Sustainable water use in
chemical, paper, textile and food
industries

Water quality demands in paper, chemical, food and textile companies

VITO, PSP, UCM, PTS, HOL, TNO, NW, ALP, UMB, ENEA, TXT, SVI

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Executive summary

When optimizing water networks and increasing water efficiency an accurate definition of the required water quality is the key to achieve this goal. Poorly defined water qualities result in either problems with product quality, safety or in a sub-optimal water network. In the first case, the constraints for the water demands were set too loose, allowing higher contaminant levels than actually permitted by the process. The latter is the consequence of a conservative approach where water quality demands are set higher than required by the process.

This report tries to give a global overview of water quality demands for common processes in each of the four sectors. These figures should be considered as guidelines when no other information is available and should not be implemented without thorough investigation. For the four sectors (paper, chemistry, food and textile) required water quality is defined based on the function of the water, not the origin, taking into account the different aspects involved in each sector (product safety, product quality, process stability, workers safety, etc.).

In the paper sector most predominant water related problems are (bio)fouling and microbially induced corrosion on the one hand and scaling on the other hand. Most of the processes and products that are used create favourable circumstances for scaling and microbial growth.

Chemical industry is known to produce a very diverse range of products, hence have a broad spectrum of processes which are applied. For many of these processes no references are available regarding required water qualities. In these cases the water quality needed was derived from the type of water which is commonly used and the possible interference of certain contaminants. The chemical sector was divided into 5 subsectors, for each subsector several processes are described. The aim was not to have a complete list *of all chemical processes, but to at least give a representation of the processes for the most important chemicals used in Europe.*

In the food sector, the water quality which can be used in the different processes is always linked to product safety issues. Hence, many of these requirements are specified in national regulations. Nevertheless it is still possible to use water of lower quality when it can be guaranteed that product quality and product safety remain at the highest level.

For textile industry critical water parameters and water usage of the different processes were described. The main issue here is the product quality and how this is affected by the quality of the inlet water. Also in this case, setting limits for certain parameters was found to be difficult as very often the affect on the process and/or the product is unknown.

Content

1 Introduction

This report is a result of the project AquaFit4Use, a large-scale European research project co-financed by the 7th framework programme of the European Union on water treatment technologies and processes.
The research objectives of AquaFit4Use are the development of new, reliable cost-effective technologies, tools and methods for sustainable water supply use and discharge in the main water using industries in Europe in order to reduce fresh water needs, mitigate environmental impact, produce and use water of a quality in accordance with the industries specifications (fit-for-use), leading to a further closure of water cycle.

For more information on AquaFit4Use, please visit the project website: www.aquafit4use.eu.

This report was written by the following partners :
VITO, Perstorp Specialty Chemicals, UCM (University of Madrid), PTS, Holmen Paper, TNO , Nestlé Water, ALPRO, University of Maribor, ENEA, Textina and Svilanit.

2 Water quality demands in the paper sector

2.1 Introduction

Biofouling is a predominant fouling mechanism in paper production. The relevant parameters leading to biofilm accumulation derive from microbiological mechanisms, e.g. temperature, pH, content of oxygen and redox potential, nutrients measured as COD, NO_3 or total N, PO_4 or total P etc.
Corrosion in the paper industry is normally significant in the wet process equipment, each manufacturing step having its specific corrosion problem. Temperature, chemical constituents, concentration, size and quality of the wood fibres and used metals are some of the factors affecting corrosion. Different form of corrosion can be emerging. One of the most frequent types of corrosion in the pulp and paper industry is the microbiologically induced corrosion (MIC).
Scaling problems are very important in the pulp and paper industry. They can occur in different areas in the process like pipes, pumps or in the waste water treatment plant. Most frequent depositions are calcium carbonate depositions. Potential of the deposition of calcium carbonate can be predicted and assessed on the basis of the Langelier saturation index using a special method for determining the m-alkalinity.
The most important **water consumers** in paper production are:

- Cleaning and lubricating showers (e.g. for wires and press felts);
- Sealing water for liquid ring vacuum pumps;
- Sealing water for shaft sealing of pumps, agitators and other aggregates;
- Preparation and dilution of chemical additives or fillers or coating paint;
- Manual cleaning and flushing of equipment;

For those consumers, quality demands have been defined as far as possible.

2.2 Fouling, corrosion and scaling in Paper industry

Water is an indispensable medium for all stages of paper production. It is used for suspending and swelling, transport, the dissolution and the rebuilding of fibre bondings. Furthermore it is employed as sealing water for pumps, as cooling medium and also for cleaning [Kappen, 2001]. Three main circulations for the water are usual in the circuits of the paper machine. A large quantity of water is led back from the wire to the headbox in the primary circuit to adjust the very high dilution of fibre suspension to the paper machine (approx. 1 % solids content). The excess water of the primary circuit flows in the secondary circuit at the paper machine untreated or cleared for consistency control or other water consumers like cleaning showers. The surplus of water goes to the effluent treatment plant or is used in counter current flow in the stock preparation department as dilution water for stock pulping and consistency control. In the tertiary circuit the biologically purified water could be circulated back to the paper machine or used for the stock preparation.

Environmental restrictions according to a more stringent environmental legislation, the increasing of water price and the lack of water resources in same places have imposed a trend towards less water consumption in paper industry [Negro, 1995]. Moreover, closure of water circuits has economic benefits such as the reduction of raw material losses and heat losses by the effluent.

In spite of its benefit, closure of water circuits has consequences that can be summarized as follows:

- Increase in suspended solids;
- Increase in colloidal and dissolved material (DCM);
- Higher temperature in the process water.

These consequences lead to some advantages and disadvantages, as described in Table 2-1. An increased concentration of contaminants, expressed for example by the COD value and salt contents, affects both the production process as well as the paper quality. Consequences could be plugging of equipment, inefficient usages of chemicals, lost production due to downtime, increased utility costs, and downgrades products from increased dirt points [Dietz 2003].

Most of the problems are caused by proliferation of deposits in machinery surfaces and pipeline walls. These deposits can be inorganic, organic and biological or mixed.

Table 2-1. Advantages and disadvantages of closure of water circuits in paper industry [Negro, 1995]

ADVANTAGES	DISADVANTAGES
Increase in suspended solids	
Reduction in raw material losses Less production of sludge	Plugging of pipes and showers Dirt and spots in the final product Deposit formation Abrasion Felt life reduction Increase of fines Modification of the drainage capacity Loss of tensile strength
Increase in dissolved solids	
Increased retention of dissolved material	Scaling Formation of deposits Increase of biological activity Corrosion Colour Bad odour Reduction in brightness Less stability in the wet-end
Higher temperature	
Better drainage processes Energy savings	Sizing problems Reduction of the vacuum pumps efficiency Increase and/or alteration of the microbiological activity

2.2.1 Fouling

Concerning fouling, biofouling is the relevant fouling mechanism in pulp and paper industry. The phenomenon is often referred to as slime formation.
Water circuits of paper mills are habitats for microorganisms with best growth conditions like pH, temperature, nutrients and process time, leading to an accretion or accumulation of microbial cells on any submerged surface, e.g. in the wet end [Lustenberger et al, 1998] and tend to partial debonding. Detached particles could attain the fresh paper web and effect a sheet break by reduction of the wet strength or specks and holes in the product. Consequences are cost intensive breakdowns of the process and impairment of product quality. While the mechanism of the accumulation of biofilms is established, the responsible microorganisms in paper industry are unknown [Hüster, 1999; Schenker, 1995].

Moreover, the closing of water systems is changing the process conditions, leading to higher concentrations of nutrients, higher temperature and lower operating pH, favourable to faster microbial population growth.

The most important sources of microbial contamination in paper industry are:

- feed water;
- raw materials;
- additives used in the process;
- reused water inside the industry;
- environment;
- paper rejects.

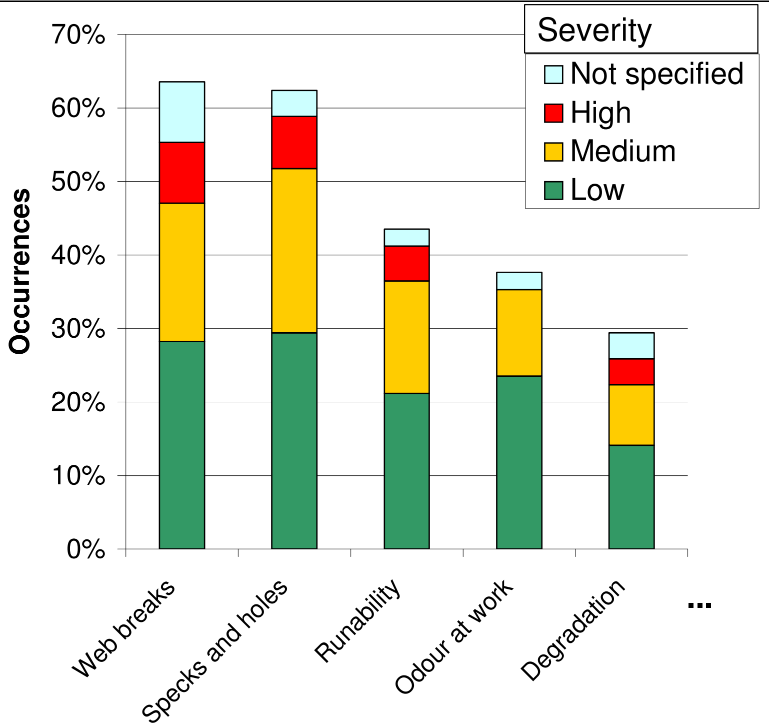


Figure 2-1. Percentage of occurrence of different problems in paper industry associated to microorganisms [Pauly and Ronninger, 2000]

According to a Europe-wide survey, a significant share of paper manufacturers evaluated microbial problems as critical. On the first places of mentioned negative effects are web breaks, specks and holes in the product, runability and odour problems as is showed in Figure 2-1 [Pauly and Ronninger, 2000].

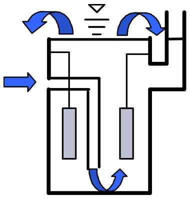
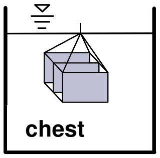
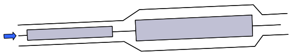
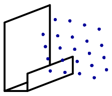
Due to diverse growth conditions between manufacturing sites like production process, additives and source of water, the composition of microorganisms between them is very different and every site must be studied separately for the identification of the more relevant microorganisms. A usual concentration of microorganisms is between 10^4 and 10^8 microorganisms/ml. Aerobic bacteria are more often present in process waters although in case of low O_2 level anaerobic bacteria are predominant. Anaerobic bacteria such as *Clostridium* produce fermentation of volatile fatty acids generating bad odour. Sulphate reducing bacteria are very usual and they are responsible for the generation of H_2S with a characteristic bad odour. Bacteria that produce spores (*Bacillus* and *Clostridium* for example) are very resistant and thus difficult to eliminate form the system. The principal sources of these bacteria are additives like starch and surface water.

Funguses are also usual in waters from paper industry, they do not form slime but different organic material could become trapped in their structure generating deposits. Yeasts are present in paper industry waters and although they do no generate slime they could produce the fermentation of additives like starch. Also algae could be present in these process waters increasing nutrients of bacteria and producing green stains in the final product. The presence of different kinds of microorganisms implies the necessity of a good identification of the microbial problem for finding countermeasures in every particular case.

Another effect is the formation of anaerobic areas at the basis of the biofilm, which leads to odour problems. Numerous paper mills have experienced considerable financial losses due to offensive odours in paper product or in their environment, although there is no connection between malodour and toxicity. The usual odours in pulp and paper industry are emitted from reduced sulphur compounds such as mercaptans produced chemically from craft or sulphite pulp mills, or microbiologically under anaerobic conditions such as sulphate reducing bacteria [Blanco, 2003]. Volatile fatty acids (VFAs) like acetate, propionate and butyrate accumulate in mill water systems as a result of the metabolism of facultative anaerobic bacteria such as methane producing bacteria [Blanco, 2003].

The following table shows some techniques to measure biofilms.

Table 2-2. Resistance

Name and layout	Description	Principle	Application
Blue Pot 	Tank with hinged stainless steel coupons	Bypass	Fixed flow rate in bypass; coupons with smooth and rough surface
Fins 	Stacks of steel plates	System used for plunge	Immersed in process water chest
Tube 	Two linked pipes with hinged stainless steel coupons	Bypass	Fixed flow rate in bypass; coupons with smooth and rough surface; Reynolds number
Plate 	Steel plate with a channel for collection	Area of aerosols	Hang up beside wire section in the area of aerosols

Beside these intermittent methods several online systems are available (e.g. from Nalco, Kolb, Ashland). By different physical methods, the thickness of the biofilm and the speed of growth are measured. With some systems it is possible to draw conclusions to the concentration of bacteria and their nature. The target is to ensure that feed points and dosing strategies are continuously optimized to prevent unnecessary downtime and product defects.

The relevant parameters leading to biofilm accumulation derive from microbiological mechanisms, e.g. temperature, pH, content of oxygen and redox potential, nutrients measured as COD, NO_3 or total N, PO_4 or total P etc. (Figure 2-2). The influence of the paper specific process on the accumulation of biofilms is determined in [Pauly and Dietz, 2005].

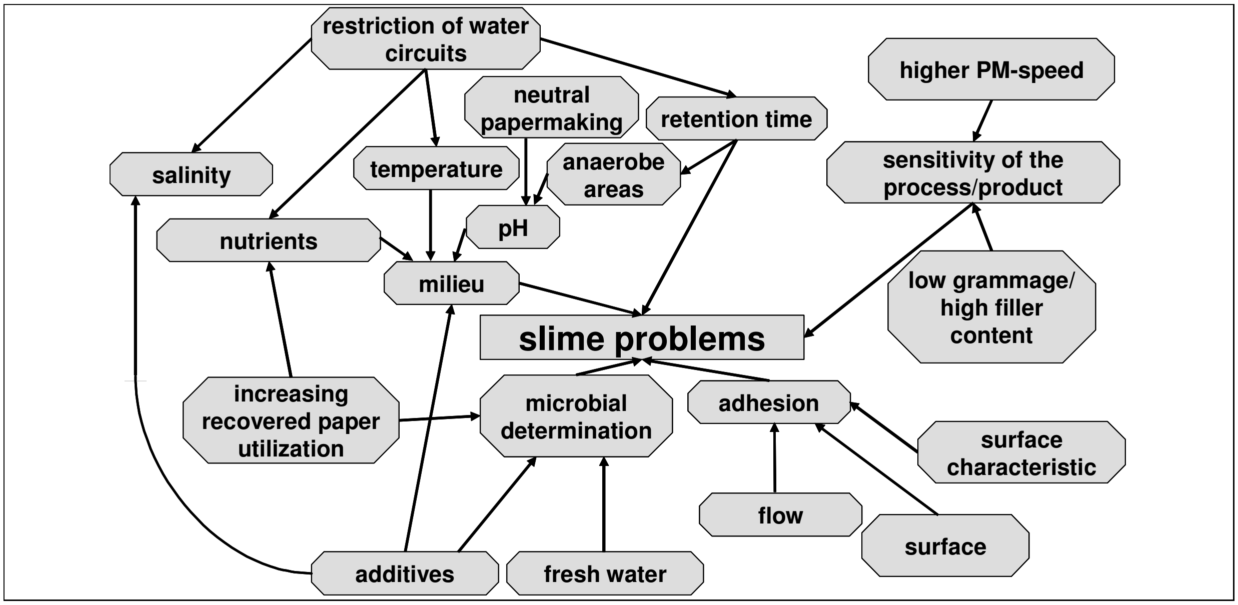


Figure 2-2. Parameters influencing biofilm accumulation

Based on inducing parameters methods to prevent or monitor biofilm formation have to be named [Pauly, 2005] like in Figure 2-3. The specific conditions and the profitability of the approach need to be checked.

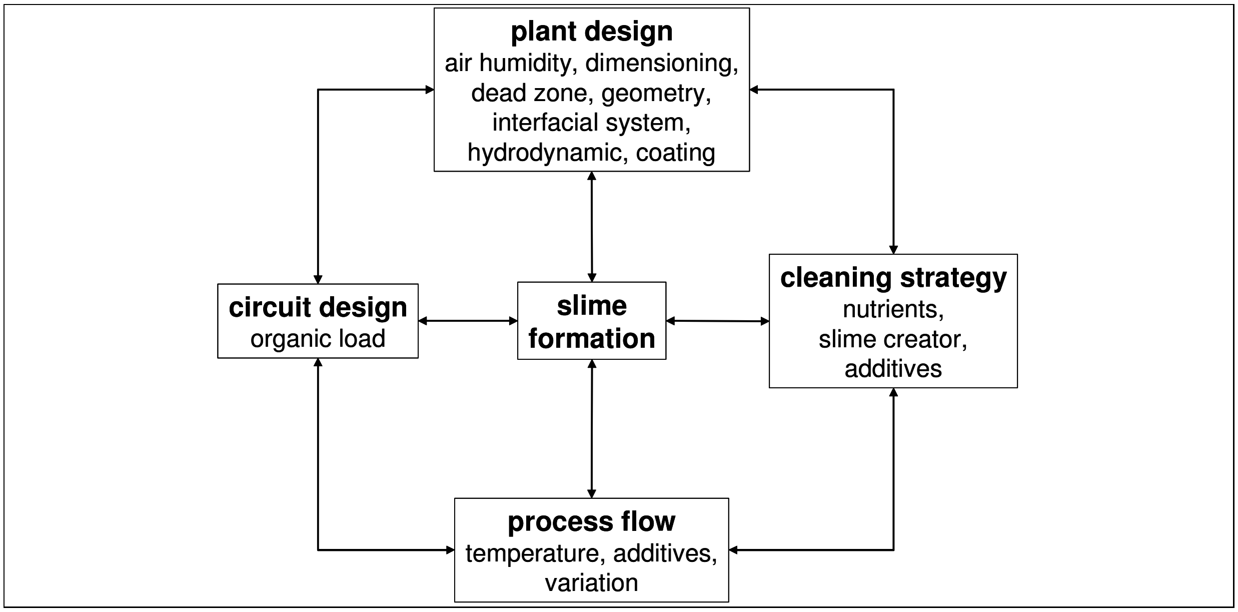


Figure 2-3. Methods to prevent slime formation [Pauly, 2005]

A qualified plant design should enable the prevention of deposits and aerosols which are good conditions for slime formation, e.g. avoiding of oversizing and dead zones or an adapted geometry of tanks. All areas with low velocity are applicable for deposits and resultant accumulation of bacteria.

The organic load in process water is very important for biofilm formation. The less the amount of nutrients (expressed in COD or TOD) the less growth substrates are available for biofilm builder. The amount of organic load is a consequence of the quality of raw materials and the degree of restriction of the water circuit.

Temperature is an important factor for production processes as well as for microorganisms. Results of investigations show that for microorganisms the typical range of temperature is between 35 °C and 50 °C. Reduction of the process temperature is in many cases not practicable, because of worse dewatering of the paper web in the press section. Higher temperatures are possible, depending on the level. However other problems like malfunction of chemical additives, work safety or discharge temperature limits could occur. Variation of pH have an effect on microbial deposits or production of EPS.

Variation of raw material could reduce both the input of COD and of microorganisms, yet this measure is not economically feasible. Changing storage conditions of recovered paper could improve this aspect.

System cleanings are expensive because of production downtime. It is possible that with “good housekeeping” and education of the staff the potential of biofilm formation will also be reduced.

A common practice for microbiological control is the use of biocides. Costs have to be compared to the costs of slime induced breakdowns or loss of paper quality. To optimize the biocide-dosage a meaningful and practicable monitoring system is required.

- bacterial counts are insufficient, measuring of ATP shows potential of biofilm accumulation;
- manual measurement of slime is applicable to assess biofilm accumulation (measurement period min. 1 week);
- online measurement of slime is able to show results after two to three days and is independent from breakdowns;
- observation of the statistic of sheet breaks to identify slime as the real cause as a sole monitoring system is not adequate, because influencing factors are numerous.

Case example

In an R&D project, biofouling has been studied under real case conditions. The project aimed at identifying the causes of undesired slime formation and of problems such as web breaks and quality defects in the paper. From the results of this investigation, measures have been derived to optimise the process design in such a way that slime problems are effectively and economically reduced.

Three industrial plants producing paperboard from recycled fibres were examined for extended periods. Raw materials, production rates, web break statistics, additives in use and the process management have been assessed, as well as organic and microbial loads in the stock and water system. Different measuring devices for slime growth measurement have been designed and applied. The composition of biofilms has been determined by conventional methods and fluorescence in situ hybridization (FISH), supplemented by biocide performance tests.

All data collected was evaluated by means of multivariate correlation and regression analysis. In this way, influences on biofilm growth could be identified. A temperature increase of about 31 °C to 36 °C was found to enhance biofilm growth by a factor of 2 to 3. Concomitantly, the process water COD increased by 25 %, and the redox potential dropped. Synergetic effects of these parameters are to be assumed. Biofilm formation in the aerosol region of the paper machine can exceed the formation in the stock and water system. In particular, humidity and fog intensity have strong influences on this [Pauly, 2005].

2.2.2 Corrosion

Paper production consists of a series of processes and can be roughly divided according to the five major manufacturing steps pulp production, pulp processing and chemical recovery, pulp bleaching, stock preparation and paper manufacturing. Each manufacturing step has its own corrosion problems related to the size and quality of the wood fibres, temperature of the process water, the concentration of the treatment chemicals and the materials used for machinery construction. Examples of corrosion affecting production are corrosion products polluting the paper and corrosion of rolls scarring the sheets of paper. Corrosion of components may also result in fractures or leaks in the machines, causing production loss and safety hazards.

Both organic and inorganic constituents in the dissolved solids influence the harshness of corrosion. Most significant among these are:

- chlorides;
- sulphates;
- lignin-related sulphur compounds;
- organic acids;
- carbonates.

Higher temperatures amplify the activation of localised corrosion and metal dissolution kinetics in uniform attack. Some of the corrosion concerns in the pulp and paper industry are listed below:

- pitting;
- crevice corrosion;
- stress corrosion cracking;
- microbiologically induced corrosion (MIC);
- fatigue corrosion.

In paper industry non biological corrosion is principally due to sulphate and chloride. Sulphate inputs are for example due to the use of chemical additives for fixing or retention agents. The use of sulphuric acid for pH control and sodium bisulphite for bleaching also increases the sulphate concentration in the water. Chlorine is used for bleaching in some paper industries although the tendency is to use free chlorine bleaching process. Fresh water intake or flocculation agents like PAC also contribute to chloride concentrations in process water.

Pitting corrosion and crevice corrosion caused by chloride and thiosulphate ions are common problems at the wet end of paper machine and predominantly at splash zones. Thiosulphate originates from hydrosolphite (dithionate) used as bleaching chemical of mechanical pulp, activities of Sulphate Reducing Bacteria [Laitinen, 2008].

Corrosion issues in the paper industry are normally most significant in the wet process equipment. Various manufacturing steps have their specific corrosion problems. Temperature, chemical constituents, concentration, size and quality of the wood fibres, and metals used in machinery components are some of the factors affecting corrosion in equipment (Figure 2-4). Paper recycling and environmental concerns regarding chemical releases have required the pulp and paper industry to change their processes.

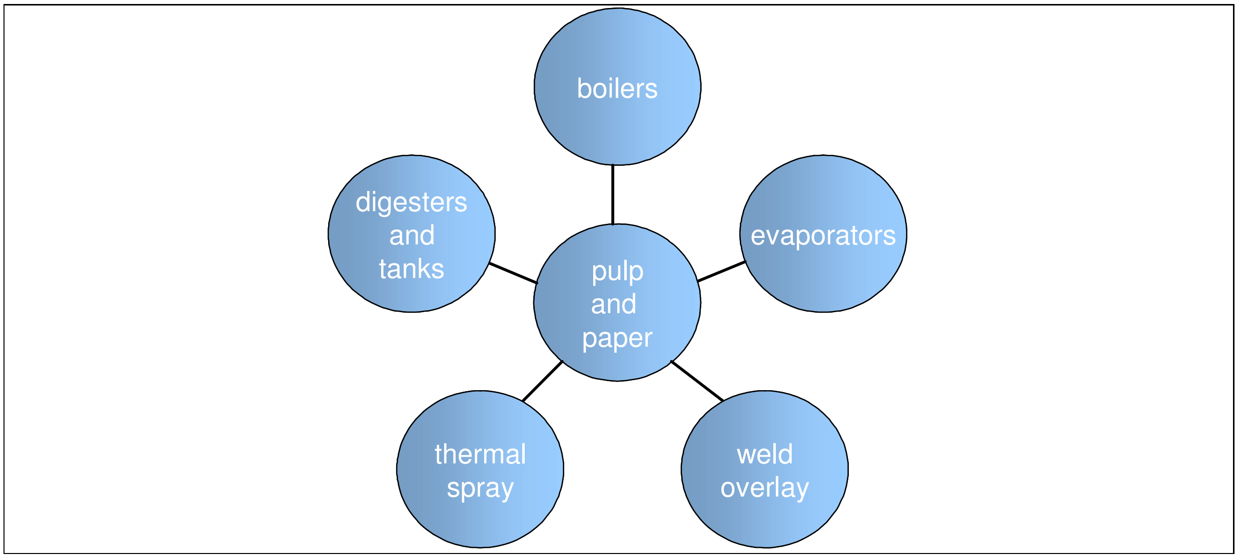


Figure 2-4. Affected equipment by corrosion

Paper mills have been historically constructed of a mixture of carbon steel and stainless steel components. There has been a trend to use more stainless steel in paper equipment. Stainless steels have their own corrosion concerns. Proper selection of stainless steels and associated welding processes for these new environments are significant issues to the pulp and paper industry. Material requisitions for different equipment or different processes are available [Acme Alloys].

An example for resistance of materials against chloride during contact with water is shown in Table 2-3.

Table 2-3. Resistance of materials against chloride during contact with water [Huber]

Application	Chloride at room temperature mg/l	Chloride at 70°C mg/l	Type of steel
drinking water, industrial water	100	50	304 (1.4301) 321 (1.4541)
drinking water, industrial water	400	200	316Ti (1.4571) 316 (1.4401)
cooling water, process water, mineral water	1 000	500	316L (1.4435) 316 (1.4436)
sea water, brackish water brine	20 000	5 000	F48 (1.4439) 904L (1.4539)
sea water, chemical water	25 000	10 000	1.4566, 1.4562

An example for the influence of material selection on corrosion is the Mestä-Rauma pulping plant, which was opened in Europe in 1996, and is one of a kind as it is made entirely of stainless steel. By using this material for each process, the maintenance costs associated with equipment are significantly reduced in comparison to those for carbon steel equipment. The capital investment for this pulping plant was $550 million. The capital investment costs for a new state-of-the-art integrated mill are estimated at $1 billion [Brongers and Mierzwa].

Corrosion control methods in the pulp and paper industry include equipment design, process design, and the use of corrosion inhibitors. Using any of these techniques reduces or eliminates corrosion within a system.

2.2.2.1 Equipment design

Pulp and paper equipment design consists of proper material selection in conjunction with the process chemicals and the prevention of stagnant process fluids in the equipment. Low-alloy carbon steel would be the material of choice if corrosion were not a problem; however, for many processes, stainless steel and even nickel-base and titanium alloys are required for better performance in corrosive environments. Within the group of stainless steels, there are several alloy grades. Their relative cost is dependent on the concentration of the major alloying elements (Cr, Ni, Mo, etc.), the volume produced, and the form in which it is supplied (tube, pipe, plate, or block). In general, stainless steels are more expensive than low-alloy carbon steels. Stagnant and slow-flowing process fluids in pulping equipment can occur in crevices and water traps. Fluid stagnation often leads to an increase in concentration of the chemicals and the local creation of a severe environment in which pitting and crevice corrosion may occur. By designing drain holes and easy access to the equipment, stagnant solution can be removed. Slow-flowing fluids containing a solid fraction of pulp may deposit a layer of pulp on the bottom of piping and reservoirs. Under-deposit corrosion mechanisms, such as crevice corrosion and pitting, may occur. If equipment is designed with sufficiently fast and/or turbulent flow, deposit formation can be controlled. In addition, regularly scheduled cleaning and proper equipment maintenance can prevent the build up of pulp and decrease the amount of stagnant solutions.

2.2.2.2 Process design and corrosion inhibitors

Corrosion rates in mill equipment also depend on the chemical composition within each section of the process. The chemical composition varies from mill to mill depending on the processes involved, the closure of the mill's water circuits, the produced paper grade, the speed of the process, and the amount of pulp or paper being produced. In general, the corrosivity of an environment will increase when the temperature is increased, when the pH is reduced, when the dissolved solids content increases, and when the chloride and sulphur compound concentrations are increased. Therefore, by monitoring the process and maintaining the proper temperature, pH, dissolved solids content, and chloride and sulphur compound concentrations, the amount of corrosion can be controlled. In some processes, corrosion inhibitors can be added to the process to mitigate corrosion. Continued measurements of the process chemistry should be made to ensure that the correct dosage of the added corrosion inhibitor is maintained. Preventive strategies for corrosion control in the pulp and paper industry include the verification of average corrosion rates, using weight loss coupons, regular inspection, and preventive maintenance. Preventive strategies are considered during the design and construction phases when new equipment is made, or when existing equipment is refurbished or repaired. Corrosion prevention techniques focus on minimizing the initiation of corrosion altogether, while corrosion control techniques are used to minimize the propagation of ongoing corrosion.

2.2.2.3 Weight loss coupons

Weight loss coupons are commonly used as a means to measure the average corrosion rate in a process or in the atmosphere of a pulp or paper plant. This technique is relatively cheap and easy to use, as it requires only a little amount of pieces of metal that are weighed, exposed for a period of time, and weighed again. Using the difference between the dry weight of the coupon before and after the test, the average corrosion rate can be calculated. Deposits have to be removed. An advantage of this technique is that several coupons of different materials can be exposed simultaneously. By performing weight loss tests, the corrosiveness of an environment can be estimated over a period of time. If the corrosion rate is determined to be too high, preventive measures can be taken to prolong the remaining life of the equipment. The preventive actions can include the addition of a corrosion inhibitor, a change in the process, an application of anti-corrosion coatings or the addition of a cathodic protection system.

2.2.2.4 Inspection and preventive maintenance

An additional method to monitor the corrosion rate is through regular visual inspection of all parts of the equipment that are exposed to corrosive environments. These inspections use non destructive examination (NDE) to reveal corrosion pits, crevice corrosion, or wall thinning before they will affect or stop the production process or degrade the paper to below its product quality specifications. Regular inspection is performed as part of the maintenance program in plants. The results of the inspections are used to plan equipment repairs during scheduled shutdowns and to take action to maintain optimum production quality and quantity.

2.2.3 Scaling

Accumulation of scale is a phenomenon that can occur in all pulp and paper making processes. The huge variety of substances present in the process lead to the formation of scale deposits on mill equipment. Scale deposits can cause a number of operational problems such as plugging of equipment, inefficient usage of chemicals, increased utility costs, lost production due to downtime and downgraded products from increased dirt counts, but can also cause a drastic reduction in heat transfer rates in equipment such as boilers, steam generators, evaporators, distillation units, heat exchangers, cooling tower fill, engine jackets etc.

Typical scaling compounds and their sources, place of occurrence and conditions for scaling in papermaking and pulp bleaching are described in Table 2-4.

Table 2-4. A summary of types, sources, location and causes of scale deposits in pulp and paper mills [Sitholé, 2002]

Scale	Source	Place of occurrence	Conditions for scaling
Aluminium hydroxides	**Aluminium**: wood, alum, sodium aluminate, polyaluminium chloride, rosin sizing	Paper machine, deinking plants	Temperature, high total dissolved solids (TDS)
Aluminium phosphates	**Aluminium**: wood, alum, sodium aluminate, polyaluminium chloride, rosin sizing **Phosphates**: starch, filler stabilizers	Paper machine, size press	Excess phosphoric acid
Aluminosilicates	**Aluminium**: wood, alum, sodium aluminate, polyaluminium chloride, rosin sizing **Silicate**: peroxide stabilizer	Recovery area	High residual alkali
Barium sulphate	**Barium**: wood **Sulphate**: sulphuric acid, white liquor, alum	Bleach plant, paper machine	Oxidation of sulphite, addition of sulphate, poor white liquor clarification, temperature, high TDS
Calcium carbonate	**Calcium**: wood, white liquor, calcium carbonate filler, hard water **Carbonate**: white liquor, calcium carbonate filler, formation in caustic extraction stages	Digesters, heat exchangers, evaporators, lime kilns, brownstock screen room, bleach plant, paper machine, deinking plants	Alkaline conditions, high temperature, high TDS
Calcium oxalate	**Calcium**: wood, white liquor, calcium carbonate filler, hard water **Oxalate**: wood, pulping, delignification	Recovery area, digesters, bleach area, deinking plants, BCTMP mills, fermentors	Acid conditions, high TDS
Calcium sulphate	**Calcium**: wood, white liquor, calcium carbonate filler, hard water **Sulphate**: sulphuric acid, white liquor, alum	Recovery area, digesters, bleach area	Oxidation of sulphite, addition of sulphate, poor white liquor clarification, temperature, high TDS

Scale	Source	Place of occurrence	Conditions for scaling
Calcium silicate	**Calcium**: wood, white liquor, calcium carbonate filler, hard water **Silicate**: peroxide stabilizer	Pulp brightening processes, refiner plates, deinking plants	Recycling of bleach effluents, drop in pH, low Mg/Ca ratio in pressate, carryover of deinking gents
Burkeit	**Sodium**: wood, water, process additives **Carbonate**: white liquor, calcium carbonate filler	Black liquor evaporators	Sulphate: carbonate ratio, residual alkali
Magnesium silicate	**Magnesium**: wood, peroxide stabilizer **Silicate**: peroxide stabilizer	Pulp brightening processes, refiner plates	Recycling of bleach effluents, drop in pH, low Mg/Ca ratio in pressate
Radium sulphate	**Radium**: wood, water **Sulphate**: sulphuric acid, alum	Associated with barium sulphate scale	Same as for barium sulphate

Replacing alum with an organic cationic donor (e.g. polyaluminium chloride - PAC) can help reduce aluminium-based scale deposits in paper machines, however the corrosion relevant compound chloride is increased. Other possibilities to prevent aluminium scale deposits are to avoid high pH values or long dwell times or high water temperatures. Chelates can also be used to tie up free metal ions that contribute to scale or inhibitors that have the ability to inhibit crystal growth. These inhibitors are capable of maintaining ion pairs in solutions well beyond their solubility limit. For example, polyphosphates can be used in the presence of calcium and carbonate ions to prevent calcium carbonate formation. In cases where crystal formation cannot be totally inhibited, a dispersant can be used to prevent the crystal from depositing on a surface. Anionic polymers such as sodium polyacrylate impart an increased negative charge to the particle as well as providing a steric barrier, thus preventing formation of the deposit.

A solution to avoid scale deposits caused by fillers are retention aids that overcome the repulsive forces that keep the filler particles dispersed. The retention aids should agglomerate the fillers and fines such that they will be retained but not over agglomerated as this results in poor formation of the paper web. Fillers should be stabilized with dispersants that do not cause scale problems.

2.2.3.1 Calcium carbonate

Calcium-based scale deposits are the main problem in the paper production process. Increasing calcium concentrations in white water in the last years are due to the fact that calcium carbonate is increasingly used as cheap filler and coating pigment. With the rise of calcium carbonate consumption in the paper production the amount of calcium carbonate in recovered paper is inevitably rising, too. As a consequence of the use of recovered paper as a secondary raw material it is also a source of calcium carbonate. The content of calcium and percentage of calcium carbonate in different grades of recovered paper is shown in Table 2-5.

Table 2-5. Calcium and calcium carbonate-contents of important sorts of recovered paper

EN 643 grade		Number of samples	Ca-content	$CaCO_3$
1.02	Mixed papers and boards (sorted): A mixture of various qualities of paper and board, containing a maximum of 40 % of newspapers and magazines.	4	33,3	8,3 %
1.04	Supermarket corrugated paper and board: Used paper and board packaging, containing a minimum of 70 % of corrugated board, the rest being solid board and wrapping papers.	3	17,0	4,3 %
4.03	Used corrugated craft 2 Used boxes of corrugated board, with liners of craft or testliners but having at least one liner made of craft.	2	5,9	1,5 %

In internal result 1.2.1.1 the relevance and calculation of the Langelier saturation index (LSI) is described. With modifications in calculation and interpretation, this parameter is applicable to specify the potential of calcium carbonate deposition in process water in the pulp and paper industry. In the process water of paper mills producing packaging paper from recovered fibres it has to be reckoned with deposition of calcium carbonate with an **LSI higher than 0,5**. Because of the frequent presence of organic acids in process waters that are vulnerable to scaling, calculation of the m-alkalinity needs to be adapted. The correlation between the calculated and measured m-alkalinity is demonstrated in Figure 2-5.

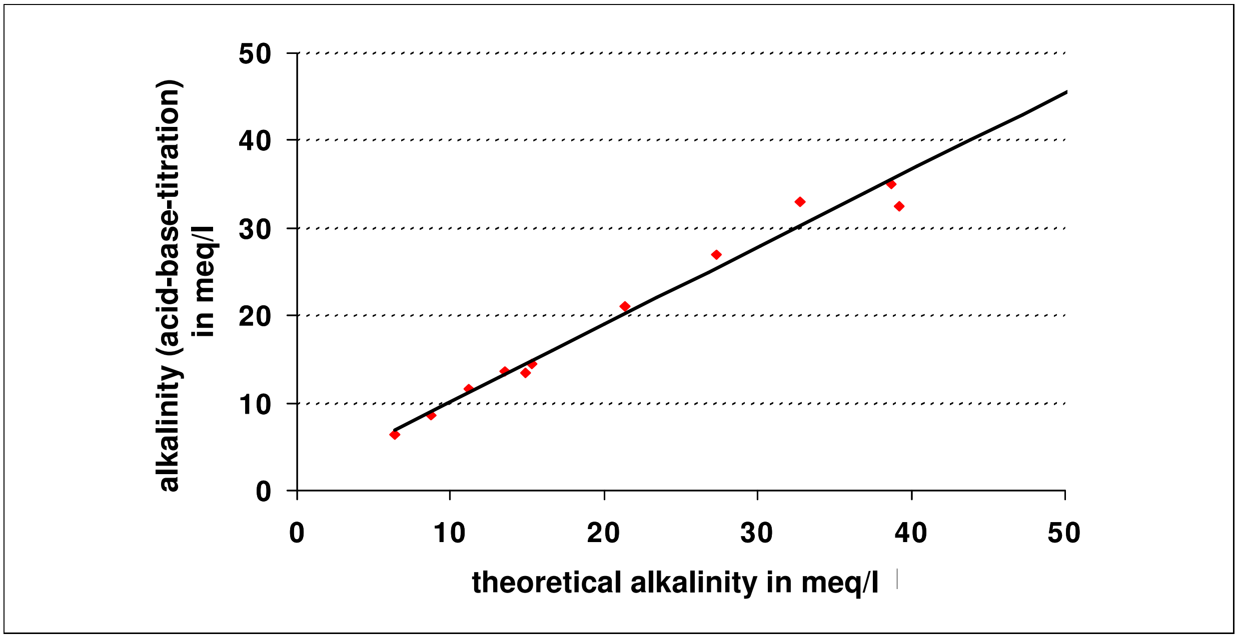


Figure 2-5. Comparison of the alkalinity (acid-base-titration) and the calculated alkalinity [Bobeck et al, 2004]

A comparison of several methods to calculate the potential of deposition of calcium carbonate is shown in Table 2-6 [Bobeck et al, 2004].

Table 2-6. Comparison of several methods to calculate the potential of deposition of calcium carbonate

	Marble resolution test	Scaling-Test	LSI
Conclusion	Max. deposition of calcium carbonate	Actual deposition (under test conditions)	Potential of deposition of calcium carbonate
Reproducibility (VK)	5-10 %	40 % within 8 parallel Coupons (estimation)	5-10 %
Source of error and limitation of the method	Test cannot be used for estimation of scaling inhibitors	Dropping off of depositions before weighing; scaling of the test system; foaming	No quantification of the deposition Index cannot be used for estimation of scaling inhibitors
Expenditure of time	Ca. 1 h	3 weeks	2 h
Equipment	Common laboratory equipment, Calcium-analysis	Test equipment, pump if necessary, common laboratory equipment	Common laboratory equipment

LSI = Langelier saturation index
VK = coefficient of variation

Strategies for controlling calcium scales can be divided into operation and elimination processes. In the majority of cases elimination processes are more expensive than operation processes.

Mostly those processes are economic only if calcium elimination can be combined with other cleaning purposes.

Operation processes are:

- by **setting of pH** in the range of 7 it is possible to reduce the deposition of calcium carbonate [Hamm et al, 1991], COD degradation is influenced by low pH (microbial activity);
- use of **inhibitors**, which influence the solubility of calcium carbonate in pulp suspension [Pang et al, 1998];
- **recirculation** of clarified waste water can effect increasing pH and dilution; additional precipitation of calcium carbonate after the anaerobic treatment is possible [DIEDRICH et al., 1997; Nivelon et al., 1998; Hamm, 1999; Pauly, 2001];
- **selection of recovered paper** as raw material with low content of calcium carbonate or inert calcium carbonate fillers; not practicable because fabricators of recovered paper cannot influence the mixture.

Elimination processes include:

- **precipitation** of calcium carbonate by different chemicals and separation, high cost due to expensive chemicals and costs of disposal [Haver et al., 1998];
- membranes with **nanofiltration** can separate dibasic ions like calcium [N.N., 1996];
- lime sludge can be separated by **hydrocylones**, no information about large scale examination;
- **evaporation** is a well suitable method to separate calcium carbonate because non volatile substances can be retained completely;
- **mechanical treatment** by high pressure.

Case example

Within an R&D project [Bobeck et al., 2004] common analysis and calculating methods concerning scaling have been investigated within several German paper mills which use recovered paper as raw material. By identification of scaling problems in the pulp-water-system and simultaneous consideration of scaling parameters thresholds should be appointed.

Paper mill A (PM A) has depositions in showers, sieves and vacuum pumps. A permanent magnet is installed. PM B has similar problems. The calcium concentration in the white water is between 620 and 900 mg/l, this means double concentration as in PM A. Due to the low pH in PM B (5,80 – 6,60) the potential of deposition of calcium carbonate is lower. PM D has no scaling problems at the paper machine or pipe system. This is demonstrated by the low LSI shown in Figure 2-6.

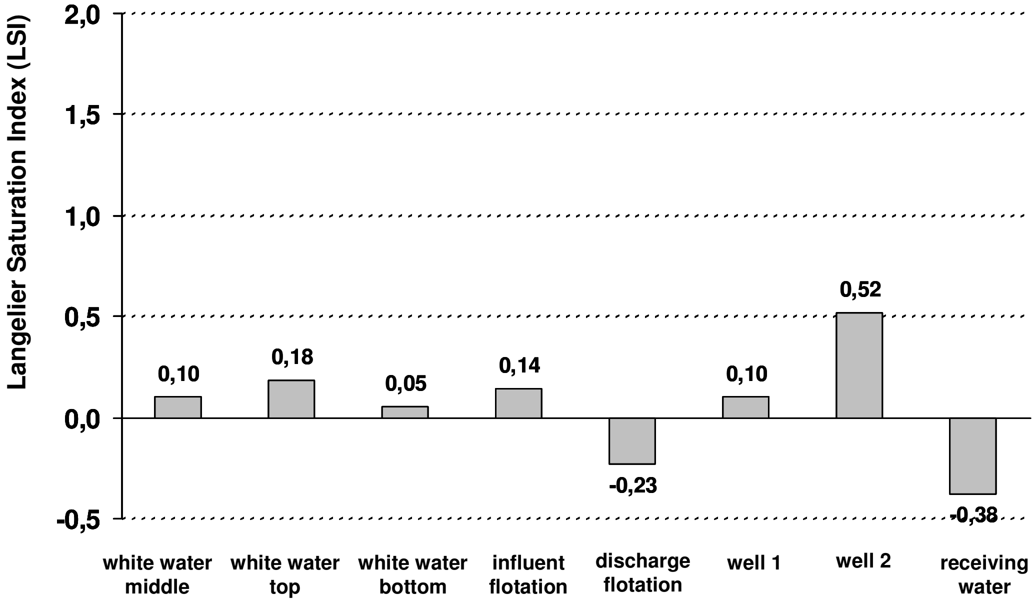


Figure 2-6. LSI measured in paper mill D

Despite of a closed water circuit PM E has no scaling problems. A permanent magnet is installed because of odour problems. The LSI measured in PM E is very low (Figure 2-7). There is no reason for scaling problems given.

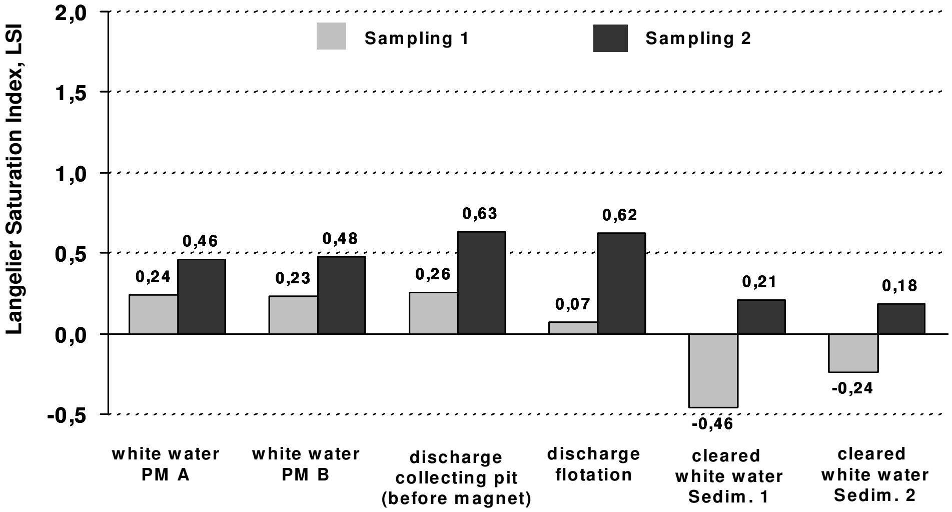


Figure 2-7. LSI measured in paper mill E

Also Figure 2-8demonstrates that despite of high calcium concentration the m-alkalinity and the pH are very low. The high load of organic matter and concentration of VFA counteract the deposition of calcium carbonate by building complexes.

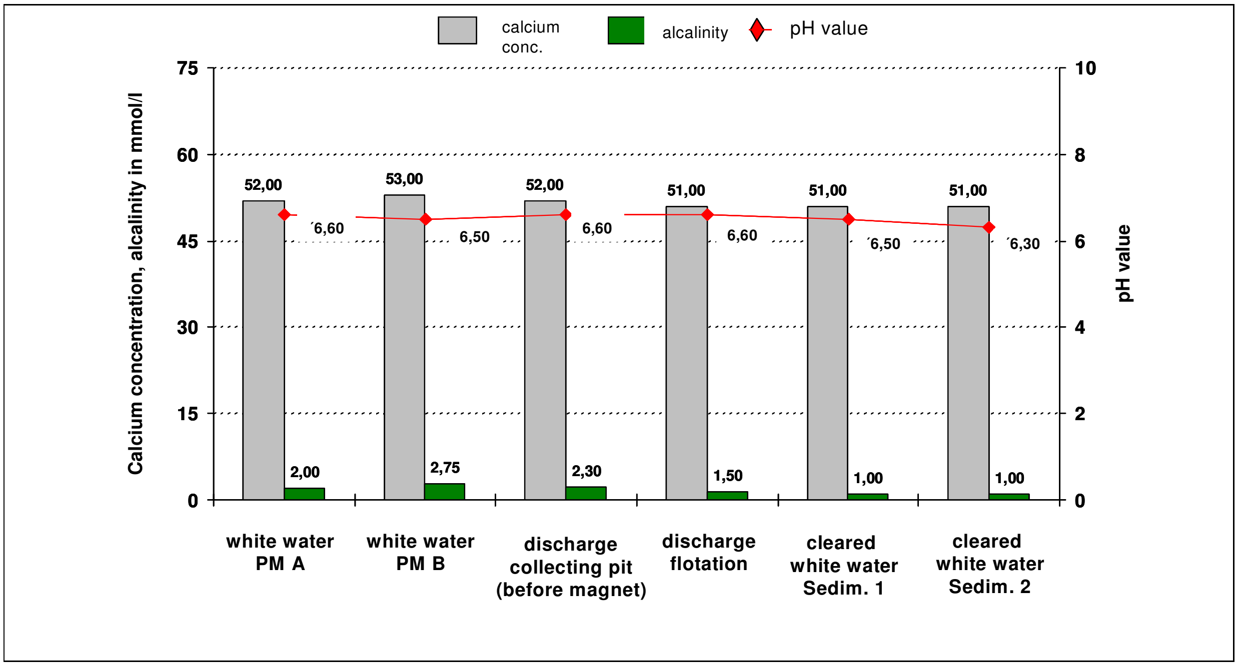


Figure 2-8. Calcium concentration, m-alkalinity and pH measured in paper mill E

A comparison of results measured in several paper mills is shown in Table 2-7.

Table 2-7. Comparison of results measured in several paper mills

		Temper-ature	pH	Calcium	m-alkalinity	IDS	Conductivity	COD	VFA
		°C	--	mg/l	mmol/l	mg/l	µS/cm	mg/l	mg/l
A	White water 1	37,9	7,2	396	4,8	3 420	5 280	2 578	928
	White water 2	37	7,2	393	9,4	3 400	5 280	2 538	593
	Clear filtrate	37,2	6,92	384	7,1	3 420	5 240	2 505	752
B	White water 1	40	6,6	634	5,75	3 760	4 920	8 140	2 460
	Clear filtrate		5,8	900	4,75	4 380	5 520	9 140	3 260
D	White water top	25	6,83	511	3	1 920	2 470	2 709	1 313
E	White water PM A	24	6,62	2 079	2	7 150	8 160	10 468	5 100
	White water PM B	24	6,46	2 118	2,75	7 090	8 500	10 442	5 274

2.3 Water consumers and quality demands in paper production

In the history of papermaking, the water circuit was created as a result of the invention of the paper machine and with it the advent of endless papermaking. As industrial papermaking evolved and developed, so did the importance and scope of water circuits as well. Factors that have shaped and influenced this development are listed below:

- A reduction in the specific water volume: As the specific water volume is reduced, the demands on the contaminant removal efficiency of the installed circulation water treatment rise, since the water must be used several times and fresh water is also replaced by circulation water at critical locations. This means that more water must be treated and higher requirements are placed on the treated water;
- Development of production capacities: The increased productivity, which in some cases is considerable, makes it necessary to hydraulically adapt the elements of the water circuit. Higher capacity also means higher machine speeds and thus growing requirements on automation, control and reliability of the systems;
- Increased product quality and greater use of recovered paper: High requirements on water quality make it necessary to separate heavily loaded and slightly loaded water and the removal of components detrimental to the product. The greater use of recovered paper significantly aggravates the above-mentioned conditions even more;
- Greater raw material efficiency: This requires the collection and recirculation of all partial flows containing solids. Only clarified water is discharged. A system that is integrated into the water system must take over solids management.

The requirements mentioned above result in practice in the construction of complex water circulation systems. Their appearance, the mode of operation of the elements contained in them and possibilities for system closure will be discussed in the following sections.

2.3.1 Designing water circulation

The functions of water in papermaking are complex and diversified. The important facet of water use is to provide the quality and volume of water necessary for the intended purpose, bearing the associated economical and ecological aspects in mind. This makes it necessary first and foremost to identify and quantify the quality requirements for the respective purpose.

In addition to the functions of sheet formation and suspension as well as the transport of fibres and fillers, water fulfils other important functions in papermaking: for instance, it serves as shower and sealing water in a number of treatment units, etc. Using fresh water for all these purposes would mean consuming more than 100 l of water per kg of paper produced. Hence, the water used in the process of making paper is usually recirculated and reused again. The important functions of water are shown in the following figure.

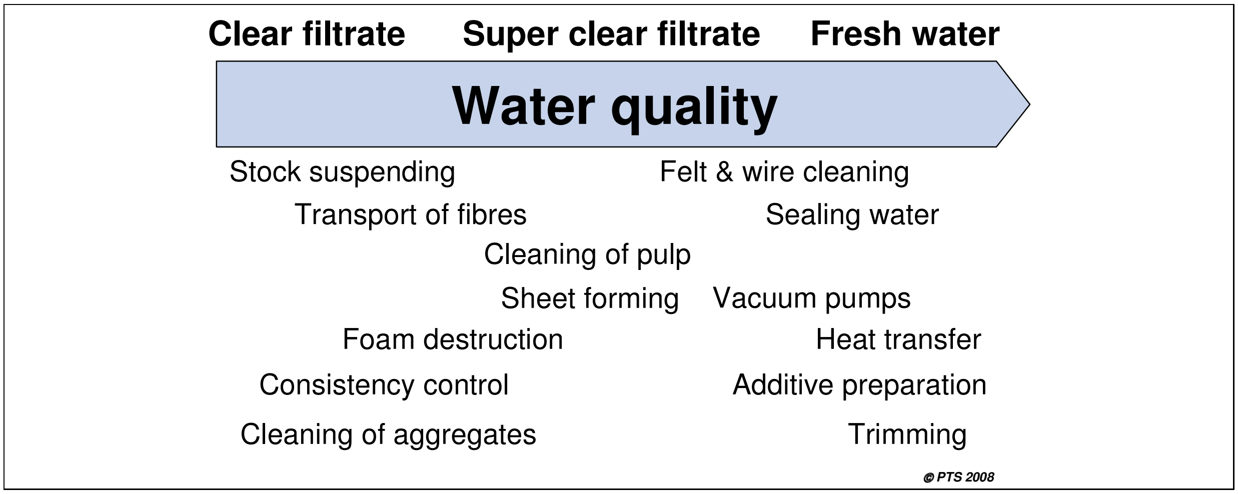


Figure 2-9. Functions of water

Fresh water is used mainly for:

- Cleaning and lubricating showers (e.g. for wires and press felts);
- Sealing water for liquid ring vacuum pumps;
- Sealing water for shaft sealing of pumps, agitators and other aggregates;
- Preparation and dilution of chemical additives or fillers or coating paint;
- Manual cleaning and flushing of equipment;
- Cooling water (e.g. for oil, steam, bearings): Usually reused for purposes listed above;
- Steam production.

In minor quantities, fresh water is also used for other purposes like cutting the web or foam disintegration. Fresh water which is used for cooling of steam condensers or oil coolers is usually directly reused for the above mentioned purposes.

All other functions in papermaking must be accomplished using circulation water. Most of the process water is used in forming the sheet on the wire. The largest amount (white water 1) is immediately recirculated again to dilute the furnish which is provided from the stock preparation to the paper machine in order to reduce the stock consistency to a value between 0,7 and 1,5 % stock consistency that is required for sheet formation. Any surplus water is usually supplied to a save-all. Smaller volumes of circulation water accumulate together with the rejects from screening in the stock approach system (centrifugal cleaners, etc.) and in other units (e.g. sealing water, rinse water, etc.). Depending on the paper grade being produced, at least some of this water is also supplied to the save-all (e.g. in the production of recovered fibre based papers) or is transported to the effluent treatment plant (fine papers, etc.).

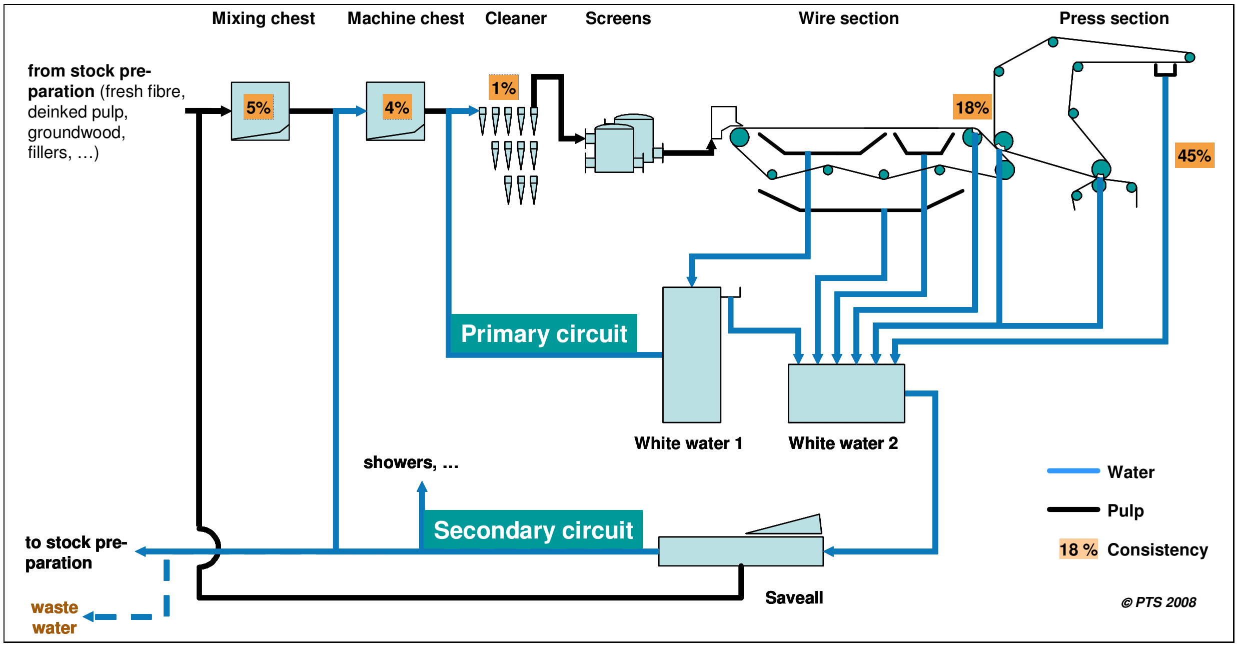


Figure 2-10. Simplified illustration of water flows at the paper machine

Generally speaking, three categories of water circulation can be defined: a primary and secondary circulation and a tertiary circulation, if one exists. The classification scheme depends on how close the circulation is to the core process. These circulation cycles are shown schematically in a block diagram in Figure 2-11.

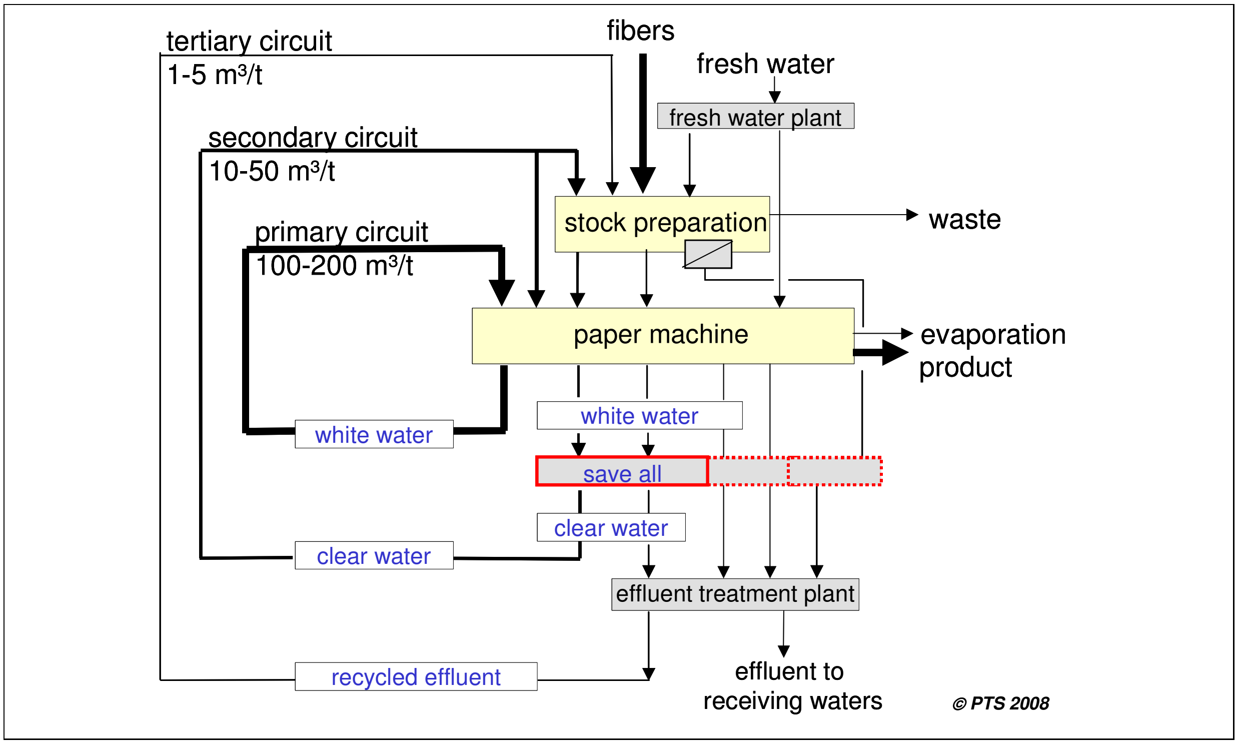


Figure 2-11. Simplified schematic illustration of global water flows in a paper mill

The primary circuit contains white water 1 and is the largest circuit as far as the volumetric flow rate is concerned. The circulating volume of water amounts to approx. 100 to 200 l/kg. The specific volumetric flow rate is dependent on the flow, retention and stock consistency at the headbox. It functions to collect the stock and form the sheet on the wire. The secondary circuit is formed from the surplus from the primary circuit. The conditions on the wire such as retention, additive addition and dewatering performance are very decisive regarding the nature of the secondary circuit.

The secondary circuit normally does not consist only of surplus white water 1. In most cases, it consists of water discharged into the wire pit, water eliminated by the suction boxes and vacuum pumps. In rare cases, water from the floor channels or from the wet broke, for example, is supplied to this circuit. The collected flow is usually directed to a save-all. The specific volumetric flow rates to the save-alls amount to approx. 10-50 l/kg. Whereas the recovered pulp is returned to the machine chest or stock preparation, the functions of the clarified water or clarified filtrate that is produced are quite wide spread. It is used for defibration in the pulper, for stock consistency control and for showers in the wire section. It is less frequently used as sealing water or for preparing additives. Depending on the save-alls used, several different qualities of treated water may be available such as in a disk filter, for example. Owing to the use of fresh water, not all of the clarified water or clarified filtrate will be reused. Any surplus forms part of the effluent.

A tertiary circuit is understood to be the at least partial recirculation of treated effluent. The entire volume is recirculated in paper mills with water closure, i.e. without any effluent discharge. The specific flow ranges between 1 and 5 m³/t. This is occasionally the case in the product group of paper for corrugated board.

The possible uses of the water from the tertiary circuit depend on the quality of the water and this quality can vary considerably. Examples include the use for showers in the wire and press sections, as sealing water for pumps and as process water for vacuum pumps. The use of fully treated water ("biologically treated water") may raise problems owing to the calcium carbonate it contains, since deposit formation and the plugging of nozzles may ensue. The water circulation of a paper machine contains more water (together with the pulp from the stock preparation and due to the addition of fresh water) than the product gives off in the dryer section. Any remaining water normally ends up in the effluent.

2.3.2 Water quality for process water

The following tables are mentioning water qualities for process water. Water qualities depend very much on the paper grade produced, raw materials used and other specific mill conditions. Therefore the given limits are not binding. Included in the table are main parameters that describe water quality. In specific cases, other parameters than mentioned may be also relevant. Nutrients like Nitrogen and Phosphorus are important for all paper grades. Their content, especially in recycled water, should be kept as low as possible in any case. Microorganisms are important, unwanted and present in water circuits of all paper grades. Their content as well should be kept as low as possible in any case. Bacterial counts give a hint on microbial presence. However, exceeding a certain limit may not inevitably lead to microbiologically induced problems, whereas under-running a certain limit may not always prevent from them.
In general, recycled water should not be of worse quality than process water.

2.3.2.1 Graphic papers

The following table is mentioning water qualities for process water. The qualities for process water are meant to be exemplary as the required process water quality is depending basically on specific mill conditions. Especially used raw materials like virgin pulp, deinked pulp (DIP) from recovered fibres or mechanical pulp show different inputs of compounds into the water system.

Table 2-8. Water quality for graphic papers

Parameter	Unit	Location			
		Process water PM loop	**1st loop DIP**	**2nd loop DIP**	**Mechanical pulp**
pH	-	7,0…8,5[1]	7,5…8,5[1]	7,5…8,5[1]	6,0…7,0[1]
Temperature	°C	40…60[1]	40…60[1]	40…60[1]	60…80[1]
Conductivity, 25°C	mg/l	1 000[2]	3 500[2]	2 000[2]	1 500…2 000 (2 000)[4]
COD	mg/l	1 000[2]	3 500[2]	2 000[2]	2 000…3 000 (10 500)[4]
Cationic demand	µeq/l	25[2]	200[2]	125[2]	n.a.
Cl^-	mg/l	100[2]	n.a.	n.a.	n.a.
SO_4^{2-}	mg/l	100[2]	300[2]	200[2]	n.a.
Hardness	mg/l ($CaCO_3$)	50[2]	200[2]	150[2]	n.a.
N-NH_4^+	mg/l	1[3]	1[3]	1[3]	n.a.
N-NO_3^-	mg/l	1[3]	1[3]	1[3]	n.a.
N-NO_2^-	mg/l	1[3]	1[3]	1[3]	n.a.
Total P	mg/l	1[3]	1[3]	1[3]	n.a.
Fungi	UFC/ml	2[3]	2[3]	2[3]	n.a.
Algae	UFC/ml	2[3]	2[3]	2[3]	n.a.
Microorganisms	per ml	10[3]	10[3]	10[3]	n.a.

[1] typical working ranges
[2] machinery and equipment are working without problems, if the given limits are not exceeded

[3] microorganisms are critical, hence nutrients and their concentration are limiting values
[4] based on data from 26 paper machines examined by PTS
n.a. no information available

2.3.2.2 Packaging papers

The following table is mentioning water qualities for process water. The qualities for process water are meant to be exemplary as the required process water quality is depending basically on specific mill conditions. The COD in the stock preparation loop is with 1 500 to 12 500 mg/l (max. 25 000 mg/l) about 50 % higher than in the PM loop. The table is giving a range within which many existing mills are working, however the given maximum value in brackets indicates that there are some mills operating at considerably higher loaded process waters. The data for process water are based on data from 48 paper machines examined by PTS.

Table 2-9. Water quality for packaging papers from recovered fibres without deinking

Parameter	Unit	Process water PM loop
pH	-	(5,9) 6,3…7,3 (7,5)
Temperature	°C	35…48 (48)
Conductivity	mg/l	2 000…6 000 (13 000)
COD	mg/l	1 000…8 000 (25 000)
Cl^-	mg/l	100…700 (1 200)
SO_4^{2-}	mg/l	200…900 (1 600)
Ca^{2+}	mg/l	200…1 200 (3 800)
LSI(1)	-	< 0,5

[1)] adapted calculation of the m-alkalinity according to [Bobeck et al, 2004]

2.3.2.3 Sanitary papers

The following table is mentioning water qualities for process water. The qualities for process water are meant to be exemplary as the required process water quality is depending basically on specific mill conditions. The COD in a fresh fibre stock preparation loop is with 200 to 500 mg/l (max. 1 000 mg/l) about 30 % higher than in the PM loop. The COD in a recovered fibre stock preparation loop is with 1 500 to 3 200 mg/l (max. 4 100 mg/l) about 100 % higher than in the PM loop. The table is giving a range within which many existing mills are working, however the given maximum value in brackets indicates that there are some mills operating at considerably higher loaded process waters. The data for process water are based on data from 19 paper machines producing tissue from fresh fibre and 15 paper machines producing tissue from recovered paper examined by PTS.

Table 2-10. Water quality for sanitary papers from fresh fibre

Parameter	Unit	Process water PM loop
pH	-	7,1…8,1 (8,1)
Temperature	°C	36…44 (44)
Conductivity	mg/l	500…1 700 (3 500)
COD	mg/l	150…450 (1 000)
Cl^-	mg/l	50…350 (700)
SO_4^{2-}	mg/l	80…200 (900)
Ca^{2+}	mg/l	50…400 (1 800)

Table 2-11. Water quality for sanitary papers from recovered paper

Parameter	Unit	Process water PM loop
pH	-	7,1…8,3 (8,3)
Temperature	°C	30…46 (46)
Conductivity	mg/l	1 000…2 500 (4 000)
COD	mg/l	500…1 500 (2 500)
Cl^-	mg/l	60…250 (700)
SO_4^{2-}	mg/l	150…350 (600)
Ca^{2+}	mg/l	80…250 (330)
LSI$^{1)}$	-	< 0,5

$^{1)}$adapted calculation of the m-alkalinity according to [Bobeck et al, 2004]

2.3.2.4 Other papers

Other papers include: decor paper, fine paper, filter paper, wall base paper, craft paper, crepe paper, technical speciality papers. The following table is mentioning water qualities for process water. The COD in a fresh fibre stock preparation loop is with 130 to 600 mg/l (max. 1 000 mg/l) slightly higher than in the PM loop. The qualities for process water are meant to be exemplary as the required process water quality is depending basically on specific mill conditions. The table is giving a range within which many existing mills are working, however the given maximum value in brackets indicates that there are some mills operating at considerably higher loaded process waters. The data for process water are based on data from 31 paper machines examined by PTS.

Table 2-12. Water quality for other papers

Parameter	Unit	Process water PM loop
pH	-	6,0…8,0 (8,0)
Temperature	°C	26…46 (46)
Conductivity	mg/l	500…2 000 (3 200)
COD	mg/l	100…600 (750)
Cl^-	mg/l	50…300 (550)
SO_4^{2-}	mg/l	100…500 (850)
Ca^{2+}	mg/l	10…80 (250)

2.3.3 Water quality for single water consumers

2.3.3.1 Showers

In the past, water quality demands for wire and felt cleaning showers have often been defined by the content of suspended solids. However, trials suggested, that it is rather the **size of particles** that is the relevant parameter [Hutter et al., 2004]. A supplier of paper machines recommends for high pressure showers in the wire section the use of super clear filtrate containing **fibres with lengths'** less than 0,3 mm and a **suspended solids concentration** less than 20 mg/l [Haavanlammi, 2001].

In order to avoid blocking the fabric of press felts it is recommended, that no particles with a **diameter** less than 10 µm are present in the water [Kershaw et al., 2004]. The temperature of shower water should be similar to white water temperature.

Table 2-13. Water quality for felt and wire cleaning according to suppliers

Parameter	Unit	
pH	-	6,7…7,3
Conductivity	mg/l	500
Total suspended solids	mg/l	10…15
Inorganic solids	mg/l	150…300
Langelier SI	-	0,5…1,0
TA	mg/l	85
Free SiO_2	mg/l	40…50
Free carbon dioxide	mg/l	10
Cl^-	mg/l	200
SO_4^{2-}	mg/l	200
Ca^{2+}	mg/l	60
Hardness	°dH	20
$N\text{-}NO_3^-$	mg/l	50
Mg^{2+}	mg/l	15
Fe	mg/l	0,2
Mn	mg/l	0,05…0,1
Microorganisms	per ml	10

Despite suppliers' requirements, showers are often operated with a water quality very different from the one in the table. Clear recommendations for other water quality parameters than solids and temperature cannot be given. Colouration and scaling potential surely have to be considered. A general requirement is that the water has to be not higher loaded than white water of the paper machine.

Showers in the wire and press section belong to the most critical water consumers concerning water quality.

2.3.3.2 Water ring vacuum pumps

The following table states water quality demands for water ring vacuum pumps.

Table 2-14. Water quality demands for water ring vacuum pumps [Paulapuro, 2000]

Parameter	Unit
Temperature	< 20 - 30℃
pH	> 7,0
Conductivity	< 2 000 µS/cm
Chloride	< 200 ppm
Sulphate	< 200 ppm
Dissolved solids	< 1 000 mg/l
Carbonate-Hardness	< 200 ppm $CaCO_3$ equiv.
Abrasive substances Ø >10 µm	< 40 - 50 ppm

The Langelier saturation index (LSI) should indicate that the water is rather slightly scaling than being aggressive, i.e. LSI = 0,5 to 1,0.

2.3.3.3 Sealing water

Stuffing boxes require a concentration of suspended solids lower than 20 mg/l [Zippel, 2001]. The Langelier saturation index (LSI) should indicate that the water is rather slightly scaling than being aggressive, i.e. LSI = 0,5 to 1,0.

2.3.3.4 Cleaning purposes

For cleaning purposes it is sufficient in many cases to provide water with a reduced content of suspended solids and colouration.

2.3.3.5 Chemicals preparation

The following table gives recommendations for the water quality for the dilution of retention and flocculation agents and starch cooking according to chemicals' suppliers.

Table 2-15. Water quality for preparation of chemicals according to suppliers

Parameter	Unit	
pH	-	6…8
Temperature	℃	10…60
Conductivity	mg/l	4 000
Cationic demand	µeq/l	350
Total solids	mg/l	500
Total suspended solids	mg/l	120
Langelier SI	-	0,5…1,0
TA	mg/l	
Free SiO_2	mg/l	
Free carbon dioxide	mg/l	
Free chlorine	mg/l	1
SO_4^{2-}	mg/l	
Ca^{2+}	mg/l	
Hardness	mg/l ($CaCO_3$)	200
$N\text{-}NO_3^-$	mg/l	
Mg^{2+}	mg/l	
Fungi	UFC/ml	2
Algae	UFC/ml	2
Microorganisms	per ml	1 000

Despite suppliers' requirements, chemicals preparation can in some cases also be done with process water from which suspended solids are removed. This is especially practised for the post dilution of chemicals.
The preparation of chemicals belongs to the most critical water consumers concerning water quality.

2.3.3.6 Cooling water

Plate and frame or shell and tube heat exchangers are common types of heat exchangers. The required water quality depends on the used material. Relevant topics in general are:

- Nutrients stimulate microbial growth and reduce heat transfer by biofouling;
- Solids cause malfunction of heat exchangers by plugging;
- Precipitation of salts reduces heat transfer by scaling;
- Corrosive conditions are to be avoided;
- The temperature level must be low enough to allow the required heat transfer.

Table 2-16. Water quality for plate heat exchanger from stainless steel AISI 316 according to supplier [Hydac, 2004]

Parameter	Unit	
Free Chlorine, Cl_2	mg/l	< 0,5
Chloride at 20°C	mg/l	< 700
Chloride at 50°C	mg/l	< 200
pH	-	> 7
SO_4^{2-}	mg/l	< 100
$[HCO_3^-] / [SO_4^{2-}]$	-	> 1
Free CO	mg/l	< 10

2.3.3.7 Steam production

The required water quality is determined by the steam generation process, not by the steam "consumers" like heating of drying cylinders or direct heating of wood chips or water. For this reason, the quality requirements described in Internal result I1.2.1.1 are applicable.

2.3.3.8 Other water consumers

For other than the above mentioned water consumers, no general recommendation for the water quality can be given.

3 Water quality demands in chemical sector

3.1 Introduction

The chemical and pharmaceutical industries are very diverse businesses. The IPPC BREFs distinguish between the following main branches:

- Large Volume Organic Chemicals;
- Large Volume Inorganic Chemicals;
- Polymers;
- Organic Fine Chemicals;
- Specialty Inorganic Chemicals
- Pharmaceutical

Even though the total amount of different substances produced in the chemical and pharmaceutical industry might be big, typically the amount of unit processes and unit operations are limited (about 20 each). Unit processes are the principles for the chemical reactions and unit operations the principles to process or to refine the products.

Water is essential in most chemical and pharmaceutical production units. It is used in many unit processes and can be used with most unit operations, either as a media or product stream to refine or as a resulting waste water. For a specific production, the choice of unit processes and operations together with the choice of raw material and process equipment define the use of water and water quality needed. The required water quality and the amount of water used in the unit operations can vary in a very wide range, depending on the substance produced, the product quality aimed at and the unit operations chosen.

Examples of usage of water in the chemical and pharmaceutical industry:

- water mixed with the raw material;
- water used as reaction medium/solvent;
- water used for product washing;
- water used for cleaning of equipment;
- water used in equipment (e.g. vacuum generation).

To this, a major part of the water is used for steam generation and cooling in the chemical and pharmaceutical industry.

The chemical and pharmaceutical industries in Europe are aware of the importance to reduce its use of water and its emissions from the production. Most companies have a commitment to reduce the amount of water used per unit product produced. However, in some branches of the sector, e.g. the pharmaceutical industry, this might not be possible due to present regulations by the authorities.

3.2 Major water consuming processes

Water is essential in most chemical and pharmaceutical production units and the water is used in a wide range of applications. The chemical and pharmaceutical industry typically uses about 20 different unit operations, i.e. technologies to refine the products or abate emissions and waste:

Typical unit operations are:

- absorption;
- adsorption;
- condensation;
- crystallisation;
- distillation;
- dilution;
- drying;
- evaporation;
- extraction;
- filtration;
- ion exchange;
- mixing/blending;
- quenching;
- scrubbing;
- settling;
- sieving;
- stripping;
- washing (of product).

Other usage of water:

- sealing water in pumps;
- cleaning of equipment, pipes, areas etc;
- steam generation;
- cooling systems;
- heat carrier.

When discussing the water quality needed and the use of water in the chemical and pharmaceutical industry several aspects have to be considered, e.g.:

- what is the quality of available water; does it have to be further treated before use?
- in what unit operation(s) will water be used; will the water have an influence on process performance?
- in what unit operation(s) will water be used; will the water have an influence on equipment, piping etc?
- what quality do we aim at for the final product; will the water have an influence on product quality?
- at what stage in the product flow do we introduce the water? will the product be further treated?
- what is the quality of other raw materials and medias in contact with the product?

All these will define the quality of the water needed for a specific use, for a specific product at a specific stage in the product flow. E.g. better water quality is needed to wash the final product than the first washing of a crystallized substance; water acceptable for scrubbing will not necessarily work as sealing water in a pump etc. This can mean that the same unit operation in some applications can use surface water without any pretreatment, but in other applications needs an ultra pure water.

All together this means that it is impossible to define any generic water quality criteria for water used in the chemical and pharmaceutical industry, even at unit operation level. Instead the manufacturer needs to understand its own production and the way the water quality interacts with its equipment, its final product quality and the environment. To give an understanding on how the water quality can interact with equipment and final product, important unit operations will be briefly presented together with an overview of some possible interactions.

3.3 Generic unit operations in the chemical and pharmaceutical industry

Typically, the reactions in the production will never achieve a perfect selectivity of the target product, so it is important to apply suitable unit operations to separate impurities, waste streams and substances for recovery etc. This separation can be split into the following categories:

- Liquid-vapour separation (e.g. distillation, evaporation, stripping, absorption);
- Liquid-liquid separation (e.g. extraction, decanting);
- Solid-liquid separation (e.g. centrifuging, filtration, settling, drying, crystallisation);
- Solid-gas separation (e.g. filtration, adsorption);
- Solid-solid separation (e.g. sieving, gravity, flotation).

Below some important unit operations and examples of considerations regarding their water quality need will be presented.

3.3.1 Unit operations with direct use of water

3.3.1.1 Absorption (Scrubbing)

The absorption process implies that one substance is absorbed into another substance, e.g. a gas into water. In this case the dissolved amount of gas is proportional to the partial pressure of the gas. Temperature and pH as well as any chemical reaction in the water phase will influence the performance of the absorption process. Absorption can be used for cleaning a gas stream (scrubbing), making the water a potential waste water, or for the transfer of a gaseous raw material to the product solution. Typically the water quality in the first case would be lower than the water quality needed in the second case. In the first case volatile substances can be an environmental problem

3.3.1.2 Adsorption

Adsorption is the physical adsorption of a substance (typically a liquid or a gas) on the surface of a solid adsorbent. The adsorbent is characterized by a large number of different seized pores to “catch” e.g. organics from a gas stream. Typical adsorbents are activated carbon, zeolites, silica gel and aluminium oxide. Water, water solutions or steam can be used to regenerate the adsorbent.

3.3.1.3 Crystallisation

Crystallisation is a separation process in which the dissolved substance, the solute, is transferred from the liquid solution to a pure solid crystalline phase by precipitation. Water can typically be the solution, but can also be used to redissolve to recrystallise the product to improve the product quality. Water can also be used to wash the crystals. The water quality is important not to incorporate impurities or colour to the product.

3.3.1.4 Dilution

Dilution can be used at the start of the production in the reaction vessel to control the conditions during the reaction in a favourable way. Dilution is also used together with the final product to achieve the right concentration of the product for different applications.

3.3.1.5 Extraction

Extraction involves the use of the partition coefficient of a substance between two immiscible liquids, and it is the most important liquid-liquid separation process in the chemical and pharmaceutical industry. Often one of these liquids is water. Examples of other liquids used in extraction are diethylene glycol, octanol and dimethyl sulphoxide. The liquid enriched in the desired product typically has to be treated by e.g. distillation.

3.3.1.6 Filtration

Filtration is a mechanical or physical operation which is used for the separation of solids from fluids by allowing the fluid to pass, but where the solids (or at least part of the solids) in the fluid are retained. The separation will depend on the pore size of the filter and the thickness of the filter layer. For product recovery water can be used to wash the product in the filter.

3.3.1.7 Ion exchange

Ion exchange is typically the exchange of ions between an aqueous ion-containing solution and a solid ion exchange resin. The ion exchange resin 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 types of ions. Typically acid or alkaline water solutions and pure water are used to regenerate the ion exchanger.

3.3.1.8 Mixing/blending

Mixing typically refer to the mixing of two or more substances in the same or different phases to achieve specified, homogenous proportions between the substances in the resulting mixture. E.g. water can be used to dilute an acid to a more suitable concentration. See also dilution.

3.3.1.9 Quenching

Quenching refers to a rapid cooling by addition of e.g. water by water sprays into a gaseous reaction vessel. In chemistry quenching is used to control reactions by only providing a narrow window of time in which the reaction is favourable and accessible. In a scrubber a hot gas stream can be quenched, not to evaporate large portions of the scrubbing liquor or to damage scrubber internal parts. Cooling the gases reduces the temperature and volume of gases, permitting the use of less expensive construction materials and a smaller scrubber vessel and fan. Depending on where in the production the quenching is used, the demands on water quality can vary in a wide range.

3.3.1.10 Scrubbing

See absorption.

3.3.1.11 Sieving

Sieving is a unit operation similar to filtration but where the size distribution of the residues is more controlled by fractioning by sieves with well defined openings in the mesh. Sieving can be performed as a dry as well as wet operation. When the sample is a very fine powder which tends to agglomerate (mostly < 45 µm), the dry sieving operation tend to lead to clogging of the sieves. In this case wet sieving of a suspension can be an alternative. The product can be rinsed directly in the sieves and it should be carried out until the liquid which is discharged through the receiver is clear. Sample residues on the sieves are typically dried.

3.3.1.12 Washing (of product)

Washing of a product can be done in many types of equipment as centrifuges, filter, sieves, settling tanks etc. Washing is typically performed to remove solids and or soluble impurities in the product.

3.3.2 Unit operations that separate water as useful water solution and/or as a waste water stream

The water quality of the feed to these unit operations is depending on the demands on the water quality used up streams. Demands up streams will also affect the effluent from the unit operations together with the processing in the unit operation itself.

3.3.2.1 Condensation

Condensation is the unit operation where components from gaseous mixtures can be separated into liquids by fractional condensation (in principle distillation the other way around). Typically this unit operation will not use water by itself but will generate water as a useful condensate or as a waste water stream.

3.3.2.2 Decanting

Decantation is an operation for the separation of mixtures, carefully pouring a solution from a container in order to leave the precipitate (sediments) in the bottom of the original container. Usually a small amount of solution must be left in the container, and care must be taken to prevent a small amount of precipitate from flowing with the solution out of the container.

3.3.2.3 Distillation

Distillation involves the partial evaporation of a liquid phase followed by condensation of the vapour phase, and is one of the most important industrial methods of phase separation. Distillation separates a mixture into to fractions with different compositions, one condensed vapour enriched in the more volatile components and one remaining liquid phase that is depleted of the same volatile components.
Water can be either a volatile component or the remaining liquid phase in this unit operation. Typically this operation will not use water by itself but will generate condensate and/or a waste water stream.

3.3.2.4 Drying

Drying is typically the operation where any residual liquid is evaporated from a solid substance by heat and/or applied vacuum to increase the solids content. Typically this operation will not use water by itself but will generate condensate as a waste water stream.

3.3.2.5 Evaporation

Evaporation is the slow vaporization of a liquid. Typically evaporation separates a liquid into two fractions; one fraction as a condensate containing the more volatile components and one fraction containing the less volatile components as well as ions of metals and salts. Water can be either a volatile component in the condensate and/or the remaining liquid phase in this unit operation. Typically this operation will not use water by itself but will generate water as a condensate or as a waste water stream.

3.3.2.6 Settling

Settling is the operation by which particles in a liquid will settle to the bottom of a vessel, forming a sediment. Settling of particles can be due to either gravity or centrifugal force.

3.3.2.7 Stripping

Stripping is a physical separation operation where one or more light components are removed from a liquid stream by a vapour stream. For a water solution with more volatile components the heavy components are removed at the bottom of the column as an aqueous waste stream. This stream typically further treated by e.g. evaporative concentration. Typically this operation will not use water by itself but will generate condensate and/or waste water streams.

3.4 Information on water quality restrictions from literature & experience

As the chemical and pharmaceutical industries in Europe are aware of the importance to reduce its use of water and its emissions from the production, large efforts are spent on minimising the water consumption and related costs and on reducing the industry's impact on the water environment.
To do this, different measures have to be considered for reduction of "fresh" water:

- using equipment using less or no water (e.g. "dry" vacuum pumps);
- new methods for cleaning reactor, equipment etc;
- reuse of water within and between plants.

In the short term reuse of water might have the biggest potential. A lot can be achieved with existing technology and even with existing equipment. In many cases the water treatment needed for more extensive reuse will also give opportunity to reduce the amount of emissions.

Closing the water cycle on unit operation level as well as on process and site level will be the main improvement option in the chemical and pharmaceutical sector as well as for other industrial sectors.

The development of methods to identify possibilities to reuse process water and to identify necessary treatment techniques will be essential to achieve reduction of "fresh" water use in the chemical and pharmaceutical industry.

3.4.1 Possible water quality restrictions for unit operations

While closing the water cycle, and ultimately aiming at a "zero water footprint", the industry needs to improve its understanding on "water fit for use", i.e. what minimum water quality can be used for a certain application in a unit operation, considering equipment, product quality and the environment. The industry needs better methods to identify possibilities to reuse process water, including improved understanding on how the water quality interacts with the production, and better methods to identify necessary treatment techniques to achieve a more extensive reuse.

An important part of the knowledge needed will be to understand how different parameters of the water quality can interact with the production. Insufficient water quality can cause many different types of problems:

- scale and fouling can restrict throughput and decrease performance;
- scale and fouling can cause corrosion;
- scale can cause abrasion;
- impurities can affect the colour, taste and other properties of the final product;
- ionic impurities can cause corrosion;
- impurities can cause abrasion;
- volatile organics can be toxic, generate smell and bad labour environment;

- bacteria/biofilm can restrict throughput and decrease performance;
- bacteria can cause corrosion;
- bacteria can cause diseases and generate smell and bad labour environment.

Common to these problems are that they will increase maintenance costs, increase the number of unplanned stops, decrease performance of the production and increase risks for the personnel and the environment.
Below (Table 3-1) an overview is given on how some parameters can interact with different unit operations.

In the following paragraphs the different sub-sectors in the chemical industry will be discussed. The most important water consuming processes are listed and if possible, the required water quality is given.

Table 3-1. Water quality and related problems in different unit processes

Water quality interaction with unit operations

S	scale	P	product
F	fouling	T	equipment, piping etc
C	corrosion	H	health
B	bacteria	E	environment

1 absorption
2 adsorption
3 condensation
4 crystallisation
5 distillation
6 dilution
7 drying
8 evaporation
9 extraction
10 filtration
11 ion exchange
12 mixing/blending
13 quenching
14 scrubbing
15 settling
16 sieving
17 stripping
18 washing (of product)
19 sealing water in pumps
20 cleaning of equipment, pipe
21 steam generation
22 cooling systems
23 heat carrier
24

	type of problem					type of interaction					unit operation & usage																						
water parameter	S	F	C	B		P	T	H	E		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Calcium	**S**						**T**								**X**		**X**	**X**			**X**		**X**	**X**							**X**	**X**	**X**
Barium	**S**						**T**								**X**		**X**	**X**			**X**		**X**	**X**							**X**	**X**	**X**
Strontium	**S**						**T**								**X**		**X**	**X**			**X**		**X**	**X**							**X**	**X**	**X**
Iron	**S**			**B**		**P**	**T**								**X**		**X**	**X**			**X**		**X**	**X**							**X**	**X**	**X**
Manganese	**S**					**P**	**T**								**X**		**X**	**X**			**X**		**X**	**X**							**X**	**X**	**X**
Magnesium	**S**						**T**								**X**		**X**	**X**			**X**		**X**	**X**							**X**	**X**	**X**
Carbonate	**S**						**T**								**X**		**X**	**X**			**X**		**X**	**X**							**X**	**X**	**X**
Bicarbonate	**S**						**T**								**X**		**X**	**X**			**X**		**X**	**X**								**X**	**X**
Chloride			**C**				**T**				**X**	**X**		**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**
Sulphate	**S**		**C**				**T**				**X**	**X**		**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**
Silica	**S**						**T**								**X**		**X**	**X**			**X**		**X**	**X**							**X**	**X**	**X**
Phosphate	**S**			**B**			**T**	**H**							**X**		**X**	**X**			**X**		**X**	**X**							**X**	**X**	**X**
Nitrate				**B**				**H**								**X**			**X**	**X**	**X**	**X**			**X**	**X**		**X**		**X**		**X**	
Ammonia				**B**				**H**	**E**							**X**			**X**	**X**	**X**	**X**			**X**	**X**		**X**		**X**		**X**	
Solid particles		**F**				**P**	**T**					**X**		**X**	**X**		**X**	**X**	**X**		**X**		**X**		**X**	**X**		**X**	**X**	**X**	**X**	**X**	**X**
Oil & Grease		**F**		**B**		**P**	**T**	**H**				**X**		**X**	**X**		**X**	**X**		**X**	**X**		**X**	**X**	**X**	**X**		**X**	**X**	**X**	**X**	**X**	**X**
Colour						**P**								**X**			**X**																
Conductivity			**C**				**T**				**X**	**X**		**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**
Proteins		**F**		**B**		**P**	**T**	**H**								**X**			**X**	**X**	**X**	**X**			**X**	**X**		**X**		**X**		**X**	
COD/BOD/TOC		**F**	**C**	**B**		**P**	**T**					**X**		**X**		**X**	**X**		**X**	**X**	**X**	**X**			**X**	**X**		**X**	**X**	**X**	**X**	**X**	

3.5 Water quality in chemical industry: Chlor-alkali manufacturing

3.5.1 Process description

The chlor-alkali industry is the industry that produces chlorine (Cl_2) and alkali, sodium hydroxide (NaOH) or potassium hydroxide (KOH), by electrolysis of a salt solution. The main technologies applied for chlor-alkali production are **mercury, diaphragm and membrane cell electrolysis**, mainly using sodium chloride (NaCl) as feed or to a lesser extent using potassium chloride (KCl) for the production of potassium hydroxide.
The overall reaction for each of the three processes is:

$$2\ Na^+(aq) + 2\ Cl^-(aq) + 2\ H_2O \rightarrow 2\ Na^+(aq) + 2\ OH^-(aq) + Cl_2(g) + H_2(g)$$

Where Cl_2 is formed at the anode and H_2 at the cathode.

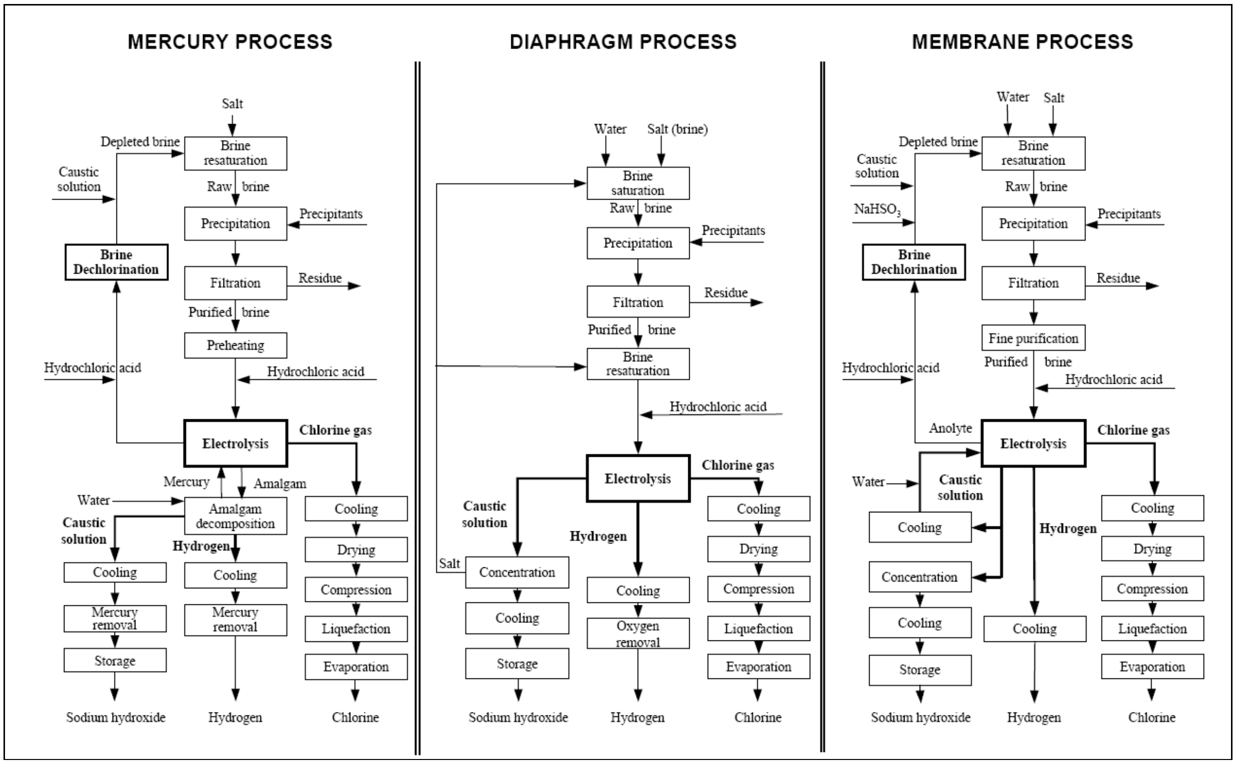


Figure 3-1. Overview of three chlor-alkali manufacturing processes

In general water is used in the processes for:

- purges;
- preparation of the brine;
- the caustic circuit: for maintaining the water balance in the reaction to form NaOH in the membrane and mercury cells;
- the chlorine absorption unit: the quantity used will depend on the amount of chlorine released to absorption.

Water can also be used for cooling. However, cooling systems are not considered in this document. Apart from the water needed for cooling, generally **2 - 2,5 m^3** of water is consumed per ton of chlorine produced for plants using a brine recalculation process. For waste brine processes, about 10 m^3 of water per ton of chlorine produced is required.

In general the brine preparation process is common for all 3 types of chlor-alkali processes. Regeneration of the brine often implies adding water. Especially for the membrane cell process the required water quality needs to be very high, to avoid impurities which can affect membrane performance.

Table 3-2. Required water quality for brine preparation

Parameter	Unit	
	Mercury cell or diaphragm	Membrane cell
pH	6,5 - 7,5	6,5 - 7,5
Conductivity	< 100 µS/cm	< 1 µS/cm
TDS	50 – 100 mg/l	< 1 mg/l
Heavy metals	< 1 ppm	< 0,1 ppm
Calcium	< 2 ppm	< 0,1 ppm
Sulphate	< 5 g/l	< 0,1 ppm
TOC	< 5 mg/l	< 0,1 ppm

3.5.1.1 Mercury Cell Process

In Figure 3-1 the mercury process is schematically drawn. Raw brine is purified by precipitation and filtration to remove undesired contaminants. The purified brine enters the mercury cell and Cl_2 is formed at the anode. At the Hg-cathode Na is formed, which reacts with Hg to form an amalgam. The Na-Hg-amalgam is treated in the decomposer, where Na^+, Hg and H_2 are formed (graphite as a catalyst). Hg is used again in the electrolytic cell.

The most important water using process is the amalgam decomposer, in which water is used to make-up for the amount of water that is being transformed to sodiumhydroxide and hydrogen gas.

Typical required water quality for the amalgam decomposer is described in the table below. Typically this water quality is achieved by treating process water with RO, ion-exchange or a combination of both.

Table 3-3. Required water quality for the mercury cell process

Parameter	Unit
pH	6 - 8
Conductivity	< 10 µS/cm
TDS	5 - 10 mg/l
Heavy metals	< 1 ppm
Carbonate-Hardness	< 200 ppm $CaCO_3$ equiv.
TOC	< 5 mg/l

3.5.1.2 Diaphragm process

In Figure 3-1 the diaphragm is schematically drawn. The diaphragm process was developed in the 1880s in the USA and was the first commercial process used to produce chlorine and caustic soda from brine. The process differs from the mercury cell process in that all reactions take place within one cell and the cell effluent contains both salt and caustic soda. A diaphragm is employed to separate the chlorine liberated at the anode, and the hydrogen and caustic soda produced directly at the cathode. Without the diaphragm to isolate them, the hydrogen and chlorine would

spontaneously ignite and the caustic soda and chlorine would react to form sodium hypochlorite (NaClO), with further reaction to produce sodium chlorate ($NaClO_3$).
The diaphragm is usually made of asbestos (or polymer containing asbestos) and separates the feed brine (anolyte) from the caustic-containing catholyte. Purified brine enters the anode compartment and percolates through the diaphragm into the cathode chamber.

The required water quality for the diaphragm process is quite similar to that of the mercury cell process (refer to Table 3-3).

3.5.1.3 Membrane cell process

In the 1970s, the development of ion-exchange membranes enabled a new technology to produce chlorine: the membrane electrolysis process. Today, it is the most promising and fast-developing technique for the production of chlor-alkali and it will undoubtedly replace the other two techniques in time.
In this process, the anode and cathode are separated by a water-impermeable ion-conducting membrane. Brine solution flows through the anode compartment where chloride ions are oxidized to chlorine gas. The sodium ions migrate through the membrane to the cathode compartment which contains flowing caustic soda solution. The demineralized water added to the catholyte circuit is hydrolyzed, releasing hydrogen gas and hydroxide ions. The sodium and hydroxide ions combine to produce caustic soda which is typically brought to a concentration of 32 – 35 % by recirculating the solution before it is discharged from the cell. The membrane prevents the migration of chloride ions from the anode compartment to the cathode compartment; therefore, the caustic soda solution produced does not contain salt as in the diaphragm cell process. Depleted brine is discharged from the anode compartment and resaturated with salt. If needed, to reach a concentration of 50 % caustic soda, the caustic liquor produced has to be concentrated by evaporation (using steam).
Table 3-4 shows the required water quality for the membrane cell process. The figures are indicative, basically demineralized water with low conductivity is used. Heavy metals and organic substances should be avoided at all times.

Table 3-4. Required water quality: membrane cell process

Parameter	Unit
pH	5 – 7,5
Conductivity	< 1 µS/cm
TDS	< 1 mg/l
Heavy metals	< 0,1 ppm
Calcium	< 0,1 ppm
Sulphate	< 0,1 ppm
TOC	< 1 ppm

3.6 Water quality in chemical industry: large volume inorganic chemicals

3.6.1 Ammonia

Ammonia is synthesized from nitrogen and hydrogen by the following reaction:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

The best available source of nitrogen is from atmospheric air. The hydrogen required can be produced from various feedstocks but currently it is derived mostly from fossil fuels. Depending of the type of fossil fuel, two different methods are mainly applied to produce the hydrogen for ammonia production: **steam reforming** or **partial oxidation**.

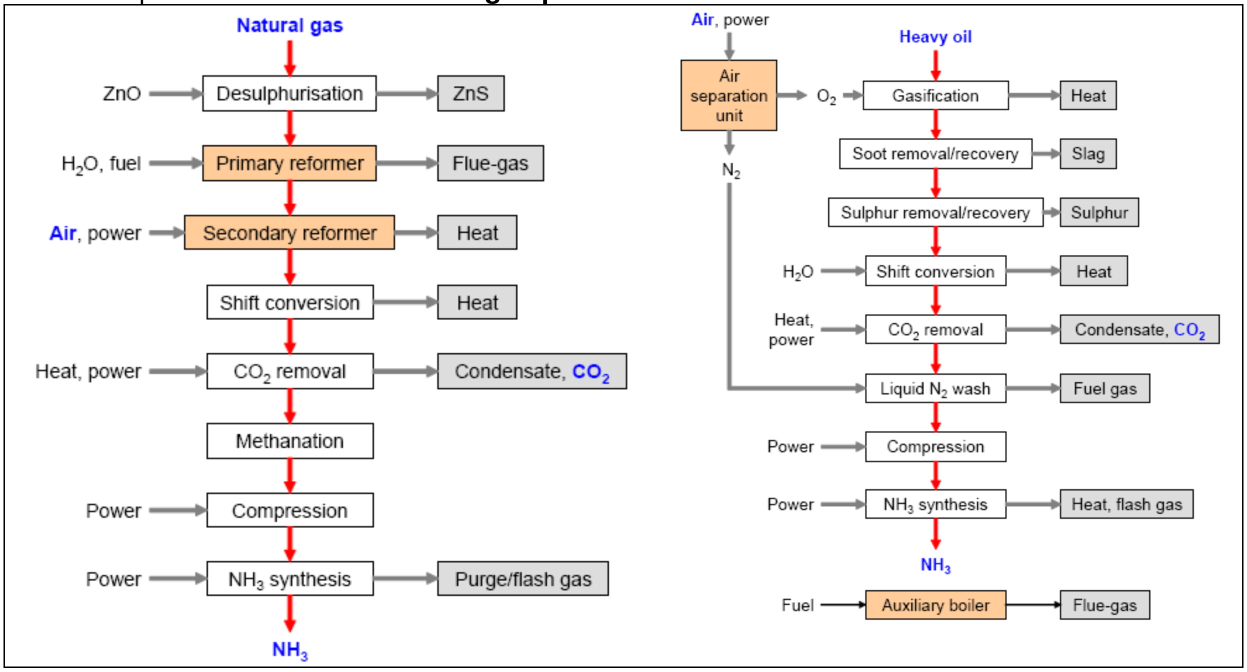


Figure 3-2. Ammonia production: schematic overview of steam reforming and partial oxidation process.

3.6.1.1 Conventional steam reforming

The reaction in the primary steam reforming unit is highly endothermic. Therefore the water needed for the reaction is added in the form of steam. The required water quality is similar to that of the boiler feed water (see I1.2.1.1). The other process steps do not use water, although in the CO_2-removal step a waste water stream is produced (i.e. condensate) which contains high levels of ammonia and methanol.

3.6.1.2 Partial oxidation

Depending on the gasification design, i.e. waste heat boiler or quench, additional steam has to be supplied ahead of the shift conversion by saturation and direct injection. The required water quality for steam production is discussed in internal result I1.2.1.1

3.6.2 Nitric acid

Nitric acid production starts from ammonia, which is oxidised and then absorbed into water. The liquid NH3 is evaporated and filtered. NH3 is reacted with air on a catalyst in the oxidation section. Nitric oxide and water are formed in this process according to the main equation:

$$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H2O$$

Nitrous oxide, nitrogen and water are formed simultaneously in accordance with the following equations:

$$4\ NH3 + 3\ O2 \rightarrow 2\ N2 + 6\ H2O$$
$$4\ NH3 + 4\ O2 \rightarrow 2\ N2O + 6\ H2O$$

Nitric oxide is oxidised to nitrogen dioxide as the combustion gases are cooled, according to the equation:

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

For this purpose, secondary air is added to the gas mixture obtained from the ammonia oxidation. Demineralised water, steam condensate or process condensate is added at the top of the absorption column. The weak acid solution (approximately 43 %) produced in the cooler condenser is also added to the absorption column. The NO_2 in the absorption column is contacted countercurrently with flowing H_2O, reacting to give HNO_3 and NO:

$$3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$$

The oxidation, absorption of the nitrogen dioxide and its reaction to nitric acid and nitric oxide take place simultaneously in the gaseous and liquid phases. Both reactions (oxidation and HNO_3 formation) depend on pressure and temperature and are favoured by higher pressure and lower temperature.

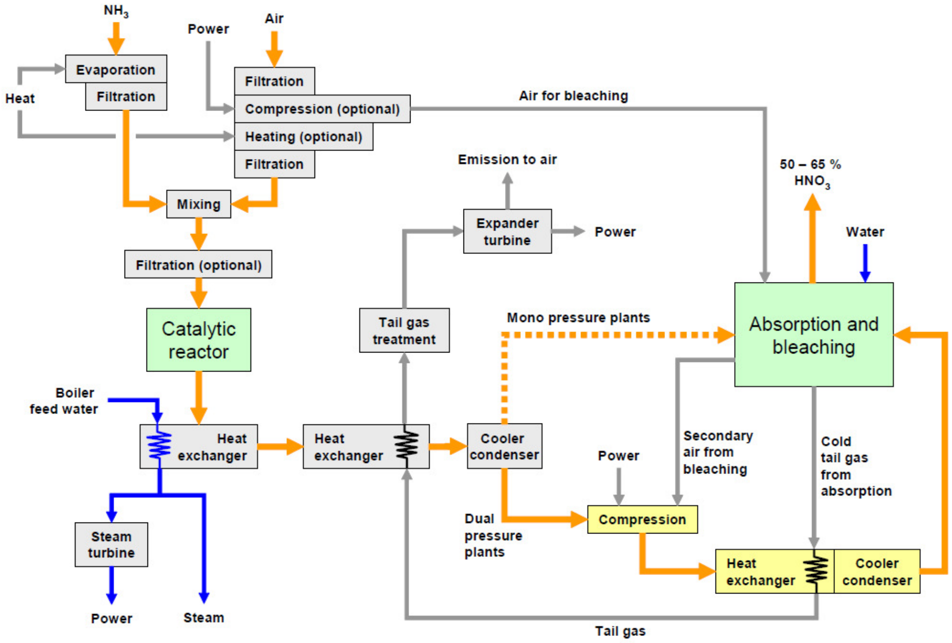


Figure 3-3. Nitric acid production : schematic overview

The formation of HNO_3 is exothermic and continuous cooling is needed within the absorber. As the conversion of NO to NO_2 is favoured by low temperature, this will be the significant reaction taking place until the gases leave the absorption column. The nitric acid produced in the absorber contains dissolved nitrogen oxides and is then ‘bleached’ by the secondary air. An aqueous solution of nitric acid is withdrawn from the bottom of the absorption tower.
The required water quality for the absorption process should be that of ‘purified’ water. This water quality is obtained generally after RO-treatment or ion-exchange with weak acid/base resins.

Table 3-5. Required water quality: nitric acid : absorption process

Parameter	Unit
pH	5 – 7,5
Conductivity	< 10 µS/cm
TDS	< 5 mg/l

Heavy metals	< 0,1 ppm
TOC	< 1 ppm

3.6.3 Sulphuric acid

More H2SO4 is produced than any other chemical in the world. In Western Europe in 1997, over 19 Mtonnes were produced, the total production worldwide being estimated at around 150 Mtonnes. The production process of H2SO4 is depicted inFigure 3-4. Starting from a sulphur source, SO2 is produced which is burned to SO3. In an absorbing unit the SO3 is absorbed into a concentrated solution of H2SO4.

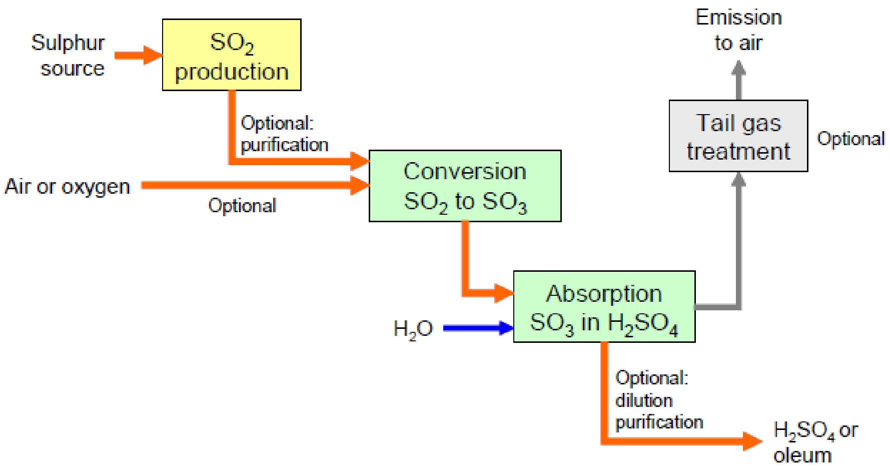


Figure 3-4 Overview of the production of H2SO4

H2SO4 is produced from SO2, which is derived from various sources, such as combustion of elemental sulphur or roasting of metal sulphides. SO2 is then converted into SO3 in a gas phase chemical equilibrium reaction, using a catalyst. The different process steps in the production of SO2 usually do not require water.

Water is only used in the absorber to maintain the desired acid concentration of 98,5-99,5%. Regarding water quality the required specifications for this water is basically dependent on the desired product quality. In any case purified water (low organic content and low suspended solids) is needed. The need for extra pure water is also coupled to the use of a purified SO3-stream in the absorber. In general terms the water quality listed below in Table 3-6 will be sufficient for the absorber.

Table 3-6. Required water quality: sulphuric acid : absorption process

Parameter	Unit
pH	5 – 7,5
SS	<10 mg/l
Conductivity	< 20 µS/cm
TDS	< 10 mg/l
Heavy metals	< 1 ppm
TOC	< 10 ppm

3.6.4 Phosphoric acid

Phosphoric acid, H_3PO_4, is a colourless, crystalline compound, that is readily soluble in water. The main product is phosphoric acid with a commercial concentration of 52 – 54 % P_2O_5. Two different processes using different raw materials can be used in the manufacture of phosphoric acid:

1. the thermal process uses elemental phosphorus as the raw material. Here, elemental phosphorus is produced from phosphate rock, coke and silica in an electrical resistance furnace (see Section 5.4.15)
2. wet processes, using phosphate minerals, which are decomposed with an acid.

For the thermal process, this is carried out in two stages. First, elemental phosphorus is produced from phosphate rock. Then the elemental phosphorus is oxidised with air to P2O5, which is subsequently hydrated to produce phosphoric acid. Hydration is carried in a similar way as for the production of sulphuric acid. P205 is absorbed in a concentrated solution of H3PO4. The concentration of this solution is maintained by adding fresh water. The required water quality is similar to the one described in Table 3-6

There are three possible subgroups of wet processes depending on which acid is used for the acidulation, i.e. HNO3, HCl or H2SO4. Since the production with sulphuric acid is preferred worldwide, only this is discussed.

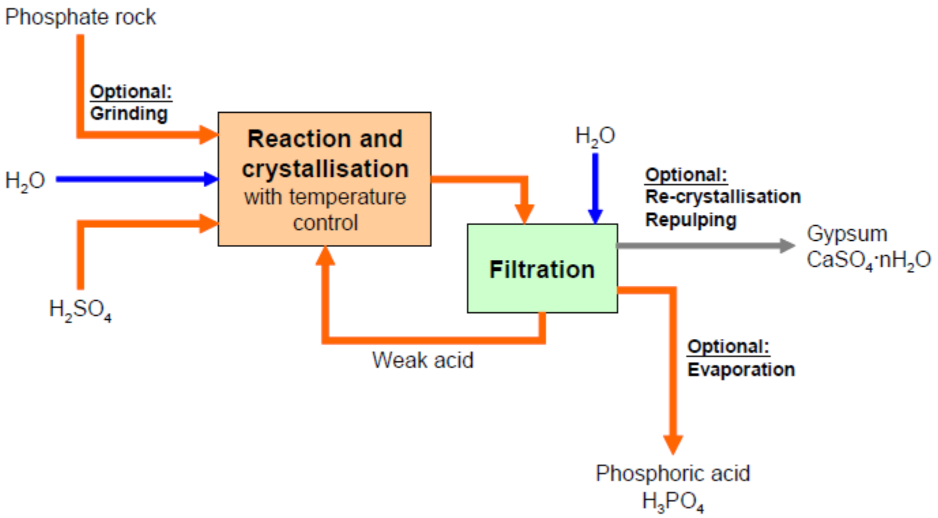


Figure 3-5 Overview of H3P04 production (wet process with H2SO4)

Figure 3-5 gives an overview of the production of H3PO4 by wet processes. The tri-calcium phosphate from the phosphate rock reacts with concentrated H2SO4 to produce H3PO4 and the insoluble salt calcium sulphate.

$$Ca_3(PO_4)_2 + 3\ H_2SO_4 \rightarrow 2\ H_3PO_4 + 3\ CaSO_4$$

The insoluble calcium sulphate is filtered from the H3PO4. The reaction between phosphate rock and H2SO4 is restricted by an insoluble layer of calcium sulphate which forms on the surface area of the rock. This restriction is minimised by contacting the phosphate rock with recirculated

H_3PO_4, thereby converting as much of it as possible to the soluble mono calcium phosphate, followed by precipitation as calcium sulphate with H_2SO_4.

$$Ca_3(PO_4)_2 + 4\ H_3PO_4 \rightarrow 3\ Ca(H_2PO_4)_2$$

$$3\ Ca(H_2PO_4)_2 + 3\ H_2SO_4 \rightarrow 3\ CaSO_4 + 6\ H_3PO_4$$

As for the production of nitric and sulphuric acid, the required water quality for the phosphorous acid production is strongly dependant of the specifications of the final product. In general the water quality described in Table 3-6 will be sufficient.

3.6.5 NPK-Fertilizer

When defining compound fertilisers, the large number of N/P/K – ratios and the numerous processes applied in their production must be taken into account. Product types are PK, NP (e.g. DAP), NK and NPK. These products might contain:

- nitrogen, expressed as % of N, in ureic, ammoniacal and/or nitrate forms
- phosphorus, usually expressed as % of P_2O_5, in forms soluble in water and/or neutral ammonia citrate and/or mineral acids
- potassium, usually expressed as % of K_2O, in forms soluble in water
- secondary nutrients, as calcium (CaO), magnesium (MgO), sodium (Na_2O) and/or sulphur (SO_3)
- microelements (zinc, copper, boron, etc.)
- other elements.

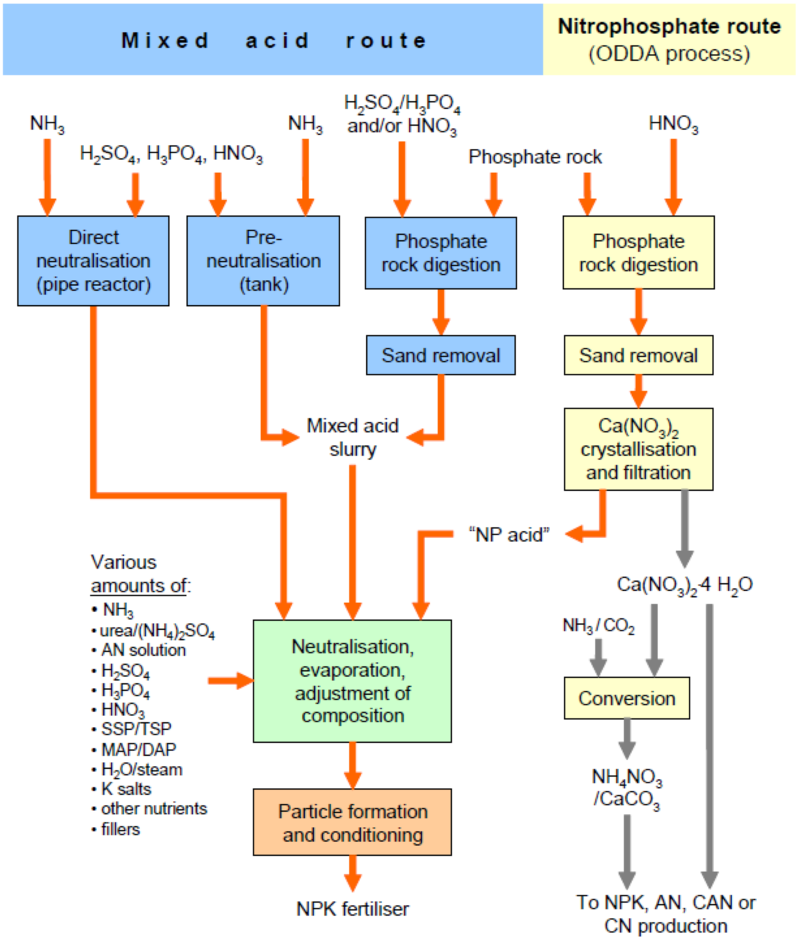


Figure 3-6 Overview of the production of NPK fertilisers

Figure 3-6 gives an overview of the production of NPK fertilisers. Compound fertilisers can be produced in four, basically different, ways:

- production by the mixed acid route, without phosphate rock digestion
- production by the mixed acid route, with phosphate rock digestion
- production by the nitrophosphate route (ODDA process)
- mechanical blending or compactation of single or multi-nutrient components (not included in the figure).

Phosphate rock digestion is carried out with nitric acid (nitrophosphate route) or with a combination of nitric, sulphuric, and/or phosphoric acid (mixed acid route). For both routes a rather low water quality is needed. Basically primary treated surface water with low organic and metal content will be sufficient. In

Table 3-7 the required water quality is listed.

Table 3-7. Required water quality: NPK fertilizer production

Parameter	Unit
pH	7-9
SS	<10 mg/l
Conductivity	< 500 µS/cm
TDS	< 300 mg/l
Chloride	<100mg/l
Heavy metals	< 1 ppm
TOC	< 10 ppm
Hardness	<20°F

3.6.6 Soda Ash

Soda ash is a fundamental raw material to the glass, detergent and chemical industries. Virtually all European soda ash is made using the Solvay process, which uses salt (NaCl) and limestone (CaCO3) as raw materials.
The Solvay process is described in Figure 3-7.

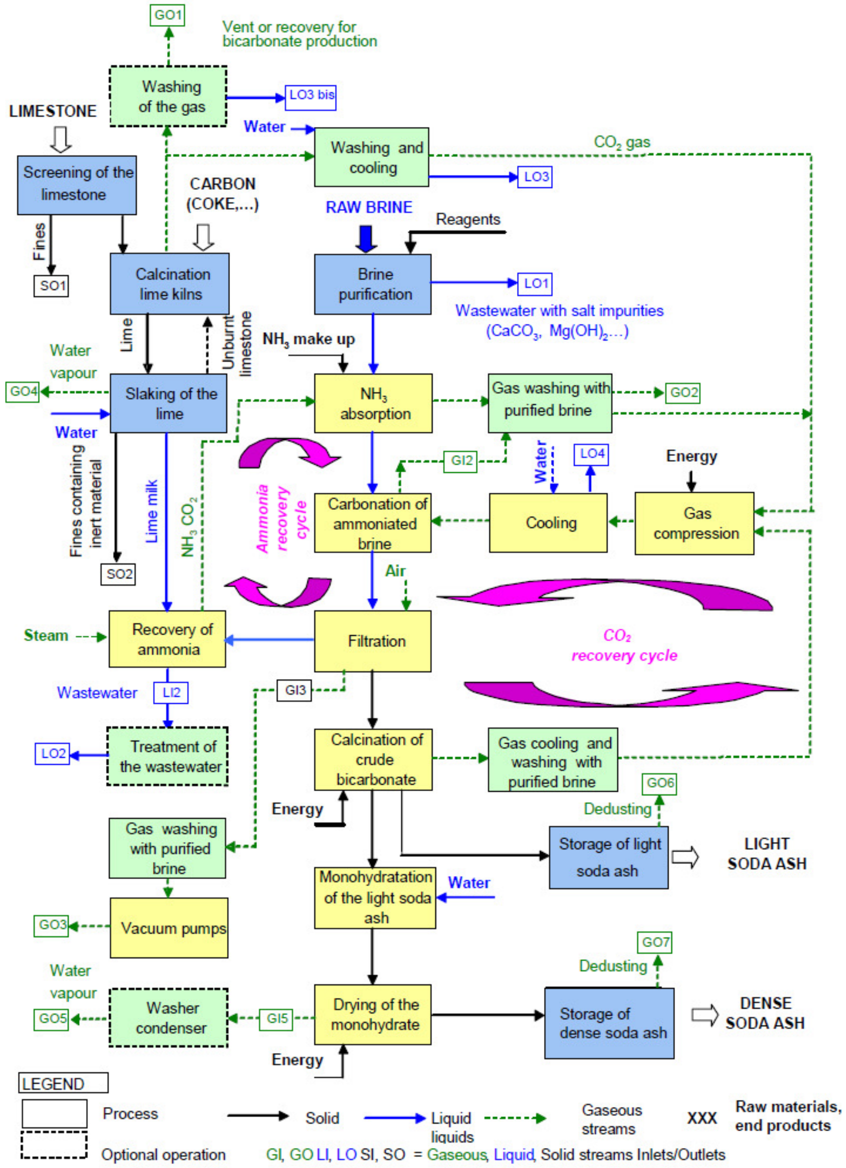


Figure 3-7 Process flow for manufacturing of soda ash by Solvay process (CEFIC-ESAPA, 2004)

The main water consuming process in the Solvay Process is the slaker in which lime reacts with water to form milk of lime. The quality requirements for this water are not high. Usually the process water is taken from the outlet of the cooling water system (see

Table 3-8)

Table 3-8. Required water quality: Solvay process : production of milk of lime (slaker)

Parameter	Unit
pH	6 – 9
SS	<50 mg/l
Conductivity	<2000 µS/cm
TDS	< 1000 mg/l
Heavy metals	< 1 ppm
TOC	< 10 ppm
Hardness	<20°F

3.6.7 Titanium dioxide

Titanium dioxide (TiO_2) white inorganic pigments are used primarily in the production of paints, printing inks, paper and plastic products. Titanium dioxide pigments are made from one of two chemical processes: the chloride route, which leads to TiO2 products by reacting titanium ores with chlorine gas; and the sulphate route, which leads to TiO2 products by reacting titanium ores with sulphuric acid.

3.6.7.1 Chloride process

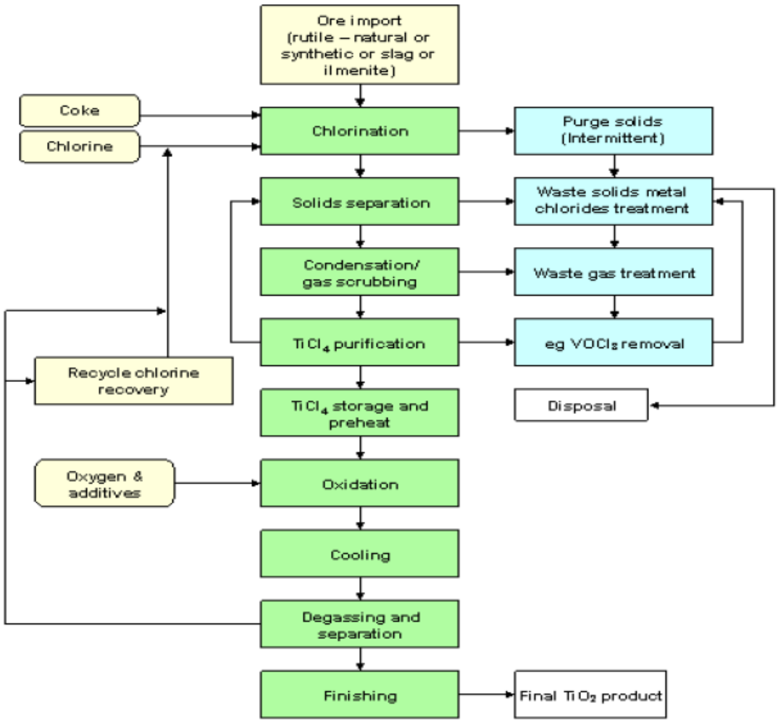


Figure 3-8 Process flow for manufacturing of TiO2 (Chloride process) [20, CEFIC-TDMA, 2004]

As illustrated in Figure 3-8, chlorine gas is used as an intermediary in the process and is recovered for re-use. During chlorination ore containing titanium dioxide and coke are fed to a fluidised-bed reactor where an exothermic reaction with chlorine gas takes place at 1000 °C. The resulting vapours of titanium tetrachloride plus other volatile metallic chloride impurities are cooled with recycled cold TiCl4, which allows the removal of some impurities. The majority of the titanium tetrachloride is condensed from the gas stream and pumped to a dedicated storage facility. Further purification of TiCl4 by distillation is carried out and the distillate product is stored for further downstream uses or export. From storage, the liquid titanium tetrachloride and oxygen are preheated before mixing. Oxidation of the TiCl4 to titanium dioxide and chlorine is carried out at between 900 – 1000 °C and 1500 – 2000 °C. The reaction involved is:

$$\mathrm{TiCl4 + O2 \rightarrow TiO2 + 2\ Cl2}$$

The oxidation phase is used to control the final quality of the TiO2 crystal size to enable the product to be used as a pigment. Light metal chlorides (usually of aluminium and alkali metals) are used to aid this process. The reaction products are cooled and the titanium dioxide powder is collected in bag filters and the chlorine is recycled. The oxidation product stream is a mixture of chlorine, oxygen and titanium dioxide powder. After exiting the reactor, these are cooled by indirect water-cooling. The titanium dioxide is slurried with water and transferred to the finishing stage. The required water quality for this process step is strongly dependant on the required specifications for the end product. In general terms the water quality listed in Table 3-9 can be used.

Table 3-9. Required water quality: TiO2 chloride process : slurrying process

Parameter	Unit
pH	6-8
Conductivity	< 500 µS/cm
TDS	< 300 mg/l
Heavy metals	< 0,1 ppm
TOC	< 1 ppm

Waste solids from the chlorination stage, which consist of metal chlorides, coke and some ores, are neutralised in a chalk or lime slurry. The metals are precipitated and stabilised, and the filter cake is landfilled, while the aqueous filtrate is discharged to the appropriate aqueous environment. For the lime slurry preparation in the waste water treatment, the water quality is given in Table 3-10.

Table 3-10. Required water quality: TiO2 chloride process: lime slurry for waste water treatment

Parameter	Unit
pH	7 – 9
SS	<50 mg/l
Conductivity	<2000 µS/cm
TDS	< 1000 mg/l
Heavy metals	< 5 ppm
TOC	< 10 ppm

3.6.7.2 Sulphate process

The sulphate process, uses concentrated sulphuric acid to digest the prepared titanium dioxide ore. The first step is the digestion of the ore which can be operated either batch wise or continuously. The ilmenite or slag (or a blend) is mixed with highly concentrated sulphuric acid (80

– 95 %) and this is necessary to digest the feedstock containing TiO2. A highly exothermic reaction is initiated by the addition of a measured quantity of steam, water or diluted acid and takes place at around 140 ºC.
The equation for the digestion reaction may be summarised as:

$$\mathrm{FeTiO3 + 2\ H2SO4 \rightarrow TiOSO4 + 2\ H2O + FeSO4}$$

During the batch process, the exothermic reaction raises the temperature of the reactor from 180 to 210 °C and water evaporates. The resulting solid cake is dissolved in water and acid recycled from a subsequent washing step. Any insoluble material is removed by flocculation and filtration. Afterwards, the titanyl sulphate (TiOSO4) in the clarified liquor is hydrolysed which results in a precipitation of the hydrated TiO2, while other sulphates, e.g. iron-sulphate (FeSO4), remain in the solution. Any suspended material is removed from the solution by flocculation and filtration. It is washed with dilute waste acid to recover the titanyl sulphate. The acidic filtrate liquors are recycled back to the process. Hydrated titanium dioxide is produced by hydrolysing the liquor with steam in rubber andbrick-lined mild steel vessels.
The hydrolysis reaction is:

$$\mathrm{TiOSO4 + 2\ H2O \rightarrow TiO(OH)2 + H2SO4}$$

Precipitation of the hydrated TiO2 is achieved by boiling the liquor for some hours followed by cooling to 60 °C. The hydrated TiO2 is filtered off from the suspension and the filter cake is washed to remove any absorbed metal ions. At this stage of the process, the spent acid with a concentration of 20 - 25 % H2SO4 and 10 – 15 % of soluble salts (mainly iron, aluminum and magnesium sulphates) arises and is either recycled or neutralised with lime/limestone to produce gypsum.

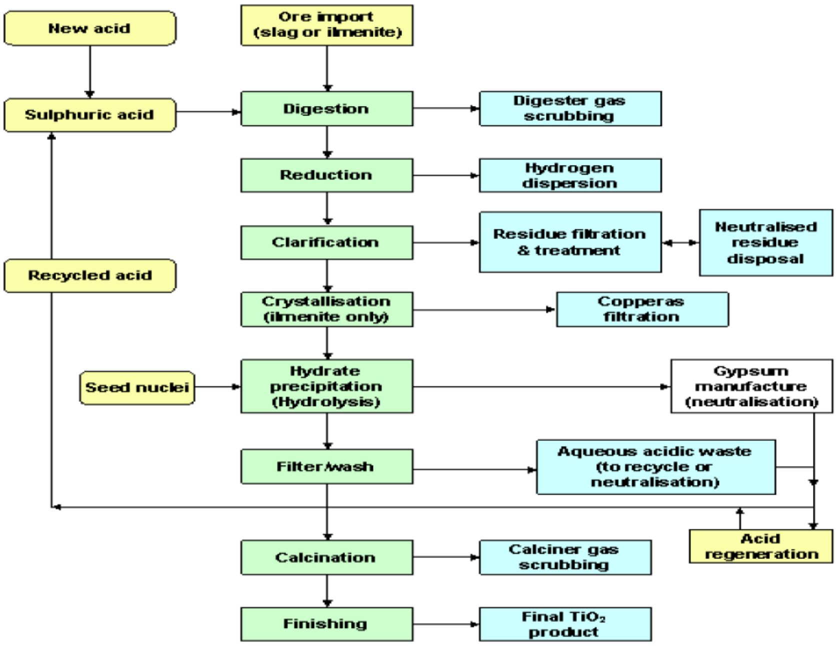


Figure 3-9 Process flow for manufacturing of TiO2 (sulphate process) [20, CEFIC-TDMA, 2004]

The precipitated hydrated TiO2 is separated on vacuum filters from the mother liquor. This acidic filtrate can either be reconcentrated andrecycled back to the digestion step or may be neutralised with lime/limestone. After the separation of the mother liquor, the filter cake is washed with water or a weak acid. The resultant solid is slurried with dilute sulphuric acid and aluminium or a solution of trivalent titanium is usually added as a reducing agent to maintain the iron in the ferrous state. The slurry is 'leached' (sometimes called 'bleaching') at 50 °C to remove final traces of iron. Thus the residual solid metals (Fe, Cr, Mn, and V) are eliminated from the hydrate by the addition of a reducer additive (e.g. trivalent titanium or aluminium) and acid (leaching agent). The use of zinc is not recommended due to its potential effect in the food chain.
The slurry then undergoes final washing and dewatering. The pulp still contains adsorbed sulphuric acid, which is impossible to remove by washing. Conditioning agents and rutile nuclei can be added at this stage to the resulting pulp to enhance crystallite growth and to determine the final crystal form during calcinations (i.e. final stage in the process where water and oxides of sulphur are driven off the pulp).

The different water using processes in the TiO2 production via the sulphate route are :

- Digestion : dilution of concentrated H2SO4 to achieve temperature raise due to exothermic reaction
- Washing after hydrolysis : the precipitated TiO(OH)2 is filtered off from the suspension and the filter cake is washed to remove any absorbed metal ions.
- Final washing : after leaching (removal of metal traces with dilute acid) the slurry is washed and conditioned.
- Washing after coating : coating involves the deposition of hydroxides (Si, Ti, Zr, Al,…) on to the surface of the TiO2-particles

Guidelines for the required water quality for the listed water consuming processes is given in Table 3-11.

Table 3-11. Required water quality: TiO2 sulphate process

Parameter					Unit
	Digestion	*Washing after hydrolysis*	*Final washing after leaching*	*Washing after coating*	
pH	7 – 9	7 – 9	7 – 9	7 – 9	Sörensen
SS	<50	<10	<5	<1	mg/l
Conductivity	<2000	<1000	<500	<500	µS/cm
TDS	< 1000	<500	<300	<300	mg/l
Heavy metals	< 5	<1	<0,1	<0,1	ppm
TOC	< 20	<10	<10	<5	ppm

3.6.8 Carbon black

Carbon black is a form of highly dispersed elemental carbon with extremely small particles. Depending on the raw materials and production processes, carbon black also contains chemically bound hydrogen, oxygen, nitrogen, and sulphur.
There are several production processes. Some are partial combustion processes :

- Furnace black process : using petrochemical oils, coal, tar oils and natural gas
- Gas black process
- Channel black process
- Lamp black process

Other are thermal cracking processes :

- Thermal black process
- Acetylene black process

In Europe the furnace black process is by far the most important process that is being used. The heart of a furnace black plant is the furnace in which the carbon black is formed. The primary feedstock is injected, usually as an atomised spray, into a high temperature zone of high energy density, which is achieved by burning a secondary feedstock (natural gas or oil) with air. The oxygen, which is in excess with respect to the secondary feedstock, is not sufficient for complete combustion of the primary feedstock, the majority of which is, therefore, pyrolysed to form carbon black at 1200 – 1900 °C.
Because of the very low density (20-60g/l) of the carbon black coming from the reactor, for certain applications (e.g. rubber black for tyres) it is necessary to pelletize the carbon powder. This can be done by mixing the fluffy powder with water and small amounts of additives. Afterwards the wet pellets are dried. The required water quality for the pelletizing process is given in Table 3-12

Table 3-12. Required water quality: Carbon black: pelletizing process

Parameter	Unit
pH	7 – 9
SS	<5 mg/l
Conductivity	<200 µS/cm
TDS	< 100 mg/l
Heavy metals	< 1 ppm
TOC	< 20 ppm
Hardness	<20°F

3.6.9 Synthetic amorphous silica

Due to their inert nature synthetic amorphous silica are used in cosmetics, pharmaceuticals, foods, pet food, rubbers and silicones, paint, paper, plastic,…
There are two different main production routes for amorphous silica : synthetic amorphous pyrogenic silica and synthetic amorphous precipitated silica and silica gel. Only the latter needs significant amounts of proceswater and will be discussed more in detail

3.6.9.1 Precipitated silica

The most important production processes –regarding water- of precipitated silica are: synthesis and washing (solid-liquid filtration. Raw materials for the production of precipitated silica and silica gels are aqueous alkali metal silicate solutions (e.g. water glass) and acids, generally sulphuric acid.

In the reaction of alkali metal silicate solutions, (e.g. water glass) with mineral acid (e.g. sulphuric acid), the silica precipitates according to the following equation:

$$\text{Na2O x nSiO2 + H2SO4} \rightarrow \text{nSiO2 + Na2SO4 + H2O (n = 2 to 4)}$$

In contrast to silica gels, which are produced under acidic conditions, in this case precipitation is carried out in neutral or alkaline media. The properties of the precipitated silica can be influenced by the design of the reactor and by varying the process parameters.

Table 3-13. Required water quality: synthetic amorphous silica : precipitation process

Parameter	Unit
pH	5 – 7,5
SS	<10 mg/l
Conductivity	< 20 µS/cm
TDS	< 10 mg/l
Heavy metals	< 1 ppm
TOC	< 30 ppm

The suspension received from the precipitation step is filtered. For this purpose, usual filter presses, membrane filter presses or belt/drum filters are used.After filtration, a washing step follows to remove salts. The level of salt retained in the product depends on the intended application of the final silica. The required water quality for the synthesis and filtration process are listed in Table 3-13

3.6.9.2 Silica gel

As with precipitated silica, silica gels are produced by the neutralisation of aqueous alkali metal silicates with acids. The first synthesis step comprises the formation of a hydrosol which is produced by the controlled mixing of water glass and diluted sulphuric acid. Occasionally, other acids are used. During the sol forming step, an unstable intermediate, monomer orthosilicic acid, is formed which then rapidly undergoes an acid-catalysed condensation reaction to form oligomers. When the molecular weight reaches approx. 6000, a sudden increase of both the viscosity and the modulus of elasticity is observed. This increase marks the transformation of the sol to a gel, that will then further develop its internal structure.

During the subsequent washing process, excess salts are removed in order to purify the gel. By an appropriate choice of the washing conditions (e.g. pH, temperature, time) different specific surface areas can be achieved for the purified hydrogel. In most cases the hydrogel is dried afterwards.

The required water quality for the washing process is listed in Table 3-14

Table 3-14. Required water quality: synthetic amorphous silica : silicagel process

Parameter	Unit
pH	5 – 9
SS	<0,1 mg/l
Conductivity	< 5 µS/cm
TDS	< 1 mg/l
Heavy metals	< 0,1 ppm
TOC	< 5 ppm

3.7 Water quality in chemical industry: large volume organic chemicals

3.7.1 Generic LVOC production process

Although processes for the production of LVOC are extremely diverse and complex, they are typically composed of a combination of simpler activities and equipment that are based on similar scientific principles.

The core activity of a chemical production process is the conversion of raw materials into the desired product(s) using the necessary chemical reactions (Unit Processes) and physical changes (Unit Operations). This typically involves the five steps described below :

1. *Raw material supply and preparation* : the receipt and storage of raw materials and ancillary reagents, and their charging into reactors.
2. *Synthesis* : the core of every process where raw materials are transformed into crude product by means of a chemical reaction ('Unit Processes'), often with the aid of a catalyst.
3. *Product separation and refinement* : using 'Unit Operations', the product is separated from other reaction components (e.g. unreacted feed, by-products, solvents and catalysts) and purified of contaminants to the necessary specification.
4. *Product handling and storage :* the storage, packaging and export of the product.
5. *Emission abatement* : the collection, re-use, treatment and disposal of unwanted liquids, gases and solids for those pollutants that have not been addressed by process-integrated measures.

The reactions used in the production of LVOC never achieve perfect selectivity of the target product and so there is considerable importance on unit operations to separate wastes from products. Many production processes need to separate individual substances from a homogeneous liquid mixture or to completely fractionate such mixtures into the component parts. Separation can be generically split into the following categories:

- liquid-vapour separation (by distillation, evaporation, steam/gas stripping)
- liquid-liquid separation (by extraction, decanting, centrifuging, multi-stage contacting)
- solid-liquid separation (by centrifuging, filtration, sedimentation, drying, crystallisation)
- solid-gas (by filtration)
- solid-solid separation (screening, electrostatic, gravity, flotation).

In the following paragraphs six of these unit processes will be discussed : absorption, distillation, extraction, solids separation, adsorption and condensation.

3.7.2 Absorption

Absorption is the uptake of one substance into the inner structure of another; most typically a gas into a liquid solvent. Absorption equipment generally consists of a column with internals for heat and material exchange in which the feed gas is brought into counter-current contact with the regenerated absorbent.

The absorbent loaded with the removed component leaves the bottom of the column and is regenerated by desorption. The solvent can be recovered (to minimize waste and reduce raw material costs). Water is often used as the solvent and the pollutants may be removed (e.g. by steam distillation, adsorption on activated carbon, extraction) to enable re-use in the process.

Water that cannot be re-used is usually biologically treated. In some cases, the absorbate itself is a commercial or intermediate product (e.g. hydrochloric acid solutions from acid gas scrubbing).

In case the absorbent is water and the objective is to absorb an unwanted organic compound from a gas stream which does not react with the water itself and is discarded as waste, typically the required water quality would be as listed in Table 3-15. Restrictions of the manufacturer of the absorbing unit can can increase the required quality

Table 3-15. Required water quality: organic chemicals : absorber

Parameter	Unit
pH	5 – 9
SS	<20 mg/l
Conductivity	< 3000 µS/cm
TDS	< 1000 mg/l
Heavy metals	< 1 ppm
TOC	< 40 ppm

3.7.3 Distillation

Distillation is the most important industrial method of phase separation. Distillation involves the partial evaporation of a liquid phase followed by condensation of the vapour. This separates the starting mixture (the feed) into two fractions with different compositions; namely a condensed vapour (the condensate or distillate) that is enriched in the more volatile components and a remaining liquid phase (the distilland) that is depleted of volatiles.

Only a limited number of separation problems may be solved by simple distillation and it is unsuitable for feeds containing components with similar boiling temperatures. Higher efficiency can be achieved by increasing the contact surface area or by contacting the liquid and vapour phases. Rectification columns provide intensive mass transfer by the repeated countercurrent contacting of the vapour and liquid streams in multiple stages. Rectification columns are of the plate or packed design, and may involve more than 100 distillation steps. Heat is required at the bottom of a distillation column for evaporating the feed and condensation energy is needed at the top of the column. The condensation energy is often transferred into cooling water or air, and this may provide an opportunity for energy recovery.

Depending of the boiling point of the components, effluents may result from aqueous bottom residues or from the top after condensation. Discharges depend on the efficiency of the distillation process and of additional steps for phase separation (preferably fractionated-condensation of top effluent, stripping of bottom residues).

During operation, the distillation process requires no water. Waste water streams can be generated as bottom or top product

3.7.4 Extraction

Extraction is the most important liquid-liquid separation process used in industrial chemistry. It is used mainly where other separation methods or direct distillation are ineffective or too expensive. Its typical uses include:
separation of components with similar boiling points (e.g. separating aromatics from hydrocarbons)

- separation of high boilers from aqueous solution

- separation of mixtures with high boiling points
- separation of temperature sensitive compounds
- separation of azeotropic mixtures (e.g. extraction of acetic acid from aqueous media)
- separation of pollutants for the minimisation of waste water streams.

In order to extract a substance, an extraction solvent must be added to form a second liquid phase solution. Generally the desired substance is then separated from the solvent by distillation and the solvent is recycled. Sometimes the selective action of the solvent is used in combination with distillation (extractive distillation or azeotropic distillation), for example in the manufacture of very pure, light aromatics. Extraction solvents like dimethyl sulfoxide, morpholines, sulfolane and diethylene glycol are widely used in the production of aromatics. Nmethyl- pyrrolidone, dimethylformamide and acetonitrile are also important solvents, especially for the extraction and separation of butenes and butadienes. Various types of mixer-settlers, centrifugal extractors and columns are used as extraction apparatus. All of them add the light phase at the bottom of the column, and the heavy phase is removed from the top. The density difference causes the light phase to rise through the heavy phase and effect the mass transfer between the two phases.

The extracting agent (raffinate) is generally recycled and only a small amount of liquid waste is generated. If water is used as the solvent, then it can be biologically treated once any highly concentrated waste components have been separated. Other extracting agents may require incineration.

In case water is used as an extracting agent, which is discharged into the waste water treatment the required water quality depends mainly of the specifications of the manufacturer of the extraction unit. Typically required water quality would be as listed in Table 3-16

Table 3-16. Required water quality: organic chemicals : extraction

Parameter	Unit
pH	5 – 9
SS	<5 mg/l
Conductivity	< 1500 µS/cm
TDS	< 500 mg/l
Heavy metals	< 1 ppm
TOC	< 20 ppm

3.7.5 Solids separation

Solid-liquid and solid-gas separations have industrial importance for product finishing and for minimising emissions of particulate matter to the atmosphere. Product finishing applications include separating heterogeneous catalysts from a product stream or separating solid products, by-products or intermediates (e. g. ammonium sulphate in the acrylonitrile-process, BTXaromatics at low temperatures). The principal solid-gas separation techniques are cyclones, fabric filters, ceramic filters, wet collection devices, electrostatic precipitators, dust separation equipment and high efficiency venturi scrubbers. The main solid-liquid techniques are centrifuging, filtration, sedimentation & clarification, drying and crystallisation. The choice of technique depends on:

- the characteristics of the particles and the carrier gas stream
- process factors such as temperature and pressure and
- operational factors such as floor space and headroom.

As such the **separation of solids does not require water input**. On the other hand water is frequently used as cleaning agent for these units.

3.7.6 Adsorption

Adsorption is the physical accumulation of material (usually a gas or liquid) on the surface of a solid adsorbent. Industrial adsorption processes are used to remove certain components from a mobile phase (e.g. air or water) or to separate mixtures. The applications can be production or abatement related and may include the removal of water from gases or the removal of organics from air streams or flue gas. The best adsorbents are characterized by a large number of different sized pores and so activated carbon, zeolites, silica gel and aluminium oxide are the most commercially important. Zeolites (molecular sieves) have a very narrow distribution of micro-pores and preferentially adsorb polar or polarisable materials (e.g. water or carbon dioxide). By contrast, activated carbon has a hydrophobic character and is especially suitable for the removal of organic substances. Other than for cleaning activities, no water is used in the adsorption process.

3.7.7 Condensation

Components from gaseous mixtures can be separated into liquids (or solids) by fractional condensation. Either the residual gas or the condensate may be the desired product. The temperature, the partial pressure of the condensing substances and their vapour pressure are linked. The recovery of 100 % of the condensing substances is not possible, whatever the temperature, when inerts are present with the condensing substances. Condensation may be used to separate products from waste streams and this often enables valuable feedstock or solvent to be returned to the production process. Condensation of volatile species is also used to minimise the emission of air pollutants, but this may require the use of cryogenic condensation to achieve the desired lower emissions. Other than for cleaning activities, no water is used in the condensation process.

3.8 Water quality in chemical industry: polymers

3.8.1 General processes and techniques

About 50-80% of the total water consumption in most polymer production plants is due to production of steam and water use in cooling towers. The requirements for these processes were elaborately discussed in I.1.2.1.1.. The rest of the water is used

3.8.1.1 Polymerisation reactions

Polymerisation is the most important reaction process and produces amongst others the plastics polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) and polystyrene (PS). The reaction principle includes the opening of the double bond of a monomer (Figure 3-10) and linking many monomeric molecules together forming a saturated long chain macromolecule. These reactions are usually exothermic, thus producing energy.

Figure 3-10 Typical polymersation reaction by opening double bond

The number of molecules combined, n, may vary from 10 – 20 (telomers or oligomers) to 1000-100000 and more (polymers). The polymer growth occurs very rapidly, in seconds or minutes.. However, the overall time required for a high conversion of monomer to polymer is often several hours.
Depending on the activation (type of reaction initiation), a differentiation is made between radical and ionic polymerisation:

- radical initiators may be oxygen, or for higher process temperatures, organic peroxides or azocompounds or simply heat as in the case of polystyrene, and for lower processing temperatures redox systems such as persulphate/bisulphit.
- ionic (including organo-metallic) catalysts are mostly of a very complex nature and often require a separate production process within the plant. Modern ionic catalysts are so effective that removal of the catalyst after polymerisation is not required for most of the applications. Only one gram of transition metal, for instance, produces more than 200 tonnes of final products. Thus, the residual concentration of the transition metal is no more than a few parts per million.

3.8.1.2 Polycondensation reaction

The reaction principle includes the reaction of a monomer with two distinctive reactive functional groups or the combining of two bifunctional monomers forming a polymer and generating a by-product which is, in many cases, water. A schematic view of the reaction is shown in Figure 3-11

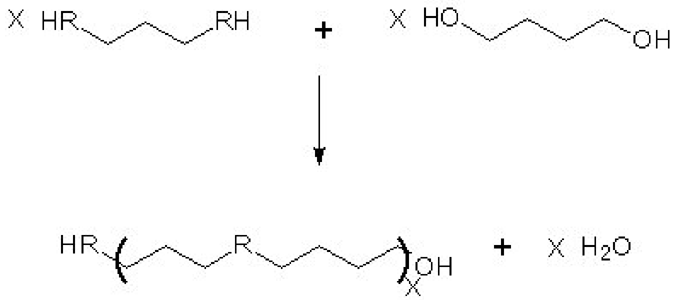


Figure 3-11 Typical polycondensation reaction

The reactive groups may be for instance:

- alcohol plus acid for polyesters
- amine plus acid for polyamides.

This process is, like most of the chemical reactions, an equilibrium process; it may be shifted in either direction depending on the conditions. High yields are achieved only by careful removal of the by-products (water or alcohols) which are formed. Otherwise, the by-product would interfere and reduce the molecular chain length. The by-product is removed by heat and by highly vacuum towards the end of the reaction. Polycondensation is considered to be a ‘step growth reaction’. The process often (but not always) needs a catalyst which is usually a metal salt or a combination of metal salts. Generally, polycondensation reactions are carried out either in bulk or in organic solvents.

3.8.2 Core production processes

Generally, the reaction of monomers to polymers may be carried out discontinuously or continuously by one of the following processes:

- suspension polymerisation
- bulk polymerisation
- emulsion polymerisation
- gas phase polymerisation
- solution polymerisation.

3.8.2.1 Suspension polymerisation

In suspension polymerisation, the chemical reaction takes places in droplets that are in suspension in a solvent. Suspension polymerisation is characterised by a good transfer of the reaction heat, a low dispersion viscosity and low separation costs on the one side but also by the fact that it is a discontinuous process, and there are relatively high amounts of waste water, significant reactor wall fouling and suspension agents remaining in the final product and in the waste streams.
Typical products are : PVC, PMMA, PS, PTFE and polyolefins.

Suspension polymerisation produces latex particles in the size range from 1 to 1000 µm. This process comprises monomer + initiator + solvent (usually water) + surfactant. The monomer and the initiator are both insoluble in the solvent (water), e.g. styrene and benzoyl peroxide; hence the monomer is dispersed as droplets (as in emulsion polymerisation), but the initiator is present in these droplets (and not in the aqueous phase). The role of the surfactant is purely to stabilise these droplets.

There are no micelles in the aqueous phase. The focus of polymerisation is now totally inside the monomer droplets. Hence, the polymerisation resembles a (micro-) bulk polymerisation, but confined to each monomer droplet separately.

High quality water is necessary to ensure optimal polymerisation. Suspended solids , heavy metals and TOC must be minimal in order not to disturb the process.

Table 3-17. Required water quality: polymer production : suspension polymerisation

Parameter	Unit
pH	7-9
SS	<5 mg/l
Conductivity	< 500 µS/cm
TDS	< 200 mg/l
Heavy metals	< 0,1 ppm
TOC	< 5 ppm
Hardness	<5°F

3.8.2.2 Bulk polymerisation

In bulk polymerisation, the polymer is produced in a reactor where only the monomer and a small amount of an initiator are present. Bulk polymerisation processes are characterised by high product purity, high reactor performances and low separation costs, but also by high viscosities in the reactors. Bulk processes cause reactor fouling, and in the case of polycondensation products, a high vacuum is required.

Typical products are:
- Polyolefins
- Polystyrene
- polyvinyl chloride
- polymethyl methacrylate
- polyamides
- polyesters.

This is the usual method for step-growth (condensation) polymerisation. The reaction is often carried out at a high temperature, but there are no real problems with heat transfer out of the reaction vessel (i.e. temperature build-up). The degree of polymerisation increases linearly with time, so that the viscosity of the reaction mixture only increases relatively slowly; this allows for efficient gas (e.g. water vapour) bubble transfer out of the system as well.

For certain monomers (e.g. vinyl chloride), the polymer is insoluble in its own monomer (above some critical molar mass). Hence, in these cases, the polymer precipitates (as aggregated, swollen particles) from the monomer after a while. Eventually all the monomer is converted to polymer.

In most cases **water input is not needed** during the bulk polymerisation process. Instead, for the polycondensation reactions, water needs to be extracted from the reaction.

3.8.2.3 Emulsion polymerisation

In emulsion polymerisation, the chemical reaction takes places in droplets that are in suspension in a solvent – like in the case of suspension polymerisation – but also in emulsion structures called micelles, and in the solvent. Emulsion processes typically show a low dispersion viscosity, good heat transfer, high conversion rates and are suitable for the production of high molar mass polymers. They are also characterised by high separation costs, reactor wall fouling and emulsifiers remaining in the product and in the waste streams.

Typical products are:

- ABS
- polyvinyl chloride
- PTFE
- SBR
- NBR
- PVA
- PMMA
- polyacrylates for paints

Emulsion polymerisation produces latex particles in the size range from 0.03 to 0.1 µm. The process comprises monomer + initiator + solvent (usually water) + surfactant (usually anionic, e.g. sodium dodecyl sulphate).
The monomer has only a very limited (but finite) solubility in the solvent (e.g. styrene in water). Most of it is present initially in dispersed droplets (hence the term emulsion polymerisation); one role of the (anionic) surfactant is to help stabilise these droplets, by adsorbing at the droplet/water interface. However, some of the monomer is present in the water phase. Most of the surfactant is present as micelles, again in the water phase, and some of the monomer will be solubilised in the micelles.
Thus, the monomer is actually distributed in three locations: droplets, aqueous solution (small amount) and micelles. The initiator is soluble (and therefore present) in the water phase. The growing, oligomeric free-radical chains will co-micellise in with the existing micelles from the added anionic surfactant. Polymerisation continues in the growing particles until all the monomer in the droplets and free solution is exhausted. The size of the final particles is controlled by the number of micelles present (i.e. the initial surfactant concentration).

For this type of polymerising reaction, very pure water is required with a minimum of disturbing compounds present. Typically deminwater will be used as solvent for the reaction. Heavy metals can interfere with the catalyst, high conductivity and hardness will disturb the emulsion,...

Table 3-18. Required water quality: polymer production : emulsion polymerisation

Parameter	Unit
pH	5-9
SS	<5 mg/l
Conductivity	< 10 µS/cm
TDS	< 5 mg/l
Heavy metals	< 0,1 ppm
TOC	< 5 ppm
Hardness	<5°F

3.8.2.4 Gas phase polymerisation

In gas phase polymerisation, the monomer is introduced in the gaseous phase and put in contact with a catalyst deposited on a solid structure. Gas phase processes allow an easy removal of the reaction heat, they are low in emissions and waste and no additional solvents are needed. Gas phase processes are not applicable for all end-products and the investment costs are relatively high, partially caused by the high pressure equipment needed for most of the processes.
Currently, gas phase processes are only applied to the polyolefins (commodity plastics):

- Polyethylene
- Polypropylene

This process is often used, e.g. in Ziegler-Natta type polymerisations of ethylene and propylene where the catalyst is supported on inert silica particles so the reaction therefore takes place at the surface. This helps control the stereochemistry (especially for isotactic polypropylene).

No water is required for the gas phase polymerisation reaction

3.8.2.5 Solution polymerisation

In solution polymerisation, the chemical reaction takes place in a solution of the monomer in a solvent. Solution polymerisation processes are characterised by a good transfer of the reaction heat, a low dispersion viscosity and little reactor wall fouling, but also by the low reactor capacities, high separation costs, often the use of inflammable and/or toxic solvents and traces of solvent contaminating the final product.
Typical products made by solution processes are:

- Polyacrylonitrile
- polyvinyl alcohol
- SBR
- BR
- EPDM
- Polyethylene

Solution polymerisation comprises monomer + initiator + solvent. This is the preferred method to use for chain-growth polymerisation. The solvent helps heat dispersal and reduces the rapid build-up in viscosity in the reaction mixture. The polymer may or may not be soluble in the solvent; in the latter case (e.g. styrene +methanol) the polymer precipitates from solution (above some critical molar mass).

In case water is used as solvent, similar water quality as for emulsion polymerisation is needed (see Table 3-18)

3.8.2.6 Viscose production process

When producing viscose fibres, the pulp – which is mainly cellulose from wood – is dissolved and subsequently precipitated under controlled conditions. The most important process worldwide is the so-called ‘viscose process’ where the alkaline pulp is treated with carbon disulphide (CS2) and dissolved by adding sodium hydroxide solution. A viscous orange-brown solution called ‘viscose’ is formed which is ripened, degassed and then pressed through spinnerets into a highly acidic spinning bath. Here, the cellulose precipitates when CS2 and the by-product H2S is released. After this, the cellulose is stretched, washed and then undergoes further processing.

At this point, a distinction has to be made between staple fibres and filament yarn. Staple fibres are cut into short pieces after the spinning bath. These short fibres, which are each approximately 4 cm long, are spun into textile yarns or processed into 'non-woven' products later on. In contrast, filament yarns are spun into endless fibres which can be used immediately.

The main processes (other than cooling and steam production) during viscose production are :

- Steeping

The cellulose sheets are saturated with a solution of caustic soda (or sodium hydroxide) and allowed to steep so the caustic solution can penetrate the cellulose and convert some of it into "soda cellulose", the sodium salt of cellulose. This is necessary to facilitate controlled oxidation of the cellulose chains and the ensuing reaction to form cellulose xanthate.

- Pressing

The soda cellulose is squeezed mechanically to remove excess caustic soda solution.

- Shredding

The soda cellulose is mechanically shredded to increase surface area and make the cellulose easier to process. This shredded cellulose is often referred to as "white crumb".

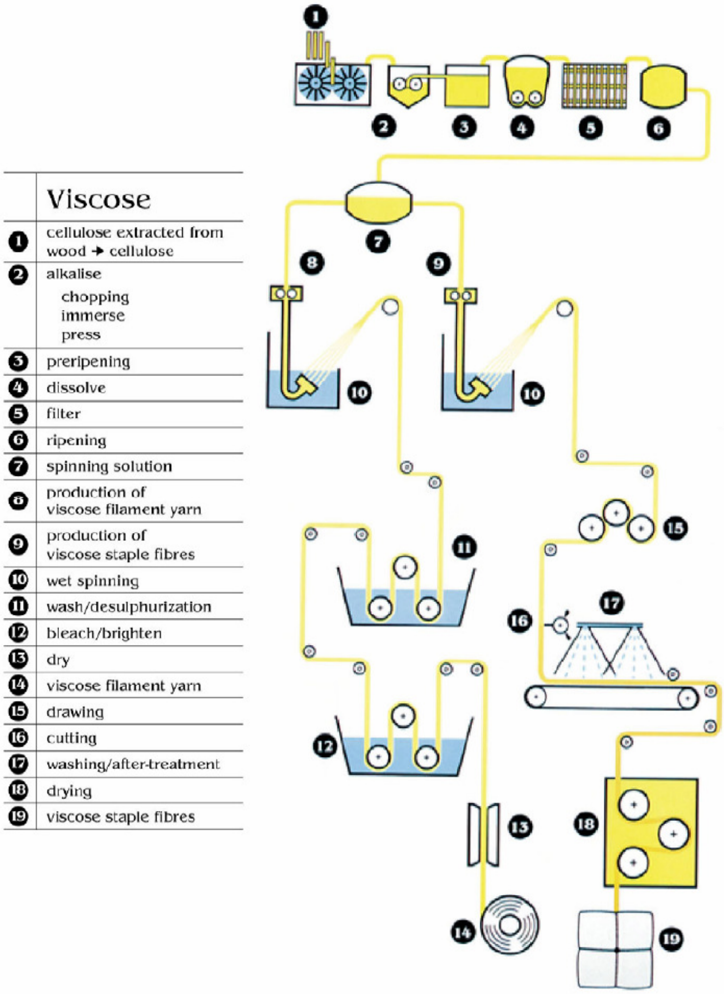


Figure 3-12 Flow diagram of viscose fibre production

- Aging

The white crumb is allowed to stand in contact with the oxygen of the ambient air. Because of the high alkalinity of white crumb, the cellulose is partially oxidized and degraded to lower molecular weights. This degradation must be carefully controlled to produce chain lengths short enough to give manageable viscosities in the spinning solution, but still long enough to impart good physical properties to the fiber product.

- Xanthation

The properly aged white crumb is placed into a churn, or other mixing vessel, and treated with gaseous carbon disulfide. The soda cellulose reacts with the CS2 to form xanthate ester groups. The carbon disulfide also reacts with the alkaline medium to form inorganic impurities which give the cellulose mixture a characteristic yellow color – and this material is referred to as “yellow crumb”.

- Dissolving

The yellow crumb is dissolved in aqueous caustic solution. The large xanthate substituents on the cellulose force the chains apart, reducing the interchain hydrogen bonds and allowing water molecules to solvate and separate the chains, leading to solution of the otherwise insoluble cellulose. Because of the blocks of un-xanthated cellulose in the crystalline regions, the yellow crumb is not completely soluble at this stage. Because the cellulose xanthate solution (or more accurately, suspension) has a very high viscosity, it has been termed “viscose”.

- Ripening

The viscose is allowed to stand for a period of time to “ripen”. Two important process occur during ripening: Redistribution and loss of xanthate groups. The reversible xanthation reaction allows some of the xanthate groups to revert to cellulosic hydroxyls and free CS2. This free CS2 can then escape or react with other hydroxyl on other portions of the cellulose chain. In this way, the ordered, or crystalline, regions are gradually broken down and more complete solution is achieved. The CS2 that is lost reduces the solubility of the cellulose and facilitates regeneration of the cellulose after it is formed into a filament.

- Filtering

The viscose is filtered to remove undissolved materials that might disrupt the spinning process or cause defects in the rayon filament.

- Degassing

Bubbles of air entrapped in the viscose must be removed prior to extrusion or they would cause voids, or weak spots, in the fine rayon filaments.

Water usage during the first stage of processing is limited to the water that is needed for the preparation of the feedstock of viscose solution. De necessary water quality for this listed in Table 3-19

Table 3-19. Required water quality: viscose production : viscose preparation

Parameter	Unit
pH	7-10
SS	<20 mg/l
Conductivity	< 1000 µS/cm
TDS	< 500 mg/l
Heavy metals	< 1 ppm
TOC	< 10 ppm
Hardness	<5

- Spinning - (Wet Spinning)

The viscose is forced through a spinneret, a device resembling a shower head with many small holes. Each hole produces a fine filament of viscose. As the viscose exits the spinneret, it comes in contact with a solution of sulfuric acid, sodium sulfate and, usually, Zn++ ions. Several processes occur at this point which cause the cellulose to be regenerated and precipitate from solution. Water diffuses out from the extruded viscose to increase the concentration in the filament beyond the limit of solubility. The xanthate groups form complexes with the Zn++ which draw the cellulose chains together. The acidic spin bath converts the xanthate functions into unstable xantheic acid groups, which spontaneously lose CS2 and regenerate the free hydroxyls of cellulose. (This is similar to the well-known reaction of carbonate salts with acid to form unstable carbonic acid, which loses CO2). The result is the formation of fine filaments of cellulose, or rayon.

The required water quality for spinning is listed in Table 3-20. Special care must be taken to avoid particle in the feed-water as these will cause blocking of the spinnerets.

Table 3-20. Required water quality: viscose production : viscose spinning

Parameter	Unit
pH	6-9
SS	<1 mg/l
Conductivity	< 1000 µS/cm
TDS	< 500 mg/l
Heavy metals	< 1 ppm
TOC	< 10 ppm
Hardness	<5

- Drawing

The rayon filaments are stretched while the cellulose chains are still relatively mobile. This causes the chains to stretch out and orient along the fiber axis. As the chains become more parallel, interchain hydrogen bonds form, giving the filaments the properties necessary for use as textile fibers.

- Washing

The freshly regenerated rayon contains many salts and other water soluble impurities which need to be removed. Several different washing techniques may be used. In most cases cascade-rinsing is practiced and fresh water is only added in the last step. Typically this is softened water. The requirements for the washing process are listed in Table 3-21

Table 3-21. Required water quality: viscose production : viscose washing

Parameter	Unit
pH	6-9
SS	<10 mg/l
Conductivity	< 1000 µS/cm
TDS	< 500 mg/l
Heavy metals	< 10 ppm
TOC	< 20 ppm
Hardness	<10

- Cutting

If the rayon is to be used as staple (i.e., discreet lengths of fiber), the group of filaments (termed “tow”) is passed through a rotary cutter to provide a fiber which can be processed in much the same way as cotton.

3.8.3 Down-stream processing of polymers

In previous sections mainly the production of the raw polymer material was discussed, i.e. the primary reaction to create polymerisation. Besides this, in most cases a considerable amount of water is also used in the down-stream processing of the polymers.
In most case the down-stream processing entails the extruder en pelletizer. Fine particles are separated from the pellets by a water flow. The requirements for this process are usually not extremely high, but do depend on the final product specifications. Table 3-22 list the water quality requirement for a PE-pelletizer

Table 3-22. Required water quality: Polymer production (PE) : pelletizer

Parameter	Unit
pH	5-9
SS	<50 mg/l
Conductivity	< 2000 µS/cm
TDS	< 500 mg/l
Heavy metals	< 10 ppm
TOC	< 50 ppm
Hardness	<25°F

3.9 Water quality in chemical industry: pharmaceutical industry

3.9.1 introduction

Water is one of the major commodities used in the pharmaceutical industry. It may be present as an excipient, used in the synthesis of pharmaceuticals, during production of the finished product or as a cleaning agent for rinsing vessels, equipment, etc.

Unlike other chemical sectors the water qualities that can be used in the pharmaceutical sector are well defined. Different grades are required depending on the different pharmaceutical uses. Control of water quality –especially microbial quality- is a major concern in the pharmaceutical sector.

The European Pharmacopoeia provides standard for grades of water for pharmaceutical use :

- Purified water
- Highly purified water
- Water for injections

Besides this, also potable water is mentioned but is not described as such in the European Pharmacopoeia.
Regarding water quality, the European Pharmacopoeia not only describes the limits for the different parameters but also the way in which the type of water has to be prepared.

3.9.2 Potable water

As already mentioned potable water is not covered by a pharmacopoeial monograph, but must comply with the regulations on water laid down by the competent authority (European or national, whichever is more stringent). Testing should be carried out at the manufacturing site (i.e. the water supplier) to confirm the quality of the water.

Potable water may be used in chemical synthesis and in the early stages of cleaning pharmaceutical manufacturing equipment, unless there are specific technical or quality requirements for higher grades of water. Potable water is **always** the prescribed source of feed water for the production of pharmacopoeial grade waters.

3.9.3 Water for injections (WFI)

WFI defined as water for the preparation of medicines for parenteral administration when water is used as a vehicle (WFI for injections in bulk) and for dissolving or diluting substances or preparations for parenteral administration before use (sterilized water for injections)

3.9.3.1 Production of WFI

Control ,of the chemical purity of WFI presents few major problems as it is always produced starting from potable water or purified water (see Table 3-24). The critical issue is to ensure microbial quality with respect to the removal of bacteria and bacterial endotoxins. The only official method for production of WFI is distillation. The water is distilled in an apparatus of which the parts in contact with the water are made of neutral glass, quartz or suitable metal and which is fitted with an effective device to prevent entrainment of droplets (i.e. possible carry-over of nonpruified water). During production and storage, appropriate measures are taken to ensure that the total viable aerobic count is adequately controlled and monitored.

3.9.3.2 Specifications of WFI

In Table 3-23 are the specifications of WFI listed, according to European and US Pharmacopeia. These specifications are on top of the requirements for drinking water.

Table 3-23. Required water quality: pharmaceutical : Water For Injection

Parameter	Unit	
	Eur.Ph.	**US Ph.**
TOC	< 0,5 ppm	< 0,5 ppm
Conductivity	<1,1µS/cm at 20℃	
Conductivity		<1;3µS/cm at 25℃
Nitrate	<0,2 ppm	
Heavy metals	<0,1 ppm	
Dry residue	<0,001	
Aerobic bacteria	<10	<10
Bacterial endotoxins	<0,25EU/ml	<0,25EU/ml

3.9.4 Purified water (PW)

Purified water is water for the preparation of medicinal products other than those that require the use of water which is sterile and/or apyrogenic. Purified water which satisfies the test for endotoxins may be used in the manufacture of dialysis solutions.

3.9.4.1 Production of PW

Purified water is prepared by distillation, ion exchange or by any other suitable method, from water that complies with the regulations on water intended for human consumption.

3.9.4.2 Specifications of PW

In Table 3-24 are the specifications of WFI listed, according to European and US Pharmacopeia. These specifications are on top of the requirements for drinking water.

Table 3-24. Required water quality: pharmaceutical : Purified water

Parameter	Unit	
	Eur.Ph.	**US Ph.**
TOC	< 0,5 ppm	< 0,5 ppm
Conductivity	<4,3µS/cm at 20℃	
Conductivity		<1;3µS/cm at 25℃
Nitrate	<0,2 ppm	
Heavy metals	<0,1 ppm	
Aerobic bacteria	<100CFU/ml	<100CFU/ml

3.9.5 Highly purified water (HPW)

Highly purified water is intended for use in the preparation of products where water of high biological quality is needed, except where water for injection is required.

3.9.5.1 Production of HPW

HPW is produced from water that complies with the regulations on water intended for human consumption. Common production methods are : double pass reversed osmosis coupled with other suitable techniques such as ultrafiltration and deionization.

3.9.5.2 Specifications of HPW

Highly purified water meets the same quality standards as WFI but the production methods are considered less reliable than distillation and thus it is considered unacceptable for use as WFI.

3.9.6 Application of water in different processes and product

Table 3-25 list a number of sterile medical products and the minimum acceptable quality of water

Table 3-25. Required water quality: medicinal products and required water quality

Sterile medicinal product	Required water quality
Parenteral	WFI
Ophthalmic	PW
Haemo(dia)filtrations solutions	WFI
Peritoneal dialysis solutions	WFI
Irrigation solutions	WFI
Nasal/Ear preparations	PW
Cutaneous preparations	PW

Non-sterile medicinal product	Required water quality
Oral preparations	PW
Nebuliser solutions	PW
Cutaneous	PW
Nasal/Ear preparations	PW
Rectal/Vaginal preparations	PW

Table 3-26 list a number of process steps during the production of active pharmaceutical ingredients (API) and the required water quality.

Table 3-26. Required water quality: productions of API and required water quality

Type of manufacture		Required water quality
Synthesis of all intermediates of API's prior to final isolation and purification	No requirement for sterility or apyrogenicity in API or the product in which it will be used	Potable water
Fermentation media	No requirement for sterility or apyrogenicity in API or the product in which it will be used	Potable water
Extraction of herbals	No requirement for sterility or apyrogenicity in API or the product in which it will be used	Potable water
Final isolation and purification	No requirement for sterility or apyrogenicity in API or the product in which it will be used	Potable water
Final isolation and purification	API is not sterile but is intended for use in a sterile, non-parenteral product	PW
Final isolation and purification	API is sterile and is not intended	PW

	for parenteral use	
Final isolation and purification	API is not sterile but is intended for use in a sterile, parenteral product	PW (with endotoxin <0,25 EU/ml and control of specified organisms
Final isolation and purification	API is sterile and apyrogenic	WFI

4 Water quality demands in food sector

4.1 introduction

The food and beverage industry is of prime importance to the economy of the European Union; it is among the largest industry sectors in the Union with more than 25 000 companies across the EU, employing some 2,6 million people, and an annual turnover of 600 billion euro (EU 2001). With a high concern for consumer safety, it is one of the most stringent areas of quality control.

The food industry has a high demand for clean and fresh water. Access to an abundant source of high quality water is one of the essential factors in designing a food plant. Food safety regulations and internal quality standards are often a significant barrier to water conservation measures. The previous EU directive and respectively the Dutch regulations strictly prohibited the use of non-potable water in the food industry. In addition and as one of the consequences of the strict regulations, the governing mentality in the food processing firms is that the use of any kind of water other than drinking water will generate substantial threat to the product quality and safety. Apart from the mentioned restrictions, due to the wide variety of compounds added to the streams from the products during the processes, the quality evaluation of the waste streams becomes more complicated. Hence, if a method could successfully cover the many relevant aspects of water quality in the food industry and supply sufficient support for the usage of lower quality of water, it can be assumed that with minor modifications it could be attuned to other industries branches, which have not so much restrictions for water reuse and less complications. Non-food industries are less complex in order of the existing variety of water quality parameters in process streams and less restricted in using lower quality of water. In most of these industries, many water reuse practices have already been carried out. This however does not apply to the food industry and the main issues in this aspect are still to be discovered.

The principal concerns in the food and beverage industry are:
- Microbiological control and product safety;
- Reducing the formation of scale and deposits;
- Maintaining product integrity;
- Lowering overall production costs.

Due to the importance of consumer health, microbiological control and product safety has an especially high precedence. Reducing the formation of scale and deposits and in general protecting machinery and pipelines is a well-documented issue. The main parameters in water which indicate its effect on the equipment are mainly recognized and can be seen as general parameters (on scaling, fouling, corrosion), which will be discussed in task 1.2.1.

Product integrity where separated from safety can be best demonstrated by product quality. In the case of food products the organoleptic characteristic of a food is an indication of its quality.

In this part an overview is given of water quality demands in the food industry. Water quality requirements or restrictions will be collected for different water functions, like washing, blanching, cooling, heating, cleaning, use in products, etcetera.

Generally speaking, it is possible to identify two main types of reuse relating to whether the water comes into contact with food product(s) or not. Typical reuse applications, where the water usually has no such contact, include its use in cooling and for the generation of “non-food steam”. Water that does have contact with food may do so at the raw product stage (e.g. washing or transport) at intermediate stages (e.g. cleaning of equipment) or in the final product itself (i.e. residual water).

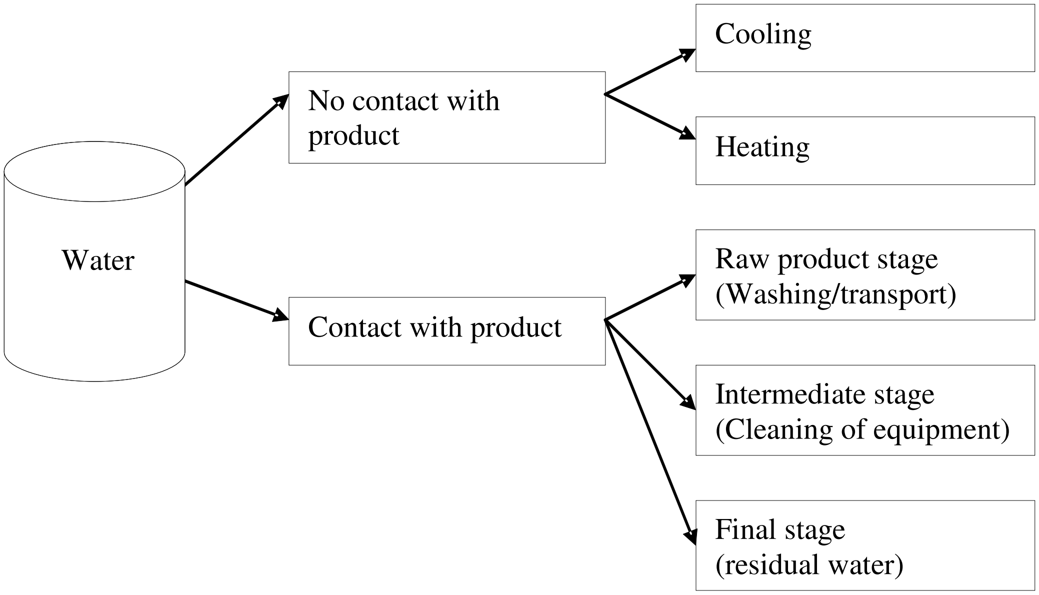


Figure 4-1. Water use in the food sector

4.2 Water functions in the food industry

Within the food industry several sectors can be distinguished. The most important water consuming sectors within the food industry are:

- Potato, vegetables and fruit preserving industry;
- Dairy industry;
- Meat industry;
- Fish processing industry;
- Beverage industry and Breweries (malting industry);
- Sugar and starch industry;
- Margarine, oil and fat industry.

For all the above mentioned sectors water is more or less used for the same main functions. In food processing plants the water use starts with conditioning raw materials, such as soaking, cleaning, blanching and chilling. It continues with cooling, sanitizing, steam generation for sterilization, power and process heating, and, finally, direct ‘in- process’ use. The main functions of water in industrial processes are:

- Washing/cleaning of (raw) products;
- Transport of products;
- Dissolving of ingredients;
- Treatment of the product (e.g. alteration, separation);
- Provision of appropriate water content in the final product/as an ingredient in the product;
- Cooling processes;
- Steam generation;

- Cleaning/rinsing of equipment;
- Abnormal incidents (e.g. fire protection);
- Sanitation.

4.3 Water Quality Parameters

In this chapter we will focus on the relevant water quality parameters for the most important water functions (water uses) in the food sector. In task 1.2.1 of WP 2.1. already attention is paid to the water quality in relation with the more general utility parameters, to avoid scaling, fouling, corrosion and parameters on environment, safety and health. Here we are more focused on the process specific parameters. The required water quality is strongly related to the process water function. Besides the process specific water function also food safety and food quality are relevant aspects for the water quality.

Critical water quality parameters can be distinguished in microbiological contaminants, chemical contaminants and physical contaminants. The following table gives an overview of relevant parameters for different water functions.

Table 4-1. General Overview of relevant water quality parameters for several water function

Water function	Contact with product	Example	Relevant water parameters
Washing/Rinsing	yes	Potato and vegetable processing	Pesticides Colour Micro-organisms Poly-phenols TSS
Transport medium	yes	Potato and vegetable processing	unknown
Pasteurizing	no		Temperature, M.O.
Disinfection (indirect)	no		Temperature, M.O.
Reactant	yes	Hydrolyses reactions	COD or TOC Hardness (Ca and Mg) pH
Separation medium	yes	Protein extraction out of potatoes	
Solvent	yes	Pickle/brine bath	
Blanching	yes	vegetables	Leaching components (e.g. nitrate)
Disinfection (direct)	yes		
Product/Ingredient	yes	Beer brewery, soft drink production	All parameters with a concentration above DWS
Cooling (indirect)	no		Temperature, hardness,
Heating (indirect)	no		Temperature
General cleaning	yes	Scrub water, Cleaning pipelines & reactors	COD or TOC Smell Colour Micro-organisms Kjeldahl-N TSS
Consumption & Facilities	yes	Canteen, WCs & showers	

4.3.1 Washing/cleaning of (raw) products

Washing is the process of selectively removing unwanted compounds from a mixture using a solvent. For a washing to be successful the unwanted materials must be more soluble in the solvent than in their current state. Water is the common solvent used in industrial washing processes. Washing is one of the major stages in the food industry.

Immediately upon receipt at the food industry, raw food materials are thoroughly washed. The objectives of washing are to:

- separate soil and other foreign materials from the product;
- reduce load of spoilage bacteria naturally present in foods;
- improve quality and appearance of food.

Reduction of the number of bacteria present increases the effectiveness of the sterilization process.

Washing is done by equipment in which the products are subject to high-pressure water sprays or strong flowing streams of water while passing along a moving belt or while being tumbled on agitating or revolving screens. Sometimes a flotation type of washer is also used to remove chaff or other extraneous material. Washing is sometimes preceded by mechanical removal of soil and other fine materials that adhere to the food. Stones and other heavy objects are also separated by density difference.

Generally, washing processes are carried out in several stages. Water with lower quality can be used in the preceding stages and the cleanest water is used for the final stage (cascade washing).

Regarding the function of the washing process, the waster used must have a sufficient diluting capacity: Relatively low load of substance, which needs to be washed (e.g. starch, in potato washing) and a low microbiological load for efficiently decreasing the initial load on the product.

4.3.2 Blanching

Blanching is the heating of fruit or vegetables for a short time with either steam or water, and is an essential step before canning, drying or freezing of food.

This heating process is not meant to cook the food but to inactivate substances that would otherwise adversely affect the nutrient content, colour, flavour or texture during subsequent processing and storage.

Blanching is a fairly mild heat treatment, which involves exposing plant tissue to some form of heat, usually steam or hot water, for a prescribed time at a specified temperature. Typical blanch times and temperatures might be in the neighbourhood of 88 ° - 100 °C for 1 - 10 minutes, depending on the product.

The two most widespread commercial methods of blanching involve passing food through an atmosphere of saturated steam or a bath of hot water. Both types of equipment are relatively simple and inexpensive. Hot gas blanching has been developed for the blanching of vegetables, partly to reduce the pollution effluent from blanching, however hot gas blanching is not normally encountered.

Thermophilic growth is a major concern with blanchers. Blanchers should be operated at temperatures in the 88 - 93 ºC (190 – 200 ºF) range. Product temperatures at or above 82 ºC (180 ºF) help to control thermophilic growth. Foam build-up in blanchers should be controlled, as the foam may allow for thermophilic growth at temperatures lower than the temperature of the blanching water.

Recycling of water does not affect the product quality or yield but substantially reduces the volume of effluent produced. However, it is necessary to ensure adequate hygienic standards for both the product and equipment by preventing a build-up of bacteria in cooling water, and the improved hygiene control may result in additional costs, which outweigh savings in energy and higher product yield.

Knowledge of the added chemicals to blancher water can contribute in determination of acceptable quality for the process: Sodium Carbonate (0,125 % w/w) or calcium oxide is often added to blancher water to protect chlorophyll and to retain the colour of green vegetables.

Enzymic browning of cut apples and potatoes is prevented by holding the food in dilute (2 % w/w) brine before blanching.

In some types of food such as certain varieties of potatoes, the time temperature conditions needed to achieve enzyme inactivation causes an excessive loss of texture in some types of food. Hence, Calcium chloride (1 – 2 %) is added to blancher water to form insoluble calcium pectate complexes and thus to maintain firmness in the tissues. (Fellows P. 2000)

4.3.3 Provision of appropriate water content in the final product (as ingredient)

The demands for water used in processes where the water contacts the product or become part of the product are generally very high. Mostly the water quality which is used is potable water quality and sometimes this water is further cleaned to softened water or demineralized water.

4.3.4 Cooling

The most frequent problems in cooling water systems are scaling, corrosion, biological growth, fouling and foaming. These problems arise from contaminants in potable water as well as lower quality water, but the concentration of some contaminants may be higher.

4.3.5 Heating (steam production)

Quality requirements for boiler feed makeup water are dependent upon the pressure at which the boiler is operated. Generally the higher the pressure, the higher the quality of water required. Very high-pressure boilers require makeup water of distilled quality.

In general even potable water must be treated to reduce the hardness of the boiler-feed water to close to zero. Removal or control of insoluble salts of calcium and magnesium and control of silica and aluminium are required since these are the principal causes of scale build-up in boilers. High alkalinity may contribute to foaming, resulting in deposits in super heater, re-heater, and turbines. Bicarbonate alkalinity under the influence of boiler heat, may lead to the release of carbon dioxide, which is a source of corrosion in steam-using equipment.

4.3.6 Cleaning and CIP

Cleaning programs are frequently combined with disinfection and involve several stages including:

1. Preparation, involving dismantling of equipment;
2. Dry removal of gross soil (small pieces of product or other residues);
3. Cleaning with chemical detergent;
4. Rinse with potable water at 40 - 50 °C;
5. Disinfection;
6. Final rinse with potable water to remove chemical residuals.

Cleaning which involves the removal of all soil, comprises four principal phases:

1. Wetting and penetration of soil and surfaces by the cleaning solution;
2. Reaction of the cleaning solution with soil to facilitate peptidization of organic material, dissolution of soluble compounds and emulsification of fats;
3. Prevention of re-deposition of dispersed soil;
4. Removal by rinsing.

The water temperature is one of the factors that can affect the cleaning procedure: too hot water results in coagulation of protein soil and too cold water will not remove the fat.

The common cleaning agents contain the following typical components:

1. Wetting agents which aid cleaning by reducing surface tension and emulsifying fat;
2. Inorganic alkalis which break down proteins, through the action of the hydroxyl ions, saponify fats and at higher concentrations kill micro-organisms;
3. Inorganic and organic acids, which solubilise carbonate and other mineral scales and proteinacous deposits;
4. Sequestering or chelating agents which soften water, e.g. EDTA and polyphosphates.

Water hardness can affect the detergents efficiency. Soft water is the best for cleaning purposes since salts present in hard water may either react with components of the cleaning agent, thereby reducing their effectiveness, or produce insoluble deposits. The rate of deposition increases with increasing temperature and so it is advisable when using hot water either to soften the water before use or to use detergent mixtures containing chelating agents.

4.3.6.1 Methods of Cleaning

- **Foam:** Foam is produced through the introduction of air into a detergent solution as it is sprayed onto the surface to be cleaned. Foam cleaning will increase the contact time of the chemical solutions, allowing for improved cleaning with less mechanical force and temperature;
- **High Pressure:** High pressure cleaning is used to increase the mechanical force, aiding in soil removal. In high pressure cleaning chemical detergents are often used along with increased temperature to make soil removal more effective;
- **Clean in Place (CIP):** CIP cleaning is utilized to clean interior surfaces of tanks and pipelines of liquid process equipment. A chemical solution is circulated through a circuit of tanks and or lines then returned to a central reservoir allowing for reuse of the chemical solution. Time, temperature, and mechanical force are manipulated to achieve maximum cleaning;
- **Clean Out Of Place (COP):** COP cleaning is utilized to clean tear down parts of fillers and parts of other equipment, which require disassembly for proper cleaning. Parts removed for cleaning are placed in a circulation tank and cleaned using a heated chemical solution and agitation;
- **Mechanical:** Mechanical cleaning normally involves the use of a brush either by hand or a machine such as a floor scrubber. Mechanical cleaning uses friction for food soil removal. (Bishop, 1997)

4.3.6.2 Important parameters in CIP

From the point of view of CIP, the most important parameters are *pH, Chlorine and hardness levels*. In some cases, water with *high iron content* can also present problems.

In CIP processes, temporary hardness and its proportion to total hardness is most important. For example a moderately hard water of 180 mg/l $CaCO_3$ total hardness but with a temporary hardness of 160 mg/l $CaCO_3$ could be more troublesome than a one of 250 mg/l $CaCO_3$ total with a temporary hardness of only 100 mg/l $CaCO_3$.

4.3.6.3 Cleaning water applications

Applications can be broadly divide into: water for non plant uses (e.g. floors, walls, yards and external cleaning of tankers and other vehicles); and water for CIP and disinfection of plant and equipment.

4.3.6.4 Non-plant uses

In general the quality of water for these applications need not be as high as that required for plant cleaning and bottle or can washing. However it is important to remember that, if badly contaminated water is used for cleaning walls and floors in a processing or a packing area, or even for external cleaning of tankers, there is always a risk that product contamination will occur.

4.3.6.5 Plant uses

This category covers both internal and external cleaning of the plant, be it raw or finished product plant. The reliable microbiological quality of water is of high significance. All water used for plant cleaning and disinfection should be soft. However the use of absolutely soft water (i.e. zero mg/l $CaCO_3$ total hardness) is not advisable since it can be corrosive and cause difficulties in machinery. Water with 5 - 10 mg/l $CaCO_3$ total hardness is ideal. The problem of scale resulting from hard rinse water can be minimized by acidifying the water at point of use by injecting a suitable acid on the delivery side of the pump, but this must be very carefully controlled and monitored.

4.3.6.6 Process validation

Validation is another essential aspect of a properly managed CIP process. There are three main aspects of the validation process. First, it is important to ensure that the CIP process is in fact operating as intended. Second, it is important to validate that the CIP process has indeed cleaned/and or sterilized the equipment to the level required. Microscopic counts, filtration tests and chromatographic analyses can be used. Kits for the rapid detection of cells have a growing importance in the CIP process. Kits based on ATP detection or immunological reactions for rapid detection have been developed and marketed.
Finally, it is also important to ensure that residual chemicals have been removed from the system. This is particularly the case where detergents are being used. The mentioned monitoring steps are significant to recognize as in cases of using non potable water, they will prevent hazards.

4.4 Water quality demands in different subsectors

In this chapter an overview is given of water quality requirements for different water functions in several sectors within the food industry.

4.4.1 Water quality Potato, vegetables and fruit preserving industry

Table 4-2. Branche specific parameters (TNO, 2001)

Parameter Microbiological contaminants, including spores	**Explanation *)** Pathogenic organism
Calcium	Scaling (M&P)
Proteins	Turbitity (PQ) and H2S and NH3 formation (PQ)
Phosphate	Scaling (M&P) and Softening (PQ)
Iron	Colouring (PQ)
Magnesia	Scaling (M&P)
Manganese	Scaling (M&P) and colouring (PQ)
Nitrate	Forming nitrite (PS)
Nitrite	Forming nitro amines (PS)
Sulphate	Forming endo toxines (PS)
Solid particles	Contamination, biofouling (M&P)
Starch	Turbidity (PQ)
Temperature	Leaching and consistency product (PQ)
Conductivity	
Colour	
COD	
Ammonium	
Pesticides	
Cleaning agents	

*) M&P = machinery & pipes; PQ = product quality; PS = product safety

Table 4-3. Relevance of parameters for different aspects*) (TNO, 2006)

Parameter			**Criteria**			
	PS	**PQ**	**PWF**	**M&P**	**Health and WC**	
Pathogenic MO	2,3				1,2	Incl.
Total MO		1,2,3	1,3	1,2,3	2	Legionella
Iron		2,3	1	1,2,3		
Manganese		2,3	1	1,2,3		
Calcium		2,3	1,2,3	1,2,3		
Magnesia		3	1,2,3	1,2,3		
Chloride		3	1	1,2,3		< DWS
Sulphate		3	1			
Ammonium		3	1			
Nitrate	2,3	3	1			
Nitrite	3					
Phosphate		3	1,2	1,2,3		
Proteins		3				
Starch		3	1			
Conductivity			1	1,2,3		
COD	2	3				
Colour		2,3				
Pesticides	2,3	2,3				
Cleaning agents		2,3			2	

1 = steam production and softened water
2 = cleaning water and HD water
3 = washing water
*) PS = product safety; PQ = product quality; PWF = process water function; M&P = machinery & pipes; WC = working conditions

Table 4-4. Standards for relevant parameters (TNO, 2006)

		Steam	Cleaning	Washing	Remarks
Pathogenic MO	#/100 ml	0	0	0	DWS
Total MO	#/100 ml	100	100	100	DWS
Iron	µg/l	200	200	200	DWS
Manganese	µg/l	50	50	50	DWS
Calcium	mg/l	150	150	150	DWS
Magnesia	mg/l	50	50	50	DWS
Chloride	mg/l	150	200	200	
Nitrate	mg/l		150	150	
Nitrite	mg/l		0,1	0,1	DWS
Phosphate	mg/l		2	2	
COD	mg/l		5	5	DWS
Colour	mg/l		20?	20?	DWS
Pesticides	µg/l		2,5	2,5	DWS = 0,5
Cleaning agents	mg/l		-	?	

Table 4-5. Requirements for water in vegetables and fruit preserving industry (IMd Micon, 1999)

Water use/process	Minimal requirements	Current water source	Additional treatment
Wash and rinse water	No SS, low temperature, bacterial count < 100/ml	Ground water	-
Transport water	No SS, bacterial count < 10.000/ml	Ground water	-
Cooling water (without product contact)	No SS	Ground water/ surface water	Chlorinate
Product water	Potable water quality, softened	Treated ground water/tap water	softening
Process water, cooling water with product contact	Potable water quality, low bacterial count	Treated ground water/ Tap water	Chlorinate (cooling water)
Cleaning water	Potable water quality	Treated ground water/tap water	
Boiler water	Not permitted: hardness, oxygen, iron, organic material	Treated ground water/tap water	Softening and degassing
Sanitary	Potable water quality	Tap water	-

4.4.1.1 Ready to cook vegetables

Table 4-6. Water quality different water streams; measured values (TNO, 2003)

Process	pH	EC mS/cm	Turbidity (FNU)	SS g/l	COD tot Mg/l	COD solved Mg/l	Germ number (Kve/ml)
Box washer	8,1	0,483	8,2	0,004	22	10	28 000
Wagon washer	7,0	0,481	8,3	0,032	45	24	480 000
Wash water lettuce	4,4	0,56	274	0,236	1 030	558	> 10.10^6
Cutting water lettuce	7,6	0,451	2,08	n.k	45	44	> 10.10^6
Wash water endive	6,0	0,717	120	0,168	434	212	n.k.
Root scraper	4,2	3,3	520	6,0	25 600	18 900	n.k
Beet water	n.k.	n.k	n.k	0,344	17 500	21 100	n.k
Waste water during production	n.k	n.k	n.k	n.k	2 740	2 050	n.k
Waste water during cleaning	n.k	n.k	n.k	n.k	1 840	1 470	n.k
Intake water buffer	n.k	0,462	0,31	0,016	6	n.k	260
Drinking water standard	7-9,5	1,25	10	1	5		100

Table 4-7. Branch specific parameters (TNO April 2005)

Parameter	Explanation
Pesticides	Negative health effects (H&WC and PS)
Disinfectants	Negative health effects (H&WC and PS)
Odour/taste additives	Negative affect product (PQ) and negative smell (H&WC)
Iron (Fe)	Corrosion (M&P)
Colour	Discoloration Product (PQ)
Legionella	Pathogenic organisms (H)
Listeria monocytogenes	Pathogenic organisms (H&WC)
Nitrate	Forming of nitrite and nitro amines (PS)
Pathogenic M.O.	Pathogenic organisms (PS, H)
Polyphenols	Discoloration Product (PQ)
Cleaning agents	Negative effect on taste of product (PQ)
Temperature	Increase pathogenic organisms (PS) and microbiological decay (PQ)
Total amount M.O.	Microbiological decay (PQ), biofouling, corrosion (M&P)
SS	Contamination, biofouling (M&P)

Table 4-8. Standards for the application of process water from production process (TNO, April 2005)

Parameter		Standards process	Standards Cleaning	Overall Standards	DWS
Ammonium	mg/l	1	-	1	0,2
Pesticides	µg/l	0,5	0,5	0,5	0,5
COD	mg/l	20	20	20	5
Disinfectants	??	0	0	0	n.k
Phosphate	mg/l	5	5	5	2
Iron (Fe)	mg/l	1	1	1	0,2
K	mg/l	50	-	50	n.k.
Colour	mg/l PtCo	Acceptable	acceptable	Acceptable	20
Legionella	??	Not admit	Not admit	Not admit	N.k
L. monocytogenes	n/100 ml	Not admit	Not admit	Not admit	
Nitrate	mg/l	150			
Nitrite	mg/l	0,3			
Pathogenic org.	n/100 ml	Not admit	Not admit	Not admit	Not admit
Polyphenols	mg/l	Acceptable	-	acceptable	Nk
Cleaning agents	??	0	0	0	n.k
N-total	mg N/l	15	15	15	1?
Sulphate	mg/l	150	-	150	150
Temperature	C	4	-	4	25
Total M.O.	n/ml	100	100	100	100
TSS/turbidity	mg/l	10	10	10	n.k

4.4.1.2 Potato processing industry

For the assessment of the possibilities for reuse of process water streams, the following water quality parameters are important by the production of chips (Arcadis, 1999).

Table 4-9. Water quality parameters for the production of chips (Arcadis, 1999)

Parameter	Explanation
COD and N-kj	Criteria for amount of organic material (pollution load). High concentrations leads to scaling
Hardness	Causes scale
Fe, Mn	High concentrations leads to deposition/scaling (of oxides)
NO_3 (as nitrate)	Supplement for quality
SO_2 (as sulphite)	Supplement as anti-oxidant and important for colour product
Temperature	Important due to process- and product quality
pH and chloride	Important due to corrosion and product quality
Odour and taste	Important in case of contact with product
Pyrophosphate (P-amount)	Pyrophosphate is used for to avoid greyness of chips and to bind iron particles
Sugars	Sugar content is important by blanching step (colour)
Micro biological quality	Risks because of infection of product
Remnant of cleaning and disinfectants	Unwanted in case of contact with end product

Table 4-10. Water quality parameters for the different process steps during the production of chips (Arcadis, 1999)

		Washing after sand filter	Cutting sorting line	Cooker	Steam Peeling	Cleaning	Boiler house
Temperature	ºC	<30	<50	<50	<100	<60	<40
Hardness	ºDH	-	-	-	-	-	<20
COD	mg/l	<20.000	<5.000	<100	<500	<1.000	<50
Nkj	mg/l	<770	<190	<4	<20	<40	<2
N-NO3	mg/l	<500	<100	<100	<100	<100	<100
SO2	mg/l	<10	<0	<10	<10	<10	<10
pH	mg/l	6-8	4,8-10	4,8-10	5-10	<6-9	6-9
Pyro-phosphate (P)	mg/l	<100	<200	<100	<100	<100	-

In the following table the water quality of the effluent of the different process steps is presented.

Table 4-11. Water quality of the effluent of the different process steps

		Washing after sand filter	Final rinse	Cooker	Condens water oven	Cleaning	Boiler house
Temperature	ºC	20	48	72	95	30	90
Hardness	ºDH	-	-	-	-	-	0,5
COD	mg/l	10.000	16.000	4.500	1.000	500	2.500
Nkj	mg/l	385	615	173	39	19	96
N-NO3	mg/l	100	10	10	10	10	0

SO2	mg/l	0	0	0	0	0	0
pH	mg/l	7,5	10,2	4,9	7	7	7
Pyro-phosphate (P)	mg/l	60	10	50	0	10	-

		Condens water steam peeling	Wash basin cutting	Sorting	Flock Line	Sorting line
Temperature	ºC	95				
Hardness	ºDH					
COD	mg/l	25.000	20.000	4.200	5.000	20.000
Nkj	mg/l	960	770	162	190	796
N-NO3	mg/l	10	200	10	10	200
SO2	mg/l	0	0	0	0	0
pH	mg/l	6	4	5,8	7	4
Pyro-phosphate (P)	mg/l	25	15	0	50	10

From the water quality criteria presented in the tables above, it can be determined whether reuse of water is possible or not. If the water quality does not meet the criteria for a certain process step, a water treatment step can be introduced.

Table 4-12. Requirements water streams Potato processing industry (IMd Micon, 1999)

Waterstream/Process	Minimal requirements	Current water source	Additional treatment
Washing/remove stones	Process water, moderate quality	Treated ground water/tap water	Sand removing installation
Cutting	Process water, moderate quality	Treated ground water/tap water	Removing starch
Sorting	Process water sufficient quality	Treated ground water/tap water	-
Blanching	Potable water quality	Treated ground water/tap water	-
Cleaning water, filling systems	Potable water quality	Treated ground water/tap water	
Cooling/freezing	Process water sufficient quality	Treated ground water/tap water	
Boiler water	Not permitted: hardness, oxygen, iron, organic material	Treated ground water/tap water	Softening, degassing
High pressure cleaning	Potable water quality	Treated ground water/tap water	-
Cooling towers	No corrosion, settling and algal growth	Treated ground water/tap water	If necessary softening

4.4.1.3 Canned mushrooms

Table 4-13. Branch specific parameters canned mushrooms (TNO May 2005)

Parameter	Explanation
Calcium	Scaling (M&P)
Proteins	Turbidity (PQ)
Phosphate	Scaling (M&P)
Carbon hydrates	Turbidity (PQ)
Magnesia	Scaling (M&P)
Total amount M.O.	Microbiological decay (PQ), biofouling, corrosion (M&P)
SS	Contamination, biofouling (M&P)

4.4.1.4 Canned vegetables

Table 4-14. Branch specific Canned Vegetables parameters (TNO May 2005)

Parameter	Explanation
Calcium	Scaling (M&P)
Proteins	Turbitity (PQ) and H2S and NH3 formation (PQ)
Phosphate	Scaling (M&P) and Softening (PQ)
Iron (Fe)	Discolouring (PQ)
Carbon hydrates	Turbidity (PQ)
Copper	Health aspects (H&WC)
Magnesia	Scaling (M&P)
Nitrate	Forming of nitrite and nitro amines (PS)
Nitrite	Forming nitro amines (PS)
Sulphate	Damage to caps
Zinc	Neg. health aspects (PS)
Total amount M.O.	Microbiological decay (PQ), biofouling, corrosion (M&P)
SS	Contamination, biofouling (M&P)

Table 4-15. Standards Canned vegetables (TNO November 2004)

Parameter		Standard washing	Standard blanching	Standard overall	DWS
Pesticides	Ug/l	O,5	0,5	0,5	0,5
Calcium	Mg N/l	150	70	70	150
Chloride	Mg/l	200	200	200	150
Chrome	Ug/l	50	50	50	50
Disinfectants		0	0	0	n.o
Proteins (Nkj)	Mg N/l	-	40	40	1
Phosphate	Mg/l	2	5	2	6
Iron	Ug/l	-	200	200	200
Lead	Ug/l	10	10	10	10
Magnesia	Mg/l	50	50	50	50
Nickel	Ug/l	20	20	20	20
Nitrate	Mg/l	150	50	50	50
Nitrite	Mg/l	0,1	0,1	0,1	0,1

Parameter		Standard washing	Standard blanching	Standard overall	DWS
Pathogene MO's	#/ml	0	0	0	0
pH	-	6-8	6-8	6-8	6-9,5
Cleaning agents	-	0	0	0	n.0
Total Mo	#/ml	1,0E+04	1,0E+04	1,0E+04	100
TSS	Mg/l	0	40	0	n.o
Starch (COD)	Mg/l	100	100	100	5
PAK (sum)	Ug/l	0,1	0,1	0,1	0,1
Org. micro	Ug/l	dws	dws	dws	dws

Table 4-16. Standards canned vegetables (TNO October 2006)

Parameter		Steam	Cleaning	Wash water	Remarks
Pathogene MO	#/100 ml	0	0	0	dws
Total MO	#/100 ml	100	100	100	dws
Iron	Ug/l	200	200	200	dws
Manganese	Ug/l	50	50	50	dws
Calcium	Mg/l	150	150	150	dws
Magnesia	Mg/l	50	50	50	dws
Chloride	Mg/l	150	200	200	
Nitrate	Mg/l		150	150	
Nitrite	Mg/l		0,1	0,1	dws
Phosphate	Mg/l		2	2	
COD	Mg/l		5	5	dws
Pesticides	Ug/l		2,5	2,5	0,5
Cleaning agents	Mg/l		-	?	

4.4.2 Water quality in dairy industry

4.4.2.1 Cheese production

For the assessment of the possibilities for reuse of process water streams, the following water quality parameters are important by the production of cheese (Arcadis, 1999).

Table 4-17. Water quality parameters for the production of cheese

Parameter	Explanation
Hardness	Causes scaling
Fe, Mn	High concentrations leads to deposition/scaling (of oxides)
COD and N-kj	Criteria for amount of organic material (pollution load)
Total micro-organisms/Coli/streptococcen	Risk because of contamination of product
pH and chloride	Important due to corrosion
Odour and taste	Important in case of contact with product
Electric conductive capacity	Indicator for total salt content

The table below is given water quality criteria for the different process steps in cheese production (Arcadis, 1999)

Table 4-18. Water quality criteria for the different process steps in cheese production (Arcadis, 1999)

		Cooling water	Product water	Utilities/ boiler water	Utilities/ Suppletion evaporators	CIP	Indirect product contact (seal water)
Temperature	ºC	<15	-	-	<40	-	<15
Hardness	ºDH	<22	-	<0,2	<22	-	<0,2
Fe	mg/l	<0,2	<0,2	<0,1	<0,2	<0,2	<0,1
Mn	mg/l	<0,1	<0,05	<0,05	<0,05	<0,1	<0,05
COD	mg/l	<100	<30	<40	<40	<250	<50
Nkj	mg/l	-	<0,5	-	-	<10	<1
pH		6,5-9	6,5-9	-	6,5-8,5	-	-
Cl	mg/l	<150	<150	-	<150	-	-
Conductivity	µS/cm	-	-	-	<800	-	-
Total Germ number	Kve/ml	<10	<10	-	-	<50	<20
Coli/Faec.	n/100 ml		0	-	-	<1	-

The water coming from the different process steps can also be characterized, see table below.

Table 4-19. Characterization of water coming from the different process steps

		Cooling water	Product water	Utilities/ boiler water	Utilities/ Suppletion evaporators	CIP	Indirect product contact (seal water)
Temperature	ºC	20	-	90	-	-	20
Hardness	ºDH	22	-	0,5	55	-	1
Fe	mg/l	0,1	0,2	0,09	0,3	0,2	0,2
Mn	mg/l	0,05	0,05	0,01	0,05	0,1	0,05
COD	mg/l	40	1060	2650	30	2650	70
Nkj	mg/l	-	44	-	0,5	88	0,7
pH		7,1	5-8	-	8,9	-	-
Cl	mg/l	50	150	-	375	-	-
Conductivity	µS/cm	-	-	-	2250	-	-
Total Germ number	Kve/ml	10	300	-	-	10	25
Coli/Faec.	n/100 ml	-	2	-	-	3	-

Analyzing the quality of the in- and outcoming streams, it can be concluded that for direct reuse cooling water and water form indirect product contact can be used. For the reuse of other water streams a pretreatment step is necessary (especially for the removal of COD).

Table 4-20. Requirements water streams production of cheese (IMd Micon, 1999)

Water stream/process	Minimal requirements	Current water source	Additional treatment
Process water, contact with product	Potable water quality	Treated ground water/tap water	-
Product water	Potable water quality	Treated ground water/ tap water	-
Cleaning water and pre rinse water	Low Hardness, Potable water quality or somewhat lower quality	Treated ground water/ tap water	-
Boiler water	Not permitted: hardness, oxygen, iron, manganese, organic material	Treated ground water/ tap water	Softening and degassing
Cooling water	Low temperature, no settling (hardness)	Treated ground water/ tap water	-
Suppletion water cooling tower	N settling parts (hardness)	Treated ground water/ tap water	Conditioning with chemicals
Sanitary and other	Potable water quality	Tap water	-

4.4.2.2 Milk processing

Table 4-21. Requirements water streams consumption milk company (IMd Micon, 1999)

Water stream/process	Minimal requirements	Current water source	Additional treatment
Process water, contact with product	Potable water quality, low bacterial count	Treated ground water/tap water	(disinfection)
Process water, no direct contact with product	Potable water quality	Treated ground water/ tap water	-
Cooling water	Potable water quality, low hardness	Treated ground water/ tap water	If necessary softening and disinfection
Boiler water	Not permitted: hardness, oxygen, iron, organic material	Treated ground water/tap water	Softening and degassing

4.4.2.3 Whey processing

Table 4-22. Requirements water streams industrial whey processing (IMd Micon, 1999)

Water stream/process	Minimal requirements	Current water source	Additional treatment
Process water	Potable water quality	Treated ground water/tap water	disinfection
Cleaning water	Not permitted: hardness, micro biological requirements	Brüden-condensate	-
Boiler water	Not permitted: hardness, oxygen, iron, organic material	Brüden-condensate	Degassing
Cooling water	Low temperature, bacterial count must be zero	Treated ground water/ surface water	Chlorinate
Suppletion water cooling tower	Low temperature, bacterial count must be zero	Treated ground water/	Conditioning with chemicals
Sanitary and other	Potable water quality	Tap water	-

4.4.3 Water quality in meat industry

4.4.3.1 (Pig, poultry and cattle))Slaughter house

Table 4-23. Water Quality Criteria for pig and cattle and slaughterhouse (Groeneveld, N. 2001)

Division	Water quality	COD (mg/l)	Conductivity (mS/m)	TSS (mg/l	Bacterial count (log/ml)
Cattle wagons and stable	Rinse water	500	GAN	GAN	2
Heating box	Process water	50	2 500	50	1
Brush and scratch machine	Process water	50	2 500	50	1
Slaughter hall	Tap water	5	250	5	0
Gut room	Tap water	5	250	5	0
Cleaning dirt line					
- pre rinse	Rinse water	500	GAN	GAN	2
- rinse	Process water	50	2 500	50	1
Cleaning clean line					
- pre rinse	Process water	50	2 500	50	1
- rinse	Tap water	5	250	5	0
Other	diverse	5 - 500	400 - GAN	5 - GAN	0 - 2

GAN = no analyse necessary

Table 4-24. Requirements water quality pig slaughter house (IMd Micon, 1999)

Water stream/process	Minimal requirements	Current water source	Additional treatment
Cleaning cattle-truck	Microbiological reliable, no infection animal disease permitted	Treated ground water/tap water	Disinfection
Stable: spraying pigs with nozzles	Microbiological reliable, no infection animal disease permitted	Treated ground water/ tap water	None
Stable: Cleaning	Micro biological reliable, no infection animal disease permitted	Treated ground water/ tap water	None
Heating box	No infection animal disease permitted	Treated ground water/	None
Process water slaughter line	Potable water quality	Tap water	None
Stomach and gut processing	Potable water quality	Treated ground water/	None
Washing meat crate	Potable water quality	Tap water	None
Cleaning slaughter line	Potable water quality	Treated ground water/	None
Warm and hot water	Potable water quality, low hardness	Tap water	Partially softening
Suppletion water cooling tower	No settlement, low hardness	Treated ground water/ Tap water	Partially softening
Boiler water	Not permitted: hardness, oxygen, iron, organic material	Treated ground water/ tap water	Degassing, softening

Table 4-25. Branch specific parameters Poultry slaughter (TNO, 2006)

Parameter	Explanation
Legionella	Pathogenic organism (H&WC)
Pathogenic organisms - Salmonella spp - Campylobacter spp - Staphylococcus aureus - Clostridium perfringens - Clostridium botulinum - Bacillus cereus - Aeomonas hydrophila - Escherichia. Coli O 157:h7 - Shigella spp. - Listeria monocytogenes	
Total M.O.	Biofouling (M&P)
Viruses - Aviaire influenza (new castle disease)	Pathogenic organism
Colour	Discolouring product (PQ)
Temperature	Grow of m.o. (PS, PQ)
SS	Contamination, blockage (M&P)
Iron (Fe)	Blockage pipes (M&P, PWF) Product quality (PQ)
Disinfectants	Health effects (PS, H&WC)
Cleaning agents	Influence taste product (PQ)
Antibiotics	Resistance problems

4.4.3.2 Meat processing company

Table 4-26. Requirements water quality meat processing (IMd Micon, 1999)

Water stream/process	Minimal requirements	Current water source	Additional treatment
Process water, contact with product possible	Potable water quality	Treated ground water/tap water	
Pasteurization water	Potable water quality	Treated ground water/ tap water	disinfection
Cooling water	Potable water quality	Treated ground water/ tap water	disinfection
Boiler water	Not permitted: hardness, oxygen, iron, organic material	Treated ground water/ tap water	Degassing, softening

4.4.4 Water quality in fish processing industry

no relevant information available

4.4.5 Water quality in beverage industry

4.4.5.1 Fruit juices

Table 4-27. Requirements water quality by production of fruit juice (IMd Micon, 1999)

Water stream/process	Minimal requirements	Current water source	Additional treatment
Product water	Potable water quality	Treated ground water/tap water	Degassing, demineralisation
Cooling water	No settling permitted, potable water quality	Treated ground water/ surface water	-
Cleaning water	Potable water quality (due to lack off disinfection step)	Treated ground water/ surface water	-
Boiler water	Not permitted: hardness, oxygen, iron, organic material	Treated ground water/ surface water	Degassing, softening
Suppletion water cooling tower	No settlement, corrosion, algal growth	Treated ground water/ Tap water	Softening, Conditioning with chemicals (prevention of corrosion and algal growth)
Sanitary and other	Potable water quality	Tap water	-

4.4.5.2 Beer brewery

Table 4-28. Requirements water quality beer brewery (IMd Micon, 1999)

Water stream/process	Minimal requirements	Current water source	Additional treatment
Brew water	Potable water quality with additional requirements (hardness)	Treated ground water/tap water	Degassing, softening
Cooling water beer residue	No settling permitted, temperature, micro biological quality	ground water	-
Cooling water wort	Potable water quality	Treated ground water/ surface water	Degassing, softening
Cooling water pasteurization	No settling permitted, temperature, micro biological quality	Ground water	Chlorine dosage
Cleaning water	Potable water quality, low hardness	Treated ground water/ Tap water	Fraction Softening
Boiler water	Not permitted: hardness, oxygen, iron, organic material	Treated ground water/ surface water	Degassing, softening
Sanitary and other	Potable water quality	Tap water	-
Carbonic acid installation	Potable water quality	Treated ground water/ surface water	

4.4.6 Water quality in sugar and starch industry

4.4.6.1 Starch processing

Table 4-29. Requirements water quality starch and glucose producing company (IMd Micon, 1999)

Water stream/process	Minimal requirements	Current water source	Additional treatment
Process water starch	Potable water quality	Treated ground water/tap water	
Process water glucose production	Potable water quality	Treated ground water/tap water	
Final rinse water demineralization unit	Potable water quality	Tap water	
Other rinse water demineralization unit	Potable water quality	Condensate glucose production	
Suppletion water cooling tower	No SS, low hardness	Condensate glucose production	
Boiler water	Not permitted: hardness, oxygen, iron, organic material	Treated ground water/ surface water	Degassing, softening

4.4.6.2 Sugar Processing

Table 4-30. Requirements water quality sugar production (IMd Micon, 1999)

Water stream/process	Minimal requirements	Current water source	Additional treatment
Wash- and transport water	Free of SS, Potable water quality	Clarified Water/condensate	Presettling/Anaerobic treatment
Water diffusion process	condensate	Condensate	
Boiler water	Not permitted: hardness, oxygen, iron, organic material	condensate	Degassing, softening

4.4.7 Water quality in margarine, oil and fat industry

5 Water quality demands in textile sector

5.1 Introduction

The textile finishing industry is the second biggest water consuming sector in Europe (after agriculture). European industries process all kind of fibres, the great part are man-made fibres, while among natural fibres cotton is the most important. Textile finishing industry also consumes high quantities of dyestuffs and auxiliaries. Processes using high amounts of water are printing and dyeing (on average 100 - 150 m^3/t). Some facts about textile finishing industry in European Union:

- Over 4 000 companies;
- Over 100 000 employees;
- Over 10 billion Euros turnover;
- Approximately 6 million tons of textile materials are processed each year with a consumption of 600 million m^3 of water;
- Considerable amount of coloured waste water with very heterogeneous composition (~128 tons of dye per day);
- More than 10 000 commercial products, corresponding to 4 000 different molecules;
- Degradation of commercial dyes in the environment is slow and complicated (high thermal and photo stability);
- Dyes cause a lot of problems in the environment:
  - high visibility (1 mg/l), absorption and reflection of sunlight;
  - harmful degradation products, POPs, metals;
  - degradation products can be toxic or carcinogenic, allergenic;
  - acute and chronic diseases.

Woven and knitted fabrics cannot be processed into finished goods without several water-intensive finishing operations to enhance the appearance, durability, and serviceability of fabrics. Finishing processes consist of four main steps: fabric preparation, dyeing, printing, and special finishing. Not all these steps are always necessary, while methods used can vary greatly in function of different end products, applications and site-specific manufacturing practices.

The quality of water is of big importance for the stability of production and quality of products. Most critical parameters are hardness, pH, and metal content. Usually softened fresh water is used for almost all wet processes although for some processes water with lower quality would also be good enough. Some additional treatments like sand filters are applied in cases of increased content of other dashes.
The principal concerns in the textile industry are:

- Maintaining product integrity;
- Reducing the formation of scale and deposits;
- Lowering overall production costs.

Beside the direct impact of the waste water produced by the textile finishing industry, the large consumption of fresh water is becoming intolerable in countries subject to real or potential water shortages.

In this chapter an overview is given of water quality demands in the textile industry. Water quality requirements or restrictions were collected for different water functions, like washing, dyeing, printing, cooling, heating, cleaning, etcetera.

A general flowchart for processes in textile manufacturing is shown on Figure 5-1.

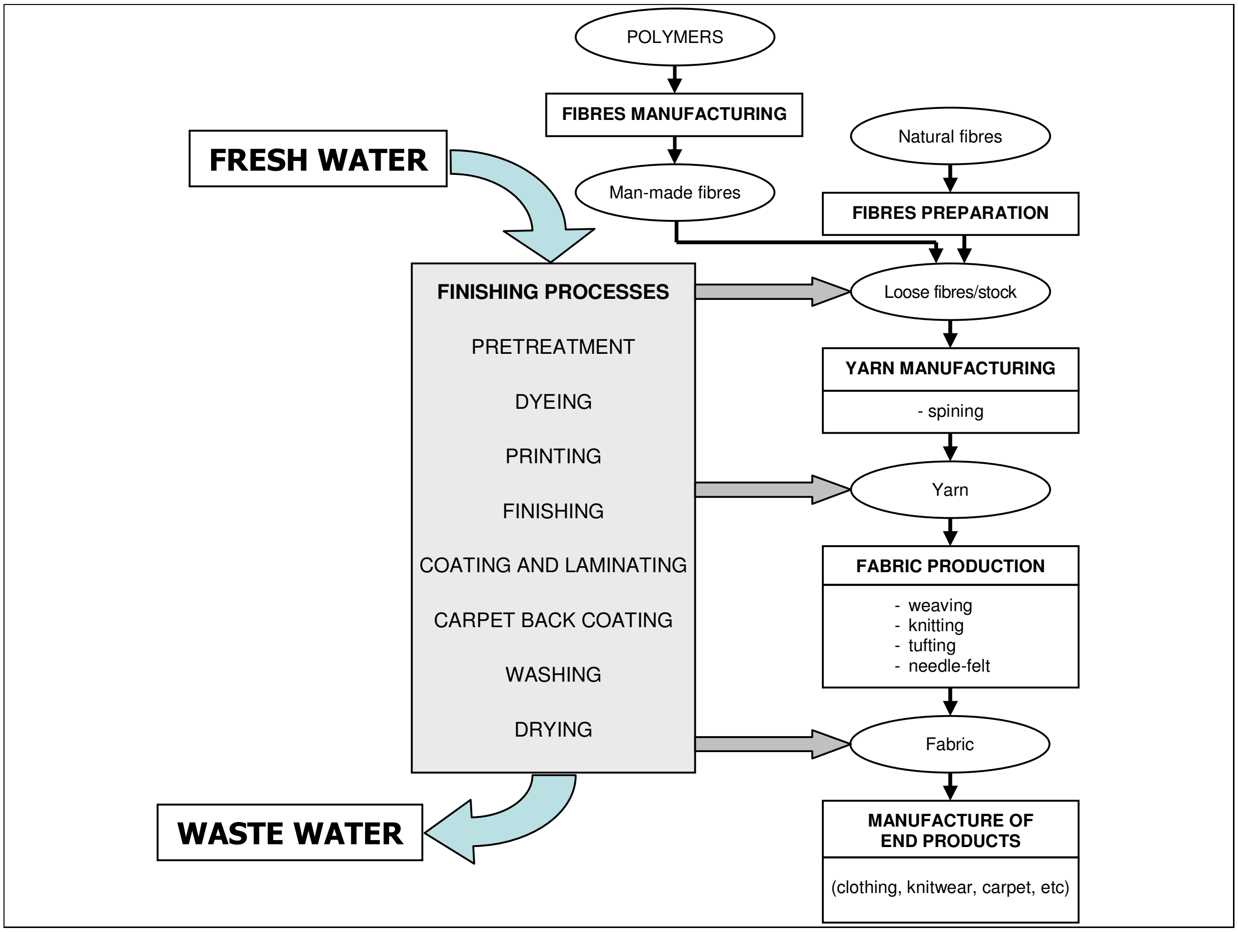


Figure 5-1. General flowchart of textile production processes

Not all processes are using water. On Figure 5-2 more detailed flowchart shows which processes need the input water (marked with rounded W).

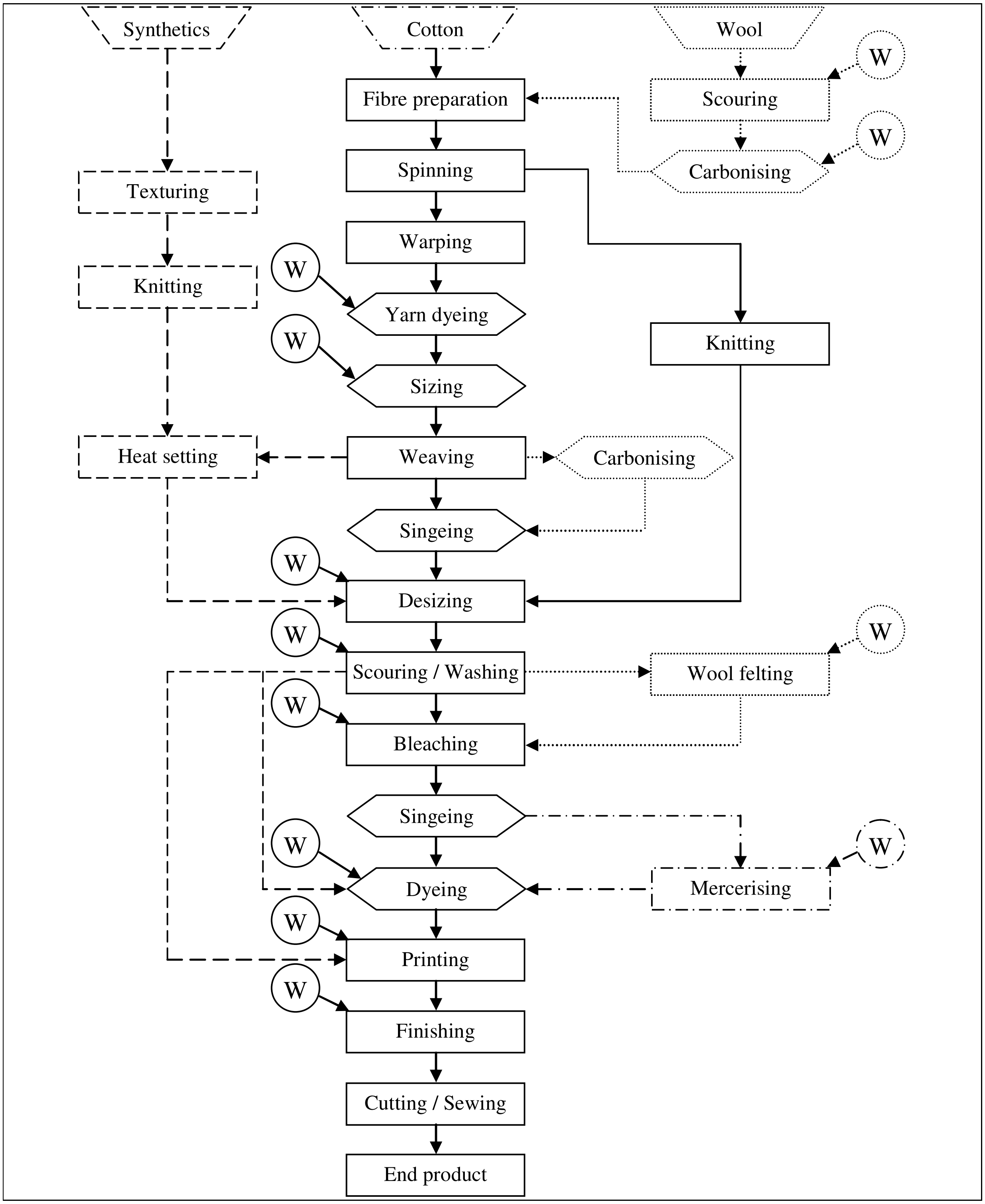


Figure 5-2. General flowchart for processes in textile manufacturing

5.2 Water Functions in the textile industry

Within the textile industry several sectors can be distinguished. The most important water consuming sector within the textile industry is textile finishing industry, where water can be used on two different ways: as a medium for textile treatment with direct contact with material or as a heating / cooling medium without direct contact. Figure 5-3 shows water circuit in textile finishing production.

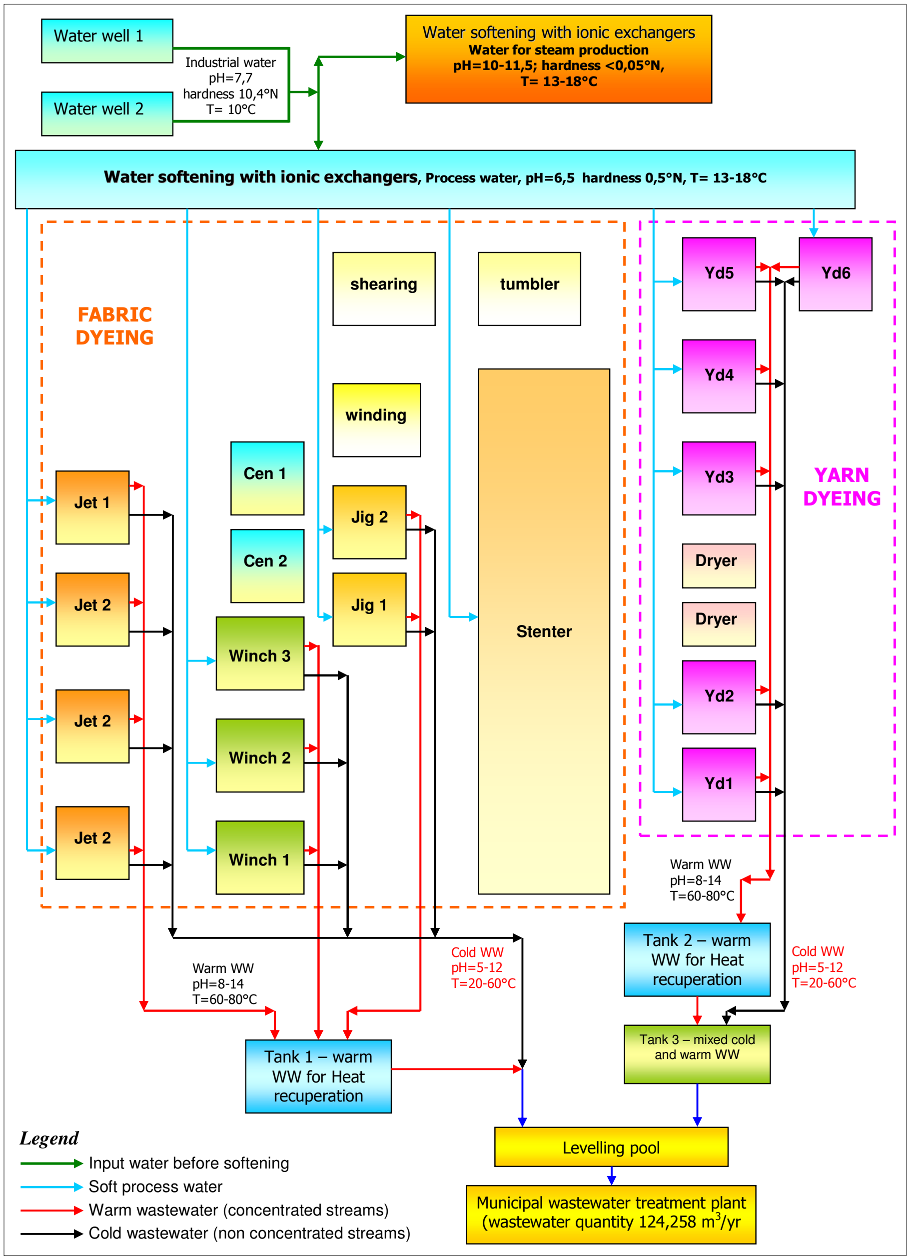


Figure 5-3. Water circuits in textile finishing production

5.2.1 Different textile processes

Wet textile finishing processes consists of operations like: pre-treatment, dyeing, printing, finishing, washing, coating and laminating, carpet back coating, ... These operations are explained more into detail below.
The major water demanding processes during textile production are:

- Fabric preparation;
- Dyeing;
- Printing;
- Special finishing;
- Cooling processes;
- Steam generation;
- Abnormal incidents (e.g. fire protection);
- Sanitation.

5.2.1.1 Pretreatment

- Cotton (singeing, desizing, scouring, mercerising, bleaching);
- Wool (carbonising, washing/scouring, fulling, bleaching);
- Silk (scouring, weighting);
- Synthetic material (washing; extraction of: surfactants, complexing agents, alkali; thermofixation).

5.2.1.2 Dyeing

- Cellulose fibres dyeing;
- Wool dyeing;
- Polyamide fibres dyeing;
- PES fibres dyeing;
- Acrylic fibres dyeing.

5.2.1.3 Printing

- Printing with pigments;
- Printing with dyes.

5.2.1.4 Finishing (functional finishing)

- Easy care treatments;
- Water repellent treatments;
- Softening treatments;
- Flame-retardant treatments;
- Antistatic treatments;
- Mothproofing treatments;
- Bactericidal and fungicidal treatments;
- Anti-felt treatments;
- Oxidising treatments;
- Treatments with resins.

5.2.1.5 Washing

- Washing with water (in the presence of wetting agent and detergent);

- Dry cleaning (with solvent, usually perchloroethylene).

5.2.1.6 Coating and laminating

- The fabric to be coated/laminated is supplied full width on a roll;
- The fabric is fed under careful tension control to a coating or laminating heat zone after application of the coating auxiliaries, the fabric is passed through an oven to cure the composite and remove volatile solvents before cooling and rolling up.

5.2.1.7 Carpet back coating

- Pre-coating;
- Foam coating;
- Textile back-coating;
- Heavy coating;
- Reinforcement;
- Back finish.

5.2.2 Environmental issues

5.2.2.1 Pretreatment

- COTTON: Water emissions which vary according to a number of factors: the make-up, the sequence adopted, the fact that some treatments are often combined in a single step, etc.;
- WOOL: Water emissions, but also specific operations where halogenated solvents are employed;
- SILK: Scouring baths present a high total organic charge; the concentration of nitrogen organic components in particular is high. The environmental issues associated with silk pre-treatment arise from emissions of washing agents to water;
- SYNTHETIC MATERIAL: When material is washed, about 80 % of preparation agents are released to the waste water and the remaining 20 % can be emitted to exhaust air in the subsequent high temperature treatments (drying and thermofixation).

The main concerns, as regards waste water, arise from the discharge of poorly or non-biodegradable substances such as mineral oils, EO/PO adducts, silicone oils, hard surfactants, etc. Furthermore, biocides, which are normally contained in the aqueous formulations, contribute to aquatic toxicity of the waste water.

5.2.2.2 Dyeing

- The dyes themselves (toxicity, metals, colour) auxiliaries contained in the dye formulation (dispersants, salts, powder-binding agents, anti-foaming agents, anti-freeze agents, thickening agents, buffer systems);
- Basic chemicals (alkali, salts, reducing and oxidizing agents) and auxiliaries used in dyeing processes;
- Contaminants present on the fibre when it enters the process sequence (residues of pesticides on wool are encountered in loose fibre and yarn dyeing and the same occurs with spin finishes present on synthetic fibres).

Water and energy consumption in dyeing processes are a function of the dyeing technique, operating practices and the machinery employed.

5.2.2.3 Printing

- Printing paste residues;
- Waste water from wash-off and cleaning operations (unfixed dye, urea, sulphates, polysaharides, polyacrylates, glycerine, polyvinyl alcohol, m-nitrobenzene sulphonate, multiple-substituted aromatic amines, mineral oils);
- Volatile organic compounds from drying and fixing (aliphatic hydrocarbons, methanol, polyglycols, formaldehyde, ammonia, phenylcyclohexene).

5.2.2.4 Finishing (functional finishing)

- Ethylene urea and melamine derivatives in their “not cross-linked form” (cross-linking agents in easy-care finishes);
- Organo-phosphorous and polybrominated organic compounds (flame retardant agents);
- Polysiloxanes and derivatives (softening agents);
- Alkyphosphates and alkyletherphosphates (antistatic agents);
- Fluorochemical repellents.

5.2.2.5 Coating and laminating

- Coating powders;
- Coating pastes (fatty alcohols, fatty acids, fatty amines from surfactants; glycols from emulsifiers; alkylphenoles from dispersants; glycol, aliphatic hydrocarbons, n-methylpyrrolidone from hydrotropic agents; aliphatic hydrocarbons, fatty acids/salts, ammonia from foaming agents; phthalates, sulphonamides/esters ex softeners/plasticisers; acrylic acid, acrylates, ammonia, aliphatic hydrocarbons from thickeners);
- Polymer dispersions (aqueous formulations: acrylates, monomers);
- Melamine resins;
- Polymer dispersions (organic solvent-based formulations).

5.2.2.6 Carpet back coating

- Foaming agents and stabilisers (surfactants);
- Cross-linkers (sulphur, but also peroxides);
- Vulcanisation accelerators (mercaptobenzothiazoles, dithiocarbamates);
- Activators (combination of zno and stearic acid);
- Gelling agent (ammonium acetate, silicon fluoride);
- Hydrophobic substances (paraffin dispersions, silicon emulsions) ;
- Complexing agents (edta, polyphosphates);
- Antioxidants;
- Thickeners (organic polymers based on polyacrylates and cellulose).

5.2.2.7 Washing

- Anionic and non-ionic surfactants;
- Impurities from material.

5.3 Water Quality Parameters

In this chapter we will focus on the relevant water quality parameters for the most important water functions (water uses) in the textile sector and on the process specific parameters. The required water quality is strongly related to the process water function. Besides the process specific water function also product quality is relevant aspect for the water quality.

5.3.1.1 Fabric preparation (washing, desizing, scouring, bleaching,…)

Most fabric that is dyed, printed, or finished must first be prepared or pre-treated. It consists of several treatment and rinsing steps. Natural impurities or processing chemicals, potentially able to interfere with following processes need to be removed. Typical preparation treatments include desizing (to remove the sizes applied to the yarn during sizing operation), scouring (to remove different substances both naturally present and artificially applied), and bleaching (to remove natural yellowish colour and increase whiteness). Preparation steps can also include processes such as singeing and mercerising, aimed to chemically or physically alter the fabric.

5.3.1.2 Dyeing

Dyeing operations are used to add colour to textiles and may take part in the process chain at different stages of production (fibres, yarn, fabric or piece dyeing). Textiles are dyed by applying a wide range of dyestuffs and by using different techniques and equipment. Dyestuffs are largely synthetic, typically derived from coal tar and petroleum-based intermediates.
Coloration of a textile material is achieved in a number of different ways:

- direct dyeing, in which the dye in the aqueous solution in contact with the material is gradually absorbed into the fibres because of its inherent substantivity;
- dyeing with a soluble precursor of the dye, which forms an insoluble pigment deep within the fibres on treatment after dyeing;
- direct dyeing followed by chemical reaction of the dye with appropriate groups in the fibre;
- adhesion of the dye or pigment to the surface of the fibres using an appropriate binder.

All of these methods but the last require that the fibres, at some stage, absorb the dye, or an appropriate precursor, from an aqueous solution. This process is essentially reversible. However, precipitation of a pigment and reaction with the fibre are irreversible chemical processes.

For different substrate specific dyes have to be used. Most common dyes are:

- acid, metalized and mordant dyes for dyeing wool and nylon;
- direct dyes for dyeing cellulose;
- disperse dyes for dyeing polyester, cellulose acetate and nylon;
- reactive dyes for dyeing cotton and wool;
- vat dyes for dyeing cellulose and cotton;
- cationic dyes for acryl, polyester and nylon.

Basic chemicals and auxiliaries used in the dyeing process are:

- sulphur-containing reducing agents (sodium sulphide, sodium hydrosulphite);
- oxidizing agents (dichromate, bromate, iodate, chlorite, hypochlorite);
- salts of various types;
- other auxiliaries;
- fatty amine ethoxylates (levelling agent;
- alkylphenol ethoxylates (levelling agent);

- quaternary ammonium compounds (retarders for cationic dyes);
- polyvinylpyrrolidone (levelling agent for vat, sulphur and direct dyes);
- cyanamide-ammonia salt condensation products (auxiliaries for fastness improvement);
- acrylic acid-maleic acid copolymers (dispersing agent);
- ethylenediamine tetraacetate (edta) complexing agents;
- diethylenetriaminepentaacetate (dtpa);
- ethylenediaminetetra(methylenephosphonic acid) (edtmp);
- diethylenetriaminepenta(methylenphosphonic acid) (dtpmp).

Dyeing can be performed by using continuous or batch processes. In batch dyeing, a certain amount of textile substrate is loaded into a dyeing machine and brought to equilibrium with a solution containing the dye. Auxiliary chemicals and controlled dye bath conditions accelerate and optimise the migration of dyeing molecules from the solution to the fibre. The dye is fixed on the fibre using heat and/or chemicals, and the tinted textile substrate is washed to remove unfixed dyes and chemicals. Common methods of batch dyeing include beam, beck, jet and jig processing.

In continuous dyeing processes, textiles are fed continuously into a dye bath. Continuous dyeing processes are typically comprised of dye application, dye fixation with chemicals or heat, and washing.

The amount of dyestuff used varies mostly according to the dye bath ratio, defined as the weight of the bath divided by the weight of the fabric. The dye bath ratio typically ranges from 5 to 50 depending on the type of the dye, dyeing system, and the affinity of the dyes for the fibres.

By chemical analysis, the following pollutant types were identified in the water samples:

- phenols (nitrophenols, bisphenol A, nonylphenol (NP), octylphenol (OP));
- nonylphenolethoxylate (NPEO) surfactants and their metabolites with endocrine disrupting potential;
- different aromatic sulphonates;
- LAS surfactants, dyes (colorants);
- pesticides;
- pharmaceuticals.

5.3.1.3 Printing

Printing, like dyeing, is a process for applying colour to a substrate. However, instead of colouring the whole substrate (cloth, carpet or yarn) as in dyeing, print colour is applied only to defined areas to obtain the desired pattern. This involves different techniques and different machinery with respect to dyeing, but the physical and chemical processes that take place between the dye and the fibre are analogous to dyeing. A typical printing process involves the following steps:

- colour paste preparation: when printing textiles, the dye or pigment is not in an aqueous liquor, instead, it is usually finely dispersed in a printing paste, in high concentration;
- printing: the dye or pigment paste is applied to the substrate using different techniques;
- fixation: immediately after printing, the fabric is dried and then the prints are fixed mainly with steam or hot air (for pigments). Note that intermediate drying is not carried out when printing carpets (too much energy would be needed for removing the highly viscous liquor);
- after-treatment: this final operation consists in washing and drying the fabric (it is not necessary when printing with pigments or with other particular techniques such as transfer printing).

When describing the different printing techniques, a distinction should be made between printing with pigments, which have no affinity for the fibre, and printing with dyes (reactive, vat, disperse, etc.). Fabrics are often printed using a variety of techniques and machine types. The printing techniques are numerous: rotary screen, direct, discharge, resist, flat screen, and roller printing.

Pigments cover about 75 – 85 % of all colouring matter used for the printing operations. Compared to dyes, pigments are typically insoluble and have no affinity to the fibres. Resin binders are typically used to attach pigments to substrates, while solvents are used as vehicles for transporting the pigment and resin mixture to the substrate.

5.3.1.4 Special finishing

Finishing encompasses chemical or mechanical treatments performed on fibre, yarn, or fabric to improve appearance, texture, or performance Mechanical finishes can involve brushing, ironing or other physical treatment used to increase the lustre and feel of textiles. Application of chemical finishes to textiles can impart a variety of properties ranging from decreasing static cling to increasing flame resistance. Chemical finishes are usually followed by drying, curing, and cooling steps.

5.3.1.5 Cooling

The most frequent problems in cooling water systems are scaling, corrosion, biological growth, fouling and foaming. These problems arise from contaminants in potable water as well as lower quality water, but the concentration of some contaminants may be higher.

5.3.1.6 Heating (steam production)

Quality requirements for boiler feed makeup water are dependent upon the pressure at which the boiler is operated. Generally the higher the pressure, the higher the quality of water required. Very high-pressure boilers require makeup water of distilled quality.
In general even potable water must be treated to reduce the hardness of the boiler-feed water to close to zero. Removal or control of insoluble salts of calcium and magnesium and control of silica and aluminium are required since these are the principal causes of scale build-up in boilers. High alkalinity may contribute to foaming, resulting in deposits in super heater, re-heater, and turbines. Bicarbonate alkalinity under the influence of boiler heat, may lead to the release of carbon dioxide, which is a source of corrosion in steam-using equipment.
Steam can be used for heating purposes and is not in the contact with processed material or can be used as direct thermal media for e.g. thermo fixation processes. In this case the quality of water used for steam preparation must also meet the general requirements for technological water.

5.4 Water quality demands in textile industry

In this chapter an overview is given of water quality specification and requirements for textile industry.

5.4.1 Water consumption

Water consumption differs strongly depending on type of processes, equipment and material processed. Some data are presented in Table 5-1, Table 5-2 and Table 5-3.

Table 5-1. Average consumption for different textile wet processes (l / kg)

Material	*Process*	*Consumption (l/kg)*
Cotton	Desizing	3 - 9
	Scouring or Kiering	26 - 43
	Bleaching	3 - 124
	Mercerizing	232 - 308
	Dyeing	8 - 300
Wool	Scouring	46 - 100
	Dyeing	16 - 22
	Washing	334 - 835
	Neutralization	104 - 131
	Bleaching	3 - 22
Nylon	Scouring	50 - 67
	Dyeing	17 - 33
Acrylic	Scouring	50 - 67
	Dyeing	17 - 33
	Final scour	67 - 83
Polyester	Scouring	25 - 42
	Dyeing	17 - 33
	Final Scour	17 - 33
Viscose	Scouring and dyeing	17 - 33
	Salt Bath	4 - 13
Acetate	Scouring and Dyeing	33 - 50

Table 5-2. Minimal and maximal water consumption (l / kg)

Category	min	med	max
1.Wool scouring	4,2	11,7	77,6
2.Wool finishing	110,9	283,6	657,2
3.Low water use processing	0,8	9,2	140,1
4.Woven fabric finishing			
Simple processing	12,5	78,4	275,2
Complex processing	10,8	86,7	276,9
Complex processing+desizing	5,0	113,4	507,9
5.Knit fabric finishing			
Simple processing	8,3	135,9	392,8
Complex processing	20,0	83,4	377,8
Hosiery processing	5,8	69,2	289,4
Stock and yarn finishing	3,3	100,1	557,1
Nonwoven finishing	2,5	40,0	82,6
Felted fabric finishing	33,4	212,7	930,7

Table 5-3. Water usage (l / kg) for different materials and processes

	Desizing	Scouring	Bleaching	Dyeing	Printing
Wool		4 – 77,5		40 – 150	280 – 520
Cotton		2,5 – 43	30 – 50	38 – 143	
Synthetic		17 – 67		38 – 143	
Not specified	12,5 – 35				20 – 300

Table 5-4. Liquor ratio for various dyeing processes

Process litres per kg	
Dyeing winches	**20-30:1**
Hank machines	**30:1**
Jet dyeing	**7-10:1**
Package dyeing	**5-8:1**
Pad batch	**5:1**
ULLR dyeing	**5:1**

Hank machines and dyeing winches are the biggest water consumers (20 - 30 l/kg) but pad-batch and ultra low liquor ratio dyeing processes need only 5 l/kg. The quantity of water used for a particular process also depends on the equipment modernisation and development. As an example, batch dyeing machines for knitwear have over last four decade gone from 30 l/kg to only 6 l/kg of treated material.

5.4.2 Water quality requirements

Water for a textile plant comes from various sources like rivers, lakes and subterranean water from wells. The water may be obtained directly from the source or from local municipality. Natural and pretreated water may contain a variety of chemical species that can influence textile wet processing. The various salts present in water depend on the geological formation through which the water has flowed. These salts are mainly carbonates (CO_3^{2-}), hydrocarbonates (HCO_3^-, also named bicarbonates), sulphates (SO_4^{2-}) and chlorides (Cl^-) of calcium (Ca^{2+}), magnesium (Mg^{2+}) and sodium (Na^+). Hard water contains calcium and magnesium ions and gives an immediate precipitate with soap. Soap is a water-soluble sodium salt of high molecular weight carboxylic acid, such as stearic acid. Its calcium and magnesium salts are much less soluble and give a gummy precipitate with a soap solution in hard water. When this happens, the cleaning efficiency of the soap decreases dramatically. The dirt in suspension, as well as the precipitated calcium and magnesium soap, can deposit back onto material being washed. This gives a dingy fabric with a poor handle that will be difficult to dye in a level shade.

Besides dissolved salts of natural origin, water may contain a variety of other salts from human or industrial activity. These include nitrates (NO_3^-), phosphates (HPO_4^{2-} and $H_2PO_4^-$) and various metal ions. The ions of certain transition metals, such as those of iron, copper and manganese, can precipitate dyes, or form complexes with them, dulling or even changing their shade. In addition many of these ions catalyse the decomposition of hydrogen peroxide in bleaching baths. It is not uncommon for a particle of iron rust on the surface of a cotton fabric to generate such rapid peroxide decomposition that the cellulose is totally oxidised and a hole results. These transition metal ions may be present in the natural or municipal water, or, in the case of iron, come from corrosion within pipelines. Both dissolved and colloidal silica in boiler feed water can lead to the formation of a hard resistant scale on the boiler's internal surfaces, considerably decreasing heat transfer efficiency. Organic compound from the decomposition of vegetable matter in the water, or from sources of pollution, can be very varied. They can have such high concentrations that the water is coloured.

The use of hard water in a textile dyeing or finishing mill can have some serious consequences. These include:

- precipitation of soaps,

- redeposition of dirt and insoluble soap on the fabric being washed – this can cause yellowing and lead to unlevel dyeing and a poor handle;
- precipitation of some dyes as calcium or magnesium salts;
- scale formation on equipment and in boilers and pipelines;
- reduction of the activity of the enzymes used in desizing;
- decreased solubility of sizing agents;
- coagulation of some types of print pastes;
- incompatibility with chemicals in finishing recipes.

In the Table 5-5 it can be seen how the presence of Water Hardness affects the various wet processing stages right from desizing to finishing.

Table 5-5. The influence of Water Hardness on wet processes

Wet Process	Problems encountered
Desizing	Deactivate enzymes and makes it in-soluble some size materials like starch and PVA.
Scouring	Combine with soap, precipitate metal-organic acids. Produce yellowing of off-white shades; reduce cleaning efficiency and water absorption.
Bleaching	Decompose bleach baths.
Mercerizing	Form insoluble metal oxides, reduce absorbency and lustre Combine with dyes changing their shades, in-soubise dyes, cause tippy dyeing, reduce dye diffusion and hence results in poor washing and rubbing fastness.
Dyeing	Dusting and white patches appear if the hardness is very high.*
Finishing	Form insoluble metal oxides, reduce absorbency and lustre Combine with dyes changing their shades, make them in-soluble, cause tippy dyeing, reduce dye diffusion and hence results in poor **washing** and **rubbing fastness.**

* Some authors demonstrated that the calcium ions could produce a strong electrolytic effect (positive or negative, depending on the nature of the fabric and pH used) on dyeing, even under very low concentrations [20].

Soft water is relatively free of calcium and magnesium ions. It produces a rich foamy lather with soap. This is essential for the soap to be an effective emulsifying agent for oils and dirt. With hard water, the soluble sodium salt of soap reacts with the alkaline earth metal ions and precipitates as the useless and undesirable calcium or magnesium soap. The cleaning ability is lost.

Water quality for all processes should be of such quality to avoid any process and final product quality problems (product quality and stability). While some impurities will adversely affect specific dyeing and finishing processes, other impurities can be tolerated at moderate levels in many processes. Critical impurities are following:

- Colour resulting from residual dyes in process water will generally be critical in most wet finishing processes. Exceptions may be found in the dyeing or rinsing of heavy or dark shade fabrics where residual colour may have a negligible effect on the ultimate shade. The nature of the colour producing dye will also determine the tolerate colour level. For example, basic dyes are a particular nuisance because they have a high tinctorical value and can stain most fabric types. Pigmented or insoluble colours (vats and sulphur dyes) have much less tendency for redeposit on fabric;

- Oxidising or reducing agents can affect the finished fabric quality as a result of chemical reaction with fibres or dyestuffs. Common oxidants used in textile processing include hydrogen peroxide, hypochlorite, and other bleaching agents; reducing agents include sodium hydrosulphite and sodium bisulphite. Most of these chemicals are destroyed by other reducing or oxidising agents and are thus removed before the water is reused;
- Process water pH is a critical factor in many wet finishing processes. However, this does not limit process water reuse since pH can be controlled at the process by chemical addition;
- Hardness-producing cations like calcium and magnesium form insoluble precipitates with soaps. The precipitates are sticky, adhere readily to fabrics, and can result in unlevel dyeing or poor hand. These cations will generally interfere with the activity of surface active agents or some finishing chemicals;
- Electrolytes can be present in recycled water in the form of inorganic salts or other textile auxiliaries. Some textile processes are relatively insensitive to electrolyte concentration while others are not. For example, anionics cannot be tolerated in process waters used to apply cationic fixing agents to direct dyes. A high salt concentration might cause direct dyes to exhaust or strike too rapidly and result in an uneven dyeing. Changes in dyeing procedures or proper dye and chemical selection can often eliminate some of these limitations for water reuse;
- Metals, like iron and manganese, can affect the shade of dyed fabric or can impart a yellowish tinge to bleached fabric. Heavy metals can also interact with process chemicals, e.g. promote catalytic decomposition of peroxides in bleaching and damage cellulosic fibres;
- Total solids – the solids content in recycled water will limit reuse only to the extent that the solids interfere with the dyes and process chemicals. Therefore, it may not be reasonable to specify a maximum solids limit of, say, 200 mg/l for general process use. Generally, it is not the amount of solids, but the nature of the solids that affects the textile process. Exceptions are the case of a final rinse in water containing a solids level high enough to give a sufficient residue after drying to result in poor fabric hand, or a high suspended solids level that in some cases can mechanically clog spray nozzles and filters. Dissolved electrolytes can only be removed by reverse osmosis so their effect on the process must be understood. In many cases much higher electrolyte concentrations can be tolerated that previously thought.

Mostly fresh softened water is used for all processes although sometimes water of lower quality could be used as well. Three types of water quality are suggested for use in textile industry: high quality water, moderate quality and low quality water.

1. High quality water can be used for all processes, such as dye baths, print pastes, finishing baths, final rinse bath. Consumption of such water is 10 – 20 % of total water consumption. Four different sources are presented in Table 5-6: fresh softened water, recycled effluent (proposed), mains drinking water prescribed concentrations or values (PCVs), Confederation of British Wool Textiles (CBWT) water specification

Table 5-6. Water quality suitable for all processes

	Fresh softened water	Recycled effluent	Mains water PVCs	CBWT specification
Colour[a] (mg/l Pt scale	None visible	None visible	20	None visible
COD (mg/l O_2)		20 - 50	5,5 - 9,5	6,0 - 8,0
pH	6,5 - 7,5	6,5 - 7,5		
Total hardness (mg/l)	50[b]	90[b]	250 (Ca), 50 (Mg)	60 - 80[b]
Chloride (mg/ Cl)	300	500	400	
Sulphate (mg/l SO_4)			250	
Fe (mg/l)	0,05	0,1	0,2	0,1
Cu (mg/l)	0,05	0,005	3	0,1
Cr (mg/l)		0,01	0,05	
Al (mg/l)		0,02	0,2	
Mn (mg/l)			0,050	0,05
Zn (mg/l)			5	0,1

a Suggested specification for water with no visible colour absorbance in 10mm cell:450 nm, 0,02-0,04; 500 nm 0,02-0-05; 550 nm, 0,01-0,03; 600 nm 0,01-0,02
b measured as ppm $CaCO_3$

2. Moderate quality water used for washing-off stages after scouring, bleaching, dyeing/printing and finishing. About 50 – 70 % of total water consumption consists of such water needs. Final rinse bath in the washing processes should be always high quality water to ensure that material is free from traces of contamination. Table 5-7 shows parameters of moderate quality water.

Table 5-7. Suggested water quality suitable for washing off processes[a]

Parameter	**Maximum recommended level**
Colour[b]	None visible
COD (mg/l)	200
pH	7,0 – 8,0
Total hardness (ppm $CaCO_3$)	100
Chloride (mg/l)	500 – 2 000
Fe (mg/l)	0,1
Cu (mg/l)	0,05
Cr (mg/l)	0,1

a Final rinse bath to use high quality water
b Specification as above

3. Low quality water can be used for washing down equipment, screen washing in print works and general washdown of print paste containers and floors. Quantity presents only 10 – 20 % of total water consumption, but it is wasteful to use high quality water for such operations. Table 5-8 presents the parameters of low quality water.

Table 5-8. Suggested water quality suitable for equipment washdown only

Parameter	Maximum recommended level
Colour[b]	None visible
COD (mg/l)	500 – 2 000
pH	6,5 – 8,0
Total hardness (ppm $CaCO_3$)	100
Chloride (mg/l)	3 000 – 4 000
Fe (mg/l)	0,1
Cu (mg/l)	0,05
Cr (mg/l)	0,1

Dyestuff producers also publish some criteria for process water. Following target specification, published by BASF, and guidelines for technological water for textile finishing by Bezema and Ciba are presented on Table 5-9 Table 5-10 and Table 5-11.

Table 5-9. Target specification for dye house process water by BASF (maximum recommended level/tolerance)

Parameter	Level	Unit
pH	7,0 (± 0.5)	
Total Hardness	50	ppm $CaCO_3$
Iron	0,05	mg/l
Copper	0,05	mg/l
Chloride	300	mg/l

Table 5-10. Guidelines for technological water for textile finishing - Bezema

Parameters	Limits
Hardness	< 5° n
Organic load	< 20 mg/l $KMnO_4$ - use
Glow residual	< 50 mg/l
Fe	< 0,1 mg/l
Mn	< 0,05 mg/l
Cu	< 0,01 mg/l
Nitrate(V)	< 50 mg/l
Nitrate(III)	< 5 mg/l
pH	pH 6 - 8
Odour	without
Colour	without

Preferably no free carbon dioxide

Table 5-11 Quality requirements of water used in production - Ciba

Parameters	Limits
Colouring	colourless
pH-value	neutral
Glow residual	< 500 mg/l
$Fe^{2+/3+}$-content	< 0,1 mg/l
$Cu^{2+/3+}$-content	< 0,05 mg/l
M^{2+}-content	< 0,02 mg/l
Cr^{-}/Cd-content	< 0,01 mg/l
Cl^{-}-content	< 300 mg/l
Sulphate-content	< 250 mg/l
Phosphate-content	< 10 mg/l
Total hardness	0-8 °dH
COD	< 50 mg O_2/l

1 °dH = 10 mg/l CaO = 7,9 mg/l MgO

According to work in SP5, considering treatability criteria ENEA proposed following characteristics as starting point only. During the tests other characteristics should be added if needed.

Characteristics for reusability

- pH: almost all the authors agree on a pH required in the range of 6,5 - 8,0. The proposed value is 6,5 - 8,0;
- Conductivity: most of the authors suggest maximum values in the range 1 - 2 mS/cm. The proposed value is 1,5 mS/cm;
- Suspended Solids: the authors suggest maximum values in the range 5 - 50 mg/l. The proposed value is 10 mg/l;
- Turbidity: Only one author proposes a maximum value of 1,0 NTU. The proposed value is 1,0 NTU;
- Total COD: Maximum values for reuse range between 10 and 160 mg/l. The proposed value is 60 mg/l;
- Colour: Most authors recommend the water should be colourless (roughly corresponding to an absorbance at each wavelength < 0,01 cm-1). The proposed value is: mean value of absorbance in the visible spectrum < 0,01 cm-1 and absorbance at three wavelengths selected < 0,01 cm-1.

Wet processes in the textile industries require water of very good quality concerning mainly content of dyes, detergents, and suspended solids. Therefore, a purification treatment to recycle water must have much better performances than for simple discharge according to the limits imposed by legislation.

Discussion with textile companies, involved in this project exposes the main concern about using recycled water: the quality and stability of final product. Until now they use only softened fresh ground water. Nevertheless weather conditions can influence the quality of such water. For example after heavy rain the content of iron ions increases, so they had to install additional filters. Also the nature of the process is of big importance on ability to use recycled water. For washing and rinsing of dark dyed material it is easier to use recycled waste water than for very light shades. And because of instant changing of production (equipment, processes, materials,) the hardware solution for reuse (pipes, reservoirs, treatment plants) could be very demanding and expensive.

According the number of characteristics needed to be controlled for water quality demand in textile sector (as discussed in Madrid), companies usually control only above mentioned parameters. Because almost every chemicals used in textile wet processes are organic source, COD should indicate the content of those chemicals in waste water. But COD does not indicate the kind of chemicals (oxidation, reduction) and influence in combinations of different chemicals. Sometimes very small concentration of one chemical can deteriorate the quality of product.

Our proposition is to consider above mentioned parameters as necessary for water quality characterisation with possibility to include additional parameters if necessary.

Some general information about parameters which can influence water quality issues for industrial reuse is presented in Table 5-12.

Table 5-12. Industrial reuse concern

Water quality parameter	Industrial reuse concern
Ammonia	Forms combined chlorines, causes corrosion, promotes microbiological growth
Minerals: calcium, magnesium, iron and silica	Scale formation
Phosphorus	Scale formation, algal growth, biofouling of process equipment
Residual organics	Bacterial growth, microbial fouling on surfaces, foaming in process waters
Total Dissolved Solids (TDS)	Corrosion
Total Suspended Solids (TSS)	Deposition on materials and surfaces, microbial growth

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