and this combination is used to bind larger dissolved organic contaminants by adsorption. Since the surface of activated carbon is hydrophobic, hydrophobic substances can be removed better than hydrophilic ones. Activated carbon comes mainly in two forms, as powder or as granules. The powder form is added directly to the water during the coagulation step and then precipitated with the sludge.

Granulated activated carbon is placed in a filter cartridge. It has a limited adsorption capacity and must therefore be replaced after a certain period of use. Granulated activated carbon is regenerated prior to reuse. Activated carbon is used e.g. in drinking water production but also in many other industrial applications.

Flotation

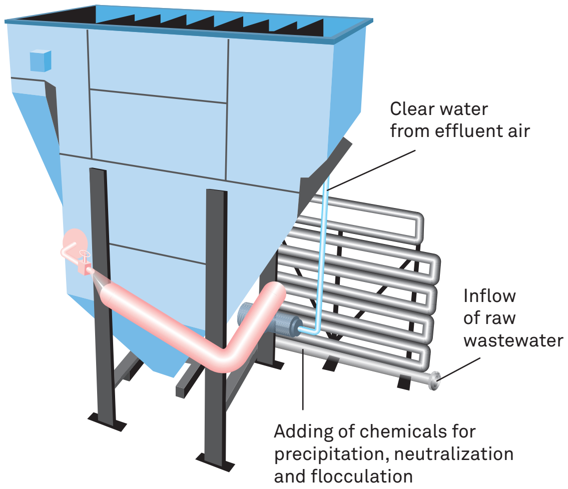
Separation by flotation is commonly used in industrial wastewater treatment applications. It requires chemical pre-treatment in a flocculator. A typical process sequence consists of the addition of a coagulant followed by pH adjustment and finally the addition of a polymer to ensure effective flocculation.

The flotation process involves adding a mix of clean water saturated with air at high pressure to the chemically treated wastewater. When pressure is released, small air bubbles are formed that attach themselves to the flocs and lift them to the surface, where they can then be scraped off as sludge.

Flotation is often used in dairies and slaughterhouses, where grease is mixed in with the incoming wastewater.

Figure 3.42

Flotation plant.

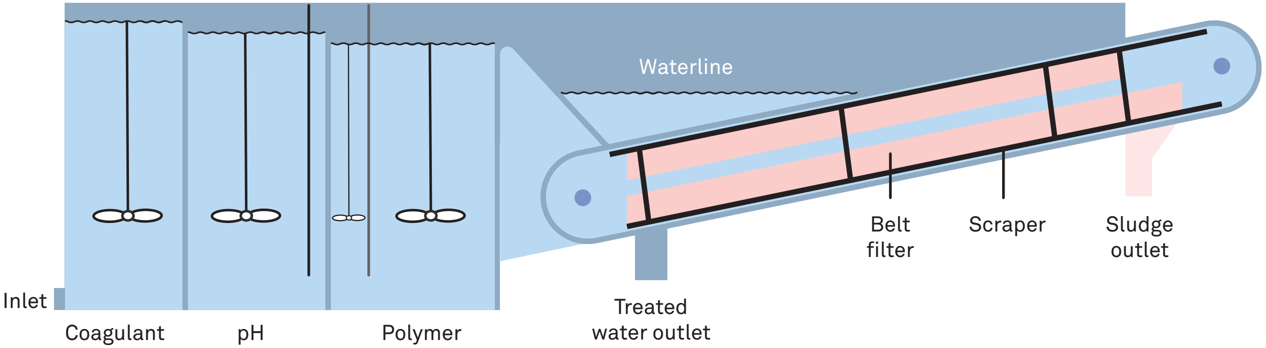


Belt filtration

Belt filtration is based on a chemical pre-treatment step followed by an endless belt filter. A typical process sequence consists of the addition of a coagulant in the first chamber followed by pH adjustment in the second chamber and finally the addition of a flocculant to ensure effective flocculation in the third chamber. The flocs are then removed from the aqueous phase by the subsequent belt filter. The sludge can be further dewatered in a filter press or centrifuge.

Figure 3.43

Belt filter.



Belt filtration is widely used in treatment processes where grease is not mixed in with the incoming wastewater.

Electrodialysis

Electrodialysis is sometimes used for recovering dissolved contaminants such as metal ions. The method is based on letting the contaminated water pass through an electric field so that the positive ions are drawn to a negatively charged electrode, or conversely, so that the negative ions are drawn to a positively charged electrode.

Between the electrodes are a number of membranes that are permeable to either positive or negative ions. This leads to the concentration of, for example, positive ions in one chamber and their reduction or complete removal from the other chamber.

Ion exchange

During ion exchange the undesirable ions in the contaminated water are replaced with other more environmentally friendly ions. An ion exchange unit works rather like a filter that traps ions in the ion exchange medium. The ion exchange unit only removes positive or negative ions. It has a limited capacity and must be regenerated once the ion exchange matrix has become saturated.

Ion exchange is often used to soften water by exchanging Ca^{2+} with Na^+ cations. Regeneration is necessary with a NaCl solution.

Reverse osmosis

Reverse osmosis (RO) is a water purification process that uses a partially permeable membrane to remove ions or unwanted molecules. High pressure is applied to overcome the osmotic pressure, forcing the ions and molecules to pass the membrane. The result is that the concentrate, retained on the pressurized side, contains all unwanted ions and molecules whereas the permeate, as ultra-clean water, has passed through the membrane.

RO requires pre-treatment (coagulation, flocculation, filtration) to remove suspended solids and other impurities that can block the membranes. Iron coagulants or high basic polyaluminum salts are preferred.

RO is used in boiler and cooling tower makeup water where very low salt concentrations are required.

Antiscalants are crucial to prevent scale forming on the surface of the membranes, and regular cleaning is needed to keep the flux (l produced water/m² surface · hour) at the highest level.

Table 3.44
Typical Kemira products for raw water and wastewater treatment.

Brand name	Active ingredient	Main use and characteristics
Kemira PIX / PAX	Fe / Al	Inorganic coagulant for raw water and wastewater treatment
Kemira Superfloc	Polyamine or poly-DADMAC	Organic coagulant for raw water and wastewater treatment
Kemira Superfloc	Polyacrylamide	Flocculant for raw water and wastewater treatment
Kemira KemGuard	Polyacrylate/formulated	Antiscalant for RO scale prevention
Kemira KemConnect		Smart process optimization
Kemira Kemisorb	Activated carbon	Adsorbent for organic contaminants
KemConnect DEX	Performic acid	In-situ disinfection unit for all kinds of water applications

Power plants

Power plants for electricity production are located in areas with a reliable supply of raw water, such as coastal areas where seawater is used and inland areas where surface water is readily available from rivers or lakes. The main application for treated raw water is cooling towers to cool down excess heat and boilers for steam production.

Power plants have two types of cooling tower systems: “once through” and “recirculating”. Once-through systems are found mainly in coastal areas, whereas recirculation systems are used inland. The main difference is the raw water demand. Once-through systems require high volumes of raw water, whereas recirculation systems need much less because they circulate the water several times until a critical salt concentration is reached.

Water treatment for a once-through system is rather simple. The first step is a mechanical cleaning, followed by disinfection to remove shellfish, algae, and any other organic material. This pre-treated seawater is used as feed water for the cooling system and after heat transfer it is released back into the sea.

Recirculating systems require more advanced raw water treatment. The treatment steps are mechanical treatment, chemical precipitation, sedimentation, decarbonization, and RO. Recirculating systems tend to concentrate all dissolved ions. If the critical ion concentration is exceeded, scale precipitation starts to occur in pipes or other surfaces, which reduces the heat transfer coefficient. This must be avoided under any circumstances. Polyacrylates are added as antiscalants to disperse high ion concentrations. Decarbonization (reduction of HCO_3^-) requires the addition of lime at a pH of 10.2, which leads to a precipitation of $CaCO_3$.

Sludges from raw water treatment processes are easy to dewater in filter presses as the main contents are inorganic components; anionic polymers are mainly used for this application.

Wastewater from power plants primarily comes from flue gas treatment processes in coal-fired plants to reduce environmentally harmful substances such as toxic metals, dioxins, and furanes. Both dry and wet processing are used for this application. Wet processes require chemicals such as caustic soda or special coagulants to remove toxic metals; iron coagulants are commonly used in these processes.

Food production (dairy and meat)

Wastewater from dairy and meat industries is processed using chemical precipitation followed by biological treatment. Large factories have their own anaerobic treatment step prior to chemical precipitation. Anaerobic treatment is very common in the food industry as this type of wastewater usually has a high concentration on easily degradable substances which can be converted into biogas for power generation.

Inorganic or organic coagulants are added to remove larger suspended particles, fats, colloidal particles, proteins, phosphorus, nitrogen, and some dissolved organic substances. Organic flocculants, which in this type of application are anionic or cationic, form large flocs. The most common method of separating sludge is by flotation since the nature of the sludge makes it suitable for this method. In order to achieve satisfactory treatment results it is important to have the right pH during the precipitation stage. The optimum pH varies depending on the type of coagulant but is usually between 5 and 6.

Table 3.45
Typical treatment results for chemically treated wastewater from dairy and meat industries.

Parameter	Treatment efficiency
Grease	95%
COD	85%
Nitrogen (N_{tot})	60%
Phosphorus (P_{tot})	95%

The excess sludge from chemical precipitation and biological treatment can be dewatered in centrifuges by adding cationic flocculants. This sludge can be processed further in an anaerobic digestor since it has a high biogas potential.

Oily water treatment

Oily water

Wastewater containing oil is generated in various industries including oil and gas production, petroleum refineries and other petrochemical facilities, food processing, and steel manufacturing. Oil is immiscible in water and two phases are eventually formed. This type of wastewater typically requires treatment because of its potentially harmful effects on the environment and human health.

Oil in water can be divided into three groups: free oil, emulsified oil, and soluble oil. Depending on the type of oil present in water, different separation/treatment methods and chemistries are applied.

Free oil

When the amount of oil in water is high or the oil droplets are large (>150 µm) it is classified as free oil. This type of oil is separated using physical separation, where the oil floats to the surface because it is less dense than the water. In applications such oil and gas production, chemicals like de-emulsifiers are added to accelerate the phase separation process.

Emulsified oil

Emulsified oil, where droplets are in the size range 10-100 µm, is more stable than free oil and requires both chemical and physical separation. De-emulsifiers are commonly used to reduce the surface charge or surface tension of oil and thus accelerate droplet coalescence, with the bigger droplets separating more quickly (Stokes' law). Physical methods like hydrocyclones and gas flotation are common processes used to separate emulsified oil.

Soluble (dissolved) oil

This type of oil includes benzene, toluene, ethylbenzene, xylenes, phenols, low molecular weight aromatic compounds, and carboxylic acid. Soluble oils are not removed effectively using oil-water separation methods; instead, they are removed by adsorption with activated carbon or a synthetic adsorbent such as organoclay. Emulsified oil can be also retained by adsorbents.

Produced water treatment

Produced water is any water stream that flows from an oil or gas-producing reservoir (Ref. 3. Walsh, J.M., Produced Water: Volume 1: Fundamentals, Water Chemistry, Emulsions, Chemical Treatment. Petro Water Technology, 2019). The sources of produced water are formations (rocks) that acts as traps for oil. In the beginning they are saturated with saline water; as time passes and the oil is released it propagates inside formations and replaces part of the saline water. This water, along with water injected during production, is called produced water and is the largest wastewater stream generated in oil and gas upstream. It is estimated to be around 250 million barrels per day (bbl/d, or about 39.7 million m^3/d) compared to 100 million bbl/d of oil produced (https://www.producedwatersociety.com/research/resources/global-hydrocarbons-production). This means that production of each bbl of oil generates about three bbl of produced water. The amount of water co-produced with oil varies during the lifetime of the reservoir. Mature reservoirs generate up to 10 bbl of water per bbl of oil. Produced water characteristics depend on several variables including formation geology, the lifetime of the reservoir, the extraction method, and the type of oil and process chemicals. It contains different organic and inorganic compounds including oil (2–600 mg/l), salt (total dissolved solids: 100–400,000 mg/l), process chemicals like corrosion/scale inhibitors, and solids from formations or corrosion/scaling (total suspended solids: 1.2–1,000 mg/l) (Ref. 4. J. Hazard. Mater. 170 (2009) 530-551)

The majority of produced water (up to 80%) onshore is re-injected into the reservoir to maintain hydraulic pressure and enhance oil recovery, while in offshore extraction the produced water is discharged directly into the sea. For re-injection, the main target of the water treatment process is to remove emulsified oil and solids to prevent plugging of the reservoir or pump damage. For direct discharge the main objective is to reduce the oil content down to the discharge limit. The treatment process offshore is different to onshore due to limitations on space and treatment time. Onshore treatment includes settling, gas flotation, and nutshell filters. In offshore treatment processes, hydrocyclones are more common because they enable highly efficient oil removal in a short space of time. A cyclone uses centrifugal acceleration to separate oil from water.

Figure 3.46 and 3.47 show a generic produced water treatment process for offshore and onshore. The average oil content in produced water is approximately 500 mg/l.

Figure 3.46

A generic water treatment process for offshore oil and gas production.

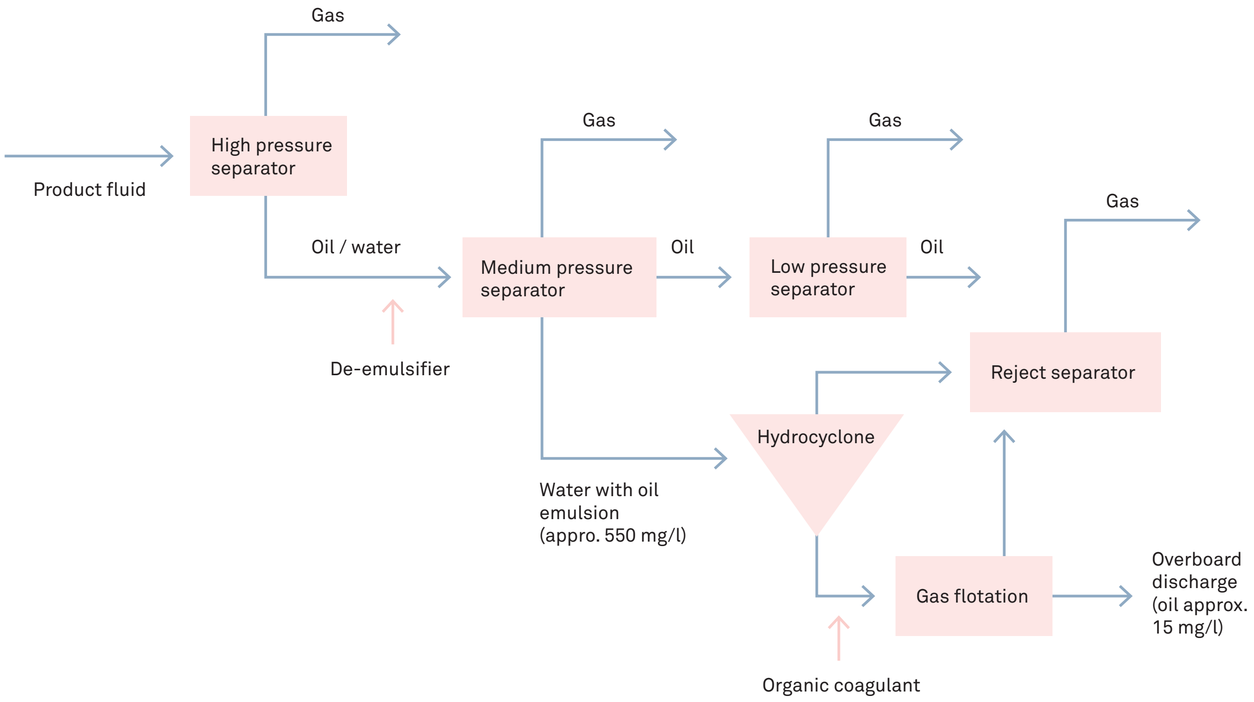
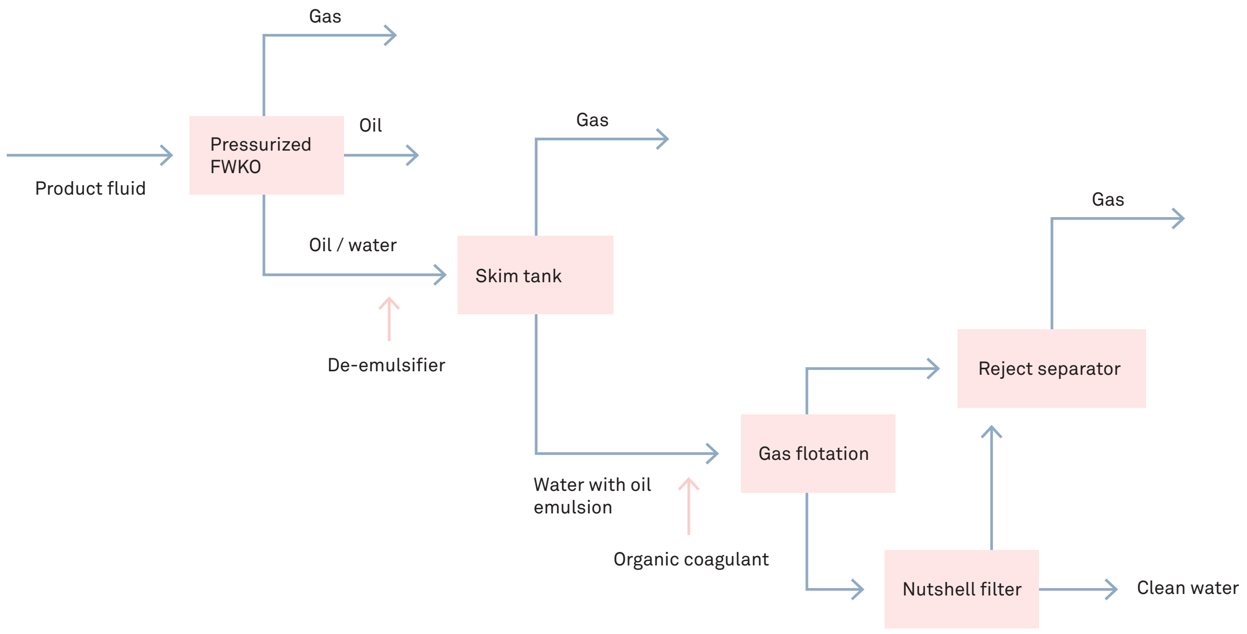


Figure 3.47
A generic water treatment process for onshore oil and gas production.



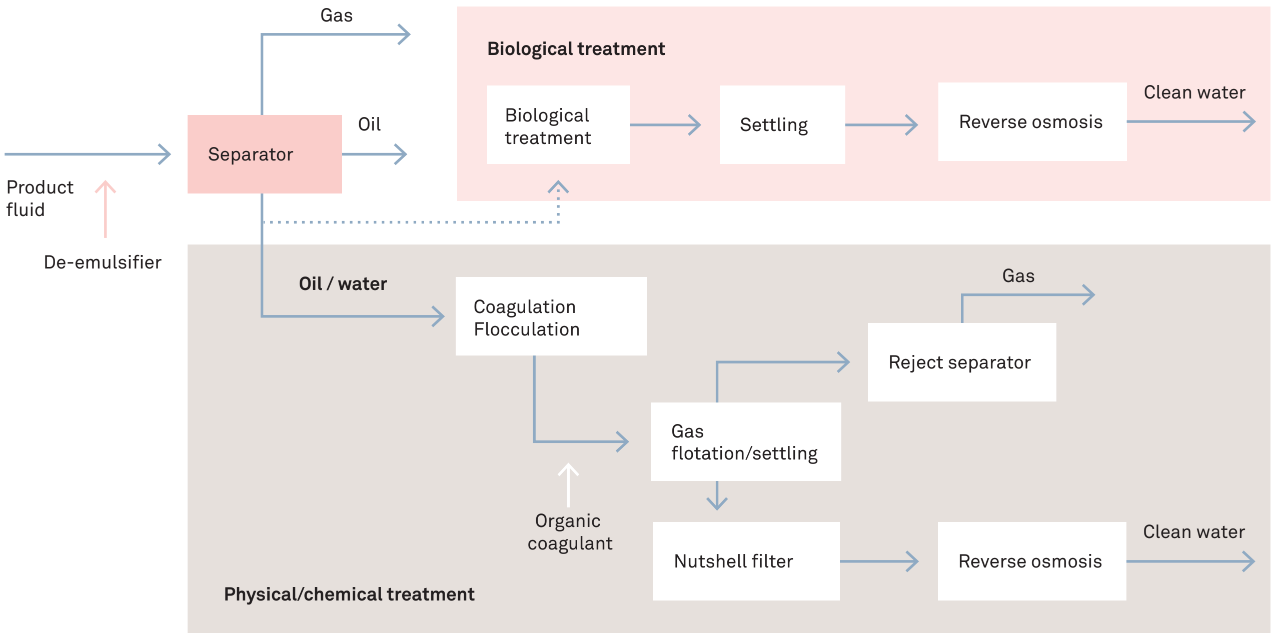
Conventional treatment results in 15–100 mg/l oil in the treated water (Ref. 5 Chemosphere 192 (2018) 186–208).

The produced water that is not re-injected cannot be directly discharge to surface or ground waters because it poses a risk to the environment and human health; discharge is therefore heavily regulated. Most regulatory policies and technical requirements focus on oil content. For example, the allowable oil in water for overboard disposal is <29 mg/l in the US, <30 mg/l in the North Sea, and 20 mg/l in Brazil (Ref. 6. Chemosphere 192 (2018) 186-208). The impurities in produced water can be removed/treated using several different physical, chemical, and biological treatment methods. The selection of the treatment method depends on several parameters including cost, location, and discharge/treatment target. For example, if the target is to reuse the treated water as process water in addition to oil, salts must be removed.

Physical methods like settling, flotation, membrane filtration, and thermal technologies are commonly used for treatment (Ref. 7. Carvalho M.S. et al., Evaluation of the Polymeric Materials (DVB Copolymers) for Produced Water Treatment, Society of Petroleum Engineers, Abu Dhabi, 2002). To improve the efficiency of treatment process chemicals like de-emulsifiers, coagulants, and flocculants, antiscalants are added at different stages of the treatment process. For example, de-emulsifiers are added in the beginning of the process to enhance separation of oil from water in primary/secondary separators. De-emulsifiers are surface-active agents that are effective in disrupting the effects of natural emulsifiers present in the oil. Organic coagulants like polyamines are also used in this step to increase the size of oil droplets and speed up separation. After this step water may go to coagulation/flocculation where inorganic coagulants like ferric sulfate, ferric chloride, polyaluminum chloride, and aluminum sulfate are used to coagulate residual oil. Flocculants like anionic/cationic polyacrylamides are used to flocculate the flocs and enhance separation. If removal of salt is required, then membrane processes like RO are used. Antiscalants (scale inhibitors) and biocides are used to prevent scale formation and biological fouling. Figure 3.48 shows a schematic of a water treatment process with both physical and biological methods. The chemicals in different steps of process are indicated in the graphic.

Figure 3.48

A generic treatment process for produced water.



Pulp and paper industry

The pulp and paper industry uses large amounts of water and production facilities are therefore often built in locations that have an excellent supply of surface water. Water is used to wash the pulp in fiber production, to carry fibers in paper and board production, and to produce chemical solutions.

The general strategy of the pulp and paper industry is to treat waste at source, i.e. within the industry, by modifying processes and thereby reducing emissions. In the past, fresh water was used in every stage of manufacturing and then discharged directly into waterways, but today's plants and processes recycle much more water and therefore have less impact on the aquatic environment. Water consumption is now considerably lower than it was just a few decades ago.

Environmental efforts have concentrated mainly on treating water at source. This means that, whenever possible, the contaminants must be removed within the process. To achieve the best possible environmental results, it is necessary to find the right balance between internal process efficiency and external treatment. The highest discharges into the water come from the fiber manufacturing process, especially pulp bleaching. This is an area where processes have also been developed to reduce the environmental burden through extended cooking and oxygen delignification. Bleaching with ECF (Elementary Chlorine Free) and TCF (Totally Chlorine Free) has also made it possible to reuse the water from bleaching plants and thus reduce water consumption. The most common bleaching agents are chlorine dioxide, ozone, hydrogen peroxide, and peracetic acid.

Environmentally harmful emissions into water from the pulp and paper industry can be divided into the following main groups:

- Oxygen-demanding substances
- Suspended solids
- Nutrient salts
- Chlorinated organic compounds

Raw water

The pulp and paper industry is a major consumer of surface water, which is also the commonest source of raw water, particularly for pulp manufacture, although groundwater may also be used. Most pulp is produced in countries with a plentiful supply of water. Water is naturally recycled to a much greater extent in countries that have poor access to water.

Treatment is carried out in the same way as for producing drinking water in municipal wastewater treatment plants, i.e. by chemical precipitation. Aluminum salts are generally used at optimal pH, while iron salts are used when the quality of the raw water is very poor, when it has a high content of humic substances, or when using a decarbonation stage if the pH is high. The temperature of raw water varies, which affects the optimum pH. In some cases, water is warmed to a constant temperature before chemical treatment. The equipment that is most commonly used is a flotation basin with a sand filter or self-cleaning sand filter.

To ensure acceptable water quality, the treatment process is adapted to suit the composition of the raw water and the product that is being manufactured. Water for certain purposes, such as feed water for steam boilers, requires special treatment such as desalination or ion exchange after chemical precipitation and filtration.

The quality of raw water varies during the year. particularly during spring and autumn floods, when the concentrations of humic substances and particles can increase drastically. This can be remedied by adding polymers, particularly the anionic type. Polymers can also be used if a treatment plant has problems with excessive loading.

Internal treatment

Internal water reuse can be increased by improving the separation in disc filters, dissolved air flotation (DAF), and membranes by purifying process filtrates inside the process close to its origin or at some other point in the process. Another option is to recirculate effluent back to raw water treatment or back to the process. Every purification process creates a reject concentrate that can either be reused or disposed of. There is a clear correlation between water consumption and runnability problems. Circulation is often opened and more water used when there are breaks and other stability problems.

Chemical pulp plants produce certain process-disrupting substances that must be eliminated in order to improve the recycling of water. They mainly include modified cooking, oxygen delignification, and bleaching agents that have made it possible to reduce water consumption. Bleaching-step carryover can be limited with high dryness in the washing press. The water can be reused in the bleaching plant and the separated contaminants then go on to chemical recovery or are used for energy production.

Development work is also being carried out in mechanical pulp production in an effort to reduce water consumption, but because this process already operates with less water than the others do, the demand is not so great.

The backwash from paper and board machines has always been reused in what are known as short and long circulation systems. Short circulation means that the water circulates around the process without being treated, while long circulation means that the water is partially treated before being recirculated. With today's effective retention systems, it is rarely necessary to resort to any other treatment than filtering.

External treatment

The forestry industry has been treating its wastewater using mechanical, biological, and chemical methods for many years now. Due to their significant production capacity and high water consumption each mill has its own treatment plant. The types of installation vary depending on the discharge requirements.

External treatment begins with a primary stage, i.e. some form of mechanical treatment that is primarily intended to remove suspended solids. The most common method is to use sedimentation basins, but flotation is also used. The efficiency of mechanical treatment can be enhanced with coagulants and flocculants. Chemical precipitation effectively removes substances that are difficult to break down biologically.

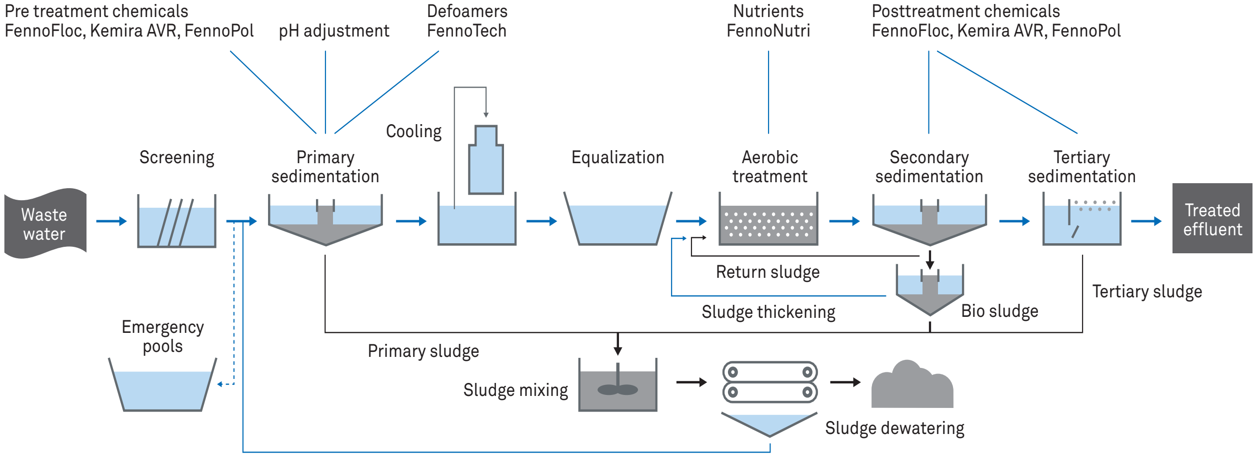
All types of biological methods are used in the pulp and paper industry, but one method that is typically used in the forestry industry is an activated sludge process with long retention times. Typical preparatory phases before biological units are pH adjustment, equalization, and cooling. Wastewater contains plenty of organics from wood and less nutrients. Nutrient dosing is based on mass balance, where the flow of substances (P, N) to and from the plant is equal and the dissolved nutrients in the treated wastewater are monitored. The current trend is to add phosphorus in the form of phosphoric acid and nitrogen in the form of urea. Sludge loss from the biological stage is a common problem and can be prevented by adding metal salts to the process. The following values are expected in treated water for a well-functioning activated sludge plant at a pulp or paper mill:

- Phosphorus dissolved in effluent: 0.1–0.2 mg P/l
- Nitrogen dissolved in effluent: 1.8–2 mg N/l
- BOD dissolved in effluent: 0–10 mg/l
- Solids in effluent: 10–30 mg/l

If biological effluent treatment is not sufficient to meet the discharge limits, tertiary treatment is needed to improve the effluent quality before it is discharged to the recipient. It may be necessary to remove solids, phosphorus, non-degradable COD, and/or color. A typical tertiary treatment step consists of chemical dosing and solids removal using a filter, DAF, or clarification; solids removal is typically enhanced with polymers. Phosphorus removal can be achieved using chemical precipitation, usually with inorganic coagulants. Chemical phosphorus removal requires only a small equipment footprint and is reliable and easy to operate. COD and color reduction can also be achieved through chemical precipitation, usually with inorganic coagulants.

In today's environmentally aware forestry industry, separate treatments methods can be used for each wastewater fraction. Treatment can then be adapted to suit the individual contaminants in the wastewater. In the case of wastewater from the coating industry, membrane treatment may be an alternative if the coating can be reused. Otherwise, chemical precipitation may be used to remove the particles from the wastewater. Another wastewater fraction that can be treated separately is the water from screening. This water contains bark particles and substances that can disrupt operation in biological plants. Wastewater from the screening process responds well to treatment by chemical precipitation and can be reused.

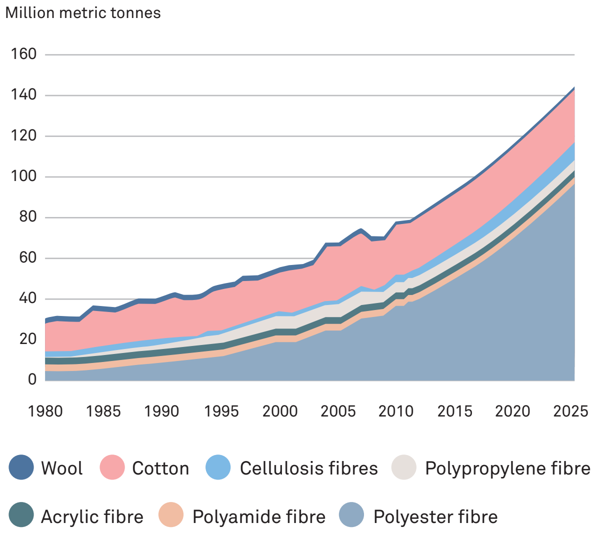
Figure 3.49
An example of external treatment at a pulp and paper mill using Kemira products.



Textile industry

The textile industry is one of the biggest industrial water consumers, with an average consumption of 20–50 l/kg of fabric produced. Textiles are put through several washing stages to give the fabric its desired characteristics. Textile fibers can be divided into two main groups: natural and synthetic.

Figure 3.50
World fiber production 1980–2025.



Depending on which group they belong to, there are several chemicals and additives that are used in textile fiber preparation (see table 3.51). The "average wastewater" from the textile industry contains the following groups of contaminants:

- Dyes
- Textile additives
- Detergents
- Chemicals
- Lanolin and oils
- Traces of textile fibers

Colored wastewater is the most typical characteristic of almost all sorts of water from the textile industry. The color is due to dye residue, i.e. dye that has not been fixed in the textile fiber, and its concentration in wastewater depends on the type of dye and the amount used during the dyeing process. The physical conditions during the dyeing process (such as temperature, pH, etc.) also have a major effect on the concentration of residual dye in wastewater. The disadvantage of these substances is that they color the water, even in low concentrations. The lowest concentration at which residual dye can be seen in water is around 0.1 mg/l. There is no evidence to show that textile dyes in water have any significant effect on the concentration of organic material in wastewater. The increased concentration of BOD and COD in this type of water is instead caused by textile additives such as starches, bleaches, foam inhibitors, enzymes, and high molecular content organic compounds.

Colored wastewater is one of the most typical characteristics of almost all types of water from the textile industry.

Chemical precipitation is widely used for treating wastewater from the textile industry. It involves adding a coagulant to precipitate out dissolved substances in the water and then remove them as a sludge. Particulate substances are also bound to the flocs that are formed when the coagulant is added. Organic flocculants are needed for floc formation. Separation takes place by sedimentation or flotation.

Iron coagulants are more effective at color removal. Organic cationic coagulants can partly replace inorganic coagulants and result in lower sludge production.

The main advantage of using chemical precipitation is the efficiency of dye reduction, especially for dyes that are insoluble in water, where a reduction efficiency of 70% can be achieved. On the other hand, this method is not especially effective for water-soluble dyes. Reactive dyes remain in the water after chemical treatment, which means that the water remains colored. Highly persistent dyes require further oxidizing methods such as Fenton´s reagent or the addition of Na-chlorate.

Table 3.51
Average concentrations of contaminants in various types of textile wastewater.

Pre-treatment	COD (mg/l)	BOD_5 (mg/l)	SS (mg/l)	pH
Animal fibers (wool washing)	50,000–150,000	20,000–60,000	5,000–20,000	7–8.5
Plant fibers (linen and cotton)	1,500–5,000	300–1,000	100–400	8–12.0
Water from dyeing	400–2,000	100–400	30–300	5–10.5

Table 3.52
Chemical treatment efficiency.

BOD_5 (%):	min.	30
	max.	60
	average	45
COD (%):	min.	35
	max.	70
	average	55
Dye reduction (%)	min.	50
	max.	90
	average	70

Choosing the right coagulant and dosage is very important. The pH of the wastewater is also very significant – the optimum pH range for precipitation with aluminum salts is between five and seven, while iron salts can be used in the range 5-11.

Biodegradability tests have shown that most textile dyes and some high-molecular additives are either non-biodegradable or biodegrade very slowly in a normal biological treatment process, i.e. the activated sludge method. Dye reduction is not particularly high, only around 50%. Some dye reduction can be achieved under anoxic conditions. In general, the activated sludge process gives a reduction of between 80 and 90% in BOD_5, but the retention time at this stage is generally longer than a day. In most cases phosphorus and nitrogen must be added, since these elements are in low concentrations in textile wastewater.

Mining industry water demand

The relationship between the mining industry and water resources is highly complex and site specific, with potential impacts on both local hydrology and water quality occurring during the different stages of a mine's life cycle. A yardstick is required to compare the production of metals to everyday objects that we take for granted and don't deem as having such a large environmental impact. Table 3.53 lists such objects.

Table 3.53
Water footprint of everyday articles

Description	Liters per article	Liters per kilogram
T-shirt	2,700	11,000 (cotton textile)
Cup of coffee	140	21,000 (roasted coffee beans)
Bar of chocolate (100g)	2,400	24,000 (40% cocoa content)
Sheet of paper	10	2,000 (80 g/m^2)

Ref. 8. Water for Food (2008) 49 - 61.
Ref. 9. van Oel P.R. and Hoekstra A.Y., The green and blue water footprint of paper products: methodological considerations and quantification, Unesco-IHE Institute for Water Education, 2010.
Ref. 10. Ecol. Econom. 64 (2007) 109 –118.
Ref. 11. Chapagain A. et al., The water footprint of cotton consumption, Unesco-IHE Institute for Water Education, 2005.

As process wastewater from the mining industry is high in salts and dissolved metals, around 90% of flocculants employed are anionic types. However, cationic types may be used if the effluent system is operating in acidic conditions. Further chemical treatment of the wastewater, including disinfection and neutralization, may also be required depending on the type of material extracted and the subsequent contaminants within the stream.

An array of water-management approaches is being used by the industry to mitigate the risks of adverse water impacts. As a result, the significant variability within the industry poses a range of challenges when attempting to quantify the water footprint of mining operations and mineral commodities. Thus, in this section the blue water footprint (WF_{blue}, amount of raw water directly linked to the production) will be used as a benchmark to measure the water demand of the leading metal mining and refining operations and processes.

Water contamination risks associated with a mine are heavily dependent upon several factors, such as the geochemistry of the ore body, the tailings disposal strategy, the mining method, and the processes used for the beneficiation of minerals from ore.

Generally, contaminated mine water is generated when rock containing sulfidic minerals is exposed to water and oxygen, resulting in the production of acidic waters with high concentrations of metals and sulfates.

Mine drainage, process water, and stormwater associated with industrial activities are the main types of water produced in mining operations. The two primary aims of the treatment of contaminated mine water are to neutralize acidity and remove metals by precipitation.

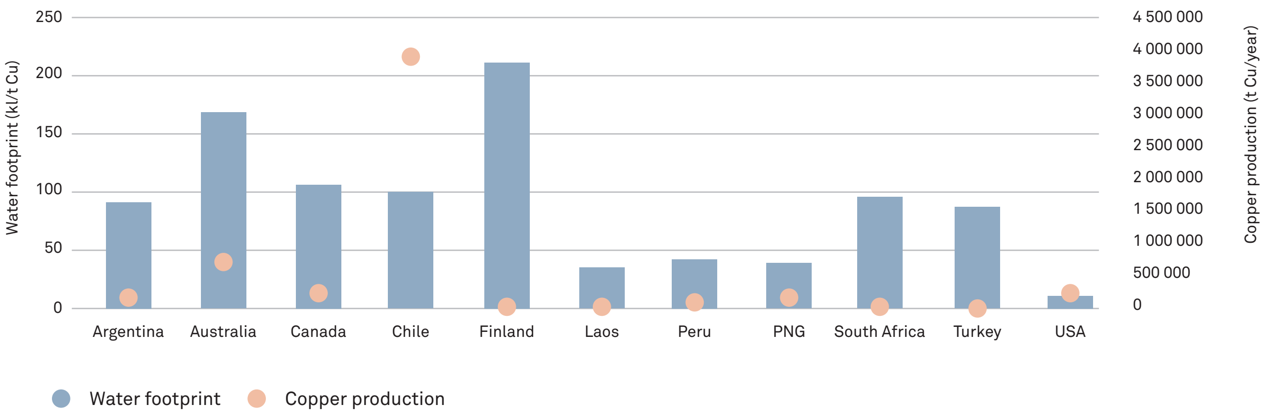
Copper

Copper is an important metal in modern society due to its wide variety of uses, including electrical wiring, heat exchangers, piping and roof construction, and, increasingly, consumer electronics. The processes for extracting copper from the two types of ore are quite different, and the WF_{blue} of the sulfide ore refining process is 2.4 times higher than that of the oxide ore refining process (Ref. 12. J. Ind. Ecol. 18 (2014) 49-58) i.e. 96 m^3/t of copper versus 40 m^3/t of copper.

The water footprint average is 70.4 m^3/t Cu but can range from several cubic meters to up to 350 m^3/t Cu. Variation in water intensity is generally due to inconsistencies in reporting methods, the geographical location of the mining operations, limited economies of scale of production sites, and the climate type, which ranges from arid regions in Australia and Chile to the sub-arctic climates in Canada or Finland (Ref. 13. J. Clean. Prod. 40 (2013) 118-128).

Figure 3.54

Primary copper production water footprint by country.



Strategies to reduce water requirements include evaporation prevention, paste tailings disposal, filtered tailings disposal, and ore pre-sorting. Research reports suggest that for some sites, water consumption reductions of up to 74% may be possible via ore pre-concentration and filtered tailings disposal (Ref. 14. J. Clean. Prod. 21 (2012) 71-82).

Gold

From ancient times to the present day, gold has been highly valued by society and has been the most highly sought-after precious metal, having been used for a variety of different purposes such as money, to back currency, in jewellery making, and in dentistry.

It is important that gold ore processing is split into two main types, namely refractory and non-refractory ores. Refractory ore processing can consume as much as 50% more water than non-refractory ore processing.

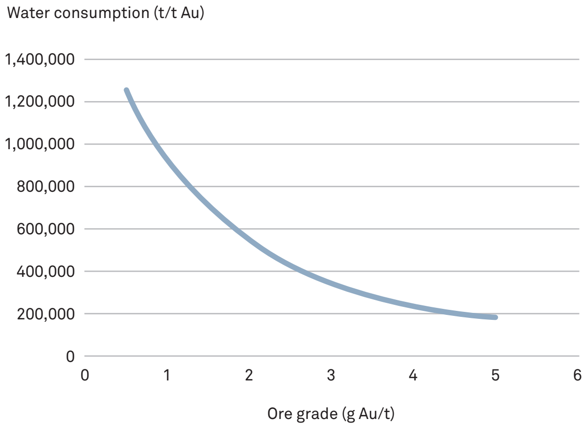
Cyanide, for example, is typically encountered in wastewater associated with gold and silver mining, and can be treated by adding sulfur, hypochlorite, or peroxide to oxidize cyanide into cyanate.

The direct WF_{blue} independent of ore type was found to be 259,290 m^3/t. The environmental footprint of gold production (per tonne of gold produced) is greater than that of other metals by several orders of magnitude. This observation is largely attributable to the low grade of ores used for gold production compared to ores used in the production of most other metals.

The effect of falling ore grades on the water footprint of gold production will be significant because of the major contribution that the mining and mineral processing stage makes to the water footprint, as noted above. Additional material will need to be handled and processed in this stage as the ore grade falls in order to produce the same amount of gold. According to a 2012 lifecycle evaluation study, the following water consumption-to-ore-grade relationship was derived.

Figure 3.55

The effect of ore grade on embodied water of gold production. Adopted and adjusted from Ref. 15. J. Clean. Prod. 29-30 (2012) 53-63.



Iron and steel

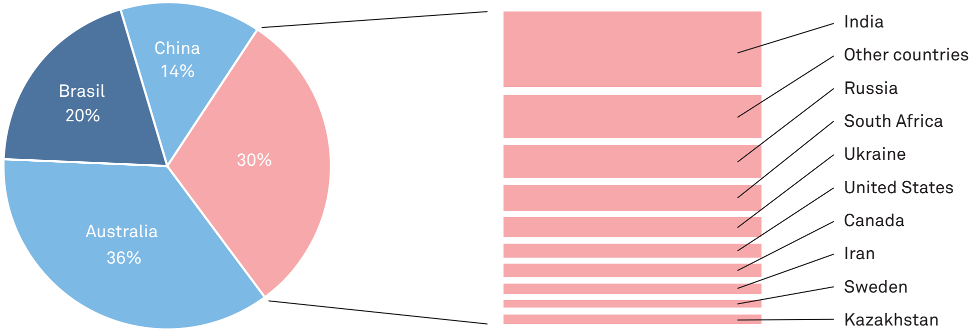
Iron (Fe) is one of the most common elements in the world and forms five percent of the Earth's crust. It is the fourth most common element after oxygen, silicon, and aluminum. Iron occurs in the form of minerals, and 98% of the iron ore mined is oxide compounds of magnetite (Fe_3O_4) and hematite (Fe_2O_3).

Although iron is a highly abundant element, it is important to understand that only three countries in the world produce 69% of the iron used globally, with Australia, Brazil, and China accounting for 36%, 20%, and 14% respectively of the total iron mined in 2018 (Ref. 16. Mineral Commodity Summaries 2019, U.S. Geological Survey). The top 15 iron-producing countries and their global contribution can be seen in Figure 3.56.

Thus, mainly water data from Australian and Chinese production facilities are considered. The extraction of

Figure 3.56

Global iron ore production in 2018 in terms of contained iron.



iron ore involves surface (open pit) or underground mining techniques. The mining method selected depends on a variety of factors, including the nature and location of the deposit as well as its size, depth, and grade. Underground mining requires more energy than surface mining due to greater requirements for hauling, ventilation, water pumping, and other mining operations. However, surface mining accounts for most of the iron ore produced worldwide. The average water requirement for open-pit iron ore in Australia is 0.21 m^3/t ore and a further 4.21 m^3 to produce a tonne of steel. In China, a WF_{blue} of 4.85 m^3 and 12.04 m^3 are required using a tonne of steel billet as the functional unit of measure.

Steel has a relatively low water footprint compared to gold and copper. The main problems faced by the iron mining industry relate to stabilizing and securing tailings disposal facilities. The water footprint of iron mining facilities can mainly be reduced by improving their thickening and water-reclamation processes.

Available wastewater treatment processes in mining

Recent population growth and rapid industrial development in Europe and the USA, particularly after 1940, have resulted in the production of increasing amounts of industrial wastewater. As a result, wastewater treatment methods and technology for the removal of contaminants, including metals, have had to be improved over time to ensure adequate protection of public health and the environment.

There are dozens of different treatment technologies available to water treatment plant operators, each with its own advantages, limitations, costs, reliabilities, and degree of effectiveness. Furthermore, like most mineral extraction technologies, it is generally not possible to say how well a given treatment system will perform on a given mine effluent until that effluent is made available for laboratory and field testing.

Chemical precipitation

Sulfide oxidation leads to the solubilization of metals. The most common form of water treatment is chemical treatment to raise the pH and precipitate metals.

Chemical treatment involves the addition of an alkali material to raise the pH of the acidic mine drainage stream to levels that cause the solubilized metals to precipitate. Two types of precipitation processes are common in mining, namely hydroxide and sulfide precipitation Reaction 0-1 and Reaction 0-2 illustrate the respective metal (M^+) precipitation processes.

$$M^+(aq)+OH^-(aq) \rightarrow MOH(s)$$
$$2M^+(aq)+S^{2-} \rightarrow M_2S(s)$$

Dissolved metals in mine waters may generally be removed from solution as metal hydroxides with the addition of caustic soda (NaOH), quick lime (CaO), or slaked lime ($Ca(OH)_2$) to a pH where a point of minimum solubility is achieved.

Hydroxide-based metal precipitation technology is proven and has been shown to be effective in consistently providing acceptable effluent quality under normal operating conditions. However, in some cases lime precipitation may not be able to remove all metals to meet water quality standards, for example cadmium, and it has little effect on the removal of metalloids such as arsenic, selenium, thallium, antimony, and cyanide. For these and other additional contaminants, other treatment technologies may be necessary.

The principle of sulfide precipitation is the addition of either hydrogen sulfide (H_2S), sodium sulfide (Na_2S), or sodium hydrosulfide (NaHS) to mine waters. It should be kept in mind that metal hydroxides are predominantly amphoteric, therefore beyond the point of minimum solubility. There is a real risk that key metals could potentially dissolve back into solution.

Membrane technology

All membrane processes separate the feed stream into a permeate and a concentrate. A drawback of this technology is the safe disposal of the dry salts created in this process, which requires specially constructed disposal facilities.

Scaling agents such as iron salts, silica, calcium sulfate, and calcium carbonate can cause fouling problems as saturation conditions may occur on the membrane surface, resulting in the precipitation of solids on the membrane. Calcium removal by ion exchange or soda softening and the addition of antiscaling agents are used to alleviate some of these scaling problems.

Reverse osmosis

RO can be used as a secondary treatment to chemical precipitation to further reduce the level of contaminants in a waste discharge.

Ozonation

Advanced Oxidation Processes (AOPs) have been proven to be very effective at remediating contaminated wastewaters containing organic pollutants and reducing arsenic. The most studied AOPs are photochemical-based processes such as UV/hydrogen peroxide, heterogeneous photocatalysis and photo-Fenton, UV plus ozone, and combinations of these technologies. The principle of AOPs is based around the creation of reactive chemical species that can degrade or transform chemical pollutants, ultimately causing mineralization. One of the major drawbacks of AOPs is their comparatively high operational cost compared to technologies such as biological treatment and the use of activated carbon.

Other treatment methods

Below is an extensive list of alternative treatment methods for treating wastewater from the mining industry. The nature of their function is discussed at various points in this handbook, so page references are provided.

- Engineered wetlands
- Carbon adsorption (page 96)
- Ion exchange (page 96)
- Electrodialysis (page 109)
- Biological treatment systems (see page 59)

Costs of wastewater treatment

Essential cost factors in wastewater treatment include investment costs, energy consumption, chemical consumption, and sludge disposal costs. The disposal of sludge represents a large part of the total operating costs for a treatment plant, and there are different approaches to reducing these costs. As the sludge has a high water content, different technologies have been developed to reduce it.

Sludge also contains valuable resources such as carbon, nitrogen, and phosphorus. Nitrogen and phosphorus can be extracted from the sludge as fertilizers or be recycled with the sludge for use in agricultural applications. The value of this is however not accounted for in WWTP budgets, while nutrient recovery is a cost for a WWTP.

The inflow composition to a wastewater treatment plant varies considerably depending on the origin of the wastewater. There are types of wastewater that originate solely from municipal sources, but in most larger towns and cities there is a higher and strongly varying ratio of wastewaters from industrial sources. Consequently, the necessary water treatment steps must be adapted according to the raw water quality and the release limits. It is therefore impossible to make a general assessment of costs due to the large variation of treatment steps used in different WWTPs. Therefore, we will limit ourselves to demonstrating how chemistry can help WWTPs reduce both OPEX and CAPEX.

Energy savings

Normally, sludge disposal represents the largest operational cost for a municipal WWTP, followed by energy. Since a lot of the energy is consumed by the biological treatment process, this is where the efforts to reduce costs should be concentrated.

First of all the biology should be unloaded when applicable. Using a pre-precipitation process will unload the biology and hence reduce the energy consumption of the blowing machines. Since less BOD needs to be degraded, bioreactors with smaller volumes can be used; this also reduces the amount of energy required to keep the biomass in suspension. Reducing biomass volumes reduces endogenous respiration of the bacteria, meaning less electricity is needed.

Using a nitrogen process will also influence energy consumption in the biological stage. With pre-denitrification, the water must be recycled as many as four or five times in order to achieve the required nitrogen levels. This means pumps running four to five times higher than the influent pumps must work constantly and this of course consumes energy. If the plant instead has combined post and pre-denitrification with a small denitrification zone before the aerobic zone, the return flow is only the flow of the return sludge, which is approximately one time the influent flow. A post-denitrification process can also be designed to be highly compact and hence more energy can be saved.

Finally, the nitrification rate is dependent on the COD/N-ratio; with a high ratio the nitrification rate drops. Pre-precipitated water has a lower COD/N-ratio than primary settled water. Volume and energy savings can be achieved here too.

Biogas production

Biogas can be a source of revenue for a WWTP, and even if the gas isn't sold to an external provider it can be used as an energy source to reduce external energy costs.

As mentioned before, biogas production increases with pre-precipitation since primary sludge has a higher biogas potential than secondary sludge. Again, a pre-precipitation process can generate energy savings or even revenue.

Investment savings

A pre-precipitation plant can be more compact than a plant with simultaneous or post-precipitation, or when operating with Bio-P. This means that a lower investment is needed for the biological treatment step; pre-precipitation can be used to increase the capacity of a plant that has reached its limit.

Chemical treatment can also be combined with low-cost separation equipment like micro-filters. These can be used to help the biological treatment step, to treat stormwater, or to polish the water during high flows. Introducing chemical treatment processes is likely cheaper than investing in a new biological train.

Many municipalities use long payback times in their investment calculations, perhaps as long as 40 years, which can result in misleading investment proposals since no WWTP would be able to operate effectively without being upgraded during that time. Realistic payback times need to be used when comparing alternatives with higher operating costs but lower investment costs.

Sludge dewatering savings

Sludge disposal is a high cost for a WWTP, so achieving the highest possible sludge dryness is beneficial in financial terms and can be done using chemical or thermal solutions to improve the dewaterability. There are many ways to do this, but in general only polymers are used for sludge dewatering. It is then highly important to find the polymer that will achieve the best DS content for a reasonable cost. Bio-P plants with anaerobic digesters have high levels of phosphate in the solution, which has a negative impact on sludge dewaterability. Phosphate levels can be reduced with the addition of an inorganic coagulant, phosphorus can be precipitated as struvite or calcium phosphate, or better still, the plant can use chemical phosphorus removal in place of bio-P, which can also generate savings in maintenance costs.

Maintenance savings

Many WWTPs that use bio-P have problems with struvite scaling in pipes and heat exchangers after anaerobic digestion. Since nothing can be done with the ammonium in the sludge liquor, phosphate has to be controlled instead, or alternatively the precipitation of struvite needs to be controlled. Phosphate is easily removed with aluminum or iron salts, which can be dosed into the digester or preferably used in the water treatment process.

An alternative is to use antiscalants, which have the same backbone as polyacrylamide polymers but a smaller molecule size. Antiscalants inhibit the crystallization formation in solutions. They do not inhibit the precipitation of the salt, for instance struvite, but ensure that no large crystals are built up, ensuring that scaling cannot occur in pipes. There are different kinds of scaling found in WWTPs, for instance struvite, calcium carbonate, and vivianite (ferrous phosphate). The correct antiscalant will depend on the type of chemical molecule that is causing the scale.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CHAPTER 4

SLUDGE TREATMENT

Sludge from wastewater treatment

The target of wastewater treatment is the production of clean water. When that is done, the impurities and contaminants to a great extent are removed from wastewater and end up in a solid fraction: sludge. Solids are separated by transforming dissolved substances and small particles into larger particles that can then be separated e.g sedimentation. When these larger particles accumulate in larger units, they form sludge. Sludge can be defined as an inhomogeneous mixture of particles and water. The total solids content of wastewater sludge varies considerably. It can be high or low, and the content will vary depending on the origin of the sludge.

A water or wastewater treatment plant consists of a number of treatment steps where the contaminants are converted into solid form so that they can be separated from the water. The result of the separation steps is a water-rich sludge that contains the contaminants and that must be processed in an economically and environmentally appropriate way. The appearance of the resulting sludge, its physical and chemical properties, and its volume show considerable variations depending on the specific composition of the treated water and the local setup of the treatment plant process. Industrial sludge can contain valuable metals, drinking water sludge can contain coagulants, and sewage sludge contains nutrients and carbon. All the useful compounds are lost if sludge is disposed of. Opinions on sludge are changing: Due to the valuable compounds it can contain, sludge is seen as a resource and an opportunity for sustainable recycling rather than as an ecological problem.

The processing of sludge is cost intensive. It is the final – and an essential – step in the wastewater treatment process as it should deliver a compact solid fraction without releasing captured contaminants back into the wastewater treatment process or environment. Sludge processing comprises a sequence of steps such as thickening, stabilization, and dewatering. Another essential element of sludge treatment is the handling of it further downstream: the disposal route. Depending on the requirements for disposal, the treatment methods must deliver the targeted specifications such as high dry solids content, hygienization, and nutrient recycling. The most widespread routes for sludge disposal are composting, incineration, agricultural use, use as a soil improver, or landfilling.

Various types of sewage sludge

Municipal wastewater that enters the wastewater treatment plant (WWTP) undergoes a sequence of treatment steps with the target to specifically remove the targeted physical and chemical sludge components one by one. The capacity and requirements determine the design. Normally two or three treatment steps are used after the preliminary treatment. For further information see chapter 3.

The solid-containing sludges from the primary, secondary, and tertiary treatment steps have specific properties and appearances depending on their biological, physical, and chemical composition, and they contain varying mixtures of contaminants. Sludges from each of these treatment steps typically have different names.

Treatment steps and their sludge types:

- Primary treatment: Primary or mechanical sludge
- Secondary treatment: Secondary, biological, surplus, or excess sludge
- Tertiary treatment: Tertiary or chemical sludge

The sludges that exit the treatment steps are in most cases collected and mixed. In a further downstream treatment, the mixed sludges often undergo anaerobic digestion to stabilize them and achieve a volume reduction by transforming organic matter into valuable biogas. More information on the production of biogas from sludge can be found in chapter 6.

The approximate quantities of sludge that are produced in the different treatment steps of a WWTP are shown in the table 4.1.

Table 4.1

Approximate mass flows of sludge from different treatment steps inside a WWTP when Al^{3+} and Fe^{3+} are applied as coagulants. The flows refer to non-stabilized sludge before it enters anaerobic digestion.

Treatment step	Flow [g/(PE·d)]	Dry solids content after thickening [% DS]	Volume [l/PE]
POST-PRECIPITATION			
Primary sludge	50	6	0.8
Secondary sludge	30	2	1.5
Tertiary sludge	25	2	1.2
Mixed sludge	105	3	3.5
PRE-PRECIPITATION			
Primary sludge	110*	5	2.2
Secondary sludge	10	2	0.5
Mixed sludge	120	4	2.7
DIRECT PRECIPITATION			
Primary sludge	110	5	2.2

** Of which 25 g/PE·d consists of metal hydroxides and phosphates.*

Sludge composition

Wastewater sludge contains solid and dissolved substances in an aqueous matrix. The total solids content is typically 2-5%, with a pH of 7-8. Solid material and dissolved substances are both organic and inorganic. Organic compounds and nutrients, phosphorus, and nitrogen, are the most important components of sludge, as they are affected by the wastewater treatment process and themselves affect the final sludge value.

Sludge largely consists of organic matter, of which a large part is micro-organisms and the metabolic products of their biological processes. Fibers such as cellulose, hair, proteins, and plastics as well as organic micropollutants are present in sludge. Examples of dissolved organic substances in sludge are polysaccharides, fatty acids, and humic substances. The amount of volatile solids, loss of ignition, and degree of mineralization are measurements that indicate the proportion of organic material.

Inorganic substances in sludge mainly originate from sand and different sparingly water-soluble metal salts, such as phosphates, sulfides, hydroxides, and carbonates. Iron, aluminum, and calcium are common metals that form these salts, with many of them originating from chemical treatment. Toxic metals are also present in sludge. Dissolved inorganic substances in sludge include nutrients such as ammonium and phosphates, and other inorganic ions like potassium, sulfates, and chlorides.

During the treatment process, most of the organic substances and nutrients are removed from wastewater. They are either released into the air or bound to the solid to be removed in the sludge.

The particle charge of sludge is typically slightly negative.

The composition of sludge varies considerably depending on the wastewater treatment process, origin of the wastewater and sludge, season, and weather. Table 4.2 presents typical measured values of some parameters of digested municipal sludge.

Table 4.2
Typical variation of some parameters of digested municipal sludge before dewatering.

Parameter	Unit	Typical variation
DS	%	2.2 – 5.0
VS of DS	%	55 – 71
pH		7.2 – 8.0
Conductivity	mS/cm	6 – 12
Charge	μeq/g	-5.2 – -1.7
CST	s	100 – 800
COD	g/l	19 – 38
P-tot	mg/l	440 – 1,300
N-tot	g/l	1.4 – 3.3

Harmful and toxic compounds in sludge

Wastewater contains different levels of harmful and toxic substances. Some of these are water soluble and remain in the purified wastewater entering the recipients in the wastewater effluent, some precipitate under the conditions of wastewater treatment and are found in the sludge, and some degrade in the wastewater process. New analysis methods have made the identification of environmentally harmful substances easier and more accurate.

Wastewater sludge contains disease-causing substances and organisms, known as **pathogens**. These are typically bacteria, such as Salmonella and Escherichia coli, the eggs of parasites (oocysts), or viruses.

Toxic metals are to a great extent separated from the wastewater, ending up in the sludge (see chapter 3). They form sparingly soluble metal hydroxides, sulfides, carbonates, and phosphates at approximately neutral pH-levels in the wastewater treatment process. The concentration of toxic metals in sewage sludge has decreased in the past decades as their use and disposal have been controlled by regulations and the industry has improved their removal at the source (Table 4.3).

Table 4.3
Typical metal concentrations in municipal wastewater sludge. Ref 1.

Metal		Concentration [mg/kg DS]
Cadmium	Cd	0.9–3.4
Chromium	Cr	20–80
Copper	Cu	130–300
Mercury	Hg	0.5–2.9
Nickel	Ni	15–31
Lead	Pb	26–110
Zinc	Zn	380–1,100

Ref. 1. https://ec.europa.eu/environment/archives/waste/sludge/pdf/part_iii_report.pdf. Environmental, economic and social impacts of the use of sewage sludge on land. Final Report. Part III: Project Interim Reports. Date 26.03.2020

Organic micropollutants include compounds like pharmaceuticals, hormones, flame retardants, biocides, and dioxins from chemical production. Many of them have low solubility in water but are still found at low concentrations in liquid wastewater. Depending on the compound, its removal efficiency from wastewater varies. Some degrade in biological processes and form degradation products whereas others are inert. Some micropollutants or their degradation products end up in the sludge, whereas others remain in the wastewater liquid and pass the treatment process without being removed. Examples of organic micropollutants in wastewater and their share in sludge are presented in Table 4.4.

Organic micropollutants can be removed from wastewater with expensive additional treatment steps at the end of the whole wastewater treatment process before the water is released to the recipient.

Table 4.4

Examples of organic micropollutants in wastewater and share of them to the sludge based on a Finnish study (Ref. 2).

Compound	Inflow mg/p/a	Degraded in treatment	Bound to sludge	In sludge mg/p/a	In effluent mg/p/a
Triclosan (TCS)	5.6	0%	68%	3.8	1.8
Carbamazepine	37	2%	4%	1.5	34
Hexabromocyclododecane (HBCD)	1.2	7%	80%	1.0	0.2
Brominated diphenylethers (BDE)	0.7	0%	92%	0.6	0.1
Perfluorooctane sulfonate (PFOS)	2.4	0%	10%	0.2	2.2
Diuron	1.8	0%	5%	0.1	1.7
Dioxins and dioxin-like compounds: PCDD, PCDF, PCB	0.2	0%	97%	0.2	0.0
Ibuprofen	1,778	98%	1%	8.9	36
Tributyltin (TBT)	0.1	9%	62%	0.0	0.0
Octylphenols and ethoxylates	53	11%	76%	40	6.9

**p = person, a = annual*

Ref 2. https://www.vvy.fi/site/assets/files/1617/haitalliset_aineen_jatevedenpuhdistamoilla_-hankkeen_loppuraportti.pdf. Date 24.03.2020. ISBN 978-952-6697-02-4

Microplastics are plastic particles smaller than five mm and up to 99% of them are removed by wastewater treatment processes depending on the method used. The removed particles typically end up in the sludge. Most WWTPs are currently not specifically equipped to remove microplastics. Although recent research has focused on the release of microplastics from WWTPs, there is still some work to be done to characterize the sizes, types, and concentrations of microplastics in wastewater, and to develop targeted methods for their removal.

Water distribution in sludge

Water is bound to the solids in the sludge in different ways. The water-containing gelatinous nature of sludge makes it particularly difficult to separate the two phases effectively.

Taking a closer look at the sludge matrix at a microscopic level, water has different appearances and physical properties depending on its relation to the particles. These properties have a decisive impact on the result of a physical solid-liquid separation step. Depending on the way water is bound or associated with the particles, higher or lower cake dryness can be achieved.

Researchers have developed the following descriptions of the various physical properties of water in the sludge phase:

Free water: Water that is not bound to any particle.

Capillary water: Mechanically bound water between sludge particles.

Surface-bound water: Physically bound layer of water molecules that adhere to the surface of sludge particles by means of hydrogen bonds.

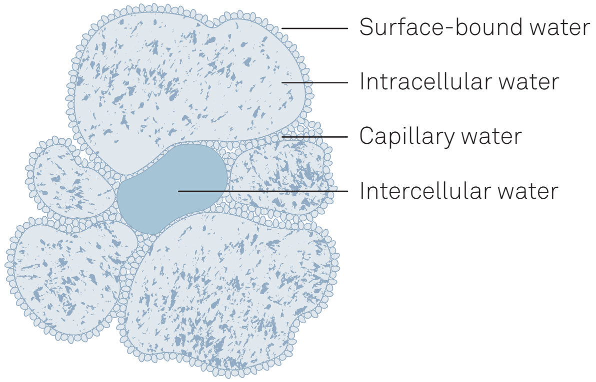
Chemically bound water: Water that is strongly bound to metal ions.

Intracellular water: Water inside cells

Intercellular water: Water between cells and particles.

Figure 4.5

The various water phases associated with sludge particles.



The normal dry solids (DS) content for dewatered and digested sludge is between 18 and 30% depending on the sludge characteristics. With advanced dewatering techniques, even higher DS contents can be achieved.

With current dewatering technology, only easily available water like free and some capillary water can be captured and separated from the sludge matrix.

As a first step, the water content of sludge can be split into free water and bound water. The dewatering properties of sludge differ considerably according to the varying amounts of those two types of water.

Intracellular water is completely bound to the sludge body. Aerobic or anaerobic digestion can degrade the cells and the cell walls, releasing the intracellular water. Thermal hydrolysis degrades the organic matter and destroys biological cell structures, releasing more intracellular water. Treatment with ultrasound destroys cell walls with high-energetic acoustic waves. Macerator pumps break down biological structures using a high-energy mechanical impact.

Intercellular and capillary water are types of water bound between dewatered cells and particles by surface effects, which are very difficult to remove using mechanical methods. Capillary forces are often stronger than the mechanical forces applied in sludge dewatering, which is why capillary bound water is difficult to remove. The quantity of water removed is determined by the size of the particles, their geometry, and how closely they are packed together.

Surface-bound water can be released using biological procedures or through the impact of physical and mechanical energy on the sludge.

Sludge treatment

Conventional sludge treatment includes stabilization or pre-treatment, thickening, dewatering and disposal.

Sludge stabilization

Sludge stabilization is a chemical or biological process to eliminate pathogens and stops the natural fermentation of the sludge. Two biological processes for sludge stabilization are aerobic and anaerobic digestion. Lime addition can be used as a chemical stabilization treatment.

Aerobic digestion

In aerobic digestion, the sludge is stabilized and degraded in aerated bioreactors. The aeration brings large amounts of oxygen from the air into the organic matter. It activates the aerobic microbes, which first start to degrade carbon-containing matter into carbon dioxide, and later also nitrogen-containing matter. The average residence time is approximately 15 days. The temperature is the same as normal wastewater treatment, 15°C on average. If the temperature is lower, e.g. in winter, the reaction time is longer, and the residence time must be increased. The oxidation of one kilogram of organic matter consumes approximately 1.5 to 2 kilograms of oxygen.

Anaerobic digestion

Anaerobic digestion is widely used for sludge stabilization. It effectively reduces organic matter, provides a valuable energy source in the form of biogas (methane, CH_4), and results in a well dewaterable sludge phase. Anaerobic digestion is one of the most widely used stabilization methods because it isn't sensitive to changes in the sludge substrate and it runs under quite a simple technical setup. You can read more about anaerobic digestion in chapter 6.

Table 4.6 shows the reactor volume requirement of different sludge types. The mixed sludge from conventional WWTPs with biological treatment produces approximately 30 liters of biogas per person per day, while the amount of sludge is reduced by about 35%.

The degradation of organic matter can be described by the formula:

$$a = 1 - [(MSi \cdot VSu) / (MSu \cdot VSi)]$$

a = Degree of degradation
MSi = Raw sludge mineral solids, % of DS
MSu = Degraded sludge mineral solids, % of DS
VSi = Raw sludge volatile solids, % of DS
VSu = Degraded sludge volatile solids, % of DS

Table 4.6
Digester volume requirements for various types of sludge.

Feed sludge to digestion	Digester volume [l/PE]
Primary sludge	30
Primary sludge + Biological sludge	45–60
Primary sludge + excess sludge	60–90
Primary sludge from direct or pre-precipitation	70–100

The sludge obtained from pre-precipitation contains considerably more readily biodegradable organic matter than the sludge from secondary treatment or mixed sludge. Pre-precipitated sludge therefore yields higher biogas volumes in digestion.

Sludge pre-treatment

Typical pre-treatment processes before sludge stabilization are thermal sludge treatment and sludge hydrolysis.

Thermal sludge treatment

In thermal treatment, sludge is submitted to temperatures above boiling point in pressurized reactors. The temperature level can exceed 150°C, the pressure level can achieve several bars, and the residence time is often between one and a few hours. Thermal sludge treatment mainly targets the solubilization of the

Table 4.7
Biogas production of different sludge types.

Sludge origin	Daily load [g/(PE·d)]	Volatile solids GF VS [%]	Load volatile solids [g VS/(PE·d)]	Gas production [l/(PE·d)]
BIOLOGICAL TREATMENT				
Primary sludge	50	75	38	
Secondary sludge	30	70	21	
Mixed sludge	80	74	59	30
PRE-PRECIPITATION				
Primary sludge	110*	60	66	
Secondary sludge	10	70	7	
Mixed sludge	120	61	73	40

** 25 g of the matter is in the form of metal hydroxides and phosphates that do not produce any gas.*

solid organic content made up of sedimented organic waste from the different treatment steps, and of microbial cells both live and dead. Both raw sludge and digested sludge can be processed. Due to better energetic control, most thermal sludge treatment processes are run continuously. Thermal sludge treatment can be supported with chemical additions.

The solid residue is composed of inert matter, mainly sand and fibers. It is easier to dewater in most cases because the water-rich organic structure of the sludge that strongly resists dewatering is almost completely hydrolyzed and transferred to the liquid phase. In addition, thermal sludge treatment disinfects sludge by eliminating all pathogenic microbes.

Sludge hydrolysis

An additional carbon source is sometimes needed to support the biological treatment step in a WWTP. It can be produced using thermal, chemical, enzymatic, or biological sludge hydrolysis as mainly the organic part of the sludge is solubilized.

Some WWTPs use biological fermentation in separate fermentation tanks or in primary settling. If the process is carefully regulated it can produce highly bioavailable fatty acids for the biological step.

Enzymatic hydrolysis involves adding external enzymes to the sludge. Elevated temperatures speed up the hydrolysis rate, and if the temperature exceeds 60–70°C there is a light pasteurization effect that prevents the sludge bacteria from immediately consuming the released short-chain compounds.

Chemical hydrolysis involves adding alkaline (alkaline hydrolysis) or acid agents (acidic hydrolysis) to the sludge. Suitable alkaline agents are sodium hydroxide, soda, or lime. In the case of acidic hydrolysis either sulfuric acid or nitric acid may be added. The easy stoichiometry of the added chemicals makes it easy to control the chemical hydrolysis process.

High yields of dissolved organic substances in the carbon source can be obtained from both raw and digested sludge. Due to its high content of easily soluble COD, pre-precipitated primary sludge is the most suitable as it releases the highest amount of bioavailable carbon in a possible hydrolysis step, which is also the easiest and cheapest way to produce a carbon source.

Sludge thickening

Sludge thickening is an intermediate step in wastewater treatment. The target is to increase the solids content in sludges of different origins and to eliminate water volumes, which drastically reduces the hydraulic load to the downstream treatment steps.

In large WWTPs, separate thickening steps are used mainly to reduce the volumes of primary and activated sludge.

The thickening of primary sludge is mainly carried out using gravity settling. The typical dry solids content after sedimentation and thickening is between 5 and 7%.

At the end of the biological treatment, the returned activated sludge has a solids content of around 0.8%, sometimes less than 0.5%. Typically, excess sludge is thickened to 3-7%. In large WWTPs, the thickened sludge fractions from primary and secondary treatment are united in one stream and then submitted to anaerobic digestion.

Sludge volume is reduced by thickening before dewatering to improve the overall economy of a WWTP.

- Anaerobic digestion – Reduced digester volumes, extended retention times, reduced heat consumption
- Sludge dewatering – Reduced hydraulic load on dewatering equipment.

Table 4.8
Equipment for thickening of activated sludge.

Equipment	Use of polymers
Gravity settling tanks	Polymers can be used to increase settling speed, increase clarity of supernatant, and to increase dry solid content
Dissolved air flotation (DAF)	Polymers can be used to increase dry solid content and to increase water clarity
Centrifuge	Polymers can be used to increase dry solid content and to improve centrate quality
Gravity belt thickener	Use of polymers is necessary
Drum thickener	Use of polymers is necessary

Gravity settling tanks

Thickening by sedimentation is often carried out in circular basins with a depth of 2.5–5.5 m equipped with surface and bottom stirrers, and in many cases gate agitators.

Table 4.9
Sludge load of various types of sludge, for sedimentation by thickening.

Sludge type	Sludge load [kg DS/(m²· d)]
Primary sludge	100–150
Secondary sludge	25–30
Tertiary sludge	25–30
Mixed sludge	30–50

Dissolved air flotation

Dissolved air flotation units are circular or rectangular. Rectangular tanks are considered easier to scrape and are therefore more common. The sludge load is 140–240 kg DS/m²·d.

Centrifuges

The main components of a centrifuge are a conical-cylinder bowl that rotates at high speed (2000–4000 rpm) and a screw that rotates at a slightly different speed (a few rpms different). The rotating bowl creates a centrifugal force which drives the solid-liquid separation, with the solids conveyed out by the screw.

Gravity belt thickener

A gravity belt thickener consists of a gravity belt that moves over rollers at an adjustable speed. The flocculated sludge is evenly distributed over the belt. The water drains through the belt and the thickened sludge is discharged at the end of the thickener.

Drum thickener

A drum thickener consists of a flocculation system and a rotating cylindrical screen. The flocculated sludge is fed into the rotating screen. The solids roll out at the end of the screen and the water drains through. Some drum thickeners are also equipped with a slowly rotating screw (variable speed). This screw conveys the sludge gently upwards through the screen and discharges it at the end.

Sludge dewatering

Municipal wastewater treatment mostly processes a mix of sludges of different origins. Some WWTPs also receive external sludge, for example from septic tanks, industrial waste, or from other wastewater treatment plants, that is processed with their other sludges. External sludge can be fed to the process before or after the sludge stabilization. In some cases, the external sludge is added to the influent water and treated together with the "normal" wastewater.

Sludge dewatering is the final treatment step for the solid fraction in a conventional municipal WWTP. The target of sludge dewatering is to achieve a sludge cake that is as dry as possible using mechanical dewatering methods.

Digested sludges from municipal WWTPs usually have a DS content of between 2 and 5% and a water content of between 95 and 98%. Conventional municipal wastewater sludges can be dewatered to DS contents between 18 and 30%, but due to local variations dewatering results can end up far above or below this range.

Important factors in sludge dewatering are:

- Sludge type, e.g. the share of primary and secondary sludge
- Type of sludge stabilization and sludge pre-treatment
- Sludge age during nitrification and denitrification
- The hydrophilic properties of metal hydroxides formed during chemical treatment
- The gelatinousness of the sludge that develops during biological treatment including biological phosphorus removal
- Improved primary separation screens in treatment plants that remove larger particles and fibers, decreasing the particle size in downstream treatment steps
- Reduced retention time during anaerobic digestion due to increased load and lower DS content in the feed sludge to the digester.

Digested sludges with a high pre-precipitated primary sludge content typically need lower polymer dosages and charge densities than sludges that are rich in biological sludge from secondary treatment. This is because primary sludges are heterogeneous in composition and structure, whereas secondary sludges from biological treatment are much more homogeneous and contain much more organic matter in the form of live and dead microbial cells. Sludge with a high loss on ignition value is more difficult to dewater than sludge with a high ash content.

EPSs can be degraded further by anaerobic digestion, but most will stay intact. Those sticky and water-rich microbial cells, in turn, form larger flocs and structures that resist any mechanical and chemical dewatering. The application of coagulants and flocculants for dewatering can only release the EPS-bound water to a small degree.

Advanced thermal or chemical treatments break up the EPS structure. But due to high costs, most WWTPs try to limit themselves to conventional dewatering methods with the help of coagulants and flocculants.

The disposal costs for wastewater sludge have increased and will continue to do so, because stricter laws and environmental regulations are increasing the cost of waste handling . Increasing costs for disposal are the main driving factor for WWTPs to deliver as high a DS content as possible. For large municipal WWTPs (> 500 000 PE), a 1% increase in cake DS, e.g. from 26 to 27%, can easily result in cost savings of more than 100 000 Euro per annum due to decreased sludge volumes for disposal.

Sludge conditioning

The microorganisms that make up the bulk of sludge surround themselves with a gelatinous layer that attracts water very strongly. It is thought that the microorganisms use this layer to store nutrients and to protect themselves from infections and drying out. When sludge is dewatered it must be processed or “conditioned” to break down this gelatinous layer. This releases the water so that it can be separated using one of the methods described below.

In general, sludge is conditioned with chemicals before dewatering. Two types of chemicals are used to enhance the dewaterability of sludge:

1. Inorganic chemicals: iron , aluminum and magnesium salts, and lime
2. Organic chemicals: polymers (flocculants) and organic coagulants

To achieve optimal results with conditioning chemicals smart control is needed. Normally the dosage of, for example, polymer is based on the sludge flow/mass flow only, but with a smart solution like KemConnect SD the chemical dosage can be optimized so that a better treatment result can be achieved with less chemicals. More about smart solutions can be found in chapter 7.

Inorganic chemicals

A common method of sludge conditioning for a filter press is with a combination of iron salts and lime. The most frequently used iron salts are ferric chloride, ferric sulfate, and ferric chlorosulfate. The correct dosage of ferric salt followed by the correct lime dosage will improve filterability by reducing the amount of bound water and increasing the mineral content of the sludge.

Ferric salts are also used in combination with organic flocculants to enhance sludge dewatering. Organic polymer consumption will decrease up to 30% and pre-dosing a ferric salt (1-3 l/m^3) will increase cake dry solids, improving both filtrate/centrate quality and process efficiency. Iron and aluminum salts are also used before sludge dewatering to control the level of soluble phosphates in the water phase in order to prevent struvite formation ($MgNH_4PO_4 \cdot 6H_2O$) and scaling in dewatering equipment or pipelines. More about struvite formation can be found in chapter 6.

Organic chemicals (polymers)

The most commonly used polymers for dewatering municipal sludge are cationic polyacrylamides and, in some cases, organic coagulants (polyamines and poly-DADMACs). These polymers will soon be partly replaced by bio-based polymers.

Characteristics of cationic polymers:

- Physical form: emulsions, dry polymers, water-based dispersions
- Charge density: number of charged units along polymer chain, usually expressed in mol percentage
- Molecular weight (length of the polymer chain): the sum of the atomic weights of the atoms in the molecules present in the polymer. The molecular weight (MW) is expressed in Dalton (5–20 million for cationic polymers).
- Molecular structure: linear, branched, and cross-linked.

Table 4.10

Emulsions versus dry powders (most commonly used).

	Active polymer content	Dissolution/aging time	Shelf life	Molecular structure
Emulsions	25–50%	Short (10–20 minutes)	6–9 months	Branching and cross-linking is possible
Dry polymers	~90%	Long (60 minutes)	24 months	Branching and cross-linking is difficult

Polymer solution preparations

Emulsions

When preparing a polymer solution from an emulsion, care must be taken to provide the ideal conditions to "invert" or "break" the emulsion and to allow the polymer to fully dissolve in the water. To make a homogenous polymer solution in water, the emulsion must be added to the water, never the other way around. Initially, a very high shear is needed.

The make-up concentration of the EPAM solution should generally be between 0.5 and 1.5% "as is". A higher concentration may reduce the required aging time up to the point where the solution becomes too viscous, which can cause problems with pumping and mixing with the sludge. A lower make-up concentration will lead to a less viscous solution, up to the point where the concentration is too low for the pump capacity and dosage required.

Once the EPAM is properly inverted, a minimum aging time of 10 to 20 minutes is recommended to ensure that the polymer will reach its maximum effectiveness (maximum performance with minimum dose level). This aging can occur in a tank with gentle mixing, in a tank with no mixing, or even within the solution feed pipe work itself. The purpose of this aging is to take advantage of the high molecular weight by allowing full dissolution of the polymer after inversion and full extension of the polymer molecules. If necessary, the EPAM solution can be further diluted with water to the optimal dosage concentration for the application.

Centrifugal pumps should be avoided for polymer transfer since they can damage the polymer chains.

Dry polymers

The single most important factor in the preparation of dry polymer solutions is the complete wetting of the individual polymer particles. Special equipment with a polymer dispersing device and agitating tanks should be used. After wetting the individual particles, the polymer should be aged for at least 60 minutes for maximum effectiveness. This can be carried out in a tank with gentle mixing.

Dry polymer solutions can be made from concentrations of 0.1 to 1.0%. Typically, a 0.5% concentration stock solution is initially prepared and the required polymer concentration reached by adding secondary dilution water prior to the addition point.

Centrifugal pumps should be avoided for polymer transfer.

Water quality for preparing polymer solutions

The water quality impacts the efficiency of the resulting solution. For optimum results the following water quality is recommended:

1. Water temperature between 10 and 30°C
2. Water hardness <350 ppm total hardness as $CaCO_3$ (<20 °dH) is recommended
3. Water alkalinity should be as low as possible to prevent hydrolysis of cationic EPAMs
4. pH level of 5.0–7.0 in the final solution
5. Iron level <0.5 ppm is recommended.

Polymer dosage, consumption, and mixing

The polymer dosage is commonly based on the active polymer content of the made-up polymer solution and on the DS content of the sludge. The dosage for an average cationic PAM for digested wastewater sludge can range from 5 to 15 kg active polymer per tonne DS [kg/t DS]. But dosages far above and below are also often reported due to local circumstances and sludge composition. The dosage of emulsion polymer solution is typically calculated as product basis.

Mixing the polymer with the sludge is one of the most important factors affecting the sludge dewatering application. As polymer solutions can be very viscous, the correct polymer concentration should be chosen to optimize mixing conditions. A good starting point would be to aim for a 10:1 ratio of sludge flow (m^3/h) to polymer solution flow (m^3/h).

Mechanical dewatering technologies

There are several types of mechanical dewatering equipment for municipal sludge, for example centrifuges, belt presses, filter presses, and screw presses.

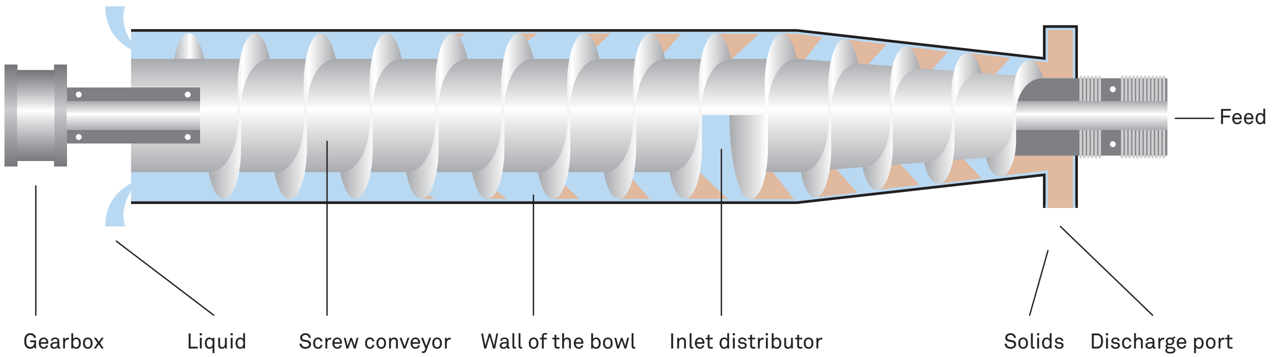
Centrifuge

Centrifuges are the most commonly used devices for municipal sludge dewatering. The main components of a centrifuge are a conical cylinder bowl that rotates at high speed (2,000–4,000 rpm) and a screw that rotates at a slightly different speed (a few rpm). The centrifugal forces created by the rotating bowl separate the liquids from the solids and convey the solids out using the screw.

Centrifuges typically need very long-chain cationic PAMs for effective flocculation. The reaction time for flocculation inside the device is very short: only a few seconds. The flocs must stay stable and withstand strong gravity accelerations and shear forces inside the device to result in effective dewatering, clear centrate, and high cake DS.

Figure 4.11

Decanter centrifuge example



Modified from Ref. 3: https://www.ebay.com/itm/Used-Alfa-Laval-ALDEC-G2-115-Two-Phase-Decanter-Centrifuge-Bowl-assembly-ONLY-/124015535672 - Date: 26.03.2020

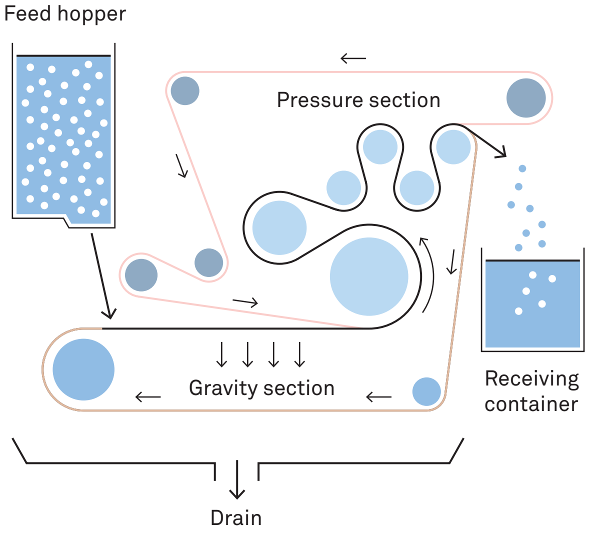
Belt press

A belt press consists of two belts. The conditioned sludge is fed on the first belt and the free water is drained using gravity. Ploughs on the belt roll the sludge around to improve the drainage and after this preliminary dewatering the sludge enters the pressing zone. The sludge is sandwiched and squeezed between the two belt filters which slowly convey the sludge over and under rollers. The forces this creates press out the excess water through the filter mesh of the belts. At the end of the press the dewatered sludge is scraped off the belt and collected.

Typically, medium-length PAMs are used for belt presses.

Figure 4.12

Belt press. Modified from Ref. 4: https://en.wikipedia.org/wiki/Belt_filter Date: 26-03-2020



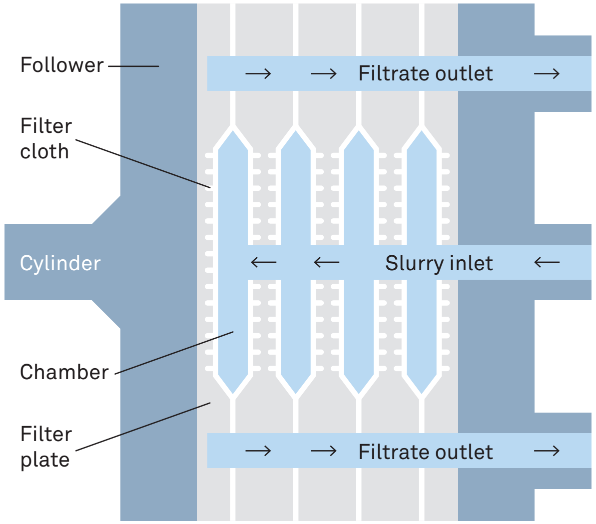
Filter press

The main components of a filter are the filter plates. The 20–40 mm space between the plates is called the chamber and this is where the filter cake is built up. Filter cloths are attached around the plates and conditioned sludge is pumped into the chamber. The filter cake builds up between the filter cloths and the clear water passes through the filter cloth pores.

Dewatering with a filter press is a batch process. At the beginning of the cycle the sludge flow is high and the pressure is low. At the end of the cycle the sludge flow is low and the pressure is high (up to 15 bar). Typically, low to medium-length PAMs are used for filter presses.

Figure 4.13

Filter press. Modified from Ref. 5: http://eco-grace-com.sell.everychina.com/p-107161099-1500x-1500mm-high-pressure-filter-press-plate-pp-membrane-filter-plate.html – Date: 26.03.2020



Screw press

A screw press is a slow-moving mechanical device that dewaters using continuous pressurized drainage. It consists of a flocculation tank, a cylindrical screen basket, and a rotating screw. The flocculated sludge enters the thickening zone and the free water is discharged through the screen basket whilst the thickened sludge is pushed by the screw towards the dewatering zone. As the sludge moves along the screen basket, the pressure increases as a result of:

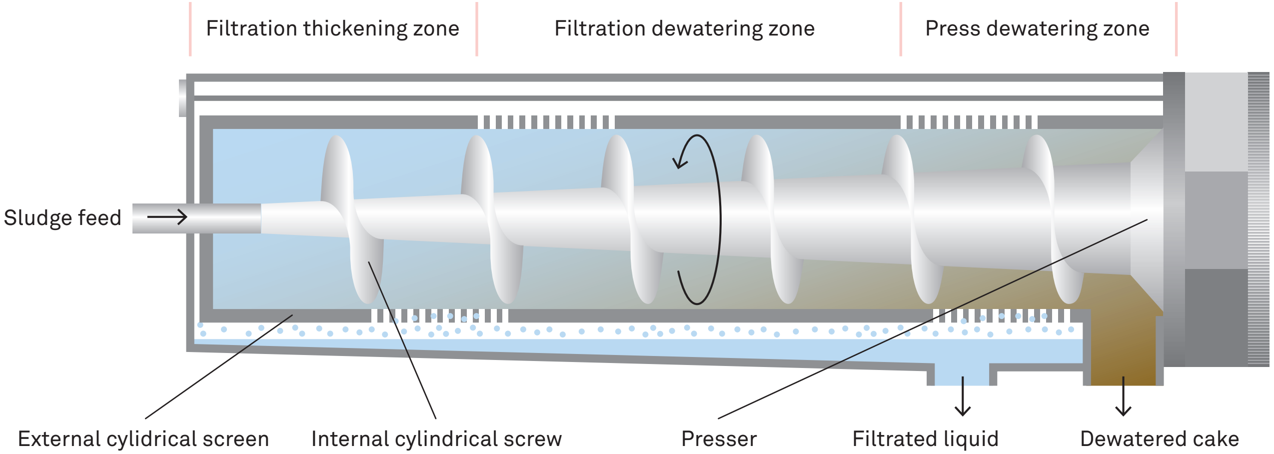
- Conical screw design
- Decreasing gaps between the flights of the screw
- Decreasing screen openings

A plate at the end creates further pressure from the outlet so that the sludge becomes drier.

Typically, low to medium-length PAMs are used for screw presses.

Figure 4.14

Screw press. Modified from Ref. 6: http://www.uboscreen.com/Mineral_Aggregate_Processing/steel-spiral-screen-1447-1.htm Date: 26.03.2020



Reject water

Reject water, also called centrate, press water, or filtrate, is produced whenever sludge is thickened or dewatered. It is normally returned to the main wastewater treatment line, often to the influent wastewater for further purification.

One of the most significant reject flows comes from sludge dewatering in wastewater treatment, e.g. from a centrifuge or filter press. These reject water streams contain elevated levels of nitrogen, phosphorus, and to a certain extent solid matter. It is wastewater from inside the wastewater treatment plant and must undergo purification treatment from the beginning of the process.

Since the reject water can contain high levels of ammonium and in some cases high levels of phosphates, some WWTPs treat the reject water before it is mixed with influent water. By doing this the internal load is reduced so the main process is stabilized.

Sludge recycling and disposal routes

There are several ways to recycle and dispose of municipal sludge. The main routes are described in this subchapter [Ref 7: https://ec.europa.eu/environment/archives/waste/sludge/pdf/sludge_disposal3.pdf - Date: 30.03.2020] .

Incineration

Incineration involves a combustion reaction and is one method of sludge disposal. The calorific value of a 100% dry sludge is around 10–20 MJ/kg of DS. Since dewatered sludge contains about 75% water, the calorific value for wet sludge is negative and it needs additional auxiliary fuel for complete combustion. To incinerate without an auxiliary fuel, the dry solids content of the sludge must be increased to around 30-45%. Therefore, in most cases, the energy generated during combustion will be counterbalanced by the energy used to reduce the water content in the sludge.

During incineration, the air supply and temperature must be carefully monitored to ensure complete combustion. If combustion is incomplete it can lead to odor problems and high emissions of pollutants such as nitrogen oxides. Flue gas has to be treated in accordance with local emission limits; ashes can be recycled.

Nowadays in Europe, sludge incineration is becoming more widespread, with three main incineration routes.

The term incineration is normally used for the combined incineration of sludge with other household waste at already existing plants requiring relatively low additional investments. This option is attractive if the calorific value of the sludge is close to that of the main waste being incinerated and the sludge source is in the vicinity of the existing incineration plant. The maximum ratio of sludge to waste has to be calculated according to the dry solids content of the sludge and proper mixing is essential to avoid process accidents. Mixing the sludge with the main waste can be done before the combustion chamber, or sludge can be injected into the furnace or at the exit of the combustion chamber under pressure.

Mono-incineration is carried out at dedicated sludge incineration plants. Building such a plant requires substantial investment so these plants are often combined with large WWTPs or are established in regions with large amounts of sludge available nearby. In mono-incineration various furnace types are used, with fluidized bed reactors becoming more widespread in recent years. This technology allows almost complete combustion of sludge at relatively low temperatures, keeps process temperatures steady, and has low maintenance costs. Additionally, sludge incineration in fluidized bed reactors is safer from an environmental point of view, as metal emissions to the atmosphere are lower. Mono-incineration is the most expensive sludge disposal route.

In co-incineration, sludge is used as a fuel at energy generating plants (e.g. coal power plants) or at plants producing certain products, such as cement. There are defined limits for the maximum feed rate of sludge to ensure quality and stability for the main process.

Other technologies involving thermal processing of sludge are pyrolysis, wet oxidation, and gasification.

Agricultural use

Sewage sludge contains compounds of agricultural value such as phosphorus, nitrogen, iron, potassium, calcium, and magnesium, as well as other macro and micronutrients necessary for plant growth. This means sludge can be recycled as an organic fertilizer or soil conditioner as a substitute for commercial fertilizers to improve yield. However, sludge must be safe, and the presence of harmful compounds, e.g. toxic metals, organic micropollutants, and pathogens in sludge must be carefully monitored. Many countries and the European Union have developed special practices and regulatory standards for the agricultural application of sludge to ensure adequate control and to manage environmental and health risks. Some factors influencing the agricultural use of sludge are culture of plants, soil quality, meteorological conditions, and field accessibility.

All sludge types (liquid, semi-solid, solid, or dried) can theoretically be applied to land. Each sludge type requires a specific method of transportation, application, and storage. The use of farmland and the option to apply sludge for agricultural purposes are seasonal. Most of the time, the agricultural sludge application can be carried out twice a year: after the harvest at the end of the summer and before ploughing and sowing in spring. This means there is a need for storage capacity if the main sludge recycling route is agricultural. Specific storage arrangements are required for each type of sludge to avoid leaching, spread of odor, particles in the air, and explosions.

Besides recycling on fields, sludge can also be applied in forestry and silviculture to fertilize soil and improve the growth of trees and other valuable plants. Quite large amounts of sludge can be spread on a relatively small area. The defining factors for sludge spreading conditions are soil type, plant species, and any other flora and fauna involved. There are certain rules for sludge quality if spreading is done in places with public access. As in agricultural applications, this alternative recycling route can be of importance if the potential spreading areas are local to a sludge source. Unlike in agriculture, sludge application in forests can be done practically all year round.

Sludge recycling to agriculture and forestry is one of the cheapest and most commonly applied methods. Transportation is the most expensive part of this sludge recycling route. Normally there is a maximum range defined depending on regional conditions that is a limiting factor for the land spreading of sludge. More about using sludge as a fertilizer can be found in chapter 6.

Composting

Composting is a widespread alternative to sludge recycling. This process is often used for the hygienization and stabilization of sludge prior to its application in landscaping, gardens, organic farming, or urban agriculture. It can also be used for land reclamation, wetlands construction, as cover for landfills, and for many other purposes. Municipal sludge can be composted separately or mixed with other household waste.

Composting is a natural process which involves biological thermal oxidation. It is carried out by microorganisms that decompose organic material. In industrial composting set-ups, sludge reaches a temperature of around 55–70°C, which kills pathogenic organisms. The sludge decomposes and results in a stable end product with a soil-like consistency and reduced odor. However, composting cannot degrade harmful organic substances or eliminate toxic metals.

Efficient composting requires a certain amount of management to maintain the necessary moisture and oxygen levels. A compost heap must have a dry content in excess of around 45%. To achieve this, sludge must be mixed with dry biodegradable material, such as sawdust, straw, or peat. The compost must also be mixed and ventilated regularly to supply oxygen and allow carbon dioxide to escape. Without such ventilation, the composting process will quickly come to a halt. The process takes several months and therefore requires a lot of space. The resulting compost is very porous, which means that transportation costs can be quite high.

Landfilling

There are two options for landfilling municipal sludge: mono depositing (just sludge) and mixed depositing (municipal waste and sludge). In mixed deposits, sludge content is around 20 to 25% of total volume. Mixed deposits are preferable because waste degradation and gas formation proceed better.

The following processes occur during landfilling:

- Aerobic degradation: consumption of available oxygen by aerobic microorganisms (approx. 14 days), increase of organics in leachate
- Acetogenesis: decomposition of easily bio-degradable substances by acetogenic and fermentative bacteria, increase in the solubility of inorganic components including toxic metals due to the decrease in pH level, leachate is highly polluted with organics

- Anaerobic degradation: production of methane by methanogenic bacteria, gas composition becomes stable, pH levels increase, lower organic content in leachate.

Landfill generates about 10 m^3 of gas per tonne of waste per year. The composition of gas produced is usually 50 to 60% methane, 40 to 50% carbon dioxide, as well as trace elements like volatile organic compounds (VOCs). Methane can be recovered on site for energy production.

Besides gas, leachate is also generated at landfills; the amount depends on landfill cover and weather conditions. Leachate can penetrate into soil and water and pose an environmental hazard as it contains organic compounds, toxic metals, different ions, and micro-organisms. However, it can be treated on site to minimize the emission risks.

In the past, landfilling has been a major disposal route for municipal sludge. Currently, European legislation only allows sludge to go to landfill in the following defined cases:

- Sludge is highly contaminated with harmful substances making landfilling the only possible route for disposal
- Agricultural application (including forestry and land reclamation) is not feasible due to location or topography
- No incineration is available in the vicinity of the site
- Total recycling costs are uneconomic.

Local country regulations define sludge disposal conditions.

Other sludge handling processes

Pyrolysis

Pyrolysis results in oil-like products and is another alternative for sludge utilization. During pyrolysis dried sludge is heated to 300–500°C and allowed to carbonize in an environment that has a poor oxygen supply. This produces tar, oil, and carbon. The oil yield from trial plants has been 16–30% of the organic content. Some financial return can be obtained from the sale of oil products.

Pasteurization and hygienization

In many countries, pathogens in sludge must be reduced to below a mandated level before it can be spread on agricultural land or disposed of in landfill sites. One method of pasteurization is to heat the sludge to at least 70°C for 30 minutes.

Stabilization with lime

All biological activity effectively comes to a stop if the pH rises above 11. This fact is exploited in lime stabilization, which involves adding enough lime to the sludge to ensure that the pH stays above 11 even after holding for around 14 days.

Stabilization with lime has several advantages. The process is easy to control, and the investment costs are modest. The phosphates and heavy metals that are present in the sludge are bound very securely by the lime, and pathogenic microorganisms are killed effectively. In order to reduce the internal nitrogen load, the high pH of the sludge can be exploited for the process known as ammonia stripping.

Lime may be added to the sludge before or after dewatering. If slaked lime is added before dewatering it results in a sludge that is odorless and has much better dewatering characteristics. If unslaked lime is added after dewatering it causes a sharp temperature increase in the sludge. This high temperature also pasteurizes the sludge.

The disadvantage of this process is its high operating costs.

Table 4.15
Amounts of lime required for sludge stabilization.

Sludge type	Lime addition [kg $Ca(OH)_2$ / tonne DS]	[kg CaO / tonne DS]
Primary sludge	100–150	70–120
Primary and secondary sludge	300–500	200–400

Kemicond

Kemicond (Kemira's sludge conditioning process) is a chemical-physical conditioning process developed for digested sludge that contains iron and phosphorus.

The sludge is acidified straight from the digester in order to dissolve ferrous salts and phosphate at a pH of between 3 and 5. By oxidizing the dissolved ferrous salts to ferric salts using hydrogen peroxide, a very strong oxidative environment can be created. The sludge is disinfected and free from odor. The oxidized iron will precipitate the dissolved phosphorus in a crystalline form. The sludge's water-retentive gel structure is broken down and the dewatering properties of the sludge are significantly improved. More than 40% DS can be achieved in a screw press.

Sludge from drinking water production

The aim of drinking water production is to separate pollutants such as clay and mineral particles, algae, and humic substances (which were discussed in chapter 2) from water.

These contaminants are separated as aqueous sludge, which can be difficult to dewater. When the treatment includes a chemical stage (coagulation and flocculation) this also produces a hydroxide sludge (chemical sludge) that can be bulky and may be difficult to dewater.

Surface water treatment plants produce the most sludge during drinking water production. As a guide figure, the sludge produced by surface water treatment is around 4.4 g DS per person per day.

There are three main disposal routes for sludge from drinking water production: return it to the water source, place on landfill, or transfer it to the sewage system.

The negative consequences of returning the sludge to the water source are the bank of sludge that builds up around the discharge area and the clouding of the water, which can have a negative effect on the ecosystem in the waterway. The option to pump the drinking water sludge to a WWTP via the municipal sewage system is considered both a good and a bad solution. The advantages are that the coagulant in the drinking water sludge can adsorb some phosphate and the chemical dosage at the WWTP can be reduced. Another advantage for iron-containing drinking water sludge is that the iron can react with sulfides in the sewer system as well as in the anaerobic digester, thereby reducing some odor and corrosion problems.

The disadvantage of bringing drinking water sludge to a WWTP is that it places a higher load on the WWTP. This could be a concern if the WWTP is at the limit of its design capacity. Another disadvantage, of course, is that sludge production increases. It takes capacity from anaerobic digestion as well as from dewatering devices. On top of that the sludge disposal costs increase.

Drinking water sludge is normally much cleaner than wastewater sludge. It mainly contains coagulant, sand, silt, and some organic matter. It could therefore be considered a source for coagulant recovery, but so far there are no commercial installations.

Sludge from industrial processes

Sludge from pulp and paper industries

The pulp and paper industry mainly generates sludge during debarking, fiber recycling, and deinking, as well as in wastewater treatment. Organic sludges are typically incinerated while mainly inorganic sludges are landfilled. The recycling of sludges as raw material is a growing trend.

External treatment produces sludge in primary, biological, and chemical tertiary steps. Typical sludge generation in external treatment is shown in table 4.18.

Table 4.18
Typical sludge generation in external treatment.

Production	External treatment primary and biological sludge kg/t product	Share of bio sludge
Pulp	10–50	35–65%
Paper & Board	5–15	20–30%

Sludge from the primary sedimentation, surplus biological sludge produced, and tertiary sludge all need to be removed effectively and in a controlled way to avoid problems. Cationic polyacrylamide polymers normally give an effective dewatering result with a dosage of 1–3 kg/t DS. However, as different types of sludge have different characteristics, effective sludge dewatering can be a challenge for many mills, especially if there are time-dependent variations in the different sludge loads.

A high DS content after sludge dewatering increases the efficiency of sludge disposal and reuse. Additional components, such as iron salts, bentonite, or organic coagulants may be used to achieve a higher dry solids content especially when sludge dewatering is difficult. Hydrogen sulfide, which is commonly produced during the dewatering of biological sludge, can be eliminated by adding iron salts.

Mineral tailings

The main target of the mineral processing industry is to recover valuable metals from metal-containing ore. These valuable metals are usually separated through processes like grinding, screening, flotation, thickening, filtration, leaching, extraction, and purification. All these processes utilize water as a carrier and their efficiency can be improved using specific chemistries.

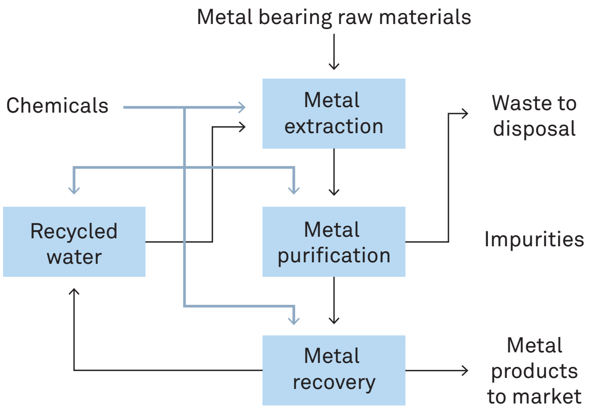
When the valuable metals have been recovered the rest of the ore is disposed of. This waste fraction is commonly known as tailings. For example, some copper ores may only contain 0.4% copper. This means that during processing, there are up to 450 times more tailings produced (as slurry) than recovered copper. Gold ores may only contain two grams of gold per tonne of ore and therefore 950,000 times more tailings are created than recovered gold. The ratio of recovered metal to waste for different metals is shown in table 4.19. The disposed tailings are usually landfilled as wet material. Sometimes some of the water can be recovered after a long natural settling period. Chemicals are not normally utilized in tailings treatment.

Table 4.19
Amounts of lime required for sludge stabilization.

Metal	Waste to mineral ratio
Bauxite	3 to 1
Iron	5 to 1
Zinc and lead	32 to 1
Copper	450 to 1
Nickel	560 to 1
Gold	950 000 to 1

The water from the metal recovery processes is separated and usually reused in the process. The process water goes through solid/liquid separation stages in thickeners and settling tanks. In these process steps, chemicals such as flocculants and coagulants are utilized. The flowsheet of utilized raw material, disposed tailings, process water, and recovered metal is presented in figure 4.20.

Figure 4.20
General raw material and process water flowsheet for mineral processing.



Power plants

Electricity production requires large amounts of raw water for cooling and boiler applications. Power plants are located in coastal areas with access to sea water, and in inland areas where surface water from rivers is available.

Significant sludge amounts are produced from inland surface water treatment. Coagulants, mostly iron based, and anionic flocculants are added to river water at pH 7.2 to precipitate soil, suspended solids, and COD. The sludge produced consists mainly of iron and other inorganic materials and can be easily dewatered in filter presses. Because of the high iron content, this type of sludge can be reused as a raw material for odor control applications in sewers to reduce hydrogen sulfide.

An additional treatment step after coagulation and sedimentation is required to reduce carbonate hardness. Lime $Ca(OH)_2$ is added at pH 10.2 to precipitate $CaCO_3$ in order to reduce HCO_3^- concentration prior to usage in a cooling tower or as boiler feed water. This sludge can also be easily dewatered in filter presses by adding anionic flocculants.

For both sludges the achieved DS content after dewatering is much higher (DS up to 60%) compared to municipal sludge because of mostly inorganic components.

The power industry also produces another sludge from flue gas treatment, but in much lower quantities. The purpose of this treatment is the reduction of substances that are harmful to the environment such as toxic metals, dioxins, and furans through precipitation with coagulants, flocculants, and sometimes the addition of powdered activated carbon. The precipitated sludge is also dewatered in filter presses and disposed of.

Food industry (dairy and meat)

Wastewater from most food production processes has high concentrations of fat, carbohydrates, and nutrients. This means sludge from the wastewater process has a high calorific value, giving it a very high biogas potential and meaning it should be treated in a biogas plant. More about biogas production can be found in chapter 6. Since sludge from the food industry is nutrient rich and has very low levels of potentially toxic elements, it is suitable to be used as an organic fertilizer after anaerobic treatment.

CHAPTER 5

PRECIPITATION, COAGULATION & FLOCCULATION

Precipitation, coagulation & flocculation

This chapter gives a comprehensive overview of precipitation, coagulation, and sedimentation processes and the differences between them. It describes the different contaminants in natural waters and wastewater that can be removed using chemical treatment. Special attention is paid to aluminum and iron-based coagulants and flocculants. This chapter also explains the mechanism of coagulant and flocculant action in water treatment and sludge dewatering, and the parameters affecting their performance. Information is also provided on how organic polymers work when cleaning water and on the differences between the actions of organic polymers and inorganic salts.

Contaminants in water can either take the form of particles or be so small that they are soluble. Dissolved substances in wastewater can include sugars or orthophosphates, while soft surface water can contain fulvic and humic acids that give it color. Moreover, both natural waters and wastewater can be contaminated with metals. Water can also contain viruses, bacteria, debris, and inorganic compounds (e.g. clays or metal oxides).

Contaminants in wastewater

Most of the contaminants in wastewater are in the form of particles.

Table 5.1 shows the distribution of TOC, COD, protein, fat, and carbohydrates in wastewater in terms of particle size.

Table 5.1
COD, TOC, fat, protein, and carbohydrate content distribution in soluble and particle form in wastewater. The figures in brackets are taken from the General Nature of Soluble and Particulate Organics in Sewage and Secondary Effluent publication referenced below.

Parameter	Soluble <0.08 μm	Colloidal particles 0.08–1.0 μm	Supercolloidal particles 1–100 μm	Sedimenting particles
% total COD	25 (40)	15 (10)	26 (21)	34 (29)
% total TOC	31 (42)	14 (11)	24 (20)	31 (27)
% total fat	12	51	24	19
% total protein	4	25	45	25
% total carbohydrates	58	7	11	24
Biochemical oxidation rate	0.39	0.22	0.09	0.08

(Ref. 1: Heukelekian, H. and Balmat, J.L., Chemical Composition of the Particulate Fraction of Domestic Sewage, Sewage and Industrial Wastes, 31(5), 1959:4, 413–423; Rickert, D.A. and Hunter, J.V., General Nature of Soluble and Particulate Organics in Sewage and Secondary Effluent, Water Research 5, 1971, 421–436; Balmat, J.L., Biochemical Oxidation of Various Particulate Fractions of Sewage, Sewage and Industrial Wastes, 1957, 29(7), 757–761.)

The significance of particle size in sedimentation

The time needed for a particle to sediment depends on its density and size, and on the gravity, density, and viscosity of the liquid in which it is dispersed.

Sand and clay often have a density of around 2.65 g/cm^3.

The density of flocs depends on their size and the amount and type of coagulant used. The floc density decreases with increasing floc size and is typically around 1.02 to 1.1 g/cm^3.

Table 5.2 shows how long it takes spherical particles of different diameters to settle 1 meter in stationary water if they have a density of 1.05, 1.10, and 2.65 g/cm^3 respectively, provided that their sedimentation behavior follows Stokes' law.

Flocs do not have a spherical form and their settling behavior therefore does not obey Stokes' law. However, the table does give a useful guide to the time required for sedimentation.

Table 5.2

Influence of particle diameter on the time required for particles to settle 1 m in stationary water at a temperature of 25°C, assuming that particle sedimentation follows Stokes' law and that particles have a density of 1.05, 1.10, and 2.65 g/cm^3 respectively. The table also shows the surface area of 1 cm^3 of particles of different sizes.

Particle diameter	Sedimentation time (1.05 g/cm^3)	Sedimentation time (1.10 g/cm^3)	Sedimentation time (2.65 g/cm^3)	Total particle surface area (m^2/cm^3)
1 mm	37 seconds	18 seconds	1 second	0.006
0.1 mm	1 hour	31 minutes	2 minutes	0.06
10 µm	4 days	2 days	3 hours	0.6
1 µm	1 year	0.6 year	13 days	6
0.1 µm	117 years	58 years	3.5 years	60

It can be seen from table 5.2 that particles with a size of 1 mm or larger settle quickly. Particles of colloidal size are, however, impossible to sediment without using centrifuges or by aggregating them into larger units by using a metal salt, a polymer, or a combination of the two.

Sedimentation time increases with decreasing water temperatures (mainly due to the increasing viscosity of water). At 5°C about 50% higher sedimentation times are needed compared to the times given in the table above.

The smaller the particle is, the larger is its relative surface area. Surface forces between small particles play a decisive role in their tendency to aggregate.

The smallest particles visible to the naked eye have a diameter of about 40 µm. Particles with smaller diameters are perceived as turbidity. Particles with a size similar to the wavelength of light, i.e. 0.4–0.7 µm, make a large contribution to turbidity. The more the particle size deviates from the wavelength of light, the less turbidity they will cause. The size of many bacteria means that they cause turbidity.

Bacteria are either spherical or rod-shaped particles, often with sizes varying between 0.35 and 35 µm. See figures 5.3–5-6.

Viruses are very small particles with sizes of about 0.02–0.4 µm.

Particles that are so small that they do not sediment naturally are called colloidal particles. They are said to be stable if they do not aggregate and unstable if they aggregate readily.

Figure 5.3
Bacteria with a spherical form (Staphylococcus aureus).

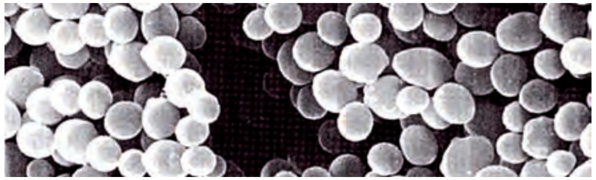
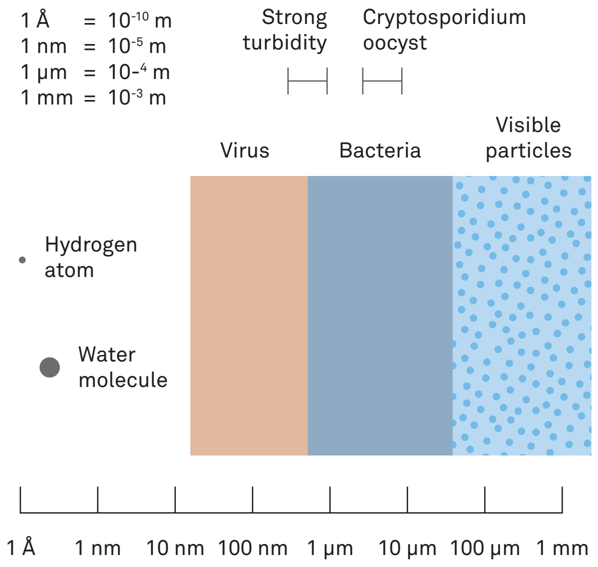


Figure 5.4
A spiral-shaped bacterium (Cristispira).

Figure 5.5
Rod-shaped bacteria.

Figure 5.6

Logarithmic size range.



Surface charge of particles in natural waters

The net charge of the dispersed particles in natural waters depends on their pH. At an ambient pH the net charge of most particles in water is usually negative.

Some microorganisms are covered by a negatively charged polysaccharide layer. The negative charge of this layer is usually due to the presence of carboxylic groups. The charge of carboxylic groups depends on their pH. At very low pHs they are non-charged but at most pHs occurring in nature they have a negative charge.

Proteins contain groups that can be either positively or negatively charged. Some groups on the surface of proteins have zero charge at low pH and a negative charge at higher pH levels.

These groups are:

- carboxylic groups (-COOH ⟷ -COO$^-$ + H$^+$)
- sulfhydryl groups (-SH ⟷ -S$^-$ + H$^+$)
- phenolic hydroxyl groups (-OH ⟷ -O$^-$ + H$^+$)

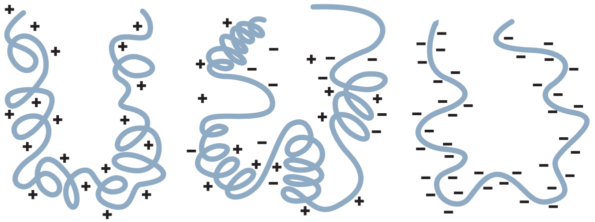
Proteins also contain groups on their surface which at acidic to neutral pHs are positively charged and at basic pHs have zero charge. These groups are:

- ε–amino groups (-NH^{3+} ⟷ -NH$_2$ + H$^+$)
- imidazole groups
- guanidine groups

The particle charge of a protein surface is strongly dependent on the pH. With increasing pH the number of negative charges increases and the number of positive charges decreases; conversely, with decreasing pH the number of positive charges increases and the number of negative charges decreases. The pH at which there are an equal number of positive and negative charges on the protein is called the isoelectric point of the protein. Different proteins have different isoelectric points, and many proteins coagulate spontaneously at their isoelectric point.

Figure 5.7 illustrates the influence of pH on the charge of proteins.

Figure 5.7
Charge of a globular protein at different pH levels. It can be seen that the configuration of proteins also changes with pH.



At very low pH

At the isoelectric point

At very high pH

Inorganic particles in natural waters are often covered by 1–20% natural organic material. Most particles in lake and river waters are negatively charged and this negative charge increases as pH increases.

Contaminants that can be removed by chemical treatment

Removal of particles

Surface water contains a variety of particles, such as insect eggs, bacteria, viruses, waste and debris products, clay, and sand. Many of them present a health hazard, and their presence increases the amount of disinfectant needed before water can be distributed to consumers. High concentrations of disinfectant can give water an unpleasant taste. Some parasite oocysts, e.g. Cryptosporidium, which have a spherical shape and a diameter of about 3–7 µm, do not seem to be killed by the most common disinfectants. In order to eliminate the risk of epidemics it is therefore important to remove them before distributing the water.

Other “particles” that must be removed include Giardia (oval to spherical shape and measures 5-15 x 8-18 µm), Legionella, Cholera, and pathogenic viruses. If they cannot be removed by coagulation only, the water needs to be disinfected.

Aluminum and iron salts have the ability to aggregate particles into sizes that can be removed.

The reason for this is that almost all particles in natural water are charged. Most of them have a net negative charge. They therefore repel each other and remain dispersed in the liquid if they cannot find something to adsorb to.

Aluminum and iron ions are positively charged. They form polymer ions and hydroxides that bind to small particles and create flocs, which can be separated from the water relatively easily.

The use of chemicals for water treatment in recent decades has improved our environment.

Figure 5.8 shows how the introduction of chemical treatment with an aluminum salt at a popular bathing lake in the south of Sweden reduced the number of tapeworm eggs in the lake. The tapeworm eggs infected fish, which in turn infected people if they were eaten without being properly cooked.

Figure 5.9 shows that viruses, which are very small particles, can be extensively removed using chemical treatment.

Figure 5.8

Tapeworm infection between 1963 and 1973 in Lake Ivösjön in Sweden. Chemical treatment was introduced in 1970. (Ref. 2: Almer, B. Bekämpning av binnikemasken, Biphyllobothrium latum. Information från sötvattenslaboratoriet, nr. 15 (1973), Sweden.)

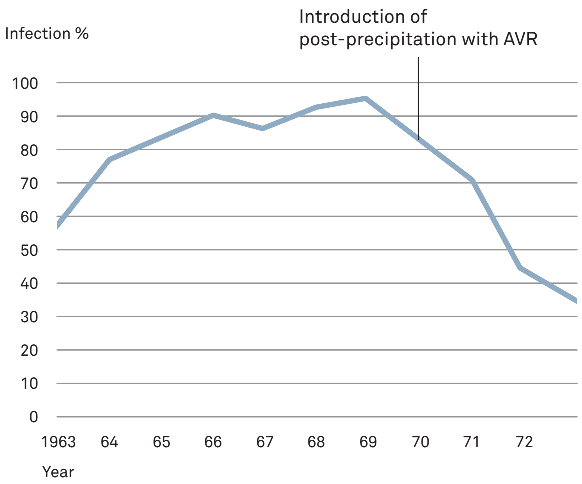
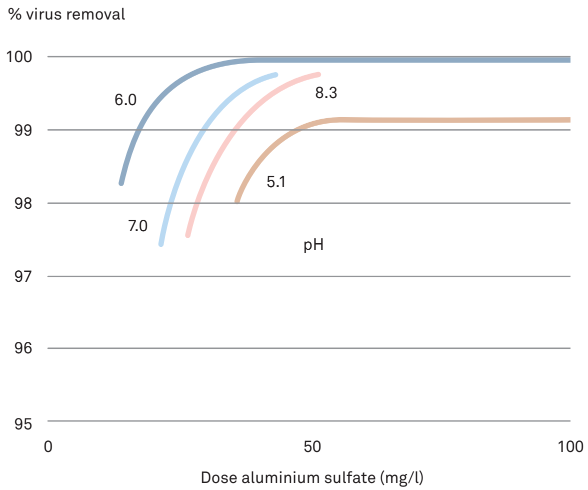


Figure 5.9

The influence of pH and the dose of aluminum sulfate on the percentage of virus removed. (Ref. 3: Chadhur M and Engelbrecht R. Removal of viruses from water by chemical coagulation and flocculation. JAWWA (1970) 31.)



Removal of dissolved substances

Most dissolved contaminants with a negative charge can be precipitated and removed using chemical treatment.

Soft surface water often has a yellowish or brownish color that comes from fulvic and humic acids. These are formed when trees, bushes, and leaves decompose. They are aromatic and contain carboxylic, phenolic, ketone, and methoxy groups. Humic acids have a higher molecular weight (1,000–1,0000 g/mol) than fulvic acids (500–2,000 g/mol). Both types of compound can be precipitated and removed using metal salts.

Various metal ions can also be bound to the hydroxides formed by the added aluminum or iron salt.

In wastewater, orthophosphate and triphosphate are examples of dissolved substances that can be removed by adding metal salts.

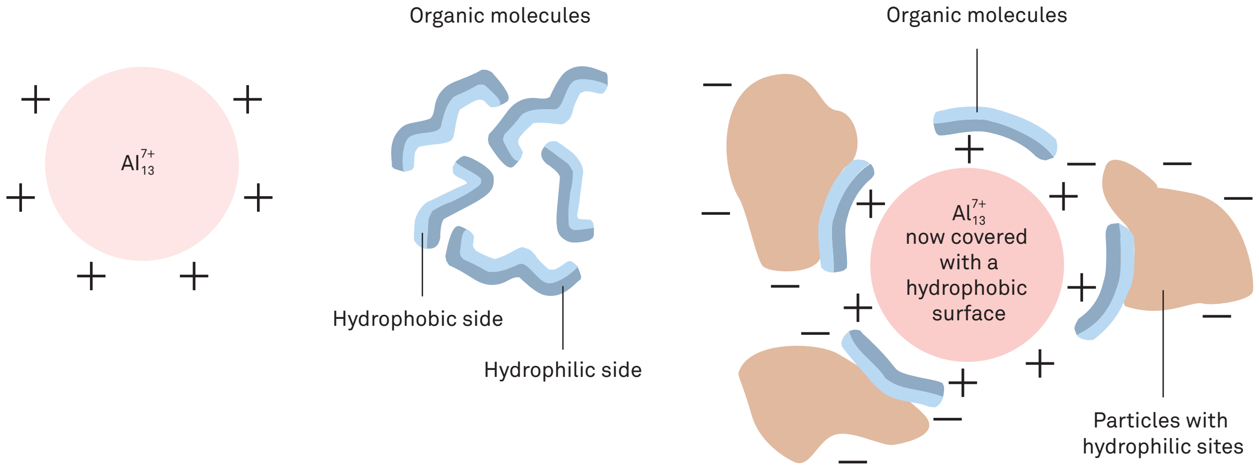
Most substances that have a low molecular weight and no charge, such as carbohydrates, are not removed by chemical precipitation. These low-molecular-weight substances can be removed efficiently using biological processes.

Aluminum and polyaluminum compounds, however, have the ability to form strong complexes with a number of uncharged, low-molecular-weight organic compounds.

These organic substances bind to the aluminum or polyaluminum ions in such a way that the hydrophilic end of the organic molecule points towards the surface of the aluminum compound, while its hydrophobic end points towards the aqueous phase (fig. 5.10). In this way, part of the surface of the aluminum compound becomes hydrophobic and can cross-link and precipitate particles that have hydrophobic sites. Some microorganisms have surfaces that are covered with hydrophilic polymers and when aluminum ions bind to some of these polymers the polymer layer becomes hydrophobic. When this happens, the microorganisms aggregate through hydrophobic interaction and precipitate. (Ref. 4: Carel J. van Oss, Interfacial Forces in Aqueous Media, Marcel Dekker, Inc. 1994).

Figure 5.10

How an uncharged organic molecule can bind to a polyaluminum ion and give it hydrophobic properties, thereby enhancing its tendency to bind to and precipitate hydrophobic material.



How easily are contaminants removed?

The higher the molecular weight of a dissolved substance or the larger a particle is, the easier it is to precipitate.

The precipitation of particles and dissolved substances is governed by different chemical rules. There are many different chemicals on the market with different relative abilities to precipitate particles or dissolved substances.

Coagulation and flocculation

Victor Kuhn LaMer originally defined coagulation as the process of reducing the electric repulsion between particles by adding simple salts. The particles then aggregate as a result of the remaining attraction forces between them.

He defined flocculation as the process of aggregating particles with the aid of polymers. He considered the bridging action of the polymers to be very important in flocculation.

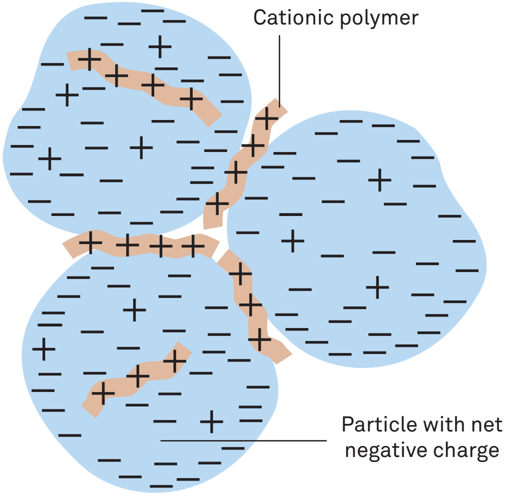
The bridging action of polymers is important, and there are many electron microscope pictures showing that polymers form thin filaments that join different particles together.

However, we now know that polymers can also aggregate particles by means of patch adsorption and cross-linking (see figure 5.11). High basicity polyaluminum ions probably aggregate particles using this mechanism. For this reason, it is now difficult to use these two words in the same way as LaMer did.

Some authors now define coagulation as the process whereby charged particles are neutralized and flocculation as the process whereby the neutralized/destabilized particles join together and form aggregates.

Other authors just use the word flocculation as a generic term to cover all aggregation processes.

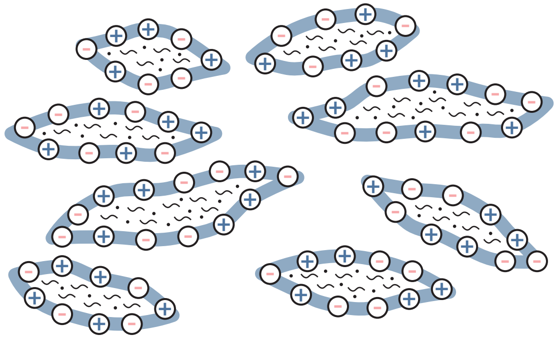
Figure 5.11
Aggregation of negatively charged particles by patch adsorption and cross-linking with cationic polymers (patch flocculation).



Reactions that occur when a solution of Al^{3+} or Fe^{3+} salts is added to water

Most impurities in water, both those in the form of particles and those in the form of dissolved substances, have a negative surface charge. Negatively charged particles repel each other and do not aggregate (see figure 5.12).

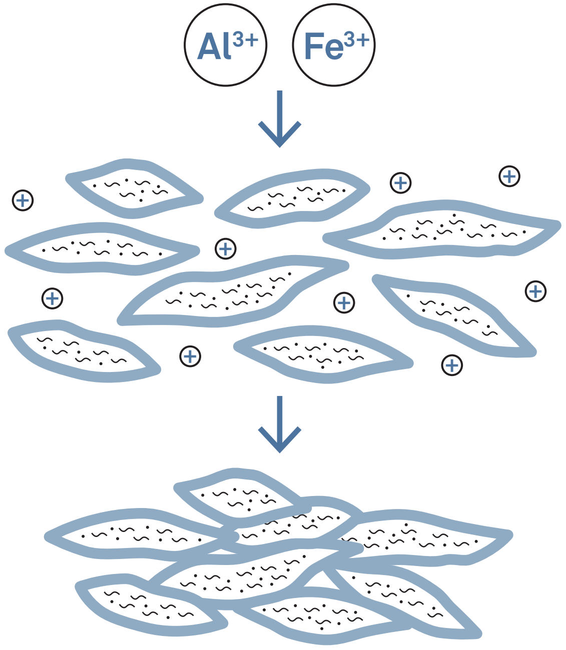
Figure 5.12
Particles have a negative net charge and repel each other.



By adding positively charged metal ions, dissolved negatively charged substances – such as phosphates, silicates, and humic and fulvic acids that give color to many waters – can be precipitated, and as explained below, most particles can be coagulated. Using this technique, microorganisms can also be aggregated into large enough sizes that they settle in sedimentation basins. Aluminum or iron salts are the most common coagulants used for this type of application.

Aluminum ions are very small ions with three plus charges. When added to water they form positively charged aluminum hydroxides and oligomeric and polymeric ions, e.g. $Al_2(OH)_2(H_2O)_8{}^{4+}$, $Al_3(OH)_4(H_2O)_{10}{}^{5+}$, and $Al_{13}O_4(OH)_{24}(H_2O)_{12}{}^{7+}$, that can crosslink and aggregate dissolved and negatively charged particulate impurities.

Figure 5.13 and 5.14
The addition of positive ions (metal salt) and creation of larger flocs – charge neutralization



Both divalent (Fe^{2+}) and trivalent (Fe^{3+}) iron ions exist. Trivalent iron salts can clean water in a similar way to aluminum salts. However, divalent iron salts can only be used for precipitating some dissolved substances, e.g. phosphate ions. Divalent iron salts do not form polymeric ions and cannot be used for precipitating negatively charged particles.

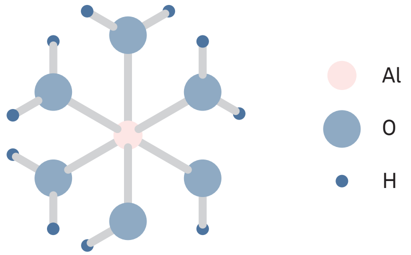
The properties of Al^{3+} and Fe^{3+} salts that lead them to form positively charged hydroxides and oligomeric ions is very important in terms of their capability to clean water.

Both Al^{3+} and Fe^{3+} are small ions with a high positive charge within a very small pH and concentration area. This high positive charge strongly attracts the two free electron pairs of water's oxygen atoms.

In acidic and neutral water solutions six water molecules bind in six directions to each Al^{3+} and Fe^{3+}. Of the surrounding six water molecules, four of the oxygen atoms are in the same plane as the aluminum or ferric ion and two are in a plane perpendicular to the one described above.

Depending on the temperature, a second layer of 10 to 12 more loosely bound water molecules exists around $Al(H_2O)_6^{3+}$ ions. Figure 5.15 shows the first layer of water around an Al^{3+} ion.

Figure 5.15
The positions of water molecules in the $Al(H_2O)_6^{3+}$ complex.



Ref. 5: Karlsson Magnus, Structure Studies of Aluminum (III) Complexes in Solids, in Solutions and at the Solid/Water Interface, Doctor's thesis, 1998, Umeå University, Sweden

Surrounding the aqueous aluminum ions are negatively charged ions that also contain some tightly bound water molecules.

Although the solution looks like ordinary water it contains very little free water with the same properties as the water you get from your tap at home. Almost all the water in a concentrated aluminum salt solution is tightly bound to the ions. The freezing and boiling points of the solution therefore differ from those of ordinary water.

When a concentrated solution of aluminum or iron salt is added to water, the Al^{3+} and Fe^{3+} ions react so strongly with the water that it is dissociated into hydrogen and hydroxide ions.

$Al^{3+} + H_2O \rightarrow AlOH^{2+} + H^+$

The above ions also contain chemically bound water molecules, but for the sake of clarity these are not shown in this or the following formulae.

The newly formed aluminum hydroxide ion reacts with water in two stages, as shown below:

$AlOH^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+$
$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3 + H^+$

Both these reactions occur very quickly.

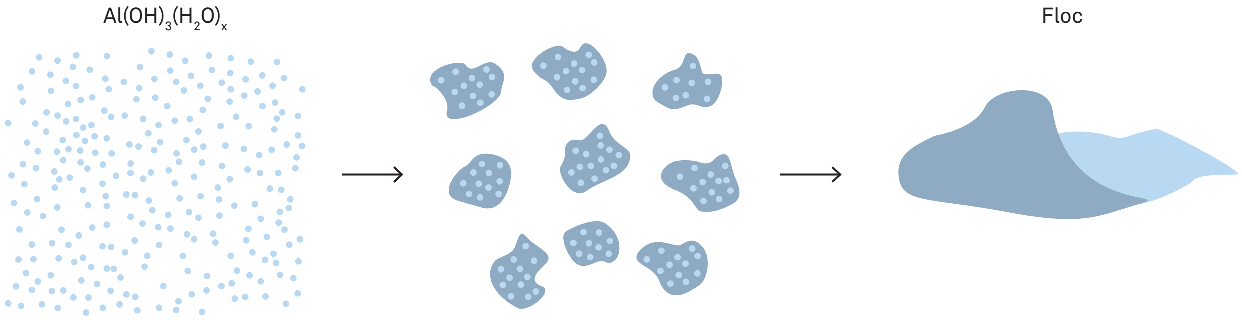
During the first second after the concentrated aluminum salt solution is added to the water, the aluminum ions exist mainly as Al^{3+} and $AlOH^{2+}$ and to a lesser extent as $Al(OH)_2^+$.

The extent of these reactions depends on pH and temperature. At pHs around neutral, each Al^{3+} and Fe^{3+} reacts with water in such a way that three H^+ ions are formed.

When freshly formed aluminum hydroxide grows, the aluminum ions become directly crosslinked by the hydroxide ions. Depending on the temperature it usually takes between one and seven seconds to form measurable amounts of aluminum hydroxide. After several minutes the hydroxides have grown large enough to see with the naked eye.

Sites with positive charge of the hydroxide repel each other. When the hydroxides grow, they therefore take on a flake-like form. Under favorable conditions the hydroxides can grow to large sizes (fig. 5.16).

Figure 5.16
Floc growth as a function of time.



Large newly formed aluminum hydroxide flocs are relatively brittle and can be easily break down by shear.

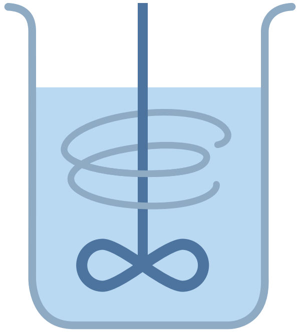
The average positive charge of each aluminum ion in aluminum hydroxide is lower than that of a fresh aluminum ion that has not had time to react with water. The charge of Al^{3+} ions added to water decreases over time.

Suppose that one liter of wastewater contains 8 mg of phosphate (P) in the form of orthophosphate. This solution contains 222,222 times more water molecules than orthophosphate ions. The wastewater contains 1,000/18 moles of water and 0.008/32 moles of orthophosphate: (1,000/18)/(0.008/32) = 222,222.

When the concentrated aluminum salt solution is added to water the likelihood that the Al^{3+} will find and react with water is much greater than the likelihood of it reacting with $H_2PO_4^-$.

In order to increase the likelihood of the metal ions in the concentrated metal ion solution binding to the contaminants in the water that is being treated, it is important to add the coagulant somewhere there is high turbulence. In turbulent locations the probability of Al^{3+} ions quickly finding a contaminant to react with is greater than in stationary water (figure 5.17).

Figure 5.17
It is important to add the metal salt solution at a point where there is high turbulence. By doing so the ions in the metal salt solution are used more effectively.



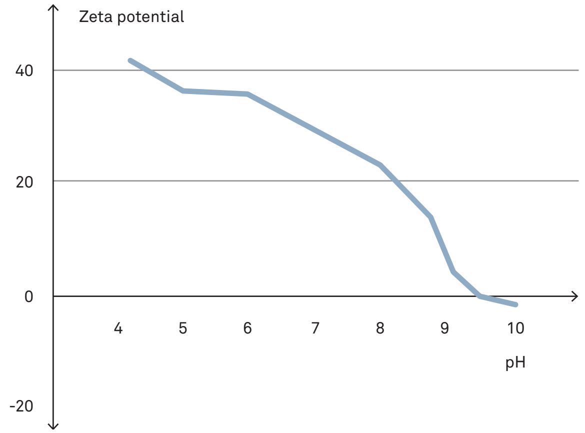
Even with good agitation it is inevitable that $Al(OH)_3$ is formed. Initially the aluminum hydroxide is formed as small clusters with loosely bound water molecules. With time the aluminum hydroxide loses more and more water molecules. Aluminum hydroxide molecules start to aggregate by hydrogen bonding. Flocs start to form and soon become visible.

Depending on the pH, the hydroxides have a net positive or negative charge. Figure 5.18 shows the influence of pH on the surface charge (zeta potential) of hydroxides produced from aluminum chloride.

The negative ion of the salt that was used to prepare the aluminum hydroxide also influences the aluminum hydroxide charge.

When hydroxide is precipitated from a solution of aluminum sulfate it takes the form of aluminum sulfate hydroxide, $Al(OH)_{3-2x}(SO_4)_x$, where x is around 0.25. The pH at which the hydroxide has zero charge is displaced about 1 pH unit towards a more acidic pH in comparison to the flocs that are formed from aluminum chloride, since the sulfate ion will reduce the positive charge.

Figure 5.18
The influence of pH on the zeta potential of hydroxides produced from aluminum chloride.

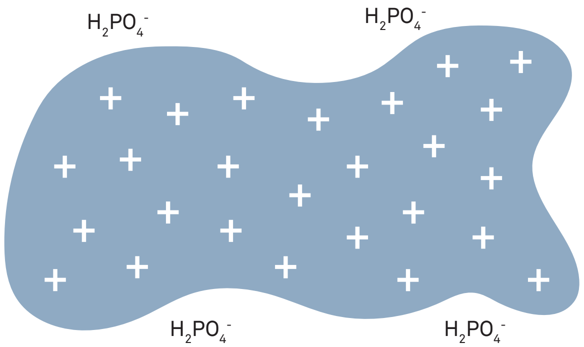


Taken from Ref. 6 Öhman L.-O. and Wågberg L., Freshly Formed Aluminum (III) Hydroxide Colloids Influence on Aging, Surface Complexation and Silicate Substitution. Pulp Paper Sci. (1997) 23(10), J475–J480.

At pH levels < 9.5, the aluminum hydroxide that is produced from aluminum chloride is positively charged and can adsorb negatively charged substances such as orthophosphate.

Aluminum hydroxide can therefore also be used for the adsorption of orthophosphate (figure 5.19). However, it is considerably less effective at removing orthophosphate than Al^{3+} and its hydrolysis products.

Figure 5.19
Orthophosphate ions adsorbed onto a positively charged aluminum hydroxide floc.



Figures 5.20 and 5.21 illustrate the influence of pH when precipitating ortho P with a constant dose of aluminum and ferric sulfates respectively. Ortho P was precipitated by adding concentrated aqueous solutions of the metal salts to solutions of ortho P, and by adding solutions of ortho P to 20-minute-old metal hydroxides.

From figures 5.20 and 5.21 it can be seen that considerably more ortho P was precipitated with direct addition of the salts than with the hydroxides.

The results show that it is important to ensure satisfactory mixing during the first few seconds after the salts are added to the wastewater being treated. The less effective the mixing, the more hydroxide will be formed, which is less effective at removing ortho P.

It is also important to ensure good mixing when adding the metal salt solution to precipitate particles.

Figure 5.20

The influence of pH on the percentage of precipitated P when 0.25 mmol of Al^{3+} is added as aluminum sulfate to 0.25 mmol of ortho P (=8.0 mg ortho P/l) and after adding a solution of ortho P to the hydroxides formed from the aluminum sulfate. The solutions of ortho P were prepared in such a way that they had the same pH as the aqueous phase of the hydroxides.

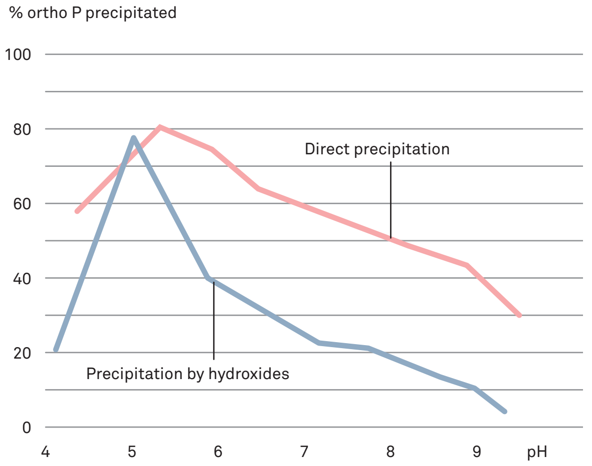
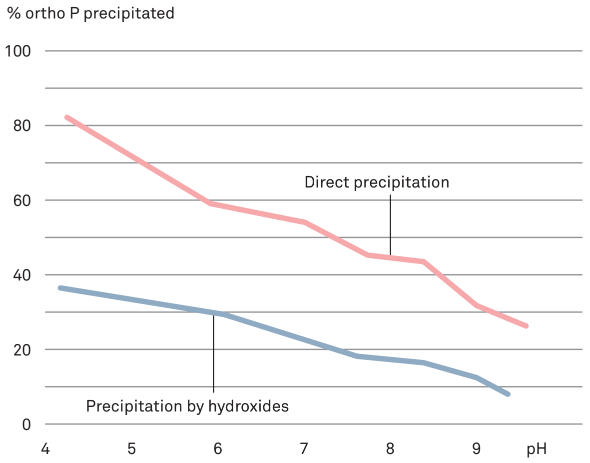


Figure 5.21

The influence of pH on the percentage of precipitated P when 0.25 mmol Fe^{3+} is added as ferric sulfate to 0.25 mmol of ortho P (=8.0 mg ortho P/l) and after adding ortho P to hydroxides formed from the ferric sulfate. The solutions of ortho P that were added to the hydroxides had the same pH as the aqueous phase of the ferric sulfate hydroxides.



Ref. 7 fig. 5.20 and 5.21: Gillberg, L., Nilsson, D., Åkesson, M., The Influence of pH when Precipitating Orthophosphate with Aluminum and Iron Salts. In: Chemical Water and Wastewater Treatment IV, Hahn, H.H., Hoffman, E., Ødegaard, H. (Eds.), Springer-Verlag, 1996, pp 95–105 (ISBN 3-540-61624.

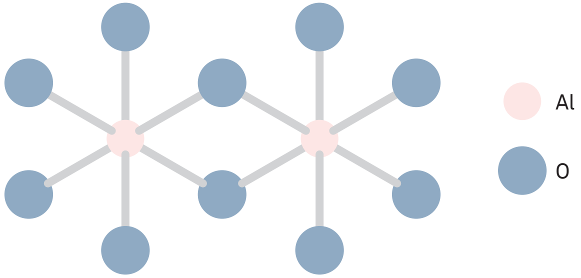
The simplest ion that is formed with more than one aluminum atom is the dimeric ion (an ion with two metal atoms, fig. 5.22).

$$2Al^{3+} + 2H_2O \rightarrow Al_2(OH)_2^{4+} + 2H^+$$

$$2Al(OH)_3 \rightarrow Al_2(OH)_2^{4+} + 4OH^-$$

Figure 5.22

Positions of aluminum and oxygen atoms in the dimeric aluminum ion. For the sake of clarity, the hydrogen atoms are not shown in the molecule.



Besides simple aluminum ions like Al^{3+}, $AlOH^{2+}$, and $Al(OH)^{2+}$ there exist oligomeric and polymeric aluminum ions. All of these contain hydroxide groups OH^-.

Oligomeric aluminum ions are unstable and have a short lifetime and are therefore difficult to identify. They include $Al_2(OH)_2(H_2O)_8{}^{4+}$ and $Al_3(OH)_4(H_2O)_{10}{}^{5+}$.

There are many other polymeric aluminum ions, many of which have a short lifetime and are therefore difficult to identify. However, some polymeric aluminum ions do exist, e.g. the well-known $Al_{13}O_4(OH)_{24}(H_2O)_{12}{}^{7+}$, which is relatively stable at certain pH levels.

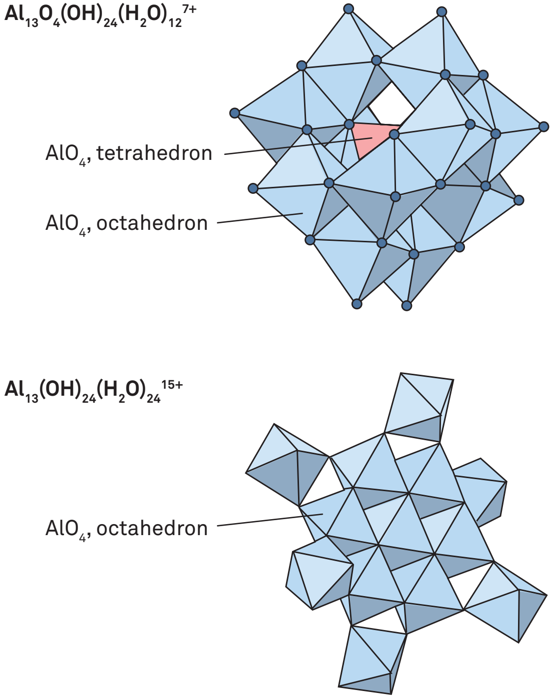
Polymeric aluminum ions have a spherical shape and contain an Al group that binds in four directions at the center. All other aluminum ions in that molecule bind in six directions.

Other polymeric aluminum ions include $Al_{13}(OH)_{24}(H_2O)_{24}{}^{15+}$ and $Al_{30}O_8(OH)_{56}(H_2O)_{24}{}^{18+}$. This latter ion consists of two spherical $Al_{13}O_4(OH)_{24}(H_2O)_{12}{}^{7+}$ ions connected by a crown of four Al ions binding in six directions. The repeating unit in polyaluminum salts is AlO^+ and $Al(OH)^{2+}$. Organic polymers can contain millions of repeating units. Polyaluminum ions therefore contain considerably fewer repeating units than organic polymers.

Commercial polyaluminum chlorides mainly contain mixtures of Al^{3+},oligomeric and polymeric ions.

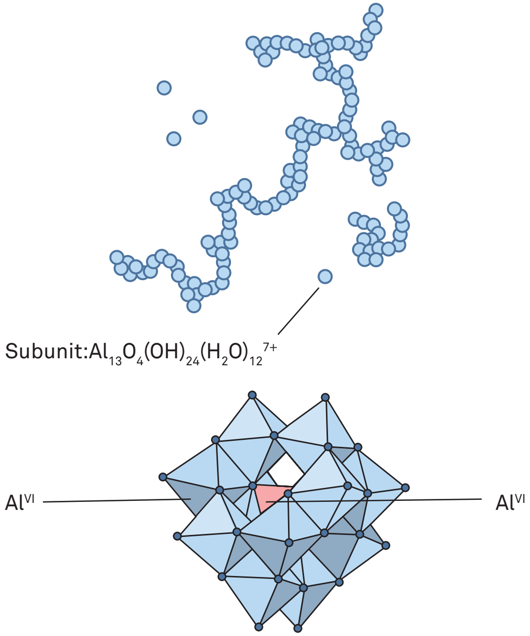
Figure 5.23 shows the molecular structure of the two known Al_{13} ions.

Figure 5.23
The molecular structure of the two known Al_{13} ions.
(Ref. 8: Karlsson Magnus, Structure Studies of Aluminum (III) Complexes in Solids, in Solutions and at the Solid/Water Interface, doctoral thesis, 1998, Umeå University, Sweden.)



Some authors believe that at least one of the Al_{13} ions is capable of polymerization. The imagined structure of polymerized Al_{13} ions is shown in figure 5.24.

Figure 5.24
Imagined structure of polymerized Al_{13} *ions.*



All these ions can precipitate ortho P. How well they do this in wastewater seems to be related to some extent on the number of positive charges per Al atom, as illustrated in the second to last column of table 5.25.

Explanation of basicity

All aluminum salts are acidic, with the exception of those that have the chemical formula $Al(OH)_4^-$. This means that hydrogen ions, H^+, are released when they are added to water. A maximum of three H^+ ions can be released for each aluminum ion that is added.

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$$

The generic formula for polyaluminum chloride is $[Al(OH)_xCl_{3-x}]_n$ where $0 < x < 3$ and $n \geq 2$. All polyaluminum salts thus contain OH^-, i.e. they contain basicity. Cl^- is very loosely bound to the positively charged aluminum ion by electrostatic forces.

The number of H^+ ions that are released per aluminum atom when a polyaluminum salt is added to pure water is (3-x), i.e. less than when a non-basic aluminum salt is added to water.

$$Al(OH)_xCl_{3-x} + (3-x)H_2O \rightarrow Al(OH)_3 + (3-x)H^+ + (3-x)Cl^-$$

Table 5.25 shows the molar ratio of OH/Al, the relative basicity of different polyaluminum ions, and the number of H^+ ions that are released when aluminum hydroxide is formed from the ions. The relative basicity of a polyaluminum salt is defined as moles OH/3 moles Al. Relative basicity is often expressed as a percentage (moles OH/3 moles Al) x 100.

The higher the basicity of a polyaluminum salt, the less it will decrease the alkalinity of the treated water and lower its ability to precipitate ortho P ions. Its ability to remove particles and turbidity passes through a maximum as the basicity increases (fig. 5.26).

Table 5.25

Basicity and other properties of some well-studied aluminum compounds

Formula	Molar ratio OH^-/Al^{3+}	Relative basicity %	Number +charges per ion	Number +charges per Al atom and number H^+ released when $Al(OH)_3$ is formed	Number H_2O molecules per Al atom
$Al(H_2O)_6^{3+}$	0	0	3	3	6
$Al_2(OH)_2(H_2O)_8^{4+}$	1	33	4	2	4
$Al_{13}(OH)_{24}(H_2O)_{24}^{15+}$	1.85	62	15	1.15	1.85
$Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$	2.46	82	7	0.54	0.92
$Al(OH)_3(H_2O)_x$	3.0	100	0	0	x

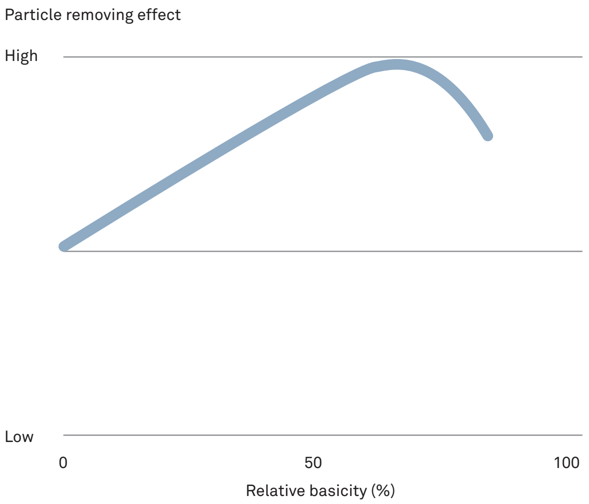
Basicity is a relatively simple parameter to measure, and all polyaluminum salts on the market are characterized by their basicity.

A polyaluminum salt with a given basicity contains a mixture of different simple and polymeric aluminum ions.

Iron (III) salts can form dimers, equivalent to one aluminum ion, but do not form the same types of polymeric ions as aluminum salts do.

Figure 5.26

The influence of the relative basicity of polyaluminum ions on their ability to remove turbidity and particles.



Precipitation of particles

Practically all surface forces between small particles (colloids) have a short range that is rarely greater than the size of the particles themselves. This means that these forces have little influence on the macromovement of particles, but are crucial in determining the outcome of collisions between particles, i.e. whether particles join together or bounce off each other.

Neutralization of charge

Almost all particles in water have a negative charge and therefore repel each other. Particles that repel each other due to their charge can aggregate when their surface charge is reduced. The surface charge can be reduced by adding (poly)aluminum or iron coagulants, or other cationic compounds.

Particles in water have different surface properties. A distinction is usually made between hydrophilic and hydrophobic particles. Aluminum and iron(III) salts can aggregate both these types of particles.

Hydrophobic particles

Hydrophobic particles have a fatty surface. As can be seen from table 5.2, most fat in wastewater exists as particles. Pure fat does not have a charge.

Negatively charged ions such as chlorides, sulfates, and orthophosphates adhere to hydrophobic surfaces by means of van der Waals forces. Hydrophobic particles in natural water therefore have a negative charge.

When the negative charge on hydrophobic particles is neutralized, the relatively strong van der Waals attraction forces come into effect. These are inversely proportional to the distance (d) between the particles, with a proportionality ratio that varies between 1/d and 1/d^3 depending on the roughness of the particle surfaces.

A more hydrophobic particle or dissolved substance, i.e. one that does not have tightly bound water molecules, is naturally adsorbed more easily onto a hydrophobic particle than hydrophilic substances that have a large number of tightly bound water molecules.

Ideal basicity for particle removal

The amount of aluminum that is needed, in the form of a (poly)aluminum salt, to neutralize and aggregate negatively charged particles depends on the basicity of the added polyaluminum salt. Polyaluminum chlorides with a relative basicity of around 65% are most effective at removing turbidity (fig. 5.26).

Sweep coagulation

When a (poly)aluminum ion is adsorbed onto the surface of a particle or dissolved substance, layers of hydroxide may start to grow from this area.

This is especially true when the concentration of contaminants is low. The contaminants that are present become enmeshed in the hydroxides (fig. 5.27). These hydroxides will be present in substantial quantities in the aqueous phase (fig. 5.28).

Almost all remaining contaminants are swept down with the settling hydroxides (fig. 5.29). This type of treatment is called sweep coagulation or sweep flocculation.

Sweep coagulation is an excellent way of treating water, but the amount of metal salt needed is greater than if the contaminants are removed using charge neutralization.

Figure 5.27
Positively charged aluminum hydroxide.

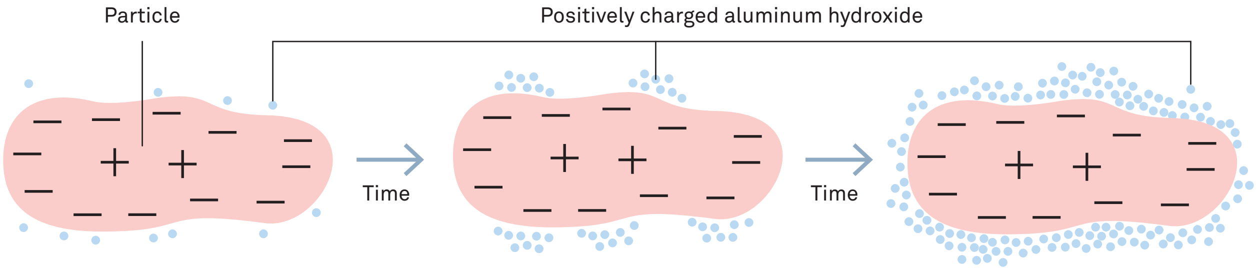


Figure 5.28
A hydroxide floc with dirt particles.

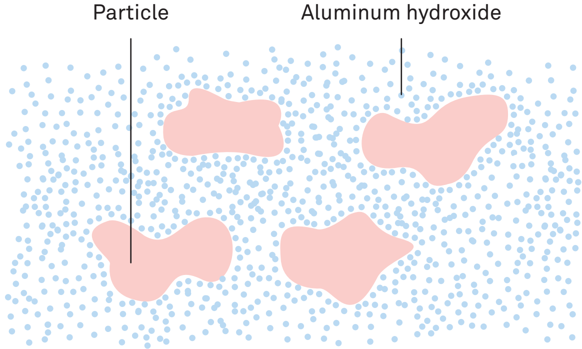
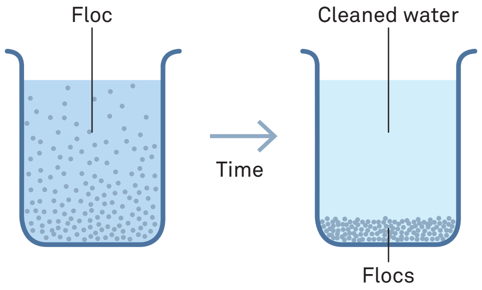


Figure 5.29
A jar of water with settling aluminum hydroxide.



Aluminum hydroxide is formed relatively quickly from low-basicity aluminum salts. It is typically formed within one to seven seconds when a low-basicity aluminum salt is added to water. However, some high-basicity salts, e.g. those containing $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$, are very stable in aqueous solutions at certain pH levels and are probably converted first to Al_{13} hydroxides, and after a considerable time to $Al(OH)_3$. As can be seen from table 5.30 below, the flocculation time that is needed to treat water to achieve a predetermined residual turbidity is shorter if a highly basic PAC is used instead of a low-basicity PAC.

Figure 5.30

Required flocculation time to achieve a final turbidity of 3 NTU when treating wastewater with 0.45 mmol Al/l in the form of aluminum sulfate, KEMIRA PAX-14, and KEMIRA PAX-XL19 respectively.

Coagulant	Molar ratio OH/Al of coagulant	Required flocculation time (minutes)
Aluminum sulfate	0	19
Kemira PAX-14	1.1	10
Kemira PAX-XL19	2.45	7

Floc size and speed of floc formation

Some treatment plants have only limited space for floc formation, so for these plants it is important to carry out flocculation in such a way that flocs are formed quickly.

During the coagulation period, flocs grow to a limited size, depending on pH, temperature, dose, shear rates, and the type of coagulant used.

In general, large flocs are obtained by:

a) using high coagulant doses
b) carrying out flocculation at relatively low shear rates
c) using a high-basicity coagulant
d) adding polymer

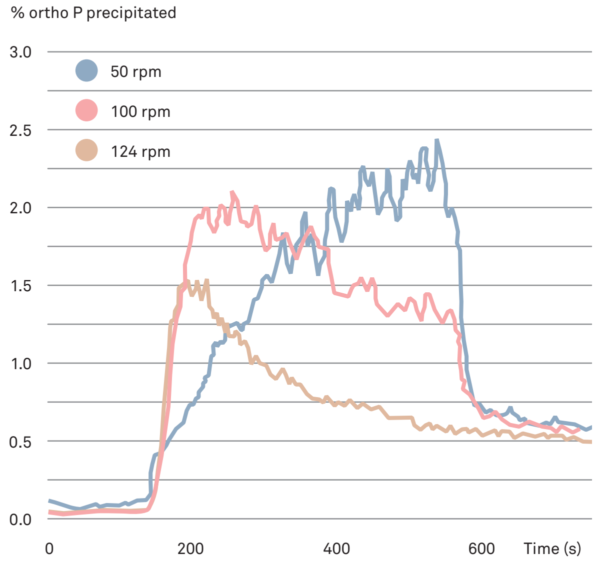
The hydroxides formed in water and wastewater treatment are relatively fluffy and easy to break. The metal salt must be added at a point with high turbulence; the high turbulence is only needed for five to 10 seconds. After the rapid mixing the mixing intensity must be high enough for the hydroxides to aggregate but not so high that they break.

Flocs are brittle and can be torn apart by shear forces, but they can reform. However, when they are formed in the fastest possible way, they have a low tendency to reform again. Flocs formed by high metal salt doses reform more easily after breakage.

Figure 5.31 shows the influence of mixing speed and flocculation time on floc size, expressed as the flocculation index.

Figure 5.31

Influence of time and mixing speed on maximum floc size during coagulation of a suspension of kaolin in mains water from London with 3.1 mg/l Al in the form of Kemira PAX-XL19. The first arrow shows the time at which the coagulant was added and the second shows the time at which the propeller speed was increased to 200 rpm.



(Ref. 9: Gregory, J. and Rossi, L., Dynamic Testing of Water Treatment Coagulants, Chemical Water and Wastewater Treatment VI, Hahn. H. H., Hoffman E. and Ødegaard H., (Eds.), Springer-Verlag 2000, pp. 57–65, ISBN 3-540-67574-4.)

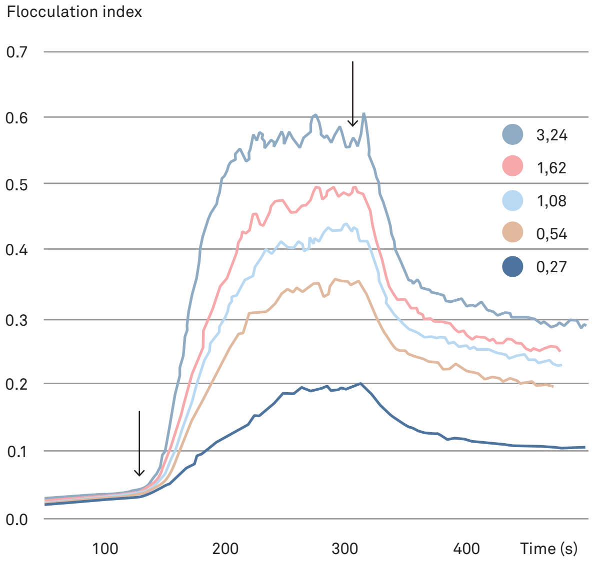
The aluminum salt was added at the time point of the first arrow with the second arrow showing where the mixer speed was increased to 200 rpm. It can be seen from the graph that when the mixer speed was increased to 200 rpm the hydroxides were sheared apart into smaller pieces.

When adding the metal salt at the two highest propeller speeds the hydroxides were quickly formed, but only a minute or two after the metal salt was added the hydroxides tended to break. As the propeller speed increased the more the hydroxides were broken up; the largest flocs were formed at the slowest propeller speed but it took a long time for them to form.

The more metal salt that is added, the larger the flocs formed. Figure 5.32 illustrates the influence of aluminum sulfate dose on the size of flocs formed in a suspension of kaolin particles, expressed as the flocculation index.

Figure 5.32

Influence of the dosage of aluminum sulfate, given in mg Al/l, on the maximum floc size achieved during flocculation of a suspension of kaolin in potable water from London with a propeller speed of 100 rpm. The first arrow shows the time at which the coagulant was added, and the second shows the time at which the propeller speed was increased to 200 rpm



(Ref. 10: Gregory, J., Rossi, L. and Bonnechi, L., Monitoring Flocs Produced by Water Treatment Coagulants, Chemical Water and Wastewater Treatment VI, Hahn H.H., Hoffman E., and Ödegaard H., (Eds.), Springer-Verlag, 2000, pp. 57–65, ISBN 3-540-67574-4.)

It can be seen from the graph that the flocs grew as increasing amounts of aluminum sulfate were added. The propeller tended to shear apart flocs formed by higher doses than illustrated, into sizes identical to the highest dose illustrated.

The basicity of the coagulant also influences the speed of floc formation. Table 5.30 shows the required flocculation time when treating wastewater with different coagulants. The higher the basicity, the less time is needed for flocs to be formed.

Other factors influencing the speed of floc formation are:

- the pH of the water being treated
- water temperature
- presence of counter ions such as sulfate, silicate, and phosphate

Ferric chloride seems to produce larger flocs than ferric sulfate, and the optimum pH for producing large flocs with ferric chloride is somewhat higher than the optimum pH for producing large flocs with ferric sulfate.

When particles are neutralized with a high-basicity polyaluminum salt, neutralization takes place within a smaller dosage range than when a non-basic aluminum salt is used. If a high-basicity metal salt is overdosed the negatively charged particles may become positively charged before they have had a chance to aggregate. This means that they will remain dispersed, i.e. they are restabilized.

It is therefore easier to overdose with a high-basicity aluminum salt than with a low-basicity one.

Floc size, strength, and sedimentation rate can all be increased considerably by adding a flocculation aid (e.g. an anionic polyacrylamide).

Different ways of aggregating particles

Aggregation due to particle motion can be caused by:

a) the thermal motion of the water (Brownian diffusion leading to perikinetic flocculation)
b) fluid motion (leading to orthokinetic flocculation)
c) differential sedimentation

The thermal motion of water is only important for aggregating relatively small particles (< 0.1 μm) and at low shear rates.

Aggregation due to fluid motion is dominant for particles with a size of about 1 μm and larger.

Differential sedimentation only becomes important when particles have a minimum size of about 5 μm.

Precipitation of orthophosphate with non-basic aluminum and iron salts

It was mentioned earlier that aluminum and iron(III) salts precipitate orthophosphate either by direct reaction or by means of hydroxides (see figures 5.20 and 5.21). As orthophosphate (ortho P) is precipitated more efficiently by direct precipitation it was stressed that the metal salt should be added at a point where the water is highly turbulent.

Iron(II) salts can also be used for the precipitation of ortho P, over a considerably narrower pH range than aluminum and ferric salts. Iron(II) salts don't precipitate particles since they don't form positively charged hydroxides. This is in contrast to both iron(III) and aluminum salts, which precipitate both particles and ortho P.

Figure 5.33 illustrates the influence of pH on the amount of ortho P that is precipitated when 1 mole of Al, Fe(III), and Fe(II) are added to 1 mole of ortho P, while figure 5.34 illustrates the influence of pH on the amount of ortho P that is bound to 20-minute-old hydroxides of the salts.

A comparison of the diagrams shows that at most pH values, considerably more P is precipitated by the direct precipitation mechanism.

Hydroxides produced from sulfate salts have less positive charge than those from chloride salts. Ferric chloride and ferric sulfate precipitate ortho P to equal extents as do aluminum chloride and aluminum sulfate. If hydroxides are formed, the sulfate bound to the hydroxides are substituted by ortho P, which binds more strongly to the hydroxides than sulfate does.

Calcium salts can also be used for the precipitation of ortho P. When ortho P is precipitated with calcium compounds, higher pH values (above 9.5–10) should be used. Figure 5.35 illustrates the influence of pH on the solubility of iron(III) phosphate, aluminum phosphate, and calcium hydroxide phosphate respectively.

When calcium hydroxide is used for water treatment, large amounts of sludge are formed.

Figure 5.33

The influence of the coagulation pH on the relative percentage of ortho P that is precipitated when solutions of aluminum sulfate, ferric sulfate, or ferrous sulfate are added to solutions of orthophosphate. One mole of metal ions was added per mole of ortho P.

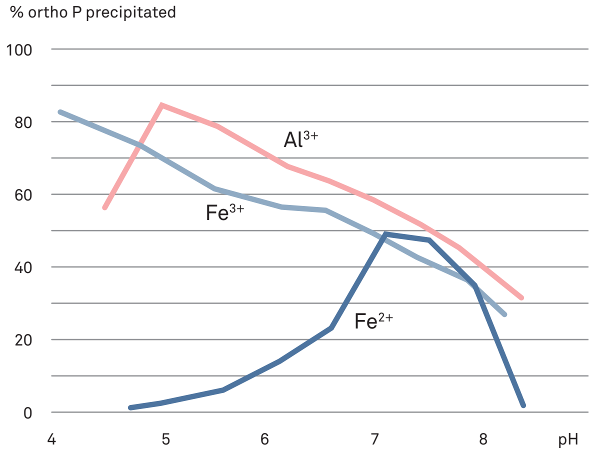
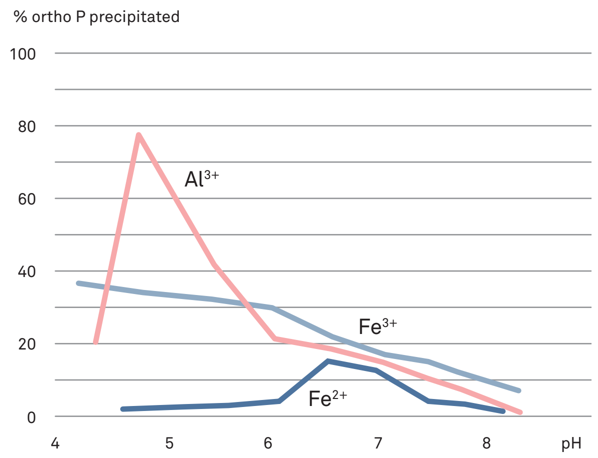


Figure 5.34

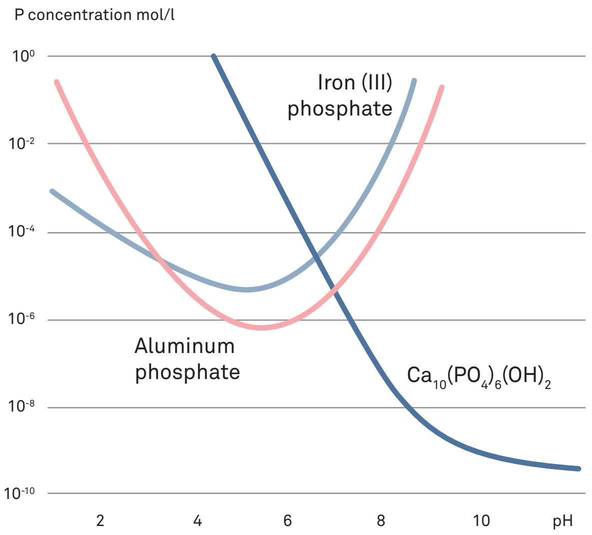
The influence of pH on the percentage of ortho P precipitated when solutions of ortho P are added to hydroxides that are prepared from the above-mentioned salts. The age of the hydroxides when the ortho P was added was 20 minutes. The pH values of the hydroxide dispersions and the ortho P solutions were identical when they were mixed.



(Ref. 11: Gillberg, L., Nilsson, D. and Åkesson, M., The Influence of pH When Precipitating Orthophosphate with Aluminum and Iron Salts. In Chemical Water and Wastewater Treatment IV, H. Hahn, E. Hoffman and H. Ødegaard (Eds.) Springer Verlag, 1996, pp. 95-105, ISBN 3-540-61624-1.)

Figure 5.35

The influence of pH on the solubility of aluminum phosphate, iron(III) phosphate, and calcium hydroxide phosphate respectively.



(Ref. 12: Leckie H and Stum W. Phosphate precipitation. Water Resources Symposium (1970) 237.)

Precipitation of triphosphate

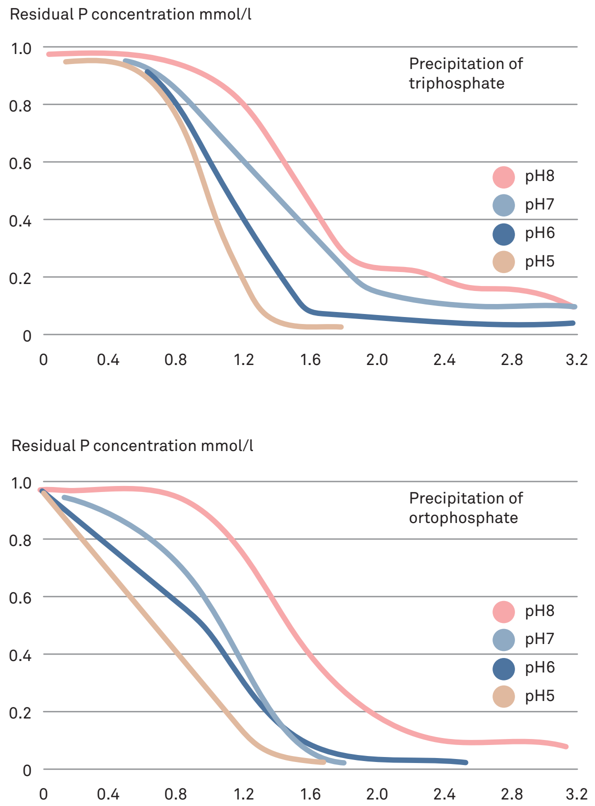
Triphosphate ($P_3O_{10}^{5-}$), sometimes called tripolyphosphate, was historically used in many detergents to sequester ions that make water hard. Today most countries have banned the use of tripolyphosphates but it can still be found in some wastewaters.

Triphosphate can be precipitated using iron and aluminum salts. When a small amount of aluminum or iron salt is added to wastewater the iron or aluminum will form soluble complexes with the triphosphate. The triphosphate will only precipitate out when it is saturated with aluminum and iron salts.

Figure 5.36 shows the influence of the dose of Kemira AVR, an iron-containing aluminum sulfate, on the residual concentration of triphosphate at different pH values. Figure 5.37 shows the corresponding curves for orthophosphate.

Figure 5.36 and 5.37

The influence of pH on the solubility of aluminum phosphate, iron(III) phosphate, and calcium hydroxide phosphate respectively.



All water that contains complexing agents demonstrates the same special precipitation behavior. When small to moderate doses of coagulant are added there is no change in the concentrations of phosphate or COD, or in the residual turbidity. It is only when the metal salt dose reaches such a level that the complex-building substances are saturated with coagulant that the water is cleaned to the same degree as if no complex-building substances had been present in the water.

Use of hydroxides for removing ions other than phosphate

Positively charged hydroxides can bind other negatively charged ions such as sulfate. The binding of sulfate to the hydroxides is strongly dependent on pH; as pH decreases more sulfate binds to the hydroxides formed by aluminum sulfate.

The hydroxides produced when treating water with aluminum sulfate at typical pHs contain approximately 0.25 mole of sulfate per mole of Al, i.e. they have the average composition $Al(SO_4)_{0.25}(OH)_{2.5}$.

Orthophosphate binds considerably more strongly to aluminum hydroxides than sulfate does. Hydroxides produced from both aluminum chloride and aluminum sulfate precipitate orthophosphate equally well.

In several places in the world groundwater is contaminated by naturally occurring arsenic. In nature, dissolved arsenic occurs both as arsenic ions (As^{3+}) and as arsenate ions (AsO_4^{3-}). Iron salts are often used to reduce the arsenic content of such waters. As a pre-treatment a small amount of an oxidizing agent, e.g. oxygen, hydrogen peroxide, or hypochlorite, is added to the water, which converts the positively charged arsenic ions into negatively charged arsenate ions. A small amount of a ferric salt is then added. The arsenate binds to the ferric hydroxide formed and most of the arsenic present in the water is recovered in the sludge. If needed, the arsenic concentration of the treated water can be reduced even further by passing the treated water through a solid bed of ferric oxide hydroxide; the same technique can be used for removing dissolved vanadium from water.

It is also possible to use solid ferric hydroxide products for the same purpose. The granulated ferric hydroxide is placed in a filter unit, where it can remove negative charge ions. Although the efficiency of the iron is lower with this method it is easier to apply in a water treatment plant and hence could be an alternative to using a coagulant.

Chemical parameters influencing the amount of metal salt needed to treat water

Several chemical parameters influence the amount of metal salt needed to treat water, including the:

- pH, alkalinity, and temperature of the water
- Type of coagulant used
- Type and amount of dissolved organic material in the water
- Presence of anions binding to the coagulant, e.g. phosphate, silicate, and sulfate
- Amount of particles in the water and their size and surface properties
- Water hardness

These factors are briefly discussed in the following sections.

The pH of the water

pH has a strong influence on coagulant demand.

With increasing pH:

- Impurities are more negatively charged, and
- The compounds formed when the metal reacts with the water are more negatively charged

As pH increases more coagulant is needed to treat the water.

Each type of metal salt has an upper pH limit for use in water treatment applications. Above this limit the products formed by the salt are negatively charged, meaning that the salt cannot be used to neutralize the negatively charged impurities in the water.

To treat water at higher pHs than usual, the effect of high-basicity aluminum salts or ferric-based coagulants should be tested.

If these salts are not available an alternative method is to mix a small amount of a cationic polymer with the available salt. However, it should be noted that the use of these polymers in drinking-water production is restricted in several countries.

The optimal pH for coagulation with sulfate salts is lower than for chloride salts.

Iron(III) salts are often used for treating water at pHs around 5, where they work using a charge neutralization mechanism. Iron(III) salts can also be used at pHs below ca. 9.5, where they work using a sweep coagulation mechanism, though at this pH more iron salt is needed.

The alkalinity of the water

Alkalinity is a measure of the buffering capacity of the water. It is defined as the amount of strong acid (H^+) needed to reach a certain pH.

Alkalinity and pH are related. Waters with high alkalinity have a higher pH than waters with low alkalinity.

Aluminum and ferric salts are acidic and decrease the pH of the treated water. With increasing coagulant basicity, the less the coagulant decreases the pH of the water.

When treating high-alkalinity water with a metal salt it can be economic to mix a strong acid with the water before adding the salt in order to reduce the amount of metal salt needed. The effect of high-basicity polyaluminum chlorides, which work at higher pHs than low and medium-basicity salts, can also be tested.

When treating low-alkalinity waters (< 30 mg HCO_3^-/l) with aluminum sulfate, the aluminum sulfate may decrease the pH too much. If this is the case, the following methods could be tested:

- using a high-basicity coagulant that does not decrease the pH of the water to the same extent as aluminum sulfate
- pre-treating the water with soda, lime, or caustic soda before adding the metal salt
- adding both carbon dioxide and a strong base, e.g. caustic soda or lime, leading to the formation of hydrogen carbonate (HCO_3^-), which provides the water with a strong buffering effect; when HCO_3^- is present in the water it is easier to reach a stable pH after adding the metal salt.

If the alkalinity is very low (<15 mg HCO_3^-/l) there might not be enough hydroxides available to form flocs even though the pH is neutral, and this is why an increase in alkalinity is needed.

The temperature of the water

The water temperature strongly influences the:

- pH and hydroxide concentration of the water
- Optimal coagulation pH
- Residual metal concentration and the pH for lowest residual Al or Fe concentration
- Viscosity of the water
- Rate at which flocs form and settle.

With decreasing temperature, the:

- Residual Al concentration decreases
- pH for optimal coagulation is displaced to higher pHs
- Flocs form more slowly
- Flocs settle more slowly due to the increased viscosity of the water and the increased time it takes flocs to grow.

In order to improve floc settling at low temperatures a coagulant aid, e.g. a polyacrylamide or activated water glass, are added to increase floc size. Usually high-molecular-weight negatively charged polyacrylamides are used, but in some cases polyacrylamides with a weak positive charge can be used.

At low water temperatures polyaluminum chlorides, especially high basic sulfated ones, and ferric coagulants often perform better than aluminum sulfate.

Dissolved organic material

When treating surface water the goal is to remove both particles (e.g. clay and pathogens) and organic dissolved material, e.g. humic and fulvic acids that give the water color, taste, and smell.

UV absorption can be used as an alternative analysis method for TOC and DOC. The recommendation is to set a UV target value of 0.02 to 0.035 cm^{-1}; this value results in treated water with a TOC content of 2 mg TOC/l or less. A relatively low level of disinfection byproduct will be formed in water with such a TOC concentration. Furthermore, the residual turbidity of filtered water will be 0.1 NTU or less.

When coagulating with aluminum sulfate, the minimum solubility is often around pH 6.0–6.2 for water at 20°C and pH 6.5–6.7 for water at 4°C; different pH conditions apply for other types of metal salts.

The UV254 absorption should be measured on non-disinfected water as high doses of oxidants such as chlorine or ozone reduce UV absorption without reducing the DOC.

Floc separation

Compared with other types of coagulants, those containing a sulfate or silicate often produce flocs that settle better.

When separating flocs using dissolved air flotation (DAF), separation is less affected by cold water temperature and the choice of metal salt is less crucial. Flocs separated with flotation can be much smaller, and a larger number of metal salt types work well. Treated water often has a lower residual turbidity when flocs are separated by flotation compared with separation by sedimentation.

Water hardness

Water hardness is caused by the presence of salts of alkaline earth metals, mainly calcium and magnesium. The harder the water the less coagulant is needed to treat it and the lower the likelihood of overdosing.

Influence of other ions on coagulation

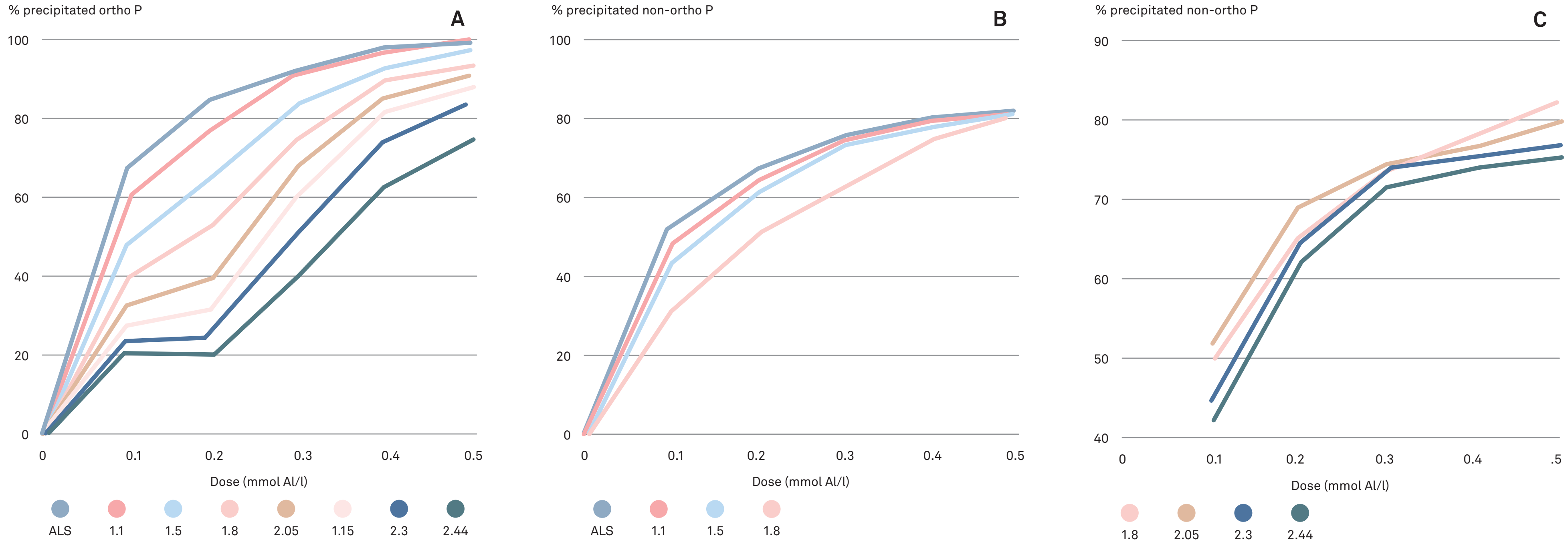
If the water contains high amounts of phosphate or silicate the coagulant demand increases and the optimal coagulation pH is often displaced in a more acidic direction. If for some reason the water contains an agent complexing aluminum or iron ions, e.g. citrate, triphosphate, or high amounts of fulvic or humic acids, the coagulant will have no effect until the complexing agent is saturated. After saturation normal coagulation behavior will be observed.

The influence of the basicity of aluminum salts on the removal of particles and orthophosphate in wastewater

Coagulant basicity influences optimum precipitation characteristics. In order to find this basicity, wastewater was precipitated using polyaluminum chlorides with different basicities. A solution of aluminum sulfate was used as a reference salt, and the residual concentrations of total phosphorus and orthophosphate were measured. The difference between these two concentrations was then used to calculate the residual concentration of non-orthophosphorus compounds. As previously mentioned, these are mainly present as particles, e.g. bacteria or viruses. Figure 5.38 illustrates the influence of the aluminum dose on these two phosphorus fractions.

Figure 5.38

Influence of the dose of aluminum sulfate and polyaluminum chloride with various molar ratios of OH/Al on the percentage concentration of precipitated orthophosphate and the percentage concentration of precipitated phosphorus that did not come from orthophosphate (mainly particles). Diagram A shows the percentage concentration of precipitated orthophosphate. Diagram B shows the percentage concentration of precipitated non-ortho P for various doses of aluminum sulfate and polyaluminum chlorides (PAC) with molar ratios of OH/Al in the range 1.1–1.8. Diagram C shows the percentage concentration of non-ortho P precipitated using PAC with molar ratios of OH/Al in the range 1.8–2.44. Diagram C has an expanded scale on the y-axis compared with diagram B.



(Ref. 13: Gillberg L., Influence of the Basicity of Polyaluminum Chlorides When Cleaning Municipal Wastewater, In: Chemical Water and Wastewater Treatment III, Klute R. and Hahn H.H. (Eds), Springer-Verlag, Berlin, Heidelberg, 1994, pp. 39–56, ISBN 3-540-58185-5.)

From diagram A it can be seen that as the basicity of the aluminum salts decreases the amount of ortho P precipitated increases.

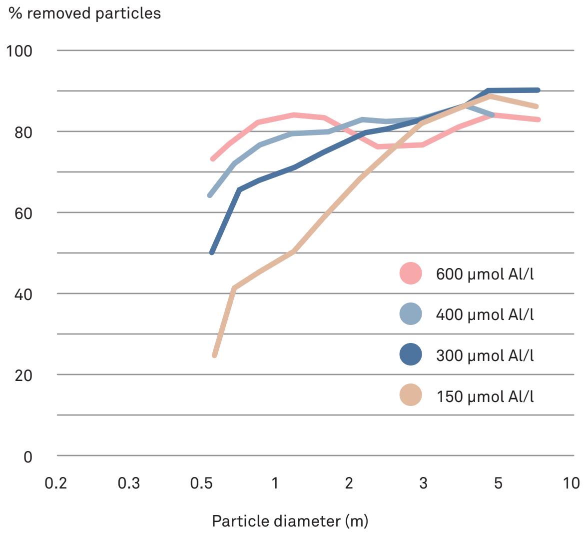
Diagram C is an enlargement of a section of diagram B. From diagrams B and C it can be seen that polyaluminum chlorides with molar OH/Al ratios of 1.8–2.05, which corresponds to a relative basicity of around 60–68%, were most effective in precipitating particles.

The lowest dose of aluminum sulfate precipitated almost 70% of the ortho P but only 30% of the non-ortho P; the lowest dose of aluminum sulfate thus precipitated more ortho P than particles. The lowest dose of PAC with a molar ratio of 2.05 precipitated little more than 50% of the non-ortho P and only 35% of the ortho P; the lowest dose of this PAC thus precipitated more particles than ortho P.

Both monomeric and polymeric ions of Al and Fe can precipitate orthophosphate. It has been shown that iron ions must be polymerized in order to be bound to a particle surface. Only Fe^{3+} can be polymerized. This is probably also true for polyaluminum salts. In order for iron or aluminum ions to be polymerized, the concentration must be sufficiently high and the pH must be within an acceptable range.

It can be seen from figure 5.39 that a given dose of coagulant precipitates relatively more large particles than small particles. In order to precipitate mostly small particles, e.g. bacteria or viruses, it is important that a sufficient dose of coagulant is added.

Figure 5.39
The influence of the dose of aluminum sulfate on the percentage of particles precipitated in different size classes.



(Ref. 14: Gillberg L., Eger L., and Jepsen S.-E. The Effect of Five Coagulants on the Concentration and Distribution of Small Particles in Sewage. In: Chemical Water and Wastewater Treatment, Hahn H.H. and Klute R. (Eds.), Springer-Verlag Berlin, Heidelberg 1990, pp. 243–256, ISBN 3-540-53181-5.)

The influence of polyaluminum salt basicity on the pH value of treated water

All aluminum salts with a basicity below 85–90% are acidic. This means that the water pH is reduced when an aluminum salt is added. The lower the basicity of the added salt, the more acidic the water becomes. When an aluminum salt with 0% basicity is added to pure water, a maximum of three H^+ ions are released:

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3(s) + 3H^+$$

The higher the basicity of the polyaluminum salt, the less the pH of the water will drop.

The number of H^+ ions released when a polyaluminum salt reacts with water is directly proportional to the average positive charge of one atom of Al in the salt used (see column 5 in table 5.25).

$$Al_{13}O_4(OH)_{24}^{7+} + 11H_2O \rightarrow 13Al(OH)_3 + 7H^+$$

i.e. 7/13 = 0.54 H^+ ions are released per Al atom.

The fact that high-basicity aluminum salts only decrease the pH of water slightly is particularly advantageous when treating water with low alkalinity.

The influence of aluminum salt basicity on the charge of hydroxides formed by aluminum and ferric salts

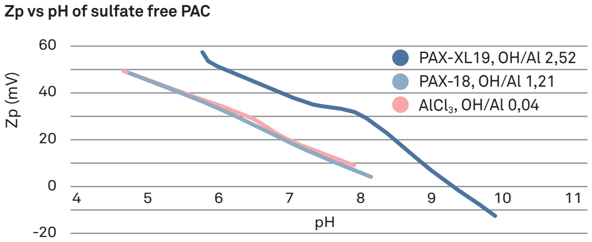
The charge of the hydroxides formed when adding aluminum and ferric salts to water has a very strong influence on the treatment result. At typical pHs the hydroxides formed by aluminum and iron salts are positively charged; the more positively charged the hydroxides are the less metal salt is needed for water treatment.

Figure 5.40 illustrates the influence of pH on the charge (expressed as zeta potential) of the hydroxides formed when adding aluminum chloride and two polyaluminum chlorides with molar OH^-/Al^{3+} ratios of 1.21 (Kemira PAX-18) and 2.52 (Kemira PAX-XL19) to deionized water slightly buffered with HCO_3^-. The relative basicities of the two polyaluminum chlorides used were 40 and 84% respectively.

From the diagram it can be seen that the charge of the hydroxides formed increases with decreasing pHs. The charge of the hydroxides formed by PAX-18 was almost identical to the charge formed by aluminum chloride.

Figure 5.40

The influence of pH on the surface charge, expressed as zeta potential, on hydroxides formed when adding aluminum chloride, PAX-18, and PAX-XL19 respectively to buffered deionized water.


Zp vs pH of sulfate free PAC

When adding aluminum chloride to water the pH drops more than when adding an identical amount of Al in the form of PAX-18. It seems that this is also the case for hydroxides formed by polyaluminum chlorides with molar OH/Al ratios in the interval 0 to 1.2.

The surface charge of the hydroxides produced from PAX-XL19 was considerably higher than the charge of hydroxides produced by the other two aluminum salts.

The influence of pH on the coagulation process

The pH value is a very important parameter in water treatment processes.

The surfaces of particles in water contain groups that change their charge according to the pH. Proteins in particular contain groups that do this, and all viruses and many bacteria have a surface made of protein.

The higher the pH, the more negative charge the surface of the protein will have and the more positive charge will be needed to neutralize and precipitate the protein, i.e. the more metal salt will need to be added. pH influences both the charge on hydroxides and particle surfaces and the type and rate at which polyiron or polyaluminum ions are formed.

The magnitude of the pH drop depends on the basicity of the coagulant used and the alkalinity of the treated water. If a coagulant with low basicity is used the metal ions must polymerize before they react with a particle surface. When iron or aluminum ions are polymerized they release H^+ and the pH drops. This means that a low-basicity coagulant will lower the pH/alkalinity considerably more than a high-basicity coagulant when they are used to treat water to the same COD/TOC level. This is illustrated in figures 5.41 and 5.42.

Figure 5.41
The influence of the molar OH/Al ratios of PAC on the alkalinity consumed when wastewater was treated to give two constant residual phosphorus concentrations.

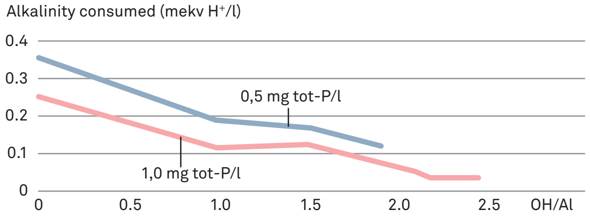
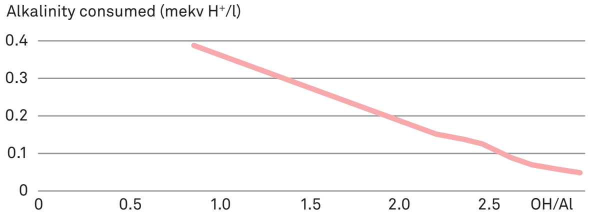


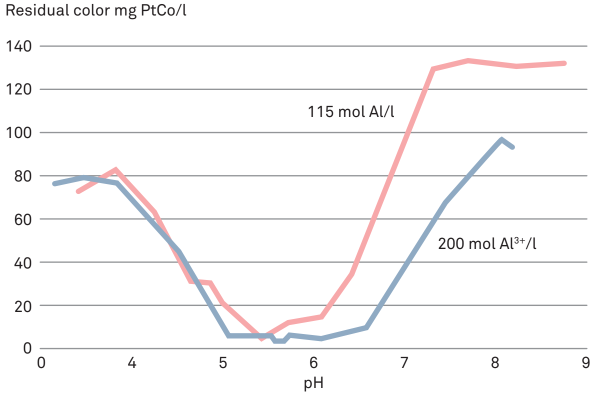
Figure 5.42
The influence of the molar OH/Al ratio of PAC on the alkalinity consumed when wastewater was treated to give a constant residual concentration of 14 mg TOC/l.



(Ref. 15 fig. 5:41 and 5:42: Gillberg L., Influence of Polyaluminum Chlorides When Cleaning Municipal Wastewater, In: Chemical Water and Wastewater Treatment III, Klute R. and Hahn H.H. (Eds.), Springer-Verlag, Berlin, Heidelberg, 1994 pp. 39–56, ISBN 3-540-58185-5.)

The lower the dose of coagulant, the more important it is to have good control of the pH; the higher the dose of coagulant, the less important it is to control the pH. This effect is shown in figure 5.43.

Figure 5.43
The influence of pH on residual color when colored surface water is treated with different doses of aluminum sulfate.



Different coagulants have their optimum treatment efficiency at different pH levels. Iron(III)salts often work better at lower pH levels than aluminum salts.

With high-basicity coagulants water can be treated at higher pH levels than with corresponding lower-basicity coagulants. This is because high-basicity polyaluminum ions are often more stable and therefore retain their high positive charge for longer than low-basicity ions.

The hydroxides grow and, over time, often reach a size at which they can be seen with the naked eye. They are considerably larger than most impurities being adsorbed into the hydroxides. All aluminum and ferric salts used for coagulation are acidic and thus decrease the pH of the treated water or wastewater.

The speed at which flocs are formed in water depends on the relation between the negative charge of the impurities and the positive charge of the components formed when adding the metal salt to the water. The speed of floc formation is quickest when the balance between these two is neutral. However, flocs can also be formed under non-neutral conditions. When this is the case flocs either become very small (e.g. too little coagulant added) or are formed slowly (e.g. too much coagulant added).

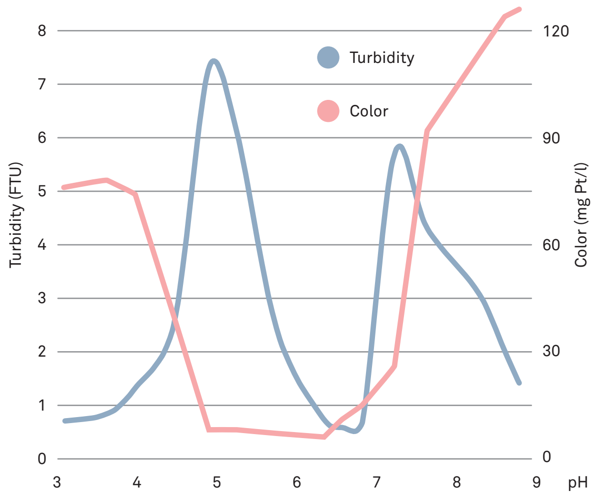
Below are the results of experiments on a strongly colored lake water using a very broad range of coagulation pHs and three doses of aluminum sulfate.

Figure 5.44 illustrates the influence of pH when coagulating the water using the highest-dose aluminum sulfate (300 μmol Al/l). Before adding the aluminum sulfate various amounts of HCl or NaOH were thoroughly mixed with the water. The pH was measured during the coagulation phase some minutes after the addition of the aluminum sulfate.

The residual turbidity was measured on non-filtered water and the residual color was measured after filtering the water through filters with a pore size of 0.45 μm.

Figure 5.44

The influence of coagulation pH when coagulating strongly colored lake water using 300 µmol Al/l dosed as aluminum sulfate.



- In the 6.3 to 6.8 pH range relatively fast settling flocs were obtained
- In the 4.9 to 6.3 pH range the color of filtered water samples was low
- In a waterworks the water would be treated at pH 6.3.

To summarize the above:

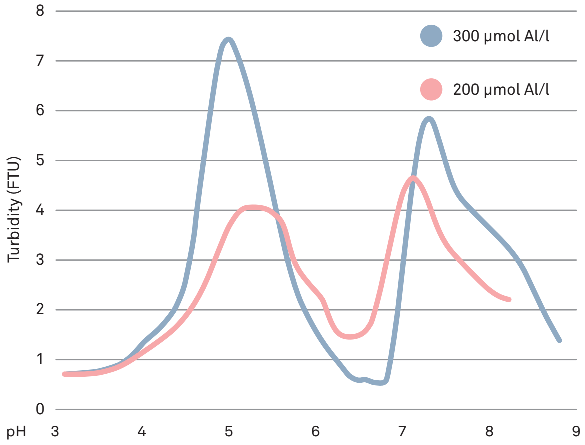
- At pHs between 6.3 and 6.8 good flocs were obtained
- The best pH for both color and floc removal was 6.3
- At pHs below 6.3 flocs became smaller and started to dissolve at pHs below 4.9
- At pHs above 6.8 flocs also became smaller as the pH increased and the charge of the flocs was not sufficient to bind the negatively charged colored humic and fulvic substances.

When a lower dose of aluminum sulfate is added compared to the previously described dose, a lower amount of positive charge is added. For this smaller amount of positive charge to precipitate most of the impurities, a lower coagulation pH has to be used. By decreasing the pH the impurities become less negatively charged.

Figure 5.45 illustrates the influence of pH on the residual turbidity of the treated water after dosing 300 and 200 µmol Al/l as aluminum sulfate.

Figure 5.45

The influence of the coagulation pH when treating strongly colored lake water with two doses of aluminum sulfate.



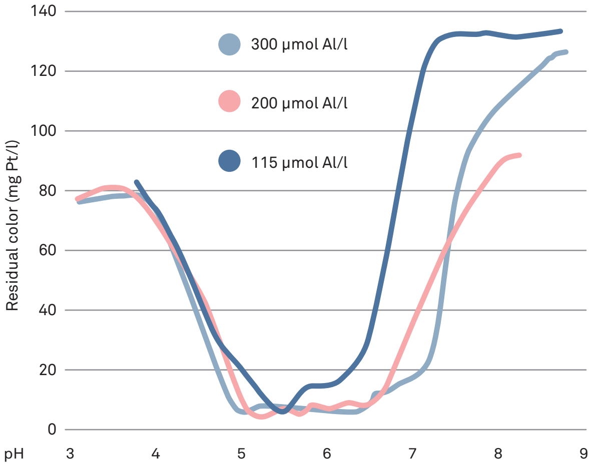
From the diagram it can be seen that with the lower dose of aluminum sulfate the best flocs were obtained just above pH 6.3 (the pH range with low residual turbidity was ca. pH 6.2–6.6). With the highest dose of aluminum sulfate the best-settling flocs were obtained at slightly higher pHs, ca. pH 6.3– 6.8).

So, when treating water with a lower dose of aluminum sulfate you need a lower pH to achieve optimum results. When you add a certain dose of aluminum sulfate you add a certain amount of positive charge, and the water contains a certain amount of impurities with a negative charge. For the best treatment result the amount of positive charge added by the metal salt needs to balance out the amount of negative charge from the impurities. If balance cannot be achieved the pH needs to be lowered because this reduces the negative charge of the impurities and increases the positive charge of the metal salt.

From figure 5.45 it can be seen that the pH range that gives well-settling flocs and low residual turbidity was also narrower for the lower dose (ca. pH 5.2 to 7) compared to the higher dose (ca. pH 4.9 to 7.2).

Figure 5:46 illustrates the influence of the three doses of aluminum sulfate on the residual color of the water.

Figure 5.46
The influence of the coagulation pH on residual color when treating strongly colored lake water with three doses of aluminum sulfate.



From the diagram it can be seen that the pH interval within which the aluminum sulfate precipitated the color decreases as the dose decreases. With the lowest dose tested the color only was precipitated in the same extent as using the higher doses only at pH 5.5.

The pH where color was precipitated best did not always coincide with the pH that resulted in the lowest turbidity and lowest residual aluminum content; in these cases a pH adjustment is needed.

The workable pH range for surface water treatment depends on the dose of metal salt added. It is not possible to decrease the aluminum sulfate dose by a considerable amount if we want treated non-filtered lake water to have a low turbidity. The optimal coagulation pH, floc size, and residual turbidities are linked.

The best pH range for coagulation not only depends on the dose of coagulant added, but also on the:

- Basicity of the metal salt added
- Type of counter ions present in the metal salt, and
- Temperature of the water to be treated

The composition of the metal salt added thus has a large influence on both the result.

Both the basicity and the type of counter ions in the metal salt strongly influence the charge of the hydroxides formed.

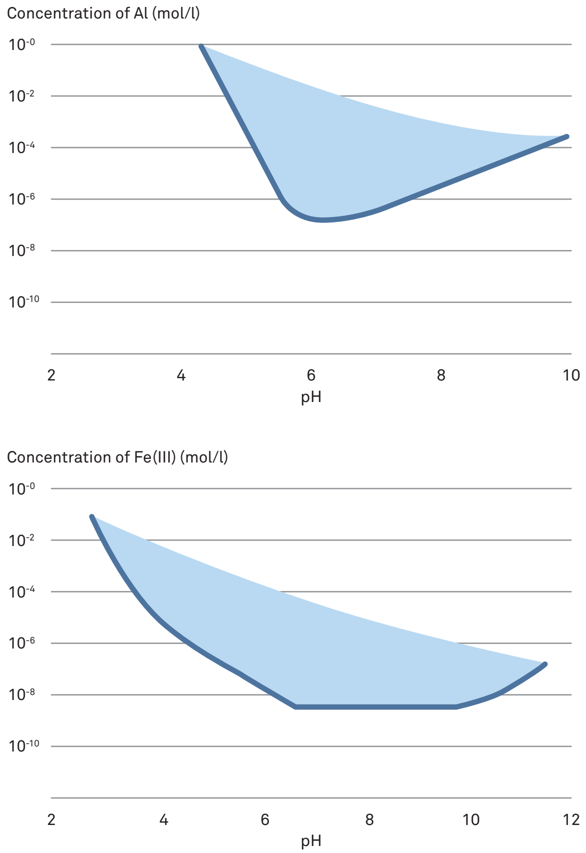
The influence of pH on the solubility of iron(III) and aluminum salts

Due to esthetical reasons, drinking water should have a low residual aluminum and iron content. The residual concentrations of Al^{3+} or Fe^{3+} in surface water after treatment with aluminum or iron salts depend on the pH. Figure 5.47 shows the influence of pH on the solubility of aluminum and iron(III) salts.

Naturally occurring water contains ions of different kinds, such as sulfate, calcium, and magnesium ions. These ions (and many others) adhere to iron or aluminum hydroxides and thereby change their charge. They therefore change the pH at which the coagulant has its lowest solubility. Adsorbed anions change the value in the acidic direction, while cations move the solubility in the opposite direction.

Figure 5.47

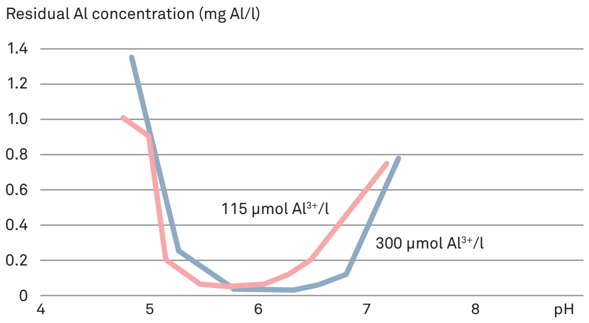
The influence of pH on the solubility of aluminum and ferric salts.



The dose of metal salt that is added to contaminated water influences the pH at which the lowest residual iron or aluminum concentration is obtained. Increasing the amount of metal salt that is added increases the pH range that gives the lowest residual iron or aluminum concentration, while also displacing it in the basic direction (see figure 5.48).

Figure 5.48

The influence of pH on residual aluminum concentration when a humic water was treated with different doses of aluminum sulfate.

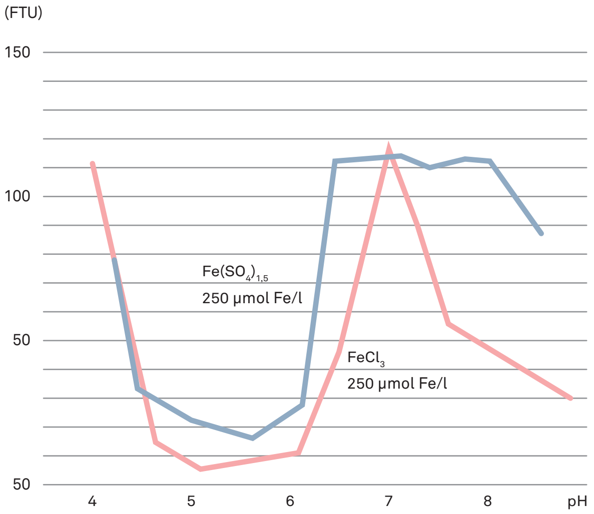


The influence of negatively charged counter ions in aluminum and iron(III) salts

All inorganic coagulants contain negatively charged counter ions. Sulfates, chlorides, and mixtures of the two are by far the dominant ones. The choice of counter ion affects the results of the treatment process. This is because the sulfate ions bind to aluminum and iron(III) hydroxides and thus reduce their positive charge. Chloride ions do not bind to aluminum ions and only to a small extent to iron(III) ions. In addition, sulfates, but not chlorides, can to some extent bind to positively charged sites on particles and hence give the particle an even higher negative charge than it would have had in the absence of sulfate. Both these phenomena mean that a higher dose of an iron(III) sulfate may be needed to precipitate particles than is the case for an iron(III) chloride.

These phenomena also mean that water can be treated at a slightly higher pH with a chloride salt than with a sulfate salt. This is shown in figure 5.49.

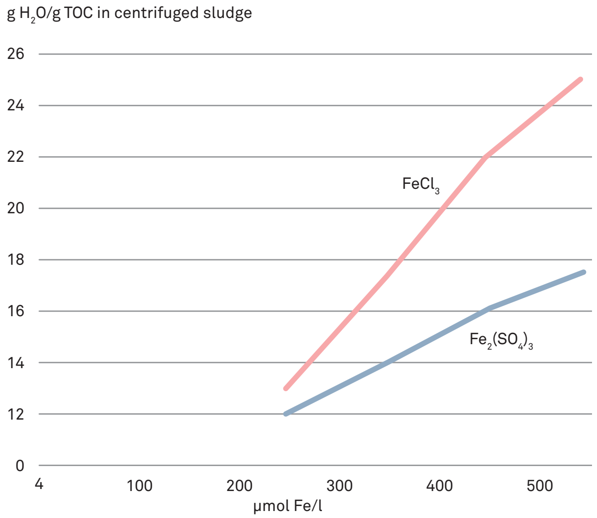
Figure 5.49
The influence of pH on the residual turbidity of synthetic wastewater treated with iron in the form of ferric chloride and ferric sulfate respectively.



Orthophosphate ions, on the other hand, are precipitated just as efficiently by iron(III) sulfate as by iron (III)chloride. This is because orthophosphate is bound more strongly to metal ions than to sulfate. When orthophosphate ions are bound to iron(III) hydroxide formed from iron(III) sulfate it releases some of the sulfate ions being adsorbed by the hydroxide.

The sludge that is formed during treatment with aluminum salts and iron salts is relatively bulky when the suspended solids (SS) level in treated water is low. One of the explanations for this is that hydroxides of iron and aluminum are positively charged. Different flocs repel each other and the space between them is filled with water. Since flocs produced by sulfate salts have a lower positive charge than those produced by chloride salts, the flocs produced by sulfate salts can get closer to each other and the resulting sludge is more compact than that produced by chloride salts. This effect is illustrated in figure 5:50, which shows the water content of centrifuged sludge obtained during the treatment of synthetic wastewater with ferric chloride and ferric sulfate respectively.

Figure 5.50
The influence of pH on the residual turbidity of synthetic wastewater treated with iron in the form of ferric chloride and ferric sulfate respectively.



The influence of silicate and sulfate on polyaluminum salts

Several procedures are available today for introducing various ligands into polyaluminum ions such as silicate or sulfate.

Incorporation of these substances in the aluminum salts increases the speed of floc formation and helps to give the treated water a low residual aluminum content; it also broadens the pH range for fast floc formation. The higher the basicity of the coagulants, the wider the optimal pH range.

When sulfate or silicate is incorporated into iron or (poly)aluminum chloride, it displaces the pH for optimum treatment in the acid direction, i.e. towards a lower pH.

Coagulants with moderate basicity that contain silicates have a very good particle-reduction effect, similar to that of high-basicity coagulants.

The influence of water temperature on the treatment process

Temperature influences several factors in water treatment and thus has a significant impact on treatment results. It influences the viscosity and density of water and its dissociation tendency to form H^+ and OH^- ions, meaning it influences the:

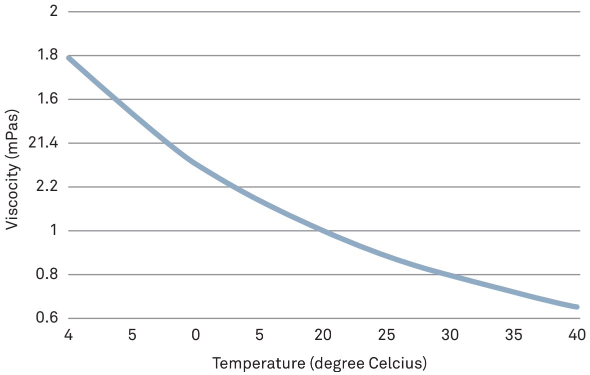
- Settling velocity of flocs
- Acidic properties of water, i.e. its pH and dissociation constant
- Velocity by which various reactions take place, e.g. the speed of hydroxide and floc formation
- Solubility of formed compounds, e.g. the residual aluminum or iron concentration of the treated water.

The influence of temperature on water viscosity

The viscosity of water decreases strongly with increasing temperature: from just above 0 to 25°C the viscosity halves (see example in fig. 5.51). With decreased viscosity flocs settle more easily and the energy needed to mix and pump water decreases.

Figure 5.51

The influence of temperature on the viscosity of water. The data taken from Ref. 16: CRC Handbook of Chemistry and Physics, 90th Edition, 2009-2010.



The influence of temperature on the sedimentation velocity of particles in water

At all temperatures the density of water increases with decreasing temperature, except in the interval from 4 to just above 0°C. With increased water density and viscosity, particles (flocs) settle slower.

By a simple calculation using Stokes law, it can be shown that particles in water settles more slowly with decreasing temperature also inside the temperature interval from 4 to just above 0°C. So, even if the density of water decreases with decreasing water temperature in that temperature interval, the increase of viscosity of water inside the same temperature interval supersedes the effect of the decreased density. So, at all temperatures, from 100 to just before the freezing point, particles in water sink slower with decreasing temperature. This is also valid for flocs in water.

The influence of temperature on the residual aluminum concentration of different salts

The solubility of aluminum hydroxide in water decreases with decreasing temperature. This means that it is possible to achieve a lower residual aluminum concentration by decreasing the temperature of the treated water.

When aluminum sulfate is added to 5°C water, the water gets a lower residual aluminum concentration and the solubility minimum is broader, typically into higher pH, than when the water temperature is 20°C.

Using higher basicity products, the pH for solubility minimum is displaced to a higher pH than at the low water temperature.

The influence of temperature on the speed of floc formation

At low temperatures flocs are formed slower than at higher temperatures, so with decreasing temperature you need a longer coagulation time for flocs to become large enough to settle. Flocculation and coagulation tanks in drinking water plants should therefore be designed for winter conditions.

Plants experiencing cold water conditions can also consider using coagulants that are more forgiving of cold water, such as high basic sulfated PAX or ferric coagulants. To further enhance the floc formation rate, many water treatment plants add a coagulation aid, e.g. a long-chained polyacrylamide or activated water glass. These chemicals cross-link and make flocs denser, converting them into sizes that settle considerably faster than ones formed without these coagulant aids.

The settling rate can be increased by up to around five times by adding long-chain polyacrylamides after the coagulation step.

If the coagulation time can be increased, flocs are formed inside wider pH ranges. This means water treatment plants with a long residence time in the coagulation sector do not need to control coagulation pH as rigorously as plants using shorter coagulation times.

Flocs can also grow in the sedimentation basin; a long sedimentation time is beneficial.

Summary

- As the temperature decreases, the optimal pH for water treatment is displaced into higher pHs
- The viscosity of water increases with decreasing temperatures, which is why the settling rate is lower
- As the temperature decreases, the solubility of aluminum salts decreases and gives lower aluminum residual
- Physical-chemical reactions proceed more slowly at decreasing temperatures and flocs are formed more slowly. Longer flocculation times are needed to form settling flocs at low temperatures compared to high temperatures
- To speed up floc formation and the settling rate of flocs, select a coagulant designed for cold water or use a coagulation aid (e.g. activated water glass or a polyacrylamide) when coagulating low-temperature water.

The removal of toxic ions with the aid of hydroxides

As previously mentioned, hydroxides are charged, and their charge depends on the pH and salt from which they were prepared. At pH levels that are neutral to acid, hydroxides have a positive charge, but at higher pHs they gain an increasing number of negative charges and eventually become negatively charged.

Ions of opposite charge bind to the charged hydroxides. This fact can be used for the removal of toxic ions.

There is a specific pH range within which coagulation can take place.

To remove positively charged toxic ions, flocculation should be carried out at as high a pH as possible. At high pH levels, the hydroxides gain a greater number of negative charges and can then bind positively charged ions, which then accumulate in the sludge.

If on the other hand you want to remove a negatively charged toxic ion, flocculation should be carried out at as low a pH as possible.

Floc strength and methods for obtaining faster-settling flocs and drier sludge

The strength of a floc produced without a flocculation aid (anionic polymer) depends on the:

- Amount of coagulant used
- Basicity of the metal salt
- Type of negative ion of the metal salt, and
- Size of the floc

Polyaluminum chlorides containing some silica have a higher floc strength than similar non-silica containing polyaluminum chlorides. Sulfate can also improve floc strength since sulfate salts have a lower water content than sludge produced using the corresponding molar amount of chloride salt. This is because sulfate ions screen the positive charges on the flocs more effectively than chloride ions. This effect allows the flocs to get closer to each other, which means there is less water between the hydroxides so the sludge is drier.

It is possible to strengthen the floc using a flocculation aid, which may also reduce the water content of the sludge.

Another advantage of using flocculation aids is that they substantially decrease the time needed for coagulation and increase the sedimentation rate of the flocs. The total time needed for coagulation and flocculation is about 25–50% of the time needed for coagulation without a flocculation aid.

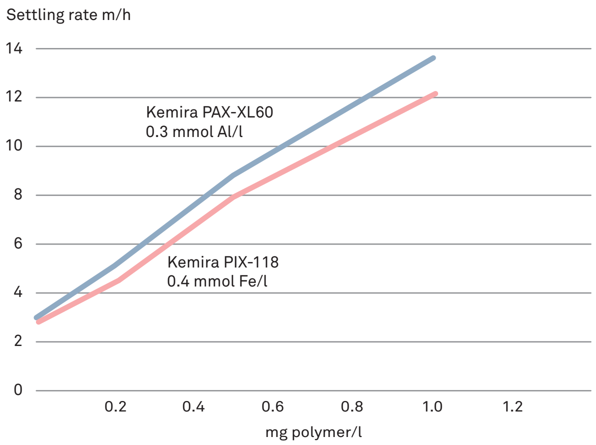
Before adding the flocculation aid the contaminants must be given time to react with the components formed from the metal salt, and the metal hydroxide flocs must be allowed to start forming. Once added, the flocculation aid cross-links and condenses the flocs, which are positively charged.

When polyacrylamides are used as a coagulation aid they are usually negatively charged high molecular weight polyacrylamides. For applications such as drinking water production, low-charge cationic polyacrylamides can also be used.

The sedimentation rate of flocs formed using a flocculation aid may be considerably higher than that of flocs formed without an aid. This effect is illustrated in figure 5.52.

If flocculation is carried out properly the flocs may be obtained in the form of a compact aggregate or pellets with a low water content that sink very rapidly.

Figure 5.52
The influence of the dose of anionic polymer on the settling rate of flocs when wastewater is treated with two metal salts.



(Ref. 17: Ødegaard, H., Grutle, S., and Ratnaweera, H., An Analysis of Floc Separation Characteristics in Chemical Wastewater Treatment, In: Chemical Water and Wastewater Treatment II, Klute R. and Hahn H.H. (Eds), Springer-Verlag, Berlin, Heidelberg, 1992, pp. 97–114, ISBN 3-540-55982-5.)

Properties of Kemira’s metal salts

Kemira produces different aluminum and iron salts with various basicity and counter ions.

Kemira has developed methods that make it possible to produce coagulants with a low heavy metal content regardless of the type of raw material. Kemira’s coagulants are among those with the lowest heavy metal content available on the market.

Tables 5.53 and 5.54 summarize the types of metal salts produced by Kemira that contain aluminum and iron. They also show the typical concentrations, basicities, and main applications. Kemira also produces salts other than those mentioned in these tables.

In general, the following can be said of aluminum salts:

- The higher the basicity of the coagulant the less it reduces the pH of the water
- Of the above coagulants the least amount of sludge seems to be produced by medium-basicity polyaluminum chlorides and aluminum sulfate
- The ability of PAC to reduce turbidity is greatest when the basicity is around 65%
- When the coagulant contains sulfate or silicate, floc formation proceeds more rapidly than in the absence of these ions
- When a coagulant contains sulfate or silicate, the optimum pH for flocculation is displaced slightly in the acidic direction
- When the coagulant includes an organic polymer, treatment can be carried out over a wider pH range.

Table 5.53
Typical aluminum salts produced by Kemira. In Pulp & Paper segment FennoFloc A trade names are in use.

Active ingredients	Form	Examples of trade name	Standards
Aluminum sulfate	Dry, granules Dry, kibbles	Kemira ALG Kemira ALK	CEN, NSF, AWWA CEN, AWWA
Aluminum sulfate	Liquid	Kemira ALS	CEN, NSF, AWWA
Aluminum iron sulfate	Dry, granules	Kemira AVR	Wastewater treatment
Aluminum chloride	Liquid	Kemira ACL-28	CEN, NSF, AWWA
Polyaluminum chloride, low basicity	Liquid	Kemira PAX-14	CEN, NSF, AWWA
Polyaluminum chloride, medium basicity	Liquid	Kemira PAX-18 Kemira PAX-40 Kemira PAX-XL 6 Kemira PAX-XL 60 SternPAC	CEN, NSF, AWWA CEN, AWWA NSF, AWWA CEN, NSF, AWWA NSF, AWWA
Polyaluminum chloride, medium basicity	Dry, powder	Kemira PAX-PS	CEN
Polyaluminum chloride, high basicity	Liquid	Kemira PAX-XL 8 Kemira PAX-XL 9 Kemira PAX-XL 10 Kemira PAX-XL 61 Kemira PAX-HP800 SternPAC	CEN, NSF, AWWA CEN CEN CEN CEN, NSF, AWWA NSF, AWWA
Polyaluminum chloride, very high basicity	Liquid	Kemira ACH Kemira PAX-XL 19 Kemira PAX-XL 1900	CEN, NSF, AWWA CEN, NSF, AWWA CEN, NSF, AWWA
Polyaluminum chloride-polymer blends	Liquid	Kemira PAX-XL 3xxx	NSF, AWWA
Sodium aluminate	Liquid	Kemira SAX-18 Kemira SAX-20	CEN NSF, AWWA

CEN - European Committee for Standardization
NSF - National Sanitation Foundation
AWWA - American Water Works Association

In general, the following can be said of iron salts:

- Chloride salts work over broader pH ranges than sulfate salts. Sometimes a lower concentration of iron is needed in the form of a chloride salt than would be needed with a sulfate salt to achieve the same effect.
- The sludge volume produced by a constant dose of iron added in the form of a sulfate salt is lower than that produced by the same amount of iron added as a chloride salt.
- Iron salts can remove odor (H_2S) by precipitating sulfides. When a ferric nitrate salt is used it removes the odor in two ways: the nitrate prevents sulfide formation, and the ferric ions precipitate sulfide through redox reactions in the form of FeS, which is black in color.
- Ferric salts decrease the pH of treated water more than aluminum salts.
- Ferric salts often work best at a slightly lower pH than aluminum salts.
- Ferric coagulants normally work across a much broader pH range than aluminum coagulants.

Table 5.54

Typical iron salts produced by Kemira. For Pulp & Paper applications FennoFloc F trade names are in use.

CEN - European Committee for Standardization
NSF - National Sanitation Foundation
AWWA - American Water Works Association

Active ingredients	Form	Examples of trade name	Standards
Ferrous sulfate	Dry, crystals	Kemira COP	Waste water treatment
Ferrous sulfate	Liquid	Kemira PIX-206 Kemira PIX-401 Kemira PIX-411	NSF, AWWA NSF, AWWA NSF, AWWA
Ferric sulfate	Liquid	Kemira PIX-113 Kemira PIX-122 Kemira PIX-312 Kemira PIX-317 Kemira PIX-322	CEN CEN NSF, AWWA NSF, AWWA CEN
Ferric sulfate	Dry, granules	Kemira FERIX-3	NSF, AWWA
Ferric chloride	Liquid	Kemira PIX-111 Kemira PIX-311 Kemira PIX-511	CEN CEN, NSF, AWWA CEN, NSF, AWWA
Ferric chloride sulfate	Liquid	Kemira PIX-118	CEN

How to carry out jar tests

Kemira Flocculator 2000

The Kemira Flocculator 2000 is used to carry out flocculation tests under laboratory conditions with effective simulation of all process stages. Up to six agitators can be connected to the control unit and the mixing procedure for each can be individually controlled.

Each agitator has a motor connected to a tachometer, which ensures that the propeller turns at the pre-determined speed for the selected time. The agitators are placed in one-liter glass beakers. Each agitator is started and then the coagulant is added. Every beaker is then treated in the same way.

Figure 5.55

Kemira Flocculator 2000.

Velocity gradients (G-values) in the Flocculator 2000

Coagulants are usually added at a dosing point where there is a high degree of turbulence. In turbulent areas the water body is subjected to velocity gradients, which have the dimension reciprocal seconds (1/s). Flocs are also subjected to velocity gradients in the coagulation step where they are formed. These gradients have an impact on the size of the flocs formed.

At turbulent points the velocity gradients (shear) fluctuate randomly in all directions, making them difficult to quantify.

It has been shown that the integrated absolute velocity gradient (G) equals:

$$G = \sqrt{\frac{P}{V\mu}}\ (1/s)$$

P/V = mixing power dissipated per unit volume (W/m^2)

μ = dynamic viscosity (kg/ms)

There are wide local variations in velocity gradients in a flocculator.

Detailed information about the local mixing zones inside a mixing tank can be obtained with computational fluid dynamics (CFD) modeling. Figure 5.56 illustrates the local velocity gradients (G-values) in a beaker connected to the Kemira Flocculator 2000. It can be seen that the highest G-values exist close to the propeller.

Figure 5.56

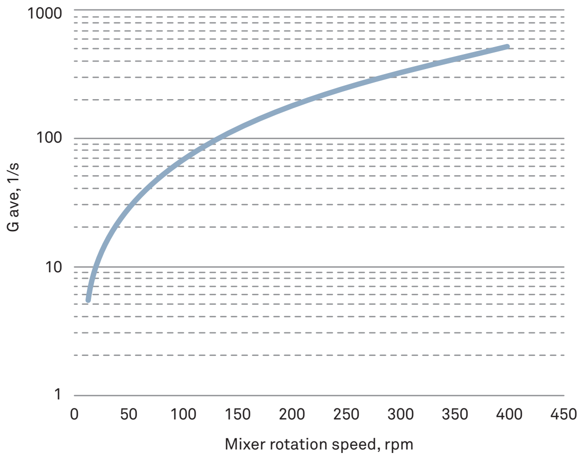
Local G-values produced by the Kemira Flocculator 2000 when the propeller is running at 250 rpm.

Designers of water treatment facilities regularly face scale-up tasks. When designing flocculators, they often use the average velocity gradient, or Gave for short.

The influence of rotational speed on G-values in one-liter glass beakers connected to a Kemira Flocculator 2000 is shown in figure 5.57.

Figure 5.57

Average G-values produced by the Kemira Flocculator 2000



It is useful to know that scaling up with the help of a diagram like the one in figure 5.57 has limitations. For example, it may lead to too much energy input when scaling up to a full-size vessel. It is also useful to know that even when two control units have identical average G-numbers, they normally have different local G-values. This may lead to different cleaning results.

Preparations for a jar test

Ensure that you handle the equipment and products in a safe manner and use personal protective equipment like goggles, a lab coat, gloves, and rubber-soled shoes that cover the entire foot. Be sure to read the relevant material safety data sheets (SDS) carefully before beginning the test, and pay attention to the quality of the tested water, since it may contain pathogenic microorganisms. Chemicals must be handled in accordance with the instructions given in the SDS. In order to prevent cuts and other injuries caused by broken glassware, always inspect glassware for flaws in advance and dispose of any cracked or chipped vessels appropriately.

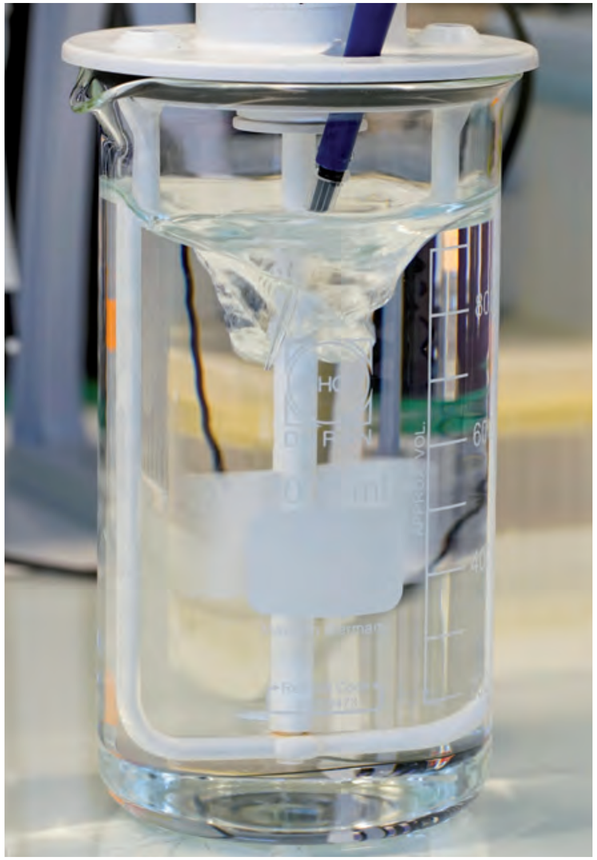
The sample must be taken at a constant depth from the water surface using a good water sampling device. The sampler should have a smooth, wide opening and preferably be dimensioned in such a way that the sample is not subjected to turbulence that breaks the flocs.

A typical sample volume is about 50 ml. A volumetric pipette turned upside down or a plastic syringe (approx. 60 ml) with a widened inlet are examples of equipment that can be used as a sampler. Place a mark on the lower end of the syringe or pipette to indicate the sampling depth.

Rapid mixing – addition of coagulant

A propeller speed of 300–400 rpm is optimal during rapid mixing. Above 400 rpm such a deep vortex is formed that air may be mixed into the treated water. Start the rapid mixing. Then directly add the coagulant into the turbulent part of the water using a micropipette (see figure 5.58). Let the rapid mixing continue for 10–30 seconds. Liquid coagulants should be fed as is.

Figure 5.58
Recommended dosing point for metal salt.



Slow mixing – coagulation

The propeller speed during the slow-mixing period should be fast enough for well-settling flocs to form in time, but not so fast that the flocs break up. The slower the propeller speed during the coagulation period, the longer it takes to reduce turbidity and the larger the flocs will be.

A propeller speed of 35–40 rpm is recommended and a coagulation time of 5–30 minutes is often sufficient depending on the water being treated. The colder the water, the longer the coagulation time needed. High-turbidity waters normally need a shorter coagulation time.

Flocs produced by iron salts can withstand longer coagulation times and higher propeller speeds without breaking than flocs produced by aluminum salts.

Sedimentation – separation of flocs

The sedimentation time will depend on the temperature of the water and the shape of the formed flocs. Sedimentation will take longer with cold water.

Let flocs settle for 10 to 30 minutes.

Recommended settings for Kemira Flocculator 2000

Wastewater treatment

- Rapid mixing: 300–400 rpm for 10 seconds
- Slow mixing: 35–40 rpm for 5–15 minutes
- Sedimentation: 10 minutes

Surface water treatment

- Rapid mixing: 300–400 rpm for 20–30 seconds
- Slow mixing: 35–40 rpm for 10–30 minutes
- Sedimentation: 15–30 minutes

How to take a sample from a beaker

Samples should be taken at the same depth in every beaker, e.g. 3 cm.

Take the sample with a steady hand using a syringe or pipette, taking care not to break the flocs or disturb settled flocs.

Jar experiments can be used to simulate different surface loads by either taking samples after different sedimentation times or by taking samples at a constant sedimentation time at different depths.

If you want to study the effect of different overflow rates it is recommended to take samples at a constant depth close to the surface after different sedimentation times. This gives a more linear response than sampling at different depths.

Practical tips

Wastewater treatment

- When collecting wastewater in a treatment station, filter it through a sieve with a pore size of ca. 1 mm to remove larger particles before pouring it into the collection vessel. Turbidity is mainly caused by very small particles with a size in the range of the wavelength of light (ca. 0.4 to 0.8 µm).
- Wastewater contains microorganisms that continuously change its composition. Sample fresh water on one occasion. Carry out the tests on the same day.
- After coagulation and floc separation, immediately analyze turbidity and the dissolved phosphorus (ortho P) concentration of the samples being filtered.
- The presence of particles disturbs the measurement of ortho P, so you should always analyze the ortho P of the samples being filtered, e.g. through Whatman GF/A or GF/C filters with pore sizes of 1.6 and 1.2 µm respectively.

- The analysis of total phosphorus (total P) doesn´t have to be carried out directly since the samples are heated and total P is converted into ortho P.

Surface water treatment

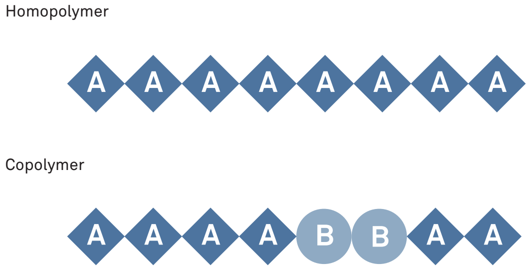
- Surface water contains considerably lower concentrations of microorganisms than wastewater. If it is stored in cold conditions surface water can be kept for several months before use.
- After coagulation and floc separation, immediately analyze turbidity.
- Always measure the residual aluminum and iron concentrations of filtered samples.
- The presence of flocs influences the residual coagulant concentration and the color when it is measured as absorbance. Carry out the measurement on filtered samples.
- When analyzing dissolved organic carbon (DOC), use a filter made of cellulose nitrate with a pore size of 0.45 µm; this pore size best resembles the effect of the sand filters used in water treatment plants.
- Do not use filters made of cellulose acetate as they will leach organic material and give too-high DOC readings.

Polymers

General background

Polymers are macromolecules consisting of several small repeating units bound to each other with covalent bonds. The repeating units can be of the same type or composed of several different types of chemical units. If the polymer consists of only one type of chemical unit the polymer is called a homopolymer. If the polymer is composed of two types of units it is called a copolymer, and if it is composed of three types of units it is known as a terpolymer (see figure 5.59).

Figure 5.59
Examples of a linear homopolymer and a copolymer.



The chemical components from which the repeating units are formed are called monomers. The number of repeating units in a single polymer molecule is called the degree of polymerization. The degree of polymerization and molar mass of the repeating units define the molecular weight of the polymer molecule. The molecular weight of polymers typically ranges from a few hundred to several tens of millions g/mol. The polymer chains are never equally long, but they form a distribution, and from this distribution different statistical average values are calculated, such as weight average molecular weight ($\bar{M}_w$) and number average molecular weight ($\bar{M}_n$).

Polymers can be made synthetically by using polymerization reactions of monomers, they can be of natural origin, or they can be produced in some other way by living organisms. The latter two types are called biopolymers.

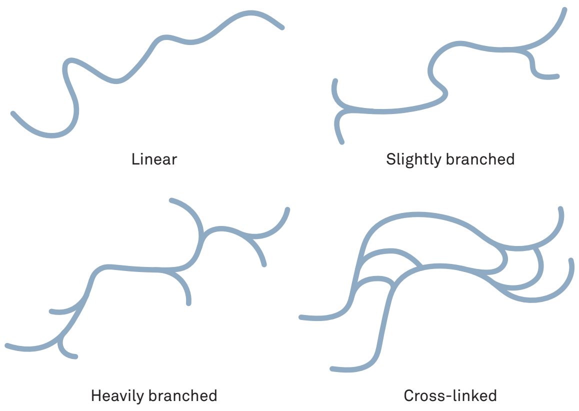
The majority of synthetic polymers are water insoluble thermoformable materials, which are used in plastics. The polymers used in water and sludge treatment are water soluble.

If the repeating unit in a polymer is charged, whether cationically or anionically, the polymer is known as a polyelectrolyte. The most important polymers used in water and sludge treatment are cationically charged copolymers of acrylamide. They are the most sold synthetic water-soluble polyelectrolytes.

The structure of polymer chains can be linear, branched, or crosslinked (see figure 5.60). The chain structure has an impact on polymer performance. If the degree of crosslinking is too high the polymer becomes insoluble in water.

Polymers are used in water and sludge treatment to floc colloidal particles in order to aid their removal or to help sludge dewatering. They can be used alone or together with inorganic coagulants to make flocs bigger and more resistant to shear forces. Floc formation due to polymer use is called flocculation, and the polymers used for this are called flocculants.

Figure 5.60
Different types of polymer chain structures.



Polymers and charges

Cationic charge normally comes from ammonium groups. There are two types of cationic charge: pH dependent and pH independent. The cationic charge is pH dependent if the amino groups in polymer are primary, secondary, or tertiary. The charge is then caused by protons at low pHs (see equation 5.61 and, e.g., figure 5.63).

Equation 5.61

$$-NR_2 + H^+ \rightarrow -N^+R_2H$$

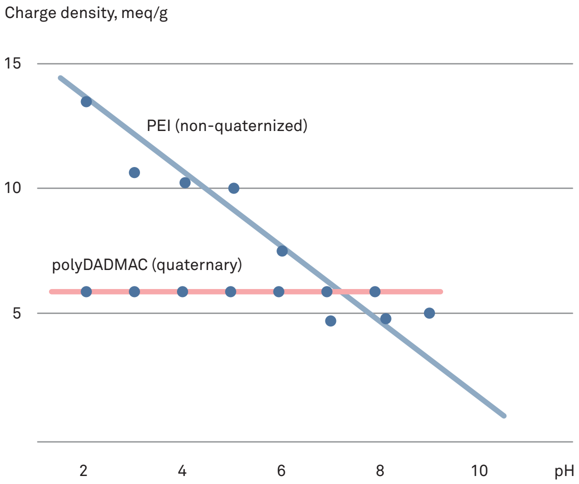
The proton-induced charge density is at its highest at low pHs and decreases when pH increases (figure 5.63).

When the cationic charge comes from a quaternary ammonium group (equation 5.62) it is not pH dependent (figure 5.63).

Equation 5.62

$$-N(CH_3)_2 + CH_3Cl \rightarrow -N^+(CH_3)_3\ Cl^-$$

Figure 5.63
Examples of the impact of ammonium group type on polymer charge density at different pHs.



A summary of the cationic charge densities of different polymers and their dependencies on polymer structure and pH is given in table 5.64.

Table 5.64
Charge densities of different polymer chemistries.

	Charge density meq/g dry polymer	Is maximum charge density dependent on polymer composition?	Is charge density dependent on pH?
Cationic polyacrylamide	Max. 5	Yes	No/Yes
Mannich polyacrylamide	Max. 7.5	Yes	Yes (figure 5.78)
Polyamine	7	No	No
PolyDADMAC	6	No	No (figure 5.63)
Polyethyleneimine (PEI)	Max. 15	No	Yes (figure 5.63)
Polydicyandiamide, chloride [Poly(DCD-Cl)]	Max. 4.5	No	to some extent (figure 5.83)
Polyvinylamine	Max. 18	Yes	Yes

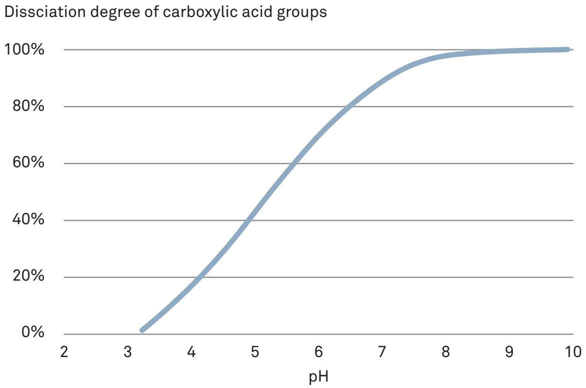
Anionic charge in polyelectrolytes is mostly based on the dissociation of carboxylic acid groups (equation 5.65). A carboxylic acid group becomes a negatively charged carboxylate group carrying a cation as a counter ion:

Equation 5.65

$$-COOH + NaOH \rightarrow -COO^{-}Na^{+} + H_2O$$

Because carboxylic acid is a weak acid, its anionic charge is dependent on the dissociation of carboxylic acid groups and the charge is thus pH dependent (figure 5.66).

Figure 5.66
Dissociation of carboxylic acid groups as a function of pH.



Anionic charge can also be based on strong acid groups such as sulfonic acid. Sulfonic acid becomes dissociated across practically the whole relevant pH range and the charge is thus essentially pH independent.

Flocculation mechanisms

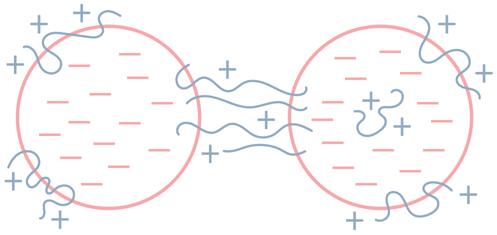
Flocculation can take place via various mechanisms utilizing electrostatic interactions and/or hydrogen bonding depending on which chemistry is used in the flocculant. Because colloidal particles normally have anionic surface charge, cationically charged flocculants can be used as such. Anionically charged flocculants need to be used together with some cationic component such as a metal coagulant or low molecular weight cationically charged polymer.

Bridging flocculation

Bridging flocculation takes place when very high molecular weight polymers such as polyacrylamide are used (figure 5.67). The molecular weight of the flocculant required is millions or even tens of millions g/mol. A very high molecular weight cationically charged flocculating polymer forms a three-dimensional structure by adsorbing onto several particles at the same time, forming a floc. The floc keeps the fine and colloidal particles from water close to each other. The cationic charge of the polymer also helps the particles to retain less water. Both these phenomena mean that the water is squeezed out and the sludge is easier to remove from dewatering equipment.

Figure 5.67

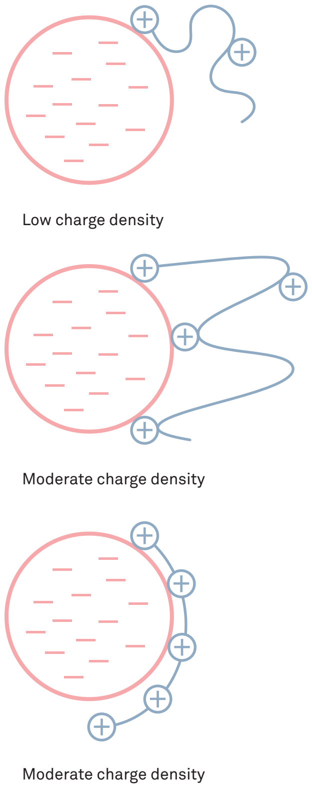
Bridging flocculation (Ref. 18: Modified from Eklund, D. and Lindström, T., Paper Chemistry. An Introduction, DT Paper Science Publications, Grankulla, Finland 1991).



Flocs formed by bridging have the highest shear force resistance but bad reflocculation ability after the shearing ceases. It is therefore important to select the correct dosing point before the dewatering equipment when using polyacrylamide flocculants.

In order to form good flocs by bridging, the polymer needs to adsorb onto the surface in an optimal way by making loops and tails. If the charge density of the polymer is too weak the interaction between the polymer and the surface will be too weak, leading to weak flocs. On the other hand, if the charge density is too high, the interaction will be too strong, meaning loops and tails for bridging cannot be formed. Thus, a moderate charge density leads to optimal flocculation (figure 5.68). The optimal charge density of the polymer depends on the sludge being treated. Sludge dewatering typically requires polymers with higher charge density than those used in, for example, paper applications.

Figure 5.68
The effect of polymer charge density on bridging flocculation.
(Ref 19: Eklund, D. and Lindström, T., Paper Chemistry. An Introduction, DT Paper Science Publications, Grankulla, Finland 1991).



Weak interaction between polymer and surface. Weak adsorption and flocculation.

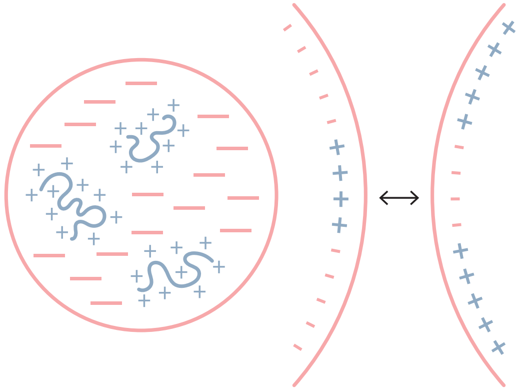
Moderate interaction between polymer and surface. Good polymer adsorption and strong bridge formation.

Strong interaction between polymer and surface. The polymer is adsorbed as flat conformation which leads to weak bridge formation (patching situation).

Patch flocculation

Patch flocculation takes place when the polymer used has high charge density. A high charge density polymer takes a flat form on particle surfaces, and the polymer can have either a high or a low molecular weight (figure 5.69).

Figure 5.69
Patch flocculation (Ref. 20: Eklund, D. and Lindström, T., Paper Chemistry. An Introduction, DT Paper Science Publications, Grankulla, Finland 1991).



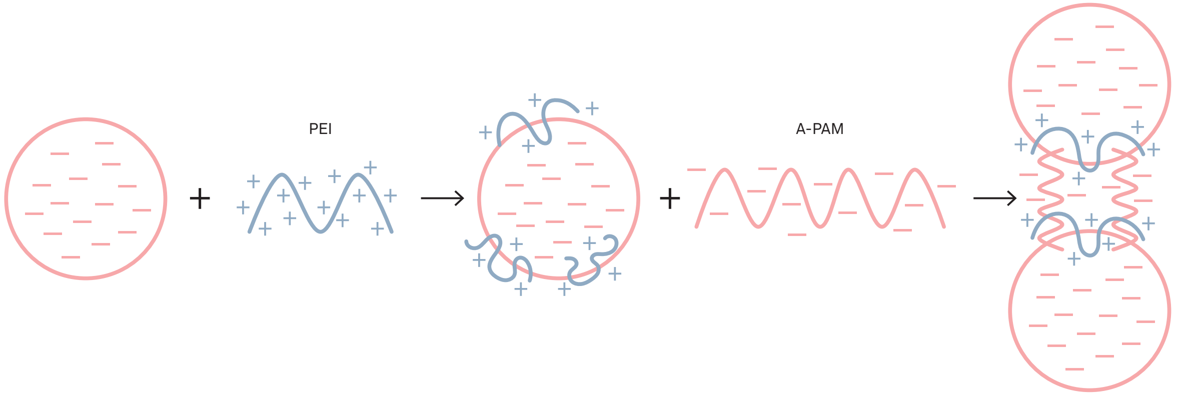
The polymer forms cationic charge-enriched patches on particle surfaces. These cationic patches attract the anionic parts of the other particles, which is inducing floc formation. Patch flocculation makes flocs that are not as shear resistant as flocs made by bridging, but which reflocculate better after shear forces cease.

Other flocculation mechanisms

Charge neutralization and heterocoagulation, where only low molecular weight cationic compounds are used, do not meet the efficiency requirements of the most demanding dewatering applications. The same is true for mechanisms where electrostatic interactions are not involved, when the polymer used has a high molecular weight but is non-ionic, such as acrylamide homopolymer or polyethyleneoxide.

Complex flocculation (figure 5.70) is a combination of patch and bridging flocculation mechanisms. It is based on electrostatic interaction, where a low molecular weight cationic component such as aluminum or iron salt, or a high charge density cationic polymer such as polyamine, polyDADMAC, or polyethyleneimine, is combined with a high molecular weight anionic flocculant polymer.

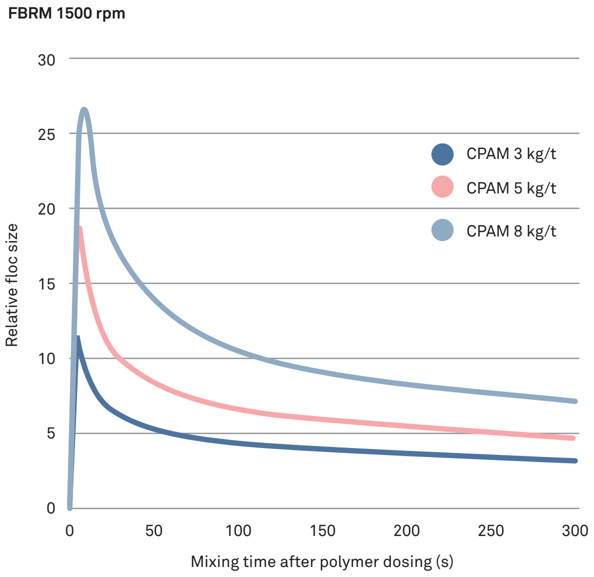
Figure 5.70
Complex flocculation based on electrostatic interaction (Ref. 21: Modified from Eklund, D. and Lindström, T., Paper Chemistry. An Introduction, DT Paper Science Publications, Grankulla, Finland 1991, modified).



The use of cationic coagulants or a cationic low molecular weight polymer produces cationically charged sites on particle surfaces. The negatively charged groups in the anionic polyacrylamide flocculant can then adsorb onto these positively charged sites and link the particles together. Flocs become denser, sink faster, are less shear sensitive, and contain less water than flocs formed without the addition of a negatively charged polymer. In dewatering applications anionic polyacrylamides are not typically used because the anionic polymer itself binds water well and thus easily retards dewatering.

The mechanism of complex flocculation based on electrostatic interaction is nonetheless a valid mechanism, especially in drinking and raw water flocculation as well as in some industrial applications.

Figure 5.71
Relative floc size using focused beam reflectance measurement (FBRM) technology.



Floc size

When a polymer is dosed the floc size in the sludge or water starts increasing rapidly (figure 5.71).

When shear forces are applied, for example when sludge flows through pipes approaching the dewatering unit, during the dewatering process, or when the sludge is mixed in a beaker in a laboratory experiment, they tend to break up flocs. The longer the shear forces are applied, the smaller the flocs become.

Floc sizes during dewatering depend on the sludge and polymer properties, the dosing amount, dosing point, and type of dewatering equipment. Some dewatering equipment, such as decanting centrifuges, perform better with large, strong flocs, while other equipment such as filter presses may get a better result with smaller flocs.

Flocculant polymers

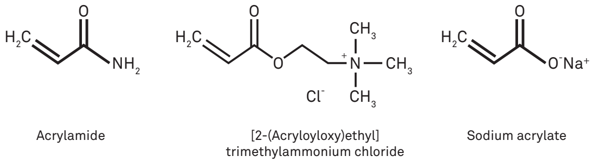
Polyacrylamides (PAM)

Industrial polyacrylamides are mostly cationic or anionic copolymers of acrylamide. Non-ionic grades also exist, i.e. homopolymers of acrylamide, but are not as widely used as charged copolymers.

The term polyacrylamide is commonly used to refer to both homopolymers and copolymers of acrylamide, although chemically it only refers to homopolymers.

The most important monomers used to make acrylamide copolymers are shown in figure 5.72.

Figure 5.72
Acrylamide and the most commonly used cationic ([2-acryloyloxyethyl]trimethylammonium chloride) and anionic (sodium acrylate) comonomers.



Polyacrylamides can be polymerized to very high molecular weights, up to several tens of millions g/mol. This specific property gives them outstanding flocculation performance, especially in high shearing systems. Low molecular weight grades of polyacrylamides can be produced, but they are not as efficient in flocculation as high molecular weight grades.

Figures 5.73 and 5.74 show the repeating unit structures in polyacrylamides.

Figure 5.73
Repeating unit structures in an anionic polyacrylamide.

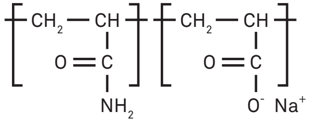
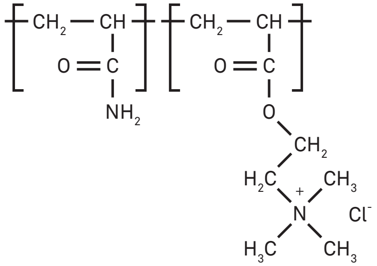


Figure 5.74
Repeating unit structures in a cationic polyacrylamide.



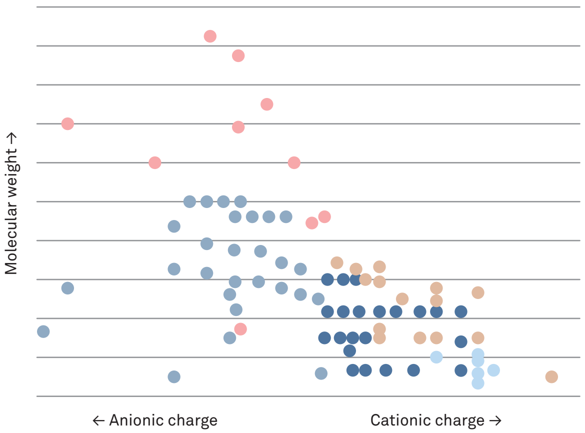
The most commonly used cationic monomer is a quaternized amino ester of acrylic acid. Other cationic monomers are used, such as amide derivatives of acrylic and methacrylic acid, but they are not as common and thus more expensive than the esters. Non-quaternary amino esters or amides can also be polymerized with acrylamide, but these are used only in special cases because the cationic charge becomes pH dependent due to a lack of quaternary amino groups.

The ester structure makes the cationic polyacrylamide sensitive to hydrolysis at elevated pHs. Hydrolysis is a problem because not only are the cationically charged groups lost, anionically charged groups are formed at the same time. This easily precipitates the polymer out of a solution because of bonding between polymer molecules. To prevent hydrolysis pH of a cationic polyacrylamide stock solution needs to be sufficiently low, preferably below pH 5. The application pH though can be higher, because flocculation takes place very rapidly (see figure 5.71).

Cationic polyacrylamides are used, among other things, for the dewatering of sludge from biological treatment processes. Typically, the higher the share of biological sludge in the total amount of sludge, the higher the cationic charge density required in the polymer.

Anionic polyacrylamides are easier to polymerize to very high molecular weights. In cationic polyacrylamides a high molecular weight becomes more difficult to achieve with high charge densities of the polymer (see figure 5.75).

Figure 5.75
Achievable relative polymer molecular weights with different charge types and at different charge density levels.



Polyacrylamide products are mostly supplied as dry powder or beads, or as water-in-oil emulsion in an aliphatic hydrocarbon medium. They can also be supplied as an aqueous dispersion in which the polymer is in precipitated form due to the high concentration of salt present in the aqueous phase.

Polyacrylamides always require specific dissolution equipment to ensure that the polymer is properly dissolved in water. The polymer concentration cannot be high; the typical maximum concentration is 0.5%.

One way to increase the molecular weight of a cationic polyacrylamide is to utilize Mannich reaction, where a non-ionic polyacrylamide is reacted with formaldehyde and dimethylamine (figure 5.76). The degree of cationization is controlled by the amount of reagents, thus it can vary between 0 and 100%.

A Mannich polyacrylamide does not contain quaternary ammonium groups, thus its charge is pH dependent (figure 5.77). The charge density decreases towards higher pHs, but at pH 7 it is still about 75% and at pH 8 about 25% of the maximum available charge (see figure 5.78).

Figure 5.76

Mannich reaction of a non-ionic polyacrylamide.

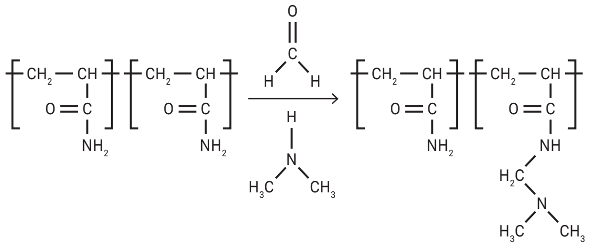


Figure 5.77

Cationic charge by protonation in a Mannich polyacrylamide.

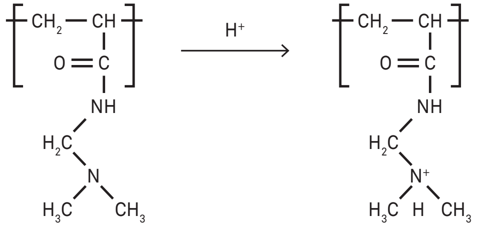
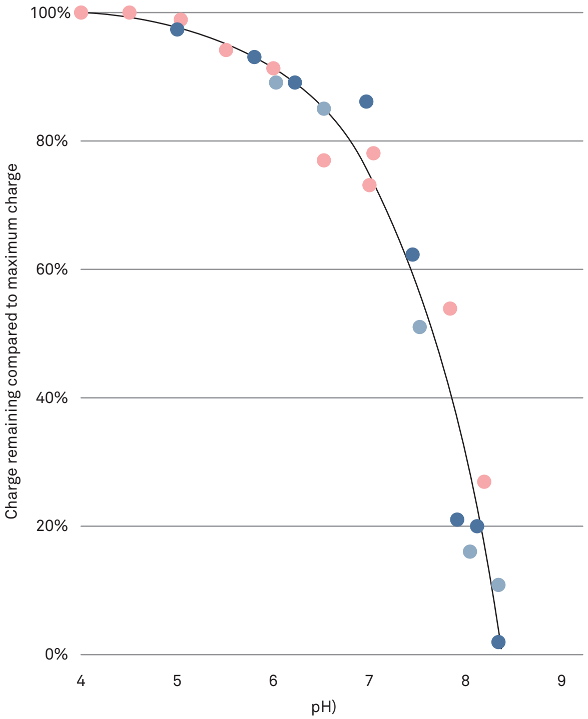


Figure 5.78

Development of charge in Mannich polyacrylamides as a function of pH.



The Mannich reaction can be made in a polymer solution. For flocculant-grade polyacrylamides this means low-end product concentration, which is why the Mannich reaction s typically made close to end use application site.. High cationic polymer consumption makes the Mannich reaction an attractive alternative because of its good cost-per-performance ratio. It is mostly used at wastewater treatment plants of big cities.

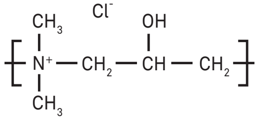
At acidic pH a Mannich polyacrylamide is a very powerful flocculant.

Polyamine

Polyamine is made by reacting trimethylamine with epichlorohydrin. Its main repeating unit is shown in figure 5.79.

Its molecular weight is not very high, only up to a few tens of thousand g/mol. Using a small amount of diamine during the polymerization creates branches on the polymer chains, and this allows the molecular weight to increase up to a few hundreds of thousands g/mol.

Figure 5.79
Repeating unit in a linear polyamine.



$$\left[-\underset{CH_3}{\overset{CH_3}{N^+}} - CH_2 - \overset{OH}{CH} - CH_2 - \right] \quad Cl^-$$

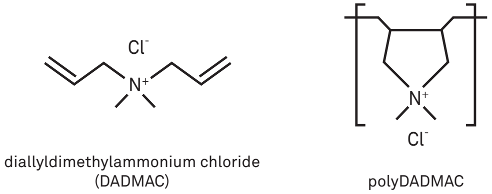
Because of their relatively low molecular weight, polyamine products are typically supplied as a solution with an active content of 30–50%.

Polyamine has a relatively high specific charge density, about 7 meq/g, and its charge is pH independent. See table 5.64.

PolyDADMAC

Diallyldimethylammonium chloride (DADMAC) monomer polymerizes by forming a specific ring structure (see figure 5.80).

Figure 5.80
DADMAC monomer and repeating structure in polyDADMAC.



PolyDADMAC can be polymerized to molecular weights of up to a few hundreds of thousands g/mol, perhaps slightly higher than that of polyamine. PolyDADMAC is also typically supplied as a solution with an active content of 20–40%.

PolyDADMAC's charge density is slightly lower than that of polyamine, about 6 meq/g, and its charge is also pH independent (see table 5.64 and figure 5.63).

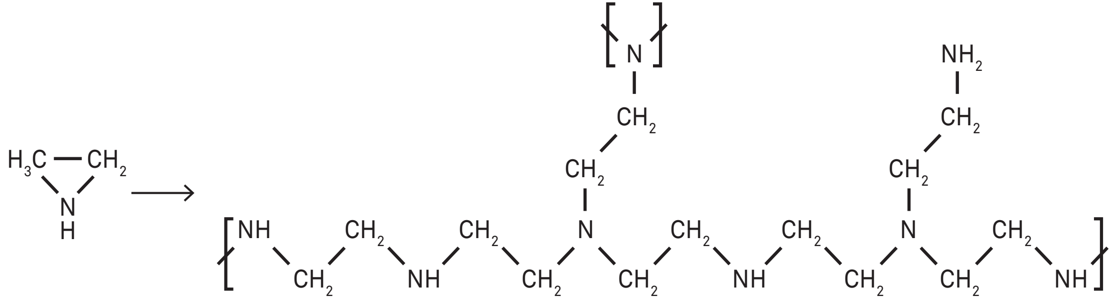
Polyethyleneimine (PEI)

When ethyleneimine (aziridine) polymerizes, its ring opens and branched polymer chains are formed carrying amino groups in chains. The amines of primary, secondary, and tertiary type (see figure 5.81).

Because the amino groups are not quaternary the charge density in polyethyleneimine is heavily pH dependent (see figure 5.63). At acidic pH polyethyleneimine has very high charge density (see table 5.64).

The molecular weight of polyethyleneimine cannot become very high, thus the product is typically supplied as a solution with an active content of 20–50%.

Figure 5.81
Formed structure in polyethyleneimine.

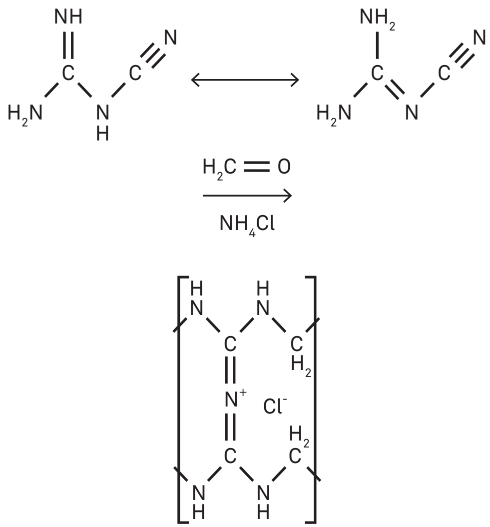


There are several different types of polymers that try to mimic the performance of polyethyleneimine. These are known as modified polyethyleneimine or ethyleneimine copolymers.

Dicyandiamide polymers

Dicyandiamide, also known as cyanoguanidine, has two tautometric forms and can be polymerized in the presence of formaldehyde and ammonium chloride into a polymeric structure with amino groups in the chain (see figure 5.82). Ammonium sulfate can be used instead of ammonium chloride to give sulfate ions as counter ions in the polymer. The sulfate version is sometimes preferred because it is less corrosive than the corresponding chloride version.

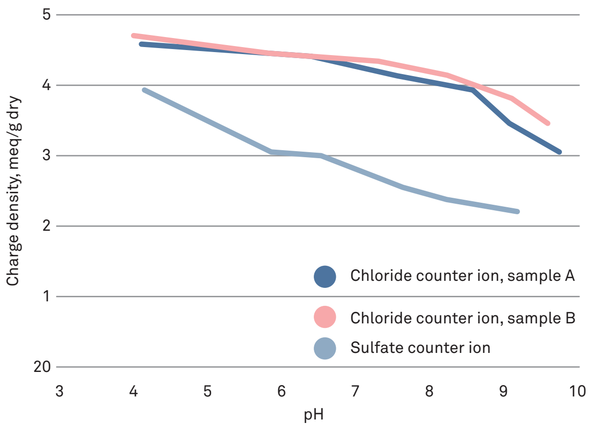
Figure 5.82
Two tautometric forms of dicyandiamide and its repeating unit after polymerization.



The charge density of dicyandiamide polymer is partly pH dependent (see figure 5.83). A sulfate ion as a counter ion gives a slightly lower charge density than chloride.

Figure 5.83

Charge density of dicyandiamide polymers as function of pH.



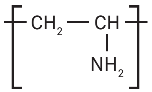
The molecular weight of dicyandiamide polymers is very low, only a couple of thousands g/mol, thus the product is typically supplied as a 50% solution.

Polyvinylamine

Figure 5.84 shows the repeating structure of polyvinylamine.

Figure 5.84

Repeating structure in polyvinylamine.

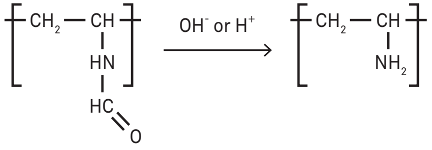


$$\left[CH_2 - \underset{\displaystyle NH_2}{CH} \right]$$

The name polyvinylamine is somewhat misleading because no stable vinylamine monomer exists. Instead of polymerizing vinylamine monomer, polyvinylamine is made by first polymerizing vinylformamide or vinylacetamide monomer and then hydrolyzing the formed polymer in alkali or acid (see figure 5.85).

Figure 5.85

Hydrolysis of polyvinylformamide to polyvinylamine.



$$\left[CH_2 - \underset{\displaystyle \underset{\displaystyle HC{=}O}{HN}}{CH} \right] \xrightarrow{OH^- \text{ or } H^+} \left[CH_2 - \underset{\displaystyle NH_2}{CH} \right]$$

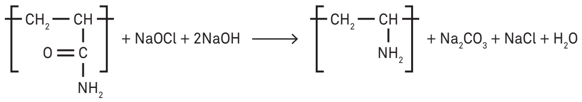
Polyvinylamine has no quaternary amino groups, thus its charge density is dependent on the pH. But because only amino groups are protonized, the charge density is also dependent on the degree of hydrolysis of formamide or acetamide groups to amine groups. In practice polyvinylamine products are never completely hydrolyzed.

At acidic pH and with a high degree of hydrolysis, polyvinylamine has very high charge density (see table 5.64). The charge density becomes lower when pH is increasing. At pH 8 about 80% of the maximum charge density remains with a hydrolysis degree of 46%, and about 60% remains with a hydrolysis degree of 89%.

Polyvinylamine is supplied both as dry powder and as a 10–20% solution.

Another way to get to the same polyvinylamine structure is to utilize the Hofmann degradation reaction for polyacrylamide. In this reaction the acrylamide monomer is first polymerized, after which the formed polyacrylamide is reacted with hypochlorite in an alkaline solution (figure 5.86).

Figure 5.86
Hofmann degradation reaction for polyacrylamide.



$$\left[\mathrm{CH_2-CH(C(=O)NH_2)}\right] + \mathrm{NaOCl} + 2\,\mathrm{NaOH} \longrightarrow \left[\mathrm{CH_2-CH(NH_2)}\right] + \mathrm{Na_2CO_3} + \mathrm{NaCl} + \mathrm{H_2O}$$

The reaction produces sodium carbonate and sodium chloride salts into a solution, thus Hofmann-type polyvinylamine products are typically supplied as a solution with salt present in the end product.

Because the Hofmann reaction takes place in alkali the reaction competes with alkaline hydrolysis of amide groups in the polyacrylamide. Therefore, the reaction is typically performed either at a very low temperature or very rapidly at a higher temperature. In practice some hydrolysis always takes place, which means that the end product has some amfoteric nature because of cationic and some anionic groups in the same polymer chain.

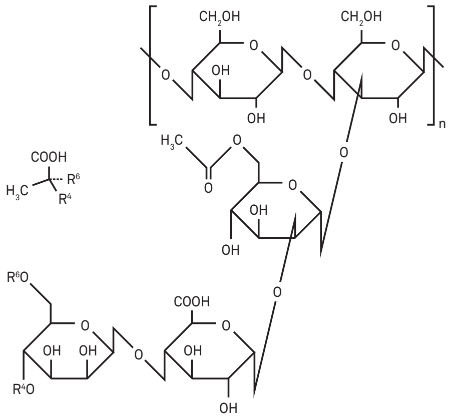
Biopolymer-based flocculants

Natural biopolymers are seldom efficient enough to be used as flocculants. Ones with the highest molecular weight, such as starch and cellulose, are either non-ionic or only very slightly anionically charged. Some natural biopolymers, such as alginate and pectin, have higher anionic charge density but their molecular weight is too low.

Man-made biopolymers with relatively high molecular weight and anionic charge density are available, and a good example is xanthan gum. Xanthan gum is a polysaccharide composed of repeating units of D-glucose, D-mannose, and D-glucuronic acid partially esterified with pyruvic and acetic acids. The structure of xanthan gum is shown in figure 5.87.

Xanthan gum is used in food, cosmetics, and oil industry applications. It also has good potential as an anionic flocculant polymer.

Figure 5.87
Structure of xanthan gum (Source: Wikipedia).



Charge can also be introduced into non-ionic biopolymers by derivatization. A good example of this is the carboxymethylation of cellulose, which produces anionically charged carboxymethylcellulose. Cellulose is naturally a water insoluble polysaccharide, but the anionic charge makes it soluble in water. The structure of carboxymethylcellulose is shown in figure 5.88.

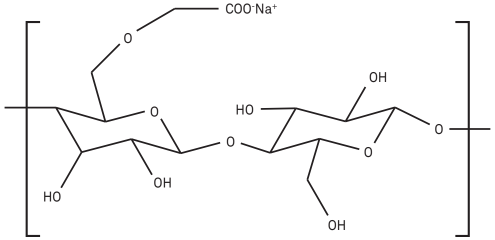
Carboxymethylcelluloses have several industrial applications. The highest molecular weight grades also have good potential as anionic flocculant polymers.

Carboxymethylated starches exist but they are not as efficient as carboxymethycelluloses.

Cationic charge is very rare in natural biopolymers. Some amino group-enriched proteins naturally have net cationic charge at suitable pH.

Figure 5.88

Structure of carboxymethylcellulose.



There are two good methods to utilize natural biopolymers as cationic flocculants: chitosan and derivatization of polysaccharides.

Chitin is a biopolymer found, for example, in the shells of several sea crustaceans such as shrimps, crabs, and lobsters. Chitin is a sidestream of food industry and this makes it an interesting option as a raw material.

Chitin is water insoluble but it can be deacetylated, leaving amino groups in the polymer chain (see figure 5.89).

When the degree of deacetylation (DDA) becomes > 50 % the polymer starts to be called chitosan. Commercial grades typically have a DDA of 75–90%.

The amino groups make chitosan soluble in acidic water and give it a cationic charge. The charge density of chitosan is dependent on the degree of deacetylation and also on pH, because the amino groups are not quaternary. Chitosan has some potential as a cationic flocculant polymer.

Derivatization of polysaccharides is another way to achieve cationic charge in biopolymers.

Starch has been cationized for many years using a well-known reaction with glycidyltrimethylammonium chloride (also called [2,3-epoxypropyl]trimethylammonium chloride) or with (3-chloro-2-hydroxypropyl) trimethylammonium chloride (see figure 5.90).

The amino group in the reagent is of the quaternary type and this makes the cationic charge density independent of pH; instead, it is only dependent on the degree of substitution (DS).

Cationized starches are used mostly in papermaking as a strength aid. For flocculation applications these strength starch grades are typically too weakly cationic, in other words they have too low DS. Cationized starches with higher DS do exist but their molecular weight is typically too low to be efficient cationic flocculant polymers.

Polymer brand names

Kemira's polymer products for water and sludge applications are sold under the following brand names:

- SUPERFLOC
- SEDIFLOC
- KemOpti

Figure 5.89

Diacetylation of chitin to chitosan.

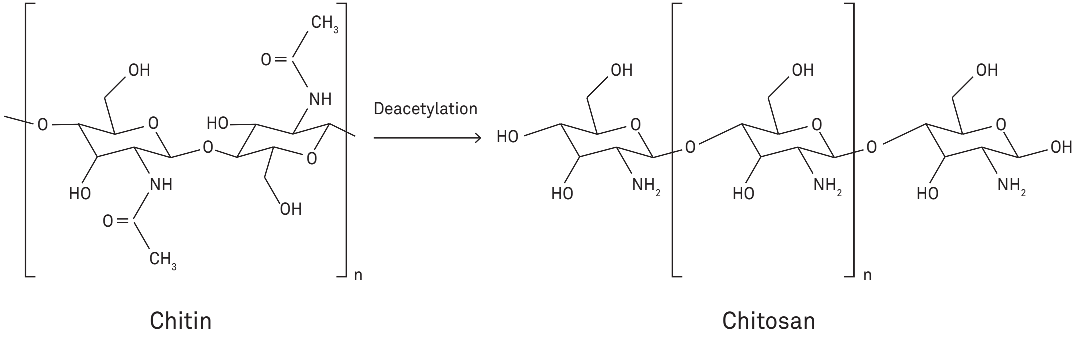
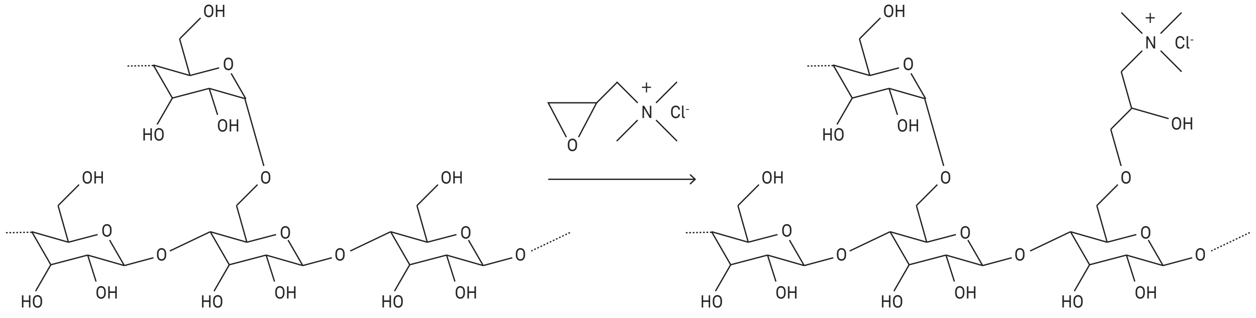


Figure 5.90

Cationization of starch.



CHAPTER 6

RESOURCE EFFICIENCY

Biogas production

Biogas is a result of degradation of organic matter in anaerobic digesters. It consists mainly of methane and carbon dioxide, and is a highly potent energy source. The organic matter (substrate) has many sources, sources including wastewater sludge that is an excellent substrate. In industrial wastewaters, the concentration is sometimes so high that it is possible to produce biogas without further pre-treatment. It is also possible to use other kinds of industrial and household waste streams as substrates. In this section, we will present biogas and the mechanism behind production; we will also highlight how different substrates can be beneficially used for effective biogas production.

Anaerobic digestion can be run at two different temperature levels: mesophilic digestion at 35 to 42°C, and thermophilic digestion at 50 to 57°C. Mesophilic digestion is highly robust against changes in sludge quality and is the most widespread digestion technology. Thermophilic digestion is more sensitive to sludge variations but generates higher biogas yields. In this chapter we refer mainly to mesophilic digestion.

Anaerobic digestion of biomass and anaerobic degradation of industrial wastewater

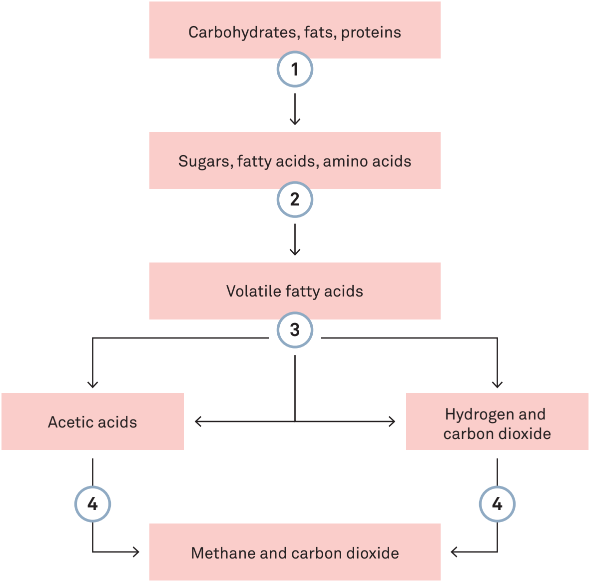
Anaerobic fermentation is a degradation process of organic material by microbial activity in the absence of oxygen, where the microorganisms transform organic substances into biogas, heat, and fertilizer. The anaerobically treated biomass, often referred to as digestate, is normally used as a fertilizer on farmlands. Anaerobically treated wastewater from industries is often distributed to municipal wastewater treatment plants (WWTPs).

Anaerobic degradation, takes place in digesters or reactors. They are designed to handle highly concentrated waste with a high amount of organic matter measured as total solids (TS). Reactors designed for treating wastewater, the amount of organic matter influent is measured as chemical oxygen demand (COD) and biological oxygen demand (BOD).

The production of biogas starts with the hydrolysis of organic material where the solid substances are degraded and dissolved and the liquified compounds are further hydrolyzed. Hydrolysis is followed by two acidification processes: acidogenesis and acetogenesis, where the dissolved organic matter is further processed. The hydrolysis forms short-chain organic compounds. The final step of anaerobic digestion is methanogenesis. It produces methane along with biomass and carbon dioxide as a result of the activity of a special type of microorganism called methanogens, which live in strictly oxygen-free environments. They produce methane from the degradation products of the preceding phases, particularly from acetic acid and hydrogen.

The anaerobic degradation pathways from organic matter to methane and carbon dioxide are illustrated in figure 6.1.

Figure 6.1
Anaerobic degradation pathways from organic matter to methane and carbon dioxide.



Substrates for biogas production

There are three main groups of substrates, also called feedstocks, for producing biogas.

Agricultural substrates:

- Manure from livestock production
- Energy crops
- Agricultural residuals

Non-agricultural substrates:

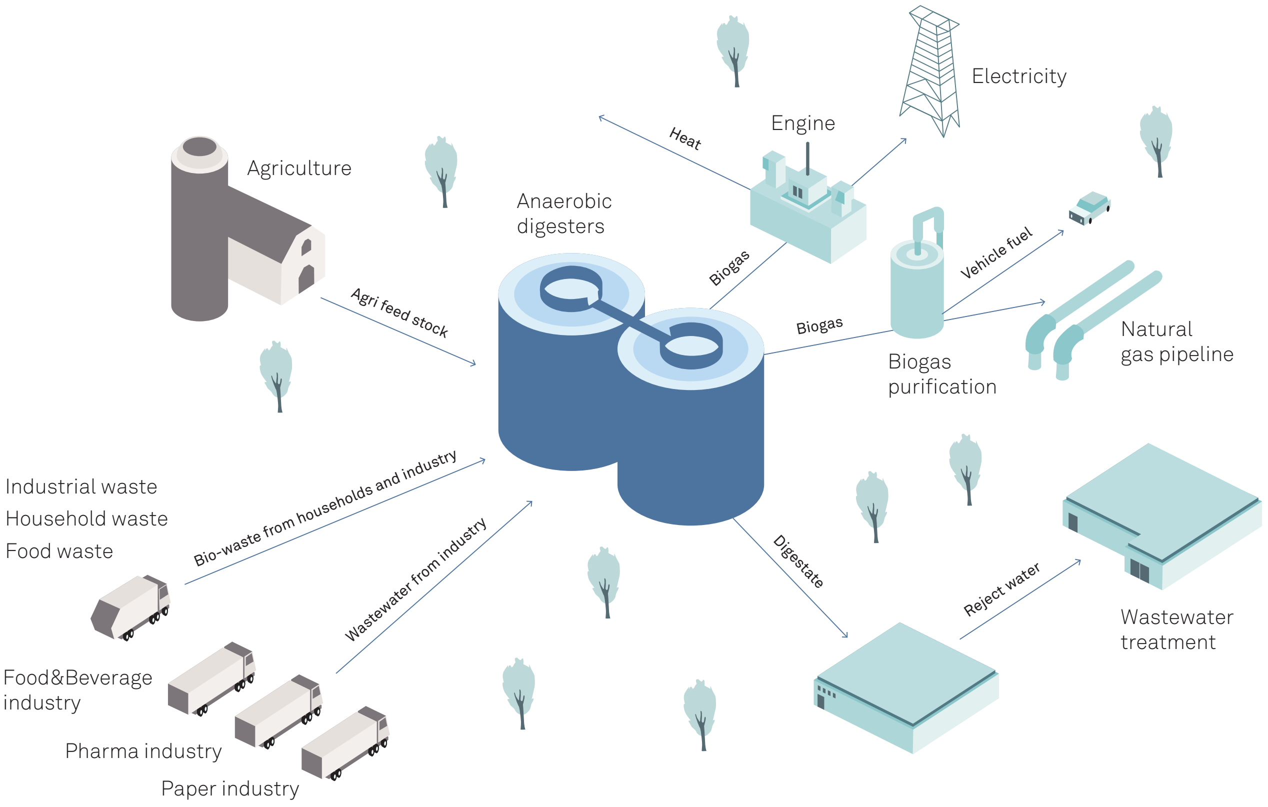
- Biowaste, household waste
- Industrial organic residues from the food industry, restaurants, and slaughterhouses
- Industrial wastewater from pulp and paper production, sugar production, pharmaceutical production, and food and beverage production

Sludge from municipal wastewater treatment

Agricultural and non-agricultural substrates are normally digested in industrial biogas plants, while wastewater sludge is typically digested at WWTPs.

In most industrial cases, different substrates are mixed in biogas plants except when treating wastewater. Biogas plants with mixed substrates practice co-digestion or co-fermentation (see figure 6.2). Most co-digestion plants use a mix of agricultural substrates, but in some countries there are plants that use non-agricultural substrates such as household waste and waste from the food industry.

Figure 6.2
Schematic picture over a biogas plant showing the utilization of substrates and biogas.



A biogas plant is normally operated with a dry solid (DS) content of 3–15% in the wet substrate. In most cases the DS is degraded by about 50% and the outlet, the digestate from the digester, typically has a DS content of 2–7%. The organic load of the digestate is normally 2–5 kg DS [kg DS / (m^3·d)].

Table 6.3 summarizes the optimal process parameters for the stable process operation of digesters.

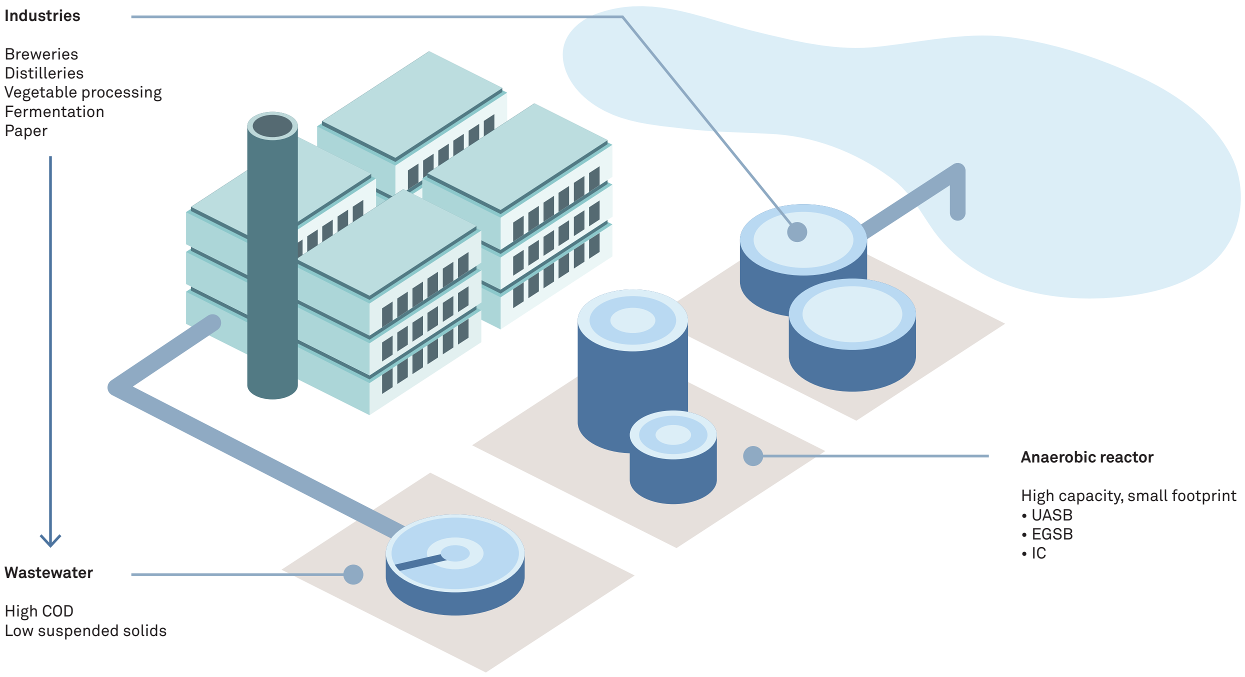
Figure 6.3
Exemplary digester process parameters.

Condition	Optimum	Common operational values for industrial digesters
Dry solids (DS), %		
In	Limited by the digester design	3-15
Out	Limited by the digester design	1.5-7
Total alkalinity (TA) mg/l as HCO_3^-	> 3,000	5,000–20,000
Gas composition	Depends on substrate	
Methane % vol		50-75
Carbon dioxide CO_2 % vol		50-25
Hydraulic retention time (HRT), days		20–80
Organic loading rate (OLR), kg VS/(m^3·d)	> 4	2–4
pH	7.2–7.5	7.2–8.5
Temperature (°C)		
Mesophilic	35–39	
Thermophilic	50–56	
Volatile fatty acids (VFA) mg/l	50–500	2,000–10,000

For wastewater treatment plants in industries such as food, beverage, pharmaceutical, sugar, and pulp and paper, the COD content of wastewater must be greater than 500–1,000 mg COD/l to be suitable for anaerobic treatment. Wastewater is treated in different types of anaerobic reactors such as UASB (Up-flow Anaerobic Sludge Blanket), EGSB (Expanded Granular Sludge Blanket), and IC (Internal Circuit Reactor). The organic loading rate is typically 10–18 kg COD/(m^3·d) depending on the reactor type. The produced biogas is used internally as an energy source for the production facility. These types of wastewaters have a high demand for trace-element supplementation, and the iron demand for hydrogen sulfide (H_2S) removal in these plants is moderate. Figure 6.4 shows examples of substrates in different parts of anaerobic WWTPs.

Figure 6.4

Examples of substrates in different parts of an anaerobic WWTP.



Hydrogen sulfide is formed during the methane production, with the level of production varying according to the type of substrate. Biogas from manure plants can have H_2S levels of up to 2,000–3,000 ppm, while the typical level in biogas from household waste is 600–800 ppm. Iron salts, which are used to remove the toxic H_2S, are dosed into the digester or into the substrate receiving tanks when needed. The amount of iron to reduce H_2S levels varies depending on the substrate. Some substrates need additives like trace elements for maintaining microbial activity.

For energy crops, agricultural residuals, and non-agricultural substrates, there is a need for trace-element supplementation. Too low trace-element contents inhibit the degradation by microbes and cause problems with the organic load and process stability and leads to high volatile fatty acid (VFA) levels in the digester. The result will be an unbalanced microbiological process in the digester and a decreased biogas yield due to low degradation of VFAs and longer fatty acids. VFA levels should not exceed 1,500 mg/l in the digester, then VFAs and longer fatty acids will be converted to methane in the treated digestate and released to the atmosphere, causing a so-called methane slip. This reduces the overall efficiency and profitability of the plant, and additionally causes an environmental issue since methane is a highly potent greenhouse gas.

Biogas yield can vary a lot depending on the energy content of the substrate. Typically, manure from pig farming has a biogas yield of 200 m^3 methane per ton of volatile solids (VS), whereas a substrate from food waste has a yield of 660 m^3 methane per ton of VS.

Process chemicals in biogas production systems

Iron as a macro-nutrient
Iron is the key component in anaerobic digestion, involved in all bacterial processes.

Different products are used to reduce hydrogen sulfide concentration in biogas production in order to protect plant equipment, gas-handling and gas-upgrading systems from corrosion. In general, if the upgraded biomethane will be used as vehicle fuel, in public gas grids or as a general energy source, hydrogen sulfide levels need to be reduced to below 100 ppm in the gas phase.

Iron-containing products, which are available commercially in liquid and solid forms, are mainly used to control hydrogen sulfide in biogas systems.

Iron reacts with the sulfide ion (S^{2-}) and forms iron sulfide, a solid component that leaves the system along with the digestate. Iron products are added either directly to the digester or before the digester.

Hydrogen sulfide equilibrium

$$H_2S \rightleftharpoons HS^- + H^+ \rightleftharpoons S^{2-} + 2H^+$$

Precipitation with iron

$$Fe^{2+} + S^{2-} \rightarrow FeS_{(s)}$$

Subject to prevailing specific site conditions, Kemira recommends a dosing of approximately 8–10 tons of Kemira BDP (biogas digestion product) per GWh for biogas plants.

Trace elements are micronutrients

The microorganisms in anaerobic digesters utilize enzymes and coenzymes for the degradation of cellulose, starch, proteins, fat, sugars, and fatty acids by the metabolism and convert the intermediate compounds into the main end products: methane and carbon dioxide.

Metals such as Co, Ni, Se, W, and Mo are important components in enzymes, coenzymes, and microbiological cofactors.

The need for trace elements in anaerobic degradation is related to the substrates natural content. Substrates coming from living creatures like municipal wastewater sludge and manure from livestock production generally don not need any additional trace elements as they are already present at sufficient levels. However, if the organic load exceeds 4 [kg VS / ($m^3 \cdot d$)] there will be a need for trace element supplementation to maintain the methane yield and the outcome of the biogas plant.

Substrates coming from energy crops, agricultural residues, industrial organic residues, household waste, biowaste, and industrial wastewater are normally very low in trace elements so these need to be added during anaerobic degradation to ensure that the microorganisms can transfer carbohydrates, protein, and fat to biogas.

Minerals as nitrogen and phosphorous

Minerals such as nitrogen and phosphorous do not need to be added in biogas production because all types of substrates contain sufficient amounts. The exception to this rule is industrial wastewater treatment plants because the untreated wastewater normally lacks both minerals, meaning they need to be added to the anaerobic reactors.

Nutrients are important in the digestate because they act like fertilizers when the digestate is spread on farmland.

Chemistry supporting the anaerobic process

As mentioned above, chemistry is needed to ensure that a biogas plant can operate properly. Kemira's BDP portfolio includes pure iron products specifically for biogas plants and industrial anaerobic wastewater treatment plants. The portfolio also includes special iron salts containing trace elements of different types and concentrations. BDP product selection is based on the substrate, the design and load of the anaerobic digestion process in question.

Iron products are added to reduce the amount of hydrogen sulfide in the produced biogas, thereby protecting devices and equipment from corrosion, and to provide biogas that is suitable for gas engines, gas grids, and for use as vehicle fuel.

BDP products containing trace elements are used to increase biogas production and yield. The organic loading rate can be increased and the VFA levels in the digester reduced; these products also help to reduce foaming problems. Improved reduction of VFA and longer fatty acids means that more acids are converted to methane and carbon dioxide. Methane slip is also reduced and the negative impact on the environment is mitigated.

In general, the addition of BDP products increases plant capacity with no additional need for infrastructure investments, improving the economic performance of the plant in terms of increased biogas yield and biogas production.

A typical dosing level for Kemira BDP products is 8–10 tonnne/GWh. In the degradation pathways shown in figure 6.1, iron is a macronutrient and the key component in anaerobic digestion. Iron is involved in all microbial metabolic processes , see figure 6.1 (1-4). It precipitates sulfide (S^{2-}) and inhibits the toxic effect of hydrogen sulfide.

The composition of the organic matter has a significant influence on the formation of biogas and the amount of methane.

Micronutrients or trace elements like cobalt, nickel, zinc, iron, selenium, molybdenum, and tungsten play an essential role as components in the enzymatically catalyzed methane formation, see figure 6.1.

Biogas utilization

There are currently three ways to use biogas efficiently:

- Energy source in a combined heat and power plant (CHP)
- Feed into the natural gas grid
- Vehicle fuel

In all cases, the raw biogas must undergo a cleaning step before application. At the biogas plant a certain amount of hydrogen sulfide is removed. For use in gas grids or as vehicle fuel, the biogas must be upgraded in a gas-upgrading unit where it is dried and cleaned from carbon dioxide, hydrogen sulfide and ammonia.

Upgraded biogas for use in public gas grids or vehicle fuel systems it must have a methane content of at least 98%.

Typically, a pre-cleaning step of the biogas is done at the biogas plant. The gas that enters an upgrading unit must have hydrogen sulfide levels below 100 ppm. The final polishing is done in the upgrading unit. Upgrading units are almost always owned and operated by energy production companies.

Biogas from municipal wastewater treatment plants

The two main products of wastewater treatment are clean water, which is released to the water supply network, lakes, rivers, or the sea; and sludge, which contains pollutants in a concentrated form and must be disposed of. Sludge disposal is costly – each person generates approximately 50 kg of solids for disposal every year [kg/(p·a)]. Anaerobic digestion can decrease this volume by up to 25 kg per year and thus decrease the cost of disposal; the produced biogas is also a valuable source of sustainable bioenergy.

The main commercial drivers for anaerobic digestion is waste volume reduction, sludge stabilization and production of sustainable biogas. Sludge is degraded to a much larger extent than raw sludge and is less sensitive to further degradation. It is stabilized and smells less than raw sludge, releases much less methane, and contains considerably less pathogens. This makes it much easier and safer to handle than raw sludge.

Most larger WWTPs in Europe (> 100,000 PE) use anaerobic digestion.

Biogas yield and volume reduction can be further improved if the non-degradable organic matter is activated by thermal methods, e.g. by thermal hydrolysis. This method is applied at some WWTPs in order to hydrolyze the organic part of the sludge and increase the biogas yield. Hydrolysis temperatures are normally between 150 and 220°C, which makes this method energy intensive. Depending on the local situation, the increased energy yield must be calculated against the consumed energy for the hydrolysis.

WWTPs that apply anaerobic digestion and utilize the gas improve the energy balance and in the best case may become self-sufficient in terms of energy.

The average amount of biogas produced is 17 cubic meters per person per year [$m^3/(p \cdot a)$]. The biogas has a methane content of approximately 60% or 10 $m^3/(p \cdot a)$. One cubic meter of methane has an energy content of approximately 10 kWh, which roughly corresponds to the energy content of one liter of gasoline.

A WWTP produces approximately 100 kWh of energy from biogas per person per year. In a combined heat and power plant this energy can be transformed into 60 kWh/(p·a) of heat power and 25 kWh/(p·a) of electrical power.

Industrial biogas production

Degradation of organic waste

Many municipalities and biogas companies have installed separate biogas facilities for energy generation and reduction of organic waste. Organic waste can originate from households, restaurants, slaughterhouses, or food processing industries. The target is to save costs by reducing the load of organic waste sent to incineration and to produce valuable biogas for use in private and public transport vehicles and as a general energy source for the public gas grid. These biogas facilities are often connected to filling stations where vehicles can be fueled with the upgraded biogas.

Cost structure – industrial biogas

Comparing biogas plants is difficult since they vary in many respects, including size, location, and type of substrate. Quite often communities run biogas plants that treat household waste, but the plant is still owned and operated as a private company. This makes it almost impossible to get any investment costs, operating costs, or income figures relating to the sale of biogas from specific companies.

The main source of revenue for a biogas plant is the sale of biogas to an energy company that makes an upgrade for utilization in a gas grid or as vehicle fuel. The gas can also be used at the biogas plant for heat and power generation.

The development of biogas industry revenues in individual countries depends on the national subsidy system. In many countries, the subsidies form the legal frame to support investments in plants and to favor the beneficial utilization of renewable energies.

Phosphorus recovery

Introduction

Phosphorus (P) is an essential substance for all life. It is used in many applications, the most important of which is fertilizer. It is one of the most important nutrients for agriculture and food growing. Kemira was established in 1920 as a state-owned fertilizer company to support agricultural production in Finland.

Phosphorus is a limited resource that is unevenly distributed around the globe with a few countries having phosphate mineral deposits. Only one phosphate mine exists in the EU and its capacity is less than 10% of EU demand, meaning that EU is highly dependent on imports. At the same time, a lot of the phosphorus in circulation is lost. Phosphate is released from agricultural fields, wastewater is not treated properly, and when phosphorus is captured from wastewater it is often not recycled.

The best phosphorus recycling options are manure from animal farms (80%) and phosphorus from wastewater (20%). Manure is already recirculated to a great extent, so more focus is needed on recovery from wastewater. To recycle a high percentage of phosphorus from wastewater, it is essential that as much as possible is captured. The best results are achieved through chemical precipitation, as described in chapter 3.

Phosphorus can be recovered from different streams and matrices at municipal WWTPs: from the water phase, directly from wastewater or reject water, from sludge when phosphorus is extracted, by using sludge as it is, or from sewage sludge ash. Figure 6.5 shows the steps at a municipal WWTP where phosphorus can be recovered.

1. Phosphorus precipitation from wastewater effluent
    - Phosphorus can be precipitated at the end of the WWTP processes after all the other impurities have been removed by iron, aluminum or calcium
    - The treated water that contains some phosphorus could be brought back to agriculture as a fertilizer
2. Phosphorus separation from digested sludge before dewatering
    - If iron is used in the wastewater process for phosphorus removal, vivianite $Fe_3(PO_4)_2.8H_2O$ is formed in the anaerobic digestion and can be separated using magnets

- If the WWTP has a Bio-P process, phosphate is released in the anaerobic digestion and can be precipitated and separated as struvite $MgNH_4PO_4.6H_2O$ after the digestion

3. Phosphorus precipitation from reject water

   If the WWTP has a Bio-P process, phosphate is released in the anaerobic digestion and can be precipitated and separated as struvite $MgNH_4PO_4.6H_2O$ after the digestion

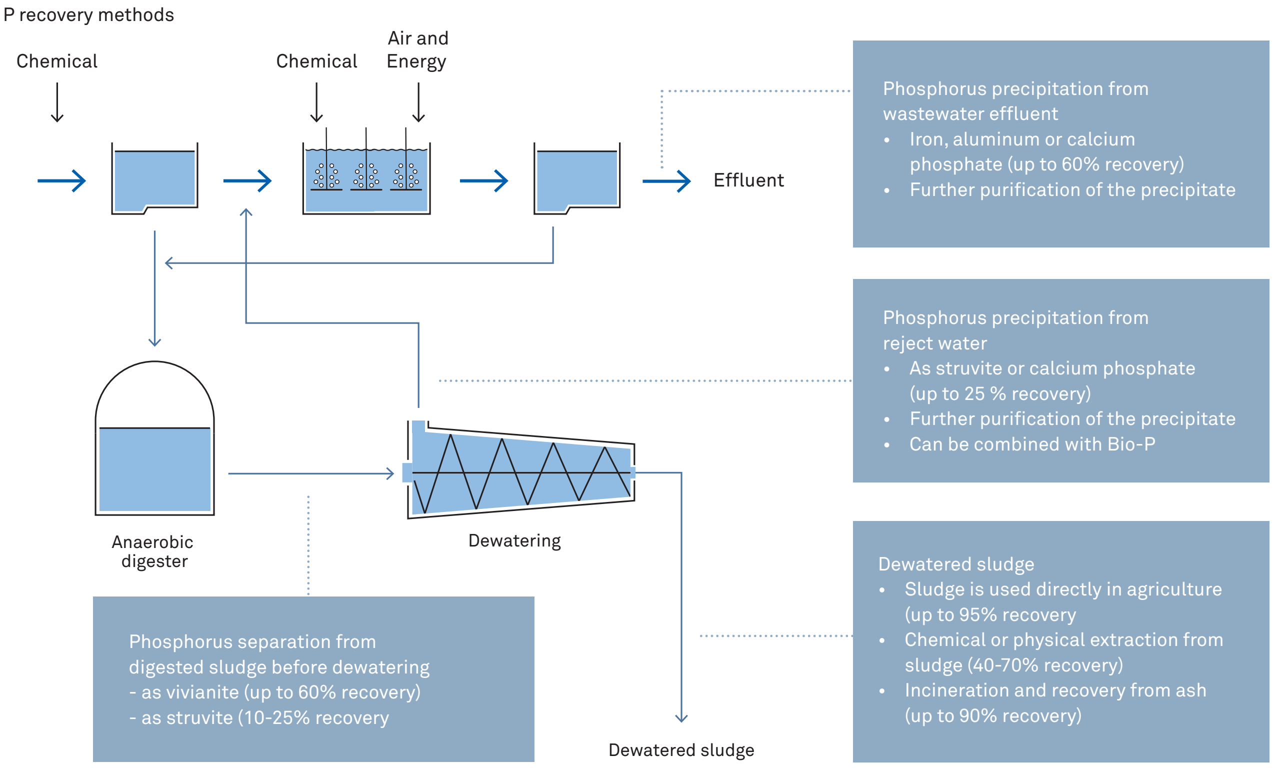
4. Dewatered sludge

   Sludge contains all the phosphorus that is captured from the wastewater. Several options are possible:

   - Sludge is used as such in agriculture
   - Phosphorus is chemically or physically extracted from sludge
   - Sludge is incinerated and phosphorus extracted from the resulting ash

Figure 6.5

Steps where phosphorus can be extracted in a municipal WWTP. Phosphorus recovery rates calculated from the influent phosphorus.



Phosphorus precipitation from wastewater effluent

- Iron, aluminum or calcium phosphate (up to 60% recovery)
- Further purification of the precipitate

Phosphorus precipitation from reject water

- As struvite or calcium phosphate (up to 25 % recovery)
- Further purification of the precipitate
- Can be combined with Bio-P

Phosphorus separation from digested sludge before dewatering
- as vivianite (up to 60% recovery)
- as struvite (10-25% recovery

Dewatered sludge

- Sludge is used directly in agriculture (up to 95% recovery
- Chemical or physical extraction from sludge (40-70% recovery)
- Incineration and recovery from ash (up to 90% recovery)

P recovery from sludge and ash

Sludge to agriculture

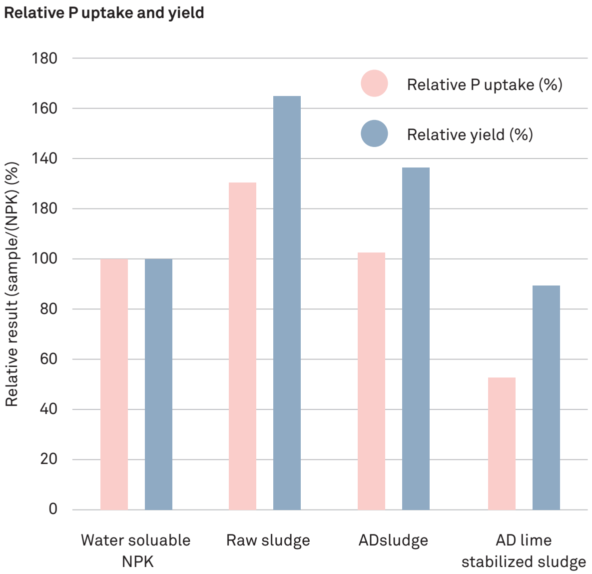
The easiest and most cost-efficient way for phosphorus recovery and recycling is the application of sludge directly on agricultural land. The more phosphorus is removed from wastewater, the lower its final concentration and the more is recovered in the sludge. When sludge is safe and clean, it is an excellent fertilizer and soil conditioner. In addition to phosphorus, the organic matter in sludge is valuable for microbial activity in the soil and in returning carbon to the soil; even small amounts of carbon have been proven to improve the phosphorus uptake by plants (Ref. 1). Sludge also contains some valuable nitrogen.

Figure 6.6 shows the agronomic value of sludge treated in different ways from a representative wastewater treatment plant using iron sulfate coagulant for phosphorus removal. The plant has a conventional activated sludge process with primary and simultaneous precipitation, and removes phosphorus in the effluent to a level of 0.3 mg/l.

In this study, Italian ryegrass was used and the phosphorus dose was kept constant. An excess of nitrogen and potassium was supplied to ensure they were not limiting growth. Phosphorus was more available to the plants in sludge than in water-soluble NPK. Phosphorus was no longer available for plants when sludge was treated with lime at 80 kg/t. (Ref. 1)

The impact of chemically precipitated sewage sludge on plant yield and agricultural land has been studied in a 30-year research project in Sweden. The study showed that using sludge had only a positive impact on yield, which increased by 16% when sludge was used in the fields without mineral fertilizers. A combination

Figure 6.6
Relative phosphorus uptake and yield of sludge treated in different ways, compared to water-soluble NPK. AD=anaerobic digestion. (Ref. 1)

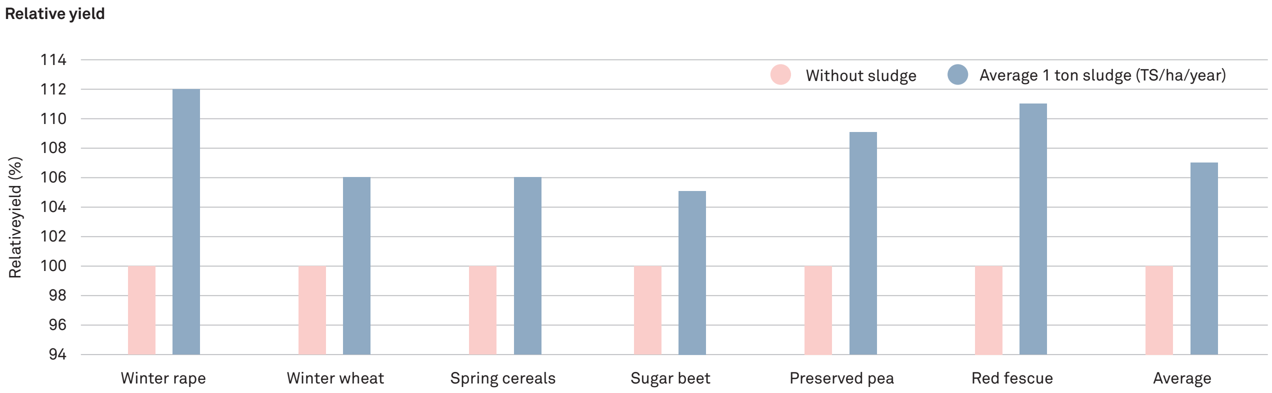


Ref. 1 Kahiluoto, H.; Kuisma, M.; Ketoja, E.; Salo, T.; Heikkinen, J., Phosphorus in manure and sewage sludge more recyclable than in soluble inorganic fertilizer. Environmental Science & Technology, 2015, 49(4), 2115-2122. DOI: 10.1021/es503387y

of sludge and mineral fertilizer resulted in a 7% increase compared with using mineral fertilizer alone (figure 6.7). (Ref. 2)

Figure 6.7

Relative yield when sludge was used in fertilization. "Without sludge" is an average when different application rates of mineral fertilizers were used. "Average 1 ton sludge" is an average when the same application rates of mineral fertilizers were used as for "Without sludge", but in addition 1 ton of sludge was used. (Ref. 2)



Ref. 2 Andersson P-G, Slamspridning på åkermark. Hushållningssällskapens rapportserie 2012, ISBN 91-88668-74-6

The nutrient value of phosphorus cannot be evaluated solely by analysing soluble phosphate in laboratory conditions. The commonly used chemical extraction methods (e.g. extraction by water, neutral ammonium citrate, sodium hydroxide, hydrogen chloride or Olsen-P method) do not reveal the sample's bioavailable phosphorus. The solubility of phosphorus in laboratory conditions has very little to do with the bioavailability of phosphorus in field conditions. Thus, the sample's bioavailable phosphorus must always be measured in real field or soil conditions.

Recovery of vivianite

ViviMag technology recovers phosphorus from digested sludge. The name of the technology is a combination of vivianite and magnetic separation – both of which are needed to separate phosphorus in this process. The recovered phosphorus is in the form of iron (II) phosphate, a mineral called vivianite with the formula $Fe_3(PO_4)_2 \cdot 8H_2O$. Vivianite is paramagnetic and can be separated from the digested sludge before dewatering by magnets similar to those used in the mining industry.

The separated vivianite can be further processed to produce fertilizer salts and iron coagulants (figure 6.8).

Vivianite is formed in the wastewater treatment process when iron coagulant is used for phosphorus removal. In anaerobic conditions when there is enough iron present, 70–90% of the total phosphorus is bound in vivianite (figure 6.9). (Ref. 3)

If the iron content in sludge is too low to support a high yield of vivianite, more iron can be dosed in the treatment process or to the digester as shown in figure 6.10. Increasing the iron content increases the share of phosphorus bound to vivianite. When more iron is dosed to the wastewater treatment process, it has an additional positive impact as it further reduces the phosphorus content in the effluent. A higher iron content in sludge also improves the biogas process by significantly reducing the hydrogen sulfide content. (Ref. 4)

It is possible to reach phosphorus recovery rates of around 60% of the influent phosphorus. A vivianite recovery rate of 80–85% from digested sludge is achievable in a full-scale process; recovered vivianite concentrate has been shown to contain up to 70% of vivianite in pilot-scale tests. Assuming vivianite is pure, it correlates to a phosphorus content of 8–9%. (Ref. 6)

The ViviMag process lowers the operating costs of wastewater treatment plants by reducing the amount of sludge produced by 10–20%.

Figure 6.8
The ViviMag process and optional further treatment process. Modified from Ref. 5 https://www.vivimag.nl/technology. (Accessed March 24, 2020)

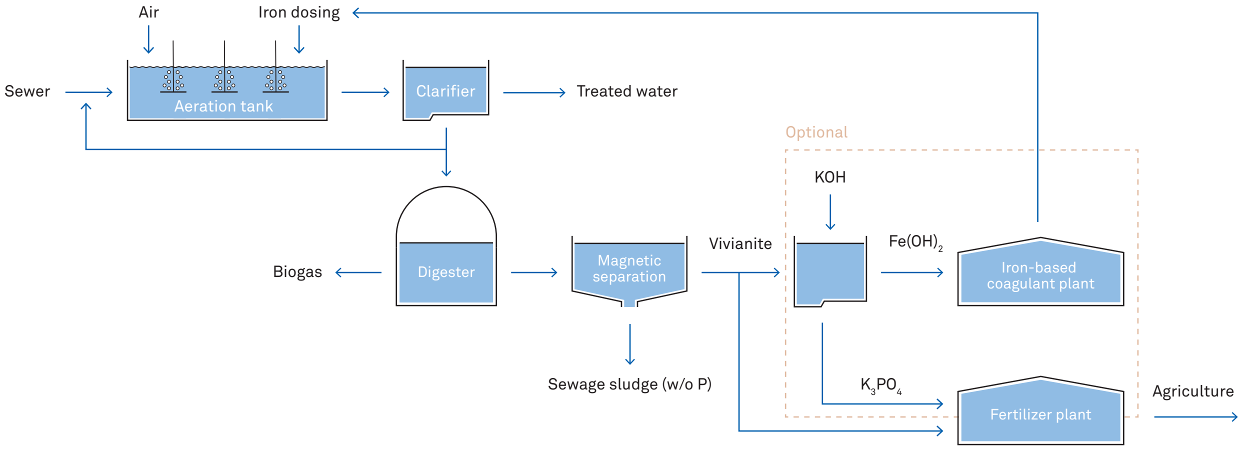


Figure 6.9

Percentage of total phosphorus bound in vivianite in digested sludge. (Ref. 3)

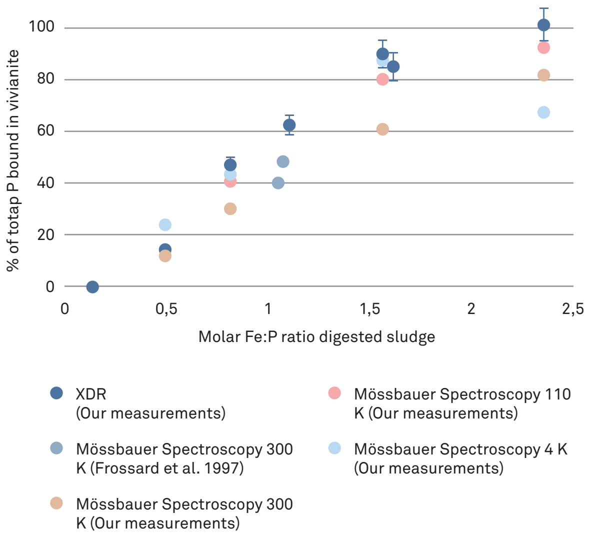
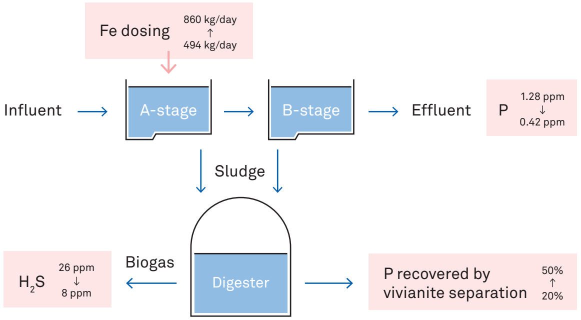


Figure 6.10

Simplified process of Nieuwveer WWTP (400,000 p.e.) and key results when iron dosage was increased. (Ref. 4)



Ref. 3 Wilfert P., Dugulan A.I., Goubitz K., Korving L., Witkamp G.J., Van Loosdrecht M.C.M, Vivianite as the main phosphate mineral in digested sewage sludge and its role for phosphate recovery. Water Research, 2018, 144, 312-321.

Ref. 4 Prot T., Wijdeveld W., Dugulan A.I., Goubitz K., Korving L., Van Loosdrecht M.C.M. Boosting vivianite recovery from digested sludge by increased iron dosage. Poster in IWA Resource Recovery Conference 2019, Venice.

Ref. 6 Wijdeveld W., Sudintas G., Prot T., Korving L., Kuntke P., Rem P., Dugulan I., Van Loosdrecth M. Magnetic recovery of the iron-phosphate mineral vivianite from anaerobically digested sewage sludge. Poster in IWA Leading Edge Conference 2019, Edinburgh

P recovery from ash

When sewage sludge is incinerated, the ash produced has a high phosphate content, with P levels around 10%, making it an attractive option as a fertilizer or fertilizer raw material. The ash also contains aluminum, calcium, and iron that has reacted with the phosphates at high temperatures, and because of this the phosphate becomes much less soluble than if it is precipitated at low temperatures as happens in a WWTP. Therefore, the ash needs to be processed before the phosphate can be utilized as fertilizer. Another concern is the heavy metal content in ash. Although the content can be high, this is not the main limitation on the use of ash as a raw material for fertilizer production.

The fertilizer industry essentially only accepts calcium phosphates as raw materials. This means that most, but not all, of the processes used to upgrade ash produce a calcium phosphate. Below we discuss three different ways of upgrading ash: one that produces calcium phosphate, one phosphoric acid, and one that produces ash with a lower heavy metal content and higher phosphate solubility.

Since many of these technologies are still under development and there are patent applications involved, we will not go into details but will rather discuss the difference between the methods.

There are several advantages to recovering phosphorus from sludge ash. The ash is highly concentrated and hence can be upgraded in a relatively compact industrial process. Another benefit is that all organic material is burnt away. When recovering from ash, there is no risk of contaminants like bacteria or viruses, or potential toxic elements like pharmaceuticals and microplastics; the recovery rate is also normally very high.

The main disadvantage is the cost. To avoid further pollution and the potential dilution of the phosphorus in the sludge ash, the sludge should be mono-incinerated, which means very high investment and operational costs. Even if a mono-incinerator already exists the recovery cost alone is higher than the cost of using mined phosphate in fertilizer production. This is the case with all available phosphorus recovery methods. It is also essential that the sludge is incinerated in the correct way to avoid toxic elements like dioxines forming in the furnace. Finally, sludge also contains nitrogen, that will be lost when the sludge is incinerated. Instead nitrogen needs to be produced in the highly energy-demanding Haber-Bosch process.

Recovery by precipitation

The principle of recovery by precipitation is to dissolve the ash and separate the different components. Dissolving the components typically requires high and/or low pH. If ash is dissolved at low pH, most of the salts are dissolved but not the silicates (sand). The first step would be to dissolve the ash in a strong acid and then separate the insoluble material, which will likely need to be disposed of. The liquid phase now contains dissolved phosphate, calcium, aluminum, iron, and heavy metals. Normally more than 90% of the phosphorus and calcium in the ash is dissolved; while iron and aluminum are dissolved to a lower level, the levels should still be sufficient to enable separation and reuse.

The different components are separated by changing the pH. For instance, aluminum and iron phosphate are very soluble at high pH, but calcium phosphate isn’t. Therefore, it is possible to separate much of the phosphate by precipitating calcium phosphate at high pH. After that aluminum and iron can be separated; iron could also be separated before the phosphate. Heavy metals are also an issue, but these can be precipitated by using sulfide or sulfide-like precipitants as long as iron isn't present.

Precipitation technology makes it possible to separate ions of phosphorus, iron, and aluminum with the by-products being heavy-metal sludge and sand; there will most probably also be residual liquid that is rich in sulfate or chlorides.

It is possible to produce a very pure calcium phosphate with precipitation technology. The quality can be even higher than mined phosphate, for instance with low cadmium and uranium content. The recycled iron and aluminum can be used as raw material for coagulant production but, depending on technology, the quality may vary.

Recovery by ion exchange

With this technology the valuable substances are separated using ion-exchange technology instead of precipitation; however, the initial step is the same – dissolving the ash and separating the sand. Ion-selective ion exchangers are used to separate the valuable substances. When the ion exchanger is saturated it is regenerated. The eluate contains a more concentrated solution of the specific ion that is separated, for instance aluminum chloride.

Using ion exchange instead of precipitation increases the opportunity to produce very clean product. The product might still be quite diluted and an evaporation might be needed to increase the concentration to a commercially viable level.

Recovery by thermal treatment

Instead of separating the phosphorus from the ash, the heavy metal content is reduced by thermal treatment, and the clean ash is used as a product.

The ash is first mixed with a reactant consisting of sodium or magnesium sulfate before being heated to around 1,000°C. Some of the heavy metals like cadmium, uranium, arsenic, and lead will then evaporate at the same time as the phosphate is converted to more soluble salts.

Because the calcined ash still contains iron and aluminum it is not an attractive raw material for the fertilizer industry; however, the phosphate is much more available than in ash and it can therefore be used as phosphorus fertilizer or be blended with nitrogen and potassium salts and converted to an NPK fertilizer.

The advantage with this method is the relatively low investment cost and simplicity of the process. The disadvantages are that the final product cannot be used as a raw material in a standard fertilizer plant and that coagulants aren't recovered.

P recovery from wastewater

An interesting solution is to separate phosphorus from wastewater before it is mixed with more complex matrices (e.g. sludge) or converted to low-availability compounds in the ash. In this case a phosphorus recovery unit is located at the end of the wastewater treatment process, ideally as the last process step before the treated wastewater is released to the recipients. If phosphorus is removed in the final treatment step, phosphorus precipitates of high purity can be obtained. Up to 60% of influent phosphorus can be recovered.

Only dissolved phosphate can be recovered; the higher the concentration, the more phosphorus is available for recovery. The incoming wastewater quality affects the recovery yield. In order to maintain as high concentration of phosphorus in the water phase as possible, minimal amounts of precipitation chemicals should be used before the recovery unit.

As with normal wastewater treatment this technology also normally uses iron and aluminum coagulants for phosphorus removal. The precipitated phosphate is then reused.

The phosphorus recovery process is presented in figure 6.11. In the primary treatment stage the separation of suspended solids and carbon is optimized and the separation of the soluble phosphate is minimized. The chemicals used – for example, organic coagulants and polymers – do not react with soluble phosphate but support solid separation. Secondary treatment can then also be run in conditions that minimize the consumption of soluble phosphates.

In the phosphorus recovery unit, phosphorus precipitation with an iron or aluminum coagulant is optimized and the precipitate is separated from the wastewater. The coagulant can be added just prior to the recovery unit or in the unit itself. Different separation methods can be used, e.g. sedimentation, flotation, centrifugation, filtration, or a combination, and the separated fraction can be further dewatered. The wastewater treatment plant may already have a tertiary settling basin available, meaning the conventional treatment process can easily be converted to a phosphorus recovery unit. P-Optimizer is used in this unit and it ensures the phosphorus level requirement of the effluent is met.

Instead of producing one sludge fraction, two different solid fractions are obtained: organic sludge and recovered phosphates (figure 6.11). The first fraction, organic sludge, is similar to conventional sludge and contains fibers and organic solids. The difference compared with conventional wastewater sludge is that it has a much lower phosphorus content. The second fraction, recovered phosphates, is concentrated in phosphorus and contains low amounts of fibers and organics. One notable advantage of recovered phosphates is that they have much lower levels of toxic metals, micropollutants, and pathogens (table 6.13).

In dry solids, recovered phosphate typically contains:

- 7–9% P
- 30-35% Fe if iron coagulant is used in precipitation
- 18-22% Al if polyaluminum coagulant is used in precipitation
- 3–10% TOC
- <5 mgCd/kgP_2O_5

The recovered phosphates can be used as a fertilizer or as a raw material in fertilizer production, or can undergo further treatment for purification or to separate the elements.

The precipitate can be pelletized or granulated. Figure 6.12 shows an example of granulated NPK fertilizer.

Figure 6.11
Wastewater treatment process with phosphorus recovery unit.

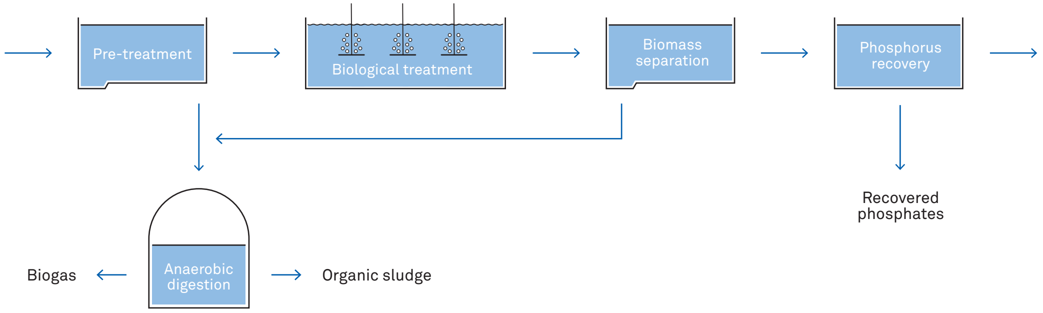


Figure 6.12
Granulated NPK fertilizer. Recovered phosphorus was used as a P-source and iron coagulant was used in phosphorus recovery.

Figure 6.13

Measured properties of recovered phosphates and a comparison to organic fertilizer and inorganic macronutrient fertilizer requirements in adopted fertilizer directive and Sewage Sludge Directive.

	Fe	P	Cd	Cd	As	Cr-tot	Cr VI	Cu	Hg	Ni	Pb	Zn	Organic C
	(% of DS)		mg/kgP_2O_5	(mg/kg of DS)									(% of DS)
FePO4, plant 1	33.0	9.3	0.2	0.05	0.9	22		32	0,2	14	1.0	100	10
FePO4, plant 2	34.5	7.1	<1.8	<0.3	36	13		17	<0.05	62	<0.3	1,100	8.5
AlPO4, plant 3	20.4	8.7	<0.5	<0.1	1.4	3.4		20	<0.1	1.2	<0.1	54	4.7
Inorganic macronutrient fertilizer in adopted fertilizer directive			60		40		2	600	1	100	120	1,500	
Organic fertilizer in adopted fertilizer directive				1.5	40		2		1	50	120		
Sewage Sludge Directive 86/278/EEC				20-40				1,000-1,750	16–25	300-400	750–1,200	2,500–4,000	

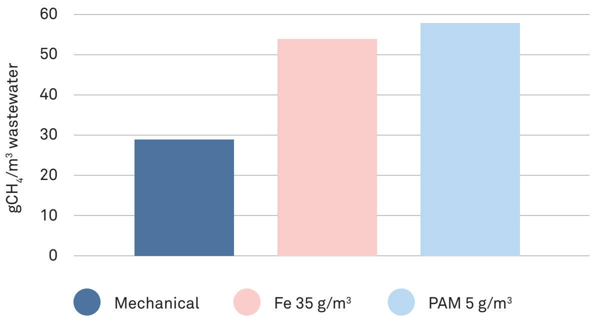
Other advantages of the process are lower sludge volumes, a lower aeration energy requirement, and higher biogas yield. It has been calculated that phosphorus recovery from wastewater reduces sludge volumes by 10–25% and the energy needed in aeration by 7–25%. Depending on the sludge disposal cost, sludge volume reduction can bring remarkable savings for wastewater treatment plants. The estimated increase in biogas production is 20–30%; in lab scale experiments an even higher increase in methane yield was obtained for primary sludge (figure 6.14).

The chemical treatment cost is similar to that of a conventional process and may vary slightly depending on chemical prices. The total operational cost of the wastewater treatment plant varies depending on the sludge disposal cost, conventional and renewable electricity prices, quality of incoming wastewater, and removal requirements.

Phosphorus recovery from wastewater at the end of the conventional wastewater treatment process is a sustainable, cost-efficient alternative: CAPEX and OPEX requirements are kept low and the recovered phosphorus is low in impurities and can be used in fertilizer applications. Moreover, it enables savings in sludge disposal costs and improves the energy efficiency of the wastewater treatment plant.

Figure 6.14

Biogas yield of primary sludge. Mechanical process without any chemicals in primary treatment, Fe in primary treatment, and polyacrylamide (PAM) in primary treatment.



P recovery from reject water

Phosphorous recovery from reject water is a process seen almost solely in municipal wastewater treatment plants that have bio-P and anaerobic digestion, since phosphate is released to a great extent in the anaerobic digesters in these plants. This is highly uncommon in plants that use chemical P recovery since the phosphorus is more strongly bound to the sludge. So this section mainly discusses phosphate precipitation from reject waters at bio-P plants but industrial waters with high phosphate content, especially in the food industry, are also included. In this case the concentration level of phosphate needed is larger than a few hundred mg PO_4-P/l.

Calcium phosphate precipitation

Calcium phosphate exists in many different forms. In nature it is mainly found as apatite – a raw material for the fertilizer industry. Since this industry is by far the largest consumer of phosphorus raw materials it is of course natural that reused phosphorus is recycled here. The fertilizer industry basically only accepts products equal to apatite, therefore calcium phosphate is the most suitable recycled raw material providing that the organic content is low.

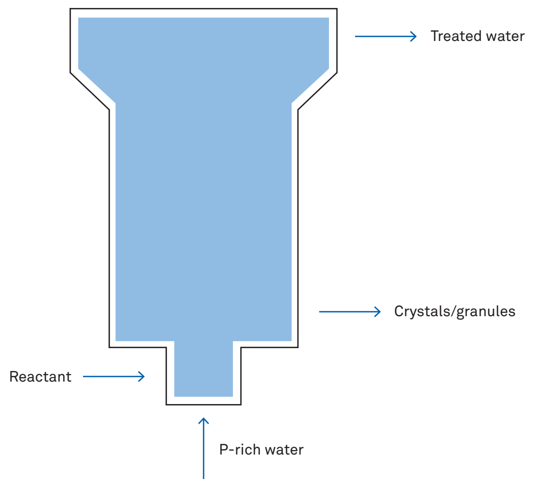
As described in chapter 4, calcium can be used for phosphorus removal but this method is not common due to the high dosage needed to increase the pH of the wastewater so that calcium phosphate can be precipitated. If the water has a high concentration of phosphate the calcium will be utilized much better as more calcium will be utilized for phosphorus precipitation.

The technology normally used to produce calcium phosphate for reuse is a crystallization process. Precipitation occurs in a tubular reactor (see example in figure 6.15) that keeps the precipitate longer than the water, which flows through. This is done by having an up-stream flow that is slower than the settling rate of the precipitate, which remains in the lower end of the reactor. To ensure that the precipitate doesn't leave the reactor with the overflow, the top of the reactor has a larger surface to slow down the vertical speed of the water and increase the settling capacity. The phosphorus-rich water enters the bottom of the reactor where calcium is added in the form of lime.

Since the water to be treated and the reagent is dosed at the entrance of the reactor, precipitation will occur in the existing precipitate concentrated in the lower part of the tank. This means that the precipitate will start to form larger and larger particles. Normally the particles will look like granules and are typically 1–5 mm in size; the final size of the granules will depend on the flow rate in the reactor and how much precipitate is taken out.

With this technology it is possible to produce a product that is easy to handle and, in many cases, has a high purity; however, the purity depends on the raw water quality. If the raw water is free of particles, the purity of the calcium phosphate normally becomes very high.

Figure 6.15
Example crystallization reactor design.



Struvite precipitation

Struvite is a double salt of magnesium ammonium and phosphate with the chemical formula $MgNH_4PO_4$. As mentioned in chapter 4, struvite precipitation sometimes occurs in WWTPs that use bio-P technology since phosphate is released when sludge becomes anaerobic. This causes problems at the WWTP that could be avoided if the phosphate is removed. One way of doing this is to control struvite formation in the plant instead of having uncontrolled precipitation that causes scaling problems. There are two main methods for struvite production, both are linked to the sludge treatment process and both use crystallization technology.

Between 7–25% of the influent phosphorous to the plant can be separated with struvite technology. Since struvite precipitation also removes ammonium, the recirculation of nitrogen is also reduced; however, the reduction is very small with 0.5–2% of influent nitrogen only.

Struvite precipitation after dewatering

In a bio-P plant the phosphate concentration is high after anaerobic digestion. This phosphate will stay in the reject water after dewatering. Now we have relatively clean water that has a high phosphate and ammonium content. The phosphate can either be recycled back to the wastewater treatment process, precipitated as calcium phosphate, or separated as struvite.

Separating struvite from reject water produces the highest end quality, with low carbon content and very low heavy metal content. The granules are normally white and can be used directly as a fertilizer or as a raw material for the fertilizer industry.

Struvite precipitation before dewatering

Struvite can also be precipitated before the sludge dewatering step; a crystallization technology is also used for this process. Since the precipitation occurs in sludge liquor with 2–5% DS, all the remaining particles remain in the reactor and the risk of contamination is greater. Even though most of the struvite precipitates without reacting with the sludge particles, the final product will be more contaminated than if struvite is precipitated after dewatering, especially in terms of carbon content.

Separating struvite from sludge particles in a particle-rich liquid is possible since the sludge particles have a lower density than the struvite precipitate. Therefore, most of the sludge particles will leave the reactor with the overflow and the struvite in the bottom of the reactor. However, the quality isn't as high as the struvite precipitated after dewatering. This is clear when you see the product, which is brownish instead of white in color. Chemical analysis also shows that the carbon content in particular is much higher when struvite is removed before sludge dewatering.

Why then do some WWTPs precipitate struvite before sludge dewatering? The answer is that the dewatering improves if struvite is separated beforehand since the phosphate-rich liquor reduces the efficiency of the polymer in the sludge dewatering. The DS content in dewatered sludge is probably 1–2% lower if the phosphate is kept in the water, and the polymer consumption is also much higher. This is where you see the true benefits of separating struvite before sludge dewatering, since the cost savings for achieving drier sludge are much greater than the value of the struvite produced.

To conclude, if struvite is precipitated after sludge dewatering the product becomes very clean but the dewatering will not work very well. Precipitating struvite before dewatering cuts the cost of dewatering but has a negative impact on the quality of the struvite.

Utilization of struvite

Struvite contains both nitrogen and phosphorus and could therefore be considered an attractive fertilizer. However, it isn't that easy. First of all, the ratio of nitrogen to phosphorus is 1:2 (W/W), whereas fertilizer plants need a ratio of 5:1. So if struvite is used as a fertilizer, farmers will need to supplement with a nitrogen fertilizer.

Another issue is the water solubility of struvite, which isn't as high as in mineral fertilizers where the phosphorus is more directly available. The solubility and plant availability of phosphate is a never-ending story that is linked not only to struvite but also to iron phosphate, which has the same level of solubility as struvite. The phosphate is available even if water solubility is low, even though it might not always be directly available. Therefore, both iron phosphate and struvite can be used as slow-release phosphorus fertilizers, which significantly reduces the risk of phosphorus leakage from fields.

If struvite is used as a raw material in the fertilizer industry the solubility normally disqualifies it as a raw material for conventional fertilizers in the same way as iron phosphate. If the struvite is produced before dewatering the carbon content will also be too high. Since many fertilizers contain nitrogen and ammonia, the carbon content needs to be low otherwise the fertilizer might be explosive.

For these reasons struvite is normally used as a special fertilizer rather than as a raw material for the mineral fertilizer industry.

Nitrogen recovery

From an environmental perspective it is important to recover nitrogen. However, nitrogen is not a limited resource and can be produced from air and natural gas. Even though it is considered a cheap process it accounts for about 5% of the global consumption of natural gas, which corresponds to 2% of global energy consumption.

It is very difficult to precipitate nitrogen salts. Instead, as mentioned in chapter 4, biological methods are used to separate nitrogen, but there are also some chemical-physical ways to separate nitrogen from wastewater.

It is basically these methods that are applied when recovering nitrogen, adsorption, stripping of nitrogen, ion exchange and struvite precipitation. Most of these methods are costly, especially if the nitrogen content is low, as it typically is in normal wastewater. If the water has a higher nitrogen content, as is the case with reject water, and the nitrogen is in the form of ammonium, stripping might be a cost-efficient solution.

There are examples of wastewater treatment plants where ammonium nitrate or sulfate are produced with stripping technologies. The ammonium sulfate is used directly in agriculture as a fertilizer while the ammonium nitrate is used to produce mineral fertilizers.

Life cycle assessment (LCA)

Our daily activities – the food we eat, the newspapers we read, the energy we use, the water we drink, etc. –have an impact on the environment. LCA is a tool used to assess the environmental impacts associated with all stages of a product’s life, from raw material extraction, materials processing and manufacturing to distribution and use. The data from an LCA study provides the information to reduce the environmental impact, for example by reducing raw material or energy consumption during the production. The method is relative, meaning that if you analyze one product or process it needs to be compared with the alternative. A comparison is made between two or more products or processes that give similar performance. For example, a diesel-powered vehicle can be compared with a petrol-powered one.

Examples of environmental impacts included in an LCA are:
- Global warming potential
- Eutrophication potential
- Acidification potential
- Abiotic fossil depletion
- Abiotic elements depletion

LCA can be used in the field of water and wastewater treatment to identify products, processes, and activities that give environmental impacts. The study needs to be done with the same borderlines. For instance, influent wastewater flow and quality and treatment results must be the same.

Simulation – comparison of three different wastewater treatment processes

Since every WWTP is unique in its design and wastewater quality it is difficult to make a true LCA comparison between different treatment processes from different WWTPs. Collecting data from many plants and benchmark the average results from the different process options could reduce the error. This might still be challenging since local conditions are never the same. For instance, two different biological treatment processes might achieve the same treatment results but the aeration might differ in terms of the type of air diffusers and blowing machines used, parameters that impact the LCA result.

Another way to compare different treatment processes is to simulate the different treatment options of the WWTP. Simulation of a WWTP in a dynamic model is an accurate way to compare different treatment processes. It is possible to design the plant and the control strategy, as well as calibrate the plant with real-time data so the simulated models will behave in the same way as a real plant.

In a study, the wastewater profile and data of a larger WWTP has been used. One year of data was modeled with three different processes: pre-precipitation, simultaneous precipitation, and biological phosphorus removal. The target was to achieve equal treatment results on BOD, phosphorus and nitrogen. On phosphorus two different treatment levels, 0.3 and 1.0 mg/l, were evaluated for all process options. All plants had a primary and secondary settling of the same volume, but the activated sludge volumes differ from case to case. All process alternatives used pre-denitrification without any external carbon source. Tertiary treatment with sand filtration was used to reach the stricter phosphorus limit in all three process solutions.

The simulated data was then evaluated in an LCA program. The energy selection has a major impact on the analysis. In this case European average electricity was used. Biogas produced was used for replacement of fossil natural gas. Figure 6.16 shows the result on carbon footprint. Pre-precipitation gives the lowest carbon footprint followed by simultaneous precipitation and bio-P. The pre-treatment saves energy and produce more biogas than the other. The energy consumption was about 20% higher with bio-P compared with pre-precipitation, and biogas production was around 20% higher with pre-precipitation.

In figure 6.16 we can also see that the stricter phosphorus demand increases the carbon footprint. Figure 6.17 shows where the increased carbon footprint originates from. Pre-precipitation with ferric chloride is used as an example.

Figure 6.16

Carbon footprint on 3 different process options with two different treatment levels for the phosphorus. Both the carbon footprint from the process and the benefits of biogas are included in the results.

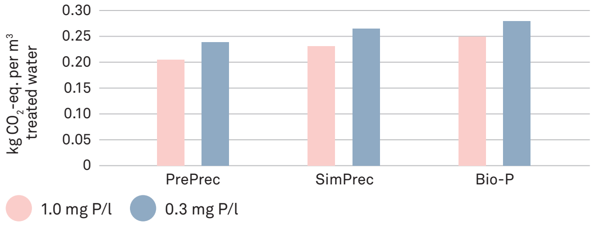
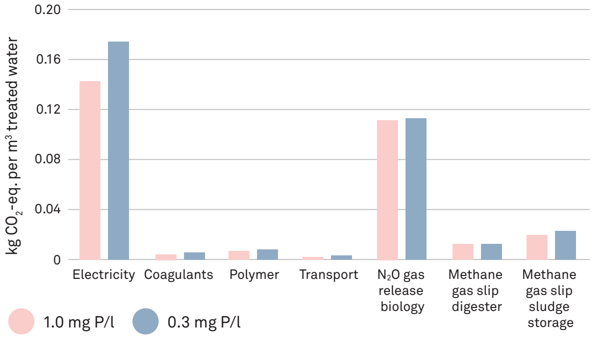


Figure 6.17

Parameters that contribute to the carbon footprint in the pre-precipitation process at two different treatment levels of phosphorus. The benefits of the biogas production is not included.



The largest carbon footprint contributor is the electricity followed by the release of laugh gas (N_2O) from the biological process, methane slip from sludge storage and anaerobic digester. Coagulant and polymer give a very low impact and, surprisingly, transport has the lowest carbon footprint.

With the stricter phosphorus demand, the carbon footprint increases. You might expect that the increase would come from the chemicals but it is the pumping energy needed to run the sand filters that contributes to almost all increase in carbon footprint.

To conclude, energy is a key factor when considering carbon footprint, followed by slip of laughing gas from the activated sludge process and methane slip from anaerobic digestion and sludge storage. Electricity production is the one that is most easy to improve with the right treatment process and the right energy source.

Alternative raw materials for sustainable coagulant production

Coagulation is an essential part of water treatment at nearly all DWTPs and WWTPs. Millions of tonnes of chemicals for water treatment need to be produced every year.

As mentioned in this handbook, there are two main groups of coagulants: iron and aluminum salts. To produce iron-based coagulants, an iron source in combination with either hydrochloric or sulfuric acid is required to dissolve the raw iron. The dissolved iron might then be oxidized using, for example, oxygen or chlorine to produce a trivalent product.

Trivalent iron salts are more efficient in water treatment as their higher valency makes them a more effective coagulant. Raw materials for iron-based coagulants can be ferrous sulfate, scrap metal, or different grades of iron oxides, which in turn can be obtained from rocks such as magnetite, hematite, and ilmenite. An example of the chemical reaction for ferric sulfate is shown in the following equation:

$$2\ FeSO_4 + H_2SO_4 + ½\ O_2 \rightarrow Fe_2(SO_4)_3 + H_2O$$

Aluminum is the most common element in the earth's crust, although much of it is in a complex form in the soil. Bauxite ore is the most commonly used source due to its high aluminum content.

Bauxite, aluminum hydroxides, and pure aluminum ingots in combination with either hydrochloric acid, sulfuric acid, or caustic, are the main raw materials used in the production of aluminum-based coagulants. An example of the chemical reaction for aluminum sulfate coagulants is shown in the following equation.

$$2\ Al(OH)_3 + 3\ H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6\ H_2O$$

Depletion of natural aluminum and iron raw resources together with an increase in raw material prices is driving coagulant manufacturers to seek out alternative raw materials, including recycled materials.

From a sustainability point of view, many raw materials used in coagulants originate from waste or industrial by-products; these are known as Alternative Raw Materials (ARMs) and they result in a lower carbon footprint for both iron and aluminum coagulants.

The two main ARMs used to produce iron salt-based coagulants are ferrous sulfate (also known as copperas) and ferrous chloride (mainly known as pickling acid). Copperas is a by-product coming from the manufacturing of titanium dioxide. Pickling acid is a by-product/wastes in large quantities in the steel industry where acid is used to pickle steel, dissolving the oxide layer of the steel in the acid. Iron salt by-products mainly occur in bivalent form. The acids used for pickling acid and/or the manufacturing of coagulants mainly come as by-product in industrial processes. In some cases, both pickling acid and/or copperas are used to directly treat wastewater.

Waste or by-product aluminum chloride $AlCl_3$ can be found for example from the chemical industry and the silica industry. The material is used as a raw material for polyaluminum chloride (PAX) production. Sodium aluminates and aluminum sulfates from the aluminum industry are also used as ARMs in the coagulant industry.

Kemira is saving hundreds of thousands of tonnes of virgin raw materials every year, making a large contribution to the recycling of by-products/wastes and improving the sustainability of its coagulants.

CHAPTER 7

SMART PROCESS MANAGEMENT

History and prerequisites

Drinking water, wastewater, and process water streams are continuously increasing in volume due to population growth, urbanization, and industrialization. Global warming is no longer refuted; it is now a known fact. Humans are changing the environment faster than the historical cyclic phenomenon of Earth's past. Drought conditions and floods are forcing major populations to move to regions that are less water-scarce and less flood-prone. This makes the accessibility of safe water resources and options for wastewater reuse a top priority. In order to mitigate the spread of diseases in these areas, proper sanitation will be paramount to future survival. Humanity therefore requires more accurate ways to measure and predict water demand versus supply, new methods to keep waste of water to a minimum and to ensure the efficacy of water treatment, and robust approaches to protecting the environment and enforcing regulations.

Around 2011 the concept of a Fourth Industrial Revolution (Industry 4.0) was proposed – a revolution that promotes the computerization of manufacturing processes through the integration of information and communication technology. It is a trend towards a complicated multi-dimensional system that includes knowledge-based automation and data exchange and processes such as cyber-physical systems, the internet of things (IoT), cloud computing, and artificial intelligence (AI). The aim is to enhance the reliability, efficiency, sustainability, seamless integration, and synchronization of all parts of large physical processes. There are a wide range of practical applications for these new systems.

Today, all industries are undergoing major changes with regards to data and how to capitalize on it. Most regulated agencies and industries collect large amounts of process and operational data; the purpose is to implement transformation and improvement via the optimization of processes, driven by real-time data in context. Even more powerful is the potential to create completely new outcomes.

Advances in sensor technologies provide further opportunities for process optimization and compliance monitoring. Field-measurement devices are becoming more accurate and capable of measuring a wide range of phenomena. Nowadays, pollution of all kinds can be

tracked – from as far away as the Earth's orbit down to physical in-vitro robotic sampling at the site of concern.

The water treatment chemical industry and the public utilities as well as private industries it serves share the goal of process optimization and improved overall productivity. The need to implement smart process management can be driven by factors such as budget constraints, new environmental regulations, sustainability, increased occurrence of severe weather events, digitalization, efficiency enhancements, or a desire to increase yields. For instance, some companies are seeking to reduce their energy consumption and increase biogas production. This may be promoted as an environmental or corporate initiative to lower the carbon footprint of an individual utility or entire industry.

Water treatment chemistry plays an essential role in most water treatment processes. Currently, the selection of suitable chemistry is achieved with laboratory and full-scale tests. Although these tests are the most common way of judging the performance of a chemistry, they are merely snapshots in time. Some may think that the characteristics of untreated influent do not change much or often; however, the ability to break down the data and examine a day or an hour's worth reveals that the changes can be dramatic. One easy way to solve issues with changing influent conditions would be to simply increase the chemical dosage as a form of "insurance policy". This is, of course, not the optimal course of action, and treatment-plant operators are a lot wiser today as a result of having access to more and better-quality data about the treatment process. They realize that real-time reaction data reveals a huge amount about the success of a product and the application it has been selected for. Thanks to advances in the interpretation and use of real-time data it is now possible to see how continuous adjustments (even minute ones) can pay off in the form of improved process efficiency and major cost savings. Smart process management allows this optimization to be automated.

Definition

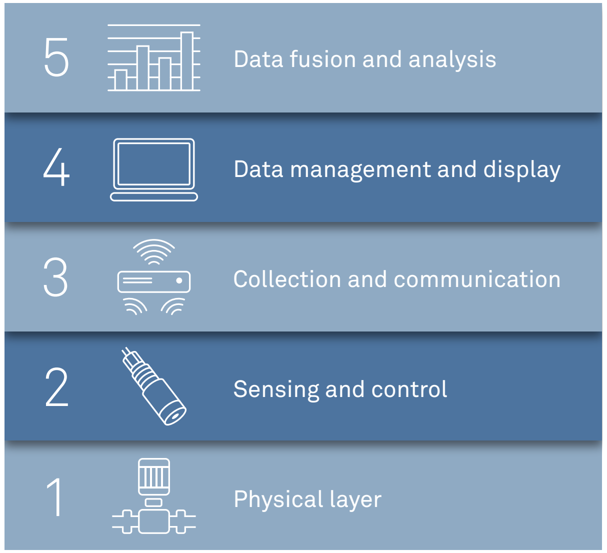


Figure 7.1
SWAN: A layered view of smart water networks (https://www.swan-forum.com/swan-tools/a-layered-view/)

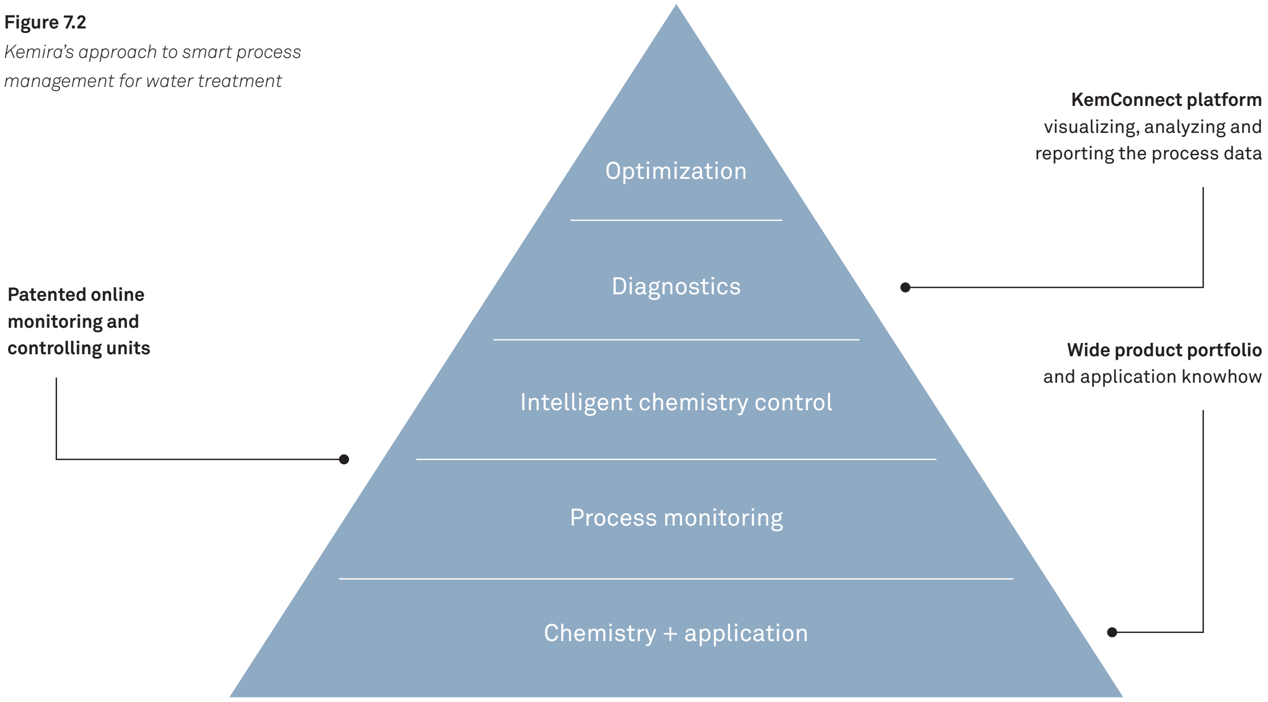
Figure 7.1 depicts a layered view of a smart water network. The physical layer comprises elements such as pipes, pumps, and valves. While this layer does not have data interfaces, it can be controlled using data collected in the next layer: sensing and control. This layer is the interface between data in the higher layers and the physical elements. The sensing and control layer consists of sensors and remote-controlled devices, and it measures parameters and enables remote control of equipment such as chemical feed pumps and flow valves. The collection and communication layer is responsible for discrete data point collection, transmission, and storage, while the data management and display layer is where data from different sources is gathered in repositories and visualizations. The highest layer, data fusion and analysis, derives predictive knowledge from the collected data. The resulting information may be displayed to humans, passed on for further analysis within the layer, or used to trigger automatic actions in the lower layers.

Smart process management in water treatment includes several components: automated dosing pumps (layer 1), accurate instrumentation (layer 2), real-time control loops (layer 2), IoT (layer 3), the data itself (layer 4), cloud-based servers (layer 5), versatile algorithms (layer 5), and data security (layers 2–5). If a contaminant or key performance indicator (KPI) can be measured accurately and a remote-controlled device meets the standards for industrial applications, then smart process management can be applied.

Applications

Kemira has invested in the development of novel and smart ways to optimize its customers' relevant processes without the need to employ additional on-site personnel. These new approaches have led to the evolution of an entirely new business model where chemistry and application expertise is offered through a suite of optimization service applications called KemConnect™. The common factor in all these approaches is a measured value for a treatable contaminant or outcome that is utilized along with the existing flow and the right choice of chemical(s) in order to have the highest impact. These values can be measured both before the control point (feed-forward mode) and after the control point (feedback mode). Each solution can be tailored according to the customer's needs and KPIs.

Figure 7.2
Kemira's approach to smart process management for water treatment



KemConnect uses local programmable logic controllers (PLCs) to run a patented control algorithm that continuously seeks to achieve an optimal condition. Customers that require an extra layer of security may choose to keep their process data private and local, with the option to grant or deny vendors access to the data. For those customers who require remote support, IoT is used to transfer the newly created data to the cloud, where it is monitored and adjusted as necessary. In this case both the vendor and customer have access to the data. Once a service application is deployed at a customer's site a continuous stream of data is created that can be used to generate alarms via SMS or email. The customer can view the treatment optimization on the KemConnect platform in real time via personalized dashboards. These dashboards can also generate predictions for both existing and forecasted operational costs.

KemConnect service applications include, but are not limited to:

- odor and corrosion control
- treatment of stormwater overflow
- chemically enhanced primary treatment
- phosphorus treatment
- COD and suspended solids removal in secondary or tertiary treatment,
- enhanced sludge dewatering, and
- wastewater disinfection.

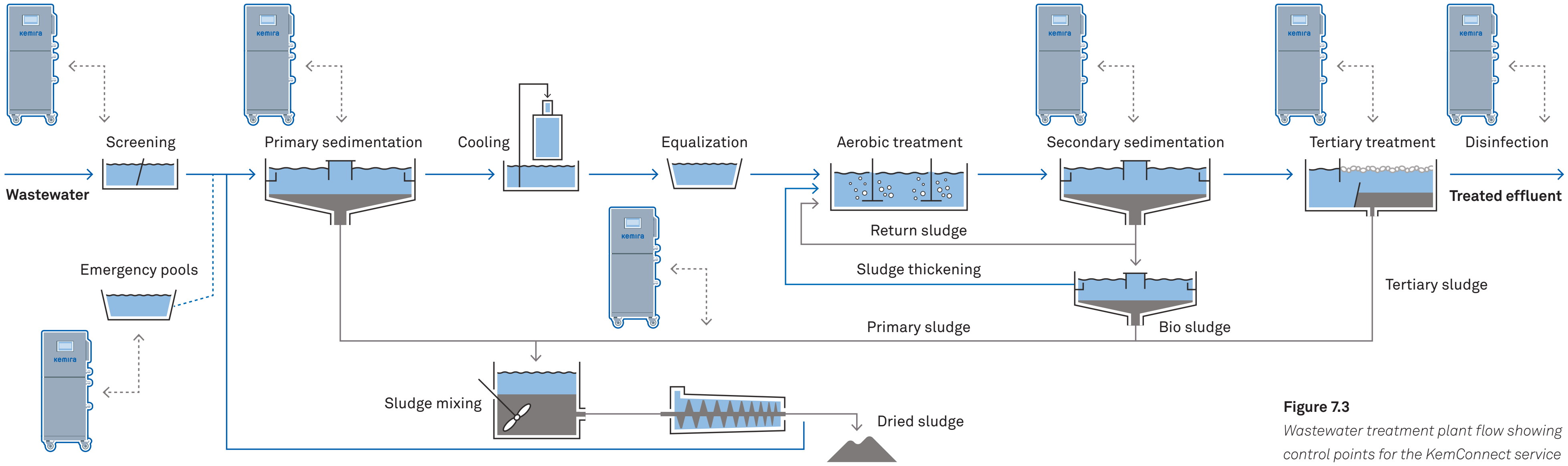


Figure 7.3
Wastewater treatment plant flow showing control points for the KemConnect service

The value that these services create and their requirements will vary from customer to customer and from industry to industry. In some cases, the value comes from OPEX savings and the possibility to delay additional CAPEX investments; in other cases the value can be in the form of increased yields. Both examples require unique solutions and tools that allow improvements over standard treatment conditions to be measured.

Odor and corrosion control

One of the first KemConnect applications was odor and corrosion control, where an algorithm was created to dose iron coagulants based on real-time dissolved sulfide and flow data. This process was designed to replace manual dissolved sulfide testing in the field. Treatment data is collected in real-time to qualify the treatment and then automatically uploaded to a customer dashboard for value quantification. KemConnect applications also utilize gas-phase sensors to control the H_2S in the sewer system.

Treatment of stormwater overflow

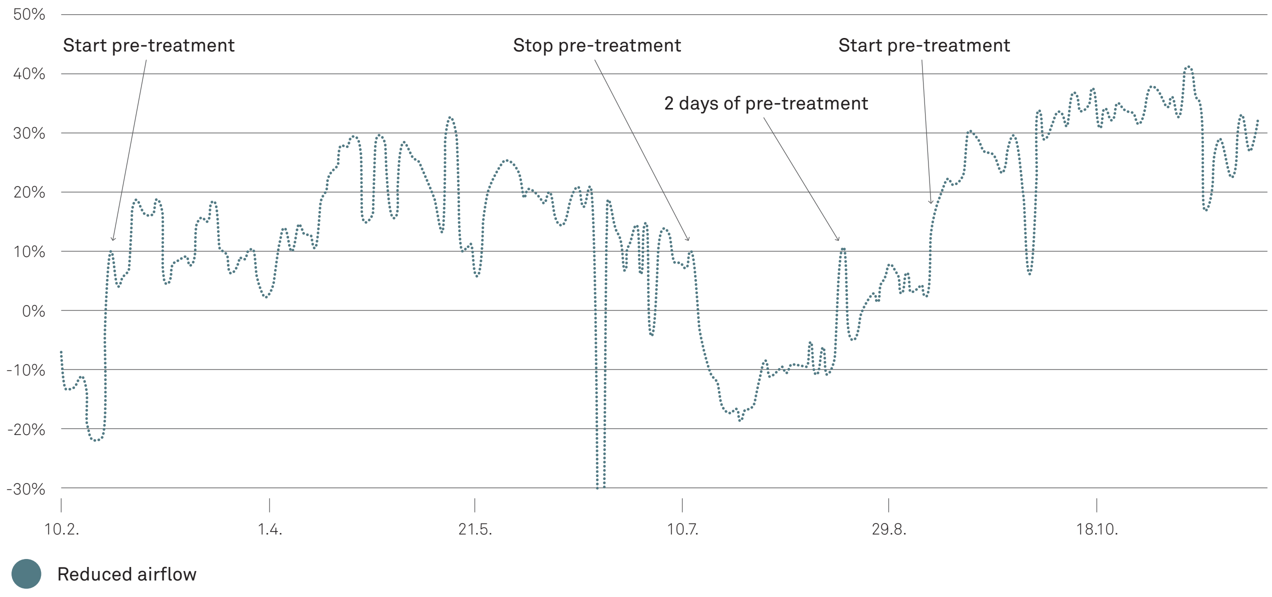
Wastewater treatment plants must be able to handle the higher hydraulic capacities and retention needed for proper treatment of excess storm flows. In the service application for storm water overflows, the surface overflow rate (SOR) along with the proper settling velocity for flocs are utilized to maintain stormwater effluent treatment requirements for total suspended solids (TSS) and particulate biological oxygen demand (BOD). Influent storm water flows, coagulant dosage rates, polymer dosage rates, untreated and treated TSS are measured and the data fed into a developed algorithm that computes the optimal dosages for the desired outcome based on the extreme conditions. The system is designed to handle the SOR with the right chemistries and settling velocities. Performance is mostly influenced by reaction time and the results of the settled effluent, utilizing feedback configuration parameters. The system is designed to provide the maximum treatment for a set time period, which could be days, weeks, or even months depending on weather patterns and seasons. Depending on the hydraulic capacity of the treatment plant, this technology can maximize the operational efficiency during extreme conditions. It can also limit or prolong the need for major plant expansion.

Chemically enhanced primary treatment

The main objective of the KemConnect offering for primary wastewater treatment is to settle just enough primary solids to alleviate most of the burden on the aeration process, hence lowering the energy required for aeration. The other objective is to increase biogas production by increasing the amount of more easily biodegradable sludge sent from the primary treatment step to the digestors as opposed to secondary sludge, which is much harder for the bacteria to digest. The system requires both feed-forward and feedback configuration parameters and includes the measurement of flow, turbidity, and suspended solids in the influent wastewater, as well as the measurement of ammonium, phosphate, COD, and nitrate and oxidation reduction potential in the nitrification/denitrification process. Feedback input loops from aeration energy and biogas production are also included. The optimal chemical dosage for the desired outcome is calculated based on the existing conditions. The system is designed to maximize the energy savings and energy production of a wastewater treatment plant and to maintain a consistent level of treatment within a minimum and maximum range. The application of such a system can limit or prolong the need for major plant expansion while addressing sustainability goals at the same time. Figure 7.4 shows the positive impact that primary chemical dosing has on aeration energy consumption.

Figure 7.4
Positive values indicate that little to no aeration energy is required when primary treatment is applied. Negative values indicate that aeration energy is required for the biological phosphorus removal process without primary treatment.

REDUCED AIRFLOW IN % VS. REFERENCE LINE



Phosphorus treatment

There are certain effluent permit limits for total phosphorous level. For wastewater treatment plants it is important to maintain a consistent low level of total phosphorus in order to meet the permit criteria; some plants have a total annual cumulative permit while others may have a daily limit. The phosphorus optimizer developed by Kemira includes measurements of influent wastewater flow, ortho and total phosphorus levels in the untreated and treated wastewater, and coagulant dosage rates. The algorithms use both feed-forward and feedback dynamic inputs to control chemical dosing and achieve the desired outcome. The system allows for flexibility in terms of treatment time and subsequent operating cost budgets. Where biological phosphorus removal processes fail to meet the lower limits required, a simple chemical tertiary application can be used to maintain reliable results. Figure 7.5 shows the impact of an automatically optimized dosing system for phosphorus control.

Wastewater disinfection

Today, some customers still struggle to meet the requirements of government directives and country-level wastewater effluent standards. In particular, there is growing concern over the increased levels of total coliforms, in particular E. coli, found in bathing waters throughout Europe. This has led to multiple beach closures, impacting the tourism industry. In response to these challenges, Kemira has developed an alternative wastewater disinfection solution that generates no by-products, eliminating the risk of harm to aquatic ecosystems. The system automatically optimizes the dosage level and allows for very quick reaction times, ensuring effluent permit compliance. The same system can be used to quickly ramp up dosing when there is sewer overflow caused by storm-surge conditions.

KEMCONNECT DOSING POINT

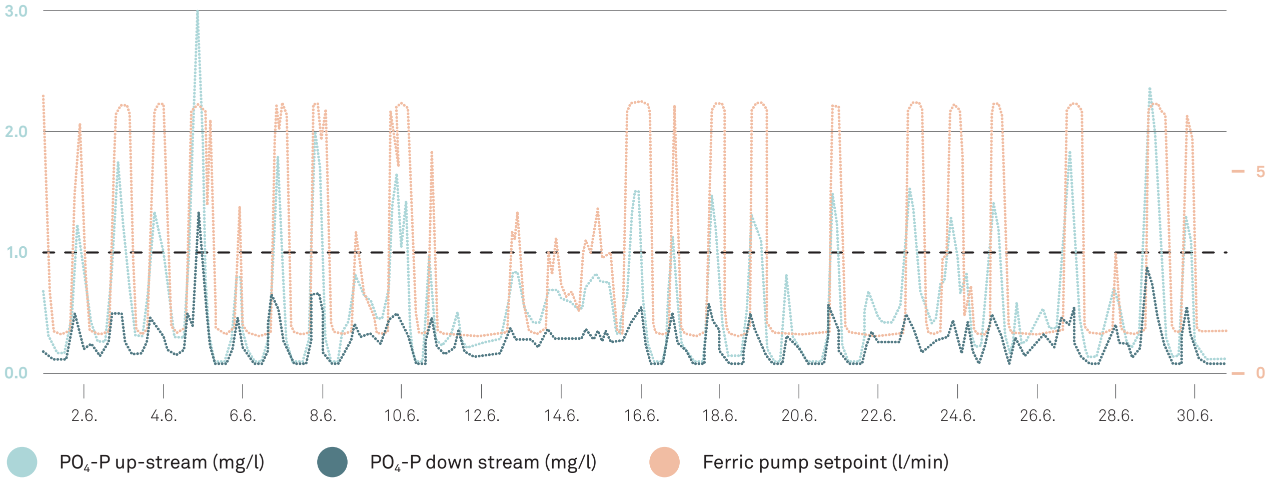


Figure 7.5
PO_4-P up-stream is the raw untreated ortho-phosphate level in the wastewater and PO_4-P down stream is the treated ortho-phosphate level in the effluent. The ferric pump setpoint shows the dosage rate of iron chemistry.

COD removal

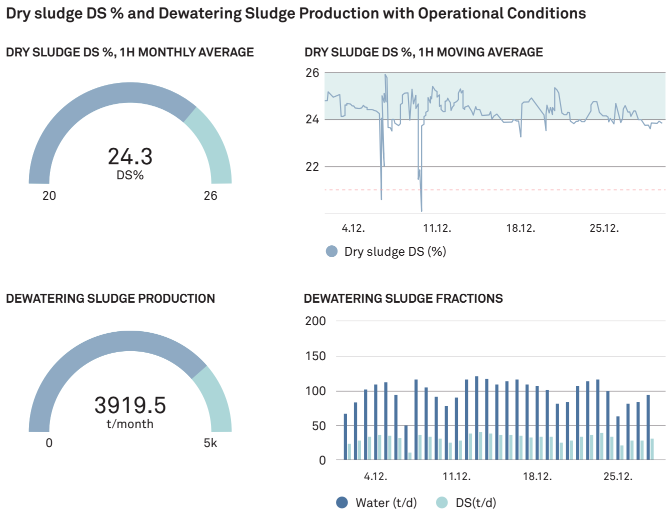
Another example of an industrial application is a smart tool for hard chemical oxygen demand (COD) removal focused on treatment processes with targeting soluble, poorly biodegradable, organic material i.e. pulp mill effluents.. The environmental regulations for COD are tightening and permit levels are being set lower than current biological treatment processes can achieve. Hard COD is defined as poorly biodegradable organic compounds that are not removed during the biological treatment stage; normally it amounts to 80 to 90% of the soluble COD remaining in the wastewater after biological treatment. In pulp mills, hard COD consists mainly of lignin-like compounds released into the wastewater during the bleaching process. In other industries the compounds are recalcitrant soluble plant material or humic compounds. The smart tool developed by Kemira offers a unique way to automatically monitor soluble COD levels and dosing coagulant when needed in order to stay within environmental permit levels.

Enhanced sludge dewatering

Modern sludge dewatering processes are mainly based on the chemical conditioning of sludge followed by mechanical treatment using dewatering equipment. The most widespread chemical method for sludge conditioning and dewatering is the addition of flocculants. Chemical application may still often be performed using manual adjustments, which in turn are based on manual sampling and retrospective tests done at regular intervals. This can lead to problems in the sludge dewatering process due to non-optimal use of the chemistry.

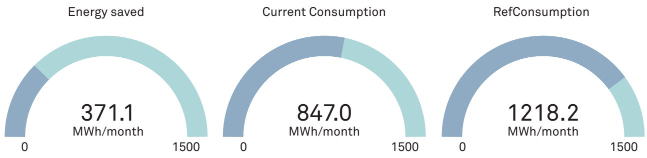
The amount of sludge sent for disposal or reuse is an important cost driver for a wastewater treatment plant. Improving the running conditions for the dewatering unit and the accurate dosage of appropriate chemicals can lead to a considerable increase in sludge dryness and decreased sludge volumes, lowering sludge handling needs and minimizing the impact on the environment. In many urban areas the dried sludge needs to be transported long distances for disposal, which adds to the treatment cost; the drier the sludge, the lower the transportation costs. In the case of sludge incineration, energy costs are usually very high. Thus, drier sludge is preferred in order to minimize the cost of pre-treatment before the incineration unit. Figure 7.6 illustrates customer KPI dashboards for enhanced sludge dewatering.

Figure 7.6
Dashboards for enhanced sludge dewatering at a wastewater treatment plant. The figure shows an improvement in dry solids from the baseline of 21% to an average of 24%. This corresponds to a heat energy reduction of 371 MWh/month in this case.

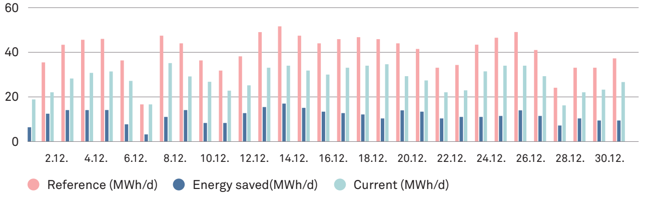

Dry sludge DS % and Dewatering Sludge Production with Operational Conditions

The system developed by Kemira for enhancing sludge dewatering is suitable for both municipal and industrial applications. It can measure total solids in the untreated sludge, iron coagulant dosage (if used), polymer dosage, total suspended solids of the treated reject water, and dry solids of the dewatered sludge. All of these parameters are continuously fed into an algorithm that calculates the optimal polymer dosage for the desired outcome based on the existing conditions. The system can be designed to optimize the polymer demand when the algorithm is heavily influenced by the feed-forward configuration parameters. Conversely, if the target is to optimize a machine's overall dewatering performance, then the algorithm will be more heavily influenced by the feedback configuration parameters.

HEAT ENERGY FRACTION (HEAT DRYER DS 35%, REFERENCE DS 21,5%)



HEAT ENERGY FRACTIONS



The system is also designed to maintain a consistent level of treatment within a minimum and maximum range of parameters. For reasons mentioned earlier, it may be that a customer can't have too dry sludge because they have a closed pipe to pump the sludge under pressure; for this reason sludge dryness limits are also set according to the application in question. In addition, some customers need a certain quality of reject water for recycling back into the wastewater treatment process. The system can be set up to achieve a very low TSS in the reject water.

Similar systems can also be used for industrial (waste) water treatment – for instance, process optimization for acidic and non-acidic thickening and clarification in the mining industry. Here, the overall goal is to optimize the metals extraction process, and the general concept is that the contaminants removed in the process have an indirect effect on the metals yield. A robust measurement device is required to withstand the harsh conditions of mining operations.

Kemira has built up its own aggregate data repository based on years of collected field performance data relating to the application of chemistry in water treatment. Collection, cleaning, and structuring the data allow the use of predictive analytics to create new digital solutions for more effective ways of working. For example, for sludge dewatering Kemira has developed a tool that identifies the optimization potential through benchmarking that quickly provides a determination of the suitable chemistry, and predicts the probable sludge dryness and chemical dosage. Selected statistical algorithms and machine learning techniques are applied to validate and adapt to new incoming data. The tool also shows how the technical optimizations translate into overall OPEX savings for the customer.

The way forward

The concept of Industry 4.0 can be applied to any municipal or industrial (waste)water treatment processes including the application of chemistry. Recent advances in this field open up tremendous opportunities for autonomous and adaptive solutions in real-world facilities. For instance, creating a “digital twin” – a virtual simulation model of a physical system – can enable real-time sensing and precise dynamic control (also remote or autonomous), with a comprehensive information service for large systems through close coordination of physical and computing resources. A digital twin can use machine learning to continuously learn and improve its own capabilities using multiple data sources.

In the age of drones and driverless cars, it is only a matter of time before water treatment processes are autonomous; the same will be true for most chemical treatment applications. Predictions based on real-time data can be used to optimize treatment processes for maximum benefit, and treatment optimizations can trigger demands that lead to further innovations.

With advances in sensor technologies, the source of contaminants will be available for all to see. Tracking where contaminations originated and are concentrated will also be possible. This will lead to targeted treatments and, hopefully, more effective enforcement.

From a human perspective, hiring civil and process engineers, operators, and laboratory staff is no longer sufficient to support the new ways of working; instead, instrumentation and electrical engineers and software and data specialists are the essential hires. With water treatment plants seldom able to attract and retain a workforce with these skills, there is an opportunity for innovative vendors to step in and fill the gap, providing customers with services that help them to optimize their processes through novel business models. As this transformation progresses there is a need for vendors to collaborate in order to avoid overlaps in their offerings and fully realize the benefits of smart process management.

Despite the many recent technological advances in the water treatment industry, business models remain largely unchanged. Smart process management should enable the development of new sustainable business models that take into account the overall value added throughout the process.

Glossary

A

Ångström measurement of length, 1 Å = 10^{-10} m.

Acid fermentation digestion of sludge under formation of organic acids.

Activated sludge sludge formed when treating sewage with microorganisms under aerobic conditions.

Adhesion the way bodies stick together by attraction between touching surfaces.

Adsorb to concentrate or attract a substance on to a surface.

Adsorption the binding of dissolved substances to the surface of a solid particle.

AOPs Advanced Oxidation Processes processes, in which formation of reactive chemical species causes mineralization of pollutants.

Aerobic in the presence of oxygen.

Affinity the tendency of substances to react with each other.

Aggregate collection of units.

Aggressive free carbon dioxide gives water corrosive properties.

ALG iron-free aluminum sulfate in granular form.

Alkali mainly sodium and potassium hydroxide.

Alkalinity buffering capacity. Ability of water to neutralize acids.

Alkaline basic, i.e. with a pH higher than 7.

Amphoteric able to act as both an acid and a base.

Ammonia NH_3, colorless gas with an acrid smell.

Ammonium NH_4^+

Anaerobic in the absence of oxygen and nitrate.

aMBR or AnMBR anaerobic membrane bioreactor technology.

Anionic negatively charged ion.

Anionic polymer polymer with negatively charged groups.

Anoxic in the absence of oxygen but in the presence of nitrate.

AOX Adsorbable Organic Halides.

ARM Alternative Raw Materials.

Artificial intelligence (AI) intelligence demonstrated by machines, in contrast to the natural intelligence displayed by humans.

Antiscalants substances preventing crystallized mineral salts (scale) from forming in the water pipes.

Ash content ash residue.

Assimilation merging or synthesis of organic compounds.

Associated free carbon dioxide the amount of carbon dioxide that is needed to prevent precipitation of calcium carbonate in water.

Autotrophic organism that produces its own nutrition; requires light energy for growth.

AVR Al and Fe(III) sulfate in granular form.

B

Bacteria single-celled, occasionally colony-forming organism in the size range 0.35–35μm. Multiplies by fission.

Basicity the molar ratio OH^-/Al^{3+} and OH^-/Fe^{3+} in aluminum or iron salts.

BDE Brominated diphenylethers.

Biocide substance inhibiting microbiological activities.

Biofilm culture of microorganisms that forms a film on a substrate.

Biological floc colony of cells.

Biological beds biobeds, tanks or containers filled with carrier material covered with biofilm.

Biomass quantity of living organisms, cell mass.

Bio P biological phosphorus reduction.

Bio-rotor rotating drum containing carrier material that is partially immersed in wastewater. Oxygenation occurs when parts of the drum pass through the air as a result of its rotation

BOD Biochemical Oxygen Demand. BOD_7 (biochemical oxygen demand over a period of 7 days) ≈ 1.15 x BOD5.

Buffer capacity ability to resist change, in pH for example.

Bulking sludge sharp rise in sludge volume in an activated sludge.

C

Capillary a hair-fine tube or very narrow gap.
Carbohydrates compound of carbon, hydrogen and oxygen, such as cellulose (starch).
Catalyst substance that accelerates a chemical reaction without being consumed in the reaction.
Cation positively charged ion
Cationic polymer a polymer with repeat units that have a positive charge.
CEPT Chemical Enhanced Primary Treatment.
CFU Colony Forming Units.
Cloud computing the on-demand availability of computer system resources including servers, storage, databases, networks, software, analytics, and data mining over the internet (“cloud”).
Coagulant relatively low-molecular substance that makes particles bind together in large groups.
Coagulate to solidify or merge to form larger particles.
Coagulating agent see coagulant.
Cyber-physical systems (CPS) a system in which a mechanism is controlled or monitored by computer-based algorithms.
CIP cleaning done in place.
CDC Centers for Disease Control and Prevention.
COD Chemical Oxygen Demand.
Coliform bacteria type of intestinal bacteria.
Colloidal particles particles that are so small that they do not form sediment.
COP c leaning done out of place.
CSO combined sewer overflow.
Composting controlled biological decomposition under aerobic conditions. Results in a rise in temperature and the formation of carbon dioxide.
Conditioning improvement.
Contaminate to pollute or infect.
Copolymer a polymer that contains at least two types of repeat unit.
Corrosive aggressive or attacking.
Culture to cultivate or refine.
Cryptosporidium parvum parasitic single-celled organisms that can cause illness in people and animals.
Cyst dormant form of Giardia intestinalis.
Cryophilic organism that develops favourably at low temperature, usually below +20°C.

D

DADMAC Diallyldimethylammonium chloride.
DAF dissolved air flotation.
DDT Dichloro-Diphenyl-Trichlorethane, a banned pesticide.
Decant to drain a liquid from the surface, of a sedimentation basin for example.
Degree of polymerisation the number of repeating units in a polymer.
Denitrification reduction of nitrate to nitrogen.
Density weight per volume, g/cm^3 or kg/m^3
Destabilisation processes, e.g. charge neutralisation, leading to aggregation and precipitation of colloidal particles.
Diffusion penetration.
Diffuser tube of fine-pored material.
Digester gas gas mixture that is formed during anaerobic digestion. Consists mainly of methane and carbon dioxide. Measured in litres at atmospheric pressure.
Digestion anaerobic sludge stabilisation process.
Dioxin name given to chlorinated derivatives of dibenzo-1,4-dioxin and dibenzofuran. There are 210 dioxins, of which around 10 are highly toxic. The most toxic is TCDD (2,3,7,8-tetrachlorodibenzo-1,4-dioxin).
Direct precipitation chemical-mechanical treatment.
Disinfection killing of pathogenic organisms.
Disperse mixing two individually homogenous phases, one of which forms particles or droplets in the other.
Dispersed finely divided.
Dissimilation the breakdown phase of metabolism.
Dissociation the division of a substance into simpler atomic groups or atoms.
Dissolved substance a substance mixed in a liquid that does not show a tendency to deposit or precipitate.
DO dissolved oxygen.
DOC dissolved organic carbon.
DS dry solid.
Duplicate systems separate systems with independent piping for wastewater and storm water.
DWTPs drinking water treatment plant.

E

Emission discharge

Endogenous respiration respiration without the external supply of fuel.

EQS environmental quality standards.

EQSD The Environmental Quality Standards Directive.

Enzymes proteins that have a catalytic action.

EPAM polyacrylamide emulsion.

EPS Extracellular Polymeric Substances.

Eutrophication increased supply of nutrients that leads to rapid growth of vegetation.

F

Feaces solid excrements from humans and animals.

Ferric trivalent iron ion, Fe^{3+}.

Ferrous bivalent iron ion, Fe^{2+}.

Filamentous bacteria thread-like bacteria.

Floating sludge a layer of sludge on the surface of liquid.

FD The Floods Directive.

Floc group of particles that adhere weakly to each other.

Flocculate to bring together small contaminants in aggregates that are large enough to be removed.

Flocculant chemical compound that produces flocculation.

Flotation the separation of flocs by means of bubbles of air or gas that bring them to the surface of the aqueous phase.

Fluidize to make solid particles float in a liquid or gas.

Fourth Industrial Revolution (Industry 4.0) the mass entry of cyber-physical systems into production that serve human needs, including life, work, and leisure.

Free-swimming bacteria individual or pair-forming bacteria that do not form a sediment.

Fresh water non-saline water resources.

FTU Formazin Turbidity Units.

G

GAC Granulated Activated Carbon.

GC Gas Chromatography.

Giardia intestinalis parasitic single-celled organisms that can cause illness in people and animals.

Grit chamber basin for separating sand from wastewater.

GWD The Groundwater Directive.

H

HBCD Hexabromocyclododecane.

Hardness the total calcium and magnesium ion concentration in water.

Heterotrophic organism one that requires organic matter for growth.

Heavy metal metallic element with a high atomic number.

Homopolymer a polymer that only contains one type of repeating unit.

Humus some organic decomposition products of plants.

Hydraulic load the total intake by a wastewater treatment plant.

HRT hydraulic retention time.

Hydrogen carbonate ion HCO_3^-.

Hydrolysis the splitting of a substance through reaction with water.

Hydrophilic water-loving, can be wetted by water.

Hydrophobic water-repelling, cannot be wetted by water.

HYPRO process a precipitation process in which the primary sludge is hydrolysed to form a source of carbon.

I

Immobilized cultures microorganisms that grow on a carrier material.

Infiltration penetration of liquid into a porous material, e.g. the penetration of water into soil, rock or gravel and sand ridges.

IC inorganic carbon.

Inorganic substances chemical compounds that do not contain carbon, the exception being carbon oxide compounds and cyanides.

Ion an atom or molecule with an electric charge.

Ion exchange medium a solid substance that traps ions and replaces them with ions having the same charge.

Internet of things (IoT) a network of physical devices connected to the internet able to collect and share data without human-to-human or human-to-computer interaction.

Isoelectric point the pH at which a substance has an equal number of positive and negative charges.

K

Kjeldahl nitrogen the total of organic nitrogen and nitrogen as ammonium.
Key performance indicators (KPI) a numerical value that demonstrates how effectively a company is achieving key business goals.

L

LCA Life Cycle Assessment.
LC-OCD Liquid chromatography – organic carbon detection.
Leachate contaminated water from collections of waste, especially landfill sites.
LC Liquid Chromatography.
Ligand ion or molecule that is bound to the central atom in a complex chemical compound. The water molecules in $Al(H_2O)_6^{3+}$ are ligands.
Limestone calcium carbonate, $CaCO_3$
LOI (Loss on ignition) the difference between the solids concentration and ash residue.
Lyophilic something that can be wetted by the surrounding liquid.
Lyophobic something that cannot be wetted by the surrounding liquid.

M

MAP magnesium ammonium phosphate.
Machine learning an application of artificial intelligence that provides systems with the ability to automatically learn and improve from experience without being explicitly programmed.
MBBR Moving Bed Bio-Reactor.
MCRT mean cell residence time.
Mechanical treatment the mechanical removal of contaminants.
Mesophilic organism that thrives at moderate temperatures.
Mesophilic digestion digestion at moderate temperatures, 30–40°C.
Metabolism chemical processes within an organism that result in energy production.
Methane gas, CH_4, the main component of digester gas and marsh gas.
Metazoa multi-celled organisms/animals.
MF microfiltration.
Micron one millionth of a metre – 1μm = 0.001 mm.
Micronutrient substance that is needed in small amounts for cell formation.
Microorganism microbe, organism that cannot be seen with the naked eye.
Mineralize to convert organic material into inorganic material.
Mineral salts inorganic compounds.
MLSS Mixed Liquid Suspended Solids, the name given to the sludge content of activated sludge.
Mole an number quantity. One mole corresponds to $6.02 \cdot 10^{23}$ molecules.
Monomers compounds that are used to manufacture polymers. The monomers react to form the repeating units of the polymers.
MFS Multi Flash stages in thermal desalination technology.
MED Multi Effect Distillation in thermal desalination technology.
MS Mass Spectrometer.
MW molecular weight.

N

NF nanofiltration.
Nitrification oxidation process in which ammonium is converted into nitrate.
Nitrifying oxidation of ammonium or ammonia to form nitrite and nitrate.
Nitrobacter autotrophic bacteria that oxidise nitrite into nitrate.
Nitrosamines a certain type of nitrogen compounds.
Nitrosomonas autotrophic bacteria that oxidise ammonium into nitrite.
NOM natural organic matter.
Non-ionic uncharged.
Non-ionic polymer a polymer that contains uncharged repeating units.

N_{tot} total nitrogen concentration.

NTU Nephelometric Turbidity Units.

Nutrient salts substances that fertilise the growth of organic matter.

O

Oligotrophic environment environment that has a very scarce supply of nutrients.

Oocyst dormant phase of Cryptosporidium parvum.

Organic matter and organic substances chemical compounds that contain carbon, with the exception of carbon oxide compounds and cyanides.

Orthophosphate PO_4^{3-}.

Osmosis the diffusion of a solvent from a solution with a low concentration to one that has a higher concentration.

Oxidation donation of one or more electrons. Connected to reduction.

Oxygenation adding air by pumping in or by means of a surface aerator.

Oxygen demand oxygen demand per unit of time and unit of organic weight content, g O_2/(kg LOI•h).

OUR oxygen uptake rate.

P

P_2O_5 phosphorus pentoxide.

PAA peracetic acids.

PAC powdered activated carbon.

PAH polyaromatic hydrocarbon.

PAM polyacrylamide – water-soluble polymer with a high molecular weight.

PAN collective name (poly)aluminum nitrates.

PAS collective name polyaluminum sulfates.

Pasteurisation (after L. Pasteur) method of heating a liquid to a temperature below the boiling point in order to kill pathogenic organisms without destroying the product.

Pathogen organism that causes illness.

PAX collective name for polymerised Al salts.

PCB polychlorinated biphenyls.

PE person equivalent.

PEI polyethyleneimine.

Percolation slow movement (of water) through layer of porous material.

Permanganate consumption chemical oxygen demand determined as mg/l $KMnO_4$.

Pesticide chemical compound used to combat pests.

PFA performic acids.

PFOS Perfluorooctane sulfonate.

pH the negative ten logarithm of the hydrogen ion activity (≈ concentration).

Phosphates salts of phosphoric acid.

Photosynthesis the formation of organic matter from carbon dioxide with the aid of solar energy.

PIX collective name for Fe(III)salts.

Polyelectrolyte a polymer that contains repeating units that are charged.

Polymer a compound made up of one or more repeat units.

Polyphosphate polymerised orthophosphate.

Post-precipitation addition of the coagulant after biological treatment.

ppb part per billion, 1/1 000 000 000.

ppm part per million, 1/1 000 000.

Pre-precipitation chemical precipitation followed by biological treatment.

Pre-aeration aeration of wastewater before any other treatment.

Pre-sedimentation sedimentation before any other treatment.

Primary sludge sludge from mechanical treatment.

Primary treatment mechanical treatment, the first stage.

Primary oxygen demand oxygen demand during the decomposition of organic matter in wastewater.

POP Persistent organic pollutants.

Proteins polymerised amino acids.

Programmable logic controllers (PLCs) industrial digital computers often used to automate technological processes. PLCs are intended for long-term autonomous use, often in adverse environmental conditions, without serious maintenance and practically without human intervention.

PTE Potential Toxic Elements.

Protozoa single-celled organisms/animals.

Pyrolysis breakdown of organic substance as a result of heating in the absence of oxygen.

R

Raw sludge untreated and unstabilised sludge from treatment.
Raw water untreated water from a groundwater source or surface water source.
Reaction when two or more substances together form one or more new substances.
Recipient receiving body of water (sea, lake, river, stream).
Recirculate return.
Redox potential equilibrium potential of an electrode of a neutral metal immersed in a solution. The potential is a measure of the oxidising ability of the solution, i.e. its ability to donate electrons.
Reduction acceptance of one or more electrons. Connected to oxidation.
Regenerate to return to original condition.
Reject (water) water from thickening, digestion and dewatering.
Repel to push away.
Repulsion the process of pushing away.
Resistant ability to resist.
Respire to breathe.
Restabilisation giving an electrically charged particle the opposite charge by adsorbing an electrically charged substance.
Return sludge sludge from biological treatment that is pumped back into the intake of the biological stage in order to take part in the treatment process again.
RO reverse osmosis.

S

Sanitation the removal of pathogenic microorganisms.
SBR biological batch reactor.
SDG Sustainable Development Goal.
Secondary treatment second stage of biological treatment.
Secondary oxygen demand oxygen demand during decomposition of dead algae to create organic cellular material, in recipient for example.
Secondary sludge sludge from biological treatment.
Sediment deposit of material.
Sedimentation basin basin for physical treatment by sedimentation.
SEM scanning electron microscopy.
Semi-bound carbon dioxide carbon dioxide dissolved in water in the form of hydrogen carbonate. Old terminology.
SBR Sequence Batch Reactor.
Simultaneous precipitation addition of coagulant directly to the activated sludge process.
Slaked lime calcium hydroxide, $Ca(OH)_2$.
Sludge age, SRT usually determined from the ratio between the existing quantity of sludge in the biological treatment system and the quantity of sludge removed each day.
Sludge content may be given as a specific sludge volume, ml/l, or sludge concentration, mg/l.
Sludge dewatering reducing the water content of sludge.
SVI Sludge volume index measuring sedimentation properties of an activated sludge. Given as a ratio of sludge volume and the mass of suspended solids. Expressed in ml/g.
Sludge load ratio between BOD added each day and the existing amount of sludge (suspended solids) in the aeration basin.
Sludge stabilisation breakdown of organic matter in sludge under controlled forms.
Slurry suspension of solid particles in a liquid.
Stripping removal by blowing in air/gas.
Substrate nutrient on which bacteria are cultivated.
Surface aerator aerator that disperses water and sprays it up into the air to promote oxygenation.
Surface load specific flow load in sedimentation basins.
Surface water rainwater and melt water that gathers on land surfaces.
Surfactants surface active agents that have at least one hydrophilic and one hydrophobic part.
Surplus sludge formed during the activated sludge process, the sludge that is removed from the biological process.
Suspended solids solid particles in wastewater, SS unit mg/l.
Suspended solid particles dispersed in water.
Suspension liquid containing finely dispersed solid particles.
SV_{30} volume of sludge after 30 minutes of settling in a 1 liter beaker.
Sweep coagulation method of trapping contaminants in metalhydroxide flocs.

T

TBT Tributyltin.
TCS Triclosan.
TC total amount of carbon.
Thermal disinfection killing infectious agents by heating.
Thermophilic digestion digestion at significantly elevated temperature > 55°C.
Tertiary treatment can be a third treatment stage, with chemical phosphorus removal.
Tertiary sludge sludge formed during tertiary treatment.
THMs trihalomethanes.
TOC total concentration of organic carbon.
Total solids TS, the weight of dry matter per weight of sample that is obtained after drying at 105°C.
TOX Total Organic Halides.
Toxic poisonous.
Trace element a micronutrient or microelement that is essential to organisms but is only needed in small amounts. Large amounts can act as a toxin.
Treatment efficiency the effect of the measures taken to treat water.
Turbidity measurement of cloudiness, expressed for example in NTU, Nephelometric Turbidity Units and FTU, Formazin Turbidity Units.
Turbulence gas or liquid in violent irregular motion.

U

UF ultrafiltration.
Unslaked lime calcium oxide, CaO.
Urea constituent of urine, organic nitrogen compound.

W

WWTP wastewater treatment plant.

V

Virus organism that multiply inside living cells and that may cause disease.
VOC volatile organic compound.
VM Volatile Matter = total solids – ash residue.
VS volatile solids.
VSS Volatile Suspended Solids, a measure of the organic matter, in activated sludge for example.

Z

Z potential potential of the electrical double layer that surrounds particles in a colloidal solution or suspension.
Zeolite aluminum silicate mineral of alkali metal or alkali earth metals with well defined porous structure.