UZWATER

Industrial Water and Wastewater Management

Editor:

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This compendium is produced for a master level course in the UZWATER project. It consists of some newly written material as well as previously published texts extracted from freely available books, reports and textbooks on the Internet, dominated by publications from the Baltic University Programme. The sources used for each chapter is listed at the end of the chapter.

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Industry and Water Use

Chapter 1
Industry and Water Use

1.1 Introduction. Water consumption statistics

The data on water consumption in the world is provided by the United Nations (UN, UNESCO, and FAO, see list of publications below).

Worldwide, agriculture accounts for 70% of all water consumption, compared to 20% for industry and 10% for domestic use. In industrialized nations, however, industries consume more than half of the water available for human use. Belgium, for example, uses 80% of the water available for industry.

Freshwater withdrawals have tripled over the last 50 years. Demand for freshwater is increasing by 64 billion cubic meters a year (1 cubic meter = 1,000 liters)

- The world's population is growing by roughly 80 million people each year.
- Changes in lifestyles and eating habits in recent years are requiring more water consumption per capita.
- The production of biofuels has also increased sharply in recent years, with significant impact on water demand. Between 1,000 and 4,000 litres of water are needed to produce a single litre of biofuel.
- Energy demand is also accelerating, with corresponding implications for water demand.

Almost 80% of diseases in so called "developing" countries are associated with water, causing some three million early deaths. For example, 5,000 children die every day from diarrhea, or one every 17 seconds.

The three types of water withdrawal are distinguished: agricultural, municipal (including domestic), and industrial water withdrawal. A fourth type of anthropogenic water use is the water that evaporates from artificial lakes or reservoirs associated with dams. Information on evaporation from artificial lakes will be available in the AQUASTAT database in the near future.

At global level, the withdrawal ratios are 70% agricultural, 11% municipal and 19% industrial. These numbers, however, are biased strongly by the few countries which have very high water withdrawals. Averaging the ratios of each individual country, we find that "for any given country" these ratios are 59, 23 and 18% respectively. (See Figure 1.1)
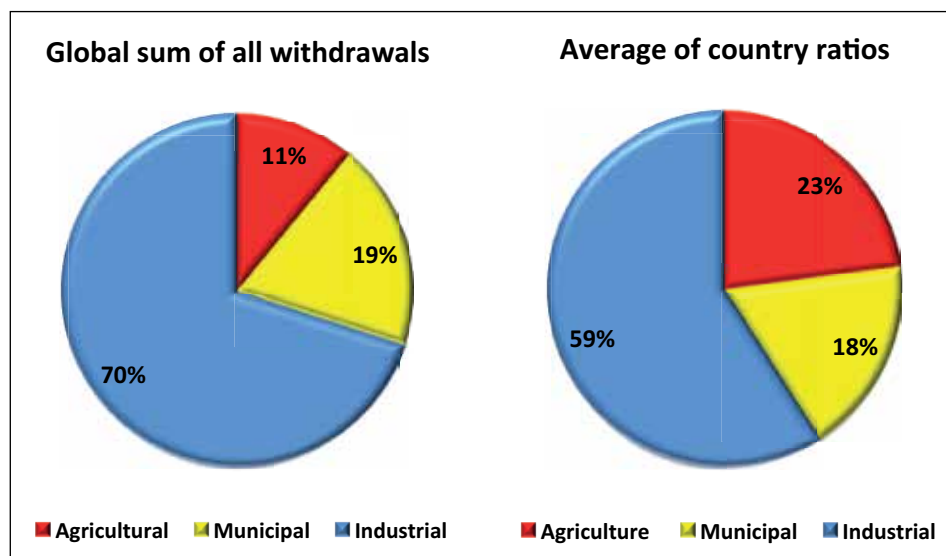
Figure 1.1 Global withdrawal ratios level and averaging the ratios (Adapted from AQUASTAT)

The ratios also vary much between regions, going from 91, 7 and 2% for agricultural, municipal and industrial water withdrawal respectively in South Asia to 8, 16 and 77% respectively in Western Europe. For more details about water withdrawal by region, please see Table 1.1.

For Africa, Asia, Latin America and the Caribbean, AQUASTAT obtains water withdrawal values from ministries or other governmental agencies at a country level, although some data gaps are filled from UN Data. For Europe and for Northern America, Japan, Australia and New Zealand, Eurostat and OECD are valuable sources of information, and also used to fill data gaps. Links to these organizations are provided below:

1.2 Water balance

The amount of precipitation falling on land is almost 110,000 km^3 per year. Almost two-thirds of this amount evaporate from the ground or transpire from vegetation (forest, rangeland, cropland). The remaining 40,000 km^3 per year is converted to surface runoff (feeding rivers and lakes) and groundwater (feeding aquifers). These are called renewable freshwater resources. Part of this water is being removed from these rivers or aquifers by installing infrastructure. This removal of water is called water withdrawal. Most of the withdrawn water is returned to the

Table 1.1 Water withdrawal by sector, around 2007 (Adapted from "Aquastat" http://www.fao.org/nr/aquastat/ Update: September 2014)

Continent Regions	Total withdrawal by sector						Total** water withdrawal	Total freshwater withdrawal	Freshwater withdrawal as % of IRWR
	Municipal		Industrial		Agricultural				
	km^3/year	%	km^3/year	%	km^3/year	%	km^3/year	km^3/year	%
1	2	3	4	5	6	7	8	9	10
World	462	12	734	19	2,722	69	3,918	3,763	9
Africa	27	13	11	5	174	82	213	199	5
Americas	130	15	288	34	430	51	847	843	4
Northern America	86	14	259	43	259	43	604	600	10
Northern America	74.4	14	252.2	48	197.2	38	523.8	520.4	9.2
Mexico	11.4	14	7.3	9	61.6	77	80.3	79.5	19.4
Southern America	36	17	26	12	154	71	216	216	2
Guyana	0.1	5	0.2	8	1.8	87	2.1	2.1	0.6
Brazil	17.2	23	12.7	17	44.9	60	74.8	74.8	1.3
Asia	228	9	244	10	2,035	81	2,507	2,373	20
Middle East	25	9	20	7	231	84	276	268	55
Arabian Peninsula	4.0	12	0.9	3	29.5	86	34.3	30.1	49.3
Near East	13.6	10	15.0	11	103.3	78	131.8	128.0	46.3
Central Asia	7	5	10	7	128	89	145	136	56
South Asia	70.2	7	20.0	2	912.8	91	1 003.1	889.6	46.0
East Asia	92.5	14	148.8	22	435.4	64	676.8	673.2	19.7
Europe	72	22	188	57	73	22	333	332	5
Northern Europe	2.7	33	4.0	50	1.3	16	8.0	8.0	1.0
Western Europe	22.8	23	72.3	73	4.6	5	99.7	99.0	15.9
Central Europe	9.7	25	25.7	66	3.8	10	39.2	39.1	15.7
Mediterranean Europe	17.6	19	26.1	28	48.0	52	91.7	90.8	21.5
Eastern Europe	6.3	22	20.6	72	1.7	6	28.6	28.5	20.9
Russian Federation	13.4	20	39.6	60	13.2	20	66.2	66.2	1.5
Oceania									
Australia and New Zealand	5	26	3	15	11	60	18	17	2
Other Pacific Islands	0.03	33	0.01	11	0.05	56	0.1	0.1	0.1

** Includes use of desalinated water, direct use of treated municipal wastewater and direct use of agricultural drainage water

environment some period of time later, after it has been used. The quality of the returned water may be less than the quality when it was originally removed.

There is an increasing recognition in industry that the reduction of water consumption and wastewater discharge is a necessary component of good environmental practice. In reality, there has been no tradition of reducing water consumption, and existing plants were not designed with water conservation in mind. Furthermore, accounting systems are designed to determine the cost of producing chemicals and raw materials and cannot easily be adapted to measuring the true cost of using water. It is very unlikely that complete water management schemes will be introduced for existing plants, although partial schemes may be attractive. Major schemes will be limited by the cost of installing long pipe runs, storage tanks and pumps, but good payback may be achieved if product or raw materials can be recovered for recycling or for sale. The need to build new effluent treatment facilities, together with further restrictions on the discharge of specific pollutants, may justify expenditure to reduce water consumption. If existing plants are to maintain their licence to operate in the next century, the case for investment in water management schemes will inevitably become more and more attractive.

1.3 Water value and quality

As a unique natural resource, the real value of water has been underestimated in many countries. The price of water has been kept artificially low, which has not stimulated people or industries to save on it. At the same time, there is a growing awareness of the impact of pollution on water quality and a demand to tighten water quality standards. Due to modern-day sophisticated analytical methods and equipment, several rather new contaminants in drinking water have been discovered, even if in very small concentrations. The public is more aware than ever before and is demanding safe drinking water.

Water quality is not synonymous with water pollution and, similarly, water quality management should not be equated with water pollution control only. Water quality management deals with all aspects of water quality problems relating to the many beneficial uses of water, while water pollution control usually connotes adequate treatment and disposal of wastewater.

For new industrial plants, it is relatively easy to incorporate water management philosophy at the design stage, given that the technical uncertainties can be overcome. The incremental cost of modifying the process may be compared with savings in long-term operational and capital costs associated with an effluent

treatment facility, as well as with an assessment of the ability of the plant to meet future environmental legislation.

For existing plants, the potential benefits of reducing water consumption may be offset by the costs associated with the installation of storage tanks and long pipe runs. Modifications to plant pipe work and supporting steelwork may be expensive and difficult to manage and there is a natural reluctance to interfere with existing plant battery units. In these circumstances, and in the absence of clear information about the direction and timing of future environmental legislation, the appeal of a stand-alone effluent treatment plant is obvious.

1.4 Water consumption

Water uses consist of intake, on-site and in-stream flow uses. Intake uses include water for domestic, agricultural and industrial purposes and uses that actually remove water from the source. On-site uses consist primarily of water consumed by swamps, wetlands, evaporation from water bodies, natural vegetation and un-irrigated crops and wildlife. Finally, flow uses include water for estuaries, navigation, wastewater dilution, hydroelectric power production, and fish, wildlife and recreation purposes.
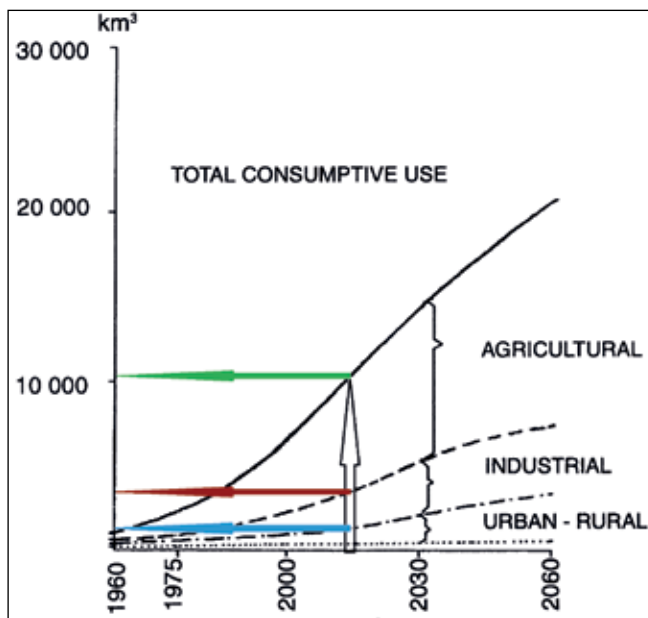

Figure 1.2 Projected uses of water in the world and real withdrawal (Adapted from Bond & Straub, 1974 and "Aquastat" 2015).

Table 1.2. Water consumption distribution (in %) in the world (Antilla et al., 1996)

Branch of economy	USA	China	Zambia	Finland	Estonia
Agriculture	42	87	26	3	9
Industry	46	7	11	85	84
Municipality	12	6	13	12	7

Intake water can be measured in two ways: by the amount withdrawn and the amount consumed. In 1975 projected uses for the world and real withdrawal are presented in Figure 1.2 and real consumption in some countries in 1990 in Table 1.2.

Worldwide water consumption at the present time is estimated at 4,340 km^3/year (surface and groundwater together). More than half of this water is used in agriculture, about a quarter in industry and a quarter for use in municipalities and rural areas. The worldwide consumption however varies considerably between regions, depending on the intensity of agriculture in relation to the humidity of the climate, on the industrialisation level and on the type of industry prevailing. In the Baltic basin industrial water use dominates the consumption. This is especially true for the regions where paper and pulp industry, as well as metallurgic and other water- intensive industry, are important. Note the high%ages for Finland and Estonia in Table 1.2. Similar figures are valid for Sweden, whereas in Poland, e.g., where agriculture is important and water not as plentiful as in the northern part of the basin, industrial water use is less dominating. The figures given for USA are representative for a region with highly developed industry but with intensive agriculture under dry conditions, whereas China represents an agriculturally dominated region with less developed industry.

Water withdrawn is water diverted from its natural course for a beneficial use. Water consumed is water that is incorporated into a product or lost to the atmosphere by evapotranspiration and thus not reusable. Consumptive use is the real indicator of water demand, inasmuch as most non-consumptive water can be, or in fact is, reused. It should be noted that water reuse is not a new concept.

The investigation and management of water resources systems for water quality must include consideration and evaluation of:
- physical, chemical and biological composition of headwaters and significant groundwater discharges;
- water quantity and quality requirements for all existing and potential water uses;
- the manner of water withdrawal and its effect on water quality and quantity;
- the existing and future water and wastewater treatment technology used to alter water quality;

- the wastewater outfall configuration and effluent mixing;
- the eutrophication status of the receiving waters;
- the ecological changes that might be caused by wastewater discharges;
- the potential effects of the discharge of heated waters.

1.5 Industrial water supply

Because of the diverse nature of industrial processes, water quality requirements are industry- dependent. In addition, water quality requirements may vary for various industrial processes within a single plant and for the same process in different plants. Quality considerations are similar, depending on cost of treatment, plant age, plant operating practices and quality and quantity of the available supply.

Because of the relative low cost of water treatment as compared to the cost of total production and marketing, industries can treat almost any water to their own specifications. However, quality characteristics that exceed those given in Table 1.3 would probably not be acceptable to most industries.

Table 1.3 Summary of specific quality characteristics of surface waters that have been used as sources for industrial water supplies (Krenkel & Novotny, 1980)

Table 1.3 Summary of specific quality characteristics of surface waters that have been used as sources for industrial water supplies (Krenkel & Novotny, 1980)

Characteristics (mg/l)	Boiler makeup water	Textile industry	Pulp and paper industry	Chemical industry	Petroleum industry
SiO_3	150	-	50	-	85
Al	3	-	-	-	-
Fe	80	0.3	2.6	10	15
Mn	10	1.0	-	2	-
Cu	-	0.5	-	-	-
Ca	-	-	-	250	220
Mg	-	-	-	100	85
Na+K	-	-	-	-	230
NH_3	-	-	-	-	40
HCO_3	600	-	-	600	480
SO_4	1,400	-	-	850	900
Cl	19,000	-	200	500	1,600
SS	15,000	1,000	-	10,000	5,000
Hardness ($CaCO_3$)	5,000	120	475	1,000	900
Alkalinity ($CaCO_3$)	500	-	-	500	500
pH	.	6-8	4.6-9.4	5.5-9.0	6.0-9.0
Colour units	1,200	-	360	500	25
COD	100-500	-	-	-	-
Temperature (γC)	50	-	35	-	-

Different industries view water, and hence water management, in different ways. At one extreme is the oil and refining industry, for which water is solely a utility and very little is used for process purposes. At the other extreme is the pulp and paper industry, for which water is an integral part of the process from the very introduction of the raw materials and continuing historically in copious quantities at every stage. For this industrial sector, water management refers only to process water use and excludes utility use.

1.6 Ultra pure water

Ultrapure water, also known as "UPW" or "high-purity water", is water that has been purified to uncommonly stringent specifications. Ultrapure water is a commonly used term in the semiconductor industry to emphasize the fact that the water is treated to the highest levels of purity for all contaminant types, including: organic and inorganic compounds; dissolved and particulate matter; volatile and non-volatile, reactive and inert; hydrophilic and hydrophobic; and dissolved gases.

UPW and commonly used term Deionized (DI) water are not the same. In addition to the fact that UPW has organic particles, and dissolved gases removed, a UPW system includes a "Polishing" loop, the most expensive part of the treatment process.

A number of organizations and groups develop and publish standards associated with the production of UPW. For microelectronics and power - "Standard Guide for Ultra-Pure Water Used in the Electronics and Semiconductor Industries". Pharmaceutical plants follow water quality standards as developed by pharmacopeias.

Ultrapure water is treated through multiple steps to meet the quality standards for different users. The primary end users of UPW include these industries: semiconductors, solar photovoltaic's, pharmaceuticals, power generation (sub and super critical boilers), and specialty applications such as research laboratories. The "ultrapure water" term became more popular in the later 1970s and early 1980s as a way of describing the particular quality of water used in power, pharmaceutical, or semiconductor facilities.

While each industry uses what it calls "ultrapure water", the quality standards vary, meaning that the UPW used by a pharmaceutical plant is different than that used in a semiconductor industry or a power station. The standards tie into the UPW use. For instance, semiconductor plants use UPW as a cleaning agent, so it is important that the water not contain dissolved contaminants that can precipitate or particles that may lodge on circuits and cause microchip failures. The power industry uses UPW as a source to make steam to drive steam turbines; pharma-

ceutical facilities will use UPW as a cleaning agent, as well as an ingredient in products, so they seek water free of endotoxins, microbials, and viruses.

Today, ion exchange (IX) and electrodeionization (EDI) are the primary deionization technologies associated with UPW production, in most cases following reverse osmosis (RO). Depending on the required water quality, UPW treatment plants often also feature degasification, microfiltration, ultrafiltration, ultraviolet irradiation, and measurement instruments (e.g., total organic carbon [TOC], resistivity/conductivity, particles, pH, and specialty measurements for specific ions).

Early on, softened water produced by technologies like zeolite softening or cold lime softening was a precursor to modern UPW treatment. From there, the term "deionized" water was the next advancement as synthetic IX resins were invented in 1935 and then became commercialized in the 1940s. The earliest "deionized" water systems relied on IX treatment to produce "high-purity" as determined by resistivity or conductivity measurements. After commercial RO membranes emerged in the 1960s, then RO use with IX treatment eventually became common. EDI was commercialized in the 1980s and this technology has now become commonly associated with UPW treatment.

Ultrapure water is used in the Semiconductor industry extensively. It is the highest UPW quality grade application: Resistivity at 25°C (>18.18 MΩ·cm) TOC (<1µg/L) (on-line for <10 ppb). The UPW consumption for the semiconductor industry can be compared to the water consumption of a small city. A single factory can utilize high purity water at a rate of ~5,500 m^3/day. The use of UPW varies between rinsing the wafer after chemicals application, to dilution of the chemicals used in production. Some UPW is used in optics of the immersion photolithography or can be utilized as make-up to cooling fluid in some critical applications. UPW is even sometimes used as humidification source for the clean room environment. It is used in other areas of the electronics industry in a similar fashion, such as display manufacturing, production of discrete components, such as LED's or the manufacturing of crystalline silicon photovoltaic's, but the cleanliness requirements in the semiconductor industry are currently the most stringent.

Quality characteristics of UPW for microelectronics and semiconductors industries would probably not be acceptable to pharmaceuticals. (For more detailed description of UPW standards and preparation see chapter 4. and 5)

1.7 Use of water in the chemical industry

The chemical industry, for its part, encompasses both extremes. Water is both a utility and a process fluid and the industry regards water management as the integration of the two duties.

When considering water use, the chemical industry is best regarded as a collection of dissimilar but related industries. The production units involved vary from the processing of heavy organic chemicals and oil derivatives through the production of basic inorganic chemicals such as alkalis and acids and of highly complex speciality chemicals to the electrolysis of sodium chloride brine to produce chlorine. Even within specific related areas, the processes may be very different. In the production of plastics, it is essential for some processes that water is excluded if the product is to have the desired properties; for other processes, polymerisation is carried out in emulsions in water and the quality of the water is critical for product quality. Plants producing the same product may use different routes, depending on the location of the plant, the availability of raw materials of the required quality, other production processes on the same site, transport and safety considerations, the age of the plant and environmental discharge permits.

Water can enter the process with the raw materials, be added or removed at different stages in the process or be added to the final product to suit specific end uses or customer requirements. It is not uncommon to purchase speciality chemical formulations that contain in excess of 90% water, while acids and alkalis may be sold with 50 to 70% water content.

It is common to find several different production processes on a single site. This is due to the integrated nature of the processes and considerations of the cost and safety of transporting potentially hazardous materials between sites. Thus water use on any particular site varies widely – some plants may use water as a utility only, while other plants may use water throughout the process. For this reason, while there are general rules that must be followed, strategies for water management are unique to production sites. For the chemical industry, therefore, it is essential to concentrate on generic solutions. This means looking at the unit operations which may find application for a range of uses, i.e. looking for the building blocks that can be used to achieve a water management scheme which is economic and, above all, robust in operation.

Chemical production sites have traditionally been located where there is a plentiful supply of cheap water and where the discharge of water has been relatively unrestricted. Environmental, safety and marketing pressures are now changing this picture and this, in turn, demands more consideration of the way water is used and discharged. Coupled with the rising costs of water and an in-

creasing awareness of the impact of water on production and product quality, the opportunities offered by water management are drawing more interest.

Chapter 1 sources:

1. "Aquastat" http://www.fao.org/nr/aquastat/ Update: September 2014
2. UN, UNESCO, and FAO publications.
3. ASTM D5127 Standard Guide for Ultra-Pure Water Used in the Electronics and Semiconductor Industries
4. SEMI F63 Guide for Ultrapure Water Used in Semiconductor Processing
5. "FDA/ICH, (CDER and CBER), Q8(R2) Pharmaceutical Development, guidance for industry, November 2009; Q9 Quality Risk Management, guidance for industry, June 2006; Q10 Pharmaceutical Quality System, guidance for industry, April 2009.". The International Conference on Harmonisation.

Chapter 2
Water Conservation

2.1 Water management in society

2.1.1 A global water perspective

Water dominates our planet and is basic to man's living conditions. Still it is a limited resource and also a threatened resource worldwide. To improve and limit water management is one of the main priorities for this century. Water is very unevenly distributed over the world. While e.g. in Africa, the Middle East, China and other arid and semi-arid areas a water access crisis is already a reality, in northern Europe, the situation is different. Here water quantity is not a large problem.

The challenge is instead to improve water quality in rivers, lakes and the Baltic Sea itself. Availability of water depends on the yearly run off, i.e. the
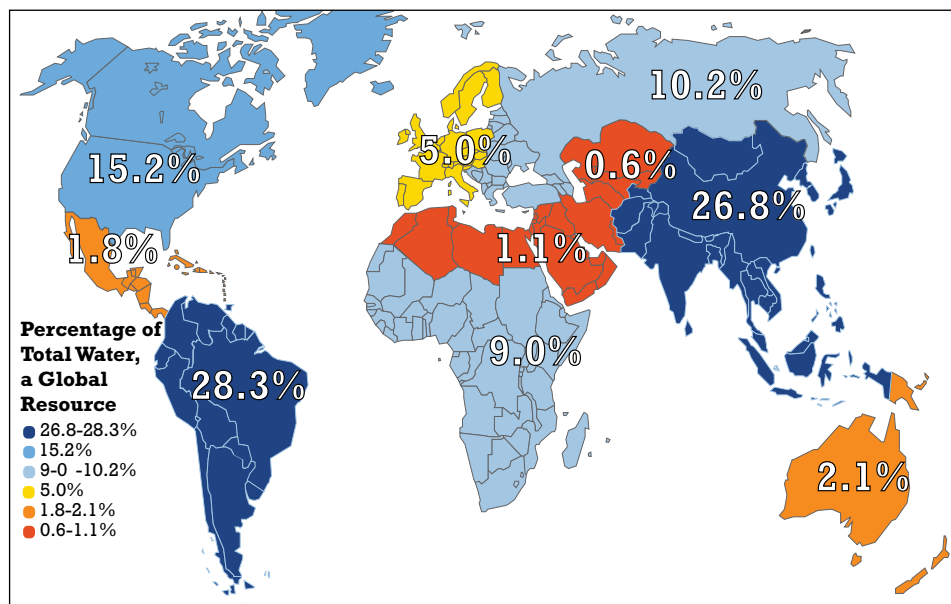

Figure 2.1. Total global water use. The map above shows the percentage of total water use in each region. Source: *http://online.sfsu.edu/rapidviz/523_infodesign_posters/523_water_miranda_bague.pdf*

amount of precipitation. In the Baltic Sea region this is very large in the north about 22,000 m^3 per person and year, while in the south, in Germany and Poland, it is about 20-fold lower.

Here water is sometimes limiting for agriculture. Water use in society is in the north, e.g. in Sweden and Finland, is about 3-4% of the runoff, or available resources, while in Poland it is about 18%. This is the level at which problems start to be visible due to the fact that water is re-circulated: wastewater emitted at some point is soon after recovered to be used for a new purpose. It is then often still too polluted. This is the water consumption cycle.

Water use is very different in different parts of the world. On the global level irrigation and agriculture account for the largest share, about 65%, followed by industry, 24%, municipal needs, 7%, and reservoirs 4%. In the Baltic Sea region irrigation is a much smaller part of water consumption.

2.1.2 Water consumption in industry

Water consumption in society has decreased significantly over a period of some 15 years. A general trend in Europe is a decline of withdrawal of water especially for industry but also for households. Many water saving strategies have been introduced with the purpose to save freshwater resources, decrease discharges of wastewater and facilitate the recovery of chemicals and energy. We will illustrate this with data from Sweden.

In total, industry is the largest water user in the region. For example, in Sweden industry accounted for close to 70% of all water use, households another 20% and agriculture 5% (data for year 2000, Figure 2.1). Three industrial branches dominate in water use. Pulp and paper industry accounts for almost half (0.9 billion m³). Together with chemical industry (0.5 billion m³) and metals work (0.4 billion m³) these three branches use 85% of all industrial water.

Industrial water use in Sweden increased dramatically from the 1940s up to a peak in 1965. Thereafter a strong decrease took place up to about 1975, and less so up the 1990s. In the period 1990-95 there was a slow decrease (just under 1% yearly) even though, at the same time, industrial production increased by about 25%. Since then (preliminary data for 2003) water use has been quite constant at around 2,200 Mm³ yearly, while the total water consumption in Sweden was 3,240 Mm³. The distribution of water consumption between different consumer groups is shown in Figure 2.2.

The withdrawal for production of potable water in the region was, around 1980, about 500-800 m^3/person and year. In the early 21 st century this figure has decreased to almost half.
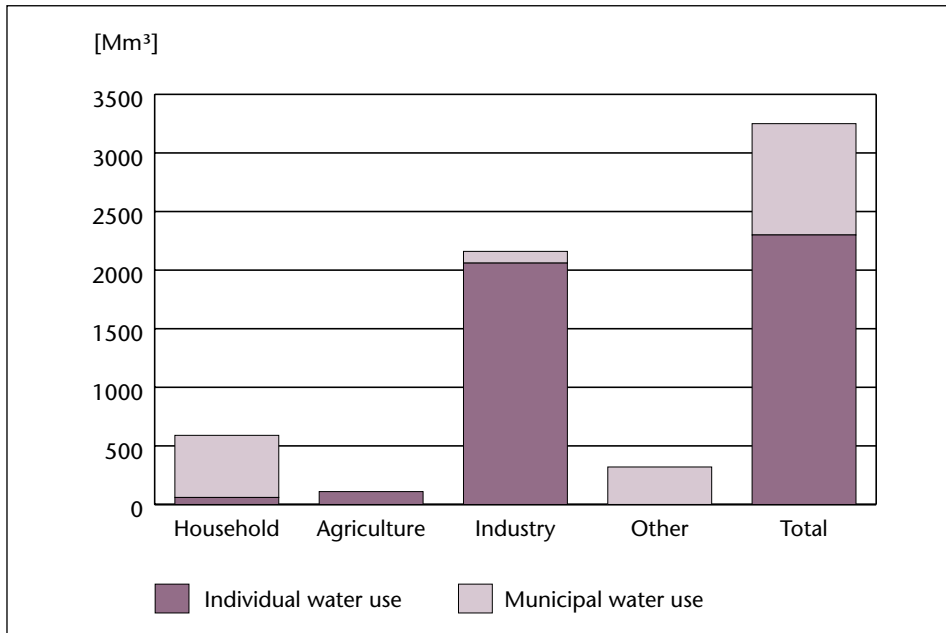
Figure 2.2 Water consumption in Sweden 2000 [SCB (Statistics Sweden), http://www.scb.se/
templates/tableOrChart_____27297.asp]

Households dominate with more than half of this consumption (57% in Swe-
den during the 1990s) while industry use no more than some 10%. Leakage in the
network is considerable and amounts to close to 25% of the total in all countries.

An important reason for decreased water consumption is the price for water.
Water companies, most of them municipally owned, charge for the provision of
potable water and treatment of sewage. Costs are mostly related to investments,
and not strongly so to the volumes. Still prices are related to consumption, which
helps reduce consumption.

Measures to save water in households are mostly trivial. This includes fixing
leakage in toilets – a running toilet uses much water over 24 hours – and kitchen
and bathrooms; the introduction of water efficient washing machines and dish
washers, and water reduction taps for e.g. showers. The reduction of water use is
coupled to reduction of warm water use.

Lower water costs thus lead to lower energy costs. Measures to reduce water
consumption in industry are partly of the same character. But more importantly a
radical new way to treat process water and other kinds of water typical for indus-
try are more important. These measures will be the topic of this chapter.
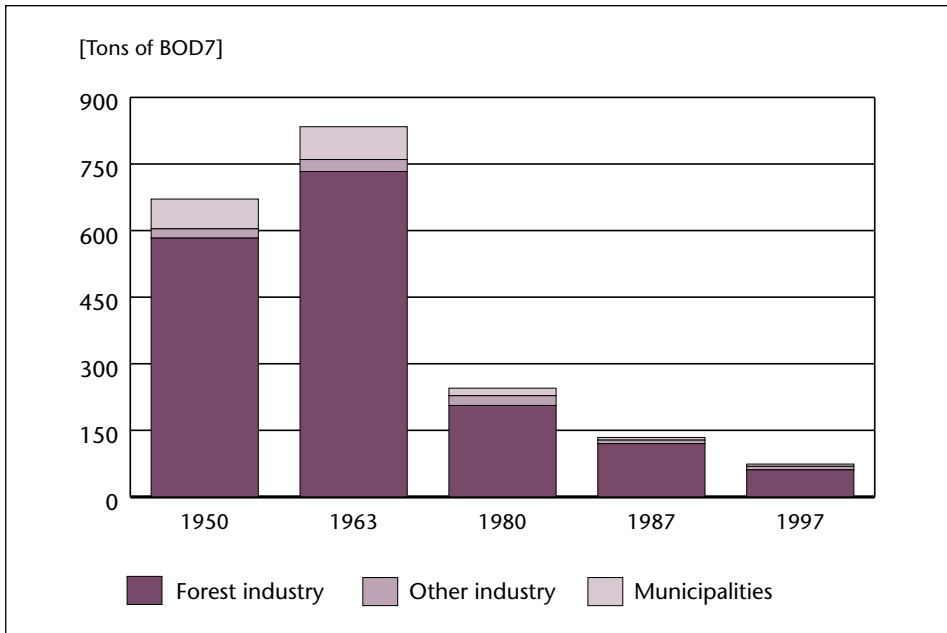
Figure 2.3 Emissions of biodegradable compounds from Swedish sources (BOD7) 1950-1997 [Persson and Nilson, 1998, compiled from the Swedish Environmental Protection Agency].

2.1.3 Integration of industrial and municipal water management

Industrial water handling, as well as solid waste treatment, has several connections to municipal water and solid waste treatment, basically because the industry often utilises the municipal wastewater treatment plants. If not, the same processes as in the municipal plants are often used. Naturally, industrial activities most often give rise to residual-product flows, entirely different from municipal waste flows, which has to be treated with its own technology.

The industry has the opportunity, already at the manufacturing stage to influence the amount and properties of the residual-flows. This possibility to process integrated solutions has, to a large extent, been used in industry. To combine internal and external measures in order to reduce emissions, at a low cost, is a very common feature of current industrial environmental protection technology. The large reduction of BOD-emissions (oxygen demanding) from the pulp and paper industry during the 70s and 80s and the very large reduction in organic chlorine compounds during later years are some illustrative examples (Figure 2.3).
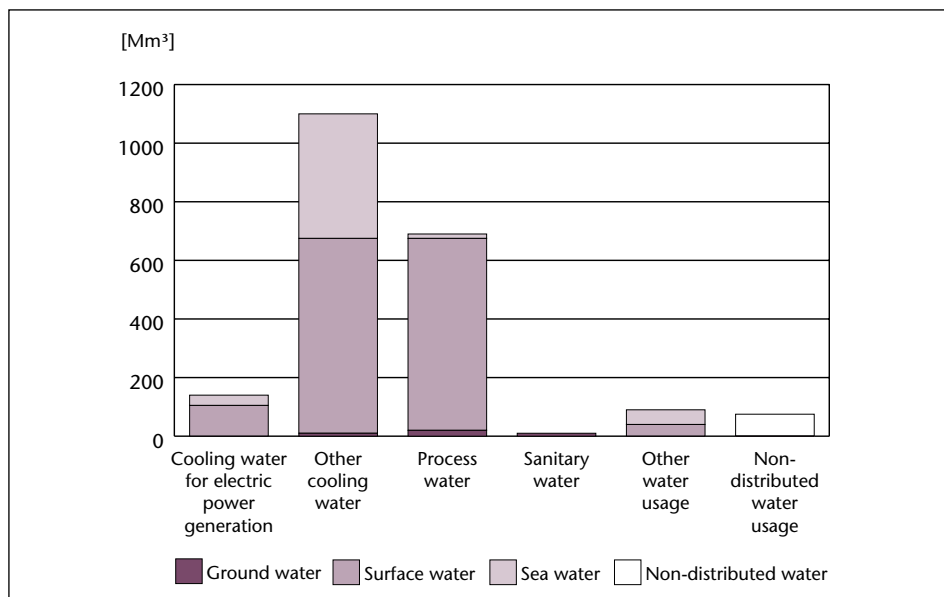
Figure 2.4. Industrial water use in Sweden in 2000 [SCB (Statistics Sweden), http://www.scb.se/templates/tableOrChart_____39386.asp].

2.1.4 Provision of water to industry

Figure 2.4 shows the details of water use in Swedish industry in year 2000 as an example. It is clear that volume-wise cooling water dominates followed by process water. Almost all of the water is withdrawn from surface water (lakes and rivers) and in a few cases as sea water. Ground water resources are thus not exploited for industrial purposes.

Industries with very large water demand have their own sources of water. However, smaller industries normally rely on municipal water. Their sources of water are thus the same as for municipal water, a mixture of ground and surface water, and artificially infiltrated water.

The volume of cooling water varies from industry to industry, depending on the amount of heat to be cooled away from the process. Industries with large demand of cooling water are situated along the coast or along rivers.

To use cleaned water from the municipal or industrial wastewater treatment plant as raw-water is one alternative that can be useful for areas with a restricted supply of water. To use reused wastewater can, however, present problems, practical as well as aesthetic. Due to variations in the inflow to the wastewater treatment plant it could become difficult to guarantee a certain quality of the

cleaned water. The wastewater treatment plant could be subject to disruptions which might mean longer or shorter production stops. An industry demanding continuous supply of raw water might therefore need an alternative raw-water source as a reserve from which, when necessary, water could be drawn.

2.2 Measures to reduce water consumption

2.2.1 Strategic choices

Water is an expensive raw material today. In earlier days water was a cheap resource that could be utilised in almost unlimited quantities, but today the costs for water supply and the treatment of wastewater have become considerable. It has thus become necessary, for economic reasons, to reduce water consumption.

Yet another reason for lowering water consumption is that emissions of pollutants from an industry depend on the wastewater production. One important step to reduce the effects of industrial emissions on the recipient and the external wastewater treatment plants is, therefore, to reduce the volume of the emissions. This can be achieved through:

- Separate handling of different kinds of wastewater.
- Process changes in order to reduce the volume of wastewater.
- Reuse of industrial wastewater as input water.
- Elimination of the intermittent emissions of process wastewater.

2.2.2 Separation of different kinds of wastewater

The kinds of water in an industry may be drastically different. Treatment of these streams separately is an important strategy. This refers to water provision, where e.g. cooling water may be withdrawn from a nearby river or lake, while process water may depend on municipal potable water. But even more so, it is important to separate the wastewater streams.

While the most polluted water should be subject to a thorough cleaning, the less polluted water may achieve a less thorough treatment or maybe even no treatment at all. This will in practice reduce the volume of wastewater significantly.

Wastewater can be divided into four classes:

Process water is part of the chemical or physical production processes. Process water may contain very specific components, pollutants, which require specific treatments. In some industries process water may be very large volumes.

Cooling water is water used to remove heat produced in the processes, e.g. in power plants. Large volumes of cooling water are used in some industries, e.g. nuclear power plants and cement industries. It is most often little, or not at all, polluted.

Sanitary wastewater is water from kitchens, toilets etc, the same as in households and residential areas. It is normally sent to the municipal sewage network.

Storm water is run-off from the industrial area, roofs and hard made surfaces. The character of storm water is dependent on the surface, and may be either similar to storm water from streets in the city or much more polluted.

Each of these streams will be discussed below.

2.2.3 Process water

Process water is the most important class of wastewater. The task is not only to reduce the cost for the used volume of water, but also to reduce the amount of pollutants in the water. In a wastewater treatment plant it is usually possible, independent of the incoming concentration, to reach a specific residual concentration in the cleaned water. It is usually rather difficult to lower the concentration under this level even if the incoming concentration is low. Since the emissions from an industry usually are calculated in kg or tonnes per day and not per litre wastewater, it is desirable to lower the amount of water to be cleaned as much as possible, even if it means that the concentration becomes higher (Figure 2.5).

From an economic point of view, it is more profitable having an as small as possible water flow, since that usually means a lower investment requirement, even if the amount of pollutants to be separated is the same.

$$F \cdot c_{in} = F \cdot c_{out} + M$$

F = volume flow of waste water [m³/d] (in and outflow)
c_{in} = incoming concentration pollutants [kg/m³]
c_{out} = rest concentration pollutants [kg/m³] (~ constant)
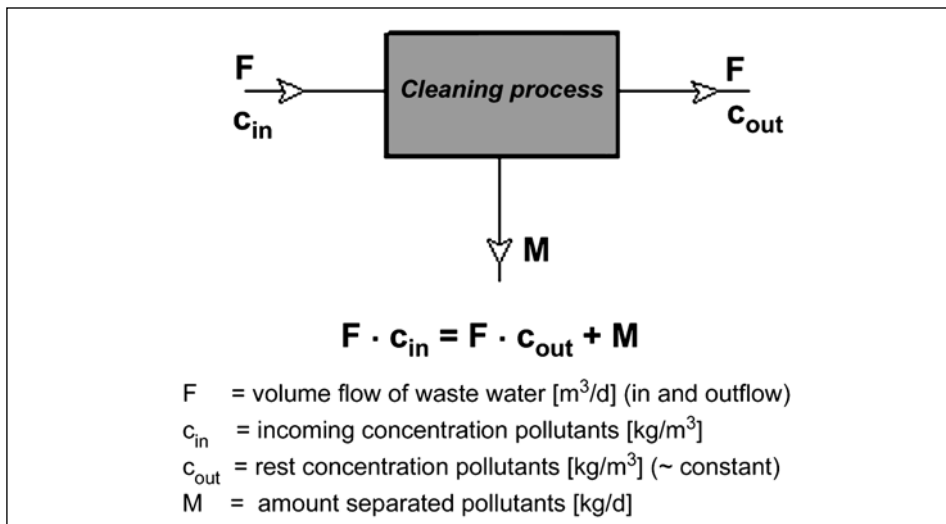M = amount separated pollutants [kg/d]

Figure 2.5 Waste watercleaning equation. A simple equation expresses how the amount of separated pollutants depends on wastewater flow. A low flow and higher concentration will improve the cleaning process.

Yet another, but equally important, point of view is to separate the pollutants from the wastewater as close to the source as possible and not to mix different wastewaters. It is always simpler and cheaper to separate one component from a solution if it is the only component present, compared to separating one component from a complex mixture.

The amount of water consumed to produce a certain amount of product is, as mentioned earlier, subject to continued reduction, among other things due to purposeful technological development towards less water consuming processes. Each unit operation in the industry demands generally as much water as earlier, but by recirculating the water within the process or reusing it after cleaning, the volumes of needed freshwater has been reduced step by step.

2.2.4 Cooling water

The volume of cooling water varies from industry to industry, depending on the amount of heat to be cooled away from the process. A large refinery, for instance, will use 500,000 m^3 per day, of which only 15,000 m^3 is process wastewater, the rest is cooling water with very small amounts of pollutants.

One possible solution for reducing the amount of cooling water is to use a closed cooling water circuit. By circulating the cooling water through a cooling tower the heat energy can be transferred from the water to air by evaporating a small part of the water. Another option is to use a heat pump to extract the heat energy from the cooling water at a higher, more useful temperature.

2.2.5 Sanitary wastewater

The volume of sanitary wastewater is normally between 75 and 150 litres per employee and day. The total amount produced depends on several factors, besides from the number of employees, for instance how much is flushed through floor drains during clean-up and what degree of personal hygiene is demanded from the personnel. Sanitary wastewater is normally sent to the municipal sewer network and treated like other wastewater. It is important that this water stream is not contaminated by industrial wastewater with pollutants not normally treated in the municipal wastewater treatment plant.

2.2.6 Storm water

Storm water is connected to the precipitation and varies therefore strongly with time. The amount of pollutants in the water depends on how much the ground in the draining area is polluted, which also decides the degree of cleaning needed. Storm water might sometimes go straight to a recipient or to a municipal waste-

water treatment plant without or after only simple pre-treatment (sedimentation) in storm water wells. In other cases the water must be treated in a separate waste-water treatment plant. The sludge from the storm water wells is treated and deposited as industrial sludge.

2.3 Process changes

2.3.1 Process changes to reduce water consumption

Just as the demand for water for human consumption can vary within certain limits the water demand for production of a certain product can vary. If there is a local shortage of water, or if its price entails large costs for a user, the user will try to save water or find substitutes. The savings are then twofold: the water costs as well as the cleaning costs are reduced. The generally most efficient way to decrease the amount of outgoing wastewater is process integration. First of all a substantial recirculation of process water is an alternative to decrease the amount of freshwater required. The prime problem is to avoid the build-up concentration of pollutants and by-products in the process water to unacceptable levels. This may be avoided by cleaning the process water after each cycle. An example is the water in a paper mill which passes the paper when it is formed. However, many changes to reduce the amount of wastewater are expensive, and the gain from the reduction has to be weighed against the costs. An alternative is a limited bleed flow, which goes to wastewater treatment.

Also important are measures which do not necessarily depend on investments, but result in a decrease in the water consumption just by "good housekeeping". Some examples are:

- Use the countercurrent principle in all washing, flushing and leaching processes.
- Re-circulate polluted water, if required after treatment.
- Use water for purposes with lower quality demands – down-classing of water.
- Flush-wash instead of dip-wash.
- Use closed cooling-water system.
- Check the actual demand for water, for instance by installing water meters to monitor consumption.
- Install magnetic valves which close off the water during production disruptions.
- Avoid leakage of water, flush over etc.

Useful examples of recirculation of water are found in the food industry, where water can be used several times starting from the "clean side" of production to the

first washing step. Sometimes an additional cleaning (intermediate cleaning) can take place, usually by sedimentation.

2.4 Cases of water conservation

Figure 2.6 shows the water cycle in a mill for recycled paper, where the evaporation losses are compensated for by re-circulating the wash water. Clean water is added only in the last washing step.

In order to achieve a recirculation of process water, substantial additional measures are required. These include desalination of the water. Evaporation would otherwise lead to a substantial increase in the salt concentration of the process water. Sludge also builds up, and measures are required to reduce it. Otherwise microorganisms would contaminate the process water.

An example of substitution of water with steam can be found in potato handling. Earlier, industrially peeled potatoes required an amount of 6 m^3 of soda per tone potatoes. Today the potatoes are peeled with steam. Water savings amounts to 60-70%. Another advantage of this new technique is that the peeling waste (about 150 kg/tonne potatoes) can be used as fodder. The amount of wastewater can be decreased by about 20% when soda, soil, and potato peels can be kept away from the wastewater.

There are many examples on production processes where water consumption has been decreased and, as a result, the amount of wastewater as well.
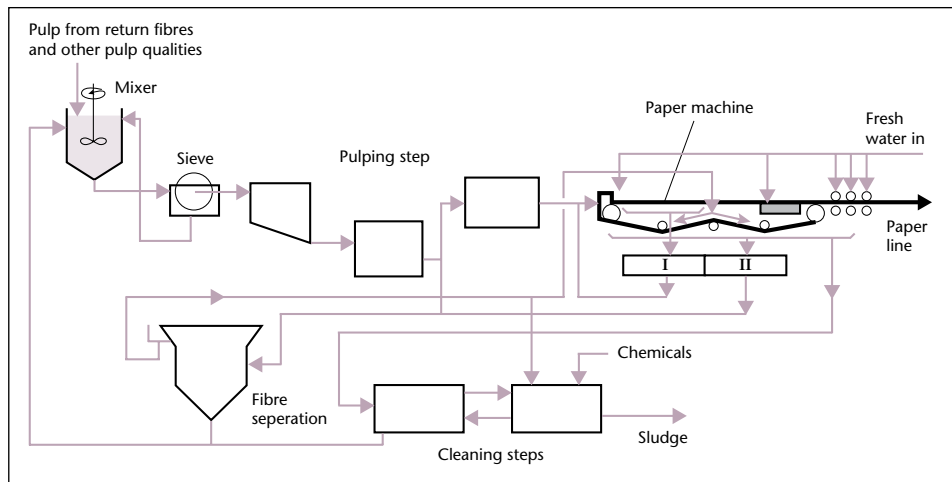
Figure 2.6 Water cycle in a mill for recycled paper.
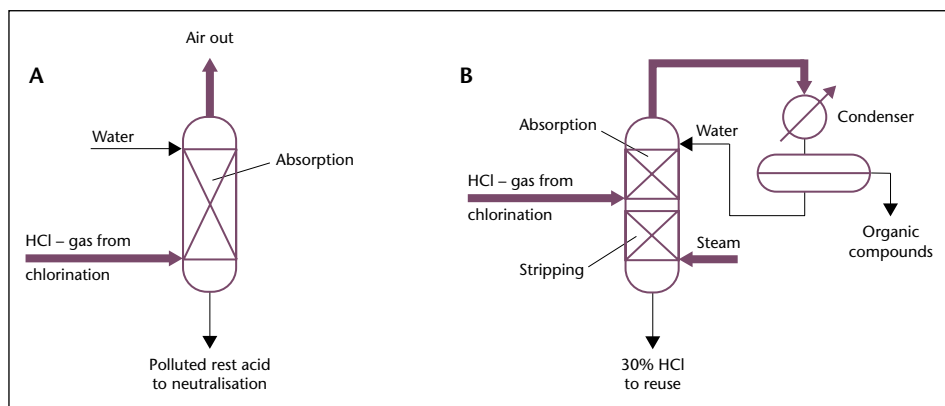
Figure 2.7 Processes for chlorinating of hydrocarbons; conventional absorption of HCl with water (A), and a new process – adiabatic absorption with evaporation (B), respectively.
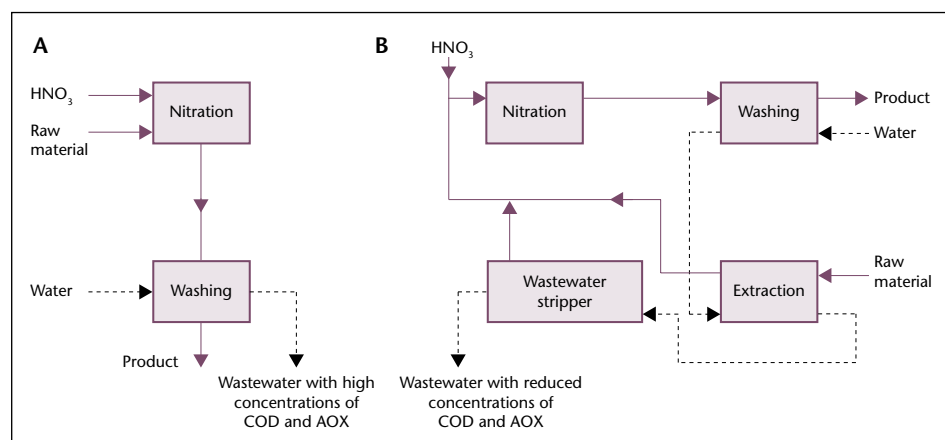
Figure 2.8 Nitration of hydrocarbons, an earlier process (A) and a developed process (B) which through reuse and recirculation of "rest"-products and unreacted raw material leads to a decreased environmental hazard potential in the wastewater.

In the classic chlorination of organic products, half of the added chlorine added to the reactor was unused and absorbed in water as dilute hydrochloric acid (HCl). (Figure 2.7). It was then included in the waste acid, which had to be neutralised. In a new chlorination process the absorption product is stripped with steam in order to evaporate the organic components, and yields a concentrated acid as by-product, to be used for other purposes.

The process has become completely free from wastewater as the separated organic compounds are recycled to the chlorination step.

Another example is shown in Figure 2.8.

An earlier process for nitration of hydrocarbons (chlorine aromatics, amines, etc.) has been improved. In the new process the organic compounds in the wash-water from the process is extracted with the incoming organic raw material in a countercurrent extraction column. The remaining hydrocarbons are evaporated and re-circulated. In addition to saving water, the environmental hazard potential of the wastewater has been decreased.

2.5 Different organizations for water conservation

2.5.1 Social movement "The Greening of Industry"

Mission

The Greening of Industry Network develops knowledge and transforms practice to accelerate progress toward a sustainable society.

Vision

The Network seeks to create new concepts and a new language that will make it possible to extend horizons and communicate across disciplines, nations, and sectors. The Network:

- Mobilizes a community of researchers to stimulate the emergence of a new strategic research area on the greening of industry.
- Creates a dialogue between this new research community and leaders in business, labour, civil society organizations, government.
- Provides an opportunity for all stakeholders, with equal voice, to develop research and action agendas on issues of industry, environment, and society.

2.5.2 Movement "Green Networking"

At the national and local level 'green networking' of a different kind has been established in many countries. It brings industry and authorities together to promote and encourage not only compliance with current legislation, including environmental licences like the EU-IPPC-licences. That is a precondition for becoming a member at all. The wider ambitions are about creating the background for 'going beyond compliance'. This means knowledge sharing and promoting new technology projects and best practices. Thus there is the Danish local 'Green Networks', which have been around for now 12-15 years. In Sweden there is the organisation Swedish Environmental Directors including many of the big companies, and there is a corresponding organisation in Finland.

There are also quite a few examples of companies entering into formal co-operation with one or more, typically nationally based, green NGOs. The subject

of the cooperation is to develop an 'Environmental Code of Conduct' or 'Environmentally best practices' in company matters like packaging, transport, waste handling, energy and water conservation etc. In this co-operation the company gets the 'blue stamp' from the NGO on its operations, when the agreed conduct or practices are complied with. It is the ethics of co-responsibility on the side of the NGOs which quite often makes NGOs hesitate to engage in such arrangements. But there are several examples from Germany.

Still, the awareness of the general public of the environmental behavior and performance of major industrial companies is as important as ever. A strong and rigorous pro-environment attitude of the general public is important to make industry comply with legislation. It is equally important for the political will to actually act and insist on compliance with current regulation in the countries where the companies operate. The NGOs have an important part to play in keeping people aware and on the alert on issues of environmental protection and sustainability and their violation. The NGOs are accepted as an influential and therefore important 'player' and partner at national, regional and international levels. NGOs are being asked for opinions on proposals, to sit on committees and help promote programmes and regulations. They also organise protests of different kinds as an instrument to influence especially regional and global, political decision-making on environmental protection issues.

Chapter 2 sources:

1- Lenart Nilsson, Per Olof Persson, Lars Ryden, Siarhei Dorozhka, Audrone Zaliauskiene, Cleaner Production – Technologies and Tools for Resource Efficient Production, Chapter 7, Water conservation, BUP Environmental management, 2007, ISBN 91-975526-1-5
2- The Greening of Industry Network (GIN) http://www.greeningofindustry.org/

Chapter 3
Water Softening and Stabilization for Industrial Use

3.1 Chemical water softening

3.1.1 Hardness definitions

The term hardness is used to characterize water that does not lather well, causes a scum in the bath tub, and leaves hard, white, crusty deposits (scale) on coffee pots, tea kettles, and hot water heaters. The failure to lather well and the formation of scum on bath tubs is the result of the reactions of calcium and magnesium with the soap. For example:

$Ca^{2+} + (soap)- = Ca(soap)_2$ s
where (s) = a solid precipitate
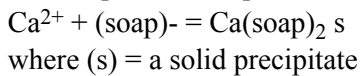
As a result of this complexation reaction, soap cannot interact with the dirt on clothing, and the calcium-soap complex itself forms undesirable precipitates. Hardness is defined as the sum of all polyvalent cations (in consistent units). The common units of expression are mg/L as $CaCO_3$ or milliequivalents per liter (meq/L). Qualitative terms used to describe hardness are listed in Table 3.1. Although all polyvalent cations contribute to hardness, the predominant contributors are calcium and magnesium. With the exception of a few other important polyvalent cations and natural organic matter (NOM), the focus of this discussion will be on calcium and magnesium.

Table 3.1. Hard water classification (Adapted from Mackenzy, 2010)

Hardness range (mg/L as $CaCO_3$)	Description	Comment
0–50	Extremely soft	-
50–100	Very soft	-
100–150	Soft to moderately hard	Acceptable to most users
150–300	Hard	-
>300	Very hard	-
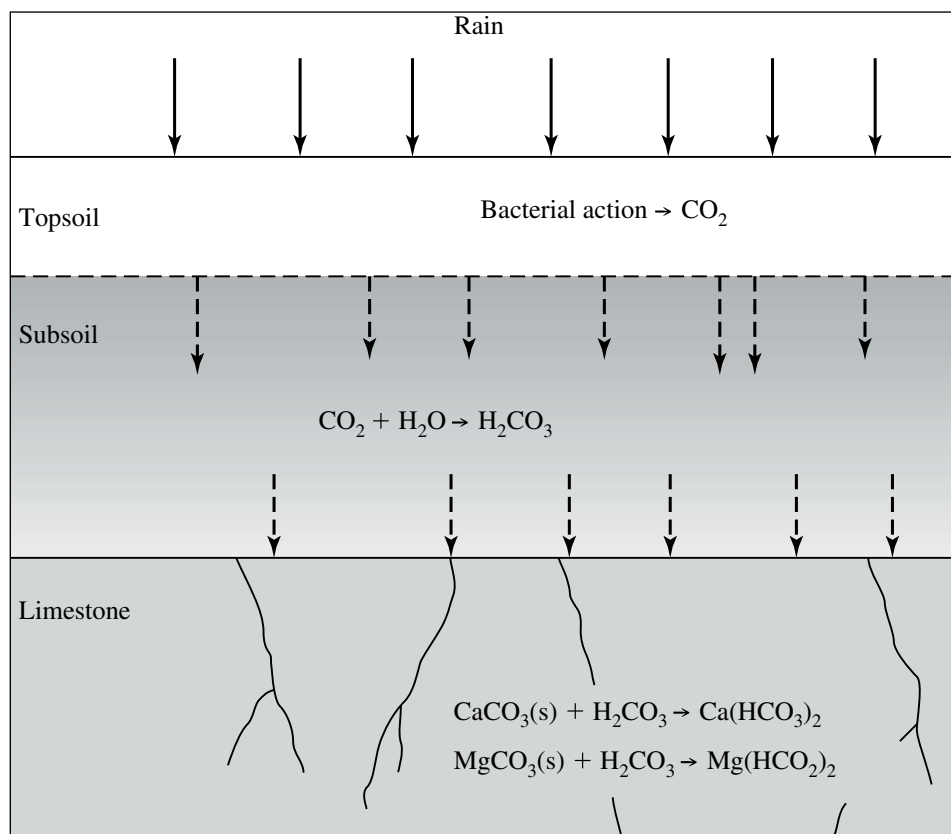
Figure 3.1 The natural process by which water becomes hard (Source: Davis and Cornwell, 2008.)

Hardness in natural waters comes from the dissolution of minerals from geologic formations that contain calcium and magnesium. Two common minerals are calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$]. The natural process by which water becomes hard is shown schematically in Figure 3.1. As rainwater enters the topsoil, the respiration of microorganisms increases the CO_2 content of the water. As shown in equations, the CO_2 reacts with the water to form H_2CO_3. Calcite and dolomite react with the carbonic acid to form calcium bicarbonate [$Ca(HCO_3)_2$] and magnesium bicarbonate [$Mg(HCO_3)_2$]. While $CaCO_3$ and $CaMg(CO_3)_2$ are not very soluble in water, the bicarbonates are quite soluble. Calcium chloride ($CaCl_2$), gypsum ($CaSO_4$), magnesium chloride ($MgCl_2$), and magnesium sulfate ($MgSO_4$) may also go into solution to contribute to the hardness.

Because calcium and magnesium predominate, the convention in performing softening calculations is to define the total hardness (TH) of water as the sum of these elements

$$TH = Ca^{2+} + Mg^{2+}$$

The concentrations of each element are in consistent units (mg/L as $CaCO_3$ or meq/L). Two components of total hardness are: (1) that associated with the HCO_3 anion (called carbonate hardness and abbreviated CH) and (2) that associated with other anions (called noncarbonate hardness and abbreviated NCH). Total hardness, then, may also be defined as:

$$TH = CH + NCH$$

Carbonate hardness is defined as the amount of hardness equal to the total hardness or the total alkalinity, whichever is less. Carbonate hardness is often called temporary hardness because boiling the water removes it. Heating drives the CO_2 out of solution and the pH increases.

Noncarbonate hardness is defined as the total hardness in excess of the alkalinity. If the alkalinity is equal to or greater than the total hardness, then there is no noncarbonate hardness. Noncarbonate hardness is called permanent hardness because it is not removed when water is heated. Bar charts of water composition are useful in understanding the process of softening. By convention, the bar chart is constructed with cations in the upper bar and anions in the lower bar.

In the upper bar, calcium is placed first and magnesium second. Other cations follow without any specified order. The lower bar is constructed with bicarbonate placed first. Other anions follow without any specified order.

The relationships between total hardness, carbonate hardness, and noncarbonate hardness are illustrated in Figure 3.2. In Figure 3.2.a , the total hardness is 250 mg/L as $CaCO_3$, the carbonate hardness is equal to the alkalinity $HCO_3^- =$ 200 mg/L as$CaCO_3$), and the noncarbonate hardness is equal to the difference between the total hardness and the carbonate hardness (NCH = TH-CH = 250 -200 = 50 mg/L as $CaCO_3$). In Figure 3.2.b , the total hardness is again 250 mg/L as $CaCO_3$. However, because the alkalinity HCO_3^- is greater than the total hardness, and because the carbonate hardness cannot be greater than the total hardness, the carbonate hardness is equal to the total hardness, that is, 250 mg/L as $CaCO_3$.

With the carbonate hardness equal to the total hardness, then all of the hardness is carbonate Hardness and there is no noncarbonate hardness. Note that in both cases it may be assumed that the pH is less than 8.3 because HCO_3^- is the only form of alkalinity present.
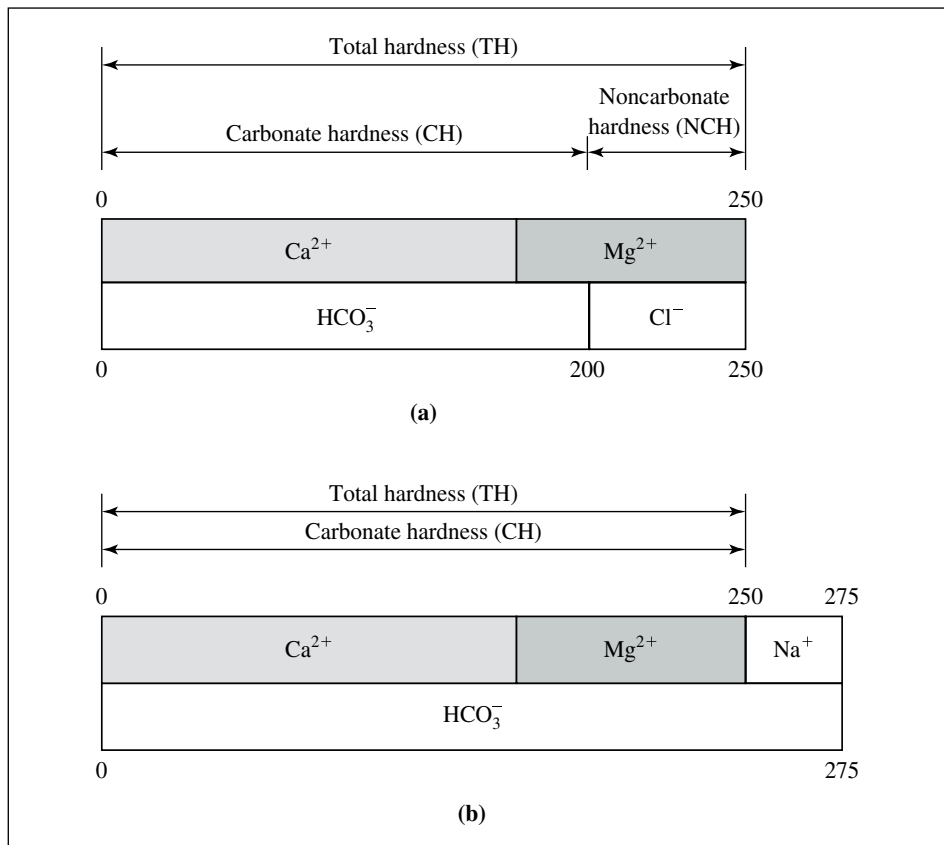
Figure 3.2. Relationships between total hardness, carbonate hardness, and noncarbonate hardness. (Source: Davis and Cornwell, 2008.)

Neutralization of carbonic acid

$$CO_2 + \mathbf{Ca(OH)_2} \rightleftharpoons CaCO_3(s) + H_2O$$

Precipitation of carbonate hardness

$$Ca^{2+} + 2HCO_3^- + \mathbf{Ca(OH)_2} \rightleftharpoons 2CaCO_3(s) + 2H_2O$$

$$Mg^{2+} + 2HCO_3^- + \mathbf{Ca(OH)_2} \rightleftharpoons MgCO_3 + CaCO_3(s) + 2H_2O$$

$$MgCO_3 + \mathbf{Ca(OH)_2} \rightleftharpoons Mg(OH)_2(s) + CaCO_3(s)$$

Precipitation of noncarbonate hardness due to calcium

$$Ca^{2+} + \mathbf{Na_2CO_3} \rightleftharpoons CaCO_3(s) + 2Na^+$$

Precipitation of noncarbonate hardness due to magnesium

$$Mg^{2+} + \mathbf{Ca(OH)_2} \rightleftharpoons Mg(OH)_2(s) + Ca^{2+}$$

$$Ca^{2+} + \mathbf{Na_2CO_3} \rightleftharpoons CaCO_3(s) + 2Na^+$$

Figure 3.3. Summary of softening reactions. (Note: The chemical added is printed in bold type. The precipitate is designated by(s). The arrow indicates where a compound formed in one reaction is used in another reaction.) (Source: David and Cornwell, 2008.)

The removal of ions that cause hardness is called softening. The majority of treatment systems that employ softening are those using a groundwater source. There are, however, a number of surface water sources with a groundwater component that is hard that employ softening as part of their treatment process. Softening can be accomplished by the lime-soda process, ion exchange, nanofiltration, or reverse osmosis. Lime-soda softening and other methods are discussed in this chapter.

3.1.2 Process limitations and empirical considerations

Lime-soda softening cannot produce a water completely free of hardness because of the solubility of $CaCO_3$ and $Mg(OH)_2$, the physical limitations of mixing and contact, and the lack of sufficient time for the reactions to go to completion. Thus, the minimum calcium hardness that can be achieved is about 30 mg/L as $CaCO_3$, and the minimum magnesium hardness is about 10 mg/L as $CaCO_3$. Historically the goal for final total hardness has been set at between 75 and 120 mg/L as $CaCO_3$. In recent years, many utilities have raised the target hardness to 120 to 150 mg/L as $CaCO_3$ to reduce chemical costs and residuals production (Horsley et al., 2005).

In order to achieve reasonable removal of hardness in a reasonable time period, an extra amount of $Ca(OH)_2$ beyond the stoichiometric amount usually is provided. Based on empirical experience, the minimum extra amount is 20 mg/L of $Ca(OH)_2$ expressed 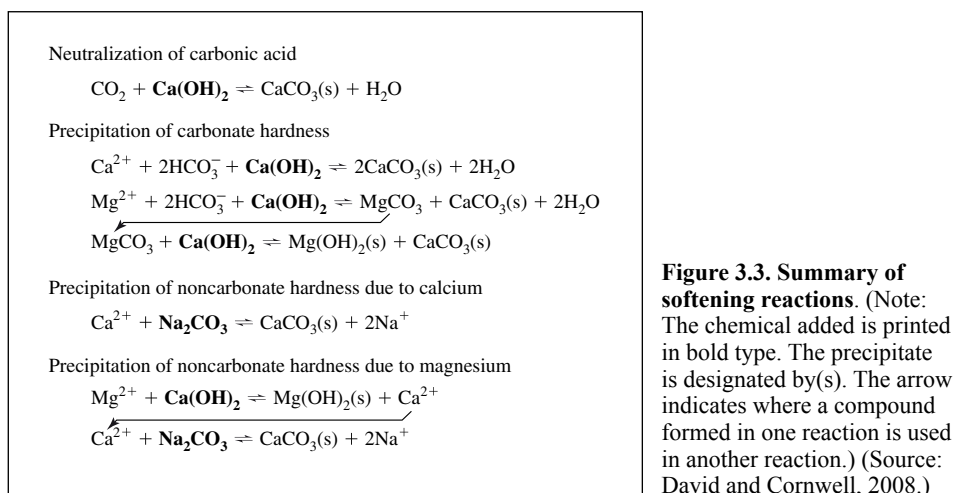as $CaCO_3$ (or 0.40 meq). Magnesium in excess of about 40 mg/L as $CaCO_3$ (0.80 meq) forms scales on heat exchange elements in hot water heaters. Because of the expense of removing magnesium, normally only the magnesium that is in excess of 40 mg/L as $CaCO_3$ is removed. For magnesium removals less than 20 mg/L as $CaCO_3$, the basic extra amount of lime mentioned above is sufficient to ensure good results. For magnesium removals between 20 and40 mg/L as $CaCO_3$, an extra amount of lime equal to the magnesium to be removed is added. For magnesium removals greater than 40 mg/L as $CaCO_3$, the extra lime addedis40 mg/L as $CaCO_3$. Addition of extra lime in amounts greater than 40 mg/L as $CaCO_3$ does not appreciably improve the reaction kinetics. Because the excess lime adds hardness in the form of Ca^{2+}, it is removed in a subsequent process step called recarbonation.

The sequence chemical additions (as $CaCO_3$) to soften water are summarized in Table 3.2.

3.1.3 Selective calcium removal

When the magnesium concentration is less than 40 mg/L as $CaCO_3$, lime softening (also called partial lime softening) can produce the desired final hard-

Table 3.2 Summary of chemical additions to soften water (Adapted from Mackenzy, 2010)

Step	Chemical addition a	Reason
Carbonate hardness		Neutralize H_2CO_3
1.	Lime = CO_2	Raise pH; convert HCO_3^- to CO_3^{2-}
2.	Lime = HCO_3^-	Raise pH; precipitate $Mg(OH)_2$
3.	Lime = Mg^{2+} to be removed	Drive reaction
4.	Lime = required excess	
Noncarbonate hardness	Soda = noncarbonate hardness	Provide CO_3^{2-}
5.	to be removed	

a The terms "Lime" and "Soda" refer to mg/L of $Ca(OH)_2$ and Na_2CO_3 respectively, as $CaCO_3$ equal to mg/L of ion (or gas in the case of CO_2) as $CaCO_3$.

ness. The alternative dosing schemes are dependent on the amount of carbonate alkalinity. In each instance CO_2 removal is shown by lime neutralization. This assumes that this is the economic alternative. In addition, it should be noted that lime must be added to the stoichiometric equivalent of the bicarbonate present regardless of the concentration of calcium. If the bicarbonate is not neutralized, the pH objective of 10.3 required to precipitate the calcium will not be achieved.

3.1.4 Split treatment
When the magnesium concentration is greater than 40 mg/L as $CaCO_3$, the flow is split to achieve a magnesium hardness of 40 mg/L as $CaCO_3$ as noted above. The portion of the flow that is treated is dosed to achieve the practical solubility limits for calcium and magnesium. The alternative dosing schemes are dependent on the amount of carbonate alkalinity. In each instance CO_2 removal is shown by lime neutralization. This assumes that this is the economic alternative.

If the total hardness after blending is above the desired final hardness, then further softening in a second stage is required. Because the split is designed to achieve a desired Mg^{2+} of 40 mg/L as $CaCO_3$, no further Mg^{2+} removal is required. Only treatment of Ca^{2+} is required. The dosing scheme for selective calcium removal is employed.

3.1.5 Use of caustic soda
Caustic soda (NaOH) is an alternative to the use of lime for softening. It has the advantages of decreased sludge production, reduction in dust generation, and the option of simpler storage and feed systems because it is purchased as a liquid.

There are several disadvantages in using caustic soda:

- the cost is four to six times higher than lime,
- the potential for hazardous chemical release is greater because it is a liquid,
- the freezing problems occur for 50 percent solutions at temperatures below 13 ºC (Kawamura, 2000).

The choice of caustic over lime will fundamentally be driven by economic evaluation of the cost of caustic, the feed system, and sludge treatment and disposal.

The stoichiometric reactions maybe derived by replacing $Ca(OH)_2$ with NaOH and rebalancing the reactions. Because Ca^{2+} hardness is not substituted for Mg^{2+}, the reactions shown in Equations 7-16 and 7-18 are not required. The sodium carbonate formed in the reactions of caustic with carbonate hardness is available to precipitate calcium noncarbonate hardness.
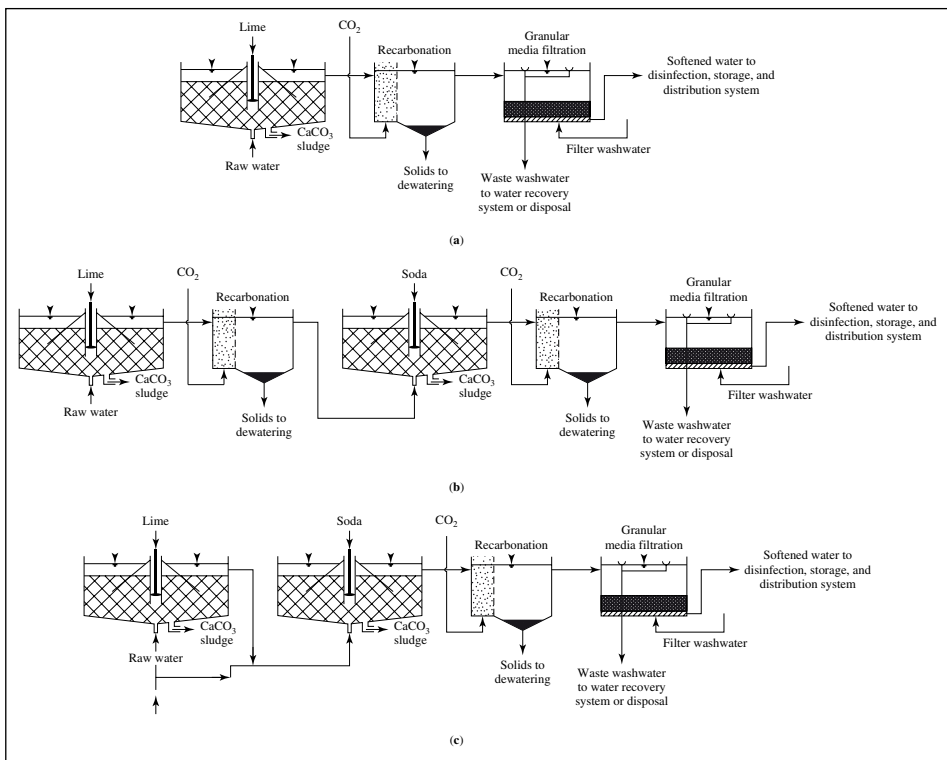

Figure 3.4. Softening process flow diagrams of common softening treatment techniques: (a) single-stage lime treatment; (b) two-stage excess lime-soda treatment; (c) split-flow lime treatment. Source: Davis, 2010.
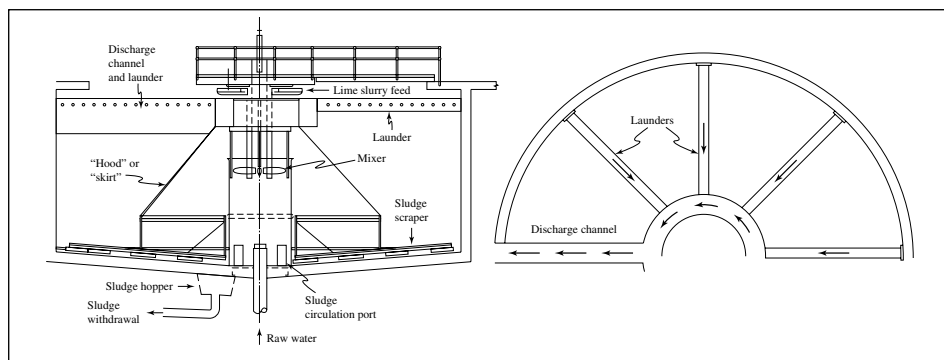
Figure 3.5. Upflow solids contact basin. The following information from Horsley et al. (2005) is provided for guidance in evaluating proprietary designs. (Source: Davis, 2010.)

3.1.6 Softening process configurations and design criteria

The process flow diagrams for three common softening treatment schemes are shown in Figure 3.4. Many other variations are possible including, for example, the use of blended raw water CO_2 to recarbonate and the use of coagulation and flocculation after the precipitation process to reduce the solids load to the filters. In the case of coagulation/flocculation, the high pH of the water coming from the precipitation process favors the use of ferric chloride as the coagulant because it is less soluble at higher pH than alum.

3.1.7 Upflow solids contact basins

Conventional softening basins are mostly found at older facilities. They provide a high degree of process stability, but the size and number of basins result in a high capital cost. Since the late 1960s most new plants have been built with upflow solids contact basins as shown in Figure 3.5.

Although rapid mixing maybe provided ahead of the solids contact unit, generally the softening chemicals are applied to the mixing zone of the contact unit. The mixing and recirculation zone is separated from the sedimentation zone by a conical baffle identified as the "hood" in Figure 3.5.

Effective solids contact units draw the settled precipitate from near the floor at the center of the basin with a large diameter turbine or impeller and recirculate it with the incoming water. When multiple units are used, the precipitate maybe recirculated from one unit to another. Because the units are sold as proprietary manufactured items, the designs are established by the manufacturer. Whenever possible, design requirements should be based on successful plants using the same or similar source water.

- The maximum recirculation rate is typically 10:1 based on the incoming raw water flow rate. The mixer is provided with a variable-speed drive to allow the operator to adjust the recirculation rate.
- The side water depth of the tank generallyvariesfrom 4.3 to 5.5 m. Contact time in the mixing zone is typically measured by the volume of water within and directly under the baffle cone.
- Overflow rate (that is, flow rate divided by the surface area, Q/ As) is generally measured 0.6 m below the water surface, based on the surface area between the baffle wall and the basin wall.

Following design criteria are recommended:

1. Flocculation and mixing period should not be less than 30 minutes.
2. Detention time should be two to four hours for solids contact clarifiers and softeners treating surface water.
3. Detention time should be one to two hours for solids contact clarifiers treating only groundwater.
4. Upflow rate (overflow rate) shall not exceed 2.4 cubic meters of flow per square meter of surface area per hour (m^3/h m^2 or m/h) at the slurry separation line for units used for clarifiers.
5. Upflow rate (overflow rate) shall not exceed 4.2 m^3/h m^2 or m/h at the slurry separation line for units used for softeners.
6. Weir loading shall not exceed 0.120 m^3/min m of weir length for units used as clarifiers.
7. Weir loading shall not exceed 0.240 m^3/min m of weir length for units used as softeners.

3.1.8 Operation and maintenance

The most important operation and maintenance task in softening is the selection of the appropriate chemicals and adjustment of the dose to changing raw water quality and plant flow. The second in the O&M monitoring of the chemical feed system is to detect clogging of the lines and maintenance of the mixers ranks need for close oversight. Encrustation is a significant problem. Annual removal of calcium carbonate build-up during seasonal low-demand periods is customary.

3.1.9 Hints from the field.

Experience suggests the following:
- Open flumes are preferred over pipelines.

- Design of pipelines and flumes should include additional capacity for encrustation.
- Sludge scraper mechanisms should be kept in operation during low-flow periods when portions of the plant are off-line but are not to be drained. This prevents the sludge blanket from settling and "freezing" the scraper so that it cannot start moving again because the settled sludge is too dense for the torque that can be applied.
- Sludge withdrawal (called blowdown) must occur regularly to keep the draft tube in an upflow clarifier open so that recirculation occurs in the mixing portion of the clarifier.

3.2 Ion exchange softening
3.2.1 Ion exchange applications
Ion exchange is widely used in the food & beverage, hydrometallurgical, metals finishing, chemical & petrochemical, pharmaceutical, sugar & sweeteners, ground & potable water, nuclear, softening & industrial water, semiconductor, power, and a host of other industries.

Most typical example of application is preparation of high purity water for power engineering, electronic and nuclear industries; i.e. polymeric or mineralic insoluble ion exchangers are widely used for water softening, water purification, water decontamination, etc.

Ion exchange is a method widely used in household (laundry detergents and water filters) to produce soft water. This is accomplished by exchanging calcium Ca^{2+} and magnesium Mg^{2+} cations against Na^+ or H^+ cations (see water softening). Another application for ion exchange in domestic water treatment is the removal of nitrate and natural organic matter.

Ion-exchange processes are used to separate and purify metals, including separating uranium from plutonium and other actinides, including thorium, and lanthanum, neodymium, ytterbium, samarium, lutetium, from each other and the other lanthanides. There are two series of rare earth metals, the lanthanides and the actinides, both of whose families all have very similar chemical and physical properties. Using methods developed by Frank Spedding in the 1940s, ion-exchange used to be the only practical way to separate them in large quantities, until the advent of solvent extraction techniques that can be scaled up enormously.

A very important case is the PUREX process (plutonium-uranium extraction process), which is used to separate the plutonium and the uranium from the spent fuel products from a nuclear reactor, and to be able to dispose of the waste prod-

ucts. Then, the plutonium and uranium are available for making nuclear-energy materials, such as new reactor fuel and nuclear weapons.

Ion exchangers are used in nuclear reprocessing and the treatment of radioactive waste.

Ion exchange resins in the form of thin membranes are used in chloralkali process, fuel cells and vanadium redox batteries.

3.2.2 Ion exchange resins and reactions

Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex. In most cases the term is used to denote the processes of purification, separation, and decontamination of aqueous and other ion-containing solutions with solid polymeric or mineralic 'ion exchangers'.

Typical ion exchangers are ion exchange resins (functionalized porous or gel polymer), zeolites, montmorillonite, clay, and soilhumus. Ion exchangers are either cation exchangers that exchange positively charged ions (cations) or anion exchangers that exchange negatively charged ions (anions). There are also amphoteric exchangers that are able to exchange both cations and anions simultaneously. However, the simultaneous exchange of cations and anions can be more efficiently performed in mixed beds that contain a mixture of anion and cation exchange resins, or passing the treated solution through several different ion exchange materials.

Ion exchangers can be unselective or have binding preferences for certain ions or classes of ions, depending on their chemical structure. This can be dependent on the size of the ions, their charge, or their structure. Typical examples of ions that can bind to ion exchangers are:

- H+ (proton) and OH− (hydroxide)
- Single-charged monatomic ions like Na^+, K^+, and Cl^-
- Double-charged monatomic ions like Ca^{2+} and Mg^{2+}
- Polyatomic inorganic ions like SO_4^{2-} and PO_4^{3-}
- Organic bases, usually molecules containing the aminefunctional group $-NR_2H^+$
- Organic acids, often molecules containing $-COO^-$ (carboxylic acid) functional groups
- Biomolecules that can be ionized: amino acids, peptides, proteins, etc.

Along with absorption and adsorption, ion exchange is a form of sorption.

Ion exchange is a reversible process and the ion exchanger can be regenerated or loaded with desirable ions by washing with an excess of these ions.
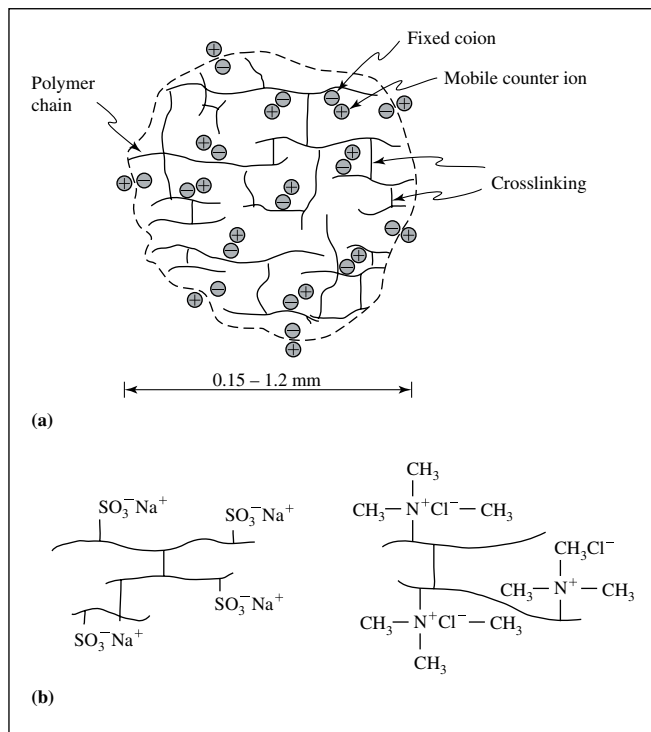
Figure 3.6. Schematic of organic cation-exchange bead (a). The bead is shown as a polystyrene polymer cross-linked with divinyl benzene with fixed coions (minus charge) balanced by mobile positively charged counterions (positive charge). (b) strong cation exchange resin on left (Na+ form) and strong-base on right (Cl- form). Source: Davis, 2010.

Typically, in water softening, sodium is exchanged for cations in solution. When the bed becomes saturated with the exchanged ion, it is shut down and regenerated by passing a concentrated solution of sodium back through the bed. Because of its large application in softening water, the focus of this chapter is on this application. The most common polymeric resin matrix is a cross-linked polystyrene to which charged functional groups are attached by covalent bonding. Divinylbenzene (DVB) is used as a cross-linking agent with the styrene. A higher DVB cross-linkage provides a more stable resin but will result in slower ion exchange kinetics. The common functional groups are in four categories: strongly acidic; weakly acidic; strongly basic; and weakly basic.

Figure 3.6 is a schematic representation of a resin bead and two typical functional groups. Cation exchange resins contain mobile positive ions, such as hydrogen or sodium that are attached to immobile functional acid groups, such as sulfonic and carboxylic groups. The functional groups are fixed to the resin matrix or backbone. These are the cation ion exchange sites. The number of sites

is finite, and when they all have been exchanged the ion exchange resin will no longer soften the water.

3.2.3 Strong cation exchange reactions.

The word "strong" in strong cation exchange does not refer to the physical strength of the resin but rather to the Arrhenius theory of electrolyte strength in which the functional group of the resin is dissociated completely in its ionic format any pH. Upper equation represents the exchange of sodium for calcium in the form of carbonate hardness and next equation represents the exchange of sodium for noncarbonate hardness where denotes the resin and the bold font represents the solid resin phase. Magnesium and other polyvalent ions are removed by similar reactions. The sulfonic group provides a strong reactive site and the exchange resin readily removes all polyvalent cations. The reactions are reversible.

$$Ca(HCO_3)_2 + 2\{\boxed{\equiv} - SO_3^- \, Na^+\} \rightleftharpoons \{\boxed{\equiv} - RSO_3\}_2 Ca^{2+} + 2NaHCO_3$$

$$CaCl_2 + 2\{\boxed{\equiv} - SO_3^- \, Na^+\} \rightleftharpoons \{\boxed{\equiv} - SO_3\}_2 Ca^{2+} + 2NaCl$$
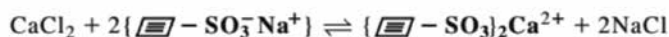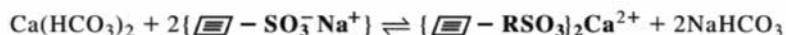
3.2.4 Weak cation exchange reactions.

The weak cation exchange resins can remove carbonate hardness as shown in equation, but they cannot remove noncarbonate hardness.

The weak cation exchange resins are regenerated with a strong acid (HCl or H_2SO_4).

$$Ca(HCO_3)_2 + 2\{\boxed{\equiv} - COOH\} \rightleftharpoons \{\boxed{\equiv} - COO\}_2 Ca + 2H_2CO_3$$
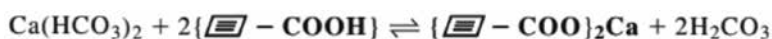
3.2.5 Ion exchange kinetics

The rate of ion exchange depends on the rates of the various transport mechanisms carrying the ion to be removed to the resin as well as the exchange reaction rate itself. The mechanisms are as follows: (1) movement of the ions from the bulk solution to the film or boundary layer surrounding the exchange solid, (2) diffusion of the ions through the film to the solid surface, (3) diffusion of the ions inward through the pores of the solid to the exchange sites, (4) exchange of the ions by reaction, (5) diffusion of the exchanged ions outward through the pores to the solid surface, (6) diffusion of the exchanged ions through the boundary layer, and (7) movement of the exchanged ions into the bulk solution.
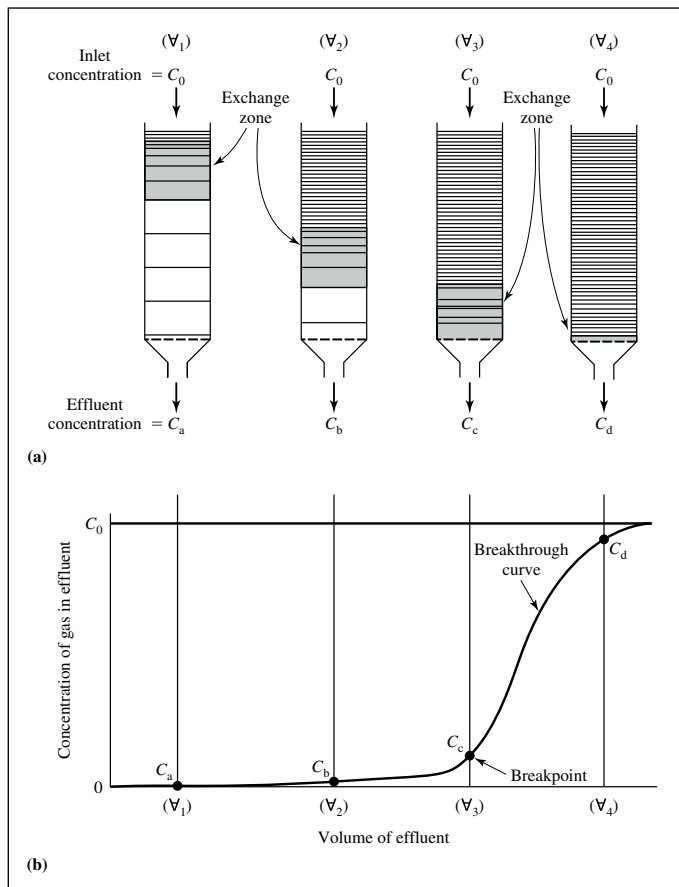
Figure 3.7 Ion exchange wave (a) and breakthrough (b). (Source: Treybal, 1968.)

For a column of resin, the exchange reactions begin to saturate the upper levels before the lower levels. The progress of this saturation through the column results in a "wave" of saturation as shown in Figure 3.7a . If samples are taken at the bottom of the column, a curve of increasing concentration is detected as shown in Figure 3.7b . This curve is called the breakthrough curve. At some point in time the effluent concentration exceeds the design criteria, for example at concentration Cc in Figure 3.7b . The column is then taken out of service and regenerated.

Exchange Capacity. One of the major considerations in selecting an ion exchange resin is the quantity of counterions that can be exchanged onto the resin. This quantity is called the exchange capacity of the resin. The total capacity is dependent on the quantity of functional groups on a resin bead. The exchange capacity maybe reported as milliequivalents per gram of dry resin (meq/g) or as

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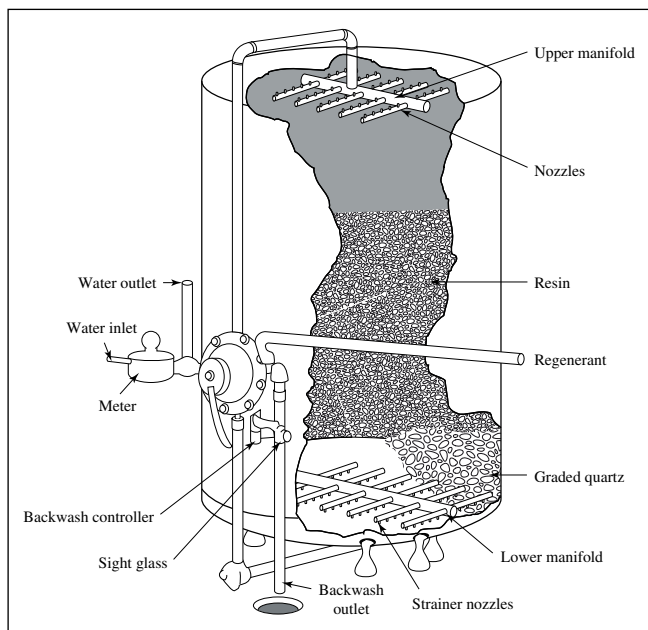
Figure 3.8 Typical ion exchange resin column. (Source:U.S. EPA, 1981.) The following steps are used in the ion exchange cycle :

milliequivalents per milliliter of wet resin (meq/mL). The typical dry-weight capacity of a strong acid cation exchange resin falls in the range of 3.6 to 5.5 meq/g. Typical wet-volume capacity is 1.8 to 2.0 meq $CaCO_3$/mL.

Resin Particle Size. Particle size has two effects on the ion exchange process. The rate of ion exchange decreases with increasing particle size. In contrast, the headloss through the bed increases as the bead size decreases. Because excessive pressure drops through the bed have the potential of causing physical damage to the resin beads, the hydraulic requirements of the resin rather than the kinetics for ion exchange govern the selection of the resin particle size. Ion exchange resin beads are spherical. They are produced in particle diameters ranging from0.04 to 1.0 mm. In the United States, the particle sizes are sold by standard sieve screen or "mesh" sizes.

The common sieve size ranges used are 16 to 50 and 50 to 100. The smaller number is the largest diameter sieve, and the larger number is the smallest diameter sieve. The manufacturer's specification is generally given the notation 16 × 50 or 50 × 100. Thus, for a 16 × 50 resin, all of the resin beads will pass the number 16 sieve, and none will pass the number 50 sieve.

Other data provided by the manufacturer includes the effective size (d10) and the uniformity coefficient. The effective size is the mesh size that passes10 percent of a sieved sample. The uniformity coefficient is the ratio of the d60 to the d10 resin sizes. These data are provided to facilitate hydraulic design.

3.2.6 Process operation

To contact the water with the ion exchange resin, it is passed through a columnar pressure vessel as shown in Figure 3.8. The water is passed through the column until the effluent no longer meets the treatment objective. The column is then regenerated.

- Service. The raw water is passed downward through the column until the hardness exiting the column exceeds the design limits. The column is taken out of service and another column is brought on line.
- Backwash. A flow of water is introduced through the underdrain. It flows up through the bed sufficient to expand the bed by 50 percent. The purpose is to relieve hydraulic compaction, and to move the finer resin material and fragments to the top of the column and remove any suspended solids that have accumulated during the service cycle.
- Regeneration. The regenerating chemical, for example, sodium chloride, flows downward through the bed at a slow rate to allow the reactions to proceed toward complete regeneration.
- Slow rinse. Rinse water is passed through the column at the same flow rate as the regenerating flow rate to push the regenerating chemical through the bed.
- Fast rinse. This is a final rinse step. The fast rinse flows at the same flow rate as the service flow rate to remove any remaining regenerating solution.
- Return to service. The column is put back in use.

3.3 Purified water stabilization

A stable water is one that exhibits neither scale forming nor corrosion properties. In the water industry, a stable water is considered to be one that will neither dissolve nor deposit calcium. The original objective of water stabilization was to adjust the pH of the treated water to prevent corrosion of the water distribution system pipes by depositing a thin film of calcium carbonate as a protective coating. Numerous investigations have revealed that although the Langelier index (a method of calculating stability) is a reasonable predictor of the potential for $CaCO_3$ to precipitate or dissolve, it does not predict how much $CaCO_3(s)$ will precipitate or whether its structure will provide resistance to corrosion (Schock, 1999).

Although its validity as a method of corrosion protection is limited, the Langelier index is still useful in predicting the potential for $CaCO_3$ to precipitate or dissolve. This is particularly valuable in designing the processes to reduce precipitation of $CaCO_3$ in the rapid sand filters and pipe network as well as those

processes used to reduce the corrosivity of reverse osmosis/nanofiltration (RO/NF) treated water.

The Langelier Saturation Index (LSI)

Langelier (1936) developed the following relationship to predict whether or not a given water will deposit or dissolve $CaCO_3$:

$$LSI = pH - pHs$$

Where: pH is in the actual hydrogen ion concentration and pHs is the pH at saturation. pHs is further defined as

$$pHs = pCa^{2+} + pAlk + C$$

where: pCa^{2+} = negative logarithm of the calcium on concentration, moles/L

pAlk = negative logarithm of the total alkalinity, equiv/L

C = an empirical constant to correct for ionic strength and the temperature dependence of the solubility of $CaCO_3(s)$

The value of the constant depends from various ionic strengths (or total dissolved solids (TDS) concentrations) and temperatures.

The state of saturation with respect to $CaCO_3$ depends on the LSI:

- If the LSI < 0, then the solution is undersaturatedand$CaCO_3$ will dissolve.
- If the LSI = 0, the solution is at equilibrium.
- If the LSI > 0, then the solution is supersaturated and $CaCO_3$ will precipitate.

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Chapter 4
Membranes for Industrial Water Filtration and Demineralization

4.1 General definitions of membrane processes

A membrane is a selective barrier. At times, it is also an outer covering of cell or cell organelle that allows the passage of certain constituents and retains other constituents found in the liquid. The influent of a membrane is known as the feed-stream, the liquid that passes through the membrane is known as the permeate and the liquid containing the retained constituents is the retentate or concentrate.

The concept of a membrane has been known since the eighteenth century, but was used little outside of the laboratory until the end of World War II. Drinking water supplies in Europe had been compromised by the war and membrane filters were used to test for water safety. However, due to the lack of reliability, slow operation, reduced selectivity and elevated costs, membranes were not widely exploited. The first use of membranes on a large scale was with micro-filtration and ultra-filtration technologies. Since the 1980s, these separation processes, along
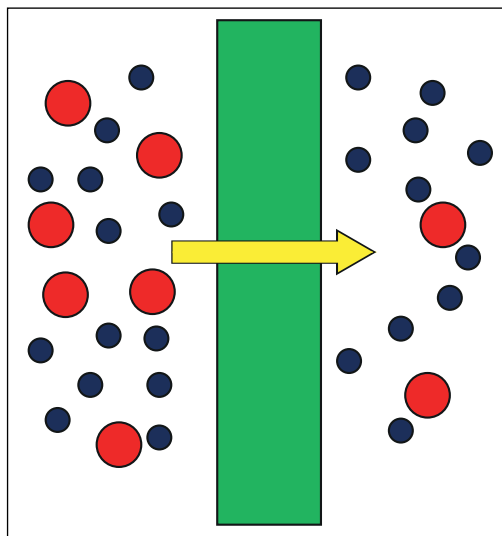
Figure 4.1. Schematic image of size based membrane exclusion (Adapted from internet http://www.separation processes. com/ Membrane)
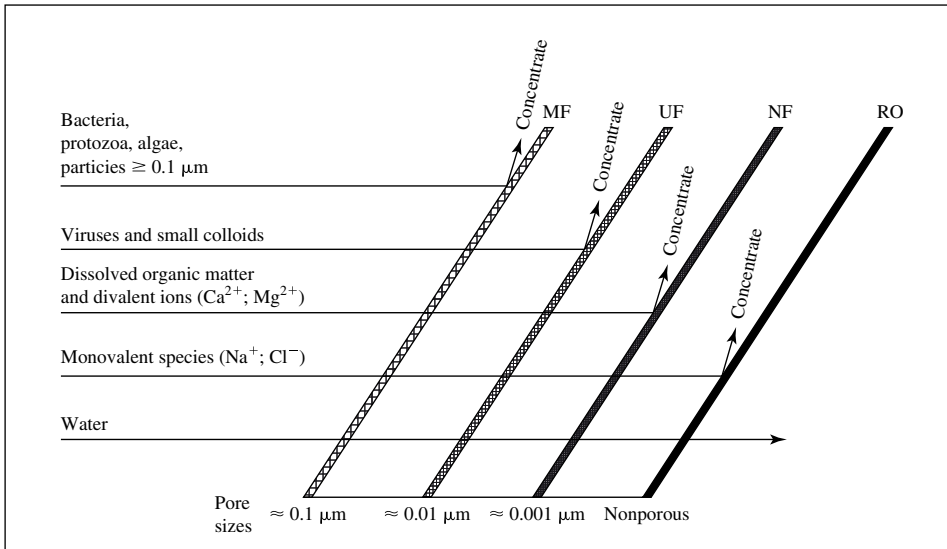
Figure 4.2 Common constituents removed by membrane processes. MF - microfiltration; UF - ultrafiltration; NF - nanofiltration; RO - reverse osmosis. (Adapted from Metcalf and Eddy.2004). Source: Davis, 2010.

with electrodialysis, are employed in large plants and, today, a number of experienced companies serve the market.

The degree of selectivity of a membrane depends on the membrane pore size. Depending on the pore size, they can be classified as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes. Membranes can also be of various thicknesses, with homogeneous or heterogeneous structure. Membranes can be neutral or charged, and particle transport can be active or passive. The latter can be facilitated by pressure, concentration, chemical or electrical gradients of the membrane process. Membranes can be generally classified into synthetic membranes and biological membranes.

4.2 Membrane processes classification

Microfiltration (MF)

Microfiltration removes particles higher than 0,08-2 µm and operates within a range of 7-100 kPa.[4] Microfiltration is used to remove residual suspended solids (SS), to remove bacteria in order to condition the water for effective disinfection and as a pre-treatment step for reverse osmosis.

Relatively recent developments are membrane bioreactors (MBR) which combine microfiltration and a bioreactor for biological treatment.

Table 4.1. Commonly used membrane techniques in industry. Source: Rosenberg 1995, Childress and Elemelech 2000, Pouliot 2000.

Type	Pore size	Molecular weight cut off	Pressure and principle	Compounds in retentate	Application in dairy industry
Microfiltration	0.2-2 μm	>200 kDa	Low pressure (below 2 bar) driven membrane process	Low retentate, separation of protein, bacteria and other particulates	- Skim milk and cheese - Dextrose clarification - Bacteria removal
Ultrafiltration	1-500	1-200 kDa	Medium pressure (1-10 bar) pressure driven process to overcome the viscosity	Large retentate with casein micelles, fat globules, colloidal minerals, bacteria and somatic cells	- Standardization of milk, reduction of calcium and lactose - Protein. whey, milk concentration
Nanofiltration	0.5-2 nm	300-1,000 Da	Medium to high pressure (5-40 bar), mass transfer phenomena by size exclusion and electrostatic interactions	Low productivity, separate monovalents salt and water	Desalting of whey, lactose free milk, volume reduction
Reverse osmosis or hyperfiltration	No pores	100 Da	High pressure, (10-100 bar)	Based on the principle of solubility, low productivity	Volume reduction, recovery of total solids and water

Ultrafiltration (UF)

Ultrafiltration removes particles higher than 0,005-2 μm and operates within a range of 70-700kPa.[4] Ultrafiltration is used for many of the same applications as microfiltration. Some ultrafiltration membranes have also been used to remove dissolved compounds with high molecular weight, such as proteins and carbohydrates. In addition, they are able to remove viruses and some endotoxins.

Nanofiltration (NF)

Nanofiltration is also known as "loose" RO and can reject particles smaller than 0,001 μm. Nanofiltration is used for the removal of selected dissolved constituents from wastewater. NF is primarily developed as a membrane softening process which offers an alternative to chemical softening.

Likewise, nanofiltration can be used as a pre-treatment before directed reverse osmosis. The main objectives of NF pre-treatment are: (1). minimize particulate and microbial fouling of the RO membranes by removal of turbidity and bacteria, (2) prevent scaling by removal of the hardness ions, (3) lower the operating pressure of the RO process by reducing the feed-water total dissolved solids (TDS) concentration.

Reverse osmosis (RO)

Reverse osmosis is commonly used for desalination. As well, RO is commonly used for the removal of dissolved constituents from wastewater remaining after advanced treatment with microfiltration. RO excludes ions but it requires high pressures to produce deionizer water (850-7000 kPa).

4.3 Membrane configurations

In the membrane field, the term module is used to describe a complete unit composed of the membranes, the pressure support structure, the feed inlet, the outlet permeate and retentate streams, and an overall support structure. The principal types of membrane modules are:

- Tubular, where membranes are placed inside a support porous tubes, and these tubes are placed together in a cylindrical shell to form the unit module. Tubular devices are primarily used in micro and ultra filtration applications because of their ability to handle process streams with high solids and high viscosity properties, as well as for their relative ease of cleaning.
- Spiral Wound, (Figure 4.3.) where a flexible permeate spacer is placed between two flat membranes sheet. A flexible feed spacer is added and the flat sheets are rolled into a circular configuration.
- Hollow fiber, consists of a bundle of hundreds to thousands of hollow fibers. The entire assembly is inserted into a pressure vessel. The feed can be applied to the inside of the fiber (inside-out flow) or the outside of the fiber (outside-in flow).
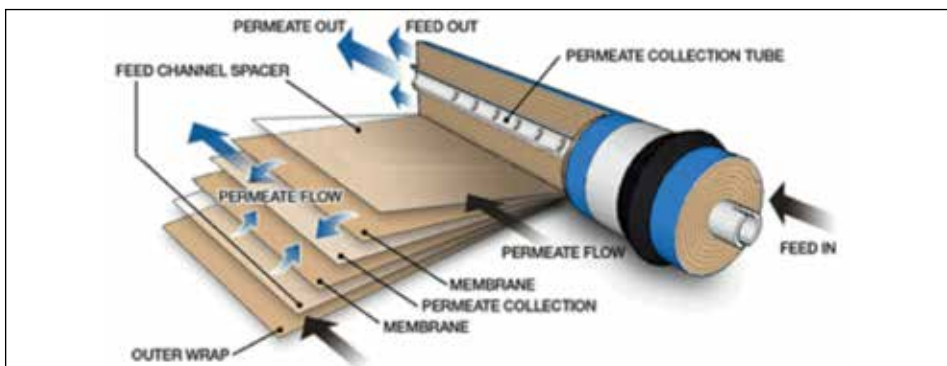
Figure 4.3. Spiral wounded membrane configurations: (Adapted from internet http://www. separation processes. com/Membrane/MT_FigGen10.htm)

- Plate and frame consist of a series of flat membrane sheets and support plates. The water to be treated passes between the membranes of two adjacent membrane assemblies. The plate supports the membranes and provides a channel for the permeate to flow out of the unit module.
- Ceramic and polymeric flat sheet membranes and modules. Flat sheet membranes are typically built-into a submerged vacuum driven filtration systems which consist of stacks of modules each with a number of sheets. Filtration mode is outside-in where the water passes through the membrane and is collected in permeate channels. Cleaning can be performed by aeration, back wash and CIP.

The key elements of any membrane process relate to the influence of the following parameters on the overall permeate flux are:
- The membrane permeability (k)
- The operational driving force per unit membrane area (Trans Membrane Pressure, TMP)
- The fouling and subsequent cleaning of the membrane surface.

4.3.1 Flux, pressure, permeability
The total permeate flow from a membrane system is given by following equation:

$$Q_p = F_w \cdot A$$

Where Qp is the permeate stream flowrate [kg·s^{-1}], Fw is the water flux rate [kg·m^{-2}·s^{-1}] and A is the membrane area [m^2]
The permeability (k) [m·s^{-2}·bar^{-1}] of a membrane is given by the next equation:

$$k = \frac{F_w}{P_{TMP}}$$

The transmembrane pressure (TMP) is given by the following expression:

$$P_{TMP} = \frac{(P_f + P_c)}{2} - P_p$$

where PTMP is the Transmembrane Pressure [kPa], Pf the inlet pressure of feed stream [kPa]; Pc the pressure of concentrate stream [kPa]; Pp the pressure if permeate stream [kPa].

The rejection (r) could be defined as the amount of particles that have been removed from the feedwater.

$$r = \frac{(C_f - C_p)}{C_f} \cdot 100$$

The corresponding mass balance equations are:

$$Q_f = Q_p + Q_c$$
$$Q_f \cdot C_f = Q_p \cdot C_p + Q_c \cdot C_c$$

In order to control the operation of a membrane process, two modes, with respect to the flux and to the TMP (Trans Membrane Pressure), can be used. These modes are: (1) constant TMP and (2) constant flux.

The operation modes will be affected when the rejected materials and particles in the retentate tend to accumulate in the membrane. At a given TMP, the flux of water through the membrane will decrease and at a given flux, the TMP will increase, reducing the permeability (k). This phenomenon is known as fouling, and it is the main limitation to membrane process operation.

4.3.2 Dead-end and cross-flow operation modes

Two operation modes for membranes can be used. These modes are:

- Dead end filtration where all the feed applied to the membrane passes through it, obtaining a permeate. Since there is no concentrate stream, all the particles are retained in the membrane. Raw feed-water is sometimes used to flush the accumulated material from the membrane surface.
- Cross-flow filtration where the feed water is pumped with a cross flow tangential to the membrane and a concentrate and permeate streams are obtained. This model implies that for a flow of feed-water across the membrane, only a fraction is converted to permeate product. This parameter is termed "conversion" or "recovery" (S). The recovery will be reduced if the permeate is further used for maintaining processes operation, usually for membrane cleaning.

$$S = \frac{Q_{permeate}}{Q_{feed}} = 1 - \frac{Q_{concentrate}}{Q_{feed}}$$

Filtration leads to an increase of the resistance against the flow. In the case of dead-end filtration process, the resistance increases according to the thickness of the cake formed on the membrane. As a consequence, the permeability (k) and the flux rapidly decrease, proportionally to the solids concentration and, thus, requiring a periodic cleaning.

For cross-flow processes, the deposition of material will continue until the forces of the binding cake to the membrane will be balanced by the forces of the

fluid. At this point, cross-flow filtration will reach a steady-state condition, and thus, the flux will remain constant with time. Therefore, this configuration will demand less periodic cleaning.

4.3.3 Fouling
Fouling can be defined as the potential deposition and accumulation of constituents in the feed stream on the membrane.

Fouling can take place through a number of physicochemical and biological mechanisms which are related to the increase deposition of solid material onto the membrane surface. The main mechanisms by which fouling can occur, are:
- Build-up of constituents of the feedwater on the membrane which causes a resistance to flow. This build-up can be divided into different types:
  Pore narrowing, which consists of solid material that it has been attached to the interior surface of the pores.
  Pore blocking occurs when the particles of the feed-water become stuck in the pores of the membrane.
  Gel/cake layer formation takes places when the solid matter in the feed is larger than the pore sizes of the membrane.
- Formation of chemical precipitates known as scaling
- Colonization of the membrane or biofouling takes place when microorganisms grow on the membrane surface.

4.3.4 Fouling control and mitigation
Since fouling is an important consideration in the design and operation of membrane systems, as it affects pre-treatment needs, cleaning requirements, operating conditions, cost and performance, it should prevented, and if necessary, removed. Optimizing the operation conditions is important to prevent fouling. However, if fouling have already take place, it should be removed by using physical or chemical cleaning.

Physical cleaning techniques for membrane include membrane relaxation and membrane backwashing.
- Back-washing or back-flushing consist of pumping the permeate in the reverse direction through the membrane. Back-washing removes successfully most of the reversible fouling caused by pore blocking. Backwashing can also be enhanced by flushing air through the membrane. Backwashing increase the operating costs since energy is required to achieve a pressure suitable for permeate flow reversion.
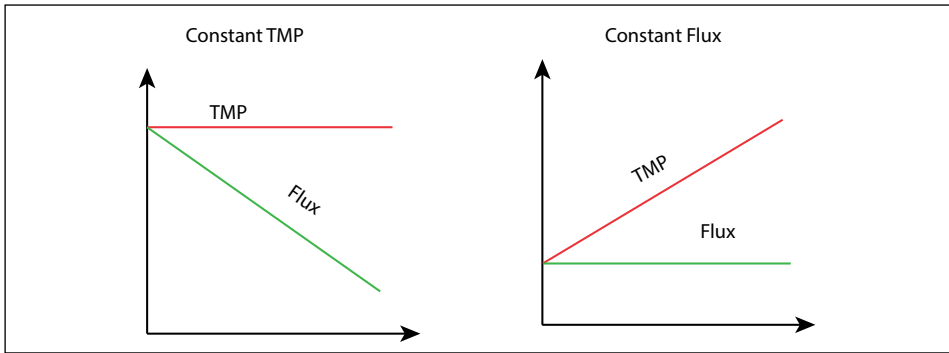
Figure 4.4. Constant TMP and constant Flux operations (Adapted from http://www./ thumb/440px-Constant_TMP_and_constant_Flux.jpg)

- Membrane relaxation consists of pausing the filtration during a period of time, and thus, there is no need for permeate flow reversion. Relaxation allows filtration to be maintained for longer period of time before the chemical cleaning of the membrane.
- Back pulsing high frequency back pulsing resulting in efficient removal of dirt layer. This method is most commonly used for ceramic membranes.

Recent studies have assessed to combine relaxation and backwashing for optimum results.

Chemical cleaning.
Relaxation and backwashing effectiveness will decrease with operation time as more irreversible fouling accumulates on the membrane surface. Therefore, besides the physical cleaning, chemical cleaning may also be recommended. They include:
- Chemical enhanced backwash, that is, a low concentration of chemical cleaning agent is added during the backwashing period.
- Chemical cleaning, where the main cleaning agents are sodium hypochlorite (for organic fouling) and citric acid (for inorganic fouling). It should be point out, though, that every membrane supplier proposes their own chemical cleaning recipes, which differ mainly in terms of concentration and methods.

Optimizing the operation condition
Several mechanisms can be carried out to optimize the operation conditions of the membrane to prevent fouling, for instance:
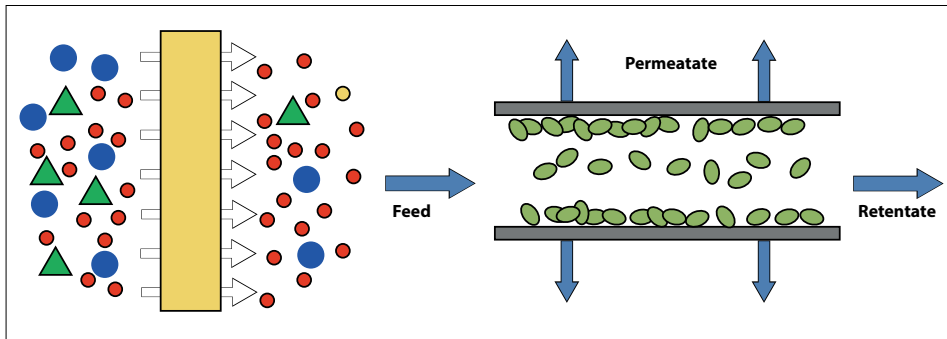
Figure 4.5. Schematic process of dead-end and cross-flow filtration (Adapted from internet http://www /Cross-flow.svg/300px-Cross-flow.svg.png)

- Reducing flux. The flux always reduces fouling but obviously it impacts on capital cost since it demands more membrane area. It consists of working at sustainable flux which can be defined as the flux for which the TMP increases gradually at an acceptable rate, such that chemical cleaning is not necessary.
- Using cross-flow filtration instead of dead-end. In cross-flow filtration only a thin layer is deposited on the membrane since not all the particles are retained on the membrane, but the concentrate removes them.
- Pre-treatment of the feed water is used to reduce the suspended solids and bacterial content of the feed-water. Flocculants and coagulants are also used, like ferric chloride and aluminum sulfate that, once dissolved in the water, adsorbs materials such as suspended solids, colloids and soluble organic.

Applications

Distinct features of membranes are responsible for the interest in using them as additional unit operation for separation processes in fluid processes. Some advantages noted include:

- Less energy-intensive, since they do not require major phase changes
- Do not demand adsorbents or solvents, which may be expensive or difficult to handle
- Equipment simplicity and modularity, which facilitates the incorporation of more efficient membranes

Membranes are used with pressure as the driving processes in membrane filtration of solutes and in reverse osmosis. In dialysis and pervaporation the chemical

potential along a concentration gradient is the driving force. Also pertraction as a membrane assisted extraction process relies on the gradient in chemical potential.

However, their overwhelming success in biological systems is not matched by their application.[1] The main reasons for this are named

- Fouling – the decrease of function with use
- Prohibitive cost per membrane area
- Lack of solvent resistant materials
- Scale up risks

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Chapter 5
Electrochemical Water Purification for Industrial Use

5.1 Electrodialysis for water purification

5.1.1 Electrodialysis method description

Electrodialysis (ED) is used to transport salt ions from one solution through ion-exchange membranes to another solution under the influence of an applied electric potential difference. This is done in a conFigureuration called an electrodialysis cell. The cell consists of a feed (diluate) compartment and a concentrate (brine) compartment formed by an anion exchange membrane and a cation exchange membrane placed between two electrodes. In almost all practical electrodialysis processes, multiple electrodialysis cells are arranged into a conFigureuration called an electrodialysis stack, with alternating anion and cation exchange membranes forming the multiple electrodialysis cells. Electrodialysis processes are different compared to distillation techniques and other membrane based processes (such as reverse osmosis) in that dissolved species are moved away from the feed stream rather than the reverse. Because the quantity of dissolved species in the feed stream is far less than that of the fluid, electrodialysis offers the practical advantage of much higher feed recovery in many applications.

In an electrodialysis stack, the diluate (D) feed stream, brine or concentrate (C) stream, and electrode (E) stream are allowed to flow through the appropriate cell compartments formed by the ion exchange membranes. Under the influence of an electrical potential difference, the negatively charged ions (e.g., chloride) in the diluate stream migrate toward the positively charged anode. These ions pass through the positively charged anion exchange membrane, but are prevented from further migration toward the anode by the negatively charged cation exchange membrane and therefore stay in the C stream, which becomes concentrated with the anions. The positively charged species (e.g., sodium) in the D stream migrate toward the negatively charged cathode and pass through the negatively charged cation exchange membrane. These cations also stay in the C stream, prevented from further migration toward the cathode by the positively charged anion exchange membrane. As a result of the anion and cation migration, electric current flows between the cathode and anode. Only an equal number of anion
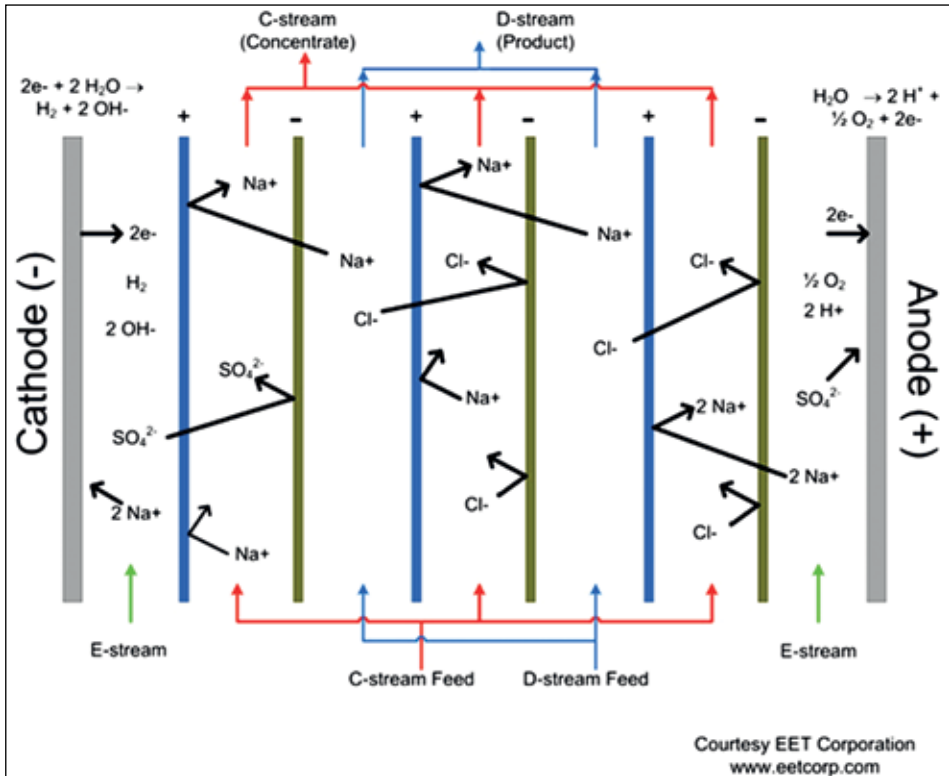
Figure 5.1. General technological scheme of electrodialysis process. (Adapted from internet http://www.a-wpt.com/productssolutions/ edi.php)

and cation charge equivalents are transferred from the D stream into the C stream and so the charge balance is maintained in each stream. The overall result of the electrodialysis process is an ion concentration increase in the concentrate stream with a depletion of ions in the diluate solution feed stream.

The E stream is the electrode stream that flows past each electrode in the stack. This stream may consist of the same composition as the feed stream (e.g., sodium chloride) or may be a separate solution containing a different species (e.g., sodium sulfate). Depending on the stack conFigureuration, anions and cations from the electrode stream may be transported into the C stream, or anions and cations from the D stream may be transported into the E stream. In each case, this transport is necessary to carry current across the stack and maintain electrically neutral stack solutions.

5.1.2 Anode and cathode reactions
Reactions take place at each electrode. At the cathode,

$2e^- + 2\,H_2O \rightarrow H_2\,(g) + 2\,OH^-$

while at the anode,
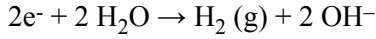
$H_2O \rightarrow 2\,H^+ + \frac{1}{2}\,O_2\,(g) + 2e^-$ or $2\,Cl^- \rightarrow Cl_2\,(g) + 2e^-$
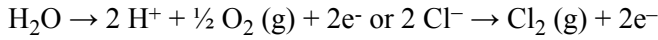
Small amounts of hydrogen gas are generated at the cathode and small amounts of either oxygen or chlorine gas (depending on composition of the E stream and end ion exchange membrane arrangement) at the anode. These gases are typically subsequently dissipated as the E stream effluent from each electrode compartment is combined to maintain a neutral pH and discharged or re-circulated to a separate E tank. However, some have proposed collection of hydrogen gas for use in energy production.

5.1.3 Efficiency
Current efficiency is a measure of how effective ions are transported across the ion exchange membranes for a given applied current. Typically current efficiencies >80% are desirable in commercial stacks to minimize energy operating costs. Low current efficiencies indicate water splitting in the diluate or concentrate streams, shunt currents between the electrodes, or back-diffusion of ions from the concentrate to the diluate could be occurring.

Current efficiency is calculated according to:

$$\xi = \frac{zFQ_f(C^d_{inlet} - C^d_{outlet})}{NI}$$

Where: ξ = current utilization efficiency; z = charge of the ion; F = Faraday constant, 96,485 Amp-s/mol; Q_f = diluate flow rate, L/s; C^d_{inlet} = diluate ED cell inlet concentration, mol/L; C^d_{outlet} = diluate ED cell outlet χ concentration, mol/L; N = number of cell pairs; I = current, Amps.

Current efficiency is generally a function of feed concentration.

5.1.4 Electrodialysis applications
In application, electrodialysis systems can be operated as continuous production or batch production (Figure 5.2.) processes. In a continuous process, feed is
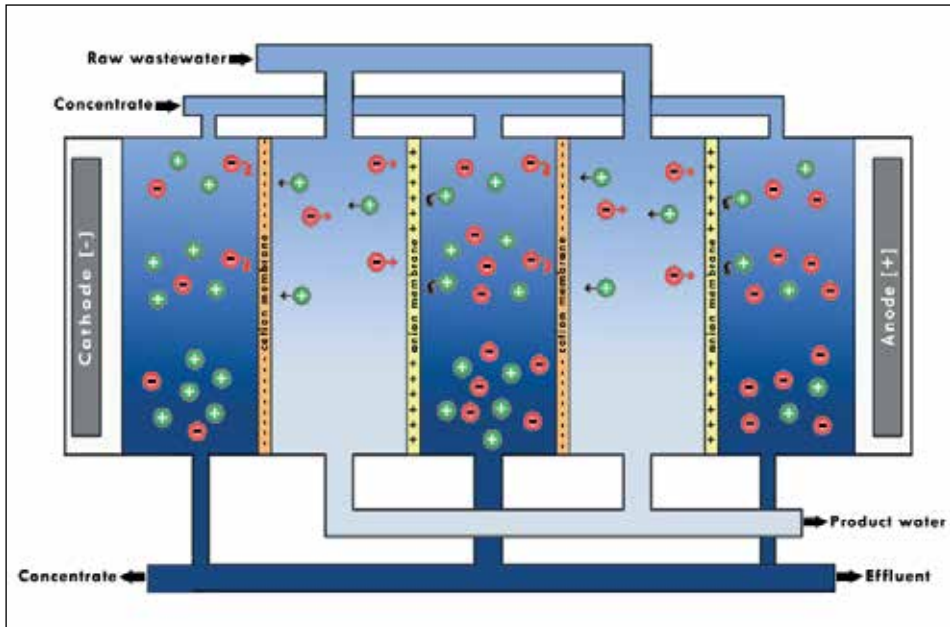
Figure 5.2. Electrodialysis continues and batch production processes (Adapted from internet http://www. electrodialysis)

passed through a sufficient number of stacks placed in series to produce the final desired product quality. In batch processes, the diluate and/or concentrate streams are re-circulated through the electrodialysis systems until the final product or concentrate quality is achieved.

Electrodialysis is usually applied to deionization of aqueous solutions. However, desalting of sparingly conductive aqueous organic and organic solutions is also possible. Some applications of electrodialysis include:

• Large scale brackish and seawater desalination and salt production.
• Small and medium scale drinking water production (e.g., towns & villages, construction & military camps, nitrate reduction, hotels & hospitals)
• Water reuse (e.g., industrial laundry wastewater, produced water from oil/gas production, cooling tower makeup & blowdown, metals industry fluids, wash-rack water)
• Pre-demineralization (e.g., boiler makeup & pretreatment, ultrapure water pretreatment, process water desalination, power generation, semiconductor, chemical manufacturing, food and beverage)
• Food processing
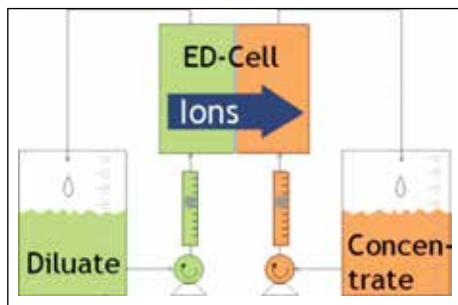
Figure 5.2. Electrodialysis continues and batch production processes (Adapted from internet http://www. electrodialysis)

- Agricultural water (e.g., water for greenhouses, hydroponics, irrigation, livestock)
- Glycol desalting (e.g., antifreeze / engine-coolants, capacit or electrolyte fluids, oil and gas dehydration, conditioning and processing solutions, industrial heat transfer fluids, secondary coolants from heating, venting, and air conditioning (HVAC))
- Glycerin Purification

The major application of electrodialysis has historically been the desalination of brackish water or seawater as an alternative to RO for potable water production and seawater concentration for salt production (primarily in Japan).[4] In normal potable water production without the requirement of high recoveries, RO (Reverse Osmosis) is generally believed to be more cost-effective when total dissolved solids (TDS) are 3,000 parts per million (ppm) or greater, while electrodialysis is more cost-effective for TDS feed concentrations less than 3,000 ppm or when high recoveries of the feed are required.

Another important application for electrodialysis is the production of pure water and ultrapure water by electrodeionization (EDI). In EDI, the purifying compartments and sometimes the concentrating compartments of the electrodialysis stack are filled with ion exchange resin. When fed with low TDS feed (e.g., feed purified by RO), the product can reach very high purity levels (e.g., 18 MΩ-cm). The ion exchange resins act to retain the ions, allowing these to be transported across the ion exchange membranes. The main usage of EDI systems are in electronics, pharmaceutical, power generation, and cooling tower applications.

5.1.5 Electrodialysis method limitations
Electrodialysis has inherent limitations, working best at removing low molecular weight ionic components from a feed stream. Non-charged, higher molecular

weight and less mobile ionic species will not typically be significantly removed. Also, in contrast to RO, electrodialysis becomes less economical when extremely low salt concentrations in the product are required and with sparingly conductive feeds: current density becomes limited and current utilization efficiency typically decreases as the feed salt concentration becomes lower, and with fewer ions in solution to carry current, both ion transport and energy efficiency greatly declines. Consequently, comparatively large membrane areas are required to satisfy capacity requirements for low concentration (and sparingly conductive) feed solutions. Innovative systems overcoming the inherent limitations of electrodialysis (and RO) are available; these integrated systems work synergistically, with each sub-system operating in its optimal range, providing the least overall operating and capital costs for a particular application.

As with RO, electrodialysis systems require feed pretreatment to remove species that coat, precipitate onto, or otherwise "foul" the surface of the ion exchange membranes. This fouling decreases the efficiency of the electrodialysis system. Species of concern include calcium and magnesium hardness, suspended solids, silica, and organic compounds. Water softening can be used to remove hardness, and micrometre or multimedia filtration can be used to remove suspended solids. Hardness in particular is a concern since scaling can build up on the membranes. Various chemicals are also available to help prevent scaling. Also, electrodialysis reversal systems seek to minimize scaling by periodically reversing the flows of diluate and concentrate and polarity of the electrodes.

5.2 Electrodeionization (EDI)
5.2.1 Electrodeionization method description
Electrodeionization (EDI) is a water treatment technology that utilizes electricity, ion exchange membranes and resin to deionize water and separate dissolved ions (impurities) from water. It differs from other water purification technologies in that it is done without the use of chemical treatments and is usually a polishing treatment to reverse osmosis (RO). There are also EDI units that are often referred to as Continuous electrodeionization (CEDI) since the electric current regenerates the resin mass continuously. CEDI technique can achieve very high purity, with conductivity being below 0.1uS/cm.

Figure 5.3 shows a diagram of the internal process of an electrodeionization device. Two electrodes are on either side of multiple EDI compartments, which are known as diluting chambers and concentrating chambers. As water flows through the EDI module and power is applied, there are three processes
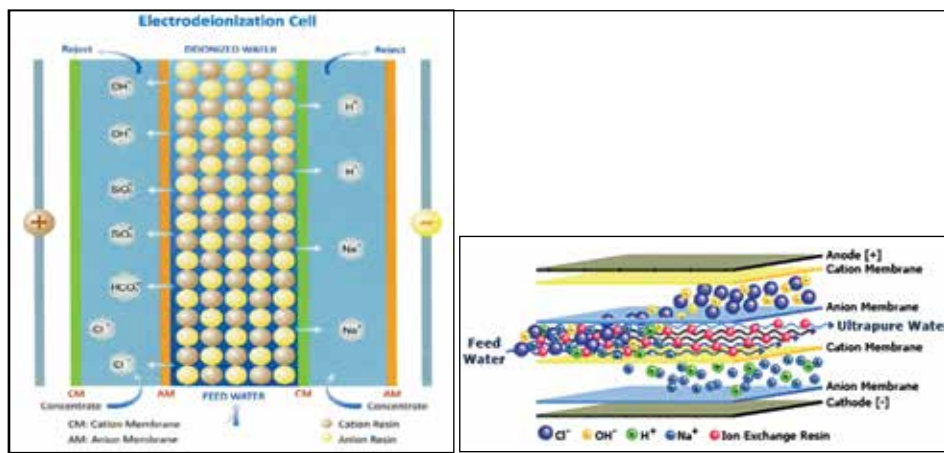
Figure 5.3. Typical electrodeionization device configuration with ion exchange resin and without. (Adapted from internet http://www.cal-water.com/pdf/EDI_Info.pdf)

occurring simultaneously: The deionization process where the water is purified by ion exchange; ion migration where the ions are removed from the resin; and continuous regeneration of the resin.

In Figure 5.3, we see there are two types of chambers in an EDI device. Diluting chambers (D-chambers) are the portion containing mixed bed ion exchange resin where water is purified or diluted of ions. Concentrating chambers (C-chambers) are the areas where water is concentrated of ions, and becomes waste water. The D-chambers contain both cation exchange resin and anion exchange resin. There are several different concentrate chamber designs; however the most efficient EDI devices contain resin-filled concentrate chambers, known as an "all filled" EDI design.

The D and C chambers are separated by ion exchange membranes. The membranes are similar in material and charge to the ion exchange resin. For example, cation exchange membranes only allow cations to pass, and anion exchange membranes only allow anions to pass. Water and oppositely charged ions may not pass across the ion exchange membrane used in EDI.

5.2.2 Deionization

Deionization is the removal of ions - both positively charged cations and negatively charged anions. Cations are positively charged ions because they have a loss of one or more electrons, very small negatively charged particles. For exam-

Figure 5.4. Electrical deionization module view. (Adapted from internet http://www. lenntech.com/library/edi/edi.htm)

ple, the sodium ion (Na⁺) is positive because the ion lost one electron. Calcium (Ca⁺⁺) has twice the positive charge of sodium because it has lost two electrons. Anions contain a negative charge because they contain one or more additional electrons. The chloride ion (Cl⁻) is formed when chlorine gains one electron, and oxide (O⁻⁻) has gained two electrons.

Figure 5.3 shows the ion exchange process. This is typical of all high purity resin, including electrodeionization. The cation exchange resin is in the regenerated hydrogen (H+) form as the charged exchange sites are bonded with hydrogen ions. As the feed water contacts the resin, the contaminant cations such as calcium, magnesium, sodium, potassium and ammonium have a higher affinity to the site charges on a resin bead than a hydrogen ion. The cation exchange resin releases a hydrogen ion to bond with the cation. Likewise, anion exchange resin is in the regenerated hydroxide (OH⁻) form as the charged exchange sites are bonded with hydroxide ions.

The contaminant anions – such as carbonate, bicarbonate, chloride, sulfate, nitrate, fluoride, silica, boron and carbonic acid – have a higher affinity to the anion exchange resin than hydroxide. The anion exchange resin releases a hydroxide ion to bond with the anion. The released hydrogen and hydroxide ions bond to form water. Water is purified, or deionized, by the removal of the cations and anions as it flows through the mixed resin bed.

5.2.3 Applications of EDI

When fed with low TDS feed (e.g., feed purified by RO), the product can reach very high purity levels (e.g., 18 Megohms/cm). The ion exchange resins act to retain the ions, allowing these to be transported across the ion exchange membranes. The main usage of EDI technology such as that supplied by Ion pure, E-cell and Snow Pure are in electronics, pharmaceutical, and power generation applications.

One important aspect in the water treatment application is that water to some kinds of EDI needs to be free from CO_2, since this in its dissolved form will put unnecessary strain on the EDI unit and will reduce performance.

5.2.4 Theory of EDI

An electrode in an electrochemical cell is referred to as either an anode or a cathode, terms that were coined by Michael Faraday. The anode is defined as the electrode at which electrons leave the cell and oxidation occurs, and the cathode as the electrode at which electrons enter the cell and reduction occurs. Each electrode may become either the anode or the cathode depending on the voltage applied to the cell. A bipolar electrode is an electrode that functions as the anode of one cell and the cathode of another cell.

Each cell consists of an electrode and an electrolyte with ions that undergo either oxidation or reduction. An electrolyte is a substance containing free ions that behaves as an electrically conductive medium. Because they generally consist of ions in solution, electrolytes are also known as ionic solutions, but molten electrolytes and solid electrolytes are also possible. They are sometimes referred to in abbreviated jargon as lytes.

Water is passed between an anode (positive electrode) and a cathode (negative electrode). Ion-selective membranes allow the positive ions to separate from the water toward the negative electrode and the negative ions toward the positive electrode. High purity deionized water results.

Disadvantages
- EDI cannot be used for water having hardness higher than 1, since the calcium carbonate would create a scab in the camera of the concentrated one, limiting the operation
- It requires purification pretreatment
- Carbon Dioxide will freely pass through an RO membrane, dissociating and raising the conductivity of water. Any ionic species formed from the carbon dioxide gas will lower the outlet resistivity of the water produced by EDI. The management of CO_2 in water is typically handled in one or two ways: the
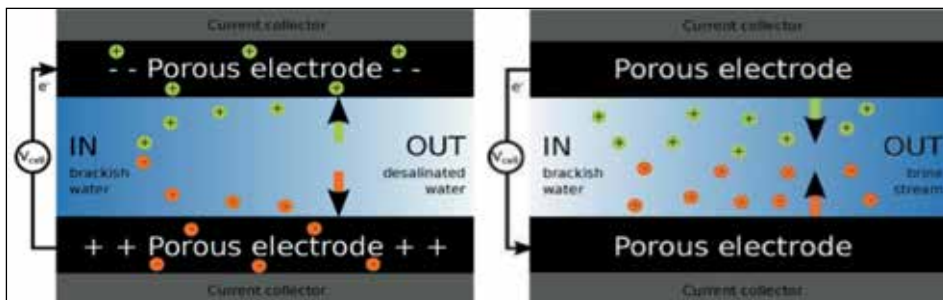
Figure 5.5. Adsorption and desorption of ions from the brackish water to desalinate water (left) and to regenerate the electrodes (right) (Adapted from Porada et al. 2013)

pH of the water can be adjusted to allow the RO membrane to reject the ionic species or the carbon dioxide can be removed from the water using a strip gas.

5.3 Capacitive Deionization process

Capacitive deionization (CDI) is a technology to deionize water by applying an electrical potential difference over two porous carbon electrodes. Anions, ions with a negative charge, are removed from the water and are stored in the positively polarized electrode. Likewise, cations (positive charge) are stored in the cathode, which is the negatively polarized electrode.

Today, CDI is mainly used for the desalination of brackish water, which is water with a low or moderate salt concentration (below 10 g/L). Other technologies for the deionization of water are, amongst others, distillation, reverse osmosis and electrodialysis. Compared to reverse osmosis and distillation, CDI is considered to be an energy-efficient technology for brackish water desalination. [2]This is mainly because CDI removes the salt ions from the water, while the other technologies extract the water from the salt solution.[1][3]

Historically, CDI has been referred to as electrochemical demineralization, "electrosorbtion process for desalination of water", or electrosorption of salt ions. It also goes by the names of capacitive desalination, or in the commercial literature as "CapDI".

Adsorption and desorption cycles

The operation of a conventional CDI system cycles through two phases: an adsorption phase where water is desalinated and desorption phase where the electrodes are regenerated. During the adsorption phase, a potential difference over two elec-
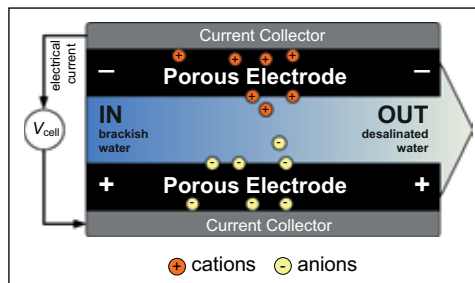
Figure 5.6. Capacitive deionization during the adsorption cycle (Adapted from Porada et al. 2013)
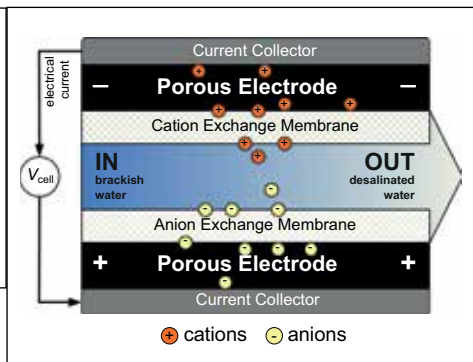
Figure 5.7. Membrane capacitive deionization during the adsorption cycle (Adapted from Porada et al. 2013)

trodes is applied and ions are adsorbed from the water. The ions are transported through the interparticle pores of the porous carbon electrode to the intraparticle pores, where the ions are electrosorbed in the so-called electrical double layers (EDLs). After the electrodes are saturated with ions, the adsorbed ions are released for regeneration of the electrodes. The potential difference between electrodes is reversed or reduced to zero. In this way, ions leave the electrode pores and can be flushed out of the CDI cell resulting in an effluent stream with a high salt concentration, the so-called brine stream or concentrate. Part of the energy input required during the adsorption phase can be recovered during this desorption step.

5.4 Membrane capacitive deionization

By inserting two ion exchange membranes, a modified form of CDI is obtained, namely Membrane Capacitive Deionization. This modification improves the CDI cell in several ways: [4]

- Co-ions do not leave the electrodes during the adsorption phase, as described above (see Ion adsorption in Electrical Double Layers for explanation). Instead, due to the inclusion of the ion exchange membranes, these co-ions will be kept in the interparticle pores of the electrodes, which enhance the salt adsorption efficiency.
- Since these co-ions cannot leave the electrodes and because the electroneutrality condition applies for the interparticle pores, extra counter-ions must pass through the ion-exchange membranes, which give rise to a higher salt adsorption as well.
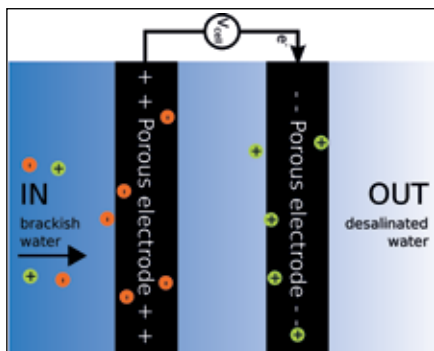
Figure 5.8. Flow-through CDI cell during the adsorption cycle (Adapted from Porada et al. 2013)
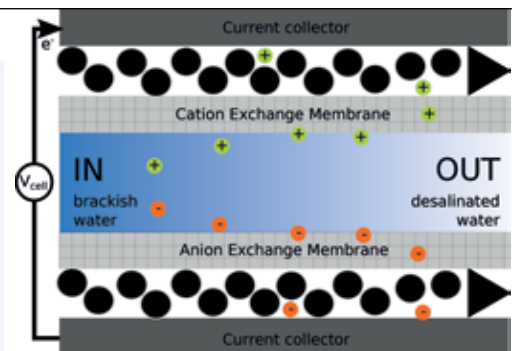
Figure 5.9. Flow-electrode CDI cell during the adsorption cycle (Adapted from Porada et al. 2013)

- Operating MCDI at constant current mode can produce freshwater with a stable effluent concentration (see constant voltage vs. constant current for more information).
- The required energy input of MCDI is lower than of CDI.

5.5 Cell geometries

Flow-by mode

The electrodes are placed in a stack with a thin spacer area in between, through which the water flows. This is by far the most commonly used mode of operation and electrodes, which are prepared in a similar fashion as for electrical double layer capacitors with a high carbon mass loading.

Flow-through mode

In this mode, the feed water flows straight through the electrodes, i.e. the water flows directly through the interparticle pores of the porous carbon electrodes. This approach has the benefit of ions directly migrating through these pores, hence mitigating transport limitations encountered in the flow-by mode.

Flow-electrode capacitive deionization

This geometrical design is comparable to the flow-by mode with the inclusion of membranes in front of both electrodes, but instead of having solid electrodes, a carbon suspension (slurry) flows between the membranes and the current collector. A potential difference is applied between both channels of flowing carbon

slurries, the so-called flow electrodes, and water is desalinated. Since the carbon slurries flow, the electrodes do not saturate and therefore this cell design can be used for the desalination of water with high salt concentrations as well (e.g. sea water, with salt concentrations of approximately 30 g/L). A discharging step is not necessary; the carbon slurries are, after leaving the cell, mixed together and the carbon slurry can be separated from a concentrated salt water stream.

Capacitive deionization with wires
The freshwater stream can be made to flow continuously in a modified CDI con-Figureuration where the anode and cathode electrode pairs are not fixed in space, but made to move cyclically from one stream, in which the cell voltage is applied and salt is adsorbed, to another stream, where the cell voltage is reduced and salt is released.

Electrode materials for CDI
For a high performance of the CDI cell, high quality electrode materials are of utmost importance. Carbon is the choice as porous electrode material. Regarding the structure of the carbon material, there are several considerations. As a high salt electrosorption capacity is important, the specific surface area and the pore size distribution of the carbon accessible for ions should be large. Furthermore, the used material should be stable and no chemical degradation of the electrode (degradation) should occur in the voltage window applied for CDI. The ions should be able to move fast through the pore network of the carbon and the conductivity of the carbon should be high. Lastly, the costs of the electrode materials are important to take into consideration.

Nowadays, activated carbon (AC) is the commonly used material, as it is the most cost efficient option and it has a high specific surface area. It can be made from natural or synthetic sources. Other carbon materials used in CDI research are, for example, ordered mesoporous carbon, carbon aerogels, carbide-derived carbons, carbon nanotubes, graphene and carbon black. Recent work argues that micropores, especially pores < 1.1 nm are the most effective for salt adsorption in CDI.

Energy requirements
Since the ionic content of water is demixed during a CDI adsorption cycle, the entropy of the system decreases and an external energy input is required. The theoretical energy input of CDI can be calculated as follows:

$$\Delta G = R * T * \Phi_{v,fresh} * (C_{feed} - C_{fresh}) \left[\frac{\ln\alpha}{1-\alpha} - \frac{\ln\beta}{1-\alpha} \right]$$

Where: - R is the gas constant (8.314 J mol^{-1} K^{-1}), - T the temperature (K), $\Phi_{v,fresh}$, - the flow rate of the fresh water outflow (m^3/s), C_{feed} - the concentration of ions in the feed water (mol/m^3) and C_{fresh} - the ion concentration in the fresh water outflow (mol/m^3) of the CDI cell. α - is defined as C_{feed}/C_{fresh}, and β - as C_{feed}/C_{conc}, with Cconc - the concentration of the ions in the concentrated outflow.

In practice, the energy requirements will be significantly higher than the theoretical energy input. Important energy requirements, which are not included in the theoretical energy requirements, are pumping, and losses in the CDI cell due to internal resistances. If MCDI and CDI are compared for the energy required per removed ion, MCDI has a lower energy requirement than CDI.

Comparing CDI with reverse osmosis of water with salt concentrations lower than 20 mM, lab-scale research shows that the energy consumption in kWh per m3 freshwater produced can be lower for MCDI than for reverse osmosis.

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Chapter 6
Ultra Pure Water Systems

6.1 Ultra pure water definitions

Ultrapure water, also known as "UPW" or "high-purity water", is water that has been purified to uncommonly stringent specifications. Ultrapure water is a commonly used term in the semiconductor industry to emphasize the fact that the water is treated to the highest levels of purity for all contaminant types, including: organic and inorganic compounds; dissolved and particulate matter; volatile and non-volatile, reactive and inert; hydrophilic and hydrophobic; and dissolved gases.

UPW and commonly used term Deionized water "DIW" are not the same. In addition to the fact that UPW has organic particles, and dissolved gases removed, a UPW system includes a "Polishing" loop, the most expensive part of the treatment process. The standards will be revised whenever the semiconductor industry develops new line widths, thereby keeping the guidelines current

A number of organizations and groups develop and publish standards associated with the production of UPW. One of them for microelectronics and power, they include Semiconductor Equipment and Materials International (SEMI). Pharmaceutical plants follow water quality standards as developed by two main pharmacopeias, United States Pharmacopeia and European. The most widely used requirements for UPW quality are "Standard Guide for Ultra-Pure Water Used in the Electronics and Semiconductor Industries" [1] and "Guide for ultrapure water used in semiconductor processing".[2]

Bacteria, particles, organic and inorganic sources of contamination vary depending on a number of factors including the feed water to make UPW as well as the selection of the piping materials to convey it. Bacteria are typically reported in colony-forming units (CFU) per volume of UPW. Particles use number per volume of UPW. Total organic carbon (TOC), metallic contaminates, and anionic contaminates are measured in dimensionless terms of parts per notation, such as ppm, ppb, ppt and ppq.

Bacteria have been referred to as one of the most obstinate in this list to control.[3] Techniques that help in minimizing bacterial colony growth within UPW streams include occasional chemical or steam sanitization (which is common in the

pharmaceutical industry), ultrafiltration (found in some pharmaceutical, but mostly semiconductor industries), ozonation and optimization of piping system designs that promote the use of Reynolds Number criteria for minimum flow [4] along with minimization of dead legs. In modern advanced UPW systems positive (higher than zero) bacteria counts are typically observed in the newly constructed facilities. This issue is effectively addressed by sanitization using ozone or hydrogen peroxide. With proper design of the polishing and distribution system no positive bacteria counts are typically detected throughout the life cycle of the UPW system.

Particles in UPW are the bane of the semiconductor industry, causing defects in sensitive photolithographic processes that define nanometer sized features. In other industries their effects can range from a nuisance to life-threatening defects. Particles can be controlled by use of filtration and ultrafiltration. Sources can include bacterial fragments, the sloughing of the component walls within the conduit's wetted stream and also the cleanliness of the jointing processes used to build the piping system.

TOC in UPW can contribute to bacterial proliferation by providing nutrients, can substitute as a carbide for another chemical species in a sensitive thermal process, react in unwanted ways with biochemical reactions in microbioprocessing and, in severe cases, leave unwanted residues on production parts. TOC can come from the feed water used to produce UPW, from the components used to convey the UPW (additives in the manufacturing piping products or extrusion aides and mold release agents), from subsequent manufacturing and cleaning operations of piping systems or from dirty pipes, fittings and valves.

Metallic and anionic contamination in UPW systems can shut down enzymatic processes in bioprocessing, corrode equipment in the electrical power generation industry and result in either short or long-term failure of electronic components in semiconductor chips and photovoltaic cells. Its sources are similar to those of TOC's. Depending on the level of purity needed, detection of these contaminants can range from simple conductivity (electrolytic) readings to sophisticated instrumentation such as ionchromatography (IC), atomic absorption spectroscopy (AA) and inductively coupled plasma mass spectrometry (ICP-MS).

6.2 Ultra pure water quality standards for electronics and semiconductor-industry manufacturing.

Different levels of quality are required for a vast range of applications, therefore different grades of water must be purified and utilized to match the required procedures or appliances.

Recommendations for water quality related to electronics and semiconductor-industry manufacturing. Seven classifications of water are described, including water for line widths as low as 0.032 micron. In all cases, the recommendations are for water at the point of distribution (POD).

Water is used for washing and rinsing of semiconductor components during manufacture. Water is also used for cleaning and etching operations, making steam for oxidation of silicon surfaces, preparing photo masks, and depositing luminescent materials. Other applications are in the development and fabrication of solid-state devices, thin-film devices, communication lasers, light-emitting diodes, photo-detectors, printed circuits, memory devices, vacuum-tube devices, or electrolytic devices.

It is used in other areas of the electronics industry in a similar fashion, such as display manufacturing, production of discrete components, such as LEDs or the manufacturing of crystalline silicon photovoltaic's but the cleanliness requirements in the semiconductor industry are currently the most stringent.

Significance:
1   High-purity water is required to prevent contamination of products during manufacture, since contamination can lead to an unacceptable, low yield of electronic devices.
2   The range of water purity is defined in accordance with the manufacturing process. The types of ultra-pure water are defined with respect to device line width. In all cases, the water-quality recommendations apply at the point of distribution. (POD)
3   The limits on the impurities are related to current contamination specifications and to available analytical methods (either performed in a suitable clean laboratory or by on-line instrumentation). On-line and off-line methods are used in accordance with current industry practice. Concentration of the sample may be required to measure the impurities at the levels indicated in Table 6.1.

6.3 Ultra pure water quality standards related to pharmaceuticals and biotechnology industries

In pharmaceutical and biotechnology industry are number places of application for UPW. A typical use of Ultrapure water in Pharmaceutical and Biotechnology industries is summarized in the Table 6.2[6]

Table 6.1 Requirements for Water at the Point of Distribution in the Electronics and Semiconductor Industries

Parameter	Type E-1	Type E-1.1	Type E-1.2*	Type E-1.3*	Type E-2	Type E-3	Type E-4
Line width (microns)	1.0–0.5	0.35–0.25	0.18–0.09	0.065–0.032	5.0–1.0	>5.0	—
Resistivity, 25°C (On-line) (MΩ-cm)	18.1	18.2	18.2	18.2	16.5	12	0.5
TOC (µg/L) (on-line for<10 ppb)	5	2	1	1	50	300	1000
On-line dissolved oxygen (µg/L)	25	10	3	10	—	—	—
On-Line Residue after evaporation (µg/L)	1	0.5	0.1		—	—	—
On-line particles/L (micron range)							
>0.05 µm				500			
0.05–0.1		1000	200	N/A	—	—	—
0.1–0.2	1000	350	<100	N/A	—	—	—
0.2–0.5	500	<100	<10	N/A	—	—	—
0.5-1.0	200	<50	<5	N/A	—	—	—
1.0	<100	<20	<1	N/A	—	—	—
SEM particles/L (micron range)							
0.1–0.2	1000	700	<250	N/A	—	—	—
0.2–0.5	500	400	<100	N/A	3000	—	—
0.5–1	100	50	<30	N/A	—	10000	—
10	<50	<30	<10	N/A	—	—	100000
Bacteria in CFU/Volume							
100 mL Sample	5	3	1	N/A	10	50	100
1 L Sample			10	1			
10 L Sample				1			
Silica – total (µg/L)	5	3	1	0.5	10	50	1000
Silica – dissolved (µg/L)	3	1	0.5	0.5	—	—	—
Anions and Ammonium by IC (µg/L)							
Ammonium	0.1	0.10	0.05	0.050	—	—	—
Bromide	0.1	0.05	0.02	0.050	—	—	—
Chloride	0.1	0.05	0.02	0.050	1	10	1000
Fluoride	0.1	0.05	0.03	0.050	—	—	—
Nitrate	0.1	0.05	0.02	0.050	1	5	500

Table 6.1 Requirements for Water at the Point of Distribution in the Electronics and Semicon-
ductor Industries (continued)

Parameter	Type E-1	Type E-1.1	Type E-1.2*	Type E-1.3*	Type E-2	Type E-3	Type E-4
Nitrite	0.1	0.05	0.02	0.050	—	—	—
Phosphate	0.1	0.05	0.02	0.050	1	5	500
Sulfate	0.1	0.05	0.02	0.050	1	5	500
Metals by ICP/ MS (µg/L)							
Aluminum	0.05	0.02	0.005	0.001	—	—	—
Antimony				0.001			
Arsenic				0.001			
Barium	0.05	0.02	0.001	0.001	—	—	—
Boron**	0.3	0.1	0.05	0.050	—	—	—
Cadmium				0.010			
Calcium	0.05	0.02	0.002	0.001	—	—	—
Chromium	0.05	0.02	0.002	0.001	—	—	—
Copper	0.05	0.02	0.002	0.001	1	2	500
Iron	0.05	0.02	0.002	0.001	—	—	—
Lead	0.05	0.02	0.005	0.001	—	—	—
Lithium	0.05	0.02	0.003	0.001	—	—	—
Magnesium	0.05	0.02	0.002	0.001	—	—	—
Manganese	0.05	0.02	0.002	0.010	—	—	—
Nickel	0.05	0.02	0.002	0.001	1	2	500
Potassium	0.05	0.02	0.005	0.001	2	5	500
Sodium	0.05	0.02	0.005	0.001	1	5	1000
Strontium	0.05	0.02	0.001		—	—	—
Tin				0.010			
Titanium				0.010			
Vanadium				0.010			
Zinc	0.05	0.02	0.002	0.001	1	5	500
Temperature Stability (K)				±1			
Temperature Gradient (K/10 min)				<0.1			
Dissolved Nitrogen On-line (mg/L)				8-18			
Dissolved Nitrogen Stability (mg/L)				±2			

*Values shown in Type E-1.3 are a result of aligning risk factors of known contaminates to the production pro-
cesses found in current semiconductor processing for the linewidth of interest and may differ in a few cases to
those found in Type E-1.2. Users who wish to use the higher numbers for Type E-1.2 water should feel free to
do so.
All values are equal to or less than with the exception of Resistivity.
**Boron is monitored only as an operational parameter for monitoring the ion-exchange beds.

In order to be used for pharmaceutical and biotechnology applications for production of licensed human and veterinary health care products it must comply with the specification of the following pharmacopeias monographs:
- European Pharmacopoeia (Ph Eur):[7] Aqua purificata
- The United States Pharmacopoeia (USP):[8]Purified water

Note: Purified Water is typically a main monograph which references other applications that use Ultrapure water

It should be noted that Ultrapure water is often used as a critical utility for cleaning applications (as required). It is also used to generate clean steam for sterilization.

The following Table 6.3. summarizes specifications for two major Pharmacopoeia requirements for 'water for injection' and 'highly purified water''.

Currently World Health Organization (WHO) [9] as well as Pharmaceutical Inspection Co-operation Scheme (PIC/S) [10] developed technical documents which outline validation requirements and strategies for water in different pharmaceutical application systems Concentration of the sample may be required to measure the impurities at the levels indicated in Table 6.4.

Table 6.2. Ultrapure water application in Pharmaceutical and Biotechnology industries
(Adapted from Rove, R.C. et al,)

Type	Use
Bacteriostatic water for injection	Diluent for ophthalmic and multiple-dose injections
Sterile water for inhalation	Diluent for inhalation therapy products
Sterile water for injection	Diluent for injections
Sterile water for irrigation	Diluent for internal irrigation therapy products
Water for injections in bulk	Water for the bulk preparation of medicines for parenteral administration

Table 6.3 European and United States Pharmacopoeias requirements for UPW

Properties	Ph Eur	USP
Conductivity	<1.1 μS/cm at 20°C,	<1.3 μS/cm at 25°C,
Total Organic Carbon (TOC)	<500 μ/L	<500 ppb
Bacteria (guideline)	<10 cfu/100 mL	<10 cfu/100 mL
Endotoxin	<0.25 IU/mL	<0.25 IU/mL
Nitrates	<0.2 ppm	N/A
Heavy Metals	<0.2 ppm	N/A

6.4 UPW system design for semiconductor industry

6.4.1 Definitions

Typically city feed water (containing all the unwanted contaminates previously mentioned) is taken through a series of purification steps that, depending on the quality of UPW wanted, includes gross filtration for large particulates, carbon filtration, water softening, reverse osmosis, exposure to ultraviolet (UV) light for TOC and/or bacterial static control, polishing using either ion exchange resins or electrodeionization (EDI) and finally filtration or ultrafiltration.

Some systems use direct return, reverse return or serpentine loops that return the water to a storage area, providing continuous re-circulation, while others use dead end systems that run from point of UPW production to point of use. The constant re-circulation action in the former continuously polishes the water with every pass. The latter can be prone to contamination build up if it is left stagnant with no use.

For modern UPW systems it is important to consider specific site and process requirements such as environmental constraints (e.g., wastewater discharge limits) and reclaim opportunities (e.g., is there a mandated minimum amount of reclaim required). UPW systems consist of three subsystems which are pretreatment, primary and polishing sections. Most systems are similar in design but may vary in the pretreatment section depending on the nature of the source water. Typical frontend treatments employed are Two Pass Reverse Osmosis, Demineralization plus Reverse Osmosis or HERO® (High Efficiency Reverse Osmosis)

Table 6.4 Requirements for UPW in different pharmaceutical application systems (Adapted from internet http://www.astm.org)

Grade of Water	Resisitivity (M-cm)	TOC (ppb)	Bacteria (CFU/ml)	*Endotoxin (EU/ml)	Typical Applications
Type 1+	18.2	<5	<1	<0.03	GF-AAS, ICP-MS, trace metal detection
Type 1	>18	<10	<10	<0.03	High Performance Liquid Chromatography(HPLC), GC, AAS, immunocytochemistry, mammalian cell culture, plant tissue culture
Type 2+	>10	<50	<10	NA	General laboratory applications requiring higher inorganic purity
Type 2	>1	<50	<100	NA	Feed to ultra pure type 1 systems, feed to clinical analyzers, electrochemistry, sample dilution, media preparation, radioimmunoassay
Type 3	>0.05	<200	<1000	NA	Feed to ultra pure water type 1 systems, feed to washing machines, dishwashers, autoclaves

[11,12]. In addition, the degree of filtration upstream of these processes will be dictated by the level of suspended solids, turbidity and organics present in the source water. The common types of filtration are Multi-Media, Automatic Back-washable Filters and Ultrafiltration for suspended solids removal and turbidity reduction and Activated Carbon for the reduction of organics. The Activated Carbon may also be used for removal of chlorine upstream of the Reverse Osmosis of Demineralization steps. If Activated Carbon is not employed then sodium bi-sulfite is used to de-chlorinate the feed water.

The Primary Section will consist of Ultraviolet light (UV) for organic reduction, EDI and or mixed bed ion exchange for demineralization. The mixed beds may be non-regenerable (following EDI), in-situ or externally regenerated. The last step in this section may be dissolved oxygen removal utilizing the membrane degasification process or vacuum degasification.

The last section (polishing) will consist of UV, Heat exchange to control constant temperature in the UPW supply, non-regenerable ion exchange, Membrane degasification (to polish to final UPW requirements) and ultrafiltration to achieve the required particle level. Some semiconductor plants require hot UPW for some of their processes. In this instance polished UPW is heated in the range of 70 to 80C before being delivered to manufacturing. Most of these systems include heat recovery wherein the excess hot UPW returned from manufacturing goes to a heat recovery unit before being returned to the UPW feed tank to conserve on the use of heating water or the need to cool the hot UPW return flow.[13]

6.4.2 Key UPW design criteria for semiconductor industry.
- Remove contaminants as far forward in the system as practical and cost effective.
- Steady state flow in the makeup and primary sections to avoid TOC and conductivity spikes (NO start/stop operation). Recirculate excess flow upstream.
- Minimize the use of chemicals following the Reverse Osmosis units.
- Consider EDI and non-regenerable primary mixed beds in lieu of in-situ or externally regenerated primary beds to assure optimum quality UPW makeup and minimize the potential for upset.
- Select materials that will not contribute TOC and particles to the system particularly in the primary and polishing sections. Minimize stainless steel material in the polishing loop and if used electropolishing is recommended.
- Minimize dead legs in the piping to avoid the potential for bacteria propagation.
- Maintain minimum scouring velocities in the piping and distribution network to ensure turbulent flow. The recommended minimum is based on a Reynolds

number of 3,000 Re or higher. This can range up to 10,000 Re depending on the comfort level of the designer.
- Use only virgin resin in the Polishing Mixed Beds. Replace every one to two years.
- Supply UPW to manufacturing at constant flow and constant pressure to avoid system upsets such as particle bursts.
- Utilize reverse return distribution loop design for hydraulic balance and to avoid backflow (return to supply).

Typical Semiconductor plants have only two drain systems for all of these rinses which are also combined with acid waste and therefore the rinse water is not effectively reused due to risk of contamination causing manufacturing process defects.

Definitions:
The following definitions are used by International Technology Roadmap for Semiconductors (ITRS):[5]
- UPW Recycle – Water Re-use in the same application after treatment
- Water Reuse – Use in secondary application
- Water Reclaim – Extracting water from wastewater

Water reclaim and recycle:
Some semiconductor manufacturing plants have been using reclaimed water for non-process applications such as chemical aspirators where the discharge water is sent to industrial waste. Water reclamation is also a typical application where spent rinse water from the manufacturing facility may be used in cooling tower supply, exhaust scrubber supply, or point of use abatement systems. UPW Recycling is not as typical and involves collecting the spent manufacturing rinse water, treating it and re-using it back in the wafer rinse process. Some additional water treatment may be required for any of these cases depending on the quality of the spent rinse water and the application of the reclaimed water. These are fairly common practices in many semiconductor facilities worldwide, however there is a limitation to how much water can be reclaimed and recycled if not considering reuse in the manufacturing process.

UPW recycling:
Recycling rinse water from the semiconductor manufacturing process has been discouraged by many manufacturing engineers for decades because of the risk

that the contamination from the chemical residue and particles may end up back in the UPW feed water and result in product defects. Modern Ultrapure Water systems are very effective at removing ionic contamination down to parts per trillion levels (ppt) whereas organic contamination of ultrapure water systems is still in the parts per billion levels (ppb). In any case recycling the process water rinses for UPW makeup has always been a great concern and until recently this was not a common practice. Increasing water and wastewater costs in parts of the US and Asia have pushed some semiconductor companies to investigate the recycling of manufacturing process rinse water in the UPW makeup system. Some companies have incorporated an approach that uses complex large scale treatment designed for worst case conditions of the combined waste water discharge. More recently new approaches have been developed to incorporate a detailed water management plan to try to minimize the treatment system cost and complexity.

Water management plan:
The key to maximizing water reclaim, recycle, and reuse is having a well thought out water management plan. A successful water management plan includes full understanding of how the rinse waters are used in the manufacturing process including chemicals used and their by products. With the development of this critical component, a drain collection system can be designed to segregate concentrated chemicals from moderately contaminated rinse waters, and lightly contaminated rinse waters. Once segregated into separate collection systems the once considered chemical process waste streams can be repurposed or sold as a product stream, and the rinse waters can be reclaimed.

A Water management plan will also require a significant amount of sample data and analysis to determine proper drain segregation, application of online analytical measurement, diversions control, and final treatment technology. Collecting these samples and performing laboratory analysis can help characterize the various waste streams and determine the potential of their respective re-use. In the case of UPW process rinse water the lab analysis data can then be used to profile typical and non-typical levels of contamination which then can be used to design the rinse water treatment system. In general it is most cost effective to design the system to treat the typical level of contamination that may occur 80-90% of the time, and then incorporate on-line sensors and controls to divert the rinse water to industrial waste or to non-critical use such as cooling towers when the contamination level exceeds the capability of the treatment system. By incorporating all these aspects of a water management plan in a semiconductor manufacturing site the level of water use can be reduced by as much as 90%

6.5 UPW transportation and piping

Stainless steel remains a piping material of choice for the pharmaceutical industry. Due to its metallic contribution, most steel was removed from microelectronics UPW systems in the 1980s and replaced with high performance polymers of polyvinylidene fluoride (PVDF), perfluoroalkoxy (PFA), ethylene chlorotrifluoroethylene (ECTFE) and polytetrafluoroethylene (PTFE) in the US and Europe. In Asia, polyvinyl chloride (PVC), chlorinated polyvinyl chloride (CPVC) and polypropylene (PP) are popular, along with the high performance polymers.

Chapter 6 sources:

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Chapter 7
Analytical Methods and Techniques for UPW Systems

7.1 On-line analytical measurements

7.1.1 Conductivity/resitivity

In pure water systems, electrolytic conductivity or resistivity measurement is the most common indicator of ionic contamination. The same basic measurement is read out in either conductivity units of microsiemens per centimeter (µS/cm), typical of the pharmaceutical and power industries or in resistivity units of megohm-centimeters (Mohm•cm) used in the microelectronics industries. These units are reciprocals of each other. Absolutely pure water has a conductivity of 0.05501 µS/cm and a resistivity of 18.18 Mohm•cm at 25°C, the most common reference temperature to which these measurements are compensated. An example of the sensitivity to contamination of these measurements is that 0.1 ppb of sodium chloride raises the conductivity of pure water to 0.05523 µS/cm and lowers the resistivity to 18.11 Mohm•cm. [1;2]

Ultrapure water is easily contaminated by traces of carbon dioxide from the atmosphere passing through tiny leaks or diffusing through thin wall polymer tubing when sample lines are used for measurement. Carbon dioxide forms conductive carbonic acid in water. For this reason, conductivity probes are most often permanently inserted directly into the main ultrapure water system piping to provide real-time continuous monitoring of contamination. These probes contain both conductivity and temperature sensors to enable accurate compensation for the very large temperature influence on the conductivity of pure waters. Conductivity probes have an operating life of many years in pure water systems. They require no maintenance except for periodic verification of measurement accuracy, typically annually.

7.1.2 Sodium

Sodium is usually the first ion to break through a depleted cation exchanger. Sodium measurement can quickly detect this condition and is widely used as the indicator for cation exchange regeneration. The conductivity of cation exchange effluent is always quite high due to the presence of anions and hydrogen ion and

therefore conductivity measurement is not useful for this purpose. Sodium is also measured in power plant water and steam samples because it is a common corrosive contaminant and can be detected at very low concentrations in the presence of higher amounts of ammonia and/or amine treatment which have relatively high background conductivity.

On-line sodium measurement in ultrapure water most commonly uses a glass membrane sodium ion-selective electrode and a reference electrode in an analyzer measuring a small continuously flowing side-stream sample. The voltage measured between the electrodes is proportional to the logarithm of the sodium ion activity or concentration, according to the Nernst equation. Because of the logarithmic response, low concentrations in sub-parts per billion ranges can be measured routinely. To prevent interference from hydrogen ion, the sample pH is raised by the continuous addition of a pure amine before measurement. Calibration at low concentrations is often done with automated analyzers to save time and to eliminate variables of manual calibration. [3]

7.1.3 Dissolved oxygen

Advanced microelectronics manufacturing processes require low single digit to 10 ppb dissolved oxygen (DO) concentrations in the ultrapure rinse water to prevent oxidation of wafer films and layers. DO in power plant water and steam must be controlled to ppb levels to minimize corrosion. Copper alloy components in power plants require single digit ppb DO concentrations whereas iron alloys can benefit from the passivation effects of higher concentrations in the 30 to 150 ppb range.

Dissolved oxygen is measured by two basic technologies: electrochemical cell or optical fluorescence. Traditional electrochemical measurement uses a sensor with a gas-permeable membrane. Behind the membrane, electrodes immersed in an electrolyte develop an electrical current directly proportional to the oxygen partial pressure of the sample. The signal is temperature compensated for the oxygen solubility in water, the electrochemical cell output and the diffusion rate of oxygen through the membrane.

Optical fluorescent DO sensors use a light source, a fluorophore and an optical detector. The fluorophore is immersed in the sample. Light is directed at the fluorophore which absorbs energy and then re-emits light at a longer wavelength. The duration and intensity of the re-emitted light is related to the dissolved oxygen partial pressure by the Stern-Volmer relationship. The signal is temperature compensated for the solubility of oxygen in water and the fluorophore characteristics to obtain the DO concentration value. [4]

7.1.4 Silica
Silica is a contaminant that is detrimental to microelectronics processing and must be maintained at sub-ppb levels. In steam power generation silica can form deposits on heat-exchange surfaces where it reduces thermal efficiency. In high temperature boilers, silica will volatilize and carry over with steam where it can form deposits on turbine blades which lower aerodynamic efficiency. Silica deposits are very difficult to remove. Silica is the first readily measurable species to be released by a spent anion exchange resin and is therefore used as the trigger for anion resin regeneration. Silica is non-conductive and therefore not detectable by conductivity.

Silica is measured on side stream samples with colorimetric analyzers. The measurement adds reagents including a molybdate compound and a reducing agent to produce a blue silico-molybdate complex color which is detected optically and is related to concentration according to the Beer-Lambert law. Most silica analyzers operate on an automated semi-continuous basis, isolating a small volume of sample, adding reagents sequentially and allowing enough time for reactions to occur while minimizing consumption of reagents. The display and output signals are updated with each batch measurement result, typically at 10 to 20 minute intervals. [5]

7.1.5 Particles
Particles in UPW have always presented a big problem for semiconductor manufacture, as any particle landing on a silicon wafer can bridge the gap between the electrical pathways in the semiconductor circuitry. When a pathway is short-circuited the semiconductor device will not work properly; such a failure is called a yield loss, one of the most closely watched parameters in the semiconductor industry. The technique of choice to detect these single particles has been to shine a light beam (a laser) through a small volume of UPW and detect the light scattered by any particles (instruments based on this technique are called Laser Particle Counters or LPCs). As semiconductor manufacturers pack more and more transistors into the same physical space, the circuitry line-width has become narrow and narrower. As a result LPC manufacturers have had to use more and more powerful lasers and very sophisticated scattered light detectors to keep pace. As line-width approaches 10 nm (a human hair is approximately 100,000 nm in diameter) LPC technology is running out of steam, and new particle measurement techniques will be required.

7.1.6 Non-volatile residue
Another type of contamination in UPW is dissolved inorganic material, primarily silica. Silica is one of the most abundant elements on the planet and is found in

all water supplies. Any dissolved inorganic material has the potential to remain on the wafer as the UPW dries. Once again this can lead to a significant loss in yield. To detect trace amounts of dissolved inorganic material a measurement of non-volatile residue is commonly used. This technique involves using a nebulizer to create droplets of UPW suspended in a steam of air. These droplets are dried at a high temperature to produce an aerosol of non-volatile residue particles. A measurement device called a condensation particle counter then counts the residue particles to give a reading in parts per trillion (ppt) by weight. [6]

7.1.7 TOC

Total Organic Carbon is most commonly measured by oxidizing the organics in the water to CO_2, measuring the increase in the CO_2 concentration after the oxidation or delta CO_2, and converting the measured delta CO_2 amount into "mass of carbon" per volume concentration units. The initial CO_2 in the water sample is defined as Inorganic Carbon or IC. The CO_2 produced from the oxidized organics and any initial CO_2 (IC) both together are defined as Total Carbon or TC. The TOC value is then equal to the difference between TC and IC. [7]

Organic oxidation methods for TOC analysis
Oxidation of organics to CO_2 is most commonly achieved in liquid solutions by the creation of the highly oxidizing chemical species, the hydroxyl radical (OH•). Organic oxidation in a combustion environment involves the creation of other energized molecular oxygen species. For the typical TOC levels in UPW systems most methods utilize hydroxyl radicals in the liquid phase.

There are multiple methods to create sufficient concentrations of hydroxyl radicals needed to completely oxidize the organics in water to CO_2, each method being appropriate for different water purity levels. For typical raw waters feeding into the front end of an UPW purification system the raw water can contain TOC levels between 0.7 mg/L to 15 mg/L and require a robust oxidation method that can insure there is enough oxygen available to completely convert all the carbon atoms in the organic molecules into CO_2. Robust oxidation methods that supply sufficient oxygen include the following methods; Ultraviolet light (UV) & persulfate, heated persulfate, combustion, and super critical oxidation. Typical equations showing persulfate generation of hydroxyl radicals follows.

$$S_2O_8^{-2} + hv \text{ (254 nm)} \rightarrow 2 \text{ } SO_2^{-1}\bullet \text{ and } SO_2^{-1}\bullet + H_2O \rightarrow HSO_2^{-1} + OH \bullet$$
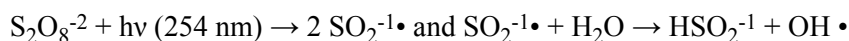
When the organic concentration is less than 1mg/L as TOC and the water is saturated with oxygen UV light is sufficient to oxidize the organics to CO_2, this is a simpler oxidation method. The wavelength of the UV light for the lower TOC waters must be less than 200 nm and is typically 184 nm generated by a low pressure Hg vapor lamp. The 184 nm UV light is energetic enough to break the water molecule into OH and H radicals. The hydrogen radicals quickly react to create H_2. The equations follow:

$$H_2O + h\nu \ (185nm) \rightarrow OH\bullet + H \bullet \ \text{and} \ H \bullet + H \bullet \rightarrow H_2$$
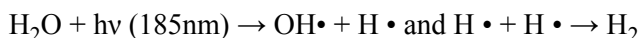
Different types of UPW TOC Analyzers
IC (Inorganic Carbon) = $CO_2 + HCO_3^- + CO_3^{-2}$
TC (Total Carbon) = Organic Carbon + IC
TOC (Total Organic Carbon) = TC – IC
$H_2O + h\nu \ (185 \ nm) \rightarrow OH\bullet + H \bullet$
$S_2O_8^{-2} + h\nu \ (254 \ nm) \rightarrow 2 \ SO_2^{-1}\bullet$
$SO_2^{-1} \bullet + H_2O \rightarrow HSO_4^{-1} + OH \bullet$
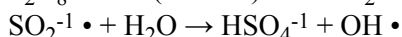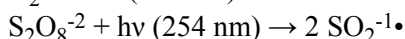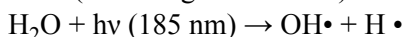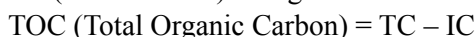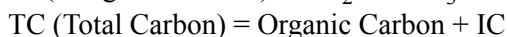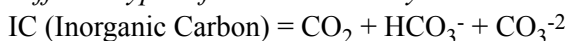
7.2 Offline lab analysis
7.2.1 Definitions
When testing the quality of UPW, consideration is given to where that quality is required and where it is to be measured. The Point of Distribution or Delivery (POD) is the point in the system immediately after the last treatment step and before the distribution loop. It is the standard location for the majority of analytical tests. The Point of Connection (POC) is another commonly used point for measuring quality of UPW. It is located at the Outlet of the submain or lateral take off valve used for UPW supply to the tool.

7.2.1 Grab sample
Grab sample UPW analyses are either complimentary to the on-line testing or alternative, depending on the availability of the instruments and the level of the UPW quality specifications. Grab sample analysis are typically performed for the following parameters: metals, anions, ammonium, silica (both dissolved and total), particles by SEM (scanning electron microscope), TOC (total organic compounds) and specific organic compounds.

7.2.2 Metal analyses

Metal analyses are typically performed by ICP-MS (Inductively coupled plasma mass spectrometry). The detection level depends on the specific type of the instrument used and the method of the sample preparation and handling. Current state-of-the-art methods allow reaching sub-ppt (parts per trillion) level (< 1 ppt) typically tested by ICPMS. [8]

7.2.3 The anion analysis

The anion analysis for seven most common inorganic anions (sulfate, chloride, fluoride, phosphate, nitrite, nitrate, and bromide) is performed by ion chromatography (IC), reaching single digit ppt detection limits. IC is also used to analyze ammonia and other metal cations. However ICPMS is the preferred method for metals due to lower detection limits and its ability to detect both dissolved and non-dissolved metals in UPW. IC is also used for the detection of urea in UPW down to the 0.5 ppb level. Urea is one of the more common contaminants in UPW and probably the most difficult for treatment.

7.2.4 Silica analysis

Silica analysis in UPW typically includes determination of reactive and total silica. [9] Due to the complexity of silica chemistry, the form of silica measured is defined by the photometric (colorimetric) method as molybdate-reactive silica. Those forms of silica that are molybdate-reactive include dissolved simple silicates, monomeric silica and silicic acid, and an undetermined fraction of polymeric silica. Total silica determination in water employs high resolution ICPMS, GFAA (Graphite furnace atomic absorption), [10] and the photometric method combined with silica digestion. For many natural waters, a measurement of molybdate-reactive silica by this test method provides a close approximation of total silica, and, in practice, the colorimetric method is frequently substituted for other more time-consuming techniques. However, total silica analysis becomes more critical in UPW, where the presence of colloidal silica is expected due to silica polymerization in the ion exchange columns. Colloidal silica is considered more critical than dissolved in the electronic industry due to the bigger impact of nano-particles in water on the semiconductor manufacturing process. Sub-ppb (parts per billion) levels of silica make it equally complex for both reactive and total silica analysis, making the choice of total silica test often preferred.

7.2.5 Although particles and TOC

Although particles and TOC are usually measured using on-line methods, there is significant value in complimentary or alternative off-line lab analysis. The value of the lab analysis has two aspects: cost and speciation. Smaller UPW facilities that cannot afford to purchase on-line instrumentation often choose off-line testing. TOC can be measured in the grab sample at a concentration as low as 5 ppb, using the same technique employed for the on-line analysis (see on-line method description). This detection level covers the majority of needs of less critical electronic and all pharmaceutical applications. When speciation of the organics is required for troubleshooting or design purposes, liquid chromatography-organic carbon detection (LC-OCD) provides an effective analysis. This method allows for identification of biopolymers, humics, low molecular weight acids and neutrals, and more, while characterizing nearly 100% of the organic composition in UPW with sub-ppb level of TOC. [11;12]

7.2.6 SEM particle

SEM particle analysis is similar to TOC and represents a lower cost alternative to the expensive online measurements and therefore it is commonly a method of choice in less critical applications. SEM analysis can provide particle counting for particle size down to 50 nm, which generally is in-line with the capability of online instruments. The test involves installation of the SEM capture filter cartridge on the UPW sampling port for sampling on the membrane disk with the pore size equal or smaller than the target size of the UPW particles. The filter is then transferred to the SEM microscope where its surface is scanned for detection and identification of the particles. The main disadvantage of SEM analysis is long sampling time. Depending on the pore size and the pressure in the UPW system, the sampling time can be between one week and one month. However, typical robustness and stability of the particle filtration systems allow for successful applications of the SEM method. Application of Energy Dispersive X-ray Spectroscopy (SEM-EDS) provides compositional analysis of the particles, making SEM also helpful for systems with on-line particle counters.

7.2.7 Bacteria analysis

Bacteria analysis is typically conducted following ASTM method F1094. [13] The test method covers sampling and analysis of high purity water from water purification systems and water transmission systems by the direct sampling tap and filtration of the sample collected in the bag. These test methods cover both the sampling of water lines and the subsequent microbiological analysis of the

sample by the culture technique. The microorganisms recovered from the water samples and counted on the filters include both aerobes and facultative anaerobes. The temperature of incubation is controlled at 28 ± 2 C, and the period of incubation is 48 h or 72 h, if time permits. Longer incubation times are typically recommended for most critical applications. However 48 hrs is typically sufficient to detect water quality upsets.

Chapter 7 sources:

1. ASTM D1125 Standard Test Methods for Electrical Conductivity and Resistivity of Water
2. ASTM D5391 Standard Test Method for Electrical Conductivity and Resistivity of a Flowing High Purity Water Sample
3. ASTM D2791 Standard Test Method for On-line Determination of Sodium in Water
4. ASTM D5462 Standard Test Method for On-Line Measurement of Low-Level Dissolved Oxygen in Water
5. ASTM D7126 Standard Test Method for On-Line Colorimetric Measurement of Silica
6. ASTM D5544 Standard Method for On-Line Measurement of residue After Evaporation of High Purity Water.
7. ASTM D5997 - 96 Standard Test Method for On-Line Monitoring of Total Carbon, Inorganic Carbon in Water by Ultraviolet, Persulfate Oxidation, and Membrane Conductivity Detection.
8. Lee, Albert; Yang, Vincent; Hsu, Jones; Wu, Eva; Shih, Ronan. "Ultratrace measurement of calcium in ultrapure water using the Agilent 8800 Triple Quadrupole ICP-MS". Agilent Technologies.
9. ASTM D4517 Standard Test Method for Low-Level Total Silica in High-Purity Water by Flameless Atomic Absorption Spectroscopy
10. ASTM D859 Standard Test Method for Silica in Water
11. Huber S. A., Balz A, Abert M., and Pronk W. (2011) Characterisation of Aquatic Humic and Non-humic Matter with Size-Exclusion Chromatography - Organic Carbon Detection - Organic Nitrogen Detection (LC-OCD-OND). Water Research 4 5 (2 011) 879-885.
12. Huber, Stefan; Libman, Slava (May–June 2014). "Part 1: Overview of LC-OCD: Organic Speciation in Service of Critical Analytical Tasks of Semiconductor Industry". Ultrapure Water Journal 31 (3): 10–16.

II

Industrial Wastewater Treatment

Chapter 8
Industrial Wastewater Characterisation

8.1 General principles of industrial wastewater characterization

The purposes of pollution control endeavours should be (1) to protect the assimilative capacity of surface waters; (2) to protect shellfish, finfish and wildlife; (3) to preserve or restore the aesthetic and recreational value of surface waters; (4) to protect humans from adverse water quality conditions.

The selection and design of treatment facilities is based on a study of
- the physical, chemical and biological characteristics of the wastewater
- the quality that must be maintained in the environment to which the wastewater is to be discharged or for the reuse of the wastewater
- the applicable environmental standards or discharge requirements that must be met

The main chemical characteristics of wastewater are divided into two classes, inorganic and organic. Because of their special importance, priority pollutants and volatile organic compounds (VOCs) are usually considered separately.

8.2 Physical characteristics

The principal physical characteristics of wastewater are its solids content, colour, odour and temperature.

The total solids in a wastewater consist of the insoluble or suspended solids and the soluble compounds dissolved in water. The suspended solids content is found by drying and weighing the residue removed by the filtering of the sample. When this residue is ignited the volatile solids are burned off. Volatile solids are presumed to be organic matter, although some organic matter will not burn and some inorganic salts break down at high temperatures. The organic matter consists mainly of proteins, carbohydrates and fats.

Between 40 and 65% of the solids in an average wastewater are suspended. Settleable solids, expressed as milliliters per litre, are those that can be removed by sedimentation. Usually about 60% of the suspended solids in a municipal wastewa-

ter are settleable. Solids may be classified in another way as well: those that are volatilised at a high temperature (600 °C) and those that are not. The former are known as volatile solids, the latter as fixed solids. Usually, volatile solids are organic.

Color is a qualitative characteristic that can be used to assess the general condition of wastewater. Wastewater that is light brown in colour is less than 6 h old, while a light-to- medium grey color is characteristic of wastewaters that have undergone some degree of decomposition or that have been in the collection system for some time. Lastly, if the colour is dark grey or black, the wastewater is typically septic, having undergone extensive bacterial decomposition under anaerobic conditions. The blackening of wastewater is often due to the formation of various sulphides, particularly, ferrous sulphide. This results when hydrogen sulphide produced under anaerobic conditions combines with divalent metal, such as iron, which may be present. Colour is measured by comparison with standards.

The determination of odour has become increasingly important, as the general public has become more concerned with the proper operation of wastewater treatment facilities. The odor of fresh wastewater is usually not offensive, but a variety of odorous compounds are released when wastewater is decomposed biologically under anaerobic conditions. The principal odorous compound is hydrogen sulphide (the smell of rotten eggs). Other compounds, such as indol, skatol, cadaverin and mercaptan, formed under anaerobic conditions or present in the effluents of pulp and paper mills (hydrogen sulphide, mercaptan, dimethylsulphide etc.), may also cause a rather offensive odour. Odour is measured by successive dilutions of the sample with odour-free water until the odour is no longer detectable.

The temperature of wastewater is commonly higher than that of the water supply because warm municipal water has been added. The measurement of temperature is important because most wastewater treatment schemes include biological processes that are temperature dependent. The temperature of wastewater will vary from season to season and also with geographic location. In cold regions the temperature will vary from about 7 to 18 °C, while in warmer regions the temperatures vary from 13 to 24 °C.

8.3 Chemical characteristics

8.3.1 Inorganic chemicals

The principal chemical tests include free ammonia, organic nitrogen, nitrites, nitrates, organic phosphorus and inorganic phosphorus. Nitrogen and phosphorus are important because these two nutrients are responsible for the growth of aquatic plants.

Other tests, such as chloride, sulphate, pH and alkalinity, are performed to assess the suitability of reusing treated wastewater and in controlling the various treatment processes.

Trace elements, which include some heavy metals, are not determined routinely, but trace elements may be a factor in the biological treatment of wastewater. All living organisms require varying amounts of some trace elements, such as iron, copper, zinc and cobalt, for proper growth. Heavy metals can also produce toxic effects; therefore, determination of the amounts of heavy metals is especially important where the further use of treated effluent or sludge is to be evaluated. Many of the metals are also classified as priority pollutants (see below).

Measurements of gases, such as hydrogen sulphide, oxygen, methane and carbon dioxide, are made to help the system to operate. The presence of hydrogen sulphide needs to be determined not only because it is an odorous gas but also because it can affect the maintenance of long sewers on flat slopes, since it can cause corrosion. Measurements of dissolved oxygen are made in order to monitor and control aerobic biological treatment processes. Methane and carbon dioxide measurements are used in connection with the operation of anaerobic digesters.

8.3.2 Organic chemicals

Over the years, a number of different tests have been developed to determine the organic content of wastewaters. In general, the tests may be divided into those used to measure gross concentrations of organic matter greater than about 1 mg/l and those used to measure trace concentrations in the range of 10^{-12} to 10^{-0} mg/l. Laboratory methods commonly used today to measure gross amounts of organic matter (greater than 1 mg/l) in wastewater include (1) biochemical oxygen demand (BOD), (2) chemical oxygen demand (COD) and (3) total organic carbon (TOC).

Trace organics in the range of 10^{-12} to 10^{-0} mg/l are determined using instrumental methods including gas chromatography and mass spectroscopy. Specific organic compounds are determined to assess the presence of priority pollutants. The BOD, COD and TOC tests are gross measures of organic content and as such do not reflect the response of the wastewater to various types of biological treatment technologies. It is therefore desirable to divide the wastewater organic constituents into several categories, as shown in Figure 8.1.

8.3.3 Volatile Organic Carbons (VOC)

Volatile organic compounds (VOC) such as benzene, toluene, xylenes, dichloromethane, trichloroethane and trichloroethylene, are common soil pollutants in industrialised and commercialised areas. One of the more common sources of
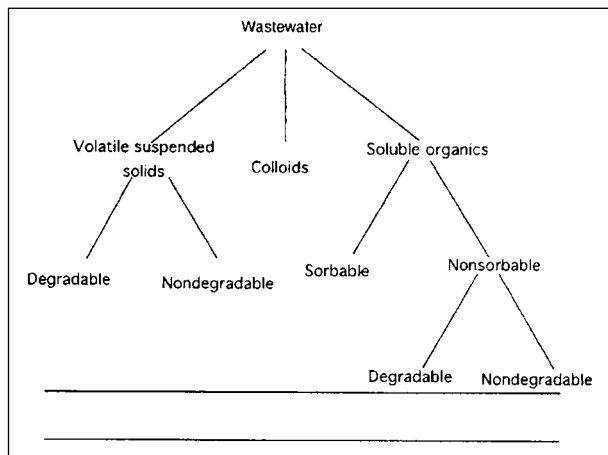
Figure 8.1. Partition of organic constituents of a wastewater (Adapted from Eckenfelder, 1989).

these contaminants is leaking underground storage tanks. Improperly discarded solvents and landfills, built before the introduction of current stringent regulations, are also significant sources of soil VOCs.

In Table 8.1 a list of typical inorganic and organic substances present in industrial effluents is presented.

8.4 Heavy metals and inorganic species

8.4.1 Heavy metal discharges

Several industries discharges heavy metals (Table 8.2).

It can be seen that of all of the heavy metals chromium is the most widely used and discharged to the environment from different sources. However, it is not the metal that is most dangerous to living organisms. Much more toxic are cadmium, lead and mercury.

These have a tremendous affinity for sulphur and disrupt enzyme function by forming bonds with sulphur groups in enzymes. Protein carboxylic acid ($-CO_2H$) and amino ($-NH_2$) groups are also chemically bound by heavy metals. Cadmium, copper, lead and mercury ions bind to cell membranes, hindering transport processes through the cell wall. Heavy metals may also precipitate phosphate bio-compounds or catalyse their decomposition.

The pollutant cadmium in water may arise from industrial discharges and mining wastes. Cadmium is widely used in metal plating. Chemically, cadmium is very similar to zinc, and these two metals frequently undergo geochemical processes together. Both metals are found in water in the +2 oxidation state. The

Table 8.1. Substances Present in Industrial Effluents (Bond & Straub, 1974)

Substances	Present in wastewaters from
Acetic acid	Acetate rayon, beet root manufact.
Acids	Chem. manufact., mines, textiles manufact.
Alkalies	Cotton and straw kiering, wool scouring
Ammonia	Gas and coke and chem. manufact.
Arsenic	Sheep dipping
Cadmium	Plating
Chromium	Plating, chrome tanning, alum anodizing
Citric acid	Soft drinks and citrus fruit processing
Copper	Copper plating, copper pickling
Cyanides	Gas manufacture, plating, metal cleaning
Fats, oils, grease	Wool scouring, laundries, textile industry
Fluorides	Scrubbing of flue gases, glass etching
Formaldehyde	Synthetic resins and penicillin manufact.
Free chlorine	Laundries, paper mills, textile bleaching
Hydrocarbons	Petrochemical and rubber factories
Mercaptans	Oil refining, pulpmills
Nickel	Plating
Nitrocompounds	Exoplosives and chemical works
Organic acids	Distilleries and fermentation plants
Phenols	Gas and coke manufact., chemical plants
Starch	Food processing, textile industries
Sugars	Dairies, breweries, sweet industry
Sulfides	Textile industry, tanneries, gas manufact.
Sulfites	Pulp processing, viscose film manufact.
Tannic acid	Tanning, sawmills
Tartaric acid	Dyeing, wine, leather, chem. manufacture
Zinc	Galvanizing zinc plating, rubber process.

Table 8.2. Heavy Metals Found in Major Industries (Bond & Straub, 1974)

Industry	Al	As	Cd	Cr	Cu	Hg	Pb	Ni	Zn
Pulp and paper mills				x	x	x	x	x	x
Organic chem.	x	x	x	x		x	x		x
Alcalies, Chlorine		x	x	x		x	x		x
Fertilizers	x	x	x	x	x	x	x	x	x
Petroleum refin.	x	x	x	x	x		x	x	x
Steelworks		x	x	x	x	x	x	x	x
Aircraft plating, finishing	x		x	x	x	x		x	
Flat glass, cement				x					
Textile mills				x					
Tanning				x					
Power plants				x					

effects of acute cadmium poisoning in humans are very serious. Among them are high blood pressure, kidney damage, destruction of testicular tissue, and destruction of red blood cells. Cadmium may replace zinc in some enzymes, thereby altering the stereo-structure of the enzyme and impairing its catalytic activity.

Cadmium and zinc are common water and sediment pollutants in harbours surrounded by industrial facilities. Concentrations of more than 100 ppm dry weight sediment have been found in harbour sediments.

Inorganic lead arising from a number of industrial and mining sources occurs in water in the +2 oxidation state. Lead from leaded gasoline used to be a major source of atmospheric and terrestrial lead, much of which eventually enters natural water systems. Despite greatly increased total use of lead by industry, evidence from hair samples and other sources indicates that body burdens of this toxic metal have decreased during recent decades. This may be the result of less lead used in plumbing and other products that commonly come in contact with food or drink. Acute lead poisoning in humans causes severe dysfunction in the kidneys, reproductive system, liver, and the brain and nervous system.

Mercury, because of its toxicity, its mobilisation as methylated forms by anaerobic bacteria, and other pollution factors, mercury generates a great deal of concern as a heavy-metal pollutant. Mercury is found as a trace component of many minerals, with continental rocks containing an average of around 80 ppb, or slightly less, of this element. Cinnabar, red mercuric sulphide, is the chief commercial mercury ore. Metallic mercury is used as an electrode in the electrolytic generation of chlorine gas, in laboratory vacuum apparatuses and in other applications. Organic mercury compounds used to be widely applied as pesticides, particularly fungicides. Mercury enters the environment from a large number of miscellaneous sources related to human use of the element. These include discarded laboratory chemicals, batteries, broken thermometers, lawn fungicides, amalgam tooth fillings and pharmaceutical products. Sewage effluent sometimes contains up to 10 times the level of mercury found in typical natural waters.

The toxicity of mercury was tragically illustrated in the Minamata Bay area of Japan during the period of 1953-1960. A total of 111 cases of mercury poisoning and 43 deaths were reported among people who had consumed seafood from the contaminated bay. Among the toxicological effects of mercury were neurological damage, including irritability, paralysis, blindness, insanity, chromosome breakage and birth defects. The milder symptoms of mercury poisoning, such as depression and irritability, have a psychopathological character and may escape detection. The unexpectedly high concentrations of mercury found in water and in fish tissues result from the formation of soluble monomethylmercury ion,

CH_3Hg^+, and volatile dimethylmercury, $(CH_3)2Hg$, by anaerobic bacteria in sediments. Mercury from these compounds becomes concentrated in fish lipid (fat) tissue and the concentration factor from water to fish may exceed 103.

8.4.2 Cyanide

Cyanide ion, CN-, is probably the most important of the various inorganic species in wastewater. Cyanide, a deadly poisonous substance, exists in water as HCN, a weak acid with the dissociation constant Ka of $6 \cdot 10^{-10}$. The cyanide ion has a strong affinity for many metal ions, forming relatively lesstoxic ferro-cyanide, $Fe(CN)_6^{4-}$, with iron (II), for example. Volatile HCN is very toxic and has been used in gas chamber executions in the United States (Manahan, 1994). Cyanide is widely used in industry, especially for metal cleaning and electroplating. It is also one of the main gas and coke scrubber effluent pollutants from gas works and coke ovens. Cyanide is widely used in certain mineral-processing operations.

8.4.3 Ammonia

Ammonia is the initial product of the decay of nitrogenous organic wastes, and its presence frequently indicates the presence of such wastes. It is a normal constituent of some sources of groundwater and is sometimes added to drinking water to remove the taste and odour of free chlorine. Since the pKa of the ammonium ion, NH_4^+, is 9.26, most ammonia in water is present as NH_4^+ rather than NH_3.

8.4.4 Other inorganic pollutants

Hydrogen sulphide, H_2S, is a product of the anaerobic decay of organic matter containing sulphur It is also produced in the anaerobic reduction of sulphate by microorganisms and is developed as a gaseous pollutant from geothermal waters. Wastes from chemical plants, paper mills, textile mills and tanneries may also contain H_2S.

Nitrite ion, NO_2-, occurs in water as an intermediate oxidation state of nitrogen. Nitrite is added to some industrial processes to inhibit corrosion; it is rarely found in drinking water at levels over 0.1 mg/l.

Sulphite ion, SO_2^{2-}, is found in some industrial wastewaters. Sodium sulphite is commonly added to boiler feed-waters as an oxygen scavenger:

$$2SO_2^{2-} + O2 \rightarrow 2\ SO_2^{2-} \qquad (1)$$

8.4.5 Organic pollutants

Effluent from industrial sources contains a wide variety of pollutants, including organic pollutants. Primary and secondary sewage treatment processes remove some of these pollutants, particularly oxygen-demanding substances, oil, grease and sol-

ids. Others, such as refractory (degradation- resistant) organics (organochlorides, nitro compounds etc.) and salts and heavy metals, are not efficiently removed.

Soaps, detergents and associated chemicals are potential sources of organic pollutants. Most of the environmental problems currently attributed to detergents do not arise from the surface-active agents, which basically improve the wetting qualities of water. The greatest concern among environmental pollutants has been caused by polyphosphates added to complex calcium, functioning as a builder.

Bio-refractory organics are poorly biodegradable substances, prominent among which are aromatic or chlorinated hydrocarbons (benzene, bornyl alcohol, bromobenzene, chloroform, camphor, dinitrotoluene, nitrobenzene, styrene etc.). Many of these compounds have also been found in drinking water. Water contaminated with these compounds must be treated using physical and chemical methods, including air stripping, solvent extraction, ozonation and carbon adsorption.

Polychlorinated biphenyls (PCB compounds) first discovered as environmental pollutants in 1966 (Manahan, 1994), PCB compounds have been found throughout the world in water, sediments and bird and fish tissue. They are made by substituting between 1 and 10 Cl atoms onto the biphenyl aromatic structure. This substitution can produce 209 different compounds.

PCBs have very high chemical, thermal and biological stability, low vapour pressure and high dielectric constants. These properties have made PCBs attractive as coolant-insulation fluids in transformers and capacitors, in the impregnation of cotton and asbestos, as plasticizers and as additives to some epoxy paints.

8.4.6 Priority pollutants

The USEPA (Keith & Telliard, 1979) has defined 129 toxic chemicals as priority pollutants:

- 31 are purgeable organics (benzene, toluene, carbon tetrachloride, chlorobenzene, chloroform, bromoform, vinyl chloride etc.);
- 46 are base/neutral extractable organic compounds (nitrobenzene, naphthalene, fluorine, chrysene, pyrene, anthracene, acenaphthene, dinitrotoluene etc.);
- 11 are acid extractable organic compounds (phenol, 2-and 4-nitrophenols, pentachlorophenol, 2-chlorophenol, 2,4-dimethyl-phenol etc.);
- 26 are pesticides/PCB's (aldrin, dieldrin, chlordane, toxaphene, heptachlor etc.);
- 13 are metals (antimony, arsenic, cadmium, chromium, copper, lead, mercury, nickel, thallium etc.);

To this list are also included total cyanides, total phenols and asbesto

8.5 Thermal pollution

Considerable time has elapsed since the scientific community and regulatory agencies officially recognised that the addition of large quantities of heat to a recipient possesses the potential of causing ecological harm.

The really significant heat loads result from the discharge of condenser cooling water from the everincreasing number of steam electrical generating plants (Figure 8.2) and equivalent-sized nuclear power reactors. Large numbers of power plants currently require approximately 50% more cooling water for a given temperature rise than that required of fossil-fuelled plants of an equal size.

The degree of thermal pollution depends on thermal efficiency, which is determined by the amount of heat rejected into the cooling water. Thermodynamically, heat should be added at the highest possible temperature and rejected at the lowest possible temperature if the greatest amount of effect is to be gained and the best thermal efficiency realised.

The current and generally accepted maximum operating conditions for conventional thermal stations are about 500 °C and 24 MPa, with a corresponding heat rate of 2.5kWh, 1.0 kWh resulting in power production and 1.5 kWh being wasted. Plants have been designed for 680 °C and 34 MPa; however, metallurgical problems have kept operating conditions at lower levels.

Nuclear power plants operate at temperatures of from 250 to 300 °C and pressures of up to 7MPa, resulting in a heat rate of approximately 3.1 kWh. Thus, for nuclear plants, 1.0 kWh may be used for useful production whereas 2.1 kWh is wasted.
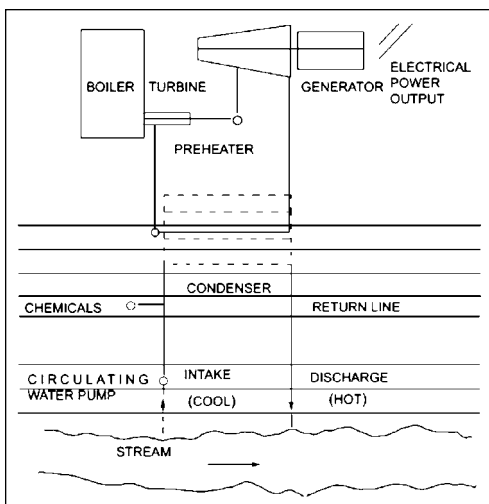

Figure 8.2. Schematic diagram of once-through cooling and steam electrical generation (Krenkel & Novotny, 1980).
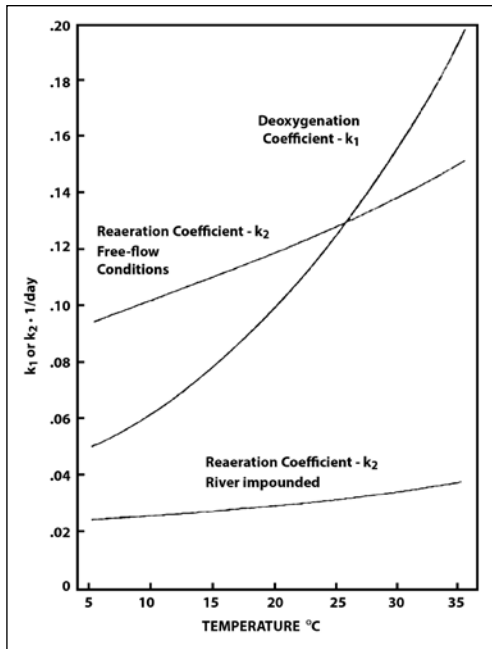
Figure 8.3. Variation of k1 and k2 with temperature (Krenkel & Novotny, 1980).

Most steam-powered electrical generating plants are operated at varying load factors, and, consequently, the heated discharges demonstrate wide variation with time. Thus, the biota is not only subjected to increased or decreased temperature, but also to a sudden, or "shock," temperature change.

The effects of temperature on the stream self-purification process in rivers are demonstrated in Figure 8.3, which shows the variation of the rate constants k_1 (deoxygenation) and k_2 (reaeration) with respect to temperature. Examination of this relationship demonstrates that an increase in temperature causes a considerable increase in k_1. While k_2 also increases with increasing temperature, this is counteracted by the combination of lesser dissolved-oxygen content and greater rate of change of k_1 with temperature. The overall effect of the impoundment on the rate of oxygen recovery is demonstrated by the lower curve, which depicts the reaeration rate constant under existing, impounded conditions. Note that, while k_1 at a given temperature is unchanged, the value of k_2 at any temperature is significantly reduced.

Increased temperature will cause remarkable reduction in the self-purification capacity of a water body. The addition of heated water to the receiving water can be considered equivalent to the addition of sewage or other organic waste

material, since both pollutants may cause a reduction in the oxygen resources of the receiving waters.

In most cases, the increases in temperature are small and probably do not cause biological harm outside the mixing zone. In fact, little data exists to support the claims of extensive heat damage from power plants on the biota. Furthermore, besides entrainment problems, few substantiated fish kills have been reported as a result of power plant operations.

The possible effects of heat on fish may be summarised here:

a Direct death from excessive temperature rise beyond the thermal death point.

b Indirect death due to:
- less oxygen available
- disruption of the food supply
- decreased resistance to toxic materials
- decreased resistance to disease
- predation from more tolerant species
- synergism with toxic substances

c Increase in respiration and growth
d Competitive replacement by more tolerant species
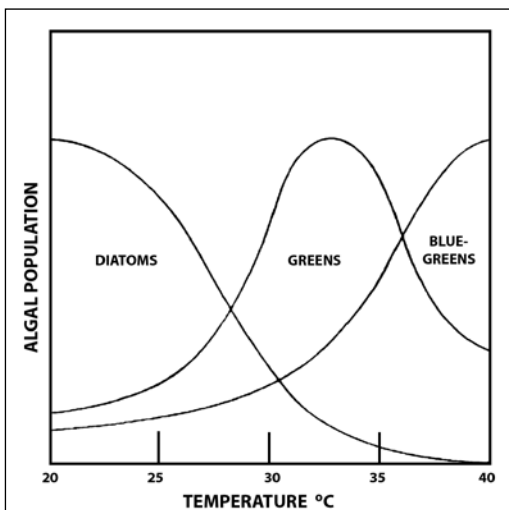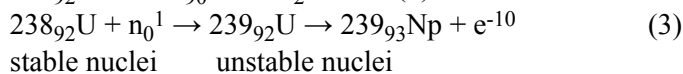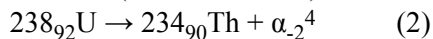e Sub-lethal effects

Figure 8.4. Algae population shifts with change in temperature (Krenkel & Novotny, 1980).

While each of these factors could be important at a specific location, the temperature rises typical of most power plants are usually not high enough to be of concern. It is interesting to note that field research studies on the effects of heat on the environment have been hindered, both in the United States and Europe, because of the lack of sufficient temperature elevations below existing power plants.

Figure 8.4 shows that increased temperatures cause the growth of undesirable algae. There are other negative results as well, e.g. Escherichia coli multiply much more rapidly at elevated temperatures.

8.6 Radioactivity and radioactive pollution

The massive production of radionuclides (radioactive isotopes) from weapons and nuclear reactors since World War II has been accompanied by an increasing concern about the effects of radioactivity upon health and the environment. Radionuclides are produced as fission products of heavy nuclei of elements such as uranium or plutonium. They are also produced by the reaction of neutrons with stable nuclei (Manahan, 1994):

$$238_{92}U \rightarrow 234_{90}Th + \alpha_{-2}^4 \qquad (2)$$
$$238_{92}U + n_0^1 \rightarrow 239_{92}U \rightarrow 239_{93}Np + e^{-10} \qquad (3)$$
stable nuclei   unstable nuclei

Radionuclides are formed in large quantities as waste products in nuclear power generation. Artificially produced radionuclides are also widely used in industrial and medical applications, particularly as tracers. Radionuclides differ from other nuclei in that they emit ionising radiation – alpha particles, beta particles and gamma rays. The levels of radionuclides found in water are typically measured in units of picocuries/litre, where a curie is $3.7 \cdot 10^{10}$ disintegrations per second.

The decay of a specific radionuclide follows firstorder kinetics:

$$-dN/dt = kN \qquad (4)$$

where N is the number of radioactive nuclei present and k is the rate constant, which has units of reciprocal time. The half-life, $t_{1/2}$, is generally used instead of k to characterise a radionuclide:

$$t_{1/2} = 0.693/k \qquad (5)$$

As the term implies, a half-life is the period of time during which half of a given number of atoms, of a specific kind of radionuclide, decays. Ten half-lives are required for the loss of 99.9% of the activity of a radionuclide.

Radiation damages living organisms by initiating harmful chemical reactions in tissues. For example, bonds are broken in the macromolecules that carry out life processes. In cases of acute radiation poisoning, bone marrow, which produces red blood cells, is destroyed and the concentration of red blood cells is diminished. Radiation-induced genetic damage is of great concern. The radionuclide of most concern in drinking water is radium, Ra. In all areas of the uranium-producing regions in the USA significant radium contamination of water has been observed. As the use of nuclear power has increased, the possible contamination of water by fission-product radioisotopes has become more of a cause for concern. Table 8.3 summarises the major natural and artificial radionuclides likely to be encountered in water.

Transuranic elements are of growing concern in aquatic (oceanic) environment. These alpha emitters (various isotopes of neptunium, plutonium, americium, curium) are long-lived and highly toxic.

Table 8.3. Radionuclides in water (adapted from Manahan, 1994)

Radionuclide	Half-life	Reaction, source
Natural reactions		
Carbon-14	5,730 years	^{14}N (n,p); ^{14}C
Silicon-32	300 years	^{40}Ar (p,x); ^{32}Si
Potassium-40	$1.4 \cdot 10^9$ years	0.0119% of natural K
Naturally occuring from ^{238}U series		
Radium-226	1,620 years	Diffusion from sediments
Lead-210	21 years	^{226}Ra, 6 steps, ^{210}Pb
Thorium-230	75,200 years	^{238}U, 3 steps, ^{230}Th
Thorium-234	24 days	$^{238}U \rightarrow ^{234}Th$ in situ
From reactor and weapons fission		
Strontium-90	28 years	Important isotopes of high biological activity
Iodine-131	8 days	
Cesium-137	30 years	
Barium-140	13 days	The isotopes from ^{140}Ba through ^{85}Kr are listed in decreasing order of fission field
Zirconium-95	65 days	
Cerium-141	33 days	
Strontium-89	51 days	
Ruthenium-103	40 days	
Krypton-85	10.3 years	
Cobalt-60	5.25 years	From nonfission reactions
Manganese-54	310 years	From nonfission reactions
Iron-55	2.7 years	^{56}Fe (n,2n), ^{55}Fe
Plutonium-239	24,300 years	^{238}U (n, γ), ^{239}Pu

8.7 Pollution load and concentration

In most industries, wastewater effluents result from the following water uses:
- sanitary wastewater (from washing, drinking and personal hygiene);
- cooling (from disposing of excess heat to the environment);
- process wastewater (including both water used for making and washing products and for removal and transport of waste and by-products); and
- cleaning (including wastewater from cleaning and maintenance of industrial areas).

Excluding the large volumes of cooling water discharged by the electric power industry, the wastewater production from urban areas is about evenly divided between industrial and municipal sources. Therefore, the use of water by industry can significantly affect the water quality of receiving waters.

The level of wastewater loading from industrial sources varies markedly with the water quality objectives enforced by the regulatory agencies. There are many possible in-plant changes, process modifications and water-saving measures through which industrial wastewater loads can be significantly reduced. Up to 90% of recent wastewater reductions have been achieved by industries employing such methods as recirculation, operation modifications, effluent reuse or more efficient operation.

As a rule, treatment of an industrial effluent is much more expensive without water-saving measures than the total cost of in-plant modifications and residual effluent treatment.

Industrial wastewater effluents are usually highly variable, with quantity and quality variations brought about by bath discharges, operation start-ups and shutdowns, working-hour distribution and so on. A long-term detailed survey is usually necessary before a conclusion on the pollution impact from an industry can be reached.

The population equivalent (PE) is used to compare how many people it would take to produce the same amount of pollution as produced by the industrial wastewater effluent under consideration. The following per capita (cap) loadings have been agreed upon for the population equivlent estimation:

Biochemical Oxygen Demand (BOD_5) PE
    1 PE = 60g of BOD_5/day

Chemical Oxygen Demand (COD) PE
    1 PE = 120g of COD/day

Table 8.4. Flow and population equivalents for some typical industrial raw wastes (Krenkel & Novotny, 1980)

Industry	Production unit	Flow/prod. unit	PE (BOD$_5$)	PE (SS)
Slaughterhouse	1 hog (0.4 cattle unit	600	18	6
Poultry	1,000 kg	18.3	300	130
General dairy	1,000 kg of raw milk	2.91	10	7
Cheese factory	1,000 kg of raw milk	1.66	16	6
Brewery	119.2 l of beer	1.78	19	13
Beet sugar	ton of raw beets	2.74	40	29
Paper mill	ton of raw paper	159	26	704
Pulp mill (kraft)	ton of raw pulp	260		
Tanning (Cr)	100 kg of hides	29	80	520
Laundry	100 kg of clothes	12.4	24	8
Oil refining	159 l crude oil	2.91	00.06	01.00

Table 8.5. Comparative strengths of wastewaters from industry (Bond & Straub, 1974)

Type of waste	BOD5 (mg/l)	COD (mg/l)	SS (mg/l)	pH
Apparel				
Cotton	200-1,000	400-1,800	200	8-12
Wool scouring	2,000-5,000	2,000-5,000[a]	3,000-30,000	9-11
Wool composite	1	-	100	9-10
Tannery	1,000-2,000	2,000-4,000	2,000-3,000	11-12
Laundry	1,600	2,700	250-500	8-9
Food				
Brewery	850	1,700	90	4-8
Distillery	7	10	low	-
Dairy	600-1,000	150-250[a]	200-400	Acid
Cannery				
citrus	2,000	-	7,000	Acid
pea	570	-	130	Acid
Slaughterhouse	1,500-2,500	200-400[a]	800	7
Potato processing	2,000	3,500	2,500	11-13
Sugar beet	450-2,000	600-3,000	800-1,500	7-8
Farm	1,000-2,000	500-1,000[a]	1,500-3,000	7.5-8.5
Poultry	500-800	600-1,050	450-800	6.5-9
Materials				
Pulp; sulfite	1,400-1,700	84-10,000	variable	
Pulp; kraft	100-350	170-600	75-300	7-9.5
Paperboard	100-450	300-1,400	40-100	
Strawboard	950	850[a]	1,350	
Coke owen	780	1,650[a]	70	7-11
Oil refinery	100-500	150-800	130-600	2-6
[a] = CODMn. mg O$_2$/l				

Suspended solids

    1 PE = 70 g/day

Population equivalents for some industrial wastes can be related to production units as shown in Table 8.4. These numbers represent only very rough estimates for planning purposes. For more precise numbers, the PE estimates should always be verified by a survey and/or by consulting the plant engineer.

    In Table 8.5 the values of typical concentration parameters (BOD$_5$, COD, suspended solids) and pH for different industrial effluents are given.

8.8 Differences between industrial and municipal wastes

The number of contaminants in industrial waste can run in a scale from zero to about 100,000 parts per million. Industrial waste varies temporally and, in the normal course of operation, is unpredictable. The strengths and volumes of municipal sewage, on the other hand, are well established and occur within the

Table 8.6. Examples of industrial wastewater concentrations for BOD$_5$ and suspended solids

Industry	BOD5, mg/L	Suspended solids, mg/L
Ammunition	50-300	70–1,700
Fermentation	4,500	10,000
Food processing	100-6,900	30-3,500
Pulp and paper (kraft)	100-350	75-300
Slaughterhouse (cattle)	400-2,500	400–1,000
Tannery	700-7,000	4,000-20,000

Table 8.7. Examples of industrial wastewater concentrations for nonconventional pollutants

Industry	Pollutant	Concentration, mg/L
Coke by-product (steel mill)	Ammonia (as N)	200
	Organic nitrogen (as N)	100
	Phenol	2,000
Metal plating	Chromium VI valent	3-550
Nylon polymer	COD	23,000
	TOC	8,800
Plywood-plant glue waste	COD	2,000
	Phenol	200-2,000
	Phosphorus (as PO$_4$)	9-15

rather narrow limits of 100 to 1,000 parts per million for the contaminants that are generally measured in volumes of 50 to 150 litres per person per day. If we take the population equivalent (PE) of domestic sewage by BOD as a unit, then the corresponding PE values for industrial effluents are in the range of about 5-1 500 depending on the branch of industry. Because of the wide variety of industries and levels of pollutants, only a snapshot view of the characteristics can be presented. A sampling of a few industries for two conventional pollutants is shown in Table 8.6. A similar sampling for nonconventional pollutants is shown in Table 8.7. (W&WE Mackenzee)

Industrial waste deoxygenates at rates that vary from negative values to about 5 times the rates at which normal domestic sewage deoxygenates. Some industrial wastes have no organic matter and thus no oxygenation rate or oxygen demand. Domestic sewage deoxygenates at a quite constant rate, seldom outside the range 0.07 to 0.20, and is usually discharged independently of the time of day or week.

And finally, a municipality views wastewater treatment as a service to the community, while industry view wastewater treatment as an imposed necessity.

Chapter 8 sources:

1- Rein Munter, Industry and water use, BUP Environmental science, Chapter 17, Lars-Christer Lundin & Lars Ryden.

2- Rein Munter, Industrial wastewater characteristics, BUP Environmental science, Chapter 18, Lars-Christer Lundin & Lars Ryden.

3- Mackenzie L. Davis Water and Wastewater Engineering: Design Principles and Practice, McGraw-Hill New York (2010) ISBN: 978-0-07-171385-6, 1301p.

4- Metcalf & Eddy (2003) Wastewater Engineering: Treatment and Reuse,4th ed., McGraw-Hill, Boston, pp. 452–453, 820–840, 1217–1343.

Chapter 9
Conventional Industrial Wastewater Treatment Methods

9.1 Pathways of industrial effluents treatment

There are many different ways of treating industrial effluent (Figure 9.1). It is often possible and advisable for an industry to discharge its waste directly at a municipal treatment plant, where a certain portion of the pollution can be removed. A municipal sewage-treatment plant, if designed and operated properly, can handle a major part of the industrial waste, with the exception of toxic substances like cyanides, phenols in high concentrations and heavy metals. The wastewater pH should be close to neutral. Generally, the industrial effluent should be free of substances that could impair the treatment process or cause violation of water quality standards of the receiving waters. Hence, one possibility that should be given serious consideration is for industry and municipalities to co-operate in the joint construction and operation of a municipal wastewater treatment plant. In many cases, the joint treatment of industrial and municipal wastewaters can be economically and environmentally beneficial to both the industry and the municipality.

There is a fine line of distinction between a volume of wholly untreatable waste and one containing only certain components that are untreatable if combined with domestic sewage. For example, wastewater from a plating plant can probably be treated together with domestic sewage if its pH value is first stabilised at about 7.0 and the cyanides and the major part of the chromium is eliminated at a local wastewater treatment unit. The shortest pathway – discharge of untreated industrial waste directly into a nearby stream – should be permitted only after a detailed survey, by competent and certified sanitary engineers, of the existing conditions and future uses of the receiving stream. Nowadays this case should certainly be considered as an exception. Complete treatment of industrial wastes prior to direct discharge or reuse at the plant is gradually receiving more and more consideration. In fact, complete treatment (or at least, advanced, tertiary treatment) has already been implemented in many large industries, for example, textile, pulp and paper, steel and chemical industries. The methods used for wastewater treatment can be classified as physical unit operations and chemical and biological unit processes.
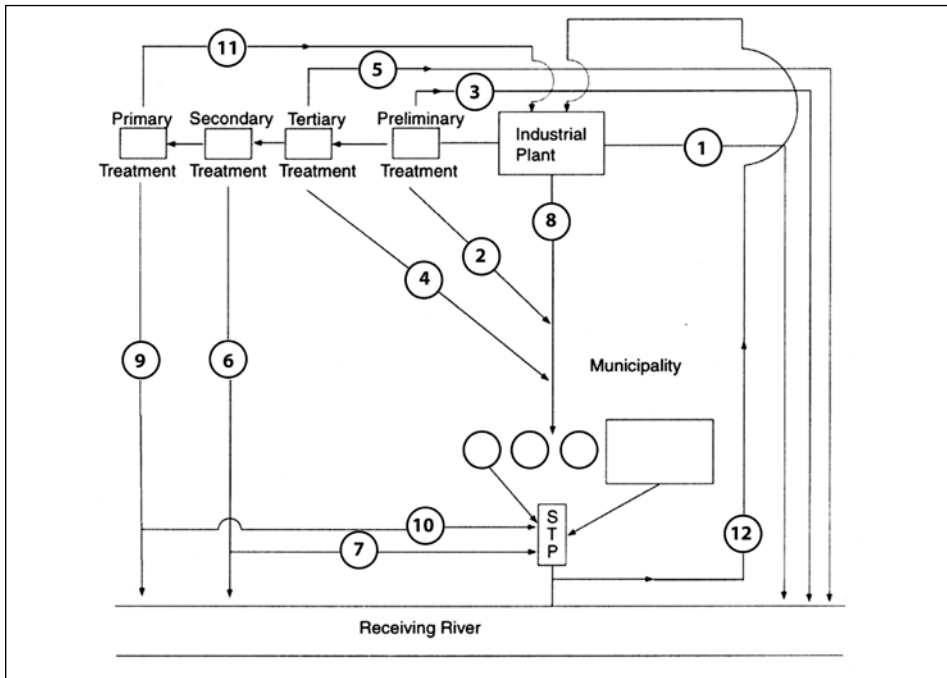
Figure 9.1. Twelve alternatives of industrial waste treatment systems (Nemerov & Dasgupta, 1991).

A summary of the unit operations and processes commonly used in wastewater reclamation and the principal contaminants removed are presented in Table 9.1.

9.2 Levels of treatment

Treatment levels of wastewater are often identified as primary, secondary and tertiary (the latter also known as advanced).

Primary treatment involves separating a portion of the suspended solids from the wastewater. Screening and sedimentation usually accomplish this separation process. The effluent from primary treatment will ordinarily contain considerable organic material and will have a relatively high BOD.

Secondary treatment involves further treatment of the effluent. Biological processes generally accomplish the removal of the organic matter and the residual suspended solids. The effluent from secondary treatment usually has little BOD_5 (15-30 mg/l as average) and a low suspended solids value (15-30 mg/l as average).

Table 9.1. Unit processes and operations used in wastewater reclamation and potential for contaminant removal (adapted from Metcalf & Eddy, 1991)

	BOD	COD	TOC	Turbid.	Color	*Coli*	NH$_3$-N
Primary treatment	x	x	x	x	o		o
Sludge	+	+	+	+	x	+	+
Nitrification	+	+	+	+		+	+
Denitrification	o	o	o	o			x
Trickling filter	+	+	x	x	o	o	
Coag.-floc.-sed.	+	+	+	+	+	+	o
Filtration A/S	x	x	x	x	x		x
GAC adsoption	+	x	+	+	+	+	x
Ion exchange	x	x	o	o			+
Chlorination						+	+
Reverse osmosis	+	+	+	+	+		+
Ozone	o	+	x			+	
Symbols: o = 25% removal of influent concentration, x = 25-50%, + = > 50%. Blank denotes no data							

Table 9.2. Biodegradability of organic hazardous waste (Leachy & Brown, 1994)

Readily degradable	Moderately degradable	Recalcitrant
Gasoline	Crude oil	TCE
Jet fuel	Lubricating oils	PCE
Diesel fuel	Coal tars	Vinylchloride
Toluene	Creosotes	PCB
Benzene	Pentachlorophenol	DDT
Isopropylalcohol	Nitrophenol	Chlordane
Methanol	Aniline	Heptachlor
Acetone	Long-chain aliphatics	
Phenol	Phtalates	
Ketone		

Most of the readily biologically degradable organic material is removed during biological treatment, but from 40 to 150 mg/l of dissolved and biologically resistant or "refractory" organic material remains in the effluent. These materials may be end products of normal biological decomposition or artificial products, such as synthetic detergents, pesticides, oils, chlorophenols, nitro-compounds, TCE, PCE, PCB, etc. The biodegradability of some organic compounds is characterised in Table 9.2.
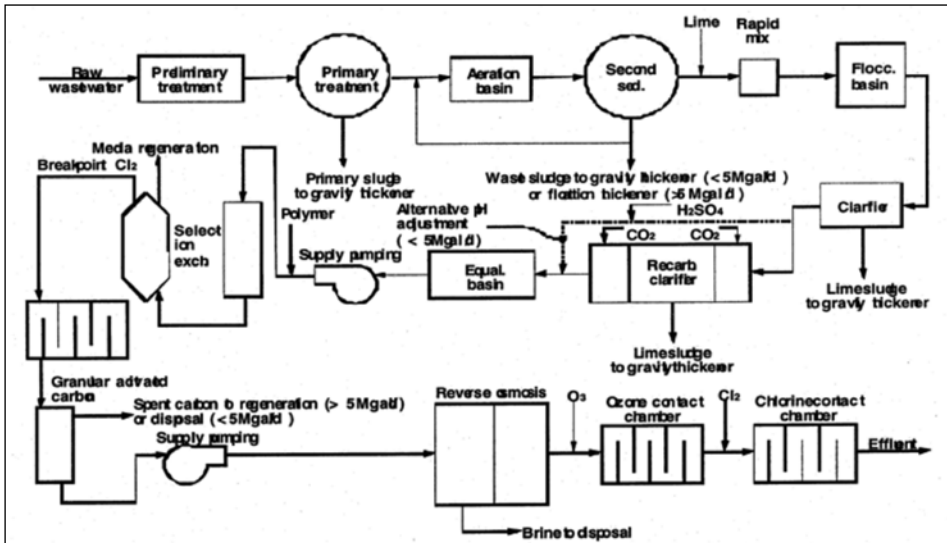
Figure 9.2. Conceptual flow diagram of advanced wastewater treatment system capable of producing potable-quality water supply (Metcalf & Eddy, 1991).

9.3 Unit operations

9.3.1 General definitions of industrial wastewater treatment

Both treatment levels, primary and secondary, have been discussed previously. The task of the present chapter is to give an overview of the third, advanced level of wastewater treatment. The united operations and processes included here (co-agulation, filtration, activated carbon adsorption, electrodialysis, reverse osmo-sis, ozonation, advanced oxidation processes etc.) are at the same time often used for industrial effluents local treatment. A conceptual flow diagram of an advanced wastewater treatment process combination capable of producing potable water from municipal wastewater is illustrated in Figure 9.2.

9.3.2 Pretreatment of industrial wastewaters

Most industrial wastes contain usually only a few harmful compounds and the removal of these leaves the remaining wastes amenable to treatment along with domestic sewage. Three steps are now necessary to complete the technical solution to the problem (Nemerow & Dasgupta, 1991):

- to ascertain the capacity of the various existing treatment-plant units;
- to reduce the incoming waste load to a minimum by proper local pre-treatment of industrial wastes at each factory, and

- to re-evaluate the present plant and suggest the additions required to handle the future waste load effectively.

Industrial wastewaters can pose serious hazards to municipal systems because the collection and treatment systems have not been designed to carry or treat them. The wastes can damage sewers and interfere with the operation of treatment plants. They may pass through the wastewater treatment plant (WWTP) untreated or they may concentrate in the sludge, rendering it a hazardous waste.

The Clean Water Act (CWA) gives the EPA the authority to establish and enforce pretreatment standards for discharge of industrial wastewaters into municipal treatment systems. Specific objectives of the pretreatment program are:
- To prevent the introduction of pollutants into WWTPs that will interfere with their operation, including interference with their use or with disposal of municipal sludge.
- To prevent the introduction of pollutants to WWTPs that will pass through the treatment works or otherwise be incompatible with such works.
- To improve opportunities to recycle and reclaim municipal and industrial wastewaters and sludge.

EPA has established "prohibited discharge standards" (40 CFR 403.5) that apply to all nondomestic discharges to the WWTP and" categorical pretreatment standards" that are applicable to specific industries (40 CFR 405-471). Congress assigned the primary responsibility for enforcing these standards to local WWTPs.

In the General Pretreatment Regulations, industrial users (IUs) are prohibited from introducing the following into a WWTP:
1. Pollutants that create a fire or explosion hazard in the municipal WWTP, including, but not limited to, waste streams with a closed-cup flash point of less than or equal to 60 C, using the test methods specified in 40 CFR 261.21.
2. Pollutants that will cause corrosive structural damage to the municipal WWTP (but in no case discharges with a pH lower than 5.0) unless the WWTP is specifically designed to accommodate such discharges.
3. Solid or viscous pollutants in amounts that will cause obstruction to the flow in the WWTP resulting in interference.
4. Any pollutant, including oxygen-demanding pollutants (such as BOD), released in a discharge at a flow rate and/or concentration that will cause interference with the WWTP.
5. Heat in amounts that will inhibit biological activity in the WWTP and result in interference, but in no case heat in such quantities that the temperature at the

Table 9.3. Chemical treatment of paper and paperboard wastes (adapted from Eckenfelder, 1989)

Waste	Influent BOD (ppm)	Influent SS (ppm)	Effluent BOD (ppm)	Effluent SS (ppm)	Effluent pH	Coagul. Alum. (ppm)	Coagul. Silica (ppm)
Board		350-450		15-60		3	5
Board		140-420		10-40		1	-
Board		240-600		35-85		-	-
Board	127	593	68	44	6.7	10-12	10
Tissue	140	720	36	10-15	-	2	4
Tissue	208		33	-	6.6	-	4

Table 9.4. Coagulation of textile wastewaters (adapted from Eckenfelder, 1989)

Coagulant	Dose (mg/l)	pH	Colour* Influent (mg/l)	Colour* Removal (%)	COD Influent (mg/l)	COD Removal (%)
Ferrisulf.	250	7.5-11	0.25	90	584	33
Alun	300	5-9		86		39
Lime	1,200	>11		68		30
Ferrisulf.	1,000	9-11	4.60	87	1,570	31
Alun	750	5-6		89		44
Lime	2,500	>11		87		44
* Colour sum of absorbances at wavelengths of 450, 550 and 650 nm.						

WWTP exceeds 40 ºC unless the approval authority, on request of the publicly owned treatment works (POTW), approves alternative temperature limits.

6. Petroleum oil, nonbiodegradable cutting oil, or products of mineral oil origin in amounts that will cause interference or will pass through.
7. Pollutants that result in the presence of toxic gases, vapors, or fumes within the POTW in a quantity that may cause acute worker health and safety problems.
8. Any trucked or hauled pollutants, except at discharge points designated by the POTW.

9.3.3 Coagulation

Coagulation may be used for the clarification of industrial wastes containing colloidal and suspended solids. Paperboard wastes can be coagulated effectively with low dosages of alum. Silica or polyelectrolyte aids in the formation of a rapid-settling flock. Typical data are summarised in Table 9.3.

Table 9.5. Colour removal from pulp and paper-mill effluents (Eckenfelder, 1989)

Coagulant	Dose (mg/l)	pH	Colour Influent (units)	Colour Removal (%)	COD Influent (mg/l)	COD Removal (%)
Ferrisulf.	500	3.5-4.5	2,250	92	776	60
Alun	400	4.0-5.0		92		53
Lime	1,500	>11		92		38
Ferrisulf.	275	3.5-4.5	1,470	91	480	53
Alun	250	4.0-5.5		93		48
Lime	1,000	>11		85		45

Wastes containing emulsified oils can be clarified by coagulation. The oil droplets in water are approximately 10-5 cm and are stabilised by adsorbed ions. Emulsifying agents include soaps and anion-active agents. The emulsion can be broken by "salting it out" with the addition of salts, such as $CaCl_2$. A lowering of the pH of the waste solution can also frequently break an emulsion. For example, polymer waste from latex manufacture has been coagulated with 500 mg/l ferric chloride and 200 mg/l lime at pH 9.6. COD and BOD reductions of 75 and 94%, respectively, were achieved from initial values of 1 000 mg/l and 120 mg/l.

The resulting sludge contained 1.2% solids by weight. Results from the co-agulation of textile wastewaters are shown in Table 9.4 and colour removal from pulp and paper-mill effluents in Table 9.5.

It can be seen from Tables 9.4 and 9.5 that while coagulation is very efficient for industrial effluents colour reduction (the removal is normally more than 85% and often reaches 92-95%), it is much less effective for COD reduction (only 30-60% removal).

9.3.4 Precipitation – heavy metals removal

Precipitation is employed for removal of heavy metals from industrial effluents. Heavy metals are generally precipitated as hydroxide through the addition of lime or caustic (NaOH) to a pH of minimum solubility. The pH of minimum solubility varies with the metal in question. For example, the solubilities of chromium and zinc are minimal at pH 7.5 and 10.2, respectively.

When treating industrial wastewater that contains metals, it is necessary to pre-treat the effluents to remove substances that will interfere with the precipitation of the metals.

Table 9.6. Effluent levels achievable in heavy metal removals (adapted from Eckenfelder, 1989)

| Metal	Achievable effluent concentration (mg/l)	Technology
Arsenic	0.05	Sulphide precipitation with filtration
	0.06	Carbon adsorption
	0.005	Ferric hydroxide co-precipitation
Barium	0.5	Sulphate precipitation
Cadmium	0.05	Hydroxide precipitation at pH 10-11
	0.05	Co-precipitation with ferric hydroxide
	0.008	Sulphide precipitation
Copper	0.02-0.07	Hydroxide precipitation
	0.01-0.02	Sulphide precipitation
Mercury	0.01-0.02	Sulphide precipitation
	0.001-0.01	Alum co-precipitation
	0.0005-0.005	Ferric hydroxide co-precipitation
	0.001-0.005	Ion exchange
Nickel	0.12	Hydroxide precipitation at pH 10
Selenium	0.05	Sulphide precipitation
Zinc	0.1	Hydroxide precipitation at pH 11
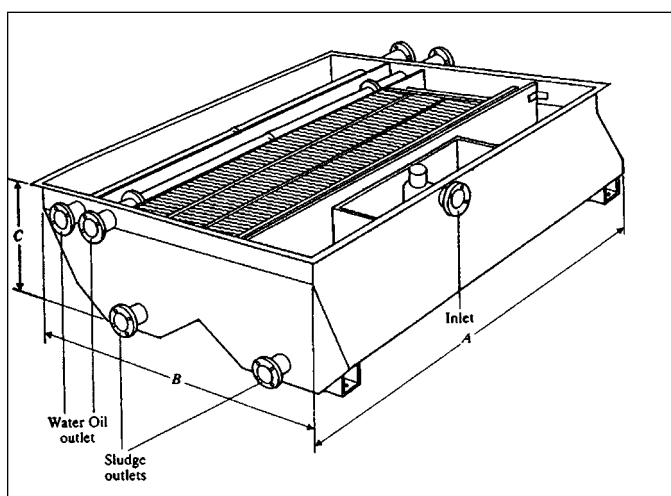
Figure 9.3. Cross-flow plate separator (from Eckenfelder, 1989).

Cyanide and ammonia form complexes with many metals, limiting the removal of them. For many metals such as arsenic and cadmium, co-precipitation with iron or aluminium is highly effective for removal to low residual levels. In order to meet low effluent requirements, it may be necessary to provide filtration to remove flock carried over from the precipitation process. Filtration should reduce effluent concentrations to 0.5 mg/l or less.
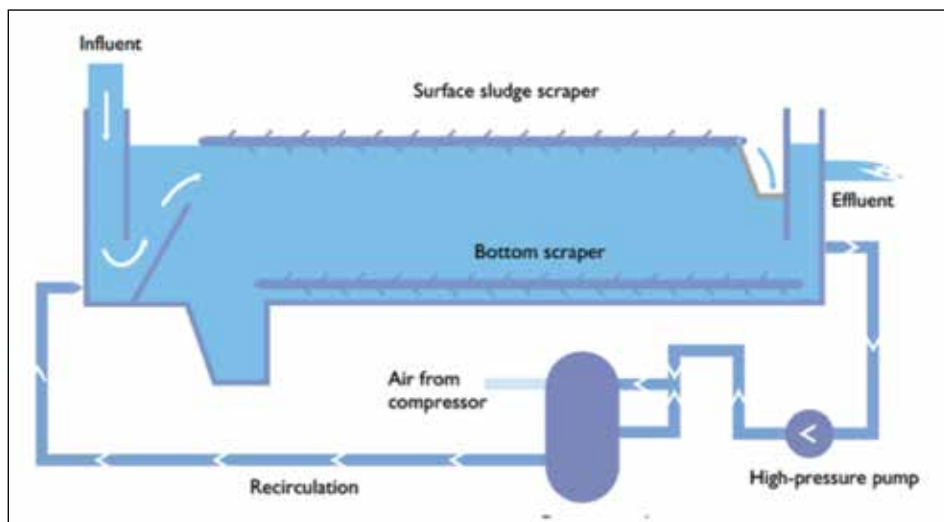
Figure 9.4. Dissolved air flotation (DAF)system.(Adapted from Gillberg et al, 2003)

For chromium wastes treatment hexavalent chromium must first be reduced to the trivalent state Cr_3^+ and then precipitated with lime. The reducing agents commonly used for chromium wastes are ferrous sulphate, sodium meta-bisulphite, or sulphur dioxide. Metals removal is summarised in Table 9.6.

9.3.5 Flotation (oil separation)

In oil separation, free oil is floated to the surface of a tank and then skimmed off. The design of a gravity separator is based on the removal of all free oil globules larger than 0.15 mm. The Reynolds number is less than 0.5, so Stokes' law applies. Typically, effluent oil concentrations in the order of 50 mg/l are achieved.

The hydraulic loading of a cross-flow corrugated plate separator (Figure 9.3) varies with temperature and the specific gravity of the oil. Nominal flow rates are specified for a temperature of 20 °C and a specific gravity of 0.9 for the oil. A hydraulic loading of 0.5 m^3/ m^2/h of actual plate area will usually result in separation of 0.06-mm droplets. Oil emulsions can be broken before separation by acidification, the addition of alum or iron salts, or the use of emulsion-breaking polymers.

Dissolved Air Flotation Equipment

Separation by flotation is commonly used in industrial water treatment. The flotation process itself involves adding a mixture of water and air to the chemically

treated water. Air bubbles attach themselves to the flocs and lift them to the surface, where they can then be scraped off as a sludge.

Figure 9.4. presents a diagram of a DAFsystem, can be completed with chemical coagulation and sludge handling equipment. As shown inFigure 9.4, raw (or pretreated) wastewater receives a dose of a chemical coagulant (metal salt, for instance), then proceeds to a coagulation-flocculation tank. After coagulation of the target substances, the mixture is conveyed to the flotation tank, where it is released in the presence of recycled effluent that has just been saturated with air under several atmospheres of pressure in the pressurization system shown. An anionic polymer (coagulant aid) is injected into the coagulated wastewater just as it enters the flotation tank.

The recycled effluent is saturated with air under pressure as follows: A suitable centrifugal pump forces a portion of the treated effluent into a pressure-holding tank. A valve at the outlet from the pressure-holding tank regulates the pressure in the tank, the flow rate through the tank, and the retention time in the tank, simultaneously. An air compressor maintains an appropriate flow of air into the pressure-holding tank. Under the pressure in the tank, air from the compressor is diffused into the water to a concentration higher than its saturation value under normal atmospheric pressure. In other words, about 23 ppm of "air"(nitrogen plus oxygen) can be "dissolved" in water under normal atmospheric pressure. At a pressure of six atmospheres, for instance, Henry's law would predict that about 6×23, or about 130 ppm, of air can be diffused into the water.

In practice, dissolution of air into the water in the pressurized holding tank is less than 100% efficient, and a correction factor, f, which varies between 0.5 and 0.8, is used to calculate the actual concentration.

After being held in the pressure-holding tank in the presence of pressurized air, the recycled effluent is released at the bottom of the flotation tank, in close proximity to where the coagulated wastewater is being released. The pressure to which the recycled effluent is subjected has now been reduced to one atmosphere, plus the pressure caused by the depth of water in the flotation tank. Here, the "solubility" of the air is less, by a factor of slightly less than the number of atmospheres of pressure in the pressurization system, but the quantity of water available for the air to diffuse into has increased by a factor equal to the inverse of the recycle ratio.

Practically, however, the wastewater will already be saturated with respect to nitrogen but may have no oxygen because of biologicalactivity. Therefore, the "solubility" of air at the bottom of the flotation tank is about 25 ppm, and the excess air from the pressurized, recycled effluent precipitates from "solution." As

this air precipitates in the form of tiny, almost microscopic, bubbles, the bubbles attach to the coagulated solids. The presence of the anionic polymer (coagulant aid), plus the continued action of the coagulant, causes the building of larger solid conglomerates, entrapping many of the adsorbed air bubbles. The net effect is that the solids are floated to the surface of the flotation tank, where they can be collected by some means, thus removed from the wastewater.

Some DAF systems do not have a pressurized recycle system, but rather, the entire forward flow on its way to the flotation tank is pressurized. This type of DAF is referred to as "direct pressurization" and is not widely used for treating industrial wastewaters because of undesirable shearing of chemical flocs by the pump and valve. Air-to-Solids Ratio

One of the principle design parameters for a DAF wastewater treatment system is the socalled air-to-solids ratio (A/S). The mass of air that must be supplied per day by the compressor and air delivery system is calculated by multiplying the mass of solids to be removed each day by the numerical value of the A/S. If the A/S is too low, there will not be sufficient flotation action within the treatment system. If, on the other hand, the A/S value is too high, there will be many more air bubbles than can attach to the solids. Many of the unattachedfine bubbles will coalesce; large bubbles will result, causing turbulence in the flotation tank. Experience has shown that A/S values in the range 0.02 to 0.06 result in optimal flotation treatment.
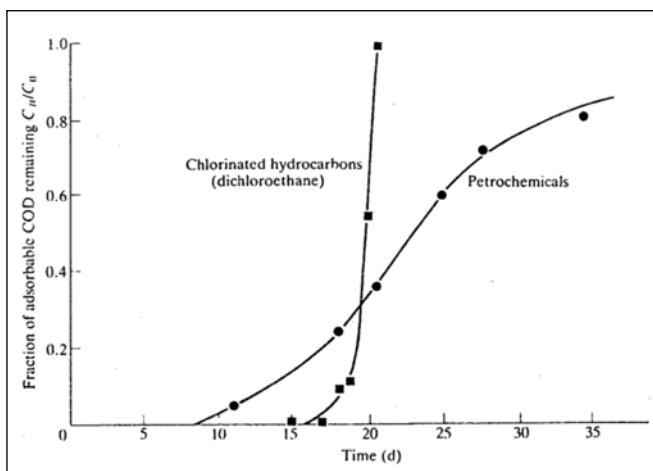

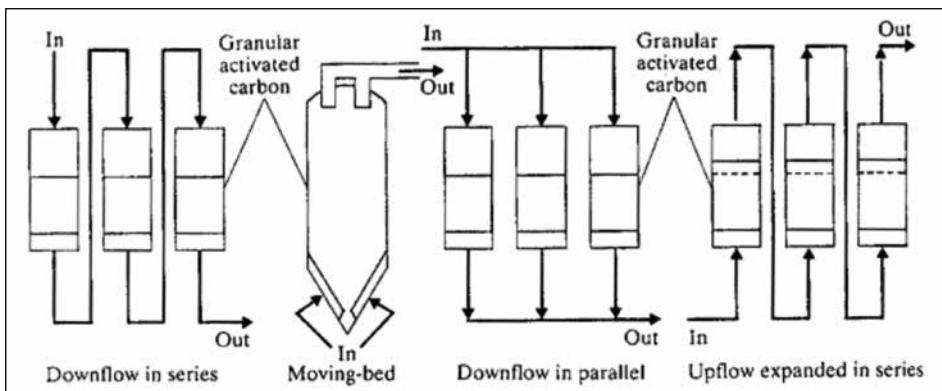**Figure 9.5. Continuous carbon column breakthrough curves** (Eckenfelder, 1989).

Figure 9.6. Types of granulated activated carbon (GAC) column design (Eckenfelder, 1989).

9.3.6 Activated carbon adsorption

Many industrial wastes contain refractory organics, which are difficult or impossible to remove through conventional biological treatment. These materials can be removed by adsorption on activated carbon or synthetic active-solid surface. The degree to which adsorption will occur and the resulting equilibrium relationships have been correlated according to the empirical relationship of Freundlich or the theoretically derived Langmuir relationship. For practical applications more suitable Freundlich isotherm is expressed as

$$X/M = kC1/n \qquad (6)$$

Where

X = weight of substance adsorbed

M = weight of adsorbent

C = concentration remaining in solution

k, n = constants depending on temperature, the adsorbent and the substance to be adsorbed.

The values of k for several priority pollutants (nitrobenzene, styrene, chlorobenzene, bromoform etc.) are in the range 60-360 mg/g and the values of $1/n = 0.12$-0.98. In granular carbon columns, the carbon adsorption capacity at breakthrough as related to exhaustion is a function of the waste complexity, as shown in Figure 9.5. A single organic substance, such as dichloroethane, will yield a sharp breakthrough curve so that the column is more than 90% exhausted when breakthrough
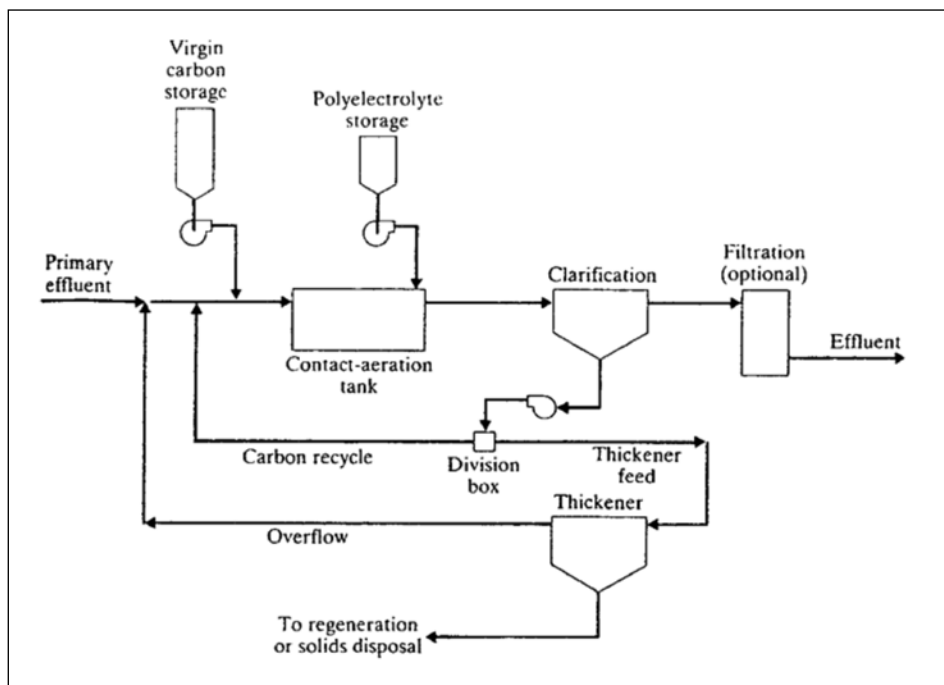
Figure 9.7. General process diagram of a powdered activated carbon (PACT) wastewater treatment system (Eckenfelder, 1989).

occurs. By contrast, a multicomponent petrochemical wastewater shows a drawn-out breakthrough curve due to varying rates of sorption and desorption.

Depending on the nature of the wastewater several modes of carbon column design may be employed: down flow in series, moving-bed, down flow in parallel, up flow expanded in series etc. (Figure 9.6).

It is generally feasible to regenerate spent carbon for economic reasons. The modes of regeneration are thermal, steam, solvent extraction, acid or base treatment, and chemical oxidation. In most wastewater cases, however, thermal regeneration is required. Thermal regeneration entails drying, thermal desorption and high-temperature heat treatment (650-980 °C) in the presence of limited quantities of water vapour, flue gas and oxygen. Multiple-hearth furnaces or fluidised-bed furnaces can be used. The regeneration process is a compromise between burning too much carbon and leaving unburned tars that clog the pores. Depending on the type of carbon and furnace operation, weight losses of carbon during regeneration usually amount to 5-10% by weight of the carbon regenerat-

ed. In practice, the greatest total surface area is obtained when about 3-5% of the original carbon is burned off each time.

Lately, powdered activated carbon (PAC) has been added to the activated sludge process for enhanced performance (the PACT process). The flow sheet for this process is shown in Figure 9.7. The advantages of the PACT process are decreasing variability in effluent quality and removal by adsorption of non-degradable refractory organics and colour. PAC also has the advantage of being able to be integrated into existing biological treatment facilities at a minimum capital cost. Since the addition of PAC enhances sludge settleability, conventional secondary clarifiers are often adequate, even with high carbon dosages (300-500 mg/l PAC).

9.3.7 Joint treatment of municipal and industrial effluent

Combined municipal and industrial waste treatment is the most desirable arrangement and at the same time it is the most difficult to achieve. Since most of the sewage plants use some form of biological treatment, it is essential for a satisfactory operation that extremes in industrial waste characteristics can be avoided and the waste be:

- as homogeneous in composition and uniform in flow rate as possible;
- free of excessive acidity or alkalinity and not high in chemicals which precipitate on neutralisation or oxidation;
- practically free of antiseptic compounds and toxic trace metals;
- low in potential sources of high BOD, such as carbohydrates, sugar, starch, and cellulose; and
- low in oil and grease content.

Chapter 9 sources:
1- Rein Munter, Industrial wastewater treatment, BUP Environmental science, Chapter 19, Lars-Christer Lundin & Lars Ryden.
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Chapter 10
Ion Remowal Technologies for Industrial Wastewater Treatment

10.1 Ion exchange

Ion exchange can be used for the removal of undesirable anions and cations from a wastewater. Cations are exchanged for hydrogen or sodium and anions for hydroxyl ions. Ion exchange resins consist of an organic or inorganic network structure with attached functional groups. Most ion exchange resins used in wastewater treatment are synthetic resins made by the polymerisation of organic compounds into a porous three-dimensional structure.

Ion exchange resins are called cationic if they exchange positive ions and anionic if they exchange negative ions. Cation exchange resins are comprised of acidic functional groups, such as sulphonic groups, whereas anion exchange resins have basic functional groups, such as amine. The strength of the acidic or basic character depends upon the degree of ionisation of the functional groups, similar to the situation with soluble acids or bases. Thus, a resin having sulphonic acid groups would act as a strong acid cation exchange resin.

For the other types of ion exchange resins, the most common functional groups are carboxyl (-COOH) for weak acid, quaternary ammonium ($R3N^+OH^-$) for strong base, and amine ($-NH_2$ or $-RNH$) for weak base.

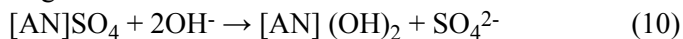Cation exchange of the hydrogen cycle can be illustrated by the following reactions:

$$Ca^{2+} + H_2[KAT] \rightarrow Ca[KAT] + 2H^+ \qquad (7)$$

Regeneration with 2 to 10% H_2SO_4 yields:

$$Ca[KAT] + 2H^+ \rightarrow H_2[KAT] + Ca^{2+} \qquad (8)$$

Similarly, anion exchange replaces anions with hydroxyl ions:

$$SO_4^{2-} + [AN](OH)_2 \rightarrow [AN]SO_4 + 2OH^- \qquad (9)$$

Regeneration with 5 to 10% NaOH will renew the exchange sites:

$$[AN]SO_4 + 2OH^- \rightarrow [AN](OH)_2 + SO_4^{2-} \qquad (10)$$

Since exchange occurs on an equivalent basis, the capacity of the bed is usually expressed as equivalents per litre of bed volume. In some cases capacity is expressed as kg $CaCO_3$ per unit bed volume or as mass of ions per unit bed volume.
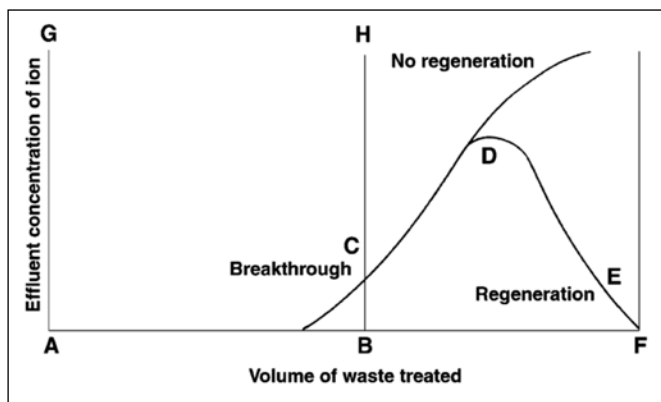
Figure 10.1. Treatment and regeneration cycle of ion exchange resin (from Eckenfelder, 1989).

Treatment of a wastewater by ion exchange involves a sequence of operating steps. The wastewater is passed through the resin until the available exchange sites are filled and the contaminant appears in the effluent. This process is defined as the breakthrough. At this point treatment is stopped and the bed is backwashed to remove dirt and to re-grade the resin. The bed is then regenerated. After regeneration the bed is rinsed with water to wash out residual regenerant.

The treatment and regeneration cycle is shown in Figure 10.1. In this figure, the area ABHG is the quantity of ions in the volume of solution treated before breakthrough. The area ABC is the quantity of ions leaking through the column and the area ACHG is the quantity of ions removed by the exchange resin. The resin utilisation is therefore area ACHG/K, where K is the ultimate capacity of the resin. The area BCDEF is the quantity of ions removed from the bed during regeneration. The regeneration efficiency is therefore area BCDEF/R, where R is equal to the concentration of the regenerant times its volume.

To ensure contact of liquid with the resin and to minimise leakage, the minimum bed depth is 61 to 76 cm. The treatment flow rate can vary between 0.27 to 0.67 $m^3/(min·m^3)$. The regenerant flow rate is 0.13 to 0.27 $m^3/(min·m^3)$.

One of the major applications of ion exchange in industrial waste treatment has been in the plating industry, where chromium recovery and water reuse have resulted in considerable savings.

For recovery of the spent chromic acid in plating baths, the chromic acid is passed through a cation exchange resin to remove other ions (Fe_3+, Cr_3+, Al_3+ etc.). The effluent can be returned to the plating bath or to storage. The recovered chromic acid from the spent regenerant will have an average concentration of 4 to 6%. The spent regenerant from the cation exchanger will require neutralisation and
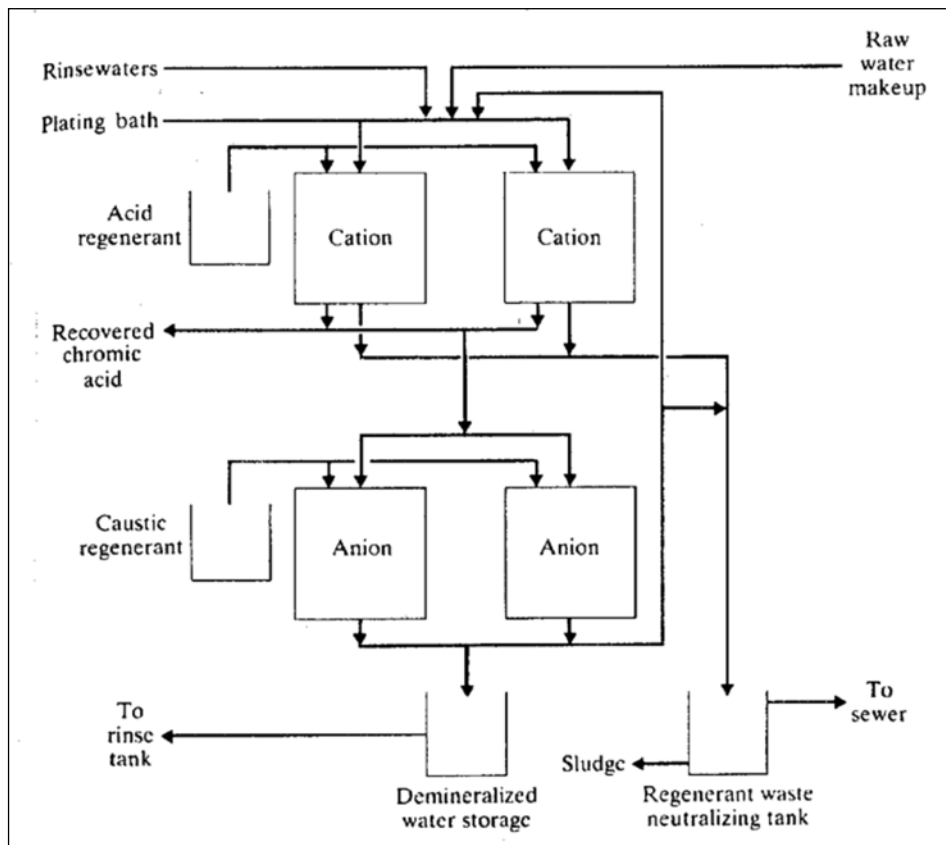
Figure 10.2. Ion exchange system for chromate removal and reuse (Eckenfelder, 1989).

possibly precipitation of metallic ions before it is discharged to the sewer. A flow diagram of an ion exchange process for a plating plant is shown in Figure 10.2.

10.2 Membrane processes

The membrane processes can be classified according to the size range of the separated species:

- Reverse osmosis is used to separate dissolved salts and small organics (size under 1 nm). Example: production of drinking water from seawater or seawater desalination.
- Nanofiltration is used to separate antibiotics (size under 10 nm). Example: selective demineralisation of water or concentration of organic solutions.

- Ultrafiltration is used to separate emulsions, colloids, macromolecules or proteins (size under 100 nm). Example: treatment of pulp and paper industry's effluents.
- Micro-filtration is used to separate small particles, large colloids and microbial cells (size under 10 mm). Example: removal of microorganisms from the fermentation products.
- Gas and vapour separation is used to isolate a gas from a mixture of gases or vapours. Example: recovery of ammonia or hydrogen from industrial gases.
- Electrodialysis is used to separate anions and cations by means of two charged membranes (anode and cathode). Example: production of pure water.

Reverse osmosis

As can be seen from the list above, membrane filtration includes a broad range of separation processes, ranging from filtration and ultrafiltration to reverse osmosis. Generally, those processes defined as filtration refer to systems in which discrete holes or pores exist in the filter media, generally in the order of 102 to 104 nm or larger. The efficiency of this type of filtration depends entirely on the difference in size between the pore and the particle to be removed. The various filtration processes relative to molecular size are shown in Table 10.1.

In normal osmosis, a semipermeable membrane separates a salt solution from a pure solvent of a less concentrated solution. This membrane is permeable to the solvent and impermeable to the solution (Figure 10.3). The chemical potential of the pure solvent is greater than that of the solvent in solution, and therefore brings the system to equilibrium. For two solutions with different concentrations, separated by a semipermeable membrane, the osmotic phenomenon will be a water flux from the most diluted solution to the concentrated one. To stop this water flux, a pressure on the concentrated solution has to be applied. By increasing the pressure above the osmotic pressure, a water flux from the concentrated solution to the diluted one is obtained. This phenomenon is called reverse osmosis.

The equation of osmotic pressure, the so-called Van't Hoff's equation, is:

$P = C\ RT$

Table 10.1. Membrane processes (Eckenfelder, 1989)

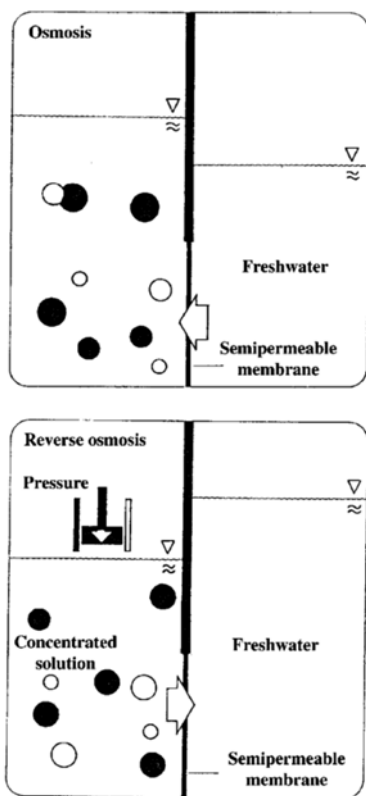| Material to be removed	Approximate size, (nm)	Process
Ion removal	1-20	Diffusion or reverse osmosis
Removal of organics in true solution	5-200	Diffusion
Removal of subcolloidal organics	200-10,000	Pore flow
Removal of colloidal matter	75,000	Pore flow

Figure 10.3 Osmosis and reverse osmosis (Eckenfelder, 1989).

where C is the concentration of the solute, R is the gas constant and T is the temperature in K. It should be noted however that this relation should be applied to dilute solutions, i.e. to solutions under low osmotic pressures.

The permeate flux can be expressed as follows:

$J = e \cdot d2 \cdot \Delta P / 32 \cdot m \cdot t \cdot z$

where e is the membrane porosity, d is the pore diameter, t is the tortuosity factor, m is the solvent viscosity, ΔP is the pressure difference across the membrane and z is the membrane thickness.

The selectivity of the membrane is defined by the solute rejection coefficient, which is given by the following expression:

$R = 1 - C_p/C_f$

where C_p is the solute concentration in the permeate and C_f, the solute concentration in the feed.

There are three different types of membrane structures: homogeneous, asymmetric and composite membrane. The homogeneous membrane is not used very often because of its considerably low permeate flow rate. It is only used for micro-filtration. Asymmetric membranes are made of two layers: a 1-2 mm thick top layer of finest pore size supported by a 100 mm thick, more porous matrix. With such an asymmetric structure, reasonable rates of permeate flux are obtained. Composite membranes are made of two layers as well: an extremely thin layer (1 mm) of finest pore structure deposited on a porous matrix. The thin layer can be made of inorganic materials.

Membranes are most commonly made of polymeric materials such as polyamide, polysulfone and poly-carbonate. The method of packing the membrane leads to a module design of a membrane separation unit. There are four types of modules commercially available: tubular modules, flatsheet modules, spiral-wound modules and hollow-fibre modules.

A typical tubular membrane type is shown in Figure 10.4. Manufactured from ceramics, carbon, or porous plastics, these tubes have an inside diameter ranging from 1/8 inch (3.2 mm) up to 1 inch (2.54 cm). The membrane is typically coated on the inside of the tube, and the feed solution flows through the interior from one end to the other, with the "permeate" or "filtrate" passing through the wall. Other membrane systems used are spiral-wound hollow-fibre and plate or frame.

The water (permeate) flux is a function of the pressure differential between the applied pressure and the osmotic pressure across the membrane. Flux rates of approximately 0.1 m^3/m^2/day are typical for tubular and spiral-wound systems. The maximum pressure is generally taken to be 1,000 $lb/in2$ (6,900 kPa) gage. The water flux increases with increasing feed water temperature. A standard of 21 °C is generally assumed and temperatures of up to 29 °C are acceptable.

Salt rejection depends on the type and character of the selected membrane and the salt concentration gradient. Rejection values of 85 to 99.5% are generally obtainable, with 95% commonly being used.

Membranes consisting of cellulose acetate are subject to hydrolysis at high and low pH values. The optimum pH is approximately 4.7, with operating ranges between 4.5 and 5.5. Generally, membranes will last up to two years with some loss in flux efficiency. The pre-treatment of water to a membrane system is vital, to maintain productivity and to obtain long membrane life. In particular, the level of fine and colloidal solids must be controlled (Figure 10.5.).
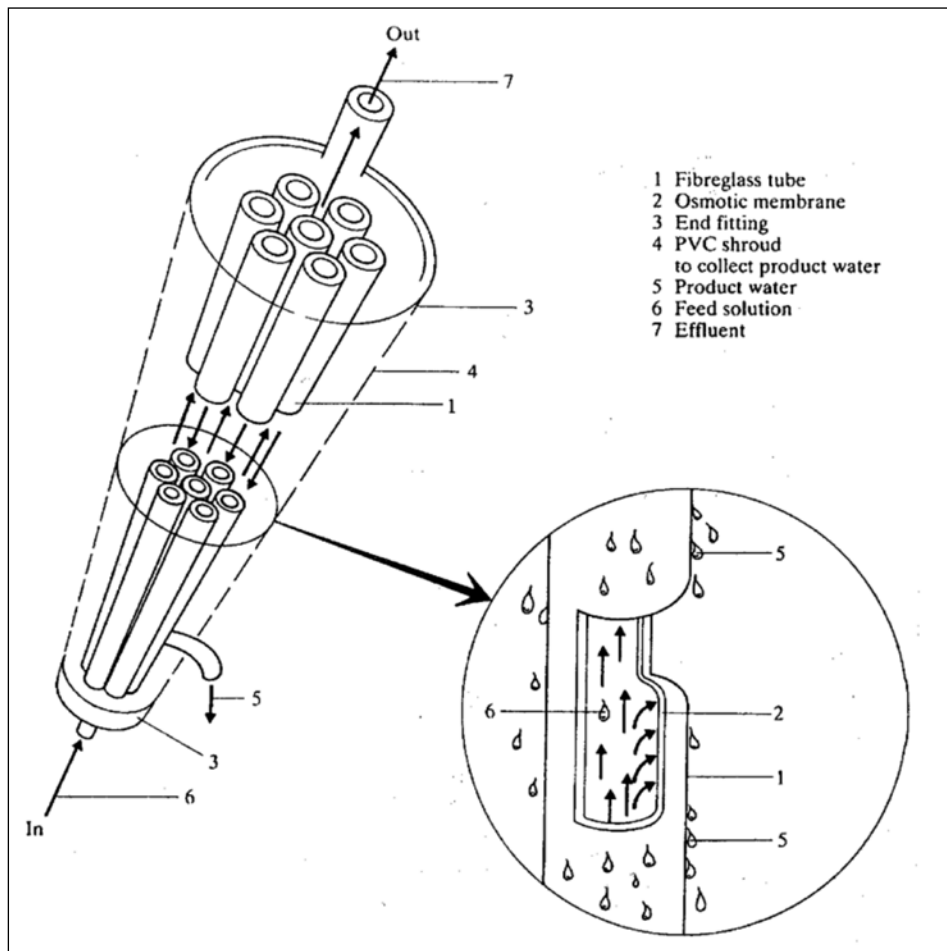
Figure 10.4. Membrane filtration system. Tubular reverse osmosis unit (Eckenfelder, 1989).

An industrial standard method called the "silt density index" (SDI) is used. The SDI test entails passing the feed water through a fine-pore membrane filter (0.45 _m) under standard conditions and measuring the rate at which the flow falls through the membrane. It is recommended not to have an SDI higher than 0.3. Membrane systems are normally turned off periodically for chemical cleaning, to allow deposits to be removed. Cleaning methods include periodic depressurisations, high-velocity water flushing, backwashing, cleaning with enzyme detergents, ethylene diamine, tetraacetic acid etc. A summary of operational parameters is given in Table 10.2.
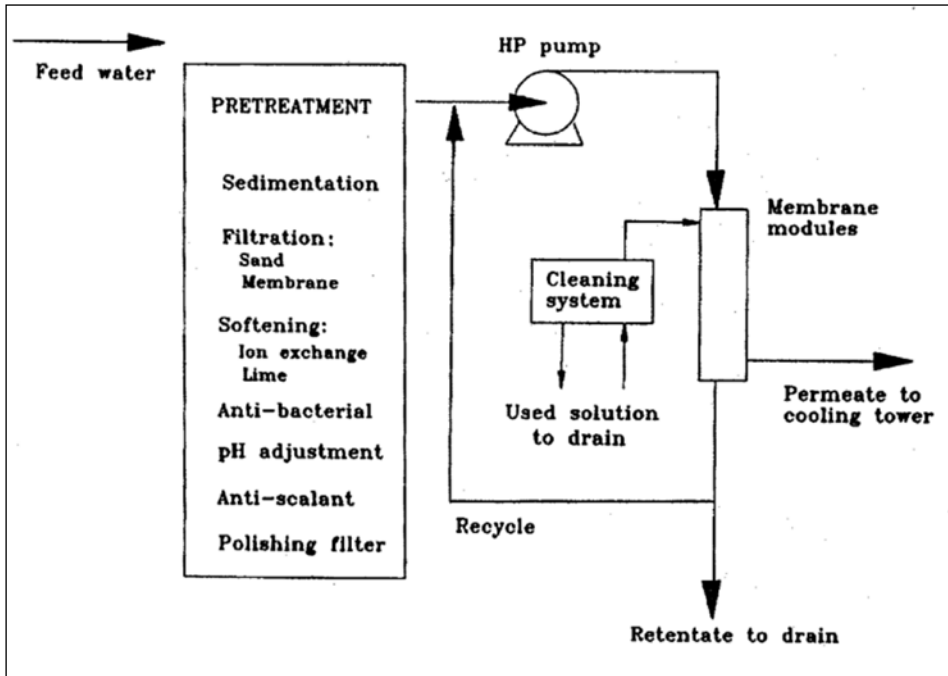
Figure 10.5. Reverse osmosis – general system (Newton & Solt, 1994).

Table 10.2. Summary of system operational parameters (adapted from Eckenfelder, 1989)

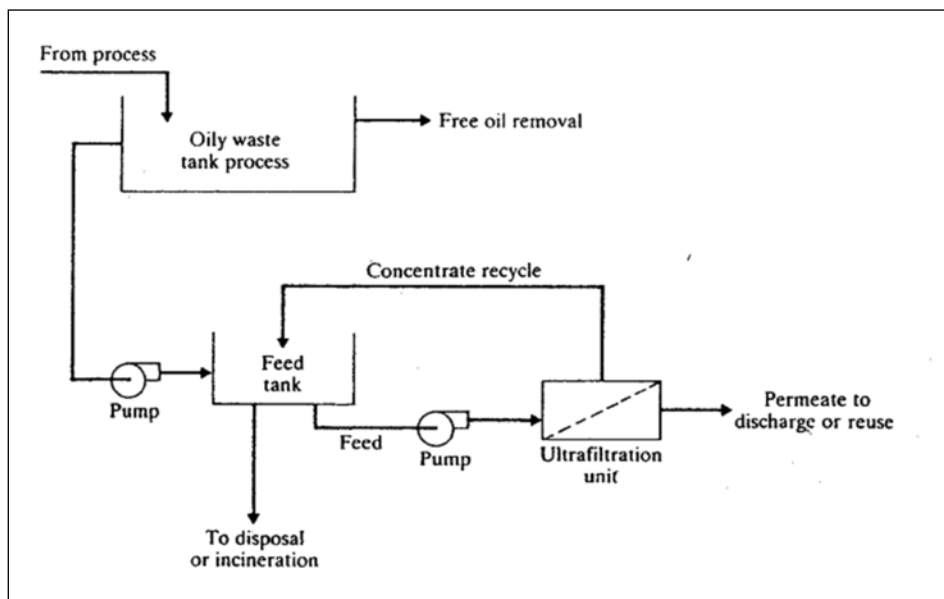| Parameter	Range	Typical
Pressure (MPa gage)	3-7	4
Temperature (^{o}C)	15-40	21
Packing density (m^2/m^3)	50-500	-
Flux (m^3/(d•m^2))	0.5-4	0.6-1.7
Recovery factor (%)	75-95	80
Rejection factor (%)	85-99.5	95
Membrane life (years)	-	2
pH	3-8	4.5-5.5
Turbidity (JTU)	-	1
Feed-water velocity (m/s)	0.01-0.75	-
Power utilization (kW•h/10^3 l)	2-3.7	-

Figure 10.6. Treatment of oily wastewaters by ultrafiltration (Eckenfelder, 1989).

Reverse osmosis systems can operate at 90% efficiency or better with respect to total dissolved solids. In addition to inorganic ions, the membranes also remove residual organic molecules, turbidity, bacteria and viruses.

In Figure 10.6. the application of ultrafiltration for oily wastewaters treatment is illustrated. The permeate is recycled as rinse water and the concentrate is hauled or incinerated.

Demands for lower freshwater consumption together with stringent environmental legislation within the pulp and paper industry have created a need for process water and effluent recycling, and thus totally or partly closed water circuits have become a reality. The membrane processes (ultraand nanofiltration) are already being used in paper machine white-water treatment and the experience has been good. The development of membrane materials like ceramics will prolong membrane lifetime and thus reduce cost. New modules are also needed, because e.g. the nanofiltration spiralwound module needs a very heavy pre-treatment, usually by ultrafiltration. During the last decade, as a result of the development of a new filter, called the CR (cross-rotational), as well as of new membrane materials, membrane applications have proved to be competitive processes for the concentration of valuable compounds or purification of water.

10.3 Electrodialysis

The electrodialysis process uses a series of membranes made from ion-exchange resins. These membranes will selectively transfer ions. They are based on polymers of materials such as styrene or polyethylene incorporating fixed and mobile charged groups. In, for example, cation-exchange membranes, negatively charged groups are fixed and positively charged groups mobile. Then, under the influence of a driving force (an electric field or a concentration gradient), positive and negative ions are attracted to the membrane, and the membrane is permeable for positive ions while rejecting negative ions. In the electrodialysis process the transport through the membrane is promoted by an electric field across the membrane. Diffusion is negligible by comparison and ion transport is directly related to the electric current. According to Faraday's law an electric current of 26.8 Ah is needed to transport 1 gram equivalent of a salt. In practice the electric current is higher, due to inefficiencies caused by electrical resistance. Generally in electrodialysis a package of membranes is used with alternate cation and anion membranes arranged in a so-called "membrane-stack" (Figure 10.7.). Membranes in an electrodialysis unit are approximately 0.5 mm thick, separated by porous spacers about 1 mm thick. Water flows through the porous spacers. Anions and cations pass through the membranes so that the original feed is desalinated and a concentrate forms on the other side of the membranes. A contact time of 10 to 20
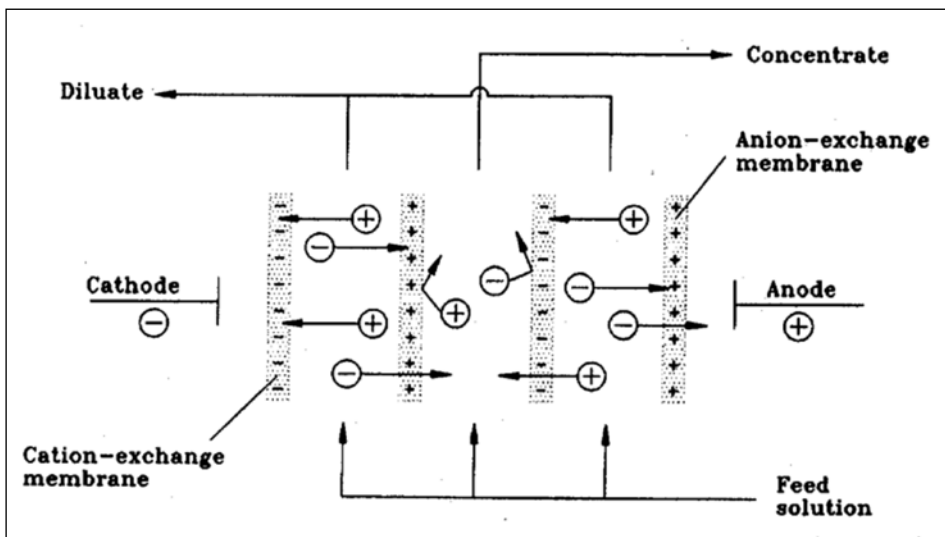

Figure 10.7. Electrodialysis stack (Newton & Solt, 1994).

s is required to obtain a removal efficiency of about 25-60%. As reverse osmosis, electrodialysis also requires a high degree of pre-treatment prior to the process. Suspended solids removal is absolutely necessary, and dissolved organics should be removed to prevent fouling.

10.4 Capacitive deionization
Method description
Providing access to affordable and clean water is one of the key technological, social, and economical challenges of the 21st century. For the desalination of water, commercially available methods include distillation, reverse osmosis, and electrodialysis. Novel approaches include ion concentration polarization in microporous media, systems based on batteries, forward osmosis, and capacitive deionization (CDI).

CDI is based on an electrochemical cell consisting of an open-meshed channel for water flow, in contact with sheets of porous electrodes on both sides. Upon applying a cell voltage between the two electrodes, ions become immobilized by an electrosorption process, that is, cations move into the cathode (the electrode into which negative electrical charge is transferred), while anions move into the anode (Figure 10.8). After sometime, when the electrodes reach their adsorption capacity (which depends on cell voltage), a discharge cycle is initiated by reducing or reversing the cell voltage, thereby releasing the salt as a concentrated stream. In the discharging step of the cell, energy recovery is possible.

Salt immobilization by CDI is considered an energy-efficient method for the desalination of water.15,18 Though typically applied to the desalination of brackish water sources, seawater can also be desalinated by CDI.In combination with ion selective membrane layers placed in front of the electrodes, CDI can be used to selectively remove a certain ionic species from a mixture of salts or to harvest compounds such as acetic acid, sulphuric acid, insulin, and boron. Such separation processes may find use in the treatment of wastewater from agriculture (mining), industry, and hospitals.

Various configurations for the design, stacking, and water management of CDI cells are possible. Most studies consider a design where the salt water is directed parallel to two equal electrodes, while a constant cell voltage is maintained, see Figure 10.8.

However, stacks of electrodes do not necessarily have to consist of symmetrical cells and, instead, varying the carbon mass between the two electrodes provides the possibility to optimize the usable voltage window. Another approach utilizes carbon rods (called wires) which are sequentially dipped and taken out
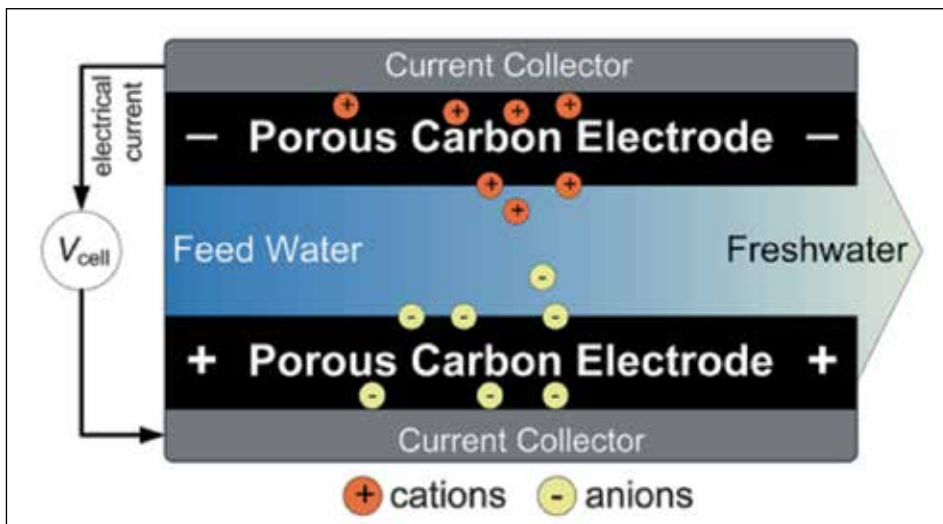
Figure 10.8. Schematic illustration of desalination via capacitive deionization (CDI). Upon applying a cell voltage between the two electrodes, anions and cations are electrosorbed within highly porous carbon electrodes to counterbalance the electrical charge. This immobilization of ions decreases the salt concentration in the flow channel, and results in the production of freshwater (Source: Porada et al 2013.)

of the water, instead of using film electrodes forming a stack through which the water flows. Instead of using bare carbon electrodes, improved energy efficiency has been reported for membrane-CDI (MCDI), where ion-exchange membranes are placed in front of one or both of the electrodes. Further modifications are the use of constant current operation, directing the water flow straight through the electrodes, or the use of flowable electrode suspensions. Recently, CDI electrodes have also been used to produce energy from the controlled mixing of river and seawater, based on a reversal of the CDI process.

Electrosorption of ions is an interfacial process and in order to have a maximum contact area between the electrode and the water, CDI employs high surface area porous carbon electrode materials. At the water–carbon interface, electrical double layers (EDLs) are formed in which ions are electrosorbed. It has been stated that for optimum performance, pores should be large enough to have only a weak EDL-overlap, that is, mesopores are to be preferred over micropores. However, some microporous carbons, such as activated carbons and carbide-derived carbons actually outperform mesoporous carbons. Recently, Porada et al. reported that CDI desalination capacity positively correlates with the volume of pores in the range below 1 nm, while obtaining a negative correlation with the

total pore volume, or with the BET specific surface area (BET SSA, ref. 48).The importance of pores <1 nm has also been demonstrated for the capacitance of EDL-capacitor electrodes, for H_2 gas storage, and for CO_2 gas removal capacity. These results relate to equilibrium conditions, and micropores (<2 nm) and especially ultramicropores (<0.8 nm) can pose severe limitations to ion transport in CDI flow cells. Thus, porous electrodes that combine a large micropore volume (for a high deionization capacity) with a network of mesopores (between 2 and 50 nm) and macropores (>50 nm) may yield a highly efficient deionization process.

Chapter 10 sources:

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Chapter 11
Advanced Oxidation Technologies for Industrial Wastewater Treatment

11.1 Introduction. Classification of advanced oxidation technologies.

The presence of recalcitrant organic pollutants such as pesticides, hormones, pharmaceuticals, phenols, surfactants and dyes in water and wastewater has been described in the literature as one of the most serious problems for human beings and the environment. The great concern is mainly that the genotoxic and mutagenic properties of these pollutants can cause bioaccumulation problems and transportation that is magnified in the food chain. They have therefore received great attention since they are released into the environment through a variety of human and industrial activities. Conventional techniques such as adsorption, precipitation, flocculation and reverse osmosis simply transfer organic pollutants from different phases or concentrate them in one phase, without actually removing them.

Such water sources pollution recently created a pressing need for the development of efficient water-treatment processes. The search for a solution to this problem has involved extensive examinations in the field of advanced oxidation processes (AOPs).

In chemical oxidation processes, reaction mechanisms change structure, and chemical properties of the organic substances. Molecules break in smaller fragments, higher percent of oxygen appears in these molecules in form of alcohol's, carboxylic acids etc. oxidation of organic compounds with oxidation such as ozone or $OH^\bullet$ radicals usually yields more oxidized ones which are in most cases more easily biodegradable than the former ones. This is the general idea that yields to the combination of a chemical oxidation processes. Oxidation with ozone or hydrogen peroxide has been found to be an important alternative to chlorination, because the oxidation does not result in toxic chlorinated organic compounds. Advanced Oxidation Technologies (AOT's), including Advanced Oxidation Process (AOP's) and other physicochemical conversion methods which are:

1   Advanced Oxidation Process (AOP's);
2   Non-Thermal Plasmas (NTP) for air and wastewater treatment;
3   Electrohydraulic cavitation and sonolysis for wastewater treatment;
4   Electron beam and gamma-ray irradiation;
5   Catalytic oxidation for air treatment;
6   Wet air oxidation for wastewater treatment;
7   Supercritical water oxidation treatment;
8   Electrochemical redox reactions for wastewater treatment;
9   Photocatalsis for wastewater and air treatment.

11.1.1 Advanced Oxidation Process (AOP's):
The concept of advanced oxidation process (AOPs), was defined by Glaze et al. In 1987 as processes that "involve the generation of hydroxyl radicals in sufficient quantity to affect water purification". In this context, advanced oxidation processes generally mean the application of either oxidation technologies using UV/O_3, O_3 /H_2O_2, UV/ H_2O_2 or the photo Fenton reaction (UV/ H_2O_2/ Fe^{++}or Fe^{+++}). Peyton gave a detailed overview and description of AOP's in 1990. The advanced oxidation process (AOP's) will discuss in details after mention of the rest advanced oxidation technologies (AOT's).

11.1.2 Non-Thermal Plasmas (NTP) for air and wastewater treatment
Non-thermal plasma technology (NPT) is a new advanced oxidation technology, which is applied to treat air pollutant and may also be applied to treat wastewater. The plasma produced by an electron beam, a pulsed corona discharge or a dielectric-barrier discharge employed to create a large quantities of high reactive free radicals (mainly atomic oxygen in the ground energy state (O^3P) and oxygen in the first excited energy state (O^1D), and hydroxyl radicals) in a gaseous medium at near ambient temperature. These radicals subsequently react with entrained hazardous organic chemicals, converting them to either nonhazardous substances (CO_2, H_2O and acids, i.e., mineralized compounds) or other easily manageable compounds. Because NTP processes can simultaneously remove or convert different types of pollutant, e.g., volatile organic compounds and oxides of sulfur and nitrogen frequently found in flue gases, it is particularly attractive for many present and future environmental applications.

11.1.3 Electrohydraulic cavitation and sonolysis for wastewater treatment
Electrohydraulic cavitation involves the formation and behavior of bubbles in liquids. It is induced by applying electrical power is provided by a pulse-powered

plasma discharge producing pulsed and/or continuous ultrasonic irradiation (i.e., sonolysis) in water. Kinetic and sonoluminescnce measurements indicate that an extremely high temperature (>500 ^{o}K) and pressure (>100 atm) are generated during the adiabatic and short-time (<1 s) implosions occurring at the cavitations sites. When a bubble fills with gas and vapor pulses and collapses, molecules inside the bubble or close to the bubble surface is fragmented, escape into the bulk of the solution and react in various ways outside (or inside) the bubble. After the production of these radicals, pollutants such as tetrachloromethane and hydrogen sulphide in the water can be oxidized to final products such as CO_2, Cl^- and SO_4^{2-}.

11.1.4 Electron beam and gamma-ray irradiation

High-energy electron beams are gamma rays (i.e., ionizing radiation) are very effective tools for water pollutant degradation. The development of new powerful electron accelerators (e.g., an energy level of 1.0 MeV and a power level of 50 KW, or an energy level of 4.5 MeV and a power level of 400 KW) enables very effective radiation processing of wastewater streams. when a high energy electron beam of gamma ray irradiates water, the water (as well as organic compounds contained in it) split into a number of primary species of e$_{aq}$ (electrons in aqueous solutions), $H^\bullet$, $^\bullet OH$, H_2, H_2O_2, H^+ and OH^-. Some of these primary species then colloid with other substrates in water to form more radical species that are oxidants and therefore able to oxidize organic pollutants. As has been observed when using this technology, many organic compounds can be promptly oxidized such as polychlorinated biphenyls (PCBs). tetrachloromethane, trichloroethylene (TCE), tetrachloroethylene (PCE) and benzene.

11.1.5 Catalytic oxidation for air treatment

Catalytic oxidation for the treatment of air pollution is an important environmental technology, which has been employed for environmental protection for twenty years. Catalytic oxidation, also known as catalytic incineration, is the complete chemical conversion of a gaseous organic compound with oxygen at a certain temperature (below or above 100 ^{o}C) and pressure (one or more than one atm.) while both substances are in contact with a solid material (catalyst) that increase the rate of oxidation reaction. This technology is used for the treatment of organic pollutants in a gas phase, such as automotive emission control and control of industrial gas emissions.

11.1.6 Wet Air Oxidation for wastewater treatment

Wet air oxidation (WAO) is a well established technology for wastewater treatment, particularly for the treatment of toxic and highly concentrated wastewaters. It is a chemical oxidation process involving organics or oxidizable inorganic components in an aqueous liquid phase at high temperatures (125-320 ^{o}C) and pressures (0.5-20 Mpa), using a gaseous source of oxygen (normally air). WAO has been demonstrated to mineralize various organic compounds to carbon dioxide, water and other inorganic end products such as ammonia, nitrate, nitrogen, chloride, sulphate and phosphate. The oxidation capability of WAO is greatly enhanced if catalysts and oxidants such as ozone and hydrogen peroxide are present. Normally, the mechanisms of WAO reactions are radical ones. Except for carboxylic acids of low molecular weight (especially acetic and propionic acid) and polychlorinated biphenyls (PCBs), most compounds are easily degradable by WAO. At a feed COD higher than 20.000 mg/L, WAO becomes energetically self-sustaining (i.e., no additional fuel is required) and may in fact produce energy in the form of high-pressure steam. One of the most important applications of WAO is the treatment of sewage sludge from municipal wastewater treatment plants.

11.1.7 Supercritical Water Oxidation Treatment

Supercritical water oxidation (SCWO) is an intensive version of the WAO process. In recent years, SCWO has become a rapidly developing innovative waste treatment technology for the oxidation of organic wastes and hazardous materials in water. The SCWO process involving the mixing of wastes with an oxidant (oxygen, air, or hydrogen peroxide). The reaction with organic pollutants is carried out at a pressures and temperatures above the water critical point (374 ^{o}C and 22.13 Mpa). The general SCWO reaction temperature range is between 400 and 650 ^{o}C. Under these conditions, oxidation occurs rapidly (within a few seconds or minutes) and simple products (such as CO_2 and H_2O, and N_2 in the case of nitro-organics) are produced.

SCWO has great advantages as regards the treatment of some refractory organic compounds, including a rapid chemical reaction and no production of nitrogen oxides. The pressure and temperature required can be attained using readily available high pressure and high temperature equipment. SCWO has proven to be successful for the disposal of phenol, halogenated organics, biopharmaceutical wastes, chemical warfare agents, hydrolyzed solid rocket propellant, and biological sledges.

11.1.8 Electrochemical redox reactions for wastewater treatment

Electrochemical methods oxidize and reduce pollutants in wastewater by means of electrode reactions (electrolysis). The electrodes needed are available in various shapes (bar, plate, porous and fiber) and are made of various materials. In wastewater, such oxidizable pollutants as organic compounds are oxidized at the anode surface, and such reducible pollutants as most inorganic metal cations are reduced and deposited (in most cases) at cathode surfaces. To bring about the required reaction, a certain electropotential is applied to the anode and cathode. Electrochemical methods are employed mainly for metal ion elimination such as the recovery of copper and lead, mercury(II) and zinc(II), cobalt(II), and cadmium, etc. Another interesting application of electrochemical method is cyanide oxidation in wastewater. In most metal finishing and hydrometallurgical industrial wastewaters containing metal ions (such as gold, silver, chromium) and cyanides, the electrochemical method has an advantage in that simultaneously cyanide is decomposed (oxidized) at the anode and heavy metals are deposited (reduced) at the cathode without causing a sludge problem.

11.1.9 Photocatalysis for wastewater and air treatment

Photocatalysis is the combination of using a photocatalyst and UV or visible light for the treatment of wastewaters and gaseous pollutants. When illuminating a photocatalyst using UV or visible light, various organic compounds (e.g., aromatic, organochloride and organophosphorous compounds) can be oxidized and mineralized at the photocatalyst surface or oxidized in solution ambient and atmospheric conditions. This is because strong oxidation and reduction sites are produced at the photocatalyst surface when this surface is illuminated with light of the appropriate wavelength. Radicals formed at the surface dissolve in solution and then react with pollutants. It has often been demonstrated that various organic pollutants can be oxidized photochemically under the influence of large amounts of free solar energy.

Photocatalysis is one of the most important advanced oxidation technologies. It can be used not only for oxidative treatment of wastewater containing various organic and inorganic compounds, but also for reductive treatment such as reductive deposition of metals from wastewater.

11.2 An overview of different advanced oxidation processes

Advanced oxidation processes is one of the most environmental friendly techniques used to remove recalcitrant organic pollutants not easily treatable by ex-
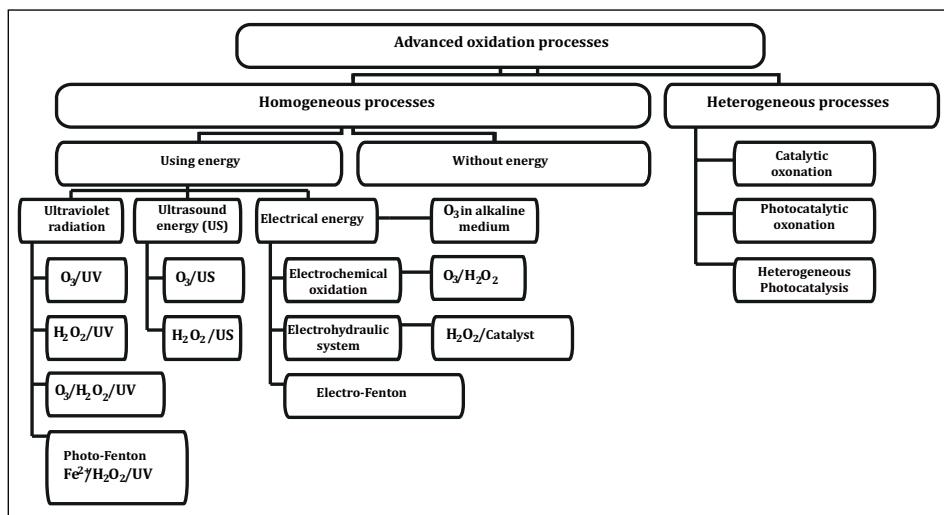
Advanced oxidation processes

Homogeneous processes — **Heterogeneous processes**

Homogeneous processes:
- **Using energy**
  - **Ultraviolet radiation**
    - O_3/UV
    - H_2O_2/UV
    - $O_3/H_2O_2/UV$
    - **Photo-Fenton** $Fe^{2+}/H_2O_2/UV$
  - **Ultrasound energy (US)**
    - O_3/US
    - H_2O_2/US
  - **Electrical energy**
    - **Electrochemical oxidation**
    - **Electrohydraulic system**
    - **Electro-Fenton**
- **Without energy**
  - O_3 in alkaline medium
  - O_3/H_2O_2
  - $H_2O_2/Catalyst$

Heterogeneous processes:
- **Catalytic oxonation**
- **Photocatalytic oxonation**
- **Heterogeneous Photocatalysis**

Figure 11.1. Various AOTs based on wastewater treatment technologies (Sourced from Sharma et al. (2011)

isting conventional process due to their chemical stability. The degradation of biologically persistent pollutants occurs in the presence of highly reactive species such as ozone, hydrogen peroxide, and hydroxyl radicals at ambient temperature and pressure.

There are two types of AOP's as shown in Figure 11.1. The two categories are further classified as either photochemical or non-photochemical processes. The basic mechanism of AOP's is centered on the generation of highly reactive hydroxyl radicals. These hydroxyl radicals are unstable, nonselective, and powerful oxidants when compared to other known oxidizing agents like potassium permanganate. The hydroxyl radical reacts efficiently to fragment organic pollutants into harmless end products, CO_2 and H_2O. Despite being a short-lived species, the hydroxyl radical attacked organic pollutants through hydrogen abstraction, electron transfer, and formation of a double bond with the organic compounds.

11.2.1 Ozonation for Organic Compound Oxidation

Advanced oxidation processes (abbreviation: AOP's), in a broad sense, refers to a set of chemical treatment procedures designed to remove organic (and sometimes inorganic) materials in water and waste water by oxidation through reactions with hydroxyl radicals ($^{\bullet}OH$). In real-world applications of wastewater treatment, however, this term usually refers more specifically to a subset of such
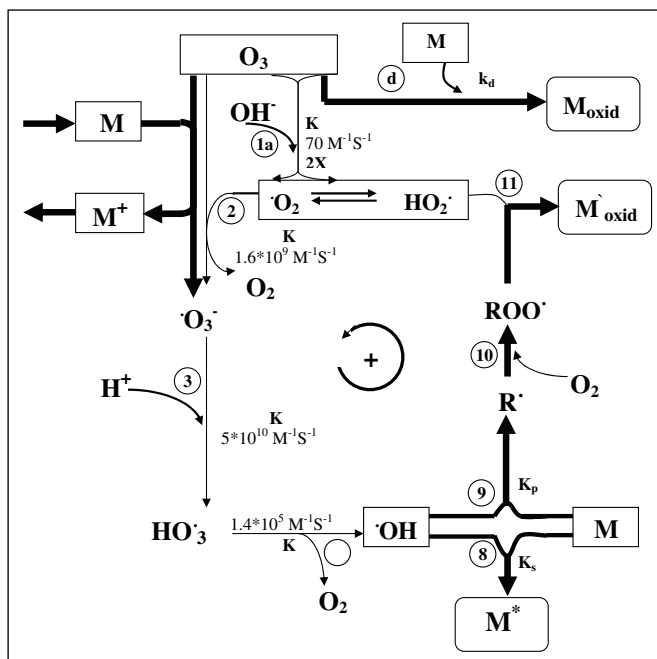
Figure 11.2. Reactions of aqueous ozone in the presence of an organic compound M which react with O_3 or interacts with •OH by scavenging it and/or converting it into HO_2• is an oxidizable substrate in solution; k, k1, kd, kp, ks are reaction constants. (Adapted from Rashed et al. 2005)
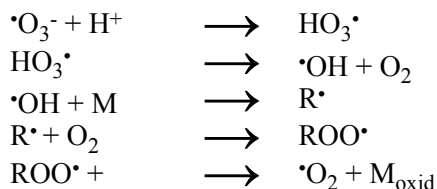
chemical processes that employ ozone (O_3). One such type of process is called in situ chemical oxidation.

Mechanisms of the ozonation of organic soluble substrate (M) in aqueous solutions were diagramed and clearly explained (see Figure 11.2). The main processes of this diagram involving radical reactions are:

Initiation steps, which generate radicals via reactions with OH and substrate (M) in an aqueous solutions:

$$O_3 + OH^- \longrightarrow O_2^- + HO_2^\bullet$$
$$O_3 + M \longrightarrow {}^\bullet O_3^- + M^+$$
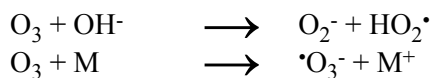
Propagation steps, which maintain the radical reaction chain:

$$^\bullet O_3^- + H^+ \longrightarrow HO_3^\bullet$$
$$HO_3^\bullet \longrightarrow {}^\bullet OH + O_2$$
$$^\bullet OH + M \longrightarrow R^\bullet$$
$$R^\bullet + O_2 \longrightarrow ROO^\bullet$$
$$ROO^\bullet + \longrightarrow {}^\bullet O_2 + M_{oxid}$$

In these steps, radical groups are propagated and maintained through reactions with H^+ and an organic substrate (M) that has alkyl groups (R)$^\bullet$ the radical propagation result in the oxidation of the alkyl groups of the substrate.

Termination step:

$$^\bullet OH + M \quad \longrightarrow \quad M^\bullet$$

In that step, M (e.g., organic substrate or bicarbonate) acts as a radical scavenger, and the radical chain reaction is ended by the formation of product $M^\bullet$.

11.2.2 Application of UV/ozone for Organic Compound Oxidation

During UV/ozone processes, ozone adsorbs UV light (wavelength shorter than 310 nm) and photolyzed to produce hydrogen peroxide and hydroxyl radicals, which able to oxidize organic compounds. For efficient ozone photolysis, UV light must have a wavelength at/or shorter than 254 nm. Fronk reported that a concentration of 50-384 µg/L of halogenated alkenes and aromatic hydrocarbons could be reduced to 87% and 82%, respectively, by applying ozone dose of 6 mg/L. Glaze et al. and Peyton et. al., found that halogenated micropollutants such as chloroform, bromodichloromethane and tetrachloroethylene were destroyed four to fifty times faster by UV/ozone than by ozone alone. During these experiments, ozone dose rates of 0.1-1.3 mg/L min and UV intensities of 0.09-0.38 watt/L were used. Since the effect of UV on ozone in an aqueous solution is the production of hydrogen peroxide, an alternative method is to add hydrogen peroxide to the ozone solution (ozone/hydrogen peroxide system) instead of producing it in situ by ozone photolysis.

11.2.3 Application of UV/hydrogen Peroxide and Fenton Reactions for Organic Compound Oxidation

Among different AOP's, Fenton and photo-Fenton for the removal of organics from wastewater have been extensively reviewed and thus have received greater attention than any other AOTs in recent years.

The processes involved in the destruction of organic compounds with UV/hydrogen peroxide are shown in Figure 11.3. hydrogen peroxide can be photolyzed to produce two hydroxyl radicals if the wavelength of the photon is shorter than 370 nm. These radicals can oxidize organic compounds containing an alkyl group R, compared with the photolysis of ozone, the photodecomposition efficiency of ozone at 254 nm. In this respect, a very promising development of the UV/hydrogen peroxide process is the development of lamps that emit efficiently at shorter wavelength (185 nm), such as the antimony halide lamp.
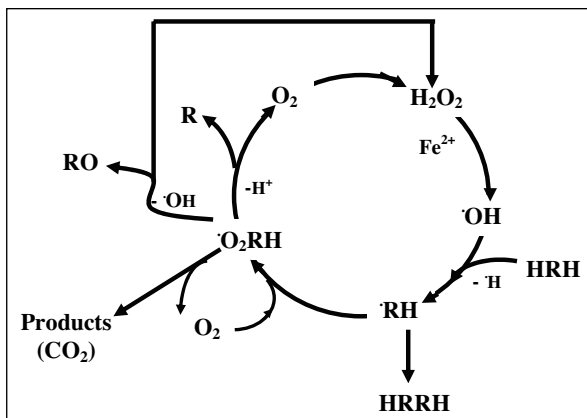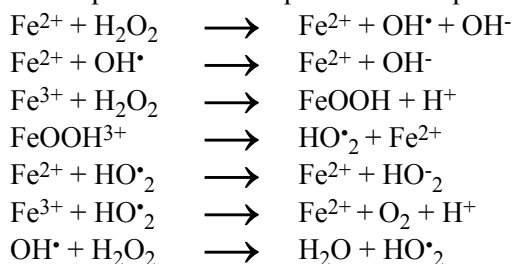
Figure 11.3. Reactions processes in hydrogen peroxide/UV systems and photo Fenton/UV systems. Source: (Adapted from Rashed et al. 2005)

Since the AOP's using hydrogen peroxide are based on hydroxyl radicals attacking organic compounds in wastewaters, the key to enhancing the oxidation efficiency of hydrogen peroxide is to accelerate its decomposition, producing as many hydroxyl radicals as possible. In addition to employing UV to decompose hydrogen, a catalyst can be used. The Fenton's reagent was discovered by Fenton in 1894. Fenton's reagent is a mixture of H_2O_2 and ferrous iron, which generates hydroxyl radicals according to the reaction:

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + OH + OH^-$$
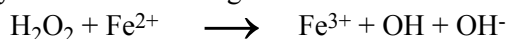
The ferrous iron (Fe^{2+}) initiates and catalyzes the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals. The generation of these radicals involves a complex reaction sequence in an aqueous solution.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{2+} + OH^\bullet + OH^-$$
$$Fe^{2+} + OH^\bullet \longrightarrow Fe^{2+} + OH^-$$
$$Fe^{3+} + H_2O_2 \longrightarrow FeOOH + H^+$$
$$FeOOH^{3+} \longrightarrow HO^\bullet_2 + Fe^{2+}$$
$$Fe^{2+} + HO^\bullet_2 \longrightarrow Fe^{2+} + HO^-_2$$
$$Fe^{3+} + HO^\bullet_2 \longrightarrow Fe^{2+} + O_2 + H^+$$
$$OH^\bullet + H_2O_2 \longrightarrow H_2O + HO^\bullet_2$$

H_2O_2 can act as an $^\bullet OH$ Scavenger as well as an initiator. Due to the formation of Fe^{3+} during the reaction, the Fenton reaction is normally accompanied by the precipitation of $Fe(OH)_3$. The primary purpose of this research was to examine the feasibility and the efficiency of using Fenton's reagent for the removal of organic compounds, which found in the resultant wastewater of some industries.

Hydrogen peroxide and ferrous iron are used for the oxidation of organic substances. It acts as a reductant when reacting with a strong oxidizing agent such as potassium dichromate, and generates the free oxygen with decomposition by itself. Consequently, the mechanism of these reactions with respect to hydrogen peroxide is very complex and may change with conditions of the reaction and the type of catalyst. Generally Fenton's oxidation process was composed of four stages, which are: pH adjustment, oxidation reaction, neutralization and coagulation, and precipitation. The organic substances are removed at two stages of the oxidation and the coagulation.

11.3 Electrochemically mediated oxidative advanced processes (EOAP's)

Over the past decades, electrochemical methods such as electrocoagulation, electrocatalysis oxidation and reduction, electro-Fenton, photoelectro-Fenton, photocatalysis and photoelectrocatalysis (Figure 11.4) have been pointed out as good alternatives to promote the degradation and mineralization of organic pollutants, since they combine the advantages of hydroxyl radicals formation and the efficiency of electrochemistry.

The basic concept of EOAP's is that when a semiconductor surface is irradiated by light (hv ≥ E_g) there is generation of electron/hole pairs (e^-/h^+) by the promotion of an electron from the valence band (lower energy level) to the conduction band (higher energy level). The electrons are forwarded to the counter electrode under positive bias potential (n-type) in order to minimize the recombination of these pairs due to the short life-time. When immersed in electrolyte the adsorbed water molecules and/or hydroxyl ions react with the holes on the valence band to generate hydroxyl radicals ($^\bullet OH$), which are a powerful oxidizing agent (+2.80 V)

The first findings, from 1839, found that the photoelectrochemistry field was stimulated by the Becquerel effect. They observed a photocurrent flow of electrons due to illumination of a material connected by two electrodes immersed in solution. In 1972, the work of Fujishima and Honda had a huge impact on this field. They studied the use of a TiO_2 semiconductor on the photoelectrolysis of water (water splitting) under anodic bias potential in a photoelectrochemical (PEC) cell . Nowadays, photoelectrocatalysis is an emerging field with many applications, such as organic compounds oxidation, inorganic ions reduction, disinfection and production of electricity and hydrogen.

In Electrochemically Mediated Oxidative Advanced Processes (EOAPs), hydroxyl radicals can be generated by direct electrochemistry (anodic oxidation)
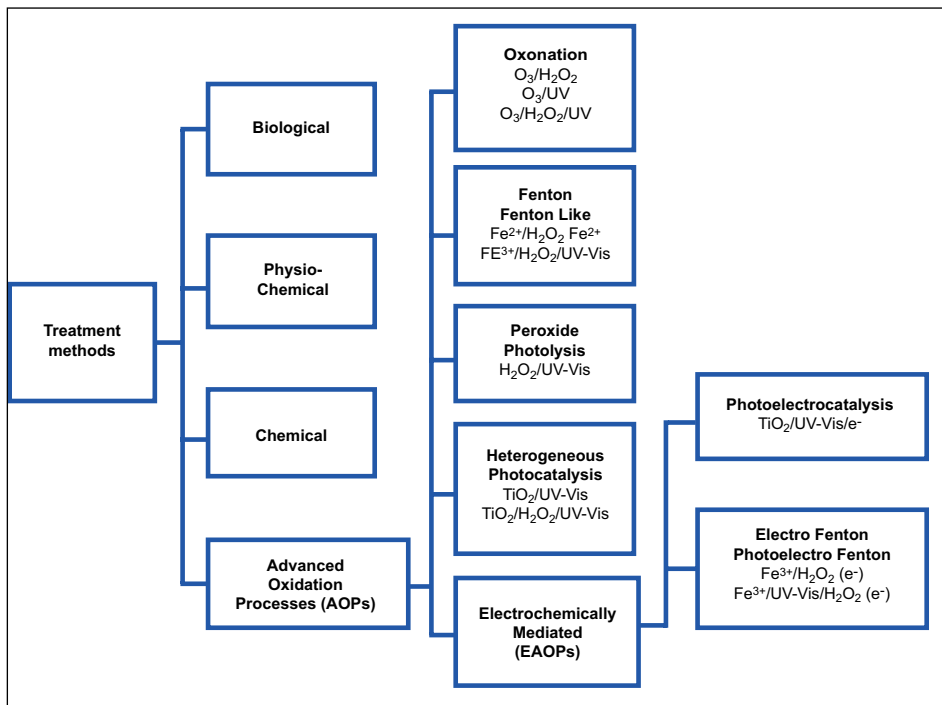
Figure 11.4. Treatment methods described for the degradation of organic pollutants, including conventional techniques and advanced oxidation processes. (Adapted from Bessegato G.G. et al. (2014) / http://www.intechopen.com/books/)

or indirectly through electrochemical generation of Fenton's reagent. In photo-electrocatalytic oxidation the $^{\bullet}$OH is generated heterogeneously by direct water discharge on specific anodes such as DSA and BDD electrodes. During the electro-Fenton reaction the hydroxyl radicals are generated homogenously via Fenton's reaction.

11.3.1 Photoelectrocatalysis: Basic concepts

Advanced oxidation processes (AOP's) have been proposed as alternative methods for the degradation of recalcitrant organic compounds in water, air and soil in recent years. AOPs are based on the generation of hydroxyl radicals ($^{\bullet}$OH) as highly oxidant species, which are responsible for the oxidation of the major pollutants. Among the AOP's, heterogeneous photocatalysis deserves particular attention. The method is based on the use of a semiconductor (mostly TiO_2) irradiated with light energy equal to or greater than its band-gap energy. Since 1972 it has been known that is possible to promote photoelectrolysis of water (water

splitting) under anodic bias potential. Since then, photocatalysis has been explored to promote organics oxidation, inorganics reduction, disinfection of water containing biological materials and production of electricity and hydrogen.

A semiconductor material is characterized by two energy bands separated by the band-gap energy, E_g. A semiconductor at absolute zero is insulating, because the valence band (lower energy level) is completely occupied and the conduction band (higher energy level) totally empty. To become conductive, charge carriers need to be created, usually by photoexcitation. The basic concept is that when a semiconductor surface is irradiated by light (hv $\geq E_g$) there is generation of an electron/hole pair (e^-/h^+) by promotion of an electron from the valence band (VB) to the conduction band (CB).

The key to obtaining success with photocatalytic and photoelectrocatalytic methods is the development of novel efficient materials as working electrodes, which present good optical, mechanical, electronic, electrochemical and catalytical properties. The choice of the synthesis method to produce the semiconductor material is of fundamental relevance, as it will determine the efficacy of the PEC treatment. All factors related to the surface material will influence the success of photoelectrochemical processes as morphological and structural features (particle size, surface area), good charge separation (e^-/h^+), suitable photonic efficiency and band-gap energy level. The oxidizing nature of the holes (h^+) in the valence band means they generate $^\bullet$OH radicals by the oxidation of H_2O molecules or OH^- ions adsorbed on the semiconductor surface, and are also able to oxidize organic molecules directly. Although heterogeneous photocatalysis is a well understood process, and despite its promising results in water decontamination, its practical exploitation has been restricted by its low photonic efficiency, which is mainly due to recombination of the e^-/h^+ pair. Therefore, there are considerable efforts being made to obtain new processes able to separate charge carriers and minimize their recombination rate. The combination of electrochemical and photocatalysis processes (photoelectrocatalysis) offers the opportunity to separate photo-generated e^-/h^+ pairs by gradient potential. Specifically, when the photocatalyst is attached to a conductive substrate (photoanode), there is the possibility to apply an anodic bias potential to the semiconductor and to modify the substrate/electrolyte interface. This alternative improves the efficiency of charge separation by driving the photogenerated electrons via the external circuit to the counter electrode. Figure 11.5 illustrates the mechanism of photoelectrocatalysis.

Furthermore, the great goal is to avoid the removal of photocatalyst suspensions. The immobilization of the photocatalyst particles on a solid substrate is
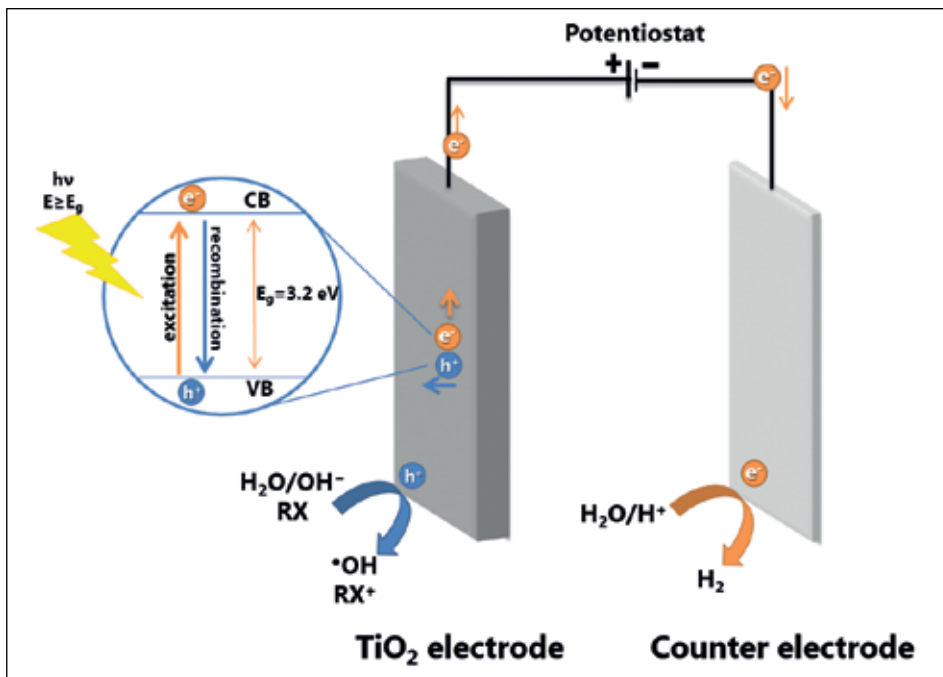
Figure 11.5. Schematic representation of the mechanism of separation and recombination of charges in the photocatalysis or photoelectrocatalysis and mechanism of charge separation in a photoelectrochemical system, where a gradient of potential is created. (Adapted from Bessegato G.G. et al. (2014) / http://www.intechopen.com/books/)

usually applied on photoelectrocatalysis and therefore the process dispense next filtration step.

It is interesting to understand why photoelectrocatalysis is efficient in charge separation. When a semiconductor is in contact with an electrolyte there is formation of a junction semiconductor/electrolyte interface, which determines the electron hole separation kinetics. The junction in a redox electrolyte causes a change in the electrochemical potential (Fermi level) due to discrepant potentials at the interface. Thus, the equilibration of this interface needs the flow of charge from one phase to another, and a band-bending is created within the semiconductor phase. The amount of band-bending in this Schottky junction will depend on the difference of the Fermi levels of semiconductor and electrolyte. The region where there is bending is called the space charge layer (SCL), which is characterized by the accumulation of electrons or holes at the surface shows the behaviour of these charges in the semiconductor before and after this equilibration when it is in contact with an electrolyte.

Photoelectrochemical methods have been intensively investigated as promising alternative methods not only to remove organic pollutants but also to decrease toxicity, since they degrade substances in a short period of time. The degradation mechanism of photocatalysis can be classified into five steps: (1) transfer of reactants in the fluid phase to the surface; (2) adsorption of the reactants; (3) reaction in the adsorbed phase; (4) desorption of the products; and (5) removal of products from the interface region.

11.3.2 Semiconductor materials

The application of semiconductor materials has received a great deal of attention in a re-emerging field: the generation of hydrogen as a clean energy carrier. Studies have described the direct water splitting process and the degradation of organic pollutants in order to obtain hydrogen. For this purpose, the use of n and p-type semiconductor materials using the photoelectrocatalysis method was investigated. The choice of the semiconductor material for hydrogen generation
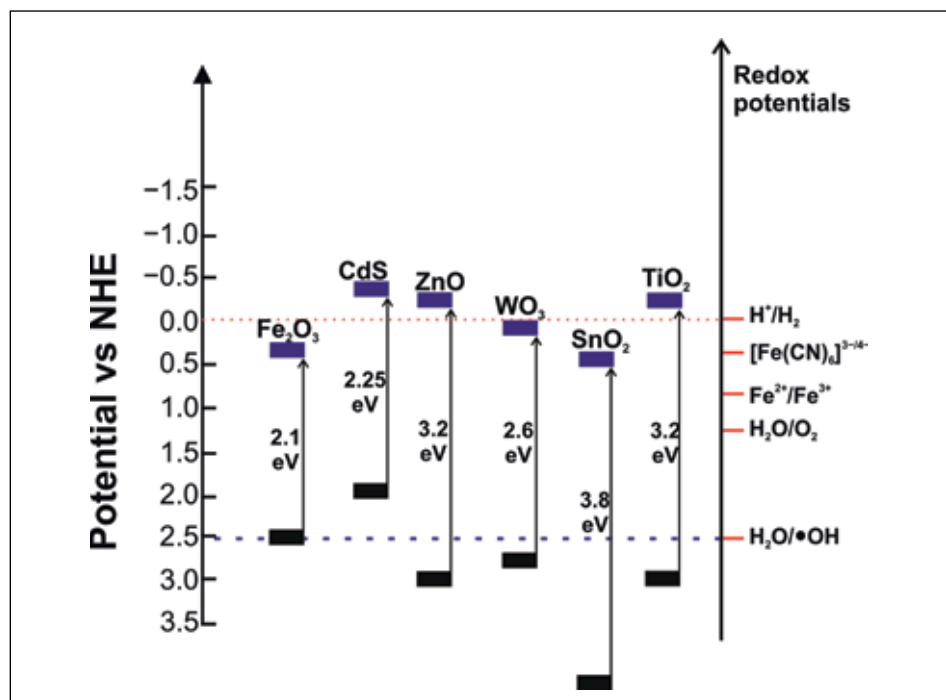

Figure 11.6. Schematic representation of E_g values (in eV) and position of CB and VB for the main semiconductors (*Adapted from Bessegato G.G. et al. (2014)* / http://www.intechopen.com/books/)

purposes depends on the valence and conduction-band energy levels, which are pH dependent (Figure 11.6)

The lower edge of the conduction band needs to be greater than the energy level for H_2 evolution (according to Equation 1). For water-splitting purposes (Figure 11.6), the upper edge of the valence band needs to have enough energy to promote the H_2O/O_2 reaction (Equation 2), while for simultaneous organic-pollutant removal the energy level must be more electropositive than the $OH^-/{}^\bullet OH$ level for hydroxyl radical formation (Equations 1,2):

$$2H^+ + 2e^- \longrightarrow H_2 \qquad\qquad\qquad 1$$

$$2H_2O \longrightarrow O_2 + 4e^- + 4\,H^+ \qquad\qquad 2$$
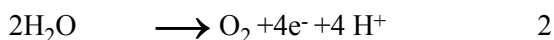
For any given semiconductor and electrolyte, there is an exact potential for which the potential drops between the surface and the bulk of the electrode is zero; in other words, there is no space charge layer. Because the band edges are flat, this potential is called flat-band potential, V_{fb}. The application of any potential greater than the flat-band potential will increase the band-bending at the n-type semiconductor electrode, such as TiO_2. In this case electrons are depleted and holes enriched at the surface. When TiO_2 is irradiated, it is observed that the photogenerated holes have an oxidizing power equivalent to the potential of the valence band edge, and are able to oxidize an RED molecule, whose formal potential is more negative than the valence band. In the case of TiO_2, the H_2O can be oxidized producing ${}^\bullet OH$ radicals. The electron in the conduction band flows via an external circuit to the counter electrode, where reduction reactions may occur, such as the reduction of H^+ ions to H_2 (Figure 11.5). It is important to note that in photo (electro) catalysis, the greater the band-bending (and therefore the SCL) the faster the electron/hole separation occurs, and then the recombination of charges is minimized.

The importance of photoelectrocatalysis has been discussed, with emphasis on recent advances in TiO_2-based materials and strategies of electrochemical synthesis and modification. Currently, TiO_2 nanotube arrays occupy a prominent position. These can be prepared by electrochemical anodization of titanium plates in fluoride-containing electrolytes. In the search for catalysts that can be photo-activated with visible radiation, doping or modification of these materials can be easily performed by electrochemical techniques. The use of these photocatalysts immobilized on conducting substrates employed in photoelectrochemical reactors is a viable strategy for increasing the efficiency of water splitting or to promote efficient degradation of organic compounds.

11.4 Advantages, limitations and perspectives of AOP's

AOP's hold several advantages that are unparalleled in the field of water treatment:

- It could effectively eliminate organic compounds in aqueous phase, rather than collecting or transferring pollutants into another phase.
- Due to the remarkable reactivity of $\cdot$OH, it virtually reacts with almost every aqueous pollutants without much discrimination. AOP's could therefore be applicable in many, if not all, scenarios where many organic contaminants are expected to be removed at the same time.
- Some heavy metals could also be removed in forms of precipitated $M(OH)_x$.
- In some AOP's designs, disinfection could also be achieved, leading AOPs to an integrated solution to some of the water quality problems.
- Since the complete reduction product of $\cdot$OH is H_2O, AOP's theoretically do not introduce any new hazardous substances into the water.

It should be realised that AOP's are not perfect and have several drawbacks (limitations):

- Most prominently, costs of AOP's are too high, since a continuous input of expensive chemical reagents is required to maintain the operation of most AOP systems.
- Some techniques require pre-treatment of wastewater to ensure reliable performance, which could be potentially costly and technically demanding. For instance, presence of bicarbonate ions (HCO_3^-) can appreciably reduce the concentration of $\cdot$OH due to scavenging processes that yield H_2O and a much less reactive species, CO_3^-. As a result, bicarbonate must be wiped out from the system or AOP's are compromised otherwise.
- Given the potential costs, AOP's may not individually handle a large amount of wastewater; instead, AOP's should be deployed in the final stage after primary and secondary treatment have successfully removed a large proportion of contaminants.

Future perspectives

Since Glaze first proposed the definition of AOPs in 1987, this field has witnessed a rapid development both in theory and in application. So far, TiO_2/UV system, H_2O_2/UV system and Fenton, photo-Fenton and Electro-Fenton systems have received extensive scrutiny. Yet there are still many research needs on existing AOPs mentioned above.

Recent trends are the development of new, modified AOPs that are efficient and economical. In fact, there has been some studies that offer constructive solu-

tions. For instance, doping TiO_2 with non-metallic elements could possibly enhance the photo catalytic activity; and implementation of ultrasonic treatment could promote the production of hydroxyl radicals.

As the need for safe and clean water increases globally, there is certainly a growing demand for technologies that could fulfill such tasks. A promising future for AOPs awaits.

Chapter 11 sources:

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2./https://www.researchgate.net/publication/265087675/A_Review_of_Combined_Advanced_Oxidation_Technologies_for_the_Removal_of_Organic_Pollutants_from_Water / Tijani J.O., Fatoba O.O., Madzivire G., Petrik L. F.: A Review of Combined Advanced Oxidation Technologies for the Removal of Organic Pollutants from Water; Water Air Soil Pollut (2014) 225:2102:1-30

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4.https://en.wikipedia.org/wiki/Advanced_oxidation_process

5.https://en.wikipedia.org/wiki/Fenton's_reagent

6.http://cdn.intechopen.com/pdfs-wm/46877.pdf

UZWATER

This compendium is produced for a master level course in the UZWATER project. It consists of some newly written material as well as previously published texts extracted from freely available books, reports and textbooks on the Internet, dominated by publications from the Baltic University Programme. The sources used for each chapter is listed at the end of the chapter. The compendia of the Uzwater project are produced exclusively for Master students free of charge at the participating Universities and is not to be sold or be freely available on the Internet.

The UZWATER project is an EU TEMPUS project. It includes 8 universities in Uzbekistan and deals with university education for sustainable water managment in Uzbekistan. Uppsala University and Baltic University Programme is one of the six EU partners in the project. Lead partner is Kaunas University of Technology.

The main objective of the project is to introduce a Master level study program in environmental science and sustainable development with focus on water management at the eight partner universities in Uzbekistan. The curriculum of the Master Programme includes Environmental Science, Sustainable Development and Water Management.

The Sustainable Development unit will include the basic methods used in Sustainability Science, in particular introduce systems thinking and systems analysis, resource flows and resource management and a series of practical tools for good resource management, such as recycling, and energy efficiency.

The specific objectives of the project are:
*   to establish study centers at the partner universities in Uzbekistan
*   to improve the capacity to train master students with expertise to address the severe environmental and water management problems of the country;
*   to support the introduction and use in Uzbekistan of modern education methods, study materials, and e-learning tools;
*   to encourage international cooperation at the partner universities;
*   to strengthen capacities to provide guidance to authorities and the Uzbekistan society at large;
*   to ensure the visibility and promotion of the Master Programme through web pages, printed material and cooperation with society;
*   to ensure continuity of the Master Programme and long-term support of the project outcomes at partner universities beyond Tempus funding.

http://uzwater.ktu.lt